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THE STRUCTURE OF THE ATOM

BY

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THIRD EDITION, REVISED AND ENLARGED

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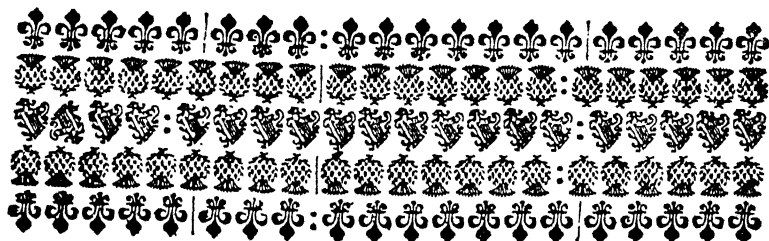
A D·E D I C A T I O N

Sir,

I fear that what I offer you here is but an indifferent
Plant, though 'tis grown from your own Seed. Since I laboured
in your Elaboratory, working small things while those Choice
Philosophers Moseley (of whom we may say, as the illustrious
Newton said of Cotes, that had he lived we had known
something) and Bohr were performing great ones, War and
the Penalties of Publick Employment have long kept me from
attempting to add to Knowledge by such Natural Experiments
as my slender Wit can devise. In studying now at length to
fit myself for a Venture I have gathered together much of
what the Learnèd of our day have discussed in the matter
of that Microscosm, the Atom, within whose exiguous
Bounds is Space and to spare for Philosophical Speculations;
and in the perhaps too Presumptuous Hope that what it
has taught me much to collect may help others as Ignorant as

Myself I have ordered my Conclusions into the Volume which I now present to You.

No Astronomer of these petty Suns and Planets has given us more and rarer News of them than Yourself, who first taught the Virtuosi to see in the Atom a Massy Nucleus controlling by electrick Laws his distant Servants the light-heeled Electrons. You will find here, then, much that is a Picture of your own Thoughts; and as there is scarce a Man whose Portrait is being limned but feels a lively Curiosity to see what the Artist, be he never so unskillful, has made of his Task, so, I trust, you will look not without Interest on much that I have endeavoured to portray of which you are the Originall. And if at times the Incompetence of my Pencil shall make you smile, I hope you will nevertheless consider that I have always wrought as well as my Ability and Exiguous Leisure allow me. I fear that it will avail me little with many, in this Censorious Age, to plead the Largeness of my Design as an Excuse for an imperfect Execution of its Particulars. But I have frequently observed that they are most contentious who are least able to perform, while others, like yourself, whose Large Atchievements might well make them Scorners of lesser Men, look leniently upon those who undertake Small Things without Great Pretensions.

I confess that I come to the Performance of this Work with much less Deliberation and Skill than the Weightiness of it requires, but Better Brains are busy about Graver Matters than such a Surveyall as I here endeavour. That the Attempt is seasonable, I think you will allow: that it is incomplete I

cheerfully acknowledge. I have not declared myself largely on such slippery Matters as the Evolution of our Great Universe from a Prime Substance, nor the Future of Mechanicall Power, for I am not one of those who would Strive, as our French Cousins say, to break an Eel across his Knee. *I have gone softly, essaying rather to show what is certain, and what less certain, leaving the Niceties of Fantastickall Speculation to those whose Pens are more Copious than mine.*

Finally I bring you humbly this Book not so much in the Belief that it is worthy your Acceptance, as in the Hope that its very Imperfections and Errours may prove of Service, by suggesting to your Perspicacious Judgement Means by which they may be amended, and Experiments to resolve what I have set down doubtfully. The Principles which you have already establisht will remain to perpetuate your Name to Future Ages, and these I have endeavoured to elucidate to the Students in our great Science of Physicks. I have, however, small Doubt that you are so extending the Bounds of Natural Knowledge as to render what I have written Meagre and Incomplete even while I Subscribe Myself,

Sir,

Your most Humble Servant,

EDWARD NEVILLE DA COSTA ANDRADE

*At the Artillery Colledge at Woolwich,
January, 1923*

PREFACE TO FIRST EDITION

IN this book I have endeavoured to give, in a form sufficiently simple to make it accessible to all serious students of the exact sciences, a critical account of the work that has been done, in various fields, on the subject of atomic structure, and to state without ambiguity the present position, which does not, of course, imply that the present position is without ambiguity. It is part of the policy of the book to indicate the inadequacies as well as the triumphs of the prevailing theories, and this has often involved the discussion of particular problems towards the solution of which little has been done. While I have tried particularly to make a comprehensive survey I cannot pretend that I have included everything of importance that touches my theme. A great deal of selection has been necessary to keep the book within the limits of size judged advisable, and, in my choice, I have been guided by the wish to give a coherent and readable exposition rather than a series of abstracts of original papers. Some admirable pieces of work have been deliberately omitted as not falling into the scheme of the book, and it is probable that others have been passed over through inadvertence. The papers cited at the end of each chapter form only a small portion of those which I have consulted, but at the same time those who know how much has been written on the subject during the past ten years will not censure me overmuch if I confess that I have found it impossible to read, even perfunctorily, all that has appeared.

A word of explanation is necessary concerning these references appended to the chapters. They have been selected with one object only, that of enabling the reader to find with the least possible trouble further information on any point in which he may be particularly interested. In consequence the list gives no indication of priority ; the latest paper of a given author is quoted in preference to the earliest, since it contains any back references needed. Again, important papers do not receive reference if the work described has been superseded, although they may have influenced subsequent research. Besides the latest papers and the general references I have occasionally quoted an old paper if it is fundamental for the subject, such as an early paper by Rutherford or Lenard. The titles of the papers have in all cases been given, since they sometimes afford a guide as to the contents. A complete bibliography could have been furnished with very little additional trouble, but it would have added very considerably to the bulk of the book, and probably diminished its value. Too many references are as bad as none at all. The general references and the papers cited will be found to furnish a body of additional reference sufficient to satisfy the most avid reader.

Where I have introduced mathematical calculations I have tried to make perfectly clear what are the physical assumptions involved and what are the results obtained, so that those unwilling, for one reason or another, to follow the actual working may omit to do so without necessarily losing sight of the nature of the argument. I have frequently had in mind an aphorism of the late Lord Kelvin, who cannot be accused of lack of understanding of mathematical methods : " Nothing can be more fatal to progress than a too confident reliance on mathematical symbols ; for the student is only too apt to take the easier course, and consider the formula, and not the fact as the

physical reality." In the case of complicated calculations whose execution involves no physical principle, but demands considerable technical mathematical skill, I have generally contented myself with quoting the result, especially when the full calculation can easily be found in Sommerfeld's *Atombau* or elsewhere.

The book includes matter published up to March, 1923. Any account of a field of science so assiduously cultivated as this is bound, in a restricted sense, to become rapidly out of date, but if the account has been properly rendered the reader will have acquired sufficient familiarity with the fundamental questions involved and the methods of attacking them to be able to follow and appreciate the next developments. Most of the matter described here seems likely to retain for some time its validity as the foundation on which more elaborate structures may be built.

It gives me pleasure to acknowledge my indebtedness to several gentlemen who have helped me in the production of this book. I have to thank Sir Ernest Rutherford for having looked over the manuscript of the first seven chapters, and for having, in particular, drawn my attention no less to certain details of scientific work than to a shrewd philosophic precept. My friend Dr. Ludwik Silberstein has read the manuscript of Chapters VIII. to XI., and I owe him my thanks for many illuminating suggestions. Professor T. M. Lowry has kindly read Chapter XII., and made some remarks which have been very valuable to me. Mr. Wilfred Jevons, senior lecturer in Physics at the Artillery College, has not only placed his considerable knowledge of spectroscopy freely at my disposal, but has performed the arduous and unattractive task of reading through all the proofs with apparent cheerfulness, and to him, and to other colleagues at the Artillery College—Professor K. C. Browning, Mr. R. H. Wright and Mr. C. E. Wright—who have

always been ready to aid me I am deeply grateful. I offer my best thanks to the following gentlemen for having supplied me with the original photographs which have been used in preparing the plates : M. le duc de Broglie for the X-ray absorption spectra, Professor Paschen for the fine structure of the helium lines, Professor Siegbahn for the X-ray emission spectra, and Mr. Blackett for the α-ray tracks. I have further to thank the Council of the Royal Society, the Proprietors of the *Philosophical Magazine,* and the Proprietors of the *Physical Review* for permission to use certain diagrams, and Dr. F. W. Aston and Messrs. Arnold jointly for permission to use the photographs reproduced in Plate II.

Finally, it will very much facilitate my work, in the event of a second edition of this book ever being called for, if authors will kindly send me separate copies of any papers bearing on the subject which have appeared in the past or may appear in the future. I shall be sincerely grateful to those who do this, as also to any readers who will notify me of mistakes which I may have committed either by ignorance or carelessness, or by both.

E. N. DA C. ANDRADE.

ARTILLERY COLLEGE,
   WOOLWICH, *April* 1923.

PREFACE TO THIRD EDITION

WHEREAS the second edition differed from the first in a few inessential points only, for this the third edition the book has been completely rewritten. Not only have extensive additions been made in view of the researches of the past three years, but the original presentation of the earlier work has been in many places drastically revised, in the hope of making the implications clearer and the treatment more consistent. Further, the scope of the book has been increased by the discussion of certain aspects of the subject treated very inadequately, or not at all, in the earlier editions. I may instance the account of the experimental work on critical potentials, of Saha's theory of ionisation, and of Born and Landé's work on the elasticity of solids. I have been largely guided as to what to discuss and what to omit by considering whether a concise account of the matter in question is already available to English readers. Thus I have included the topics just mentioned, but have said nothing of the experimental determination of X-ray wave lengths, which has been so adequately discussed by other writers.

In endeavouring to avoid an undue extension of the book I have neglected a variety of interesting subjects, and in particular I may have laid myself open to reproach by saying nothing of band spectra. My excuse is that the book is primarily intended to deal with the atom, and that the valuable work on band spectra has not so far yielded any precise informa-

tion as to atomic structure or, in particular, as to the method by which atoms combine. When the subject has developed a little further it is possible that Dr. Jevons and I may essay to give a short account of it, as, in some sense, a supplement to this book.

The correspondence principle has been treated at much greater length than before, and illustrated by detailed examples, and something has been said of the principle of adiabatic invariance. The whole theory of line spectra has been discussed in very much greater detail, and the description of the periodic table in terms of orbits, which had only just been initiated by Bohr when the first edition appeared, has been much extended. Chapters which are entirely new are those dealing with Multiplets and Anomalous Zeeman Effect, and with Quantum Theory and Wave Theory. The discovery of the Compton effect rendered a chapter on the lines of the latter necessary, while the work embodied in the former has mostly been carried oút in the past three years. In treating the general problems of multiplet lines, theories have been discussed which are plainly of a provisional nature. Here, as elsewhere, it has been my particular endeavour to set out clearly the experimental results, so that the reader may gather what regularities have been actually established, independently of any attempted explanation. If this policy has been adequately pursued the book may retain some value even when theories exposed in it have been superseded.

The new quantum mechanics of Heisenberg, Born, Jordan, and Dirac, and of Schrödinger has been mentioned in the last chapter, but not discussed in the body of the book. The papers dealing with the new mechanics in its different aspects were appearing when the account of the problems to which they apply was substantially completed. The best plan therefore appeared to be to bring the account of the quantum

theory of spectra down to the point attainable without invoking the newest theories, exposing the difficulties and systemizing them as far as possible, so that the reader might have before him the problems which have shown the inadequacies of the older quantum mechanics. Some such treatment is needed to pave the way for the novel ideas. No doubt it will shortly be—may even be now—possible to rewrite Chapter XV. completely in terms of the new mechanics and the spinning electron, in such a way that many of the dilemmas do not arise. The book has, however, already been so long delayed that it was not judged advisable to hold it up still further, especially as the new ideas have not yet so far crystallised as to render this task a short one.

It is clear that, since the work has inevitably occupied all my leisure time for two years, all parts of it cannot claim to be equally representative of the latest researches. Any attempt to bring the whole treatment up to date would have entailed repeated rewriting of the chapters first completed, and no final form would ever have been reached. Certain papers which appeared as late as the autumn of 1926 have received consideration in the later parts of the book.

I owe especial thanks to two gentlemen for help in preparing the new edition. My kindly critic Mr. R. H. Fowler, of Trinity College, Cambridge, has on several occasions placed his extensive knowledge of modern spectral theory at my disposal, and I am particularly indebted to him in respect of Chapter XV. He read the proofs of this chapter, and made many valuable suggestions : the imperfections of the chapter, of which I am keenly conscious, I must claim as my own. Dr. Wilfred Jevons, senior lecturer in Physics at the Artillery College, has read with meticulous care the whole of the proofs, both in the slip and in the page state, and has frequently saved me from obscurity and error. Other colleagues at the Artillery College

to whom I offer my best thanks for assistance rendered are Professor H. C. Plummer, Mr. C. E. Wright, who has read through the page proofs, and Mr. J. W. Farmery. I am indebted to Professor W. Wilson, of Bedford College, Dr. L. Silberstein, Dr. C. D. Ellis, and Professor E. V. Appleton for friendly counsel.

I have to thank Dr. Blackett, Professor Gerlach and Dr. Foote for original photographs from which plates have been reproduced : the Council of the Royal Society and Professor C. T. R. Wilson for permission to use Plate III. : Messrs. Hirzel and Professor Stark for permission to use the photograph of the Stark effect in Plate V. : Messrs. Springer and Dr. Back for the anomalous Zeeman resolutions in Plate VII. : Messrs. Gyldendal and Drs. Kramers and Holst for the folding plate at the end of the volume : the Proprietors of the *Philosophical Magazine* for Fig. 25. I have used the library of the Royal Institution extensively for reference to journals, and it would be ungracious not to acknowledge the courteous services of the staff, and especially of Mr. Cory, the librarian.

Finally, I feel that I must express my thanks for the very friendly and encouraging reception accorded to the book as it originally appeared, and my hopes that it may in its present form prove of service to students of our lofty subject of atomic physics.

<div style="text-align:right">E. N. DA C. ANDRADE.</div>

ARTILLERY COLLEGE,
WOOLWICH, *October* 1926.

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PART I

THE NUCLEUS

CHAPTER I

Introductory. The triumph of the atomic hypothesis is the epitome of modern physics. Since the time of Democritus the discontinuous, or granular, structure of matter has been eloquently argued by learned speculators like Gassendi, and, later, by experimental philosophers like Dalton, but it is only in our time that the existence of atoms and molecules has, from the point of view of the physicist, been placed beyond doubt. The last quarter of a century or so has also seen the definite establishment of the atom of electricity, the electron, and the wide acceptance of the enigmatic atom, or quantum, of radiant energy. Matter, electricity, and radiant energy are, then, not continuous in structure, but made up of discrete units. Whereas, however, the two latter are considered to possess the attribute of old assigned to the atom of matter, namely, indivisibility, the atom of matter itself is no longer an unbreakable entity. We believe that it has a structure, and in this structure the electron and the quantum of radiant energy play essential parts.

The first speculations as to the structure of the atom are due to the English chemist Prout (1785-1850). The hypothesis known by his name laid down that the atoms of all elements are built up of hydrogen atoms, and at the time when it was put forward it had a considerable measure of support, largely due, no doubt, to an inherent desire among scientists for simplicity. Prout's hypothesis gratified the wish for one fundamental substance expressed in the πρώτη ὕλη of the ancients and the *materia prima* of the alchemists. He based his speculations on the then possible belief that the atomic

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weights of all elements were simple multiples of that of hydrogen, and when later it was objected that the atomic weight of chlorine, for instance, was 35·5, the supporters of the hypothesis took as their fundamental unit a substance of half the weight of the hydrogen atom. Later determinations forced them to reduce the weight of their unit, until the work of Stas finally drove the supporters of the hypothesis to the fantastic shifts which immediately precede the death of a theory. Prout's hypothesis served a useful purpose, however : firstly, in stimulating speculation as to a possible sub-structure of the atom, and secondly, in promoting the exact study of atomic weights.

It is interesting to note that, in a modified form, Prout's hypothesis has now returned. The nuclear atom, in which the mass is supposed to be concentrated in a comparatively small nucleus, surrounded by a cloud of electrons, is now occupying the attention of physicists and chemists. It is believed that this nucleus is built up of positively charged hydrogen nuclei, the so-called *protons*, while the other constituent of the hydrogen atom, the electron, is the only other irreducible entity entering into the structure of even the most complex nucleus. Old objections based on the fact that atomic weights are not expressible in whole numbers, if oxygen be taken as 16, are set aside by the recent work of Aston and others on isotopes, which allows us to ascribe the fractional part of the atomic weight to the fact that the elements possessing such a weight are really mixtures of isotopes of different whole-number atomic weights. So the old theory reappears in a form more suited to the needs of to-day. Similarly, in the quantum theory the old corpuscular theory of light takes on a new garb and light is shown to exert a pressure and to have weight. Certain conceptions seem to have an innate attractiveness for the scientific mind, and just as the constitution of our bodies will probably always dictate certain general forms for the material tools wherewith we attack the gross manifestations of nature, so the constitution of our minds may be supposed to render desirable and convenient certain general forms of theories wherewith to attempt the explanation of her hidden principles.

Discussion of the hypothesis that the atoms of the various

elements are built out of some one or two fundamental substances was revived by the enunciation of the periodic law, which remains one of the fundamental guides for all speculation on the subject. Mendeléeff himself, to whom we chiefly owe the periodic table, was, it is interesting to note, opposed to all such speculations, and considered them an abuse of the knowledge which he had systematised, but many of his contemporaries and their successors were strongly impressed by the suggestion that the periodically recurring properties must be due to some periodically recurring feature in the structure of the atoms. In general terms, it is reasonable to suppose that as more and more of the hypothetical elementary particles of which all atoms are built are added to make heavier and heavier atoms there must be certain features of the pattern formed which present themselves at regular intervals. As J. J. Thomson has said : " That the atoms of the different elements have a common basis, that they behave as if they consisted of different numbers of small particles of the same kind, is proved to most minds by the periodic law of Mendeléeff and Newlands." The establishment of the nature of the " small particles of the same kind," the electrons, was, perhaps, the most important stage in the doctrine of atomic structure. The discovery of the Zeeman effect came at a fortunate time, as its simplest manifestation was at once explained by Lorentz in terms of vibrating electrons present in the atom.

The modern theories of atomic structure may, in fact, be said to have begun with the experimental establishment of the existence of the electron. As soon as it was shown that the mass of the electron was only about $1/1700$ of that of the hydrogen atom, and that all electrons, no matter of what origin, were of the same kind, it was realised that a suitable brick of which to build all atoms was to hand, and speculation as to the arrangement in the atom of electrons, and of the positive electricity necessary to make the atom neutral, began.

Oliver Lodge, summarising in 1906 various hypotheses, enumerated five possibilities :

(1) The main bulk of the atom may consist of ordinary matter associated with sufficient positive electricity to neutralise the charge of the electrons present.

(2) The bulk of the atom may consist of a multitude of positive and negative electrons, interleaved, as it were, and holding themselves together in a cluster by their mutual attractions, either in a state of orbital motion, or in some static geometrical configuration, kept permanent by appropriate connexions.

(3) The bulk of the atom may be composed of an indivisible unit of positive electricity, constituting a presumably spherical mass in the midst of which an electrically equivalent number of point electrons are scattered : these electrons may distribute themselves in rings, after the fashion of Alfred Mayer's floating magnetic needles, and revolve in regular orbits about the centre of the mass, with a force directed to that centre, and varying as the direct distance from it.

(4) There may be a kind of interlocked admixture of positive and negative electricity incorporated together in a continuous mass in the midst of which one or two more isolated and individualised electrons may move about and carry on that display of external activity which confers upon the atom its observed properties.

(5) A fifth view of the atom would regard it as a " sun " of extremely concentrated positive electricity at the centre, with a multitude of electrons revolving in astronomical orbits, like asteroids, within its range of attraction.

The first hypothesis and the fourth (which is extremely indefinite) do not call for further mention. The other three will be very briefly considered, as they bring out certain points which have to be taken into account in any atom model.

Lenard's Dynamids. A great advance was made by Lenard when he showed that the cathode rays could be made to penetrate a thin aluminium window and so pass out into the air. His further experiments on the absorption of the rays led him to the conclusion, which retains its great importance, that swift cathode rays can pass freely through thousands of atoms, assuming for the size of the atom the magnitude deduced from the kinetic theory of gases. The greater part of an atom must therefore be empty, at any rate so far as these fast travelling electrons are concerned. Lenard assumed that every atom was built up of what he called *dynamids, i.e.* couplets

consisting of a positive and negative electron, of fixed moment. These dynamids were surrounded by a field of electric force, which captured very slow-moving electrons : swift electrons, however, could pass by uncaptured, and, unless they passed very close, undeflected. From the absorption of the fast-moving electrons Lenard calculated that the dynamids had a certain small cross section absolutely impenetrable to any cathode rays, and that the total impenetrable volume due to all the dynamids in one atom was less than 10^{-9} times the volume of the atom. The scattering he attributed to deflection of the rays passing close to dynamids, this deflection being, of course, greater for the slower rays. He also deduced, from the fact that the absorption of cathode rays is roughly proportional to the mass of matter traversed, that the number of dynamids in an atom is proportional to the atomic weight of the atom. As to the arrangement in space of the dynamids in the atom Lenard offered no definite suggestion.

This work of Lenard's is of great interest, since, although his atom is not now accepted, in view of the much wider successes of Rutherford's type of atom, it presents many features embodied in Rutherford's atom. In both models most of the atom is empty. The size of Lenard's impenetrable dynamids is not very different from that of Rutherford's impenetrable nucleus, although in Lenard's atom of atomic weight N there are N dynamids, in Rutherford's atom there is only one nucleus with a charge equal to, not the atomic weight, but the atomic number. Lenard's atom was evolved by considering the passage and scattering of cathode rays through solid matter, Rutherford's mainly from considerations of the scattering of α particles by solid matter.

J. J. Thomson's Atom. J. J. Thomson's atom model consisted of a sphere of uniformly distributed positive electricity, in which are embedded a number of electrons whose total charge equals that of the positive electricity. This model proved very successful in representing in outline the chemical properties of atoms as exhibited in the periodic table. It can be shown that the electrons will have certain stable arrangements in rings. Starting with one electron, and putting in more electrons one by one, it is found that until we reach five

they arrange themselves in one ring. When a sixth is added the ring is no longer stable : one electron goes to the centre. The outer ring is then stable until it contains eight electrons : after that further electrons go to the centre to form another ring until when there are eleven in the outer ring, and five in the inner ring, the next electron added goes to the centre to start a third ring. In this way successive rings are built up, and a periodicity is obtained which is very suggestive of the periodic law of chemistry. Abegg's law of valency, that the sum of the positive and negative valencies of an atom is 8, is well represented. J. J. Thomson also worked out a theory of scattering of moving electrified particles in passing through small thicknesses of matter made up of such atoms. His results, however, did not agree so well with experiment as those given by Rutherford's model, and, further, the atom has had no success in the way of representing spectroscopic results (including in this term X-ray spectroscopy). It represented, however, the most elaborate and successful attempt to construct an atom model susceptible of detailed mathematical treatment until Rutherford, in 1911, enunciated his theory of the atom in a celebrated paper on the scattering of α and β particles by matter.

Rutherford's Atom.* Rutherford's atom consists of a positively charged nucleus, very small compared to the size of the atom, surrounded by a distribution of electrons, whose number equals the nuclear charge. It is often compared to a planetary system with a central " sun." The essential mass of the atom is concentrated in the nucleus. In the paper in which Rutherford first advocated this form of atom he stated that the central charge was approximately proportional to the atomic weight, and calculated that in one or two cases it had values which were about half the atomic weight. Later work has shewn that the central charge is equal to the atomic number, *i.e.* the number pertaining to an element when all the elements are arranged in order of increasing atomic weight, and numbered successively, starting with hydrogen as 1. Moseley's brilliant

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* The Rutherford type of atom was suggested by Nagaoka in 1904, but as he only investigated its stability, and brought forward no compelling evidence in its favour, it is usually known by the name of the man whose convincing presentation, based on crucial experiments, first exhibited its possibilities.

investigations on the X-ray spectra of a series of different elements first established this important feature of the theory. The atom was originally devised to account quantitatively for the observed scattering of a rays. It has since proved remarkably successful in accounting for a large number of atomic phenomena. It is by far the most fruitful of all atomic models, and most of the considerations of this book will be devoted to it.

A clear separation of the mass properties from the chemical properties is provided by the nucleus atom, the mass being given by the *mass* of the nucleus, while the chemical properties are determined by the nuclear *charge*, which conditions the distribution of the surface electrons of the atom. This feature of the model has proved particularly valuable for the interpretation of the modern work on isotopes, that is, for giving a theoretical account of the experimental discovery that there exist atoms of different masses which have the same chemical properties, and are therefore chemically inseparable.

The Dynamical and the Statical Nucleus Atom. For some problems the behaviour and distribution of the electrons surrounding the nucleus is of no great importance : they play no appreciable part, for instance, in the large angle scattering of a particles which has proved of such importance for speculation on atomic structure. For many purposes, however, it is essential to consider in detail the extra-nuclear part of the atom. There have been, in the main, two rival hypotheses. To account for the structure of line spectra, both optical and X-ray, a theory has been built up on the assumption that electrons circulate in certain stable orbits round the nucleus, the selection of the orbits, and the deduction, from the orbits selected, of the frequencies of the radiations being governed by special hypotheses. This theory owes its inception, and many of its developments, to Bohr, and is generally known by his name : we may refer to the model in question as the dynamical atom. Bohr and others have elaborated the model with a view to accounting for the chemical properties of the atom, especially those expressed in the periodic table.

An atom model in which the electrons are moving in complicated orbits is, however (in the present state of the theory, at any rate), not easy to deal with from the point of view of

chemical combination. Naturally enough the chemists have received more warmly the second hypothesis, that of the static atom model, which has been developed by Lewis, Langmuir, and others. This assumes a distribution of electrons in shells round the nucleus, but these electrons are considered to be stationary. Such a model has proved useful not only for the game of molecule building (a pastime not altogether unlike the glorified dominoes recently described by Major MacMahon *), but also from the point of view of atomic and molecular sizes, as concerned in the viscosity of gases, and crystal structure. By a variety of fantastic assumptions it can be forced to give a rough account of spectral series, but it cannot interpret any of the details so successfully explained by the dynamical model, such as the relation of the hydrogen to the ionised helium spectrum, the " fine structure " of the lines of hydrogen and helium, and the effect of an external electric or magnetic field on the spectral lines.

The claims of the rival theories are reviewed in the course of the book.

Duties of an Atom Model. It is a truism, but one which, perhaps, can bear repetition, that an atom model is only of use, and deserving of retention, when it describes quantitatively experimental observations, and proves fruitful in suggesting new lines of research. Some of the main phenomena which an atom model is expected to represent, and which have directed thought and speculation on the subject, are :

Scattering of α and β rays, and of X-rays, by matter.

The series spectra, both in the visible and invisible regions, including in this the X-ray spectra.

The phenomena of radioactivity.

The existence and properties of isotopes.

The non-existence of atoms of certain masses.

The periodic law, and the associated periodic variations.

The laws of chemical valency and chemical combination.

A completely satisfactory atomic model, which is an un-realisable ideal, would, of course, have to account for all the observed phenomena of physics and chemistry, which are

* *New Mathematical Pastimes*, by Major P. A. MacMahon. 1921. Cambridge University Press.

sciences of the atom. Many phenomena beyond those just enumerated have furnished helpful material for the criticism of atomic models. Crystal structure, magnetism, the viscosity of gases, the compressibility of crystals, the ionisation of gases, and various other subjects of study in chemistry and physics will be cited as witnesses for or against certain views of atomic structure, and there is little doubt that with sufficient ingenuity almost any experiment can be made to furnish some evidence on so comprehensive a subject. Those mentioned above have been selected as having, possibly, proved most fruitful so far. There is doubtless much evidence near at hand whose bearing has hitherto escaped notice, but may be revealed in the near future to some mind combining the imagination, knowledge, and balance which are necessary for fertile speculation.

CHAPTER II

General Behaviour of α Particles and Electrons passing through Matter. The physicist attempting to construct an atomic model from considerations of spectral data has been compared to a man who, never having seen a musical instrument, should essay to construct a model of a piano by listening to the sounds made by it when thrown downstairs. To help him in his task, however, the physicist has other guides besides the vibrations ; he has, for instance, probes of various strength which he can thrust through the case of the instrument, noting the resistances and deflecting forces which they experience. These probes are the swift α particles and electrons of various speeds, which in their passage through the atom undergo a variety of forces. Both the electron and the α particle are, of course, exceedingly small compared to the gas-kinetic * size of the atom, and hence the nature of their interaction with the atom during very close encounter is especially significant, since, except in certain cases, the moving particle may be considered as a point charge. A consideration of the behaviour of these flying corpuscles gave the essential features of the atom model which at present claims what is almost universal confidence.

The α particles are atoms of helium with a positive charge of two units, whose initial velocities vary from $2 \cdot 22 \times 10^9$ cm./sec. to $1 \cdot 45 \times 10^9$ cm./sec., according to the radioactive substance which gives rise to them. The corresponding kinetic energies

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* Perhaps the introduction into English of this expression may be allowed, since it is desirable to have some short way of indicating the size of an atom deduced from the kinetic theory of gases.

are 1.53×10^{-5} and $.645 \times 10^{-5}$ ergs. Moving electrons are at our disposal with velocity varying from nothing to the very high velocities of the β particles, approaching for the swiftest that of light. The velocity corresponding to a free fall through a potential difference of $.5$ volt,* which is about the lowest used in the class of experiment in question, is 4.2×10^7 cm./sec. or $.0014\ c$: that of the swiftest β particle is about $.998\ c$, where c is the velocity of light, and the corresponding energy is 1.2×10^{-5} ergs. For convenience we shall often refer to moving electrons, no matter what their origin, as cathode particles.

There are wide analogies between the behaviour of swift electrons and of α particles in passing through matter. If a narrow beam of α rays or of cathode rays—the latter, from the window of a Lenard tube, for instance—passes through a high vacuum it preserves a well-defined conical or cylindrical form, and gives a spot with sharp boundaries on a phosphorescent screen or photographic plate. The introduction of matter, either in the form of a gas or of a thin metal foil, causes the beam in either case to become diffuse, like a ray of light in a turbid liquid : the spot on a screen loses its sharp edges, the rays being spread over a comparatively large area and presenting the phenomenon known as *scattering*. In the case of both α rays and cathode rays an apparent reflexion of the rays takes place at solid surfaces, which proves to be, however, due to particles which have been turned back through more than $90°$ by the scattering process.

Both classes of particle in general produce ionisation in gases through which they pass, due to the release of electrons

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* The velocity of a cathode particle is generally given in volts, the meaning of this being that the velocity in question would be acquired by an electron moving *freely* through a potential difference of the specified number of volts. For low electronic velocities $\frac{1}{2}m_0v^2 = eP$, where P is the potential difference, or $\frac{1}{2}\frac{m_0}{e}v^2 = P$. Remembering that 1 volt $= 10^8$ electromagnetic units we have

$$v^2 = \frac{2\,Pe}{m_0} = 2 \times 1.760 \times 10^7 \times 10^8 V \quad \text{or} \quad v = 5.93 \times 10^7 \sqrt{V}$$

where V is the potential in volts.

For large velocities this simple formula does not hold, since the mass then increases with the velocity. The kinetic energy of the electron is then given by $m_0c^2\left(\dfrac{1}{\sqrt{1-\beta^2}} - 1\right)$, where $\beta = \dfrac{v}{c}$, and c is the velocity of light. In Appendix II. is given a table comparing the velocity of an electron expressed as a fraction of the velocity of light, and in volts.

from the atoms encountered : these electrons become attached
to other atoms, and so positive and negative carriers—generally
called ions, although their method of production is not that of
ions in electrolytic solutions—are formed.   If the velocity of
the particle fall below a certain limit no ionisation is produced.
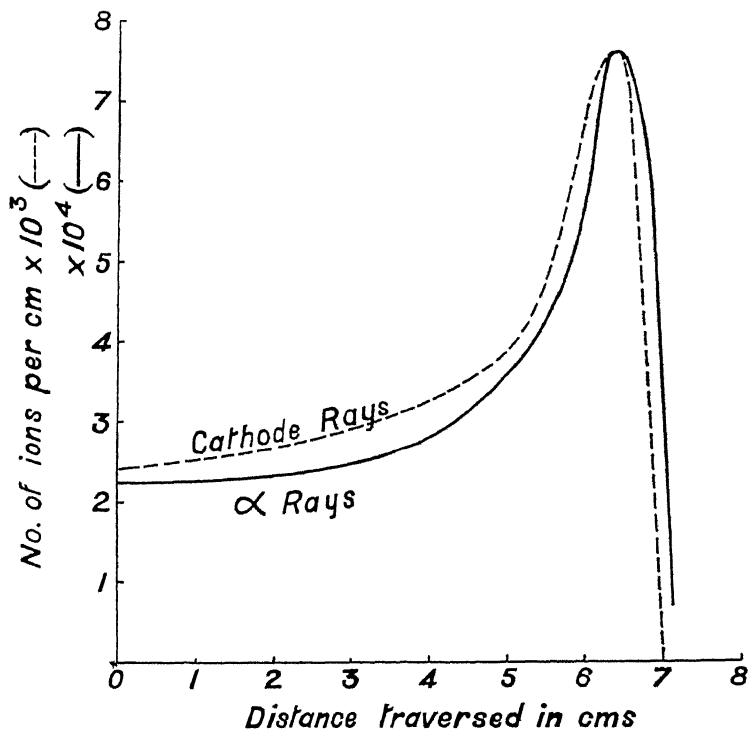
FIG. 1.

Comparison of ionisation produced by a moving electron and by an
α particle.   The ordinates are to be multiplied by 10^3 and 10^4
respectively to give the number of ions.

Further, there is an optimum velocity, approximately the same
for α particles and electrons, for which the greatest number of
carriers are produced per centimetre run of the particle, this
velocity being about $8\cdot4 \times 10^8$ cm./sec.   There is, in fact, a general
correspondence, pointed out by Ramsauer, between the two
classes of particles as ionisers.   The continuous line in Fig. 1
shows the number of pairs of ions produced by a single α

particle at different points of its path in air, which terminates at 7 cm.; the range of the particles in question. The velocity of the α particle at each point of its range can be calculated from Geiger's formula $v^3 = \cdot143(7-x)$; so that to every abscissa may be attached a velocity. If the number of pairs of ions produced by an *electron* of this velocity be plotted as ordinate, the dotted curve is obtained which, with suitable adjustment of ordinate scale, agrees very closely with the α particle curve. A single α particle gives rise to about ten times as many ions as an electron of the same velocity.

Both classes of particles are absorbed in passing through matter.* With both classes the velocity is gradually reduced by successive encounters with atoms. In the case of the α particles this reduction of velocity continues until the particle is reduced to gas-kinetic velocities, which happens after a certain approximately constant distance—the *range* of the particle—has been traversed. Very few particles are stopped or otherwise removed from the beam : the absorption is, for α particles, mainly a reduction of velocity. The flying electron also has its velocity reduced by passing through matter, but the absorption is here mainly a reduction of the number of particles, owing to a large number of them being abruptly removed from the beam in a way that will be considered later.

The fundamental idea to be found in all modern theories of the absorption and scattering of corpuscular radiations by matter is that the atom contains certain discrete centres of force—dynamids in Lenard's theories, electrons embedded in a uniform distribution of positive charge in J. J. Thomson's older theories, electrons and a heavy positive nucleus in Rutherford's atom—which deflect the moving corpuscle when it passes near them, and, in general, change its velocity. Both deflection and change of velocity obviously depend on the mass of the atomic centres of force in question, or, in the case of the electron, what comes to the same thing, the forces holding it in equilibrium in the atom. It is in the treatment of these forces, and

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* The question of absorption is often unnecessarily obscured by neglecting to distinguish between two different effects—a diminution of velocity of the particles, due to successive encounters with atoms, and a diminution of number of particles, consequent upon the stoppage and removal from the beam of some of them.

in the space distribution of the positive charge, that the various theories differ. Lenard's work will be described first, not only on account of its historical importance, but also because it enables us to make an estimate of the size of the nucleus, if we apply it to the nucleus theory. The remainder of the chapter is devoted mainly to the consideration of experiments establishing Rutherford's nucleus atom, which dominates present-day physics.

The Absorption of the Cathode Rays. When cathode particles pass through matter they issue from the absorbing sheet diminished firstly in number, and secondly in velocity. The two effects are best discussed separately, but unfortunately experimenters have not always been clear as to which effect they are observing. Measurements made by receiving the rays either in a Faraday cylinder or on a paraffin-wax-covered plate measure the charge, and hence the number of electrons : measurements—such as those of Whiddington—made with a cathode stream whose velocity is measured, before and after passage, by a magnetic field give the diminution of velocity ; but measurements made with the ionisation chamber give neither the one nor the other in the general case. For the number of carriers produced is a complicated function of the velocity of the primary beam (see Fig. 1), although for a fixed velocity it is proportional to the number of flying particles. Hence if measurements are made with beams of different velocity careful correction is necessary.*

Lenard has shown from a detailed study of the experimental results that the absorption of cathode rays, namely, the reduction to gas-kinetic velocity, is due in the main to the sudden removal of an electron from the beam by a single atomic encounter, and in a much less degree to the gradual reduction of velocity by repeated encounters. He therefore defines the absorption coefficient by the equation $J = J_0 e^{-ax}$, where J is the intensity, defined as the number of electrons falling per second on unit surface at right angles to the beam, x is the thickness

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* With sufficiently high velocity there is tertiary radiation produced by the secondary electrons liberated by the primary beam. If the chamber is deep, there are appreciable changes of velocity in the passage through the chamber itself of a penetrating radiation. These and other such-like effects are not always taken into account.

of absorbing material and a is the coefficient   This equation has been experimentally confirmed by Lenard and Becker: since the coefficient a is a function of the velocity it is necessary to work with thicknesses of absorbing material which do not much reduce the velocity, and to correct for such reduction as takes place.* Taking the coefficient of absorption as defined, measurements show an astonishing decrease of absorption with increasing velocity of the cathode beam. The following table, borrowed from Lenard, exhibits this. The values are smoothed values taken from curves embodying the observations of Lenard, Becker, Rutherford, H. W. Schmidt and others, made with photoelectric electrons, rays from a Lenard tube, and β rays from radioactive substances. The coefficient a is shown divided by the density of the absorbing substance. Absorption is approximately proportional to density—Lenard's "mass-absorption law"—and for the substances most used in absorption measurements, namely, air and aluminium, the proportionality is particularly close.

VARIATION OF ABSORPTION COEFFICIENT WITH VELOCITY

$\dfrac{v}{c}$	$\dfrac{a}{D}$	$\dfrac{v}{c}$	$\dfrac{a}{D}$	$\dfrac{v}{c}$	$\dfrac{a}{D}$
·90	6 gr.$^{-1}$ cm.^{2}	·55	1·3 × 10^2	·15	1·5 × 10^5
·85	9	·50	2·2	·10	8·0
·80	13	·45	4·0	·08	14
·75	19	·40	7·4	·06	25
·70	29	·35	14	·04	58
·65	49	·30	29	·03	86
·60	83	·25	86	·02	130
·55	130	·20	360	·01	180
		·15	1500		

Curves expressing the variation of absorption with thickness of foil, and also the loss of velocity of the flying electrons in passing through matter are given in Appendix I.

Now, from the kinetic theory of gases the number of encounters of a flying electron with gas molecules can be easily

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* a is a constant in the ordinary physical sense, for most constants—except universal constants—are parameters which vary with the defining conditions. Thus thermal conductivity varies with temperature, and at the same time demands a difference of temperature for its measurement.

calculated, assuming for the gas molecules the size found from considerations of viscosity and the like. It appears at once that a swift electron can encounter thousands of atoms without being either appreciably turned aside or stopped. A simple method of deducing this is to apply a theorem of Clausius, according to which, if small swift particles be fired through a layer of gas x cm. thick, having for the total cross-section of all the molecules in unit volume a value a, then a fraction e^{-ax} will get through without an encounter. Our coefficient a may therefore be taken to represent the absorbing cross-section per unit volume. Consider, for example, the rays of velocity 1.2×10^{10} cm./sec. in the table, for which $\frac{a}{D} = 740$, whence a for air at N.T.P. $= 740 \times .00129 = .95$. For air at N.T.P. the total molecular cross-section is about 18000 sq. cms. per c.c. of gas, and hence the cross-section which is effective as an absorber for rays of velocity 1.2×10^{10} cm./sec. is about a twenty-thousandth of the cross-section of the molecule. For swifter rays it is still smaller.

Sufficiently swift cathode rays can, therefore, pass freely through atoms. Over twenty years ago Lenard explained this result by supposing that atoms contain certain centres of force which he called *dynamids*, and considered to be composed of a single positive and a single negative charge, closely connected together. The electric force is very large in the neighbourhood of a dynamid, and comparatively weak elsewhere in the atom, so that swift cathode particles can pass freely through the "empty" bulk of the atom while the dynamids themselves behave as impenetrable to the swiftest rays. From the limiting coefficient of absorption a certain impenetrable cross-section of the atom may be calculated which gives the size of the hypothetical dynamids. Thus in the table given the least value of $\frac{a}{D}$ is 6, or for air at N.T.P. $a = .0078$. Comparing this with the total cross-section 18000 referred to above, we have

$$\frac{\text{cross-section of dynamids}}{\text{cross-section of atom}} = \frac{.0078}{18000} = 43 \times 10^{-8}.$$

Lenard supposed the dynamids to be distributed throughout the atom. If we adopt the Rutherford model, and consider that there is in each atom one nucleus which we may take for the moment as impenetrable to the fastest cathode ray, we have for its linear dimensions a quantity of the order 7×10^{-4} times the linear dimensions of the atom, or, since the diameter of the molecule of nitrogen is about 3×10^{-8} cm., the diameter of the impenetrable part, taken as a whole, is of the order 2×10^{-11} cm.—or rather is less than 2×10^{-11} cm., since the least coefficient of absorption in the table has been taken, while for still faster rays the coefficient may be somewhat less. Rutherford's latest estimate of the diameter of the nucleus of light atoms is approximately 5×10^{-13} cm., or about one-fortieth of this. For so indefinite a thing as the diameter of the nucleus this is very fair agreement. Rutherford's estimate is based upon the behaviour of the nucleus towards the α particle, our adaptation of Lenard's upon that towards the cathode particle, and there is no particular reason to expect the two to agree exactly. The nucleus is not a minute, round, hard billiard ball.

It may well be asked by what mechanism the absorbing cross-section of which we have spoken removes an electron from the beam. The assumption already used, that the removal is due to a single encounter, is strongly supported by the observation that a beam of homogeneous velocity retains approximately its homogeneity after passage through a sheet of matter, if the experimental conditions exclude disturbing forces, such as electro-magnetic waves. If the removal of an electron from the beam were the result of a *gradual* diminution of velocity to gas-kinetic magnitude by successive encounters, there would always be present in the emergent beam electrons of different velocities; for instance, those of very small velocity, which would have been removed had the sheet been a little thicker. Supposing then that the removal is the result of a single encounter, are we to assume that the electrons passing near the nucleus are turned through a large angle with practically undiminished velocity, as we shall see is undoubtedly the case with α particles, or are they removed from the beam by a sudden diminution of velocity? Lenard believes in the latter alternative. Of course

if the nucleus be a positively charged sphere,* and the original direction of the electron pass through, or within a certain small distance of the sphere, the electron will be captured and so removed. If the original direction pass a little further from the sphere, the large change of direction of velocity will take place without diminution of velocity, as considered in greater detail when the α particle is discussed. Both effects probably contribute to the absorption. The question, so far as I know, has not been carefully discussed, and it is much too complicated for discussion here.

The cathode ray absorption experiments have not so far yielded the clearer and more detailed information supplied by Rutherford's experiments on the α particle, but they supplied the first evidence of the " empty " behaviour of the atom towards high-speed particles, and, as we have seen, can be made to furnish a rough estimate of the size of the nucleus, whatever may be the exact mechanism by which the absorption is effected.

The α Particle. Single and Multiple Scattering. The nucleus atom model was originally put forward by Rutherford on the evidence of his experiments on large angle scattering of α particles. The scattering which these undergo can be investigated in much more detail than that of cathode particles. It is well known that α particles, falling on a phosphorescent screen, usually of zinc sulphide, produce discrete scintillations which can be observed through a low-power microscope, and it has been proved that the arrival of a single α particle produces one scintillation. Hence we have a method of counting, and observing the position of, single particles which is denied us in the case of the cathode particles. That the radioactive elements supply strong sources of α rays of fixed initial velocity has its advantages, since there is no need to use any device, such as the magnetic resolution usual with cathode rays, to obtain a homogeneous pencil: on the other hand, we have not the wide range of velocity available with cathode rays.

When a narrow beam of homogeneous α rays from a thin film of Radium C, say, falls on a metal foil the rays are scattered,

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* *I.e.* if the non-uniformity of the field close to the nucleus, which contains both positive and negative electricity, be neglected.

and the distribution can be quantitatively fixed by counting the scintillations produced in directions making various angles with the original beam. This method was extensively used by H. Geiger, and by Geiger and Marsden, in their pioneer investigations on the subject. Now, it is observed that not only do some of the particles which penetrate the foil make large angles with the original direction, but that also a certain very small fraction of the incident particles are scattered through so large an angle that they do not penetrate the foil, but emerge on the side of the incidence. The greater the atomic weight of the metal of the foil, and, within limits, the greater the thickness of the foil, the greater the fraction turned back, which shows that the " reflection " is a volume, and not a surface, effect. The number of particles scattered through a large angle, say 30° (a small range of angles about a mean deflection is, of course, taken) in the forward direction, is, within experimental error, proportional to the thickness of the foil, as is shown in the following table for gold foils.

Number of foils.	Air equivalent ($= T$).	No. of scintillations in given direction ($= N$).	$\dfrac{N}{T}$
1	·11	21·9	200
2	·22	38·4	175
5	·51	84·3	165
8	·81	121·5	150
9	·90	145	160

Similar results have been obtained with other metals. This result is a decisive one for the theory of single scattering.

If, with a given foil, the number of particles scattered through various *small* angles (a few degrees) be observed, which can be done by counting the number of scintillations on a given small area taken at different distances from the centre, it is found that the distribution obeys the laws of probability. There is a most probable angle of scattering varying, with the material and thickness of the foil, from half a degree or so to a few degrees, and the number of particles scattered through angles on either side of this is compatible with the theory that the scattering is due to a *large number of random small deflections* undergone

by each particle as it traverses the foil (a mechanism usually referred to by the name of multiple scattering). The most probable angle for a given foil having been found, the chance of a deflection of 90° or more can be calculated on the assumption of multiple scattering, and is found to be vanishingly small, so small that the large angle scattering of 30° or more would never be observed in the ordinary course of experiment. This fact, that the number of large angle deflections observed is incompatible with the relative number and distribution of small deflections observed, if the final scattering be assumed to be the result of a large number of small scatterings, forms the starting-point of Rutherford's reasoning. From it he deduced the essential consequence that the large angle deflections are due to encounters with a single atom.

To get the intense field of force necessary to deflect an α particle through the large angles observed Rutherford assumed a massive nucleus, very small in comparison to the atom itself, the remainder of the atom being made up of rings of electrons whose rotation prevents them being drawn in by the positively charged central sun, though there is nothing in the scattering experiments alone to indicate a rotation rather than a statical distribution. The swift α particle, which is itself a nucleus,* and hence very small, can pass freely through the bulk of the atom, just as can the swift electron. It suffers very small deflections when passing near the electrons of the atom, but will experience a large deflection when passing very close to the nucleus. For the present purpose, which is to consider the large angle scattering, we can neglect the electrons. To examine the angle of deflection due to the nucleus consider a massive point K, with a positive charge Z times the electronic charge e, which repels a particle of mass M and positive charge E approaching with velocity v along a path which, far removed from K, has a direction PO (Fig. 2). If the inverse square law be assumed, the path will be a hyperbola, of which PO is one asymptote, and $P'O$, which gives the path of the emerging particle when a long way from K, the other asymptote. Let p

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* The α particle is a helium atom with two positive charges. Since, as we shall see, the neutral helium atom has only two extranuclear electrons, a doubly charged atom has no extranuclear electrons, or is nucleus only.

be the length of the perpendicular KS, which we may call the impact parameter, $\varphi = P'OS$ be the angle through which the particle is deviated, and a the semi-transverse axis.
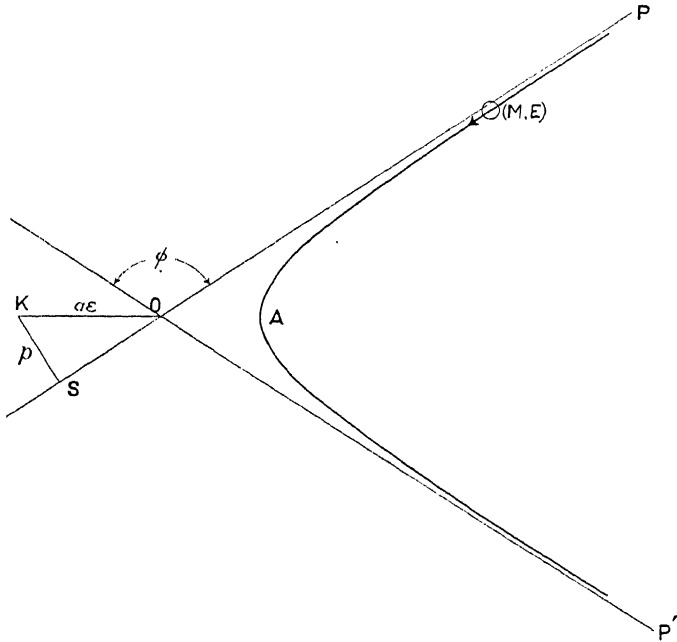

FIG. 2.

Then from the geometry of the hyperbola the eccentricity =

$$\epsilon = \operatorname{cosec} \tfrac{1}{2}\varphi$$

and

$$p = a\epsilon \cos \tfrac{1}{2}\varphi = a \cot \tfrac{1}{2}\varphi.$$

By the simple dynamics of the central orbit, if μ is the acceleration at unit distance, then

$$v^2 = \frac{\mu}{a} = \frac{ZeE}{Ma};$$

$$\therefore \ p = \frac{ZeE}{Mv^2} \cot \tfrac{1}{2}\varphi, \quad \dots\dots\dots\dots\dots\dots(1)$$

which gives the angle of deflection corresponding to a given impact parameter and a given velocity. It is to be noted

that if b be the distance from K at which the particle would be brought to rest momentarily if it were fired direct at K, then

$$0 = \frac{\mu}{a} - \frac{2\mu}{b}$$

or

$$b = 2a = \frac{2\,ZeE}{Mv^2} \; .$$

Equation (1) can therefore also be written

$$\cot \tfrac{1}{2}\varphi = \frac{2p}{b} \; . \quad \dots\dots\dots\dots\dots\dots\dots (1a)$$

The formula (1) or (1a) for the deflection holds, it so happens, whether the charges of the nucleus and approaching particle be of the same or of opposite signs.   In the case of the a particle there is no doubt that they are of the same sign.

Now if n be the number of atoms per unit volume and t the thickness of the foil, then $1/nt$ is the average area of foil surface dominated by one nucleus. Hence the chance that an a particle in traversing the foil passes at a distance between p_1 and p_2 from a nucleus is*

$$q = \pi(p_1{}^2 - p_2{}^2)nt,$$

and the fraction deviated between angles φ_1 and φ_2 is

$$q = \frac{\pi}{4}\,ntb^2\,(\cot^2 \tfrac{1}{2}\varphi_1 - \cot^2 \tfrac{1}{2}\varphi_2).$$

Since the scintillations are usually counted on a screen perpendicular to the direction of the scattered rays, for all angles, we will express the scattering as the number of scintillations on a small unit area distant r from the point of incidence of the rays on the scattering foil, and normal to the radius vector r.   The area cut off between angles φ_1 and φ_2 on a sphere of radius r is

$$2\pi r^2 (\cos \varphi_1 - \cos \varphi_2) = 4\pi r^2 (\cot^2 \tfrac{1}{2} \varphi_1 - \cot^2 \tfrac{1}{2}\varphi_2) \sin^2 \tfrac{1}{2}\varphi_1 \sin^2 \tfrac{1}{2}\varphi_2.$$

Hence, out of a total number of particles Q falling on the foil, the number per unit area at distance r on a screen normal to r is

$$\frac{Qnt\,b^2}{16r^2 \sin^2 \tfrac{1}{2}\varphi_1 \sin^2 \tfrac{1}{2}\varphi_2} \; .$$

* Rutherford in his original paper uses m for both mass of particle and probability.

When the area is small, so that φ_1 and φ_2 can be taken as sensibly equal, this becomes

$$\frac{Qnt\, b^2 \cosec^4 \tfrac{1}{2}\varphi}{16r^2}.$$

Hence the number of particles per unit area of phosphorescent screen (always normal to the particular direction considered) at a distance r defined as above, should be, on the assumptions made, proportional to

(1) $\cosec^4 \tfrac{1}{2}\varphi$;

(2) thickness t of scattering material, provided that this is so small that the α particles scattered through large angles have only a small chance of a second encounter ;

(3) square of the central charge Ze ;

(4) the reciprocal of $(Mv^2)^2$, or $1/v^4$ if M be constant.

Experiments by Geiger, both working singly and in collaboration with Marsden, have confirmed these results very well. The number of α particles emerging from a scattering foil at an angle φ has been found to vary as $\cosec^4 \tfrac{1}{2}\varphi$ for angles ranging from 5° to 150°, for which the number of particles varies from 250,000 to 1 (the distances had to be increased considerably at small angles to reduce the scintillations to countable numbers). For small thicknesses the number scattered is directly proportional to the thickness, but for larger thicknesses the decrease of velocity causes a somewhat more rapid increase in the amount of scattering. This proportionality is of particular importance, for the relation between scattering and thickness forms a crucial test of the theory of single scattering, which itself is essential to the nucleus atom. Single scattering gives a direct proportionality between the number scattered and the thickness. The hypothesis of multiple scattering, on the other hand, leads to the conclusion that the number of α particles scattered in a given direction should be proportional to the square root of the thickness.

The scattering per atom, when foils of different materials are in question, is approximately proportional to the square of the atomic weight. It will be shown later that from this, and from the quantitative results as to the numerical fraction of particles

scattered through a large given angle (45°, say), it can be deduced with the help of Rutherford's equation (1) that Z is equal to the atomic number, which is in agreement with later very reliable results. A proportionality to Z^2 is thus indirectly confirmed. The proportionality to the inverse fourth power of the velocity of the incident α particle was directly confirmed.

Rutherford's assumption of a heavy, positively charged nucleus, and consequent occasional single scattering through a large angle, has been strikingly confirmed by photographs of the tracks of α particles in gases. These can be made visible by the method, devised by C. T. R. Wilson, in which, by means of a sudden expansion, condensation of water in minute drops is produced on the ions formed by the passage of the α particle. C. T. R. Wilson's well-known photographs show towards the end * of some of the α-ray tracks in air abrupt changes of direction through large angles, quite inconsistent with multiple scattering, but in accord with the theory developed above. These photographs do not allow of quantitative calculations, but exhibit other interesting features, such as a short " spur " at the point where the direction of track changes abruptly, to be attributed to ionisation produced by the struck nucleus in its path. Recently Blackett, by an elaboration of the method, has obtained valuable quantitative results. To find the angle through which the particle is turned at a close encounter it is not sufficient to take a single photograph, since this is in general a perspective picture of the true track, the plane containing the path before and after impact not being parallel to the plane of the plate.† Blackett, following Shimizu, takes, by means of an arrangement of mirrors, two views of the same tracks, as seen from mutually perpendicular directions, through the same lens on the same plate. By geometrical methods it is possible to deduce, from the two

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* Since the chance of a deflection through a given large angle is inversely proportional to the fourth power of the velocity, such deflections are to be expected near the end, rather than the beginning, of the range.

† This perspective effect has been held by Lenard (*Quantitatives über Kathodenstrahlen*, p. 240), to invalidate the general conclusions drawn by Rutherford from C. T. R. Wilson's original photographs. Such criticism has been completely stultified by the work of Shimizu and of Blackett.
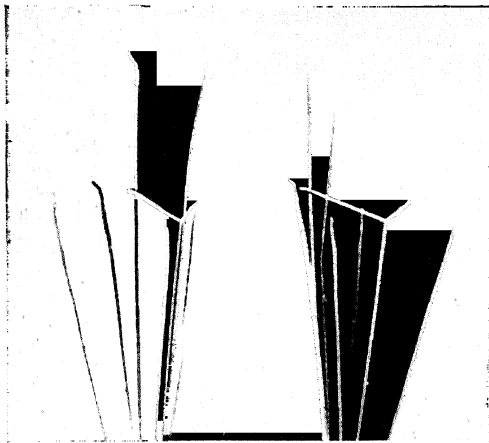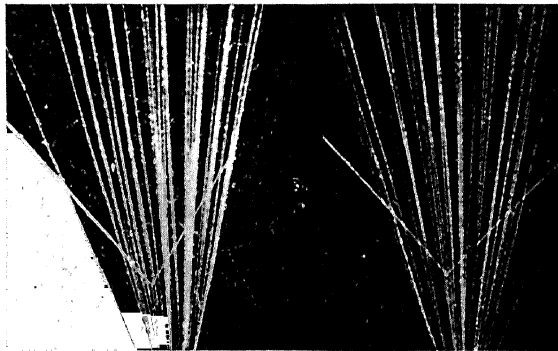
PLATE I

FIG. 1.

FIG. 2.

Double Photographs of Forked α-Ray Tracks.   (Blackett.)

Fig. 1.   Forked Track in Oxygen.
Fig. 2.   Forked Track in Helium.

projections thus obtained, the true angle. Fig. 1, Plate I., shows one of Blackett's photographs of α particles in oxygen. The second track from the right in the right-hand group, and the fourth track from the right in the left-hand group are the two different views of the same very definite forked track.   The long branch of the fork represents the track of the α particle after collision, the shorter branch the track of the struck oxygen nucleus.   For this particular track the true angle which the former makes with the original direction of the α particle is 76° 6', the angle which the latter makes is 45° 12'. Knowledge of these angles enables us to calculate the relative masses of the striking particle and the struck particle, if we assume that the ordinary laws of mechanics for perfectly elastic bodies (conservation of energy and of momentum) govern the impact.*   The mass of the recoil atom in the case of oxygen here considered is in this way found to be 16·72, with a probable error of ·42, which is in sufficiently good agreement with the known mass of the oxygen nucleus, 16.

Interesting results have likewise been obtained by Blackett with helium.   Here the mass of the striking and the struck nucleus are equal, and it can easily be proved that in this case the paths of the two after collision must be at right angles double to one another.   Fig. 2, Plate I., is one of Blackett's more recent photographs of α rays passing through helium ; a splendid forked track will be seen well represented in each of the two views.   The angle between the two branches of the fork is 89° 27', which gives for the ratio of the mass of the struck helium nucleus to that of the α particle ·981 instead of 1. In general we may say that these experiments not only make visible the large single scattering postulated by Rutherford, but also confirm the assumption that it is due to close impact between nuclei, governed by the ordinary laws of mechanics for perfectly elastic spheres.   Each forked track provides, among other things, a determination of the mass of a single nucleus.   A sufficiently large number of photographs could be made to afford a quantitative determination of isotopes in a gas like chlorine, but the method is not very practicable.

* Cf. the second of the two equations (1), Chapter IV., which also leads at once to the result for impact on a helium atom quoted on the next page.

Size and Charge of Nucleus from Scattering Experiments.
It will have been observed that, in the deduction of equation (1), Coulomb's inverse square law was assumed. The close agreement with experiment furnishes a very strong reason for presuming that the law holds down to the subatomic distances (in the case of gold it holds apparently for distances between 36×10^{-12} and 3×10^{-12} cms.) considered in these calculations. This is somewhat astonishing in these days when the general tendency is to explain all difficulties by reference to the limited validity of the classical laws of electricity and mechanics.

It is important to form an estimate of the size of the positively charged nucleus which, from the assumptions already made, is small compared to the size of the atom, as deduced from ordinary kinetic theory The experimental confirmation of the assumption that the force exerted by an atom is $X = \dfrac{Ze}{r^2}$ (neglecting the action of the extranuclear electrons), where r is the distance from the centre of the nucleus, allows us to make a simple calculation of the distance b within which an α particle can approach a heavy nucleus. Taking the gold nucleus, the motion of which when struck by an α particle can be neglected, we have for b

$$\tfrac{1}{2}Mv^2 = \frac{ZeE}{b} ,$$

or $\qquad \tfrac{1}{2} \times 6 \cdot 56 \times 10^{-24} \times 2 \cdot 09^2 \times 10^{18} = \dfrac{79 \times 2 \times 4 \cdot 77^2 \times 10^{-20}}{b} \cdots ,$

the atomic number (nuclear charge) of gold being 79, and the velocity of the α particles from Radium C, with which the experiments were carried out, being $2 \cdot 09 \times 10^9$ cms./sec.

From this $b = 3 \times 10^{-12}$ cms. Since the distribution law deduced for scattered α particles holds right up to angles of deflection of $150°$, when the α particle must approach within about this distance, we know that the inverse square law must hold even for such close approach, which enables us to infer an upper limit for the size of the nucleus. The diameter of the gold nucleus must, thus, be less than 3×10^{-12} cms. Incidentally the distance of approach for the smallest

scattering angle measured, $5°$, is about 36×10^{-12} cms. for gold, which indicates that the space between these two limits is free from all forces except that of the nucleus, and so cannot contain any concentration of electrons. From the photographic study of forked tracks Blackett has deduced that the inverse square law holds between the nucleus and the a particle when their distance apart lies between about 7×10^{-12} and 10^{-9} cm. for argon, and 3×10^{-12} and 5×10^{-10} cm. for air.

Collision with light atoms also affords us information as to nuclear magnitudes. Considerations similar to those given above, but allowing for the motion of the struck nucleus, would lead us to deduce for the hydrogen nucleus a radius of about 10^{-13} cms. But the experiments on firing a particles into hydrogen molecules, and knocking hydrogen nuclei forward, which are discussed in Chapter IV., have been made by Rutherford to show that the inverse square law no longer holds when the approach is within a distance of 3×10^{-13} cms. This points to a deformation of the nucleus by the enormous forces set up, and we may take this distance as being the diameter of the nucleus. Of course no very precise meaning can be attached to the expression " diameter of the nucleus," any more than to the " diameter of an atom," but just as in the kinetic theory there is, for ordinary velocities, a certain distance of closest approach (varying somewhat with the variations of velocity which accompany changes of temperature) which we call the diameter of the molecule, so in subatomic physics we may call the distance of closest approach, without deformation, obtained with a particles, in the case of whose energy the extranuclear electrons have a vanishing influence, the diameter of the nucleus. The quantity obtained is actually radius of helium nucleus +radius of struck nucleus, but for rough measurements of this kind all nuclear radii may be taken as equal as a first approximation. Rutherford gives it as his opinion that the nuclei of light atoms other than hydrogen are of the order 5×10^{-13} cms. in diameter. Taking 10^{-8} cms. as approximate atomic diameter the minuteness of the nucleus at once appears.

A somewhat more elaborate scheme has been adopted by Bieler in discussing his recent experiments on the large-angle

scattering of a particles by light nuclei. The object of these experiments is to investigate quantitatively the failure of Coulomb's law in the case of close approach of the nuclei, and it can easily be proved that the lighter the struck nucleus the smaller the apsidal distance corresponding to a given angle φ (see Fig. 2), or, in general terms, the less the atomic weight of the substance of the foil, the closer the approach of the nuclei. Foils of aluminium and magnesium were therefore used, the experimental arrangement being that adopted by Chadwick and Bieler for investigating the distribution of expelled protons (see page 84). The immediate object was to compare the number of a particles scattered at various angles with that to be expected if the inverse square law held at all distances. Since it is known from the experiments of Chadwick that the scattering by heavy nuclei, such as gold, gives the distribution to be anticipated if Coulomb's law were obeyed, the plan adopted was to compare the number of particles scattered by the light metal foil with the number scattered by a gold foil through the same angle, the angle being varied by using annuli of different sizes, isolated by suitable diaphragms.

It was found that while for small angles of scattering (where, of course, the approach of nuclei is not very close) the ratio was constant, for large angles the number scattered by the nuclei of the light elements was smaller than it should be if the inverse square law were obeyed. Bieler concludes that the divergence from this law manifested in the scatter ing results can be expressed quantitatively by supposing that the nucleus possesses, superposed on the Coulombian field, another field of force of the reverse sign (*i.e.* corresponding to an attraction of the positive charge), varying as the inverse fourth power of the distance. The result of such a field is that at a certain distance from the centre of the nucleus there is a neutral surface, outside which there is a net repulsion on a positive charge, while inside there is a net attractive force for the positive charge. The radius of this surface works out as $3 \cdot 44 \times 10^{-13}$ cms. for aluminium. Hence at a distance of $3 \cdot 44 \times 10^{-12}$ cms. this additional inverse fourth power force is only one hundredth of the Coulombian force, while at a distance no

greater than $3 \cdot 44 \times 10^{-11}$ cms. it has sunk to one ten thousandth of the Coulombian force. This general result, that the inverse square law holds to within one per cent. or so for distances greater than 3×10^{-12} cms. from the centre of the nucleus, but breaks down at smaller distances, is consistent with what has gone before.

It has been mentioned that, on the assumption of single scattering, which has been so abundantly justified, it is possible to calculate the nuclear charge from the fraction of particles scattered through a given angle under definite conditions. In the equation (1), putting in the value of b, we have: fraction of incident particles which, having been deflected through angle φ, fall on unit area of phosphorescent screen,

$$= \frac{y}{Q} = \frac{nt 4 Z^2 e^2 E^2 \operatorname{cosec}^4 \frac{1}{2}\varphi}{M^2 v^4 \, 16 r^2} .$$

The number n of atoms in unit volume of the metal of the scattering foil is known from the atomic weight and the density, and e, E and M are accurately known, so that counts of the number of particles scattered at a known large angle enable Z to be calculated. Chadwick, repeating in modified form earlier less accurate experiments, has measured by such counts Z for three different metals, namely, platinum, silver and copper. He finds values 77·4, 46·3, and 29·3 respectively. The atomic numbers of the elements in question are 78, 47, and 29, so that these experiments give a direct proof that the nuclear charge is equal to the atomic number, a fact which is fundamental for modern atomic theory. It will be noted that the formula contains the assumption that the struck nucleus does not move : as a matter of fact the correction necessary if the movement of the struck nucleus is considered has been calculated, but for the lightest atom in question, copper, it is quite negligible.

In short, the scattering of the α rays has been worked out fully on the assumptions that

(1) the atom consists of a nucleus very small in comparison with the atom, surrounded by electrons with large interspaces ;

(2) the mass of the atom is concentrated in the nucleus ;

(3) the net positive charge on the nucleus is equal to the atomic number ;
and the calculated results are everywhere in accord with experiment. Rutherford's original paper is a striking example of the confidence of the great investigator—of the neglect of inessential detail which has its root in intuitive perception, and which seems rash to the timid until repeated experimental support furnishes abundant justification. Rutherford takes no account of the action of the surrounding electrons on the a particle either by electrostatic or by the magnetic action implied in the rotation of the electrons in closed orbits. The possibilities that the accelerated passage of the a particle shall be accompanied by a radiation of energy either from the particle or the atom traversed are not discussed. In spite of the alarming complexity of the problem presented by, say, a gold atom, the simplicity of the assumptions has not prevented them covering in outline, at any rate, the many different numerical aspects of the scattering of a rays, and offering the foundation for a large body of successful work in other directions.

It may be added that Rutherford and Nuttall deduced the nuclear charge of hydrogen and helium from measurements of the scattering of a rays by gases. A beam of rays is sent between close parallel glass plates, immersed in the gas under investigation, and the ionisation produced by the emergent beam measured in a separate chamber. The gas atoms deflect a certain fraction of the a particles against the plates, which fraction is accordingly absent from the emergent beams, with corresponding loss of ionising power. Allowance being made for absorption in the gas a number is finally obtained which is a measure of the scattering, not, of course, through one fixed angle, but through a range of angles the same in all experiments, which allows the deduction of a relative scattering coefficient for different gases. The scattering was found to vary directly as the pressure and inversely as the fourth power of the velocity, which indicates that the effect is mainly due to single scattering rather than multiple scattering. From the numerical results it was calculated that, assuming the carbon atom to contain six electrons, the hydrogen atom contains one, the helium atom two electrons. In calculating the scattering through the small

angles in question in these experiments* the effect of the scattering by the electrons has to be considered, although it can be neglected in the case of large angle scattering, since encounter with an electron cannot turn an α particle through a large angle.

The Scattering of β Particles. Experiments show that, like the α rays, electrons travelling with high velocity undergo scattering in their passage through both solid foils and gases, and that both small angle scattering, and the rarer large angle scattering (Lenard's " Rückdiffusion ") occur. The study of the scattering in the case of β particles has not led to results of such fundamental importance as in the case of α particles, yet the large amount of work carried out has provided some valuable supplementary information, and deserves consideration here on account of the more precise treatment of the scattering problem to which it has led. Detailed experimental investigation is more difficult with β particles than with α particles, since with the former no method of detecting single particles, corresponding to the scintillation method used with the latter, is available, nor is a source of β particles of homogeneous velocity obtainable without magnetic resolution. Again, the question of single as against multiple scattering is less easily disentangled for β than for α particles, and the effect of the electrons of the scattering atoms comes into more prominence than it does for the single scattering of α particles. There are further points, such as the variation of the mass of the β particles with velocity, which will receive mention as they occur.

The realisation of the conditions for single scattering with β particles is very troublesome. Experiments have been carried out by Geiger and Bothe, and by Bothe. Homogeneous rays were obtained by resolution in a magnetic field, and the distribution of the scattered rays was measured photographically, the blackening of the plate for rays scattered through different angles being compared with the blackening obtained under standard conditions. For large angles, where long exposures are needed on account of the relatively few particles scattered, the γ rays give trouble by their action on the plate, so for these experiments a strong deposit of radium E, which

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* With the apparatus used the angles of scattering mainly effective were of the order of one-tenth of a degree.

gives very feeble γ rays compared to the other radium products, was used. For very small thicknesses of scattering foil proportionality of the number of particles scattered in a given direction to the thickness of the foil was established, which indicates single scattering. The other laws expounded in the discussion of the large angle scattering of α rays have also been, by these experiments, confirmed in outline, but not in detail, for the large angle scattering of β rays, allowance being made for certain complicating factors. The same series of experiments showed clearly that for larger thicknesses of scattering foil the laws deduced theoretically for single scattering do not hold. Subsequently Chadwick and Mercier, using a somewhat different method, have confirmed these results with increased accuracy. The source used was radium E, adopted for the reasons just specified, but no magnetic resolution was utilised. The scattering foil was in the form of a ring, as in the experiments described on p. 84, and the number of particles scattered between 20° and 40° was measured by the ionisation produced in a hemispherical chamber as compared with that produced by the direct pencil, cut down to a suitable fraction by a rotating disc with a gap in it. The experimenters found, as did Geiger and Bothe, that the scattering through a given angle is proportional to the thickness as long as the foils are very thin, but that a departure from proportionality sets in for thicker foils ; that the scattering is proportional to the square of the atomic number ; and that the amount of the scattering is in agreement with the theory of single scattering, if the relativity correction necessitated by the high velocity of the β particles be taken into account. It may be held, then, that by using very thin foils the single scattering of β particles has been satisfactorily demonstrated.

Crowther and Schonland, both independently and in collaboration, have also carried out many experiments on β ray scattering, which they interpret in terms of single scattering. The method which these investigators use is to measure the angle Φ, which is such that half the total number of scattered particles are deflected through an angle greater than Φ ; Φ may, perhaps, be called the angle of half scattering. The disagreement of their results with the theory for single scatter-

ing led them to suppose that Coulomb's law breaks down in the neighbourhood of the nucleus at distances for which a ray experiments indicate that it still holds. Considerations which are now to be developed show, however, that the experimental conditions are not such that single scattering is to be anticipated, and it will be seen that there is no need for this assumption.

To reduce the various experiments on β ray scattering to order it is necessary to bear in mind, as has been pointed out independently by Wenzel and by Bothe, that single scattering and multiple scattering are merely two limiting cases of what may occur, the term "multiple scattering" being taken to imply a scattering brought about by a sufficient number of small independent deflections for statistical methods of computation to be valid, and a Gaussian distribution to be assumed. Between these two extreme cases there is the possibility that the number of deflections suffered by a single particle may be neither one nor very large; this is the case which Bothe calls *Mehrfachstreuung*, and which we may call plural scattering.* This case is naturally very troublesome to handle mathematically, and for a rays, when both extremes can be realised experimentally, it is of little interest. For β rays, however, as has already been stated, it is difficult to obtain the experimental conditions for single scattering, and the consideration of plural scattering has simplified the interpretation of certain results of Crowther's, and, in general, brought the various investigations into a unified scheme.

The factors which determine whether in any particular case single scattering may be taken as the effective mechanism are the thickness of the scattering foil, and the smallest angle included in the distribution to be covered by the theory. This is immediately evident when it is considered that deflection at a single impact through a given angle means passage within

*The Germans use the words *Einzel-*, *Mehrfach-*, and *Vielfach- streuung*, corresponding to which, if the above suggestion be adopted, we shall have single, plural and multiple scattering. The notation is not very satisfactory, since there is no real distinction in the meaning of the words, as ordinarily used, either between *mehrfach* and *vielfach*, or between plural and multiple. Few-fold scattering would convey clearly what is meant for the intermediate case, but I hesitate to propose such a word.

a certain distance of a nucleus, and so for single scattering to prevail the scattering foil must be so thin that the chance of the particle passing within this distance of more than one nucleus is very small.   More definitely, it may be said that for a thickness t of foil the condition for single scattering is fulfilled if it is improbable that the swift particle passes more than once within a certain distance p of a nucleus, where p is fixed by the condition that, if a deflection ψ corresponds to passage at this distance from the nucleus, then 4ψ is less than φ, φ being the smallest angle of deflection included in the experimental data.   For a foil of given material and thickness p can at once be found, since $nt\pi p^2 = 1$, while formula (1) gives the angle ψ corresponding to distance p.   Hence the minimum φ can be calculated for any given experimental conditions.   For instance, in Chadwick's experiments on the scattering of α particles ψ turns out to be somewhat less than $1°$, whereas the smallest angle of scattering considered was about $21°$, so that the hypothesis of single scattering is amply justified in these experiments.

In the case of Crowther and Schonland's experiments, however, similar considerations lead to the conclusion that the hypothesis of single scattering is not justified, but that rather, for the angles measured, plural scattering must occur, the degree of departure from single scattering varying, of course, with the thickness and material of the foil.   Wenzel and Bothe have both concluded that the results are not in conflict with Coulomb's law, if the effect of the electrons in the scattering atom be taken into account.   The simplest assumption to make for the purpose of calculation is that the negative electricity is uniformly distributed throughout a sphere of the size of the atom, surrounding the nucleus : this will give a first approximation to the distribution to be anticipated on Bohr's present views of interpenetrating orbits.   Since only the electrons in a cylinder described about the path of the β particle as axis with a radius small compared to the size of the atom have an appreciable direct effect on the particle, it can be shown that the direct deflection produced by this distribution of electricity is negligible, so that the only effect of the electrons which need be considered is the shielding of

the nuclear charge. Bothe has deduced for small deviations the formula

$$\varphi = \frac{aZ}{p}\left(1 - \frac{p^2}{R^2}\right)^2,$$

where $a = \dfrac{2e^2}{mv^2}$ and φ is the angular deflection, assumed small, R is the radius of the atom, and p the distance of the path from the nucleus. If Φ is Crowther's "angle of half scattering," then for single scattering

$$n\pi p^2 t = \tfrac{1}{2}$$

and

$$\Phi = \sqrt{2} \cdot a\, Z \sqrt{\pi n t}. \qquad\text{..........................(2)}$$

For multiple scattering, which occurs for comparatively thick foils, the Gaussian law of distribution is obeyed, and calculation shows that, approximately

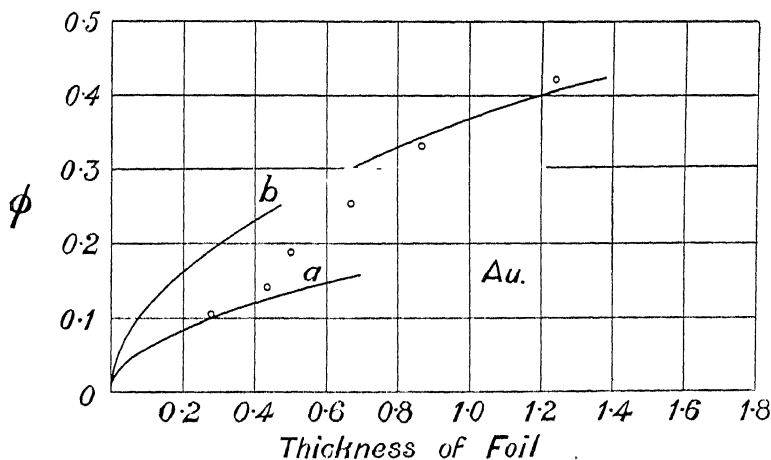$$\Phi = 2 \cdot 6\, a\, Z \sqrt{\pi n t}. \qquad\text{..........................(3)}$$

FIG. 3.

Scattering of β rays by gold foils, compared with theory.

Hence both for single and multiple scattering Φ is proportional to $\sqrt{t}$,* but the constant of proportionality is about

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* Of course for single scattering the number of particles scattered in a given direction is proportional to t, and not to $\sqrt{t}$, but this number must not be confused with Φ.

1·8 times as great in the latter case as in the former, for the same scattering material. For plural scattering the value of the constant is intermediate between $\sqrt{2}$ and 2·6. Bothe has shown that, when Φ is plotted against t, the results of Crowther and of Crowther and Schonland lie, in fact, between the parabola given by (2) and that given by (3), being on the single scattering curve for small thicknesses and on the multiple for large thicknesses, as is to be expected from theoretical considerations. Fig. 3 shows the results for gold foils. In short, whether single, plural, or multiple scattering occurs or not is merely a question of the thickness of the foil and the magnitude of the angles measured. Detailed considerations, of which the type has been sketched above, show that there is no need to question the validity of Coulomb's law,* nor to consider a magnetic moment of the nucleus, as suggested by H. S. Allen, in order to explain the β particle scattering results.

The *small* angle scattering of a particles, studied by Geiger, can be calculated theoretically on the same lines as the scattering of the β particles, by treating the atom as a massive nucleus surrounded by a sphere of uniform negative electrification. According to the theory developed by Bothe the expression $\dfrac{\Phi}{\sqrt{t}} \cdot \dfrac{Mv^2}{E}$ is constant for a given scattering material, where Φ is the angle of half scattering, and M, E and v are the mass, charge and velocity of the scattered particle. The following table shows that the agreement between the results obtained with α and β particles is very fair. It is

Ray.	Experimenter.	$\dfrac{\Phi}{\sqrt{t}} \cdot \dfrac{Mv^2}{E} \times 10^{-14}$
α	Geiger.	3·3
β	Crowther.	3·87
β	Crowther and Schonland	3·81
β	Schonland.	3·92
β	Geiger and Bothe	4·4

* For the exceedingly close approach to the nucleus which occurs with a swift α particle fired straight at the nucleus, Coulomb's law does, however, break down. See Chapter IV.

assumed that true multiple scattering takes place in both cases, which is justified by the thickness of the foil and the small angles considered in Geiger's experiments.

The theory of the scattering of α and β particles so far considered still makes considerable assumptions, even when the nature of the scattering—single, plural, or multiple—has been taken into account. It has already been pointed out that, while the shielding action of the atomic electrons on the nuclear charge has been estimated,* the direct deflecting action of the electrons has been neglected. This has been justified, since it is shown that this action must be very small compared to that of the nucleus. It is further assumed that the collision is governed by the same laws as the impact of perfectly elastic bodies, which is equivalent to neglecting all loss of energy due to possible radiation or absorption : this assumption has been strongly supported in the case of swift α particles by experiments already described. It is well known, however, that it would lead to erroneous results in the case of the passage of slow electrons through matter, for which Franck and Hertz have shown experimentally that inelastic collisions take place, but for the very fast β particles the percentage loss of velocity in the passage through thin foils is exceedingly small; and, again, experiments of D. L. Webster on the excitation of characteristic X rays have shown that for high electron velocities the chance of a quantum absorption of the electronic energy is very small. The consideration of the excitation of radiation by slower electrons, and their general behaviour on passing through matter, receives further attention later on in the book.

Of interest in connection with the swift electrons are certain recent experiments carried out independently by C. T. R. Wilson and by Bothe on the paths of β rays through gases, the tracks being photographed with the help of a Wilson expansion chamber. Both experimenters obtain three types of tracks : (a) those showing abrupt changes of direction through large angles, sometimes exceeding 90°, (b) forked tracks, similar

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* In the case of scattering through small angles. In the case of scattering of the α particles through large angles, i.e. of very close approach to the nucleus, experiment indicates that the space between the nucleus and the moving particle at its distance of closest approach is free from electrons, so that there is no shielding action. See p. 27.

to those exhibited in Blackett's photographs of α rays, even if not quite so sharply defined, (c) tracks showing a gradual curvature, due to a large number of small imperceptible deflections. The three types are illustrated in the photographs, taken by C. T. R. Wilson, reproduced in Plate II. The upper photograph shows a track with an abrupt change of direction of type (a), which elsewhere in its path shows the gradual curvature of type (c). The stereoscopic pair below show a fork of type (b). Tracks of type (a) correspond to deflections of the particle due to close approach to a nucleus, and Rutherford's theory can be applied to them, although, strictly speaking, a correction, which has been worked out by Darwin, should be applied to express the effect of the change of mass with velocity of the electron on the shape of the orbit. Wilson, using the simple theory, has deduced, from the fraction of the β particles observed in his photographs to be deflected through more than $90°$, the nuclear charge of the scattering atoms, and finds for it $6 \cdot 5e$, which is as close to $7e$, the nuclear charge of the nitrogen atom, as can be expected from the experimental conditions. Similarly Bothe, taking the nuclear charge as $7e$, calculates the fraction of the particles which should suffer deflections exceeding $45°$ in a given length of path, and gets fair agreement with his experiments. The forked tracks (b) are due to the close collision of the β particles with an atomic electron, which itself acquires so large a velocity that it constitutes a secondary β ray and produces ionisation of the same order as that attending the original particle, which proceeds with diminished velocity. The angle between the two prongs of the fork is approximately $90°$, which, as pointed out in connection with Blackett's experiments, is the angle corresponding to elastic impact of a particle upon one of equal mass. Bothe takes account of the relativity change of mass of the β particle, which makes the angle somewhat less than $90°$, $e.g.$ for an original velocity of $\cdot 7$ that of light the angle works out to be $85°$. The agreement with experiment is good. Both calculation and experiment, again in fair agreement, show that forked tracks which entail appreciable diminution of velocity of the primary β ray due to the origination of a secondary β ray, are of comparatively rare occurrence, so that
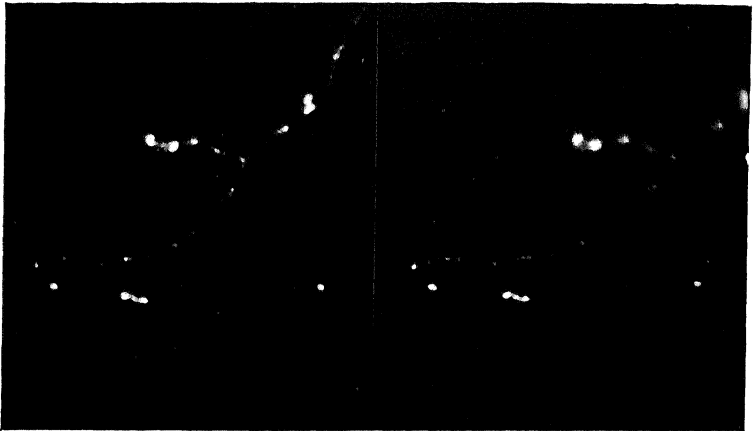
PLATE II

FIG. 1.

FIG. 2.

β-Ray Tracks. (C. T. R. Wilson.)

Fig. 1. Track showing both Abrupt Change of Direction and Gradual Curvature.

Fig. 2. Double Photograph of Forked β-Ray Track.

in considering the multiple scattering and absorption of β rays the secondary radiation may be neglected. It has, however, disturbed some of the experiments on large angle—single—scattering of β rays. The tracks of type (c) often appear to exhibit a persistent curvature in one direction, to explain which somewhat strained quantum considerations have been invoked, but a careful study of the tracks by Bothe has shown that the effect is a physiological one, due to some tendency in the eye to join up random points into a smooth curve. Tracks made up artificially, by a draughtsman, of a large number of purely random small deflections show the same general character as the curved β rays track. The mechanism assumed for multiple scattering is therefore justified by the photographic records.

Loss of Velocity in Passage through Matter. In considering the multiple scattering which occurs when a particle passes through matter under conditions which have been specified, the main difficulty lies in the summation of the individual small deflections, which themselves have to be averaged. These cannot, of course, be added, since they are in random directions, but have to be compounded in a way which involves difficult considerations of the Gaussian distribution law, discussed by Bothe in the course of the investigations to which reference has been made in the previous section. The question of the loss of velocity, or absorption, of the swift particles is in a sense less complicated, since the elementary losses of velocity at separate encounters with atoms can be simply added. Since work on the diminution of velocity in passing through matter has led to certain estimates of the nuclear charge it may be well to outline certain methods of investigation. It is assumed, both in calculating the small angle scattering and the decrease of velocity of the particles, that the single deflections are very small—the paths of the particles, although slightly bent, are taken as straight lines in calculating the action of a single atomic electron. The force between an electron* and a rapid

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* C. G. Darwin has shown that only if the particle passes very close to the nucleus is the influence of the central charge on the velocity important. The cases of close passage are comparatively rare, and for absorption, in the sense of diminution of velocity, the effect of the nucleus may be neglected. The mechanism of single scattering and of absorption of particles is thus essentially different, which explains why we can treat them separately as different phenomena.

particle will have a resultant component at right angles to the
path of the particle, and this will lead to a transfer of energy
to the electron, and a consequent loss of velocity of the particle,
as well as a small deflection.   The calculation of this loss of
energy gives the loss of velocity of the particle with which we
are now concerned.

It is obvious that the effect of the passage of a particle past
an electron will depend upon whether the electron be assumed
to move so as to be in equilibrium at any instant with the
forces acting (the interatomic forces and the force due to the
moving electron) or whether it be assumed that the passage
of the particle is so rapid that the electron will not move appreci-
ably during the short time of near passage of the particle.*
The difference is that considered in the theory of the ordinary
and of the ballistic galvanometer.   J. J. Thomson, in a pioneer
investigation, assumed the electron to be at rest and very
weakly bound, so that the effect of the interatomic forces
was at most to add slightly to the inertia of the electron.
A simple calculation shows that if the particle (mass M,
charge E, velocity v) be deflected through an angle 2θ with
communication of energy l to the electron (mass m, charge e),
then

$$\sin^2 \theta = \frac{1}{1 + p^2/\lambda^2} = \frac{\lambda^2}{\lambda^2 + p^2}$$

and

$$l = \frac{2mM^2v^2}{(M+m)^2} \sin^2\theta,$$

where

$$\lambda = \frac{Ee}{v^2} \frac{M+m}{Mm}.$$

Now the probability of passage at a distance between p and
$p + dp$ from an electron is

$$2\pi p \cdot dp \cdot nZt,$$

since nZ is the total number of electrons per unit volume.

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* The time of collision is not a definite quantity, but is considered to be of
the same order of magnitude as the time taken by the particle to travel a
distance comparable with the quantity p called the impact parameter.

Hence the loss of energy for passage at this distance is

$$\frac{2E^2e^2}{mv^2}\frac{1}{p^2+\lambda^2}2\pi p\,.\,dp\,.\,nZt$$

or total loss of energy $=L=\dfrac{4\pi E^2e^2nZt}{mv^2}\displaystyle\int_0^{p_0}\frac{p\,dp}{p^2+\lambda^2}.$

The difficulty is to decide as to the upper limit of the integral: if it be taken as ∞ the loss of energy is ∞. J. J. Thomson fixed p_0 more or less arbitrarily. He obtained the result that the square of the energy of the particle, *i.e.* the fourth power of the velocity, diminishes proportionally to the length of the path in matter. This law has been verified by Whiddington for cathode rays, and the formula

$$v_0{}^4-v^4=kx$$

is sometimes known as the Thomson-Whiddington relation.

Following on this investigation of J. J. Thomson's, Bohr showed how to avoid the difficulty as to the limit of the electron's sphere of influence to which allusion has just been made. He has worked out the loss of velocity of a high-speed particle passing through matter on the assumptions:

(1) That it is due to transfer of kinetic energy to the electrons of the atoms traversed.

(2) That the electron is bound in the atom by forces which give it a free period, the free period being large compared to the time of collision (see footnote, p. 40) for collisions in which p is of the order of magnitude of $\lambda=\dfrac{eE\,(M+m)}{v^2mM}.$

The second assumption enables us to neglect the influence of the atomic forces, and treat the electron as free, except for collision in which p is great compared to λ, since in other cases the collision is over before the electron has been appreciably displaced.* Bohr deduced the formula

$$\frac{dv}{dx}=-\frac{4\pi e^2E^2n}{mMv^3}\sum_{s=1}^{s=r}\log\frac{v^3kMm}{v_seE\,(M+m)},$$

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* If p is large, so that the particle passes at a great distance from the electron, then a continuous equilibrium is established between the two forces acting on the electron—the interatomic force and the force due to the passing particle —and after the passage the electron returns to equilibrium without having acquired energy from the particle.

where v is the velocity, and there are r electrons in each atom, of frequencies $v_1, v_2, \ldots v_r$, n being the number of atoms per unit volume. This is in agreement with the empirical formulae for the diminution of velocity of the a rays in passing through matter, if the effect of the logarithmic term, which cannot in general be exactly evaluated, be approximately estimated. The chief interest here is that Bohr, assuming (a) the nuclear atom, and (b) the frequency of the electrons to be that deduced from the refraction and dispersion of gases, was able to show that the experimental values for the absorption of a rays in hydrogen and helium agreed with those found from this formula, taking the number of extranuclear electrons to be 1 in the hydrogen atom, 2 in the helium atom. These numbers are those found by Rutherford from a consideration of the scattering of a particles by the gases, and all evidence obtained since has confirmed them.

The Behaviour of very slow Electrons. Before closing this chapter it may be well to say a word of the behaviour towards atoms of moving electrons of low velocity in contrast to the swift electrons so far considered. We have seen that the cross-section per atom which is—whatever mechanism may be assumed—effective in absorbing cathode rays increases rapidly as the velocity of the electron diminishes. For rays below a certain critical velocity, which varies for different gases, but is of the order of 10 volts, the absorbing cross-section reaches a constant value, which is roughly equal to the whole gas-kinetic cross-section of the atom. (In the case of hydrogen, which behaves anomalously with reference to absorption in general, the absorbing cross-section is greater than the gas-kinetic cross-section.)

The question is bound up with the ionisation potential and the resonance potential, which are further discussed in Chapter XII. in connection with series spectra. It has been shown by experiments of Franck and Hertz that for very low velocities the electron behaves as if it were itself a minute gas molecule : the effective cross-section of the gas molecule is that deduced from the kinetic theory, and the impact follows elastic laws, with practically no loss of velocity of the electron, since the mass of the molecule is relatively so great. In this case there

is no ionisation or radiation. For the rare gases, metallic vapours of small electron affinity, and certain other gases, as the velocity of the electron is increased certain values are reached, for greater velocities than which the electron loses energy on impact, the energy being converted into light energy. The corresponding potentials are the *resonance potentials.*
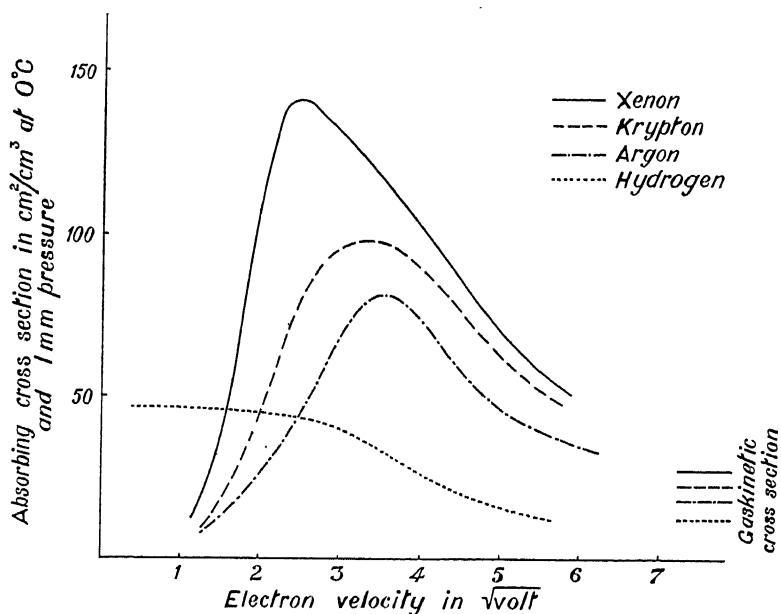

FIG. 4.

Behaviour of inert gases towards very slow electrons.

Further increase of velocity brings us to a point at which ionisation sets in : electrons possessing this or greater velocities remove an electron from the atom when they traverse it, and lose a corresponding amount of energy.

Elastic impact takes place, then, for electrons having velocities below a certain limit, which varies for different gases. For all such velocities the absorbing cross-section is in general roughly equal to the gas-kinetic cross-section : for somewhat higher velocities the electron passes more or less freely through the bulk of the atom, and loses energy, which appears as

radiation. Ramsauer has recently shown, however, that there are striking anomalies with the inert gases.

As the velocity of the incident electrons is diminished the absorbing cross-section first increases to a maximum which is many times the gas-kinetic cross-section, and then diminishes to a value which is only a small fraction of it. Thus with argon the cross-section is only one-seventh of the gas-kinetic value for electrons of velocity ·75 volt. Fig. 4 shows the behaviour of the gases xenon, krypton and argon : the same abnormality is observed, but to a less degree, for neon and helium. The curve for hydrogen, which has an abnormal absorption for electrons of low velocity, is also shown in Fig. 4. Attempts have been made to explain this unexpected behaviour of the inert gases. Hund, for example, has put forward a theory in which the very slow electrons are deflected within the atom through angles of 2π or multiples of 2π, so that they appear to pass freely through. His theory is open to a great many objections, and, in general, it may be said that no valid explanation has so far been offered. The phenomenon is obviously one that must be taken into account in any attempt to construct a theory of the passage of very slow electrons through matter.

As this matter is going to press Brode has published an account of investigations on the absorption of slow electrons which confirm Ramsauer's results for the inert gases, and further indicate a similar maximum of absorption for methane, so that the inert gases are not alone in their behaviour.

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CHAPTER III

RADIOACTIVE CONSIDERATIONS

Introductory. The importance of the phenomena of radio-activity for speculation on atomic structure is not far to seek. In the first place radioactivity is an atomic property, all radio-active changes being entirely independent of the state of chemical combination of the radioactive atom, and of the physical condition of the compound, so that the changes and eruptions can be referred direct to the atom itself. The fact that helium nuclei and electrons are shot out by radioactive substances indicates that they must be constituents of the atomic structure, at any rate of the heavy atoms in question.* Since we cannot, by the most drastic physical and chemical means at our disposal, affect in any way † the quality or quantity of the main radiations from radioactive substances these processes must have their first origin deep down in the atom, in or near the nucleus. In fact it may be said, summaris-ing results to be discussed, that radioactivity and mass are properties dependent on the nucleus ; chemical nature and spectra are connected with the distribution of the extra-nuclear electrons, and only indirectly with the charge on the nucleus.

Radioactivity also provides us with a means of studying directly the properties of single atoms. The energy of the a particle is so great that one particle produces ionisation, or (on impact with a phosphorescent screen) luminosity sufficient

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* There is, of course, a possibility that the helium nucleus may be formed of four hydrogen nuclei during the process of emission, but this hypothesis has nothing to recommend it, and so is, at present, a needless complication.

† Presumably the soft γ radiations, which have been identified with the L radiation of lead and bismuth, could be excited to a small extent by heavy bombardment.

to reveal its presence. In the foregoing chapter we have seen what important conclusions have been drawn from experiments on the scattering of α particles observed by this latter method. In Chapter IV. will be described the way in which the α particle has been used to break up the nuclei of other atoms. In the present chapter we consider among other things the origin of this projectile and of the β particle, and certain evidence as to the constitution of the nucleus obtained by a study of the properties of radioactive substances.

Origin of the α and β Particles. The α particle comes from the nucleus. Its security from external influences, its enormous energy, and, above all, the fact that (taking the nuclear theory as established) there is nowhere else for it to come from, since outside the nucleus are only electrons, fix this origin.

In a single radioactive change, accompanied by α radiation, one α particle is lost per atom. This has been proved by counting the number of α particles expelled per unit time by a given mass of radioactive element, either by counting scintillations or by Rutherford and Geiger's method of detecting the passage of single α particles.* The number so counted is found to be equal to the number of particles breaking down per unit time, deduced from the radioactive constant λ in the ordinary decay formula $N = N_0 e^{-\lambda t}$. Strictly, this only proves that when a large number of radioactive atoms undergo one α ray transformation an equal number of α particles are ejected, but the assumption that each atom emits one particle follows naturally, and has been abundantly justified by the simplicity which it has introduced.

An important property of the α particle is that in the transformation of a given kind of atom it has a single fixed velocity of emission, and consequently a fixed *range* in a given gas, characteristic of the atom in question. Thus radium changing to radium emanation (niton) emits α particles of initial velocity $1 \cdot 61 \times 10^9$ cm./sec. and range $3 \cdot 30$ cms. : radium C emits α

* This method utilises the ionisation by collision, which takes place when ions are accelerated in a strong electric field, to measure the direct ionisation produced by the passage of a single particle. The momentary current so originated by each particle is detected by a string electrometer. See *Radioactive Substances and their Radiations*, by E. Rutherford. Cambridge University Press.

particles of initial velocity $2 \cdot 06 \times 10^9$ cm./sec. and range $6 \cdot 94$ cms. This range, given for air at normal pressure and $15° C.$, is an extremely important constant, and is connected with the life-period of the radioactive atom.

The origin of the β particle is not as immediately evident as that of the α particle, since electrons are present both in the nucleus and outside the nucleus. The question is discussed at the end of the chapter, when further evidence has been considered, but a few well-established facts which bear on the question may be called to mind here. The β particles have no single velocity of emission for a given atom, but a range of velocities. In the case of certain radioactive elements there are, in addition to particles having a continuous range of velocities, others with selected homogeneous velocities. When the β rays are spread out in a magnetic field, so that rays of different velocities follow different paths, and allowed to fall on a photographic plate, there is obtained a so-called β ray spectrum in which the rays of homogeneous velocity appear as lines, analogous to spectral lines, upon a continuous background. There is, in consequence of this lack of uniform velocity, a possibility—which has been recently shown to be a very strong probability—that the β particles do not all originate in the same part of the atom. Certain β particles proceed from the nucleus, while others are ejected from the extranuclear parts of the atom.

It is an observed fact that atoms which give a line spectrum of β rays also emit characteristic γ rays, or, in other words, a well-marked line spectrum of γ rays, while those which give a continuous β ray spectrum give only a weak γ radiation. This is important in view of the mechanism of emission of β rays, which remains to be discussed.

Although the non-homogeneity of velocity of the β rays contrasts with the homogeneous velocity of the α rays, there is a feature which both classes of ray have in common. Experiment has indicated that only one β particle is emitted from a single atom undergoing a β ray change. This is not established by direct experiment within so small a margin of error as the similar proposition for the α rays (the possible error is round about ten per cent.), but indirect evidence from the theory of isotopes offers a strong confirmation.

Radioactive Isotopes and their Importance for Nuclear Theory.
We now consider the very important generalisation, which
was put forward by several investigators independently in
1913, concerning the α and β ray changes, and the place in
the periodic table of the products of these changes. Early
in the history of radioactivity it was discovered that certain
of the radioactive elements, detected as such by their unique
radioactive properties, could not be separated chemically. The
case of thorium and ionium, which Boltwood, later supported
by Auer von Welsbach, pronounced inseparable, and the case
of the thorium products radiothorium, mesothorium 1, and
thorium X, of which radiothorium is chemically inseparable
from thorium, and thorium X inseparable from radium and from
mesothorium 1, may be especially cited, and many other
instances are now known.

All the radioactive elements may be arranged in the columns
of the periodic table according to their chemical and electro-
chemical properties : from what has just been said the same
place will, in general, be occupied by more than one element.
The generalisation to which reference has been made then
appears. The product of an α ray change is shifted by two
places in the table, as compared to the parent element, the
shift being in the direction of diminishing atomic weight or
increasing negative valency. The product of a β ray change
is shifted by one place as compared to its parent, the shift being
in the opposite direction, that of increasing positive valency.
Thus an α ray change followed by two β ray changes will lead
to a product occupying the same place in the periodic table as
the original element, while at the same time the total alteration
of charge is zero.

The change of mass to be expected on the loss of an α particle,
whose mass is roughly four times that of the hydrogen atom,
is four units : that on the loss of a β particle, of negligible mass,
is negligible. Hence we arrive at the conclusion that *atoms
of different mass can have the same chemical properties*, and
so occupy the same place in the periodic table. From this
property they are called *Isotopes*.

Of the radioactive elements, the atomic weight has been
directly determined for thorium, uranium, radium and niton

only, and these determinations confirm the hypothesis. Uranium I has an atomic weight 238, and three α particle transformations with two β particle transformations produce radium, atomic weight $226 = 238 - 3 \times 4$. Radium is transformed to niton with the loss of one α particle only, and the atomic weight of niton is 222. Thorium is in a different series, and so cannot be used for this check.

Fig. 5 shows the distribution of the radioactive elements in the periodic table in accordance with this theory of α and β ray transformations. The number at the head of the vertical column gives the charge, which we take to be the nuclear charge; it is diminished by 2 for an α ray transformation and increased by 1 for a β ray transformation. The horizontal rows give the atomic weight. This figure exhibits, then, the radioactive isotopes. The method of positive ray investigation initiated by J. J. Thomson, and continued with such success by Aston, which is discussed in Chapter V., has shown that isotopes exist for a large number of elements other than radioactive ones.

It will be seen, from inspection of Fig. 5, that there are various leads (by a " lead " is meant any product of the same atomic number as ordinary lead) of different origin, such as the final product of the uranium-radium series, formed when radium F loses an α particle, and the final product of the thorium series, formed from each of the two branches of the thorium chain. These should have different atomic weight : the number of α ray changes involved in the transformation of radium, of atomic weight 226, to uranium lead, is five, whence the atomic weight of the latter product should be 206, while similar considerations show that the atomic weight of the thorium lead should be 208. Now, it has been experimentally established that lead found in thorite (which has presumably been formed by the degeneration of thorium) has atomic weight 207·77, while uranium lead has atomic weight 206·08. This is a striking confirmation of the theory of isotopes. (Ordinary lead has atomic weight 207·19, and is presumably a mixture of isotopes.)

The nuclear theory identifies the mass of an element with the mass of its nucleus, and refers the chemical and spectroscopic properties to the distribution and number of the extra-nuclear electrons, which is governed by the nuclear charge.

To agree with this the α particle and β particle concerned in the radioactive change must both come from the nucleus

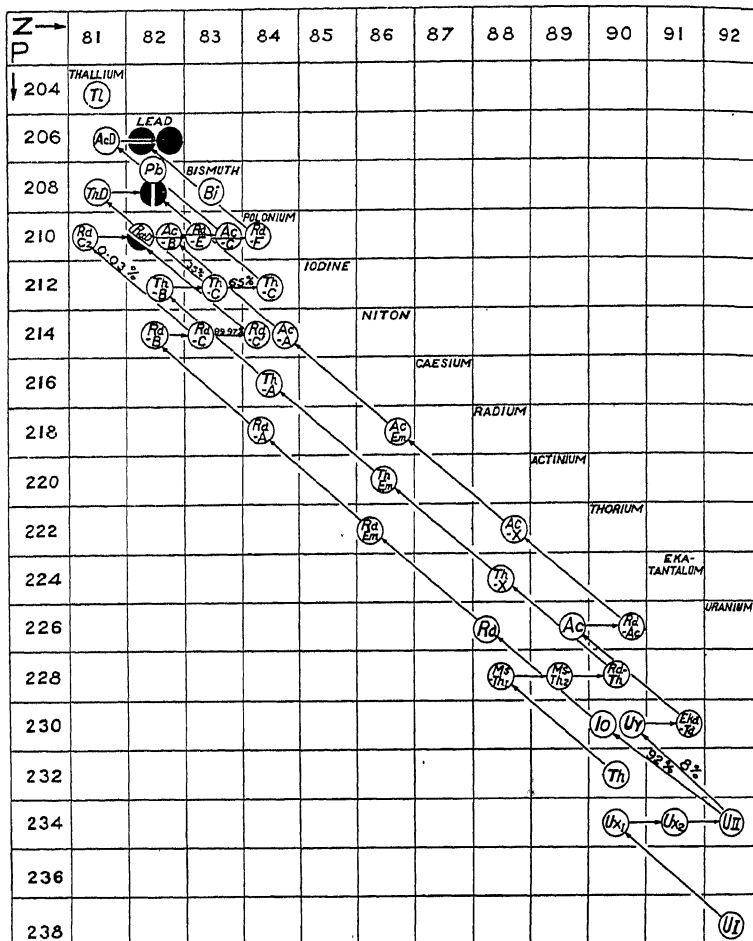

FIG. 5.

Distribution of radioactive elements, showing isotopes.

(although, of course, the possibility still remains that the β particle which leaves the nucleus is not the same particle which issues, but remains in the extra-nuclear structure of the atom, and dislodges an electron from it). The fact that the α particle

is always emitted with the same velocity, and that an α ray change is never accompanied by γ rays except when β rays are also emitted, indicates that the α particle must be able to escape without appreciable communication of energy to the extra-nuclear electrons, a fact remarkable enough. The non-uniform velocity of the β particle when it finally leaves the atom may be attributed to interchanges of energy with these electrons, accompanied by γ radiation.

That the electrons constituting the β rays do not in all cases, at any rate, come from the nucleus is, however, indicated by certain experiments of Hahn and Meitner, who have shown that though radium and radiothorium both emit α and β radiation, in each case only the product corresponding to the α radiation can be detected. If the radium nucleus lost an electron it should give rise to an isotope of actinium, and the percentage of radium atoms which lose electrons is large enough to make the detection of such an isotope, should it exist, quite feasible. Careful search has failed to reveal it, or the product to be expected if the β particle emitted by radiothorium came from the nucleus. It seems natural to suppose that the β particle in both these cases is somehow ejected from the extranuclear electrons. The highest velocity of a homogeneous β radiation is in each case about ·65 times the velocity of light, so that we can have electrons discharged with this velocity from the extranuclear structure. We shall see later that all but the hardest of the homogeneous γ rays also originate in the extranuclear structure.

The Range of the α Particle. One of the most striking properties of the α particle is that it is expelled with a definite velocity characteristic of its parent element. This velocity varies for different elements from $1 \cdot 45$ to $2 \cdot 22 \times 10^9$ cm./sec., and the corresponding energies of a single α particle are $\cdot 645 \times 10^{-5}$ and $1 \cdot 53 \times 10^{-5}$ ergs.* Another characteristic of a

* The energy corresponding to the hardest γ rays measured by Ellis (see page 59 *et seq.*) is in the neighbourhood of 10^{-6} ergs; the energy corresponding to removing an electron from the K orbit of a radioactive atom is round about $1 \cdot 6 \times 10^{-7}$ ergs. Variations in velocity corresponding to the first named would easily be detected, so that it appears that all α rays are emitted from the nucleus under similar conditions, rather than, as might be alternatively supposed, some with lesser velocities than others, the difference between the greatest and the lesser values of the energy being radiated as hard, or nuclear, γ rays. The possibility that some of the α rays may lose energy in exciting

radioactive element is the half value period, and there is an important empirical connection between this and the velocity of
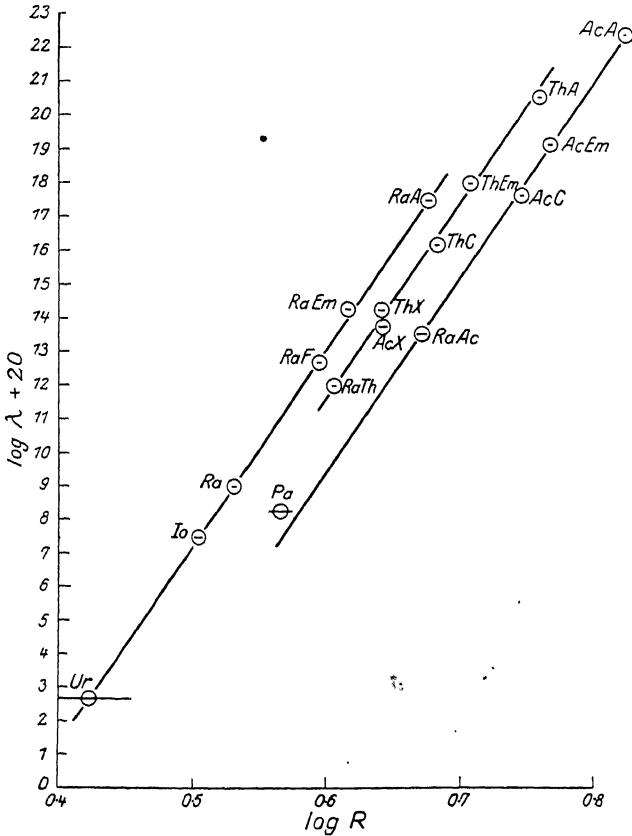

FIG. 6.

Connection between range of α particle and transformation constant for radioative elements.

(The lengths of the horizontal lines in the circles indicate the degree of precision of the measurements, being twice the mean error of several determinations, expressed on the logarithmic scale of the diagram.)

the α particle, which is qualitatively expressed by saying that the shorter be the period of the element, the greater the velocity of

γ rays in the K and L levels does not seem to be excluded, since the loss of energy occasioned would not lead to sufficient variations of velocity to be detected by present methods.

the particle. Quantitatively Geiger and Nuttall have found that the relationship is approximately expressed by the formula

$$\log \lambda = A + B \log R, \quad \dots\dots\dots\dots\dots\dots\dots(1)$$

where λ is the transformation constant of the element, R is the range of the α particle (in air at N.T.P., say) and A and B are constants. The range R is a function of the velocity, increasing rapidly with it : empirically $aR = v^3$, where v is the velocity. Formula (1) therefore expresses a relationship between the period of transformation and the velocity with which the α particle is discharged. B is a constant which has the same value for all three radioactive families, but the constant A has different values for the uranium, thorium and actinium series. Fig. 6 exhibits the facts graphically according to the latest determinations of Geiger.

The relationship holds very well for the uranium series, and not quite as well for the others. It is in any case a good enough formula to begin with, and considering the scarcity of quantitive relationships in the field of radioactive change, has considerable value. It obviously bears upon the properties of the nucleus, and will have to be considered in any theory of nuclear structures.

Lindemann has sketched a suggestive theory to account for formula (1). He supposes that the nucleus contains particles executing periodic motions, and that it becomes unstable when N independent particles pass some unspecified critical position in time τ. Further, the frequency of oscillation of the particles is assumed to be given by the quantum relationship $h\nu = E$, where E is the energy of the expelled particle. These assumptions lead at once to the result that, the greater E, the greater the instability of the nucleus, but they are entirely *ad hoc*. They give λ quantitatively in terms of τ and h. To get a value for τ somewhat fantastic assumptions are made— τ is assumed to be comparable with the time taken by a wave of strain to traverse the nucleus (which for *this* purpose is treated as a homogeneous positive charge), and is thus obtained in terms of the radius and mass of the nucleus. Substituting in the empirical formula, the constants of that formula are obtained in terms of the nuclear charge, mass and radius, in the form

$$\log \lambda = N \left(30\cdot 819 + \log \frac{\sqrt{M r^3}}{Z} \right) + \tfrac{2}{3} N \log R.$$

Comparing with the empirical value for B, we find that $N=80$, and taking the empirical value of A for the radium family, we find that the radius of the nucleus $r = 3 \cdot 85 \times 10^{-13}$ cms., which agrees with Rutherford's estimate. The theory is obviously only tentative, but in the absence of any more precise ideas of the mechanism of the nucleus, it is well worthy of attention.

The γ Rays and the β Rays.[*] The γ rays are electromagnetic waves of the same nature as visible light waves, but much shorter wave-length. The γ ray spectrum of radium B and radium C has been investigated by Rutherford and Andrade, who made use both of the reflexion at a crystal face and the method of transmission through a crystal.[†] The spectrum so determined consists of a number of discrete lines, whose wave-lengths vary between $\cdot 72 \times 10^{-9}$ and $1 \cdot 4 \times 10^{-8}$ cm. : it is not yet definitely established if there is a continuous background to the spectrum. The softer rays coincide within the limit of experimental error with lines in the L series of the X-ray spectra of lead and bismuth ; of the harder rays some, *but not the most penetrating*, coincide with lines in the K series of the same elements. This fact, which is firmly established, is a very important confirmation of the theory of isotopes, which bears so closely upon the question of atomic structure. For, according to the radioactive transformations in the radium series, radium B should be an isotope of lead, radium C an isotope of bismuth, as can be seen from Fig. 5. Now, the ordinary X-ray spectra are governed by the nuclear charge and not by the nuclear mass, since it is the charge which determines the number and motions of the extranuclear electrons. Isotopes should therefore have the same X-ray spectra : the identity of the spectra which can be excited by cathode bombardment or by hard X-rays in lead and bismuth with some of the lines of the self-excited γ ray spectrum of radium B and C confirms the results reached from chemical evidence.

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[*] In the rest of this chapter a certain knowledge of modern work on X-ray spectra is assumed, although the work is not discussed until Chapter XIII., which may be consulted, if necessary, before reading further, as to the meaning of the K and L levels.

[†] For details consult *X-Rays and Crystal Structure*, by W. H. and W. L. Bragg. G. Bell and Sons.

COMPARISON OF γ RAY SPECTRA OF RADIUM B AND C
WITH X-RAY SPECTRA OF LEAD AND BISMUTH.

Radium B and C.		Lead.	Bismuth.
$\lambda = \cdot72 \times 10^{-9}$ cms.		(Nuclear origin.)	
$\cdot99$			
$1\cdot15$			
$1\cdot37$		$1\cdot42\ K.$	$1\cdot39\ K.$
$1\cdot59$		$1\cdot59\ K.$	—
$1\cdot69$		—	—
$1\cdot96$		—	—
$2\cdot29$		(Nuclear origin.)	
$2\cdot42$		—	—
$2\cdot62$		—	—
$2\cdot96$		—	—
$3\cdot24$		(Nuclear origin.)	
$4\cdot28$		—	—

Radium B.			Lead.		Bismuth.	
$\cdot793 \times 10^{-8}$	m		—		$\cdot793\ L.$	vf
$\cdot809$	m		—		$\cdot810\ L.$	f
$\cdot838$	m		$.837\ L.$	m	—	
$\cdot853$	m		(Nuclear origin.)			
$\cdot917$	f		—		$\cdot922\ L.$	f
$\cdot953$	m		$\cdot950\ L.$	f	$\cdot953\ L.$	m
$\cdot982$	s		$\cdot980\ L.$	s	—	
$1\cdot006$	m		$1\cdot005\ L.$	f	—	
$1\cdot029$	m		—		—	
$1\cdot055$	f		—		$1\cdot057\ L.$	vf
$1\cdot074$	f		—		—	
$1\cdot100$	f		$1\cdot087\ L.$	f	—	
$1\cdot141$	m		—		$1\cdot141\ L.$	vs
$1\cdot175$	s		$1\cdot172\ L.$	vs	—	
$1\cdot196$	m		$1\cdot184\ L.$	m	—	
$1\cdot219$	f		—		—	
$1\cdot266$	f		—		—	
$1\cdot286$	f		—		—	
$1\cdot315$	f		—		$1\cdot313\ L.$	f
$1\cdot349$	m		$1\cdot345\ L.$	f	—	
$1\cdot365$	m		—		—	

In this table the letters K and L denote the X-ray series in
which the lines, whose wave-lengths are given, are found for
the element named at the head of the column. The letters
s, m, f denote intensities as strong, medium, and faint ; the
v prefixed denotes very. It will be noted that, especially when
intensities are considered, the spectrum of radium B corresponds
much better to the L spectrum of lead than to that of bismuth.
The attribution of nuclear origin is based upon the work of Ellis,
to be described.

We see that while a majority of the homogeneous

γ radiations measured by Rutherford and Andrade can be set down as belonging to the ordinary X-ray spectra of the atoms in question, spectra which have their origin in interchanges of electrons among the extranuclear system,* a few of the most penetrating cannot be attributed to this source, but must be referred to the nucleus. Recently still more penetrating γ rays have been detected by a method which has been much used of late for measuring the wave-length of radiations of X-ray frequency. When such radiations fall on a metal electrons are liberated with a velocity which depends not on the intensity but on the frequency of the incident waves. The method utilises the quantum relationship which exists between the frequency and the velocity, namely

$$E = h\nu - P, \quad\text{.....................................(2)}$$

where E is the energy of the liberated electron, ν is the frequency, and h is Planck's constant. This equation is sometimes known as Einstein's law, since it was first applied by Einstein to the photoelectric effect. For electrons whose velocity does not approach that of light, $E = \frac{1}{2}m_0v^2$, where v is the velocity with which the electron leaves the atom, and m_0 is the rest-mass of the electron. P represents the work required to remove the electron from the influence of the atomic forces : if the electron were not bound at all it would acquire the full velocity given by $\frac{1}{2}m_0v^2 = h\nu$.

This quantity P has not a single fixed value, but for a given atom may have any one of a series of discrete values, since, as is discussed more fully in the second half of the book, the extranuclear electrons fall into certain groups, or energy levels, characterised each by a different strength of binding of its electrons. P is greater for the so-called K level than for the L levels, greater for the L levels than for the M levels, and so on.

Equation (2) has been verified by experiments on the photoelectric effect, and incidentally its confirmation gave strong support to the quantum theory before the great rush of evidence *au secours du vainqueur*. Measurements of the velocity of the liberated electron can, then, be made to give the frequency of the liberating radiation, so long as there is some way of

* See Chapter XIII.

fixing the appropriate P : they have been so applied by O. W. Richardson and others in the case of ultra-violet light of very short wave-length, and especially by de Broglie in the case of X rays. On the other hand, if the frequency of the liberating radiation be known, and the velocity of the liberated electrons be measured, the value of P, the work required to remove an electron from the various levels of energy within the atom, can be obtained. This method has recently been applied by H. Robinson with great success. Now, it has been shown by Rutherford that if the general γ radiation from radium B and C be allowed to fall upon heavy metals, such as gold, then electrons are emitted from the metal in groups, each of which has a well-defined velocity. From this velocity, by suitable methods, can be deduced the wave-length of the γ rays.

In the experiments carried out on the subject by C. D. Ellis the velocity of the liberated electron—which will be referred to as secondary β radiation—is measured in the usual way, by letting it travel in a strong magnetic field which produces a curvature of path dependent on the velocity. The photographic plate is so arranged that all rays of a given velocity, *i.e.* of given curvature of path, come to a comparatively sharp focus upon it, in spite of variation of direction of projection ;* it records the spectrum of the secondary β radiation as a series of well-defined lines. The source of the β radiation is generally a piece of metal foil rolled round a fine glass tube containing a large amount of radium emanation, which, of course, deposits radium B and C on the walls of the tube. Suitable lead screens are employed to protect the plate from direct radiation, and the whole apparatus is enclosed in an evacuated box. In Fig. 7, S is the source, AB the photographic plate, L a lead block protecting the plate from direct radiation, and F_1, F_2, F_3, lead screens for the same purpose.

With the metals tungsten, platinum, lead and uranium exposed to the γ rays the secondary β ray spectrum is found to contain in each case a group of three main lines, but the velocity corresponding to a given line in the spectrum is not independent of the metal, but increases somewhat as we go from heavier to lighter atoms. This is to be expected, for, turning to equation

* Cf. p. 112.

(2), while $h\nu$ is the same in all cases, being determined by the exciting γ ray, P, the work required to remove the electron from the atom will depend upon the position of the electron in the atom, and, for corresponding positions in different atoms, will depend upon the nuclear charge, which varies from atom to atom. As is explained in Chapter XIII., measurements of the X-ray spectrum of an element* enable us to calculate the work
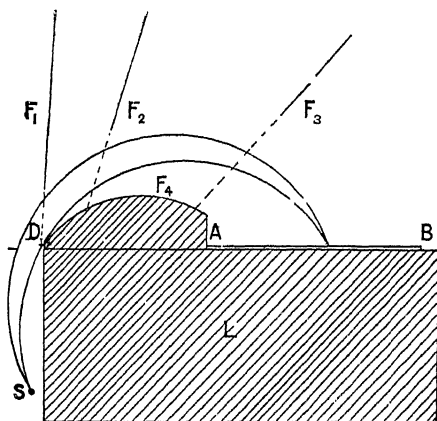

FIG. 7.

Ellis' apparatus for spectrum of the β rays excited by γ rays.

required to remove an electron from a given orbit, or energy level, within the atom, to infinity. (By infinity we indicate a fraction of a millimetre sufficiently large to remove the electron from atomic influences.) Hence P can be obtained from the different metals in question (1) when the electron is removed from the K level, (2) when the electron is removed from an L level. It may be noted here that there are three L levels, denoted by the symbols L_{I}, L_{II}, L_{III},† and the fact that they

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* The K and L absorption edges are the factors here in question.

† The task of following the work of the investigators of these levels is not facilitated by the fact that the same symbols are used by different authors with different meanings, Bohr and Coster and others, including Robinson and Ellis, use the symbols L_{I}, L_{II}, L_{III} where, for corresponding quantities Sommerfeld uses the reverse order, L_{III}, L_{II}, L_{I}. Readers should beware of this. With the notation here used L_{I}, L_{II}, L_{III} are in diminishing order of strength of binding of the electron in question.

do not differ very greatly adds to the difficulty of interpreting the β ray spectra, as we shall see, especially as great precision in the experimental determination of the β ray velocities is very hard to attain.

E, the energy of the electron when well free of the atom, is calculated from the given line in the secondary β ray spectrum. When P for the element in question is added to E an energy is obtained whose value should be independent of the element, and characteristic of an exciting γ ray. The necessity of fulfilling the condition of independence of element renders it possible to find by trial whether the electron is emitted from the K or from an L level, since the energy required to send an electron from the K level to the surface varies considerably more from element to element than the corresponding energy in the case of the L level. Hence a comparison of the spectra of secondary β rays excited by the same group of γ rays in various metals can be made to yield (1) the work done to free the electron from the atom, and consequently the energy level from which the electron originates, (2) the true initial velocity of the electron, which is the same for all heavy atoms, and gives the frequency of the γ ray liberating that electron.

A numerical example may be given for the two metals platinum and uranium. The energy P, in volts, required to send an electron from the K level to the surface is $\cdot782 \times 10^5$ and $1\cdot178 \times 10^5$ respectively. We find, corresponding to the three main lines in the secondary β ray spectrum, three values of $E+P$ which are independent of the metal, as will be seen from the following table taken from a paper by Ellis :

Observed energy E deduced from β ray spectrum.		$E + P$	
Platinum.	Uranium.	Platinum.	Uranium.
$1\cdot58 \times 10^5$	$1\cdot22 \times 10^5$ volts.	$2\cdot36$	$2\cdot40 \times 10^5$ volts.
$2\cdot12$	$1\cdot74$	$2\cdot90$	$2\cdot92$
$2\cdot69$	$2\cdot31$	$3\cdot47$	$3\cdot49$

The existence of three γ rays, of wave-lengths $\cdot0519$, $\cdot0423$,

·0354 × 10⁻⁸ cms.,* corresponding to the three energies $E+P$, is therefore demonstrated, together with the fact that the rays can liberate electrons from the K level of heavy atoms.

It has been shown experimentally that the strong lines of the magnetic spectrum of the secondary β rays excited in lead by the γ rays coincide with lines of the spectrum of the natural β rays of radium B.† It is therefore reasonable to assume that the natural β rays are excited by the γ rays from the nuclei of their own atoms. The three γ rays found experimentally in the way just described may be expected to give six lines of the natural β ray spectrum of radium B, if we consider that each ray releases electrons from the K and from the L level. The lines calculated on this assumption are, in fact, found to be represented in the β ray spectrum of radium B, which, however, also contains other lines.‡

Six of these can be accounted for by choosing suitably three other wave-lengths for γ rays, and assuming that each can

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* Calculated from the energy by the formula $E = h\nu$, which, if E be expressed in volts, gives

$$\lambda = \frac{3 \times 10^{10} \times 6 \cdot 55 \times 10^{-27}}{E \times 1 \cdot 59 \times 10^{-12}} = \frac{1}{E} 12 \cdot 36 \times 10^{-5} \text{ cm.}$$

The values of $E + P$ used in deducing the above wave-lengths are means which include values for metals not embodied in the above table.

† As this part of the book is going to press I have received from M. Jean Thibaud, working in the laboratory of M. de Broglie, a very interesting paper entitled *La Spectrographie des Rayons* γ, presented as a doctorate thesis at the University of Paris in June 1925. Thibaud has carried out extensive investigations on the secondary β ray spectrum excited in many different metals by the γ rays from the radioactive elements. In particular he has shown that *all* the important lines on the natural β ray spectrum of radium B and radium C (with the solitary exception of a line of energy $1 \cdot 334 \times 10^6$ volts which occurs in the natural spectrum of radium C) appear in the spectrum excited in lead by the γ rays of the radium family, the agreement in energy (or wave-length) being exact for radium B, and the energy of the excited rays being slightly greater than that of the natural rays for radium C, the excess being exactly that to be anticipated if the natural β rays were excited in an atom of $Z = 83$ (bismuth) instead of $Z = 82$ (lead). This confirms the results of Rutherford and Andrade, deduced from measurement of the natural and excited γ rays. Thibaud's numerous measurements of excited β ray spectra emphasize the confidence which can be placed in Einstein's law $E = h\nu - P$ over a range of electron velocities from a fraction of a volt to a million or more volts. The wave-lengths deduced by him agree well with those obtained from the natural β ray spectra.

‡ This spectrum has recently been re-examined in great detail by Ellis and Skinner (*Proc. Roy. Soc.*, A, **105**, 165, 1924).

release an electron from the K level and from the L level. (One of these lines falls so close to one of the other six that it cannot be distinguished experimentally from it.) We thus have six homogeneous γ rays deduced from these considerations of the secondary β rays produced by the γ rays, and of the natural β ray spectrum of radium B, all of which are considerably shorter than the γ rays measured by Rutherford and Andrade by the crystal method. The existence of such very penetrating γ radiations is further indicated by measurements of the absorption of the γ rays in aluminium. It may be noted that there are certain further natural β rays of radium B not accounted for by the six penetrating rays, but numerical manipulation shows that these can be attributed to γ rays measured by the crystal method.

L. Meitner has at the same time carried out numerous experiments on similar lines, especially with thorium B. In agreement with Ellis she deduces two γ rays, of wave-length ·0523 and ·0417 A.U. respectively, but her theory of the origin of β and γ radiations differs widely from his. The two theories are considered in the last section of this chapter. Hahn and Meitner have further deduced from the three β rays of radium itself that this element emits a nuclear γ ray of wave-length $6\cdot6 \times 10^{-10}$ cm., which releases electrons from the K, L, and M levels of the radium atom.

Energy Levels of the Nucleus. It has already been pointed out that the K series for radium B is fully represented by the γ ray lines measured by Rutherford and Andrade, so that the γ rays detected by the analysis of natural and secondary β rays spectra are harder than the K series for an element of atomic number 82. They must therefore originate in the nucleus, since experiments on the deflection of the α particle by other atoms have indicated that the space between the K electrons and the nucleus is empty. The six hard γ rays, with their energies, deduced from the β ray spectrum by Ellis, are given in the following table * :

* In this table the values given are from Ellis' paper of 1922. The values have since been slightly modified, as given in the table at the end of this chapter. The older values are set down here to .correspond to the 1922 diagrams of nuclear levels, which are retained for simplicity (see Fig. 8). Those seeking the most recent values should consult the paper of Ellis and

NUCLEAR γ-RAYS OF RADIUM B (FROM β-RAY SPECTRA).

Intensity.	λ in A.U.	Energy in volts.
s	·0519	$2·385 \times 10^5$
m	·0488	2·529
s	·0423	2·918
s	·0354	3·492
m	·0339	3·639
f	·0308	4·000

It will be seen by inspection that these can be arranged in pairs, which show a constant energy difference, thus :

4·000	3·639	3·492
2·918	2·529	2·385
1·082	1·111	1·107

If, then, it be supposed that there are energy levels within the nucleus, and that in some way the difference of energy between
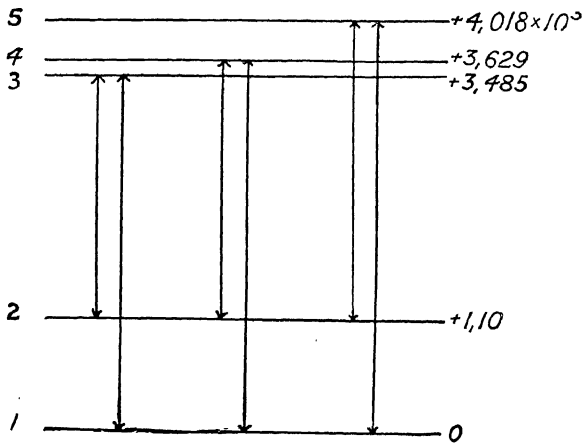
FIG. .8.
Energy levels of radium B nucleus.

any two levels, $E' - E''$, can be radiated as a homogeneous radiation of frequency given by $h\nu = E' - E''$, then all the nuclear

Skinner quoted in the references, and the thesis by Thibaud to which reference is made on p. 62.

rays can be accounted for by supposing three outer levels and two inner levels, the inner levels differing from one another by energy $1\cdot 10 \times 10^5$ volts. Such levels, and the six energy changes corresponding to the radiation tabulated above, are indicated in Figure 8.

If these levels, and this mechanism, do in fact exist, energy changes from level 5 to 4, 5 to 3, 4 to 3, and 2 to 1 would also seem possible, with radiation of homogeneous γ rays of corresponding frequencies. It is a striking fact that wave-lengths calculated from these transitions do actually agree with wave-lengths recorded by Rutherford and Andrade, and not represented in the K and L spectra of lead, with which, except for the structure of the nucleus, radium B is identical. This is shown in the following table :

NUCLEAR γ RAYS FROM SCHEME OF LEVELS AND
FROM CRYSTAL MEASUREMENTS.

Energy levels concerned.	Energy in volts	λ in A.U. calculated from energy levels.	λ in A.U. measured by Rutherford and Andrade.
5 − 4	$\cdot389 \times 10^5$	$\cdot318$	$\cdot324$
5 − 3	$\cdot533$	$\cdot231$	$\cdot229$
4 − 3	$\cdot144$	$\cdot857$	$\cdot853$
2 − 1	$1\cdot10$	$\cdot112$	$\cdot115$

The experiments have, then, led to a scheme of nuclear levels which accords well with the facts. The experimental device of determining wave-length by the velocity of the electrons liberated seems to be likely to assume great importance as a general method. De Broglie states that already wave-lengths can be measured by corpuscular spectra with an accuracy approaching that attainable by crystal gratings.

The method of determining the wave-length of the nuclear γ rays from the natural β ray spectra of radioactive elements, based upon the well supported hypothesis that the β rays are due to the conversion of γ ray energy in the extranuclear electron structure of the same atom, is being pursued further at the present time by Ellis and by Meitner. Recently Ellis and Skinner have redetermined the β ray spectrum of radium B and radium C, and, from consideration of the new data,

slightly changed the wave-length of some of the rays determined by Ellis as just described, and added a few new ones of lesser intensity.   As a result, the scheme of nuclear levels shown in Fig 8 has been modified in certain inessential particulars, but the old scheme has been retained here, since it exemplifies all the principles involved, and is less complicated than the new. Readers who wish to consider the problem in detail should consult the original paper.   In the words of Ellis and Skinner : " The modifications introduced have changed some details of this interpretation but, on the other hand, the general correctness of the view has been greatly strengthened.   But still it appears unlikely that any definiteness in our knowledge of this level structure can be obtained by a mere search for numerical agreement, at least not until the general accuracy has been greatly increased.   Evidence of a more fundamental nature will have to be found before we can settle this question of the exact level structure in the nucleus."

The Mechanism of the Nucleus and Radioactive Change. As a result of the work so far described we know that the nuclei of heavy (radioactive) atoms contain α and β particles, which may be ejected.   We know further that, accompanying either an α or a β transformation, the nucleus can emit in some cases very penetrating γ radiations.   These γ radiations lead, by an extension of Bohr's theory of energy levels in the extra-nuclear parts of the atom, to the conception of energy levels within the nucleus, differences between which give, by the quantum relation, the frequency of the penetrating rays.   The hypothesis that one, and only one, electron leaves the radio-active atom per disintegration, which has received reference on p. 49, has recently been confirmed by the work of Emeléus, who measured directly the number of electrons emitted by radium E, and of Gurney, who did the same for radium B and C.

We have now to discuss certain problems concerning the mechanism by which the α, β and γ radiations are emitted by radioactive atoms.   As a help to understanding this mechanism we must enquire if the β particle which escapes from the atom is the one which left the nucleus, or if this latter is retained in the outer structure of the atom, and another dislodged : if all the particles leave the nucleus of a given kind of atom with one

fixed velocity, as do the α particles ; if the γ rays are emitted before, during, or after the disintegration of the atom. In considering these general questions it must be remembered that the line spectrum of β rays represents only a small part of the energy of β ray emission, the greater part, as shown by Chadwick, being represented by a continuous background, *i.e.* by electrons of a continuous range of velocity, on which the groups of homogeneous velocity, which give the line spectrum of β rays, are superimposed. Radium E, which gives no γ rays, exhibits a continuous β spectrum without accompanying lines. In the view of the origin of the β rays which form the continuous background theories differ widely. Ellis supposes that the β rays leave the nucleus with a continuous distribution of velocities, which throws the difficulty back upon the mechanism of the nucleus rather than solves it. Meitner supposes, however, that all disintegration electrons leave the nucleus with a fixed velocity characteristic of the nucleus, which is in a sense a more attractive assumption, since it merely extends to the β particles the property possessed by the α particles. On her view the departure of the disintegration electron is the first step in the process : it is followed by a readjustment within the nucleus which may either be rayless (as in the readjustment which immediately follows the *removal* of an outer, or ionisation, electron from the periphery of an atom), or may involve quantum changes of energy, corresponding to the emission of one or more γ rays. The existence of the continuous background is explained by arguing that the disintegration electron, after it has left the nucleus, must be subject to various impacts and other secondary influences which cause losses of velocity of varying amounts. There are, however, grave difficulties in the way of such an assumption.* For instance, if every β ray which left the nucleus of radium C possessed the maximum velocity measured in the β ray spectrum of that element, the heating effect should be greater than that actually measured for the β and γ rays together of radium B and

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* Ellis and Wooster (*Proc. Cambridge Phil. Soc.*, **22**, 849, 1925) have shown that it is very hard to see how a sufficient broadening of an originally homogeneous β ray line could be produced in this way to account for the continuous background of, say, radium E, which stretches from 1,000,000 volts to small energies of the order 40,000 volts.

radium C. It has seemed to me that a partial reconciliation between the continuous background theories of Ellis and of Meitner may be effected by allowing the nucleus to eject β particles of not one velocity, but of a few different velocities, just as it emits γ rays of a few fixed wave-lengths. In such a case the broadening of the individual β ray lines produced by interchanges of energy in the extranuclear structure need be far less than it would have to be if only one nuclear β ray line were emitted, and a background might be produced which our present resolving power would leave as continuous. However, in the absence of further experimental evidence, speculation in this direction has limited value. Ellis has suggested that the accurate measurement of the heating effect produced by radium E, which has a continuous β ray spectrum only, and emits no γ rays, would provide valuable evidence. The average energy of break up of a radium E atom might prove to be equal either to the maximum energy, or to the average energy of the continuous β ray spectrum. Either result would offer difficulties to a theoretical explanation, but not the same difficulties, so that in a restricted sense a slight advance seems possible in this direction.

While the continuous background, then, is the subject of opposing theories (although it seems likely that the particles which form this background come direct from the nucleus), there is general agreement that the natural β ray line spectrum has its origin in the ejection of electrons by nuclear γ rays from various energy levels in the extranuclear structure of the atom. The fact that the artificial β ray line spectra obtained by subjecting heavy elements to γ rays agree numerically with the assumption that the β rays are ejected from the various levels of the atoms of these heavy elements, coupled with the fact that all γ ray emitters give a β ray line spectrum, offers strong evidence on this point, and both Ellis and Meitner have obtained satisfactory estimates of the wave-lengths of nuclear γ rays on this assumption. However, in the case of the natural β ray spectrum of a radioactive element the β rays cannot be ejected by the nuclear γ rays from one atom of this element falling upon another atom, because the atoms of the element are so sparse that no appreciable intensity would be reached in

this way. Rather, as Ellis and Skinner have showed,[*] there must frequently be a conversion of the γ ray into β ray energy inside the atom, which they call internal conversion.

There remains to be discussed the question as to the sequence of the phenomena. Meitner urged that the ejection of the disintegration electron from the nucleus is the first step in the changes which lead to γ ray emission and the natural β ray spectrum. In support of this she invokes the behaviour of the rays of the so-called C group.[†] Ellis was originally of the opinion that the nuclear γ ray was first emitted, but the work of Black made this view difficult to hold, and recently Ellis has, in conjunction with Wooster, carried out experiments which have led to a definite decision in favour of the primary emission of the nuclear electron. The argument upon which the experiments are founded is as follows. What is observed in the case of the β ray line spectrum excited by γ rays in a foreign element is the velocity of the secondary β rays, and this depends not only upon the frequency ν of the nuclear γ ray, responsible for the ejection according to equation (2) on p. 58, but also on the work required to release the electron, *i.e.* to withdraw it from the atomic field of force. This work is conditioned by the net positive charge on the nucleus. It should therefore be possible by accurate measurement of the β ray spectrum of radium B, say, and a comparison with the artificial β ray spectrum excited in a non-radioactive element of known atomic number by the γ rays from radium B, to decide whether the nuclear charge against which the work is done is 82 or 83 in the case of radium B, which would answer the question as to whether the secondary β ray is ejected before or after the disintegration of the nucleus.

Ellis and Wooster, adopting a very ingenious device, have been able to make measurements sufficiently accurate to answer this question. They surround a tube containing radium B with a sheath of platinum, so that the γ rays from the radium B excite secondary β rays in the platinum ; at the same time they deposit radium B on the outside of the platinum tube.

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[*] See also Gray, *Nature*, 3rd Jan., 1925.

[†] Ellis divides the β rays from radium B into three groups, called, in order of increasing speed, the C, D and E groups.

The secondary β rays from the platinum must, owing to their absorption coefficient, have their source in, and very near to, the surface, so that in this way it is possible to obtain secondary β rays from platinum, $Z=78$, and the primary β rays from radium B from the same source as far as position is concerned. Analysis of the spectra of these β rays in a magnetic field enables a decision to be made as to the Z which corresponds to the primary β rays, since with comparison lines for $Z=78$ present the difference between $Z=82$ and $Z=83$ becomes quite appreciable. The result of the experiments is definitely that the natural β rays from radium B have energies corresponding to excitation by the nuclear γ rays in an atom of nuclear charge 83, so that the atom of radium B ($Z=82$) must have lost a nuclear electron before a β ray line is emitted, and the γ rays must be due to internal conversion. The repetition of Rutherford and Andrade's experiments, by Rutherford and Wooster, involving the careful measurement of the γ ray L spectrum of radium B, have led to the same conclusions.

The work of Ellis and his collaborators has shown that the energy levels in the radioactive nuclei are similar in different atoms of the same family, that is, similarly spaced levels occur, but they all experience a displacement in the same direction as we go down the radioactive series. It is supposed that these levels are in some way due to various rings, or, generally speaking, separated systems of nuclear electrons. The first stage in an instability of the radium B type is the emission of a disintegration electron from one of these rings : this issues from the atom with a certain velocity, which varies in the case of different atoms of the same kind, and when all atoms are statistically considered is responsible for the continuous background. The emission makes the nucleus unstable, and the readjustment leads to the emission of the γ ray. It is, of course, indifferent for the γ ray what happens to the disintegration electron once it is out of the nucleus. What causes electrons of different velocity to leave the atom is still uncertain, and we cannot say for certain at present whether they first leave a given nuclear level, or the whole nucleus, or the atom with variable velocity, $i.e.$ at what stage or by what mechanism the continuous distribution is produced.

The assumption of various levels from which the disintegration electron may come is useful in that it enables us to assume similar energy level schemes for unlike emissions. As far as the α ray emission is concerned, we are still completely in the dark as to where the α ray comes from, or how it is that an α ray body, such as radium, emits γ rays.

In conclusion, a table of some of the most important nuclear rays for the radium family is appended. The values for radium B and C are those recently deduced by Ellis and Wooster from measurements of the β ray spectra. Measurements for radium and radium D have been made by Meitner.

NUCLEAR γ RAYS OF THE RADIUM FAMILY

Radioactive Substance.	Type of Disintegration.	γ Rays.	
		Wave-length in cms.	Energy in Volts.
Radium	α Ray	$6 \cdot 6 \times 10^{-10}$	$1 \cdot 87 \times 10^5$
Radium B	β Ray	23·03	·536
		5·07	2·433
		4·75	2·600
		4·16	2·970
		3·49	3·540
Radium C	β Ray	4·49	2·75
		3·71	3·33
		3·17	3·89
		2·88	4·29
		2·02	6·12
		1·31	9·41
		1·092	11·30
		·990	12·48
		·866	14·26
		·694	17·78
		·556	22·19
Radium D	β Ray	26·4	·467

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CHAPTER IV

THE DISRUPTION OF THE NUCLEUS BY α PARTICLES

Introductory.   Early in the history of radioactivity it became clear that, for a given mass, the energy associated with the radium emanation was enormous.   I c.c. of the emanation with its products evolves in the course of its lifetime some six million times the heat given out by an equal volume of an explosive mixture of hydrogen and oxygen when detonated, and the energy is emitted not as a radiation uniformly distributed round the source, but localised along the paths of individual particles.   Such simple considerations of the great concentration of energy afforded by the emanation led Ramsay, in 1907 and 1908, to attempt a disintegration, or transformation, of the atom by means of the radiations from radioactive substances.   Alone, and together with Cameron, he subjected various atoms to the action of the radiation by dissolving emanation in a solution of the salt of the atom in question. He came to the conclusion that the radiation produced neon and argon from water and lithium from copper, evidence for the products being obtained spectroscopically.   Working in this way it is extraordinarily difficult to avoid traces of impurity, especially of the substances in question, since neon and argon are present in air, and lithium and sodium can be dissolved in minute quantities from glass and quartz by the action of pure water.   Other experimenters were unable to reproduce Ramsay's result when working with more rigorous exclusion of possible sources of contamination, and it is generally accepted to-day that the evidence is against the transformations announced by Ramsay.   Nevertheless the experiments are interesting historically. as showing an early realisation of the

powerful agent offered by radioactive energy for attempts to break up the atom.

The greatest concentration of energy is offered by the fast α rays emitted by the radioactive elements. Although the velocity of these rays is small compared with that of the fastest β rays (being not more than about one-fifteenth of the velocity of the high-speed β particles from radium C) the great mass of the α particles compared to that of the electron (even when the increase of the mass of the electron with velocity is considered) makes the energy of the faster α particles greater than that of any of the homogeneous β particles. Thus the energy of a single α particle from radium C is about 13×10^{-6} ergs, while that of a β particle of velocity $0.98c.$, emitted by the same element, is about 3×10^{-6} erg. Further, the α rays are emitted with a uniform velocity from a given product, and so afford particles of definite energy. By the aid of such α rays Rutherford has succeeded in breaking up the nuclei of certain atoms, and thus obtaining evidence both of their structure and their size. The method consists in the observation of single atoms, which permits a much more detailed quantitative investigation of the properties of the products of disruption than the spectroscopic method. Further, the method admits of easy controls, by which the source of the products of disruption can be determined with some certainty. In essence it consists in letting the α particles strike the atoms whose nuclei are to be investigated. In the case of direct, as distinct from glancing, impact the nucleus struck will be thrown forward with a velocity depending upon its mass and charge, and an investigation of the range of the nucleus, which can be carried out by the method of counting the scintillations produced on a zinc sulphide screen, enables an estimate of the nature of the nucleus to be made. The ratio of the charge to the mass of the nucleus can also be investigated by the ordinary method of magnetic deflection.

When α particles are fired into hydrogen, it has been proved that the hydrogen nucleus is thrown forward. In the case of nitrogen it is not the whole nucleus, but once more a hydrogen nucleus, or proton,* which constitutes the long-range particle

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* The hydrogen nucleus is so important an entity in modern physics that the special name of *proton* has been suggested for it, and is now generally adopted.

produced, and it can be shown that the source of the particle must be the nitrogen nucleus, and not a hydrogen contamination. Similarly, a positively charged hydrogen nucleus has been shown to enter into the structure of other heavier nuclei besides that of nitrogen, and a way has been opened along which the question of the laws of force in the neighbourhood of the nucleus may be approached.

Theory of Impact of an α Particle on a Light Nucleus. As a preliminary to the consideration of the experiment let us examine the theory of the impact of an α particle on any nucleus. If the nucleus is heavy we have the case already considered in Chapter II., when there was a question of the scattering of α particles. Even if the nucleus be as light as that of copper ($Z=29$) its motion when struck is negligible, as has been confirmed experimentally by Chadwick in experiments on scattering, so that for all heavier atoms it is justifiable to consider the struck nucleus as fixed. Such an assumption is, however, obviously untrue for the passage of α rays through hydrogen, to which attention is now devoted.
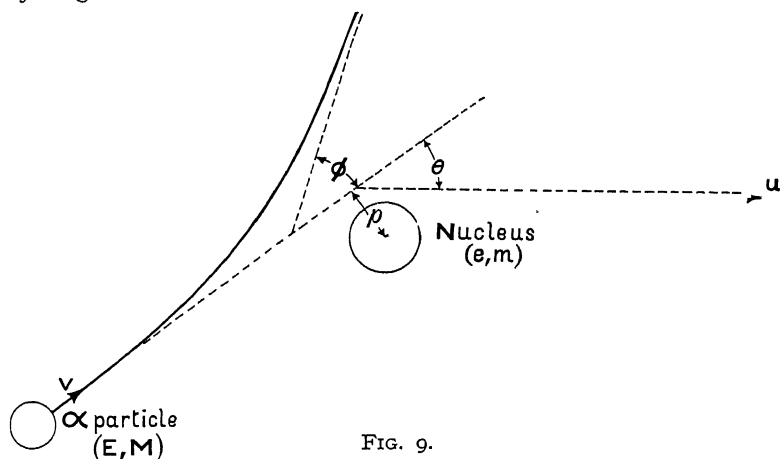
FIG. 9.

Suppose that the mass and charge are M, E for the α particle, and m, e for the struck nucleus; that the initial velocity of the α particle is v, and the velocity of the nucleus after impact u; further, that after impact the velocity of the α particle makes an angle φ, the velocity of the nucleus an angle θ with the original direction of the α particle. (Fig. 9.)

Treating the two bodies as charged points, which involves neglecting the electron or electrons attached to the struck nucleus (a neglect justified by the small mass and large distance from the nucleus of the electron) and assuming no loss of energy at the collision,* we have

$$\left. \begin{array}{l} u=2v\dfrac{M}{M+m}\cos\theta \\[2ex] \tan\varphi=\dfrac{m\sin 2\theta}{M-m\cos 2\theta} \end{array} \right\} \quad \dots\dots\dots\dots\dots\dots(1)$$

so that for the hydrogen nucleus $\left(m=\dfrac{M}{4},\ e=\dfrac{E}{2}\right)$

$$u_H=1\cdot 6\,v\cos\theta. \quad \dots\dots\dots\dots\dots\dots\dots(1a)$$

To calculate θ we must use the orbit, for which a law of force must be assumed. We have seen that experiments on scattering have shown that the inverse square law is justified if the smallest distance of approach be not too small.

With this law, $\qquad p=\mu\tan\theta \quad \dots\dots\dots\dots\dots\dots\dots(2)$

where p is the impact parameter, and

$$\mu=\frac{Ee}{v^2}\left(\frac{1}{m}+\frac{1}{M}\right).$$

Assuming a stream of α particles of homogeneous velocity all travelling in the direction of the x axis, the velocity of the struck hydrogen nucleus (the single electron presumably becomes detached by the violent impact) will depend only upon p, which conditions θ; the velocity of the nucleus conditions its range. The connection between range and velocity is known empirically in the case of the α particle, or helium nucleus, and is expressed by the formula $v^3=aR$, where a is a constant; or the range is proportional to the cube of the initial velocity. This result can be extended to the hydrogen nucleus by the help of Bohr's formula (see page 41)

$$\frac{dv}{dx}=-\frac{4\pi e^2E^2n}{mMv^3}\sum\log\frac{v^3kMm}{v_s eE(M+m)}.$$

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* Such as would be involved in radiation were it set up. It is also assumed that the energy of motion is purely translational.

The mass of the proton (hydrogen nucleus) is one quarter that of the helium nucleus, its charge one half. This means, that except for a corrective term log 2 to be added inside the summation sign, the range of a proton in hydrogen should be the same as that of a helium nucleus of equal velocity in the same gas, and should obey approximately the same law of decrease of velocity. The correction makes the range of the hydrogen nucleus 28 cms. in hydrogen, as compared with a range of 31 cms. for the α particle in the same gas.

For passage through heavier atoms, such as aluminium, where there are more electrons, and so more terms under the summation sign, correspondingly higher multiples of log 2 will occur, and the range will be relatively less. Speaking generally, however, we may expect the range of a proton to be a little less than that of an α particle of the same initial velocity.

There are two important cases which have been examined experimentally, with the object of gaining knowledge of the laws which govern the impact of nuclei when the approach is very close, as distinct from the case where the collision is less intimate and the inverse square law holds. Rutherford, in the first paper on the subject, investigated, for the long-range protons obtained by the impact of α particles on hydrogen atoms, the frequency of occurrence of different long-ranges among a given number of particles. (This distribution of ranges obviously depends upon the collision mechanism; for instance, to take an extreme case, if, by some peculiar inter-action, all the struck protons were thrown forward in the same direction, independent of the impact parameter, we should have one range for all the protons.) Chadwick and Bieler, on the other hand, have since investigated the number of struck protons thrown forward at various angles to the original direc-tion of the α particle. This distribution of angles is another aspect of the same problem, since both the magnitude and the direction of the velocity of the proton are functions of the impact parameter. We shall now consider in outline the theory which covers the two cases.

It is assumed that the hydrogen atoms through which the

α particles pass constitute a comparatively thin layer,[*] a distribution which is most easily attained in practice by using a thin sheet of hydrogen-containing material—say paraffin wax,—the phenomenon being a purely atomic one. The velocity of the impinging α particles may then be taken as the same for all impacts. If the impacts be governed by the laws expressed in equations (1) and (2), then the nuclei struck will go forward in directions making various angles θ with the original direction of the α particles. The velocity will vary as $\cos \theta$, and hence the range in the direction of travel as $\cos^3\theta$, or in the direction normal to the zinc sulphide screen as $\cos^4\theta$.

That is

$$\frac{R}{R_0} = \cos^4\theta \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

where R_0 is the maximum range, i.e. the range of a particle projected at $\theta = 0$.

Hence with increasing effective range (distance in air or air equivalent from source to screen) there will be a rapid falling off of the number of particles, due to the short ranges of the more deflected particles. The number can be obtained in terms of the range by observing that, in passing through a layer of hydrogen 1 cm. thick, the number of protons projected between 0 and θ by Q α particles is

$$n = Q\pi p^2 N = Q\pi N \mu^2 \tan^2\theta \quad \dots\dots\dots\dots\dots\dots(4)$$

where N is the number of hydrogen atoms per c.c. at N.T.P. The numerical value of μ for an α particle of velocity $1 \cdot 922 \times 10^9$ cm./sec. is $9 \cdot 27 \times 10^{-14}$, the numerical value of N is $5 \cdot 41 \times 10^{19}$, whence

$$\frac{n}{Q} = 1 \cdot 46 \times 10^{-6} \tan^2\theta$$

$$= 1 \cdot 46 \times 10^{-6} \left(\sqrt{\frac{R_0}{R}} - 1 \right) \quad \text{from (3)}.$$

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[*] In the case of a thick layer of hydrogen, such as was used in Rutherford's early experiments, where the gas extended more than 3 cms. in front of the source, the absorption of the α rays in the gas itself comes into question. K. Compton (Phys. Rev. **19**, 234, 1922) has worked out the case of the thick layer, and has obtained a correction which can be applied if necessary. As it appears from his calculation that this correction does not affect the general validity of the results obtained by applying the thin layer theory to a layer that is actually of the thickness used in Rutherford's experiments, we shall, for simplicity, follow Rutherford in treating the layer as thin.

The number of protons is proportional to p^2, *i.e.* proportional to $1/v^4$. Considering, therefore, α particles of other velocities than that assumed above, we see that for an α particle of any range r other than the range r_0 of the α particle from radium C, the formula becomes modified to

$$\frac{n}{Q} = 1 \cdot 46 \times 10^{-6} \left(\frac{r_0}{r}\right)^{4/3} \left(\sqrt{\frac{R_0}{R}} - 1\right). \quad \ldots\ldots\ldots\ldots\ldots (5)$$

This formula expresses the number n of protons of range R to be expected, when α particles of range r in air traverse a layer of hydrogen, r_0 being the range of the α particles from radium C in air, and R_0 being the maximum range of struck protons, which is about four times r. It gives a very rapid rate of decrease of the number of swift protons with increasing range.

Formula (4) gives the number of particles projected at angles between o and θ, formula (5) the number projected of given range R. The deduction of these formulae has involved assumptions that the nuclei can be treated as charged points for all collisions, even very close ones, and that the inverse square law of repulsion holds throughout. It has been further assumed that the projected proton travels linearly right up to the end of its path. We know that the α particle of range 7 cms. travels linearly up to within 1 cm. of the end of the range, and in the last centimetre is scattered, and, from analogy, there should be a similar effect with the hydrogen nucleus. This modifies somewhat the law of falling off of the number of projected nuclei at the end of the range, but has been neglected in deducing the formula. We shall see that it appears experimentally that many of the swifter protons are, in certain circumstances, projected forward in the direction of the incident α particle. If all the hydrogen nuclei struck were thus thrown forward in the same direction, then the falling off of the number at the end of the range would be entirely due to such scattering effect, and we should expect a curve similar to that found for the α particle itself, as shown in Fig. 10, which represents the number of scintillations produced on unit area of a phosphorescent screen at various ranges by a narrow beam of α particles passing through air.

Whatever be the law of force, or the nature of the collision, for a direct impact we have from (1)

$$u = 1 \cdot 6v.$$

An α particle of velocity 2×10^9 cm./sec. has range 31 cms. in hydrogen : we have already seen that, applying Bohr's formula, the range for a hydrogen nucleus of the same velocity should
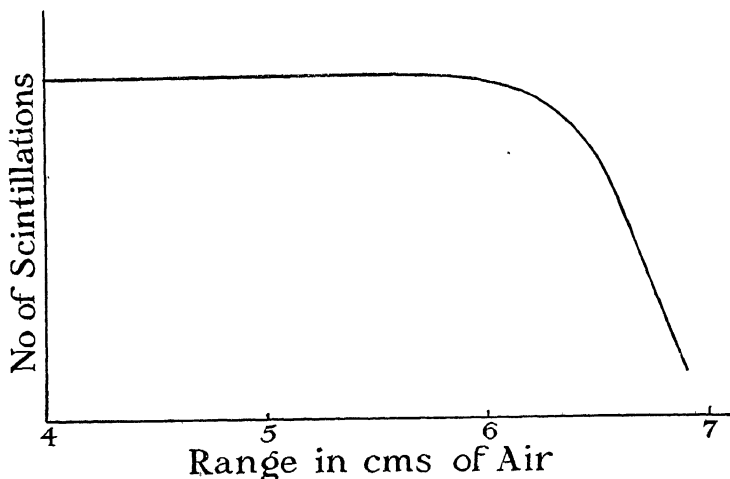
FIG. 10.

Diminution of the number of scintillations produced by α particles from radium C towards end of range.

be 28 cms. in hydrogen. Since the range is roughly proportional to the cube of the velocity, the range of the projected hydrogen nucleus of velocity $1 \cdot 6v$ should be $(1 \cdot 6)^3 \times 28 = 117$ cms. in hydrogen, or about four times that of the α particle projecting it. It has been pointed out that the range of a proton through atoms other than hydrogen is a little less than that of an α particle of the same velocity, so that we can extend this result to air or aluminium, and say that the range of the proton *thrown straight forward by direct impact* of an α particle should be roughly four times that of the α particle itself.

Experimental Observation of Long-Range Hydrogen Particles. Thus, assuming, as has been done, that there is no loss of energy in collision and that the range is proportional to the cube of the velocity, the passage of α particles through a layer of hydrogen should be expected to produce

a few protons of ranges four times that of the α particles themselves. The existence of high-speed particles beyond the range of the particles in hydrogen has been detected by the scintillations produced in a zinc sulphide screen. Using the apparatus shown in the diagram (Fig. 11) Rutherford has carried out a series of experiments on the projected hydrogen nucleus which have led to important results.
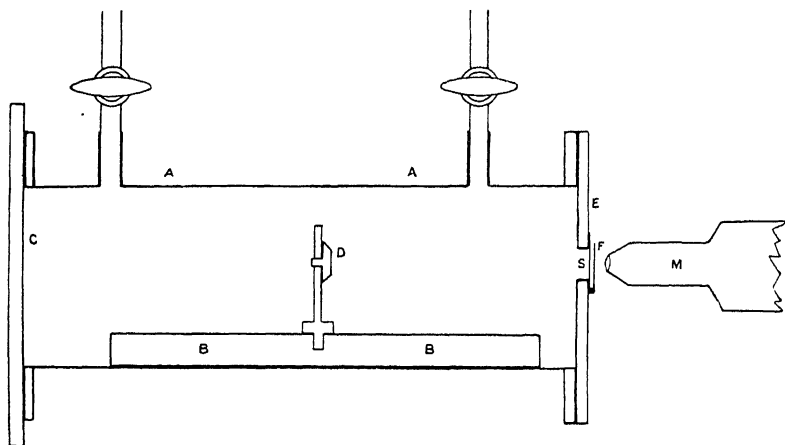
FIG. 11.

Rutherford's apparatus for measurements on long-range protons.

D, the source of radiation, is a brass disc on which radium C is deposited, mounted to slide on the bar BB. This is enclosed in the rectangular brass box, which can be exhausted or filled with any gas. The plate E, which closes one end, is pierced by an opening S which is covered by a thin metal foil, whose stopping power for the α particles varies from 4 to 6 cms. of air. The zinc sulphide screen is outside the window at a distance of a millimetre or two, so that further screens can be introduced between the two. The microscope M for observing the scintillations commands a field of view 2 millimetres in diameter. All the foils used for absorption were heated in an exhausted furnace to get rid of occluded hydrogen as far as possible. Various velocities of α particles were produced by letting the α particles from the radium C pass through appropriate screens. With this apparatus scintillations were observed

for absorptions, produced by screens, equivalent to about 28 cms. of air, which is the range to be expected for directly struck hydrogen nuclei.   But when the relation between the number of long-range particles and the range was investigated, it was found that the distribution varied with the initial velocity of the α particle producing them.   Fig. 12 exhibits the results.

Observed curves	of absorption of H atoms		
	A. range of incident		
	α particles		7 cms
B	,,	,,	6·8 ,,
C	,,	,,	6·1 ,,
D	,,	,,	5·7 ,,
E	,,	,,	4·8 ,,
F	,,	,,	3·9 ,,
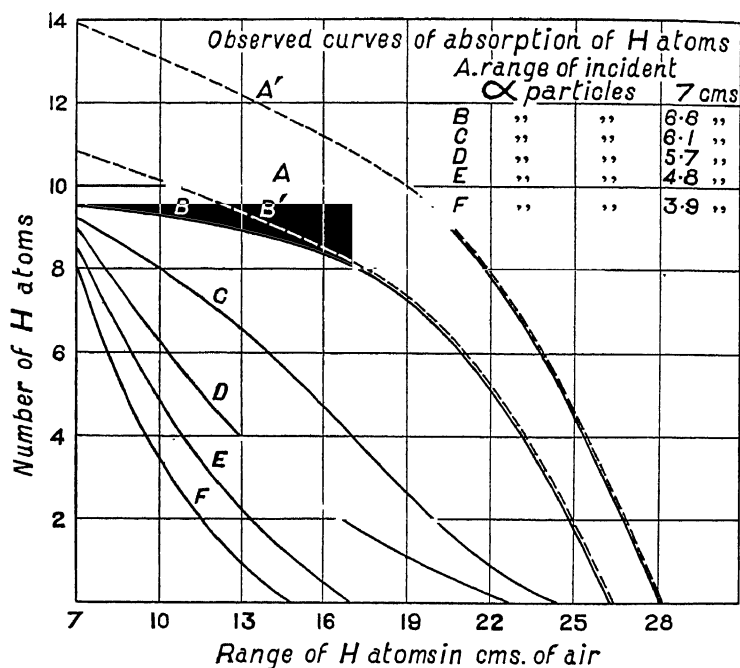
Fig 12.

Distribution of long-range protons produced by α-rays of various velocities.

Curve F for α particles of 3·9 cms. range in air shows a rapid falling off of the number as the range increases, which corresponds closely to the theoretical form given by equation (5). Curves E and D approximate to the same form, but for the full velocity of the α particle the distribution, given by A',* is

* The curves A and B, shown in unbroken line, are the forms given by Rutherford in his original paper.   Later researches in the Cavendish Laboratory have shown that a certain number of slower protons are always

absolutely different. The number of long-range hydrogen particles diminishes comparatively slowly for all ranges up to 22 cms., and then falls off rapidly, there being no particles of range greater than 28 cms. Such a result obviously cannot be reconciled with the assumption that the struck hydrogen nuclei are projected in all directions, at angles varying with the parameter p, according to the assumptions made in deducing equation (5). The nature of the departure of curves A' and B' from the theoretical form followed by D, E and F, indicates that there are far more projected particles of extreme range, corresponding to direct impact, than should be anticipated from application of the inverse square law. It must be remembered that, even if all the protons were thrown directly forward, the distribution curve would not show a sharp drop at 28 cms., but would, on account of scattering at the end of the path, show a falling off of the type exhibited in Fig. 10 for a particles. When allowance is made for the difference between charge and mass of the hydrogen as compared with the helium nucleus, the drop should be expected to set in at 19 cms. Hence the departure from the form indicated by the inverse square law is even more pronounced than appears at first sight, since the curve A' is not very different from what we should expect in the extreme case of all protons thrown straight forward, no matter what the impact parameter. This extreme case is represented by the continuous curve A.

A general explanation suggests itself at once. The simple laws assumed for the deduction of equations (4) and (5) may hold when the two nuclei are separated by a distance large compared with their size, but break down for very close approach. The greater the velocity of the a particles, the closer is the approach, and the greater the departure of the laws of collision from the simple forms valid at greater distances. On the simple assumptions

present, and have indicated that the curves A and B should be modified to the forms A' and B', shown in broken line. A' and B' are therefore considered in the discussion, but it is clear that Rutherford's original conclusions are but little affected by the modification. Instead of inferring that *all* the protons struck by the swift a particles are thrown directly forward we must conclude that *nearly all* the protons are thrown directly forward, but that some are projected at an angle. The essential point, that far more are thrown forward than can possibly be explained on an inverse square law, maintains its validity.

the nuclei must get within a distance of about 3×10^{-13} cms. of one another for the case of α particles of range 7 cms., and although the assumptions are, from what has just been said, not justified, they probably give us about the right order of distance. By counting the number of long-range particles, and comparing with the total number of α particles emitted in the given direction, Rutherford estimated that, for these fast α particles, any one striking a hydrogen nucleus within a perpendicular distance of the centre $= p = 2 \cdot 4 \times 10^{-13}$ cms. projects the nucleus straight forward. This is another expression of the failure of the simple laws of impact to apply for near approach. The most recent work has tended to show that this estimate is rather too small.
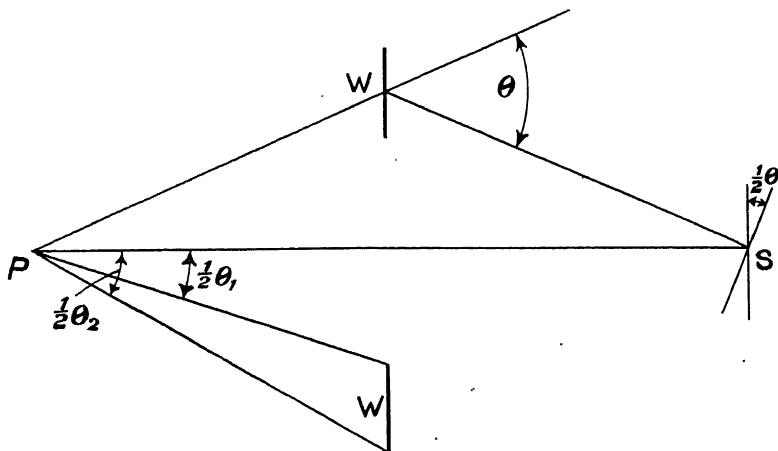
FIG. 13.

Disposition of source of α particles P, source of protons WW, and phosphorescent screen S in Chadwick and Bieler's experiments.

Chadwick and Bieler have confirmed these general results by determining the distribution of number of protons projected at various angles. Suppose that the source of protons be a thin flat ring (of paraffin wax) WW, whose plane is midway between the source of α particles P and the zinc sulphide screen S. Then if R be the number of α particles per second emitted equally in all directions by P, and $n = F(\theta)$ be the number of

protons projected at all angles between o and θ,* by a single α particle passing through a layer of hydrogen gas at N.T.P. I cm. thick, a simple calculation shows that the number x of protons falling on unit area of a screen normal to PS is

$$x = \frac{R\bar{t}}{16\pi\bar{r^2}}[F(\theta_2) - F(\theta_1)],$$

where $\bar{t}$ is the mean value of t sec $\tfrac{1}{2}\theta$, $\bar{r^2}$ is the mean value of r^2, t being the thickness of the paraffin-wax film expressed as a
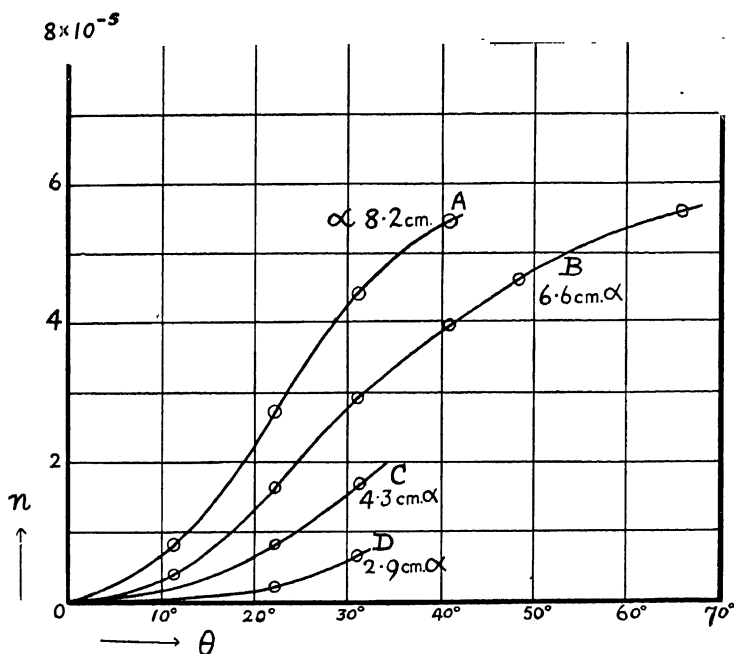
FIG. 14.

Number of protons projected at different angles by α particles of various velocities.

layer of hydrogen gas containing the same number of hydrogen atoms, and r the distance of a point of W from S. By using different annuli of wax, having various values of θ_1, θ_2, and counting scintillations on S, Chadwick and Bieler have been

* This number is the n of equation (4), which, of course, only holds for the inverse square law.

able to find $F(\theta)$, which they express by plotting n against θ.* Direct impact of scattered α rays on the zinc sulphide screen was, of course, prevented by a suitable absorbing screen of aluminium foil placed close to S, so that all scintillations counted were due to projected protons. Fig. 14 shows the results for various velocities of α particles, expressed in the diagram as ranges in air. It will be seen at once that far more protons are projected through small values of θ by fast α particles than by the same number of slower α particles. For the slowest α particles the curve approaches that to be expected on the inverse square law, expressed in equation (4), and the results for α particles of ranges from 2 cms. of air to 1 cm. of air (not shown in the diagram) agree closely with calculation from the simple law, with regard to the absolute number of particles to be expected at various angles as well as with regard to the general form.

Further evidence pointing to the failure of the inverse square law for close collisions has been supplied by experiments of a different type. A. L. McAulay has measured the ionisation produced by the protons projected from a paraffin-wax film by a homogeneous beam of α particles. A shallow ionisation chamber connected to a particularly sensitive electrometer is used, and the ionisation measured with various thicknesses of absorber between the wax film and the chamber. From the figures obtained the number of projected protons of various ranges can be deduced, and from this the number of protons projected at various angles in the collision. McAulay has concluded that the closer the collision the greater is the proportion of protons projected straight forward, but that only for very close collision are all the protons sent straight on.

The preference of the projected protons for the direction of the original α particles cannot be reconciled with a spherical nucleus, and has led to various conjectures. It can either be supposed that the nucleus is normally aspherical—flattened,

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* Following a notation of Darwin's, $\bar{p}$, instead of n, may be plotted against θ. $\bar{p}$ is a length defined by $P = \pi \bar{p}^2$, where P is the probability that a collision will lead to an angle of projection less than θ. This is convenient for comparison with the detailed mathematical calculation, but exhibits the general result less directly.

let us say—or that it is deformed to a flattened shape by the stresses set up by the near approach of another nucleus. Darwin, discussing the question at length, has tried various model nuclei, including one in the form of an elastic plate, which is supposed to set itself with its plane normal to the path of the nucleus. This is Rutherford's original assumption, and obviously gives a greater preference to the forward direction for the struck particle. (Since the helium nucleus is the more complicated, it is taken as the plate-like one, the hydrogen nucleus being assumed to be a point charge.) The agreement is not exact, and the assumption that the nucleus consists of a bipole, *i.e.* two equal charges of the same sign separated by a finite distance, has been tried, and also gives a rough agreement with experiment. The experimental data are not very precise, which, considering the experimental difficulties, is not astonishing, and this, combined with the fact that we know nothing at all of the behaviour of charges at the distances considered here, makes speculation as to the shape of the nucleus more a matter of fancy than for sober computation. For instance, the charges in the bipole which are assumed to be separated by a distance of the same order as the distance of closest approach, cannot act on one another with forces anything like the ordinary electrostatic forces, or the nuclei would be unstable. Chadwick and Bieler, comparing their result with Darwin's calculations, have come to the conclusion that the best agreement with experiment is given by the assumption that the α particle behaves in these collisions as an elastic oblate spheroid, of semi-axes 8×10^{-13} cm. and 4×10^{-13} cm. respectively, moving in the direction of its minor axis. The repulsion between α particle and proton, on this view, obeys the inverse square law until the proton (treated as a point) reaches the spheroidal surface, when it encounters a very powerful field of force, and recoils as from an elastic body. Speaking generally, the anomalous behaviour sets in at a distance between proton and α particle of the order 5×10^{-13} cm., while scattering experiments have shown that for distances about ten times this the nucleus can apparently be regarded as a point charge in all cases.

It need scarcely be said that many control experiments have

been made to see if the long-range particles are really to be attributed to hydrogen. They are produced in all hydrogen compounds, such as paraffin wax. To make sure that the projected long-range particles are really hydrogen nuclei they were subjected to electrostatic and magnetic deflection, according to the principle used for finding $\dfrac{e}{m}$ and v for the electron. The deviation is, of course, small, of the order of that for the α particle ; for details of the experimental arrangement, Rutherford's original paper must be consulted. It was found that $\dfrac{e}{m}$ had the same value as for the hydrogen atom in electrolysis, making it reasonable to assume that the long-range particles are hydrogen atoms with a single positive charge, or, in other words, hydrogen nuclei, or protons. The velocity agreed within experimental error with that calculated on the assumption that there is no loss of energy on impact. This shows that there is no sensible radiation of energy in the collision.

Collision of α Particles with Oxygen and Nitrogen Atoms. Nuclei of Mass 3 ? We have seen that when an α particle strikes a hydrogen atom it communicates to it a velocity which has a value 1·6 times that of the α particle, corresponding to a direct impact, or smaller values corresponding to oblique impacts, and that accordingly we have long-range hydrogen atoms of various ranges not exceeding a fixed maximum. If we turn to consider impact with other atoms, the question becomes much more complicated.

When the α particle strikes an atom it will not communicate large velocities to it unless its original path passes near the nucleus. If it does this, so that the nucleus is suddenly accelerated, we do not know how far the extranuclear system of the atom is disturbed. We know that the α particle produces ionisation in all gases, and in general the ions carry a single charge.* But calculation shows that a swift α particle produces ionisation in, or separates an electron from, roughly every

* In positive ray work carriers with multiple charges are frequently detected. Carbon and oxygen, for instance, give some carriers with two charges, while with mercury vapour carriers with eight charges have been found.

atom which it traverses, and so few of the paths through the atom pass near the nucleus that if such paths did, in fact, remove more than one electron from the atom, it would not be detected. We have, then, little to guide us as to the state of the atom whose nucleus is struck.

Even supposing, however, that this were definitely settled, the formulae, due to Rutherford, Bohr and Darwin, which have been worked out to give the change of velocity, and hence the range, of a swift particle, all assume the swift particle to be simple and small, of the nature of a nucleus or an electron. If the nucleus carries electrons with it they will modify the interaction between the moving particle and the electrons of the atom through which it is passing, an interaction which is responsible for the diminution in velocity (see page 40). As far as I know, nothing has been worked out in any detail on this point.

Suppose, for example, that α particles are shot through nitrogen, producing a few swift nitrogen atoms by direct impact with nitrogen nuclei. We have no precise theoretical ground for expecting any particular range for a nitrogen atom so produced, since to the action of the electrons of the stationary nitrogen atoms on the moving nucleus we have to add the interaction of the electrons, and the action of the electrons of the moving nitrogen atom on the fixed nucleus. Rutherford originally assumed that the moving nitrogen atom may be treated as a nucleus of nitrogen mass, but with unit charge, on which hypothesis a range can be worked out for swift nitrogen atoms moving through nitrogen in terms of the range of the incident α particles. For direct impact the range so found exceeds that of the α particles.

Experiments have shown that the α particles from radium C, when allowed to pass through oxygen, nitrogen, or air do, in fact, produce scintillations beyond the normal range. Taking air at normal pressure and 15° C., for example, the normal range of the α particles is 7·1 cms., but scintillations are observed up to 9 cms. These scintillations would at first sight appear to be due to struck oxygen and nitrogen atoms originating in the volume of the gas. The question then arises as to whether the actual particles producing the scintillations are oxygen and

nitrogen nuclei, or fragments of these nuclei ? When pure oxygen and nitrogen are tried separately the limit of range (9 cms.) is found to be about the same in the two cases, which tends to show that the particles are not actual oxygen and nitrogen nuclei, since we should scarcely expect the heavier oxygen nuclei to travel as far as the nitrogen nucleus. It has been pointed out, however, that so little is known of the laws which govern the behaviour of a struck nucleus of the mass in question, with an unknown number of electrons still adhering to it, that it is unwise to be dogmatic on this point.

Carrying out experiments of the type described in the section which deals with the rupture of the nitrogen nucleus, in which the magnetic deflection is measured by a special device, Rutherford originally concluded that his results with nitrogen and oxygen were compatible with the existence as a separate entity of a nucleus of mass 3, carrying a charge 2, projected from the atom with a velocity $1 \cdot 19 \, v$, where v is the velocity of the impinging α particle. Such particles must, to agree with experiment, be assumed to come from both oxygen and nitrogen with about the same velocity, since the shorter range particles from oxygen and nitrogen have about the same range. It seemed, then, possible that the nuclei contain particles of mass 3, corresponding to an unknown gas.

The existence of such a new element must be considered very doubtful, or, at least, not beyond question. It is true that Bourget, Fabry and Buisson have concluded that there exists in the nebulae an element of atomic weight about 3, basing their estimate on the broadening, by Doppler effect, of the lines of unknown origin in the spectra of the nebulae, to account for which the gas nebulium has been postulated. Rydberg, too, decided some years ago, on spectroscopic grounds, to create two new elements between hydrogen and helium. But on other grounds there is no place for a new element in this position : all experiment tends to show that hydrogen has nuclear charge 1 and helium nuclear charge 2. There is, of course, the possibility of an isotope of helium, with atomic weight 3 and nuclear charge 2, but such an isotope should give approximately the same line spectrum as helium.

Rutherford himself has since announced that he is not

contented with his original experiments on this point, and does not consider that they establish the existence of particles of mass 3. It appears that a marked variation of the thickness of films of metal foil used as absorbers tended to falsify the fixing of the source of the particles which produced the scintillations. It has since been found that some parts of a foil whose average stopping power, deduced from the weight, was 3·8 cms., had a stopping power of only 2·5 cms. Rutherford and Chadwick have shown quite recently that radium C itself emits, in addition to the α particles of range 7 cms. which have long been recognised, other α particles of range 9·3 cms. and 11·2 cms. The nature of the particles has been proved by their magnetic deflection. These appear whatever material is used to absorb the main beam of α rays, and are to be regarded as two groups of swift α rays from the radium C nucleus which, in all probablity, represent new types of disintegration of that element. Now when the particles come from the radioactive source, the method of determination of mass, based upon the assumption of a production in the volume of the gas, is no longer valid. It may be said, therefore, that there is no unexceptionable evidence in favour of the particles of mass 3. Their possible existence has been discussed here firstly on account of the great interest which centres on the subject, and secondly to indicate the extraordinary difficulty of the experimental investigations of these points.

Systematic photographs of the tracks of α particles towards the end of their paths have been taken by Shimizu, and, quite recently, by Blackett, using the C. T. R. Wilson method of rendering the ionisation produced visible by cloud production. These photographs show that recoil nitrogen and oxygen atoms are comparatively numerous, but too little is at present known of the behaviour of such slow-speed particles to enable detailed conclusions to be drawn.

The Rupture of the Nitrogen Nucleus. More striking results derived from observations on the passage of α particles through nitrogen are now to be considered. There are always a certain number of very long-range * scintillations observed with a

* By this is indicated ranges far beyond that of the α particle, up to, in fact, 28 cms. and more in air.

radium C source, due either to hydrogen atoms shot out from the nucleus of the radium C atom—there is no other reason to believe that radioactive atoms themselves emit swift hydrogen atoms, but, on the other hand, the few atoms in question could scarcely be detected by any other method—
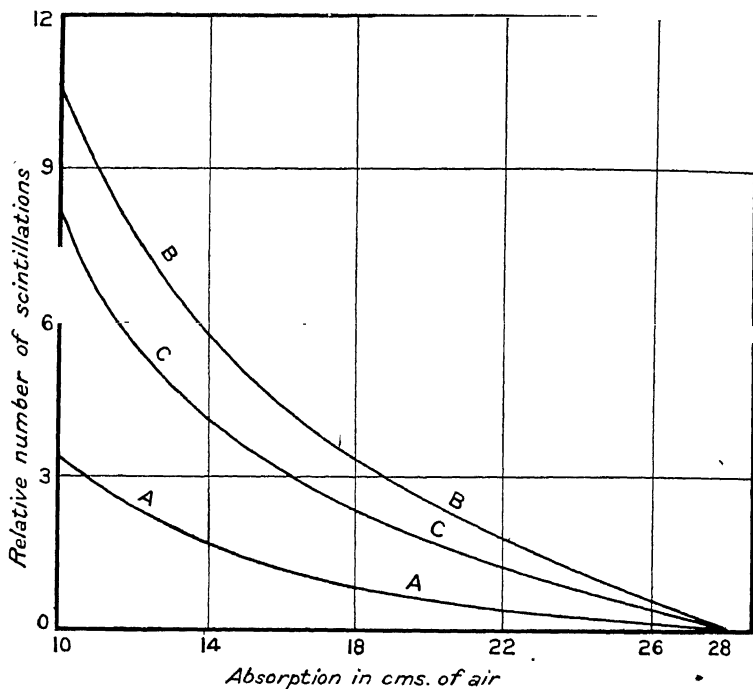
FIG. 15.

Long-range protons from nitrogen.

or to α particles striking hydrogen atoms contained in contaminations of the source. The introduction of nitrogen between source and screen increases the number of long-range scintillations, in proportion to the pressure of the gas, while oxygen, or oxygen compounds such as carbon dioxide, do not increase the number. Air produces an effect proportional to its nitrogen content. A series of checks have shown that the increased number of long-range particles is really due to the nitrogen and to no other cause. Since the range is far beyond that possible for struck nitrogen atoms on any reasonable

assumption, and is approximately equal to that to be expected for struck protons, Rutherford has concluded from his experiments that when a swift α particle strikes a nitrogen nucleus it can knock a proton out of it. The nitrogen nucleus must, then, contain a proton as part of its structure. From the experiments it appears that only one impact out of twelve close collisions, giving rise to a swift nitrogen atom of maximum range 9 cms., can liberate a proton from the nitrogen nucleus.

Fig. 15 expresses the way in which the number of long-range particles diminishes with absorption. Curve B is for air, curve A gives the " natural " long-range scintillations due to the source (with carbon dioxide at a pressure calculated to give the same absorption of α rays as ordinary air), while curve C, expressing the difference of B and A, shows the scintillations arising from the presence of the nitrogen.

The long-range particles from nitrogen have been definitely proved to be hydrogen nuclei by deflection in a magnetic field.
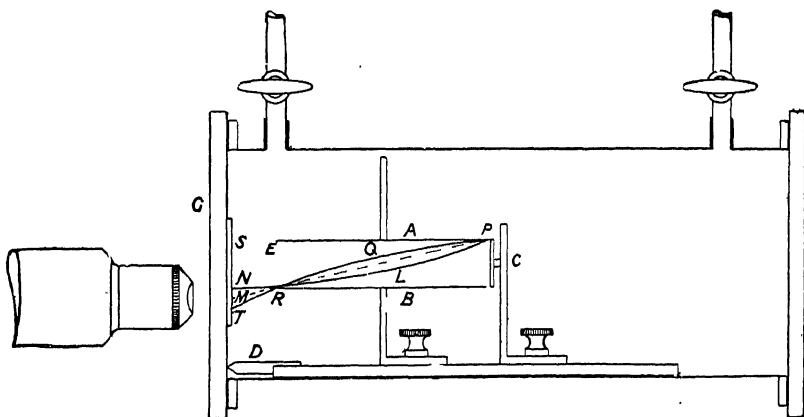
FIG. 16.

Rutherford's apparatus for identifying long-range protons.

The apparatus used by Rutherford is shown in Fig. 16. The disc held by the stand C is the source of the α particles. A and B are two parallel plates 6 cms. long and 1·5 cms. wide, separated by a distance of 8 mm., so as to allow struck atoms which go off at an angle enough room to emerge. S is the zinc sulphide screen ; absorbing screens inserted between S and R

stop the nitrogen or oxygen atoms of 9 cms. range. When there is no magnetic field the boundary between the region in which scintillations are frequent and that where they occur only occasionally is given by the line *PRM*, cutting the screen at *M*. The effect of the field is to displace this boundary,
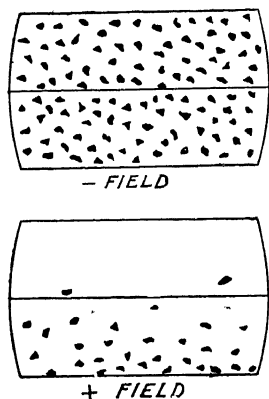
− *FIELD*

+ *FIELD*

FIG. 17.

Change of appearance of screen effected by reversal of magnetic field.

either downwards or upwards according to the direction of the field. In this experiment the strength of the field is adjusted so that the screen is just covered with scintillations for one direction, while when the direction of the field is reversed scintillations are mainly confined to the region below a horizontal cross-wire in the observing microscope. Fig. 17 shows the appearance in the two cases.

No very precise deductions can be made from this experimental result alone, since the long-range particles are produced at all parts of the range from one end of the plates to the other, although in greater quantity near the source, where the velocity of the particle is high. Rutherford, however, has adopted the device of repeating the experiments with a mixture of hydrogen and carbon dioxide, adjusted to have the same stopping power for α particles as air, when the effect of the magnetic field on the scintillations is indistinguishable from the effect with air. Since in the case of the hydrogen mixture the long-range particles can, from results already considered, be nothing but hydrogen nuclei, this affords a proof that the long-range particles produced from nitrogen are in fact protons. The only possible source for them is the nitrogen nucleus.

Long-Range Particles from other Light Elements. When nuclei are disintegrated the laws of conservation of energy and of momentum do not necessarily connect the velocity of the α particle before collision with the velocities of the α particle, main body of the nucleus, and fragment of the nucleus after collision. The potential energy which the nucleus may be supposed to possess in virtue of the state of tension between

its parts, or the kinetic energy which it perhaps possesses in virtue of a possible motion of the nuclear constituents, may be involved in the rupture. Theoretical considerations, therefore, lead us to believe that an a particle of given velocity may produce long-range protons whose velocity is in excess of that calculated from simple mechanical considerations.

It has been shown by Rutherford and Chadwick that the long-range protons struck on by $\dot{a}$ particles from radium C have a maximum range of 29 cms. (in air) if produced from hydrogen, but a maximum range of 40 cms. if produced from nitrogen. Various other light elements have been tried with a view to the production of long-range protons. In their experiments of 1921 and 1922 Rutherford and Chadwick usually subjected the elements to the action of the a rays by placing a film of the solid oxide, deposited on a gold foil, between source and screen. Long-range protons from the nuclei were detected with boron, nitrogen, fluorine, sodium, aluminium and phosphorus. That the long-range particles so produced are actually hydrogen nuclei has been proved by deflection in a magnetic field, and that they are not due to chance atoms of hydrogen present as contamination in the film is evident from their ranges, which in the case of all the elements just mentioned notably exceeds the 30 cms. range in air characteristic of free hydrogen nuclei set in motion by a particles from radium C. Particles of range less than 30 cms. were observed with films of certain other light elements, but the inevitable presence of hydrogen contaminations made it impossible to attribute them with any confidence to the nuclei of the elements in question so long as this method of observation was used.

An important characteristic of these particles struck out of complex nuclei by a rays has, however, enabled Rutherford and Chadwick to modify the method so as to deal with protons of range less than 30 cms. Whereas with hydrogen as the bombarded material nearly all the protons are thrown directly forward, it was found that with the other elements nearly as many long-range protons proceed backwards as forwards. The velocity of the forward protons is always somewhat greater than that of the backward ones, but the effect clearly indicates that the release of the protons from the nuclei is due to some

kind of trigger action.   In support of this it may be noted that the energy of the protons of 90 cm. range released from aluminium is greater than the total energy of the releasing α particle.   It follows that whereas the protons due to hydrogen contaminations are to be found only in the forward direction, protons released from complex nuclei by trigger action initiated by α particles are to be expected in any direction in numbers not very different from those in the forward direction.   It is by taking advantage of this possibility of distinguishing between the two that Rutherford and Chadwick have been enabled to make a further advance.   In the new method the nuclear protons are looked for at right angles to the powerful beam of α rays which liberates them.   The source and the material to be investigated are in an evacuated box, and the zinc sulphide screen is placed outside, over a hole covered with a sheet of mica of stopping power equivalent to 7 cms. of air.   That no hydrogen nuclei from hydrogen atoms, or α particles from the source, can reach the screen under these conditions is clearly shown by the fact that no scintillations are observed when a sheet of paraffin wax is bombarded.

With this arrangement it has been found that, in addition to the elements already mentioned, the following give rise to protons of range exceeding 7 cms. : neon, magnesium, silicon, sulphur, chlorine, argon and potassium.   The numbers of protons from these elements are small compared to that from aluminium under the same conditions, varying between $\frac{1}{3}$ and $\frac{1}{20}$ of the latter.   The maximum ranges have not been accurately determined at the time of writing, but appear to lie between 18 and 30 cms. for all elements in question except neon, for which the range is less, about 16 cms.   The following elements have been tested for long-range protons with negative results : helium, lithium, carbon, oxygen, iron, nickel, copper, zinc, selenium, krypton, molybdenum, palladium, silver, tin, xenon, gold and uranium.

The range of a scattered α particle is less than that of the original α particle whenever the deflecting nucleus is light enough to take up an appreciable fraction of the energy of the incident particle.   This range depends, of course, upon both the angle through which the particle is deflected and the mass of

the scattering nucleus * ; for instance, with carbon as scattering material, and the angle a right angle, as in these experiments, the range of the α particle is reduced from 7 cms. to 2·5 cms. by the interchange of energy at deflection.   Hence a sheet of mica of very small stopping power can be used to stop all scattered α particles, and protons of range down to 2 or 3 cms. can be looked for by this method.   No protons even of this short range were detected with carbon.

The results are summarised in the following table :

NUMBER AND RANGE OF LONG-RANGE PROTONS
FROM VARIOUS ELEMENTS.

Element.	Atomic Number.	Mass Numbers.	No. of Particles per minute per milligram.	Maximum range of particles in cms. of air.		
				Forward.	At right angles.	Backward.
Lithium - -	3	7, 6	—	—	—	—
Beryllium- -	4	9	—	—	—	—
Boron - -	5	11, 10	>·15†	58	—	38
Carbon - -	6	12	—	—	—	—
Nitrogen - -	7	14	·7	40	—	18
Oxygen - -	8	16	—	—	—	—
Fluorine - -	9	19	·4	65	—	48
Neon - -	10	20, 22	—	—	16	—
Sodium - -	11	23	·2	58	—	36
Magnesium - -	12	24, 25, 26	—	—	About 25	—
Aluminium - -	13	27	1·1	90	—	67
Silicon - -	14	28, 29, 30	—	—	About 25	—
Phosphorus - -	15	31	. ·7	65	—	49
Sulphur - -	16	32	—	—	About 28	—
Chlorine - -	17	35, 37	—	—	About 30	—
Argon - -	18	40, 36	—	—	About 23	—
Potassium -	19	39, 41	—	—	About 23	—

Fig. 18 gives a graphical representation of the same results. For convenience of distinction the columns corresponding to elements of odd atomic number are black, and the columns for even atomic number are white.   The heights of the columns are, of course, approximate, since for some elements the range has been measured only at right angles to the bombarding beam of α particles, while in other cases the forward range is taken.   There is probably not much difference between the

* See page 75 *et seq.*

† ·15 is given by Rutherford and Chadwick in their first paper (*Phil. Mag.* Nov. 1921), but in a later paper (*Phil. Mag.* Sept. 1922), they state that ·15 is too small.

forward and right-angle range for a given element, and in any case a high degree of accuracy cannot be hoped for at present in such measurements.

Kirsch and Pettersson have carried out certain experiments on the artificial disintegration of elements by exposing thin copper foils spread with layers of the substances to the action of radium emanation in contact with them. They have found long-range protons from magnesium and silicon, for which they
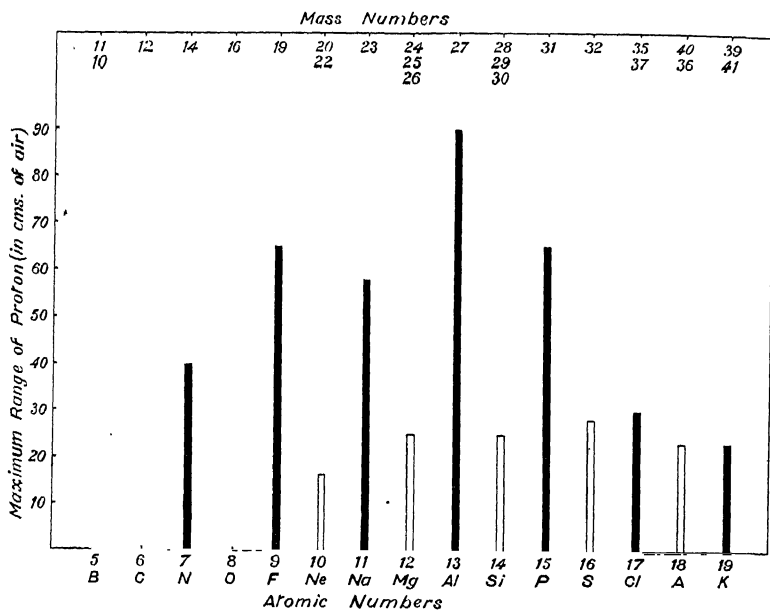
FIG. 18.

Range of protons expelled from different elements by bombardment with α particles.

give a forward range of 12 cms. and 13 cms. respectively, and also protons from lithium, beryllium, and carbon, the range in the case of the last mentioned being only 6 cms. These latter results are in direct contradiction to the results of Rutherford and Chadwick. Whether Kirsch and Pettersson have succeeded in establishing their contention is a matter on which the experts in this particularly difficult type of work must judge for themselves : if any others feel in doubt as to whether they

or Rutherford are more likely to be in error on this point, these doubters must await the test of time.

From the earlier results it was supposed that a proton could not be separated from nuclei of elements of mass $4n$, where n is a whole number, but the most recent experiments have shown that this is not true. The most striking general feature of the results of Rutherford and Chadwick, readily visible from Fig. 18, is that protons from elements of even atomic number either do not occur or are of much shorter range than those from elements of odd atomic number. They are also, in general, fewer in number. These points are further discussed in Chapter VII.
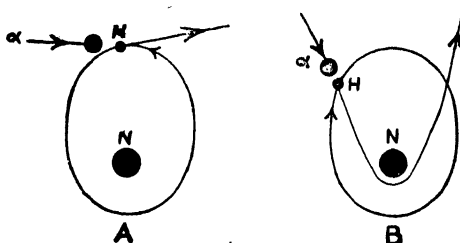
FIG. 19.

Release of a proton from a nucleus : A, in the forward direction ; B, in the backward direction.

The fact that the direction of emission of the liberated proton is largely independent of the direction of the incident α particle and that the energy of the liberated particle occasionally exceeds the total energy of the incident α particle, points to a release of nuclear energy. The mechanism of this release has been the subject of speculation. Rutherford and Chadwick suppose that within the nucleus a proton revolves as a satellite, being held in its orbit by a central attraction. (There may, of course, possibly be more than one such satellite.) This implies that somewhere within that vague central region which we term the nucleus the force on a positive charge is an attraction, which changes to a repulsion as we go further out, a conclusion to which Bieler has also been led, as described in Chapter II. The impact of the particle drives the satellite outside the critical surface at which the force is zero, and the proton is then repelled, acquiring a high velocity. Fig. 19

clearly expresses the mechanism contemplated. Against this Pettersson has put forward what he termed an explosion hypothesis, which supposes that the effect of the impact of the a particle is to initiate a disturbance by which the proton is shot out with a velocity, *relative to the residual nucleus*, independent of the direction. The difference between forward and backward velocity is due to the forward motion communicated to the nucleus as a whole. The only figures which he invokes to support the hypothesis show the kind of partial agreement and disagreement which scarcely carries conviction. The experimental facts are not yet sufficiently numerous or sufficiently precise to bear the load of speculation that willing hands are ready to heap upon them. The advantage of the satellite hypothesis is that it does give a mechanism, artificial as it may be, by which the emission might be supposed to be obtained : the explosion hypothesis gives no picture.

The information afforded by these astonishing experiments of Rutherford's is considered further in Chapter VII., when the constitution of the nucleus is discussed. This playing billiards with nuclei is a remarkable technical feat, and the whole series of experiments depends upon our ability to deal with single atoms. The amount of disintegration taking place in the atoms exposed to rapid a particles is excessively small : for instance, it can be calculated from the scintillation results that if the whole a radiation from 1 gram of radium were allowed to fall upon nitrogen atoms for a year, only 5×10^{-4} cubic millimetres of hydrogen would be set free, a quantity which it would be troublesome to detect by ordinary means, to say the least.

The scintillation method no longer provides the sole evidence for the disruption of the nitrogen nucleus by favourable impact of an a particle. Blackett has recently succeeded in photographing by the Wilson method collisions resulting in the expulsion of a proton. The general method is the same as that by means of which the tracks in oxygen and helium were photographed in the earlier experiments (see p. 24), two photographs being taken simultaneously from directions at right angles, which enables the tracks to be located in space. Since Rutherford and Chadwick have shown that for a million a particles of range 8·6 cms. the expulsion of a proton from a

PLATE III
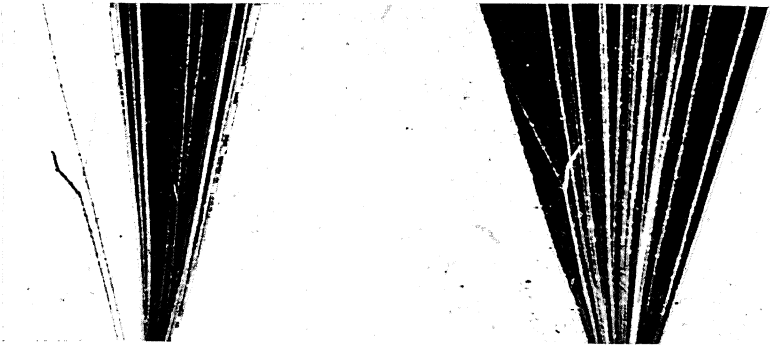
Double Photograph of α-Ray Tracks, showing Disruption of Nitrogen
Nucleus and Expulsion of Proton. (Blackett.)

The track showing the disruption is the one on the extreme left in the left-hand
photograph; the same track appears next to the extreme left in the right-hand
photograph. The thin straight branch is the track of the proton; the short bent
branch is the track of the struck nucleus.

nucleus takes place in only about twenty cases, it was necessary to take a very large number of photographs. Actually Blackett, using the α rays from a deposit of Thorium $B + C$ (which gives particles of range 8·6 cms. and of range 5 cms.), has taken about 23,000 photographs, showing some 270,000 tracks of α particles of range 8·6 cms. and 145,000 tracks of range 5 cms., and among these has obtained record of 8 tracks resulting in the expulsion of a proton. This agrees as well with Rutherford and Chadwick's estimate of the frequency of occurrence of such collisions as can be expected, considering the large probability variations of such small numbers.

An example of Blackett's results is given by the beautiful double photograph reproduced in Plate III. The desired track is seen on the extreme left in the left-hand photograph, and is the extreme left but one in the right-hand photograph. The track of the expelled proton is very thin compared to the main track, and presents a beaded appearance, characteristic of small ionisation. This agrees with expectation, since the ionisation due to a moving particle is proportional to the square of its charge, and is inversely as the velocity, both of which factors contribute to make the ionisation produced by the proton considerably less than that produced by the impinging α particle. The appearance of the anomalous track is not the only evidence that it is produced by a proton. The angles which it makes with the other components of the fork are not consistent with elastic collision. The three limbs are, however, coplanar, which supports the natural hypothesis that, although kinetic energy of translation is not conserved in such a collision, owing to the internal nuclear energy being involved, yet the conservation of momentum still holds. Calculation based on this assumption shows that the velocity of the proton, of mass 1, deduced from measurement of the angles of the fork agrees well with Rutherford and Chadwick's deduction from the range in their experiments. Blackett has obtained, among the eight pictures of nuclear rupture, a photograph of a proton ejected backwards, which constitutes another proof of the nature of the collision.

It is remarkable that the fork shows two prongs and not three, as might be expected to correspond to proton, broken

nucleus, and α particle after collision. The conclusion that the α particle is captured by the nucleus, and that the heavy branch of the fork represents the path of the new nucleus so formed, seems inevitable. The α particle cannot lose enough energy in the collision for it to cease to ionise, since, if it leaves the struck nucleus at all after the close approach necessary to eject a proton, it must acquire a high speed in the repelling field. The length of the track of the heavy nucleus is consistent with an atomic number 8, but can only fix the mass within fairly wide limits, as lying between 12 and 20 say. The positive evidence, then, indicates that the result of a destructive collision of an α particle with a nitrogen atom is that a proton is expelled from the nucleus, and that the α particle remains sticking to the shattered nucleus, forming a new nucleus of atomic number $7 - 1 + 2 = 8$, and mass $14 - 1 + 4 = 17$. Such a nucleus would characterise an isotope of oxygen. This isotope cannot be of frequent occurrence, since its existence is not indicated by Aston's mass determinations, nor by atomic weights. Little can be profitably said about it at the present moment.

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See also References, Chapter II.

CHAPTER V

POSITIVE RAYS

Introductory. By various devices the positively charged atoms which are always present in a low-pressure tube through which a discharge is passing can be separated out into a beam, consisting of discrete atoms or molecules flying all in one direction. Of recent years this beam has been much studied with a view to obtaining information as to the charges which atoms can carry, and the mechanism of light emission. For our purpose, the chief importance attaches to the researches of J. J. Thomson and of F. W. Aston, who have shown how from the positive rays the masses of atoms and molecules, and the charges carried, can be accurately deduced. The recent results of positive ray analysis have proved the existence of isotopes of a variety of common elements, and that, when the existence of these isotopes is taken into consideration, the atomic weights of all elements, except hydrogen, are exact whole numbers when expressed in terms of oxygen, taken as 16. This has introduced a far-reaching simplification into the theory of the nucleus.

Older methods of determining the masses of atoms are indirect, and give what is, in effect, the average mass for the very large number which go to make up weighable quantities of matter. The positive ray method has, for the first time, established definitely that a small series of whole numbers represent the weights of all atoms—that the atoms of a given substance do not have a continuous range of weights, with a most probable value, like the velocities of molecules in the kinetic theory of gases, which was hitherto a possible belief. The method has also established the existence of new molecules, such as H_3. It deals, of course, with extraordinarily small

quantities of matter, for, while any ordinary chemical method needs at the very least 10^{12} atoms, it has been estimated that 10^3 atoms are sufficient to give a well-marked record by the positive ray method. We are in it approaching the results possible in the case of those " natural " positive rays, the a particles, where single atoms can be detected.*

Nature and Production of Positive Rays. The term " positive rays " does not describe accurately the radiations with which we are now concerned, for the positively charged particles are accompanied by negatively charged and neutral particles. What is truly characteristic of the rays is that they consist in all cases of flying material atoms, or groups of atoms, there being no transport of free electricity. It is probably now too late to modify the nomenclature, but it would be more consonant with the facts to use the expression " molecular rays " (the term molecule including single atoms) or, by analogy with Aston's term " mass spectrograph," " mass rays."†

Positive rays can be produced in different ways. In the case of the familiar canal rays, which make their appearance when a pierced cathode is used, the rays stream through the holes and travel in the opposite direction to the cathode rays : it is with rays so produced that most of the important experiments to be discussed have been carried out. It may be well to recall, however, that they can also be produced with cathodes made of two parallel plates metallically connected, or with two thin parallel wires used together as cathode. In a canal ray tube there is also a material radiation which travels in the same direction as the cathode rays, from which it can be separated by deviating the cathode rays magnetically. This constitutes what Goldstein called K_1 rays : J. J. Thomson speaks of it as retrograde rays. Rays of a material character have also been produced, by W. Wien, from a pierced anode, and by Gehrcke and Reichenheim

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* It is perhaps worth while recalling in this connection the fact that von Dechend and Hammer claim to have obtained discrete scintillations with canal rays of high velocity. Energy considerations, however, make it doubtful if true scintillations have been obtained, or, at any rate, if they can be due to the impact of single atoms.

† I am much gratified to note that, since the publication of the first edition of this book, Dr. Aston has approved the nomenclature here suggested, and adopted it himself.

from an anode containing an enclosure of, or impregnated with, a metallic salt. These rays are generally called anode rays. Gehrcke and Reichenheim's method of production has the advantage that atomic rays of the light metals can be comparatively easily produced by using a hollow anode filled with a salt of the given metal, and it has been utilised recently by Aston and by G. P. Thomson. The salt is usually mixed with powdered graphite for convenience in manipulation. Another method of obtaining mass rays, also due to Gehrcke and Reichenheim, which has been used with much success by Dempster and by Aston, is to employ a hot anode coated with a metallic salt.

W. Wien and J. J. Thomson have shown by independent methods that in the canal rays positive, neutral and negatively charged material particles co-exist, and, further, that if the positively charged particles are separated out of the beam by a magnetic field they are subsequently regenerated in the remaining beam, as may be shown by a second magnetic field. Some particles remain positively charged throughout their path, others become neutral or negative, and particles that have once become neutral may acquire a charge again. In fact, however the rays be treated, an equilibrium is speedily established in which the ratio of the number of the charged to the uncharged particles is constant under given conditions. Wien showed that the lower the pressure the smaller the effect of a magnetic field in diminishing the heating and phosphorescent action of the original beam, which indicates that at very low pressures particles which have once become neutral remain so. In short, a great body of experimental facts points to the following mechanism. The mass rays which pass through the pierced cathode in a discharge tube at low pressure are atoms, or combinations of atoms, which have acquired a positive charge by loss of electrons in the region of strong ionisation in front of the cathode, and have consequently been accelerated towards the cathode by the large potential gradient in the dark space.*

* The total drop of potential is practically concentrated in the dark space. Positive particles generated at the far boundary of the dark space will therefore have a velocity which corresponds approximately to the total drop : particles generated in the dark space will have lesser velocities varying with the distance of their point of generation from the cathode.

They shoot through the hole in the cathode into a region of low pressure, where, however, they make in general a certain number of collisions with free electrons.* These collisions lead to the neutralisation of the positive atom, or the acquisition of a positive or negative charge by the neutral atom, according to circumstances. A great deal of work has been done on the theory of these changes which need not detain us here. We content ourselves with stating that the whole question is bound up with the mean free path of the charged and uncharged atoms shot through a very low concentration of stationary particles. Ordinary gas-kinetic methods can be applied with some success.

The fundamental results are obtained by considering the record of such particles as retain their positive charge throughout their path from the deflecting system to the photographic plate on which they are received. Both particles with a constant negative charge, and particles which have been positively charged for part of the path only, also, in general, leave their traces, and for the full interpretation of the photographs some consideration of the mechanism sketched above is necessary.

The Method of Crossed Electric and Magnetic Deflection. J. J. Thomson evolved a powerful method of determining the mass and charge of all the flying atoms and molecules present, by making use of an electric field superimposed on a magnetic field. The lines of electric and magnetic force have the same direction, and therefore the deflections of a moving charge due to the two fields are at right angles to one another. The apparatus is represented in Fig. 20. The bulb A is made very large, since this is found to facilitate the passage of the discharge at the low pressure necessary in these experiments. B is the pierced cathode, cooled by the water jacket C. M is the magnet producing the magnetic field: the pole pieces are insulated electrically, so that the electric field required can be

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* That it is collisions with electrons, and not with atoms, which causes the changes of charge is indicated by, for instance, the experiments of Königsberger and Kutschewski. They showed that the velocity of the rays is independent of the pressure over a considerable range (5×10^{-5} mm. to 5×10^{-3} mm.), whence it is concluded that the changes of charge have no appreciable effect on velocity, and so that they cannot be due to impacts with the comparatively heavy atoms.

maintained between them. D is the anode : H is the photographic plate, normal to the undeflected beam, on which the rays record themselves.

We consider the trace left on the plate when the two fields are acting, the mutually perpendicular deflections, measured on the plate from the spot where the undeflected beam strikes it as origin, being x and y.   Let e, m, and v be the charge, mass,
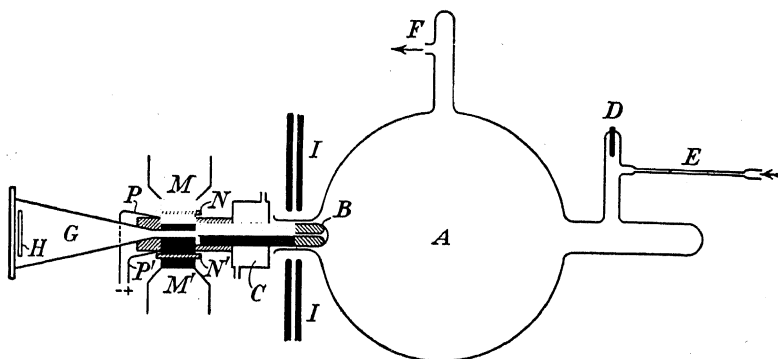
FIG. 20.

Positive ray apparatus for parabola method.

and velocity respectively of the particle.   If the deflections are not large, we have for that due to the electric field of strength X

$$x = C_1 \cdot \frac{Xe}{mv^2},$$

and for that due to the magnetic field of strength H

$$y = C_2 \cdot \frac{He}{mv}.$$

C_1 and C_2 are constants which depend only on the dimensions of the apparatus used.*   Hence

$$\frac{y}{x} = \frac{C_2 H}{C_1 X} \cdot v, \qquad \frac{y^2}{x} = \frac{C_2^2 H^2}{C_1 X} \cdot \frac{e}{m}.$$

Particles moving with a fixed velocity will give on the plate a

* For instance, if the fields be considered to extend over a distance b, and to begin and terminate sharply, and if the distance of the photographic plate from the remoter end of the field be l, then $C_1 = C_2 = b\left(l - \dfrac{b}{2}\right)$.   If allowance is

straight line passing through the origin, no matter what their charge and mass. Particles for which e/m is constant will give a parabola passing through the origin. Reversing the sign of e reverses, of course, both deflections, and gives a parabola in the opposite quadrant, so that negatively charged particles give separate traces.

Königsberger and Kilchling, and others, have made use of the parabolae for investigating e/m, but the most fruitful experiments have been carried out by J. J. Thomson, in whose hands the method of positive ray analysis has been made to yield very elegant and important results. The constants of the apparatus being known, it is clear that every parabolic trace obtained gives a numerical value for e/m. It may be noted that for measurement it is convenient to reverse the magnetic field during the experiment, so as to obtain pictures symmetrical about the axis of x.

Good photographs taken by this method, examples of which are given in Figs. 1 and 2 of Plate IV.,* show a series of clearly defined parabolic arcs, all terminating on a line parallel to the y axis. Different points of the same arc correspond to different energies, the value of x being inversely as the energy. The sharp termination of the parabolae comes from the fact that there is for all particles in a tube run under given conditions a maximum possible value of the energy, corresponding to the full potential drop. In addition to the parabolae due to the positively charged particles there are others, much fainter, due to negatively charged particles, which can also be seen in Figs. 1 and 2 of Plate II. There are also certain faint lines connecting the origin to the parabolae, which are examples of the so-called secondary rays. These must be set down to particles which, owing to collisions, have been positively charged for part of their journey only, and therefore have, effectively, a reduced value of e/m. The full consideration of the different possible cases, and their experimental representation, does not concern us here.

to be made for the fact that in reality the fields do not begin and terminate sharply, then obviously C_1X and C_2H are to be replaced by integrals involving the variable X and H.

* My thanks are due to Dr. F. W. Aston for permission to use these photographs.

From a consideration of mass ray photographs J. J. Thomson deduced various possible masses of atoms and molecules.* The ratio e/m does not, of course, fix m immediately, since the possibility of multiple charges has to be considered, but the uncertainty so introduced can be eliminated by other considerations. Let us, for example, take the case of neon. On the assumption of a single charge, a parabola is found which gives m corresponding to atomic weight 20 ; this is obviously due to neon atoms with one positive charge, and not to calcium with two charges, since it is only found strong when neon is deliberately introduced into the tube. Accompanying this is a parabola which gives an atomic weight of 22 if one charge be assumed. No gas of this atomic weight was known at the time of J. J. Thomson's original experiments, so the possibility that this was due to doubly charged atoms of carbon dioxide (atomic weight 44) had to be considered. It was found, however, that while washing out the discharge tubes with gases which had been drawn through a tube immersed in liquid air completely removed the line corresponding to atomic weight 44, it left the brightness of the 22 line undimmed. This showed that the line was not due to doubly charged carbon dioxide atoms, and, with other considerations, led J. J. Thomson to consider the existence of a gas of atomic weight 22 probable. Since then it has been definitely proved by Aston that there is an isotope of neon with this atomic weight.

Some of the main results obtained by the parabolic method may now be summarised. The existence of triatomic hydrogen, H_3, which has been confirmed by other methods, has been established. The hydrogen atom with one positive charge is also easily detected, but, while with other elements doubly charged atoms are found, this is never the case with hydrogen. Whereas, of course, the fact that hydrogen atoms with two positive charges are never found by this method does not necessarily prove that they cannot exist, it should be noted that if they had been found the whole accepted theory of the hydrogen atom would have been jeopardised. For it is funda-

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* The fact that the parabolae were sharp constituted the first *direct* proof that a given kind of atom has a definite mass rather than a continuous range of mass.

mental for modern theory that the hydrogen nucleus—the proton—has only one positive charge, and if this is true a particle of atomic weight one can never have more than one positive charge. Hydrogen atoms with a negative charge are found, which shows that the hydrogen nucleus can hold two electrons in certain circumstances. The hydrogen molecule H_2 has been detected with one positive charge, but never with two charges, which may be taken to indicate that at least one extranuclear electron is needed to hold the two hydrogen nuclei together. The molecule H_3 likewise can have one positive charge, but apparently never two.

While negatively charged atoms of many elements are easily detected, negatively charged atoms of the inert gases have never been found, which indicates that the nuclei of these gases have normally as many electrons as they can hold. This confirms the views that will be expressed later. In general negative charges are only found with elements or compounds having marked electronegative properties.

With many elements atoms with multiple positive charges are found. Carbon and oxygen atoms with two positive charges may be cited, but atoms of krypton and other elements which have lost three electrons have been detected, and mercury atoms can have any charge from one to eight.

The most important results of the mass ray method have, however, been the detection and ordering of a large number of isotopes, which has shown incidentally that certain definite masses only are possible for atoms, and that a continuous range of masses never occurs. Aston, using an anode consisting of an electrically heated platinum strip coated with a metallic salt—the hot anode method of Gehrcke and Reichenheim—has employed the parabola method for preliminary investigation of the isotopes of the alkali metals. G. P. Thomson, producing anode rays from a cold metallic salt by the other method of Gehrcke and Reichenheim, has utilised the parabola method to demonstrate the existence of isotopes of light metals, such as lithium and beryllium, for which a difference of one unit in atomic mass represents a large percentage difference. The recent great advances in our knowledge of isotopes which have been made by the method of mass rays are, however, essentially

bound up with certain improved experimental methods. These must now be indicated in outline.

Focussing Methods. The most important object of the method of mass rays is to determine the masses of atoms and molecules. For this purpose the parabola method has certain disadvantages, of which one of the most serious is that the beam proceeding from the fine hole in the cathode spreads somewhat, producing, in effect, an umbra and penumbra, as would a beam of light from an extended source sent through the same hole. The result is that the lines produced can never be sharp. Again, the total number of particles of the same e/m are distributed over a long line ; shorter exposures would be possible in a method which brought the rays to a more restricted spot, whose position should give the information required.

Two methods of focussing rays of fixed e/m, so that all particles of a beam, initially slightly divergent, are collected to one spot, have been devised. That of Dempster makes use of rays of homogeneous velocity, which are obtained by producing charged atoms of negligible velocity,[*] and accelerating them in a known electrostatic field. The particles to which a known kinetic energy has thus been given are then analysed in a magnetic field. To focus sharply on the detecting device particles which have followed different paths use is made of the fact that, if a slightly divergent beam of similar particles of homogeneous velocity from a small source be allowed to pass in a uniform magnetic field, then the particles of different initial directions are reunited after describing approximately semicircles : this method of focussing has been employed in obtaining β ray spectra, and used by Ellis in the experiments described in Chapter III.[†] The radius of curvature r of the path in a magnetic field of strength H being accurately obtained, e/m can be determined. For if P be the accelerating potential, the energy with which the particles enter the magnetic field is given by

$$\tfrac{1}{2}mv^2=eP,$$

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[*] Such atoms without initial velocity can be originated, for instance, by heating salts on a strip of platinum.

[†] It was, I believe, first utilised by Rutherford and H. Robinson. (The Analysis of β-Rays from Radium B and Radium C, *Phil. Mag.*, 26, 717, 1913.)

while in the magnetic field

$$mv = eHr.$$

Hence $$\frac{e}{m} = \frac{2P}{H^2r^2}.$$

The latest form of Dempster's apparatus is shown in Fig. 21. The charged particles come from a hollow anode, in which the
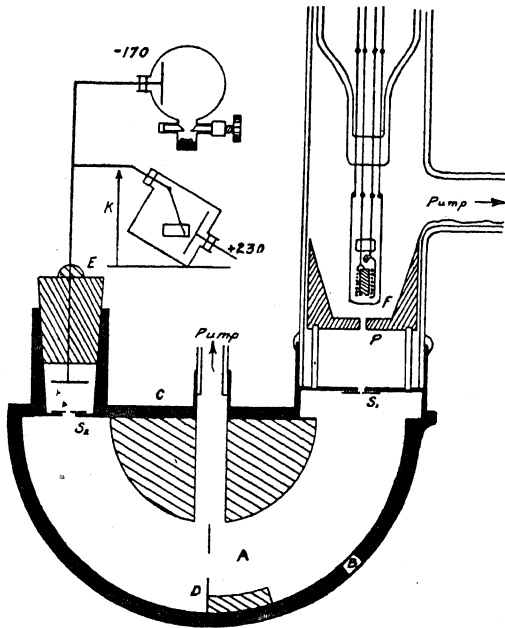
FIG. 21.

Dempster's apparatus for positive rays.

given salt is electrically heated, and, further, bombarded with electrons from a coated platinum cathode F, which can be seen just in front of the anode. The main accelerating field acts between P and S_1. S_1 is the slit through which the charged particles issue into the uniform magnetic field, which bends their paths through the diaphragm D to the slit S_2, in the plane of which particles of given e/m are focussed. Particles passing through S_2 are detected by a plate connected to an electrometer.

A.S.A.   H

The whole apparatus is, of course, highly exhausted, and placed between the poles of a magnet, which produces the uniform field. This field is maintained constant, while the accelerating potential is varied. The potential difference, magnetic field, and fixed radius of curvature corresponding to the maximum reading on the electrometer give, by the above formula, the value of e/m for the positive particles. With this apparatus Dempster has analysed magnesium, lithium, calcium and zinc into their isotopes.
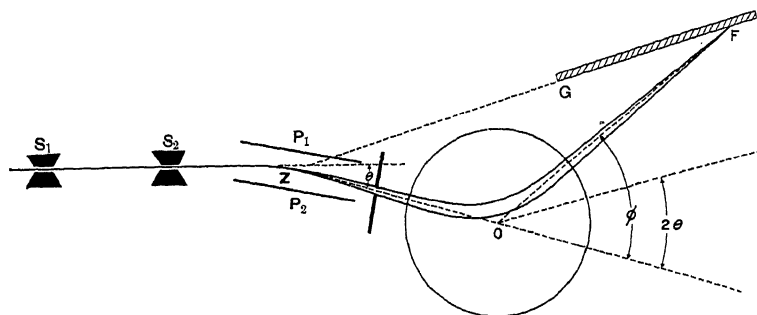
FIG. 22.

Diagrammatic representation of Aston's method of focussing positive rays.

The method used by Aston with such success employs the rays of mixed velocities obtained with a discharge tube, as in the parabola method. An electric and a magnetic field are used, through which the rays pass successively, but the fields are normal to one another, so that the deflections are in the same plane. The electric field bends the rays in one direction, and at the same time disperses the rays of different energies : the magnetic field, whose direction is such as to bend the rays in the opposite direction, brings the dispersed rays together again at one point. In Fig. 22 S_1 and S_2 are two parallel straight slits used to form a beam of rays : P_1 and P_2 are the plates producing the electric field, which bends the rays as shown. The circle of centre O represents the poles of the magnet whose field bends the rays back, and brings them to a focus at F. The paths shown are, then, followed by rays all of which have one value of e/m. Simple geometrical considerations * show that if the

* See Aston, *Isotopes*, Chapter V.

plane photographic plate, *GF*, be arranged so as to make the same angle θ with the original direction of the beam as does the electrically deflected beam *ZO*, but on the opposite side, as shown in the figure, then all rays of the same e/m come to one point on the plate, but rays of different e/m are focussed at different points. The linear dispersion, or separation of rays of different e/m, is very large.

The actual apparatus is represented diagrammatically in Fig. 23. *B* is a bulb some 20 cms. in diameter, in which the
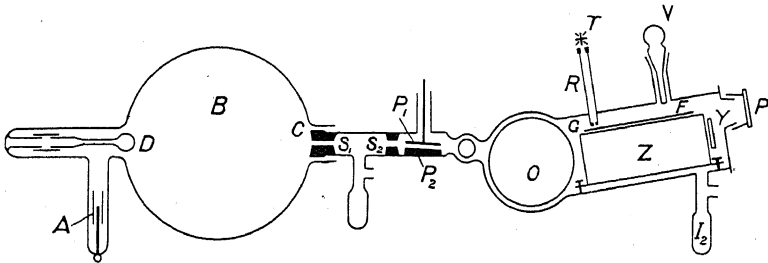
FIG. 23.
Aston's mass spectrograph arranged for use with canal rays.

discharge is produced in a gas containing the element or elements to be investigated, the gas being slowly admitted through a side tube (not shown) between S_1 and S_2, and removed through a similar side tube opposite it (also not shown). The rate at which the gas leaks in is adjusted so that the right pressure is maintained when the vacuum pump is run continuously. *A* is the anode, *C* the cathode, *D* a silica bulb which protects the wall of the bulb from the cathode rays, which would otherwise melt a hole opposite the cathode. S_1 and S_2 are the slits through which the charged atoms are shot, and P_1 and P_2 are the plates between which the electric field is maintained, as in Fig. 22. The circle, centre *O*, represents the pole pieces of a large electric magnet which produce the magnetic deflection. *GF* is the photographic plate, held in a special carrier *Z*. *Y* is a phosphorescent (willemite) screen for visual observation, which is seen through the window *P*. *T* is a small lamp by means of which a fiducial mark can be put on the plate. I_2 is a charcoal tube which can be immersed in liquid air for help at certain stages of the exhaustion.

The plate shows, in accordance with what has been said, a series of short lines, which are images of the slit, each line corresponding to a fixed value of e/m, but representing all velocities.   Such a series of lines may therefore be called a mass spectrum, and Aston has in fact called his instrument the mass-spectrograph.   Some typical mass spectra obtained by Aston with his apparatus are shown in Fig. 3, Plate IV., with the masses corresponding to the lines marked at the side of the record.   Spectra II., III. and IV. were all obtained with phosgene, $COCl_2$, which was the compound selected for the investigation of chlorine : spectrum I., inserted for comparison, was obtained with a tube free from chlorine.   It will be seen that the introduction of the chlorine compound gives rise to lines corresponding to masses 35, 36, 37 and 38, of which 35 and 37 belong to isotopes of chlorine, 36 and 38 to the hydrochloric acids formed from the two isotopes.   Spectra II., III. and IV. exhibit different dispersions because they were obtained with fields of different strength.

Methods of obtaining Mass Rays of Given Elements.   The apparatus of Fig. 23 is suitable for investigating the isotopes of any element of which volatile or gaseous compounds can be obtained.   There is no need for the element to be in an uncombined state, since a large part of the molecules is split up into the component atoms in the discharge, so that both the atoms and different compounds are represented in the mass spectra.   As examples it may be mentioned that while hydrogen and nitrogen were introduced into the tube as uncombined gases, chlorine, bromine, and fluorine, on account of their chemical activity, were investigated by using phosgene, methyl bromide, and boron trifluoride respectively ; phosphorus and arsenic were obtained from phosphine and arsine ; while for iron the carbonyl was used.   Often the gas containing the element under investigation was mixed with some other gases giving convenient reference lines.

With certain elements no convenient volatile compounds can be obtained, and other methods have to be adopted.   Reference has already been made to G. P. Thomson's work on the anode rays of lithium and beryllium, in which the element is introduced as a solid metallic salt in an anode paste.   Aston attempted

PLATE IV.
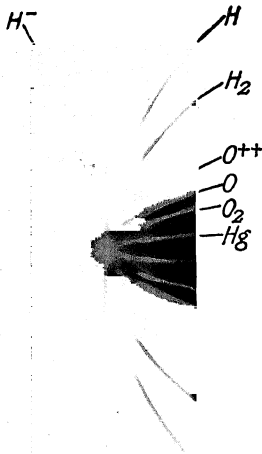
FIG. 1.
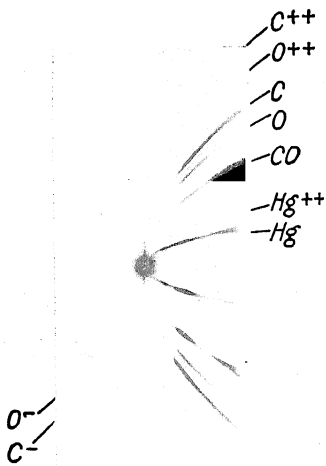
FIG. 2.
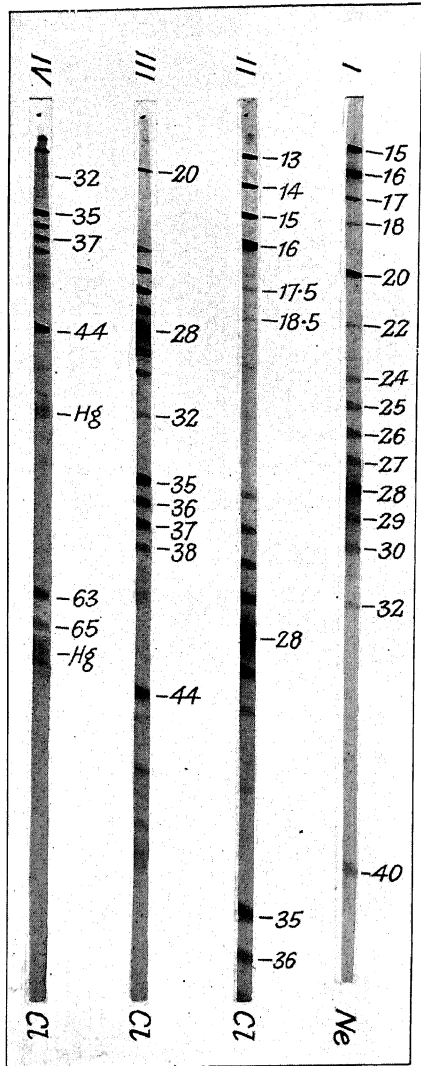
FIG. 3.

Records made by Positive Rays. (F. W. Aston.)

Figs. 1 and 2. Positive Ray Parabolas.

Fig. 3. Mass Spectra by Aston's Method.

Reprinted from Dr. Aston's *Isotopes*. (By kind permission of Messrs. E. Arnold.)

to obtain metallic ions by maintaining a metallic arc in the discharge bulb by means of a special device, but this method was not successful. He has, however, been able to extend his measurements to a large number of metals not accessible as volatile compounds by the use of accelerated anode rays. The apparatus with which these new measurements have been carried out is shown in Fig. 24, which represents the arrangement for generating the rays, the mass spectrograph itself,
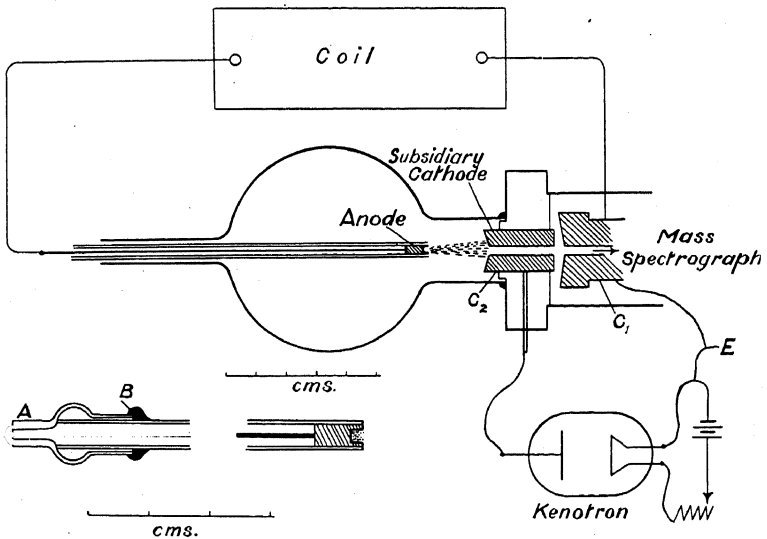
FIG. 24.
Aston's apparatus for producing anode rays for mass analysis.

into which they pass, being the same as in Fig. 23. The bulb is quite small, as can be seen from the scale in the drawing. The anode consists of a small steel cylinder into which is pressed a paste made of powdered graphite and metallic salt. It is carried in a long glass tube, as shown, so that it can be easily removed by melting the wax seal shown in detail at B. A subsidiary cathode is used to concentrate the cathode rays on the anode, and so produce a good supply of charged atoms. The instability of the discharge, due to the fact that any increase of current through the tube raises the temperature of the anode, which then releases more gas and so leads to a

further increase in current, was avoided by an ingenious use of a kenotron. This empty device ($\kappa\epsilon\nu\acute{o}\varsigma$, empty) is, in essence, an evacuated bulb containing a thin wire, which can be maintained at a high temperature by a subsidiary circuit, and a plate opposite to it, or, in other words, it is an electronic valve without the usual grid. As indicated in the diagram the hot filament is earthed and connected to the cathode of the mass spectrograph, while the plate is connected to the subsidiary cathode. The current which the kenotron will carry has a fixed limit determined by the temperature of the filament only, so that the kenotron controls the potential difference between the two cathodes, of which C_1 is connected to the negative, earthed, pole of the induction coil, while C_2 is connected through the kenotron only. If now, owing to release of gas, the tube becomes softer, the potential difference between anode and C_2 automatically diminishes, the anode cools, and the tube hardens again. In a similar way, if the tube hardens unduly the kenotron automatically leads to softening.

By this method of accelerated anode rays Aston has investigated a large number of metallic elements for which the gas bulb method had not yielded results. Of the first sixty elements only six at the present time have not been satisfactorily tested for isotopes. Of all the non-metallic elements, leaving the radioactive elements out of the question, not one has failed to give a mass spectrum.

Recent Results of Mass Analysis. With his improved methods of experiment Aston claims to be able to measure atomic masses with an accuracy of 1 in 1000, which is an astonishing feat when it is considered that, in the discharge tube experiments the total mass of gas present in the bulb is less than $\frac{1}{10}$ milligram, and that only an exceedingly minute fraction of this is actually used—that is, projected on to the plate—to determine the atomic mass of several elements.

Undoubtedly the most important results of the experiments is the establishment of the " whole number rule," *i.e.* that all atomic masses, except that of hydrogen, are whole numbers, taking oxygen as 16. This abolishes what was the fundamental objection to Prout's hypothesis, and allows us to assume that

besides the electron, there is only one other fundamental body, the proton, concerned in the structure of the atom.*

The chief elements whose atomic weights, as ordinarily determined, depart markedly from whole numbers, have been shown to contain various isotopes of whole number atomic weights. The atomic weight of the chemical tables is, in the case of fractional values, an average of weights of isotopes present in different proportions. The table on the following page contains Aston's results, supplemented in a few cases by those of Dempster. It will be seen that the chlorine, for instance, whose chemical atomic weight is 35·46, is really a mixture of two chlorines of the same chemical properties (same atomic numbers), but masses 35 and 37. For krypton six isotopes have been definitely established, and so on.

Separation of Isotopes. Various methods of separating isotopes by making use of their different masses have been suggested, and, in many cases, tried, such as separation by mass diffusion, by thermal diffusion, by pressure diffusion produced by centrifuging, evaporation at low pressure, and so on. The methods are all very slow and laborious, but a partial separation of the two neons has been effected by diffusion, and of the two chlorines, as *HCl*, by the same method. As an indication of the scale of the experiments it may be stated that with the latter gas Harkins, starting with about 20,000 litres, effected a separation into two gases whose densities indicated a change of ·055 unit in atomic weight.

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* Recently it has been found by Aston that there are one or two other elements for which the masses of all, or of certain, isotopes depart from whole numbers by a small amount which cannot be explained away as experimental error. Thus all the isotopes of tin appear to differ by 2 or 3 parts in 1000 from whole numbers, while rubidium has an isotope of mass 87·8, and barium one of mass 137·8 At present too little is known on the subject of these deviations to warrant the hazarding of speculations on the subject here. In the case of the isotopes in question, and of hydrogen, it is the nearest whole number to the experimentally determined mass which has a fundamental meaning, for it certainly represents the number of protons in the nucleus. This number, which for all other isotopes is exactly given by the determined mass, is called the mass number, and is tabulated for the various elements in the last column in the table on p. 120. By this convention the appearance of fractional numbers differing slightly from whole numbers is avoided even in the case of the few anomalous elements mentioned.

According to his latest paper (June, 1925), Aston is about to embark on a special investigation of the divergencies from the whole number rule.

TABLE OF ELEMENTS AND ISOTOPES.

Element.	Atomic Number.	Atomic Weight.	Minimum Number of Isotopes.	Mass-numbers of Isotopes in order of decreasing Intensity.
H	1	1·008	1	1
He	2	4·00	1	4
Li	3	6·94	2	7, 6
Be	4	9·02	1	9
B	5	10·82	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22
Na	11	23·00	1	23
Mg	12	24·32	3	24, 25, 26
Al	13	26·96	1	27
Si	14	28·06	3	28, 29, 30
P	15	31·02	1	31
S	16	32·06	3	32, 34, 33
Cl	17	35·46	2	35, 37
A	18	39·88	2	40, 36
K	19	39·10	2	39, 41
Ca	20	40·07	2	40, 44
Sc	21	45·1	1	45
Ti	22	48·1	1	48
V	23	51·0	1	51
Cr	24	52·0	1	52
Mn	25	54·93	1	55
Fe	26	55·84	2	56, 54
Co	27	58·97	1	59
Ni	28	58·68	2	58, 60
Cu	29	63·57	2	63, 65
Zn	30	65·38	4	64, 66, 68, 70
Ga	31	69·72	2	69, 71
Ge	32	72·38	3	74, 72, 70
As	33	74·96	1	75
Se	34	79·2	6	80, 78, 76, 82, 77, 74
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
Rb	37	85·44	2	85, 87
Sr	38	87·63	2	88, 86
Y	39	88·9	1	89
Zr	40	91·25	3	90, 94, 92, (96)
Ag	47	107·88	2	107, 109
Cd	48	112·41	6	114, 112, 110, 113, 111, 116
In	49	114·8	1	115
Sn	50	118·70	7	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121·77	2	121, 123
Te	52	127·5	3	128, 130, 126
I	53	126·92	1	127
X	54	130·2	7	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132·81	1	133
Ba	56	137·37	1	138, (136), (137)
La	57	138·91	1	139
Ce	58	140·25	2	140, 142
Pr	59	140·92	1	141
Nd	60	144·27	3	142, 144, 146, (145)
Er	68	167·7	Several	164 to 176
Hg	80	200·6	6	202, 200, 199, 198, 201, 204
Bi	83	209·00	1	209

(Numbers in brackets are provisional only.)

Another successful separation was carried out with mercury by Bronsted and Hevesy, using the method of evaporation at very low pressures. If an evaporating liquid consist of atoms
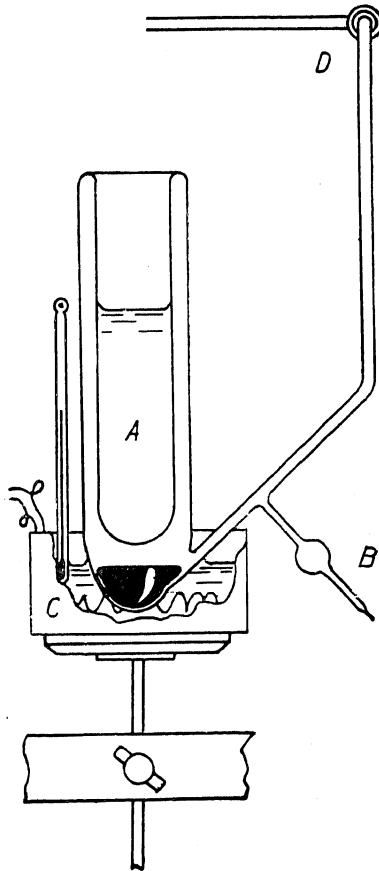
FIG. 25.

Bronsted and Hevesy's apparatus for partial separation of isotopes of mercury.

of different masses, then the number of lighter atoms which leave the surface in unit time is to the number of heavier atoms inversely as the square root of the atomic masses, so that the liquid surface acts much as a porous diaphragm in ordinary diffusion experiments. Now by placing over the surface of the

liquid a cold surface to act as a condenser, and by keeping the pressure between liquid and condenser so low that the atoms pass from one to the other without collision in the interspace, it can be ensured that all atoms which leave the surface are permanently separated from the original liquid. The condensed liquid should be rich in light atoms, and the evaporating liquid itself rich in heavy atoms. The experimenters, using the apparatus shown in Fig. 25,* evaporated mercury at about 50° C., condensed it at very low pressure on the surface A cooled by liquid air, and repeated the fractionation several times. At the end of each fractionation the mercury was thus separated into two parts, one solid on the bottom of A, and the other liquid at the bottom of the vessel. The liquid was removed by rotating the apparatus about the ground joint D and so running it into the bulb B. From the original 2700 c.c. were produced final fractions of volume ·2 c.c., one of density 1·00023, and the other of density ·99974, taking the density of normal mercury at the same temperature as 1. This, of course, does not constitute a complete separation into the isotopes, of which there are certainly more than two, but is a partial separation into a fraction containing an excess of heavy isotopes, and one containing an excess of lighter isotopes. Hönigschmidt and Birckenbach, separating by this method mercury into a lighter fraction of density ·999824 and a heavier fraction of density 1·000164, find corresponding atomic weights of 200·564±·006 and 200·632±·007 respectively, while for ordinary mercury they find 200·61±·006. Since the heaviest isotope of mercury is of atomic weight 204, it will be seen that the separation is very incomplete, even after the large number of fractionations undertaken.

The mass ray method has given results so consistent and uniform that the call for confirmation is scarcely urgent enough to justify the immense labour which any attempt at separation so far adumbrated demands.

The significance of the whole number rule and the other results of mass-ray analysis will be considered in Chapter VII.

*A modification of the apparatus on a larger scale was used for the early separations.

It may, however, be pointed out, before leaving the subject, that the existence of isotopes explains the existence of chemical anomalies when the elements are arranged in order of their (average) atomic weights, since isotopes of various elements are actually intermingled with one another on an atomic mass scale.

REFERENCES, CHAPTER V

GENERAL REFERENCES.

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CHAPTER VI

CLASSICAL X-RAY CONSIDERATIONS

Introductory. It is well known that the radiations which can be excited by the incidence of X rays on a substance fall into two classes :

(a) A radiation whose penetrating power, or hardness, is the same as that of the primary radiation, and therefore independent of the nature of the substance. This is analogous to the light scattered by a white matt surface, and is generally termed scattered radiation.

(b) A radiation whose hardness depends only on the nature of the atoms comprised in the substance. This can only be excited by a radiation harder than itself, and it is sometimes called fluorescent radiation, from the analogies which it exhibits with ordinary fluorescence. It is as characteristic of the substance in which it is excited as is an ordinary optical spectrum, and it is better called the characteristic radiation, especially as, unlike fluorescent radiation from solids or liquids, it possesses a line spectrum.

Both classes of radiation can, of course, be excited by the direct incidence of a stream of electrons of suitable velocity. The investigation of characteristic X rays has led to results which have profoundly influenced modern speculation on atomic structure. Bohr's quantum theory of spectra has shown that they can be made to yield information as to the arrangement and behaviour of the extranuclear electrons, in a way which is described in the second part of this book. Moseley's pioneer investigations formed the starting-point of the researches into X-ray spectra which are considered in this connection, but the main conclusions which he drew from his experiments are

independent of quantum theory. For this reason, as well as on account of their importance for the general theory of the nuclear atom, to which the first part of this book is devoted, they will be considered here. In historical order, his results precede much of the work that has already been described, and the fundamental importance of the atomic number, which he was the first to establish, has already received attention. The work has become so well known that an apology may be considered by some to be due rather for redirecting attention to the familiar than for having postponed it.

Again, certain results have been obtained with scattered radiation which do not involve the quantum theory, but are dependent on classical considerations only. Barkla's experiments gave an early indication of the number of electrons in an atom, and, although they are now chiefly of historic interest, deserve more than a passing reference for the originality and suggestiveness of the method. Recently W. L. Bragg * has carried out experiments which it is hard to classify. He takes a beam of homogeneous (and so characteristic) radiation, and investigates the intensity of the reflection from various faces of a crystal. The reflected beam is, of course, of the same quality as the primary beam, but can scarcely be termed " scattered," as it is regularly reflected. The formulae used are based upon the amount of radiation scattered by a free electron, which is calculated by classical electrodynamic method. This is the calculation upon which Barkla's deductions are based ; it has been elaborated by Darwin, A. H. Compton, and Bragg to cover the case of the regular arrangement of electrons which occurs in a crystal.

The conclusions to which this chapter is devoted are, then, all independent of Bohr's assumption, and are therefore taken together.

Moseley's X-ray Work. The Atomic Number. Moseley's work first revealed the importance of the atomic number, as distinct from the atomic weight, and formed the basis for the later work of Sommerfeld, Kossel and others, which interprets the structure of the X-ray spectrum in terms of the electron orbits of Bohr's hypothesis. He excited the characteristic

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* In collaboration with R. W. James and C. H. Bosanquet.

radiation in a series of elements, ranging in atomic number from aluminium to gold, by bombarding a target containing the atoms in question with cathode rays, and took advantage of the then recently discovered method of crystal reflexion to measure the wave-length of the X rays so produced.*   Barkla had already shown, by absorption measurements, that each element gave characteristic radiations of two very different penetrating powers, and had called the harder radiations of the various elements the K series, the softer the L series.   Moseley photo-graphed the lines corresponding to both K and L series, and expressed more exactly, substituting a wave-length or frequency for the hardness as measured by absorption, the general results of Barkla.   He speedily confirmed Barkla's discovery that the characteristic radiation is an atomic, and not a molecular, pro-perty, a fact which is fundamental to the great power of the X ray method.

His great discovery, however, was that expressed by him in the form that a certain quantity Q " increases by a constant amount as we pass from one element to the next, using the chemical order of the elements in the periodic series."   Here $Q = \sqrt{\dfrac{\nu}{\frac{3}{4}\nu_0}}$, where ν is the frequency of a given line, which can be identified in the X-ray spectrum of each element considered, and ν_0 is a frequency of fundamental importance in ordinary line spectra.   If by ν we understand, as is usual in spectro-scopy, not the true frequency $\dfrac{c}{\lambda}$, but the reciprocal wave-length $\dfrac{1}{\lambda}$, then $Q = \sqrt{\dfrac{\nu}{\frac{3}{4}R}}$, where R is Rydberg's constant.†

From the linear relation found when $\sqrt{\dfrac{\nu}{R}}$ is plotted against the atomic number Z, but not against the atomic weight A (see Fig. 26), Moseley concluded that " we have here a proof that there is in the atom a fundamental quantity, which increases by

* See W. H. and W. L. Bragg, *X Rays and Crystal Structure*.   G. Bell & Sons.

† Consult, if necessary, the Digression on Optical Spectra, Chapter VIII.

regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus." This hypothesis, fundamental for the modern theory of the atom,
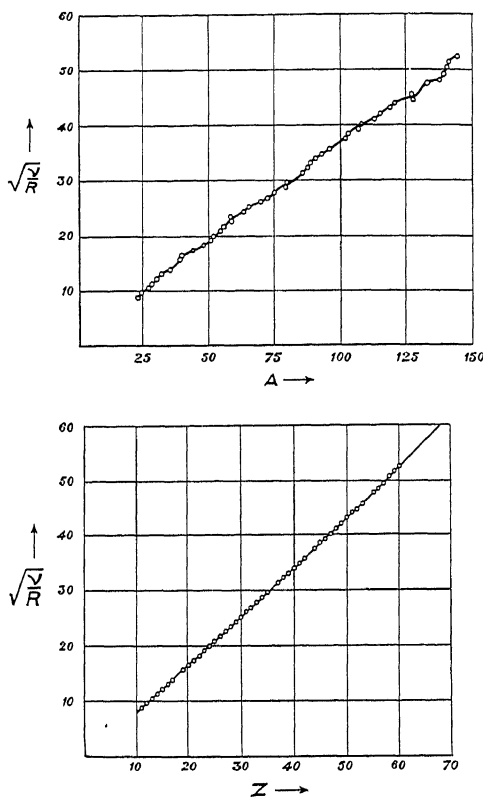
FIG. 26.

$\sqrt{\dfrac{\nu}{R}}$ plotted against atomic weight (above) and against atomic number (below), showing the linearity to exist in the latter case only.

is given in Moseley's own words, because it is not always recognised how clearly he saw the implication of his results. It was enunciated as a result of the measurement of the α and β lines of the K series for twelve elements : all subsequent work has gone to strengthen it. Moseley himself extended his measurements to many other elements, and confirmed his law for them.

The proportionality of $\sqrt{\nu}$ to the atomic number is generally known as Moseley's law.   The formula can be written

$\frac{\nu}{R} = \frac{3}{4}(Z-z)^2$, the value found for z by Moseley being 1, so that

$$\frac{\nu}{R} = \frac{3}{4}(Z-1)^2 = (Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right). \quad \dots\dots\dots\dots\dots(1)$$

Moseley identified in the K series the two lines which he called α and β : α is the stronger, and the above formula represents the frequency of the $K\alpha$ line.   In the L series he identified five lines, and for the $L\alpha$ line found the formula

$$\frac{\nu}{R} = (Z-7\cdot4)^2\left(\frac{1}{2^2}-\frac{1}{3^2}\right). \quad \dots\dots\dots\dots\dots\dots\dots(2)$$

Graphs exhibiting $\sqrt{\dfrac{\nu}{R}}$ plotted against Z are shown in Fig. 68, Chapter XIII.   The linear relation is not exact, the departure from linearity having been explained by Sommerfeld on relativistic grounds.   This, and the meaning of the constant in formulae (1) and (2), are matters dealt with in the second part of the book.

The atomic number is more fundamental for the chemical properties and the electrodynamic properties of the atom than the atomic weight.   It is equal to the net positive charge on the nucleus. The establishment of these fundamental points is Moseley's great achievement.

Barkla's Estimate of the Number of Electrons.   When X rays fall upon light atoms (*i.e.* atoms whose weight does not exceed that of sulphur) then (*a*) the scattered radiation is of the same hardness as the incident radiation,* and (*b*) the intensity of the scattered radiation is roughly proportional to the mass of the scattering atom if equal numbers of atoms take part in the scattering in all cases.   For example, in the case of gases the intensity of the scattered radiation is proportional to the density, and does not depend on the nature of the gas.   We can therefore assume that the scattering is effected by the extranuclear electrons of the atom, vibrating freely under the influence of the

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* But see the discussion of the Compton effect, Chapter XVIII.

periodic electric force in the wave front of the primary beam.*
This assumption will account for (a); we can explain (b) by
supposing that the number of electrons in an atom is a constant
multiple of the atomic weight. It may be mentioned that this
mechanism of scattering gives results agreeing well with the
observed facts of polarisation of X rays.†

The energy radiated by an electron, of varying velocity v,
in a time dt, through unit area at a distance r from the electron
is given by the formula, due to Abraham,

$$dE_\phi = \frac{1}{4\pi} \frac{e^2 \dot{v}^2}{r^2 c^3} \frac{\sin^2 \varphi}{(1 - \beta \cos \varphi)^6} dt,$$

where φ is the angle between the radius vector r and the direc-
tion of motion of the electron, while $\beta = \dfrac{v}{c}$, c being the velocity
of light. If we consider only electronic velocities small com-
pared to c, so that we can neglect β in comparison with 1, and
then integrate over a sphere, we get for the total energy radiated
by the electron in unit time

$$E = \frac{2}{3} \frac{e^2}{c^3} \dot{v}^2.$$

Let there be Y electrons in each atom, and consider a unit cube
of the radiator, containing n atoms of substance of atomic
weight M. Then we have nY electrons vibrating freely under
the influence of the electric force F of the primary beam. Then
$\dot{v} = -\dfrac{Fe}{m}$, and the whole scattered energy

$$= E_s = \frac{2}{3} \frac{e^4}{m^2 c^3} F^2 n Y.$$

* It is reasonable to suppose the electrons to behave as free for periodic
forces of X-ray frequency, although restoring forces have to be considered
when dealing with optical frequencies.

† In the simple form here represented it implies, of course, that the
intensity distribution of the scattered rays in directions making various
angles with the direction of the primary beam will be symmetrical about a
plane at right angles to this direction. This distribution was actually found
in the experiments of Barkla with which we are dealing at the moment, but
in general it is not observed. This lack of symmetry, which need not trouble
us here, has been explained by Debye from consideration of the mutual
interference between the radiation scattered from different electrons. This
receives reference in connection with W. L. Bragg's work, described on p. 132
et seq., and elsewhere later in the book.

The energy E_p of the primary beam falling on unit area of the radiator is $\dfrac{c}{4\pi}\,F^2$, and hence

$$\frac{E_s}{E_p}=\frac{8\pi}{3}\,\frac{e^4}{m^2c^4}\,nY,$$

e being measured throughout in electrostatic units. The scattering coefficient s is defined by the equation

$$E_s=sE_p\,dx,$$

where dx is the thickness of the radiator traversed, which has been taken here as unity. Hence

$$s=\frac{8\pi}{3}\,\frac{e^4}{m^2c^4}\,nY$$

or

$$\frac{s}{\rho}=\frac{8\pi}{3}\,\frac{e^4}{m^2c^4}\,\frac{Y}{Mm_H},$$

where ρ is the density of the scattering material, and m_H is the mass of an atom of hydrogen. The numerical values of all the terms of the factor $\dfrac{8\pi}{3}\,\dfrac{e^4}{m^2c^4m_H}$ are known. Putting in these values we have

$$\frac{s}{\rho}=\cdot40\times\frac{Y}{M}$$

Barkla measured $\dfrac{s}{\rho}$ for various substances, by comparing electroscopically the intensity of the beam scattered through various angles with the intensity of the primary beam, which consisted of fairly soft rays.* For light substances (air, carbon, aluminium), where there is no appreciable characteristic radiation, he found $\dfrac{s}{\rho}=\cdot2\,\dfrac{cm^2}{gm}$ in each case, which gives $\dfrac{Y}{M}=\cdot5$, or the number of extranuclear electrons in an atom is about half the atomic weight. This is in agreement with recent theory, since for the elements in question the atomic number is half the atomic weight, within two per cent. in the case of aluminium.

* $\left(\dfrac{\mu}{\rho}\right)$ with aluminium for the hardest rays used being 2·5, which corresponds to $\lambda=\cdot56\times10^{-8}$ cm.

The experiments are of great interest as bringing a fresh class of evidence to bear on the subject, and their description forms a suitable preliminary to the consideration of W. L. Bragg's recent work.
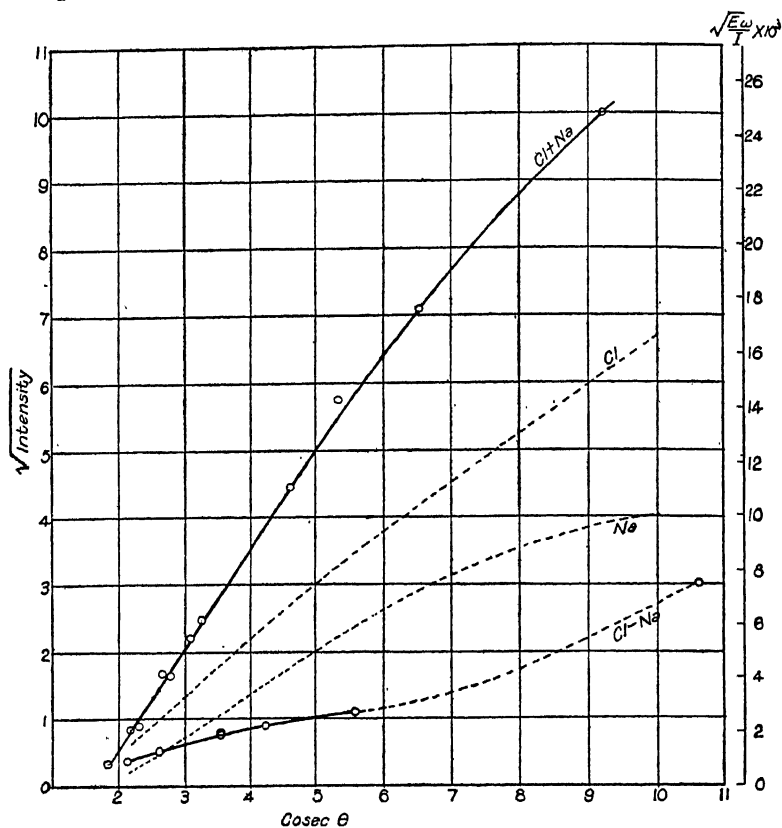
FIG. 27.

Intensity of X rays reflected at various angles from a crystal of rock salt.

Electronic Distribution without Quantum Theory. We now turn to the experiments of W. L. Bragg and his collaborators, which, without appeal to quantum theory, have yielded certain rough estimates of the distribution of the extranuclear electrons. The experiments in question consist in measuring the comparative intensity of a beam of homogeneous X rays after reflexion at various angles from a given cubic crystal of a two-element

compound.   For one face of the crystal and one order of reflexion it is well known that there is only one angle of reflexion for X rays of given wave-length, namely, that given by the formula $\lambda = 2d \sin \theta$.   If, however, various crystal faces be used (previously prepared by grinding a surface parallel to the planes in question, to avoid adding to the already great difficulties presented by the absorption question) and, in addition, various orders of reflexion, then a large number of angles can be obtained for the one crystal, and the intensity of the reflected beam for each measured.   It is found that when intensity is plotted against angle a smooth curve of simple form is obtained. In Fig. 27 the square root of the intensity is plotted against $\csc \theta$, where 2θ is the angle through which the incident beam is turned.

We will now consider interelectronic interference.   As was mentioned in a footnote on p. 130, Debye, from considerations of the lack of symmetry of the distribution of the scattered X radiation, was led to the conclusion that with short wave-lengths there is interference between the radiations set up by the various electrons of the atom vibrating under the influence of the electric vector of the exciting X rays. Obviously, if the wave-length is comparable with the distances between these electrons there will be, in consequence of the regularity of the electron grouping, certain definite phase differences between the vibrations originated by one atom, in spite of the fact that the atoms themselves may be irregularly oriented in amorphous substances.   Debye deduced the formula

$$V = \frac{Ne^4}{m^2c^4}\frac{1}{R^2}\frac{1+\cos^2\theta}{2}\sum_n\sum_m\frac{\sin[2KS_{nm}\sin\frac{1}{2}\theta]}{[2KS_{nm}\sin\frac{1}{2}\theta]},$$

where V is the fraction of the incident energy observed as scattered energy at a large distance R from the radiator, θ is the angle between the incident ray and R, N is the number of atoms radiating, and

$$K = \frac{\text{frequency of the plane polarised incident wave}}{\text{light velocity}},$$

$S_{nm} =$ distance of the nth from the mth electron, which, of course, depends on the distribution assumed.

Applying this formula to a ring distribution of electrons Debye was able to account for the observed fact of asymmetry of scattered radiation for hard exciting rays, and for the fact that for long waves the scattered intensity is proportional to the square of the atomic weight, for short waves to the atomic weight itself. The asymmetry begins to make its appearance when the wave-length is only slightly shorter than the diameter of the ring. For our present discussion these experiments on scattering are chiefly important as supporting the assumption of interelectronic interference. It may, however, be added that owing to the difficulty of obtaining an " amorphous " powder that did not exhibit a microcrystalline structure Debye could not confirm all his results quantitatively on solids, but it is of interest to note that, assuming for the benzene ring an inter-ference between the scattered radiation from the regularly grouped *atoms* analogous to the interference between the electrons considered above, he was able to obtain an estimate of the diameter of the benzene ring, viz. $12 \cdot 4 \times 10^{-8}$ cms.

For a crystalline substance Debye's formula does not apply, since it assumes a random distribution of atoms. In its place Bragg uses a formula derived by Darwin from application of Fresnel's classical theory of diffraction to atoms arranged in parallel planes, special allowance being made for

(1) the general absorption ;

(2) the special absorption which takes place when the rays absorbed are incident at the reflecting angle, due to multiple reflexion within the crystal ;

(3) the heat motion of the atoms, expressed by the so-called Debye factor $e^{-B\sin^2\theta}$;

(4) crystal imperfections.

In addition the essential factor F is introduced to express the fact that the scattering is not effected by a continuous sub-stance, but by discrete electrons, which, for short wave-lengths, set up definite phase differences in the waves which they scatter. It gives the ratio of the amplitude of the wave scattered by the whole atom to the amplitude of the wave scattered by a single electron ; at zero glancing angle it equals the total number of electrons. It is this factor F which is the object of

W. L. Bragg's researches. It may be pointed out that the nucleus is assumed to play no part in the scattering, on account, presumably, of its large mass, but it is not clear that, even if it be immovable as a whole, the electrons which it contains may not play some part in diffracting incident waves.

This brief account may suffice to indicate that the formula is dependent on many assumptions, and cannot claim a high degree of certainty. If the rotation method is employed to get over the effects of crystalline imperfections,* and the crystal have an angular velocity of ω radians per second, and E be the energy reflected from the given face, I the total energy of the incident beam passing into the ionisation chamber† in 1 second, then

$$\frac{E\omega}{I} = \frac{N^2\lambda^3}{2\mu\sin 2\theta}\, F^2 \,\frac{e^4}{m^2c^4}\,\frac{1+\cos^2 2\theta}{2}\, e^{-B\sin^2\theta}, \quad \ldots\ldots\ldots\ldots(3)$$

μ being the linear coefficient of absorption and N the number of molecules in unit volume of the crystal. From this formula, and experimental determinations of $E\omega/I$ for various values of θ, W. L. Bragg and his collaborators calculate F, which is a function of $\sin\theta$.

A crystal of rock salt is used. The values of F for the two different kinds of atoms, sodium and chlorine, are deduced from the following considerations. When $\sqrt{E\omega/I}$ is plotted against cosec θ the values lie on two curves, one corresponding to reflexions from planes whose indices are all odd—(111), (311), (331), etc.—and the other to the remaining planes. The first set of planes contain alternately sodium atoms only and chlorine atoms only, the reflexions from the chlorine atoms being 180° out of phase with the reflexions from the sodium atoms. With the other set of planes the reflexions from the sodium atoms reinforce the reflexions from the chlorine atoms. Hence we have the effect which can be symbolised as $Na - Cl$, and the effect $Na + Cl$. From these the effectiveness of the two kinds of atoms can be separated (cf. Fig. 27).

Having obtained experimentally F as a function of $\sin\theta$ for sodium and chlorine separately, Bragg assumes various distributions of electrons, and calculates the corresponding values

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* Consult, if necessary, W. H. and W. L. Bragg, *X Rays and Crystal Structure*.

† The reflected and incident energies are measured by the ionisation method.

of F. The assumption of electrons uniformly distributed throughout a sphere gives curves which do not even approximately resemble those derived from experiment. An assumption of electrons arranged in shells—three shells of 2, 8, and 8 electrons respectively for the ionised chlorine atom, and two shells, of 2 and 8 electrons respectively, for the ionised sodium atom—in accordance with an atom model of Lewis-Langmuir type is equally unsuccessful. Good agreement has, however, been obtained on the following basis :

<div align="center">

Sodium.

7 electrons on a shell of radius ·29 × 10⁻⁸ cm.

3   ,,   ,,   ,,   ·76

Chlorine.

10 electrons on a shell of radius ·25 × 10⁻⁸ cm.

5   ,,   ,,   ,,   ·86

3   ,,   ,,   ,,   1·46   ·

</div>

This does not accord very well with any accepted view of the structure of such atoms. More interesting are the calculations made on the basis of the type of arrangement of electrons proposed by Bohr, which is described in Chapter XIV. This postulates for ionised sodium 2 electrons describing one-quantum (circular) orbits, 4 electrons describing two-quantum circular orbits, and the remaining 4 describing two-quantum ellipse-like orbits. Assuming for sodium :

as the radius of the 1-quantum circle   ·05 × 10⁻⁸ cm.,

as the radius of the 2-quantum circle   ·34

and as the major semi-axis of the ellipse   ·42

an approximate evaluation has been made for the values of F at different angles, an arrangement of circular segments being used to account roughly for the elliptical orbits. The variations of F with $\sin \theta$ so obtained accord pretty well with experiment considering the necessarily rough nature of the calculation.

The method awaits further development. It seems to open a promising way for investigating the general distribution of the electrons in individual atoms, but in its present form, at any rate, it can only yield information as to the average distance of electrons from the nucleus—the average volume density of electrons, as it were, throughout the space surrounding the

nucleus. It cannot distinguish between a static and a dynamic distribution : it averages in time as well as in space. Different distributions being assumed, the values of F must be calculated for comparison with experimental values, though I understand that, with practice, the general type of distribution necessary to fit a given curve can be rapidly ascertained. In any case the method offers, of course, a distinctly original procedure for checking any theoretical distribution reached by other means. For example, it speaks, as we have seen, strongly against the physical reality of the type of distribution assumed by Langmuir.

Recently Hartree has calculated the factor F in equation (3) from the electronic core orbits, the dimensions of which have been approximately worked out for certain types of atoms, as described in Chapter XI. He has tabulated results both for the original Bohr scheme of electronic distribution, and for the modified scheme proposed by Stoner, which is now generally accepted (see Chapter XIV.) : in general the results obtained are not very different in the two cases. The agreement with W. L. Bragg's observations is not altogether satisfactory. Underlying Hartree's work is the assumption, widely adopted, that the electrons in the atom scatter X-rays just as free electrons in their instantaneous positions would do on the classical theory. It is by no means established beyond doubt that this procedure is justified, at any rate for all the classes of orbits, with varying degrees of firmness of binding, present in the atom.

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CHAPTER VII

THE STRUCTURE OF THE NUCLEUS

Some General Considerations. The work described in the previous chapters has furnished a great body of evidence for the nuclear type of atom. We have seen that the nucleus must be very small compared to the size of the atom, its linear dimensions being of the order 10^{-12} cm.; heavy, in the sense that practically the whole mass of the atom is concentrated in it; positively charged with a net charge equal to the atomic number. We cannot, however, always treat it as a small indivisible charged sphere, although for certain classes of problems, such as the structure of spectra, the scattering of particles when the approach is not too close, and chemical combination, such an approximation is sufficient. The general nucleus must contain charged helium nuclei *; charged hydrogen nuclei, or protons; and electrons. Its constitution must be governed by laws which permit these to be assembled together in a stable manner over a range of varied proportions, so that there can be changes of net charge without changes of mass, and changes of mass without changes of net charge. The nucleus must, further, in the case of certain heavy atoms, have a mechanism for emitting α and β particles, and the very penetrating γ radiations which we have discussed as nuclear γ rays.

The nucleus itself, then, must obviously have a structure which is more rather than less complicated than that of the extra-nuclear part of the atom, since it has a greater variety of

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* It has. been suggested that the α particle is manufactured by the protons in the act of discharge, but, although this cannot be definitely disproved, it will be seen in the course of this chapter that many facts point to the nucleus containing ready-made helium nuclei of great stability.

components and even more varied functions to perform. Within the intricate structure of extranuclear electrons we have, on a very much smaller scale, a second structure of electrons and protons, whose number is comparable to that of the extra-nuclear electrons. There is, it may be said, an atom within the atom. Further, the structure of the nucleus seems likely to find its first satisfactory statement in terms of helium nuclei, treated as separate entities, as well as protons and electrons. The structure of those components of the nucleus will have to be cleared up before the whole atom can be expounded in terms of the two fundamentals, protons and electrons. Whether, as fresh experimental results are obtained, the mind will rest con-tented with two ultimates instead of one is a matter rather for philosophic speculation than physical argument. At present we would be well content if we could make a rough working model with helium nuclei, protons and electrons.

Having indicated the problem, we must hasten to add that not very much has so far been done towards its solution. Certain generalisations are possible, certain tentative sugges-tions have been made, which seem helpful. On the other hand, the subject has offered a vast field for what the Germans call *Arithmetische Spielereien*, which serve rather to entertain the players than to advance knowledge. On this delicate point it is easy to say too much.

Fundamental for all discussion of nuclear structure is Aston's proof that, for all elements so far investigated, the atomic weights, given in terms of oxygen, can be expressed by whole numbers, since elements whose atomic weights, as determined chemically, show fractional parts, consist of mixtures of isotopes of whole number weights. (Cf. the table in Chapter V.) The only definite exception is hydrogen, whose atomic weight is 1·008, and this will be discussed later.* Fundamental, also, is Ruther-ford's proof that certain classes of nuclei, at any rate, contain hydrogen nuclei as a component. Various other pieces of evidence will be supplied in the course of discussion, but these experimental results are at the basis of all speculations.

Stable Assemblages. The whole number rule allows us to suppose that all nuclei are built up of the same mass elements,

* See, however, footnote to p. 119.

i. protons, assuming, for the moment without discussion, that the mass of the proton when combined with other protons is slightly less than that of the free proton. If the nucleus consisted only of protons the charge would equal the atomic mass, whence it is clear that the nucleus contains, besides protons, electrons. Further, we know that the heavy nuclei eject a particles, of mass four and charge two, which must consist of four protons combined with two electrons. We shall see that much evidence points to the extreme stability of this group, which we shall call the a group, and it will be considered as a separate unit.

Since we can alter the charge of the nucleus without changing its mass, by adding or subtracting an electron, and can alter the mass without changing the charge, by adding or subtracting a (proton+electron), we can obviously, on paper, make a nucleus of any mass with any charge. Reference to experimental fact, however, shows that not only does a given charge have, even in the most extreme case,* a comparatively small range of possible masses, but also that certain atomic masses have never been detected, i.e. that all combinations which would give a nucleus of that mass are unstable. The table overleaf shows the atomic masses from 1 to 44, a region that has been searched for isotopes, with those which are unstable indicated.

Non-occurrence is an indication of very great instability. But within the range of atomic masses which do occur there must be various degrees of stability, and for this there are three main lines of evidence. For heavy nuclei we have the radioactive atoms, whose half-value periods give a measure of stability. For light elements we have Rutherford's experiments, showing that some nuclei give up protons when bombarded by a particles, while others do not.† In the third place, an indication as to relative stability has been sought by Harkins in the

* Such as xenon, which has, associated with charge 54, isotopes whose masses range from 128 to 136.

† The fact that heavy nuclei are not disrupted by a particles is not significant of stability, since in the case of such nuclei the net positive charge is also large, and the a particle is repelled or deflected before it gets close enough to be able to exert a great force on one particular proton. When, however, as in Rutherford's experiments, a range of light nuclei is taken, in which the atomic numbers of the disruptable and non-disruptable nuclei prove to be intermixed, the result must throw light on the relative stability.

ATOMIC MASS AND NATURE OF ATOM.

Atomic Mass.	Atomic Number.	Description of Atom.
1·008	1	Hydrogen.
2	—	Unstable.
3	—	Unstable.
4	2	Helium.
5	—	Unstable.
6	3	Lithium. Isotope.
7	3	Lithium. Isotope.
8	—	Unstable.
9	4	Beryllium.
10	5	Boron. Isotope.
11	5	Boron. Isotope.
12	6	Carbon.
13	—	Unstable.
14	7	Nitrogen.
15	—	Unstable.
16	8	Oxygen.
17	—	Unstable.
18	—	Unstable.
19	9	Fluorine.
20	10	Neon. Isotope.
21	—	Unstable.
22	10	Neon. Isotope.
23	11	Sodium.
24	12	Magnesium. Isotope.
25	12	Magnesium. Isotope.
26	12	Magnesium. Isotope.
27	13	Aluminium.
28	14	Silicon. Isotope.
29	14	Silicon. Isotope.
30	14	Silicon. Isotope.
31	15	Phosphorus.
32	16	Sulphur. Isotope.
33	16	Sulphur. Isotope.
34	16	Sulphur. Isotope.
35	17	Chlorine. Isotope.
36	18	Argon. Isotope.
37	17	Chlorine. Isotope.
38	—	Unstable.
39	19	Potassium. Isotope.
40 ⎫	⎰ 18	Argon. Isotope.
40 ⎭	⎱ 20	Calcium. Isotope.
41	19	Potassium. Isotope.
42	—	Unstable.
43	—	Unstable.
44	20	Calcium. Isotope.

comparative abundance in which the different kinds of atoms occur in nature. It is well known that the radioactive elements when are stable are relatively abundant, and the contention is that this rule can be extended to the elements which are not radioactive. The widest fields available for investigations of this kind are afforded by the crust of the earth and by meteorites, and Harkins has found that these two offer fairly concordant evidence for the relative abundance of atomic species.

It need hardly be emphasized that no great precision is to be attached to any figures of relative abundance, since our sources of information are very limited. As regards the universe at large the spectroscope, while it tells us of the elements present in the surface of suns, can give us no information as to relative abundance. As regards the earth, it has been argued by Weichert and others, notably F. W. Clarke, who has collected a large amount of information on the subject under discussion, that it consists of a core of iron and an outer layer of rock, or lithosphere, as it is called, the two being about equal in volume. To get the average composition of the lithosphere, Clarke, assuming that lower parts of it approximate to an average basalt, takes a mean between the composition of the latter and that of an average surface rock. The atmosphere, and the thin film of water and organic matter, are neglected. Meteorites can be divided roughly into two kinds, stone meteorites and iron meteorites, the former being supposed to be fragments of lithosphere from some planet or planets similar to the earth, the latter to be fragments of the iron core : in any case they are samples of non-terrestrial matter, and therefore valuable. The average composition of stone meteorites approximates to that of the lithosphere : if the iron meteorites be included in the average, the result is to raise the iron and nickel percentages at the expense of the other elements. If the hypothetical iron core be included in the earth average, the effect is similarly to raise the relative importance of iron and nickel. Of a large number of possible ways of treating the results I have judged best to exhibit in Fig. 28 the atomic percentages of the elements (1) in the lithosphere, shown by the right hand of the two columns corresponding to a given atomic number ; (2) in the average meteorite, shown by the

left hand column. As in Fig. 18 for elements of even atomic number the columns are white, for elements of odd atomic number they are black. It must be understood that alternative methods of averaging modify the figure, but leave unchanged its essential features. By atomic percentage is meant the relation which the number of atoms of the given element bears to the total number of all kinds of atoms in the mass considered:
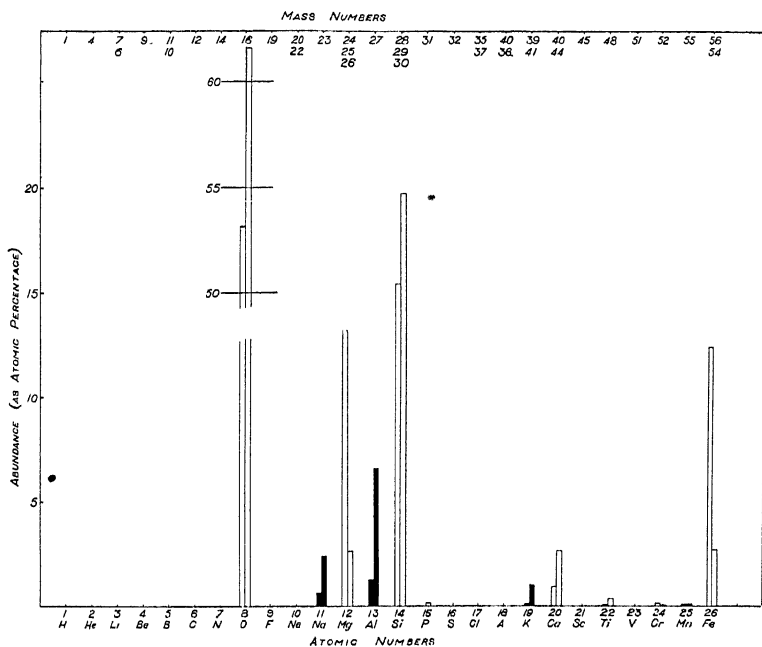
FIG. 28.

Relative atomic abundance of elements (1) in the lithosphere (right-hand columns), (2) in average meteorite (left-hand columns).

it is, of course, obtained by simply dividing the number expressing the abundance by weight of the element, estimated by the geologists, by the atomic weight. It may be noted incidentally that over 99·8 per cent. by weight of the earth's crust and of meteorites consists of light elements of atomic weight less than 60, which may be taken to indicate an evolution of the heavier nuclei from light nuclei, a question which is too speculative for discussion here.

Harkins has pointed out that atoms for which Z is even are much more abundant than atoms for which Z is odd, as is readily seen from Fig. 28. Further, in 13 out of 14 atoms in meteorites, and a proportion only slightly less in the crust, the atomic mass P is divisible by 4. This indicates a particular stability of groups of 4 protons. It is interesting to compare these deductions with the results of Rutherford and Chadwick on the artificial disintegration of nuclei. These also point to a relative stability of nuclei for which Z is even, for from such nuclei either no protons could be ejected, as in the case of carbon and oxygen, or else protons were ejected in relatively small numbers and of relatively short range, as with the even number nuclei from neon to argon. So far no definite results have been obtained from the bombardment of elements from calcium to iron, but, as pointed out in the footnote on p. 141, increasing Z will tend to prevent artificial disintegration quite apart from all questions of stability. Originally no protons were obtained with atoms for which $Z = 4n$, which seemed to confirm the special stability of such nuclei in accordance with Harkins' deduction, but the new disintegration results show no particular difference between these and intermediate elements of even number charge. In any case there seems no doubt that there is an essential distinction between elements of odd and even atomic charge, which is further confirmed by certain results of Aston. His work has shown that elements of odd atomic number never consist of more than two isotopes, and that, after atomic number 9, when two isotopes occur for odd elements their masses always differ by two. Even number elements often contain a large number of isotopes, and when there are only two their masses sometimes differ by four. The significance of these differences is not yet clear.

There are certain general rules, independent of abundance or radioactivity considerations, which deserve attention. To begin with, it may be pointed out that the atomic number Z is never greater than half the atomic mass P, or

$$Z \leqslant \tfrac{1}{2}P.$$

Further, the quantity $\tfrac{1}{2}P - Z$ tends to increase as P increases. It is not a one-valued function of P, since for the same P we may

have different Z (the case of isobares), and a smooth curve cannot be drawn accurately through the points when $\frac{1}{2}P - Z$ is plotted against P, but the points lie about a straight line cutting the axis of P in the neighbourhood of $P=35$. For all values of P less than 22 either $P=2Z$ or $P-1=2Z$. The interpretation of such a graph is that the number of nuclear electrons in excess of $\frac{1}{2}P$ tends to increase steadily with P.

If the number of α particles in a nucleus be denoted by α, and the number of protons and electrons not combined as α particles be respectively p and e, while P is the atomic mass, we can write

$$Z=2a+p-e,$$

$$P=4a+p,$$

p having as possible values 1, 2, 3 only.

This gives that e, the number of the electrons outside α particles, is

$$e=2\frac{P-p}{4}+p-Z,$$

p being chosen so that $\dfrac{P-p}{4}$ is a whole number. It is found that when P is even Z is even, and when P is odd Z is odd, for most atomic species, so that in most cases e is an even number. This indicates that the nuclear electrons tend to occur in pairs, even when not intimately combined with protons to form α particles, a supposition which is supported by the fact that, when there are several isotopes of one "element," the one that occurs in the largest proportions in the standard mixture is, in general, that which has an even number of nuclear electrons. This hypothesis of the existence of electron pairs is embodied in the form of an assumption which is becoming widely accepted, and which is used in the following sections of this chapter, namely, that the nucleus contains as special units α particles neutralised by the attachment of two electrons.

Of course, if to protons, electrons and α particles a fourth nuclear constituent, the so-called isohelium (*i.e.* an assemblage of mass 3 and positive charge 2) be added, as is done by many nucleus builders, general equations can be made up expressing P, Z and the number of constituents N of the nucleus in terms

of these four.   Neuburger, for instance, has made play with a general formula giving relations between P and Z in terms of a, e and s, the number of isohelium nuclei.   It does not seem to me that this takes us much further.   The evidence for the existence of isohelium is inconclusive—Aston has found no trace of it.   Neuburger contends that, even granting that it is not found free, this cannot prevent his assuming its existence in the nucleus.   On these lines nucleus-building takes on an airy charm denied to ordinary scientific speculation.

In short, very little is definitely known as to the composition of the general nucleus.   It seems undoubted that the a particle is a particularly stable entity : further evidence of this stability is offered at the end of this chapter.   Such particles take part in the composition of all nuclei, and exceedingly stable nuclei can be made up of a particles only,* such as the nucleus of oxygen.   Until Rutherford and Chadwick published (in July 1924) their newer results on artificial disintegration, all elements of mass $4n$ were recorded to have withstood bombardment by swift a particles without detachment of a proton, but the results in question place neon, magnesium, silicon, sulphur and oxygen on the list of disruptable nuclei.   Of these elements all but sulphur contain isotopes of atomic mass other than $4n$, to which the detached proton might be attributed, but sulphur, of mass 32, is single, and definitely shows that a nucleus of mass $4n$ may be broken artificially.†   It may, of course, be supposed that the sulphur nucleus contains seven a particles, and a looser collection of four protons and two electrons, from which the proton is detached, but this is very speculative, and it seems best simply to recognise that we are no longer justified in saying without qualification that all nuclei for which $P=4n$ have a greater stability than other nuclei,

* Of course it is not certain that all the protons and electrons of the oxygen nucleus, for example, are combined in four a particles because $P=16$.   There may be separate particles, composed of two protons and an electron, but the fact that nuclei for which $P=4n+2$, such as, in particular, nitrogen, are much more easily broken than those for which $P=4n$ has been considered to speak for the pure a particle structure of the $P=4n$ nuclei.

† Since this was written Aston has shown that sulphur has isotopes of mass 33 and 34, although the two together amount to only about 3 per cent. of the whole.

although such a stability is on the whole indicated. The existence of isotopes for many of the light elements concerned in the disintegration experiments makes the connection of stability and atomic mass more difficult to trace, but there is no doubt that nuclei for which $P = 4n + 3$ have an easily detachable proton. A few of the deductions which have been made concerning the number of nuclear electrons have been indicated, and some investigators have attached significance to the fact that with increasing atomic mass, and increasing excess of electrons, isotopes occur more frequently and in larger groups. We now turn to the radioactive atoms, for which a theory has been put forward by Meitner which is both simple and suggestive.

Meitner's Model for Radioactive Nuclei. Meitner's model has the merit that it expresses in a direct manner certain features of the sequence of the radioactive charges, and of the branching of series. In other words, it does describe by means of a simple hypothesis, not in conflict with other observations, a collection of hitherto unrelated facts, and so deserves to be taken more seriously than many of the speculations which are merely restatements of isolated facts by means of an *ad hoc* hypothesis for each of them.

Meitner supposes that a nucleus of atomic number Z, atomic mass $P = 4a + p$, contains $\frac{1}{2}Z$ ordinary a particles, and $(a - \frac{1}{2}Z)$ particles neutralised by $2(a - \frac{1}{2}Z)$ electrons combined with them in some looser manner than the electrons which actually form part of the a particles. Further, it contains p protons neutralised by p electrons. In other words, the net positive charge, which determines Z, is supplied entirely by $\frac{1}{2}Z$ ordinary a particles. Z is here assumed even ; if Z is odd there is probably an extra electron. The a particles which are neutralised in the way described are denoted, for convenience, as a' particles ; they are, of course, exactly the same as a particles once they get loose from their environment. The heavier the atom, the more of these a' particles there must be, since for lighter atoms Z is not very different from $\frac{1}{2}P$.

For lighter atoms there is no particular evidence in favour of such a type of atom more than in favour of any other type which gives a number of a particles and a number of neutralised protons. But radioactive changes find a good description in terms

of such an atom, and Meitner suggests the following mechanism. If an α particle is emitted, there follows a series of α changes before one of the neutralised (α') groups becomes unstable. When such a group does eventually break up, we have either (a) the α' particle emitted, leaving two electrons in excess, which afterwards leave the nucleus successively in two β ray
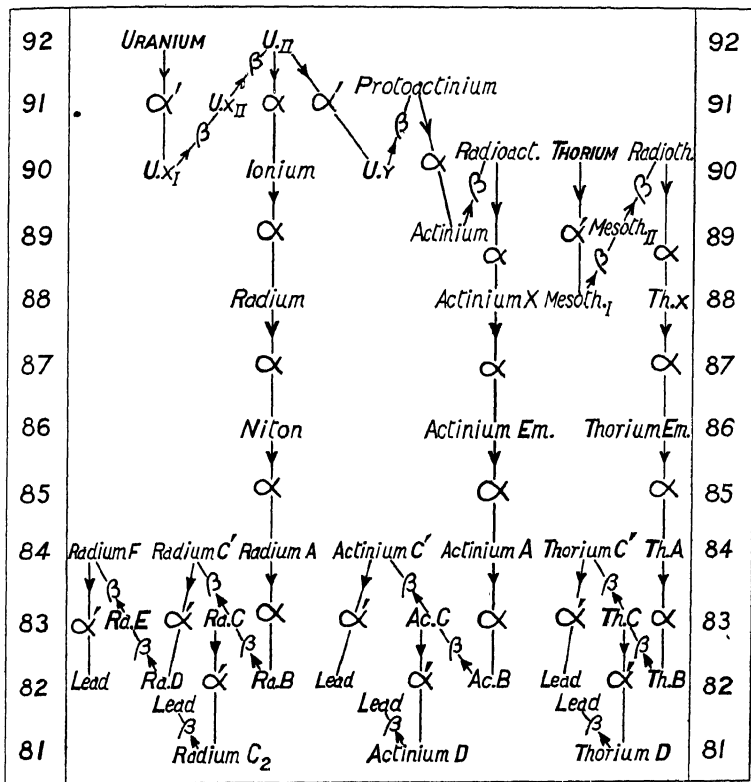
FIG. 29.

Table of radioactive changes, showing α and α' transformations.

transformations, or (b) one of the electrons emitted, when either a second β change or an α' change may follow, leaving respectively an α' or a β particle to be emitted later. That is, in case (b) two classes of change can take place for the same species of atom: some of the atoms will give a β and later an α' change, while others will give an α' and later a β change.

We have a branching and reuniting of the series such as is found experimentally.

On this theory, then, a β change either follows an α' change (in which case a second β change succeeds) or it precedes an α' change, this latter alternative being attended by branching.

A glance at Fig. 29 (produced by applying Meitner's theory to a diagram of Darwin's) will show how far the theory represents the facts. There is one weak spot at the branching of Uranium II., where we have the sequence $\alpha'\beta\alpha\beta$ instead of $\alpha'\beta\beta\alpha$, as we should expect. Apart from this, the agreement is good. There are never more than two consecutive β changes, which are always preceded by an α, or, as we call it, an α' change. A single β change always precedes a branching. The fact that the model makes it easier to remember the sequence of changes shows that it is of definite value, and, although it has not yet been extended to nuclei other than radioactive ones, it deserves an honourable place as having achieved some success in a limited field.

Instability Rules. The question as to why certain atomic masses are unstable and do not occur has been attacked by extending to the non-radioactive elements certain rules deduced for the properties of the radioactive elements. Fajans seems to have been the first to make a systematic attempt along these lines, and he has been followed by A. S. Russell who, as a result of somewhat involved analogies, has had success in predicting isotopes.

We consider as an essential part of nuclear structure the α particles neutralised by two electrons each, combined in a manner less intimate than the two which form part of the α particle itself, which have been called α' particles in discussing Meitner's theory, to distinguish them after they have lost their two electrons from the α particles which have never had such electrons. Such neutralised particles when existing in the nucleus we shall call $\alpha\beta\beta$ particles : they have mass 4 and charge 0. The other components of the nucleus are unneutralised α particles, of mass 4 and positive charge 2 ; protons, of mass 1 and positive charge 1 ; and electrons, of mass 0 and negative charge 1. Since $Z \leqslant \frac{1}{2}P$, we can with α and $\alpha\beta\beta$ particles build

up a nucleus which will differ in atomic mass by not more than 3 units, and in net nuclear charge by not more than 1 unit from any given actual nucleus. By adding therefore to the α and $\alpha\beta\beta$ particles not more than 3 protons and not more than 1 electron, any given nucleus can be imitated as far as mass and charge are concerned. The following table shows how Fajans divides up nuclei into eight series,* and the number of electrons and protons which must be added to assemblages of α and $\alpha\beta\beta$ particles to make up nuclei of the series in question.

NUCLEAR SERIES.

Series.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Atomic weight	$4n$	$4n$	$4n+1$	$4n+1$	$4n+2$	$4n+2$	$4n+3$	$4n+3$
Nuclear charge	Even	Odd	Even	Odd	Even	Odd	Even	Odd
Number of protons	0	0	1	1	2	2	3	3
Number of electrons	0	1	1	0	0	1	1	0

The table shows that in all series but series II. the number of loose protons exceeds the number of loose electrons (the term "loose" being applied to units not forming part of α or $\alpha\beta\beta$ particles), or, for definiteness, it may be said that the loose electron is neutralised in all nuclei but those of series II. Now this series consists of three elements only, $Th\ D$ ($P=208$, $Z=81$), $Th\ C$ ($P=212$, $Z=83$), and $Ms\ Th_2$ ($P=228$, $Z=89$), which are all short-lived β radiators, i.e. very unstable. Generalising from this it may be assumed that all nuclei which could be made up to fall into series II., or, in other words, all nuclei of atomic mass $4n$ and odd nuclear charge are unstable. Examples of such nuclei are Li_8, N_{16}, F_{20}, Na_{24}, Cl_{36}, and isotopes of the masses indicated by the suffixes have, in fact, never been detected. Still more striking is the non-occurrence of a silver isotope of mass 108, or copper isotope of mass 64. Turning to the question of isobares, which are elements having the same atomic mass, but different nuclear charges, we note that adding an electron to a nucleus produces a new nucleus of the same mass, but charge differing by 1 unit, and such a nucleus with an unneutralised electron we hold to be unstable.

* There are four possible types of atomic weight, since the step of mass in adding α or $\alpha\beta\beta$ particles is four units, and to each type of atomic weight corresponds two series, one for even and the other for odd, nuclear charge.

Accordingly, isobares whose atomic numbers differ by 1 are not to be expected among the stable elements, and they do not, in fact, occur, although ten certain pairs of isobares are now known. Pairs of isobares provisionally indicated, but not certain, also obey this rule. That a whole class is thus excluded helps to explain the relative scarcity of isobares.

Russell also bases his arguments as to the relative stabilities of the isotopes of inactive elements on analogies drawn from the radioactive series, but he starts from four radioactive series the members of which have atomic weights $4n+3$, $4n+2$, $4n+1$, and $4n$ respectively. The third series is a purely hypothetical one whose end products may be bismuth ($P=209$) and thallium ($P=205$). The reasoning is not always easy to follow. Several interesting results are derived, many of which await confirmation, but they are not of a nature that can be briefly exposed.

In short, all speculation on the subject of stability is based on the known properties of the radioactive elements. Suggestive regularities have been pointed out, but the guiding facts are scanty, and no great certainty as to the underlying meaning of the rules put forward can yet be claimed.

Nuclear Dynamics. Attention is devoted to nuclear dynamics rather to indicate the tasks of the future than to describe the triumphs of the present. At present the problem offers what is termed by some writers an almost virgin field. Obviously some theory of the motion of the nuclear constituents will have to be elaborated eventually. Rutherford and Chadwick's work gives a strong indication of an orbital motion of at least one proton, and it is probable that a complicated system of moving parts will have to be devised to give a stable nucleus. Any successful model which will explain radioactivity will have to contain moving protons and electrons. It is quite possible that the nucleus will be definitely divided into inner and outer parts, and a kind of nucleus within the nucleus assumed. A start in this direction has, in fact, already been made.

Rutherford has recently put forward a provisional scheme of nuclear structure, guided largely by a suggestive result obtained in investigating the scattering of α particles by aluminium. The experiments of Bieler, to which reference was

made in Chapter II., showed that the closer the approach of the α particle to the scattering nucleus the smaller becomes the ratio which the number of particles scattered through a given angle bears to the number indicated by the inverse square law. Rutherford and Chadwick, using α particles of greater energy, have found that for still closer approach
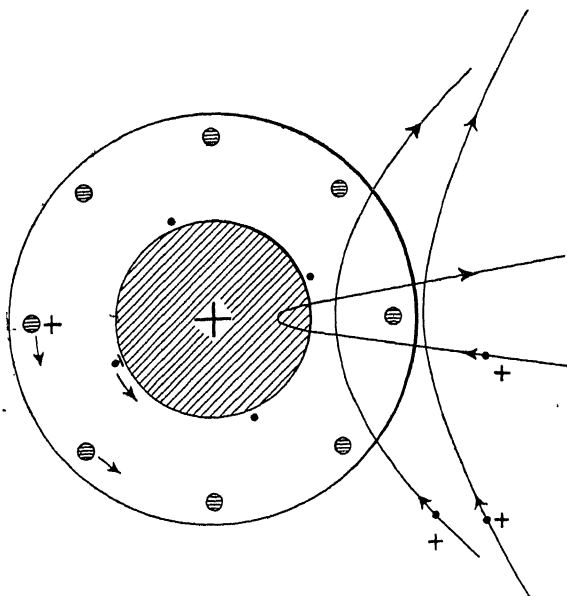
FIG. 30.
Rutherford's nuclear scheme.

than Bieler obtained this ratio suddenly increases again. This result was obtained with aluminium : with heavier elements, where, owing to the large nuclear charge, such close approach does not occur, the inverse square law was found to retain its validity within the limit attainable. For example, with silver and gold the distance of closest approach is 2×10^{-12} cms. and 3×10^{-12} cms. respectively with the swiftest α particles used.

The aluminium results can be explained by supposing that the nucleus consists of a positively charged inner core, surrounded by a ring or shell of circulating electrons, and a system of still larger radius of circulating protons, as represented crudely in Fig. 30. An α particle which does not penetrate

the outer shell will be subjected to a force which follows approximately the inverse square law.* An α particle which penetrates within the proton system will then be subjected to a repulsion smaller than would be the case on the inverse square law (supposing, of course, the net nuclear charge to be concentrated at the centre of the nucleus), and for such particles the scattering will be less than that calculated on the inverse square law. α particles which possess˙ sufficient energy to penetrate the inner system of satellites represented in Fig. 30 will be exposed to a bigger field, and the scattering ratio will increase. The quantitative departure from the inverse square law will depend upon the exact distribution of the nuclear electricity. When the laws of scattering for very close approach are more completely worked out no doubt an attempt will be made to represent this distribution more exactly.

The scattering results alone do not, of course, demand that the electrons and protons of Fig. 30 shall be in motion, since a statical distribution will effect the same thing. However, if we are to retain the inverse square law of force between the inner core and outside electric charges, as we shall do unless we are irresistibly driven from this position, they must be in motion to secure stability. Further, as we remember, Rutherford was led to assume circulating protons in the outer part of the nucleus to explain the behaviour of the protons expelled by impact of α particles (Fig. 19). Other nuclear properties also seem to call for a dynamical rather than a statical model of the nucleus. Lindemann, by a combination of very wide generalities and very special assumptions, has, as we have seen, devised a nucleus in which there are moving parts, which gives some account of Geiger's law connecting range of α particle and half-value period, but which does nothing else. Ellis has brought forward strong evidence for energy levels within the nucleus, differences between which can be emitted as γ rays, and assumed that these levels are due to circulating electrons, like those in the extranuclear structure, but has not referred to other nuclear properties. The approach to the

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* If the distribution of electricity be assumed azimuthally continuous and spherically symmetrical the inverse ˙square law will, of course, be exact as long as the α particle does not cross the boundary.

problem from various directions is beginning to indicate certain wide features of nuclear structure ; but we are a long way from having any sure ground on which to build a more precise dynamical theory, since it is improbable that ordinary electro-dynamic laws, even as limited by the quantum theory, hold within the inner part of the nucleus, whatever may be the case in the outer regions.   The fact that a heavy nucleus, containing some tens of electrons, appears to be of the same order of size as the electron itself, as ordinarily estimated, shows how much more complicated the problem of the nucleus is bound to be than that of the extranuclear structure, where the distances are large compared to the dimensions of the parts.

Whereas in 1923, when the first edition of this book was published, practically all the few experiments bearing on nuclear structure were concerned with the spontaneous radiations from the nucleus, and so applied only to very heavy nuclei, containing a large number of units, Rutherford and Chadwick's latest experiments have indicated how information can be obtained as to the outer parts, at any rate, of light nuclei.*   The continuation of these experiments is likely to furnish us soon with further information as to nuclear structure.

The nucleus may, of course, have a rotation as a whole, in addition to any internal motions.   In fact, small as it is, it offers an unbounded field for speculation, which, however, in the absence of experimental information, has a limited value.

Shape of the Nucleus.   When we say that a nucleus has a certain size, say 5×10^{-13} cms., we do not mean anything very determinate.   A nucleus is a centre of complicated forces, which, at a great distance, may be taken as a minute charged sphere, but even at a great distance it is not certain that the field of force has spherical symmetry about the centre, although in the investigation of Bohr and his school it is always assumed to possess it.   Near the nucleus it is practically certain that

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* " Unfortunately, at present the main experimental information bearing on the dynamical problem is from the radioactive side, and so applies to nuclei of such a complicated character and large number of constituents that the task is of exceeding difficulty.   The greatest hope at present seems to lie in extensions of Rutherford's work on α particles, which has indicated a revolution of a proton within the nucleus, and may enable us to explain, at any rate, the outer parts of a simple nucleus." (*Structure of the Atom.* First Edition.)

it has not : the mere fact that a particle emission is accompanied by so slight γ radiation seems to indicate that there are certain preferred paths along which the particles leave, without coming close to extranuclear electron orbits. By the diameter of the nucleus we indicate the distance between the centres of two nuclei at which the inverse square law breaks down. In speaking of the shape of the nucleus what has generally been meant so far is that nuclear charges, distributed in a certain configuration, and acting on external charges with an inverse square law, give one or other of the experimentally established results : the configuration is then called the shape of the nucleus. We shall indicate now a few of the attempts which have been made to devise an aspherical nucleus.

The first, perhaps, was made by Silberstein in 1919, when he showed that a theory of the fine structure of spectral lines could be based upon an axially symmetrical nucleus, any departure from spherical symmetry producing a splitting of a line into close components. He assumed an inverse square law between each individual charge of the nucleus and external electrons, and disregarded relativistic complications : the helium nucleus, for instance, he took as two positive point charges separated by a distance $2a$, upon which the separation of the components of a line is shown to depend. Preliminary work only has been carried out along these lines, but it is interesting as showing that a departure from sphericity not exceeding the order of size laid down by Rutherford for nuclear magnitudes can produce appreciable results on the electronic orbits. It may be noted that Darwin found a nucleus of Silberstein's type, a " bipole " of two like charges, fairly satisfactory from the point of view of the collision relation between an a particle and a proton.

Rutherford's work, showing that for close collision between a flying a particle (helium nucleus) and a nucleus the helium nucleus behaves as if flattened, has been considered in Chapter IV., where it has been indicated that there is nothing to decide whether the helium nucleus is permanently flat or deformed from a spherical to a flattened shape by the near approach of the a particle. It has been recorded that Chadwick and Bieler, using Darwin's calculations, have concluded that the helium nucleus behaves—in collision—as an elastic oblate

spheroid, moving in the direction of the minor axis, the semi-axes being respectively 8×10^{-13} cm. and 4×10^{-13} cm. At present most speculation as regards shape has been restricted to the helium nucleus, since it is only for the swift α particle that close collisions with that minute proof-body, the proton, have yet been studied in detail. The difficulties connected with the collision between an α particle and a heavier atom have been indicated in Chapter IV. As a general conclusion we may say that it is rather early to expect to get a decision on the shape of even the simpler nuclei—the necessary accurate experimental work is not yet to hand. Heavier nuclei have, in general, been treated as spherical in explaining the scattering results. There are, however, one or two interesting pieces of speculation as to the possibility of other shapes which may be mentioned before leaving the subject.

Chwolson has made a suggestion that the ultimate density of electricity, positive or negative, is always the same, *i.e.* that a given elementary charge always occupies a given volume. He adopts the disc form for the nucleus, and shows that for a given charge in disc form the mass is inversely as the thickness of the disc. He suggests that the positive elementary disc is the α particle, and calls it a *petalon* : he calculates for its radius $70s$ and for its thickness $\cdot 00055s$, where s is the radius of the electron. The nucleus is then supposed to consist of petalons sandwiching electrons between them, a nucleus of atomic number Z containing $Z - 1$ petalons and $(Z - 2)$ electrons. This hypothesis is mentioned for its novelty rather than for any positive achievements to which it has led.

Considerations of a different kind have led H. T. Wolff likewise to assume a disc form for the heavy nucleus at least. He starts from the assumption that, just as optical and X-ray spectrum lines are due to quantum transitions in the extra-nuclear electronic orbits, so the emission of nuclear γ rays is to be attributed to the passage of circulating electrons in the nucleus from one quantum state to another. This agrees with the views of Ellis. He then shows that, if the nucleus be assumed spherical, and it be further assumed that Coulomb's law of force prevails, then the Sommerfeld-Wilson quantum condition*

* See Chapter X.

for angular momentum leads to the result that, if the radius of the smallest electron path is to be not greater than 10^{-12} cm., then the nuclear charge must be at least $139e$, which is out of the question. He concludes that Coulomb's law and the quantum condition may be retained if the nucleus, instead of being spherical, is assumed to be a positively charged disc of radius 4×10^{-13} cms., round which the nuclear electrons circulate in a coplanar, concentric orbit. The positive charges in the nucleus are supposed to hold together by themselves, which, of course, means that Coulomb's law cannot hold for them amongst themselves for distances less than 4×10^{-13} cms., but that the repulsion must change to an attraction. The radius of the electron orbit works out at the reasonable value of 10^{-12} cm. These values, it may be noted, show a certain rough agreement with Bieler's estimates of distances at which the inverse square law holds and breaks down. On Wolff's calculations one of the electrons detached from its orbit will leave the sphere of atomic influence with a velocity of about $\cdot998c$ in the case of radium B, a value which agrees pretty well with the measured velocity of the swiftest β particle from this element. Wolff has also considered the problem of α ray emission on the basis of a disc nucleus, without any very striking result. There has been no attempt to adapt the disc nucleus to the scattering results.

Too much attention must not, of course, be paid to these deductions, as the number of unconfirmed, if plausible, hypotheses on which they rest is great. At the same time, it is noteworthy that certain independent lines of reasoning are, in a very general sort of way, pointing to the conclusions : firstly, that the field of force which surrounds the nucleus loses spherical symmetry and assumes an axial symmetry as the centre of the nucleus is approached ; and secondly, that the law of force, which obeys the inverse square far out from the nucleus, modifies its form and ultimately reverses sign as the centre of the nucleus is approached. Much work is likely to centre on the investigation of these points in the near future.

Effect of Packing on Mass of Protons. There remains to be discussed the question as to why hydrogen does not comply with the whole number rule, that is, why the mass of a proton when

isolated is 1·0077, while in any complex nucleus it is 1·000 ± ·001. This effect of " close packing " of protons, or " mass defect " (*Massendefekt*) has been explained on the supposition that all the mass, of proton as well as electron, is electromagnetic. Classical theory shows that the electromagnetic mass is a function not only of the charge, but of the distribution of the charge : the more concentrated a given charge, the greater the force needed to accelerate it. Thus the electro-magnetic mass of a charge e on a sphere of radius a is $m = \dfrac{2}{3}\dfrac{e^2}{a}$. To obtain the experimental mass of the electron the charge must be considered concentrated on a sphere of diameter $3·8 \times 10^{-13}$ cms.: to get the greater mass of the proton the diameter must be 2×10^{-16} cms. This, of course, assumes that these ultimate particles behave like macroscopic charged spheres, which is a considerable assumption.

On the electromagnetic theory, then, the mass depends on the capacity of the system. If we bring two small charged spheres of opposite sign close together the mass of the two so placed will be less than the sum of the mass of the two separately. The diminution of mass which attends the packing of the protons in the nucleus (which is in general ·76 per cent. of the mass of the isolated protons) can, then, be attributed to their close packing with electrons. That the packing must actually be close is indicated by the size of the electrons as compared with the estimated size of the nucleus.

The mass defect is shown in the simplest case by the helium nucleus, which, containing four protons and two electrons, has mass 4, ·76 per cent. less than that of four isolated protons, 4·0308. That this is a very stable combination has been proved experimentally, and we have also seen that the helium nucleus is probably the chief unit of which nuclei are built. It may be that only in the helium nucleus is the packing close enough to produce the ·76 per cent. mass defect, and that for the one, two or three odd protons, and the electrons more loosely held in the nucleus by both α particles (on Meitner's theory) and elsewhere, there is no appreciable packing effect. The heavy nuclei are, however, so largely composed of helium nuclei that there is so far no hope of a decision on this point.

We can get a numerical estimate of the stability of the helium nucleus from the mass defect, by taking into account Einstein's relation between mass and energy. According to this, energy and mass are connected by the relation

$$m = \frac{E}{c^2},$$

where c is the velocity of light: if a system loses energy it loses mass, and *vice versa*. Hence the loss of mass which takes place when four protons are combined to give a helium nucleus must, *whatever be its cause*, be accompanied by an output of energy given by

$$E = \cdot 0308 \times 9 \times 10^{20} = \cdot 28 \times 10^{20} \text{ ergs}$$

$$= 7 \times 10^{11} \text{ (small) calories}$$

per gram molecule (4 grams) of helium. Thus, in the language of the chemist, a helium nucleus is an exothermic compound, giving out $1 \cdot 75 \times 10^{11}$ calories per gram as compared with, for instance, the $1 \cdot 6 \times 10^3$ calories given out when a gram of carbon dioxide is formed from its elements. To resolve a gram of helium into protons would, of course, require the input of this amount of energy, and a substance which requires some 10^{11} calories to dissociate a gram of it may justifiably be called stable.

A single helium nucleus would require

$$\frac{\cdot 28 \times 10^{20}}{6 \cdot 1 \times 10^{23}} \text{ ergs} = 5 \times 10^{-5} \text{ ergs}$$

approximately. This is more than three times the kinetic energy of the swiftest α particle (that for thorium C_2 with range 8·6 cms. in air at 15° C.). Hence there seems little likelihood that the helium nucleus will be dissociated at present, since the α particle offers by far the greatest local concentration of energy at our disposal.

It is not surprising that the enormous energy which would be at our disposal if we could make protons combine to helium nuclei (4 grams of helium in the course of formation from hydrogen would give about a million horse-power for an hour), has led to many brilliant flights of fancy. A comparatively

small rate of formation of helium from protons in the sun would give a sufficient supply of energy to compensate for that lost by radiation.   Delightful or horrible pictures of what could be done were such a source of energy at our disposal are easily (and profitably) drawn.   It has been suggested that if once a single helium atom could be built up from protons the energy liberated would detonate in some way all neighbouring substances, and blow the world—possibly the universe—to pieces.   I confess that I do not know quite what is intended by this detonation ; presumably it is meant that all neighbouring protons would combine, and the output of energy be cumulative.   It seems to me, however, that the fact that, in spite of the existence in nature of radioactive changes, electric forces, enormous pressures and temperatures, and plenty of protons to work upon through all geological time, no detonation of the world has yet taken place, assures us some degree of security.   It must be remembered that nature is continually carrying out experiments— Rutherford has done nothing new in disrupting nitrogen nuclei, which nature has been doing in the same way for millions of years, wherever air is in contact with radioactive matter. Rutherford was the first to demonstrate it, to show it going on.

Speculations as to the evolution of all elements from original protons and electrons are entertaining, but hardly come within the scope of this book.

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CHAPTER VIII

A DIGRESSION ON OPTICAL SPECTRA *

Importance of Spectral Evidence. The experimental study of spectra, both optical and X-ray, has led to the discovery of numerical laws which are of the utmost importance for modern atomic theory. As the account of the regularities revealed in series spectra is either entirely lacking or else very meagre in the ordinary text-books of physics, a short description of the chief properties of such spectra may, perhaps, be permitted here, as a preliminary to considering the motion of the electrons which run their courses round the nucleus.

The optical spectra of gases under ordinary pressures consist of a number of discrete lines, each corresponding to a characteristic frequency of vibration. In some cases the lines are arranged in obvious groups,† within which they crowd up towards a limiting line, or head : these, the well-known band spectra, appear channelled or fluted to a low dispersion instrument, and reveal their true nature only to spectrographs of high resolving power. The band spectra are always associated with the emission of light by undissociated molecules, that is, by combinations of atoms and not by single atoms, although sometimes these combinations may be relatively unstable.

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* This chapter is inserted for the benefit of those who are not acquainted with the results of modern spectroscopy, and can be omitted by those who are. Readers seeking relevant experimental data are referred to A. Fowler's *Report on Series in Line Spectra,* published by the Physical Society of London (hereafter called " Fowler's Report "), or to the book *Seriengesetze der Linienspektren,* by F. Paschen and R. Götze, published by Springer, of Berlin.

† That the lines belonging to an ordinary line series—say one of the series of lithium—form a single group is not *obvious* to the casual observer. In fact, a prolonged investigation is often necessary to assign lines to their proper series.

Ordinary line spectra are of atomic origin, and thus demand an atom model capable of emitting a large number of separated frequencies. On the classical theory of electrodynamics this calls for a large number of degrees of freedom of the vibrating centres which the atoms must be supposed to contain. No theory assumes that all the frequencies are emitted at once by a single atom, but, all atoms being supposed similar, any one of them must be capable of emitting singly any one of the lines.

The characteristic X-ray spectra are strictly atomic in their origin : if a large number of different kinds of atoms are present, either as a mechanical mixture or a chemical combination, in the substance which is made to give out its characteristic X-radiations, each kind of atom will emit its own spectrum exactly as if it alone were present.* The X-ray spectra have been conclusively shown to be connected with disturbances in the inner groups of electrons, which accounts for their independence of chemical combinations, while the outer electrons are concerned in the emission of optical spectra. Since chemical combination is also an affair of the outer electrons † the molecule does not give the optical line spectra of its component atoms, but a band spectrum of its own.

Dispersed through a range of wave-lengths stretching from about 10^{-9} cms. to 1.9×10^{-4} cms. we have, then, certain series of vibrations which are characteristic of the particular atom concerned in their emission. The X-ray series are of comparatively simple structure, the modifications which take place as we go from the lighter to the heavier atoms being easily followed. The optical spectra, on the other hand, are often of so great complexity that the laws which govern them have not yet been hunted down : the iron spectrum, to take the worst example, with its thousands of lines, long defied all attempts to unravel it and, although considerable progress has recently been made in classifying a proportion of the lines, is still only partially ordered. The lines of the spectra of hydrogen and helium, and in general the spectra of elements in columns I, II and III of the periodic tables, have been resolved into

* But cf. the work of Lindh, p. 385. ·   † Cf. Chapter XII.

series governed by comparatively simple laws. These regularities will now be described, starting with hydrogen, which, although the simplest case, exemplifies many of the properties of series spectra. It must not, however, be forgotten that the spectra of many of the elements have not yet been satisfactorily ordered into series, although the work now being so vigorously prosecuted is fast bringing order into columns IV to VIII, in which until recently only isolated relationships had been established.

Hydrogen. It has been found that the regularities of spectral series are always much more simply expressed in terms of the *frequency* than of the wave-lengths of the lines concerned. If λ be the wave-length, c the velocity of light, the frequency is, of course, $\dfrac{c}{\lambda}$, but spectroscopists have found it more convenient to employ the simple reciprocal of the wave-length expressed in centimetres, which is called the wave number and will be denoted by ν. In other words, it is the number of waves per centimetre. When the true frequency, which is $c\nu$, is required it will from now on be denoted by ν_T.

Balmer was the first to show that chosen lines of a spectrum could be represented by a simple law, when he announced that the wave numbers of the hydrogen lines then known were represented by the simple formula*

$$\nu = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right), \quad \dots\dots\dots \dots\dots\dots\dots(1)$$

when n' has the value 2, and n takes successively the values 3, 4, 5 . . . to give the wave numbers of the different lines.†

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* This is not the exact form in which this discovery was expressed, but is the equivalent modern form.

† Fowler uses the notation $\nu = N\left(\dfrac{1}{m_1^2} - \dfrac{1}{m^2}\right)$, and others use $\nu = N\left(\dfrac{1}{n^2} - \dfrac{1}{m^2}\right)$. It is not considered advisable to use m for the integer in spectral formulae since m is generally adopted for the mass of the electron, which occurs in all modern discussions of the theory of spectra. n has been widely used in developing expressions for the general term of spectral formulae to represent the general integer in the quantising equations. It is therefore adopted here for the general term, the particular value for the limit being denoted by n'.

The constant R,* which is of the utmost importance for our subject, is known as Rydberg's constant, and has the value, according to Houstoun's recent determination, of 109677·70 ±·04 (on the international scale).† The accuracy of the formula may be seen by comparing the values given by the formula for the first six lines with the experimental values.

WAVE NUMBERS OF THE FIRST SIX LINES OF THE
BALMER SERIES OF HYDROGEN.

Observed	15233·22	20564·79	23032·54	24373·06	25181·34	25705·96
Calculated‡	15233·17	20564·77	23032·54	24373·06	25181·35	25705·97

The formula expresses a property of line series which is quite general. As the lines are taken in succession from the red to the violet they crowd up together, approaching a *limiting wave number* given by putting $n=\infty$ in the formula. Fig. 31
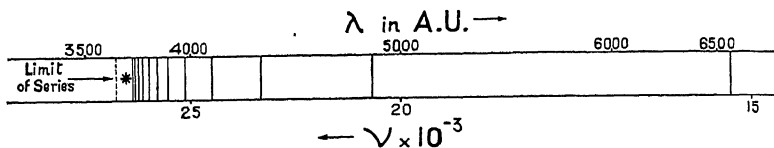
FIG. 31.

Balmer's series for hydrogen.

(Some 23 lines have been measured in the gap denoted by *, but are too close together to be represented on this diagram.)

shows the lines of the Balmer series with a scale of wave-lengths above and wave numbers below : the lines of any other single

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* Professors Siegbahn, Sommerfeld, and others, having decided to use R to denote Rydberg's constant, this notation is here adopted in preference to the N sometimes used. R, it may be noted, is of dimensions $\left[\dfrac{\mathrm{I}}{\text{length}}\right]$, since n and n' are pure numbers, and $\nu = \dfrac{\mathrm{I}}{\lambda}$.

† W. V. Houstoun, *Nature*, April 24, 1926. R. T. Birge earlier concluded that the best value of R was 109677·6 (*Nature*, March 3, 1923).

‡ Using the value $R = 109678·8$. The wave numbers have actually been measured to eight figures, instead of the seven given, and for closest agreement the value $R = 109678·3$ adopted, while the formula has been slightly modified by the addition of a very small term to n' and n. This is not of importance for our considerations.

line series have a similar general appearance. The diagram offers no indication of the relative intensities of the lines, which actually fall off in a regular manner as the limit is approached. This decrease of intensity towards the limit is a regular feature of all spectral series.

Three other series are now known for hydrogen, namely, the Lyman series, in the ultra-violet, and the Paschen series and Brackett series in the infra-red. These are expressed by putting

$$n'=1, \; n=2, \, 3, \, 4 \ldots \quad \text{(Lyman series)}$$

$$n'=3, \; n=4, \, 5, \, 6 \ldots \quad \text{(Paschen series)}$$

and $\qquad n'=4, \; n=5, \, 6, \quad \ldots \quad \text{(Brackett series)}*$

in the general Balmer formula.

These three series exemplify in a very simple way a principle whose general conformation for all spectra which have been ordered is one of the most important results of modern spectral work—the *combination principle* first pointed out by Ritz. The formula (I) gives the wave number as the difference of two *terms*, both of the form $\dfrac{R}{x^2}$. Now considering the sequence of terms $\dfrac{R}{1^2}, \; \dfrac{R}{2^2}, \; \dfrac{R}{3^2}$, etc., it will at once be seen that as a consequence of the fact that any line can be expressed as the difference of two of them, the wave number of a line can be represented as the difference of wave number of two other lines. For the spectra of other elements the terms have not quite so simple a form, but they are always functions of whole numbers, and the wave numbers can always be expressed as a difference of two terms, with certain consequent relationships. In general it may be said that the terms are the fundamental characteristics of a line spectrum, for from them all the lines

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* This series has only recently been observed by F. S. Brackett (*Astrophys. Jour.*, **56**, 154, 1922), who, using a long hydrogen tube viewed end on as a source, measured two lines in the far infra-red which may be represented by

$$n'=4, \; n=5, \, 6$$

in the general Balmer formula. The wave-lengths of these two lines are $4·05\mu$ and $2·63\mu$ respectively. At the same time Brackett observed for the first time the third, fourth and fifth lines of the Paschen series.

of the different series into which it may be resolved are obtained. The constant R appears with slight changes in the terms of all series.*

In addition to these four series there is a " secondary," or band, spectrum of hydrogen, consisting of thousands of lines now in course of disentanglement, but this is due to a hydrogen molecule, and may be put aside for the present.†

Arc and Spark Spectra. Classification of Spectra. The series spectrum of hydrogen is particularly simple, corresponding, as has been shown by all modern theory, to the very simple structure of the hydrogen atom, which in its normal state contains only one electron. Heavier atoms are capable of emitting two or more distinct classes of spectra, each of which has its own several series. When subjected to moderate agitation the atoms give one class : when subjected to very rough handling they give another class, either accompanied by, or unaccompanied by, the first. By careful search and selection of conditions, the existence of further spectra has been established during the past few years. In general, in the Bunsen flame, or in the arc, the disturbances suffered by the atom are comparatively mild ; in the spark, with a condensed discharge from Leyden jars or other condensers, the disturbance is more violent. The spectrum produced in the first case is therefore called the arc spectrum ; in the second case lines which are shown only faintly in the arc are enhanced, and fresh lines appear. The new lines and the enhanced lines constitute the second class, the spark spectra. Some spark lines, of course, sometimes appear in the arc : the complete ordering of the lines into these two classes is a matter of careful investigation. It may be stated at once that modern research has shown that the arc spectra result when an electron is removed from a neutral atom, while the spark spectra result when an electron is removed from an atom which has already lost an electron. The existence of only one line spectrum with

* Thus, for instance, $R = 109722 \cdot 3$ for neutral helium. (See Chapter IX, p. 197.)

† With respect to the conditions necessary for the production of the Balmer and the many-line spectrum of hydrogen in separated regions of a discharge tube, a very interesting paper by R. W. Wood (*Phil. Mag.*, **44**, 538, 1922) may be consulted.

hydrogen is thus simply explained, for the hydrogen atom has only one electron to lose.

The further classes of spectrum to which reference has been made are excited, one when two electrons are removed from the atom, another when three electrons are removed from the atom, and so on. The existence of spectra emitted by the aluminium atom which has lost two electrons has been established by Paschen, and of spectra due to the silicon atom which has lost three electrons by Fowler. The names arc and spark spectra are therefore not particularly desirable in the light of modern knowledge, since they fail to emphasize the real distinction between the classes of spectra to which they are applied. It is, theoretically, preferable* to speak of the spectra of the neutral atom (arc spectrum) and of the singly ionised atom (first spark spectrum), continuing the notation by referring to the further classes of spectra as of the doubly ionised atom, of the trebly ionised atom, and so on. It is usual to abbreviate this description by using symbols whose nature can be made clear by taking as an example silicon. The four classes of spectra, due to the neutral, singly, doubly and trebly ionised atoms are called respectively Si_I, Si_{II}, Si_{III} and Si_{IV}. This notation goes back to Norman Lockyer. It is to be noted that the spectrum of *singly* ionised silicon is Si_{II}, not Si_I. By another notation the spectra are spoken of as Si, Si^+, Si^{++}, Si^{+++}. In the case of arc and spark spectra this form is general; for instance, the two magnesium spectra are often described as the Mg spectrum and the Mg^+ spectrum.

In general, most of the lines of either the arc or the spark spectra fall into four distinct series, which are named the principal, diffuse (or first subordinate), sharp (or second subordinate), and fundamental series † respectively. In the general case the lines of the different series are intermixed, and the series overlap. If all the lines had the same physical character it would be difficult to sort them out; fortunately there are

* But often, for brevity, one is compelled to use the older nomenclature.

† The fundamental series is sometimes called the Bergmann series on the continent, but the name is dying out. As a matter of fact, Saunders and Fowler independently discovered such series in the visible region for calcium and strontium before Bergmann measured a number of them in the infra-red for other atoms.

certain guides, in the appearance of the lines and their physical behaviour, which aid the separation into series. The terms diffuse and sharp series, for instance, originate in the fact that for many elements the lines of the diffuse series are comparatively ill-defined and "washy," the lines of the sharp series clear and definite. (This is not the case for all elements, but the names have been extended from the elements where the lines are actually diffuse and sharp respectively to those where these differences are not marked.) Continuing the physical characteristics of the different series, we note that the lines of the principal series are strong and easily reversed by absorption. When the series consist of doublets, the separation (*i.e.* differences of wave number of the two components), in the case of the principal series, becomes less and less as the wave number of the line increases, whereas for the sharp and diffuse series the separation is constant throughout. In triplet series there are analogous guides which need not be detailed. The relative ease with which given lines are excited is also a guide to the series to which they belong. Another test indicating the series to which a line is to be attributed consists in observing the Zeeman effect : in a strong magnetic field all lines which belong to the same series behave similarly, showing identical resolution if the scale of frequencies be adopted. In these ways, even when the lines of different series are mixed up, they can be allotted to their series. It may be added that there is nothing particularly fundamental about the fundamental series except that it is more Balmer-like than the other three ; and the name does not seem particularly happy, as if a series is principal it might also be supposed fundamental. However, the name is generally used, and is accepted in Fowler's report, so it will be adopted here.

A comparison of Fig. 32, on which are represented the wave numbers of the hydrogen lines with Fig. 33, on which are represented the wave numbers of the four main series of lithium, will show how the series which are separated for hydrogen, overlap for lithium, as they do in the general case.

Series Relationships. Since in all spectra which have been ordered the wave number of any line is expressed as the difference of two terms, the problem is to find a satisfactory

general formula for the terms. The simple form $\dfrac{R}{n^2}$ suffices for hydrogen and ionised helium alone : for other elements a somewhat more complicated function of the whole number n is required. Various types of formulae have been suggested by Rydberg, Hicks, Rummel, Ritz, Nicholson, Paulson, Johanson and others ; * for present purposes the simplest of them, that of Rydberg, will suffice. His expression for a typical term is $\dfrac{R}{(n+\mu)^2}$, where R is the constant which we have already seen in Balmer's formula,† n is a whole number and μ is a number which has a fixed value for a given series, but different values for the different series of one element, and, of course, still other different values for the series of other elements. Its values, as allotted by the practical spectroscopists, are usually not very different from unity—that is, they lie between ·3 and 1·7. For instance, for lithium μ is ·9596, ·5921, ·9974 respectively for the principal, sharp and diffuse series.‡

Thus for one element any term is determined by a whole number n, and by a constant μ characteristic of the series. The whole number n is called the *sequence number* (German *Ordnungszahl* or *Laufzahl*), the body of terms determined by giving n successive whole number values in the term formula being called a *sequence* of terms, in contradistinction to a series, which expression is restricted to lines, not terms. The particular values which the constant μ adopts for the principal, sharp, diffuse and fundamental sequences are generally denoted by P, S, D, F, and a term of the principal sequence

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* See Fowler's Report.

† R varies very slightly from element to element, owing to the fact that the mass of the nucleus, though large compared to that of the electron, is not infinite. (See p. 195 *et seq.*)

‡ The form $\dfrac{R}{(n+\mu)^2}$ is characteristic of arc spectra. For spark spectra the constant is not R but $4R$, a fundamental point. Of course, by taking n not as a whole number, but as a multiple of ·5, it would be possible to express the spark series with the constant R ; this, however, as subsequent considerations will show, would be to destroy a simplicity of expression which is in the best accord with theory. Similarly, since not n but $n+\mu$ is determined in fitting an arc series, the value of n can be changed by a unit if the corresponding adjustment is made in μ. (See p. 173 *et seq.*)

is written as nP, which is an abbreviated notation for $\frac{R}{(n+P)^2}$. Similarly, an nth order term of each of the other three series is written nS, nD, nF. If there were no interrelation between the series, typical *wave numbers of lines* written as $P(n)$, $S(n)$, $D(n)$, $F(n)$ would be

$$P(n) = P_\infty - nP$$
$$S(n) = S_\infty - nS$$
$$D(n) = D_\infty - nD$$
$$F(n) = F_\infty - nF,$$

where P_∞, S_∞, D_∞, F_∞ are the limits of the different series which the wave numbers of the lines $P(n)$, $S(n)$ ... attain when n is put $= \infty$, causing the second term to vanish in each expression. The limiting frequencies are, however, connected by simple relationships. In the first place, the limiting frequencies of the sharp and diffuse series are identical: $S_\infty = D_\infty$. Further, the limiting frequencies of the principal and the sharp series are expressed in a very simple way by the so-called Rydberg-Schuster law. The limit P_∞ of the principal series is equal to the value of the term nS, the variable part of the expression for $S(n)$, where n is put 1, while the limit S_∞ of the sharp series is equal to the value of nP where n is put 1. A further law, discovered by Runge, states that the limit of the fundamental series is given by putting $n = 2$ in the term nD. Thus the wave numbers of lines of the four series are given by

$$P(n) = 1\,S - nP \qquad n = 1, 2, 3 \ldots$$
$$S(n) = 1\,P - nS \qquad n = 2, 3, 4 \ldots$$
$$D(n) = 1\,P - nD \qquad n = 2, 3, 4 \ldots$$
$$F(n) = 2\,D - nF \qquad n = 3, 4, 5 \ldots$$

The possible values of n are indicated on the right. It will be seen that the first, or lowest frequency, line of the principal series is given by $1S - 1P$, while the first line of the sharp series is $1P - 2S$. If we put $n = 1$ in the expression for $S(n)$ we get $1P - 1S$, which is the negative of $P(1)$. Thus $-P(1)$ behaves as if it were the "*first*" line of the sharp series: it is not, of

course, observed, because a negative frequency is only a fiction. If, however, $S(n)$ be plotted against n, $-P(\mathrm{I})$ at $n=\mathrm{I}$ will fall into line with the other terms.*

The different series are thus expressible by the difference between a fixed limiting term and a variable term containing a characteristic constant. There are, however, various other lines whose wave numbers are expressible as the difference between some value of the variable term of the series and a value of the variable term of another series. These are the so-called "combination lines," a further example of the fact that the terms are the important things, since they can be assorted in various ways so that their differences give observed wave numbers. As an example of combination lines, with strontium a series of lines $\mathrm{I}D\text{-}nP$ is observed ; a single line $\mathrm{I}S\text{-}\mathrm{I}D$; and other combinations involving lines of triplet series which have not yet been mentioned. Speaking generally, it accords best with modern theoretical views to lay stress on the terms, and to say that a spectrum of a given class can be represented by a certain number of term sequences. The four sequences nP, nS, nD, nF are the most important, but, as will be seen later, there is no theoretical reason for limiting the number of sequences to four, and recently, for the representation of certain lines, other sequences $G, H. \ldots$ (for which the lowest value of n is greater than it is for the F sequence) have been introduced. A further consideration of this point is best postponed until we take up the theoretical aspect of the subject in Chapter XI. ·The fact that any spectral line can be represented by the difference of two selected terms is embodied in the Combination Principle of Ritz, to which reference has already been made.

It should be stated clearly that the allocation of the whole numbers to the leading terms in the above series is to a certain degree arbitrary, since the value of n in $(n+\mu)$, which is the quantity determined by the experimental data, obviously depends upon the values selected for μ, so that adding or

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* It may be noted that sometimes the value $n=\mathrm{I}$ will give a negative wave number for the P series, which means that the first *observed* term is given by $n=\mathrm{2}$. In this case $n=\mathrm{I}$ will give a positive wave number, *i.e.* an observed term, in the S series.

subtracting 1 from μ changes the value of n by 1 for all terms of the sequence. We are considering here Rydberg's formula for the term $\dfrac{R}{(n+\mu)^2}$; formulae used for more accurate fitting of the experimentally found values of the terms embody a third corrective term in the denominator, which term involves n, and so is slightly modified by a difference of allocation of n, but not sufficiently to serve to fix n unequivocally. The allocation of n in the leading lines given above (*i.e.* $1S$, $1P$,
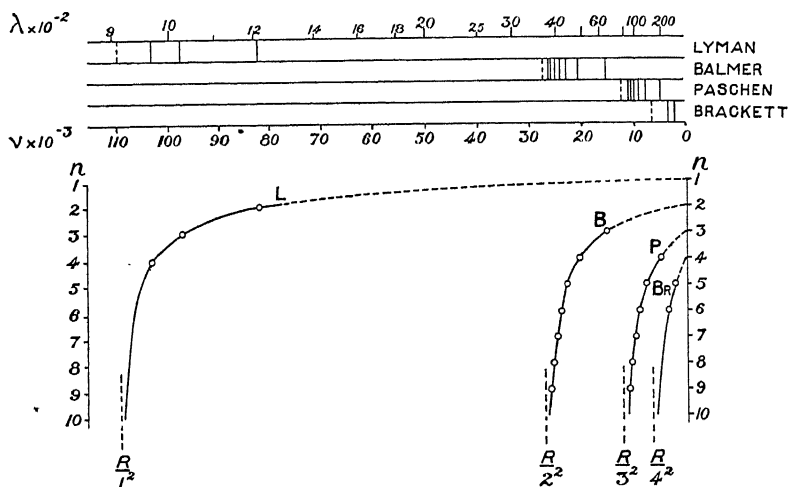
FIG. 32.

Diagrammatic representation of series for hydrogen.

$2D$ for the limiting terms) is Rydberg's notation, adapted by Fowler. In Paschen's notation the $1P$ is replaced by $2P$, and $2D$ by $3D$, which affects the value of μ, of course, but does not affect the fitting to experiment. Rydberg and Paschen's notations are the only two used by practical spectroscopists. It will be pointed out later that Bohr, on theoretical grounds, allots n still differently : on his notation the value of n to be given to the leading terms varies from element to element. This notation, great as is its theoretical significance, has proved unmanageable for descriptive purposes, and need not be considered at this stage. The Rydberg-Fowler notation is adopted in this book, since most English readers rely on Fowler's report for

the mass of important reference which it contains. Those who consult Paschen-Götze must keep in mind the difference of notation.

Graphical Expression of Series and Series Relationships. Fowler exhibits the series by plotting the wave numbers of the *lines* against n, the frequency scale increasing from right to left, and n increasing downwards. Fig. 33 prepared for lithium is typical. Above are the lines of the four series, exhibited on a wave-number scale; below, the graphs of ν against n. The lines approach the limits indicated as n tends
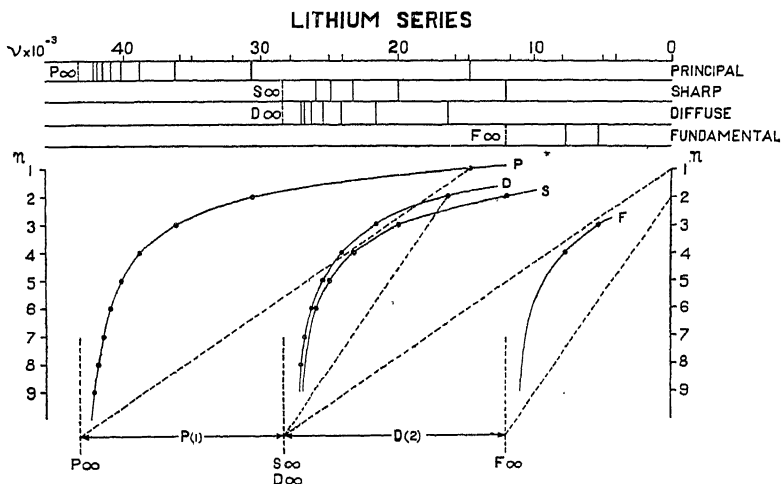
FIG. 33.

Diagrammatic representation of series for lithium.

to ∞ . The common limit of $S(n)$ and $D(n)$, and the relationships $P_{\infty} - S_{\infty} = P(1)$ and $S_{\infty} - F_{\infty} = D_{\infty} - F_{\infty} = D(2)$, indicated by dotted lines in the diagram, are immediately obvious. For comparison the simpler hydrogen relationships are exhibited in the same way in Fig. 32.

Bohr, on the other hand, plots the ν-values of the *terms* and not of the lines. This type of diagram is sometimes known by the name Grotrian.*

* Grotrian first employed a " Grotrian diagram " in a paper on regularities in the neon spectrum, published in the *Physikalische Zeitschrift* for November 1st, 1920. However, as Grotrian himself clearly states, Bohr had used the method some months previously in a lecture in Berlin, and had published it in the *Zeitschrift für Physik*, where it appeared a little before Grotrian's paper (vol. ii, p. 423).

The terms nS, nP, nD, nF of each different sequence are plotted on a scale of wave number ν, from right to left on a horizontal line, one line being used for each sequence, and the different lines being spaced vertically in the order named, with the S sequence uppermost. Fig. 34 shows the lithium spectrum
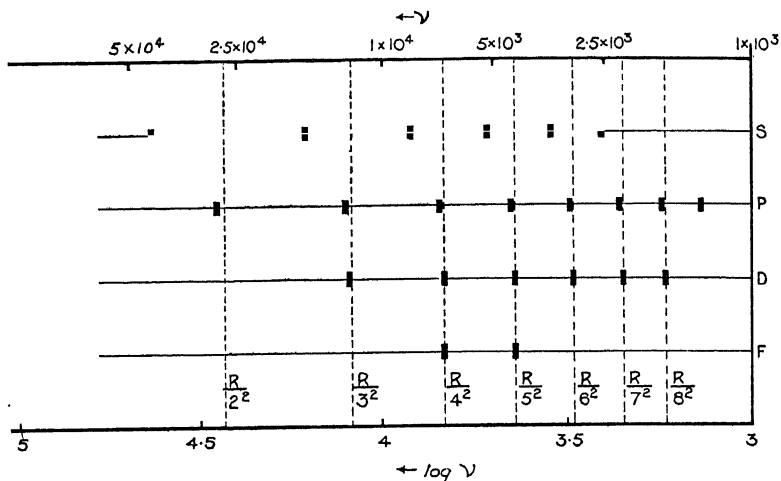
FIG. 34.

Bohr-Grotrian diagram for lithium spectrum.

exhibited in this manner, a logarithmic scale being, however, used for ν in order to open out the scale for the higher terms of the sequences. For comparison the hydrogen terms are represented by the vertical broken lines. The advantages of this method will appear when Bohr's general theory of spectra is discussed.

Doublet and Triplet Series : Fine Structure. Actually, things are not, in general, as simple as they have so far been described to be. Series consisting of single lines—so-called singlet series—are in a minority. The lines of a series may occur in pairs, known as doublets : the best known example of such a doublet is the yellow sodium lines, $\lambda\lambda = 5896$, 5890, which constitute the first pair of the sodium principal (doublet) series. In the case of doublets each series is then duplicated, since the shorter wave-length components of each doublet, taken together, form one series, the longer components a second series of the same kind. Again, the lines may occur in threes,

known as triplets: the series are then triplicated. Many relations, fundamental for the spectroscopist, have been obtained experimentally, and explained theoretically, regarding the separation of the lines in doublet and triplet series, relations which distinguish in a characteristic way any selected series from each of the other series. Thus the frequency difference of doublets of a principal series decreases with increasing frequency of the lines, so that the two series have the same limit, while the frequency difference of doublets of the diffuse and sharp series is constant throughout the series. Further, some lines have satellites, or fainter companions, which were formerly regarded as, in a sense, a subsidiary complication, but have now been shown to be an essential feature of the multiplet mechanism.

Doublet and triplet series are not the only types of multiple series. Recent research has shown that lines can occur in groups resulting from combinations of terms of far greater complexity, known as quartets, quintets, sextets, septets and octets, any such groups being known, generally, as a multiplet. The lines which go together to form a single multiplet are all characterised by the same value of n: they are not, in general, readily distinguishable as belonging together, but have to be hunted out by special methods, such as a consideration of the relative intensities of the different components of the multiplets, of the temperature classification, and of the Zeeman effect. The characteristics of multiplets are considered in greater detail in Chapter XV, which deals largely with their properties.

The spectrum of an alkali metal consists of doublets: although in many cases the two components are too close to be resolved it is perfectly clear, on both theoretical and experimental grounds, that each member of the various series is double. When we turn to the spectra of neutral atoms (arc spectra) of the alkaline earth metals we find triplets, lines of the S, P, D and F series being all triple.* Besides these triplets, however, there are for the same atom quite distinct

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* It has been usual hitherto to reserve different types for the terms of different systems: thus both Fowler and Paschen always used small letters, s, p, d, f, for triplet terms, while Fowler used Greek letters, σ, π, δ, ϕ, for double terms. See, however, p. 302 *et seq.*

and different series of single lines, which can be classed as S, P, D and F series. It must be clearly understood that all these lines, triplets and singlets, are emitted by the same light source, and that they are quite separate from the spectra of the ionised atom (spark spectra) of the same element. In such a case we say that the spectrum comprises a triplet *system* and a singlet *system*, each system consisting of the usual four series and combination lines (together with possible other series, G, H, and so on, to which reference has been made). The spark spectrum may also comprise different systems, though the detection of more than two is, so far, exceptional. Recent research has shown that the arc spectra of elements of the higher columns of the periodic table may comprise several systems : for instance, quartet, sextet and octet systems have been identified for neutral manganese, Mn_{I}.

The subject of multiplet series will be further considered later in connection with the " inner quantum number." Their systematic representation with the help of this third quantum number is one of the recent descriptive successes of the theory. The present brief account is designed to elucidate casual references to such series which will have to be made before that chapter is reached. It is also important that the multiplets should not be confused with the fine structure of spectral lines which, in the case of hydrogen and ionised helium, have proved of great importance for the quantum theory.

The use of instruments of very high resolution, in the hands of skilled workers, has shown that lines of hydrogen and ionised helium, which under lower resolution appear to be of simple structure, *i.e.* to have a maximum of intensity, dying off on either side, are really complex, having several components. The effect is more clear cut with ionised helium than with hydrogen, as is indicated by theory should be the case. The exact nature of the resolution is discussed further when Bohr's theory is considered : the fine structure is mentioned here merely as an experimental fact of spectroscopy. Figs. 1 and 2 of Plate V. show the fine structure of, respectively, the 4686 and the 3203 lines of ionised helium, as photographed by Paschen in the third and fourth order, respectively, of his big concave grating. With 4686 five components can be distin-

guished in the reproduction, of which three are strong : with 3203 four components, of which three are strong.   This fine structure is discussed at length in Chapter X.

The Helium Spectrum.   Now that the general nature of line series has been indicated, there are one or two facts about the helium spectrum which call for further mention. Non-ionised helium—which gives the " arc " spectrum—has two complete sets of series, a doublet system, with principal, sharp, diffuse and fundamental series and also combinations, and a singlet system, likewise with four series and combinations. This fact was originally interpreted as indicating that ordinary helium was a mixture of two hypothetical gases—" ortho-helium," giving the doublet system, and " parhelium," giving the singlet system.   There is no corroborative evidence of any kind for this supposition, which is now abandoned.   Bohr has indicated a method of accounting for the two systems, without any need for supposing two gases.

The lines of the spectrum of neutral helium cannot be expressed by terms of the Balmer type, but call for terms of the Rydberg, or, for better agreement, of the Hicks type,

$$\frac{R}{\left(n+\mu+\dfrac{a}{n}\right)^2}.$$

The agreement is not always satisfactory, but this is the most generally useful type of formula.

In addition to the systems associated with the non-ionised atom there are, of course, series associated with ionised helium which were originally attributed to hydrogen.   These are expressed by the formulae of the type $4R\left(\dfrac{1}{n'^2}-\dfrac{1}{n^2}\right)$, where R has a value slightly different from that which it has for hydrogen, namely, 109722 instead of 109678.   (Cf. p. 168.) Series have been detected for which, in the formula just given, $n'=1$ and $n'=2$ (Lyman) ; $n'=3$ (Fowler) ;   and $n'=4$ (Picker-ing).   Lines of the Fowler series (also known as the " 4686 series," from the wave-length of the first observed line) show the fine structure to which reference has just been made.

The account here given of series spectra is, it must be understood, incomplete. Only those points which are necessary for the understanding of the developments of the theory handled in subsequent chapters have been considered. Much very beautiful work has been done on the regularities exhibited in spectra containing systems of different multiplicities and on the systematic variation of spectra for different elements of the same period, and for different elements of the same column, of the periodic table. Some of these have not yet been brought under the theoretical scheme to be outlined in this book, others will be mentioned as occasion arises, in connection with the particular theoretical results that concern them.

PART II

THE EXTRANUCLEAR STRUCTURE

CHAPTER IX

THE DYNAMIC MODEL OF AN ATOM WITH ONE ELECTRON

Introductory. There is, we have seen, general agreement that the atom has a nuclear structure, and that the number of units of net positive charge on the nucleus, which is the same as the number of extranuclear electrons, is equal to the atomic number. The question of the distribution and behaviour of the electrons is very difficult to answer in a way calculated to please everybody and to satisfy nature. The configuration and conduct of these electrons govern the series spectra, both optical and X-ray, of the atom ; the chemical properties of the atom ; the magnetic properties of the atom ; and other physical properties, of which the compressibility is one that has received special attention. In general the fields of investigation indicated have tended to grow different atoms —the extranuclear structure has been designed by each school to suit particular phenomena, or groups of phenomena, at the expense of others.

It is clear enough that if the forces between the nucleus and the electrons are governed by the ordinary inverse square law the atom cannot be stable if the electrons are supposed to be at rest. For, if an electron is to be in stable equilibrium, there must, corresponding to a small displacement in any direction, be a force tending to restore it to its equilibrium position. Such a system of electric forces, all tending to move a negative charge towards one point, is, by Gauss's Theorem, only possible if the small sphere enclosing the point contains, a positive charge, which is contrary to hypothesis. There are various alternatives. We may assume, with J. J. Thomson, that the law of force is not the simple inverse square, but one adapted

to give an equilibrium position for electrons. A very simple type of such law supposes that the force due to the central charge E is given by $\dfrac{E}{r^2}\left(1-\dfrac{c}{r}\right)$, which changes from an attraction to a repulsion when $r = c$, and J. J. Thomson has worked out the stabilities of various numbers of electrons on these lines, and calculated compressibilities from his models. Or we may simply assume that certain configurations are particularly stable, feeling that it is not ours to reason why when it comes to forces within the atom, of whose nature we have no direct evidence ; that the object is to make an easily visualised picture. Langmuir, extending the work of Kossel and Lewis, has acted in this sense, and assumed certain " cells," arranged in an order dictated by the periodic table, for the reception of electrons. Or we may endeavour to extend to the atomic structure new principles which have already found a wide application in molecular physics, using as general a dynamical scheme as possible, and striving to keep in touch with classical electrodynamics by making the classical scheme a limiting case. This is the method adopted by Bohr and his school, the relation with classical procedure being given by the so-called correspondence principle, which will be discussed later.

In the main the Bohr atom has been evolved by considering the characteristic radiations, using the term to cover optical spectra, of different atoms, while the statical atom models have been elaborated from the chemical point of view. No successful attempt has been made to explain the details of spectroscopic observation on the basis of a static atom, and until very recently the Bohr atom had but little application to chemistry. Within the last few years, however, Bohr has extended his theory, and, while obtaining valuable results on the theory of optical spectra, has also indicated how it can be adapted to give the periodic properties indicated in the modern forms of Mendeléef's table. There are strong indications that the general features of the Bohr scheme are capable of covering a very wide range of phenomena.

The Bohr atom is a dynamical one in that the extranuclear electrons are assumed to be in rapid motion round the nucleus. On the classical theory of electrodynamics this implies in-

stability, since any acceleration of an electron must be accompanied by radiation, by which the energy of the atom would be continually dissipated, the electrons finally falling into the nucleus. Any orbit would be possible, the actual one depending upon initial conditions and the time during which radiation had taken place, and we should expect not a series of sharp lines, but a continuous spectrum. Bohr avoids the difficulties of the classical theory by assuming a limited number of stable orbits in which the electrons can revolve without radiating ; these orbits are subject to certain quantum conditions involving the generalised momenta of the electrons. The atomic system as a whole can, then, exist only in a number of so-called *stationary states,* to each of which pertains a certain total energy. States intermediate between these stationary states, although dynamically possible, are excluded by hypothesis. Radiation takes place only when an atom passes from one state to another of lesser energy, the frequency of the radiation being determined by the quantum relationship between frequency and energy. This, of course, is avoiding the difficulties presented by the question of dynamical stability by denying that the classical relationships hold within the atom, but the quantum theory has proved its worth in so many branches of electronic physics that its invocation has not the *ad hoc* character of Langmuir's cells. Bohr has introduced into the world of spectra Planck's universal constant h, invoked to account for very different phenomena.

In dealing with the dynamical atom we have to discuss both the distribution and motions of the various electrons, that is, to decide not only upon the possible orbits, but upon which— or how many—electrons are executing each. The way in which the quantum principle is introduced is a matter for arbitrary decision, to be followed by a checking of the results of the decision against the measurements of the spectroscopists. Since the dynamics within the atom are certainly not subject to the ordinary laws of mechanics there is no way of deciding *a priori* if a particular method of " quantising " is correct, a truism, which, with other truisms, is occasionally overlooked.*

* Similarly, of course, there is no *a priori* reason for saying that the mechanics of the Schoolmen, which supposed that the state of a system was

Besides the optical and X-ray emission spectra we have as a guide the various absorption phenomena, and the effect of electric and magnetic fields. Finally, the question of periodic chemical properties has to be considered.

The Fundamental Assumptions of Bohr's Theory. Before Bohr put forward his theory of atomic radiation, which has had such success in representing spectroscopic fact in the widest way, all scientists who had worked on the fascinating problem of making an atomic model which should emit a spectral series had assumed the Maxwellian relation between the motion of the electron and the emitted radiation. This states, we may say, that if an electron describes a periodic orbit* which can be resolved into a series of vibrations of frequencies $\nu_1, \nu_2, \nu_3, \ldots$, then radiations of the same frequencies will be emitted. Thus, to take the simplest case, an electron describing a circular orbit of frequency ν_T would, on the classical theory, emit a radiation of frequency ν_T.

The physics of the present century has been marked by severe attacks on the general validity of classical mechanics and electrodynamics. In considering the radiation from a black body Planck has been led, by the necessity of describing experimental fact, to assume that there are elementary oscillators, of frequency ν_T, which, instead of being able to vibrate with all amplitudes, and consequently emit any specified amount of radiant energy, can only emit energy in discrete quanta. The quantum of energy which such an oscillator can emit is proportional to the frequency ν_T, the coefficient of proportionality being the same for oscillators of different frequency, in fact, a universal constant. This universal constant, called Planck's constant, is always denoted by h; its value is 6.545×10^{-27} C.G.S. units. The quantum of radiant

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specified by the position of the parts alone, without their velocities—that there was no such thing as inertia—is less reasonable than the mechanics of Newton. It is the appeal to experiment, in this case largely to observations of the behaviour of that big atom which is our solar system, that decides for Newton. If the scholastic conception had proved moderately competent to deal with terrestrial experiment—which, of course, it was not—the analogy would be better than it is. It is interesting to note that Kepler, who did not understand the principle of inertia, provided the planets with souls to guide them, and prevent them falling into the sun. We have provided the electrons with quanta to prevent them falling into the nucleus.

energy is thus $h\nu_T$. It is to be noted that h is of dimensions (L^2MT^{-1}), which are those of a moment of momentum or an angular momentum. In general a quantity of these dimensions is spoken of as an action,* and h is sometimes called a quantum of action.

Bohr assumes the Rutherford atom, in which electrons are distributed around a small massive nucleus, and further assumes that the electrons circulate in orbits under the inverse square law of force, which prevails in ordinary electrostatics. He further makes three bold assumptions, of which two are in direct contradiction to the classical theory, the third not so much in contradiction to, as entirely unrelated to, the previously accepted—or, to coin one of the pleasant compounds now in favour, pre-Planckian—theory. Preliminary reference has already been made to these assumptions.

The first is that within the atom electrons can circulate in closed † orbits *without radiating energy at all*, whereas on classical theory every acceleration of an electron must be accompanied by radiation.

The second assumption is that of all the infinite number of different orbits which, according to the initial conditions, classical theory indicates as being able to occur, only certain discrete orbits are possible, these possible orbits being determined by certain quantum conditions. An atom in which electrons are describing orbits permitted by the quantum conditions is said to be in a stationary state, and to each particular stationary state pertains a certain energy. Thus, for a given atomic system, a series of energies E_1, E_2, E_3 ... alone is possible. Frequently, to make the problem manageable, it is necessary to fix the attention on a certain electron, and to assume that the energy of the rest of the atom is unaffected for a whole series of stationary orbits of this electron.

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* The name being derived from the " principle of least action " used in general dynamics.   In the simplest case the action takes the form $\int mv \,.\, ds$, which is of the above dimensions.

† In Bohr's original theory the orbits were all closed. Later, as we shall see, paths have been considered which are not closed, the electron tracing, in the simplest case, a Keplerian or quasi-Keplerian ellipse with progressive motion of perihelion—or rather perinucleon. The assumption still holds for this class of orbits.

In such a case, since we are solely concerned with the difference of energies between two different stationary states, it suffices to calculate the energies of the different stationary orbits of the one electron. The assumption of stationary states is the very essence of the theory, and constitutes an advance which, in spite of difficulties as to details, has brought order into all branches of spectroscopy.

The third assumption specifies the frequencies of the radiations which the atom containing the orbits can emit; it has been justified by its very considerable success in accounting for experimental relations in line spectra. It is assumed that under certain conditions (the conditions which provoke the emission of the spectral series, whatever they happen to be) an atom can be put into a stationary state of energy E_n greater than the normal energy of the atomic system, to pass later from this stationary state to another stationary state of less energy $E_{n'}$, and that this sudden passage, sometimes termed a " quantum switch," is accompanied by a radiation of energy $E_n - E_{n'}$, of which the frequency is given by the condition :

$$h\nu_T = E_n - E_{n'} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(\text{I})$$

Before E. T. Whittaker put forward the theory described in Chapter XVI no way had been suggested by which a radiation of this frequency could be connected with the machinery of classical electrodynamics, and Whittaker's model is rather cumbersome. After all, there is no particular reason why the process should be explained. " Explained," in this connection, means usually " described in terms of the classical theory " ; as the classical theory has been thrown overboard in postulating stationary states it should not distress us greatly if, for the moment, such explanation is lacking.

At the same time, certain applications of the theory of stationary states at present generally made (in connection with the ordering of multiplets in line spectra and the abnormal Zeemann effect) are purely empirical, and hard to reconcile with the model valid for simpler cases. Here some extension is certainly desirable, since the restricted applicability of the model tends to diminish its use.

As the theory is developed it will be seen that while the

break with classical mechanics is absolute in respect of the postulates to which attention has been directed, yet it is less universal than is sometimes hastily assumed. The motion of the electrons in their stationary orbits is, by hypothesis, governed by the ordinary laws of celestial mechanics (with, when necessary, a relativity correction), although the quantum conditions impose the restriction that out of all the states mechanically possible only a certain number are permissible. Further, the conditions which fix the stationary states are such that a continuous and slow variation of the external forces, such as of the electric or magnetic field in which the atoms may be placed, while it affects, in general, the kinetic energy of the motion, does not affect the value of the expression (or expressions) which determines the stationary state, or, in other words, the stationary states possess a peculiar stability deducible on mechanical grounds, once the quantising conditions are admitted. The principle which establishes this is known as the principle of Adiabatic Invariance, to be explained in due course. Finally, by considering the case when the difference of energies between the successive stationary states becomes very small (which is the same thing as saying when the total quantum number is very large) it is found that in the limit the frequency given by the quantum theory approaches that given by the classical theory. This leads to the tracing of a correspondence between the motion of the electron in its orbit and certain properties of the radiation emitted, although, as has been emphasised, the frequency of the radiation is not, in any case but the limiting case, the same as that of the periodic motion of the electron.

For instance, the simple character of the hydrogen spectrum is connected with the simple character of the orbital motion of the electron in the hydrogen atom, although not by the relations deducible from the classical theory. If the simple nature of the orbital motion be disturbed, the spectrum presents new features. This result, in its most general form, is embodied in the so-called Correspondence Principle of Bohr, which is of the utmost importance for the whole quantum theory. By means of certain rules expressed in a Selection Principle, it leads to a limitation of the number of transitions

mathematically possible between the various stationary states. Excellent agreement with experiment has been established, the lines excluded by the Principle being, in general, missing in the actual spectra.

The case of the general atom, when the nuclear sun is surrounded by a large number of planetary electrons, is obviously very complicated, and only to be attempted at all by making simplifying assumptions, since the mechanics of even three bodies is not capable of a solution in finite terms. The simplest case of the quantum theory of spectra is afforded by the atomic system in which the nucleus is associated with a single planetary electron ; the atom of neutral hydrogen is an example. An atom of helium from which one electron has been altogether removed, and an atom of lithium from which two electrons have been altogether removed, constitute similar systems, and may be called hydrogen-like. We shall, to begin with, confine ourselves to such hydrogen-like atoms, and use them to introduce in a simple form various conceptions which will have to be thrown into a more general form later.

In the case of circular orbits the calculation is straightforward, and will be given in detail as an illustration of the fundamental method of the quantum theory of spectra.

Hydrogen-like Atom with Circular Orbits. We consider an atom consisting of a nucleus with a single electron rotating round it and, for generality, take the nuclear charge as Ze, to cover cases such as that of ionised helium. Let M be the nuclear mass ; e, m the charge and mass of the electron ; and r the radius of an orbit, all orbits being supposed circular for the present.

Since the potential energy is involved some arbitrary zero of energy must be taken, the selection of which will not affect the final result, since this involves differences of energy only. It is usual, for simplicity, to take the energy of the electron as zero when it is at rest at an infinite distance from the nucleus. Then, since in an elliptic orbit the velocity of projection is well known to be less than the velocity from infinity, the total energy of an electron in an elliptic (or circular) orbit will, on this convention, always be negative, and the numerically

greater the expression for the energy, the less the energy will be.* Let M be so large compared to m that the nucleus may be considered at rest (in an inertial system of reference). This may be done without any loss of generality, since if the problem be considered as a two-body problem instead of a one-body problem the bodies move about their fixed centre of mass, and all we have to do is to replace the mass m by μ, where $\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$. In any circular—or elliptic—orbit the potential energy will be negative, to wit $-\frac{Ze^2}{r}$; the kinetic energy $\frac{1}{2}mv^2$. In a circular orbit with an inverse square law of force, equating the centrifugal force to the attraction, we have

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

from which

$$\frac{Ze^2}{r} = mv^2 \ .$$

The total energy is therefore $-\frac{Ze^2}{r} + \frac{1}{2}mv^2 = -\frac{1}{2}mv^2,$

which is always negative, as just stated. It will be observed that the smaller the orbit the greater the kinetic energy, but the less the total energy. It is convenient to introduce a quantity W, the negative total energy of the system ; then

$$W = \frac{1}{2}mv^2 = \frac{1}{2}\frac{Ze^2}{r} \ .$$

We now have to introduce the quantum condition which will determine the permissible orbits, restricting them to certain selected values of r. In the simple case of circular or elliptic orbits the condition which fixes the possible stationary orbits can be expressed by saying that the orbits which are stable are those, and only those, for which the angular momentum of the electron is equal to $\frac{nh}{2\pi}$, where n is any whole number and h is Planck's constant. The generalisation of this condition for

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* Failure to grasp this point often leads to confusion with beginners as to which orbit represents the greater *total* energy.

the case of orbits which are not closed is a matter which will demand a detailed discussion later, but, quite generally, the stationary states are fixed by restricting the values of certain determining expressions, of the dimensions of action, *i.e.* energy × time, to being whole number multiples of h.

In this simple case, then, the quantising condition is

$$2\pi m v r = n h \quad\text{................................(3)}$$

where n is a whole number.

With (2) this gives

$$r = n^2 \frac{h^2}{4\pi^2 m Z e^2}, \quad v = \frac{2\pi Z e^2}{n h}$$

or frequency of revolution $= \omega = \dfrac{4\pi^2 m Z^2 e^4}{n^3 h^3}$.

Also

$$W = \tfrac{1}{2} m v^2 = \frac{2\pi^2 m Z^2 e^4}{h^2} \cdot \frac{1}{n^2} \quad\text{....................(4)}$$

For successive possible orbits as we go outwards from the nucleus W has values inversely as the squares of the successive whole numbers. W, of course, diminishes as we go out from the nucleus, which corresponds to an increase of energy. When an electron passes from an outer orbit to an inner orbit there is a change of energy $-\Delta W$, which, by the fundamental assumption of the theory, (1), appears as radiation of frequency $\nu_T = -\dfrac{\Delta W}{h}$, or of wave-number $\nu = -\dfrac{\Delta W}{hc}$. W is proportional to $\dfrac{1}{n^2}$, and therefore gives a sequence of terms depending on n in the way required for the hydrogen spectrum.

We must suppose that when the hydrogen atom is excited to radiation the electron is removed from the innermost orbit, which, having the closest binding, *i.e.* least energy, corresponds to the normal state, to some outer orbit permitted by the quantum condition (3). When the electron passes from this outer orbit to a permitted inner orbit, of less energy, monochromatic radiation takes place. Using the relation (1) we see that the frequency of the lines emitted by a system consisting of a nucleus of

charge e, and a single circulating electron, is therefore given by

$$\nu_T = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

and the wave number by

$$\nu = \frac{2\pi^2 me^4}{ch^3}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

.............................(5)

where n' and n are whole numbers characteristic of the two orbits in question. Comparing this with Balmer's formula $\nu = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$ we find that $R = \frac{2\pi^2 me^4}{ch^3}$. The numerical value of this expression is

$$R = 109800 \text{ cm.}^{-1},$$

which compares well with the experimental value 109678. This numerical agreement, which involves only universal constants whose value had been previously determined, is a very strong support of Bohr's theory, and helped considerably to establish it in the early days. The fact that W is proportional to $\frac{1}{n^2}$ would not by itself have been very convincing, as the hypotheses were obviously directed to obtain this result. It will be noted that the Balmer series is given by quantum switches from various initial orbits to one final orbit, of quantum number 2. This final orbit is not the most permanent, or most closely bound orbit, since for this the quantum number is 1. This innermost orbit, which is normally occupied by the electron, is the final orbit for lines of the Lyman series.

The results so far obtained have been deduced on the assumption that the orbits are circular. It is noteworthy that if the case of Keplerian, strictly elliptic orbits be investigated exactly the same results follow : a single quantum number n fixes the major axis a of the ellipse, which determines uniquely the energy and the period of revolution of the electron.* Thus the

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* By the familiar equations of elliptic orbits

$$\tfrac{1}{2}v^2 = \frac{\mu}{r} - \frac{\mu}{2a} \cdot \text{ and } \quad T = 2\pi\sqrt{\frac{a^3}{\mu}}$$

where μ is the central acceleration at unit distance.

energy of the electron describing a Keplerian ellipse is exactly the same as if it were describing a circle of radius a, and it is characterised by the same quantum number, so that it leads to the same frequency laws. This case of simple elliptic orbits is not considered in detail here because it is a so-called degenerate case of a class of orbits which require two quantum numbers for their specification : that is, it is an orbit with two degrees of freedom, r and θ (whereas the circular orbit only has one, θ) and only one periodicity. Such orbits are discussed in Chapter X.

The absolute size of the orbits involves some interesting considerations. For the innermost orbit, for which $n = 1$, we have $r = \dfrac{h^2}{4\pi^2 me^2}$, the numerical value of which is $\cdot 54 \times 10^{-8}$ cms. This is of the order found for the size of the hydrogen atom from gas-kinetic, and other, considerations. Now we have seen that the radius r of the optical orbits increases as the square of n, so that when a hydrogen atom is in the stationary state preliminary to the emission of a higher member of the Balmer series, say, the orbit must be very large—for instance for the 20th member $n = 22$, $n' = 2$, and the radius of the orbit is $22^2 = 484$ times that of the orbit in the normal atom, *i.e.* the diameter is about 5×10^{-6} cms. For the hydrogen atoms to have 5×10^{-6} cms. as their mean distance apart, the pressure of the gas must be about $\cdot 22$ mm. of mercury, so that it is to be expected that at pressures of this order, or higher, the 20th member will only show itself in feeble intensity, if at all. It need not be entirely absent, since a certain small fraction of the hydrogen atoms are always much further apart than the mean distance, and also because the orbits, being plane, have more room than is indicated by considering them as spherical surfaces. In general, however, we should expect the higher members of the series to have a better chance of showing themselves at very low pressure. Now in stellar spectra as many as 33 lines have been observed (Pickering in ζ Puppis): the diameter of the orbit in the higher stationary state for the 33rd line is about $1 \cdot 3 \times 10^{-5}$ cms. The low pressure prevailing in the outer regions of stars would be expected to render the temporary existence of an atom of this size possible. Further, considering different stars, recent research seems to indicate

clearly a correlation between pressure and number of Balmer lines observed.

Normally in the laboratory only the first four members of the Balmer series of hydrogen—the so-called α, β, γ and δ lines— are observed in any intensity.   R. W. Wood, however, working with a special disposition, at a pressure where "Crookes' dark space is about 6 mm. long," has obtained 20 lines, but he found that as the pressure was raised the higher numbers of the series disappeared successively. Again, Whiddington has found that by reducing the pressure from 1 mm. to ·001 mm. of mercury, and arranging for suitable excitation he can raise the number of lines from 4 to 20.   Although no very precise quantitative results are ·available, there is, then, no doubt that low pressure favours the appearance of higher members of the Balmer series, as required by Bohr's theory.   It may be added, however, that Llewelyn Hughes has pointed out that when the pressure is lowered the mean free path of the electron is increased, and consequently, if the collisions are inelastic, the energy which it acquires is increased.   He is inclined to attribute the appearance of the higher terms to the relative preponderance of swifter electrons at lower pressures, since he has shown that when electrons with low energies collide with molecules of hydrogen the lines of higher term number are relatively much weaker than when the impact energy is high. This may well be a contributing cause to the effect under discussion.   The presence of atomic, instead of molecular, hydrogen in the stars must also be taken into account.

Effect of Finite Mass of Nucleus.   The discovery by Pickering of certain lines in the spectrum of ζ Puppis, lines which were at first attributed to hydrogen but have since been shown to be due to ionised helium, was the first step in a series of investigations which has led to another important confirmation of Bohr's simple theory.   The lines in question are represented fairly closely, but not within the limits of experimental error, by putting $n = p + \cdot 5$ (where p is a whole number) in Balmer's formula, and were therefore originally supposed to belong to hydrogen.   Fowler showed that the lines only occurred in the laboratory with hydrogen containing helium, and it was later shown that they were produced in helium in the entire absence

of hydrogen. Fowler further observed in helium tubes subjected to a condensed discharge lines whose frequencies agreed approximately with those obtained by putting in equation (5) $n'=\frac{3}{2}$, $n=2$, 3, 4 . . . , and others given by putting $n'=\frac{3}{2}$, $n=\frac{5}{2}$, $\frac{7}{2}$, $\frac{9}{2}$, . . . All these facts can be simply explained in the following way.

The helium atom is supposed to consist of a nucleus with a positive charge of two units and a mass approximately four times that of the hydrogen nucleus, accompanied by two circulating electrons. If the gas be exposed to a powerful discharge the atoms may become ionised, and lose, each, one electron, thus becoming a kind of hydrogen atom with a heavier, and doubly charged, nucleus. Putting $E=2e$ we have, instead of (5),

$$\nu=\frac{8\pi^2 m e^4}{c h^3}\left(\frac{1}{n'^2}-\frac{1}{n^2}\right)=4R\left(\frac{1}{n'^2}-\frac{1}{n^2}\right). \quad\ldots\ldots\ldots\ldots(6)$$

The double nuclear charge makes the constant $4R$ instead of R. The spectrum of ionised helium is, in this sense, a typical spark spectrum. The above formula gives approximately Fowler's lines if we put $n'=3$, $n=4$, 5, 6 . . . , and Pickering's lines if we put $n'=4$, $n=5$, 6, 7 . . . * Thus all the lines can be referred to ionised helium, but the value of R in (6) is not quite the same as R in (5). This fact is beautifully accounted for if we remember that the mass of the nucleus, while large compared to that of the electron, is not infinite, as assumed in deducing (5) and (6). The centre of mass of the system, about which nucleus and electron rotate, is not at the nucleus, but at a close position determined by the ratio $\dfrac{M}{m}$, and it has already been pointed out that the modification which this introduces is expressed mathematically by substituting for m

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* The original Pickering series included only alternate lines, beginning with $n=7$. The failure to identify the other lines was due to their closeness to Balmer lines of hydrogen, from which they were first separated by E. J. Evans (*Phil. Mag.* **29**, 284, 1915). Since then H. H. Plaskett (*Publications of the Dominion Astrophysical Observatory*, I. 325, 1922), investigating the spectra of certain *O* type stars, has succeeded in obtaining Balmer lines (in the case of 10 Lacertae the first four, H_α, H_β, H_γ, H_δ) and the neighbouring Pickering lines on the same plate, and has measured the separation accurately, obtaining excellent agreement with Bohr's theory.

in the equations the factor $\dfrac{mM}{M+m}$. If we put R_H, R_{He}* to represent the values of R in (5) and (6) respectively, we have

$$\frac{R_{He}}{R_H} = \frac{\dfrac{3 \cdot 97mM}{3 \cdot 97M+m}}{\dfrac{mM}{M+m}} = \frac{1+\dfrac{m}{M}}{1+\dfrac{1}{3 \cdot 97}\dfrac{m}{M}}.$$

Fowler's determinations give for $\dfrac{R_{He}}{R_H}$ the numerical value 1·0004095, which gives for the ratio $\dfrac{m}{M}$ the value $\frac{1}{1831}$.† This value, calculated by applying the quantum theory of spectra to spectroscopic data, agrees closely with the accepted value, deduced from very different experimental evidence. In the face of this agreement it is hard to deny that the conception of the revolving electron must correspond closely to reality (as understood by the physicist), at any rate as far as the hydrogen-like atom is concerned.

It is of interest to note that an accurate determination of the ratio e/m can be derived from the comparison of R_{He} and R_H. For we have

$$\frac{M}{m} = \frac{e}{m} \bigg/ \frac{e}{M}.$$

Now $\dfrac{e}{M}$, or the ratio of the charge to the mass for the hydrogen ion, can be very accurately determined by electrolytic methods : it has the value 9571 E.M.U. gm⁻¹.

Hence $\dfrac{e}{m} = 9571 \times 1847 = 1 \cdot 768 \times 10^7$ E.M.U. gm⁻¹,

* With this notation the spectrum of ionised helium is given by

$$\nu = 4R_{He}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right).$$

† Paschen, as a result of further investigation of the spectroscopic constants, finds by this method $\dfrac{M}{m} = 1847$. His value for R_{He} is 109722·14 ± ·04, which is, of course, derived from laboratory measurements. H. H. Plaskett's value, derived from astrophysical measurements, is 109722·3 ± 0·44, agreeing within estimated experimental error.

using the value of $\dfrac{M}{m}$ determined by Paschen from spectro-scopic data. This value of $\dfrac{e}{m}$ is probably correct to within ·5 per cent., and as reliable as any at present available.*

It may be remarked that with helium the value of R differs by about 1 part in 8,000 from the value R_∞ which R has when the mass of the nucleus is taken as infinite.

The Principle of Adiabatic Invariance. By the funda-mental postulate of Bohr's theory the laws of classical electro-dynamics are violated when an atom is excited to radiate. The exciting cause may be either a swift electron or a suitable radiation. The result is that the system is thrown from one stationary state to another, with absorption of energy equal to the energy difference between the states. In other words, any sufficient *sudden* disturbance, such as that produced by an electron of sufficient energy, or a sufficiently rapid oscillation of electric force, produces a quantum change in the atomic system.

Suppose, however, that external forces are comparatively slowly brought to bear on the atomic system, for example, that an ordinary macroscopic (*i.e.* large scale, as distinct from one of atomic magnitude) electric or magnetic field is created in its neighbourhood. The result of this field will be to modify gradually the electron orbit, or, speaking quite generally, to produce a new system of electronic motions in the atom. It cannot, however, send the atom from one stationary state to another, and, therefore, if the quantum conditions are to retain any meaning, the expression which is quantised, *i.e.* set equal to nh, must not change. This expression is of the dimensions of an action. The kinetic energy may, however, and will in general, change. We proceed to show that, in the simple case under consideration in this chapter, the expression quantised is invariant when the external forces are slowly changed. By analogy with the reversible adiabatic changes of thermo-dynamics, which also imply a slow continuous change of ex-ternal agents, such an expression is called an adiabatic invariant.

To make clearer the nature of the problem to be discussed, a simple mechanical case, which was actually the first for which

* See also a letter of R. T. Birge in *Nature*, quoted in footnote on p. 166.

the question was raised,* may be taken. Suppose a simple pendulum, of given frequency, to possess an energy of vibration which is a given multiple of the frequency, and thus to represent a vibrating system obeying a quantum condition. Now suppose that the pendulum be shortened, say by displacing a small ring, which embraces the thread near the top, slowly downwards : the frequency of the pendulum will increase. Does the quantum condition still hold ?   The answer is that if the change be carried out continuously and so slowly that the motion of the ring during a single period is very small compared to the length of the pendulum, then there will be work done on the pendulum, and its energy will increase so as to be still the original multiple of the frequency.   Similarly, if the pendulum be lengthened, there will be work done on the ring by the pendulum, and its energy will decrease along with the frequency.   If, however, the motion of the ring be not slow and steady—if, for instance, it be lowered suddenly through a finite distance just at the moment when the thread is vertical, so that no work is done—then the adiabatic condition is violated, and the constancy of the ratio of energy to frequency no longer holds.

To prove that the expression $T.\bar{E}_{\text{kin}}$ is adiabatically invariant in the case of the simple pendulum, T being the time period and $\bar{E}_{\text{kin}}$ the average value of the kinetic energy over a complete period, let l be the length from ring to bob, θ the angle which the thread makes with the vertical, α the angular amplitude.

Then
$$\theta = \alpha \sin \frac{2\pi}{T} t,$$

$$T = 2\pi \sqrt{l/g}.$$

The tension in the thread
$$= S = mg \cos \theta + ml\dot{\theta}^2,$$

and the vertical component of the force produced by the
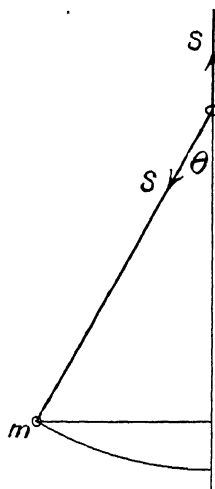
FIG. 35.

* By H. A. Lorentz, and at once answered by Einstein, at the first Solvay Congress, 1911.

two equal tensions S, making an angle of $\pi - \theta$ with one another, on the ring is

$$S(\mathrm{I} - \cos \theta).$$

Against this a vertical displacement δl of the ring does work, so that the increase of energy of the pendulum due to the movement of the ring is

$$\delta E = - \delta l \,.\, S(\mathrm{I} - \overline{\cos \theta}),$$

the bar denoting mean value with respect to time over a vibration. Taking small vibrations,

$$\mathrm{I} - \cos \theta = \tfrac{1}{2}\theta^2$$

and

$$\delta E = - \delta l \,.\, mg \,.\, \tfrac{1}{2}\overline{\theta^2} = - \delta l \,.\, mg \,.\, \tfrac{1}{4}a^2$$

to the second order, since the term in $\dot{\theta}$ disappears to this order.

Now total energy of pendulum

$$= E = 2\overline{E}_{\mathrm{kin}} = \tfrac{1}{2}ml^2\left(\frac{2\pi a}{T}\right)^2 = \tfrac{1}{2}mgla^2 \, ;$$

$$\therefore\ \frac{\delta E}{E} = - \tfrac{1}{2}\frac{\delta l}{l} = - \frac{\delta T}{T} \, ;$$

$$\therefore\ TE = \text{constant} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots(7)$$

or

$$2T \,.\, \overline{E}_{\mathrm{kin}} = \text{constant} \quad\dots\dots\dots\dots\dots\dots\dots(7\mathrm{a})$$

This is a particular case of an important theorem of Boltzmann, that, for any periodic system of period T obeying the classical laws of mechanics,

$$\delta Q = \frac{2}{T}\ \delta(T\overline{E}_{\mathrm{kin}})$$

where δQ is the heat, or total energy, supplied to the system.* If $\delta Q = 0$, the adiabatic case, this takes the form (7a).†

* More generally

$$\delta\left(\frac{\mathrm{I}}{T}\int_0^T (E_{\mathrm{kin}} + E_{\mathrm{pot}})dt\right) = \frac{2}{T}\ \delta\left(\int_0^T E_{\mathrm{kin}} \,.\, dt\right).$$

† The case of the conical pendulum presents an interesting illustration of the principle, which can be worked out without the approximation for small angles involved above. In Fig. 35 the mass m must now be supposed to be rotating so that θ may be taken as constant during a single revolution, the ring being displaced downwards so slowly that any modification of θ in a

Another way in which condition (7a) may be written is that

$$\int_0^T 2E_{\text{kin}}\, dt = \frac{2\overline{E_{\text{kin}}}}{\omega} \text{ is invariant, where } \omega = \frac{1}{T}$$

which is a form to which reference will have to be made.

A word of explanation is needed as to the sense in which the word adiabatic is used in the mechanical case. In the thermo-dynamic case a change is adiabatic if there is no *direct* communi-

time comparable with the period is negligible. This is necessary to make the case an adiabatic one.

$$S \sin \theta = ml \sin \theta \cdot \omega^2,$$

where ω is the angular velocity.

$$mg = S \cos \theta = ml \cos \theta \cdot \omega^2,$$

$$E_{\text{kin}} = \tfrac{1}{2}ml^2 \sin^2 \theta \cdot \omega^2$$

$$= \tfrac{1}{2}mgl \frac{\sin^2 \theta}{\cos \theta} \cdot \quad\quad\dots\dots\dots\dots\dots\dots\dots\dots\dots(A)$$

We now require a relation between θ and ω. We have

$$E_{\text{kin}} = W + K + mg(l_0\overline{1 - \cos \theta}_0 - l \cdot \overline{1 - \cos \theta}), \quad\dots\dots\dots\dots(B)$$

where W is the work done in displacing the ring from the initial time, when l was l_0 and K is a constant, depending upon the zero taken for E_{pot}.

$$W = -\int_{l_0}^{l} S(1 - \cos \theta)dl = -mg\int_{l_0}^{l} (\sec \theta - 1) \cdot dl.$$

Differentiating (A) and (B) with respect to l and equating

$$-mg(\sec \theta - 1) - mg(1 - \cos \theta) + mgl \frac{d \cos \theta}{dl}$$

$$= \tfrac{1}{2}mg(\sec \theta - \cos \theta) + \tfrac{1}{2}mgl(-\sec^2 \theta - 1) \frac{d \cos \theta}{dl},$$

or putting

$$z = \cos \theta,$$

$$\frac{3}{l} - \frac{3z^2 + 1}{z(1 - z^2)} \frac{dz}{dl} = 0.$$

Integrating, we get

$$l^3 = C^3 \frac{z}{(1 - z^2)^2} = C^3 \frac{\cos \theta}{\sin^4 \theta}.$$

Hence

$$E_{\text{kin}} = \tfrac{1}{2}mgC \sin^{\frac{2}{3}} \theta \cos^{-\frac{2}{3}} \theta = \tfrac{1}{2}mgC \tan^{\frac{2}{3}} \theta,$$

$$\omega^2 = g/l \cos \theta = g/C \cdot \tan^{\frac{4}{3}} \theta:$$

$$\therefore\ 2T \cdot E_{\text{kin}} = \frac{4\pi}{\omega} E_{\text{kin}} = 2\pi \cdot mg^{\frac{1}{2}} \cdot C^{\frac{3}{2}} = \text{constant}.$$

I am indebted to my colleague Professor H. C. Plummer for suggesting this example. A further very simple illustration is afforded by a heavy particle attached to a string executing a circular motion on a smooth horizontal table. The period is modified by gradually decreasing the radius of the circle, by drawing the string through a hole in the table.

cation of heat to the system, that is, if the factors expressing the
energy of thermal agitation are not directly changed, but only
affected by the change of some such coordinate as the volume
or the pressure. The energy of thermal agitation decreases,
of course, during the adiabatic expansion of a gas (we restrict
the term adiabatic to reversible processes—the unresisted
expansion of a gas is not considered) but only as a result of
changes of external conditions, work being done against ex-
ternal pressure. Similarly, in the adiabatic changes contem-
plated in the quantum mechanics, the external forces which
change do not affect directly the coordinates of the system
which determine its energy (θ and $\dot{\theta}$ in the pendulum case) but
concern parameters which remain constant as long as these
forces are constant (the length l in the pendulum case). The
energy of the system may change, but it is not as the result of
a direct communication of energy as such. Again, the adia-
batic change must take place very slowly in both thermo-
dynamic and mechanical cases. Finally, in the mechanical
case, there must be no systematic relationship between the
variation of the external forces and the periods of the system.
For instance, in the pendulum case the external forces must
not vary slowly but harmonically with a period connected with
that of the pendulum. In the thermodynamic case, the number
of degrees of freedom of any material body, considered as a
system of molecules, is so large that this point does not arise.

We have, then, for any simple periodic system an expression
$2T.\bar{E}_{\text{kin}}$ which is adiabatically invariant. Now the quantum
condition for Bohr's atom with one electron and a circular orbit,
which we have so far considered, is

$$2\pi m v r = 2 \cdot \tfrac{1}{2}mv^2 \cdot \frac{2\pi r}{v} = 2\bar{E}_{\text{kin}} \; T = nh.$$

The function which is restricted to be an integral multiple of
h is, therefore, an adiabatic invariant. An orbit allowed by
the quantum theory remains an allowed orbit when it is
modified by any change of external forces carried out con-
tinuously and sufficiently slowly for the change which takes
place during a single period of the atomic system to be negligible.
The general hypothesis of "mechanical transformability," as

Bohr terms it, *i.e.* that an allowed orbit always remains an allowed orbit, corresponding to the prevailing field, when the external conditions are slowly changed is often known as Ehrenfest's adiabatic hypothesis, after its first promulgator.

The expression $J = \int_0^T 2E_{kin}\, dt$ can be generalised, as will be seen later, to apply to systems which are not simply periodic. Its invariant property is of great importance. In virtue of this property the laws of classical mechanics can, without any violation of quantum conditions, be assumed to apply to the orbital motion as long as the external forces are varied but slowly : on the other hand, if J were not invariant and the basis of classical mechanics were retained, we could, by suitably changing these forces, cause the atomic system to emit or absorb energy without passing from one stationary state to another, which would render our quantum system nugatory. The quantum conditions would be impracticable if they lost their validity whenever a gradual change, even a small one, was made in the external forces, and in general when we have to seek expressions to quantise in the more general case of atomic systems these expressions must be adiabatically invariant. The invariant property also allows us to pass from a stationary state of a simple periodic motion of a given kind to a stationary state of a motion of another kind which is also simply periodic. Thus, for the simplest of all quantised systems the Planckian oscillator, which is an electron, bound to an equilibrium position by a quasi-elastic force, vibrating in a straight line,

$$J = \int_0^T 2E_{kin}\, dt = 2T\bar{E}_{kin} = \frac{E}{\omega} = nh,$$

since the average potential energy is equal to the average kinetic energy, so that E, the total energy, is $2\bar{E}_{kin}$. Hence, if the principle of adiabatic invariance be assumed, it follows at once that the quantum condition for any periodic system which can be formed in a continuous manner from a Planckian oscillator by gradual alteration of external forces is that $J = nh$. Further, Ehrenfest has shown that the *a priori* probability of a given stationary state of a system is unaffected by an adiabatic transformation which modifies it into a

stationary state of a different system.   Planck established that
all possible states of an oscillator, *i.e.* all values of n in the
expression $W = nh\omega$ had equal *a priori* probability.   Hence
it follows that all the stationary states in the transformed
system have equal *a priori* probability.

If a hydrogen atom with a circular orbit be transformed
adiabatically to a system with an elliptic orbit of the same
time period, which can be done, then $\overline{E}_{kin}$ must be the same
for the two orbits.   It is well known that in an elliptic as in a
circular orbit the average value of the negative potential
energy is equal to twice the average value of the kinetic
energy, and therefore the total energy of the elliptic orbit is
the same as that of the circular orbit of the same quantum
number.   Hence a system of elliptic orbits will give the
same frequencies as a system of circular orbits of the same
periods, which is equivalent to saying that a permitted
elliptic orbit is energetically equal to a circular orbit whose
diameter equals the major axis of the ellipse.*   We see,
then, that Bohr's theory applied to ordinary Keplerian orbits,†
with one degree of periodicity, would give the same spectra
as it does with circular orbits.   This point has already been
mentioned, and shows that in considering circular orbits only
we have not lost generality to the extent that might be
expected.

However, there is no need to work, in this case, the adiabatic
transformation directly.   If the quantising condition be given
in the form now under discussion, viz. $2\int_0^T E_{kin}\, dt = nh$, then it
can be shown quite simply that the stationary elliptic orbit
and the stationary circular orbit, in the same system, corre-
sponding to the same value of n have the same total energy
and the same a.   As the equivalence of the elliptic and
circular orbits is a point of some importance it may be well
to prove this from first principles.

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* Since, for an ellipse, $T = 2\pi\sqrt{\dfrac{a^3}{\mu}}$ (Kepler's Third Law).

† *i.e.* orbits in which the electron is attracted by a central force, obeying the
inverse square law, and the mass of the electron is assumed independent of
the velocity.

For the elliptic orbit the following results are well known :

$$\frac{I}{r}=\frac{me^2}{p^2}(I+\epsilon\cos\theta), \quad p=mr^2\dot\theta=\frac{2m\pi ab}{T}$$

and
$$\tfrac{1}{2}mv^2=\frac{e^2}{r}-\frac{e^2}{2a}\,.$$

Hence
$$2\int_0^T E_{\mathrm{kin}}\,dt=2c^2\int_0^T\frac{dt}{r}-\frac{e^2}{a}\,T,$$

$$\int_0^T\frac{dt}{r}=\frac{m}{p}\int_0^{2\pi}r\,.\,d\theta=\frac{p}{e^2}\int_0^{2\pi}\frac{d\theta}{I+\epsilon\cos\theta}=\frac{p}{e^2}\frac{2\pi}{\sqrt{I-\epsilon^2}}=\frac{2\pi m^{\frac{1}{2}}a^{\frac{1}{2}}}{e}$$

substituting the value of p and remembering that $T=2\pi\sqrt{\dfrac{a^3m}{e^2}}$.

Hence the quantising condition becomes

$$2\int_0^T E_{\mathrm{kin}}\,.\,dt=2\pi em^{\frac{1}{2}}a^{\frac{1}{2}}=nh \quad\text{or}\quad em^{\frac{1}{2}}a^{\frac{1}{2}}=\frac{nh}{2\pi}\,,$$

while the total energy $=-W=\tfrac{1}{2}mv^2-\dfrac{e^2}{r}=-\dfrac{e^2}{2a}\,.$ ....(8)

For future reference, it may be noted that (4), together with (8), gives for the semi-major axis

$$a=\frac{h^2n^2}{4\pi^2Ze^2m}\,.$$ ....(9)

For the circular orbit, of radius a, the quantising condition is

$$2\int_0^T E_{\mathrm{kin}}\,dt=mv^2\frac{2\pi a}{v}=2\pi mav=2\pi em^{\frac{1}{2}}a^{\frac{1}{2}}=nh\,,$$

and the total energy is $-\tfrac{1}{2}mv^2=-\dfrac{e^2}{2a}\,.$

This proves our point.

Finally, a further property of J, to which future reference will have to be made, may be noted. Suppose two *mechanically* possible states of the system (all external forces being the same in each case) differing very little from one another, and denote differences between the two states by δ.

Then
$$\delta J=\delta\int_0^T 2E_{\mathrm{kin}}\,dt=\delta\frac{2\overline{E}_{\mathrm{kin}}}{\omega}=\frac{\delta E}{\omega}\,,$$

since the total energy $E = 2\bar{E}_{\text{kin}}$, and E has a value in each of the states which is constant for that state.

Hence
$$\delta E = \omega \, \delta J.$$

The Correspondence Principle. The quantum theory, as we have so far considered it, gives information as to the frequency of the radiation emitted by an atom, in terms of the energy of the stationary states of the atom, but gives no information as to other properties which characterise a radiation, namely, intensity and polarisation. It also leaves unsettled the question as to whether frequencies corresponding to every transition (quantum switch) mathematically possible are to be expected, a question which is, of course, merely an aspect of the intensity problem, since if a given frequency is not to occur its intensity would be given as zero by any adequate theory. These questions cannot be settled on the basis of the postulates which we have discussed, since these tell us nothing as to the probability of a transition taking place, which would govern questions of intensity, nor give us any indication of polarity in the way in which the transition takes place, to correspond to polarisation in the radiation. We can, perhaps, illustrate the position as regards intensity by drawing an analogy from the field of radioactivity. We do not know what makes a given radioactive atom break down, and so have no means of calculating when it will do so. However, we know empirically the percentage number of atoms of a radioactive element which suffer a given disintegration in unit time, and so can attribute a so-called *a priori* probability (based on no dynamical causality) of a disintegration to every atom. In the same way, the probability of a transition between two stationary states must be allotted by some *a priori* principle ; and the question before us is as to how this can be done.

Bohr has answered this question by assuming a certain correlation between the motion of the electron in its atomic orbit and the radiation emitted. On the classical electrodynamic theory the radiation from an electron is governed by the electric moment er, or, in the case of a system of several electrons, Σer, the frequency of the radiation being the same as the frequency of oscillation of this moment. The postulates

of the quantum theory are, of course, in direct contradiction to this : the frequency of the radiation cannot be equal to that of the electric moment. Nevertheless, when the quantum numbers are very large the frequencies of the electronic motion in two consecutive states are very nearly equal, and also approximate to the frequency of the radiation which the quantum theory requires. In other words, as the quantum numbers of the orbits tend to infinity the frequency calculated on the quantum theory tends to equality with that calculated on the classical theory. Starting from this limiting case, in which there is a close connection between the frequency of the radiation given by the quantum theory and the frequency of the motion of the electron in its orbit, Bohr has traced a correspondence between (a) a quantum switch leading to a given monochromatic radiation, and (b) a selected harmonic component of the motion of the electron in its orbit, the motion being resolved by Fourier's theorem into a sum of oscillations whose frequencies are multiples of the fundamental frequency. The frequency of the radiations and the frequency of the harmonic component are no longer equal, as they are in the classical case, but yet, on Bohr's hypothesis, the presence of the given harmonic component conditions, in some way which is not understood, the occurrence of the " corresponding " quantum switch. Rules are given for the selection of the harmonic component of electron motion corresponding to the quantum switch in question. The correspondence is assumed to be so complete that, if the *polarisation* and *amplitude* of the given radiation are calculated by the classical method from the amplitude and direction of the harmonic component, then they will be approximately correct for the actual radiation, although the *frequency* of the radiation must be obtained by quantum methods, and is equal to that given by classical methods only in the limiting case indicated. The applications of the correspondence principle are most striking in the case of periodic motions of two or more degrees of periodicity, but the case of simply periodic motions considered in this chapter may be used to provide an introduction to the principles, and to elucidate what has just been said.

Consider, then, the case of the hydrogen-like atom, for which the frequency of revolution

$$= \omega = \frac{4\pi^2 m e^2 E^2}{n^3 h^3}.$$

This we deduced for the circular orbit, but it has already been pointed out that for a simple Keplerian ellipse, of major axis r, the frequency and the energy are the same as for a circle of radius r, the nucleus being, of course, assumed the same in both cases.

The wave number of the radiation given out in passing from the n to the n' quantum orbit is

$$\nu = \frac{R}{n'^2} - \frac{R}{n^2}$$

$$= (n' - n)R\frac{n + n'}{n^2 n'^2}.$$

If n' and n are very large compared to their difference $n - n'$, we have approximately

$$\nu = (n' - n)R\frac{2}{n^3}$$

$$= (n - n')\omega \frac{Rh^3}{2\pi^2 m e^2 E^2},$$

using the expression for ω given above; or since

$$R = \frac{2\pi^2 m e^4}{ch^3}$$

and for simplicity we may take the hydrogen atom itself, where $e^2 E^2 = e^4$

$$\nu_T = (n - n')\omega. \quad \dots\dots\dots\dots\dots\dots\dots\dots(10)$$

That is, the frequency of the emitted radiation, as deduced from the quantum theory, becomes, when $\dfrac{n - n'}{n}$ is very small, a whole number multiple of the fundamental frequency of the orbital motion of the electron.*

* It is interesting to note another way of expressing the equivalence of classical and quantum theory in the limit. If the motion of the electron in its orbit, of fundamental frequency ω, contains harmonics of frequency $\tau\omega$, where τ is

In the case of *any* singly periodic motion. (*i.e.* motion in a closed orbit which repeats itself with fundamental frequency ω *), the displacement in a given direction, say ξ along the x axis is, of course, a periodic motion with the same fundamental frequency ω.   Such a motion can, as is well known, be expressed as a Fourier series, *i.e.*

$$\xi = \Sigma C_\tau \cos 2\pi(\tau\omega t + c_\tau).$$

There will, of course, be a similar expression for η, the displacement along the y axis, viz.

$$\eta = \Sigma B_\tau \cos 2\pi(\tau\omega t + b_\tau).$$

Now the frequency of the radiation emitted, on classical theory, is the frequency of oscillation of the electric moment, and therefore, in general, any orbit of one degree of periodicity will give rise to radiations of frequencies $\tau\omega$, *i.e.* radiations whose frequencies are whole number multiples of the fundamental frequency.   Hence, referring to equation (10), we can make the quantum and the classical theory agree in the limit which we are discussing by assuming that the occurrence of a transition from an n-quantum to an n'-quantum orbit is connected with the presence of a harmonic component of frequency $(n - n')$ in the orbital motion of the electron.   If there is no such component, then, to preserve our correspondence, we must suppose that the transition in question cannot occur.

Starting from this point Bohr has developed a principle which lays down a correspondence between (*a*) the proba-

a whole number, then, in the classical case, the radiation will contain a frequency

$$\nu_T = \tau\omega = -\tau\frac{\partial W}{\partial J} = -\frac{\partial W}{\partial J/\tau} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots(a)$$

where $J = nh$. This may be verified from (4), p. 192, remembering that nh, which occurs in the expressions for ω and W, may be treated as continuously varying in the classical case.

In the quantum case we have, generally, $\nu_T = -\dfrac{\Delta W}{h}$,

where Δ refers to the *finite* difference in W between two permitted orbits. But $\Delta J = (n - n')h = \tau h$, so that in the quantum case

$$\nu_T = -\frac{\Delta W}{\Delta J/\tau} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(b)$$

If $\dfrac{\Delta J}{\tau}$ tends to 0, which is the case when τ is indefinitely increased, $n - n'$ being kept constant, then the two expressions (*a*) and (*b*) become equivalent.

* Such a motion is also called a motion of one degree of periodicity.

bility of a transition occurring between two given stationary states, of whatever quantum numbers, and (b) the coefficient of a certain harmonic term in the expression for the electric moment of the electron, which is a periodic function of the time. The frequency of the orbital motion of the electron is, of course, in any case but the limiting case, different in the initial and in the final orbit pertaining to the transition, and it is the essence of the quantum theory that the frequency of the emitted radiation is equal to neither of these, so that there is no question of equality of frequencies of electronic motion and of radiation except in the extreme case where n is very large compared to $(n - n')$. Nevertheless it is assumed that there is a correlation between the harmonics and the transitions such that an estimate not only of the intensity of the radiations, but also of their state of polarisation, can be obtained by a harmonic analysis of the orbital motion. The existence of a harmonic term corresponding to a given value of τ will condition the occurrence of a transition for which $n - n' = \tau$: in other words, if $C_\tau = 0$, no such transition can take place. And if conditions are such that the harmonic term is, for instance, a linear vibration for all states of the atom, then the radiation emitted during the transition corresponding, in the sense which has been indicated, to this term will be plane polarised. If the harmonic term represents a circular vibration the corresponding radiation will be circularly polarised.

It is only in the limit $n \to \infty$ that the frequency obtained by applying the classical theory to the orbital motion actually coincides with that given by the quantum theory, and similarly it is only in this limit that we can suppose that the square of the amplitude of a particu'ar harmonic in the orbital motion gives an *exact* measure of the intensity of the corresponding radiation. The nature of the assumption made in applying the correspondence principle is that, as the frequency can be deduced correctly, *i.e.* in agreement with quantum considerations, from classical consideration of the orbital motion in the limit, it may be assumed that in this limit the whole of the properties of the radiation can be deduced from classical considerations—the intensity of a given line from the amplitude of the corresponding harmonic component, and the

polarisation from the nature of the motion expressed by the harmonic term. The further assumption is then made that, in other cases than the limiting case, just as the frequency of the radiation is still to some extent conditioned by the frequency of the orbital harmonic component, though not equal to it,* so the intensity and polarisation of the harmonic components allow an estimate to be made of the relative intensities and of the states of polarisation of the different components.

A very simple illustration of the principle is offered by a Planckian oscillator, *i.e.* an electron executing a linear simple harmonic motion, under the influence of some elastic restoring force. For such an oscillator $\xi = C \cos 2\pi \, (\omega t + c)$. Planck's hypothesis is that the energy of the oscillator is restricted to values given by $W = nW_0$, where n is a whole number and $W_0 = h\nu$. According to Bohr's quantum theory of spectra it would appear that such a system could emit radiations of any frequency ν given by $h\nu = (n - n')h\omega$ where n and n' are any two whole numbers, that is, a radiation of the frequency of the oscillator itself, or any multiple of this. Planck assumed, however, that this oscillator could emit only monochromatic radiation of frequency ω.

To apply the correspondence principle, we note that the expression for the motion of the electron contains a single harmonic term, for which, with our general notation, $\tau = 1$. Hence, by hypothesis, only transitions for which $n - n' = 1$ are possible, and thus the radiations are strictly monochromatic, as Planck desired. It may also be noted that a circular electronic orbit only contains one harmonic term, so that if this

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* To express the frequency ν_{qu} deduced from the quantum theory in terms of the frequency ν_{cl} given by the classical theory, consider J expressed as a linear function of some quantity λ, so that $J = J_0 + \tau\lambda$, where τ is a whole number. As λ increases continuously, so J takes up a series of values specifying mechanically possible states : when $\lambda = h$ we have a stationary state on the quantum theory. In the classical case of a periodic motion of fundamental frequency ω, we have for any harmonic $\nu_{cl} = \tau\omega$.

Now from $J = J_0 + \tau\lambda$, $\tau = \dfrac{\partial J}{\partial \lambda}$, and we know that $\delta E = \omega \, . \, \delta J$ (see p. 206).

$$\therefore \; \nu_{cl} = \tau\omega = \frac{\partial J}{\partial \lambda} \cdot \frac{\partial E}{\partial J} = \frac{\partial E}{\partial \lambda}.$$

Now
$$\nu_{qu} = \frac{1}{h}(E_n - E_{n'}) = \frac{1}{h}\int_{n'}^{n} dE = \frac{1}{h}\int_0^h \frac{\partial E}{\partial \lambda} \cdot d\lambda = \frac{1}{h}\int_0^h \nu_{cl} \cdot d\lambda$$

or ν_{qu} is a kind of mean value of ν_{cl} over a region in which J varies continuously.

were the only possible type of orbit for hydrogen the correspondence principle would imply that each of the hydrogen series could consist of one line only. The elliptic orbit, with its complete series of harmonics, permits, however, a plurality of transitions.

The Correspondence Principle has found wide application in the hands of Bohr, and examples of its use will be found in subsequent chapters. Like other fundamental hypotheses of the quantum theory, it has no justification in the way of logical deduction : it cannot be explained in the sense of being deduced from wider and universally accepted laws. It is founded on analogy, and its success entitles it to respect. It in no sense reconciles the quantum theory and the classical theory of radiation, since it is additional to the fundamental hypotheses of the quantum theory, and does not replace or modify any of them : it does not bear at all on the great question originally handled by the quantum theory, namely, that of frequency. It provides a method, based on an assumed correspondence between the results given by classical analysis and quantum condition, of estimating a probability of transition governed by quantum laws taking place, but it gives us no insight into the physical causes which bring about such transitions. It but adds to the paradoxes of the quantum theory, giving us another example of the way in which classical and quantum laws have to be assumed side by side, each governing part of the whole mechanism of radiation, to enable us to give a manageable description of observed facts. The ultimate simplification is still to come.

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CHAPTER X

Introductory.—We have seen how the normal line spectra of hydrogen-like atoms can be described, on Bohr's assumptions, with the help of one quantum number n, which can take a series of whole number values, and how the same simple machinery gives a rough representation of the radiating properties of the general atom. The electronic orbits considered were in all cases simply periodic, that is, the periodicity of the motion of the electron could be described in terms of one constant, ω, giving the number of revolutions in unit time. The case of circular orbits is perfectly straightforward : the case of elliptic orbits was given as an extension of that of circular orbits, and appeared to be just as simple, the single periodicity being, on Bohr's view, the factor responsible for the identity of the term values obtained from circular and elliptic orbits. An essential mechanical difference between the circular orbits and the elliptic orbits is that the former have only one degree of freedom, θ, while the latter have two, r and θ. We shall see that the simplicity of the singly periodic elliptic orbit is due to the fact that it is a limiting, or so-called degenerate, case, of a class of orbits, to be considered in this chapter, which have two fundamental frequencies to go with the two degrees of freedom.

As long as the inverse square law holds exactly and the electronic mass is taken as constant, the orbits described are, in a frame of reference through the centre of mass of the system nucleus-electron, simply periodic Keplerian ellipses, including the circle as a particular case. When, however,

there is any departure from the law, whether owing to external causes, such as an applied magnetic field ; structural causes, such as the presence of a distribution of electrons round the nucleus ; or a factor which makes the equations depart from those of the Keplerian orbit, although, strictly speaking, the inverse square law of attraction still holds, *e.g.* a variation of the mass of the circulating electron with its velocity—whenever there is such a departure the orbit ceases to be simply periodic, and revolves as a whole with a periodic motion involving a new period.   In other words, in any central field, with a law of force departing from the inverse square form, the motion is no longer in an ellipse, but consists in a libration of r combined with a uniform motion of the perihelion, or rather perinucleon : the path is a rosette, as shown in Fig. 36.   It can be described
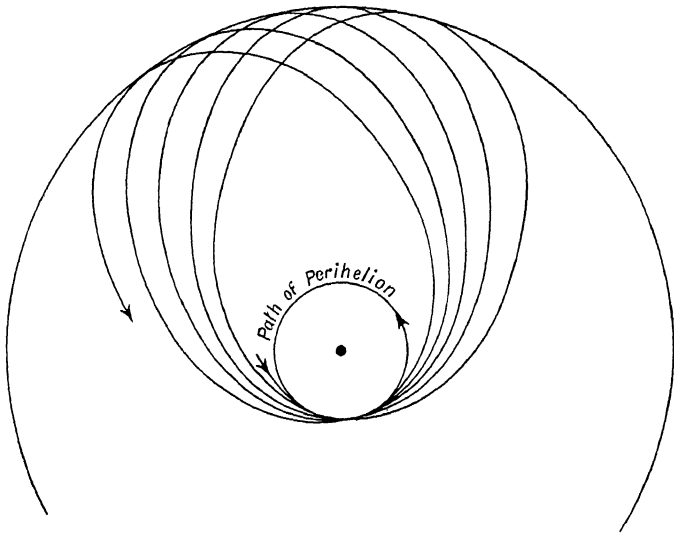
FIG. 36.

Orbit of electron in a central field departing from the inverse square law.

with the aid of two fundamental periodicities, ω_1 and ω_2, one describing the periodicity of the electron in an elliptic orbit approximating to the quasi-elliptical loop, and the other the motion of the perihelion.

One quantum condition no longer suffices to describe the motion : two are required, each involving an independent quantum number. That is, two quantum numbers, n_1 and n_2, will appear, each of which can take a series of whole number values. The fixation of the quantum conditions is a question of great difficulty, which has given rise to much discussion. The point of view of Bohr differs somewhat from that of Sommerfeld : both will receive mention in this chapter, which will deal with the case of the hydrogen-like atom alone.

The main effects to be discussed are that of the relativity changes of mass of the electron ; that of an external magnetic field (Zeeman effect) ; and that of an external electric field (Stark effect). In the last-mentioned case the resultant field of force is not central, since the electric field produces a parallel field of force imposed on the actual field, due to the nucleus. The path is not a rosette, but still has the general character of a Lissajous motion, that is, a motion produced by compounding two simple harmonics at right angles to one another, whose periods are, in general, incommensurable. Such a motion touches an enclosing figure, which in the Lissajous case is a rectangle whose sides touch the various successive loops that constitute the path. In other cases the sides of the enclosing figure may be curves. In the course of time the path comes as near as may be desired to any chosen point in the enclosed area, except in the degenerate case where the two periods are commensurable, when the path becomes a closed figure. A motion of non-degenerate type occurs in the Stark effect, in which case the enclosing figure is a quadrangle whose sides are parabolic arcs.

Such motions as we have just glanced at are often called conditionally periodic, because under certain conditions they repeat themselves exactly after a finite time. Thus in the Lissajous case if the frequency of the one simple harmonic is a simple multiple of the other simple harmonic at right angles to it, or if in the rosette case the period of rotation of perihelion is a simple multiple of that in the quasi-ellipse from apse to apse, then the motion is in a closed curve.

Hamiltonian Mechanics.—For dealing with the astronomy of the atom the system of generalised mechanics known by

the name of Hamilton, which has rendered such great services to celestial astronomy, has proved particularly well adapted. The equations do not, of course, give expression to any fundamental dynamical principle not contained in Newton's laws of motion, but they express the content of Newton's laws in a particularly general and convenient way, without the need of specifying any particular system of coordinates, such as Cartesian, polar or curvilinear coordinates.

We suppose that the positional configuration of the system can be completely specified by r coordinates $q_1, q_2 \ldots q_r$. These may be of any nature and their number is equal to the number of degrees of freedom of the system; for instance, in the case of a single particle whose position in space is given by polar coordinates they are r, φ, θ. The motion of the system at any instant is given by further specifying so-called momentum-coordinates or impulse-coordinates, denoted by p_1, p_2, $\ldots p_r$. These p's are strictly defined by r relations of the type

$$p_m = \frac{\partial L}{\partial \dot{q}_m}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\text{I})$$

where L is the Lagrangian function $E_{\text{kin}} - E_{\text{pot}}$.* If the E_{pot} does not involve any $\dot{q}_m$ (it never does in the ordinary cases with which we have to deal), then

$$p_m = \frac{\partial E_{\text{kin}}}{\partial \dot{q}_m}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\text{Ia})$$

For example, in the case of a single particle, and Cartesian coordinates,

$$q_1 = x, \ q_2 = y, \ q_3 = z; \quad E_{\text{kin}} = \tfrac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

and by definition (Ia)

$$p_1 = m\dot{x}, \ p_2 = m\dot{y}, \ p_3 = m\dot{z},$$

the ordinary momenta. With a single particle and polar coordinates

$$q_1 = r, \ q_2 = \theta, \ q_3 = \varphi$$

and

$$E_{\text{kin}} = \tfrac{1}{2} m (\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2\theta \cdot \dot{\varphi}^2).$$

* The equations of motion in terms of the Lagrangian function are

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_m} - \frac{\partial L}{\partial q_m} = 0.$$

Here
$$p_1 = \frac{\partial E_{\text{kin}}}{\partial \dot{r}} = m\dot{r},$$

$$p_2 = \frac{\partial E_{\text{kin}}}{\partial \dot{\theta}} = mr^2\dot{\theta},$$

$$p_3 = \frac{\partial E_{\text{kin}}}{\partial \dot{\varphi}} = mr^2 \sin^2\theta \cdot \dot{\varphi},$$

so that p_2, p_3 are components of angular momentum, or of moment of momentum, about the origin, corresponding to the angular coordinates θ and φ. The definition (1a) applies, of course, to any type of coordinate.

To express the properties of the motion a function called the Hamiltonian function is formed. This is defined by the equation

$$H = \Sigma p_m \dot{q}_m - L.$$

But E_{kin} is a homogeneous quadratic function of the generalised velocities $\dot{q}$, so by Euler's theorem

$$2E_{\text{kin}} = \Sigma \dot{q}_m \frac{\partial E_{\text{kin}}}{\partial \dot{q}_m} = \Sigma p_m \dot{q}_m ; \ldots\ldots\ldots\ldots\text{by (1a)}$$

$$\therefore H = 2E_{\text{kin}} - E_{\text{kin}} + E_{\text{pot}} = \text{total energy.}$$

If L does not contain t explicitly, the Hamiltonian function is, we see, identical with the total energy of the system, which we generally write hereafter as E.

In terms of the function H the equations of motion assume the form

$$\dot{q}_m = \frac{\partial H}{\partial p_m}, \quad \dot{p}_m = -\frac{\partial H}{\partial q_m}, \quad \ldots\ldots\ldots\ldots\ldots(2)$$

which we will not prove here : they can easily be verified by taking any simple case. This system of equations is called the canonical* or Hamiltonian form of the equations of motion.

In the cases with which we have to deal the motion may be expressed with the help of coordinates of a particular type, called cyclic. Such a cyclic coordinate is an angular coordinate

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* " Canonical. Standard—said of various simplest and most significant forms to which general equations and expressions may be brought without loss of generality " (Webster's Dictionary).

θ, which does not occur in the expression for the energy. Thus, in the simple elliptic orbit, the energy is

$$E_{\text{kin}} + E_{\text{pot}} = \frac{m}{2}\left(r^2 + r^2\dot{\theta}^2\right) - \frac{eE}{r}$$

and θ does not occur explicitly, although $\dot{\theta}$ does. The elliptic motion can, however, by a suitable transformation be expressed by *two* cyclic coordinates just as the Lissajous motion.

In certain cases a motion is possible (and is of particular interest for us) for which the cyclic coordinate q_m can be expressed in the form

$$q_m = \omega_m t + \delta_m,$$

where ω_m and δ_m are constants ; the energy then involves p_m, but not q_m. Using equation (2), we have

$$\frac{\partial H}{\partial p_m} = \frac{\partial q_m}{\partial t} = \omega_m, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2a)$$

a result to which we shall have to refer later.

Sommerfeld's Method for Systems of Two Degrees of Freedom. We have seen in Chapter IX. that the quantising condition for systems with one quantum number is

$$\int_0^T 2\dot{E}_{\text{kin}}\, dt = nh \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

and from above $\qquad 2E_{\text{kin}} = \Sigma p_m \dot{q}_m = p\dot{q}$

for a system of one degree of freedom, so that for such a system (3) is equivalent to

$$\int_0^T p\, dq = nh = J. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Now Sommerfeld has assumed, generalising from this, that, in the case of more than one degree of freedom, there is for each degree of freedom a quantising condition expressed by

$$\oint p_m\, dq_m = n_m h = J_m, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where n_m is a whole number. Thus a system of r degrees of freedom requires for its quantisation r quantum numbers, $n_1, n_2 \ldots n_r$, each of which can take a range of whole number values. The condition (5) was enunciated independently by W. Wilson, and is sometimes called the Sommerfeld-Wilson quantum condition.

This method of quantisation is arbitrary in the sense that its main justification is to be found in the agreement of the results with experiment: there is no *a priori* reason for it. The J_m's, as defined by (5), have, however, the same important property as was discovered for the single J in Chapter IX.: they are adiabatically invariant, that is, if the system be exposed to slowly varying forces, and the effect of these on the motion be calculated according to classical mechanics, then the value of each J_m remains constant. The lines of a proof have been sketched by J. M. Burgers, but a complete proof presents grave difficulties. The importance of this condition for the quantum theory has already been pointed out in connection with one quantum number, and exactly similar considerations apply in the case of more than one quantum number. There is a limitation incurred with degenerate systems which will be mentioned when such systems are discussed a little later.

In the case of multiply periodic motions the range over which an integral $\int p_m\, dq_m$ is to be taken is that of a complete oscillation of the coordinate. As regards the question of the selection of the coordinates, cases can be imagined in which difficulties arise, but in the cases with which we shall deal here an obvious choice generally presents itself, as r and θ for the central orbit.

In general, a momentum p_m may be a function of all the coordinates $q_1, q_2 \ldots q_r$. In certain cases, however, the coordinate can be so chosen that p_m is a function of q_m alone, that is, each momentum is a function of its " own " coordinate and not of the other coordinates. In such cases we speak of a " separation of the variables." * Such a separation of the variables is always possible in the case of the multiply periodic system with which we shall deal. Each integral $\int p_m\, dq_m$ is then a function of one coordinate alone, and this is the essence of Sommerfeld's method. It is of interest to note that in these cases it can be shown that each q librates between fixed limits.

* Apparently first discussed by Jacobi, *Vorlesungen über Dynamik*, Chapter XX.

Bohr's Method with Multiply Periodic Systems. With Sommerfeld's method each degree of freedom leads to a separate quantum condition, so that for a system of s degrees of freedom it appears that we must have s quantum numbers. We have seen, however, that a Keplerian ellipse only requires one quantum number to specify its energy in a stationary orbit, just as does a circular orbit, yet it has two degrees of freedom. The Keplerian ellipse is a particular case of a motion of two degrees of freedom, a so-called degenerate case, in which there is only one periodicity, and when we come to consider this ellipse on the basis of Sommerfeld's theory it will be seen how the two quantum numbers degenerate into one in this case. Bohr's method of handling the problem provides a much more direct connection between the quantum conditions and the periodicities, specifying, for instance, that one quantum number is required for each true periodicity. This tells us at once that the Keplerian ellipse will only require one quantum number. The method is more physical than Sommerfeld's, in the sense that the general character of the motion in the orbit is made to yield almost without calculation immediate information of a general kind as to the quantising conditions and general nature of the spectrum to be anticipated. Sommerfeld's method is, however, often simpler to follow.

We start by considering the variation with time of the component ξ of the displacement of the electron in its orbit resolved along any given direction, say that of x : in other words $e\xi$ is a component of the electrical moment of the electron. If the motion is simply periodic, *i.e.* if it repeats itself exactly with a frequency $\omega = \dfrac{1}{T}$, then we have, by Fourier's theorem

$$\xi = \Sigma C_\tau \cos \left(2\pi\tau\omega t + \gamma_\tau\right) \quad\dots\dots\dots\dots\dots\dots\dots(6)$$

where τ is any whole number, and C_τ, γ_τ are constants, corresponding to each value of τ. In the simplest case of all, the simple harmonic motion, $\tau = 1$ only, and the summation sign is dropped. Expressions of the same form as (6), but with different values of the constants, can be written down for the displacements η, ζ along the axes of y and z.

Now suppose a multiply periodic motion, which needs for

its specification a number r, say, of frequencies ω which are such that no relation of the type

$$m_1\omega_1 + m_2\omega_2 + \dots + m_r\omega_r = 0 \quad \dots\dots\dots\dots\dots\dots(7)$$

exists between them, where the m's are whole numbers.* Then the displacement ξ is given in the most general case by

$$\xi = \Sigma C_{\tau_1\dots\tau_r} \cos\left\{2\pi(\tau_1\omega_1 + \tau_2\omega_2 + - + \tau_r\omega_r)t + \gamma_{\tau_1\dots\tau_r}\right\} \quad \dots\dots(8)$$

$\tau_1, \tau_2 \dots \tau_r$ are all whole numbers, and the constants are endowed with many suffixes to indicate that for any given selection of τ's there is a particular C and a particular γ. Thus, if there were three frequencies only, ω_1, ω_2, ω_3, and a particular term was considered for which $\tau_1 = 2$, $\tau_2 = 2$, $\tau_3 = 5$ say, then C_{225} would denote the coefficient of that term, and γ_{225} the phase constant. There are, of course, in the most general case ∞^r terms in the series. Similar expressions, with say A and a, and B and β in place of C and γ can be written down for η and ζ, but there is no point in doing so.

To specify the stationary state we have as before certain integrals of action J which are put equal to whole number multiples of h,

$$J_1 = n_1 h, \ J_2 = n_2 h, \text{ etc.}, \quad \dots\dots\dots\dots\dots\dots(9)$$

where n_1, n_2,...are quantum numbers in the sense described on page 219. Each of these can take a series of whole number values. As we are expressing the motion differently from the Sommerfeld-Wilson scheme, we have to discuss what we mean by the J's. The J's are now generalised momenta corresponding to the ω's in the expression (8); in fact, J's and w's can be regarded as momenta and coordinates replacing p's and q's, where $w_m = \omega_m t + \delta$. They satisfy the canonical equations

$$\frac{\partial J_m}{\partial t} = -\frac{\partial E}{\partial w_m} = 0$$

and
$$\frac{\partial w_m}{\partial t} = \frac{\partial E}{\partial J_m} = \omega_m.$$

---

* Taking for simplicity only two periods ω_1 and ω_2, then if there is a relation $m_1\omega_1 + m_2\omega_2 = 0$ both frequencies are simply harmonics of one fundamental frequency, and the motion degenerates into the case covered by formula (6). If there are more than two frequencies, and the relation (7) holds between two of them the degeneration is not complete.

The number of J's is now equal, of course, to the number of ω's, which is an essential feature of the Bohr scheme. The ω's belong to cyclic coordinates, or angle variables, as they are sometimes called, to which we have already referred, and the equation last written corresponds to (2a).   We have

$$\frac{\partial E}{\partial J_1} = \omega_1, \quad \frac{\partial E}{\partial J_2} = \omega_2, \ \ldots$$

and

$$\delta E = \frac{\partial E}{\partial J_1} \cdot \delta J_1 + \frac{\partial E}{\partial J_2} \cdot \delta J_2 + \ldots,$$

where the symbol δ denotes the difference of the quantity concerned in two neighbouring states which are mechanically possible, but not, of course, necessarily stationary states.   We thus reach the expression

$$\delta E = \Sigma \omega_m \, \delta J_m, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

which we use as defining the J's.

In the case of a simply periodic system the two neighbouring states would be two near ellipses with the same nucleus as focus: we have seen that the relation $\delta E = \omega \, \delta J$ holds in that case.   Equation (10) does not suffice to specify the J's, since the constants of integration are unspecified.   To fix the J's Bohr does not connect each one separately with a coordinate, as does the Sommerfeld-Wilson condition, but puts

$$\sum_r \omega_m J_m = \sum_i \overline{p_i \, \dot{q}_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

where the p's and q's are, as before, generalised coordinates and momenta.   The stroke over the right-hand member indicates an average value with time over a time very large compared to the fundamental periods of the motion, $i.e.$

$$\sum_i \overline{p_i \, \dot{q}_i} = \frac{1}{t - t_0} \sum \int_{t_0}^{t} p_i \frac{\partial q_i}{\partial t} \cdot dt,$$

where $t - t_0$ is very large.

It should be emphasised that these conditions come to Sommerfeld's conditions, when the latter can be formulated, and that, when the calculations can be carried out, Bohr's

and Sommerfeld's methods are equivalent and lead to identical results about observable quantities. For one periodicity

$$\omega J = \Sigma \frac{1}{T} \oint p \, dq = \Sigma \omega \oint p \, dq,$$

which is the quantum condition for a simple periodic system, and if the variables are separable, equation (11) is equivalent to the conditions $J_m = \int p_m \, dq_m$ as long as the number of co-ordinates, or degrees of freedom, is equal to the number of periods. Equations (10) and (11) together do not involve any equality between the number of J's and of p's, but rather that the number of J's and consequently of quantum numbers, shall equal the number of fundamental frequencies. On the other hand, Sommerfeld's method implies that the number of quantum numbers shall be equal to the number of degrees of freedom. Now it sometimes happens that the number of fundamental frequencies is less than the number of degrees of freedom, as in the Kepler ellipse to which reference has so often been made : this is the distinguishing feature of the class of motion called degenerate. This class of motion illustrates well the difference of the two viewpoints, and the simple case of the Keplerian ellipse will be treated by each method in a subsequent section as an illustration.

The Principle of Correspondence : General Case. The chief difference between Bohr and Sommerfeld is that Bohr strives to retain a physical meaning for the frequencies of the electron in its orbit, which on classical theory determined the frequencies of the emitted radiation ; these, in the physical sense, are the real things. We have already discussed the way in which a given transition is correlated by Bohr with a certain harmonic component in the orbital motion, in the simple case of a simply harmonic system. We now attempt to show how the method which has just been sketched extends this correspondence, or, to put it the other way round, how an extension of the correspondence principle may be made to imply the method.

By the fundamental postulate

$$\nu_T = \frac{1}{h} \big\{ E\left(n_1, n_2...n_r\right) - E\left(n'_1, n'_2...n'_r\right) \big\},$$

where the n's denote that the energies now involve several quantum numbers. Now in the case where the quantum numbers themselves are very large compared to their differences in the two orbits considered, the difference of energy between the two orbits is very small, and may be considered as given by δE in the equation

$$\delta E = \Sigma \omega_m \, \delta J_m. \quad\dots\dots\dots\dots\dots\dots\dots(10)$$

Then, in the limiting case,

$$\nu_T = \frac{E - E'}{h} = \frac{\delta E}{h} = \frac{1}{h}\Sigma \omega_m \, \delta J_m = \Sigma \omega_m \frac{J_m - J_{m'}}{h}$$
$$= \Sigma \omega_m (n_m - n'_m).$$

But, on the classical theory, the complex radiation given out by a system represented by equation (8) would consist of harmonics of frequencies given by expressions $\omega_m \tau_m$.

Hence in the limiting case where $\dfrac{n_m - n'_m}{n_m}$ is very small

$$\tau_m = n_m - n'_m$$

and the frequencies given by classical and quantum theory agree. By the same argument as was used in the simple discussion of the correspondence principle in Chapter IX. the presence of a harmonic component, for which the whole number

$$\tau_m = n_m - n'_m$$

in equation (8), conditions the possibility of a transition from quantum state n_m to quantum state n'_m, even where $\dfrac{n_m - n'_m}{n_m}$ is not small. The arguments used in the discussion of Chapter IX. also apply again to the question of polarisation.

The Case of the Kepler Ellipse : Bohr's and Sommerfeld's Methods Contrasted. We have already said, in Chapter IX., that in the case of the Kepler ellipse the energy depends upon the major axis only, and is independent of the eccentricity, so that if one quantum number suffices to fix the major axis it will give the Balmer series. This is Bohr's point of view which we now consider in a slightly different manner from before, on the basis of the general conditions set out in this chapter.

If $2a$ be the major axis, ω the frequency of revolution, and W the negative energy of the electron in its orbit, as considered on page 191, then it follows from Kepler's laws that

$$\omega = \sqrt{\frac{2W^3}{\pi^2 e^4 Z^2 m}}, \quad 2a = \frac{Ze^2}{W}.$$

If the mass of the nucleus is considered finite m must be replaced by

$$\frac{mM}{m+M}.$$

By (10)*
$$\delta E = \omega \delta J$$

or
$$\frac{\partial E}{\partial J} = -\frac{\partial W}{\partial J} = \sqrt{\frac{2}{\pi^2 e^4 Z^2 m}} \cdot W^{\frac{3}{2}};$$

whence
$$J = \frac{1}{\sqrt{2}} \cdot \sqrt{\pi^2 e^4 Z^2 m} \cdot 2W^{-\frac{1}{2}},$$

so that
$$W = \frac{2\pi^2 Z^2 e^4 m}{J^2},$$

the constant of integration being zero, since when $J = 0$, $W = 0$. For J is, by definition (11) on page 223, given by

$$\omega J = \frac{1}{T}\left\{ \oint p_r \cdot dr + \int_0^{2\pi} p_\theta \cdot d\theta \right\},$$

choosing r and θ as coordinates for the ellipse; and if $J = 0$, p_r and p_θ must be each zero, and hence $W = 0$.

Also we have the quantising condition

$$J = nh;$$

$$\therefore \ W = \frac{2\pi^2 Z^2 e^4 m}{h^2} \cdot \frac{1}{n^2},$$

which is the same formula as is obtained in the case of circular orbits. Hence Balmer's series and all the other considerations.

---

* Cf. in case of circular orbit.

$$E = -\tfrac{1}{2}\frac{Ze^2}{r}, \quad J = 2\pi(mZe^2)^{\frac{1}{2}}r^{\frac{1}{2}}, \quad \omega = \frac{1}{2\pi}\left(\frac{Ze^2}{m}\right)^{\frac{1}{2}}r^{-\frac{3}{2}};$$

$$\therefore \ \delta E = +\tfrac{1}{2}\frac{Ze^2}{r^2}\,dr = \left(\frac{Ze^2}{m}\right)^{\frac{1}{2}}r^{-\frac{3}{2}}(mZe^2)^{\frac{1}{2}}\tfrac{1}{2}r^{-\frac{1}{2}} \cdot dr$$

$$= \omega \cdot \delta J.$$

It is to be noted that, on this view, all that the quantum condition does is to restrict the major axis a, and consequently the energy, which is a function of a alone, to certain stationary values. Corresponding to a given a, fixed by the quantising condition, we can have ellipses of all possible eccentricities. We now turn to Sommerfeld's method, which does not allow this, although, as we shall see, from the point of view of the series spectra the result is the same.

Sommerfeld's method attaches a separate quantum condition to each degree of freedom, so that while the circular orbit, with fixed r and only one degree of freedom, has but one quantum condition, the ellipse, with variable r and θ, must have two quantum conditions, which will be, as we have seen,

$$\int_0^{2\pi} p_\theta \cdot d\theta = n_a h, \quad \oint p_r \, dr = n_r h,$$

where
$$p_\theta = \frac{\partial E_{\mathrm{kin}}}{\partial \theta}, \quad p_r = \frac{\partial E_{\mathrm{kin}}}{\partial r}$$

by definition of the p's. n_a is called the azimuthal quantum number, n_r the radial quantum number, and the sum $n_a + n_r$ the total quantum number, denoted by n.

For the ellipse
$$E_{\mathrm{kin}} = \tfrac{1}{2} m \left(r^2 \dot{\theta}^2 + \dot{r}^2 \right),$$

which gives p_θ and p_r at once, or they can be written down directly if it be remembered that they are the momenta depending on $\dot{\theta}$ and $\dot{r}$ respectively. The quantising conditions are then

$$\left. \begin{array}{l} \int_0^{2\pi} p_\theta \, d\theta = 2\pi p = n_a h, \\[2mm] \oint p_r \, dr = \int_0^{2\pi} m\dot{r} \frac{dr}{d\theta} \, d\theta = n_r h, \end{array} \right\} \quad \cdots\cdots\cdots (12)$$

where $p = mr^2\dot{\theta}$ is the constant of areal velocity.

Now the equation of an elliptic orbit of eccentricity ϵ expressed in polar coordinates with respect to the focus as origin is usually given in the form

$$\frac{\mathrm{I}}{r} = \frac{\mu m^2}{p^2}(\mathrm{I} + \epsilon \cos \theta),$$

where $\dfrac{\mu}{r^2}$ is the central attraction. In the case of a nucleus of charge Ze, with a revolving electron

$$\frac{1}{r} = \frac{mZe^2}{p^2} (1 + \epsilon \cos \theta), \quad \dotfill (13)$$

$$\dot{r} = \frac{Ze^2}{p} \epsilon \sin \theta, \quad \frac{dr}{d\theta} = \frac{p^2}{mZe^2} \frac{\epsilon \sin \theta}{(1 + \epsilon \cos \theta)^2}$$

or $\quad \displaystyle\oint p_r \, dr = \int_0^{2\pi} p\epsilon^2 \frac{\sin^2 \theta}{(1 + \epsilon \cos \theta)^2} \, d\theta$

$$= 2\pi p \left(\frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right) = n_r h.$$

Substituting the value for p

$$1 - \epsilon^2 = \frac{n_a}{(n_a + n_r)^2} \quad \dotfill (14)$$

The total energy is

$$E = -W = \tfrac{1}{2}m \left(r^2 \dot{\theta}^2 + \dot{r}^2 \right) - \frac{Ze^2}{r}$$

$$= -\frac{mZ^2 e^4}{2p^2} (1 - \epsilon^2),$$

using (13), or, from (12) and (14),

$$W = + \frac{2\pi^2 m Z^2 e^4}{n_a^2 h^2} \frac{n_a^2}{(n_a + n_r)^2}$$

$$= hZ^2 R \frac{1}{(n_a + n_r)^2} \, .$$

Hence $\quad \nu = Z^2 R \left\{ \frac{1}{(n'_a + n'_r)^2} - \frac{1}{(n_a + n_r)^2} \cdot \right\} \dotfill (15)$

Equation (15) shows that elliptic orbits, treated in Sommerfeld's way, give exactly the same series spectra as do circular orbits or elliptic orbits treated by Bohr's method, since $(n_a + n_r)$ and $(n'_a + n'_r)$ take a series of whole number values. Equation (14) shows that there is a formal difference, however, for it restricts the eccentricity, unrestricted from Bohr's point of view, to certain quantised values. Denoting a given orbit by the total quantum number n and by the azimuthal quantum number,

which we will now call k, *i.e.* by $(n_a + n_r)$ and by n_a, Sommerfeld allows, for a given n, n different ellipses, since k may have the value n (which gives a circular orbit, because, if the azimuthal quantum number equals the total quantum number $n_r = 0$, which means that there is no radial momentum and so the value of r must be constant) or any lesser whole number value. The value $k = 0$ is excluded, because this gives $\epsilon = 1$, *i.e.* a straight line through the nucleus, which is physically impossible—it would either precipitate the electron into the nucleus or eject it from the atom. Thus for total quantum number 4 the four orbits shown in Fig. 37, which, of course, all have the
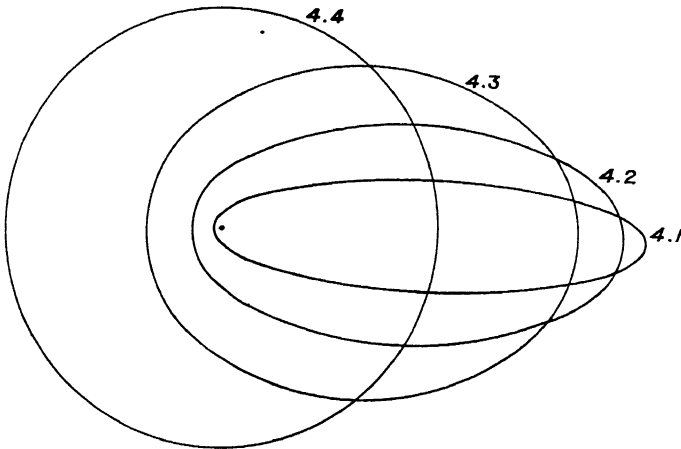
FIG. 37.

Ellipses of same total quantum number, but different azimuthal quantum number.

same major axis, are possible : in this figure to each orbit is affixed a pair of numbers, of which the first denotes the total quantum number, the second the azimuthal quantum number. On Bohr's view any ellipse with the nucleus as focus and the given length as major axis is possible, since the one quantum number which he uses for one degree of periodicity determines the energy only.

The difference, however, between the two *results* is purely formal, since, if the orbit departs ever so slightly from the Keplerian ellipse, a second periodicity is introduced. Such a

departure may, for instance, be caused by any departure of the central attraction from the inverse square law, such as is caused by the relativity variations of mass of the electron : the perihelion of the orbit then rotates slowly, as in the celebrated astronomical case of the orbit of Mercury.   The second periodicity is, in such a case, the periodicity of the motion of perihelion, or perinucleon, rather.   As soon as there is a second periodicity, however slow, Bohr has to introduce a second quantum number, when, in effect, the eccentricity becomes quantised, just as in Sommerfeld's treatment.   However, Bohr's method in general has the great advantage that it has a physical significance, the conditions being uniquely determined by absolute properties of the orbits.   Sommerfeld's conditions have no physical meaning in the sense that they are mathematically dependent upon the coordinates chosen.   While it is true that a particular set of coordinates are, in general, indicated by the conditions of the problem, as in the example just worked out, this dependence is a weakness of the method.

The case of the strictly elliptic orbit is a so-called degenerate case.   Bohr's point of view is the more physical, since it gives in this case a degeneration, as it were, of the orbits.   Their discipline is dissolved, they lose their class consciousness, and we find every possible degree of eccentricity represented, in contradistinction to the general case of a periodic orbit of two degrees of freedom, where we have two periodicities, and a limited number of discrete eccentricities conditioned by the value of k.   This point of view is all part of the correspondence principle, as has been pointed out on page 225, and enables us to make deductions as to the general nature of the spectra to be expected as soon as we know the general nature of the orbit. . It is also applicable to cases where the variables have not been separated.   The Sommerfeld-Wilson conditions $\oint p_m dq_m = n_m h$ demand a separation of the variables.   They have the advantage of being mathematically more straightforward.   In most cases, where they are equivalent to Bohr's conditions, it is convenient to use them.

Sommerfeld's Theory of the Fine Structure of Spectral Lines. We shall now consider a feature of the line spectra of

hydrogen-like atoms, the explanation of which by Sommerfeld in 1916 constituted one of the early triumphs of the quantum theory of spectra. Sommerfeld applied his quantising conditions to work out the effect of the relativity change of mass of the electron moving in a given orbit on the energy of that orbit. We have seen how, on his method, elliptic orbits of certain eccentricity only are allowed, as represented, *e.g.* in Fig. 37, the energies of all orbits of a given total quantum number being equal. When the relativity effect is taken into account the energies of these orbits are modified slightly, but the modification depends upon the eccentricity, being greater for those whose eccentricity is greater. This is clear on general grounds, since the relativity change of mass, negligible when the velocity is very small compared to that of light, increases very rapidly with increase of velocity, and the maximum velocity, at perihelion, is much greater for large eccentricities than for small. The single energy corresponding to orbits of a given n is therefore replaced by a group of n energies differing slightly from one another when the relativity effect is considered, and consequently a single spectral line is replaced by a group of close lines. We shall indicate very briefly the way in which Sommerfeld derived his formula, to which we shall have frequent occasion to refer in considering the structure of X-ray spectra. Subsequently we show how Bohr later derived the formula from his method of quantisation.

The relativity increase of the mass of the electron is expressed by the well-known formula

$$m = \frac{m_0}{\sqrt{1 - \beta^2}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(16)$$

where m_0 is the mass of the electron at very slow velocities (the so-called "rest mass") and $\beta = \frac{v}{c}$, v and c being the velocities of the electron and of light respectively. We still have, rigorously (if the nucleus be infinitely heavy), the central force $\frac{Ze^2}{r^2}$ acting upon the electron, and the areal constant

$$p = mr^2\dot{\theta} = \text{constant},$$

but m now varies according to (16) instead of being constant.

The effect of this upon the orbit can be shown to be that the equation

$$\frac{1}{r} = \frac{mZe^2}{p^2}\,(1 + \epsilon \cos\theta), \quad \dots\dots\dots\dots\dots\dots(13)$$

which expresses the relation between r and θ when the mass is constant, becomes

$$\frac{1}{r} = C\,(1 + \epsilon \cos\gamma\theta), \quad \dots\dots\dots\dots\dots\dots(17)$$

where $C = \dfrac{Ze^2m_0}{\gamma^2p^2}\Big(1 + \dfrac{E}{m_0c^2}\Big)$, E is the total energy, and

$$\gamma^2 = 1 - \Big(\frac{Ze^2}{pc}\Big)^2.$$

From (17), the orbit when the relativity effect is considered, we must find the new quantising conditions. For the first we have

$$\oint p_\theta\,d\theta = \oint p\,d\theta = n_a h = kh,$$

n_a or k being written alternatively for the azimuthal quantum numbers. p is constant, and the complete range of integration for θ is 2π .

Hence we have, as in the simple case,

$$p = \frac{kh}{2\pi}.$$

For the second quantum condition $\oint p_r\,dr = n_r h.$

Now

$$p_r = m\dot{r} = -mr^2\frac{d}{dt}\frac{1}{r} = -mr^2\frac{d\theta}{dt}\frac{d}{d\theta}\frac{1}{r}$$

$$= -p\frac{d}{d\theta}\frac{1}{r}.$$

From equation (17) we see that r no longer passes through a complete cycle when θ passes from 0 to 2π, but when θ passes from 0 to $\dfrac{2\pi}{\gamma}$, that is, the perihelion rotates through an angle

$2\pi\left(\dfrac{1}{\gamma} - 1\right)$ per revolution.*   Hence the radial quantum condition now is

$$\oint p_r \cdot dr = -p \int_0^{\frac{2\pi}{\gamma}} \frac{d}{d\theta}\left(\frac{1}{r}\right) \cdot \frac{dr}{d\theta} \cdot d\theta.$$

Using (17) the integral becomes

$$\int_0^{\frac{2\pi}{\gamma}} \frac{\epsilon^2\gamma^2 \sin^2 \gamma\theta}{(1 + \epsilon \cos \gamma\theta)^2}d\theta = \epsilon^2\gamma \int_0^{2\pi} \frac{\sin^2 z \cdot dz}{(1 + \epsilon \cos z)^2}$$

$$= \epsilon^2\gamma\left[\frac{1}{\epsilon} \cdot \frac{\sin z}{1 + \epsilon \cos z}\right]_0^{2\pi} - \epsilon\gamma \int_0^{2\pi} \frac{\cos z}{1 + \epsilon \cos z} \cdot dz.$$

In the right-hand side of the equation the first member is zero, while the second member $= \gamma \int_0^{2\pi}\left(\dfrac{1}{1 + \epsilon \cos z} - 1\right)dz.$

$\int_0^{2\pi} \dfrac{dz}{1 + \epsilon \cos z}$ is a known integral † and equals $\dfrac{2\pi}{\sqrt{1 - \epsilon^2}}.$

Hence

$$\oint p_r \cdot dr = p\gamma\left(\frac{2\pi}{\sqrt{1 - \epsilon^2}} - 2\pi\right)$$

$$= 2\pi p\gamma\left(\frac{1}{\sqrt{1 - \epsilon^2}} - 1\right) = n_r h. \quad \ldots\ldots\ldots(18)$$

This quantises the eccentricity of the stationary orbits, p and γ being fixed by k.

We now require the expression for the energy of the relativity orbit, which is

$$E = m_0 c^2\left(\frac{1}{\sqrt{1 - \beta^2}} - 1\right) - \frac{Ze^2}{r},$$

the potential energy being the same as in the Newtonian case. After some transformation this becomes

$$E = m_0 c^2\left\{\sqrt{\frac{p^2 - p_0^2}{p^2 - \epsilon^2 p_0^2}} - 1\right\},$$

where p_0 is put for $\dfrac{Ze^2}{c}.$

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* This rate of rotation of perihelion is, of course, very small.   For the orbits for which it is greatest in the hydrogen atom the orbit is described about 40,000 times to one complete revolution of perihelion.

† See, *e.g.*, Silberstein's *Synopsis of Applicable Mathematics* (G. Bell), p. 111.   Sommerfeld shows in appendix 6 to his *Atombau* how to evaluate this and similar integrals by contour integration.

It then only remains to substitute for ϵ in terms of k and n_r, which is given by equation (18). When this is carried out we get finally

$$1 + \frac{E}{m_0 c^2} = \left\{ 1 + \frac{a^2 Z^2}{(n_r + \sqrt{k^2 - a^2 Z^2})^2} \right\}^{-\frac{1}{2}} \quad \cdots\cdots\cdots\cdots (19)$$

where $a = \dfrac{2\pi e^2}{hc}$ is called the fine structure constant. The numerical value of a is $7 \cdot 29 \times 10^{-3}$.

This is Sommerfeld's complete expression for the energy E in the relativity ellipse. The somewhat lengthy calculation has been considerably shortened here by the omission of several steps in the working for which the reader is referred to Sommerfeld's book. The object has been to indicate the nature of the modification introduced into the mechanics by the relativity change of mass, and the form taken by Sommerfeld's quantum conditions.

To make the formula more manageable, it may be developed in powers of Za. We have

$$1 + \frac{E}{m_0 c^2} = 1 - \frac{1}{2}\frac{a^2 Z^2}{n^2} - \frac{1}{2}\frac{a^4 Z^4}{n^2}\left[+\frac{1}{n^2} + \frac{n_r}{n^2 k} - \frac{3}{4n^2} \right]$$

+ terms in higher powers of aZ,

whence, remembering $n = n_r + k$,

$$E_{n,k} = -\frac{m_0 c^2 a^2 Z^2}{2n^2}\left[1 + a^2 Z^2 \left(-\frac{3}{4n^2} + \frac{1}{nk} \right) \right]$$

$$= -\frac{R Z^2 hc}{n^2}\left[1 + a^2 Z^2 \left(-\frac{3}{4n^2} + \frac{1}{nk} \right) \right], \quad \cdots\cdots\cdots (20)$$

neglecting in the final formula $a^4 Z^4$ and higher powers. In the case of hydrogen and ionised helium aZ is of the order 10^{-2}, so that formula (20) is correct to a very high degree of approximation. If the formula be applied to X-ray spectra, where Z may have a large value, the full formula (19) may have to be used. The value of $E_{n,k}$ depends not upon n alone, as in the case of the Keplerian orbit, but upon n and k.

Now the frequency of any spectral line is given by the differences of two terms of the form $E_{n,k}$, one constant throughout the series, the other variable. Considering the constant

term alone, it is clear that if the inner orbit has $n=2$ (and consequently can be either elliptical, $k=1$, or circular, $k=2$), there are two energies, and consequently each line might be expected to be a doublet. If the inner orbit has $n=3$, a triplet series might be expected. The Balmer series of hydrogen is given by the return of an electron from an outer orbit to an orbit of quantum number 2, and therefore each line should be, on account of the duplicity of the final orbit, a close doublet. The separation of the lines in wave numbers is given by

$$\Delta\nu_2 = Z^4\frac{R\alpha^2}{2^2}\frac{1}{2^2} = \frac{R\alpha^2}{2^4} = \cdot365 \text{ cm.}^{-1}, \quad \ldots\ldots\ldots\ldots(21)$$

since $Z=1$ for hydrogen. This is exceedingly small, as can be seen by comparing it with the separation of the familiar sodium doublet, which is $17\cdot18$ cm.$^{-1}$. Observation of an effect of this order is very difficult, as the Doppler effect of the moving centres of emission in the gas broadens every line.* However, by working with the gas at liquid air temperature results have been obtained by several observers. Among recent results may be quoted the following :

Line.	Observer.	Date.	$\Delta\nu$
H_α			$\cdot293$
H_β	Gehrcke and Lau	1922	$\cdot293$
H_γ			$\cdot293$
H_γ	Wood	1922	$\cdot307$
H_α			$\cdot33$
H_β			$\cdot36$
H_γ	Shrum	1923	$\cdot37$
H_δ			$\cdot36$
H_ϵ			$\cdot35$

The mean of several older measurements by distinguished observers, such as Michelson, Fabry and Buisson, and others, is $\cdot298$ cm.$^{-1}$. It will be seen that while the earlier measurements, including those of Gehrcke and Lau, and of Wood, gave a value of about $\cdot30$ cm.$^{-1}$, which is nearly 20% too low, Shrum's results, obtained in McLennan's laboratory, agree with Sommerfeld's theory, and the separation has been measured for as many as five lines. This excellent confirmation is all the more welcome in that the lack of agreement between the earlier experiments and the theory was already being made a

* The effect is further complicated by the electric field in the discharge, which tends to produce a Stark effect.

basis for criticism of the theory,* in spite of the agreement furnished by ionised helium, to which we refer later. †

We have so far tacitly assumed that the initial orbits are simple. For a total quantum number 3, however, we should expect three close energy levels, corresponding to different values of k; for total quantum number 4, four levels; and so on. Each line of the doublet should therefore, it appears, have a fine structure of its own, owing to multiplicity of levels in the initial orbit. To begin with, however, the correspondence principle excludes some of the transitions, since k can only change by $+1$ or -1 in a quantum switch. ‡ To the final orbit 2_1 we can only have a return from one initial orbit, for which $k=2$, since $k=0$ is excluded. To the final orbit 2_2 we can only have a return from an initial orbit for which $k=1$ or $k=3$. That is, for all lines of the Balmer series we should apparently have a triplet when the structure of the higher levels is considered.

It is clear, however, from formula (20), that the energy differences between the various levels corresponding to different values of k for a fixed value of n become smaller as n increases. The wave number difference for a given n between orbits for which $k=1$ and $k=3$ is

$$\Delta\nu_n = RZ^4\alpha^2\frac{1}{n^2}\left[\frac{1}{n \cdot 1} - \frac{1}{n \cdot 3}\right]$$

or

$$\frac{\Delta\nu_n}{\Delta\nu_2} = \frac{1}{n^3} \cdot \frac{32}{3} \qquad\text{using (21)}$$

For $n=5$ $\Delta\nu_n = \cdot085\Delta\nu_2$; for $n=7$ $\Delta\nu_n = \cdot031\Delta\nu_2$.

---

* Cf. E. Lau, "Über die Frage der Feinstruktur ausgewählter Spektrallinien," *Phys. Zeitschr.* 25, 60, 1924.

† Since this was written Shrum's results have been criticised by L. Janicki ("Über die Balmerserie des Wasserstoffs," *Ann. d. Physik*, **76**, 561, 1925), who considers that they are vitiated by a neglect of certain physiological and photographic factors. As a result of a measurement of Shrum's photographs with a photometer free from subjective effects Janicki reduces Shrum's separations for H_α, H_β, H_γ to $\Delta\nu = \cdot302$, $\cdot322$, $\cdot318$ respectively. On the other hand, P. H. van Cittert ("Zur Messung der Feinstruktur der Wasserstofflinien," *Ann. d. Physik*, **77**, 372, 1925) criticises Gehrcke and Lau's measurements. He holds that a neglect of certain positive corrections has led to all their separations being too small. Still more recently W. V. Houstoun (*Nature*, **117**, 590, 1926) has measured the separations with great precision; his results are H_α $0\cdot316 \pm 0\cdot002$, H_β $0\cdot329 \pm 0\cdot005$, H_γ $0\cdot353 \pm 0\cdot007$.

‡ See Chapter XI., "The Selection Principle."

Hence for H_γ and H_ϵ the separation of two of the lines of the triplet is only 8 per cent. and 3 per cent. respectively of the doublet separation as calculated by considering the final orbit alone. The separation of the lines of the theoretical triplet are shown in Fig. 38 for H_α and H_ϵ. There is reason theoretically to suppose that the line shown strong in Fig. 38 is the most intense line. A fine structure of three components has not been obtained for any hydrogen line, even H_α, for which, as we have seen, the separation of the two closer lines is greatest.
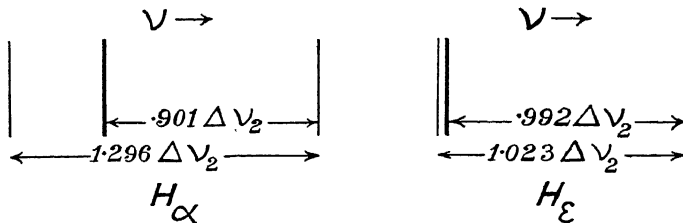
FIG 38.

Theoretical fine structure of hydrogen lines H_α and H_ϵ.

This is not surprising, when the smallness of the effect in question is taken into account. Hence what is measured experimentally is the separation of a line representing the two lines on the left, unresolved, and the line on the right. In the case of the higher numbers of the series, the two unresolved lines are so close that it makes little difference which part of the compound line is selected for measurement : in the case of H_α if the measurement is made from the stronger line of the unresolved pair the separation is smaller than if some point between the two lines be selected. Hence there is more uncertainty in the measurement of H_α than of the other lines.

It will be noted that, in Shrum's measurements, the result for H_α shows the greatest departure from the theoretical value.

It is interesting to observe that for the Lyman series the theory indicates no fine structure. The final orbit is here single, since $n=1$, and so k can only $=1$. For each initial orbit only one value of k is indicated, for by the correspondence principle $\Delta k = \pm 1$, and $k=0$ is excluded. Hence there is only one initial orbit, n_2, for each n, and only one final orbit, 1_1. No fine structure has been experimentally detected.

We turn to the case of ionised helium, where, since the effect in question is, from formula (20) or (21), proportional to Z^4, evidence of the details of fine structure should be somewhat easier to obtain. Again, the helium atom is heavier than the hydrogen atom, whence a smaller gas-kinetic velocity and sharper lines. Even in the case of helium, however, the problem is one to tax the powers of a skilled spectroscopist.

The detailed structure has been observed with the Fowler series of ionised helium, represented by the formula

$$\nu = 4R_{He}\left(\frac{1}{3^2} - \frac{1}{n^2}\right).$$

The final orbit has a quantum number 3 : the initial orbit has a quantum number 4, 5, 6, 7 and 8 for the lines of wave-length 4686, 3203, 2733, 2511, 2385 A.U. respectively. The line 4686 should therefore be a triplet, and, if all transitions were permitted, each line of the triplet should have four components. However, the selection principle ($\Delta k = \pm 1$) permits only five lines in place of twelve, the possible transitions being :

Final Orbit: $n' = 3$ Initial Orbit: $n = 4$

$$
\begin{array}{ccc}
k' = 3 & \longleftarrow & 4 = k \\
2 & & 3 \\
1 & & 2 \\
& & 1
\end{array}
$$

Actually Paschen, to whom we owe the investigation of the fine structure of the lines in question, has obtained, with a heavy spark discharge, *seven* components for $\lambda 4686$, of which two appear to be pairs of close lines, but with a direct current only six, two being very faint. The position of the components agrees excellently with the values theoretically computed by Sommerfeld in the way described. The occurrence, in feeble intensity, of components forbidden by the selection principle must be attributed to the beginning of a Stark effect : the electric field is more powerful for the spark discharge, which accounts for the new components which appear with the spark, but not with direct current. The *position* of the lines is the same in the case of spark discharge as with direct current. The strong

PLATE V.
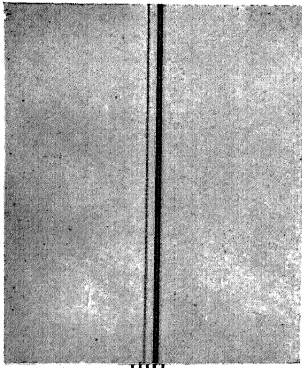
4685 6

Fig. 1.
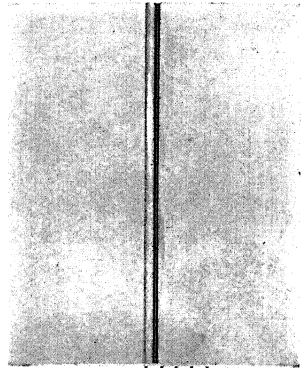
3203   4

Fig. 2.

Fine Structure of the Ionised Helium Lines 4686 and 3203.   (Paschen.)
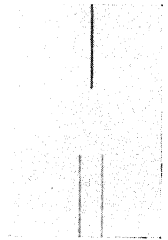
Fig. 3.

Normal Zeeman Effect.   (E. Back.)

p

s

Hδ   Hγ   Hβ
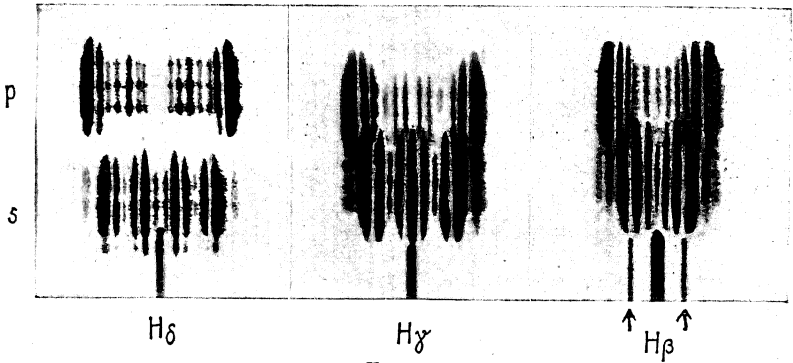
Fig. 4.

Transverse Stark Effect in Hydrogen.   (Stark.)

(The two lines indicated by arrows are ghosts of Hβ.)

components correspond in both cases to transitions permitted by the selection principle. Very good agreement has also been obtained in the case of the fine structure of $\lambda 3203$. Fig. 1 of Plate V. shows the fine structure of $\lambda 4686$, and Fig. 2 the fine structure of $\lambda 3203$, as obtained by Paschen with a helium tube of special construction excited by a 1000 volt accumulator battery. The former was obtained in the 3rd order of Paschen's large concave grating, the latter in the 4th order. Both photographs have been enlarged, but not retouched, for reproduction : 1 A.U. is represented by 4 mm. for $\lambda 4686$ and by 8 mm. for $\lambda 3203$. Of the six components detected for $\lambda 4686$ with direct current five can be distinguished in the reproduction : three plainly, and two with difficulty. The three strong components are representatives of the three groups due to the triple nature of the orbit of quantum number 3 : that at 4685·8 corresponds to the transition 4_4 to 3_3, while those at 4685·7 and 4685·4 correspond to transitions 4_3 to 3_2 and 4_2 to 3_1 respectively, all permitted by the selection principle. The three strong, easily visible components of $\lambda 3203$ likewise correspond to the three possible final orbits, the transition being, in order of decreasing wave-lengths, 5_4 to 3_3, 5_3 to 3_2, 5_2 to 3_1.

Paschen's investigation of the fine structure of the helium lines was carried out at the instigation of Sommerfeld, to test his theory of fine structure. The agreement, complete when the selection principle is considered, is one of the most brilliant confirmations of the quantum theory of the spectra of hydrogen-like atoms.

The Method of Secular Perturbations. For the cases of hydrogen-like atoms with orbits of two degrees of periodicity, which we consider in the remaining sections of this chapter, we shall use the method of Bohr. We have to deal with the important cases (1) of a hydrogen-like atom when the relativity change of mass of the moving electron is taken into account, a case which we have already treated by Sommerfeld's method ; (2) a hydrogen-like atom in a magnetic field, the case of the Zeeman effect ; (3) a hydrogen-like atom in an electric field, the case of the Stark effect. In all these cases we are concerned with a Kepler ellipse, which is a degenerate orbit of two degrees of freedom and one degree of periodicity, rendered

non-degenerate * by a disturbing influence which introduces a second degree of periodicity. Two quantum numbers are then required. When the second degree of periodicity is characterised by a frequency small compared to that of the original degree of periodicity, *i.e.* to the frequency in the undisturbed Kepler ellipse, Bohr's method admits of certain simplified and approximate methods of solution which suffice for the type of problem in hand.

In celestial mechanics elliptical orbits on which are imposed certain very slow progressive changes—in the most general case in size, shape and position—periodic with a period very long compared to that of the motion in the undisturbed orbit, are said to be subject to secular perturbations, and the same expression may be used in speaking of the class of atomic orbits under discussion. The orbit of the hydrogen electron when the relativity correction is taken into account is such an orbit, exemplifying a slow progressive change in the position of the orbit. The case where the shape of the orbit also undergoes a slow periodic change is illustrated by the Stark effect. An essential feature of Bohr's method is that the frequency of the slow variation of the orbit introduced by the disturbing field determines the additional energy due to the presence of this field. It may be added that the problem, obviously, cannot be treated by the method of adiabatic invariants, because the stationary states of the perturbed system have an extra quantising condition, compared to the undisturbed orbit.†

Fundamental for the method is the fact, pointed out by Bohr, that for systems subject to a small ‡ secular perturba-

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* Strictly speaking, we should say less degenerate, since a third degree of periodicity is possible for an orbit in space.

† Or, in other words, it may be said that for a change in the field to be adiabatic it must be small during a time in which the particle has come near to every point in the two-dimensional field which would be covered by the particle when executing a complete cycle of its disturbed motion. As the disturbances are made smaller and smaller the time which must elapse before the particle comes near to a point chosen at random in the field becomes longer and longer, and when at last the motion becomes simply periodic this time becomes infinite, since the particle never leaves the one ellipse. Hence the rate of change of the forces for an adiabatic transformation in this case is infinitely slow.

‡ The secular perturbation is small when λ, the ratio of the external disturbing forces to the internal forces, is small. The result is true, neglecting quantities of the order λ^2.

tion the additional energy E_F, due to the work done by the disturbing field on the particle during the establishment of the field, is equal to the mean value of the potential of the disturbing force taken over a period of the motion of the undisturbed state. Expressed in symbols, if Ω be the potential energy of the disturbing forces, then

$$\psi = \frac{1}{T}\int_0^T \Omega \, . \, dt = E_F. \quad \dots\dots\dots\dots\dots\dots(22)$$

The cycle of changes which the orbit executes does not depend upon the magnitude of Ω, which merely governs the rate at which the cycle is executed, *i.e.* the new frequency ω_F. The potential of the particle with reference to the external field will, in general, vary with the time during a period, but its mean value over a period will be constant. These are results which Bohr has deduced mechanically: they will here be taken as proved.

We may call the energy of the particle, apart from the potential energy due to the disturbing field, the internal energy of the system. Since the total energy of the particle must be constant with the time for a given field, from the conservation of energy, it follows that the mean value of the internal energy does not vary with the time, and also, since the additional energy depends only on the magnitude of the field and the undisturbed motion of the system (to the approximation considered), that this mean value does not change when the field changes. It is the external potential which changes with the field.

We have stated that the additional energy depends upon the frequency of the periodic disturbance introduced by the disturbing field. We now proceed to consider this point a little closer, by examining what simplification can be introduced into the general equation when the second periodicity is produced by a small disturbance of a degenerate system.

For two periodicities we have from (10) the general condition

$$\delta E = \omega_1 \, \delta J_1 + \omega_2 \, \delta J_2, \quad \dots\dots\dots\dots\dots\dots(10a)$$

where δE is the difference in total energy, and δJ_1, δJ_2 the differences in J_1 and J_2, between two near orbits of the kind

characterised by the frequencies ω_1 and ω_2. In a degenerate system we have from (7) $\omega_1 = s\omega_2$, where s is a whole number.* Using as coordinates of the degenerate curve r and θ, we have from (11)

$$\omega_2 J = \omega_1 \oint p_\theta \, d\theta + \omega_2 \oint p_r \, dr,$$

where J is the whole action in the degenerate system, since the frequency of the degenerate motion will be the lesser frequency, and hence

$$J = sJ_1 + J_2,$$

where J_1 is the generalised momentum corresponding to θ. We can write (10) in the form

$$\delta E = \omega_2(s \, \delta J_1 + \delta J_2) + (\omega_1 - s\omega_2)\delta J_1 \quad \ldots\ldots\ldots\ldots (23)$$

where now ω_1 is the frequency corresponding to θ. In the undisturbed, degenerate state $\omega_1 = s\omega_2$; in the disturbed state $(\omega_1 - s\omega_2)$ differs from zero by a small quantity which expresses the frequency of the slow variations which the orbit undergoes in consequence of the disturbing field. We shall denote this frequency by

$$\omega_F = \omega_1 - s\omega_2.$$

Now consider various states of the perturbed system corresponding to a state of the undisturbed system for which

$$J = sJ_1 + J_2 = nh,$$

n being the principal quantum number, by definition. For any two neighbouring states the difference of J

$$= \delta J = s \, \delta J_1 + \delta J_2 = 0,$$

since the motion in a stationary state of a perturbed system differs only slightly at any moment from the motion in the unperturbed system. Hence, if the energy of the perturbed system $= E_n + E_F$, where E_n is the energy in the state of the unperturbed system for which

$$J = nh,$$

---

* For instance in the Kepler ellipse $J = J_r + J_\theta$, since r and θ complete a cycle together, while in the case of an elliptic orbit with the attracting body at the centre of the ellipse, which is well known to be the case when the attraction varies directly as the distance, $J = 2J_r + J_\theta$, since the radius completes a cycle twice while the angle does a cycle once. In the most general case $J = s_1 J_1 + s_2 J_2$, where s_1 and s_2 are whole numbers, but the above is assumed for simplicity.

then from (23)

$$\delta E_F = \omega_F \, \delta J_1. \quad \ldots\ldots\ldots\ldots\ldots\ldots(24)$$

J_1 is, of course, the angular momentum of the electron in its orbit, as distinct from J, which is the total action, and includes the radial part. In our application of (24) we shall therefore require to find the angular momentum.

Equation (24) is fundamental for the treatment of perturbed systems. It connects the energy due to the disturbing field with the frequency of the disturbance introduced by the field. If there be more than one kind of disturbance the formula can be shown to be

$$\delta E_F = \sum_1^{s-1} \omega_F \, \delta J_F;$$

but this generalisation will not concern us here.

Fine Structure by the Method of Perturbations. We proceed to consider the way in which the method of perturbations can be made to give the fine structure of lines for a hydrogen-like atom.

In discussing Sommerfeld's work on this subject it was stated that the effect of the relativity change of mass is to make the perihelion rotate at such a rate that the angle at which r attains its maximum value advance by $2\pi\left(\dfrac{1}{\gamma} - 1\right)$ for each revolution of the electron in its orbit, where $\gamma^2 = 1 - \left(\dfrac{Ze^2}{pc}\right)^2$. At the end of a complete cycle, *i.e.* when the orbit has returned to approximately its original position, the angle will have advanced by 2π, while the electron has made $2\pi / 2\pi\left(\dfrac{1}{\gamma} - 1\right) = \dfrac{\gamma}{1 - \gamma}$ revolutions. Hence the frequency of the motion of perihelion

$$= \omega_F = \omega \frac{1 - \gamma}{\gamma} = \tfrac{1}{2}\omega\left(\frac{Ze^2}{pc}\right)^2, \quad \ldots\ldots\ldots\ldots\ldots(25)$$

neglecting squares and higher powers of small quantities.

Now such a rotation of perihelion can be produced with a particle whose mass is *not* a function of the velocity by adding to the central force $\dfrac{Ze^2}{r^2}$ an inverse cube term $\dfrac{A}{r^3}$, and by adjusting A the rate of rotation can be made the same as in the

relativity case. This can easily be shown from the theory of the central orbit. Starting with the standard equation

$$\frac{d^2u}{d\theta^2} + u - \frac{m}{p^2u^2}P = 0,$$

where $u = \frac{1}{r}$ and P is the central force, we have

$$\frac{d^2u}{d\theta^2} + u - \frac{m}{p^2}(Ze^2 + Au) = 0.$$

Hence
$$\frac{1}{1 - \frac{Am}{p^2}} \cdot \frac{d^2u}{d\theta^2} + u - \frac{Ze^2m}{p^2 - Am^2} = 0 \; ;$$

$$\therefore \; u - \frac{Ze^2m}{p^2 - Am^2} = a \cos\left(1 - \frac{Am}{p^2}\right)^{\frac{1}{2}} \cdot \theta,$$

or
$$u = \frac{1}{r} = \frac{Ze^2m}{p^2 - Am^2}\left\{1 + n \cos\left(1 - \frac{Am}{p^2}\right)^{\frac{1}{2}}\theta\right\},$$

where n is an arbitrary constant.

To make this give the same frequency of rotation of perihelion as obtains in the rotating orbit, we must put

$$1 - \frac{Am}{p^2} = \gamma^2 = 1 - \left(\frac{Ze^2}{pc}\right)^2.$$

Hence
$$A = \frac{Z^2e^4}{mc^2}.$$

We wish to treat the problem as the case of a degenerate motion, of one degree of periodicity, slightly disturbed. If we impose on the orbit in which a relativity change of mass is making itself evident an inverse cube term of the magnitude just derived, then we shall annul the relativity motion of the perihelion, and have an orbit of one degree of periodicity. The shape of the orbit is not, however, left unaffected, although the period is, and the moment of momentum no longer bears the same relation to the energy as it does in a simple Keplerian ellipse described under the inverse square law alone, so that the

quantum condition is modified. The energy of a stationary state of this system can be shown to be

$$E' = -\frac{2\pi^2 Z^2 e^4 m}{h^2 n^2}\left(1 - \frac{3\pi^2 Z^2 e^4}{c^2 h^2 n^2}\right),$$

which, of course, involves one quantum number, n, only.

This expression is derived most simply by considering a circular orbit, with inverse cube terms and relativity effect; since we have an orbit of one degree of periodicity the result obtained for the circle will have general validity. The equations for the circular orbit are

$$\frac{m_0}{(1-\beta^2)^{\frac{1}{2}}}\frac{v^2}{r} = \frac{Ze^2}{r^2} - \frac{Z^2 e^4}{m_0 c^2}\frac{1}{r^3}$$

(equation of motion),

$$\frac{m_0}{(1-\beta^2)^{\frac{1}{2}}}\,vr = \frac{nh}{2\pi} \quad \text{(quantising equation)},$$

since the relativity mass $= m = \dfrac{m_0}{(1-\beta^2)^{\frac{1}{2}}}$.

Further, using the relativity expression for the kinetic energy,

$$\text{total energy} = E = -\frac{Ze^2}{r} + \frac{Z^2 e^4}{2c^2 m_0}\cdot\frac{1}{r^2} + m_0 c^2\left(\frac{1}{(1-\beta^2)^{\frac{1}{2}}} - 1\right).$$

We are considering an approximate solution only, since we are going finally to apply the method of perturbations, which only applies if the ratio of the disturbing force to the internal forces is small. We shall therefore neglect in the final result for the circular orbit higher powers of β than the square. To this approximation, remembering $v = \beta c$, we have

$$\frac{m_0}{(1-\beta^2)^{\frac{1}{2}}}\cdot c^2\beta^2 = m_0 c^2\beta^2 = \frac{Ze^2}{r} - \frac{Z^2 e^4}{m_0 c^2 r}, \quad \ldots\ldots\ldots\ldots(1)$$

$$\frac{m_0}{(1-\beta^2)^{\frac{1}{2}}}\cdot \beta cr = m_0\beta cr\left(1+\tfrac{1}{2}\beta^2\right) = \frac{nh}{2\pi}; \quad \ldots\ldots\ldots\ldots(2)$$

$$\therefore \frac{1}{r} = \frac{2\pi m_0 c\beta}{nh}\left(1+\tfrac{1}{2}\beta^2\right). \quad \ldots\ldots\ldots\ldots(3)$$

From (1),
$$c^2\beta^2 = \frac{Ze^2 2\pi m_0 c\beta}{nh}(1 + \tfrac{1}{2}\beta^2) - \frac{Z^2e^4}{c^2} \cdot \frac{4\pi^2 m_0 c^2 \beta^2}{n^2 h^2}.$$

This gives, to our order of approximation,

$$c\beta\left(1 + \frac{Z^2\alpha^2}{n^2}\right) = \frac{Zac}{n}(1 + \tfrac{1}{2}\beta^2)$$

$$= \frac{Zac}{n}\left(1 + \tfrac{1}{2}\frac{Z^2\alpha^2}{n^2}\right)$$

or

$$\beta = \frac{Za}{n}\left(1 - \tfrac{1}{2}\frac{Z^2\alpha^2}{n^2}\right),$$

where we have put $a = \dfrac{2\pi e^2}{hc}$, as we did earlier (p. 234).

From (3),
$$\frac{1}{r} = \frac{2\pi m_0 c Z\alpha}{n^2 h}(1 - \tfrac{1}{2}\beta^2)(1 + \tfrac{1}{2}\beta^2) = \frac{2\pi m_0 c Z\alpha}{n^2 h}.$$

Total energy
$$= -\frac{Ze^2}{r} + \frac{Z^2e^4}{2c^2 m_0} \cdot \frac{1}{r^2} + m_0 c^2(\tfrac{1}{2}\beta^2 + \tfrac{3}{8}\beta^4)$$

$$= -\frac{Z^2\alpha^2 c^2 m_0}{n^2} + \frac{Z^4\alpha^4 c^2 m_0}{2n^4}$$

$$+ m_0 c^2\left\{\tfrac{1}{2}\frac{Z^2\alpha^2}{n^2}\cdot\left(1 - \frac{Z^2\alpha^2}{n^2}\right) + \tfrac{3}{8}\frac{Z^4\alpha^4}{n^4}\right\}$$

$$= -\tfrac{1}{2}\frac{Z^2\alpha^2 c^2 m_0}{n^2}\left(1 - \tfrac{3}{4}\frac{Z^2\alpha^2}{n^2}\right)$$

$$= -\frac{2\pi^2 Z^2 e^4 m_0}{h^2 n^2}\left(1 - \frac{3\pi^2 Z^2 e^4}{c^2 h^2 n^2}\right)$$

$$= E',$$

as required.

If we now remove the inverse cube field we shall have the true case of the relativity effect. To do this we have to add an inverse cube term of opposite sign, which gives us the case of an orbit of one degree of periodicity perturbed by a small force. We know that the additional energy in such a case is given by

$$\delta E_F = \omega_F\, \delta J_F. \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots(24)$$

J_F, which is the azimuthal J, is given by the J_θ for the undisturbed system, or

$$J_F = \int p \, d\theta = 2\pi p,$$

since the modification of J_θ caused by rotation of perihelion will affect E_F to the second order of small quantities only.

Hence, using (24) and (25),

$$\delta E_F = \omega_F \cdot \delta J_F = \tfrac{1}{2}\omega \left(\frac{Ze^2}{c}\right)^2 \frac{1}{p^2} \cdot \delta J_F$$

$$= \tfrac{1}{2}\omega \left(\frac{Ze^2}{c}\right)^2 4\pi^2 \frac{\delta J_F}{J_F^2};$$

$$\therefore E_F = -2\pi^2 \omega \frac{Z^2 e^4}{c^2} \cdot \frac{1}{J_F}.$$

But
$$\omega = \frac{4\pi^2 m Z^2 e^4}{n^3 h^3}, \quad \text{p. 192,}$$

and the quantising condition for J_F is $J_F = kh$;

$$\therefore E_F = -\frac{8\pi^4 m Z^4 e^8}{h^4 c^2} \cdot \frac{1}{n^3 k}$$

$$= -\frac{RZ^2 hc}{n^2} \cdot \frac{4\pi^2 e^4 Z^2}{h^2 c^2} \cdot \frac{1}{nk}.$$

Adding this to the expression for E', the energy of the orbit of one periodicity which we have perturbed, we have

$$E = E' + E_F = -\frac{RZ^2 hc}{n^2}\left\{1 + \frac{\pi^2 Z^2 e^4}{c^2 h^2}\left(-\frac{3}{n^2} + \frac{4}{nk}\right)\right\}$$

$$= -\frac{RZ^2 hc}{n^2}\left\{1 + \alpha^2 Z^2\left(-\frac{3}{4n^2} + \frac{1}{nk}\right)\right\},$$

where $\alpha = \dfrac{2\pi e^2}{hc}$, as before. This agrees with the formula (20) derived by Sommerfeld.

It must be noted that this formula is an approximation only, just as formula (20) is an approximation, derived from (19) by neglecting the fourth power, and higher powers, of αZ. When greater accuracy is required, as in applications of the formula

to X ray spectra, where Z may be large, Sommerfeld's full formula must be used.

The Zeeman Effect. Zeeman's celebrated discovery that a magnetic field influences the spectral character of the light emitted by atoms in its neighbourhood not only provided the first experimental indication that light is generated by the movement of atomic electrons, but has ever since afforded one of the most important guides in all spectral theories. We shall have to speak of the transverse and of the longitudinal Zeeman effect. It may therefore be recalled that the former refers to the appearance of a given spectral line when the observer looks along a direction at right angles to the magnetic field, while the latter refers to the appearance when the observer looks along the lines of magnetic force.

We must now distinguish between the normal and the anomalous Zeeman effect. Taking first the normal effect, which is of comparatively rare occurrence, in the longitudinal case the single line is replaced by a circularly polarised doublet, the two lines of the doublet being polarised in opposite directions, and symmetrically disposed about the position of the original line. In the transverse case we have a plane polarised triplet, the central line of the triplet coinciding in position with the original line, and the other two being symmetrically placed. The vibration in the case of the central line is parallel to the lines of force of the magnetic field, in the other two lines at right angles to the lines of force. The effects are diagrammatically represented in Fig. 39. The transverse and longitudinal effects are, of course, not two different modifications of the behaviour of the luminous atoms, but different ways of looking at the same luminous atoms with respect to the direction of the magnetic field, the appearance varying with

Direction of observation

Direction of observation

FIG. 39.

Normal Zeeman effect.

Above, longitudinal effect; below, transverse effect.

the direction of observation. For instance, on H. A. Lorentz's original explanation of the effect, which, in accordance with classical electro-dynamics, attributed the light emission to electrons executing periodic motions with frequencies equal to those of the observed light, the central line in the transverse effect is due to an electron vibrating parallel to the magnetic field : electrons executing such a motion, which are clearly the only ones whose periods will be unaffected by the magnetic field, will not emit any radiation in the direction of the lines of magnetic force, so that in the longitudinal effect the central line is missing. Fig. 3, Plate V., shows the normal Zeeman effect in the transverse case, observed through a polarising prism, set in one case parallel to, in the other case across, the direction of the magnetic field. (The upper picture corresponds to electric vibrations parallel to the lines of magnetic force, the lower one to vibrations at right angles to the lines.) In general it suffices to consider the transverse effect, since the longitudinal appearance can be deduced from it.

The anomalous Zeeman effect is characterised by the appearance of a greater number of components than three. The normal Zeeman effect is shown by hydrogen lines and also by singlet lines in other spectra, such as lines of the singlet series of cadmium, of which the line $\lambda = 6438 \cdot 71$ A.U. shown in Fig. 3, Plate V., is one, although in the case of these singlet lines the simplicity is rather adventitious than inherent, as will be seen in Chapter XV. The anomalous Zeeman effect was long without any quantitative explanation, but during the last few years the various phenomena have been explained, or described rather, by the help of additional quantum numbers. Consideration of the anomalous effect is postponed to Chapter XV.; it is mentioned here merely to warn the reader that the theory about to be developed is of application only to the simple case of the normal effect. In the case of both normal and anomalous effect the shifts are accurately proportional to the strength of the field.*

It may be mentioned here that the normal effect was explained many years ago by the well-known theory of H. A. Lorentz,

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* In the case of the anomalous effect, so long as the field is not too strong. Cf. the discussion of the Paschen-Back effect in Chapter XV.

already mentioned. It is necessary now to show that it can be equally well explained on the quantum theory. We restrict ourselves here to the case of the hydrogen-like atom, as throughout this chapter.

The quantum explanation given by Bohr rests upon the method of perturbations, taken in conjunction with a theorem of Larmor's. This theorem* states that the effect of a magnetic field H on a system of electric charges revolving round one another under their mutual forces is simply to impose on the undisturbed motion of the system a rotation with angular velocity $\dfrac{eH}{2mc}$ around the direction of the field as axis, e being measured in electrostatic and H in electromagnetic units.†
Instead of the angular velocity $\alpha = \dfrac{eH}{2mc}$ we generally use the frequency $\omega_H = \dfrac{\alpha}{2\pi} = \dfrac{eH}{4\pi mc}$.

The Larmor precession is represented diagrammatically in Fig. 40, where the upper circle represents the path of aphelion, the lower the path of perihelion.

* *Aether and Matter*, p. 341. *Phil. Mag.*, **44**, 503, 1897.

† The theorem is easily proved in the simple case where the magnetic field is perpendicular to the plane of the orbit. Let the magnetic field be along the axis of z: then the equations of motion of an electron are

$$\left.\begin{array}{l} m\ddot{x} - \dfrac{eH}{c}\,\dot{y} = X, \\[2mm] m\ddot{y} + \dfrac{eH}{c}\,\dot{x} = Y, \end{array}\right\} \quad \dots\dots\dots\dots\dots\dots\dots(A)$$

X and Y being the components of the forces, due to the presence of other charges, acting on the electron. Now if we refer the original motion, without magnetic field, to axes rotating about z, α being the angular velocity of rotation, we have

$$\left.\begin{array}{l} m\ddot{x} - 2\alpha m\dot{y} - mx\alpha^2 = X, \\[1mm] m\ddot{y} + 2\alpha m\dot{x} - my\alpha^2 = Y. \end{array}\right\} \quad \dots\dots\dots\dots\dots\dots(B)$$

If we put $\dfrac{eH}{c} = 2\alpha m$ equations (A) and (B) become identical except for terms in α^2, which are negligible, since $\alpha = \dfrac{eH}{2mc}$ is small for any practicable field : in other words, the added velocity due to the rotation is small compared to the velocity in the orbit. We see, then, that a rotation of the angular velocity $\dfrac{eH}{2mc}$ is equivalent to the effect of the magnetic field H.

The effect of a slow rotation of the plane of the orbit on an orbital motion of original frequency ω is to introduce new frequencies $\omega \pm \omega_H$. For suppose the axis of z taken along
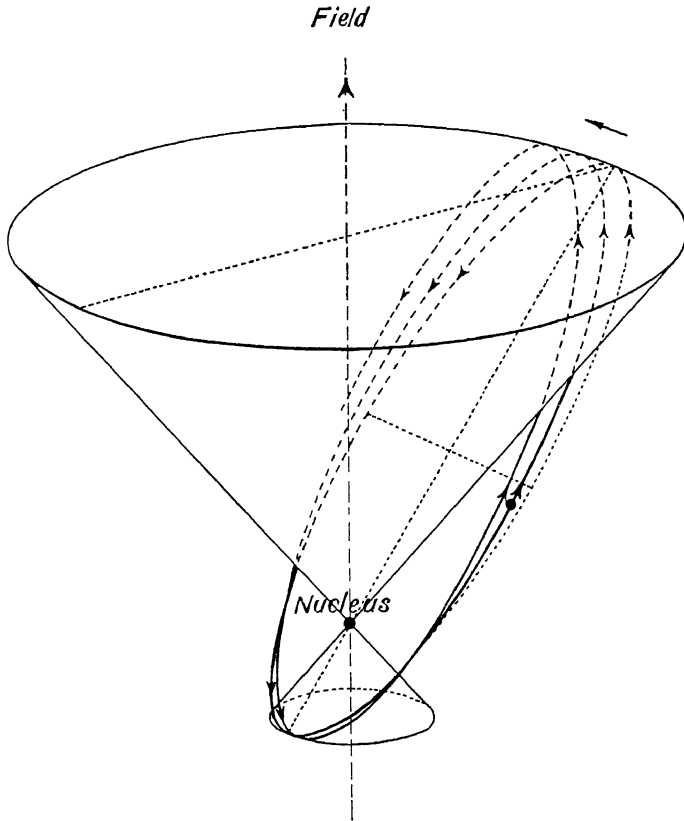
Field

FIG. 40.

Larmor precession.

the magnetic field, and that the x and y components of the original periodic motion be written, as before,

$$\begin{aligned} \xi &= \Sigma C_\tau \cos\left(2\pi\tau\omega t + \gamma_\tau\right), \\ \eta &= \Sigma B_\tau \cos\left(2\pi\tau\omega t + \beta_\tau\right). \end{aligned} \right\} \quad \ldots\ldots\ldots\ldots\ldots(26)$$

Owing to the rotation, with angular velocity $2\pi\omega_H$, of the xy

frame of reference, any harmonic component of the x coordinate becomes

$$\xi = C_\tau \cos\left(2\pi\tau\omega t + \gamma_\tau\right)\cos 2\pi\tau\omega_H t$$
$$- B_\tau \cos\left(2\pi\tau\omega t + \beta_\tau\right)\sin 2\pi\omega_H t$$
$$= M_\tau \cos\left\{2\pi(\tau\omega + \omega_H)t + \mu_\tau\right\} + N_\tau \cos\left\{2\pi(\tau\omega - \omega_H)t + \nu_\tau\right\},$$

where M_τ, N_τ, μ_τ, ν_τ are fresh constants, easily obtainable in terms of C_τ, B_τ, γ_τ, β_τ by simple trigonometry. Similarly, the τ constituent of the y coordinate becomes

$$\eta = M_\tau \sin\left\{2\pi(\tau\omega + \omega_H)t + \mu_\tau\right\} - N_\tau \cos\left\{2\pi(\tau\omega - \omega_H)t + \nu_\tau\right\}.$$

Hence the harmonic of frequency $\tau\omega$ of the elliptic vibration expressed by (26), where $C_\tau \neq B_\tau$, is replaced by two circular harmonic vibrations, of different amplitudes, one of which is of frequency $\tau\omega + \omega_H$, while the other is of frequency $\tau\omega - \omega_H$, while the rotation is in opposite directions. Using Bohr's notation, by which the constant corresponding to the value $\tau\omega + \omega_H$ is written $C_{\tau, +1}$, and the constant corresponding to the value $\tau\omega - \omega_H$ is written $C_{\tau, -1}$, we may summarise this result by saying that owing to the superposed rotation the motion becomes

$$\xi = \Sigma C_{\tau, \pm 1} \cos\left\{2\pi(\tau\omega \pm \omega_H)t + \gamma_{\tau, \pm 1}\right\} \quad\ldots\ldots\ldots\ldots(27)$$

with a similar expression for η. The periodicity of ζ is, of course, unaffected by the magnetic field.

The transformation of (26) into (27) as the result of the superposition of a rotation of frequency ω_H on the periodic orbit of frequency ω is of very great importance for the general theory of spectra, and will be used in Chapter XI.

The result of the magnetic field is, then, neglecting quantities of the order $\left(\dfrac{eH}{2mc}\right)^2$, to make of the simply periodic orbit an orbit of double periodicity, with the fundamental frequencies ω and ω_H. We therefore have two quantum conditions

$$J = nh, \quad J_H = n_H h,$$

and also $\qquad\qquad \delta E_H = \omega_H \delta J_H.$

Now this integrates at once, for ω_H is, we have seen, independent of J_H, and the constant of integration zero, from the conditions.

Hence $\quad E = E_n + \omega_H J_H$

$$= -\frac{2\pi^2 Z^2 e^4 m}{h^2}\frac{1}{n^2} + \frac{heH}{4\pi mc} n_H$$

$$= -W$$

and $\qquad \nu = \frac{1}{hc}\,(W' - W)$

$$= \frac{2\pi^2 Z^2 e^4 m}{ch^3}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) + \frac{eH}{4\pi mc^2}\,(n'_H - n_H),\;\;\ldots\ldots\ldots(28)$$

where the second expression on the right-hand side represents the difference of wave number between the original line and the components occasioned by the magnetic field. Since n'_H and n_H can have any whole number values, it might be supposed at first that our theory would indicate as components in the Zeeman effect lines whose wave number difference was any whole number multiple of $\dfrac{eH}{4\pi mc^2}$. The correspondence principle, however, shows us that this is not so. According to this principle a transition such as that denoted by (28) is conditioned by the presence of a harmonic component of frequency $(n' - n)\omega + (n'_H - n_H)\,\omega_H$ in the expression (27) for the electric moment of the orbital motion of the electron. Now, whereas we have in (27) all possible frequencies $\tau\omega$, where τ is any whole number, we have as multiples of the frequency ω_H only 1 and -1. Hence, by the principle, only transitions for which $n'_H - n_H = \pm 1$ are possible. Equation (28) must therefore be interpreted as follows : the result of a magnetic field H is to give in place of a line of wave number $Z^2 R \left(\dfrac{1}{n'^2} - \dfrac{1}{n^2}\right)$ two lines of wave number

$$Z^2 R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) \pm \frac{eH}{4\pi mc^2}\,.$$

Since the components of the moment which have been considered in deriving this expression were normal to the direction of the field the two lines will be plane polarised if the direction of observation be normal to the direction of the field : on the other hand they will be circularly polarised in opposite directions if the observer looks along the lines of magnetic force,

as can be seen by considering the argument preceding equation (27). This deduction illustrates the application of the correspondence principle to questions of polarisation.

The ζ component has not yet been considered : its frequency, as was pointed out, is unaffected by the field. On classical theory a vibration along the z axis will emit no radiation along that axis, but will send out a plane polarised radiation along any line in the xy plane. Hence, by the correspondence principle, we have, in addition to the two components mentioned above, a plane polarised component (whose plane of polarisation is at right angles to that of the other two components) for transverse observation, but no additional component for longitudinal observation. The quantum theory, with the help of the correspondence principle, furnishes, therefore, a complete explanation of the normal Zeeman effect.

We have already mentioned that an explanation of the effect, based on classical electrodynamic theory, was furnished by H. A. Lorentz at the end of the last century. Accordingly we should expect the expression for the displacement of the components to be free from quantum constants, and it may be noted that this is the case, h having divided out in the second expression in equation (28).

The Stark Effect. In contradistinction to the case of the normal Zeeman effect, the Stark effect of an electric field on spectral lines, discovered by Johannes Stark in 1913, cannot be satisfactorily treated on the classical theory : its explanation is one of the triumphs of the quantum theory.

The experimental difficulty, owing to which the discovery was long delayed, of establishing the effect, is due to the fact that the spectral emission usually takes place in the presence of strongly ionised gas, which is too conducting to allow the establishment of the necessary strong electric field. The canal rays, however, may be made to pass in a low vacuum, where a special disposition of electrodes enables the effect to be observed. The arrangement adopted by Stark is shown in Fig. 41. AA is the anode : close behind the pierced cathode CC is placed a parallel plate FF. Between AA and CC is established the field which produces the canal rays passing through the holes in CC ; between FF and CC the field which produces the

Stark effect. The distance of FF from CC is about 3 mm. or less, and the gas pressure such that the length of the cathode dark space is several cms. In such a case a very large potential gradient can be maintained between FF and CC without a discharge setting in, since the mean free path of the ions is much greater than the distance between the plates, and so there is no cumulative production of secondary ions by collision.
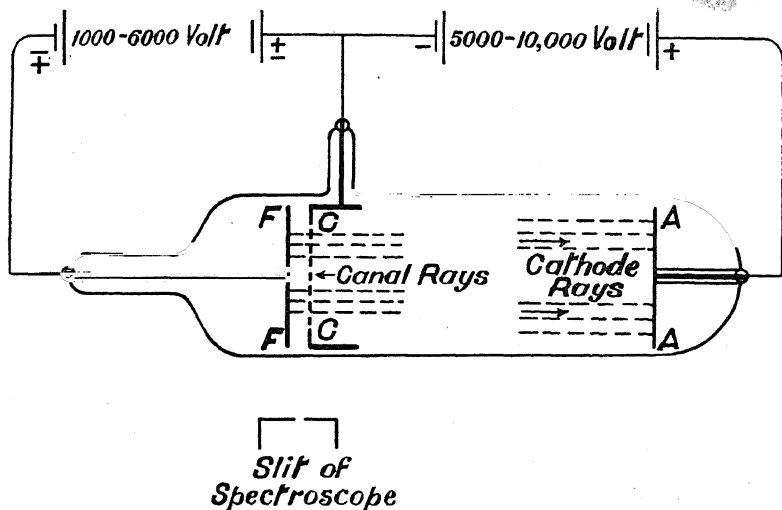
FIG. 41.

Experimental arrangement for obtaining the transverse Stark effect.

The closeness of FF and CC is a necessary condition for the success of the method.* Shortly after Stark announced the discovery of the effect Lo Surdo showed that the effect could be observed in front of the cathode, where the canal rays, accelerated towards the cathode, pass through the strong field which exists between the cathode and the negative glow (the region of the well-known cathode fall of potential). Lo Surdo's

* Professor R. W. Whiddington, lecturing in May, 1925, at the Royal Institute on the discharge of electricity through exhausted tubes, showed an experiment which illustrates admirably the fact of which Stark took advantage. A tube, actuated by a very steady potential difference, was furnished with parallel plate electrodes, the distance between which could be gradually varied without disturbing the pressure of the residual gas in the tube. When the electrodes were approached so that the anode came within the edge of the cathode dark space, the discharge went out.

method has the advantage that the spectral emission is of considerable intensity, but it is not so well adapted as Stark's for quantitative work.

Just as with the Zeeman effect there is a longitudinal and a transverse Stark effect. The arrangement of Fig. 41 is adapted for the observation of the transverse effect, for which the direction of observation is normal to the direction of the electric field. The longitudinal effect is not so important, again as in the case of Zeeman effect, since in the transverse effect we observe light corresponding on the classical theory to vibrations both parallel to and across the lines of electric force, whereas in the longitudinal case we observe only light corresponding to vibrations across the lines. Stark has, however, obtained the longitudinal effect by the special disposition of the anode represented in Fig. 42, which is self explanatory.
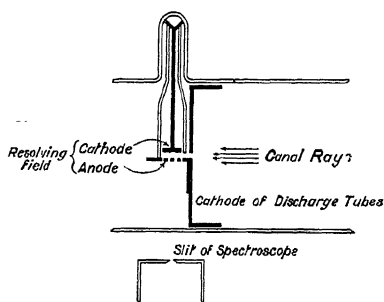
FIG. 42.

Experimental arrangement for obtaining the longitudinal Stark effect.

In the transverse case the components are linearly polarised, some, the so-called s components, at right angles to the field ; others, the p components, parallel to it. In the longitudinal case there are only unpolarised components, which coincide in position with the s components of the transverse case. These features are represented diagrammatically in Fig. 43, which represents the effect in the case of the hydrogen line H_a in a very strong field. Fig. 44 exhibits the transverse effect, which, as explained, includes all the information, for H_a and H_β, s and p components being shown separately. The lengths of the lines in this figure represent the intensities of the components. Fig. 4, Plate V., shows the actual photographs of the transverse effect in this field for the hydrogen lines H_β, H_γ, H_δ, the uppermost part of each picture showing the p components, for which the electrical vibration is parallel to the field, the middle part the components vibrating across the field, and the lower part the unresolved line without field.

To explain the Stark effect we have to consider the nature of the perturbation of the elliptic orbit brought about by a uniform electric field. Unlike the case of the relativity correction, of the Zeeman effect, and the case, to be considered in the next chapter, where a symmetrical distribution of electrons round the nucleus disturbs the field,
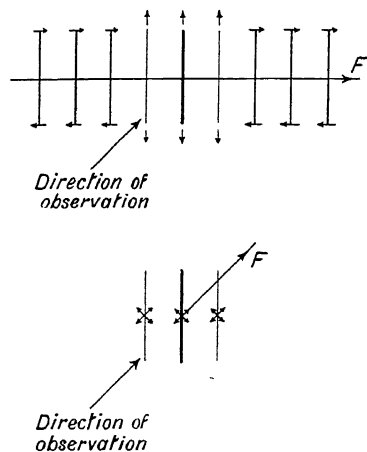
FIG. 43.

Transverse and longitudinal Stark effect contrasted : transverse effect above, longitudinal below.
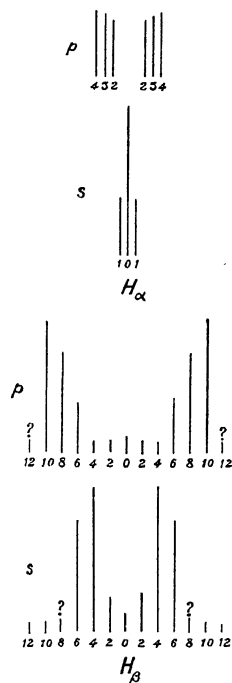
FIG. 44.

Experimental transverse Stark effect for H_α and H_β lines.

the force is here no longer a central force, and the disturbance is correspondingly more complicated. We shall take some of the results of calculation for granted, and indicate in outline the method by which Bohr has treated the problem.

It is necessary first of all to consider what is known as the "electrical centre" of the orbit, *i.e.* such a point that, if the electron were permanently fixed there, the value of the potential energy, due to the external field, would be the same as the actual time average of the potential energy when the electron describes its orbit. As usual in the method of perturbation, to a first approximation we can, for this purpose, take the orbit as being

truly elliptical, although it is actually disturbed. Considerations of symmetry show that the electrical centre must lie on the major axis : let it be distant d from the nucleus, the occupied focus, and let φ be the angle which the major axis makes

FIG. 45.

The orbit in the Stark effect.

with the axis of z, which we take as the direction of the electric field, strength F. Let r, θ be the polar coordinates of the electron in the plane of the elliptic orbit. Then if T is the undisturbed period of the motion in the ellipse, by definition of d,

$$\text{average potential energy} = \psi = Fe\,d\cos\varphi$$

$$= \frac{1}{T}\int_0^T eFz\,dt = \frac{1}{T}\int_0^T eFr\cos\theta\cos\varphi\,.\,dt$$

$$= eF\cos\varphi\,\frac{1}{T}\int_0^T r\cos\theta\,.\,dt.$$

If u is the eccentric angle, measured, like θ, from aphelion, and n be the mean angular speed with which the radius vector rotates, then

$$r \cos \theta = a(\cos u + \epsilon), \quad nt = \epsilon \sin u + u$$

and

$$n \, dt = (1 + \epsilon \cos u) \, du.$$

Hence

$$\psi = eF \cos \varphi \, \frac{1}{Tn} \int_0^{2\pi} a(\cos u + \epsilon)(1 + \epsilon \cos u) \, du$$

$$= eF \cos \varphi \, \frac{1}{2\pi} \, a3\pi\epsilon = eF \cos \varphi \, \tfrac{3}{2}\epsilon a, \quad \ldots\ldots (29)$$

so that

$$d = \tfrac{3}{2}\epsilon a,$$

or the electric centre is on the major axis midway between the centre of the ellipse and the empty focus.

By the general properties of the orbit subject to secular perturbations, as described on p. 241, ψ must be constant throughout the motion, so the electric centre must move in a plane $z = \tfrac{3}{2}a\epsilon \cos \varphi$ normal to the direction of F. Further, the additional energy due to the disturbing field is equal to the time average of the potential energy due to the field, or, if E_0 is the energy of the undisturbed elliptic orbit, and the value of a, given by equation (9) of Chapter IX., be substituted in (29),

$$\text{total energy} = E_0 + \psi = \frac{-2\pi^2 m e^4 Z^2}{h^2 n^2} + \frac{3h^2 n^2}{8\pi^2 Z e m} \, F \, \epsilon \cos \varphi. \quad \ldots\ldots (30)$$

Since this is not to vary with the time, the orbit must move so that $\epsilon \cos \varphi$ is constant, but ϵ and φ may change with the time. This is not, of course, the final solution of our problem of the total energy, since we have not yet seen how to quantise $\cos \varphi$. We proceed to introduce the second quantum number.

The actual movement of the ellipse has been worked out by Bohr. Let NN' be the nodes, where the orbit cuts the x, y plane through the nucleus S. The line NN' will rotate, while at the same time the perihelion P librates about the line SR, perpendicular to NN' and in the plane of the orbit. For one revolution of NN' there are two vibrations of P. The eccentricity and the inclination φ of the orbit both vary, but the electrical centre C maintains a constant distance from the xy plane. It is with the periodic motion of this centre that we are

concerned, for its period is the secular period which is connected with the additional energy in the way which has been utilised in the other secular disturbances which we have considered. This motion is simply periodic in a closed ellipse : the secular motion is therefore degenerate. The frequency turns out to be independent of ϵ and φ : it is given by the expression

$$\omega_F = \frac{3}{2} \frac{eF}{4\pi^2 ma\omega}$$

$$= \frac{3F}{8\pi^2 m} \frac{nh}{Ze}.$$

Since the additional energy due to the electric field and the secular period are connected by the equation $\delta E_F = \omega_F \, \delta J_F$, and ω_F is independent of J_F, we have

$$E_F = \omega_F J_F = \frac{3Fnh}{8\pi^2 mZe} n_F h,$$

since $J_F = h n_F$

or $$E = \frac{-2\pi^2 me^4 Z^2}{h^2} \frac{1}{n^2} + \frac{3h^2 F}{8\pi^2 meZ} n n_F . \quad \ldots\ldots\ldots\ldots(31)$$

Before Bohr worked out the method of perturbations this value for the energy was obtained independently by K. Schwarzchild and by P. Epstein, who used the method of separation of the variables.*

* Take a meridian plane through the z axis as zy plane, and take as the third coordinate the angle α between this plane and some fixed meridian plane. Then the parabolic coordinates given by

$$y = \xi\eta, \quad z = \tfrac{1}{2}(\xi^2 - \eta^2)$$

effect a separation of the variables for ξ, η, p_ξ, p_η, so that the Sommerfeld-Wilson conditions

$$\oint p_\xi \, d\xi = n_\xi h, \quad \oint p_\eta \, \delta\eta = n_\eta h$$

can be applied. The angular momentum about z, which is constant, is given by

$$\int_0^{2\pi} p_\alpha \, d\alpha = 2\pi p_\alpha = n_\alpha h .$$

We have thus three quantum numbers n_α, n_ξ, n_η : only two appear in (31) because the problem is degenerate, owing to the fact that the motion of the electrical centre of the orbit has only one periodicity for two degrees of freedom.

If in (31) we put

$$n = n_\xi + n_\eta + n_\alpha$$

$$n_F = n_\eta - n_\xi$$

we get the result in the form in which Schwarzchild and Epstein gave it.

Comparing formula (30) with (31) we see that

$$n^2 \epsilon \cos \varphi = n n_F$$

or

$$\epsilon \cos \varphi = \frac{n_F}{n}$$

so that

$$\xi = \tfrac{3}{2} a \epsilon \cos \varphi = \tfrac{3}{2} a \frac{n_F}{n}.$$

The distance of the electrical centre from the plane through the nucleus perpendicular to the electric field is quantised to be a whole number multiple of $\frac{3}{2} \frac{a_n}{n}$, where a_n is the major axis of the ellipse of total quantum number n. $\frac{3}{2} a_n$ is the maximum possible distance of the electrical centre from the nucleus, corresponding to $\epsilon = 1$, and $\varphi = 0$, when the motion is a straight line through the nucleus. This case, in which $n_F = n$, is therefore excluded. The electrical centre of the orbit may clearly be on either side of the xy plane. Hence we conclude that n_F can have the values $0, \pm 1, \pm 2, \ldots \pm (n-1)$.

For a given spectral line equation (31) shows that the Stark components are given by

$$\Delta \nu = \frac{1}{h} (W' - W) = \frac{3hF}{8\pi^2 m e Z} (n' n'_F - n n_F), \quad \ldots \ldots (32)$$

when n' and n are fixed. Before applying this to the experimental observations of Stark on hydrogen we must consider the question of polarisation, on the basis of the correspondence principle, that is, we must discuss the nature of the new periodicities introduced into the orbital motion by the periodic rotation of the electrical centre of the orbit. Let us refer the motion of the electron to axes through the nucleus rotating about the z axis with the frequency ω_F of the motion of C, the electrical centre, but with *uniform* velocity. Thus if the rotating xz plane contains C initially it will contain it four times in every complete revolution, or the motion of C describes an orbit with frequency $2\omega_F$ with reference to the rotating axes. The motion of the electron in the orbit will be doubly periodic, with frequencies ω_1 and ω_2, where $\omega_1 =$ mean frequency of revolution of the electron in its orbit referred to the moving axes, and

$$\omega_2 = 2\omega_F \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (33)$$

This motion can be expressed in a Fourier series, as on p. 222,

$$\xi = \Sigma C_{\tau_1, \tau_2} \cos \left\{ 2\pi (\tau_1 \omega_1 + \tau_2 \omega_2) t + \gamma_{\tau_1, \tau_2} \right\}.$$

The motion relative to the original fixed axes is obtained by superposing on this in a contrary sense the uniform rotation of frequency ω_F with which we endowed the moving axes. We have seen the effect of such an added uniform rotation in considering the Zeeman effect : there results a series of linear harmonic vibrations, of frequency $\tau_1 \omega_1 + \tau_2 \omega_2$, parallel to the axis of the uniform rotation, *i.e.* the z axis, and two series of circular harmonic rotations in the xy plane of frequencies

$$(\tau_1 \omega_1 + \tau_2 \omega_2 + \omega_F) \quad \text{and} \quad (\tau_1 \omega_1 + \tau_2 \omega_2 - \omega_F).$$

This expresses the motion in terms of the frequency ω_F of the electrical centre, and the mean frequency ω_1 of the electron in the nearly closed orbit which it describes with reference to the rotating axis.

Now, the motion can also be expressed in terms of the frequency of revolution ω of the electron about the z axis, and of the frequency ω_F : here

$$\omega = \omega_1 + \omega_F \quad \text{or} \quad \omega = \omega_1 - \omega_F, \quad \ldots\ldots\ldots\ldots(34)$$

from the definition of ω_1, according as the electrical centre rotates in a direction the same as, or opposite to, that of the electron in its own orbit. If we write

$$\xi = \Sigma D_{\tau_1 \tau_F} \cos \left\{ 2\pi (\tau \omega + \tau_F \omega_F) t + \delta_{\tau_1 \tau_F} \right\}$$

for the periodic change of the ξ coordinate perpendicular to the z axis (and, of course, a similar expression differing only in the values of D and δ for the η coordinate) we have therefore

$$\tau \omega + \tau_F \omega_F = \tau_1 \omega_1 + \tau_2 \omega_2 \pm \omega_F,$$

which becomes

$$\tau \omega_1 \pm \tau \omega_F + \tau_F \omega_F = \tau_1 \omega_1 + \tau_2 2\omega_F \pm \omega_F,$$

using (33) and (34).

This gives $\tau = \tau_1$, $\tau + \tau_F = 2\tau_2 \pm 1$ or $= 2(\tau_2 + \tau_1) \pm 1$. Hence for a periodic motion in the plane normal to the direction of the field, $\tau + \tau_F$ must be an *odd* integer. For the vibration parallel to the electric field

$$\zeta = \Sigma E_{\tau_1 \tau_F} \cos \left\{ 2\pi (\tau \omega + \tau_F \omega_F) + \epsilon_{\tau_1 \tau_F} \right\}$$

where now, since this vibration is unaffected by the field,

$$\tau\omega + \tau_F\,\omega_F = \tau_1\,\omega_1 + \tau_2\,\omega_2$$

or $\qquad\qquad \tau\omega_1 \pm \tau\omega_F + \tau_F\,\omega_F = \tau_1\,\omega_1 + 2\tau_2\,\omega_F$

which leads to $\tau = \tau_1, \quad \tau + \tau_F = 2(\tau_1 + \tau_2)$ or $= 2\tau_2$.

In this case, therefore $\tau + \tau_F$ must be an *even* integer.

The interpretation of this gives another example of the elegance of the correspondence principle. A transition from a state characterised by the two quantum numbers n and n_F to a state characterised by n' and n'_F is conditioned by a harmonic component of frequency $(n-n')\omega + (n_F - n'_F)\omega_F$ in the orbital motion. Now $(n-n') = \tau$ and $(n_F - n'_F) = \tau_F$ in the problem just discussed. We have seen that if, in the orbital motion, there is a vibration parallel to the field $\tau + \tau_F$ is even ; for a motion in a plane normal to the field $\tau + \tau_F$ is odd. For an observer looking along a direction normal to the field, these motions correspond to polarisation parallel and normal to the field respectively, *i.e.* they correspond to the p and s components in the transverse effect. For an observer looking along the lines of electric force it would seem, at first consideration, that circularly polarised components, identical in wavelength with the s components of the transverse effect, would be seen. However, when there are a large number of atoms, a rotation in one sense is as likely as that in the other : there is not, as in the case of the Zeeman effect, a difference of wavelength according as whether the component is circularly polarised in one direction or the other, with consequent separation of the oppositely polarised components. The light therefore appears unpolarised in the longitudinal Stark effect. Summarising the polarisation results we have, therefore :

In the case of the transverse effect

$\qquad (n - n' + n_F - n'_F)$ even, p components.

$\qquad (n - n' + n_F - n'_F)$ odd, s components.

In the case of the longitudinal effect

$\qquad (n - n' + n_F - n'_F)$ even, no components

$\qquad (n - n' + n_F - n'_F)$ odd, unpolarised components.

These are the polarisation rules.

The general experimental results, that the components are symmetrically placed about the position of the unresolved line, and that they are spaced at distances which are whole number multiples of a separation factor, follow from the formula (32); the observed polarisation rules, that in the longitudinal effect there are only unpolarised components, whereas in the transverse effect there are s and p components, we have just deduced by applying the correspondence principle. To illustrate the more detailed agreement between theory and experiment we will apply formula (32) and the polarisation rules to the cases of two lines of Balmer series of hydrogen, H_a and H_β.

For H_a $\qquad\qquad$ $n'=2,\ n=3$:

for H_β $\qquad\qquad$ $n'=2,\ n=4$.

Beside the rules just discussed we must remember that the case $n_F = n$ is excluded for both initial and final states (see p. 261), so that, for instance, in the case of H_a, $n_F = \pm 2,\ \pm 1,\ 0$, and $n'_F = \pm 1,\ 0$. In the case of H_a, $n - n'$ is odd, and therefore $n_F - n'_F$ must be odd for p components and even for s components. In the case of H_β, $n - n'$ is even, and therefore $n_F - n'_F$ must be even for p components, and odd for s components. We tabulate $s = n'n'_F - nn_F$, which gives the position of the components in multiples of $\dfrac{3hF}{8\pi^2 meZ}$. Since the components are symmetrical about the original line it will suffice to take all possible negative values, say, of n_F and to allot to each value all values of n'_F permitted by the rules; brief consideration will show that the positive values of n_F, with the permitted values of n'_F, give the same components with reversed sign. Since the longitudinal effect can be at once deduced from the transverse effect the latter only will be considered.

H_a. p components: $(n - n' + n_F - n'_F)$ even, $n_F - n'_F$ odd.

n	n_F	n'	n'_F	nn_F	$n'n'_F$	$s = n'n'_F - nn_F$
3	-2	2	$+1$	-6	2	8
3	-2	2	$+1$	-6	-2	4
3	-1	2	± 0	-3	0	3
3	0	2	-1	0	-2	2

H_a.   s components : $(n - n' + n - n'_F)$ odd, $n_F - n'_F$ even.

n	n_F	n'	n'_F	nn_F	$n'n'_F$	$s = n'n'_F - nn_F$
3	-2	2	0	-6	0	6
3	-1	2	1	-3	2	5
3	-1	2	-1	-3	-2	1
3	0	2	0	0	0	0

H_β. p components : $(n - n' + n_F - n'_F)$ even, $n_F - n'_F$ even.

n	n_F	n'	n'_F	nn_F	$n'n'_F$	$s = n'n'_F - nn_F$
4	-3	2	-1	-12	-2	10
4	-3	2	$+1$	-12	2	14
4	-2	2	±0	-8	0	8
4	-1	2	$+1$	-4	2	6
4	-1	2	-1	-4	-2	2
4	0	2	0	0	0	0

H_β.   s components : $(n - n' + n_F - n'_F)$ odd, $n_F - n'_F$ odd.

n	n_F	n'	n'_F	nn_F	$n'n'_F$	$s = n'n'_F - nn_F$
4	-3	2	±0	-12	0	12
4	-2	2	$+1$	-8	2	10
4	-2	2	-1	-8	-2	6
4	-1	2	±0	-4	0	4
4	0	2	$+1$	0	2	2

Stark's experimental results for H_a are represented in Fig. 44, the p components being above and the s components underneath. The numeral under each line indicates the difference of wave number between that line and the unresolved line expressed as a multiple of $C = \dfrac{3hF}{8\pi^2 meZ}$: the lengths of the lines represent intensities. It will be seen that all the experimental components are represented in our theory, which in addition gives an 8 component in the p, and a 5 and 6 component in the s effect. This need not throw doubt on the validity of the theory, for we have said nothing of the relative intensity of the various components. Kramers has investigated the

question of intensity very fully by the use of Bohr's correspondence principle, and finds that the components missing in the
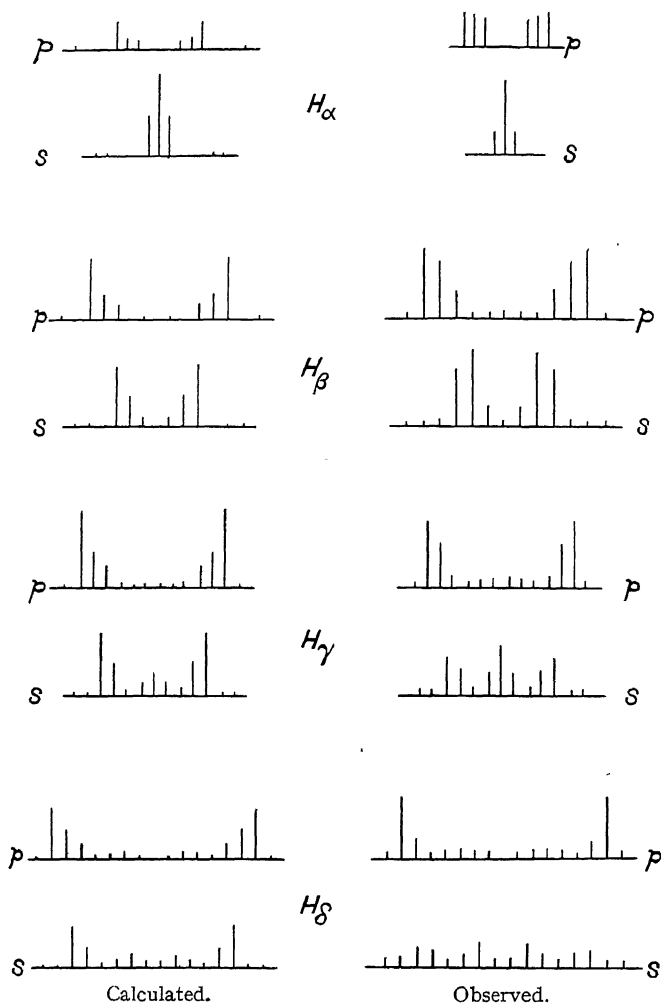
FIG. 46.

Stark effect in the Balmer lines of hydrogen.

Stark photographs are theoretically of feeble intensity, and so might well escape detection. As regards H_β, for which the

experimental results are also shown in Fig. 44, the agreement with theory is striking. All the theoretical components are represented. The lines given by Stark as questionable do not occur theoretically, and a very weak line in the p and one in the s are also theoretically excluded. In the case of H_γ and H_δ, which are not worked out here on account of limitations of space, the agreement between theory and experiment is perfect. Since these lines give round about fourteen components, the theoretical explanation of the effect is a striking triumph for the quantum theory, especially as classical theory has proved powerless in the domain of the Stark effect. The results, calculated and observed, for the first four Balmer lines are summarised in Fig. 46.

The exposition given here has been chosen with the particular object of illustrating the significance of the correspondence principle. It may be mentioned in conclusion that Kramers has handled the question of a combined relativity and Stark effect in the case of hydrogen lines. He finds that in the presence of a weak electric field the components of the fine structure split into one or more sharp, polarised components, which are displaced by amounts proportional to the square of the electric force. As the electric field is increased new components appear; when the field is strong the components coincide with those given by the theory, without relativity effect, which we have just discussed.

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CHAPTER XI

THE OPTICAL SPECTRA OF THE GENERAL ATOM

Introductory. The characteristic of the model of the hydrogen-like atom is a spherically-symmetrical central nucleus, of negligible dimensions, attracting a single electron with an inverse square law of force, and, as we have seen, this gives satisfactory results, not only as regards the quantitative structure of the line spectra of hydrogen and ionised helium, but also in respect of the resolution of the individual lines into components produced by various disturbing causes. When we turn to the general atom, with a large number of, or even only two,* electrons, the problem becomes much more complicated. No spectrum of an atom holding more than one extranuclear electron has been fully worked out, but important work has been done in the direction of explaining the general features of optical spectra, and from a consideration of the characteristics of the optical and X-ray spectra of the atoms taken in order of their atomic numbers an astonishing body of information as to the extranuclear structure of the non-hydrogen-like atoms has been won.

It has already been pointed out that no scheme of circular orbits can give even a rough description of the line spectra of the general atom, since it only provides one series of terms. The consideration of elliptic orbits did not lead to any new features in the spectrum when the field of force was a Coulombian one, since in this case the orbits are Keplerian ellipses, the problem is a degenerate one, in the sense which we have defined, and all orbits of the same major axis (which is, in effect, the parameter quantised) have the same energy. When, however,

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* Neutral helium, for which no fully satisfactory theory is yet to hand.

the field of force departs markedly from the inverse-square law, orbits of the same major axis, but different eccentricities, have different energies. *For a first attempt* on the problem of the line spectra of the general atom, the following assumptions are made. One particular electron, which we may call the " optical electron," or " series electron," is assumed to be responsible for the differences of energy between one stationary state of the atom and another, considered in the general Bohr formula $h\nu_T = E_n - E_{n'}$. It is not meant that one ticketed electron of the atom is necessarily always the optical electron, but rather that there is a privileged rôle for one electron. This electron describes orbits in which it is, for a greater part of the time, at any rate, far removed from the rest of the atom, which we will call the core of the atom.*

It is assumed further that there is no interchange of energy between the core and the optical electron : in other words, the core, consisting of the true nucleus and a grouping of extra-nuclear electrons, behaves as a kind of complex nucleus, differing from the true nucleus considered in the hydrogen-like atom, in that it exercises a more complex field of force, since the dimensions of the group of positive and negative charges are no longer, in the case of the core, negligible compared to the perihelion distance of the orbit. That the electrons of the core should be unaffected by the near passage of the optical electron is an assumption which is at variance with what we should expect from classical mechanics, and must be considered as a manifestation of some quantum property. Its justification is that on the simple assumption laid down we reach results in general agreement with experiment.

For the first great problem, which is to explain the general features of the various series—sharp, principal, diffuse and fundamental—of the line spectrum of an atom, it is assumed that the field of force produced by the core is spherically

* To be distinguished from the kernel of the atom (see pp. 552, 637), which is what is left of the atom when the electrons forming the incomplete groups of highest total quantum number are removed. Of course, in the case of the atoms of the alkali metal groups, or ionised atoms of the alkali earth group, and so on, the core and the kernel are the same thing, but in the case of, say, a neutral atom of Column III. of the periodic table, the core contains two outer electrons in addition to the kernel. What I have called the core is the German *Atomrumpf*.

symmetrical, or, still more definitely, that this field can be considered as due to a central nucleus surrounded by a spherically symmetrical distribution of negative electricity invariable with the time. This is clearly only a first approximation, since the electrons of the core are all in motion in quasi-elliptical orbits of various dimensions and eccentricities.

It should also be noted that an assumption of this kind cannot give an explanation of the multiplet structure of spectral lines, *i.e.* of the existence of doublets, triplets, quad-ruplets, and so on, in the place of single lines in most of the series. To explain this feature, and the anomalous Zeeman effect, it is necessary to consider the core as having about an axis a moment of momentum specified by the introduction of a new quantum number, and to consider the various possible positions which the plane of the orbit of the optical electron can take up with reference to this. Detailed consideration of such points is postponed to Chapter XV. On the assumption of central symmetry the orientation of the plane of the orbit obviously has no effect on the energy of the atom, and two quantum numbers, n and k, suffice to specify the orbit, and to give the energy of the terms which we require.

We have, then, to consider the behaviour of the electron in a central conservative field of force which does not obey the inverse-square law. We can specify the nature of the field a little more closely. The core consists of the central charge Ze surrounded by $Z - 1$ electrons in the case where the neutral atom is emitting light, $Z - 2$ electrons in the case of the singly ionised atom, and, in general, $Z - s$ electrons in the case of an atom ionised to the $(s - 1)$th degree. The net charge on the core is therefore se in the general case of the ionised atom. At a distance from the nucleus large compared to the dimensions of the core this net charge may be considered as concentrated at a point, or at such distances we have a field which approximates to the inverse-square law field produced by a nucleus of charge se. The fact that the same constant R occurs in all spectral formulae can now be easily explained. For very large orbits, that is, for large quantum numbers, the term must have the same value as for a hydrogen-like atom of nuclear charge se, *i.e.* must be given by Rs^2/n^2. The formula

for the general term must, then, approximate to Rs^2/n^2 when n is large, which is easily effected by substituting for n any function of n which tends to the value n^2 when n is large. Any of the empirical spectral formulae, such as those quoted in Chapter VIII., obey this condition. In the case of the first spark spectrum, which is given by a singly ionised atom, the constant is $4R$. For the spectra of doubly ionised aluminium, ordered by Paschen, and of doubly ionised silicon, ordered by A. Fowler, to which reference has been made in Chapter VIII., the constant is $9R$: for the trebly ionised silicon of Fowler it is $16R$; and so on. It is, perhaps, preferable to say that the fact that series have been found which require for their representation the constant $9R$ and $16R$ respectively indicates, on the above reasoning, that doubly and trebly ionised atoms are concerned in their emission.

Spectral Significance of the Two Quantum Numbers. A closed elliptic orbit is only possible in the case of an inverse square law of force.* When the central force departs from the inverse square law, the quasi-elliptic orbit rotates about an axis through the focus normal to the plane of the orbit. If the orbit is large, and only a small part of it lies in a field in which there is a marked departure from the inverse square law, there may be a large rotation of perihelion, although the greater part of the orbit closely resembles a Keplerian ellipse. We have in general a rosette, as in Fig. 36, but often the rotation of perihelion is so large that orbits of the appearance illustrated later in Fig. 47 occur for an actual atom. The orbit, considered as a plane orbit, is no longer a degenerate case, for corresponding to the two degrees of freedom we have two periodicities : a motion of frequency ω in the quasi-elliptic orbit, and a motion of the apse of frequency ω_k, the second periodicity being introduced by the presence of the core electrons.

We have a multiply periodic system to which we can apply Bohr's method, described on p. 221 *et seq.* Corresponding to the two periodicities we have two quantum numbers, n and k, defined by

$$J_n = nh, \quad J_k = kh. \quad \dots\dots\dots\dots\dots\dots(\text{I})$$

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* Or, of course, in the case of a force varying directly as the distance from the centre, which latter case never concerns us.

We choose J_n so that in the limiting case where, the departure of the field from the inverse square law tending to zero, the central orbit becomes a Keplerian ellipse, J_n becomes the total (*i.e.* radial+azimuthal) action J with which we dealt in considering the case of the truly elliptic orbit of one periodicity, to which corresponds a frequency ω_0. In other words, when ω_k tends to o, J_n must tend to J, which was defined by

$$J = \oint p_r dr + \oint p_\theta d\theta.$$

In the general case represented in equation (1), we have

$$\delta E = \omega \, \delta J_n + \omega_k \, \delta J_k. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

J_n being chosen as above, n is defined by equation (1), and is the principal quantum number. Bohr's general method of defining the J's and n's is designed for any periodic motion, and gives no particular quantum number preference over any other. When, however, we are dealing with disturbed elliptic orbits we can define a principal quantum number pertaining to the undisturbed orbit, as just done. This is what we did, effectively, in treating orbits by the method of secular perturbation. If ω_k is small compared to ω, that is, if the electron executes a large number of loops while the major axis of the quasi-elliptic loop moves through an angle 2π, then, since also J_k can never exceed J_n, the energy is determined to within a small percentage by J_n, that is, by the principal quantum number n as distinct from k. ω_k is not always small compared to ω, and in such cases the energy correction due to the second periodicity is large.

k is the new quantum number introduced by the rotation of the apses. Whereas in the case of the simple ellipse, the quantising of the angular momentum p_θ, carried out in the Sommerfeld-Wilson method by putting $\int_0^{2\pi} p_\theta \, d\theta = 2\pi p = n_\theta h$, led to no new term in the energy, and so was unnecessary for the Bohr point of view, now that we have two periodicities the energy is modified by the second quantum condition, as expressed in equation (2), and the second quantum number corresponding to ω_k is indispensable. The second equation of

(1) expresses the quantisation of the angular momentum in the case under consideration :

$$J_k = 2\pi p_\theta = kh, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

where p_θ is the angular momentum of the electron in its *actual* orbit about the nucleus, which is, of course, constant for any central orbit in a conservative field of force.

This follows at once from Bohr's fundamental equation

$$\sum_m \omega_m J_m = \sum_i \overline{\dot{p}_i \dot{q}_i} = \sum_i \omega_i \oint p_i \, dq_i,$$

which becomes in our case

$$\omega_n J_n + \omega_k J_k = \omega_n \oint p_r \, dr + (\omega_n + \omega_k) \oint p_\theta \, d\theta.$$

J_n tends to the value $J = \oint p_r dr + \oint p_\theta d\theta$ when ω_k tends to o, and the orbit becomes degenerate, and $J_k = \omega_k \oint p_\theta \,.\, d\theta = 2\pi p_\theta.$

k is called the azimuthal quantum number of the orbit.

We can, of course, express the general case of the elliptic orbit with rotation of perihelion in the Wilson-Sommerfeld manner, by putting

$$\oint p_r dr = n_r h, \quad \int_0^{2\pi} p_\theta d\theta = 2\pi p = kh$$

and $n = n_r + k.$

This is just what we did in the degenerate case of the Keplerian ellipse considered in the Sommerfeld way, and is, perhaps, the more straightforward way of approaching the problem. It lacks, however, something of the generality of Bohr's method, and does not bring out so clearly the fact that the second quantum number is bound up with a second periodicity.

Referring back to Fig. 37, which represents orbits of total quantum number $n=4$, and azimuthal quantum numbers $k=4, 3, 2, 1$ in the case of an inverse square field, we remember that k can have any whole number value $\lessgtr n$ except o, since $k=0$ gives a straight line through the nucleus. The case $k=n$ gives a circular orbit ; it is obvious that when r is constant the whole momentum is azimuthal. As k diminishes the ellipses become more and more eccentric. The modification which a

departure from the inverse square law introduces is that the apses of these orbits of varying degrees of eccentricity rotate, but k still conditions the eccentricity of the ellipse to which the loops approximate. It must be borne in mind that although k may be equal to n, and in any case can only exceptionally be neglected in comparison to n, the modification of the orbital energy conditioned by k is frequently small compared to the total energy, which is fixed to a first approximation, but to a first approximation only, by n. Equation (2) expresses that the additional energy term fixed by k is proportional to the frequency with which the apse rotates, and can only be considerable when this frequency approaches that of the electron in its quasi-elliptic loop.

The energies of the orbits, that is, the terms from which the various spectral series are derived, are, then, expressible in terms of two numbers, n and k. Fixing a value of k and letting n vary, we have one sequence of terms : fixing another value of k and letting n vary, we have a second sequence, and so on. Now we have seen in Chapter VIII. that to account for the various series—principal, sharp, diffuse, fundamental ...—we require four or more sequences of terms, nS, nP, nD, nF ..., of which we know empirically the following : the terms of each sequence become Balmer-like, $i.e.$ take the form R/n^2, for very large values of the sequence number n, while the departure of a term of given sequence number n from the value R/n^2 is progressively smaller as we go from sequence to sequence in the order nS, nP, nD, nF ... given above. The sequences show increasing resemblance to hydrogen terms in the order given.

The hypothesis naturally occurs, then, that a fixed value of k, with varying n, gives one of the required sequences, and that the value of k corresponding to the different sequences increases in the order in which the sequences have been set down above. Firstly, for very large values of n, the orbits are very large, whatever the value of k, and therefore lie almost entirely so remote from the atomic core that the field of force in their neighbourhood approximates closely to an inverse-square law field produced by a single nucleus whose charge equals the net positive charge on the core. For very large values of n the terms therefore become Balmer-like, as required. Secondly,

for a low value of k, say $k = 1$, all the orbits except the first one or two have a high degree of eccentricity, and consequently a small perihelion distance compared to orbits of the same n for which k is greater. Hence, for a given n, orbits of small k lie partly in a field which departs from the inverse square law more than it does at any point of the orbits of larger k, so that the greater k the closer the approximation of the term to R/n^2. Since empirically the first term of the S sequence has the value $n = 1$, for which k must be 1 (since k cannot exceed n, nor be zero), and the value of n for the first term of the other sequences increases,* it seems natural to assume that $k = 1$ for the S sequence, $k = 2$ for the P sequence, $k = 3$ for the D sequence, and $k = 4$ for the F sequence. This was Sommerfeld's original assumption, which has been well supported by the experimental results. Certain difficulties which it encounters are discussed in Chapter XV. We shall see that k must differ by 1 from sequence to sequence when we come to consider the correspondence principle, and we have seen that k must be 1 for the S sequence, and increase for the various sequences in the order given. Hence this allotment of the k's seems inevitable.†

There is, of course, no reason why k should stop at 4, since for $n \geqslant 5$ corresponding values of $k \geqslant 5$ are permitted. Hence theoretically there can be any number of term sequences corresponding to values $k = 5$, 6, 7 .... Terms for which $k = 5$ or 6 have actually been found by Fowler and Paschen ; Paschen calls them respectively " Über-Bergmann " and " Über-über-Bergmann " terms, which Fowler renders as Super-Fundamental and Super-super-Fundamental terms : they are indicated by nG and nH. They have been discovered in the case of atoms ionised to a multiple degree, and the reason is clear. Such spectra have as constant Rs^2, where $s - 1$ is the degree of ionisation, so that the terms are all displaced to the violet compared with those of the neutral atom. In the neutral atom, just as the lines of the Bergmann, or fundamental,

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* See, however, remarks on notation, page 172 *et seq.*

† The consideration of the introduction of half odd integer values for the k's, which has no satisfactory theoretical basis on the orbit scheme, is best postponed to Chapter XV.

series lie in the infra-red, the lines of the G, and still more of the H series, lie, if excited, in the very far infra-red, and we cannot hope to observe them. A high degree of ionisation brings them into a region where they can be photographed: thus the G-series lines measured for Si_{III} and Si_{IV} lie in the ultra-violet.

To correspond with the theory, then, we can write the possible term-sequences for a complete line spectrum as follows. The term of principal quantum number n, azimuthal quantum number k is written n_k, for example 4_2. The upper row of each pair of rows gives the spectroscopic, the lower the quantum notation. To avoid the difficulty caused by the fact that the principal quantum number of the leading term is differently allotted by Fowler, by Paschen, and by Bohr, an arbitrary whole number $(n_s, n_p \dots)$ is added to the principal quantum number, this arbitrary whole number being the same throughout a sequence. By suitably choosing its value any notation can be satisfied.

S sequence	$1S$	$2S$	$3S$	$4S$	$5S$	$6S \dots$
	$(n_s+1)_1$	$+2)_1$	$+3)_1$	$+4)_1$	$+5)_1$	$+6)_1 \dots$
P sequence		$2P$	$3P$	$4P$	$5P$	$6P \dots$
		$(n_p+2)_2$	$+3)_2$	$+4)_2$	$+5)_2$	$+6)_2 \dots$
D sequence			$3D$	$4D$	$5D$	$6D \dots$
			$(n_d+3)_3$	$+4)_3$	$+5)_3$	$+6)_3 \dots$
F sequence				$4F$	$5F$	$6F \dots$
				$(n_f+4)_4$	$+5)_4$	$+6)_4 \dots$
G sequence					$5G$	$6G \dots$
					$(n_g+5)_5$	$+6)_5 \dots$

Derivation of the Rydberg and Ritz Formulae. We have seen how the different series of the general line spectra can be expressed, apart from any multiplet structure, by two quantum numbers, n and k, of which k is constant in any one series, while n takes up a sequence of whole number values. We know also, from experience, that the general term can be expressed to a first approximation by Rydberg's expression

$\nu = \dfrac{R}{(n + \mu)^2}$, where μ has a constant value in any one series, and n takes up a sequence of whole number values, or more closely by Ritz's expression $\nu = \dfrac{R}{\left(n + \mu + \dfrac{\beta}{n^2}\right)^2}$ where μ and β are both constants in any one series. We now have to show that these formulae can be derived from the general scheme of n_k orbits in a central field which we have been discussing.

We assume that the dimensions of the core are small compared to the dimensions of the orbit, so that a comparatively
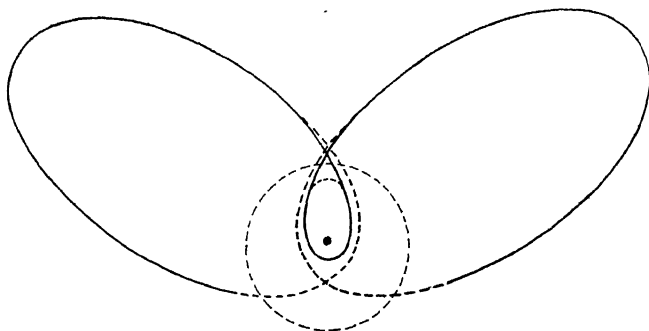
Fig. 47.

Orbit when the field near the nucleus is non-Coulombian.

large part of the orbit lies in a field approximating to the inverse square law, and consequently may be treated as part of a true ellipse. Within the core, however, as we approach the nucleus the field increases much more rapidly than would be indicated by the inverse square law. If the orbit be of marked eccentricity there will consequently be very high velocity at perihelion, and a large rotation of perihelion, the orbit taking the form shown in Fig. 47. It is represented by the full line, and consists of (a) a main outer loop, which lies in a field differing very little from that given by a charge se concentrated at the nucleus, supposing the atom to be $(s - 1)$ply ionised, and (b) an inner loop, lying mainly within the core, where the field, still central, varies much more rapidly than indicated by the inverse square law. The broken circle indicates the

boundary of the core, outside which the field is approximately Coulombian. The Keplerian ellipse of which the outer loop forms part is completed by the broken line. The inner loop is formed between the two outer loops shown by the large rotation of perihelion, and the ellipse to which it is a first approximation is also completed by a broken line. There is, of course, one inner loop to every outer loop.

The quantum number which characterises the true elliptic orbit, of which the outer loop is part, is not n, the total quantum number of the true n_k orbit, for the total energy of the electron, which does not vary with the time, must be the same in the elliptic loop as in the actual orbit, and we know that the energy E of the actual orbit is not determined by n alone, but depends also on k. Clearly, however, we can define a number n_e such that

$$-E = W = \frac{chRs^2}{n_e{}^2}; \quad \dots\dots\dots\dots\dots\dots\dots\dots(4)$$

n_e will then be the number specifying an elliptic orbit, described round a central point charge se, which has the same energy and the same moment of momentum p_θ as the actual orbit : *n_e will not, of course, in general be a whole number.* This statement is not in conflict with the assumptions of the quantum theory, since the elliptic orbit which n_e specifies is not one actually existing in an atom, but is a fictitious, mechanically possible, orbit, described about a massive point charge, and defined to have the same energy as an actual orbit. n_e is called the *effective quantum number*, and is given by equation (4) directly from the empirical spectral term, of wave number ν, which happens to be in question, since $hc\nu = W$. It is a very important conception in recent quantum theory, and its meaning should be clearly grasped.

Corresponding to n_e we have in the elliptic orbit $J_e = n_e h$. Now for the actual orbit $J_n = nh \neq J_e$. Let $J_e = J_n - ah$, where, as far as we know at present, a may be a function of n and k. Then

$$n_e h = nh - ah \quad \text{or} \quad n_e = n - a.$$

Hence $$W = \frac{chRs^2}{(n-a)^2}. \quad \dots\dots\dots\dots\dots\dots\dots\dots(5)$$

Now suppose the orbit varied in such a way that the outer loop, but not the inner loop, changes; this can clearly be done, since corresponding to a small change of velocity just outside the core a small change in direction can be made in such a way that the inner loop remains the same.   Then

$$\delta E = \omega_e \, \delta J_e = \omega_e (\delta J_n - h \delta a),$$

where ω_e is the frequency in the fictitious elliptic orbit.   We can alternatively suppose the orbit varied in such a way that only n, and consequently J_n, varies, while the other quantum condition which exists for the true orbit, namely $J_k = kh$, remains unchanged.   In this case

$$\delta E = \Sigma \omega \, \delta J = \omega_n \, \delta J_n + \omega_k \delta J_k$$
$$= \omega_n \, \delta J_n.$$

As a first approximation, ω_n, the frequency of revolution of the electron in the true orbit, from aphelion to aphelion, equals ω_e, the frequency of revolution in the elliptic orbit, since the portion in the abnormal field (the time of describing which differs from the time of describing the corresponding part of the elliptic orbit) is small, and, in addition, the velocity in this portion is very large.   To this approximation, with the conditions that we have postulated, namely that only n varies,

$$\omega_e(\delta J_n - h \delta a) = \omega_e \delta J_n,$$

so that $h \, \delta a = 0$ or $a = $ constant.

In other words, when n changes, but k is kept constant, the quantity a in formula (5) remains constant, or a constant corresponds to a given spectral series.   Formula (5) becomes Rydberg's formula, which we have deduced on the simple assumptions that the field is central and that the dimensions of the core are small compared with those of the orbit of the optical electron.*

We have assumed as a first approximation that $\omega_n = \omega_e$. To a second approximation the difference of the time periods in the two orbits will be a small quantity ψh, which does not

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* We assumed that the eccentricity of the orbit was marked, but this was only to get a departure from the Balmer form.   Obviously, if the eccentricity is zero, and the orbit large, we have circular orbits in an approximately Coulombian field, and the Balmer form holds.

depend on n, the number which conditions the size of the Keplerian loop when the inner loop is fixed, but on k, which determines the perihelion distance.

Then
$$\frac{1}{\omega_e} - \frac{1}{\omega_n} = \psi h \; ;$$

$$\delta E = - \delta W = \omega_e \delta J_e = \omega_n (1 - \omega_e \psi h) \delta J_e$$
$$= \omega_n (\delta J_e + \psi h \, \delta W).$$

For variations in which k is constant, $i.e.$ for a given spectral series,
$$\delta E = \omega_n \delta J_n \; ;$$

so that
$$\delta J_n = \delta J_e + \psi h \, \delta W,$$
$$n - a = n_e + \psi W,$$

where a is a constant of integration.

Hence
$$W = \frac{chRs^2}{n_e{}^2} = \frac{chRs^2}{(n - a - \psi W)^2},$$

or
$$\nu = \frac{Rs^2}{(n - a - \psi W)^2} \cdot$$

This is one form of Ritz's formula : remembering that ψ is small, we can take W as $\dfrac{chRs^2}{n^2}$, and, writing β for $-\psi chRs^2$, we get the form quoted on p. 278, namely

$$\nu = \frac{Rs^2}{\left(n - a + \dfrac{\beta}{n^2}\right)^2}$$

It may be recalled that all through these proofs * we have assumed that there is no interchange of energy between core and optical electron. This implies that the electrons in the core, which are part of the atomic structure, have quantum numbers which remain invariable in spite of the periodic incursions of the optical electron into the region which they traverse. This invariance, or lack of interaction, cannot be explained on the basis of ordinary mechanical laws, and would

* In connection with these proofs I am much indebted to Mr. R. H. Fowler, who kindly lent me some manuscript notes on unpublished work of Bohr's.

seem to be essentially in the nature of a quantum postulate. It is referred to by Bohr as the postulate of the *invariance and permanence of the quantum numbers*, and receives further striking illustration in the consideration of X-ray spectra, since it would seem that the removal of an inner electron which takes place when such spectra are excited does not affect the quantum numbers of the remaining electrons which form part of the atomic structure.

Returning to the proof which we have given of the Rydberg formula, we may devote a little more consideration to the distinction between the effective quantum number n_e and the principal quantum number n of the given orbit corresponding to a given term in a given sequence. n_e is found at once from the value of ν by the defining formula (4) : there is no ambiguity as to its value. n, however, cannot be found directly in this way from the empirical data. We know that it must be a whole number, and we know that $n + a = n_e$, but this does not fix n. Only when the value of n to be assigned to one term, say the first term of the sequence, has been determined, is a, previously known only to within a whole number, determined. The spectroscopists fix the value of n by using one of the more complicated formulae in which there is a corrective term depending on n, such as Hicks' formula for the term

$$\frac{R}{\left(n + \mu + \dfrac{\beta}{n}\right)^2},$$

and selecting n so as to get the best fit for the whole sequence ; they also make use of subsidiary empirical relations with the same object. Even so there is no unanimity as to the value of n to be assigned to the first term in certain series : Fowler's numeration given on p. 172 is a usual one, but is not the same as Paschen's. We shall see later that Bohr's theory assigned a definite n to the first term in each series for most atoms, but the practical spectroscopists have decided not to adopt this for descriptive purposes, and for the moment we need not further consider it.

It can easily be shown on general theoretical grounds that when in the central, non-Coulombian part of the field the force

is more intense than indicated by an inverse-square law, corresponding to central charge se, as is the case with our atomic model, then $n > n_e$,* so that a in (5) is a positive quantity. a, the amount by which the principal quantum number exceeds the effective quantum number (which is the same thing as the amount by which the actual radial quantum number exceeds the effective radial quantum number) is called the quantum defect.

An evaluation of the effective quantum number for the first few terms of the series of an atom enables us to see rapidly how far the series approximates to Balmer form. For nearly all atoms, in which series have been disentangled, the first F term has $n_e = 4$ to within less than 1 per cent. For the lighter atoms the first D term has $n_e = 3$, but for most of the heavier atoms it has definitely smaller values. The values of n_e for the early terms of the principal and sharp sequences are not whole numbers : they vary from atom to atom. This confirms very strongly our allotment of $k = 1$, 2, 3 and 4 to the S, P, D and F sequence. On this basis, for the F sequence in a hydrogen-like atom the smallest possible value of n_e is 4 :

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* To show that n is greater than n_e, consider the part of the actual orbit within the broken circle in Fig. 47, as compared with the corresponding position of the Keplerian ellipse, shown broken. The velocity at any point of a central orbit depends solely upon the intensity of attraction, the distance of the moving point from the centre of attraction, and the velocity and distance of projection. The projection conditions are the same for Keplerian and actual orbit, since the outer loops are identical, so that at a given distance we have to take into account only the intensity of attraction, which within the dotted circle is always greater for the actual than for the Keplerian orbit. It follows at once from this that, at a given distance, $v_A > v_K$, where v is the velocity of the electron and the suffixes A and K refer to the actual and Keplerian orbit respectively. At a given r,

$$(r^2\dot{\theta}^2 + \dot{r}^2)_A > (r^2\dot{\theta}^2 + \dot{r}^2)_K,$$

and $r^2\dot{\theta}$ is the same in both orbits, since it is the same in the outer loops. Hence

$$\dot{r}_A > \dot{r}_K.$$

Now if we take $\int_Q^P m\dot{r}\, dr$ from any point P where the two orbits practically coincide to the apse Q, and compare the result in the two cases, we have that in the actual orbit the apsidal distance is less than it is in the Keplerian orbit, so that the range of integration is greater, while, at a given r, $m\dot{r}$ is always greater in the actual orbit than in the Keplerian.

Hence $\oint_A m\dot{r}\, dr > \oint_K m\dot{r}\, dr$, while $\oint p_\theta\, d\theta$ is the same in both orbits, so that $n > n_e$.

while for the D, P and S sequences in order $n_e = 3$, 2 and 1. The first F term is therefore a circular 4_4 orbit whose radius is $4^2 = 16$ times that of the orbit of the electron in the normal 1_1 orbit in the hydrogen atom. For higher terms $k = 4$, $n > 4$, and the orbits are elliptical, with the result that the perihelion distance is less than this radius of the circular orbit.

To make this clear, it is well to derive first an expression for the perihelion distance of a truly elliptical orbit for a nucleus of charge Z in terms of k, n and a_H, the radius of the 1_1 hydrogen orbit, which may be called the radius of the hydrogen atom, as pointed out in Chapter IX. The radius a of a circular orbit of a hydrogen-like atom is

$$a = \frac{n^2}{Z} a_H$$

by the equation for r on page 190.

a is also known to be the semi-major axis of any elliptic orbit of the same n, whence

$$\text{perihelion distance} = d_p = a(1 - \epsilon)$$

$$= \frac{a_H n^2}{Z}\left(1 - \sqrt{1 - \frac{k^2}{n^2}}\right); \quad \ldots\ldots\ldots\ldots(7)$$

$$\text{aphelion distance} = d_a = a(1 + \epsilon)$$

$$= \frac{a_H n^2}{Z}\left(1 + \sqrt{1 - \frac{k^2}{n^2}}\right). \quad \ldots\ldots\ldots\ldots(8)$$

(7) shows that the perihelion distance must lie between $\frac{a_H k^2}{Z}$ when $n = k$, and $\frac{1}{2}\frac{a_H k^2}{Z}$ when $n = \infty$. The greater the value of k the greater the minimum perihelion distance for any term of the sequence corresponding to that value of k. This is for a Coulombian field : if the perihelion part of the orbit penetrates into a non-Coulombian field of the type we have considered, the perihelion distance is diminished, but clearly the diminution is the more marked the less the value of d_p. The smaller the value of k, then, the more markedly should we expect the energy of the orbit to depart from that of a Keplerian ellipse

of the same n. Now the order of departure of n_e from whole number values for the different series being in the order S, P, D, F, we have our k allotment confirmed.

The general run of the n_e values of the first term of the general sequence will come up for consideration in Chapter XIV.

Quantitative Applications of Theory of Central Orbits. It is not possible at present to work out in detail the spectra of any but hydrogen-like atoms, that is, systems in which the central nucleus is attended by only one electron. Even the neutral helium atom, in which there are two electrons in attendance, presents a problem which, in its full generality, is beyond the scope of present-day dynamics, although certain guesses at a possible arrangement of the orbits of the two electrons have been made the basis of extensive calculations, to which further reference occurs in Chapter XIV. Heavier atoms are naturally even less accessible to refined quantitative treatment. By means of certain simplifying assumptions it has, however, been possible to obtain rough numerical results by applying the theory of central orbits to certain classes of atoms. It must always be remembered, however, that the theory of coplanar central orbits, specified by two quantum numbers, is inherently incapable of explaining multiplet structure, such as, to take a simple example, the doublet nature of the series of the alkali metals, and consequently no very detailed agreement can be expected.

The classes of atoms for which numerical calculations of series properties have been attempted are those for which the optical electron occupies a preferential position even when it is describing its stable orbit, or orbit of least energy. To make this clear, it must be explained that, in general, the atom contains, in its normal or unexcited state, a small number of comparatively loosely bound electrons, all of which are more or less associated with the changes of energy involved in the quantum switch. (See Chapter XV.) There is, however, every reason to believe that the normal neutral atom of any alkali metal contains only one such valency electron, whereas the atoms of elements of the alkaline earth column in the periodic table contain two valency electrons, and the atoms of the next column three such electrons, although all three are not neces-

sarily moving in equivalent orbits. These matters are discussed more fully when the question of the systematic changes in structure from element to element are considered. For present purposes all that is required is the knowledge that a neutral atom of an alkali metal, a singly ionised atom of an alkaline earth, a doubly ionised atom of a column III. earth element, and so on, consists of a core of a high degree of symmetry and one electron, moving in a special orbit, more loosely held than any of the other electrons. Such a system corresponds more closely to the arrangement considered in deducing the Rydberg and Ritz type of formula by the general method which we have described, whereas for a system in which the symmetrical core is attended by two or more outer electrons, only one of which is removed to a remote orbit on excitation, we can obviously not hope for such good agreement by the same elementary method.

The method by which various workers, among whom may be mentioned Hartree, Fues and Thomas, have obtained numerical results for orbits in which the electron penetrates the core (called orbits of the second kind to distinguish them from orbits of the first kind, in which the whole orbit is external to the core), is based on a consideration of the radial quantum condition, which gives a connection between the energy of the orbit and the potential of the atomic field. The Sommerfeld quantum conditions are used, but, as has been pointed out by Bohr himself, in the case of central orbits these are exactly equivalent to Bohr's method of quantising.

The field due to the atomic core, of net charge se, is assumed to be radially symmetrical : let the function of r which expresses the potential of the force due to the core be Ve.* Ve, of

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* The potential is written as Ve instead of V, so that V may be a function of r only, and not involve the dimensions of the charge. This is a mere matter of convenience. It may also be pointed out that e, the electronic charge, is always taken as a positive number in these equations. Hence the value of the potential energy of the optical electron is $-Ve^2$ instead of $+Ve^2$, as it would be if e were taken positive or negative according to the sign of the charge it represented, as a charge symbol usually is. Similarly the electric force is $\dfrac{\partial Ve^2}{\partial r}$ instead of $-\dfrac{\partial Ve^2}{\partial r}$. Different authors adopt different conventions as to what V represents, so that the reader must be careful in comparing formulae.

course, is zero at infinity. In a central field p_θ is constant, and $2\pi p_\theta = kh$, the azimuthal quantum condition. The energy equation is

$$\frac{1}{2m}\left(p_r{}^2 + \frac{p_\theta{}^2}{r^2}\right) - Ve^2 = -W,$$

where W is, as usual, the negative total energy. Then

$$p_r = \left[-2mW + 2mVe^2 - \frac{k^2h^2}{4\pi^2r^2} \right]^{\frac{1}{2}}.$$

Let n_r be the radial quantum number : then $n_r = n - k$, and, in a given series, where k is constant, n_r increases by unity as we go from term to term. Sommerfeld's radial quantum condition is

$$n_r h = \oint p_r \, dr = \oint \left[-2mW + 2mVe^2 - \frac{k^2h^2}{4\pi^2r^2} \right]^{\frac{1}{2}} dr. \quad \dots\dots(9)$$

From spectral measurements we know the value of the term energy, $-W$, corresponding to a whole number value of n_r, for a whole series of values of n_r. The task before us is to find V as a function of r so that equation (9) may be satisfied for all these values. There is, of course, no sufficient reason for supposing *a priori* that this is possible, since the assumption that the function V is spherically symmetrical might be so far from representing the atomic truth that agreement with experiment could not be obtained on this basis. In fact, not the least interesting thing about the problem is the general question as to how far the hypothesis of central symmetry is reasonable. Fues, Hartree and Thomas, among others, worked on the problem of finding an empirical distribution of force round the nucleus for certain atoms which shall give the right spectral lines for those atoms.

Fues splits the potential V into two parts, putting

$$V = V_1 + V_2,$$

where V_1 is the potential due to a nucleus of charge *se*, so that V_2, the added potential, represents the unlikeness of the atomic field to that of a type of hydrogen atom—represents the hydrogen-unlikeness, to imitate the German phraseology. V_1 is

then the function $\dfrac{-e^2s}{r}$, for which numerical values can be calculated straight off for every r. He puts

$$P = -2mWr^2 - 2mV_1 e^2 r^2 - \frac{k^2 h^2}{4\pi^2}, \quad Q = 2mV_2 e^2 r^2,$$

so that

$$n_r = \frac{1}{h} \oint \frac{\sqrt{P-Q}}{r} \, dr \quad \dots\dots\dots\dots\dots\dots(10)$$

It is required to find the curve Q against r, which gives the nature of the added field due to the electronic distribution in the core. In the case of sodium (atomic number 11), Fues assumes that the core can be represented by a nucleus attended by two close electrons, which is roughly equivalent to a nucleus of charge 9, and 8 electrons arranged at the corners of a cube surrounding the nucleus symmetrically.* The cube is supposed to move so that the radius vector from the nucleus to the optical electron is always normal to the same face of it. The arrangement assumed is necessarily rather arbitrary and artificial. Fues has considered various other plausible symmetrical arrangements, and found that they all lead to somewhat the same type of curve for Q. An important point which he emphasises is that with none of these can the field be developed in powers of $\dfrac{1}{r}$, which accounts for Sommerfeld's failure to get satisfactory values of the constants when he assumed such a development.†

P is fully determined for each n_k orbit, since W is known empirically and V_1 is given by definition. The general form of

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* Cf. the structure of the sodium atom discussed in Chapters XIV. and XVII.

† Sommerfeld, using the simple model in which the electrons are arranged in a ring in one plane, developed an expression for V in powers of $\dfrac{1}{r}$, viz.

$$V = \frac{se^2}{r} \left[1 + \frac{1}{4}\left(\frac{a}{r}\right)^2 + \frac{9}{64}\left(\frac{a}{r}\right)^4 + \dots \right] - \frac{Ze^2}{r},$$

and from this deduced the Rydberg and Ritz formulae as successive approximations. The lines of the proof were sketched in the first edition of this book. However, Weihnacht has shown that the integration as carried out by Sommerfeld does not, in general, lead to a convergent result, which accounts for the difficulties which arose. The type of proof given on p. 279 et seq. of this book has since been evolved, so the account of this particular part of Sommerfeld's work has been omitted in this edition.

Q having been obtained, it is possible by a graphical method to find the quantum defect α in the formula

$$\frac{W}{ch} = \frac{R}{(n-\alpha)^2} \, .$$

Fues finds α always positive, as we have shown on general grounds that it should be, and the numerical values of α which he calculates are in good agreement for all terms with those experimentally determined.

He also finds the Ritz correction $\alpha - \beta/n^2$ positive for orbits of the first class, and negative for orbits of the second class. In general it may be said that the central symmetrical field gives a fair numerical representation of the sodium spectrum. In a later paper Fues uses this method of separating the field into two parts given by the functions P and Q to determine from the atomic field values of the X-ray terms of sodium, and fair agreement is obtained.

Fues has also used this method to determine from the sodium terms the way in which Q varies with r, that is the structure of the atomic field. In Fues' graphical method the circular orbits give certain parabolas which the curve of Q against r must touch ; and conditions are such that the points of contact are approximately known. By this means the Q curve can be approximately fixed : for the integration required in the formula

$$n_r = \frac{1}{h} \oint \frac{\sqrt{P-Q}}{r} \, dr$$

the Q curve is cut up into parabolic arcs, which enables the integration to be carried out. As a result Fues finds that all the terms of the optical spectrum of sodium are given to within 6 per cent. by one and the same central field, following the law obtained by him graphically.*

Hartree imagines the field at any distance r to be expressed in terms of an effective nuclear charge eZ_e, which is defined so that the force at this distance $= \dfrac{\partial V}{\partial r} = \dfrac{e^2 Z_e}{r^2}$. Z_e has, then, a different value at each distance r : it tends to s for large values of r, and tends to Z for small values of r. The charge to which

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* Not a simple curve.

the added field is due is clearly $(Z_e - s)e$. It is convenient to express the distance r in terms of the radius a_H of the 1_1 hydrogen orbit, introducing for the purpose the variable $\rho = \dfrac{r}{a_H}$.

Remembering $a_H = \dfrac{h^2}{4\pi^2 m e^2}$, $R = \dfrac{2\pi^2 m e^4}{c h^3}$, (9) becomes

$$n_r = \frac{1}{2\pi} \oint \left[-\frac{\nu}{R} + 2v - \frac{k^2}{\rho^2} \right]^{\frac{1}{2}} d\rho,$$

where $v = \dfrac{W}{hc}$ is the wave number of the term in question corresponding to the orbit specified by quantum numbers $n = n_r + k$ and k, and

$$v = \int_r^\infty \frac{Z_e}{\rho^2} d\rho. \quad \dots\dots\dots\dots\dots\dots\dots(11)$$

Expressing things in this way in terms of the scale of the hydrogen orbit, the constants e, m, h are eliminated. For calculation we can put

$$n_r = \frac{1}{\pi} \int_{\rho_2}^{\rho_1} \left[-\frac{\nu}{R} + 2v - \frac{k^2}{\rho^2} \right]^{\frac{1}{2}} d\rho, \quad \dots \dots\dots \dots\dots(12)$$

where ρ_1 and ρ_2 are the apsidal distances, which must be roots of the quantity in square brackets, since at an apse $\dot\rho = 0$ and the radial momentum is zero.

Hartree works with equations (11) and (12), his problem being to determine v as a function of r so as to satisfy both equations. The assignment of quantum number n adopted is that of Bohr, discussed in Chapter XIV. In his computations he makes great use of the circular orbits, for which $k = n$, since for these orbits Z_e and v have one value only, corresponding to the fixed value of r, and the integral involving values of v over a range of values of ρ is not needed. The method adopted is to choose the value of Z_e to fit a large circular orbit ; then to fix approximately a range of values of Z_e to fit other orbits of same k : then to fit a circular orbit of the next smaller value of k, and so on, proceeding inward. In this way, a curve of Z_e against ρ is built up for the given atom.

Hartree finds, as does Fues, that the central radial field allows in general a good approximation to be made to the.

empirical terms, but he has extended his work to include not only sodium, but also potassium and ionised calcium. The agreement is not good for orbits for which $k = 1$, which is to be anticipated, since such orbits, of high eccentricity, penetrate far into the core, where, on account of the innermost group of two electrons whose existence is discussed in Chapter XIV., the deviation from a central field must be large. Another interesting result is that the added field is appreciable a long way outside the boundary of the atom. Now, if Laplace's equation $4\pi\rho = \mathrm{div}\, E$ is to hold, such a deviation would appear to be incompatible with absence of electric charge, which emphasises the fact that the assumption of a radial field is only an approximation, or, alternatively expressed, that the radial field approximately equivalent to the core-field demands a distribution of electricity outside the actual bounds of the atom. However, a deviation of the field from the inverse square law outside the boundary of the atom can also be accounted for by a polarisation of the core by the approaching electron, to which reference is made a little later on.

Hartree has also deduced quantitative relations between sodium-like atoms, by which is meant atoms with the same core-structure as sodium but different core-charge, $i.e.$ $\mathrm{Na_I}$, $\mathrm{Mg_{II}}$, $\mathrm{Al_{III}}$ and $\mathrm{Si_{IV}}$. For orbits of the first kind, the outsiders, he assumes that the added field can be represented by

$$A(\rho) = B\rho^{-m}, \quad \dots \quad \dots \dots \dots \dots \dots \dots \dots (13)$$

and proceeds to see if agreement with experiment can be obtained by the suitable choice of m. For this purpose he considers the term excess for an n_k orbit, denoted by $a(n, k)$ and defined by

$$\frac{\nu}{R} = \frac{s^2}{n^2} + a(n, k),$$

where ν is the wave-number of the term. The ratio of the term excess for a given orbit to that for the circular orbit of the same k, which is $\dfrac{a(n, k)}{a(k, k)}$, is found for different terms from the experimental data, and proves to be much the same, for a given value of n and k, for all the sodium-like atoms. As

orbits of the first class are in question, the values of k chosen for consideration are $k=3$ and $k=4$. The theory of the central field indicates this constancy of the ratio, and it is further found that putting $m=4$ in (13) gives the experimentally found relation between different terms in a given sequence.

Born and Heisenberg have obtained a similar result for orbits of the first kind by a totally different method. They consider the atomic core not as a rigid whole, but as a rigid system of negative electricity which can be displaced by electric forces relatively to the positive nucleus. The optical electron exercises on the core an electric force which produces such a displacement, or polarisation of the core, and the electric moment so induced must be $d=\dfrac{ge}{r^2}$, where g is a coefficient of proportionality. It is well known from the elementary theory of magnetism that a small dipole of this kind produces in the direction of its axis a force $\dfrac{2d}{r^3}$, or the force f on the electron produced by this polarised core is $f=\dfrac{2ge^2}{r^5}$ with a potential $-\dfrac{ge^2}{2r^4}$. The addition of such a term to the ordinary Coulombian potential enables us to calculate the constants α and β of Ritz's formula in terms of g, or, conversely, the experimentally found values of α and β give us a value for g, which can be compared to the value of g deducible from the dielectric constant of the inert gases.* Fair, but not more than fair, agreement is obtained. We may say, then, that as far as alkali metal atoms, or alkali-metal-like atoms, are concerned, the effect of the core on orbits lying wholly outside the core can be approximately expressed by adding to the ordinary potential of the Coulombian field a term in r^{-4}. It may be added that certain quantitative results for penetrating orbits have been obtained by Hartree, but they are somewhat involved for consideration here.

W. Thomas has applied the method of Fues to calculate the actual orbits for the optical electron in the sodium atom, and

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* The structure of the core of alkali metal elements is similar to the structure of the inert gases. See Chapter XIV.

has further, by obtaining the Fourier coefficients of these orbits and by applying the correspondence principle, obtained figures to express the probability of the various transitions.
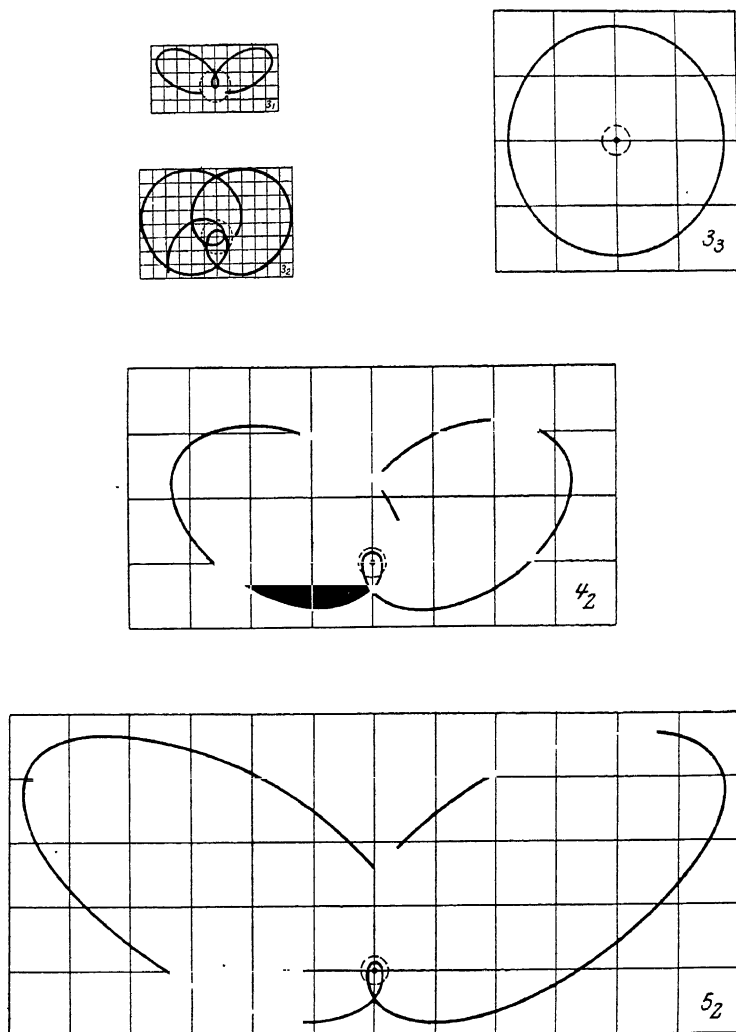
FIG. 48.

Possible orbits of the optical electron in the sodium atom.
(Normal orbit is 3_1.)

The intensities calculated in this way for the first three absorption lines in the spectrum of sodium, corresponding to the displacement of the electron from the normal 3_1 orbit to 3_2, 4_2 and 5_2 orbits (on Bohr's attribution of principal quantum numbers), show fair agreement with the measurements of Bevan for these lines. The forms of the orbits obtained by Thomas are shown in Fig. 48, to illustrate the general nature of the electron paths.

The various examples given in this section show that in the comparatively simple case where the atom consists of a symmetrical core and one valency electron, the assumption of a radial field permits an approximate representation of observed term values. At the same time they will serve to illustrate how far we are from a quantitative solution of the general problem of calculating spectral terms, since even this case can be handled in a very general way only.

The Selection Principle. We have seen that the term sequences can be explained by considering n_k orbits, a fixed value of k corresponding to a given sequence. There are limitations, theoretical and experimental, as to the combinations of terms which are possible in the expression

$$h\nu_T = W(k', n') - W(k, n), \quad \dots\dots\dots\dots\dots(14)$$

$W(k, n)$ indicating the negative energy corresponding to an n_k orbit, and these limitations have to be considered.

The disturbance of the Coulombian form of the field due to the presence of the core electrons causes, as we know, a uniform rotation of the apse with a frequency which we have denoted by ω_k. The x moment of the electron we have developed in the series

$$\xi = \Sigma C_\tau \cos\left(2\pi\tau\omega t + \gamma_\tau\right),$$

and we have seen, in considering the Zeeman effect, that the imposition of a uniform rotation is expressed by the formula

$$\xi = \Sigma C_{\tau, \pm 1} \cos\left\{2\pi(\tau\omega \pm \omega_k)t + \gamma_{\tau, \pm 1}\right\}, \quad \dots\dots\dots\dots(15)$$

which denotes that the original harmonic component of periodicity ω is replaced by the harmonic components of frequency

$$\tau\omega + \omega_k, \ \tau\omega - \omega_k.$$

Now by equation (2) we have

$$\delta E = \omega \, \delta J_n + \omega_k \delta J_k,$$

where ω is the frequency from perihelion to perihelion in the periodic orbit and ω_c is the frequency of the superimposed rotation, while

$$J_n = nh, \; J_k = kh.$$

In the limit where n and k are very large compared to the differences $(n-n')$ and $(k-k')$ in the two orbits contemplated

$$\nu_T = \frac{E-E'}{h} = \frac{\delta E}{h} = \omega \frac{\delta J_n}{h} + \omega_k \frac{\delta J_k}{h} = (n-n')\omega + (k-k')\omega_k.$$

By the correspondence principle such a transition is in general conditioned by the presence of frequencies $(n-n')$ and $(k-k')$ in the orbital motion. We see, therefore, from (15) that, while $(n-n')$ can have any whole number value, $(k-k') = \pm 1$. In other words, the only energy differences possible in (14) are those between terms for which k, the azimuthal quantum number, differs by 1. It may be noticed that in the hydrogen spectrum, where, on the point of view represented by the correspondence principle, there is only one quantum number, n, not only do all the term sequences degenerate into one sequence, but the condition which limits the choice of pairs of terms loses all significance, and lines corresponding to the difference of any two terms are possible.

The selection rule $\Delta k = \pm 1$, where Δk denotes the difference between the value of the k in the initial and in the final orbit, implies, of course, from its method of deduction, not only that there is no interchange of energy between core and optical electron, but also that there is no exchange of angular momentum.

The usual series are given by transition between P and S, S and P, D and P, and F and D terms. Hence k must differ by $+1$ or -1 for any two series of terms here paired together, which agrees with our allotment of $k=1$, 2, 3 and 4 to S, P, D and F. A reason for the allotment was, in fact, that the correspondence principle necessitates k changing by 1 as we go from one term sequence to the next.

It is instructive to contrast the case of the orbits as modified by the non-Coulombian central field of the atom itself with

that of the orbits as modified by an external magnetic field, since in both cases the result is a uniform rotation of the perihelion. Corresponding to $\Delta k = \pm 1$ we have, on the correspondence principle, a circularly polarised radiation, the rotation being in the one sense for $\Delta k = +1$ and in the other for $\Delta k = -1$. In the case of the Zeeman effect the imposed rotation is about a fixed direction, parallel to the magnetic lines of force, for all atoms, and therefore the statistical result for a large number of atoms is circularly polarised light of two different frequencies, corresponding to $\Delta k = +1$ and to $\Delta k = -1$,* the sense of the polarisation being opposite in the two cases. In the case of the atomic field, the imposed rotation is about an axis normal to the plane of the orbit itself, and the direction of the plane of the orbit is distributed at random among the different atoms in any actual body of luminous gas. Hence taking *either* $\Delta k = +1$ *or* $\Delta k = -1$, the rotation corresponding to the polarisation is as likely to be in the one sense as in the other when the average is taken over a large number of atoms. The radiation is unpolarised. Of course, transitions for which $\Delta k = +1$ and for which $\Delta k = -1$ correspond to lines of different series. In the Zeeman effect, since any component of rotation in the plane containing the direction of the field is unaffected by the field, we can have transitions corresponding to $\Delta k = 0$, which are obviously impossible in the case of a centrally symmetrical field.

The application of the correspondence principle which has been considered in this section is sometimes called the Selection Principle (*Auswahlprinzip* or *Auswahlregel*), or, since that expression may be extended to cover the selection of terms involving other quantum numbers, the k Selection Principle (*k-Auswahlregel*). It is worthy of record that a first attempt in this direction was made by Rubinowicz from a very different point of approach. He developed somewhat complicated considerations of the moment of momentum of the emitted spherical electromagnetic wave, which is connected with the moment of momentum of the atom itself by the conservation of moment of momentum, a principle which, with the conservation

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* The second quantum number was called n_{II} when we were discussing the Zeemann effect : it is now called k to emphasise the analogy.

of energy, has survived the relativistic reforms.* It is the azimuthal quantum number which is involved in the evaluation of the moment of momentum of the atom. Putting the change of moment of momentum of the atom equal to the negatived moment of momentum of the emitted spherical wave, without in any way considering the machinery by which the transformation of momentum is effected, it is found that

$$\Delta k = \frac{2ab \sin \gamma}{a^2 + b^2},$$

where a and b give the amplitude of the two mutually normal components of vibration in the wave front (or rather in the substituted Hertzian oscillator), γ the difference of phase. The expression on the right cannot exceed 1; Δk, the change of azimuthal quantum number, cannot be other than a whole number; and therefore we have the following possibilities:

$$\Delta k = \pm 1; \quad a = b, \quad \gamma = \pm \frac{\pi}{2},$$

which corresponds to circularly polarised light,

$$\Delta k = 0; \quad a = 0, \text{ or } b = 0 \text{ or } \gamma = 0,$$

which gives linearly polarised light, either along b or a, or bisecting the angle between a and b.

Returning after this brief digression to our application of the Correspondence Principle, we have seen that the assumption of a centrally symmetrical atom field led to the k-selection rule, namely $\Delta k = \pm 1$, and, conversely, the satisfaction of this rule might be considered as strong evidence for the centrally symmetrical nature of the atomic field. However, while the rule is obeyed by the four chief series (and also by the G series

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* With regard to the conception of the moment of momentum of a wave, it is well known that light exerts a pressure. Again, on the relativity theory energy possesses inertia, and hence light has inertia. Both theory and experiment indicate, then, that to radiation must be attributed momentum. The electromagnetic moment of momentum per unit volume at a given point of, say, a spherical wave is given by the vector product of the momentum G (proportional to the Poynting vector or flux of energy), and the radius vector r from the centre of the wave to the point, and, for the whole sphere it is

$N = \int [rG] \, d\tau$, where $d\tau$ is an element of volume, and $[rG]$ the vector product of the two vectors. In general the direction of the momentum G does not coincide with that of the radius vector r, and N has a non-vanishing value.

discovered by Paschen and by A. Fowler) there are certain combination lines, found experimentally, for which $\Delta k = 0$, and others for which $\Delta k = 2$. The lines of the sodium spectrum discovered in 1903 by Lenard during his investigation of the arc are examples of $\Delta k = 0$, being represented by $1P - nP$ (Fowler's notation).* Lines recently found by Foote, Mohler and Meggers in the spectra of sodium and potassium, and also by Datta for potassium, are represented by $1S - 3D$, and consequently for them $\Delta k = 2$. These combinations appear in circumstances which may be called exceptional, in general in the presence of either a strong electric field or a strong magnetic field. In either of these cases new constituents are introduced into the harmonic motion, and the possibility of fresh combinations follows from the correspondence principle. In the case of the lines discovered by Foote and his collaborators there is no applied electric field, but the current density is very high. The experimenters suggest that the interaction of atomic fields of neighbouring atoms, presumably ionised to a high degree, is responsible for the appearance of the new lines. It is noteworthy that Hansen, Takamine, and Werner have obtained in the case of mercury a certain line, forbidden by an extension of the selection principle, by applying a magnetic field.

General Scheme of Spectra. The question of multiplet structure of spectra, to which reference has been made in the Digression on Optical Spectra, will be treated in Chapter XV., but it is now necessary to take a preliminary glance at the problem of the representation of actual spectra by terms. For if we are to consider in any detail the behaviour of, for instance, the alkali metals, which have doublet series, or the alkaline earths, which have triplet series, we are forced to take account of the separate components of the doublets and triplets. The n_k levels have to be divided into various sub-levels, and the limitation of the transitions between these sub-levels by a selection principle is a very important feature of modern spectral theory, to which we shall frequently appeal to account for observed peculiarities.

* Actually by $1\pi - n\pi$, since the terms are double, and so Greek letters were used by Fowler in his *Report*.

In addition to n and k a third quantum number j is invoked, to specify the sub-levels : it is called the inner quantum number, and was first introduced by Sommerfeld as a number which could be allotted empirically to certain terms, in such a way that a simple selection principle, governing the changes of j in possible transitions, gave results in agreement with observation. Attempts have been made to give j a particular meaning in the atomic model, and we can go some way in this direction. It is essential to Bohr's theory that the quantum numbers should each be connected with some periodic motion in the atom. Thus n is connected with the periodic motion of the electron in its orbit, k with the periodic motion of perihelion ; extending the scheme, j is connected with a precessional movement of the plane of the orbit. This plane must then be assumed to be inclined at a fixed angle φ to some axis about which it rotates. Obviously if the core has spherical symmetry, and exerts a purely central force on the optical electron, there is no reason why this angle should have one value rather than another ; the energy of the system is the same for all values of φ. We must assume, in order to get a third quantum number j, that the core itself has, as a whole, an angular momentum about some axis, and that there is some kind of coupling between core and optical electron, as to the nature of which we cannot profitably speculate at present. Once we have in the atom a preferential axis we have something with respect to which we can impose a further quantum condition : we can, for instance, take the total angular momentum of the atom—core + optical electron—which will be found by compounding vectorially the angular momentum of the core and of the electron, and quantise it, by putting

$$\text{total angular momentum} = \frac{jh}{2\pi} .$$

Since, attributing a fixed angular momentum to the core, this total angular momentum will, for a given angular momentum of the electron in its path, depend upon the angle φ, we are, in effect, quantising the orientation of the plane of the orbit with respect to the axis of the core, or with respect to the total angular momentum : we restrict the inclination

to a few definite values. This gives us our third quantum
condition.

In Figure 49, $AAAA$ is the plane of the orbit, the vector CD,
representing the angular momentum of the electron in its
orbit, being inclined at an angle φ to OC, the direction of the
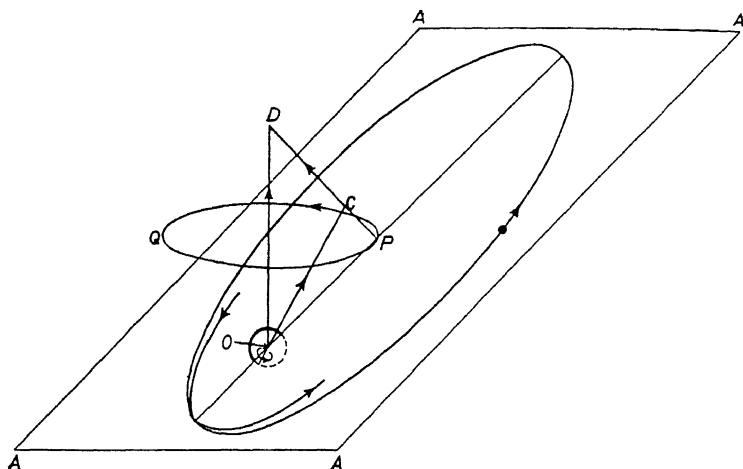
FIG. 49.

Atomic scheme where core has moment of momentum.

vector representing the angular momentum of the core. The
plane precesses, rotating round OD, the axis of total angular
momentum, as represented by PQ, while the electron circulates
in its orbit with motion of perihelion. φ is restricted to have
one of a few discrete values. This is Sommerfeld's "space
quantisation." Of course, the preferential direction necessary
in order to carry out such a space quantisation may be supplied
either by a field of force within the atom, as in the case just
considered, or by an external electric or magnetic field, as in
the case of the Zeeman or Stark effect. In the case of the
Stark and Zeeman effect we took as the orbit of the electron a
Kepler ellipse (one quantum number only) and the second
quantum number was introduced by what is virtually a space
quantisation with reference to the direction of the field of force.

This brief description of a mechanical model has been given
to reconcile the reader to the introduction of the inner quantum

number. The inner quantum number must express a coupling between the core and the electron which is capable of being effected in a finite number of different ways, a different energy of the whole atom corresponding to each way, so that we can have different term values for the same n and k. The model gives a pictorial representation of an imaginary mechanism by which this can be effected. The problem is further discussed in Chapter XV., where the quantisation of the moment of momentum of the core receives discussion. It must be said at once, however, that this model cannot be maintained in detail, and must be considered rather as a mnemonic than as a mechanically valid system. It must also be remarked that we are forced later to attribute to j in certain cases values which are whole number multiples of $\frac{1}{2}$, *i.e.* to put $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots$ instead of $1, 2, 3, 4, \ldots$, and to modify the values chosen for k similarly. We are here reaching a stage when the theory is obviously not very happy, and needs some drastic modification. For the moment, however, since we are only going to deal with differences of two values of j, it will not matter whether we take half-odd-integral values or integral values. It also does not matter for our present purpose exactly what mechanical meaning is to be attributed to j : we can treat a value of j as a label serving to distinguish a given level, so chosen that the selection rule which we are about to discuss gives results agreeing with theory.

We have seen that the selection rule for the k's is that k can change by 1 or -1 in a quantum switch. The rule found to be valid for the j's is that a quantum switch is only possible if the values of j for the initial and final orbits differ by 1, or by 0. We can express the limitations imposed by the selection rule as follows :

Principal.	Azimuthal.	Inner quantum number.
$n \rightarrow n'$,	$k \begin{array}{c} \nearrow k+1 \\ \searrow k-1 \end{array}$,	$j \begin{array}{c} \nearrow j+1 \\ \rightarrow j \\ \searrow j-1 \end{array}$.

It must be further noted that the particular transition $j = 0$ to $j' = 0$ (permitted by the rule $j' - j = 0$) is excluded. Using the model given, the selection principle for the j's can be justified by the correspondence principle. If the frequency of

the electron in its periodic orbit be ω, and the frequency of the superposed rotation in its own plane which gives the motion of perihelion be σ, then the motion is represented by *

$$\xi = \Sigma C_{\tau, \pm 1} \cos\left\{2\pi\left(\tau\omega \pm \sigma\right)t + \gamma_{\tau, \pm 1}\right\}.$$

Now let the frequency of the precessional motion of the plane of the orbit be ρ. If ξ is the component of the motion parallel to the axis of precession it will obviously be unaffected by the precession : on the other hand η, a component normal to the axis of the precession, will have a single added frequency ρ owing to the uniform circular rotation. This frequency will have to be added or subtracted according to the direction of the precession. Accordingly we have

$$\xi = \Sigma C_{\tau, \pm 1} \cos\left\{2\pi(\tau\omega \pm \sigma)t + \gamma_{\tau, \pm 1}\right\}, \quad\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

$$\eta = \Sigma C_{\tau, \pm 1, \pm 1} \cos\left\{2\pi(\tau\omega \pm \sigma \pm \rho)t + \gamma_{\tau, \pm 1, \pm 1}\right\}. \quad\ldots\ldots(17)$$

A quantum switch from an orbit characterised by j to one characterised by j' is conditioned by the occurrence of a harmonic term $(j'-j)$. From (16) $j'-j=0$, from (17) $j'-j=\pm 1$. Now in an actual source the axes of the cores must be oriented at random for the various atoms, so that we receive light corresponding to both (16) and (17). Hence we have the rule already laid down.

We can see from general reasoning that the particular transition $j=0$ to $j=0$ is excluded, as already mentioned. For $j=0$ means that the angular momentum of the core and of the electron are equal and collinear, but in the opposite sense. Since k must change in a transition the angular momentum of the electron must change, while that of the core is constant, so that after a transition j can no longer be zero.

Notation. As we are now attempting the discussion of spectra containing doublet or triplet series the notation of the *Digression*, Chapter VIII., which provided for a single term for each value of n in a given series (principal, sharp, diffuse, or fundamental) is no longer sufficient. The question of notation is, unfortunately, still in flux, and we may say, in the words of Russell and Saunders, that the present state of notation for spectroscopic terms is chaotic. In the first place, as has been

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* Cf. formula (27), page 252.

pointed out already, the serial number n is assigned differently by different practical spectroscopists among themselves, and again differently by Bohr. This, however, is a comparatively minor point, which we can postpone. Turning to general notation, and taking first the doublet terms, Fowler used in his *Report* little Greek letters with suffixes. Thus for first terms of the sharp, principal, diffuse and fundamental sequences ($k = 1, 2, 3, 4$) Fowler wrote 1σ; $1\pi_2$, $1\pi_1$; $2\delta'$, 2δ; 3φ; the π and δ terms being double.* π_1 refers to the stronger component, π_2 to the weaker one, and similarly for triplets the lowest suffix indicates the strongest component. For the same terms, Paschen and Sommerfeld use ordinary little letters, and write $1s$; $2p_2$, $2p_1$; $3d_2$, $3d_1$; $4f$. Recently Russell and Saunders have put forward a new notation, which is here adopted.

We use the letters S, P, D, F for the terms of the four main series, whether singlets, doublets, triplets, or multiplets of higher order. The serial number is written before the letter. The degree of multiplicity of the system is indicated by an index on the upper left hand of the letter ; thus a doublet term is indicated by the 2 in ^2P.† The different terms belonging, in the case of a multiplet, to the same value of n and k (*i.e.* to one serial number in one sequence) are indicated by writing the value of j, the inner quantum number, as a subscript on the right. Thus the leading P terms in a principal doublet series are written 1^2P_1, 1^2P_2; in a principal triplet series 1^3P_0, 1^3P_1, 1^3P_2. The notation has the great advantage that only one kind of letter is used, and that the system is recognised at once by the figure giving the multiplicity. The space on the upper right-hand side is left free for any further indices that may be necessary. Of late Fowler has adopted a similar notation, using, however, little letters instead of capitals.

For conversion a table comparing the various notations is given. It is particularly to be noted that the order in which the suffixes distinguishing the various terms of a multiplet (*i.e.* the lower right-hand figures) run from term to term is reversed in the new notation, as compared to the older notation. Thus,

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* Later he adopted δ_2, δ_1 in place of δ', δ.

† Read " doublet P."

for the doublets, $1\pi_2$ is 1^2P_1, $1\pi_1$ is 1^2P_2 : for the triplets the suffixes 3, 2, 1 become 0, 1, 2.

The notation of Landé is also included in the table, for comparison. Landé denotes a term by n^r_{kj}, where n is the principal quantum number, r is the multiplicity of the term.* A disadvantage of this notation is that the main symbol is the n, about the allotment of which the greatest divergencies exist.

TABLE OF SPECTROSCOPIC NOTATIONS.

System.	Landé n^r_{kj}.	Rydberg-Fowler.	Paschen-Sommerfeld.	Russell and Saunders.
Singlets (Ca$_I$)	4^1_{10}	$1S$	$1S$	1^1S_0
	4^1_{21}	$1P$	$2P$	1^1P_1
	3^1_{32}	$1D$	$3D$	1^1D_2
	4^1_{43}	$3F$	$4F$	3^1F_3
Doublets (K$_I$)	4^2_{11}	1σ	$1s$	1^2S
	4^2_{21}	$1\pi_2$	$2p_2$	1^2P_1
	4^2_{22}	$1\pi_1$	$2p_1$	1^2P_2
	3^2_{32}	$2\delta', 2\delta_2$	$3d_2$	2^2D_2
	3^2_{33}	$2\delta, 2\delta_1$	$3d_1$	2^2D_3
	4^2_{4j} $(j=3, 4)$	3φ	$4f$	3^2F_j
Triplets (Ca$_I$)	5^3_{11}	$1s$	$2s$	1^3S_1
	4^3_{20}	$1p_3$	$2p_3$	1^3P_0
	4^3_{21}	$1p_2$	$2p_2$	1^3P_1
	4^3_{22}	$1p_1$	$2p_1$	1^3P_2
	3^3_{31}	$1d'', 1d_3$	$3d_3$	1^3D_1
	3^3_{32}	$1d', 1d_2$	$3d_2$	1^3D_2
	3^3_{33}	$1d, 1d_1$	$3d_1$	1^3D_3
	4^3_{4j} $(j=2, 3, 4)$	$3f$	$4f$	3^3F_j

Optical Absorption. Valuable information as to the quantum mechanism and the stationary states can be won by passing radiation through a vapour or gas, and observing the conversion of the energy of radiation into energy of the optical electron which takes place in a quantum switch, of which the ionisation of the atom is an extreme case. This can be done by studying the selective absorption of the radiation by the vapour, since if a given frequency is missing in the

* The core quantum number (see Chapter XV.).

transmitted radiation we have evidence of its conversion. We proceed to consider the particular way in which absorption measurements can be interpreted in terms of stationary states.

By the fundamental assumption of the quantum theory each series represents a succession of transitions from various possible quantum orbits to one and the same final orbit, and we know from our consideration of the empirical laws of line spectra that at least three such final orbits, pertaining to the terms $1S$, $1P$ and $2D$ commonly occur for each spectrum which an atom can emit. Of these only one can be the most stable orbit, that is, the orbit which the optical electron occupies in the unexcited atom, and it is very important to know which this orbit may be. It is to be assumed that the largest term which occurs in all the series corresponds to the most stable orbit, since for it the work of removing the electron is greatest (*i.e.* the term pertains to the stationary state in which the atom has least energy). For this term to be known, however, the spectrum must have been ordered and satisfactorily analysed into terms, and, further, the possibility has to be considered that there may be an unknown term, involved in the emission of unobserved lines in the extreme ultra-violet. It is desirable to have a direct experimental method of determining the normal orbit of the optical electron, and such a method is afforded by the absorption spectra of cold or unexcited gases or vapours. Light passing through such a vapour finds the atoms with all their optical electrons in their normal orbits : if it contains frequencies corresponding, by the quantum relation

$$h\nu_T = E_{n'} - E_n$$

to transitions from the normal orbit to other possible orbits, *i.e.* orbits for which k differs by unity, then light of these frequencies will be absorbed. All the lines of a series whose greatest term corresponds to the normal orbit will be absorbed; but the lines of other series, whose greatest term corresponds to electron orbits not occupied in unexcited atoms, will not appear as absorption lines. The fact that only certain of the emission lines appear in the absorption spectrum of non-luminous vapours has long been known as an experimental fact, which appeared inexplicable on the older spectral theories.

The electron ejected by the incident light from the normal orbit cannot, of course, so long as it remains in the atom, occupy any final orbit other than one of the quantised orbits; its final energy is tied down to certain discrete values, and we get lines, and not a continuous band, in absorption. If, however, the frequency of the incident light be so great that the electron is thrown right out of the atom its final energy can have any value, since there are no limits imposed upon the kinetic energy with which the electron leaves the atom. Radiation of any frequency greater than that required just to ionise the atom can therefore be absorbed, and we should expect a continuous absorption band, extending from the limit of the series of absorption lines in the direction of diminishing wavelength. Such an absorption band was first observed by R. W. Wood for sodium vapour, and has been further studied by Holtsmark.

As examples of the absorption by non-luminous vapour the experiments of R. W. Wood and Fortrat on sodium vapour may be quoted. With a column of sodium vapour 2·8 m. in length, and a spectrograph of very high dispersion (at the limit of the sodium P series, $\lambda\,2414$, one Ångstrom unit was represented by 3·5 mm. on the plate), they obtained 58 members (doublets) of the principal series $1^2S_1 - n^2P_j$ ($j = 1, 2$), and members of the principal series only. 1^2S_1 is clearly the basic term. It has been shown with the other alkali metals and alkaline earths by R. W. Wood, McLennan and others that the only absorption lines which appear with non-luminous vapours are lines of the principal series. Results have been obtained with elements of other columns of the periodic table which will be considered when the table is discussed.

In certain circumstances, however, it is well known that lines which do not belong to the principal series can appear as absorption lines. The lines of the Balmer series appear sharply reversed in stellar spectra, and Hartmann has observed a continuous absorption band at the limits of the Balmer series in the spectrum of stellar hydrogen. The Balmer series, however, for which the final orbit is a $n' = 2$ orbit, does not correspond to a return to the most stable orbit; it is the Lyman series for which the limit corresponds to the stable 1_1 orbit. Again it

is not only the principal series which appears reversed in arc spectra : lines of other series are commonly reversed with the arc under ordinary conditions.*   The quantum theory explains at once how it is that *luminous* vapours or gases can absorb other lines than those which, in emission, correspond to a return to the normal orbit.   For if an atom happens to be not in the normal state, but, owing to exciting causes, in some other stationary state, then incident radiation of suitable frequency can cause the electron to move from the orbit which it happens to occupy at the moment to any other orbit permitted by the selection principle.   Corresponding to this there will be an absorption line of the series for which the initial orbit in this absorption process is the final orbit in the emission process. There is therefore no difficulty in seeing how a luminous vapour can absorb all the emission lines ; such is the case with the arc reversals,.and with the Balmer series of absorption lines produced by the very thick layers of luminous hydrogen which are effective in the stellar spectra.   A reversal of H_a was produced in the laboratory by Pfluger in 1907, and subsequently Ladenburg and Loria were able to reverse both H_a and H_β by means of a hydrogen tube at low pressure electrically excited.   R. W. Wood has demonstrated the absorption of H_a in the laboratory with a long discharge tube.   The presence of such absorption lines, then, is not in contradiction to the quantum theory, but to confirm the mechanism fully it would be desirable to produce absorption lines deliberately (in contrast to the arc reversals, which are fortuitous) in the laboratory in the following way.   Let a long column of vapour be excited by electrons of velocity just exceeding the first resonance potential, so that a comparatively large number of atoms may have an electron in a stationary state next above the normal, *e.g.* the 2^2P_1 state for the alkali metals.   This tube should then emit only the one line corresponding to the resonance potential, but when light is allowed to traverse it, it should absorb the whole series based on the 2^2P_1 orbit, *i.e.* the sharp and diffuse series.   Such an experiment is very difficult to

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* Reversed lines make their appearance as narrow black lines down the centre of the emission lines, the emission lines being broad owing to the greater heat of the middle region.

carry out : the column of vapour must be long, and the bombardment intense, since, as will be discussed a little later,
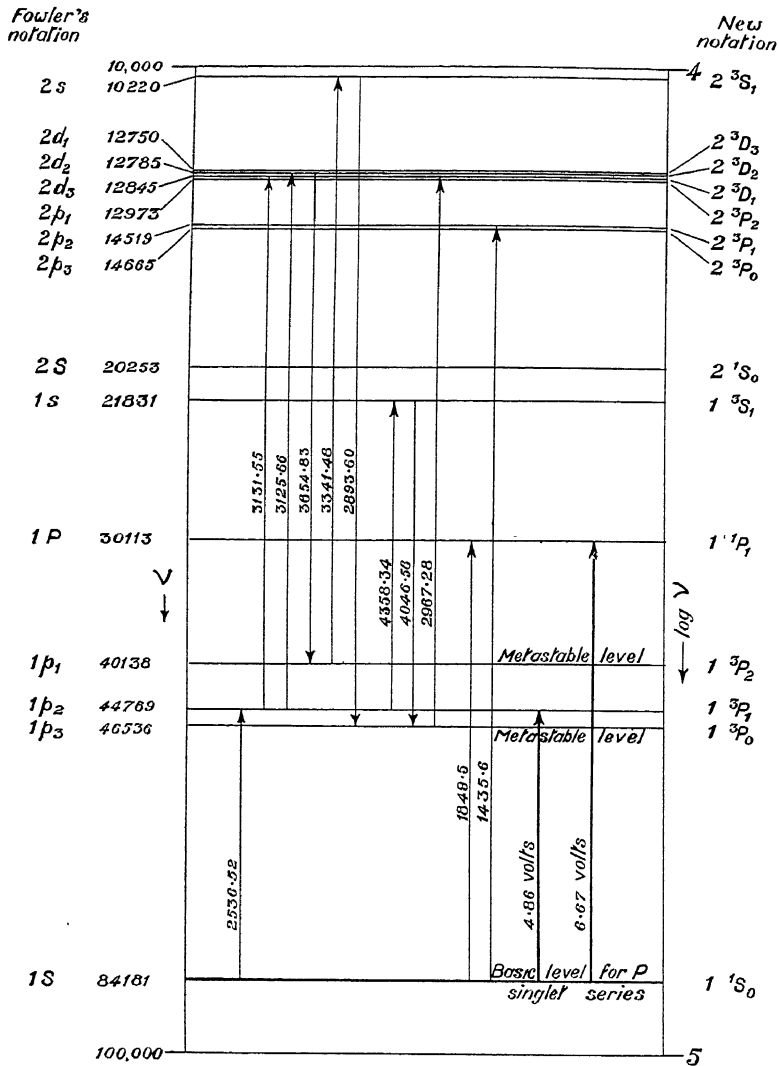
FIG. 50.

Energy level diagram for the neutral mercury atom.

the electron does not in general remain long in the stationary states other than the normal. However, certain experiments

have been carried out which approximate to these conditions, among which we may quote those of Metcalfe and Venkate-sachar on mercury vapour. They have shown that mercury vapour at low pressure, made very faintly luminous by the passage of a small current, absorbs strongly the lines

$1^3P_1 - 1^3S_1$, $1^3P_2 - 1^3S_1$, $1^3P_3 - 1^3S_1$, $1^3P_1 - 2^3S_1$, $1^3P_1 - 2^3D_3$.

The mechanism by which these lines can be absorbed can be best understood by a study of Fig. 50, in which the energy levels of some of the terms of high wave-number of the arc spectrum of mercury are shown. In order to space out the lower terms somewhat, which are crowded if the distance between the levels is plotted on a scale of wave-numbers, the wave-numbers are plotted on a logarithmic scale. The low current means that there is comparatively little ionisation in the vapour, as is to be further expected from the small potential difference (some 30 volts) between the electrodes, so that the arc spectrum is very feebly developed, but slow electrons, whose velocity is below the ionisation potential and above the first resonance potential, may be supposed to be present in comparatively large numbers. The first resonance potential of mercury, directly measured by Franck and Hertz, and later by Mohler, Foote and Meggers, is 4·76 volts, corresponding to $\lambda 2537$; * hence the resonance potential electrons raise the optical electron from its normal level to the 1^3P_1 level, as can be seen from the diagram. Atoms with a 1^3P_1 electron are in a position to absorb $\lambda\lambda 4358$, 3132, 3126, lines which are in fact found to be particularly strongly absorbed in these experiments, the final level being respectively 1^3S_1, 2^3D_1 and 2^3D_2. From 2^3D_2 the electron can return to 1^3P_2, emitting $\lambda = 3655$, but it cannot return from 1^3P_2 to 1^1S_0, such a transition $(\Delta j = -2)$ not being a possible one on theoretical grounds, confirmed by experiment. The atom, therefore,

* $h\nu_T = 4\cdot76 \times 10^8 \times 1\cdot59 \times 10^{-20}$.

$$\therefore \lambda = \frac{c}{\nu_T} = \frac{6\cdot54 \times 10^{-27} \times 3 \times 10^{10}}{4\cdot76 \times 1\cdot59 \times 10^{-12}} = \frac{19\cdot62}{4\cdot76 \times 1\cdot59} \times 10^{-5} \text{ cm.} = 2592 \text{ A.U.}$$

The experimental error in the determination of the resonance potential is about 2%, so that the transition produced by the resonance potential clearly corresponds to the well-known line $\lambda 2537$. The computed value of resonance potential to correspond to $\lambda 2537$ is 4·86 volts.

remains in the so-called metastable state (to be further considered in the last section of this chapter) until incident radiation transfers the electron to a higher level. A transition from 1^3P_2 to 2^3S_1 corresponds to absorption of $\lambda = 3341$, which is naturally very strongly absorbed : other transitions from 1^3P_2 correspond to lines which are also observed as absorption lines. A return from 1^3S_1 to 1^3P_0 with emission of $\lambda\,4047$, or from 2^3S_1 to 1^3P_0 with emission of $\lambda\,2894$, puts the atom in another metastable state, in which it can absorb $\lambda\,2967$, as can be seen from the figure. This line is also strongly absorbed. It is clear, therefore, that, on the quantum theory, the putting of atoms in the 1^3P_1 state by low velocity electrons enables the vapour to absorb strongly just those lines which are actually observed. On the other hand, lines whose basic term is 1^1P_1 are not observed as absorption lines, which indicates that the second resonance potential, 6·45 volts,* is not attained by the electrons. This is to be expected, since at the pressure which prevails in the vapour tube a velocity of a few volts is only attained in a length of path which involves several collisions. As long as the collisions are elastic, the velocity of the electron continues to increase as it proceeds, but as soon as it makes an inelastic collision, as it does once it has attained the first resonance velocity of 4·76 volts, it loses its velocity and has to start again. Thus it is extremely unlikely that an electron will ever attain a velocity of 6·45 volts under the conditions of this experiment.

It may be asked why the incident radiation of $\lambda\,2537$ does not raise the electron from 1^1S_0 to 1^3P_1 in the cold vapour, quite independent of preliminary excitation by electrons. No doubt it does in a few atoms, but with the intensity of illumination and the pressure prevailing in Metcalfe's experiment the number so excited must be negligible. However, by making the illumination very intense this effect can be produced, when the whole arc spectrum of mercury should be produced in the vapour tube.

A very instructive experiment on these lines, in which the preliminary excitation was purely optical, has been carried out by Füchtbauer with mercury vapour, in which the mechanism

* Computed value 6·67 volts.

outlined has been beautifully confirmed. A tube of mercury vapour at low pressure was irradiated by light from a mercury arc : to obtain the radiation in sufficient intensity the mercury lamp was made up so that the discharge passed in the space between two coaxial tubes, and the plain cylindrical tube containing mercury vapour was placed axially inside the inner tube, as diagrammatically illustrated in Fig. 51. All the tubes
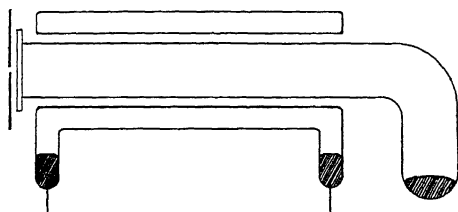
FIG. 51.

Füchtbauer's disposition for exciting mercury vapour by irradiation.

were of quartz glass. When the pressure was suitably adjusted, the vapour emitted with some intensity all the arc lines of mercury, under the stimulus of the radiation alone. When, however, a thin glass tube was inserted between the lamp and the vapour tube the emission ceased. The explanation is not far to seek. The atoms in the vapour tube, whose normal state is characterised by the term 1^1S_0, can only be excited by some radiation whose basic term is 1^1S_0. There are two series of lines in the radiation from the mercury lamp which involve this term, namely the principal singlet series $1^1S_0 - n^1P_1$, and the inter-system combination series $1^1S_0 - n^3P_1$, the observed lines of these series being $\lambda\lambda$ 1850, 1403 and $\lambda\lambda$ 2537, 1436 respectively. (See Fig. 50. The term 2^1P_1, which gives λ 1403, is not shown : it is ν 12889 close to 2^3D_1.) Of these the fused silica transmits only λ 2537, while glass absorbs all the lines. Hence, when there is no glass between the lamp and the vapour tube, the incident radiation causes transitions from 1^1S_0 to 1^3P_1 in the cold vapour, which is then prepared to absorb any line in the series for which 1^3P_1 is the limit. In this way the atoms can be set in a variety of stationary states by absorption of arc lines such as $1^3P_1 - n^3S_1$, return from which to the various possible states of smaller energy is accompanied

by the emission of arc lines. The process can be followed out in detail with the aid of Fig. 50. When, however, glass is inserted between the lamp and the vapour tube $\lambda 2537$ is cut off, and there is no incident radiation which can initiate the necessary preliminary step of transference from 1^1S_0 to 1^3P_1. Hence none of the other lines is absorbed, and in consequence there is no subsequent emission of arc lines by the vapour. There seems to be no way of explaining this effect, which follows so directly from the quantum theory, on the classical theory.

So far we have discussed cases in which the absorption spectra have been used to confirm the quantum mechanism already elaborated from a consideration of the optical emission spectra. However, the absorption spectra can be used not only to check results, but also to disentangle spectra which have not been ordered, since they give direct information as to the lowest optical level, and much work is now being carried out on these lines. Before leaving the subject, the work of Grotrian on absorption spectra of elements of the third column may be mentioned, since it will be needed for reference in Chapter XIV. For aluminium, gallium, indium and thallium the optical spectra indicate that not a ^2S term but a ^2P term is the normal level, but the question arises as to whether for these group III. earths an unknown ^2S term, greater than the ^2P term, may not exist, which might be involved in unobserved emission lines lying in the extreme ultra-violet. Grotrian showed, however, that the absorption spectra of unexcited thallium and of unexcited indium vapour consist of lines not of the principal series, but of the two series based on the term 1^2P_1, showing that 1^2P_1 is the normal level. Another very interesting point arises in connection with these experiments. The term 1^2P_2 is but very little less than 1^2P_1 (e.g. $\nu = 44455$ and $\nu = 46667$ respectively in the case of indium), but a transition from one term to the other by absorption or emission of radiation is excluded by the k selection rule. However, the energy difference being small, it can be supplied to the atom by the kinetic energy of impact of another atom (or, in the case of a transition corresponding to a loss of energy, it can be transferred from the atom as kinetic energy at impact). Now

Grotrian was able to show that on heating the vapours absorption lines appeared corresponding to an initial level 1^2P_2, and, further, that the difference of the temperature at which the two different series of lines corresponding to the initial levels 1^2P_1 and 1^2P_2 appeared was greater the greater the difference, spectroscopically deduced, between the two levels.

Nature of Emitters. Duration of Excited State. Since the arc spectrum is caused by quantum switches of the optical electron in an atom which has its normal number of electrons, or in the extreme case of the series limit by the return of an electron to replace the optical electron removed in the excitation process, the atom at the moment of emission of an arc line must be neutral. It may be recalled that Lenard, many years before the enunciation of the quantum theory of spectra, put forward the assumption that the return of a displaced electron to an atom was the cause of light emission, a conclusion which he reached as a result of the study of the electrical properties of flames and phosphorescent solids. In the case of the spark spectra, however, the atom has already lost an electron before the excitation process (in the extreme case, perhaps, the two electrons may be simultaneously detached in the excitation process, the return of one only accompanying the emission), so that at the moment of the emission of a spark line the atom should be positively charged.

Wien has verified this fundamental feature of spectral theory by direct experiment, using for the purpose the canal rays, in the manipulation of which he has long shown such skill. The rays are projected through a narrow slit into a space kept, by means of powerful high vacuum pumps running continuously, more highly exhausted than the bulb in which the rays are produced. There is, of course, a slow leak of gas from the discharge tubes, where a pressure of a few thousandths of a millimetre of mercury is necessary in order to maintain the discharge, through the slit into the observation tube, but modern pumps can remove small quantities of gas so fast that there is no difficulty in maintaining a very high vacuum.* In

* This device of maintaining a slight difference of pressure between two vessels communicating by a narrow opening was first used by Wien in 1908 in his investigations of the alternating charges of the canal rays.

the highly evacuated space the charged particles travel large distances without a collision, and consequently do not suffer changes of charge on their way through the vessel.   The light-emitting atoms, after traversing the slit, form a narrow beam which passes between the plates of a small condenser which can be charged at will to potentials of the order of 1000 volts : the electric field so established deviates charged particles, but of course leaves neutral particles unaffected.   The beam is examined with a slitless spectroscope, an image of the beam itself, which is sharp and comparatively narrow, being formed by an achromatic lens to take the place of the slit.   Each line in the spectrum so formed, then, tells us of the behaviour of the emitter of that particular line in the electric field : if the line is bent in comparison with the same line taken with the same disposition, but no field, then the emitter must be charged. Wien found that with the Balmer lines of hydrogen the field had no effect, but that, in the case of oxygen, lines known to be spark lines were deflected, while lines of the arc spectrum were not.   Similar results were obtained with one or two other gases, confirming by direct experiment our belief that during emission the atom is neutral in the case of arc lines, and positively charged in the case of spark lines.

A question of great importance now arises for consideration. We know that as a preliminary to excitation an electron is removed from its normal position to a higher quantum state, and that from this state it returns to the normal state with emission of radiation.   So far we have, however, said nothing about the time which it spends in the higher stationary state, or, in other words, about the life of the excited atom.   This point has been the subject of extensive researches by Wien, who has been followed by Dempster and others.

Wien's method is to observe the luminosity of different points of a fine beam of canal rays obtained in a highly evacuated space by the method just described.   The beam is brightest just when it issues from the fine aperture, and dies off in luminosity as it proceeds until it becomes imperceptible. By photometric measurement with a wedge device Wien finds that the decay of intensity follows accurately an exponential law.   The pressure in the space traversed by the beam is so

low that, once an atom has returned to its normal state, the chance of an impact which may re-excite it is exceedingly small.

On the classical theory this dying out of the beam would be explained by supposing the atoms to contain vibrating systems which are damped, so that the emission of a given line becomes fainter and fainter as time goes on at exactly the same rate in all atoms. We cannot admit this picture in the quantum theory, but must rather suppose that the atom remains in an excited stationary state for a finite time. Of a large number of atoms existing at a given instant in this state a given fraction must be assumed to return to the normal state in a given time interval, just as of a number of radioactive atoms a given proportion breaks down in unit time. This assumption gives an exponential falling off of light intensity indistinguishable from that predicted by a classical theory, but the effect is a statistical one on the quantum theory.* Again, whereas on the classical theory to fit the experimentally found exponential law we are forced to assume that the life of the excited atom is negligibly small, on the quantum theory we have to suppose that the time during which the emission takes place, *i.e.* the duration of the actual quantum switch, is negligible compared to the average life of the excited atom. This is a point of some importance since Einstein, in his theory of radiation, makes this assumption, which has been criticised. Wien's results offer an experimental confirmation of it, if the quantum theory of the phenomenon be accepted : we shall, of course, adopt the quantum explanation, although Wien himself discusses his results in terms of the classical theory.

On the quantum explanation the number n_t of excited atoms existing at any time is given in terms of the initial number n_0 by the formula

$$n_t = n_0 e^{-t/\tau},$$

where τ is the average life of an excited atom.† Applying this

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* For detailed consideration of this point, see G. Mie, " Über die Abklingung der Lichtemission eines Atoms," *Ann. d. Phys.*, **66**, 237, 1921.

† This formula, of course, is the exact counterpart of that giving the activity of a radioactive substance after time t,

$$I_t = I_0 e^{-t/L},$$

where L is the average life of the radioactive atom.

formula to Wien's latest experimental results, obtained with Balmer lines of hydrogen, and certain other lines, the following values are obtained for τ :

Line measured.					Value of τ.
Hydrogen $\begin{cases} H_\alpha \\ H_\beta \end{cases}$	-	-	-	-	$1 \cdot 85 \times 10^{-8}$ seconds.
	-	-	-	-	$1 \cdot 85 \times 10^{-8}$,,
Helium $\quad \lambda\,4478 \cdot 5$	-	-	-		$1 \cdot 84 \times 10^{-8}$,,
Mercury $\begin{cases} \lambda\,4358 \\ \lambda\,2536 \end{cases}$	-	-	-		$1 \cdot 82 \times 10^{-8}$,,
	-	-	-		$9 \cdot 8 \ \times 10^{-8}$,,

From certain earlier results of Wien we have

Oxygen spark lines	-	-	-	$1 \cdot 53 \times 10^{-8}$,,
Oxygen bands emitted by positively charged molecules -		-		$3 \cdot 1 \ \times 10^{-8}$,,

Hence we may say, in general, that the average life of an excited atom, which appears to be about the same in all cases for which measurements are to hand, is about 2×10^{-8} seconds, and this value is generally adopted at the present time. The value obtained from the mercury line $\lambda\,2536$ is the only one that departs markedly from this value. It may be added that Dempster, making measurements on canal rays in hydrogen, gives as the upper limit of this life 10^{-7} seconds, and finds that the duration of the actual radiation process is less than 3×10^{-10} seconds, which is negligible compared to the life of the excited atom.

E. A. Milne has made an estimate of the average life of an excited calcium atom from astrophysical data. At heights greater than 8500 kilometres above the surface of the sun, the solar atmosphere consists of calcium atoms only, which Saha's theory show to be singly ionised. These Ca^+ ions emit only the H and K lines of calcium ; for our present purpose we can speak as if but one line of frequency ν_T were emitted.* Milne assumes that these calcium atoms maintain their great height,

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* The passage from the stationary state which is the initial level for the one line to that which is the initial level for the other line, happens to be a forbidden transition. Hence an excited atom is either in the one state or the other of the two in question, and from either state it can only pass to the normal state. The frequencies of the two lines are very near one another, so a single frequency may be taken without altering the problem.

in spite of their heavy nature, in virtue of a communication of momentum $h\nu_T/c$ which takes place in the outward direction every time an atom absorbs a quantum of radiation of frequency ν_T, coming from the sun. Such an absorption is the only mechanism for converting the atom to the excited state at the exceedingly low pressure, of the order of 10^{-13} atmosphere, which prevails at the heights in question ; impacts, of electrons or atoms, are too infrequent to be considered. If τ' be the duration of the normal state, and τ, as before, the duration of the excited state, τ/τ' can be worked out from reasoning similar to that used by Einstein in deriving Planck's distribution law,* while $\tau + \tau'$ is given by considering that the momentum acquired under gravity during time $\tau + \tau'$ is equal to the momentum $h\nu_T/c$ gained during one absorption of radiation of frequency ν_T if the atom is to be in mechanical equilibrium. Milne finds for τ a value which must be less, but not very much less, than $5\cdot4 \times 10^{-8}$ seconds; this agrees with Wien's values as far as the order of the magnitude is concerned. From other considerations he has deduced as the mean life of a hydrogen atom in the two-quantum state in a typical stellar atmosphere the value 10^{-8} seconds.

The Metastable State. We have seen that a large number of transitions which would at first sight appear possible are excluded by the j selection principle. For certain elements a return from the level next above the normal is not permitted. We may take as an example the spectrum of mercury, for which the levels are exhibited in Fig. 50. The level 1^1S_0, which is the basic level of the principal (singlet) series is the normal level : next above it we find a group of three levels, 1^3P_0, 1^3P_1, 1^3P_2, which belong to the triplet series of mercury. The only combination between these and 1^1S_0 which is allowed by the j selection rule is $1^3P_1 \to 1^1S_0$: $1^3P_0 \to 1^1S_0$ is excluded because, although a switch in which j does not change is in general permitted, the particular switch $j = 0$ to $j = 0$ is excluded, as has been pointed out. $1^3P_2 \to 1^1S_0$ is excluded because j changes by 2. This is merely the expression in quantum language of the observed fact, which is, of course, independent of any allotment of inner quantum numbers. The line

* See p. 353 *et seq.*

$I^3P_1 \rightarrow I^1S_0$, which has $\nu = 39412$, $\lambda = 2536 \cdot 52$, is a strong emission line, and also the strong resonance line in mercury vapour, while lines corresponding to the other transitions have never been observed.

While, however, the correspondence principle, as expressed in the selection rules, forbids these transitions to be affected by incident radiation, this principle only applies, by its very essence, to transitions which are connected with a periodic disturbance, *i.e.* with emission or absorption of radiation. We know that an atom can be transferred from one stationary state to another by the impact of an electron, as is discussed more fully in Chapter XII. : in this case the transition is affected presumably by the strong inhomogeneous field round the electron, to which no periodic feature can be attributed. Hence, impact of an electron with sufficient energy, that is, an energy not necessarily equal to $h\nu_T$, but equal to or greater than $h\nu_T$, can transfer the atom from the normal I^1S_0 state to any higher state, and in particular to I^3P_2 or I^3P_0. When the atom is in this state it cannot return spontaneously to I^1S_0, as it would from I^3P_1 : it must first go from these states to some higher excited state from which a return to I^1S_0 is permitted by the selection principle. If the analogy may be permitted, it is as if a man who had wandered from the stalls of a theatre to the pit by some irregular passage should find that he had to spend some time in vain argument, and then go up to the box-office for a fresh ticket before he could get back to the stalls.

We might expect, therefore, a certain spurious stability for states such as I^3P_2 and I^3P_0, from which a direct return to the normal state is impossible. There is, in fact, a body of evidence that such is the case, and these states are called *metastable states*. We proceed to consider the experimental justification for this hypothesis.

The term " metastable state " was first used by Franck and Knipping, who obtained an indication of it in investigating the resonance potentials of helium. Neutral helium has two distinct systems of series, a doublet and a singlet system.* Transitions between terms belonging to the singlet (parhelium)

* Cf. Chapter VIII. page 179.

system, and terms belonging to the doublet (orthohelium) system are unknown. The normal level, corresponding to the undisturbed atom, belongs to the singlet system ; on the newer notation it is called 1^1S_0. This level is involved in the new principal series $1^1S_0 - n^1P_1$, discovered by Lyman in 1922.* On Fowler's numeration this would have to be $0S - nP$, so that the newer notation is here adopted. The level next above is an S level belonging to the doublet system, called on the newer notation 1^2S_1, from which a transition to the normal state with emission of radiation is impossible. No line has ever been detected corresponding to such a switch. Now Franck and Knipping found indications of a resonance potential corresponding to a transition from 1^2S_1 to the next doublet P level, which would not, in the ordinary way, be expected, since the 1^2S_1 state, not being the normal state, would be represented by very few atoms. If, however, an atom, once in this state, remained in it for an abnormally long time, an abnormally large proportion of atoms would be at any moment in this state, and hence the resonance potential corresponding to switches from this state to a higher state would be detected. The view that the state 1^2S_1 is unexpectedly stable, considering that it is not the normal state of the atom, is also indicated by the fact that, as discovered by Paschen in 1914, the infra-red line $\lambda\,10830$, which corresponds to a transition from 1^2S_1 to the first P term of the doublet series, is a resonance line. In other words, $\lambda\,10830$ behaves just as the first member of an absorption series, and 1^2S_1 behaves as a stable state of the atom.

This metastable state is of considerable importance in considering the chemical behaviour of the helium atom. The helium atom in the normal state is well known to be particularly inert, a fact which is explained theoretically by the closed nature of its structure, the group of extranuclear electrons being complete, and neither of them having a preferential position. In the metastable 1^2S_1 state, however, one of the electrons is displaced to an outer orbit, and the helium atom has, in the sense that it then possesses one outside or valency electron, a hydrogen structure, and should be capable of

chemical combination. Now helium, under suitable excitation, gives a band spectrum, which indicates that, in these circumstances, a helium molecule can be formed. Further, there are many indications that with certain conditions, and under the influence of an electric discharge, chemical compounds of helium may be formed. J. J. Manley claims that by the help of a glow discharge he has produced a compound of mercury and helium in quantities sufficient for analysis, and finds that it is represented by the formula HgHe, while E. J. Boomer has obtained evidence of solid compounds of helium with mercury, iodine, sulphur and phosphorus. Metastable states have also been found for neon by G. Hertz and by Lyman and Saunders.

The metastable state is a stationary state, other than the normal state, which persists for a much longer time than do the stationary states in general. The latter, as we have seen, have an average life of the order 10^{-8} seconds. The question naturally arises as to the duration of the metastable state. The most precise determinations have been made by K. W. Meissner, and by H. B. Dorgelo. The principle of Meissner's method is to use two tubes filled with the gas under investigation, one of which is used as an emission tube, and the other for absorption. The tubes are excited alternately so that the light from the emission tube passes through the absorption tube after the excitation of the latter has ceased. If an appreciable fraction of the atoms in the absorption tube have persisted in a stationary state an absorption line corresponding to a switch from that state will be observed : if all the atoms have returned to the normal state only absorption lines based on the normal state can be expected. By reducing the interval which elapses between the cutting off of the absorption tube and the excitation of the emission tube until the absorption lines corresponding to the metastable state are observed, the average duration of this state can be estimated.

The apparatus is indicated diagrammatically in Fig. 52. An alternating current is used ; with the help of two rectifiers one half-wave is sent through one tube, and the other half-wave through the other tube. The frequency of the current at which absorption is observed is noted. Dorgelo used the same

method, and also a second more accurate method in which the current is sent intermittently through the absorption tube by means of a contact carried on a revolving disc ; the disc was provided with a slit so arranged that the light admitted to the observing spectroscope was that which had passed through the tube some time after the excitation had ceased.   The emission tube was run continuously.   Meissner found from two different
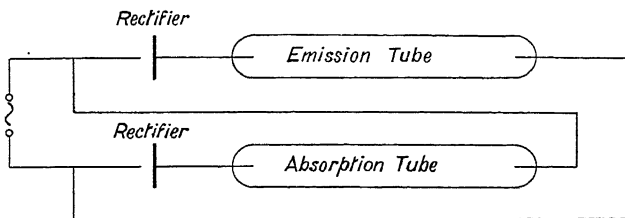
FIG. 52.
Disposition for measuring duration of metastable state.

lines based on one metastable state of neon the average life ·0048 sec. and ·0036 sec. respectively, while Dorgelo found for the life of this state ·0042 second.   Neon has a second metastable state for which Dorgelo found the average life to be less, namely, ·0005 sec.   Kannenstine has estimated the average life of metastable helium to be ·0025 sec.   We may say, then, that the life of the metastable state is of the order of a hundred thousand times that of an ordinary stationary state.

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CHAPTER XII

EXCITATION POTENTIALS AND ABSORPTION

Introductory. Very striking direct confirmation of Bohr's fundamental hypothesis of stationary states has been afforded by certain experiments on the collisions of electrons with gaseous atoms. On the older theories, which regarded the electrons in the atom as bound by quasi-elastic forces, and capable of vibrating with any amplitude, however small, we should expect an electron, on striking an atom, to transfer a certain fraction of its energy to the atom, the amount of energy transferred depending in a continuous fashion on the velocity of the moving electron and other conditions. On Bohr's theory, however, an atom can increase its energy by finite amounts only, corresponding to the passage of the atom from one stationary state to another of greater energy. Hence if the incident electron possess energy less than that corresponding to the transition of the atom from its normal state to the next stationary state, it cannot transfer any energy at all to the atom. Only the internal energy of the atom has here been considered : the type of collision just adumbrated corresponds to the collision of perfectly elastic bodies in ordinary mechanics, and there is, of course, an interchange of ordinary translational energy, just as there is in the impact of perfectly elastic spheres. However, owing to the very large mass of the atom compared to that of the electron, the loss of energy of the electron in an elastic collision is very small. To be precise, a simple calculation shows that the fraction of the kinetic energy of the electron transferred to the atom is $\dfrac{2m}{M}$, where m is the mass of the electron, and M that of the atom. This

quantity is negligble in all actual cases, so that we may expect an electron whose energy is below a certain critical value, determined by the nature of the struck atom, to proceed with practically undiminished energy after collision.

On the other hand, if the energy of the electron exceed a critical value, it may, by interaction with an atom, transfer to the atom a certain definite amount of energy, or rather, in general, one of certain definite amounts of energy, corresponding to the transition of the atom from its normal state to one of the possible stationary states. In the extreme case an electron is completely removed from the atom as the result of collision, and the atom is ionised. When the impact changes the stationary state of the atom the electron may be said to have experienced an inelastic collision, but it must be remembered that the loss of energy is not, as in the case of the collision of imperfectly elastic bodies in ordinary mechanics, a continuous function of the energy of the moving body, but has, independently of this energy, certain discrete values determined by the nature of the struck body.

The minimum potential which suffices to give a freely moving electron the energy required to ionise an atom which it strikes is called the *ionisation potential* of that atom. The minimum potential which suffices similarly to transfer an atom from the normal state to another stationary state is called a *resonance* or *radiation potential*, the latter term referring to the fact that the subsequent return of the atom to its normal state is accompanied by radiation. An atom, of course, has several resonance potentials. It is often convenient to refer to ionisation and resonance potentials inclusively as *critical potentials*, or *excitation potentials*.

The examination of the passage of comparatively slow electrons, *i.e.* electrons whose velocity is of the order 10 volts, through gases and vapours consisting of atoms with no electron affinity (*i.e.* atoms which have no tendency to form negative ions), has clearly proved the existence of both elastic and inelastic collisions of the type to be expected on Bohr's theory. There are two chief experimental methods of investigating the phenomena : the purely electrical, in which the velocities of the electron after impact, or the ionising results of the impact

on the atoms, are measured by electrical methods ; and the optical, in which the radiation produced by the return of the struck atom from its new stationary state to the normal state is examined. The excitation of spectral lines and groups of spectral lines by electrical impact is intimately connected with the question of the spectrum of the general atom, and will have to be discussed at some length. It seems advisable, however, to describe first certain general results of the electrical methods.

Electrical Methods of Investigating Excitation Potentials. Lenard was the first to show, in 1902, that an electron must possess a certain minimum energy before it can produce

$$V_R > V_A$$
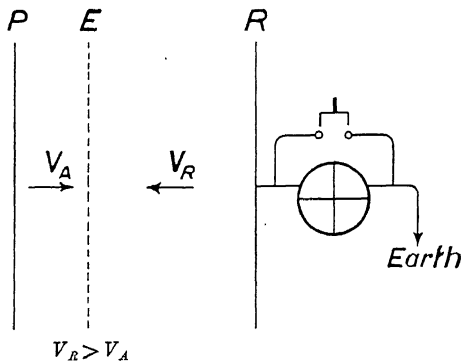
FIG. 53.

Lenard's method of investigating ionisation potentials.

ionisation by its passage through a gas, and he estimated this velocity at about 11 volts in the case of all three gases which he used, viz. air, hydrogen and CO_2. His method was to liberate electrons photoelectrically from a plate P, and accelerate them by means of a potential difference which we will call V_A, maintained between P and a gauze E, parallel to P (Fig. 53). The gas pressure is so low that the distance between P and E is less than the mean free path. The electrons, most of which, therefore, possess the full energy V_A, pass through the gauze into a retarding field due to a difference of potential V_R between E and a second plate R. Now V_R is always, arranged to be greater than V_A, so that no electrons can reach the plate R direct. If, however, the electrons have gained on

their passage from P to E sufficient energy to ionise the gas molecules which they strike, the positive ions so formed will be attracted to R, and can be detected electrometrically. The method, then, consists in observing the current from R as a function of V_A : the value of V_A for which a passage of positive charges to R sets in is a critical potential. This original arrangement of Lenard's is typical of a large number of recent experiments. The electrons to-day are, however, usually produced by a glowing wire, instead of by an illuminated plate, and more elaborate arrangements of gauzes in front of the receiving plate R have been introduced with the object of disentangling various effects. Franck and Hertz used a modification of Lenard's method to measure critical potentials before they adopted the so-called partial current method. Their source of electrons was a glowing platinum wire round which as axis the gauze was bent in the form of a cylinder, the plate R being in the form of a larger co-axial cylinder.

It was originally believed by the experimenters that the critical potential indicated by experiments of the Lenard type was the ionisation potential, the sudden change in the current from R being attributed to the movement of positive ions to R. It was pointed out by Bohr, and by van der Bijl, that if the electronic impact did not actually ionise the atoms, but merely excited them to emit light of short wave-length, this light would act photoelectrically upon R, and cause it to release electrons which would be removed by the field. This loss of electrons would account just as well as a gain of positive ions for the change in the current curve at a critical potential, and we know now that, for instance, electrons of velocity 4·9 volts do not ionise the mercury atom, as was originally believed, but put it in a stationary state, return from which to normal gives a line in the mercury spectrum. To distinguish experimentally between resonance and ionisation potentials Davis and Goucher modified Lenard's method by the introduction of a second gauze E' close to the receiving plate R. The source of electrons is a heated wire W (Fig. 54). The accelerating potential V_A is maintained between W and E as before : the retarding potential V_R, which is greater than V_A, between E and E'. Between E' and R a small potential V_1, which can be reversed, is main-

tained. This potential, when E' is negative to R, suffices to prevent the escape of photoelectric electrons from R, but attracts to R any electrons liberated from E' on the side towards R, by reflected radiation or otherwise. The current from R therefore reverses sign when the sign of V_1 is reversed, as far as the effect of radiation on R is concerned. The effect produced by the positive ions, *i.e.* the effect contemplated in the original Lenard method, is, however, but little affected by
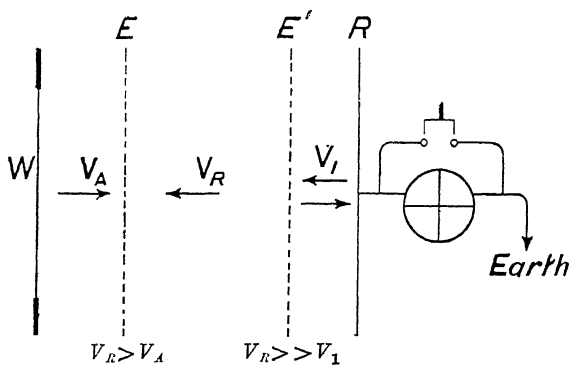
FIG. 54.

Davis and Goucher's arrangement for distinguishing between ionisation and resonance potential.

the change of sign, since V_R is large compared to V_1, and so the positive ions, all but those produced very close to E', acquire sufficient velocity in the space between E and E' to overcome the small opposing field. The curve in Fig. 55 shows the nature of the result obtained with this apparatus. It refers to mercury vapour, and indicates 10·4 volts as the true ionisation potential, with 4·9 volts and 6·7 volts as radiation potentials.

Lenard's method has been improved in a different way by the addition of a second gauze, so as to give much greater sensitiveness, although here again, as in the original method, no distinction between resonance and ionisation potential is provided. The gauzes are arranged as indicated in Fig. 54, although the disposition of the potentials is different. The accelerating field is between W and E, and the main retarding field V_R between E' and R. Between E and E', however,

there is a small, accurately adjustable retarding field V_r of a few tenths of a volt. The advantage of this method is that the electrons making collision in the main body of the gas all have the same velocity within a small fraction of a volt.
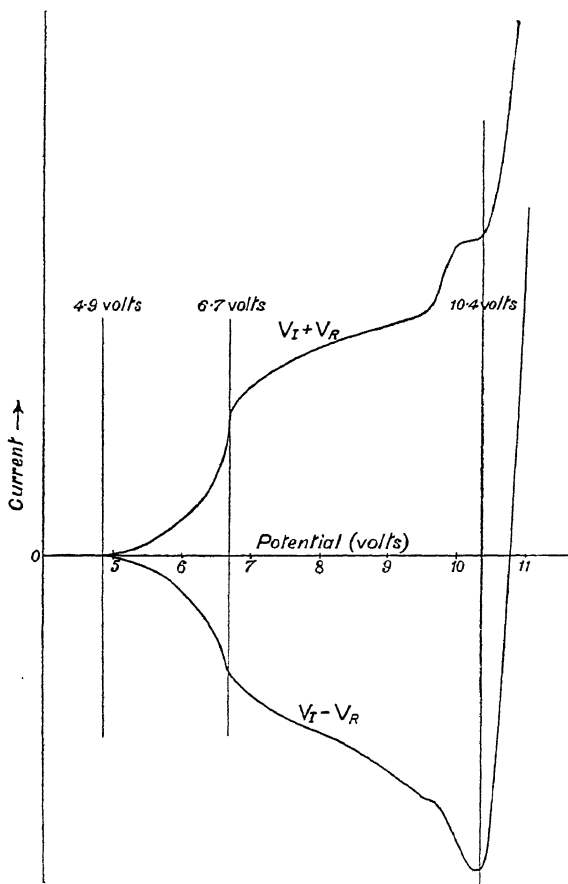
FIG. 55.

Davis and Goucher's results for mercury vapour.

The pressure is chosen so that most of the electrons experience a collision between E and E'. Franck and Einsporn have used this disposition with good results for helium and mercury vapour, and the same arrangement, called by them a four-electrode tube, has been used by Mohler, Foote and Meggers.

They use a small accelerating field between E and E' : whether this fine adjustment, as it may be called, is positive or negative is clearly indifferent.   Davis and Goucher's small reversible field, to distinguish between radiation and ionisation potentials, may, of course, be applied in this type of apparatus by inserting a third gauze, near the plate R.

The method by which Franck and Hertz carried out many of their investigations differs somewhat from Lenard's : it is usually called the partial current method, and detects the inelastic collisions by the loss of velocity of the electron.   The source of electrons is an electrically heated wire (Fig. 56a) :
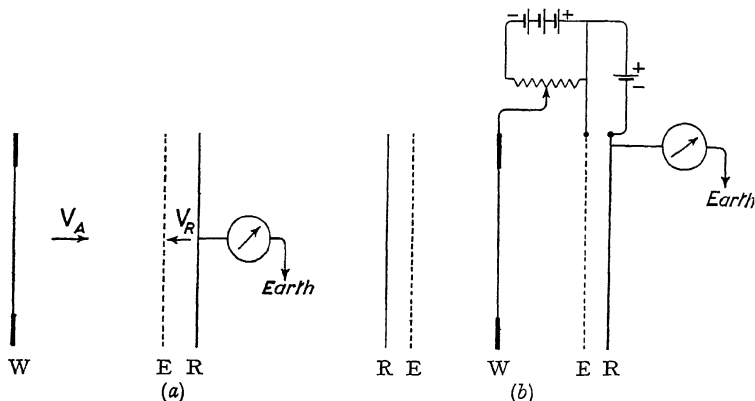
FIG. 56.

Partial current method of Franck and Hertz.

between W and the gauze E there is an accelerating potential difference V_A, while between E and the receiving plate R, which is relatively close to it, a retarding potential V_R is maintained.   It is an essential feature of Lenard's method that V_R shall be greater than V_A : in the present method, however, V_R is small.   In the actual experimental disposition E and R are cylindrical in form, surrounding the wire W as axis, as indicated in Fig. 56b.   This is the usual disposition with a hot wire as source of electrons, and was adopted in the experiments previously described, in which a hot wire is used.

V_R is kept constant, and V_A varied.   If V_A is less than V_R the current should be zero.   As V_A is increased the current should increase until V_A reaches a critical value, say V_C.   As

soon as this occurs the electrons near E, which have attained the full acceleration due to V_A,* suffer inelastic collision, losing their velocity. Since the collisions take place near E, the acceleration which the electrons experience before passing through E is very small, and the retarding potential V_R, though small, is sufficient to prevent them reaching R. As V_A
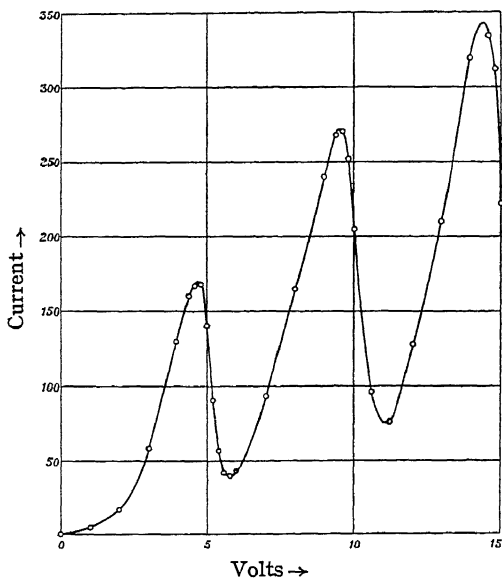
FIG. 57.
The results of Franck and Hertz with mercury vapour.

is increased from this first critical value V_C the region in which inelastic impacts first take place retreats from E towards R : the electrons which have lost their energy at inelastic impact experience a greater subsequent acceleration due to a potential $V_A - V_C$, some of them reach R, and the current again increases, until V_A reaches the value $2V_C$, when the electrons experience a second inelastic impact close to E, and the current drops once more. As V_A is further increased, the

* As long as the collisions are elastic, i.e. unattended by loss of energy of the electron, they do not affect the energy which an electron acquires in passing through a given potential difference.

current grows, to drop again at $3V_C$, and so on. The results which Franck and Hertz obtained with mercury vapour are shown in Fig. 57, and it will be seen that they are in accordance with this mechanism. There are sharp maxima at multiples of 4·9 volts : minor factors, which need not be here discussed, prevent the drop of current from being truly vertical. This 4·9 volts is a resonance potential of mercury corresponding to the switch $1^1S_0 - 1^3P_1$. More delicate experiments carried out with a slightly modified method have shown secondary maxima corresponding to other resonance potentials, e.g. 4·66 volts, which can be referred to the switch $1^1S_0 - 1^3P_0$, and 6·67 volts, ascribed to $1^1S_0 - 1^1P_1$. (Cf. Fig. 50.) The method is not adapted to distinguish between ionisation potential and resonance potential, although indications can be obtained on the point from intensities. It has been variously modified by recent workers.
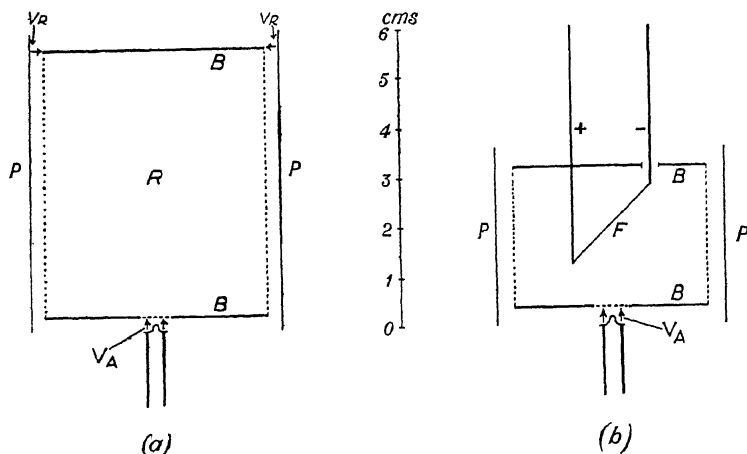
Fig. 58.

G. Hertz's new methods:
(a) for resonance potentials; (b) for ionisation potentials as well.

Hertz has shown great ingenuity in devising delicate methods for the measurement of critical potentials. Brief allusion may be made to two of them. The first is designed to detect the sudden loss of velocity which the incident electrons suffer when the accelerating potential V_A reaches a critical value, and is diagrammatically illustrated in Fig. 58a. The space R is

enclosed by a box BB with gauze sides and a small gauze window, opposite which is the hot wire source of electrons. Surrounding the box is a cylinder PP, connected to earth through a galvanometer ; between PP and BB a very small retarding field V_R of, say, ·1 volt, is maintained. If V_A is less than the critical potential, electrons make elastic impacts in the space R, and pass through the sides of BB with sufficient velocity to carry them to the cylinder PP in quantities which practically are independent of whether V_R is switched on or off. When, however, V_A is increased to a critical value the electrons make inelastic impacts, and pass through the sides of BB with a very small velocity. There is, then, a very big difference in the current flowing from PP to earth according as V_R is switched on or off, since, unless V_A exceeds the critical potential by more than ·1 volt, none of the electrons which suffer inelastic impact can make head against V_R. The fact that, except for a very small range in the neighbourhood of the critical potential, the current is largely independent of the establishment of V_R indicates very precisely the value of the critical potential. The difference of the current readings with V_R on and with V_R off is plotted against the potential : we then have a sharp maximum in the current-potential curve to indicate this potential instead of merely an elbow in the curve, as in most other methods.

The other method is illustrated diagrammatically in Fig. 58*b*, and measures the ionisation potential, as distinct from the resonance potentials, which are revealed by the method just described. Inside the box BB is a very fine wire F, the positive end of which is connected directly to the box, while the negative end is connected to it through a galvanometer and cells. It is maintained at a high temperature, so that the current flowing from F to the walls of BB is limited by the swarm of electrons which surrounds it, the so-called space charge. If, however, the accelerating potential V_A is raised to the ionisation potential electrons enter the box with sufficient energy to produce positive ions, which annul the space charge, and cause the current between F and BB, measured by the galvanometer, to increase suddenly.

If this method alone were being utilised the box BB could be

made with sides completely closed. However, to enable the method of Fig. 58a to be applied with the same apparatus the sides of *BB* are made of gauze, and the box *BB* surrounded by a cylinder *PP*, as in Fig. 58a. When resonance potentials are being measured *F* is left cold, and the apparatus used exactly as that of Fig. 58a. With such an apparatus Hertz has made very accurate measurements on neon and argon, and, in collaboration with R. K. Kloppers, on the other inert gases.

It is interesting to note that the elastic impact on gas molecules of electrons possessing small velocity was some years ago directly established by Franck and Hertz. They used the disposition represented in Fig. 59. *W* is the hot wire source
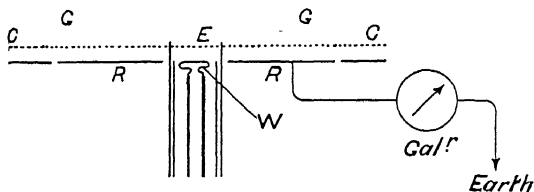
FIG. 59.

Apparatus for direct establishment of elastic impact of electrons on gas molecules.

of electrons : the accelerating field, of some 4 volts, is applied between *W* and a gauze *E*. Electrons thrown back by impact with gas molecules in the space *GG* reach the plate *RR*, where their arrival is detected quantitatively by a galvanometer. Parallel to *RR* is a gauze *CC*, and the velocity of the electrons arriving at *RR* can be measured by applying a retarding potential between *RR* and *CC*. It was found that these electrons had the full velocity of 4 volts, and collision without loss of energy was thus proved.

Before considering further details, the fundamental significance of this class of measurements for Bohr's theory may be again emphasised. The fact that the electron is elastically reflected from atoms of an electropositive gas if its energy is below a certain limiting value, whose magnitude depends upon the nature of the gas atom concerned, is in itself sufficiently striking ; the sharply defined values of energy at which in-

elastic collisions of different types set in (different types in the sense that each type corresponds to a different loss of energy) is very strong evidence for a quantum theory of energy interchange between atoms and electrons. Qualitative considerations confirm the belief in a quantum mechanism. Considering mercury vapour, for instance, the critical potential 4·9 volts, detected by Franck and Hertz, was shown not to be an ionisation potential, but a radiation potential. Now from the fundamental equation of the quantum theory

$$\text{Energy} = eV \, \frac{1}{300} = h\nu_T = \frac{hc}{\lambda},$$

where V is the potential in volts, and e is in electrostatic units, 4·9 volts correspond to a wave-length of 2520 A.U., which is, within the experimental error of the potential determination, $\lambda\,2536\cdot5$, a strong line of the mercury spectrum corresponding, on all spectroscopic evidence, to a transition involving the normal state of the atom. Davis and Goucher found another resonance potential at 6·7 volts, which corresponds to $\lambda\,1844$, or within experimental error $\lambda\,1849\cdot5$, another strong line involving the normal state of the atom. (See Fig. 50.)

A further excellent confirmation of the interpretation placed upon critical potentials has been furnished by the recent work of G. Hertz on neon. Neon has a very complicated spectrum, which has been analysed by Paschen into an elaborate system of series : the term corresponding to the normal state of the neon atom is not included in the system, since the lines involving this basic term lie so far in the ultra-violet that observation is difficult. By means of the disposition depicted in Fig. 58a, Hertz found critical potentials which indicated the value 174000 ± 1000 cm.$^{-1}$ for the wave-number of the basic term. He then looked for extreme ultra-violet lines in the spectrum of neon, using a special vacuum spectrograph made by building a small grating (1 metre radius of curvature) into a highly evacuated glass tube, the neon discharge taking place in a separate tube communicating with the spectrograph tube by a slit only.* The pressure in the spectrograph was, by means

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* The pressure in the neon tube was 4·5 mm. ; in the spectrograph about a thirtieth of this.

of a diffusion pump, kept much lower than that in the discharge tube : this maintenance of a difference of pressures between two vessels connected by a narrow opening, originally used by Wien in his work on canal rays, is a common feature of modern vacuum technique.   Hertz obtained two neon lines at 735·7 and 743·5 A.U. respectively. The difference of wave number agreed with the difference between two of Paschen's terms, called by him $1s_2$ and $1s_4$, and these lines were attributed to combinations between $1s_2$ and the basic term, and $1s_4$ and the basic term respectively.   The value of ν for the basic term was found by this optical method to be 173970 ± 100 cm.$^{-1}$, which agrees surprisingly well with the value found from consideration of critical potentials.   It may be added that the selection principle shows that the basic term in neon is a P term.

Quantitatively, then, the confirmation of Bohr's theory furnished by critical potentials is convincing, and we now place full confidence in the quantum interpretation of such experiments.

Optical Methods of Studying Critical Potentials.   Instead of investigating the fate of the electron (and of the positive ions, if such be produced) by electrical methods, we can study the result of the impact of electrons on atoms by examining the radiation resulting from the collisions. The general method is to control the velocity of the bombarding electrons by means of the accelerating potential difference, care being taken that the pressure is so low that the collision of the electrons with atoms is comparatively infrequent in the narrow space over which the potential difference is applied, and to observe the changes in the nature of the radiation which can be produced by varying the energy of the electron.   It must be remembered that the effective potential difference is that which accelerates an electron over its mean free path (or, more generally, the distance between two inelastic collisions), and that the actual potential difference between the electrodes if the gas is at atmospheric pressure (or, indeed, any pressure at which the mean free path is very small compared to the electrode distance) tells us very little, if anything, about the ionisation potential.

If the energy of the impinging electron equals or exceeds the ionisation potential, then certain of the atoms should lose an electron, the subsequent recapture of the electron in steps which vary from atom to atom leading to the emission of the whole arc spectrum. If the energy be less, then the optical electron may be thrown from its normal state into any one of several other stationary states, return from which leads to the emission of part only of the arc spectrum. The spectrum may thus be excited in stages, and the study of the so-called resonance potentials, at which definite changes in the development of the spectrum take place, furnishes important evidence as to the energy levels of the virtual orbits. Of course, electrons of sufficient energy may remove two electrons from an atom, either in two steps, by acting upon an atom which has already lost an electron, or in one step, by removing two electrons at a single collision, greater energy being required for the latter process. In either case we have the arc spectrum developed as well as the spark spectrum.

The first to study the radiation excited by electrons of given energy were Franck and Hertz, who showed that electrons of velocity 4·9 volts caused low pressure mercury vapour to emit a spectrum consisting of the one line $\lambda 2536$ only, which is in perfect accord with the theory, since the energy corresponding to this potential should raise the optical electron to a level from which the only return to normal state possible corresponds to that line. This was the first example of a so-called one-line spectrum, and initiated the researches into the quantum conditions of excitation of the optical series, which have done so much to strengthen the quantum theory of optical spectra. Franck and Hertz were followed by McLennan and his students. McLennan and Henderson, using a heated platinum plate, coated with barium or calcium oxide to produce electrons in quantity, photographed not only the one-line spectrum of mercury, but also similar spectra of cadmium and zinc by using vapours of these metals at low pressures in place of mercury vapour. McLennan and Ireton were also able to excite two-line spectra of zinc and cadmium, which were the first examples of an intermediate step between the one-line spectrum and the complete arc spectrum. Since then G. Hertz has shown the

existence of a large number of critical potentials for lines, or groups of lines, in mercury, neon, and helium, the lines which suddenly appear when a given exciting potential is reached agreeing exactly with the anticipations to be made by applying Bohr's theory to the terms.

A large number of investigations on the critical voltages required to produce various types of spectra have been carried out by Foote, Meggers, and Mohler, whose experimental disposition is of the same type as Franck and Hertz's original apparatus. It is represented in Fig. 60. The distance between the hot wire, of hairpin shape, which acts as the source of electrons, and the grid which serves to apply the potential, must be small, so that the chance of a collision in the interspace may be small, and the electrons may attain the full velocity corresponding to the voltage : the field-free space between the grid and the cylinder must be large, so that the collisions which produce the spectrum may be frequent. As an example

FIG. 60.

Apparatus for critical voltages (Foote, Meggers, and Mohler).

of the results obtained the spectra of magnesium * given in Plate VII. may be considered. At 3·2 volts the single line $\lambda 4571$ is produced : this corresponds to a transition between the normal 1^1S_0 and the 1^3P_1 level, as does the resonance line in mercury, the level scheme of which (Fig. 50) may be consulted. The voltage calculated (by the simple method employed for mercury on page 335) to correspond to $\lambda 4571$ is 2·70 volts, which agrees with the value 2·65 found experimentally by more delicate methods. (The apparatus of Fig. 60 is not adapted for accurate measurements of the resonance potentials.) At 6·5 volts a two-line spectrum is produced, the fresh line being $\lambda 2852$, $1^1S_0 - 1^1P_1$: the calculated resonance potential for the line is 4·327 volts, and the value observed by more delicate methods 4·42. The complete arc spectrum

* Reproduced from a photograph kindly sent to me by Dr. Foote.

appears at 10 volts. The last three spectra show the enhanced spectrum, which, according to calculation, should appear for voltages exceeding 15 volts. This very beautiful series of photographs shows that we can experimentally toss the spectral electron from its normal level to any one of a series of higher levels, the spectrum produced indicating, by its degree of completeness, the energy range through which the electron has been displaced.* A rough analogy may perhaps be pardoned here, in spite of the obvious imperfections. Imagine the right-hand side of a piano to be raised and supported a foot or two from the ground, so that the keys corresponding to the higher notes are actually the higher. Then if a heavy ball be pitched from the lower end of the piano on to the keys, it will strike a given note, and roll down, presumably striking other notes on its way back. The higher the ball be tossed up the keyboard, *i.e.* the greater the energy communicated to it, the more extensive a scale will be produced, and the listener would determine by the completeness of the range of notes the initial energy of the ball. The analogy is good in that the mechanism of the piano, like the mechanism of the atom, does not permit a continuous range of notes, but only of certain definite ones—a line spectrum, but it offers nothing to correspond to the inner mechanism of spectral emission, expressed by the relationship $h\nu_T = E - E'$. If the black keys be supposed stiffer than the white, we can get a somewhat strained analogy for the production of the spark spectrum.

Before leaving this part of the subject reference may be made to Franck and Einsporn's very complete determination of the resonance potentials of mercury vapour. The radiation produced by the electronic impact was detected not spectroscopically, but by the photoelectric effect on a subsidiary iron electrode, connected with a galvanometer. A sharp change in the rate of increase of the photoelectric current as the accelerating potential is raised corresponds to the production of a new

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* Recently (*Phil. Mag.*, **50**, 165, 796 and 1276, 1925) Newman, working with three-electrode discharge tubes, has succeeded in producing the spectrum of neutral sodium, potassium and rubidium respectively in line by line emission.

emission line in the ultra-violet as a consequence of the increased velocity of the exciting electron. Franck and Einsporn's results have indicated no fewer than eighteen critical potentials. These can, of course, be converted into wave-lengths of corresponding lines. When this is done it is found that eleven of those lines correspond to transitions involving the basic term 1^1S_0, while one of them represents a transition from the 1^3P_0 orbit to the periphery, showing that occasionally ionisation takes place in two steps. It is noteworthy that excitation potentials corresponding to the transitions $1^1S_0 - 1^3P_0$ and $1^1S_0 - 1^3P_2$ were measured : these lines have never been detected optically, and are excluded by the selection rules. Perhaps a confirmation by an independent method of the existence of these transitions might be desirable before attempting a theoretical explanation. Leaving out detailed discussion, it may be stated that the measurements of Franck and Einsporn, by establishing critical potentials corresponding to a whole range of lines involving the basic term, have strikingly confirmed the quantum theory of spectra.

Temperature Radiation of Gases. The quantum theory of spectra has been particularly successful in explaining why in many cases certain parts of the optical spectrum, and certain parts only, appear in the light from sources not deliberately designed for the production of special effects. Conversely, it has been possible to deduce from the relative intensities of the lines, including in this expression the question of the non-appearance of certain lines, much information about the physical conditions prevailing in the source. Among the questions of importance which we now have to consider are the emission of certain lines by restricted regions of the arc only, the limited spectra developed in ordinary flames, and the very important astrophysical deductions made by Saha. We will first of all neglect the question of the pressure, and make a few general deductions as to the effect of changing the temperature under constant pressure conditions.

We have seen that the impact of electrons possessing sufficient energy can cause the optical electron to pass from its normal level to any one of certain selected higher levels, with the subsequent emission of one or more or all the lines of the

spectrum, according to the level. Now it is reasonable to assume—by which we mean that the deductions from this assumption fit in well with observed facts, since there is no *a priori* inevitability about it—that the impact of another atom, provided it had the same energy, can produce the same effect as the impact of an electron.* Owing to the fact that the gas-kinetic energy of the atoms at ordinary temperature is very small compared to the energy which an electron needs to excite an atom, we cannot expect any light emission in a gas at room temperature which is not subjected to electronic bombardment or radiation from outside. Thus the mean kinetic energy of an atom at 17° C. is about 6×10^{-14} ergs, which is equal to the energy of an electron falling through a potential difference of about $3 \cdot 8 \times 10^{-2}$ volts. Now the lowest measured resonance potential is the first critical potential for caesium, which is 1·448 volts, or thirty-eight times the average energy of the atom, due to thermal agitation, at 17° C. Although, of course, there are atoms of all velocities, including some greatly exceeding the mean, present in a gas, the fraction whose energy exceeds the mean by thirty-eight times can be shown to be only ε^{-57}, and so is quite negligible. The mean energy of the atoms being proportional to the absolute temperature may, however, at higher temperatures approach sufficiently near to the critical energy for a pure temperature emission to take place. At the same time, as the first critical potential varies from element to element, we should expect some elements to be excited at lower temperatures than others. Again, a given element has various critical potentials, corresponding to the excitation of various lines, and we should expect raising the temperature to have just the same effect as raising the voltage of the electrons used in the bombardment method of exciting spectra, *i.e.* as the temperature is raised the number of lines of the spectrum should increase, shorter and shorter wave-lengths being progressively included.

* It is really not the energy of translation of the striking atom alone that comes into play, but also the energy of translation of the struck atom, since the relative energy of translation must obviously be the effective factor. The mean value for the relative energy, however, does not differ appreciably from the mean value of the translational energy of an atom, and for simplicity we will consider the latter alone.

These anticipations are fulfilled by the behaviour of the alkali metals in the flame. At a temperature of $1700°$ C. attained in the Bunsen flame the mean energy of the molecules is already equivalent to an electron of about ·25 volt, and the fraction of the molecules whose energy exceeds ten times this value is 3×10^{-7}, which is appreciable from the point of view of light excitation. Franck states that in the Bunsen flame at a place where the temperature is about $1550°$, lithium shows only one line, sodium two, potassium three, rubidium four and caesium six lines of the spectrum. Now, within a given arbitrary limit of wave number, $\nu = 30300$, it will be found that lithium has one line, sodium two, potassium three, rubidium four, and caesium eight lines, so that, assuming that the greatest relative energy of translation of molecules present in sufficient numbers to be effective corresponds to about 3.74 volts (equivalent to $\nu = 30300$) we have good agreement. Further, as the temperature is raised, by passing from the Bunsen burner to the blowpipe flame, and from the blowpipe to the oxyhydrogen flame, more and more lines appear, as is to be expected. Again, A. S. King, in the course of his extensive investigations of spectra produced by metallic vapours in furnaces, where the excitation is purely thermal, has shown that with rising temperature the leading line of the series appears first, and then successively series lines of shorter and shorter wave-length, which also becomes relatively stronger compared with the first line.

Reference may be made here to the *raies ultimes* of de Gramont, which are of such practical importance for chemical analysis by spectroscopic means. These ultimate lines are those which are the last to vanish when the quantity of the element producing them, in a flame, say, is made very small, and they are for this reason also called *persistent lines*. They are not necessarily the strongest lines in the spectrum as usually produced. It was at one time generally believed that they originated in the return of an electron to the normal level from the first possible energy level above the normal, or, in other words, that they were the first resonance lines of their respective spectra. If this were so they would be the most easily produced lines, in the sense that they require electronic

or atomic impacts of comparatively low energy, such as take place in a flame, to excite them, and their persistence could be attributed to this ease of excitation. However, many discrepancies were observed when this view was adopted, and Meggers, Kiess, and Walters * have recently put forward a rule which has been found to hold accurately for all spectra which have been sufficiently investigated for test to be possible. The rule in question is that *raies ultimes* are due to an electron returning to the basic level from the first higher non-metastable level of the same series system as the basic level : *i.e.* if the basic level belongs to a singlet system, the other level concerned must also belong to the singlet system, and the transition must be allowed by the selection rules. As an example we may take the arc spectrum of calcium, for which the *raie ultime* of the arc spectrum is $\lambda\,4226 \cdot 73$, corresponding to the switch $1^1S_0 - 1^1P_1$. The levels immediately above the basic 1^1S_0 term are, however, the three triplet P levels 1^3P_0, 1^3P_1, 1^3P_2, of which 1^3P_0 and 1^3P_2 are metastable. (Cf. the arc spectrum of mercury, Fig. 50.) The first resonance line is therefore $\lambda\,6572 \cdot 78$, for this corresponds to the switch $^1S_0 - {}^3P_1$. With the arc spectrum of potassium, on the other hand, where there is only one system, the *raie ultime* and the first resonance line are the same, viz. $\lambda\,7664 \cdot 94$, corresponding to the switch $1^2S_1 - 1^2P_2$. In the case of the arc spectra, then, the *raie ultime* does not in general coincide with the first resonance line, if there is more than one system : with the spark spectra, however, the two fall together, for here the normal state of the atom belongs, in general, to the system of highest multiplicity, as does the next higher term. There is so far no simple theoretical explanation of the rule of Meggers, Kiess, and Walters, although it can be brought into accord with certain rules established for complex spectra by Hund.

Effect of Pressure on Temperature Excitation of Gases. We have considered the excitation which can be produced by the collision of atoms possessing sufficient relative energy, and found that theory and experiment agree to show that the

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* See O. Laporte and W. F. Meggers, " Some Rules of Spectral Structure," *Jour. Opt. Soc. Amer.*, **11**, 459, 1925, which gives the reference for the earlier paper of Meggers, Kiess, and Walters.

higher the temperature, the greater will be the proportion of atoms of a given kind which are excited or ionised, and that the higher the ionisation potential of an element, the greater will be the temperature at which it is excited. It was, however, first pointed out by Saha that in calculating the proportion of ionised atoms in an equilibrium state at a given temperature the pressure is a very important factor, and he showed how to calculate the equilibrium ionisation in terms of pressure and temperature. This work, which has been extended considerably by H. N. Russell, R. H. Fowler, E. A. Milne and others, has proved of the greatest importance for astrophysical spectroscopy, and it is hardly too much to say that it has placed the determination of stellar temperatures on a new footing.

The method which Saha adopted does not involve the assumption of any particular machinery of ionisation. He treats the splitting up of a neutral atom into a positive ion and an electron as a reversible chemical reaction, of which the equilibrium conditions can be fixed by the thermodynamic methods developed by Nernst, and referred to by him as the reaction isobar. The work required to separate the electron from the atom, *i.e.* the ionisation potential, appears in place of the usual heat of dissociation. For calcium, for instance, the reaction considered can be represented by the equation

$$Ca \rightleftarrows Ca^+ + e - U, \quad \dots\dots\dots\dots\dots\dots\dots(1)$$

where Ca represents a neutral atom of calcium, in the state of vapour, Ca^+ the singly ionised calcium atom, e the electron and U the energy involved. The problem is to determine the percentage ionisation under given conditions.

Now if a chemical reaction takes place according to the chemical equation

$$n_a A + n_b B + \dots = n_m M + n_n N + \dots ,$$
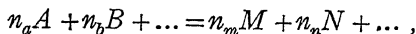
where $n_a, n_b \dots n_m, n_n$ represent the numbers of molecules of the reacting substances $A, B, \dots M, N, \dots$, then the equilibrium constant of the law of mass action is

$$K = \frac{p_M^{n_m} p_N^{n_n} \cdots}{p_A^{n_a} p_B^{n_b} \cdots},$$

where the p's are the partial pressures of the gaseous substances

$A, B, \ldots M, N \ldots$. The equation derived by Nernst fixes K in terms of the heat of reaction, the pressure, and the absolute temperature. It is

$$\log K = -\frac{U}{4 \cdot 571\, T} + \Sigma n C_p \frac{\log T}{R} + \Sigma n C,$$

where the summation signs imply the addition of quantities pertaining to the various n's, denoted by n_a, $n_b \ldots$ in the preceding equation, C_p is the specific heat at constant pressure, and C is the so-called Nernst's chemical constant of the given kind of molecule. For a proof of the equation the reader is referred to Nernst's book.*

To apply the equation to the reaction (1), we note that all the n's have the value unity, while C_p is the same for Ca and for Ca^+. The swarm of free electrons which is one of the partners in the equilibrium is treated as a monatomic gas; this swarm is referred to as " electron gas." For e we therefore have $C_p = 5/2R$. Hence

$$\Sigma n C_p = (C_p)_{Ca^+} + (C_p)_e - (C_p)_{Ca} = 2 \cdot 5R.$$

As far as the term $\Sigma n C$ is concerned, the chemical constant of Nernst can be worked out by a formula, known as the Sackur-Tetrode-Stern relation,†

$$C = \log \frac{(2\pi M)^{3/2} k^{5/2}}{h^3 N^{3/2}} = -1 \cdot 6 + \tfrac{3}{2} \log M, \quad \ldots\ldots\ldots\ldots(2)$$

where M is the molecular weight, N is Avogadro's number, and k is Boltzmann's constant. C is the same for Ca and Ca^+: for electron gas $M = 5 \cdot 5 \times 10^{-4}$, and $C = -6 \cdot 5$.

Let us now call x the fraction of calcium atoms ionised, which is what we wish to find, and let P be the total pressure, and p_+, p_-, p be the partial pressures of Ca^+, e, and Ca respectively, so that $P = p_+ + p_- + p$.

Also
$$\frac{p_+}{x} = \frac{p_-}{x} = \frac{p}{1-x} = \frac{P}{1+x};$$

$$\therefore K = \frac{p_+ \cdot p_-}{p} = \frac{x^2}{1-x^2} P. \quad \ldots\ldots\ldots\ldots\ldots(3)$$

* W. Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes.* 1918. Wilhelm Knapp, Halle. Chapter XI.
† Nernst, *loc. cit.* page 152.

Also U, which is the work, expressed in calories, done in separating the electrons, is $\dfrac{VeN}{300 \cdot J}$, where V is the ionisation potential in volts, N is Avogadro's number, and J is the mechanical equivalent of heat. To use a striking phrase of Milne's, the ionisation potential can be regarded as the latent heat of evaporation of the electron from the atom. Putting in the numerical values, we then have

$$\log \frac{Px^2}{1-x^2} = \frac{-5050\,V}{T} + 2\cdot5 \log T - 6\cdot5, \quad \ldots\ldots\ldots\ldots(4)$$

where P is measured in atmospheres, T is the absolute temperature, and V is in volts, while the logarithms are to base 10.

This equation expresses the degree of ionisation in terms of the pressure, the temperature, and the ionisation potential. The pressure and the temperature being fixed, the greater V the less the ionisation, as can be anticipated without calculation. High temperature and low pressure both favour ionisation. The following table, prepared for calcium, will serve to indicate the nature of the variation with pressure and temperature for a given atomic species.

IONISATION OF CALCIUM ATOMS AT VARIOUS PRESSURES
AND TEMPERATURES.

Ionisation Potential $= 6\cdot09$ Volts.

TEMPERA-TURE (Abs.)	PRESSURE (in Atmospheres)					
	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-5}
3000	Less than 1% ionisation					1
4000				3	9	26
5000		2	6	20	55	90
6000	2	8	26	64	93	99
7000	7	23	68	91	99	
8000	16	46	84	97		
10000	46	85	99			
11000	63	93				
12000	76	97				
13000	84	99	More than 99% ionisation			
14000	90					

Saha has applied his theory to two great problems of astrophysics, firstly the explanation of the spectral emission of the

sun's surface and atmosphere, and secondly that of the physical significance of the different spectral types into which the stars have been classified. Considering the sun first, we are confronted by the following facts : that the spark lines of certain metals, especially calcium, strontium and barium, and spark lines alone, are strongly emitted in the higher levels of the sun's atmosphere (the chromosphere), whereas the normal, or arc, absorption lines of these metals are observed in the Fraunhofer spectrum, which has its origin in the reversing layer. The atoms of these metals must then be largely unionised at the surface of the sun, and completely ionised at the higher levels of the chromosphere, *i.e.* some thousands of kilometres above the surface. If the effect of pressure be neglected we should be forced to assume that the temperature was higher in the upper layers of the sun's atmosphere than at the surface, which is in contradiction to all reasonable supposition. In applying his theory Saha takes for the temperature of the photosphere, *i.e.* the surface temperature, Biscoe's value, 7300° C.,* which is rather above the generally accepted value, but a variation of this temperature by 1000° C. or so does not affect the general conclusions. Little stress should be placed on the actual values of temperature and pressure adopted by Saha : they need adjustment in the downward direction.† With a surface temperature of 7500° absolute the temperature of the upper layers of the chromosphere works out as about 6000° absolute. The pressure Saha takes to be from 10 to 1 atmospheres in the reversing layer, and to diminish to 10^{-12} atmosphere in the outermost layers of the chromosphere. Consulting the table for calcium we see that for 1 atmosphere and 7600° absolute about 35 per cent. of the atoms should be ionised, and at lower levels, where higher pressures prevail, the percentage will be less. The ionisation increases as we go up from the surface until at temperature 6000° or higher and pressure 10^{-4} atmosphere the ionisation of calcium is practically complete. These conditions correspond to a height of about

* See F. Biscoe, *Astrophysical Journal*, **43**, 197, 1916, and **46**, 355, 1917.

† Cf., *inter alia*, H. N. Russell and J. Q. Stewart, " Pressures at the Sun's Surface," *Astrophysical Journal*, **59**, 197, 1924. The pressure in the reversing layer is probably more of the order 10^{-4} atmospheres than 1 atmosphere.

5000 kilometres, up to which height the calcium lines H and K, which are spark lines, and the Fraunhofer line g, an arc line, are observed, while above this height only H and K are observed. The agreement is therefore good. Strontium and barium have lower ionisation potentials, so that complete ionisation is reached at higher pressures and lower levels, and, in fact, flash spectrum observations show that the arc lines of those elements appear at very low levels only. Before Saha's theory it appeared very strange that the lines of these heavier elements should appear at a greater height than those of lighter elements. The following table illustrates the behaviour of the three metals :

Element.	Atomic weight.	Line (λ).	Type of spectrum.	Height at which observed.
Calcium -	40	H3969 K3934	Spark ⎫ Spark ⎭	14000 km
		g4227	Arc	5000
Strontium -	88	4216 4078	Spark ⎫ Spark ⎭	6000
		4607	Arc	350
Barium -	137	4934	Spark	750
		4554	Spark	1200
		5536	Arc	400

As regards hydrogen (which exists in the atomic state only in the sun), Saha's formula shows that, on account of its high ionisation potential, it will not be completely ionised for a temperature of 6000° C. or so except at very low pressure, *i.e.* in very high levels of the chromosphere. When hydrogen is completely ionised it cannot, of course, emit any spectrum at all, so that we can understand that, in spite of the lightness of hydrogen, in the very highest levels ionised calcium alone is detected.* Interesting observations on the spectral emission of sun spots, which are cooler than the rest of the chromosphere, and on the relative abundance, as judged by the spectroscope, of the alkali metals have also been explained. For instance, rubidium and caesium are not represented among the Fraun-

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* Milne's radiation pressure (cf. p. 317) must also be taken into account in discussing this question properly. An ionised hydrogen atom does not, of course, experience such a pressure, and is not supported by the solar radiation.

hofer lines, but it is not necessary to assume on that account that these metals are absent in the sun. For their ionisation potentials are so low (4·1 volts and 3·9 volts respectively, as compared to 6·1 volts for calcium) that they must be practically completely ionised in the reversing layer. Again, arc lines of the alkali metals are stronger in the sunspots than elsewhere.

In general it may be said that we must not conclude from the absence of lines of an element that that element is missing in a star, for if the atoms are completely ionised only the spark lines will be in evidence, and these are often in regions of the ultra-violet which are absorbed by our atmosphere. For second stage, and, in general, multiple ionisations the lines are still further in the ultra-violet. In attempting estimates of the relative proportions in which elements are present in stars, the relative ionisation potentials must be taken into account.

Saha's formula (4) involves the assumption that the number of electrons per unit volume is equal to the number of positively charged metal ions, *i.e.* that all the electrons present have been split off from atoms of the metal under consideration. Fowler and Milne, however, assume that in most astrophysical problems, owing to the presence of a large number of different kinds of atoms, the free electrons exceed in number the ionised atoms of a given kind : if, as frequently happens, there are present atoms which are much more easily ionised than the kind considered, then the electron excess must be very marked. From such considerations they are led to regard the partial pressure P_e of the electron gas as fundamental, and practically independent of the degree of ionisation of the element under discussion. If we make this assumption, we must write (3) in the form

$$K = \frac{p_+ \cdot p_-}{p} = \frac{x}{1-x} P_e, \quad \text{since } \frac{p_+}{p} = \frac{x}{1-x};$$

(4) then becomes *

$$\log \frac{x}{1-x} P_e = \frac{-5050V}{T} + 2\cdot5 \log T - 6\cdot5. \quad \ldots\ldots\ldots(5)$$

* Fowler and Milne's full formula is

$$\log \frac{x}{1-x} P_e = \frac{-5050V}{T} + 2\cdot5 \log T + \log \frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}} \sigma}{h^3} - \log b(T),$$

where k is Boltzmann's constant and σ is the number of valency electrons in

It may be mentioned that whereas Saha takes as his criterion the just detectible appearance or disappearance of a given absorption line (to which Fowler and Milne refer as the " method of marginal appearance "), Fowler and Milne prefer to consider the place in the stellar sequence at which a given line attains its maximum intensity. This method of approach eliminates many of the difficulties inherent in the method of marginal appearance, which involves assumptions as to the smallest fraction of atoms which will just give the line, and as to the relative abundance of the element giving the line.

A single diagram can be constructed from which the percentage ionisation may be determined for a given pressure, temperature, and ionisation potential. The pressure is usually only required to the approximation given by the nearest whole number power, positive or negative, of 10, which eliminates reference even to a book of logarithms. To prepare the diagram (4) is used to plot T as ordinate against $\log \dfrac{Px^2}{1 - x^2}$ as abscissa for a constant value of V, the ionisation potential; a large number of different values of V are selected, to each of which belongs a curve on the diagram. Just below, and parallel to, the axis of $\log \dfrac{Px^2}{1 - x^2}$, a scale is constructed such that under each value of $\log \dfrac{Px^2}{1 - x^2}$ is found the corresponding value of x, P being taken as 1: thus under the value 0 for $\log \dfrac{Px^2}{1 - x^2}$ will be found the value $\sqrt{\cdot 5}$ on the x scale. To use the diagram to find x for given values of P, V and T, V and T are first taken, and from them $\log \dfrac{Px^2}{1 - x^2}$ can at once be determined. From this subtract $\log P$, which, if P be given to the approximation suggested, will be a whole number.* We thus

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equivalent orbits. This equation differs from (5) only in that the logarithmic term is multiplied by σ (cf. equation (2)) and that a term $\log b(T)$ is added. This last term, which cannot be discussed here, is negligible for all atoms except H and He^+, so that, if $\sigma = 1$, (5) may be taken to be Fowler and Milne's formula.

* If P be not a whole number power of 10 the diagram can still, of course, be used, but reference to a book of logarithm tables will be necessary.
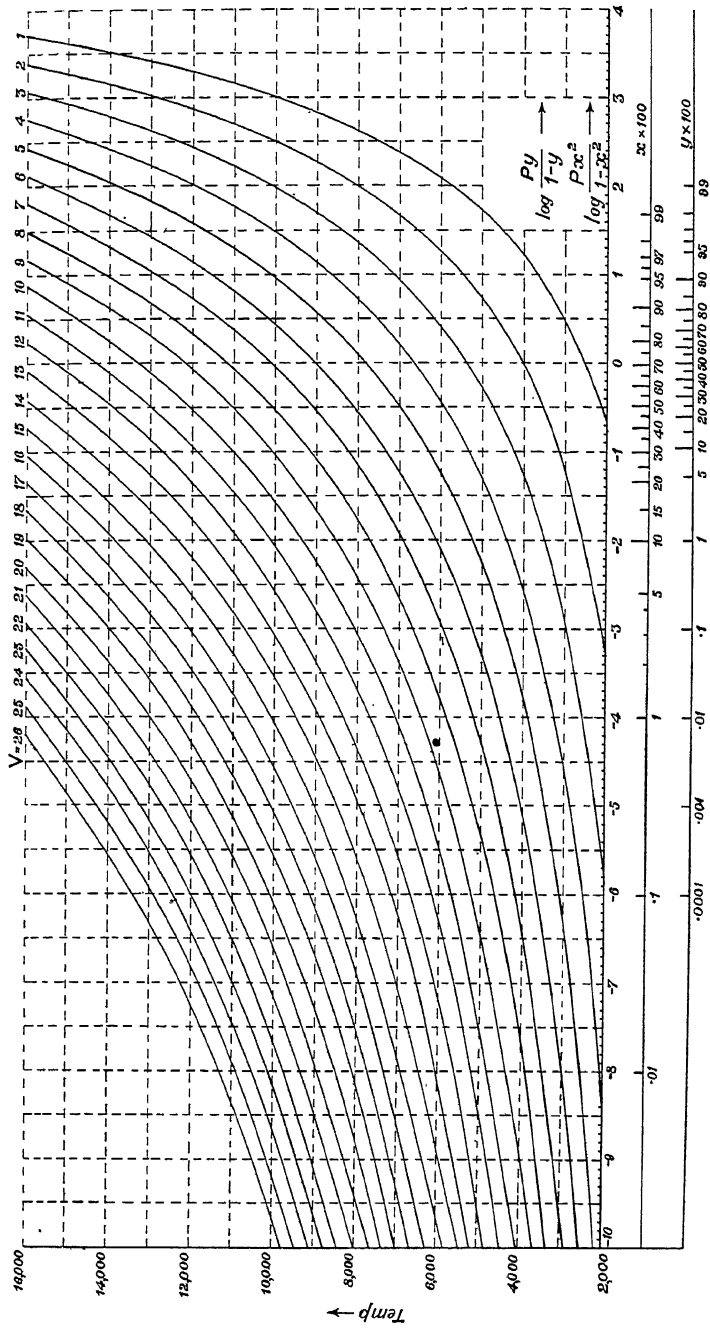
FIG. 61.

Diagram for determining percentage ionisation at a given temperature and pressure for an atom of given ionisation potential.*

* The drawing from which this diagram was reproduced was kindly executed for me by Mr. A. V. Kerrison.

get a value of $\log \dfrac{x^2}{1-x^2}$, and the number found vertically below this on the x scale is the required value of x.

In Fig. 61 such a diagram is given. Not only, however, does this express the results given by equation (4), but it can also be used if Fowler and Milne's equation (5) be adopted. For this a second scale, marked as a y scale, is given: the procedure is exactly the same as before, P being now the partial pressure of the electron gas, and y the fraction expressed in (5) by x. A new symbol is adopted on the diagram to avoid confusion.

As far as stellar spectra are concerned, we must content ourselves with the briefest reference to the large body of important work which has been based on Saha's theory.* It is clear that the appearance of characteristic lines in the spectra of stars of a given class will enable us to make an estimate of the temperature, and that in the light of the theory we can trace a connection between the density of the star, the temperature, and the spectral emission. Thus the fact that giant stars of a given spectral type have lower effective temperature than dwarfs of the same type, and yet give a spectrum in which the spark lines are stronger, is at once explained by the lower pressure prevailing in the atmosphere of the giant, which leads to increased ionisation. E. A. Milne and R. H. Fowler, both together and independently, have developed and extended Saha's work, and obtained a variety of interesting results which are beyond the scope of this book. The object of this brief astrophysical disquisition has been rather to indicate the nature of the application of atomic theory to astronomical problems than to describe, even in outline, the results obtained. The opportunity to discuss Eddington's fascinating work on the physical conditions prevailing in stars is tempting, but would lead us too far afield.

Thermodynamics and Atomic Structure. The essential features of the Bohr atom—the existence of stationary states, transition between which attends the emission or absorption of

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* Reference may be made to a paper by E. A. Milne, " Recent Work in Stellar Physics," *Proc. Phys. Soc. London*, **36**, 94, 1924. A full account of stellar spectra in the light of modern atomic theory is given by C. H. Payne in *Stellar Atmospheres*, Harvard University Monographs, Cambridge, Massachusetts.

radiation ; of a definite minimum energy of the atom which corresponds to the most stable state ; and of a definite additional amount of energy which corresponds to the complete separation of an electron from the atom—have been introduced into the treatment of thermodynamical problems, to provide a mechanism for the interchange of energy between radiation and matter. Investigations of the equilibrium between atoms, electrons and radiation have led to results of fundamental importance, especially for astrophysical problems.   To attempt anything like an adequate summary of what has been done in this direction would obviously take us far outside the plan of this book, but since these advances are essentially connected with the theory of atomic structure, a brief account of the principles from which they start will now be given.

The first application of Bohr's theory to problems of thermodynamic equilibrium was made by Einstein, who showed how the assumption of stationary states could be made to yield Planck's law for the distribution of black-body radiation, represented by the well-known formula

$$I_\lambda d\lambda = C \frac{\lambda^{-5} \cdot d\lambda}{e^{a/\lambda T} - 1},$$

where $I_\lambda d\lambda$ is the energy of radiation whose wave-lengths lie between λ and $\lambda + d\lambda$. Einstein's deduction involves two theoretical results which have long been established.   The first is Wien's law, which says that in a uniform temperature enclosure the energy is distributed among the wave-lengths according to the formula

$$I_\lambda d\lambda = C \lambda^{-5} f(\lambda T)\, d\lambda,$$

where $f(\lambda T)$ is the function whose form we have to find.   Wien's formula is derived from consideration of the thermodynamic behaviour of black-body radiation enclosed alone in a chamber with perfectly reflecting walls, and its validity is, in consequence, quite independent of any mechanism assumed for the interaction between atoms and radiation, i.e. for the emission or absorption of the radiation by matter.

The second is a theorem of Boltzmann's,* which refers to a system of gas molecules, possessing potential energy, in

* Boltzmann, *Vorlesungen über Gastheorie*, 1896, page 136.

thermal equilibrium at a temperature T. This states that the ratio of the number N_1 of molecules possessing energy E_1 to the number N_2 possessing energy E_2 is given by

$$\frac{N_1}{N_2} = e^{-(E_1 - E_2)/kT},$$

where k is Boltzmann's constant.* Thus, to take a very simple example, in an atmosphere under gravity the pressures at different places are proportional to the numbers of molecules per unit volume at those places, and the difference of potential energy is mgx per molecule, where x is the vertical distance between two levels and m is the mass of the molecule. Hence

$$\frac{p_1}{p_2} = \frac{N_1}{N_2} = e^{-mgx/kT} = e^{-Mgx/RT},$$

where M is the gram molecule and R the gas constant, which is the familiar result.

Instead of considering, as in Planck's original proof, a linear oscillator as the system by which radiant energy is transformed and equilibrium maintained, we now consider a Bohr atom, for which various stationary states, possessing negative energies, $E_1, E_2, E_3, \ldots E_n$, are possible. E_1 is the negative energy corresponding to the stable, normal state. It is an essential feature of Bohr's theory that the atom in an excited state, which we may take as state n, has an inherent tendency to return to the normal state 1 : for this return there is a certain probability, independent of the temperature or density of radiation, which we will call $A_{n \to 1}$. Einstein refers to this spontaneous radiation as "issuing radiation" (*Ausstrahlung*). The atom has no tendency of itself to pass from state 1 to state n : under the influence of radiation, however, we know that it can do so with absorption of radiation of frequency ν_T, say. The probability of the transition is proportional to the intensity I_ν of the radiation : let the coefficient of proportionality be $B_{1 \to n}$. The field of radiation will also have its effect on the probability of transitions from state n to state 1, since it is reasonable to assume that the phase equality between the radiation emitted

* $k = \dfrac{R}{N} = 1 \cdot 37 \times 10^{-16}$. In other words, k is the gas constant for a single atom.

in the transition and some of the radiation existing in the field will have a disturbing effect on the atomic system. This gives an additional probability, proportional to the density I_ν of radiation of frequency ν_T. We will denote the probability of transition, due to this radiation, by $I_\nu B_{n\to1}$. It is to be noted that two of the probabilities considered are proportional to I_ν, while the third is independent of I_ν. Einstein speaks of the effects which are proportional to the intensity of the field of radiation as due to " entering radiation " (*Einstrahlung*).

Let the number of atoms in state 1, when equilibrium is established, be q_1 : the number of atoms in state n will depend upon the energy difference $E_1 - E_n$ between state n and the normal state, and upon the temperature, in a way given by the theorem of Boltzmann's already quoted. Let this number, then, be $q_n e^{-(E_1-E_n)/kT}$, where q_n is the *a priori* probability, or weight, of the state n. q_n is, of course, independent of T. For equilibrium the number going from state n to state 1 must equal that going from state 1 to state n, or

$$q_1 I_\nu B_{1\to n} \cdot dt = q_n e^{-(E_1-E_n)/kT}(A_{n\to1} + I_\nu B_{n\to1})\, dt. \quad \ldots\ldots(6)$$

We can get a relation between $B_{n\to1}$ and $B_{1\to n}$ by making the very natural assumption that I_ν increases indefinitely with T : making T very large, we get, from (6),

$$q_1 B_{1\to n} = q_n B_{n\to1}.$$

Using this relation, we have, from (6),

$$I_\nu = \frac{q_n}{q_1}\frac{A_{n\to1}}{B_{1\to n}}\frac{1}{e^{(E_1-E_n)/kT} - 1} = F\frac{1}{e^{(E_1-E_n)/kT} - 1}, \quad \ldots\ldots\ldots(7)$$

where F is independent of the temperature, but a function of ν. From Wien's law we have : (a) I_ν must involve T only in the form $f(\lambda T)$, *i.e.* $f(T/\nu)$, and (b) F must be proportional to λ^{-5}. From (a) we have $E_1 - E_n = ak\nu$, where a is a constant. This represents Bohr's fundamental assumption. From (b) we then have

$$I_\nu \cdot d\nu = I_\lambda \cdot d\lambda = C\frac{\lambda^{-5} \cdot d\lambda}{e^{a/\lambda T} - 1},$$

which is Planck's formula as usually given. We have expressed

it in wave-lengths rather than frequencies, because it is usually so given in the text-books.   In terms of frequencies it becomes

$$I_\nu \cdot d\nu = C \frac{\nu^3 \cdot d\nu}{e^{a\nu/T} - 1}.$$

Recently Eddington has shown how, by an adaptation of Einstein's method, Planck's law can be deduced without assuming Boltzmann's equation.   Eddington assumes Wien's law, and that I_ν increases indefinitely with T, just as does Einstein, and further invokes the Bohr condition $ak\nu = E_1 - E_n$, which Einstein proves.   This last assumption makes up for renouncing Boltzmann's formula, which Eddington derives from his assumption.

This method of Einstein's has formed the starting-point of several investigations on the interaction of radiation and gaseous atoms.   Thus both E. A. Milne and R. H. Fowler have considered the equilibrium of atoms, electrons and radiation, thereby introducing a third party into the equilibrium.

Essentially involved in such problems, where the collisions of electrons and atoms, and the related radiations, have to be statistically considered, are certain deductions for which we are indebted to Klein and Rosseland.   They distinguish between *impacts of the first kind* and *impacts of the second kind* ; the nature of the distinction will now be discussed.

We know that when an electron possessing energy greater than the resonance potential strikes an atom it may (but need not necessarily) transfer energy to the atom, producing a higher stationary state, return from which is accompanied by radiation.   Such an impact, in which the energy of translation of particles is wholly or partly converted into energy of excitation, is called an impact of the first kind.   Now Klein and Rosseland have shown, by thermodynamic reasoning, that the reversed process must also take place, *i.e.* that if collision takes place between an atom in an excited state and a particle, the excited atom may return to its normal state *without radiation,* the energy which would appear as radiation if the atom were to pass spontaneously from the higher stationary state to the lower appearing as kinetic energy of the particles.   We then have an impact of the second kind.   We may summarise this

by referring to the process as reversible, and expressing the collision between an atom and an electron by $e \underset{\rightarrow}{\leftarrow} (E' - E) + e'$, where e, e' are kinetic energies of the electron, e being greater than e', and E', E are the energies of the atom in the excited and normal states respectively. The arrow pointing to the right corresponds to an impact of the first kind, the arrow pointing to the left corresponds to one of the second kind.

The necessity for the impacts of the second kind can be seen from a quite simple argument. Suppose we have atoms, electrons and radiation shut up in a perfectly reflecting uniform temperature enclosure. We have already seen how, for the case of no electrons present, Einstein was able to deduce Planck's radiation law from the equilibrium. Now suppose that the electrons which we have introduced can only carry out impacts of the first kind. They have then a mechanism by which they can lose energy, and no mechanism by which they can gain it, so that the electrons as a whole will fall in temperature, while the atoms and the radiation will increase in temperature, until all the electrons have energy equal to the lowest resonance potential. The establishment of such an inequality of temperature would violate the second law of thermodynamics, so that if we wish to retain this law we must assume the reverse mechanism which we have described.

Milne and R. H. Fowler independently have extended these ideas to the mechanism of ionisation by collision between atoms in a gas at high temperature in equilibrium with its surroundings. If an atom possessing sufficient relative energy strike another atom, it may ionise it, producing an ion and an electron, both possessing a certain amount of energy. The reverse process demanded in this case is a three body encounter between an electron, an ion, and an atom, in which the electron returns to the ion, the balance of energy appearing as kinetic energy of the atom. If I be the energy of the ion, A and A' the energy of the striking atom before and after impact, we can write as above

$$A \underset{\leftarrow}{\rightarrow} (I - E) + e + A'.$$

Discussion of the use to which Milne and R. H. Fowler have put considerations of this kind would take us too far afield.

The case of a gas in temperature equilibrium with its surroundings must, of course, be carefully distinguished from that of a gas excited to radiation by some outside influences, such as a stream of electrons whose individual energy is high compared to that of a gas molecule, or a radiation from an external high temperature source. Such cases will be discussed when we come to deal with the problems of resonance radiation, to which Klein and Rosseland's theory has been applied by Franck and his students.

Resonance Radiation. Striking confirmation of the general theory of spectra has been afforded by the study of resonance radiation. When sodium vapour at a suitable pressure is illuminated by light of the two D lines of sodium, that is, the first pair of the principal series, it re-emits light of the wave-length of the D lines in all directions, and it is to such a re-emission without change of wave-length that R. W. Wood, who has carried out extensive investigations on the subject, gave many years ago the name resonance radiation, since on the classical theory such radiation had to be attributed to resonating systems in the atom which responded to waves of their own free period. Such a radiation could, of course, be explained on any theory in which the atoms contained vibrating electrons of certain periods, and the somewhat complicated polarisation phenomena observed when the resonant light is excited by a plane polarised beam, both with and without magnetic field, do not compel a decision in favour of either classical or quantum theory.*

Results which speak clearly for the quantum theory, and are inexplicable on the classical theory, have been obtained by the present Lord Rayleigh, who excited the sodium vapour not by the first pair of the principal series of sodium, but by the second pair which lie in the ultra-violet, $\lambda\lambda\,3302 \cdot 34,\,3302 \cdot 94$, and correspond to the transitions 2^2P_2, 2^2P_1 to 1^2S_1. This radiation, obtained in strength by means of a sodium vacuum arc, excites the vapour on which it falls to a strong emission of the D lines; there is no connection between the frequencies of

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* For a discussion of R. W. Wood and A. Ellett's very interesting discoveries of the remarkable effect of weak magnetic fields on the polarisation of resonance radiation, see G. Joos, *Phys. Zeitschr.*, **25**, 131, 1924, and P. Pringsheim, *Zeitschr. f. Phys.*, **23**, 324, 1924.

the two pairs which admit a mechanical explanation of this fact. On the quantum theory the D lines are to be expected, as can be seen at once from a study of the level diagram for sodium, Fig. 62. The exciting light sends the optical electron
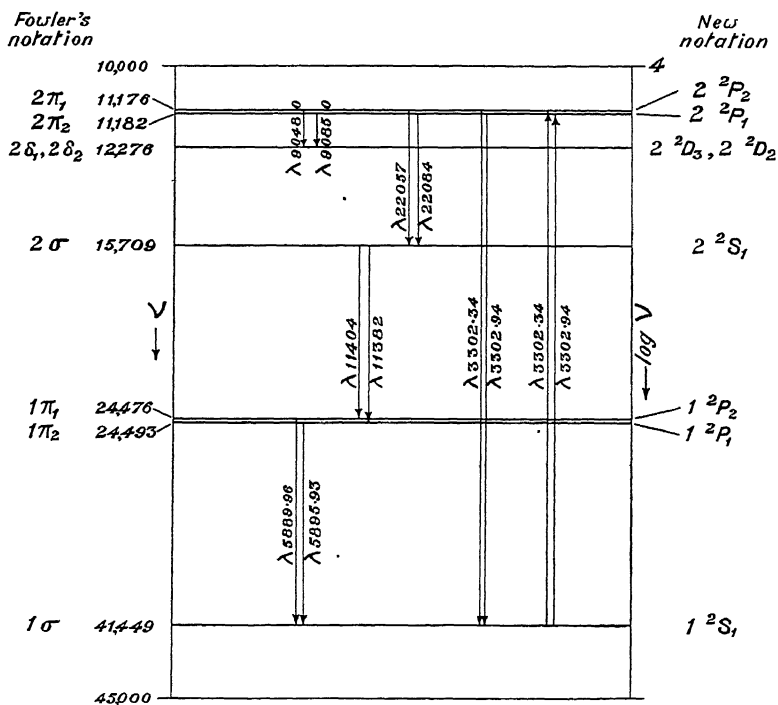
FIG. 62.

Level diagram for the sodium atom.

to the 2^2P levels. From here it can return direct to 1^2S_1, emitting $\lambda\,3302$, which was, however, not observed by Lord Rayleigh. It can also pass to 2^2S_1, and from here to 1^2P_1, 1^2P_2, but not direct to 1^2S_1, since this transition would not change k. The radiations involved in thus passing to the 1^2P levels would not be observed, as they lie in the infra-red. The return from the 1^2P levels to the basic level gives the D lines, as observed.

Among a number of other interesting resonance radiation experiments we select a group which are of particular impor-

tance as furnishing strong confirmation of the theory of impacts of the second kind put forward by Klein and Rosseland. They considered the impacts between an atom and an electron : Franck extended the same notions to the impact between atom and atom, so that in an impact of the second kind a collision between an excited and an unexcited atom results in the excited atom returning to its stable state without radiation, the energy so set free appearing as energy of translation shared between the atoms according to the laws of momentum.* He deduced from this many striking results which have been confirmed by experiment, as will now be discussed.

We consider first the quenching of resonance radiation by the admixture of a foreign gas. Some years ago R. W. Wood, whose researches opened up this fascinating field of experiment, showed that a trace of air diminished markedly the resonance radiation excited in dilute mercury vapour by the mercury line $\lambda 2537$, and that by increasing the amount of air the intensity could be decreased in exponential fashion. The absorption suffered by the primary beam was little affected, which would seem to indicate on the quantum theory that the mercury atoms are actually excited, but return to the normal state without radiating. Franck's view is that the mercury atoms are excited, but that when there is an appreciable quantity of foreign gas present impacts of the second kind may take place before the atoms have radiated : at these impacts the mercury atoms return to their stable state without radiation, the (internal) energy of excitation being shared between the mercury atom and the foreign atom as (external) energy of translation. Cario has carried out interesting experiments on the quenching of mercury resonance by admixture of an inert gas which confirm this view. If, say, argon be added the intensity diminishes according to an exponential law as the pressure of the argon increases. A relation can be obtained between the number of impacts of the second kind and the duration of the excited state, since the diminution of intensity of the resonance radiation is due to impacts taking place

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* In the case of molecules the energy might be converted into energy of rotation or vibration, but this leads us into the theory of band spectra, with which we are not concerned.

between argon and mercury atoms before the latter have had time to return to their stable state. Cario assumes that every impact between an excited mercury atom and an argon atom is an impact of the second kind, takes for the mean duration of the excited state a value 10^{-8} sec. (see p. 316), and calculates the number of impacts of the second kind. From this the ordinary considerations of the kinetic theory enable an effective diameter to be calculated for the *excited* mercury atom, taking the ordinary value for the diameter of the inert gas atom. The value for mercury derived from experiments in which the quenching was effected by a mixture of helium and neon is about three times the value ordinarily taken for the diameter of the atom : a similar result was found from calculations applied to Wood's original experiment. Now in the excited state, corresponding to $\lambda\,2537$, where the optical electron occupies a 1^3P_1 orbit much larger than that in the unexcited atom, the effective diameter must be increased, and this value seems reasonable. The assumption that all the impacts between excited and unexcited atoms are of the second kind is therefore justified, or to be cautious, one can at least say that the ratio of the number of impacts of the second kind to the total number of impacts between excited and unexcited atoms cannot be small compared to 1. The results with argon gave for the mercury atom a diameter about five times the normal : this seems to indicate that for this gas the percentage of impacts of the second kind is somewhat smaller.

Of course, atoms of any one kind can make impacts of the second kind among themselves, and it is well known that the intensity of resonance radiation diminishes rapidly as the pressure of the vapour itself is raised. At very high pressure the number of quantum switches which should take place in a given time is very small compared to the number of impacts between excited and unexcited atoms, and hence there is no appreciable resonance radiation. A very good example of the effect of these impacts of the second kind in an uncontaminated vapour is furnished by another experiment of R. W. Wood. He has shown that, when mercury vapour is excited by $\lambda\,1849$ $(1^1S_0 - 1^1P_1)$, besides the line $\lambda\,1849$ the line $\lambda\,2537$ $(1^1S_0 - 1^3P_1)$ can also appear in the resonance radiation. Now the transition

$(\mathrm{I}^1P_1 - \mathrm{I}^3P_1)$, accompanied by radiation, is forbidden by the selection principle (cf. Fig. 50). The selection principle, however, does not apply to radiationless charges. Hence we may suppose that mercury atoms which have been excited by $\lambda\,1849$ to the I^1P_1 state can, on impact with normal atoms, pass to the I^3P_1 state without radiation, the energy appearing in the way characteristic of an impact of the second kind. The line $\lambda\,2537$ can thus be emitted.

A very pretty example of impacts of the second kind is furnished by what Franck calls sensitised fluorescence. Consider two different species of atoms, A and B, and a given excited state in each : the energy corresponding to the excited state will be different in the two atoms. Let ν, ν' be the frequencies corresponding to a quantum switch from the normal state to the excited state for A and B respectively, and suppose
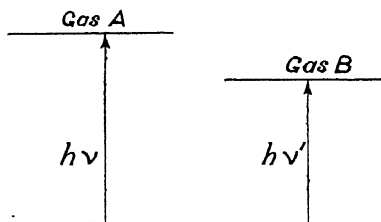
FIG. 63.

To illustrate sensitised fluorescence.

$\nu > \nu'$. Then an excited atom of A, possessing internal energy $h\nu$, can, on an impact of the second kind, transfer the whole or any fraction of this energy to a normal atom of B, and so can excite the atom of B, the balance of energy $h(\nu - \nu')$ appearing as translational energy of the atoms. Hence if to a vapour A excited to fluorescence by monochromatic radiation from an external source be added a second vapour B possessing an excited state, or states, of less energy, then atoms of this second vapour, which would not respond to the incident radiation at all, should themselves emit a radiation which we may speak of as sensitised by the presence of the vapour A. Such sensitised radiations have been produced experimentally by Cario and by Cario and Franck. Cario used mercury vapour to sensitise the radiation of thallium. The two metals were put in separate

branches of a tube, the mercury being heated to 100° C. and the thallium to 800° C., and the mixed vapour was irradiated by $\lambda 2537$ from a mercury lamp. The mercury should then be able to excite any atom possessing the requisite stationary states to emit wave-lengths greater than $\lambda 2537$. Cario obtained with thallium the lines $\lambda\lambda 5351$, 3776, 3520, 3519, 3230, 2918, *i.e.* all the lines theoretically possible if $1^2 P_1$ be taken as the normal state, as indicated by other arguments. A very beautiful extension of these experiments was made by Cario and Franck. They found that thallium could be made in this way to give a line $\lambda 2238$, which has greater energy than $\lambda 2537$. This they explained by supposing that an excited atom, taking part in an impact of the second kind, could hand over not only its internal energy of excitation, but, together with that, the whole or part of its energy of translation : this energy of translation was sufficient, in the case of the mercury atom, to account for the excess energy of $\lambda 2238$ over $\lambda 2537$. The explanation was substantiated by experiments in which the resonance radiation was sensitised, once more by mercury, in cadmium vapour. With this vapour certain lines, originating in stationary states higher than would be accounted for if the energy of $\lambda 2537$ were alone taken into account, appeared at high temperature, and not at lower temperatures, quantitative agreement being obtained.

The general conclusions as regards the radiationless impacts, or impacts of the second kind, are as follows. Two atoms, in stationary states, can, on collision, pass to other stationary states without radiating. The transitions which can take place are conditioned by the total amount of energy owned jointly by the two atoms ; it is indifferent whether this energy exists as internal quantum energy (energy of stationary states) or as external translational energy. Changes of internal energy can only take place in quantum jumps : the translational energy provides a stock from which energy may be drawn to make up the necessary quantum amount, and to which energy remaining over when the internal energies have been adjusted may be returned.

Of importance for chemical theory is still another type of sensitising which Franck showed was to be expected as a result

of impacts of the second kind. It is well exemplified by experiments which he has carried out in conjunction with Cario on the dissociation of the molecular hydrogen into atomic hydrogen. If an excited mercury atom strikes a molecule it seems possible that it may hand over its energy to the molecule in such a way that the molecule is dissociated, provided always that the energy to be disposed of is in excess of the dissociation energy. Franck and Cario actually demonstrated that, if mercury vapour is mixed with hydrogen, and irradiated with $\lambda 2537$, atomic hydrogen is formed, which will make its presence known by reducing cold copper oxide with production of water vapour and reduction of pressure. They were, in fact, able to produce all the reactions which Langmuir gives as characteristic of atomic hydrogen.

Franck has also explained by an appeal to impacts of the second kind certain peculiarities connected with the sensitising of photographic plates in the red by means of dyes.

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CHAPTER XIII

X-RAY SPECTRA AND THE INNER ELECTRON GROUPS

Introductory. It has been pointed out that X-radiation can be divided into scattered radiation, whose frequency is decided rather by the distribution of energy in the exciting radiation than by the nature of the substance in which the radiation is excited, and characteristic radiation, whose frequency depends upon, and characterises, the emitting element. The problems connected with the former are of great interest, but their consideration has done little to throw light upon atomic structure. We will therefore put them aside, and devote our attention to the characteristic radiation, which is of the highest importance for our subject.

The investigations initiated by Moseley showed that the characteristic radiation has a line structure, and to-day, as a result of improvements in the technique of the crystal method, due especially to Siegbahn and his school, the line spectra of X-rays have been measured with great accuracy and detail. In place of the six lines measured by Moseley well over sixty have been detected. X-ray spectra are in one respect much simpler than optical spectra. The monochromatic radiations given out by a typical atom fall into series, just as do the lines of the optical spectra, but whereas in the general optical case the lines belonging to the different series are intermixed, and have to be sorted out by the methods glanced at in the " Digression on Optical Spectra " (Chapter VIII.), in the X-ray case, as with the optical spectrum of hydrogen, there is no overlapping of the series. The lines belonging to one X-ray series cover a range of wave-lengths which is quite small compared to the gap between two different series, so that there is

never any doubt or difficulty attached to the attribution of a line to a given series. Fig. 64 shows diagrammatically the X-ray spectrum of tungsten, and it will be seen that the series are well separated. This attribution of the different groups of lines to different series finds complete support in the theories which will be developed. So physically distinct are the $\acute{K}$ and L series that they were discovered by Barkla from the different penetrating power of their radiations long before the
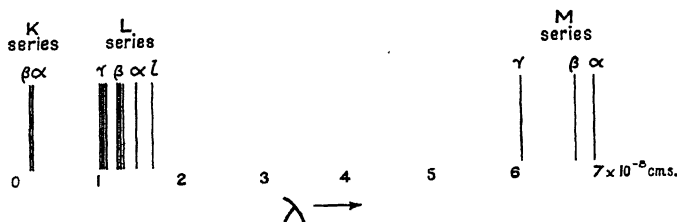
FIG. 64.

General type of X-ray spectrum, as exemplified by the tungsten spectrum.

wave-lengths of X-rays were measured, and, in fact, the nomenclature of K and L series goes back to him.

The three main series in the general X-ray spectrum are, then, known as the K, L and M series, of which the M series was discovered by Siegbahn in 1916 for the elements uranium to gold : since then measurements of the M lines have been made down to dysprosium by Stenström. More recently (1922) representative lines of a fourth series, of still lower frequency than the M series, have been measured by V. Dolejšek and by Hjalmar. This series has been named the N series, and has been obtained with the three very heavy elements uranium, thorium and bismuth.* In a given atom all the lines of the

* Barkla has of recent years discovered and discussed, in a long series of papers, some published in conjunction with Mrs. Sale and with Khastgir, an effect to which he refers as the J phenomenon. It is characterised by a sudden increase in absorption of a primary beam of X-radiation, accompanied, when the absorbing substance is a gas, by a sudden increase in ionisation. It was originally suggested by him that the phenomenon was connected with the emission of a characteristic radiation of a new series, to be called the J series, since it was found to occur at a frequency higher than that associated with the K radiation of the absorber. Further experiment has, however, convinced Barkla that the J phenomenon is not associated with a characteristic radiation of the K, L, M, N type, so that the choice of J to denote the effect

K series are more penetrating, *i.e.* of greater frequency, than any line of the L series, and all lines of the L series more penetrating than any line of the M series. The similarity of
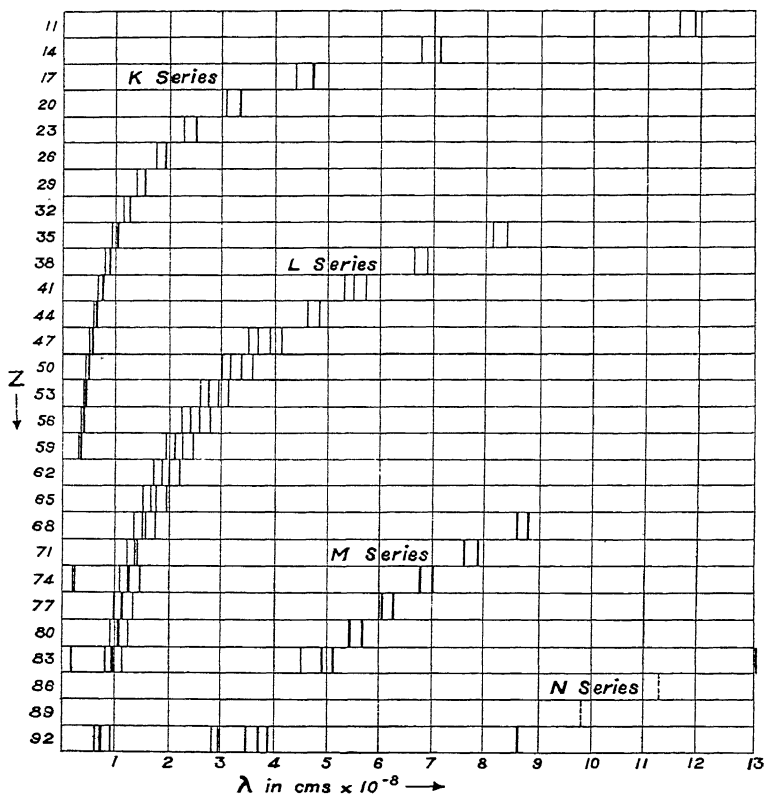
FIG. 65.

Scheme of X-ray spectra.

structure of all X-ray spectra enables us to trace a given line from atom to atom : if we do this we find that the line increases

is unfortunate. In any case, all theoretical reasoning is against the existence of a characteristic radiation more penetrating than the K radiation. The phenomenon is intriguing, but its theoretical bearing at present quite uncertain, so it will not be further discussed. To quote Barkla himself : " It is too new and too comprehensive to describe in a few words." The interested reader is referred to " The J Phenomenon in X-Rays," *Phil. Mag.* **49**, 1033 ; **50**, 1115, 1925.

in frequency with increasing atomic number. These funda-
mental properties of the K, L and M series are exhibited in
Fig. 65, where the wave-lengths of the chief lines of the dif-
ferent series are plotted against atomic number for a range of
elements from $Z = 11$ to $Z = 92$. Moseley's law, connecting the
frequency of a given line with the atomic number, has already
received reference in Chapter VI. The simple nature of the
general change in the X-ray spectrum as we go from atom to
atom is in strong constrast to the optical case.

There is much general evidence to show that, broadly speak-
ing, the origin of the X-ray spectra is to be sought in the
behaviour of the inner electrons of the extra-nuclear part of
the atom, as distinct from the superficial electrons which are
responsible for the optical spectra. The distinction between
inner and superficial electrons is not a rigid one, since we know
that the optical electron can penetrate into the core, although
most of its path lies remote therefrom, and, moreover, the
electrons which are concerned in the emission of X-ray spectra
may, in certain cases, have part of their orbit in the surface
region of the atom. Such points, however, are minor ones,
which can be best elaborated after the general features of the
X-ray spectrum have been described : they are discussed when
the connection between optical and X-ray spectra is handled,
and further in Chapter XIV. It is significant for the point
under consideration that the X-ray spectra emitted by a given
atom are, except for slight influences to be detailed later, inde-
pendent of the state of chemical combination of the atom, of
the state of aggregation, and of the temperature of the emitting
body—the same X-ray spectrum is given by an anti-cathode
when cold, and when it has become white-hot. These are
strong indications that the superficial electrons, which are
concerned in chemical combination, cohesion, and thermal
collision, play an insignificant part in the emission of the X-ray
line spectra. It is true that the radioactive properties of an
element are similarly independent of the influences just
specified. These properties are, however, unaffected by a
bombardment of swift electrons, which excite the X-ray
spectra. These electrons, while their energy is insufficient to
enable them to reach the nucleus, penetrate into the inner

parts of the extra-nuclear structure. X-rays, then, possess properties midway between optical spectra and nuclear γ rays as regards their dependence on laboratory influences, and must be supposed to originate between the nucleus and the periphery of the atom. Moseley's law supplies further evidence to the same effect, since if the outer electrons were concerned we should expect strongly marked periodicities corresponding to the occurrence of the periodic chemical properties. This law may further be taken to furnish an indication that, to a first approximation in any case, the inner structure of the atom is steadily built up in such a way that, as we proceed from atom to atom in the direction of increasing Z, certain groups of inner electrons are formed which remain as a feature of subsequent atoms. As will be expounded later, this hypothesis is generally accepted.

Preliminary Scheme of Internal Structure : Circular Orbits. To form a rough preliminary idea of the structure of the atom, as indicated by X-ray spectra, we need consider only the chief lines and the most fundamental results. Denoting for the moment by $K\alpha$, $K\beta$, $K\gamma$; $L\alpha$, $L\beta$, $L\gamma$; $M\alpha$, $M\beta$, the frequencies of the more intense lines of the K, L and M series,* consideration of the experimental data shows that the following combination relations are approximately, but not quite, true : the lack of exactness is important, and its origin will appear in the more detailed discussion that follows, but may be temporarily neglected.

$$K\beta - K\alpha = L\alpha, \; K\gamma - K\alpha = L\beta, \; K\gamma - K\beta = M\alpha \text{ and } L\gamma - L\alpha = M\beta. \quad (\text{1})$$

Next, a definite minimum energy in the form of X-rays or cathode rays is needed to excite a given X-ray series ; if the exciting agent is X-rays, the energy in question is, of course, $h\nu_T$, while if it is cathode rays the energy may be measured by the accelerating potential, as in the case of the optical ionisation potential. In contrast to the optical case, however, no single line of a given X-ray series can be excited independently of the others, but whole groups appear at once.

These facts may be provisionally explained on the supposition that the electrons are arranged in successive rings, that is,

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* This notation is temporarily adopted for simplicity, and does not correspond in all particulars to that in current use, e.g. the lines due to a transition from the N level to the K level (cf. Fig. 66) is in current notation $K\beta_2$.

in circular orbits, each of which may contain several electrons. Our experience with optical spectra suffices to warn us that circular orbits are adequate for a rough general description only, and this crude representation will be replaced later by a more elaborate scheme. The ring nearest the nucleus is known as the K ring, and the others, proceeding out, as the L, M, N ... rings, the rings being named by these letters because each one pertains in a special way to the series so denoted. The (total) quantum number of the K ring is taken as 1, of the L rings as 2, and so on, as with the orbits of the hydrogen atom, which, however, in contrast, are in general unoccupied by electrons. To excite a given series, say the K series, it is necessary as a preliminary to remove an electron from the K ring to the periphery of the atom, by which is meant to some orbit outside the occupied rings of electrons. The gap so created is filled not by the return of the original electron, but by an electron from the L, M or N ring ; such a quantum switch will give rise to, respectively, the α, β or γ line. The further out the ring from which the electron is replaced, the bigger the energy change and the greater the frequency of the emitted line. Similarly, to excite the L series an electron must be ejected from its seat in the L ring to an unreserved seat outside the atom, and replaced by an electron from the M, N or higher ring.* This simple scheme is expressed in Fig. 66, where the different rings, or energy levels, are exhibited diagrammatically. The circles must not be taken as representing the relative sizes of the orbits, but only the classes of transitions corresponding to the excitation and emission of the different series. This scheme, which was first put forward by Kossel, accounts for :

(a) The fact that all the lines of a given series have the same limit of excitation energy.

(b) The fact that for a given atom a greater energy is needed to excite the K than the L series, and a greater to excite the L than the M series.

(c) The combination relations expressed in equation (1).

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* The gap so caused in a higher ring must, of course, be in its turn filled by an electron : ultimately by a peripheral electron, which will be captured to make the atom neutral again.

(*d*) The fact that the greater the atomic number of an atom the greater is the energy needed to excite a given series.   With
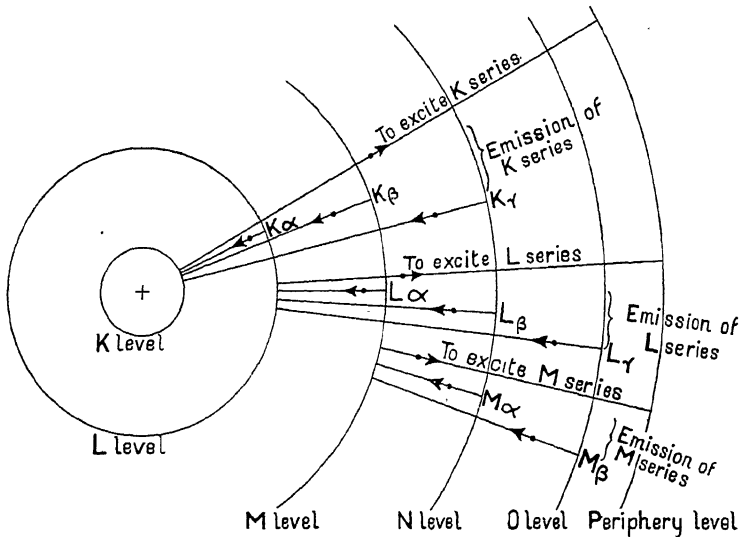
FIG. 66.

Preliminary scheme of energy levels within the atom, with corresponding X-ray emissions.

a greater nuclear charge more work is required to remove an electron from a given inner ring.

Another way of representing the quantum transitions, which is often adopted, is shown in Fig. 67.   Here a horizontal line represents each energy level, whatever the shape or nature of the corresponding orbit may be, and the transitions are indicated as before.   This method of representation has already been used for optical spectra.

The combination relations (1), which are represented in these simple diagrams, do not hold exactly for the lines given, nor, indeed, for any lines of the X-ray spectrum, when the spectra are carefully measured, though the deviations are never large.   One of the chief objects of the more elaborate models which will be described is to account exactly for the frequency relations between lines of different series of the same atom, and in general, to represent by properly chosen energy levels all the lines of the X-ray spectrum.   Another task is to

link up the X-ray spectra with the facts expressed in the periodic table.

It is to be noted that one of the chief distinctions, on this theory, between optical and X-ray spectra, is that the
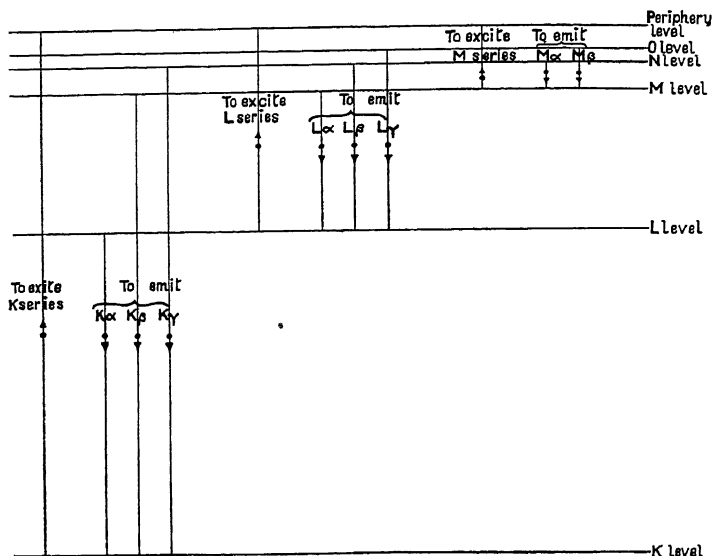
FIG. 67.

Alternative representation of energy levels.

orbits between which transitions take place are, in the optical case, of such a class that, in general, only one of them is occupied at a time, and that by the optical electron. In the X-ray case a place has to be made for an electron in a group of occupied orbits by the removal of an electron, and the electron which replaces it comes, in general, from one of a group of occupied orbits. This fact is sometimes expressed by calling the optical orbits virtual orbits, as distinct from the real orbits inside the atom. The question of the border relations between optical and X-ray spectra is discussed in a special section at the end of this chapter.

If we could suppose that the atoms of higher atomic number behaved simply as hydrogen atoms of higher nuclear charge, *i.e.* if we could neglect the effect of all the other electrons on

the electron concerned in the quantum switch, then by formula (4) of Chapter IX.,

$$W = \frac{2\pi^2 m Z^2 e^4}{h^2} \cdot \frac{1}{n^2} = RZ^2 hc \cdot \frac{1}{n^2}.$$

The wave number of the $K\alpha$ line, due to the passage of an electron from the L ring to the K ring, would be given by

$$\nu_{K\alpha} = RZ^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

and of $L\alpha$ by

$$\nu_{L\alpha} = RZ^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right).$$

Moseley gave the formulae

$$\frac{\nu_{K\alpha}}{R} = \frac{3}{4}(Z-1)^2 = (Z-1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$\frac{\nu_{L\alpha}}{R} = (Z-7.4)^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

as representing his measurements on the K_α and L_α line, *i.e.* formulae of the general type

$$\frac{\nu}{R} = (Z-z)^2 \left(\frac{1}{n'^2} - \frac{1}{n^2} \right).$$

These formulae do not represent the frequencies quite accurately; when $\sqrt{\dfrac{\nu}{R}}$ is plotted against Z the line shows a slight but systematic curvature. Fig. 68, to which reference has already been made in Chapter VI., exhibits the so-called Moseley graphs for the chief lines of the K, L and M series. The nature and degree of the departure from linearity can be seen from inspection of the diagram ; this feature has been explained on relativistic grounds, discussed later. For the moment, Moseley's formulae represent the facts closely enough.

The constant z which is to be subtracted from Z represents the action of the other electrons present in diminishing the effect of the nuclear charge on the particular electron concerned in the switch, the so-called *screening effect*. The extreme case of screening occurs, of course, when a single electron is removed to a great distance outside an atom, a case which we

have considered in connection with optical spectra. The nuclear charge is then reduced to an effective charge of one unit. In the general case of the simple ring theory we have for the term value to consider the energy of the atom when one particular electron is removed from its orbit. The presence of the electrons in rings internal to this orbit clearly diminish
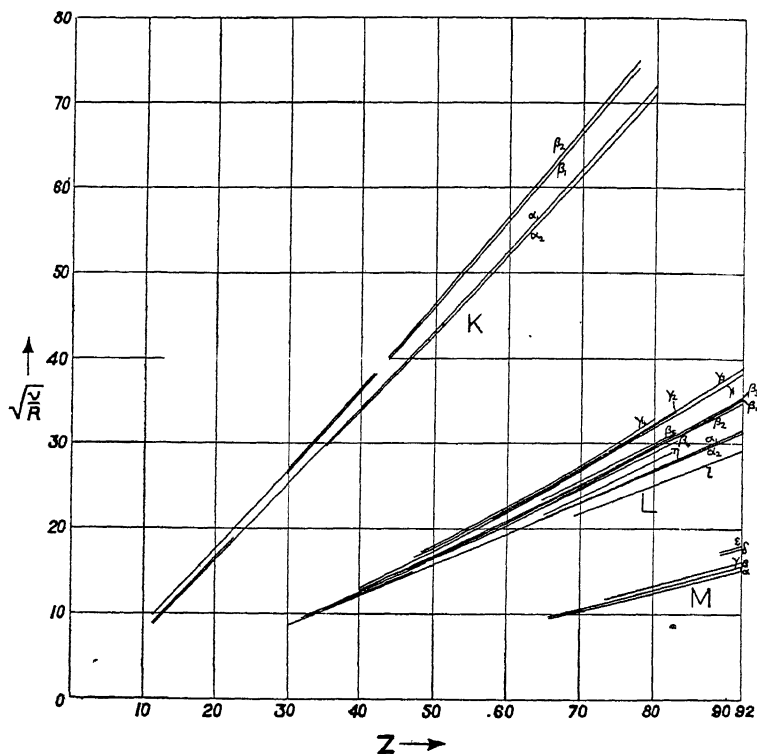
FIG. 68.

Moseley graphs for all the chief lines of X-ray spectra.

the effective nuclear charge by a quantity approximating to their total charge, and the electrons sharing the circular orbit with the switching electron also play a part in the screening effect, since they exert repulsive forces which have a radial resultant. The external rings of electrons have also to be considered; they exert a screening influence which finds an expression in the increased firmness with which they are bound

when an electron internal to them is removed. Hence it is clear that, for the circular orbit scheme, the *term* energy can be expressed in the form

$$W = Rhc(Z - \sigma_n)^2 \frac{1}{n^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where σ_n is constant for a given nth ring, but clearly increases from ring to ring as we go out. Various calculations were at one time made on the basis of the ring model as to the magnitude of this screening constant, but it is now generally realised that the ring model is quite inadequate to do more than give a quantitative description of the most important facts, and that such numerical computations are of little value. On general grounds the screening constant would be expected to be different for terms belonging to different K, L, M ... levels, as expressed in (2), and therefore Moseley's formula, which takes one screening constant for a combination of two terms, is a compromise which does not express the most general relationship. In considering later the relation between frequency and atomic number, the terms, rather than the lines, will be discussed.

Moseley's formulae, however, were the expression of a clearly realised analogy between the X-ray spectra and the hydrogen line-spectrum, and sufficient to enable him to draw the most important theoretical conclusions from his measurements. His formula for $L\alpha$, which gives a very fair representation over the range of his measurements ($Z = 40$ to $Z = 79$), is the formula for the hydrogen line H_a with a screened Z charge in place of unit nuclear charge.

Excitation and Absorption. Very important information as to the grouping of the electrons has been derived from the study of the absorption phenomena connected with X-rays. Closely connected with absorption is the question of excitation, since if radiant energy in traversing the atom is converted into a characteristic radiation it must disappear in its original form, and be absorbed. Both X-ray and optical lines may be excited either by appropriate radiation, or by moving electrons of appropriate energy, but there are characteristic differences between the two cases. As already mentioned, the lines of a

given X-ray series cannot be excited separately. Considering the K series, as the potential of the tube is raised, with corresponding increase in the energy of the individual electrons of the cathode stream, no K line appears until a certain critical potential is reached, when the whole K series appears simultaneously. When the critical exciting frequency is calculated in terms of the potential V from the usual quantum formula,

$$\text{kinetic energy} = Ve = h\nu_T,$$

it is found to be slightly harder than any observed K line—to correspond, in fact, to the limit of the K series.

This is well exemplified in Fig. 69, which shows the variation of intensity (as measured by the ionisation produced) of the
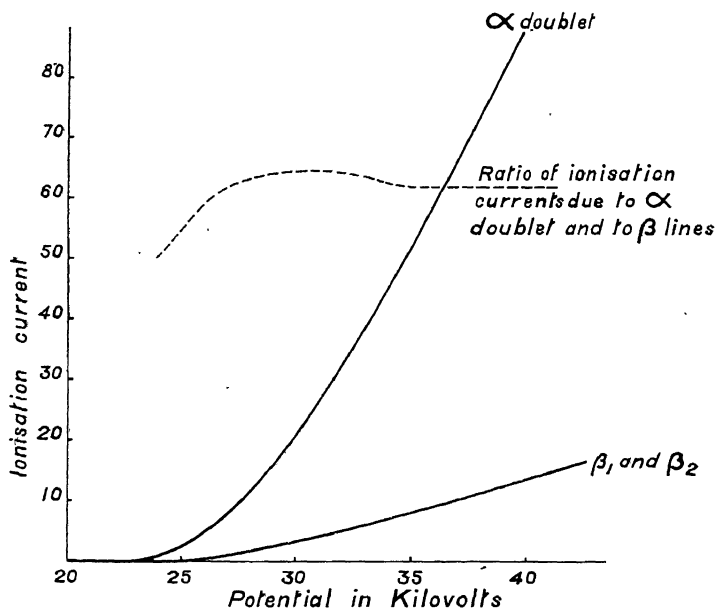
FIG. 69.

Variation of intensity of lines of K series with potential.

a and β lines of the K radiation of rhodium with the potential in the X-ray tube producing the radiation. It will be seen that both radiations set in sharply at about 23·25 kilovolts. The β radiation corresponds to about 23·1 kilovolts, according to

the quantum relation, while the α radiation corresponds to about 20 kilovolts, yet at 20 kilovolts there is no sign of its appearance. (It is interesting to notice that the relative intensity of the two radiations is approximately constant at different exciting potentials.)

If X-rays be used for the excitation of the K series they must exceed in frequency the hardest K line, whence the term " fluorescent radiation." They then excite the whole K spectrum.

Turning to the question of absorption, it is to be expected that if a heterogeneous beam of X-radiation be sent through a sheet containing atoms of a given element, there will be a sharp absorption edge, since all rays of wave-number less than a critical value ν will be unable to excite the characteristic radiation, and so will presumably be comparatively little absorbed. The absorption has been examined experimentally by letting X-radiations of a continuous range of wave-lengths from, say, the tungsten anti-cathode of a Coolidge tube,* fall upon the reflecting face of a crystal, of rock salt, for instance, which is slowly rotating. To each wave-length corresponds a particular angle of reflexion, so that the different angles successively presented by the rotation reflect selectively each a different wave-length from the continuous range, and the radiation is spread out into a continuous spectrum, on which, of course, will also appear the characteristic lines of the metal of the anti-cathode.† If now a thin sheet of the material to be investigated is introduced between the crystal and the photographic plate used to register the radiation, the wave-lengths at which special absorption takes place are recorded. It is found that sharp absorption *edges* do appear on the plate, representing the boundary between frequencies which are transmitted and frequencies for which there is characteristic absorption. Similar results have been obtained using the ionisation chamber instead of the photographic plate to register the transmitted radiation, successive measurements being made at different angles. There

* It must be remembered that the characteristic radiations are always accompanied by heterogeneous, or " white,' radiation, which, in fact, constitutes the greater part of the energy of X-radiation.

† For details of methods of X-ray spectroscopy, including the rotating crystal method, see W. H. and W. L. Bragg, *X-Rays and Crystal Structure*.

is always an edge separating two regions ; the very narrow absorption regions, typified by the Fraunhofer lines, which occur in the optical region, do not appear with X-rays. These absorption edges were first studied by de Broglie.

The sensitive emulsion of the plate contains silver and bromine, which also exert their characteristic absorption on the incident X-rays. This absorption in the plate manifests itself, of course, as an additional blackening of the plate, while, on the other hand, absorption by a foil interposed between plate and crystal is represented by a *diminished* blackening of the plate. Edges corresponding to silver and bromine appear in all plates, with light and dark regions reversed in comparison to results obtained by the ordinary method. Fig. 1, Plate VI.,* shows the K absorption edge for the three elements cadmium $(Z=48)$, antimony $(Z=51)$, and barium $(Z=56)$. Ag is the absorption edge for silver $(Z=47)$, on the left of which we have increased blackening due to the fact that all wave-lengths shorter than that corresponding to the edge Ag are selectively absorbed. The absorption edges of the three different metals are represented by the stepped boundary which divides a darker region on the right from a lighter on the left. Fig. 2, Plate VI., exhibits on a single photograph the K absorption edges of neodymium $(Z=60)$, praseodymium $(Z=59)$ and lanthanum $(Z=57)$. The K emission lines of the tungsten composing the anti-cathode are also visible on the photograph.

For the K series one absorption edge, corresponding to the limiting frequency of the K emission spectrum, is observed, as expected. For the L series, however, in the most general case —for heavier elements—*three* distinct absorption edges have been detected. Fig. 3, Plate VI., shows the edges in the cases of uranium and thorium, all three (L_I, L_{II}, L_{III}) being visible for uranium, while for thorium L_I is too faint to show in reproduction. The three L absorption edges have been measured for silver and practically all the heavier elements. Corresponding to these three absorption edges Webster and Clark, employing a tube with a platinum anti-cathode, have detected three different excitation potentials for the L series.

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* I am indebted to M. le duc de Broglie for all three photographs of Plate VI.

PLATE VI

Ag
↓
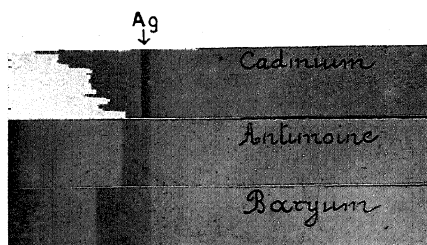
FIG. 1.

The K Absorption Edge for Cadmium, Antimony, and Barium. (de Broglie.)
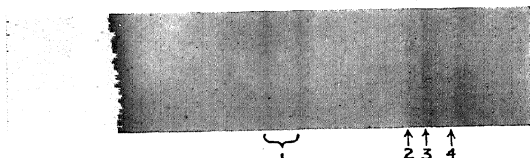
FIG. 2.

The K Absorption Spectrum of a Preparation of Didymium. (de Broglie.)

1. K Emission of Tungsten.   2. K Absorption Edge of Neodymium.
3. K Absorption Edge of Praseodymium.   4. K Absorption Edge of Lanthanum.
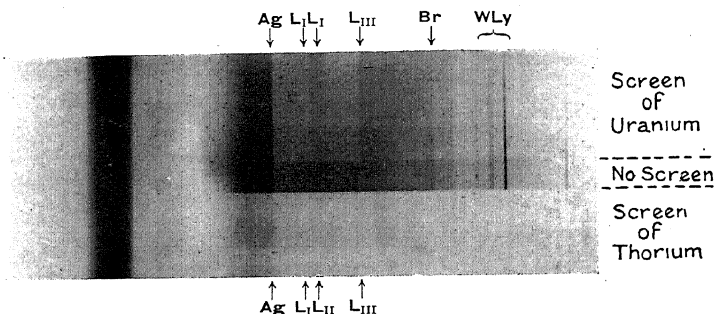
FIG. 3.   The Three L Edges of Uranium and Thorium.   (de Broglie.)
(L_I for Thorium is very faint.)
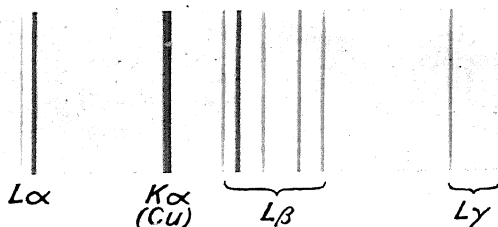
FIG. 4.   The L Series of Ytterbium. (Siegbahn.)

At about 11·45 kilovolts certain selected ·L lines appear·
together ; at 13·20 kilovolts another batch of lines appears ;
while a somewhat higher potential is needed to excite the
complete spectrum.   Hoyt has found similar results with
tungsten, the critical potentials being for this metal 10·2, 11·6
and 12·0 kilovolts.   The excitation measurements have not
been carried out systematically with a series of atoms, as have
the absorption measurements, but they confirm the general
result, that three different limiting frequencies are concerned
in the L series.   For the M series *five* different absorption edges
have been measured by Coster for the heaviest elements.   The
character and number of the absorption edges is of the utmost
importance in connection with the arrangement of the electrons
in different groups, and the existence of multiple edges for a
series is the surest indication of the subdivision of the series
into groups associated with different energy levels, which will
have to be discussed in some detail subsequently.

The energy necessary to excite a given series, say the L
series, is that required to remove an electron from the L ring,
or group, to the periphery of the atom ; corresponding to this
energy is a critical frequency given by the absorption edge.
The triple nature of the L edge indicates that there are three
different energy levels within the group, from any one of which
an electron can be removed to a final level which is the same
in all cases, *i.e.* the energy at the periphery.   Similarly, the
five M edges indicate a subdivision of the M group into five
energy levels.   Obviously this subdivision will have an effect
on the emission lines to be anticipated, increasing their possible
number, and giving us a freedom of adjustment to try to fit
the combination principle.

Another way in which the levels and their subdivisions can
be quantitatively determined is by investigating the secondary
corpuscular radiation released from a given kind of atom by
homogeneous X-radiation.   In discussing the work of C. D.
Ellis we pointed out that a single γ ray would release secondary
rays of more than one velocity from a given metal, since the
issuing velocity, neglecting relativistic correction, is given by

$$\text{Energy of liberated electron} = \tfrac{1}{2}m_0v^2 = h\nu_T - P,$$

where P is the work required to remove the electron from the

influence of the atomic forces, and hence has a different value for each of the various energy levels from which the electron may come. In the experiments of Ellis the object was to measure the wave-lengths of the incident radiation by observing the various energies in the line spectrum of the secondary β radiation, and the available knowledge of the energies of the different levels was used to distinguish which of the lines of the corpuscular spectrum were produced by a single homogeneous γ radiation. If, however, a homogeneous X-radiation, of *known* frequency, be allowed to fall on a given atomic species, and the energy spectrum of the electrons ejected from the atoms under the influence of this radiation be measured, then the differences between the $h\nu_T$ of the radiation and the various energies represented in the corpuscular spectrum will give us the energy levels from which the electrons originate.

Early experiments by Kang Fuh Hu and Lewis Simons indicated the existence of different levels. The method has been used by M. de Broglie and by Whiddington, who both obtained line spectra for the secondary corpuscular radiation when the incident radiation was homogeneous, but the most extensive and accurate measurements we owe to H. Robinson. The disposition which he used was similar to that of Ellis, illustrated in Fig. 7, the source S being a slit, through which passed the electrons released from a comparatively wide target by the incident X-rays. The necessary homogeneous and strong beam of X-rays was obtained by filtration, the radiation actually used being that from a copper anti-cathode filtered through a nickel foil, which results in the $K\alpha$ doublet alone being transmitted.* The two lines of this doublet being extremely close, the radiation may be taken as consisting of copper $K\alpha_1$, that being the intenser and harder line of the pair.

With this method of resolving the secondary corpuscular radiation by a magnetic field, and measuring the line spectrum

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* This filtration offers a good example of the general laws of X-ray absorption. The values of ν/R for the copper K radiation are 592·77 and 591·28 for α_1 and α_2 respectively, and 655·91 for β_1. The hardest radiation emitted by nickel, viz. $K\beta$, has $\nu/R = 613·48$; the frequency required to excite the nickel K spectrum will, as we know, practically coincide with this. Any ray harder than $\nu/R = 614$ will therefore be absorbed. Hence copper $K\alpha$ will be transmitted, copper $K\beta$ stopped. Any K rays of zinc proceeding from the brass parts of the X-ray tube will also be stopped, since $\nu/R = 636$ for zinc $K\alpha$.

so produced, Robinson was able to demonstrate the triple nature of the L level down as far as strontium ($Z=38$), whereas the absorption measurements had only followed it down as far as silver ($Z=47$). Furthermore, all five M levels were identified for bismuth, lead, gold and tungsten ($Z=83$, 82, 79, 74), and, except for imperfect resolution of two of them, also for barium ($Z=56$), which is a considerable extension of the range over which they were identified by the absorption edge method (thorium and uranium). The seven N levels to be later assumed, for which there was previously no *direct* experimental evidence, were identified for bismuth. Robinson's work, therefore, furnishes strong confirmation of our allotment of numbers of sub-levels in the L, M and N groups.

The absorption edges have hitherto been said to be sharp, but on close investigation they have proved not to be sharp in the strictest sense, but to have a finite breadth which has been alluded to by some writers as the fine structure of the absorption edge. That is, the edge is not only a boundary between a region of greater and less absorption, but exhibits, on careful inspection, a few close separated maxima : on the photographic plate the region of strong blackening, corresponding to little absorption by the foil, has a sharp boundary, but the comparatively light region which succeeds it exhibits one or two alternations of density, appearing as close darker and lighter lines, before it settles down. This fine structure has received a very instructive explanation at the hands of Kossel. For heavier atoms, with orbits of electrons actually occupied (in contrast to the unoccupied orbits of the hydrogen atom, for instance) an inner electron must be sent straight to the surface of the atom, there being no free orbits on the way ; this has already been pointed out in connection with the excitation of X-rays. When it has reached the surface, however, there are various external, or virtual, orbits which it may occupy. The work required to bring it to the surface is nearly as great as that required to send it to infinity, since the internal field is very strong compared to the external field, for which at some distance, at any rate, the effective nuclear charge is unity ; the small excess of work required to take the electron from the surface to infinity should, for a neutral atom, clearly approxi-

mate to Rh. Starting within the region of good transmission, and increasing the frequency, we should expect to find a sharp absorption edge at the frequency required to take the inner electron to the surface of the atom, and later, at a slightly higher frequency, corresponding to the removal of the electron to infinity, the region of continuous absorption should begin. Between these two frequencies, separated by $\Delta\nu$, say, should be a whole complex of absorption lines corresponding to the various virtual orbits, *i.e.* to the whole optical absorption series, but owing to the smallness of $\Delta\nu$ compared to ν, the wave-number of the absorption edge in question, the presence of only a few of the chief absorption lines can be detected, and that only in special favourable cases. A precise analogy to the effect may be found in the continuous absorption band observed by R. W. Wood and by Holtsmark with sodium vapour, cited in Chapter XI. Radiations of any frequency greater than that required to ionise the sodium atom are absorbed in a continuous band : between the limiting ionisation frequency and the first resonance frequency we have the complete absorption series of sodium.

If ν_K be the wave-number corresponding to the K absorption edge, then approximately $\nu \doteq RZ^2$ and $\dfrac{\Delta\nu_K}{\nu_K} = \dfrac{1}{Z^2}$.

For the L and M absorption edges,

$$\frac{\Delta\nu_L}{\nu_L} = \frac{4}{(Z-\sigma_L)^2}, \qquad \frac{\Delta\nu_M}{\nu_M} = \frac{9}{(Z-\sigma_M)^2}.$$

Hence small Z, and an initial level near the surface of the atom, are favourable to the observation of the effect, as can be seen at once from general considerations of the energy of the levels. The two conditions are not compatible, since the L and M edges are not observed with small Z, but we conclude that for heavy atoms the region of selective absorption would be most easily detected for the M series : for lighter atoms, where Z is small, it should be detectible for the K series. All these points have been confirmed experimentally. The narrow region of selective absorption at the edge of the absorption band has been detected in certain cases for all three X-ray series (not, of course, all three for the same element), and has

even been resolved into one or two close lines. The wave-number separation between these lines is of the order of R. For the M series the effect was first obtained with uranium ($Z=92$) and thorium ($Z=90$) ; for the K series for the elements from chromium ($Z=24$) to magnesium ($Z=12$). Thus the general conception of orbits of different quantum number occupied inside the atom, and unoccupied, but possible, outside the atom has been prettily confirmed. We see, too, that for very small Z a " K resonance potential " as distinct from a " K ionisation potential " should be capable of demonstration.

In connection with the fine structure of the absorption edges attention may be directed to the fact that the position of the absorption edge may be slightly affected by the state of aggregation or of chemical combination of the atoms concerned. Bergengren has shown that the wave-number of the K edge is measurably different for the different allotropic modifications of phosphorus, and Lindh has shown that the wave-number of the absorption edge for chlorine varies markedly with the valency of the chlorine in the compound used to effect the absorption. These effects are no doubt to be attributed to modification of the energy of the external orbits by the forces of crystallisation and of chemical combination respectively.

X-Ray Doublets. In dealing with the simple theory of X-ray spectra based on circular orbits we have selected certain important X-ray lines from among the many which have been measured. As a preliminary to a fuller discussion of the internal electronic structure a brief consideration of the general line structure and its analysis into energy levels is necessary. This leads straightway to a discussion of the so-called X-ray doublets, which are of great significance for the theory.

The nomenclature of the lines of the X-ray spectrum varies somewhat with different authors. That of Siegbahn is here adopted. In order of increasing wave-number the four main lines of the K series are α_2 and α_1, β_1 and β_2, forming two close pairs ; other lines detected for the light element sodium and its followers have been called α', α_3, α_4, α_5, α_6, and β_3, β', β'', which are close companions of the main α and β lines respectively. These lines have not, however, been identified from vanadium ($Z=23$) onwards, and are not further considered

here.   The L spectrum comprises two lines, l and η, and groups of α, β, and γ lines : l is the softest line in the L spectrum. There are three α lines—α_1, α_2, α_3—and, in the most general case, some ten or more β and γ lines respectively, indicated, like the α lines, by suffixes.   The M lines are denoted by α, β, γ, δ, ε, ζ, η, θ, χ, with dashes for distinction when the same letter is used for more than one line.*   It will be seen that the notation is not particularly uniform or satisfactory, but we must accept what is provided by the workers in this field.

The details of structure of the X-ray spectra have been revealed as a result of the great advances made during the past few years in the technique of accurate X-ray spectrometry, especially by the school of physicists working under Siegbahn. An example of an X-ray spectrum photograph is offered by Fig. 4, Plate VI., which represents the L series of ytterbium ($Z = 70$) as obtained by Siegbahn.

When the wave-numbers of the emission lines are considered in detail, it is found that certain of the lines can be associated in pairs to form doublets, the association in general being indicated not only by the internal structure of the spectrum itself, but also by the behaviour of the selected lines as we proceed from element to element. $K\alpha_1$ and $K\alpha_2$ constitute the K doublet.   For a given element there are, in the general case, five L doublets with a constant difference of frequency, namely η-l, β_1-α_2, γ_5-β_6, γ_1-β_2, γ_6-β_5.   These doublets are called, for a reason which will soon appear, the " relativity doublets."   The common difference of frequency for a given element is the same as the difference of frequency for the K doublet of the same element, which indicates that the association of the two $K\alpha$ lines has a physical significance.   For instance, $\Delta\nu/R$ for the K doublet is 98·5 and 125 for tungsten and platinum respectively, which values may be compared with the L doublet separations in the following table.   This table shows the frequency difference, expressed as $\Delta\nu/R$, of the L doublets of the heavier atoms, for most of which all

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* Lately the custom of indicating new lines by the two levels concerned in their emission, as $M_V P_I$, has been introduced, which, in the case of unimportant lines, which are not constantly being quoted, is convenient.

five have been measured. The L doublet $\beta_1 - \alpha_2$ has been traced down to atoms as light as niobium ($Z=41$), and $\gamma_5 - \beta_6$ as far down as rubidium ($Z=37$). The lighter atoms are not included in the table because the measurements made with them are not so complete.

TABLE OF L DOUBLETS.

Element		$\eta - l$	$\beta_1 - \alpha_2$	$\gamma_5 - \beta_6$	$\gamma_1 - \beta_2$	$\gamma_6 - \beta_5$	$L_{II} - L_{III}$
73	Ta	93·33	92·68	91·99	91·64	92·33	—
74	W	98·76	98·54	99·00	98·05	98·52	98·71
76	Os	—	111·08	—	110·67	—	—
77	Ir	—	118·64	—	117·59	119·49	—
78	Pt	126·18	125·92	125·19	124·97	126·30	126·38
79	Au	134·34	133·80	134·50	132·37	133·42	135·55
81	Tl	—	150·49	149·65	148·96	151·22	150·76
82	Pb	159·20	160·02	160·33	158·39	160·25	160·97
83	Bi	168·25	169·73	168·78	167·82	169·57	168·81
90	Th	—	250·86	—	247·81	251·26	250·00
92	U	279·11	278·73	—	276·28	279·33	276·66

The doublet relationship between the lines of the spectrum of a given element is exhibited in Fig. 70, where the L spectrum
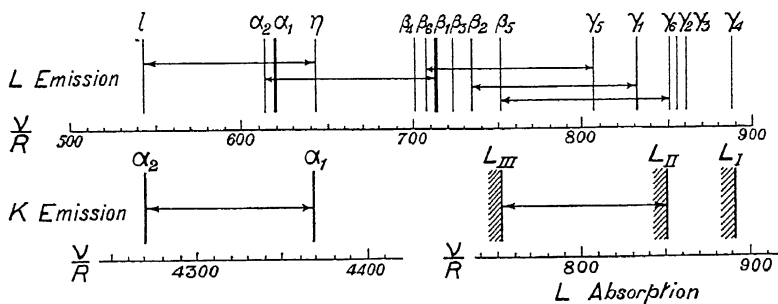
FIG. 70.

Doublet relationship as exemplified by X-ray spectrum of tungsten.

of tungsten is set out on a wave-number scale. The various pairs of lines which exhibit the doublet interval are indicated by the lines terminating in arrow heads, and the $K\alpha$ pair is shown on the same scale. For comparison the three L absorption edges are also given.

Turning from the relation between lines of one and the same element to consider how the difference of frequency

varies from element to element, we have the noteworthy experimental relation that the fourth root of $\Delta\nu$ varies linearly with Z to a first approximation.   Fig. 71 exhibits this relation-
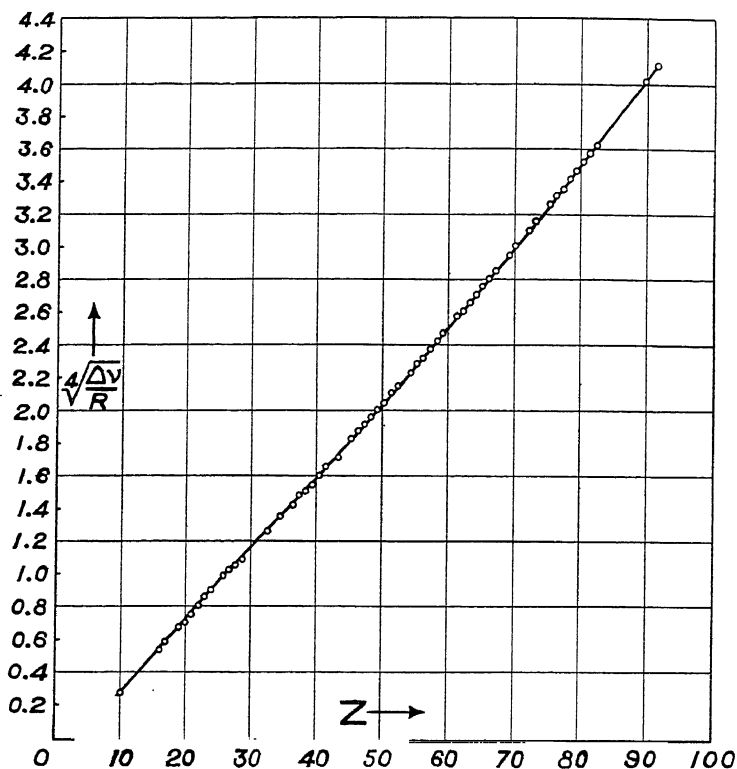
FIG. 71.

ship : for small values of Z, where the L doublet has not been measured, $\Delta\nu$ is taken for the K doublet.   The value for neon $(Z=10)$ is taken from a paper by Grotrian ; the justification for its inclusion will appear when the relationship between X-ray and optical spectra is discussed.   The curve in Fig. 71 is not quite a straight line, but the linear formula,

$$\frac{\Delta\nu}{R}=C\,(Z-s)^4 \ \dots\dots\dots\dots\dots\dots\dots\dots(3)$$

is a sufficiently close expression for a first discussion.   This formula will be developed from simple considerations, and the

significance of the small departure from linearity considered later.

It is clear that the existence of two different L levels, L_{II} and L_{III} (the third L level, L_{I}, will be discussed later), will suffice to explain both the L doublets just considered and the K doublet. If these two levels act as initial levels, the final level being the single K level, we have the $K\alpha$ doublet; if, on the other hand, a single higher $(M, N, O \ldots)$ energy level acts as the initial level, from which an electron can pass either to L_{II} or to L_{III} as final level, we have an L doublet, the various L doublets, all of equal wave-number separation corresponding to various initial levels. The equality of $\Delta\nu$ for K and L doublets is obvious on this scheme,* and it is also clear that the doublet separation must equal the interval between the L_{II} and L_{III} levels, as shown by the last column in the table.

We can clearly account for two different energy levels of total quantum number 2 by assuming orbits corresponding to azimuthal quantum numbers 1 and 2, and invoking the relativity effect to which the fine structure of the hydrogen and ionised helium lines has been attributed. Assuming a nuclear charge Z, and neglecting for the moment all the electrons but one, we have the possibility of a circular 2_2 orbit, and an elliptic 2_1 orbit, with which (as explained in Chapter X.) different energies are associated. Since the perihelion velocity, and consequently the relativity change of mass increases rapidly with increase of Z, the wave-number difference $\Delta\nu$ between circular and elliptic orbit increases rapidly with Z. This is quantitatively expressed by the theoretical formula

$$(\Delta\nu)_Z = (\Delta\nu)_H Z^4,$$

which follows at once from formula (21) of Chapter X.

This formula is based on the assumption of a hydrogen-like atom of nuclear charge Z, and expresses the relativity L doublet as an enormous magnification of the optical fine structure. Actually, there is every reason to suppose that the

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* Actually a slight difference between K and L doublets might be anticipated owing to the difference of excitation in the two cases. For the K doublet one K electron has been removed, which must slightly change the energy of the L levels, as compared with the case where both K electrons are present, and one L electron is removed. With atoms for which the L doublet has been measured $(Z \geq 39)$ the effect is too small to make itself evident.

inner electrons of the atom will produce, on any theory of distribution, a screening effect which causes the *effective* nuclear charge for an L transition to be diminished by some constant s. It is not necessary here to discuss the contribution of the various electrons to this screening constant. Assuming its existence, we have a relation of the form

$$\Delta\nu = \Delta_H(Z-s)^4,$$

which agrees with the approximate empirical relation already set down.

Sommerfeld has considered the relativity correction to a higher order of approximation. He obtains for an orbit of total quantum number n, azimuthal quantum number k, the expression :

$$\frac{\nu}{R} = \frac{Z^2}{n^2} + \frac{\alpha^2 Z^4}{n^4}\left(\frac{n}{k} - \frac{3}{4}\right) + \frac{\alpha^4 Z^6}{n^6}\left[\frac{1}{4}\left(\frac{n}{k}\right)^3 + \frac{3}{4}\left(\frac{n}{k}\right)^2 - \frac{3}{2}\frac{n}{k} + \frac{5}{8}\right]$$

$$+\text{terms in } \alpha^6 \text{ and higher powers, } \quad\dots\dots\dots\dots\dots(4)$$

which has already been discussed in Chapter X., and given as far as terms in α^4 in equation (20) of that chapter. α is $\dfrac{2\pi e^2}{hc}$

This refers to a hydrogen-like atom of nuclear charge Z : if we are considering the general atom we must allow for the screening effect of the electrons.   We should not be justified in introducing the same screening constant in the first term, which expresses the energy of a slowly moving electron, as tacitly assumed in the Moseley formula, and in the higher terms, which express the relativity modification, since for the latter practically only the perihelion part of the orbit is concerned, while for the former the whole orbit is in question.   It is found, in fact, that to express the small systematic departure of the frequencies from Moseley's law for higher atomic numbers, to which reference has already been made, quite different values of the constant must be taken in the term in Z^2 and in the higher terms, and that if this is done good agreement can be obtained.   We therefore take a formula of the type :

$$\frac{W}{Rh} = \frac{\nu}{R} = \frac{(Z-\sigma)^2}{n^2} + \frac{\alpha^2(Z-s)^4}{n^4}\left(\frac{n}{k} - \frac{3}{4}\right) + \frac{\alpha^4(Z-s)^6}{n^6}\left[\quad\quad\right] + \dots . \ (5)$$

Turning to our L doublet, for which $n=2$, and $k=1$ and 2 respectively for the two L levels, we have

$$\frac{\Delta \nu_L}{R} = \frac{a^2}{16}(Z-s_L)^4 \left[1 + \frac{5}{2} \cdot \frac{a^2}{4}(Z-s_L)^2 \right.$$

$$\left. + \text{terms in } (Z-s_L)^4 \text{ and higher powers} \right]. \quad \ldots(6)$$

which, if we neglect all but the first term, gives equation (3).* From this, if the empirically found values of $\Delta \nu_L$ for a given element be substituted, s_L for that element can be calculated. If this be done, it is found that s_L is remarkably constant for all elements for which accurate experimental data are available, namely, for those from niobium $(Z=41)$ to uranium $(Z=92)$, the most accurate value of s_L, obtained by Hjalmar, being 3·5100. The departures from this value seldom exceed two per cent. This remarkable result not only offers very strong evidence in favour of the relativistic origin of the doublets and the attribution of $n=2$ to the L system, but also confirms our belief that the K and L system is the same in number and arrangement of electrons for all the atoms in question, *i.e.* for all heavier atoms.

When the ring model was accepted attempts were made, without much success, to calculate theoretically the value of the shielding constant, σ. The ring model is now known to be so far from representing the facts that these early investigations have lost their significance. Apparently nothing has so far been done towards detailed calculation of the screening constant σ with the more complicated new model.

The L doublets so far considered are due to the existence of two L levels, the higher level concerned in the transition being the same for both lines of the doublet, but, as we shall see, when the complete level scheme is discussed, there are other L doublets which are due to transitions from two different M levels to the same final L level. The obvious thing to do is to assume three different M levels, corresponding to 3_1, 3_2 and 3_3 orbits respectively, which, with the two L levels, would give a triplet corresponding to the hydrogen fine structure

* The numerical value of a^2 is $5 \cdot 3 \times 10^{-5}$, so that $a^2 Z^2$ is small even for the higher values of Z.

triplet. (See page 236.) Investigation of the data, however, shows that this is not the case. Rather, there is a doublet corresponding to transitions from a 3_3 and from a 3_2 M orbit to a 2_2 L orbit, for which the screening constant works out empirically to be 13·0, and another doublet corresponding to transitions from a 3_2 and from a 3_1 orbit to a 2_1 orbit, for which the screening constant is very different, namely 8·5. This is remarkable as indicating, firstly, that the 3_2 orbit is, in some way, double, and secondly, that the selection rule, $\Delta k = \pm 1$, which forbids k to be the same for initial and final orbit, is violated for the k's which we have attributed to the orbits, although they give doublets whose $\Delta \nu$ changes with Z in good accord with experiment. This is a first introduction to one of the most puzzling features of the modern theory, namely the fact that while the relativity theory of n_k orbits gives a surprisingly good representation of some experimental facts it introduces grave difficulties in other respects. Further examples of this general enigma will soon appear.

Besides the relativity doublets just described, which appear both as emission lines and as absorption edges, there is another type of doublet in the X-ray spectrum, known as the screening doublet. These doublets were discovered by G. Hertz. They are not observed directly as pairs of emission lines, since the transition from a given level to both the levels, whose difference gives the shielding doublet, is forbidden by the selection principle which we shall elaborate when the complete level scheme is discussed. We know that experimentally three L absorption edges are found, L_I, L_{II}, L_{III}, and in considering the relativity doublet we have only invoked two, namely L_{II} and L_{III}, to which we have so far attributed 2_2 and 2_1 orbits respectively. The L screening doublet is constituted by the two absorption edges L_I and L_{II}, and its significance is first apparent when we consider how the separation varies with Z; the recurrence of the doublet in the emission spectrum of a single element, which is a striking feature of the relativity doublet, is denied us.

The difference of $\sqrt{\dfrac{\nu}{R}}$ for the L_I and L_{II} levels is approximately constant as we pass from element to element, exhibiting,

however, a slight increase for higher values of Z.   The general distinction between the two classes of doublet is well shown in Fig. 72, where $\sqrt{\dfrac{\nu}{R}}$ for the three levels is plotted against Z. The lines for L_{I} and L_{II}, the screening pair, are parallel, while
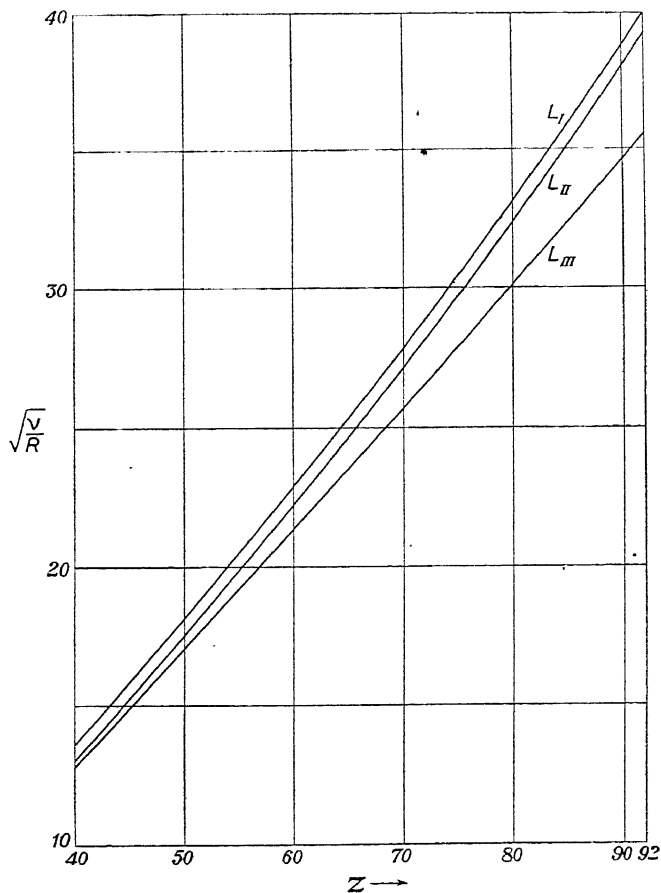
FIG. 72.

Moseley graphs for the three L levels, illustrating the distinction between screening doublet and relativity doublet.

the lines for L_{II} and L_{III}, the relativity pair, diverge in accordance with the laws discussed.   Assuming for simplicity the

Moseley formula for ν, *i.e.* the first term only of equation (5), we have

$$\frac{\nu}{R}=\frac{(Z-\sigma)^2}{n^2}, \quad \sqrt{\frac{\nu}{R}}=\frac{Z-\sigma}{n}. \quad \dots\dots\dots\dots\dots(7)$$

If σ is different for L_{I} and L_{II}*, then clearly

$$\Delta\sqrt{\frac{\nu}{R}}=\frac{\sigma_1-\sigma_2}{n},$$

and n being constant for all orbits of one (in this case the L) group, the wave-number difference of L_{I} and L_{II} is constant, and given by a difference of screening constant only between the levels. The reason for calling this doublet a screening doublet is now apparent.

From (7) it is clear that for the screening doublet

$$\Delta\nu=\frac{2R(Z-\sigma)}{n^2}$$

or the wave-number interval for this doublet increases linearly with the atomic number to the approximation in question. For the relativity doublet the interval increases, as we have seen, approximately with the fourth power of the atomic number. An elementary calculation shows that the *wave-length* interval for the screening doublet decreases as the cube of the atomic number, while for the relativity doublet it is approximately constant. It may be noted that the screening doublet was at one time called, in some quarters, the irregular doublet, but this nomenclature no longer has any significance.

The small systematic increase of the $\Delta\sqrt{\dfrac{\nu}{R}}$ value with Z for the screening doublet can be exactly accounted for by applying a relativity correction, with the *same* value of k in both cases, to the term values for L_{I} and L_{II}, the screening constant being different. Using the full formula (5) a reduced value for $\dfrac{\nu}{R}$, *i.e.* the value to be expected if there were no relativity effect, can be obtained; such reduced values obey, accurately, a

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* We have already seen in discussing the relativity doublets that an M level corresponding, on the n_k theory, to one value of k, had to be subdivided into two levels with different values of the screening constant.

Moseley type of formula (7).   With these reduced values $\Delta\sqrt{\dfrac{\nu}{R}}$ for the L screening doublet is constant within experimental error for all values of Z.   This relativity correction, which is a minor effect, must not be confused with the true relativity doublet, for which k is given a *different* value for each of the levels concerned.

The question of screening doublets in the M series is best postponed until the complete level scheme has been considered.

The Complete Level Scheme.   We have seen that there is strong direct experimental evidence for the existence of one K energy level, three different L energy levels, and five different M energy levels, these having been identified, both by absorption measurements * and by the measurements of the spectra of the secondary electronic emission carried out by H. Robinson.   Further, Robinson has demonstrated the existence of seven N levels.   In the case of the higher levels, O, P, which exist for the heavier elements, there is no direct evidence for the number of subdivisions.

With these facts, and the doublet relations as guides, the wave-numbers of the K, L and M and N emission lines have been very carefully studied with a view to their representation by a level scheme, on which all observed lines shall be represented as transitions.   It is found that the number of K, L, M and N levels just specified, together with five O levels and three P levels, will give all the observed X-ray frequencies of even the heaviest atoms.   That is, in contrast to the optical case, only twenty-four levels in all are required for the representation of the most complete X-ray spectrum : the comparatively small number is connected, of course, with the fact that for X-ray spectra only orbits actually occupied by electrons in the neutral atom come into question, whereas in the optical case we have an unlimited number of virtual orbits.   Similarly, for the lighter atoms, the higher levels are not invoked, the absence of lines involving such higher levels confirming the general evidence on this point.

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* So far the five M levels have only been observed with thorium and uranium by the absorption method, but Robinson detected all five as separate down as far as tungsten ($Z = 74$).

Fig. 73 shows the level scheme for the radon atom,* $(Z=86)$, slightly adapted from that given by Bohr and Coster. Radon completes the last full period in the periodic table. The figure also gives information as to the classes of levels occurring in the case of xenon and of krypton, which, respectively, complete the two previous periods, since the levels which disappear in passing from radon to xenon $(Z=54)$ are marked with a heavy vertical stroke near the left-hand side, while the further levels which disappear on passing to krypton $(Z=36)$ are marked with two heavy vertical strokes. Thus for the elements immediately preceding krypton no P and O levels, and only three N levels, are needed to express the observed lines. The spectrum of the lightest element for which lines have been observed by X-ray methods, *i.e.* sodium $(Z=11)$, consists of K lines only, and can be expressed without any N or higher levels, and with only one M level.

The various levels are indicated by Roman numerals as suffixes, the lowest level being denoted by the lowest suffix. This is now generally accepted, but is in contradiction to the older convention. (Cf. footnote, page 60.) The diagram is, of course, purely schematic, and not quantitative : all levels are represented as equally spaced, which is far from being the case if an energy scale be adopted. A strong confirmation of the scheme, as far as the L levels are concerned, is furnished by the experiments of D. L. Webster and of Hoyt on the different excitation potentials of the L series, to which reference has already been made. For platinum and tungsten the following lines were found to appear, in groups as shown, as the appropriate ionisation potential was reached.

	Platinum.								Tungsten.					
L_{III}	l	α_2	α_1	β_2	β_5	β_6			l	α_2	α_1	β_2	β_5	β_7
L_{II}			η	β_1	γ_1						η	β_1	γ_1	
L_{I}				γ_4							β_3	β_4	γ_4	

The lines forming the L relativity doublets can easily be picked out, since they are represented by transitions from a

* The inert gases are chosen for representation in these level diagrams since although measurements are not actually made with them, they represent on all theories the completion of a definite stage in the building up of the atoms. The scheme is, of course, derived from measurements in the neighbouring elements. It may be remembered that radon is now the official name for radium emanation, formerly known as niton.

common higher level to L_{II} and L_{III} respectively: the K doublet is represented by transitions from L_{II} and L'_{III} to K.
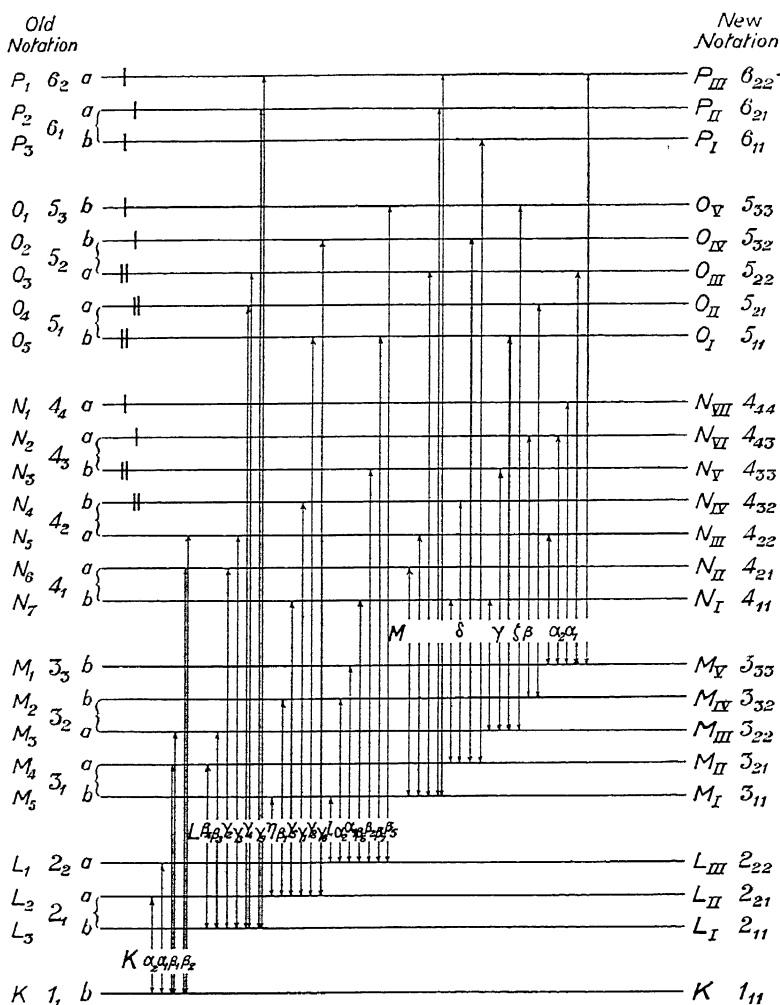
Fig. 73.
Complete level scheme for X-ray spectra.

The screening doublets are not represented by emission lines, since it will be seen that a level that is connected with L_{II} by a transition is never also connected to L_{I}. This leads us to the

consideration of the selection rules which apply to the X-ray levels.

It will be seen that to each level is affixed a number with two suffixes, such as 3_{32}. The main number is the principal quantum number, which is 1, 2, 3, 4 ... for the K, L, M, N ... levels, as in the simple diagram with circular orbits. Of the two suffixes the second, which we will denote in general by k_2, gives the value of k which has to be allotted to the levels concerned in order to give quantitatively the separation of the relativity doublet on the n_k orbit scheme which we have considered. Thus for L_{II} and L_{III} k_2 is 1 and 2 respectively. Lines corresponding to transitions from M_{II} and M_{III} to a common L level also form a relativity doublet, while transitions from M_{IV} and M_V to a common L level form another relativity doublet, as mentioned on page 392. On the n_k scheme k, which is now our k_2, had to be 1 for M_{II} and 2 for M_{III} ; 2 for M_{IV} and 3 for M_V, as represented in the diagram. The screening constant turned out to be very different in the two cases, which pointed, as we said, to a doubling of the level for which k_2 is 2. Such a doubling is represented, since both M_{III} and M_{IV} have $k_2 = 2$. It will be seen that, in general, in the scheme of Fig. 73, there are always for a given n, two levels corresponding to a given value of k_2, except for the highest level of the group.

We now turn to the first suffix, which we will call k_1. This number is always the same for both levels forming a relativity pair : thus for both L_{II} and L_{III} it is 2. For two levels forming a screening pair, however, k_2 is the same, but k_1 is different ; thus, k_1 is 1 for L_I, and k_1 is 2 for L_{II}, while k_2 is 2 for both L_1 and L_{II}. Differences of k_1 express, then, two levels which are the same, regarded as n_k levels, for relativity doublet purposes, but differ somehow in respect of the screening. For the moment this will be accepted as a direct interpretation of experimental results, and discussion of the theoretical significance, or lack of significance, of this new conception will be postponed, since it cannot be too strongly emphasised that, quite apart from any theory, the allotment of the two azimuthal quantum numbers, k_1 and k_2, is demanded by the facts, k_1 being constant for a relativity pair (by which we simply mean

a pair whose separation is governed by the relativity formula ; possibly a similar formula might be deducible without invoking relativity), and k_2 constant for a screening pair.

Inspection of Fig. 73 shows that we have the rule

$$n \gtrsim k_1 \gtrsim k_2.$$

Further, we have selection rules, first established by Wenzel, involving both k_1 and k_2. To k_1 applies the selection principle established for k in optical spectra, viz. $\Delta k_1 = \pm 1$; transitions for which k_1 decreases by 1 give much stronger lines than those for which k_1 increases by 1. For k_2 we have the rule $\Delta k_2 = \pm 1$ or 0 : thus transitions are allowed which leave k_2 unchanged, but these as well as those for which k_2 increases give weak lines compared to those for which k_2 decreases. This selection rule for k_2 is the same as that for j in the optical case.

Since k_1 must change by $+1$ or -1 a given level can only be associated in a quantum switch with two different levels of another group if for these two levels k_1 is the same, or differs by 2. In this way the selection rules express the fact that the screening doublet never appears as emission lines. The reason for the lack of exactness of the crude combination relations cited on page 371, as a preliminary to the elementary model, is also apparent.

The scheme of $n_{k_1 k_2}$ levels, with appropriate selection rules for k_1 and k_2 gives, then, an excellent representation of the observed regularities and describes all the levels needed to classify the X-ray spectra, while an n_k scheme is insufficient. When we turn to consider the theoretical significance of the $k_1 k_2$ classification, things are not so satisfactory.

The Screening Constants. The electrons of the atom are classed in groups, those of one group occupying orbits all distinguished by the same total quantum number. The number of electrons in each group is discussed at length in Chapter XIV.; there are, for instance, two in the K group, for which $n = 1$: eight in the L group, for which $n = 2$: eighteen in the completed M group, for which $n = 3$. We may suppose these orbits of a given total quantum number to be distinguished among themselves by differences of azimuthal quantum number k,

some of the electrons of a given group occupying orbits pertaining to one value of k, and others corresponding to the other value of k, k being always equal to or less than n, as in our general discussion of n_k optical orbits.   If such n_k orbits be accepted, it is clear that the paths of some electrons of one group, occupying orbits of high eccentricity, will penetrate within the orbits of electrons of a lower group (smaller n). We have to some extent the state of affairs considered when discussing optical orbits penetrating the core.   For a given n_k orbit we can consider the nuclear charge Z diminished to an effective value Z_e by the screening action of certain inner electrons.   The orbit will depart somewhat from a Keplerian ellipse owing to the fact that the whole of the screening electrons are not concentrated within a sphere whose radius is appreciably less than the perihelion distance, but extend so that the forces at the different parts of the orbit depart from the inverse square law, although when Z is large, and the complete orbit confined to the inner parts of the atom (n small) the extreme departures are small compared to those considered in the case of the optical orbits.   In the optical case of a neutral atom, the nuclear charge is screened down to 1 well outside the atom, but has an effective value several times this even a very short way inside the atom : in the case of orbits right in the interior of the atom the screening at both perihelion distance and aphelion distance will be fairly small compared to Z itself.   The departure of an n_k orbit of energy W, major axis (greatest linear dimension) $2a$, from a Keplerian form may be expressed by taking an effective quantum number n_e in place of n ; Z_e and n_e are then defined by the equations : *

$$W = Rh \frac{Z_e^{\,2}}{n_e^{\,2}}, \quad 2a = \frac{e^2}{Rh} \frac{n_e^{\,2}}{Z_e}.$$

By the arguments above, n_e is not very different from n. As far as the dependence of the energy of the orbit on Z is concerned, the departure of n_e from n can be approximately expressed by adjusting the screening constant.   If this be

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* For a Keplerian orbit about an unscreened nuclear charge Z,

$$W = Rh \frac{Z^2}{n^2}, \quad 2a = \frac{e^2}{Rh} \frac{n^2}{Z}.$$

done, W, the work required to remove the electron to infinity can be expressed in the form

$$W = Rh \frac{(Z - s_{nk})^2}{n^2},$$

where s_{nk} is a screening constant peculiar to a given n_k orbit. The total quantum number n being fixed, s_{nk} will vary markedly with k, since obviously both Z_e and n_e depend upon the eccentricity of the orbit.

So far we have only considered the effect of the electrons in the neighbourhood of nucleus and orbit on the strength of binding * of the electron. Electrons completely exterior to the orbit under consideration must, however, as Bohr pointed out, be taken into account, for when an inner electron is removed these electrons become more strongly bound, owing to the increase of effective nuclear charge. Another way of making clear the effect of outer electrons is to remember that they exert a repulsive effect on the special electron as it is being removed. This consequent diminution of W we can express by a second screening constant, which Bohr calls the outer screening constant, as distinct from s_{nk}, the inner screening constant ; by considering the number of electrons in the outer groups for a given Z he has shown that this outer screening constant depends upon Z and n, and has expressed it in the form $n^2 S_{Zn}$. The point of not including the n^2 in the S_{Zn} is that, if this separation be made, S_{Zn} as so defined is approximately equal to the number of groups for which $n > p$, where p is the value of n for the electron to which W pertains.

We then have

$$W = Rh \frac{(Z - s_{nk} - n^2 S_{Zn})^2}{n^2} . \quad \dots\dots\dots\dots\dots (8)$$

This treatment of the screening constant is of some importance for our discussion of electron groups in the next chapter.

The screening constant s_{nk} is a function of k, as is also the relativity correction, which we have not yet considered.

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* The strength of binding is a convenient phrase to denote the work required to remove the electron completely, *i.e.* W as used throughout the book.

Putting $s_{nk} + n^2 S_{Zn} = \sigma$, and taking the relativity correction into account, we have the expression already given in (5).

Any theory based on a straightforward consideration of n orbits can only give two L levels, three M levels, four N levels, and so on. Also, since both the relativity correction and the screening constant vary with k, between the two levels provided for the L group there will exist a difference of v whose variation with Z should exhibit a relativity effect added to a screening effect. Such a difference actually exists between L_{I} and L_{III}, as is clearly exhibited in Fig. 72, and similar differences are exhibited by M_{I} and M_{III}, and between M_{III} and M_{V}. For all the levels just named $k_1 = k_2$ in the $n_{k_1 k_2}$ classification which has been discussed. Bohr calls such levels normal levels, since they can be explained by n_k orbits for which $k = k_1 = k_2$. Levels for which $k_1 \neq k_2$ are abnormal: there is no place for them on a simple n_k scheme, but all experiment points to their existence.

The existence of these abnormal levels, which have their counterpart in optical spectra, is one of the problems of atomic structure for which no straightforward theoretical explanation has been found. Much important work is being carried out in the way of generalising the difficulty, and showing that it finds expression in many of the finer features of optical spectra, and many suggestive theories have been put forward, all of which, however, are forced to invoke new and non-mechanical principles for the interaction of the electron groups. For the moment, we will merely point out once more the functions of the two quantum numbers, k_1 and k_2, allotted to a level that on the simple orbital theory would have in their place but one quantum number k. Between each pair of normal levels, for which $k = k_1 = k_2$, is inserted another level, for which k_1 is equal to the k_2 of the higher normal level, and k_2 is equal to the k_1 of the lower normal level: thus between M_{III} (3_{22}) and M_{V} (3_{33}) is inserted M_{IV} (3_{32}). The abnormal level forms a screening doublet with the normal level with which it has k_1 in common, a relativity doublet with the normal level with which it has k_2 in common.

Connection between Optical and X-Ray Spectra. The longest X-ray wave-lengths measured by the ordinary crystal method

are about 12 A. (Ka for sodium, $\lambda = 11\cdot88$ A.; La for copper, $\lambda = 13\cdot3$ A.). The shortest optical wave-length measured by Lyman in a vacuum spectrograph was about 510 A. (515·7 A.); and there have been various optical measurements in the region of 350 A. by Lang, Simeon, and others. The closing of this gap between optical and X-ray spectra has been the subject of many interesting researches. Theoretically we should expect to trace a transition from X-ray to optical spectra. We distinguish X-ray spectra as consisting of lines due to an electron passing from one orbit of a class normally occupied to an orbit of another class normally occupied, while optical spectra are due to an electron passing from a virtual orbit to another virtual orbit, or to an orbit normally occupied, but belonging to the group and sub-group least firmly bound in the normal atom. Thus for the optical spectrum of sodium, the unexcited neutral atom of which has all possible orbits of its K and L groups fully occupied (by two and eight electrons respectively) and one electron in an orbit of the M group, the lines of the principal series are given by transitions from virtual orbits to the M orbit, freed during excitation: for the X-ray spectrum of any heavy atom, say tungsten, the M spectrum is given mainly by transitions from occupied N levels to an M level freed during excitation. In the optical spectrum of an atom of the lithium-neon period there are lines corresponding to transitions from virtual orbits to a normally occupied L orbit, the L group being incomplete for all the elements preceding neon: in the X-ray spectrum of heavy elements, lines of the L series are given by the passage of an electron from an occupied M or N or O orbit to an L orbit freed during excitation.

Now suppose that we trace a given line down through the spectra of the elements, starting with heavy ones and progressing towards the lighter ones, and, for definiteness, let it be an L line. So long as there are complete occupied groups outside the L groups we have two influences to consider: a primary one, the diminution of nuclear charge, which leads to a progressive diminution of $\sqrt{\dfrac{\nu}{R}}$, approximately according to Moseley's law; and a secondary influence due to the outer screening

constant, which changes as the outer groups are removed. This latter influence we consider in the next chapter : it is not important for our present purpose. Certain lines of the L spectrum will disappear : when the N group electrons have been removed, there will be no X-ray lines due to transitions from an N orbit, and as we evict different electrons of the M group, so that a given M level becomes wholly untenanted, the lines corresponding to that level will disappear. This is actually observed : the lines whose survival at any given stage is to be anticipated can be traced by considering Fig. 73. When, however, we have so far progressed in the direction of diminishing atomic number that there are no electrons left external to the L group (neon) the line which we have been considering must become an optical line. So far, however, there is no reason to expect the curve connecting $\sqrt{\dfrac{\nu}{R}}$ with Z to show any primary departures from Moseley's law, since we have only successively diminished the number of electrons in outer groups. As soon, however, as we begin to remove electrons from the L group itself, we are clearly producing large changes in the energy of the final orbit, since all the L levels are closely interconnected. It should therefore be possible still to trace the L line in the optical spectra of atoms from $Z = 9$ to $Z = 3$, but a noticeable change in the form of the curve is to be expected to set in when the L group is first attacked.

Attention was first called to the continuous transition from X-ray series to visible spectra by Kossel, who plotted $\sqrt{\dfrac{\nu}{R}}$ for the K, L and M lines of which measurements were then available against Z for the light elements. Clearly, as in all spectral questions, it is simpler to consider the behaviour of the terms than of the lines. The problem is, then, to measure the wave-lengths of lines in and near the gap already mentioned, to decide upon what transitions they represent, and hence, using the known values of ν for higher levels concerned, to deduce the value of ν for the lower levels of the lighter elements, and to examine how they compare with the values for the same

levels in heavier elements. Throughout we have to be guided by the level scheme, with its selection rules, and all the facts as to doublets and other regularities embodied in it. We shall also have occasionally to invoke information which has been won as to the number of electron orbits belonging to each level, *i.e.* the number of electrons for which n, k_1 and k_2 have given values in an atom. This is a matter more fully discussed in Chapter XIV.

The measurements of the wave-lengths of the lines in question—very long X-ray waves or very short ultra-violet waves, according as they are regarded—presents peculiar difficulties, not only because the rays are so easily absorbed, but also because the diffraction methods generally used are very difficult to apply. As regards the first point, Holweck has shown that a sheet of celluloid ·00027 mm. thick absorbs 97 per cent. of the radiation in the neighbourhood of 310 A., the region in which the absorption has its maximum, while the absorption per unit density of celluloid is relatively low compared to other substances. As regards the second point, the crystal method, as used for ordinary X-ray measurements of wave-length, breaks down for wave-lengths greater than 14 A.

By the use of special gratings, ruled with a very light touch, so as to leave a portion of the original surface functioning in the production of spectra, with about 5000 lines per cm., Millikan has been able to extend optical measurements down to 136 A (which corresponds to about 91 volts.) As regards the production of the radiations he has shown that at very low pressure (less than 10^{-4} mm. mercury) very high fields are needed to produce sparks even when the electrodes are close, and these sparks, when produced, are necessarily very energetic. Millikan terms them "hot sparks." He and his collaborator Bowen have worked with an electrode separation of from 2 mm. to ·1 mm., and have applied potential differences of several thousand volts with a condenser battery worked by a powerful induction coil. Since the spark can be operated at so low a pressure it can be built into a vacuum spectrograph, so that there are no windows and only a trace of residual gas between the source and the photographic plate: in this way the

difficulties which generally arise owing to the high absorption of all substances for the extreme ultra-violet are avoided.*

To deal with wave-lengths of the order just cited, and still shorter, special methods have been utilised. One of the most favoured, used, in various modifications, by Horton and his collaborators, McLennan and his collaborators, Kurth, Holtsmark, Hughes, and others, is to bombard the given element, in solid form, with electrons accelerated by a given voltage drop, and detect the excited radiation by its photoelectric effect on a metallic plate. A very high vacuum is maintained in the apparatus, so that the energy of the primary cathode stream exciting the radiation is accurately measurable by the voltage, and no solid diaphragm of any kind is inserted between anti-cathode and the detecting plate, since the rays in question are so soft that the diaphragm would have to be exceedingly thin to let them pass at all. The shielding of the plate from the charged corpuscles of both signs produced in the main discharge tube is one of the main difficulties, since the primary current is of the order 10^{-3} amps., while the current to be measured in the photoelectric part of the apparatus is 10^{-13} amps. or smaller, so that a relatively small diffusion of charges would completely upset the measurements. The shielding is effected in all the modifications of the apparatus by suitably charged gauzes, or condenser plates, or both, which remove the charges by a strong electric field. The principle of the measurement is to measure the photoelectric current, which, divided by the primary electric current, gives a measure of the efficacy of the radiation in releasing electrons. The primary voltage is gradually increased, and it is found that at certain voltages kinks or changes of curvature appear in the curve showing the connection between photoelectric current

* In view of the reports that helium has been " produced " by exploding metal wires by means of the sudden application of very high potentials, it may be noted here that Millikan and Bowen did not find a trace of any helium line of the ultra-violet series with any of their metal electrodes. The energy to which the tips of the electrodes are subjected during the passage of the hot spark is very much more concentrated than that prevailing in the exploded wires, so that there seems little doubt that the helium lines detected with the wires must be due to traces of helium present in the metal. This supposition is confirmed by the fact that Millikan and Bowen did once obtain helium lines with fresh electrodes, which disappeared after repeated discharges.

and voltage. These kinks are attributed to the sudden appearance of a new type of radiation, and the corresponding voltages are called critical potentials, in the sense in which the phrase has already been employed with regard to optical spectra.

The same method has been applied to gases by Foote and Mohler, who bombard the gas (which may be called a gaseous anti-cathode) with electrons from a hot wire, and measure the photoelectric current released from a grid by the radiations excited in the gas atoms. The gas pressure is, of course, very low in the vessel, and the hot wire is close to the accelerating grid, so that the electrons can acquire the full energy corresponding to the accelerating potential, while a strong field is used to prevent charges diffusing to the photoelectric surface. Richardson and Bazzoni have utilised a similar disposition.

Holweck has employed a different method, avoiding the difficulty of the diffusion of ions from one part of the apparatus to the other by using a diaphragm to divide the vessel in which the soft rays are produced from that in which their effect is measured. The source of radiation is a metal anode (molybdenum is used in the latest experiments) bombarded by electrons from a short glowing wire in the highest possible vacuum, the accelerating field being carefully measured. The rays so produced constitute a continuous spectrum, whose highest frequency corresponds to the accelerating potential : in order to make the results as definite as possible the radiation is filtered through very thin films of celluloid or other substance, so as to isolate the high frequency end of the spectrum. The radiation is detected by a gold-leaf electroscope, containing a gas at low pressure, the electroscope gas being separated from the highly exhausted space of the radiation vessel by the very thin celluloid window, prepared by a special technique. If the element is in gaseous form it is introduced into the electroscope and the ionisation current is measured : a discontinuity is observed when the critical potential of the gas is reached, on account of the increased absorption. If the element is in the solid form, *e.g.* aluminium, a thin foil is introduced between anode and electroscope, and the electroscope is filled with air at a pressure sufficient to absorb all the radiation. The absorption of the foil for the rays produced by different

potentials is measured : a discontinuity then corresponds to a critical potential of the metal.

A large number of measurements of critical potentials for elements of low atomic number have been carried out by highly skilled experimenters, using the photoelectric method in its various modifications, but the agreement between results obtained in different laboratories is not very satisfactory. A suprisingly large number of critical potentials are found in some cases : thus O. W. Richardson and Chalkin give fifteen critical potentials for iron, Rollefson gives eight, and C. H. Thomas gives twenty-three,* while Horton and his collaborators give six and Kurth five. There is fair, but not more than fair, agreement between two or more observers in the case of thirteen values, but the large number of values 'found, which are more or less evenly distributed over the range, renders this agreement less significant than it would be were there fewer determinations. For all the elements from chromium to zinc, inclusive, a large number of critical potentials have been detected ; for instance Thomas has found forty-seven for nickel, forty-eight for cobalt. Various reasons have been put forward to account for this profusion of potentials, such as that, while some of them correspond to the removal of an electron from given levels (such as M_I, say) to the periphery of the atom, others correspond to the removal of the electron from these levels to various virtual orbits, or, in other words, the hypothesis is that the various critical potentials should be capable of arrangement in groups corresponding to the fine structure of the various absorption edges. It is difficult to maintain this in view of the more or less uniform spacing of the potentials : if the hypothesis were correct it appears to the writer that the crystalline state of the metals, which must influence the virtual orbits, would have a marked influence on the determinations.† Another suggestion is that atoms which have already lost one or more electrons are concerned in some of the quantum jumps which lead to experimentally detected critical values. In any case it seems, at the present time, unjustified to pick out (as

* Exceeding 40 volts, and others below this value.

† This would, of course, account for the different values obtained by different observers. It might be worth while to investigate this point.

the writer at first was tempted to do) certain critical potentials which suit our purpose, and to call them ionisation potentials. In the consideration of the energy levels of the group titanium to zinc which follows, the critical potentials obtained by the photoelectric method are not taken into account.

The energy levels of the elements just specified can, however, be obtained without ambiguity, if not with great accuracy, in another way. We wish in particular to find values for M_I, $M_{II\ III}$, $M_{IV\ V}$;* although M lines have not been measured for the light elements in question this can be done, by considering combinations of known X-ray lines and absorption edges, using the results exhibited in Fig. 73. Thus it is clear from Fig. 73 that

$$M_{IV\ V} = L_{III} - L a_1,$$

and similar relations, involving only L or K series measurements, can be found for the other M levels. Values obtained by Stoner for the M levels, using among other results the measurements recently made by Thoraeus for the L series of light elements ($Z = 37$ to $Z = 24$) are included in Fig. 74.

Fig. 74 shows the transition of X-ray levels into optical levels. In this diagram are embodied energy values deduced from optical and X-ray measurements for the lighter atoms, including critical potential results where the interpretation is straightforward. The curves represent $\sqrt{\dfrac{\nu}{R}}$ for the terms corresponding to complete removal from the atom of an electron belonging to the level in question, plotted against Z. In the case of the X-ray terms many of the points represent direct measurements on absorption edges, and in the other cases the level scheme is so clear that there can be very little doubt that the numbers plotted are energy levels. Similarly in the case of the optical measurements the different resonance potentials have been in general fully worked out, and it is practically certain ·that the values selected are ionisation potentials, corresponding to the complete removal of an outer electron (a K electron for $Z = 1$, 2 ; an L electron for $Z = 3$ to $Z = 10$; an

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* Within the region considered M_{II} is experimentally indistinguishable from M_{III}, and M_{IV} from M_V, and the common $M_{II}M_{III}$ level is written $M_{II\ III}$ for short.
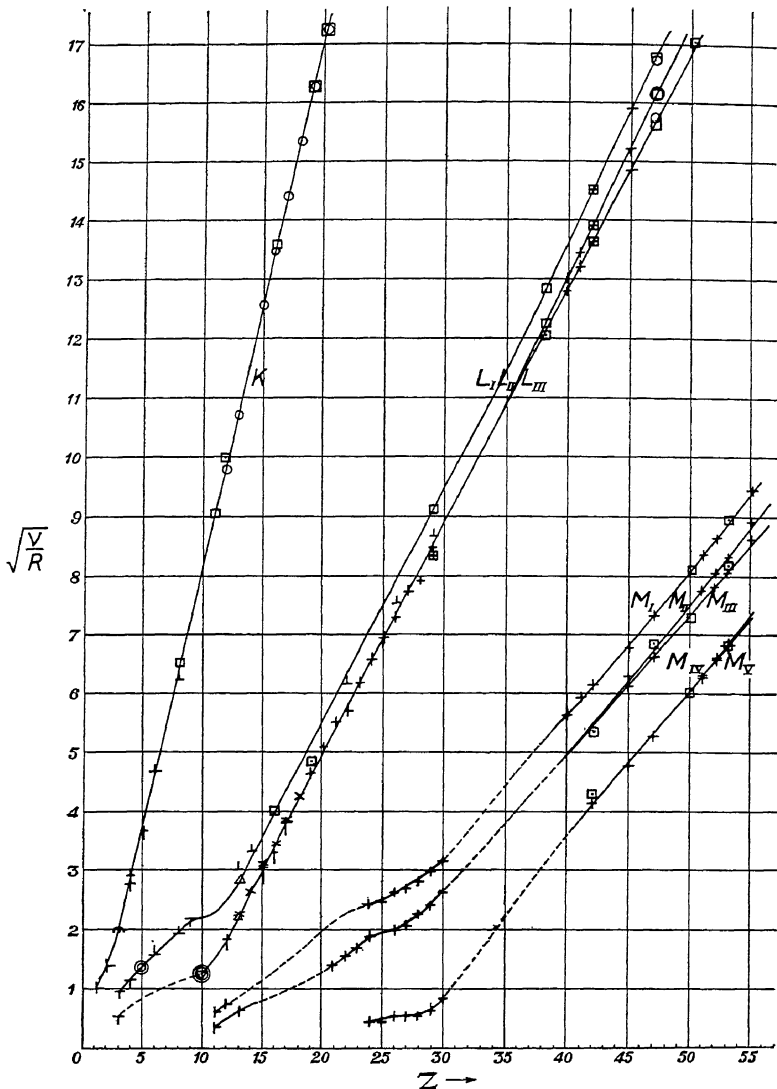
FIG. 74.
Transition of X-ray into optical spectral terms.
⊙ X-ray absorption edges.   ⊥ Kurth.   ＋ X-Ray levels.
† Foot and Mohler.   ⊢ Ionisation potentials and spectral
terms.   ✕ Holweck.   ⊡ Robinson's corpuscular spectra.
△ Horton.   ⊤ McLennan and collaborators.   ◎ Average
of several close determinations.

M electron for $Z=11$ to $Z=18$). In the case of the elements between $Z=21$ and $Z=30$, on account of the difficulties of selection and interpretation already mentioned, the photo-electric measurements in the neighbourhood of the M levels have been omitted in favour of the values deduced by Stoner.

It will be seen that the X-ray values of the terms run directly into the optical values, but that at the point where the optical values begin, *i.e.* where the electron group to which the level question belongs first becomes incomplete, there is a departure from the approximately straight line form. With the K level this point is at $Z=2$, and the change of form is comparatively slight ; with the L levels this point is at $Z=10$, and the L_I line shows a very pronounced change here. For $L_\mathrm{II\ III}$ there are not sufficient points on the optical branch to establish the break with certainty, but the course of the curve is regular down to $Z=10$. For M_I and $M_\mathrm{II\ III}$ there is a departure from the approximately straight line form which sets in, not very sharply, in the neighbourhood of $Z=28$: for $M_\mathrm{IV\ V}$ the course of the curve changes more abruptly, indicating a departure precisely at $Z=28$ from the regularity which exists with all heavier atoms. Now, as we shall see in Chapter XIV., the M_V grouplet of electrons is completed at $Z=28$, and the imperfection which begins at $Z=27$ would be expected to affect the M_V energy level more than the other energy levels. In general we may say that the transition from the X-ray to optical spectra, exemplified by the levels considered, furnishes good confirmation of the general features of spectral theory.

For comparison Fig. 75, which is taken from the first edition of this book, and represents $\sqrt{\dfrac{\nu}{R}}$ for the $K\alpha$ and the $L\alpha$ *line*, is retained.

The correspondence between optical and X-ray spectra has been further emphasised by Landé, who has shown that similar theoretical difficulties arise in both cases. On Bohr's theory of n_k orbits both lines of an optical doublet are given by orbits with the same value of k. Suppose, however, that we neglect this for the moment, and consider how a relativity doublet might arise in the optical case between orbits of different k, but the same n. Consider two orbits of azimuthal

quantum number k and $k-1$, which lie for the greater part outside the core, but penetrate for a comparatively short time within the curve. We have already discussed such orbits in Chapter XI, where we have spoken of the orbit as consist-
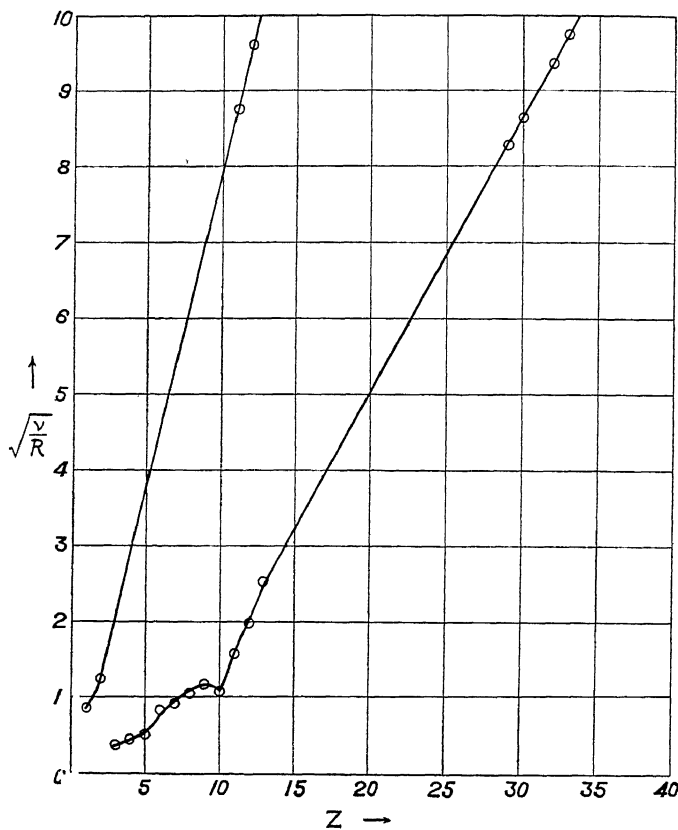
FIG. 75.

Transition of X-ray lines into optical spectral lines.

ing of an inner and an outer loop. The inner loop alone is exposed to a large effective nuclear charge, so that the velocity of the electron in the loop is higher than the perihelion velocity corresponding to the outer Keplerian loop, and practically the whole relativity effect is due to the inner loop.

For simplicity we can regard the inner loop as being governed by an inner effective nuclear charge Z_i, and the outer loop by an outer effective nuclear charge Z_o, which is 1 for a neutral atom. There is, strictly speaking, some transition value of Z, but, if we regard the inner loop as comparatively short, Z_o will govern to a first approximation the time of describing the orbit, while Z_i will govern the relativity effect, the high perihelion velocity playing its part in both cases.

If t_i and t_o are the periodic times for Keplerian orbits of quantum numbers n_i and n_o, semi-major axes a_i and a_o, described in a Coulombian field produced by the same central charge, then

$$\frac{t_i}{t_o} = \left(\frac{a_i}{a_o}\right)^{\frac{3}{2}} = \frac{n_i^3}{n_o^3},$$

since $n^2 \propto a$. Considering the n_i orbit to be described entirely in a Coulombian field produced by a central charge Z_i, and the other orbit in a field produced by central charge Z_o, we have

$$\frac{t_i}{t_o} = \frac{n_i^3 Z_o^2}{n_o^3 Z_i^2}.$$

The actual orbit, of course, comprises an outer loop consisting of the nearly complete Keplerian ellipse corresponding to Z_o and an inner loop consisting of the major part of the ellipse corresponding to Z_i. If we regard the relativity effect as due to a perturbing inverse cube field of force, then the effect of the perturbation on the energy is the time mean of the disturbing potential (cf. Chapter X). Hence it is clear that, for the case of the actual orbit, we can calculate the relativity effect for the Z_i orbit, in which alone it is considerable, and then multiply it by t_i/t_o to get the time average which we require, t_o being approximately the time of description of the whole actual orbit.

To a first order the relativity interval between two orbits of azimuthal quantum number k and $k-1$, and total quantum number n in a Coulombian field due to central charge Z_i is given by

$$\Delta \nu_i = \frac{R a^2 Z_i^4}{n_i^3 k (k-1)}$$

as follows at once from equation (20), Chapter X.

Hence, for the penetrating orbits considered,

$$\Delta \nu = \frac{t_i}{t_o} \Delta \nu_i = \frac{n_i^3 Z_o^2 R a^2 Z_i^4}{n_o^3 Z_i^2 n_i^3 k(k-1)}$$

$$= \frac{R a^2 Z_o^2 Z_i^2}{n_o^3 k(k-1)}, \quad \dots\dots\dots\dots\dots\dots (9)$$

n_o is, by the way in which it has been chosen, the effective quantum number of the optical orbit, so that

$$\nu = \frac{R Z_o^2}{n_o^2}.$$

Hence (9) can be written

$$\Delta \nu = \frac{\nu a^2 Z_i^2}{n_o k(k-1)} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (10)$$

or
$$Z_i = \left\{ \frac{\Delta \nu \cdot n_o^3 k(k-1)}{R a^2 Z_o^2} \right\}^{\frac{1}{2}} = \left\{ \frac{\Delta \nu \cdot n_o k(k-1)}{\nu a^2} \right\}^{\frac{1}{2}} . \quad \dots\dots (10a)$$

If, then, the optical doublets can be represented on the basis of the relativity correction, azimuthal quantum numbers k, k', differing by 1, being attributed respectively to two orbits belonging to the same sequence (which is in direct contradiction to Bohr's classification previously discussed), we can either put in values of Z_i and Z_o, k, k', and n_o, and calculate $\Delta \nu$, and then compare with observation, or we can use the observed value of $\Delta \nu$ to calculate one of the above quantities. Z_o is known, being 1 for the neutral atom, 2 for the singly ionised atom, and so on. For the L doublets in the X-ray spectrum $k=1$, $k'=2$, and it seems natural to try these values for the optical doublets. n_o is determined by the (mean) value of ν for the doublet in question. Perhaps the easiest method of exhibiting the regularity which is then obtained is to plot Z_i, the effective quantum number for the inner loop, against Z, using formula (10a). The result is shown in Fig. 76 ; the crosses refer to ionised atoms $(Z_o = 2)$, and the dots to neutral atoms $(Z_o = 1)$. Each point is the average of the values of Z_i calculated from different values of $\Delta \nu$ belonging to the same series, but different values of ν. It will be seen that there is a linear relation, showing that

$$Z_i = Z - \sigma.$$

The screening constant is about 4 for most of the elements, but there are indications that it is less, viz. about 2, for the lightest elements. It will be remembered that the screening constant for the L relativity doublet is 3·5, so that the optical results agree well with the assumption that the inner loops of
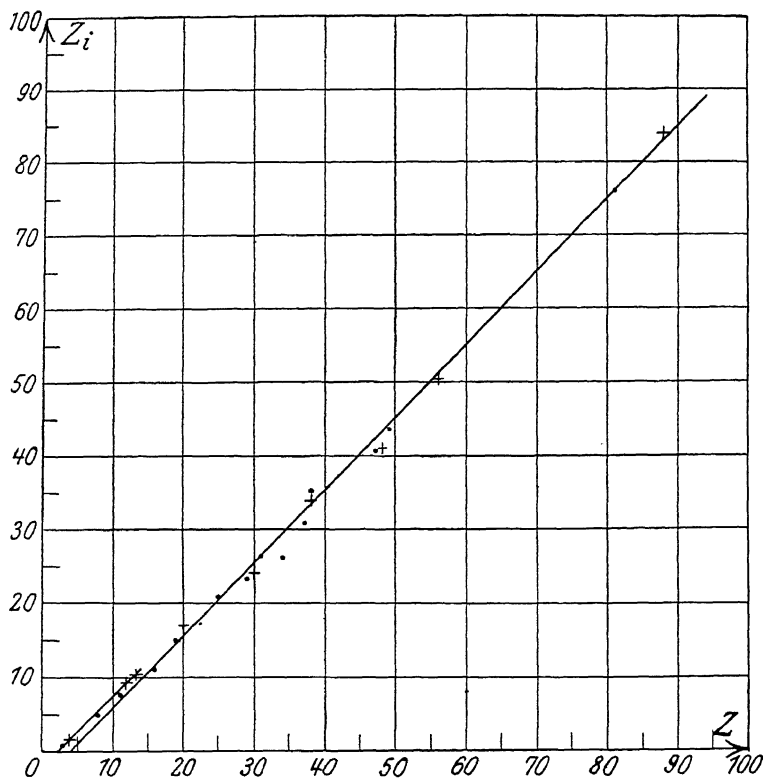
FIG. 76.

The inner effective nuclear charge Z_i for optical doublets, treated as relativity doublets.

the two orbits practically coincide with the orbits of L_{II} and L_{III} electrons. It is only to be expected that there will be somewhat greater divergencies from the formula deduced in the case of the optical doublets than in the case of the X-ray doublets, since the assumptions made in treating a penetrating orbit are clearly rough approximations. For the very lightest

elements the shielding constant may well be somewhat smaller than for the heavier elements, since the L shell is incomplete for them.

The agreement between experiment and the relativity theory of doublet origin is striking when the number of facts expressed in formula (9) is considered. The proportionality of $\Delta\nu$ to Z_o^2 and to Z_i^2 is confirmed respectively by the agreement between values deduced from the doublets of arc and spark spectra, and by the general linearity of the relation expressed in Fig. 76, which covers a range from $Z=3$, $\Delta\nu=\cdot36$, to $Z=88$, $\Delta\nu=4658\cdot6$. The proportionality of $\Delta\nu$ to Z_i^2 has long been known, being expressed by the empirical rule of Kayser and Runge, which states that in elements of the same column in the periodic table the wave-number separations are roughly proportional to the squares of the atomic weights (atomic numbers). For such homologous elements (Na, K, Rb, Cs) n_o does not vary much from one to the other for a given term, and the other factors entering into the expression for $\Delta\nu$ are constant. For the heavier elements Z_i differs from Z by a relatively small constant only, so that for these equation (9) embodies Kayser and Runge's rule. When Z is small the screening constant becomes of prime importance, which accounts for the fact that the observed value of $\Delta\nu$ for lithium is less than that given by the rule. But, above all, the absolute value of the doublet interval is expressed by (9).

The relativity interval also applies to triplets, if for $\Delta\nu$ be taken the wave-number interval between the extreme terms $^3P_0$ and $^3P_2$.

This method of accounting for the optical doublet allows us to draw a very close analogy between the terms used to describe a doublet system and to describe the X-ray spectrum. In both cases we have to use three quantum numbers, which we have called n, k, j in the optical case, n, k_1, k_2 in the X-ray case. The selection rules are the same in both cases,

$$\Delta k = \Delta k_1 = \pm 1, \quad \Delta j = \Delta k_2 = 0 \text{ or } \pm 1.$$

The analogy between optical and X-ray terms can be further expressed by the following scheme. The n of the optical terms is that of the Bohr notation, the principal quantum number of

the first term of the principal sequence being 2 for lithium, 3 for sodium, 4 for potassium, and so on. This makes the correspondence very close.

X-ray term - · -	K	L_I	L_{II}	L_{II}	M_I	M_{II}	M_{III}	M_{IV}	M_V
$n_{k_1k_2}$, n_{kj} -	1_{11}	2_{11}	2_{21}	2_{22}	3_{11}	3_{21}	3_{22}	3_{32}	3_{33}
Optical doublet term -	1^2S_1	2^2S_1	2^2P_1	2^2P_2	3^2S_1	3^2P_1	3^2P_2	3^2D_2	3^2D_3

The applicability of the conception of both screening doublets and relativity doublets to optical spectra has been strikingly illustrated by the work of Millikan, and of Millikan and Bowen, on the very short ultra-violet. Millikan and Bowen have investigated the hot spark spectra of some twenty lighter elements, the heaviest being copper, and obtained a large number of new lines. These lines they attribute to atoms in various stages of ionisation. Neutral atoms of elements of the period lithium to fluorine, inclusive, consist of a completed K group of two electrons, which we may call the helium structure, together with one electron of the L group in the case of lithium, two electrons of the L group in the case of beryllium, and so on. Similarly neutral atoms of the period sodium to chlorine consist of a completed K and a completed L group, constituting the neon structure, together with 1, 2, 3 ... M electrons as we pass up the period in the direction of increasing Z. The inert gas structure possesses a peculiar stability, and is hard to break up, but the existence of Al_{III} and of Si_{IV}, demonstrated by Paschen and by Fowler respectively, shows that all the outer electrons may be removed by a spark discharge, leaving in both cases a structure of neon form with a single loosely attached optical electron. Such atoms reduced to the inert gas form by the removal of all outer electrons are called by Millikan " stripped " atoms, and evidence of stripped atoms, to produce which as many as seven electrons have been removed (Cl_{VII}), has been deduced by him from the new lines.

To illustrate the work of Millikan and Bowen we may consider the elements of the first period of eight. With boron to nitrogen inclusive, they have obtained new doublets, while doublets due to Li_I and Be_{II} were already known. The new

doublets are attributed to B_{III}, C_{IV} and N_V respectively[*] and their wave-number separation for the doublet in each system is given in the following table :

	Li_I	Be_{II}	B_{III}	C_{IV}	N_V
$\Delta\nu$ - - -	·338 cm.$^{-1}$	6·61	34·4	107·4	259·1
$(\Delta\nu/·365)^{\frac{1}{4}}$ - -	·981	2·063	3·116	4·142	5·162
s_L - - -	2·02	1·94	1·88	1·86	1·84

The value of s_L given in the last row is found by applying the relativity formula (6), in its approximate form,

$$\Delta\nu_L = \frac{a^2 R}{16}(Z - s_L)^4.$$

Since the orbits do not penetrate within the K group, this formula is appropriate. It will be seen that, considering the large range of $\Delta\nu$, agreement is quite good : s^L is to a first approximation constant, with value 2, which indicates that in all the cases considered the atomic core does, in fact, consist of the nucleus with two closely associated electrons, the K group. The small progressive decrease of s is easily explicable, since the optical electron is, relatively to the K ring, more remote for a small nuclear charge than for a large one.[†] The screening is therefore more complete for the earlier elements than the later ones. The fact that the screening constant is slightly greater than 2 for lithium has no significance, since for this element the doublet separation is not measured with sufficient accuracy to render the last figure reliable.

Millikan and Bowen have applied the same formula to doublets obtained with the elements sodium to sulphur, attributable to stripped atoms of sodium-like structure, $i.e.$ all consisting of a completed K and L group, and one external electron. In this case, however, the orbits concerned are probably penetrating orbits, which pass within the L group,

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[*] Doublets occur with $neutral$ atoms of Columns I, III, V ... only. The displacement rule of Kossel and Sommerfeld states, in effect, that the nature of the system is governed by the number of electrons in the incomplete groups, so that stripped atoms ($i.e.$ one-valence-electron atoms) should all give doublets. (See p. 435.)

[†] Approximately the radius of the circular K orbits decreases as $\frac{1}{Z}$, while the perihelion distance of the optical orbits decreases as $\frac{1}{Z-2}$.

and in the present writer's opinion Landé's formula should be applied instead. If this be done the following screening constants are obtained :

Na_I	Mg_{II}	Al_{III}	Si_{IV}	P_V	S_{VI}
3·49	2·44	1·98	1·96	1·92	1·78

which agree well with the general run obtained with the lithium period. In the case of Na_I and Mg_{II} the electrons of the L group play little part in the shielding, the effective part of the orbit being close to the K group, while in the case of S_{VI} the effective part is, apparently, so near to the K group that the two electrons do not exercise their full screening effect.

By extending the method it has been possible to attribute various lines to atoms not completely stripped, but having two valence electrons (P_{IV}, S_V and Cl_{VI}) and three valence electrons (P_{III}, S_{IV}, Cl_V). By the Kossel-Sommerfeld displacement rule the former all give a triplet system, the latter a doublet system. In the case of the triplet system the extreme lines are taken as constituting the relativity doublet, as indicated by Landé, and it has, in fact, been shown that this leads to regular results. Another very interesting feature of Millikan's work is the establishment of screening doublets, which, from the table on p. 417, we should expect between a 2^2S and a 2^2P_1 term, corresponding to L_I and L_{II} in the case of the lithium group, and between 3^2S and 3^2P_1 and between 3^2P_2 and 3^2D_2 in the case of the sodium group. Such screening doublets have actually been traced for stripped atoms. All the doublet laws discovered with X-ray spectra can, then, be traced in optical spectra.

The detection of the higher stages of ionisation has allowed us to compare atoms of different nuclear charge, but similar electronic structure (same number of electrons, and same grouping). This makes it easier to trace regularities than in the case where different nuclear charge is accompanied by modifications of electronic structure, as when a sequence of neutral atoms is compared.

The realisation that both doublets exhibiting the relativity interval, and others exhibiting the screening interval, can be detected in optical as well as X-ray spectra, and the close analogy between X-ray and optical levels as specified by

quantum numbers, constitutes an important advance. It does not solve the fundamental difficulty of explaining how both kinds of doublets can exist separately, but it shows that the difficulty is fundamental, and not of the limited significance which might at first appear.

On the Bohr theory of n_k orbits we should have levels exhibiting an interval which is the sum of a screening and a relativity effect : such are the L_{I}, L_{III} levels, the M_{I}, M_{III}, M_{V} levels, and, in general, all levels for which, in the $n_{k_1 k_2}$ notation used, $k_1 = k_2$. These are what Bohr has called the normal levels, and they could be expressed by n_k orbits in which $k = k_1 = k_2$. In the optical case we should then have nothing but sequences of singlet terms, as follows not only from the considerations developed in Chapter XI. but also from the table on p. 417, which shows that the optical levels corresponding to normal X-ray levels comprise only one term each of the doublet P, D ... terms. The introduction of a second subordinate quantum number is needed to describe the existence of abnormal X-ray levels, and of doublet (in general multiplet) optical terms. The quantisation of the inclination of the plane of the electron orbit with respect to the axis of moment of momentum of the core, which may be referred to as the inclination hypothesis, has been suggested as a means of introducing this quantum number : it is discussed in Chapter XI., and further in Chapter XV. The trouble is that if the inclination hypothesis is used to account for the $L_{\mathrm{II}} L_{\mathrm{III}}$ doublet and the optical doublet, the same azimuthal quantum number being attributed to both levels concerned, there seems no reason why the relativity formula should be applicable, as it is. On the other hand, this attribution of azimuthal quantum numbers is satisfactory as far as the selection rules are concerned : it makes k_1 the azimuthal quantum number in the X-ray case, for which the rule $\Delta k_1 = \pm 1$ holds, and gives the same value of k to both terms of a doublet, as required by the optical sequence laws. If, on the other hand, we attribute the interval between L_{II} and L_{III}, and other relativity·pairs, and also the optical doublet interval, to a relativity effect, we must attribute different values of azimuthal quantum number to the two levels, which would make k_2 the azimuthal

quantum number in the X-ray case. This violates the appropriate selection rule, since empirically $\Delta k_2 = 0$ or ± 1 : in the optical case this attribution involves the abandonment of the scheme by which $k = 1, 2, 3, 4 \ldots$ respectively for the $S, P, D, F \ldots$ sequences.

It has been suggested that a way out is to abandon the relativity explanation of the " relativity " doublet, and to substitute for it no explanation. This, of course, is true, just as another way is to abandon the selection rules, and the attribution of a single k to each sequence of optical terms. Either expedient involves the renunciation of principles which have ordered successfully a large body of information, and the substitution of nothing in their place. The subject is further discussed in Chapter XV., but so far no generally satisfactory way out has been found.

As a final point of resemblance between X-ray and optical spectra, it may be mentioned that " spark " lines, so-called by analogy from the optical spectra, have been found in the X-ray spectrum, that is, lines which are excited by the removal of more than one electron from the atom. Wenzel showed that certain weak lines which accompany Ka_1 on the side of greater frequency—*i.e.* the pairs of lines a_3, a_4, and a_5, a_6, to which reference was made in describing the K series—can be explained by supposing that both electrons are expelled from the K group during excitation. These electrons are then replaced from the L group one by one : the first transition, which leaves the L group one electron short, gives a_4, and the second, which leaves the L group two electrons short,* gives a_3. It appears that, in addition to both K electrons, one L electron may be removed ; the subsequent transitions give rise to a_5 and a_6. These a_3, a_4, a_5, a_6 lines have been measured, by Hjalmar, for three elements only (magnesium, aluminium, silicon) : the experimental results available fall in with Wenzel's theory. Certain weak lines accompanying $K\beta$ and a few lines found in the L series, are also capable of explanation on the basis of multiple excitation.

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* In this transition a single electron passing from the L group completes the K group, as it does in the a_1 switch, but in the latter the L group is left only one electron short, which accounts for the difference between a_3 and a_1.

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CHAPTER XIV

THE PERIODIC SYSTEM AND THE THEORY OF QUANTUM ORBITS

Introductory. One great object of any scheme of atomic structure must be to offer some account of the regularities expressed in the periodic table, that is, of the recurring features which physical and chemical properties exhibit as we pass the atoms in review before us in the order of their atomic numbers. Among the regularities discussed in pre-quantum days which retain their great significance we may mention the valency properties and general facts of chemical combination ; the Lothar-Meyer curve of atomic volumes ; and such general physical properties as the boiling-point. Further, we have to consider paramagnetism, the formation of coloured salts, and other properties peculiar to restricted regions of the periodic scheme. Particular attention, however, must be paid to the quantitative relationships afforded by optical and X-ray spectra, which have proved so significant for Bohr's theory.

There will be occasion to make frequent reference to the periodic table, a modern form of which is given on the next page. To each element is attached its atomic number and atomic weight.* Each period is ended by one of the inert gases, and there is abundant evidence to show that these gases have an electronic structure of peculiar stability, represented by the completion of certain electronic sub-groups, so

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* Certain elements still rejoice in two names, which are both in common use. These are : beryllium = glucinum, columbium = niobium, lutecium = cassiopeium, niton = radon. In the last-mentioned case the name radon has now been made official, but in the other cases choice is free. The writer has no particular preferences, and it is likely that he has in different places used different names for the same element. There seemed no reason to be at pains to avoid this, since the student will meet with both names in the literature.

PERIODIC CLASSIFICATION OF THE ELEMENTS.

	I	II	III	IV	V	VI	VII	VIIIa	VIIIb	VIIIc	O
1	1 H 1·008										2 He 4·00
2	3 Li 6·94	4 Be 9·02	5 B 10·82	6 C 12·00	7 N 14·01	8 O 16·00	9 F 19·0				10 Ne 20·2
3	11 Na 23·00	12 Mg 24·32	13 Al 26·96	14 Si 28·06	15 P 31·02	16 S 32·06	17 Cl 35·46				18 A 39·88
4	19 K 39·10	20 Ca 40·07	21 Sc 45·1	22 Ti 48·1	23 V 51·0	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84	27 Co 58·97	28 Ni 58·68	
	29 Cu 63·57	30 Zn 65·38	31 Ga 69·72	32 Ge 72·8	33 As 74·96	34 Se 79·2	35 Br 79·92				36 Kr 82·92
5	37 Rb 85·44	38 Sr 87·63	39 Y 88·9	40 Zr 91·25	41 Nb 93·1	42 Mo 96·0	43 Ma	44 Ru 101·7	45 Rh 102·9	46 Pd 106·7	
	47 Ag 107·88	48 Cd 112·40	49 In 114·8	50 Sn 118·7	51 Sb 121·77	52 Te 127·5	53 I 126·92				54 Xe 130·2
6	55 Cs 132·81	56 Ba 137·37	RARE EARTHS	72 Hf 178·6	73 Ta 181·5	74 W 184·0	75 Re	76 Os 190·9	77 Ir 193·1	78 Pt 195·2	
	79 Au 197·2	80 Hg 200·6	81 Tl 204·4	82 Pb 207·20	83 Bi 209·0	84 Po (210·0)	85 —				86 Rn (222·0)
7	87 —	88 Ra 226·0	89 Ac (226)	90 Th 232·15	91 Pa (230)	92 U 238·2					

RARE EARTHS.

57 La 139·0	58 Ce 140·25	59 Pr 140·9	60 Nd 144·3	61 Il	62 Sm 150·4	63 Eu 152·0	64 Gd 157·3
65 Tb 159·2	66 Dy 162·5	67 Ho 163·5	68 Er 167·7	69 Tm 168·5	70 Yb 173·5	71 Lu 175·0	

that in the succeeding elements, the alkali metals, the outermost electron belonging to the neutral atom is the first of a new group. The lack of all chemical activity which gives the inert gases their name ; the complexity of their spectra, especially striking in comparison to the simplicity of the spectra of their immediate successors, the alkali metals ; their high ionisation potentials, and other properties to be discussed in due course, all go to indicate that with these elements an outer electronic sub-group is concluded.

The number of the period is indicated in the extreme left-hand column. The first period consists of the two elements hydrogen and helium : the second period consists of the next eight elements, ending with neon : the third period likewise consists of eight elements, ending with argon. After this come two periods of eighteen elements, ending respectively with krypton and xenon. With these periods there are in each case three transition elements closely resembling one another in chemical behaviour, placed together in Column VIII, which is subdivided into Columns VIIIa, VIIIb, VIIIc.* Further, for each period there are two elements in each column. The two elements of the one period in the same column resemble one another in valency and in certain general chemical properties : they also exhibit analogies with the elements of the two short periods in the same column, which are more marked for the one element than the other. Elements showing close resemblance are placed vertically beneath one another in the columns, in which some elements will be seen to be displaced to the left, others to the right. Thus all the alkali metals are very like one another, and are placed on the left-hand side of Column I : the alkaline earths are also very similar among themselves, and are placed on the left-hand side of Column II. The strong analogues, zinc, cadmium and mercury, all occur in Column II : they are displaced to the right-hand side of the column, since they do not resemble the alkaline earths so

* Although the chemists place all three elements in an undivided Column VIII, on account of their similarity of chemical properties, spectroscopic evidence gives three distinct columns here (see table on page 435). In course of time we shall probably find Column VIII and O replaced by Columns VIII, IX, X and XI, but for the present, to avoid shocking the susceptibilities of the chemists, we will content ourselves with the above notation.

closely as they do one another. In Column IV titanium, zirconium, and the newly-discovered element hafnium are to one side, germanium, tin and lead to the other, but the Column IV elements of the short periods, carbon and silicon, are placed in the middle, to indicate that they resemble one another more closely than they do the quadrivalent element of either the titanium or germanium character. In one and the same period the two elements in one column always occupy opposite sides.

The sixth period comprises thirty-two elements, and resembles the periods of eighteen, except that in place of the two trivalent elements it has a whole group of trivalent elements, the rare earths, which are placed together in Column III. The seventh period is incomplete.

Corresponding elements of the two short periods resemble one another markedly. In the two long periods of eighteen, elements at the beginning and end of the period correspond particularly closely as regards chemical properties to elements of the shorter periods. The eight elements from copper to krypton behave similarly to corresponding elements of the short period, the analogies becoming more and more marked as we approach the inert gases at the end of the period.*

Turning to the beginning of the third period, potassium and calcium are very close homologues of sodium and magnesium respectively : after calcium the correspondence, though it can still be definitely traced, becomes less and less marked until we come to the three transition elements which have no fellows in the short period. Similar considerations apply to the other long periods. Bohr exhibits these facts by means of the scheme shown in Fig. 77, where straight lines connect elements of markedly similar chemical properties, and "interpolated elements," if they may be so called, are enclosed in oblong frames. This method of classification is adopted to emphasise the features which correspond to changes of distribution of the electrons in orbits of different principal and azimuthal quantum numbers, which we are about to consider as taking place when successive elements are built up ; in particular the segregation

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* Copper does not resemble the alkali metals very closely. This point is discussed later.

of scandium and its followers is mainly supported by evidence from spectroscopic results. Speaking generally, the elements on either side of the inert gases show very analogous properties as we go from inert gas to inert gas, but the longer periods depart from the simple patterns of the shorter periods when a certain stage of the building up by added electrons is reached.
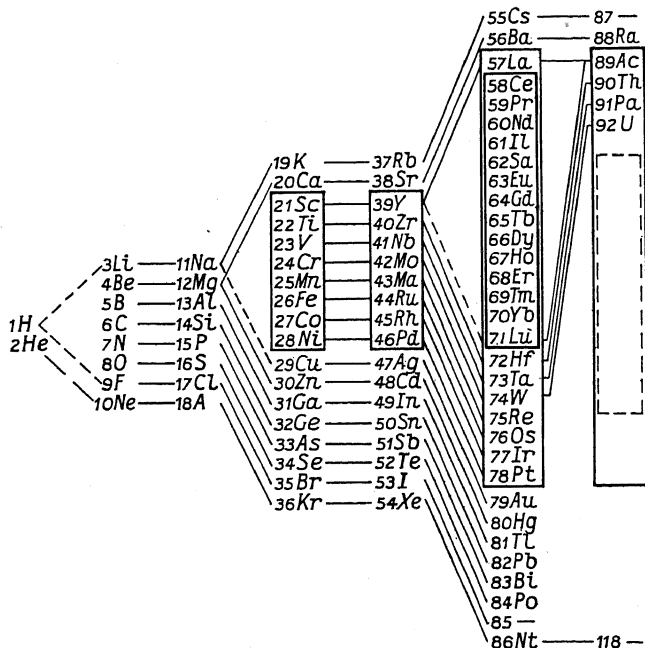
FIG. 77.
Bohr's survey of the periodic system.

It is one of the chief tasks of Bohr's model to account for this, not by assumptions which are merely a restatement of the observed periodicities, but by the application of the general principles invoked for explaining spectral and allied phenomena.

We turn to another aspect of the normal valencies of the elements. An element is said to have a positive valency when it combines with an electro-negative element, such as chlorine or oxygen, and a negative valency when it combines with an electro-positive element, such as hydrogen or a metal. Many elements exhibit both positive and negative valencies, and also

valencies of different values.   On all electro-chemical theories of valency, salts, such as metallic chlorides, are formed by the metal giving up one or more electrons, and becoming positively charged, while the atom combining with it takes up an equal number of electrons and becomes negatively charged :   the ions so formed then combine.   The number of electrons given up or taken up is the measure of the value of the valency : thus there is one such electron for monovalence, two for divalence, and so on.   This number can therefore be deduced from a study of the compounds formed, or, more directly, from the electro-chemical behaviour, which gives a measure of the charge on the various ions.   A consideration of the maximum positive and negative valencies exhibited by an element leads to the conclusion that there is a tendency for an atom to gain or lose electrons until the external group has a certain number of electrons, the same for several near elements, which represents a very stable state.   To elucidate this point, reference may be made to Fig. 78, which is due to Kossel. The number of electrons in the atom is plotted against the atomic number ; for neutral elements this gives, of course, a straight line inclined at 45° to the axes.   We consider, how-ever, the maximum and minimum number of electrons which is ever associated with a given atom.   Thus, chlorine, which electrolytically forms an ion with a single negative charge, or, otherwise expressed, takes up one electron, combines with elements of the second period (sodium to argon) to give the compounds $NaCl$, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5, SCl_6,* while oxygen forms with the same elements Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3.   Hence sodium can give up one electron, magnesium two, and so on, sulphur giving up six.   Also chlorine can form the compound Cl_2O_7, showing that it can give up seven electrons. Chlorine, then, can either take up one, but not more, electron, or give up seven electrons :   the sum of its positive and negative valencies is eight, as demanded by Abegg's rule.   Similarly sulphur can form either SH_2 or SO_3, and so can either take up two electrons or give up six electrons.

In the diagram the maximum and minimum number of electrons which can be held by each atom are indicated for all

* SCl_6 has not actually been made, but the analogous compound SF_6 has.

atoms up to $Z=57$. It is at once clear that the atoms of elements on either side of each inert gas tend, in combination, to hold as many electrons as that gas : thus the elements which neighbour on argon, from silicon $(Z=14)$ to manganese
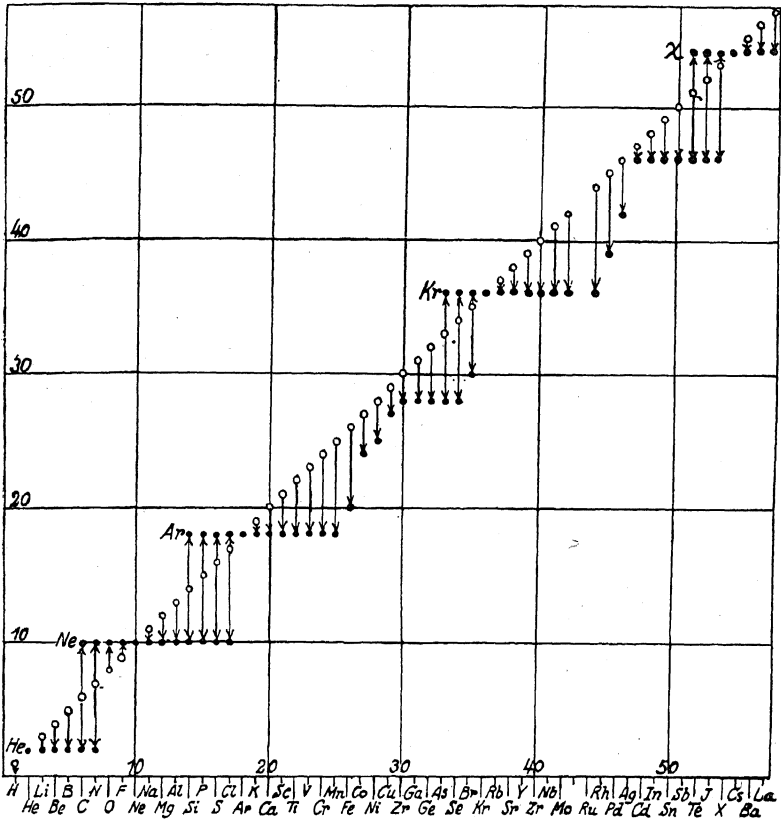
FIG. 78.

Diagram of maximum valencies, illustrating the stability of the inert gas form.

$(Z=25)$, tend to hold,. in compounds, eighteen electrons. There is, then, something particularly stable about the electron configuration of the inert gases, which enables it to co-exist with various different nuclear charges. The inert gases form a turning-point, elements immediately before them having predominant negative valencies, and those immediately after

them having predominant positive valencies. The fact that *varying* nuclear charge is stable with a *fixed* number of electrons for the series of elements forming what may be called one inert gas system (*i.e.* the series of elements which tends to have the same number of electrons as one particular inert gas) must be considered responsible for the various powers of combination of the atom. Within the inert outward form, the sheep's clothing of, say, argon, may be concealed the active and wolf-like sulphur.

Another illustration of the periodic properties, to which we shall have occasion to refer, is given by the atomic volumes. The variations of atomic volume with atomic number is illustrated in Fig. 79, the upper part of which is adapted from Ladenburg. Certain other facts are there made available for rapid reference, namely, which elements are paramagnetic, and which form coloured salts : further, the interpolated elements enclosed in frames in Fig. 77 are shown by double-headed arrows. The lower half of the diagram shows the atomic dimensions as deduced by W. L. Bragg from considerations of crystal structure. The precise physical significance of these atomic dimensions is a matter for detailed discussion, since the figures were obtained by considering that each atom occupies a spherical domain, the size of which is the same for the same atom in all simple salts, and assuming that the atomic spheres are in contact in the crystalline salt. The meaning of the atomic volume in the upper curve is still vaguer : it is defined as the specific volume (volume occupied by 1 gram) multiplied by atomic weight. The general periodic nature of the curves, and the flat minima between the maxima must, however, be significant.

In concluding this section it may be noted that the periodic system, as represented in any form of the tables, is by no means perfect. The actual variation of chemical properties from element to element is not so regular as to render any simple representation possible except as a rough approximation. Thus copper, silver and gold are placed in Column I, although of these silver is the only one which is strictly monovalent, and even this element does not resemble the alkali metals very closely. It must be our final aim to account for such departures

from the simple scheme, and already, as will subsequently appear, the scheme of atomic structure now prevailing has proved successful in explaining certain of the irregularities.
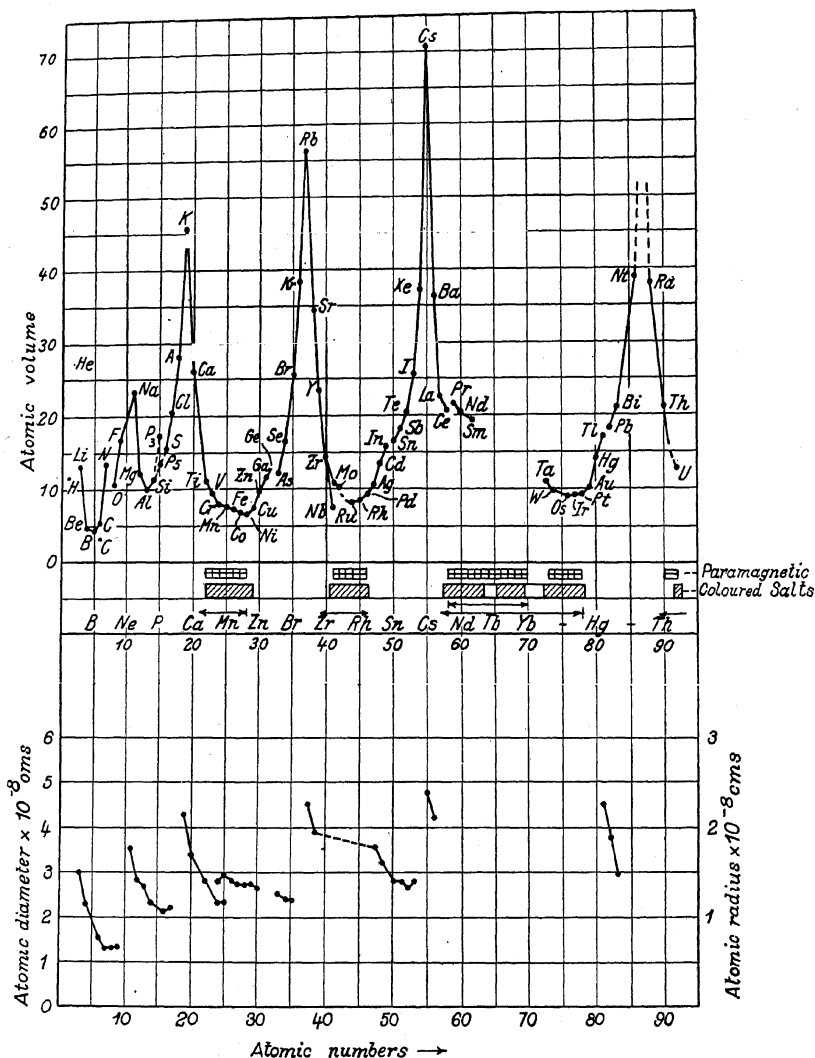
FIG. 79.

Atomic volume curves.

General Periodic Properties of Spectra. The optical spectra, which have been the subject of such searching investigation in recent years, exhibit certain regular quantitative and qualitative changes as the atomic number increases. These will be invoked as occasion arises, but one very important generalisation calls for immediate notice. The type of series spectrum, as given by the multiple structure of the lines (*i.e.* whether singlets, doublets, triplets, or higher multiplicities occur) shows a sudden variation as we pass from group to group, as first indicated by Rydberg in his law of alternations, which stated that doublet and triplet spectra were to be expected alternately as we pass from column to column in the periodic table. Thus the neutral alkali metals give doublet spectra, the spectra of the neutral alkaline earths exhibit triplets, the neutral elements of Column III have doublets, and so on. Recent progress in ordering spectra, initiated by Catalán, and continued by Gieseler, Walters, Meggers, Kiess, Laporte, Sommer and other workers, has shown that this is but a special case of a more general law. Spectra, as has long been known, do not, in general, consist of a single system of principal, sharp, diffuse and fundamental series, but comprise distinct systems of different multiplicities. The alkali metals, it is true, have but one system, the doublet system, but, for instance, the alkaline earths have a complete system of four series of single lines, and, in addition, a complete system of triplets. Both these systems belong to the neutral atom ; in addition to these we have, for the same elements, a spark spectrum of doublets. The spectroscopists just mentioned have succeeded in establishing the existence of systems of high multiplicity in the spectra of the elements of the higher groups, *i.e.* of Columns III, IV, V, VI, VII, VIII. The nature of these systems of high multiplicity is discussed in Chapter XV : for our present purpose the fact that they characterise the nature of the spectra suffices. The generalisation of Rydberg's rule which has resulted from these analyses is that odd and even multiplicities alternate as we pass from column to column. The regularities established are expressed in the following tables, which include the work of Meggers and Kiess and of Beals. The multiplicities of the systems are indicated by simple figures—thus

5 indicates quintets. The brackets indicate that the multiplicity in question is to be anticipated, but had not, at the time of writing, been observed. It will be seen that no spectrum contains more than three systems, and that the table is symmetrical about the elements of Column VII.

NEUTRAL ATOMS OF FOURTH PERIOD.

Column	I	II	III	IV	V	VI	VII	VIIIa	VIIIb	VIIIc	I	II	III
Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
At. number	19	20	21	22	23	24	25	26	27	28	29	30	31
Multiplicities	2	1	2	1	2					1	2	1	2
		3	4	3	4	3		3	2	3	4	3	
				5	6	5	4	5	4	5			
						7	6	7	6				
							8						

NEUTRAL ATOMS OF FIFTH PERIOD.

Column	I	II	III	IV	V	VI	VII	VIIIa	VIIIb	VIIIc	I	II	III
Element	Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In
At. number	37	38	39	40	41	42	43	44	45	46	47	48	49
Multiplicities	2	1	2	1?	2?					1	2	1	2
		3	4	3	4	3?		3	2	3	(4)	3	
				5	6	5	(4)	5	4	(5)			
						7	(6)	(7)	(6)				
							(8)						

The above tables apply to the neutral elements. When we come to consider the spectra of the ionised atoms, we have a further important principle enunciated by Kossel and Sommerfeld under the name of the Displacement Law* (*Verschiebungssatz*). This law states that the spectrum of an ionised atom resembles in multiplet structure that of a neutral atom of an element of the preceding column in the periodic table, while the spectrum of a doubly ionised atom resembles in structure that of a neutral atom preceding it by two places in the

* The law is so called by analogy from the displacement law in radioactivity, which states that the loss of an electron (β particle) gives an element with the properties of the element in the next (higher) column.

periodic table. Quite generally, the law may be taken as laying down that the type of spectrum, as far as the nature of its system is concerned, depends upon the number and grouping of the electrons and not upon the nuclear charge, a result which will henceforth be assumed without discussion. As an example of the Kossel-Sommerfeld displacement rule we may take the spectra of Na_I, Mg_{II}, Al_{III}, Si_{IV}, which all exhibit doublets, a result extended by Millikan and Bowen to even higher states of ionisation, as mentioned in Chapter XIII. The rule is well illustrated by a diagram originally prepared by A. Fowler, Fig. 80, in which the electron groups are represented for simplicity as rings. The outermost circle represents the incompleted group, containing 1, 2, 3 or 4 electrons as we go across from left to right in the diagram.
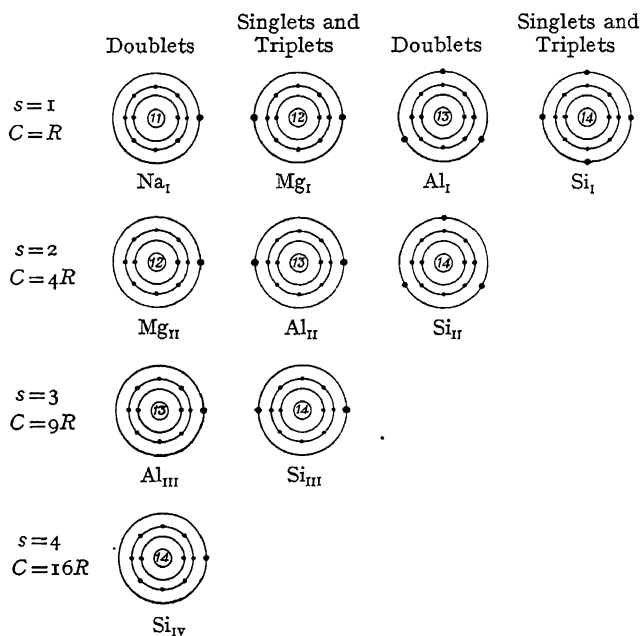
FIG. 80.

Pictorial representation of displacement rule.

For the present these regularities are merely recorded. A discussion of various features of the scheme will be undertaken as occasion arises.

General Features of Orbit Scheme. In the very simplest orbit scheme, to which reference was made in the first discussion of X-ray spectra, the orbits were circular, and shared each by several electrons. Only one quantum number was needed to specify each orbit, and the values 1, 2, 3 ... were chosen for this number for the K, L, M ... groups. We now know that three quantum numbers, n, k_1, k_2, are needed to specify an X-ray orbit in full, or, if we consider only normal levels, two quantum numbers n and k. We may, then, work out a scheme of n_k orbits, and consider the possible subdivision of these by the allotment of different k_2 values later.

The fundamental idea of Bohr's method of considering the general problem of atomic structure is, for an atom of given nuclear charge Ze, to take the bare nucleus, and add successively, one by one, the Z electrons which complete the neutral atom. The assumption to which we have already referred as the Postulate of the Invariance and Permanence of Quantum Numbers states that if to an atom in a given stage of completion (*i.e.* possessing a number of electrons each of which is specified by quantum numbers n and k), we add a further electron, then the addition of this further electron leaves unchanged the quantum numbers of the electrons already bound. This is an assumption to which we are led by the general stability of the atomic structure, and has no mechanical justification : it has the *ad hoc* character of the other assumptions of quantum mechanics. It is to be particularly noted that this is not the same thing as taking a given neutral atom, and, to form the next higher atom, adding one unit to the nuclear charge, and a fresh electron, for the changing of the nuclear charge may affect the quantum numbers of the electrons already bound, as may be seen by comparing the spectrum of, say, neutral potassium and doubly ionised scandium (both with 19 electrons, but with nuclear charges of 19 and 21 respectively), which are considered later. Rather, the spectrum of doubly ionised scandium helps to fix the quantum numbers of the first 19 electrons of scandium, which the addition of the two remaining electrons leaves unchanged. The importance of the spectra of multiply ionised atoms for the theory becomes obvious.

Within a group of orbits of the same principal quantum number n we have orbits of different eccentricity, according to the value of k. For small k the perihelion distance is small, being given quantitatively, in the case of a hydrogen-like atom of nuclear charge Ze, by the formula (7), Chapter XI., viz.

$$d_p = \frac{a_H n^2}{Z}\left(1 - \sqrt{1 - \frac{k^2}{n^2}}\right).$$

If we consider an actual atom, the field is not Coulombian until we are some distance outside the boundary; for any orbit whose d_p works out to be within the core radius the perihelion part lies in a stronger field than that assumed in the above formula, and therefore d_p is actually less than that given by the above formula, if for Ze be taken the effective nuclear charge for the aphelion parts of the orbit. In any case it is clear that orbits of a given n, and small k, may penetrate within orbits of lesser n, but greater k. We no longer have a spatial separation of the region in which orbits of a given n lie from the region in which orbits of another n lie, as in the case of circular orbits, but interpenetration of orbits of different n, both in the case of real and of virtual orbits. An important consequence of this is that we can no longer conclude that every orbit of a given n is more firmly bound than any orbit for which n has a greater value, as was true in the case of circular orbits; owing to the intense field which prevails at perihelion the binding of an orbit for which k is small may be closer than that of an orbit for which n is smaller, but k larger. It follows from this that if we take a nucleus of charge Ze, and add electrons one by one, we may reach a stage at which, t_u orbits being occupied (t and u are particular values of n and k, u being equal to or less than t), the next electron may go to a $(t+1)_1$ orbit in preference to a t_t orbit. It is perhaps best to consider the particular example to which reference has just been made. As we shall see later, it appears that with argon, at the end of the second period of eight, 3_1 and 3_2 orbits are fully occupied by electrons. With potassium ($Z = 19$) we add a new electron: if it went to a 3_3 orbit this would be a circular orbit lying outside the core, or, as we have called it, an orbit of the first kind. A 4_1 orbit,

however, penetrates deeply within the core, or is an orbit of the second kind, and spectral evidence points in fact to such an orbit being more firmly bound than a 3_3 in the case of a nuclear charge of 19, so that the last added electron for potassium goes to a 4_1 orbit, and no 3_3 orbit is occupied. If the nuclear charge is greater than 19, however, while the field well within the core is increased by a small proportion only, the field outside the argon group of 18 electrons is very much increased : the effective nuclear charge outside the kernel is about 1 for potassium, and about 3 for scandium. The result is that the strength of binding of a 3_3 orbit, still of the first kind, is very much increased compared to that of a 4_1 orbit, and actually exceeds it, as we pass from potassium to doubly ionised scandium. We understand, therefore, that whereas a group of orbits, such as the 3_3 orbits, may, as we increase Z, be temporarily passed over on account of the weakness of binding, a stage will later be reached at which the relative strength of binding of these orbits is so much increased that they will be occupied in preference to 4_1 orbits. This addition, as it were, to a group of orbits of a given quantum number after a beginning has been made with orbits of a higher quantum number is made to explain the presence of interpolated elements in the longer groups. It is a most essential feature of Bohr's scheme of interpenetrating n_k orbits, and will receive further reference when the periodic groups are discussed.

For the general discussion of the spectral evidence the effective quantum number plays a very important part, and it may be well to revise and extend what has already been said on this subject. The orbit of the optical electron may either lie entirely outside the core, when it approximates to a Keplerian ellipse, and is said to be of the first kind, or it may penetrate within the core, when it is said to be of the second kind. The parts of orbits of the second kind which lie well outside the core are described in a field which is approximately Coulombian, and therefore all of the orbit except the perihelion part may be considered as a Keplerian ellipse. Near perihelion, however, the electron is subjected to a field very much stronger than that to be anticipated on an inverse square law fitting the remoter field : the result of this is a very high

velocity and a very large rotation of perihelion. The general type of the orbits of the second kind has already been illustrated in Fig. 48, showing the orbits actually calculated for the sodium atom : it is again represented in Fig. 81, which serves to bring out details which must now be discussed.
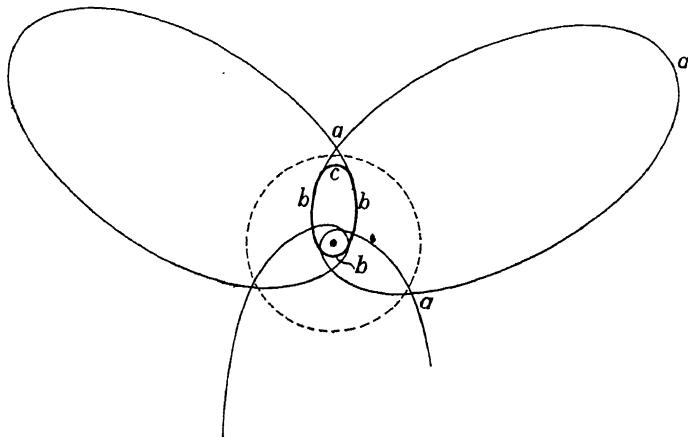
FIG. 81.

Typical orbit of the second kind.

Owing to the large rotation of perihelion the orbit consists of alternate small loops, lying either entirely or nearly entirely within the core, and large loops extending far beyond the core —the inner and outer loops to which reference has already been made in Chapter XI. In obtaining the principal quantum number $n = k + n_r$ we have to remember that the radial quantum number n_r is found by taking the integral

$$\int p_r dr = \int m \left(\frac{dr}{dt}\right)^2 dt$$

over a complete range of r values, or by taking it for a very large number of complete cycles, and dividing by the number. We can therefore consider that to obtain n_r the integral has to be taken over an inner and an outer loop, the outer loop being *aaa* in Fig. 81, and the inner loop *babb*. A large contribution to the radial integral will be given by the inner loop. The azimuthal quantum number k is given by the moment of

momentum about the nucleus, which is, of course, constant throughout the orbit.

The outer loop is nearly a Keplerian ellipse, executed in a field which, especially in the remoter parts, approximates very closely to that given by a single central charge se, if the atom is $(s-1)$ply ionised. We can, then, by suitable projection conditions, obtain a truly elliptic orbit about a central charge se which shall coincide with the outer loop except in the neighbourhood of perihelion. Let the negative energy of the orbit be W: then we define an effective quantum number n_e such that

$$W = \frac{chRs^2}{n_e^{2}},$$

as in equation (4), Chapter XI. This effective quantum number, which, as there explained, will not in general be an integer, serves to give the energy of the outer loop, treated as an orbit of a hydrogen-like atom. W, we know, is the work required to remove an electron from such an orbit to infinity, by our definition, so that n_e gives the work required to remove the electron from its actual orbit. n_e, then, may be said to measure the firmness of binding of the electron. It is, of course, the square root of the Rydberg denominator found by experiment.

n_e is not, however, the true quantum number of the actual orbit, since the inner loop contributes essentially to the radial quantum number n_r: in fact we have already proved in Chapter XI. that $n_e < n$. A corollary to this is that the dimensions of the outer loop are less than those of a hydrogen-like orbit of total quantum number n about a central charge se. The inner loop coincides approximately, as far as all but the remoter part is concerned, with the quasi-elliptic orbit (indicated by $bbbc$ in Fig. 81) executed by a core electron which never " breaks away " as it were. We will suppose that the principal quantum number of this core electron is n_c, while its azimuthal quantum number k will clearly be that of the optical electron considered.* The radial impulse, in the

* While n_c is always greater than n_e, the binding of the core electron is, of course, much firmer than that of the optical electron, since the effective nuclear charge for it is much greater than se.

neighbourhood of perihelion, will also be the same for both the electrons, but remote from perihelion the velocity of the optical electron is clearly greater than that of the core electron, since at a given distance the central force is the same in both cases, and the optical electron escapes. As k is the same in both orbits, the radial integral over the inner loop must be rather greater than that over the core orbit, or the contribution of the inner loop to the n of the optical orbit, which accounts for the excess of n over n_e, is somewhat greater than $(n_c - k)$, the radial quantum number of the core electron. The contribution of the outer loop to the radial quantum number is somewhat less than that of the *whole* Keplerian ellipse which coincides with it in the aphelion region, *i.e.* less than $n_e - k$, so that we have the approximate relation :

$$n = n_r + k = (n_c - k) + (n_e - k) + k$$
$$= n_c + n_e - k$$

or $\quad n_e = n - n_c + k.$ ....(1)

Here n_c is the greatest total quantum number of an orbit actually forming part of the atom (as distinct from a virtual orbit) for which the azimuthal quantum number is k.

The principal quantum number n tells us to which group an orbit belongs, starting with $n = 1$ for the K group, and proceeding outwards with increasing n, passing from real to virtual orbits. For real orbits n gives the energy, or closeness of binding, to a first approximation. Thus a study of the X-ray terms, as represented in Figs. 87 and 88, shows that up to $Z = 57$, all real orbits of a given n are more firmly bound than any orbit of a greater n : for greater Z we have for a time the circular N orbits, N_{VI}, N_{VII}, less firmly bound than the O orbits of highest eccentricity, which can be explained on the lines sketched above for optical orbits, since, although the circular N orbits are within the atom, they are entirely in a region for which the effective nuclear charge is very small compared to that at perihelion distance for O_I, O_{II} or O_{III} orbits ($k = 1$ or 2). For optical orbits the closeness of binding is given by n_e in the case of penetrating orbits, which, owing to the inner loop, is considerably less than n : in the case of orbits of the first kind it is approximately given by n. Whether an orbit of a given n

penetrates or not may depend upon the value of k, and an orbit for which k is large (say, the extreme case of a circular orbit, $k=n$) may not penetrate, while one for which n is larger and k smaller may penetrate, with corresponding diminution of n to n_e, as far as the outer loop is concerned.

We now see how it is that although on Bohr's scheme the principal quantum number n of the basic term, and other corresponding terms, of the optical spectra of homologous elements increases by steps of 1 as we go from element to element, the spectra are closely similar to one another. The term values are given not by n, but by n_e, and formula (1) shows that if k be fixed, changes of n_e are to a first approximation given by the changes of $n-n_c$, where n_c is the highest value of the principal quantum number for an orbit within the atom which has the same k. Both n and n_c increase by 1 as we go from one atom to the next one in the same column of the periodic table, so that n_e differs but little for similar terms of homologous elements. According to our rough formula, n_e should be respectively 2 and 3 for the first terms of the S and P sequences : the first D and F orbits are not, in general, of the second kind, or, in other words, with most atoms the 3_3 and the 4_4 orbit lie outside the core, and $n_e=n$ approximately. Hence, very roughly, we expect n_e to be 2, 3, 3, 4 for the first term of the S, P, D, F sequences. Actually, for the alkalis and alkaline earths (singlet system) we have $1<n_e<2$ for the first term of the S sequence, $2<n_e<3$ for the first term of the P sequence, as shown in the table on the next page. On the conventional spectroscopic notation a value of n is selected for the first term of the different sequences which makes the Rydberg correction small. It has been pointed out that on Paschen's notation the values $n=1$, 2, 3, 4 ... are selected for the first terms of the S, P, D, F ... sequences, while on the Rydberg-Fowler notation $n=1$, 1, 2, 3. It will be seen that in Paschen's notation the values selected differ, in general, by less than unity from n_e, while on Rydberg-Fowler the divergencies are somewhat greater. The fact that, as far as the S and P terms are concerned, n as allotted on the rational orbit system by Bohr does not give, even to the roughest approximation, the values of the terms, explains why this notation is unlikely to

be adopted practically. Taking the alkali metals as an example, it would demand a Rydberg correction for the first

Element	Quantum numbers of first term of each sequence				Effective quantum number n_e of first term				Negative Rydberg correction for large values of n			
	S	P	D	F	S	P	D	F	S	P	D	F
1 H	$\mathbf{1_1}$	2_2	3_3	4_4	1·00	2·00	3·00	4·00	0·00	0·00	0·00	0·00
2 He	$\mathbf{1_1}$	2_2	3_3	4_4	0·74	2·01	3·00	4·00	0·14	0·01	0·00	0·00
	2_1				1·69	1·94	2·99	4·00	0·30	0·07	0·00	0·00
3 Li	$\mathbf{2_1}$	2_2	3_3	4_4	1·59	1·96	3·00	4·00	0·40	0·05	0·00	0·00
8 O {	3_1	3_2	3_3	4_4	1·82	2·27	2·98	—	1·14	0·70	0·02	—
					1·74	2·17	2·97	—	1·13	0·78	0·04	—
11 Na	$\mathbf{3_1}$	3_2	3_3	4_4	1·63	2·12	2·99	4·00	1·34	0·85	0·01	0·00
12 Mg {	$\mathbf{3_1}$	3_2	3_3	4_4	1·33	2·03	2·68	—	1·52	1·04	·56	0·06
	4_1				2·31	1·66	2·83	3·96	1·63	1·12	·17	
13 Al	4_1	$\mathbf{3_2}$	3_3	4_4	2·19	1·51	2·63	3·97	1·76	1·28	0·93	0·05
19 K	$\mathbf{4_1}$	4_2	3_3	4_4	1·77	2·23	2·85	3·99	2·17	1·70	0·25	0·01
20 Ca {	$\mathbf{4_1}$	4_2	3_3	4_4	1·49	2·07	2·00	3·97	2·33	1·93	0·95	0·09
	5_1				2·49	1·79	1·95	3·92	2·44	1·95	0·92	0·10
24 Cr {	4_1	—	3_3		1·42	1·88	2·99	—	2·45	—	(0·01)	—
						2·03	—	—	—	—	—	—
25 Mn	5_1	—	3_3	—	2·31	1·63	2·89	—	2·60	—	0·08	—
29 Cu {	$\mathbf{4_1}$	2_2	3_3	4_4	1·33	1·86	2·98	4·00	2·58	(0·09)	0·02	0·00
30 Zn {	$\mathbf{4_1}$	—	3_3	4_4	1·20	1·94	2·87	—	2·62	—	0·20	—
	5_1				2·34	1·60	2·90	3·98	2·72	—	0·08	0·04
31 Ga	5_1	—	3_3	—	2·16	1·52	2·84	—	2·78	—	0·24	—
37 Rb	$\mathbf{5_1}$	5_2	3_3	4_4	1·80	2·27	2·77	3·99	3·13	2·66	0·35	0·03
38 Sr {	$\mathbf{5_1}$	5_2	4_3	4_4	1·54	2·13	2·06	4·14	(3·26)	(2·59)	1·75	0·10
	6_1				2·55	1·87	1·99	3·91	3·77	2·85	1·80	0·12
47 Ag	$\mathbf{5_1}$	2_2	3_3	4_4	1·34	1·90	2·98	3·99	3·52	(0·05)	0·01	0·01
48 Cd {	$\mathbf{5_1}$	—	3_3	4_4	1·23	1·95	2·87	—	3·57	—	0·21	—
	6_1				2·28	1·62	2·89	3·97	3·67	—	0·07	0·03
49 In	6_1	—	3_3		2·21	1·55	2·82	—	3·73	—	0·29	—
55 Cs	$\mathbf{6_1}$	6_2	3_3	4_4	1·87	2·35	2·55	3·98	4·05	3·57	0·45	0·04
56 Ba {	$\mathbf{6_1}$	6_2	5_3	4_4	1·62	2·14	1·89	2·85	4·43	(3·73)	2·45	(0·92)
	7_1				2·63	1·94	1·82	3·84	4·28	3·67	2·77	0·12
80 Hg {	$\mathbf{6_1}$	—	3_3	4_4	1·14	1·91	2·92	—	4·63	—	0·08	—
	7_1				2·24	1·59	2·93	3·97	4·71	—	0·05	0·03
81 Tl	7_1	—	3_3	4_4	2·19	1·56	2·90	3·97	4·74	—	0·10	0·03

In the above table the basic orbit is indicated by heavy type.

S terms of − ·40, − 1·34, − 2·17, − 3·13 and − 4·14 for neutral lithium, sodium, potassium, rubidium and caesium respectively, while on Paschen's or Fowler's notation the correction

is ·60, ·66, ·83, ·87, ·86 respectively, or varies little from element to element, which best emphasizes the similarity of the spectra of the neutral atoms of alkali metals.

The Inert Gases. The inert gases, placed together in Column O at the end of the periodic table, are of such importance for any systematic theory of atomic structure that it may be well to say something of them as a preliminary to the fuller discussion of the periods. Their chemical inertness, with which must be classed their monatomic nature,* indicates that all the outer electrons are tightly bound in a closed grouping, so that no one of them is available for interaction with other atoms. The valencies of the neighbouring elements likewise indicate that these gases form, as it were, turning-points in the scheme of atomic structure. As expressed in Kossel's diagram, Fig. 78, the atoms of the elements preceding or following an inert gas tend to take up or lose, respectively, a number of electrons sufficient to make their electronic structure resemble that of the inert gas in question. It is of great significance in this connection that the atoms of hetero-polar compounds are demonstrably not neutral, but consist of positive and negative ions, held together by electric forces, as is proved by the existence of free periods in the infra-red region, established by the experiments of Rubens and his collaborators on *Reststrahlen.* Such experiments have demonstrated for crystalline halogen compounds, for instance, the existence of a single region of metallic reflection corresponding to a vibration of a frequency only to be explained on the ground of such electrically coupled atoms. The halogen atoms do, then, actually take an electron, and the atoms which combine with them lose electrons, as demanded on Kossel's theory, and the experiments of Debye and Scherrer, and of W. H. Bragg, cited on page 638, offer further proof in this direction.

The actual existence of the high degree of symmetry which this closed and particularly stable inert gas structure might be expected to possess is proved by the lack of magnetic moment of the inert gases, which are all diamagnetic. Further evidence

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* The band spectrum of helium indicates that this gas can be exceptionally provoked to form molecules, but the atoms so combining must be supposed to be not in the normal state, but the metastable state.

for the completed nature of the electron grouping may be found in the extremely high ionisation potentials of the inert gases, and their very complex spectra : the former indicates the difficulty of breaking up the structure by removing an electron, and the latter that the outer electrons left in the incompleted group when an electron is actually removed are many in number. With the exception of helium and neon no success has so far been achieved in ordering the spectra of the inert gases, although some regularities have been found with many of the preceding elements. Again, while the ordinary spectra of the alkali metals are particularly simple as spectra go, very intense spark excitation produces with sodium and potassium a new and very complicated spectrum, as clearly demonstrated by Goldstein. He realised that this new spectrum must be due to a new state of the emitting atom, and called it the Basic Spectrum (*Grundspektrum*). Now if, as we have supposed, the alkali metals consist of an inert gas structure and a single outer, or valency, electron, we should expect the ordinary, or arc, spectrum to be simple compared to that of the succeeding elements, with more outer electrons. The ionised atom, however, must have an inert gas structure, so that a spark spectrum, produced by removing a second electron, should be very rich in lines, and resemble the arc spectrum of the inert gases. This relation between the spectra has been definitely established by recent work in Konen's laboratory at Bonn, where Sommer has demonstrated a general similarity between the spark spectrum of caesium and the arc spectrum of neon and of xenon, while Dahmen has proved a qualitative resemblance between the spark spectrum of potassium and the arc spectrum of argon. These observations, together with the earlier work of Goldstein, confirm, therefore, our view of the inert gases as closed structures, the addition of a further electron to which begins a fresh group.

The atomic numbers of the inert gases, from helium to radon, are 2, 10, 18, 36, 54, and 86, the numbers of elements in the succeeding groups in the table being 2, 8, 8, 18, 18 and 32, if hydrogen and helium be taken as the first group. These numbers might at first seem to represent on our scheme the numbers of electrons having, respectively, $n = 1, 2, 3, 4, 5$ and 6,

or, in other words, the numbers of electrons in the K, L, M, N, O and P groups. This, however, is not the fact, since, as we have already indicated, in the longer groups there occurs, when we reach the interpolated elements, a further building up of inner groups which were left at an intermediate stage of great stability when the new group first began. With each inert gas the number of electrons in the outermost group is 8, as we shall see later, a fact foreshadowed in Abegg's rule that the sum of the maximum positive and negative valencies of an element is eight. So fundamental is the number eight for our present subject that Ladenburg has spoken of it as " sanctified " (*geheiligt*) by the periodic system.

The only inert gas with which an attempt has been made to calculate quantitative results from a mechanical model is helium, which might at first sight seem simple, compared to, say, a sodium atom, consisting as it does of a nucleus and but two electrons. (We speak, of course, of the neutral atom.) The simplicity is, however, in appearance only, for whereas in the case of sodium we can obtain fairly satisfactory numerical results by treating one electron as privileged, and the rest as constituting a core, in the helium case such a separation is not justified. At the present time there is, in fact, no fully satisfactory model, so that we must be content to indicate some of the facts which must be explained, and the attempts which have been made to devise an adequate model.

One demand made of a model of the helium atom is that it shall give a correct value for the ionisation potential, *i.e.* the work required to remove one electron to infinity from the atom in its normal or basic state. Another is that it shall give an approximate representation of the spectrum of neutral helium. It is to be remembered that this consists of two distinct systems, one of doublets and the other of singlets, each system containing a principal, sharp, diffuse and fundamental series. (See page 179.) These two systems are sharply separated, in the sense that each is represented by separate sequences of terms, and that no lines are known corresponding to combinations between terms drawn, one each, from the two different families. In the case of other spectra containing different systems intercombinations are common, *e.g.* with

mercury, which contains a singlet system and a triplet system (see Fig. 50), combinations between triplet and singlet terms occur freely. Besides representing these qualitative facts, a satisfactory model should allow some quantitative calculation of these values.

One early assumption was that the two electrons revolved in the same circular orbit, at opposite ends of a diameter. This has been definitely abandoned as a result of criticism based upon the fact that it gives too high a value for the ionisation potential, and upon a disagreement with spectroscopic results which need not be here set out at length. In another model proposed, one electron forms a " double star " with the nucleus, while the second revolves round the pair as the single electron revolves round the nucleus in the hydrogen atom, but this is mathematically intractable, and has won no support. In the only models that have had any success both electrons are bound in equivalent orbits. That which has received most consideration is the so-called crossed orbit model, which will accordingly be briefly discussed here, but its success is very limited, and Sommerfeld has proposed a variant which will also be mentioned.

In accordance with Bohr's method, we take a nuclear charge of two units. We consider one electron to be firmly bound in a circular 1_1 orbit, as in the normal state of the hydrogen atom, and enquire how the second can be added. First of all, the second electron may have, for orbits of higher quantum number, its orbit in the same plane as the first electron. In this case, however, the closest possible binding is expressed not by a 1 quantum orbit, but by a 2_1 orbit, for the correspondence principle indicates that there can be no passage from a state where the second electron executes orbits about the first electron and nucleus to one where it shares a circular orbit with the first electron. The series of harmonic terms which covers the transitions for the former class of motion will not cover the latter transition. This movement of the second electron in the same plane as the first, with a 2_1 orbit as its final state, corresponds to the orthohelium (doublet) system. Clearly, however, the 2_1 orbit for the second electron cannot represent normal helium, because the binding is far too weak

to give the observed ionisation potential. It corresponds rather to the metastable state found by Franck, from which no direct transition to the normal state is possible.

If, however, the second electron does not move in the same plane as the first, the transition process when the second electron passes to a 1_1 orbit whose plane makes an angle with that of the first 1_1 orbit, is not fundamentally different from that when it passes to a 2_1 or any other orbit, and a detailed consideration of the correspondence principle shows that such a transition can be included in the scheme. The plane of the final 1_1 orbit of the second electron is assumed to make an angle of 120° with the plane of the equivalent 1_1 orbit of the first electron. The parhelium system of singlets corresponds to transitions among the class of stationary states in which the final one is this inclined 1_1 orbit. It may be asked why, since the energy of this 1_1 orbit is so much smaller than that of the 2_1 orbit which represents the closest binding of the orthohelium orbits, the singlet system does not include lines of much higher frequency than the doublet system. The answer is that it does, but that these lines have only recently been observed in the optical spectrum, being Lyman's extreme ultra-violet series ($1^1S - n^1P$), alluded to on page 319, where the connection between optical and X-ray spectra is discussed.
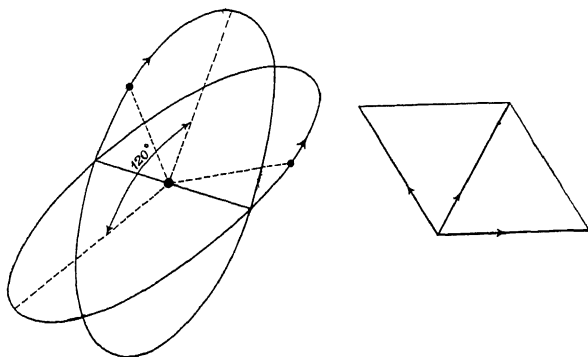
FIG. 82.
Crossed orbit model of neutral helium.

Fig. 82 indicates the chief features of the crossed orbit model, or the Bohr-Kemble model, as it is sometimes called,

since E. C. Kemble proposed it independently of Bohr. By assumption the two electrons have orbits equal in all respects, and will be at opposite ends of the common diameter simultaneously. The sense of the motion in each orbit is such that the angle between the two vectors representing the angular momentum is 120°, and not 60°, which is why the inclination of the orbits is said to be 120°. A consequence of this is that the resultant angular momentum is equal in magnitude to the angular momentum in either orbit, as can be seen by a glance at the vector diagram, viz. equal to $h/2\pi$. With this must be associated a magnetic moment. Now the neutral helium electronic structure forms the K group of all heavier atoms, while all higher completed groups or sub-groups have no resultant moment on account of their high degree of symmetry. Every inert gas should therefore possess unit moment of momentum, and the corresponding magnetic moment, on account of its crossed orbit K group. It is an experimental fact, however, that all the inert gases, including helium, are diamagnetic, which implies that the atoms have no magnetic moment (see Chapter XVI). Bohr has attempted to get over the difficulty by supposing that all the atoms set with their moment across the direction z of the field, but in random directions in the xy planes, which would give no resultant momentum. There are, however, other difficulties. Reference may be made to a paper by J. H. van Vleck on the subject ; a more comprehensive investigation has been published by H. A. Kramers, who shows that the model gives an ionisation potential of 20·63 volts, which is less by 3·9 volts than the experimentally determined value of 24·5 volts. This experimental value is particularly well supported, having been found independently by Horton and Davies, by Franck and Knipping, and by Mackay. The series limit extrapolated from Lyman's extreme ultra-violet helium lines ($1^1S - n^1P$) also confirms this value, being 24·6 volts. Kramers further showed that the model is unstable, if the question of stability is determined by the ordinary laws of mechanics. He considers that, while we might have hoped that in so simple a case these laws would hold for the purposes of the investigation, yet we have no reason to be surprised—although possibly we

may be pained—if they appear not to do so. He prefers abandoning the laws of classical mechanics to abandoning the model, and urges that the criticism which argues that the helium atom can have no moment of momentum as a whole, because the atom is not paramagnetic, is not cogent, since, for one reason, the anomalous Zeeman effect has shown that considerations of classical mechanics do not suffice to describe the magnetic properties of atoms.* It is true that we have abandoned many principles of classical mechanics at the bidding of the quantum theory, but it is not clear yet how we are to investigate stability without them.

A further criticism brought against the crossed orbit model by Pauli is that, if the K orbits had a resultant moment, the relativity effect in the case of atoms of large nuclear charge would produce a large influence on the ratio of magnetic moment to moment of momentum, and hence on the Zeeman effect—an influence which is not experimentally found. Finally, no success has so far been obtained in attempts to calculate the terms of the series of neutral helium.

The crossed orbit helium model, although it has been widely accepted, is, then, not by any means free from reproach. Sommerfeld in particular has protested against its adoption, and proposed in its stead a model in which the orbits of the two electrons are co-planar and equal, while the sense of the circulation of the electron is opposite in the two orbits, so that
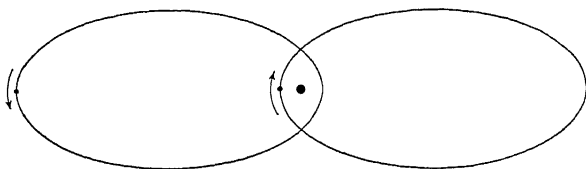
Fig. 83.
Sommerfeld's proposed model for neutral helium.

on the whole there is no moment of momentum, and no magnetic moment. The proposed scheme is represented in Fig. 83. Sommerfeld applies the quantum condition in an unusual way

* But although the relation between moment of momentum and magnetic moment is not that demanded by classical theory, nevertheless a moment of momentum is always accompanied by a magnetic moment. See Chap. XV.

by equating the sum of the radial momenta of the two electrons to $n_r h$, and the sum of the azimuthal momenta of the two electrons to kh :

$$\oint p_{r_1} dr_1 + \oint p_{r_2} dr_2 = n_r h,$$

$$\oint p_{\theta_1} d\theta_1 + \oint p_{\theta_2} d\theta_2 = kh.$$

The smallest physically possible values for n_r and k are 1, if we deny that the two electrons can move in the same circular orbit, for $n_r = 0$ would imply that both radial integrals were independently zero. If the two electrons move in equivalent orbits, we therefore have

$$\oint p_{r_1} dr_1 = \oint p_{r_2} dr_2 = \oint p_{\theta_1} d\theta_1 = \oint p_{\theta_2} d\theta_2 = \tfrac{1}{2} h.$$

If we neglect the interaction of the two electrons, the orbits are ellipses of total quantum number $n = n_r + k = 1$, azimuthal quantum number $\tfrac{1}{2}$, which we can write in our usual notation as $1_{\frac{1}{2}}$ ellipses. A simple calculation shows that for these orbits the minor axis is half the major axis, and the major axis half that of the hydrogen 1_1 orbit.

The two spectral systems Sommerfeld explains by supposing that one corresponds to orbits with half integral k, the other to orbits with integral k : since the normal state of the atom is in Sommerfeld's model given by $k = \tfrac{1}{2}$, it must be the par-helium system that belongs to the half-integer k orbits. Since the correspondence principle allows only transitions for which $\Delta k = \pm 1$, there can be no combinations between terms of the different systems, so that this fact is explained on Sommerfeld's model as well as on Bohr's. Sommerfeld's model further explains the experimentally established lack of magnetic and electric moment of the helium atom.

The other difficulties, of calculating the terms and the ionisation potential, remain ; for this the disturbing effects of the electrons one on another must clearly be considered. The atom may start with the phase relationship shown in Fig. 83, but as a result of the interaction of the two electrons (one screening the other from the nuclear charge in Fig. 83) the simple periodicity will be disturbed, and one electron will gain

on the other until the original configuration is approximately reached again. There is a double periodicity. Sommerfeld refers to an unpublished calculation of Heisenberg's, which takes account of the multiple periodicity, and gives an ionisation potential of 24·5 volts, but also shows that the model is unstable. We must therefore be content to follow Sommerfeld, and speak of the helium problem rather than the helium model. We may add that Sommerfeld himself is convinced that the solution is to be sought on the lines of a model in which both orbits are co-planar.

Before leaving the helium atom reference may be made to an important experiment of Millikan's which has a bearing on the subject. Millikan showed by means of his droplet method that a swift α particle does not knock more than one electron from a given atom, whether it is of comparatively low atomic number, such as carbon or oxygen, or of high atomic number, such as mercury. This seems to prove that the electrons within an atom are in independent orbits, in accordance with modern belief, and not in rings of four or eight as in the older theory. The one exception to the experimental rule is helium, from which both electrons can be removed in a single collision—in fact, one in every six effective collisions does remove both electrons. This indicates that, while the electrons are in separate orbits they are, for about a sixth of the period of revolution, so close or so intimately associated that the passing α particle influences both equally. This general result could, then, be explained by either the Sommerfeld or the Bohr model, but does not offer any decision between the two.

No attempt has been made so far to carry out quantitative calculations for any other inert gas.

The Periodic System : Short Periods. We have now to consider how, by the study of physical and chemical properties, especially the nature of the spectra, the orbital schemes corresponding to the different elements can be deduced. In other words, we have to decide the number of electrons in each group and sub-group, relying at every step on empirical results for a decision.

Starting with lithium, we take a nucleus of charge 3 to which two electrons have been added, arranging themselves in a

manner resembling neutral helium. For convenience we will assume the crossed orbit model, so that the two electrons occupy 1_1 orbits : the nature of the helium model assumed is of secondary importance for the present considerations, and can be changed without affecting the general argument. In the lithium spectrum the P terms differ but little from hydrogen terms, e.g. n_e for the first P term is $1\cdot96$ (cf. table on page 444), approximating closely to 2, while succeeding P terms are very nearly 3, 4 ..., the divergence becoming less and less as n becomes greater. This indicates that the circular 2_2 orbits, and further the elliptic 3_2, 4_2 ... orbits, lie entirely outside the core, which consists of the nucleus and the first two electrons : for these orbits the screening by the two electrons is nearly complete, so that we have an approximation to a hydrogen-like field. The S sequence of lithium, however, departs markedly from hydrogen-like values for the earlier terms, the value of n_e for the first S term being $1\cdot59$. The limit of the principal series of lithium, i.e. the ν value for the first S term, which is the greatest term in the spectrum, is 43485, while the limit of the Lyman series for hydrogen is $\nu = R = 109678$. Denoting by W_H the work needed to take a 1_1 hydrogen electron to infinity, we find from the figures just quoted that the work required to remove the third electron from the closest bound lithium orbit is $\cdot396W_H$, whereas for a 2_1 or 2_2 hydrogen orbit it is $\cdot25W_H$. These facts are consistent with the supposition that the orbit of the most firmly bound electron in lithium is a 2_1 orbit, which penetrates within the region of the 1_1 orbits, so that the screening is incomplete, and the binding is much firmer than that of a hydrogen orbit of the same principal quantum number. Fig. 84, which gives the Bohr-Grotrian diagram * for lithium, shows clearly the general magnitudes of the various terms, on which the argument is based that the third electron is normally bound in a 2_1 orbit.

* In all the Bohr-Grotrian diagrams in this chapter a logarithmic scale is adopted for ν, to avoid overcrowding of the higher terms. In the case of doublet lines the short line representing the (mean) frequency is broken into two, since in general the doublet is too narrow for the components to be shown separately on this small scale. In the one or two cases (cf. Cs_I, Cu_I, Fig. 84) where the doublets are wide the two halves of the broken line have been staggered to show the separation.

The hydrogen terms, for which $n_e = 2, 3, 4 \ldots$, are shown on the diagram. All the D and F terms approximate very closely to the hydrogen values, since the smallest D and F orbits, 3_3 and 4_4, are large compared to the core.

The experimental data show that a third 1_1 orbit completely external to the two 1_1 orbits of the helium group, and thus
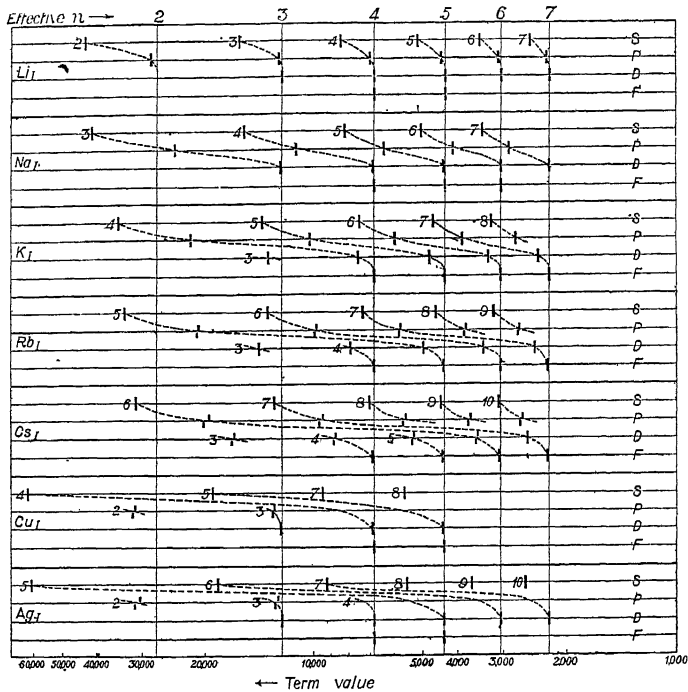
FIG. 84.

Bohr-Grotrian diagram for spectra of neutral alkali metals, and of copper and silver.

described in a partly screened field, cannot exist. Bohr states that the polarisation of the core which would be produced by such a circular orbit, could it exist, would result in the external 1_1 orbit being drawn into the region of the inner 1_1 orbits, and, by assumption, three equivalent 1_1 orbits are impossible. The whole argument as to possible orbits is an intimate mixture of experimental and very general mathematical reasoning, the properties of the orbits in complicated atoms

being, with the hypotheses so far elaborated, only vaguely deducible on a dynamical basis.

The alkali metals readily form compounds in which the metal acquires a single positive charge, as indicated by the results of electrolysis. They have a low ionisation potential for single ionisation, but it is exceedingly difficult to produce a doubly ionised atom. We have seen that in the case of lithium the third electron is bound in a 2_1 orbit. When we turn to sodium, we must consider a nucleus for which $Z = 11$, and that the first ten electrons have been bound two in the K group and eight in the L group, which, with this number of electrons, attains the highly symmetrical and closed inert gas form. We have to enquire as to the normal orbit of the eleventh electron : by our hypothesis its principal quantum number cannot be 2, the L group being complete, but must be 3 or higher. The first S term is the largest in the sodium spectrum, so that the most closely bound electron must have a 3_1 orbit. This orbit must be of the second kind, for its effective quantum number n_e is 1·63, while n is 3, or, otherwise expressed, the work required to remove the electron is much greater than that for a hydrogen-like orbit for which n is 3. That this orbit does indeed penetrate the core may be confirmed either by taking for the core a diameter found from other measurements, and showing that the perihelion distance is less than this, or, conversely, by assuming penetration, and enquiring at what distance from aphelion the inverse square law must be assumed to break down in order to get a term value approximating to that observed. This gives an estimate of the core size which can be compared with that obtained in other ways.

Many estimates have been made of atomic diameters, and anything like a thorough discussion is obviously superfluous here. We have, however, particularly in the case of the alkali metals, to distinguish between assessments calculated to give the size of the ionised atom, and those which give the size of the neutral atom. For the alkali metals the latter must be appreciably larger than the former. In any case the expression " size of the atom " is vague enough, since an atom has no definite edge, and different methods of approaching the problem must be expected to give results differing within certain limits.

since they implicitly take different criteria to define the boundary. Without considering the problem in detail we may cite the estimates of Wasastjerna, based on ionic refraction, and of Fajans, Herzfeld and Grimm, based on an elaborate consideration of Born's lattice theory, both of which apply to the ion. For the radius of the sodium ion the former method gives $\cdot74 \times 10^{-8}$ cm., the latter $\cdot52 \times 10^{-8}$ cm.* The radius of the neon atom, which should very slightly exceed that of the sodium ion (it has the same electron structure, but a nuclear charge less by 1 unit), is $\cdot65 \times 10^{-8}$ cm. according to an estimate of W. L. Bragg's, and $1\cdot17 \times 10^{-8}$ cm. according to Rankine's estimate based on viscosity measurements. We may take, then, $\cdot75 \times 10^{-8}$ as the approximate ionic radius for sodium. (For the neutral atom considerations of atomic volume, and of ionisation potential, lead independently to $1\cdot4 \times 10^{-8}$ cm. as radius.) Assuming a penetration of the core by the S orbits, Hund has estimated the radius of this ion by calculating the distance at which the inverse square law must be supposed to break down in order to obtain the right term energy, a method referred to above. He estimates the deviation from the Coulombian field by methods similar to those of Hartree (see Chapter XI.), and arrives at a value about 2×10^{-8} cm. for the radius. If, instead of $k=1$ for S orbits, he takes half-integer values (this has to be done in many cases : see Chapter XV.) he gets $1\cdot6 \times 10^{-8}$ cm., which is nearer the radius obtained by the other method, but still too large. However, exact agreement can scarcely be expected in view of the indeterminate nature of the radius.

From formulae (7) and (8) of Chapter XI. we can find at once the perihelion and aphelion distance of a given n_k orbit in a truly inverse square field of force, and we have, as there deduced,

$$\frac{a_H k^2}{Z} > d_p > \tfrac{1}{2}\frac{a_H k^2}{Z},$$

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* Contrast W. L. Bragg's estimate from crystal structure, which is $1\cdot8 \times 10^{-8}$ cm. for the radius of the sodium atom. From the method adopted it cannot be definitely said whether this applies to the ion or the neutral atom, although the bulk of the evidence points to the sodium atom being ionised in crystalline salts. The definite maxima shown at the alkali metals in the lower part of Fig. 79 would indicate, however, that the neutral atom is in question, as far as the estimate has a physical meaning.

the limit on the left being attained for $n = k$ (circular orbits), while that on the right is approached as n tends to ∞, *i.e.* as the eccentricity increases. Now at aphelion for the 3_1 orbit the effective Z is 1, so that, if the orbit were a true Keplerian ellipse, d_p would be less than a_H. The estimate given above of the radius of the sodium ion is about $1 \cdot 4 a_H$, so that there can be no doubt about the penetration of the core by the S orbits, the non-Coulombian nature of the actual field always increasing the tendency to penetrate. The value of d_p for the first virtual P orbit, *i.e.* a 3_2 orbit, is $2 \cdot 3 a_H$ for an effective nuclear charge of 1. Thus this orbit would pass outside, but close to, the core if the inverse square law prevailed everywhere, but actually, owing to the more rapid increase of the field in the neighbourhood of the core, we expect a certain degree of penetration ; this is confirmed by the value of n_e, which is $2 \cdot 12$ for the first P orbit, while n is 3.

The first D orbit is a 3_3, or a circular orbit of radius $9 a_H$, if the field be inverse square. At such a distance we should expect the screening to be nearly complete, and hence the radius of the orbit to approximate very closely to this, with consequent lack of penetration. n_e for the first D orbit is $3 \cdot 00$, *i.e.* is equal to n. Higher D orbits will have a lesser perihelion distance, tending to $4 \cdot 5 a_H$ as n tends to ∞, but even for this limiting value the distance still exceeds the core radius, and we should expect the effective quantum number to be approximately the same as the total quantum number, or, in other words, the terms to be very nearly hydrogen-like, starting at $\frac{1}{9} R$. This is the case, the sixth D term ($n = 8$) being $1718 \cdot 45$, while $\frac{1}{64} R$ is $1717 \cdot 16$. It can easily be seen without discussion that the F terms would be expected to be even more hydrogen-like, the radius of the first, the 4_4 orbit, being $16 a_H$. Fig. 84 shows the general run of the S, P, D and F terms for all the alkali metals, and should be consulted in connection with these arguments.

Although with sodium and the other alkali metals the core is sufficiently small for all the F orbits to be clear of it at perihelion, it is possible for an F orbit of low eccentricity to be entirely free of the core, while a higher F orbit, of greater eccentricity (for which the perihelion distance tends to be only

half that of the circular F orbit) may penetrate, or at any rate come very near, the core. Thus it is conceivable that the first F term might have an exceedingly small Rydberg correction, while higher F terms have a larger Rydberg correction. This is actually the case with Al_{II}, measured by Paschen, the following table giving the values of n and n_e for the ^3F terms. The core of Al_{II} is, of course, larger than the core of Na_I, since it has an electron above the inert gas structure.

n -	4	5	6	7	8	9	10
$v/4$	7109·90	4603·27	3325·30	2679·98	2144·95	1682·06	1340·31
n_e -	3·93	4·88	5·74	6·40	7·15	8·08	9·05

Turning to the remaining alkali metals, the first S orbit, which is respectively 4_1, 5_1 and 6_1, for potassium, rubidium and caesium, is always the most firmly bound, and is clearly always of the second kind, since the perihelion distance of a hydrogen orbit for which $k=1$ decreases with increasing n, while for homologous elements the core increases in size as Z increases. Similarly the P orbits must all be of the second kind. Whether the D and F orbits are of the first or second kind is a question to be examined, since, while they are of the first kind for sodium, with the increasing size of the core it becomes possible that they may penetrate it, or, in other words, the class of orbit for which penetration first occurs should, with homologous elements, be displaced towards the F orbits. We may consider the question empirically, with the help of the Bohr-Grotrian diagrams of Fig. 84. It will be seen that with lithium and sodium n approximates very closely to n_e (orbits are of the first kind) for D and F terms : with potassium n_e is somewhat less than n for D terms, and the departure becomes progressively greater as we proceed to rubidium and caesium. From the fact that n_e approximates closely to n for all the elements in the case of the F orbits, we conclude that these orbits are always of the first kind. Even for the largest core and the most eccentric F orbit (caesium 12_4 orbit) the term value is $765·77$, as compared with $761·65$ for the hydrogen $R/12^2$ term.

It is instructive in this connection to compare the spectra of Na_I, Mg_{II}, Al_{III}, Si_{IV}, all of which have the same electron structure, while the net charge on the core, se, is, respectively,

1, 2, 3 and 4. (Cf. also Fig. 80.) The Bohr-Grotrian diagram of these spectra is shown in Fig. 85 : since the constant in the spectral formula is R, $4R$, $9R$, $16R$ for Na_I, Mg_{II}, Al_{III}, Si_{IV} respectively, the terms as derived from analysis of the experimental data are divided by 1, 4, 9, 16 respectively, to facilitate comparison. From the diagram it may be seen that, as s
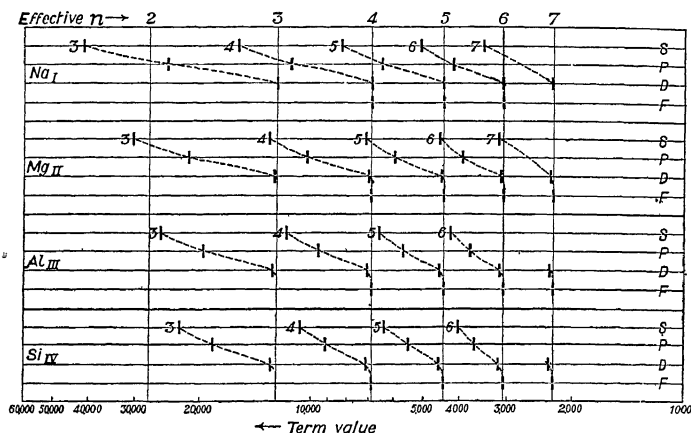
FIG. 85.

Bohr-Grotrian diagram for spectra of atoms of same electron structure, but different atomic number.

increases from 1 to 4, the S terms tend to become more hydrogen-like, or, in other words, n_e approaches n steadily ; the same holds good of the P terms. But the D terms, which for Na_I are very close to hydrogen values, depart from this and increase somewhat as s increases, until with Si_{IV} the departure is quite marked. A trace of this effect can be found with the F terms. A simple explanation of these features can be given in terms of the orbit scheme.

As the net core charge se increases, the contrast between the field inside and outside the core becomes less marked, for while, e.g., for Si_{IV} the field at a given distance outside the core is approximately four times that for Na_I at the same distance, inside the core the field is increased by a comparatively small fraction, depending on the position with respect to the minor electron groups. Thus for orbits of the second kind the increase

of core charge tends to make the terms somewhat more hydrogen-like : on the other hand, for orbits of the first kind, lying outside the core, increase of core charge diminishes the size and tends to bring them within the region where the inverse square law fails, with consequent departure of n_e from n. D and F terms being of the first kind with the atoms considered, we see that the general nature of the behaviour expressed in Fig. 85 follows from this argument.

With the alkali metals, then, everything is straightforward, and we consider that for these the normal orbit of the last
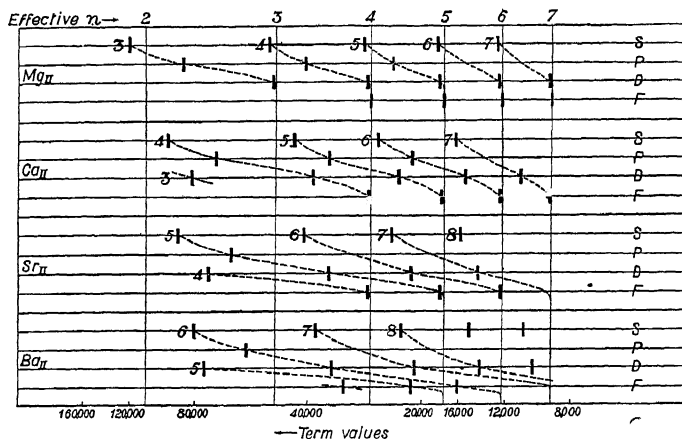
FIG. 86.

Bohr-Grotrian diagram for spark spectra of the alkaline earth metals.

added electron has $k = 1$, and n greater by 1 than its value for the preceding inert gas. To determine the orbits for the alkaline earths we must consider the spark spectrum of these elements, as was explained in discussing Bohr's general method. The spectrum of beryllium is not sufficiently known to make its consideration easy : we therefore start with magnesium. In the spectrum of Mg_{II} the first S term is the largest, so that we assume the electron last added to the inert gas core to be most firmly bound in a 3_1 orbit. The P orbits also penetrate the core, but the D and F orbits are of the first kind, as shown by a consideration of Fig. 86. With the spark spectra of the higher homologues of magnesium, the S orbit is still always

the firmest bound. The P orbits always penetrate, and from calcium onwards the D orbits do the same, but the F orbits are always of the first kind. Estimates of the dimensions of the orbit show that with Sr_{II} the 4_3 orbit, although lying within the core neighbourhood, is less firmly bound than the 5_1 (but more firmly bound than the 5_2 orbit), since, in spite of the fact that it has a lower total quantum number, the small eccentricity makes its approach to the nucleus much less close than that of the 5_1 orbit. We shall see later that no 4_3 orbits are permanently occupied for strontium. Similar considerations apply to the 5_3 orbits of barium.

With all the alkaline earths, then, the first electron added to the inert gas form has an orbit for which $k = \mathrm{I}$. Consideration of the arc spectrum shows that the second electron also has an orbit for which $k = \mathrm{I}$, so that for neutral magnesium, calcium, strontium, barium the last two electrons added have 3_1, 4_1, 5_1 and 6_1 orbits respectively. We assume by analogy that for beryllium the two electrons have 2_1 orbits.

To discuss the binding of the electrons for elements of Column III we require the spectrum of the doubly ionised atom, which is known only in the case of Al_{III}. For this the S term is again the basic term, so that the first electron is bound in a 3_1 orbit. For Al_{II} the basic term is also an S term. For Al_I, however, the basic term is a P term. We are therefore led to believe that the three outer electrons of neutral aluminium are, as far as two are concerned, in 3_1 orbits, while the third is in a 3_2 orbit.

We have now considered the first three elements in the short periods. Fowler has shown that the basic term of the spectrum of C_{II} is a $^2P_1$ term, and for Si_{II} it is also a $^2P_1$ term. This is what we should expect if the first two electrons were bound in 2_1 and 3_1 orbits respectively for the two elements, while the third electron went to a 2_2 for carbon, a 3_2 for silicon. Recent work indicates that for the neutral atom of carbon there are two 2_1 and two 2_2 electrons, and in neutral silicon two 3_1 and two 3_2 electrons. The little that is known of the elements of the higher columns will be mentioned later, and we now turn to the long periods.

The Periodic System : Long Periods. In the first long period, potassium to krypton, we have already discussed the first

two elements, which fall into line with the first two elements of the short periods. To decide upon the distribution of the outer electrons for the third element, scandium, we require to know the basic term of the spectrum of the doubly ionised atom, which gives us the binding of the first of the outer electrons. We have already pointed out that, as the nuclear charge is increased, the relative strength of binding of an electron in a 3_3 and in a 4_1 orbit varies, since increasing Z by 1 (without changing the number of electrons) increases the strength of the field at points inside the L group, where the S orbit penetrates, by a comparatively small percentage, but at points nearer the surface, where the perihelion of the D orbit lies, by a very large percentage. Now the spectrum of Sc_{III} has not been directly analysed, but we can deduce something as to its behaviour by comparing the spectrum of K_I and of Ca_{II}, which are shown in Fig. 84 and Fig. 86 respectively. We see that, whereas with K_I the first D term is less than the first P term, with Ca_{II} it has advanced to a value exceeding the first P term, and only a little less than the first S term. It is to be presumed from this that a further increase of the nuclear charge by 1 would suffice to make the D term the basic one, or, in other words, that if to an atom consisting of a nucleus of charge 21, and 18 electrons arranged in neon form, be added a further electron, it will go to a 3_3 orbit,* in preference to a 4_1 orbit. There are arguments to show that the next two electrons added go to 4_1 orbits, the effect of the one 3_3 electron being to weaken the external field. For neutral scandium, then, one electron is in a 3_3 and the other two are in 4_1 orbits.†

This binding of the nineteenth electron of scandium in a 3_3 orbit, although with the preceding elements 4_1 orbits have been already occupied, is typical of the radically new conception introduced by Bohr. In it the modification of chemical properties found with the interpolated elements enclosed in frames in Fig. 77 finds expression. Scandium is, it is true, positively trivalent, just as is aluminium, but it differs in

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* It must be the $k = 3$ orbit which is vacant and most firmly bound; this is the 3_3 orbit.

† All through the discussion in this section it may be helpful to refer to the table of n_k orbits on p. 476, to which attention is accordingly directed in advance.

certain respects from the elements on the left of Column III. In many ways it resembles the rare earths. Thus the double alkali sulphates of scandium, *e.g.* $3K_2SO_4 . Sc_2(SO_4)_3$, differ from those of aluminium, *e.g.* $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$, but are comparable with some of the double sulphates of the rare earth elements. Scandium resembles the cerium group in the insolubility of its double potassium sulphate in saturated potassium sulphate solution. Further, scandium platino-cyanide exists in two states of hydration, which are homologous with the corresponding compounds of the cerium group, having 18 molecules of water, and of the terbium group, having 21 molecules of water, respectively. In its carbonate, also, scandium resembles the rare earths rather than aluminium. This deviation from the aluminium type is to be expected if the three outer electrons are, as we have argued, bound in scandium in a somewhat different manner from that prevailing with the tervalent elements of the short periods.

The elements from scandium to nickel are all peculiar in possessing very markedly the property of variable valency. If their highest valencies are considered, the valencies run normally, exhibiting the same steady increase as in the short periods, up to manganese, which last, for example, has a valency of seven in Mn_2O_7 or $KMnO_4$. It has also, however, a valency of two in MnO, three in Mn_2O_3, four in MnO_2 and six in potassium manganate K_2MnO_4. After manganese we have the well-known iron triad—iron, cobalt and nickel—the elements of which have properties falling right outside anything found in the short periods. The elements from titanium to nickel further possess properties which demonstrate the occurrence of a new feature in the structure : they all form coloured salts, and are all paramagnetic, while, as can be seen from Fig. 79, they all have very much the same atomic volume, the curve exhibiting a flattish minimum in this first period of eighteen, which is not found in the groups of eight. Scandium, it is true, forms colourless salts, but since, when an electron is first bound in a 3_3 orbit, the strength of binding is but little greater than that in a 4_1 orbit, it is not remarkable that the characteristic properties of the interpolated elements should not appear so markedly with the first element as they

do further on. We shall find, in general, that the element initiating or closing a group of interpolated elements has properties of both normal and interpolated elements.

Spectroscopic data, then, indicate that with scandium we begin to build up a sub-group of electrons having 3_3 orbits, which has no representative in potassium and calcium for reasons already given. Taking up the tale at titanium, we have to account for a cluster of elements with chemical properties not represented in the short periods. Ladenburg in 1920 emphasised the existence of the interpolated clusters titanium-nickel (22-28), niobium-palladium (41-46) and rare earths (58-71) with the following elements to platinum. Speaking in terms of the early theory in which the electrons were arranged in spherical shells, one shell corresponding to each periodic group, he proposed to account for these clusters by the formation of "intermediate shells" of electrons (*Zwischenschale*), built up to completion as we pass from one end to the other of the interpolated cluster. Bohr's theory shows how such intermediate groups of electrons are to be expected in terms of n_k orbits, owing to the different energies associated with orbits of the same n, but different k, and how spectral evidence can be invoked to show, for example, the point at which a 3_3 orbit would become more firmly bound than a 4_1 orbit. Bohr both extended the scope of the evidence, and introduced a general dynamical, or empirically speaking, spectral criterion which offered some guide as to the intermediate groupings. On Bohr's theory we must suppose that from scandium to nickel a group of 3_3 orbits is built up, and that the building up of this group is associated with the formation of coloured salts and with paramagnetic properties. As regards the formation of coloured salts, this indicates that within the atom (which cannot, when forming part of a solid compound or existing as an ion in solution, be excited by driving an electron to a virtual orbit, as it can when in the gaseous state) transitions are possible which involve comparatively small changes of energy, corresponding to visual frequencies. When the 3_3 orbits are being filled in preference to the 4_1 orbits there is probably not a great difference of energy in the binding for the two classes, since the greater energy of the 3_3

orbits is only a transitory affair. In other words, the balance between the 3_3 and the 4_1 is fairly close, the 3_3 starting to over-come at scandium, and ceasing to be the stronger at nickel, after which the 4_1 rapidly increases in firmness of binding. Generally, therefore, we should expect transitions of small energy difference to be possible during the completion of the 3_3 groups. Of course the outer electrons are involved in the chemical combination, so that the colour of different salts will be different, but the colour of the ion in solution is more or less fixed. The relatively slight difference in the closeness of binding between the two classes of electrons is also respon-sible for variable valency. As regards paramagnetism, this must be in some way associated with the *internal* asymmetry of the atom which appears while an internal group is being built up. With the first electron going to a 3_3 orbit a wound, so to speak, appears in the *internal* symmetry which continues until sufficient electrons have been bound to heal the wound by forming a symmetrical structure.

When the scandium-nickel group is completed we come to copper, where we find both spectral and chemical evidence for a new stage in the structure. Chemically, there is a sudden decrease of valency after nickel, copper being monovalent in many compounds, such as Cu_2O. It is placed in Column I with the alkali metals, although it has many important dif-ferences, forming, for instance, cupric salts in which it is di-valent, like nickel. It also forms coloured salts. It therefore has properties midway between nickel and the Column I elements, and shows that ambiguity which we have already mentioned as characteristic of elements at the beginning and end of interpolated groups. We may, perhaps, be allowed to call such elements ambiguous elements. The chemistry text-books seem to keep a discreet silence as to why copper is placed in Column I. The chief reason would appear to be that the following element, zinc, clearly belongs to Column II, so that, to make a symmetrical table, there seems nowhere else to put copper. Spectrally, copper is also peculiar ; it gives a doublet system, like the alkali metals, but it also gives a quartet system, as recently established by Beals, so that once more it only half belongs to Column I. In the doublet system the first

S term is the greatest. We believe that with copper the 3_3 sub-group is complete, with 10 electrons,* forming a complete core with 18 electrons of total quantum number 3 : the 29th electron is in a 4_1 orbit. This would account for the spectral and chemical properties which copper shares with other elements of Column I, the single privileged electron being responsible for them. After the intermezzo, so to speak, we begin again on the same theme as at the beginning of the period. It is, however, reasonable to suppose that the 4_1 electron and the more loosely bound 3_3 electrons (supposing the 3_3 sub-group subdivided into grouplets of different firmness of binding) do not differ much in firmness of binding. The explanation of the fact that, although copper behaves similarly to the alkali metals in some respects, yet it also has a certain resemblance to the late interpolated elements, must be sought for along these lines.

The copper ion is very small, much smaller than that of sodium or potassium, as may be gathered, without detailed discussion, from Fig. 79. (Other considerations lead to the same conclusion.) This has a remarkable result with regard to the principal quantum number of the first P term. A circular 2_2 orbit will be completely clear of the core, in an approximately Coulombian field, and so be a possible virtual orbit. Accordingly we find for this term n_e is nearly 2, as can be gathered from the table on page 444, or from Fig. 84. We may thus have, in the case of a small core, both real and virtual orbits of the same n. The first D and F terms are, of course, represented by 3_3 and 4_4 orbits.

As we take Z larger the relative firmness of binding of the deeply penetrating 4_1 orbits, or even 4_2 orbits, increases in comparison to the outlying 3_3 orbits, and the properties of the elements of the short period are more closely imitated. Thus zinc is positively divalent, and has no other valency, just like calcium. The. basic term of the Zn_I spectrum is an S term. The basic term of the Ga_I spectrum, on the other hand, is a P term. We conclude that, starting at copper, the building up of the $n=4$ orbits proceeds just as does the building up of

* The number of electrons in each n_k orbit is discussed hereafter, when the subdivision of the n_k orbits is in question.

the $n=2$ orbits for the lithium period, or of the $n=3$ orbits for the sodium period.

The following table of n_k orbits for the potassium-krypton period embodies very recent results obtained by Hund from a detailed theory of complex spectra, which receives mention in Chapter XV. It will be seen that the 3_3 sub-group starts with scandium, and reaches its full and symmetrical completion with copper. Under each n_k value is tabulated the number of electrons in that class of orbit for the given element.

n_k SCHEME FOR ATOMS OF THE FIRST LONG PERIOD.

Element.		n_k Values.							
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2
18	Ar -	2	2	6	2	6	—	—	—
19	K -	2	2	6	2	6	—	1	—
20	Ca -	2	2	6	2	6	—	2	—
21	Sc -	2	2	6	2	6	1	2	—
22	Ti -	2	2	6	2	6	2	2	—
23	V -	2	2	6	2	6	3	2	—
24	Cr -	2	2	6	2	6	5	1	—
25	Mn -	2	2	6	2	6	5	2	—
26	Fe -	2	2	6	2	6	6	2	—
27	Co -	2	2	6	2	6	7	2	—
28	Ni -	2	2	6	2	6	8	2	—
29	Cu -	2	2	6	2	6	10	1	—
30	Zn -	2	2	6	2	6	10	2	—
31	Ga -	2	2	6	2	6	10	2	1
36	Kr -	2	2	6	2	6	10	2	6

The general nature of Bohr's interpretation of the long periods is expressed in the first long period which we have just considered, and we can now pass over the remaining periods comparatively quickly. The spectra of neutral rubidium, neutral strontium, and ionised strontium show the same features as those of their lower homologues (cf. Figs. 84 and 86), and lead to the conclusion that the first two electrons of the new O group are bound in 5_1 orbits, while the first electron of yttrium is bound in an orbit of lower n, namely a 4_3 orbit. The interpolated elements from yttrium to palladium, which correspond element for element so closely to the scandium-nickel group (cf. Fig. 77), are interpreted as accompanying the building up of the 4_3 sub-group to a total of 10 electrons, just as the interpolated

elements of the first long period are represented by a building up of the 3_3 sub-group. We again have paramagnetism and coloured salts as soon as the 4_3 sub-group is established. When we come to the first element following the interpolated group, namely silver, we find a closer correspondence to the alkali metals than we do in the case of copper in the period before. Spectroscopic and chemical properties agree on this point in a remarkable way. Silver is strictly monovalent; it does not form argentous and argentic salts. Similarly its spectrum consists of a doublet system only, no quartet system having yet been established. If the S terms be omitted, the spectral terms of silver have the same n, and nearly the same n_e, as those of lithium : the S terms have much higher n for silver than for lithium (first S term for silver is 5_1, for lithium 2_1), and also markedly greater n_e (cf. Fig. 84). It may be noted that lithium metal decomposes water much more slowly than sodium, while silver does not decompose water at all, a fact which may be a chemical expression of this feature of the structure. In other chemical properties in which it differs from the other alkali metals lithium resembles silver. Silver has, however, well-known chemical analogies to copper, and is therefore placed under copper in the periodic table, the three " coinage metals " being always grouped together. The elements from cadmium to xenon correspond closely to those from zinc to krypton, and are represented in the model by the completion of the. 5_1 and 5_2 sub-groups to 2 and 6 electrons respectively.

When we come to the period of 32, caesium to radon, which contains the rare earths, new features appear. With xenon we have three completed groups—the K, L and M groups—and two incompleted groups : the N group, in which all the 4_1, 4_2 and 4_3, but no 4_4, orbits are occupied ; and the O group, in which all the 5_1 and 5_2 orbits are occupied. By analogy with the other periods we anticipate that with caesium and barium, which are chemically and spectrally completely analogous to sodium and magnesium, the first two electrons of the new period are bound in 6_1 orbits, belonging to the P group. There exists the possibility of two interpolated assemblages, corresponding to the further building up of the

N and O groups, and this in fact is what we find. The chemical properties of lanthanum indicate that a further development of an inner group begins with this element. Lanthanum resembles calcium and magnesium in many general properties ; for instance, lanthanum hydroxide has all the properties of calcium hydroxide, and is a stronger base than the other rare earth hydroxides. On the other hand, lanthanum agrees with the other rare earths in many ways : the heat of formation of its oxide is particularly high, and its oxalate is soluble with difficulty in mineral acids, to mention two typical rare earth properties. According to Bohr's scheme (Fig. 77) lanthanum, however, is not grouped with the other rare earths, cerium to lutecium. A discussion of this point would take us into a detailed chemical description of the element, without any very decisive result, for lanthanum is certainly very like cerium in many respects. However, the two elements differ in respect of certain oxide properties : for instance, La_2O_3 can be made by igniting the hydroxide, nitrate, oxalate or carbonate, while Ce_2O_3 cannot be made by this method ; and, further, while lanthanum only forms this one definite oxide, cerium forms CeO_2 and possibly other oxides.* Lanthanum stands alone in that all the rare earths, except lanthanum, give sulphates crystallising with 8 molecules of water. On Bohr's view the fifty-fifth electron added to the lanthanum nucleus is bound in a 5_3 orbit, thus initiating the 5_3 sub-group. With cerium, however, the last bound electron goes to a 4_4 orbit, and the group of rare earths from cerium to lutecium corresponds to a building up of the 4_4 sub-group to a total of fourteen electrons. All these rare earths form coloured salts † and have high paramagnetism : lanthanum forms colourless salts and is feebly, if at all, paramagnetic.

The binding of the 4_4 electron with cerium seems reasonable. Adding the fifty-fifth electron to a xenon-like structure about a nucleus of $Z = 58$, we have an external field which is relatively strong, and, owing to the small size of the core, a 4_4 orbit will lie comfortably clear of it. The N group is completed to a

* Quite generally lanthanum forms only one series of salts, while cerium gives rise to ceric and cerous salts.

† Ce^{III} salts are colourless, but Ce^{IV} salts are coloured, yellow to red.

total of thirty-two electrons with lutecium,* which should therefore, if the n_k interpretation of the periodic system be correct, close the rare earth group. This completion of the rare earths with $Z=71$, first deduced by Bohr, is a very important point, which led to the discovery, announced in 1923, of the element hafnium. The very feeble paramagnetism of lutecium might, in any case, have led to a suspicion that the rare earths closed with this element : it is a further confirmation of Bohr's theory.

Once the N group is completed we must suppose, in order to account for the chemical analogy between tantalum, niobium (columbium) and vanadium (which form respectively tantalates, columbates and vanadates, and tantalic, columbic and vanadic acids) that the building up of the 5_3 orbits is in progress, just as for the homologous elements the occupation of the 3_3 or 4_4 orbits occurs. In accordance with chemical analogies summarised in the periodic table, from tantalum to platinum we add successive electrons in 5_3 orbits, until with platinum $(Z=78)$ we have ten electrons in such orbits. There is only general chemical evidence for this. When we reach gold $(Z=79)$ we have an element exhibiting certain analogies with the other coinage metals, silver and copper, which have already been discussed. However, besides the monovalent compounds, such as AuCl, gold forms compounds in which it is trivalent, such as $AuCl_3$, so that the Column I properties are not so marked with gold as with silver. In fact, were it not for the behaviour of the succeeding elements, the evidence for putting gold in Column I would be slight : it is one of the ambiguous elements. The analysis of the Au_I spectrum recently made by McLennan and McLay indicates that with gold we have a single outer electron in a 6_1 orbit. The gold ion is about the same size as the silver ion, so that we may expect P terms with an effective quantum number not differing much from 2, and D and F terms with effective quantum numbers 3 and 4. The mercury and thallium spectra, to discuss which would occupy too much space, indicate that with mercury the last

* In Bohr's original diagram the frame stops below ytterbium. The evidence seems to show, however, that it should include lutecium, and in Fig. 77 it has, accordingly, been so shown.

two electrons are bound in 6_1 orbits, while with thallium the additional electron is in a 6_2 orbit. Then follow elements about which too little is known to allow a definite allocation of orbits. The period concludes with radon, with an outer group of two electrons in 6_1 orbits and six in 6_2 orbits, an arrangement analogous to that of the other inert gases.

A word may be said as to the periodic table, printed on page 426, which, with slight differences, is given in the standard text-books of chemistry. In these text-books the more obvious chemical analogies, such as those existing between the various halogens, are stressed, but very little is done in the way of discussing the reasons for the placing of less obvious elements in their columns. The fact is that, when all the chemical properties are considered, the arguments are often far from conclusive for a given element. In such cases it is only by considering the neighbouring elements that a place can be allotted. Elements in one column, but on different sides, such as copper and potassium, are often markedly unlike, while even elements on the same side of a column, as copper and silver, are often dissimilar.

The table has, of course, been presented in many forms, differing more or less from that printed at the beginning of the chapter, for each of which advantages are claimed. One that appears to the writer to have points of interest is given as an example on the opposite page. The general scheme is due to Rydberg ; slight modifications have been introduced to bring it into conformity with modern views. Each column contains, in general, two vertical series of elements, placed to the left hand and the right hand respectively. The maximum positive valency of the one series added to the maximum positive valency of the other series gives 8 : as a consequence of Abegg's rule, elements which have negative valencies have a maximum negative valency equal in magnitude to the maximum positive valency of the other series in the same column. The elements in a period run across the table from left to right until the mid element is reached, when they double back on themselves and run from right to left. This method of representation stresses the important point that the inert gases are turning-points, separating electronegative from electro-

MODIFIED FORM OF RYDBERG'S PERIODIC TABLE.

Period	o	+1 / -1 / +7	+2 / -2 / +6	+3 / -3 / +5	+4 / -4 / +4	+5 / +3	+6 / +2	+7 / +1	+8	o	
1	2 He	1 H									
2	10 Ne	3 Li / 9 F	4 Be / 8 O	5 B / 7 N	6 C						
3	18 A	11 Na / 17 Cl	12 Mg / 16 S	13 Al / 15 P	14 Si						
4	36 Kr	19 K / 35 Br	20 Ca / 34 Se	21 Sc / 33 As	22 Ti / 32 Ge	23 V / 31 Ga	24 Cr / 30 Zn	25 Mn / 29 Cu	26 Fe	28 Ni	27 Co
5	54 Xe	37 Rb / 53 I	38 Sr / 52 Te	39 Y / 51 Sb	40 Zr / 50 Sn	41 Cb / 49 In	42 Mo / 48 Cd	43 Ma / 47 Ag	44 Ru	46 Pd	45 Rh
6	86 Rn	55 Cs / 85	56 Ba / 84 Po	Rare Earths / 83 Bi	72 Hf / 82 Pb	73 Ta / 81 Tl	74 W / 80 Hg	75 Re / 79 Au	76 Os	78 Pt	77 Ir
7		87	88 Ra	89 Ac	90 Th	91 Pa	92 U				

Maximum valency (column headers, left to right): o ; +1 / −1 / +7 ; +2 / −2 / +6 ; +3 / −3 / +5 ; +4 / −4 / +4 ; +5 / +3 ; +6 / +2 ; +7 / +1 ; +8 ; o

positive elements : it also throws into relief the peculiar position of carbon and silicon, which have no chemical analogues. It emphasises Abegg's law, and is particularly suited to be considered in conjunction with Fig. 78. The uniform spacing of the elements in columns agrees better with the spectroscopic evidence than the bunching together of the triad elements in Column VIII in the usual table, as a protest against which we divided Column VIII into three. While, however, the law of alternation of odd and even multiplicities demands a regular progression of the elements in the middle of the long periods it seems to demand a turning-point at manganese, which the table does not show. The elements to the right and to the left in one column have, in this form of table, no chemical analogies to one another, and this is, in a way, an advantage, since the attempt to trace chemical analogies between the right and left hand divisions in the column in Mendeléeff's table has been the cause of much confusion.

The table just described does not, of course, any more than any of the other forms, overcome the general difficulties, such as the fact that the first (uppermost) element in a column is not the typical element. This must be of fundamental structural significance. In fact, in all its forms the periodic table is generally represented as expressing regularities of chemical behaviour to an extent which actually it fails to achieve.* Rather, it is a bridge to knowledge consisting of a series of spans whose ends rest firmly upon the alkali metals and the inert gases ; the superficial resemblance of the spans to one

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* Occasionally, however, a chemist, irritated by the imperfection of the table, has rebelled against it altogether, and gone to the length of denying its value. Thus two French chemists, Wyrouboff and Verneuil, reject considerations based on the periodic classification, which they accuse of being a metaphysical (rather than a physical) conception. Supporting the divalence of the rare earths as against the trivalence they write (*Ann. de Chim. et de Phys.*, 6, 466, 1905), " Parmi les arguments présentés jusqu'ici, en bien petit nombre d'ailleurs, celui qui dans l'esprit des partisans de la trivalence domine de beaucoup tous les autres, *est d'ordre purement métaphysique,* c'est l'exigence du système périodique qui n'a de place pour les terres rares que si elles consentent à devenir des sesquioxides.... Il a fallu recourir à toutes sortes d'artifices ... c'est à dire à des hypothèses qui ne sont même plus de la métaphysique, et appartiennent au domaine de la fantaisie pure, sur lequel la science exacte n'a aucune prise."

Tant de fiel entre-t-il dans l'âme des dévots ?

another often conceals special structural features dictated by local stresses of which we can see nothing.

The general scheme of n_k orbits is given in the table on the following page, which may be supplemented by Hund's recent table for the first long group, given on page 468. Reference should also be made to the table constructed by McLennan, McLay, and Smith, given in Appendix V., which appeared too late to be discussed in the body of the book. In Bohr's original scheme, which first indicated the origin of the interpolated elements, and the meaning of the spectra in terms of n_k orbits, the distribution was somewhat different, in that, once a group was completed, the same number of electrons were supposed to exist in each class of orbit—thus the completed L group consisted of four electrons in 2_1 and four electrons in 2_2 orbits ; the complete M group consisted of six electrons in each class of orbit for which $n=3$, viz. 3_1, 3_2, 3_3 ; the completed N group contained eight electrons in each class of orbits for which $n=4$. The work of Stoner and Main Smith, discussed later in connection with the subdivision of the n_k sub-groups, has, however, indicated the distribution here given, which is now in a fair way to being generally accepted.

The folding sheet at the end of the volume * gives schematic diagrams of the structure of certain atoms, prepared by Kramers in accordance with Bohr's views. These show the old idea of electronic distribution, with equal numbers of electrons in, e.g., 3_1, 3_2 and 3_3 orbits when the M group is completed. Although this is now discredited, the diagram retains much of its interest, as showing the interpenetration of the orbits, the structure of elements of Column I as regards the privileged orbits, the approximate dimensions of the outer orbit as compared with the core, and other general features.

The Missing Elements. In order to discuss the most spectacular triumph of this scheme of Bohr's, we may digress for a moment to consider the discovery in 1922 of the element $Z=72$, hitherto unknown. Previously to Bohr's discussion of the periodic table, it had been assumed that this element must be a rare earth, to which is due the somewhat involved con-

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* Inserted by kind permission of Messrs. Gyldendal, the publishers of *The Atom*, by Kramers and Holst.

Group	K	L	M	N	O	P	Q
Quantum Numbers	1_1	2_1 2_2	3_1 3_2 3_3	4_1 4_2 4_3 4_4	5_1 5_2 5_3 5_4 5_5	6_1 6_2 6_3	7_1 7_2
Element							
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 1					
10 Ne	2	2 6					
11 Na	2	2 6	1				
12 Mg	2	2 6	2				
13 Al	2	2 6	2 1				
18 A	2	2 6	2 6				
19 K	2	2 6	2 6	1			
20 Ca	2	2 6	2 6	2			
21 Sc	2	2 6	2 6 1	2			
22 Ti	2	2 6	2 6 2	2			
29 Cu	2	2 6	2 6 10	1			
30 Zn	2	2 6	2 6 10	2			
31 Ga	2	2 6	2 6 10	2 1			
36 Kr	2	2 6	2 6 10	2 6			
37 Rb	2	2 6	2 6 10	2 6	1		
38 Sr	2	2 6	2 6 10	2 6	2		
39 Y	2	2 6	2 6 10	2 6 1	2		
40 Zr	2	2 6	2 6 10	2 6 2	2		
47 Ag	2	2 6	2 6 10	2 6 10	1		
48 Cd	2	2 6	2 6 10	2 6 10	2		
49 In	2	2 6	2 6 10	2 6 10	2 1		
54 X	2	2 6	2 6 10	2 6 10	2 6		
55 Cs	2	2 6	2 6 10	2 6 10	2 6	1	
56 Ba	2	2 6	2 6 10	2 6 10	2 6	2	
57 La	2	2 6	2 6 10	2 6 10	2 6 1	2	
58 Ce	2	2 6	2 6 10	2 6 10 1	2 6 1	2	
59 Pr	2	2 6	2 6 10	2 6 10 2	2 6 1	2	
71 Lu	2	2 6	2 6 10	2 6 10 14	2 6 1	2	
72 Hf	2	2 6	2 6 10	2 6 10 14	2 6 2	2	
79 Au	2	2 6	2 6 10	2 6 10 14	2 6 10	1	
80 Hg	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
81 Tl	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1	
86 Rn	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
87 —	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
88 Ra	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
89 Ac	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2 1
90 Th	2	2 6	2 6 10	2 6 10 14	2 6 10		
118 (?)	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 10	2 6

troversy which centred about the discovery. The situation is now tolerably clear, and a short summary may not come amiss.

. According to Bohr's argument, the rare earths end at $Z=71$, lutecium. The naming of this element itself has been a subject of controversy. In 1878 Marignac isolated a substance which he considered to be an element of rare earth nature : he named it ytterbium, after Ytterby in Sweden, where gadolinite * is found. Auer von Welsbach succeeded in 1905 in proving that this reputed element was really a mixture of two elementary rare earths, to which he later gave the names aldebaranium and cassiopeium. In 1907 Urbain published an investigation of these two earths, containing particulars of their optical spectra, and proposed the names neo-ytterbium and lutecium. The " neo " was afterwards dropped, and the elements are to-day usually known as ytterbium $(Z=70)$ and lutecium $(Z=71)$. In 1911, as a result of further investigation of his specimens, Urbain announced the discovery of a further rare earth, which he named celtium. He attributed to it a group of unknown lines in the optical spectrum. This celtium preparation was investigated in 1914, in the course of his X-ray researches, by Moseley, who pronounced it to be a mixture of known earths, and not a new element.

It being clearly established that there was a missing element at $Z=72$, and the suspicion being that this must be a rare earth, it was held by Urbain and his supporters that celtium was, in fact, this element, and in some periodic tables it actually appears as Ct in the Column IV. Moseley's result was attributed to imperfect technique. In 1922 Dauvillier, an expert in X-ray technique, announced that he found with Urbain's preparation not only the characteristic X-ray lines of the elements 70 and 71, and a few weak lines of 69, but also two extremely weak lines attributed to 72. The French school held accordingly that Urbain's celtium with its optical lines was established as the unknown element 72.

About this time, Bohr's theory, of which a short account has just been given, led to the definite conclusion that 72, instead of being a rare earth, must be an analogue of zirconium, and

* A mineral containing various rare earths named in its turn after the Finnish chemist, Gadolin.

so suggested a radically different method of search for the missing element. Coster and Hevesy undertook an investigation based on the new conception in Bohr's Institute in Copenhagen. With the first specimens of zirconium investigated with the X-ray spectrograph they were able to establish the presence of two lines exactly in the position which interpolation from known spectra would indicate for La_1 and La_2 of 72. They then undertook a chemical separation of the new element from zirconium, which Hevesy calls " un des problèmes les plus ardus de la chimie inorganique," making use of the intensity of the X-ray lines to obtain an estimate of the concentration of element 72 at various stages of the process of isolation. They adopted the ingenious process of mixing known quantities of tantalum ($Z=73$) with their specimens, and finding what percentage of tantalum was required to give equal intensity of selected lines of the X-ray spectrum of 72 and of tantalum. In this way a quantitative analysis was performed without chemical manipulation, a fact which is mentioned here to draw attention to the power of the X-ray method. After having prepared a specimen of zirconium which gave no trace of the lines attributable to 72, while the concentrated preparation of the new element gave such lines very strongly, Coster and Hevesy definitely claimed the discovery of a new element, which they named Hafnium, after the old Latin name for Copenhagen, Hafnia. Bohron might have been an appropriate name, but would be liable to confusion with $Z=5$.

Since then extensive investigations of the chemical and physical properties of hafnium have been carried out, and specimens sufficiently pure for atomic weight determination have been prepared, the best value for the atomic weight being 178·6. It is interesting to note that, since all ordinary zirconium preparations contain hafnium, determinations of the atomic weight which take no account of this fact must, if carried out correctly, give values which are too high. It so happens that all the determinations previous to that of Venable and Bell gave values which were too low (about 90·6), owing to defective methods. Venable and Bell in 1917 found, using modern principles, the value 91·76. Hevesy found a hafnium

content varying between ·7 and 1 per cent. in Venable and Bell's samples, allowing for which the atomic weight of zirconium reduces to 91·3. This agrees excellently with Hönigschmidt and Zintl's value obtained since the discovery of hafnium, namely 91·25.

It is estimated that hafnium forms nearly ·001 per cent. of the earth's crust, which may be compared with the estimate ·005 per cent. for nickel. Its terrestrial occurrence is probably about the same as that of lithium and copper, and much greater than that of silver and gold. In zirconium minerals the ratio of hafnium dioxide to zirconium dioxide varies from 5 per cent. (thortveitite) to ·7 per cent. (favas), Hevesy giving the mean as about 3 per cent. It is therefore astonishing that hafnium was not discovered as a result of systematic atomic weight determinations, as was argon. Argon in the atmosphere is about 1·9 per cent. by weight of its associated nitrogen. It is remarkable that these two common elements were both discovered by physical methods, owing to their chemical similarity to elements with which they co-exist.

The claims of the French school that Dauvillier's lines were actually due to a trace of hafnium, and that therefore Urbain's preparations contained hafnium, and that therefore hafnium is really celtium, can scarcely be upheld. Coster and Hevesy have shown that the relative intensities of the lines detected by Dauvillier are all against their hafnium origin, and the fact that the preparations had been carefully freed from zirconium by ordinary chemical methods renders it practically certain that all hafnium had been removed. In any case, as Paneth has emphasised, the observation of two very feeble X-ray lines, wrongly attributed to a non-existent rare earth, can scarcely rank as the discovery of an element. If we have discussed rather more fully than is perhaps justified by the scope of this chapter the discovery of hafnium it is because, in view of the confusion that has existed, and the fact that nothing is yet to be found on the subject in English text-books, it seemed that this brief exposition might be of interest.

A word on the subject of the other missing elements may be inserted here, although their discovery has not the interest associated with the hafnium investigations for the immediate

subject of discussion, *i.e.* the explanation of the periodic table in terms of electronic orbits. The elements in question are those of atomic number 43, 61, 75, 85 and 87 (and all for which the atomic number exceeds 92). Of these, 43 and 75 fall under manganese in the periodic table, and should be homologues of this metal : their existence was predicted by Mendeléeff, who named them eka-manganese and dwi-manganese, the prefixes being Sanskrit numerals indicating first and second.* 61 is a rare earth, 85 is a homologue of iodine (eka-iodine), and 87 is a homologue of caesium (eka-caesium).

The discovery of the eka-manganeses was announced in 1925 by Noddack and Tacke, and by Berg and Tacke, the former pair having carried out the chemical work, and the latter pair the X-ray spectrographic work, upon which reliance was placed for the identification. W. Hausser, in whose laboratory in the Siemens and Halske concern the latter part of the work was carried out, seems to have initiated the investigation. The investigators decided on grounds of general chemical analogy with neighbouring elements that both eka-manganeses would be found together and that platinum ore, which contains a collection of neighbouring elements (atomic numbers 24 to 29, 44 to 47, and 76 to 79), would offer a likely source, while colombite, which contains a different set of neighbouring elements, might be another. Suitable chemical methods were employed to concentrate elements of the properties to be anticipated in the eka-manganeses, colombite being used, as a supply of platinum ore originally accessible was lost. A content of the new elements in the neighbourhood of 1 per cent. was anticipated in the final preparations, and the X-ray method of identification was adopted. The substance was mixed with a niobium compound (niobic acid) to give standard lines for comparison. The identifications of 43 and 75 appear to be satisfactory. The investigators suggested the names Masurium (Ma) for 43 and Rhenium (Re) for 75, after the Masurian district of East Prussia and the German Rhine respectively. The elements are showing a strong sense of nationality. Since then Dolejšek and Heyrovsky claim to

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* For convenience the two are often referred to together as the eka-manganeses.

have identified 75 in manganese salts by electrolytic methods, and have isolated by electrolytic means a substance which they have identified by X-rays as 75.*

Quite recently (June 1926) J. H. Harris, L. F. Yntema and B. S. Hopkins have announced the discovery of the rare earth 61, to which they have given the name Illinium, since it was discovered at the University of Illinois. The number 61 falls in the so-called cerium group of the rare earths, distinguished from the other, or yttrium, group by many properties, among which the solubility of the double potassium sulphates may be cited. Monazite sands were selected for the investigation : they contain a predominance of elements of the cerium group, and are, in fact, used in commerce for the preparation of cerium products for gas mantles. The presence of the new element, concentrated by re-crystallisation of a bromate preparation rich in neodymium, was progressively traced by the optical absorption spectrum of the solutions. The proof of the presence of 61 in the final fractions was delivered by the X-ray spectrum. It appears that illinium, for which the symbol Il is proposed, is present in very small quantities even in rare earth minerals.

X-Ray Periodicities. Although the frequency of the X-ray lines shows no perceptible periodic properties when plotted against Z, valuable evidence as to the building up of groups and sub-groups can be drawn from X-ray results, by considering the term values. Bohr and Coster, after a careful analysis of all available X-ray results, both emission lines and absorption lines being studied, plotted $\sqrt{\nu/R}$ against Z (ν being the wave-number of a given term) for the various levels K ; L_I, L_{II}, L_{III} ; M_I, M_{II}, M_{III}, M_{IV}, M_V, and so on. The results are shown in Figs. 87 and 88, Fig. 88 being the right-hand lower portion of Fig. 86 shown on a larger scale. It will be seen at once that, while the K curve has the approximately straight line form demanded by Moseley's law for X-ray line values,

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* Druce has prepared from crude manganese sulphate a sample which he claims to be rich in 75. Loring and Druce have pushed the X-ray method to, and slightly beyond, the limit, having asserted the presence of 75, 85, 87 and 93 in their preparation from lines on X-ray plates without near comparison lines, and they still have some lines in hand. This discovery awaits confirmation.
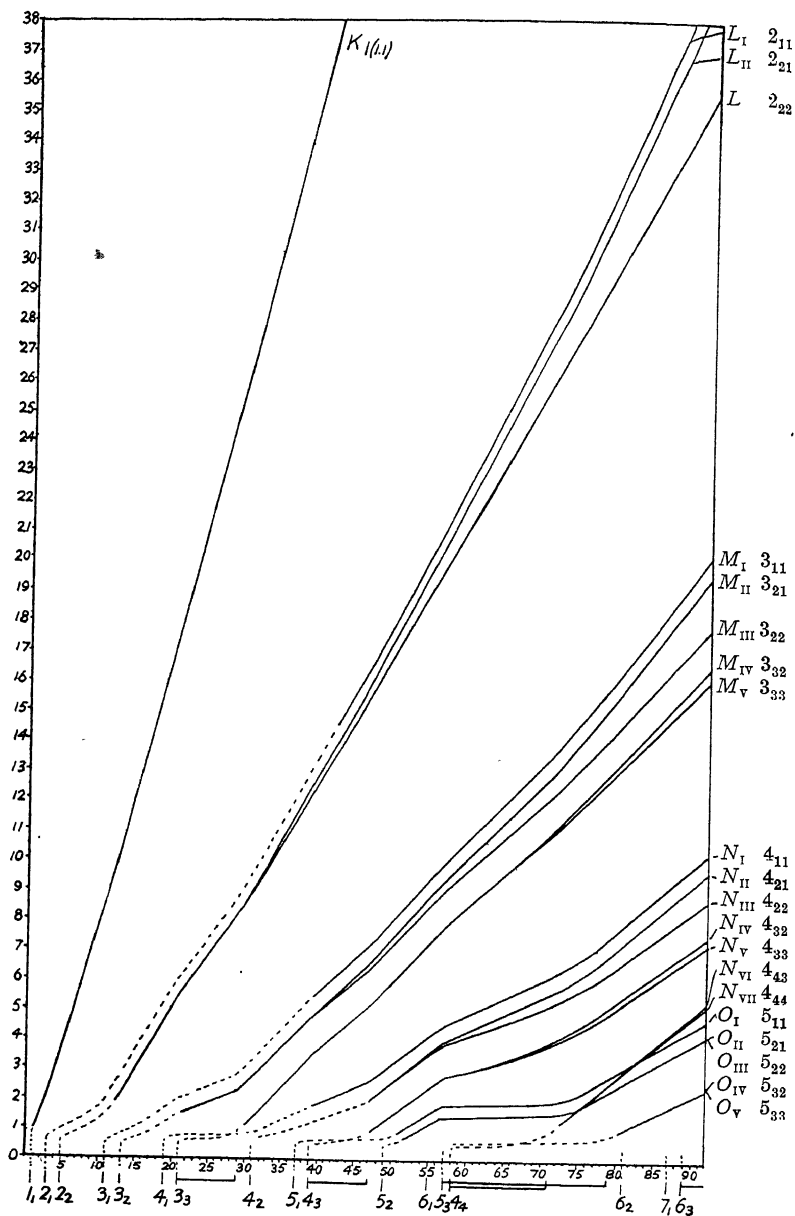
FIG. 87.

$\sqrt{\nu/R}$ for X-ray terms plotted against atomic number.
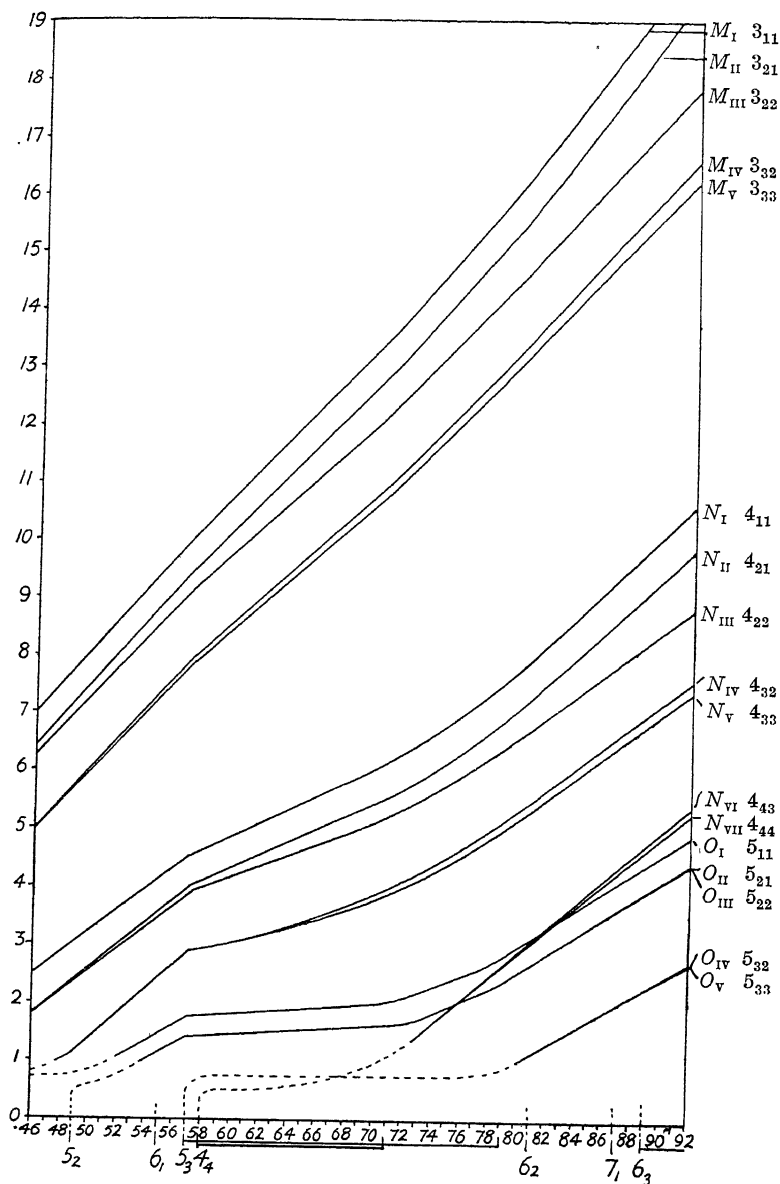
Fig. 88.

$\sqrt{\nu/R}$ for X-ray terms plotted against atomic number. (Part of Fig. 87 enlarged.)

the other curves all exhibit abrupt changes of direction at certain points. These discontinuities of direction obviously mark certain stages in the building up of the atom : their significance will now be somewhat more closely discussed.

In Chapter XIII. we referred to the screening produced by the outer electrons, *i.e.* those less firmly bound than the electrons of the particular level whose energy is in question, and expressed the effect, to a first approximation, by an outer screening constant $n^2 S_{Z_n}$, n being the principal quantum number of the screened group. Considering the outer screening constant as an expression of the increased firmness of binding of the outer electrons consequent on the removal of an electron from the n_k level, we see that the electrons in the level immediately above n_k are mainly concerned in the outer screening : electrons far out can have little effect, since in any case their energy of binding is relatively small, so that the change in it must also be small. It follows that when a level just above the n_k level is being built up, the outer screening constant is increasing rapidly, so that the slope of the curve exhibiting the change of term energy with Z for the given level must be relatively small. When the level in question is completed, and the next electrons go to a level of higher n, the rate of increase of the outer screening constant becomes suddenly smaller, and the slope of the curve should increase. We expect, then, that, on a $\sqrt{\nu/R}$ against Z curve, a region in which there is a smaller slope, inserted between two regions where the slope is larger, should correspond to the building up of an internal, or interpolated, family.

Such regions of smaller slope are indicated in Figs. 87 and 88 as follows :

Regions of small slope.	Curves indicating region.
$Z = 21$ to $Z = 29$	$M_{\text{II III}}$, $L_{\text{II III}}$
$Z = 39$ to $Z = 47$	N_{I}, all M levels
$Z = 57$ to $Z = circa\ 71$	O_{I}, $O_{\text{II, III}}$, all N levels and M levels

21 to 29 * is the region in which the interpolated group of elements scandium to nickel is built up in the potassium-

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* In all cases the last named value of Z, at which the change of slope occurs, may be considered to belong to the region of greater slope, and so to the next level, and not to the interpolated level.

krypton period: the new orbits belong to M_{IV} and M_V, and the most marked effect would be expected in the immediately preceding levels M_{II}, M_{III}, with a smaller effect in the L levels,
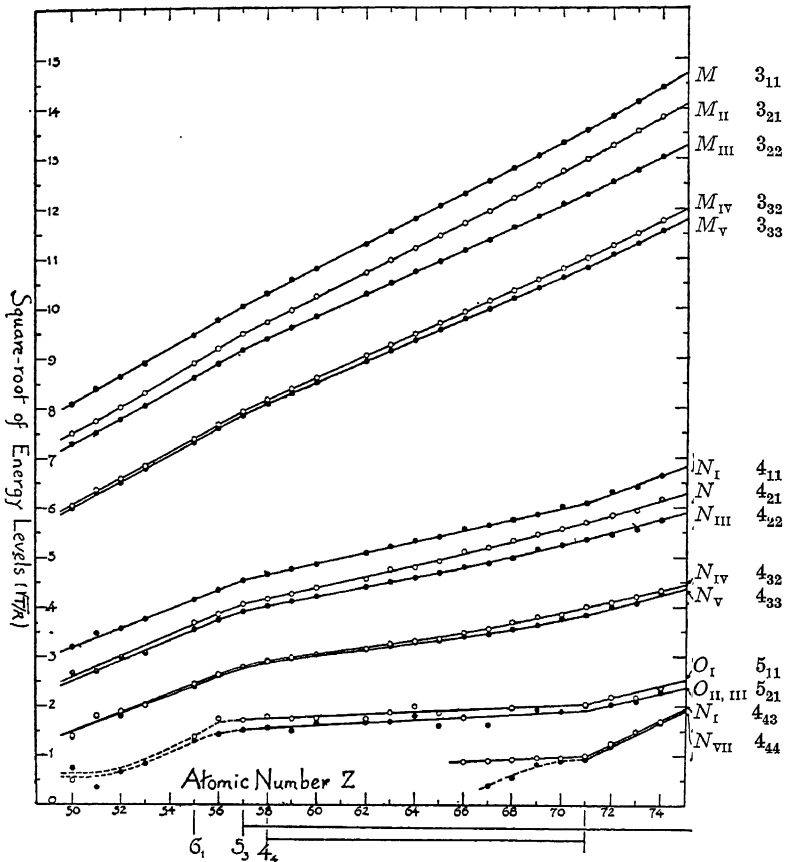
FIG. 89.

$\sqrt{v/R}$ for X-ray terms plotted against atomic numbers, for region $Z=50$ to $Z=74$.

as is seen to be the case (Fig. 87). 39 to 47 is the region of the interpolated yttrium-palladium group, the corresponding new levels being N_{IV} and N_V. 57 to 71 is the lanthanum-lutecium family, new levels N_{VI} and N_{VII} being built up. (The interpolated groups are indicated in Figs. 87 and 88 by

horizontal lines just under the Z axis.) The beginning of the interpolated group at $Z=57$ is particularly plainly shown in the O_{I} and $O_{\mathrm{II\,III}}$ levels, and also very well in the N_{I} to N_{V} levels. The termination of the group is not so plainly shown in Fig. 88.

Recently, however, Nishina, as a result of measurements of the L absorption spectra, has obtained values of the different energy levels in the region from $Sn(Z=50)$ to $W(Z=74)$, which are more accurate than those hitherto available. In particular he has provided values for the N_{VI} and N_{VII} levels, resolved separately, in the region $Z=66$ to $Z=74$, where they are only guessed in Fig. 88, and the corresponding curves show a very sharp change of direction at $Z=71$, marking the end of the rare earth family. Nishina's results are exhibited in Fig. 89. The behaviour of the other N curves, and the two O curves, in the neighbourhood of $Z=57$ is also instructive. On the whole, then, the X-ray level diagram gives strong evidence for interpolated levels just in the region where Bohr originally deduced them.

Interesting, but less precise, results can be obtained by noting the lowest value of Z for which a given line, and hence level, occurs, and comparing with the value of Z for which the level in question is, theoretically, first to be expected. The method is very rough, since it is difficult to say when a line first appears; as Z is diminished a given line becomes very faint before it actually disappears. According to Coster and Hjalmar, L lines involving the N_{IV} and N_{V} levels can be traced down as far as $Z=40$, while L lines involving O_{II} and O_{III} levels can be traced as far as 49. According to our scheme, 4_3 electrons first appear at 39, and 5_2 electrons at 49, which is in good agreement. Generally lines first appear perceptibly at a stage when, according to our scheme, the level has already been established for some few elements.

The Subdivision of the Sub-groups. So far we have considered only n_k orbits. In discussing the X-ray spectra, however, we have seen that n_k orbits will not suffice to give the observed number of levels, which are (taking K, L, M, N levels in order) 1, 3, 5, 7, instead of 1, 2, 3, 4. Each of these levels must be supposed to be represented by a certain number

of electrons. We have also seen that the levels may be represented by allotting two subsidiary quantum numbers k_1 and k_2 in place of the single k, the scheme being shown in the following table:

Level	K	L_I	L_{II}	L_{III}	M	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}
Quantum numbers	1_1	2_{11}	2_{21}	2_{22}	3_{11}	3_{21}	3_{22}	3_{32}	3_{33}	4_{11}	4_{21}	4_{22}	4_{32}	4_{33}	4_{43}	4_{44}
Optical doublet terms	1^2S_1	2^2S_1	2^2P_1	2^2P_2	3^2S_1	3^2P_1	3^2P_2	3^2D_2	3^2D_3	4^2S_1	4^2P_1	4^2P_2	4^2D_2	4^2D_3	4^2F_3	4^2F_4

Our task is now to decide how many electrons execute orbits belonging to each of these levels, which will, of course, incidentally tell us how many electrons occupy each n_k sub-group, since k is the first of the two subsidiary quantum numbers. For example, if the number of 3_{32} electrons is found to be a, the number of 3_{33} electrons b, then we may say that there are $a+b$ electrons in the 3_3 sub-group. We have called the electrons of the same n a group, and the electrons of the same n and k a sub-group: we shall call electrons belonging to a given energy level, say M_{III}, a grouplet. For electrons of a grouplet n, k_1, k_2 all have the same value.

The answer to the problem which at present holds the field was given in 1924 by Stoner and by Main Smith independently, the former approaching the problem from the physical, mainly spectral, point of view, the latter relying on chemical arguments. It is satisfactory that such different methods of attack should have led to the same result.

Considering the optical terms, the second subsidiary quantum number is the inner quantum number j already mentioned, which is usually taken as giving the moment of momentum of the atom as a whole. The anomalous Zeeman effect gives the number of possible different energy states of the atom in a weak magnetic field, i.e. the number of different positions, determined by space quantisation, of the moment axis of the atom in a magnetic field. This number is found to be equal to $2j$. These facts are discussed in Chapter XV.,* which we must anticipate here. We may say that $2j$ gives the statistical

* The question of half-odd-integer values of j, which need not trouble us here, is there discussed.

weight of the state represented by the n_{kj} orbit. Stoner proposed to interpret this experimental fact by making the hypothesis that, for a given grouplet specified by j (for which there are $2j$ possible orbits when the degeneracy is removed by a magnetic field) there are $2j$ different electrons when it is completed, or, in other words, electrons can be allotted to the grouplet until every possible orbit, revealed by the magnetic field, has an electron. When this stage has been reached the grouplet is complete, and the atom possesses a structure having a high degree of symmetry.

If we extend this idea to the real, as distinct from the virtual, orbit, we must suppose that each grouplet possesses, when completed, electrons to the number $2k_2$. Thus the number of electrons in each completed level will be given by the bottom line in the following table, obtained by multiplying the second suffix by 2.

K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}
1_{11}	2_{11}	2_{21}	2_{22}	3_{11}	3_{21}	3_{22}	3_{32}	3_{33}	4_{11}	4_{21}	4_{22}	4_{32}	4_{33}	4_{43}	4_{44}
2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	8

On this scheme the $2n^2$ electrons which exist in a completed group will be sub-divided into $n_{k_1 k_2}$ grouplets in a way represented by the formula :

$$2n^2 = 2 + 2 + 4 + 4 + \ldots + 2\,(n-1) + 2\,(n-1) + 2n$$
$$= 2\{2 + 4 + 6 + \ldots + 2\,(n-1)\} + 2n,$$

where n takes the value 1, 2, 3 ... for the $K, L, M \ldots$ group.* In the n_k scheme as originally put forward by Bohr, described in earlier editions of this book, the number of electrons in each n_k orbit of a completed group was $2n$, there being n different values of k, making $2n^2$ electrons in all. For example, take the N group. On Stoner's scheme the 4_1 orbit has 2 electrons ; the 4_2 orbit $2 + 4 = 6$ electrons ; the 4_3 orbits $4 + 6 = 10$ electrons ; the 4_4 orbit $6 + 8 = 14$ electrons ; making 32 electrons in all. On Bohr's original scheme, the 4_1, 4_2, 4_3,

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* The completion of a $K, L, M \ldots$ group does not represent the completion of a period in the periodic table, since for the rare gases (omitting helium and neon) the last group, although possessing a high degree of symmetry, is never complete, one or more sub-groups being vacant. Cf. table on page 476.

4_4 orbits each had 8 electrons when the group is complete, making 32 electrons as before. There is little doubt that the Stoner—Main Smith scheme gives a better representation of fact.

It is important to note that on the older schemes the outermost sub-groups reached a temporary stability, or partial degree of completion, with each inert gas, only to be built up further at a certain stage in the development of the next period. Thus the argon atom was supposed by Bohr to have 4 electrons each in the 3_1 and 3_2 sub-groups, this arrangement being very stable, but somewhere between titanium and copper two electrons each were added to these sub-groups, so that with krypton there were 6 electrons each in the 3_1, 3_2 and 3_3 sub-groups. In other words, the already stable 3_1 and 3_2 sub-groups had to be reopened, so to speak, at a later stage of the building up so as to admit 2 further electrons. Similarly the 4_1 and 4_2 sub-groups were stable with 4 electrons each in krypton, reached a second stable state with 6 electrons each in the rubidium-xenon period and a third stable state with 8 electrons each in the caesium-radon period. On Stoner's view a grouplet, once closed, is never reopened, further developments taking place by the addition of electrons to new grouplets. Instead of the 10 electrons added to the $n=3$ group between calcium and copper going 2 each to the 3_1 and 3_2 sub-group, and 6 to the 3_3 sub-group, the 3_1 and 3_2 sub-groups remain closed with 2 and 6 electrons respectively, as in argon, and the 10 electrons go to the 3_3 sub-group—4 to the 3_{32} grouplet, and 6 to the 3_{33} grouplet. The unpleasant tampering with an already closed sub-group is avoided.

Support for the 2, 2, 4 arrangement in the L group can be deduced from the X-ray spectra. In the first place we may consider the relative intensities of X-ray lines of the same series. If we select for discussion lines arising from transitions from different sub-levels of one group to the same final sub-level of another group, then, on the considerations of equal weight underlying Stoner's argument, we should expect the intensities of the lines to be proportional to the number of electrons in the initial sub-level considered. Complications due to intervening groups are avoided if we restrict ourselves to transitions

between adjacent main levels. Thus, taking the simplest case of $K\alpha$ lines, due to switches from L sub-levels to the K level, we compare the intensity of $K\alpha_1$ $(L_{\text{III}} \to K)$ with that of $K\alpha_2 (L_{\text{II}} \to K)$, which is one of the very few cases where reliable measurements of X-ray line-intensities are available. For a range of metals in different periods and different columns (iron, copper, zinc, molybdenum, tungsten) it is found that the ratio of intensities of $K\alpha_2$ to $K\alpha_1$ is the same in all cases, and has the value ·5 within experimental error. This is interpreted to mean that there are twice as many electrons in the L_{III} sub-level as in the L_{II} sub-level, no matter what the value of Z may be, which agrees with the attribution of 4 electrons to L_{III}, 2 to L_{II}, once the L group is completed.

Some interesting considerations based by L. de Broglie on X-ray absorption measurements have led to a similar result. This investigator, by applying considerations of thermodynamic equilibrium to the problem of absorption of X-rays, and making certain subsidiary assumptions for which justification is sought in empirical results, has calculated a theoretical expression for the absorption coefficient for a given ν. Each band is considered to pertain to an atomic absorption whose intensity varies as the cube of the wave-length (in accordance with the law of W. H. Bragg and Peirce) up to the edge of the band where the absorption discontinuity takes place, and the absorption suffered by a radiation of a given ν is due to the superposition of all bands whose edge is of frequency less than ν. The formula obtained is

$$\text{atomic absorption} = \frac{\tau A}{\rho} = \frac{\pi}{c^4}\frac{e^2}{m}\,\lambda^3\sum_p n_p \nu_p{}^2,$$

where A is the atomic mass, τ the absorption coefficient in question : n_p is the number of electrons in a completed grouplet of energy $h\nu_p$, and the summation is extended to all grouplets for which $\nu_p < \nu$. As, with increasing ν, we pass through a critical frequency corresponding to an absorption edge, the absorption changes abruptly, due to the sudden inclusion of a fresh grouplet under the summation sign.

It is clear, then, that the change of the absorption coefficient (allowance being made for changing λ) which takes place on

passage through an absorption edge furnishes a method of estimating the relative number of electrons in the different grouplets. Dauvillier has measured the intensity of absorption within the L absorption band, which contains the three absorption edges L_I, L_{II}, L_{III}, corresponding to the substructure of the L group. The measurements were carried out for gold, and gave

$$\frac{n_1}{n_2} = \cdot 78, \quad \frac{n_2}{n_3} = \cdot 495,$$

where n_1, n_2, n_3 are respectively the number of electrons in the 2_{11}, 2_{21}, and 2_{22} grouplets. Dauvillier states that $\cdot 78$ is approximately 1; this is, perhaps, a little optimistic, but in any case the actual ratio must be very simple, since

$$n_1 + n_2 + n_3 = 8,$$

and the value 1 is compatible with possible distributions.* Admitting this, we must have 2, 2 and 4 electrons in the 2_{11}, 2_{21} and 2_{22} grouplets respectively. The work has been carried out for one metal only, and the experimental agreement is not striking, but the method is ingenious.

There is chemical evidence for a first grouplet of two electrons only in all the groups, as pointed out by Main Smith. Elements of Columns I and II form oxides which are strongly basic, while characteristic elements of Column III, such as boron, aluminium and gallium, form oxides which are weakly acid, such as B_2O_3, or amphoteric, such as Al_2O_3. There is an abrupt cessation of characteristic alkaline properties on leaving Column II. The elements of Column II never behave as if univalent, *i.e.* will not part with one electron only in chemical combination, so as to give compounds such as Ca_2O. Main Smith states that elements of Column III, on the other hand, have properties which indicate that one valence electron is less firmly held than the other two. Possibly he is alluding to the supposed existence of aluminium sub-chloride $AlCl_2$, and sub-fluoride, and the ionic explanation of the behaviour of $Al(OH)_3$ as an acid hydroxide. The evidence brought

* *E.g.* if the number of electrons were 2, 3, 3, we should have $\frac{n_1}{n_2} = \cdot 66$, but $\frac{n_2}{n_3} = 1$, which is in even worse agreement with experiment.

forward does not appear overwhelming to the writer,* a fact
to which he would hesitate to confess were it not that many
experienced physical chemists appeared to appreciate his
difficulties. The decision must be left to the chemists.

As regards the long periods, the general arguments cited
apply to the first two electrons. The division of the 3_3 and
the 4_3 sub-groups into grouplets of 4 and 6 is not particularly
indicated by chemical properties, but the paramagnetic pro-
perties † of the elements of the first long period can be inter-
preted in favour of the 3_3 sub-group containing 10 electrons,
rather than 6 (with a completion of 3_2 and 3_1 to 6 each) as
on Bohr's original scheme. In the long period of 32, the
rare earth group is particularly interesting, because here
both paramagnetic susceptibilities ‡ and chemical properties
indicate a subdivision of the group into two parts. Chemically
the rare earths are divided into so-called cerium earths and
yttrium earths, the cerium group comprising the elements up
to and including samarium, while the yttrium group comprises
the elements from europium to lutecium.§ If the para-
magnetic susceptibilities of the solid salts are plotted against
atomic number the resulting curve shows two distinct maxima,
the susceptibility being zero at the beginning and end of the
whole rare earth group, and having a pronounced minimum
at samarium and europium. The chemical and physical
properties would appear to indicate a division of the fourteen
elements from cerium to lutecium into a first group of five and
a second group of nine, which agrees pretty well with our
theoretical division into six and eight, since the interpretation
of the empirical results allows a little freedom. It would
appear, then, that either the grouplet of six 4_{43} electrons is built

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* After stating that the chemical evidence by which it can be shown that
the first two valency electrons differ in firmness of binding from the third
and fourth is so vast that only a tithe need be cited, Main Smith starts by
referring to di-pyridino-compounds and acetylacetone fluorides. It is perhaps
then admissible for a physicist to assume that simpler compounds give little
evidence in this direction.

† See Chapter XVII.

‡ See Chapter XVII.

§ Chemically the yttrium group is often divided into terbium, erbium, and
yttrium (proper) sub-groups.

up first, and then the grouplet of eight 4_{44} electrons, or else, possibly, that the first grouplet is built up to five, and the second grouplet then begun, the sixth 4_{43} electron being added at a later stage. The fact that the yttrium group is often sub-divided, its first three elements—europium, gadolinium and terbium—being put in a sub-group, may mean that this sixth electron is added to dysprosium. A precise pronouncement is not justified at the present stage, but we may say that experimental fact indicates clearly a division of the rare earths into two groups roughly corresponding to the Stoner—Main Smith scheme. The fact that the interpolated elements of the periods of eighteen are not divided into two groups probably means that the two grouplets of electrons are not built up consecutively, but concurrently.

Sommerfeld has indicated how the spectroscopic facts confirm the Stoner scheme, and later, in collaboration with Grimm, has considered the connection between chemical and spectral properties in some detail.* We have emphasised that each sub-group attains a closed structure with an inert gas, and that on account of the high symmetry of this closed structure the moment for such a gas is zero. Now the subdivision into grouplets indicates various stages of comparative stability within the sub-group. In the short periods we have an n_{11} grouplet of two completed in Column II, with Be and Mg : a n n_{21} grouplet completed in Column IV, with C and Si ; the completion of the n_{22} grouplet of four gives us the inert gas. In the long periods we have the first or n_{11} grouplet completed in Column II, but for the completion of an outer n_{22} grouplet we must look to Ge, Sn and Pb in Column IV, and not Ti, Zr and Hf. Now at the completion of each grouplet we must expect, from considerations of symmetry, no moment of momentum for the atom as a whole : the inert gas form having clearly no moment it is only necessary to consider the other electrons in pairs circulating in similar orbits, but opposite sense. In other words, at the stages indicated we should find that zero values of j for the whole atom, allotted as described hereafter in Chapter XV., pertain to the basic terms of the spectra.

* This paper appeared too late for more than a passing notice. It should be consulted.

This is found to be the case. From absorption measurements of Meissner it has been deduced that the basic term of the inert gases, neon, argon and krypton, is a $^1S_0$ term. For neutral atoms of the alkaline earths, and for zinc, cadmium and mercury, the basic term is likewise a singlet S term for which $j=0$, indicating that the first grouplet of 2 is completed with these elements, as we expect. In Column IV we have evidence of zero moment in the spectrum of neutral silicon, for which McLennan and Shaver's work yields a $^3P_0$ term as basic term : Grotrian has shown that the basic term for neutral lead has $j=0$, and Sponer has found the same for neutral tin. Ionised nitrogen should have the electron structure characteristic of Column IV, and Fowler's analysis of the spectra of N_{II} does, in fact, indicate a $^3P_0$ term as the basic term. We may say, then, that the spectroscopic results point to the closing of a grouplet in Column IV, where the fourth electron is added, the left-hand elements being taken in the long periods, in accordance with our scheme of atomic structure. Further, as pointed out by Sommerfeld, elements which immediately follow or precede closed groups have basic terms for which $j=1$. For instance, for neutral atoms of the alkali metals which follow the inert gases, the basic term is a $^2S_1$; for neutral atoms of the elements of Column III, which follow the closing of the first grouplet of two (*i.e.* for the elements on the right-hand side of the column), the term is a $^2P_1$.

Work on the distribution of the electrons among the sub-groups is proceeding rapidly, hand in hand with the ordering of the complex spectra. Spectra have the advantage of giving quantitative criteria for the electronic arrangement which are seldom afforded by the present kind of chemical evidence. No doubt it will not be long before a complete distribution scheme for all the elements, together with the basic terms of their spectra, is available.*

Interesting deductions showing the bearing of the grouplet scheme on crystal form have been given by Grimm and Sommerfeld, but they have appeared too late for an attempt at adequate discussion here.

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* Since this was written McLennan, McLay and Smith have published such a table, which is printeind Appendix V, *q.v.*

Co-ordination Compounds and Co-valency. Attempts have been made to interpret the class of chemical compounds known as co-ordination compounds in terms of the Bohr atom. The most characteristic of these compounds are the complex salts, in which the metal atom has valency properties quite different from those normally exhibited by it. In a typical complex salt, such as the cobaltammine $CoCl_3(NH_3)_6$, there exist in combination a metal atom, an acidic atom, and normally saturated molecular groups such as NH_3 or H_2O. The acid atoms, Cl in the example taken, and the NH_3 molecules are, however, bound to the metal atom in essentially different ways. The ionic and chemical behaviour of the complex salt show that in the so-called luteo-cobaltic chloride $CoCl_3(NH_3)_6$ the three chlorines can be separated as ions from the rest of the group : in the compound in which one of the ammonia groups has been removed, $CoCl_3(NH_3)_5$, only two chlorines are ionically separated. This, and a large number of other facts established by Werner and his successors, detailed discussion of which is out of place here, have proved that a metal atom such as cobalt can collect round itself a certain number of ammonia molecules (to adhere to our original example), the whole forming a group which behaves as a radical and can unite with acidic atoms. This is expressed in Werner's notation by writing the compound $CoCl_3(NH_3)_6$ as $[Co(NH_3)_6]Cl_3$. The six ammonias are connected round the cobalt in such a way that its ordinary combining properties are disguised, and, in order to have a distinguishing name, we may speak of them as being bound by co-ordinating valencies, or internal valencies. The essential difference between the internal and ordinary valency bond can be seen in the second cobaltammine chloride mentioned above, purpureo cobaltic chloride $CoCl_3(NH_3)_5$, where the chemical properties show that only two of the chlorines are bound by external valencies, while the third has replaced an ammonia in the complex radical. We therefore write it as $[CoCl(NH_3)_5]Cl_2$.

In these complex radicals the number of atoms or molecules (for, as we have seen by the chlorine replacing the ammonia, the co-ordinated members may be either) has, for a given central atom, certain definite values. In general this co-

ordination number is either six or four, another example of a co-ordination number of six being offered by a ferrocyanide such as $[Fe(CN)_6]K_4$ in which a CN can be replaced by CO, forming potassium carbonyl ferrocyanide $[FeCO(CN)_5]K_3$, or potassium cobaltinitrite $[Co(NO_2)_6]K_3$, while a co-ordination number of four is exhibited by antimony in $[SbS_4]Na_3$ or gold in $[Au(NH_3)_4]Cl_3$. The same atom may form compounds in which its co-ordinatio nnumber is six, and others in which it is four, as platinum in $[PtCl_6]H_2$ and in $[Pt(NH_3)_4]Cl_2$, or cobalt in $[Co(NH_3)_6]Cl_3$, and in $[Co(NH_3)_4]I_2$.

This very sketchy description must suffice to indicate the distinction between co-ordinating and ordinary valency ; or, to use different terms, between internal and external valency, or auxiliary and principal valency, in Werner's terminology. Sidgwick was the first to attempt an explanation in terms of Bohr's atom. The co-ordinating valency must be attributed not to the outermost electrons, commonly called the valency electrons, but to electrons of an incompleted inner group, whence the appropriateness of the term internal valency. Elements which have well-established co-ordination compounds belong to the long groups. Sidgwick based his explanation on the original Bohr theory, where the completed M group contains three sub-groups of 6, and the completed N group four sub-groups of 8. He supposed that the molecules or atoms of the complex ion, like those of unionised molecules, are bound to the central metallic atom by a sharing of two electrons, a concept originally due to G. N. Lewis and subsequently emphasised by Langmuir and christened co-valency.* (The sharing of two electrons is often referred to as a non-polar bond, in contradistinction to the polar bond which unites an electropositive and an electronegative atom, as exemplified in ordinary salt, NaCl.) In general the orbits of shared electrons must be supposed to embrace both nuclei, but not much can be said as to the nature of the sharing. It was originally suggested that, as the atoms must be neutral on the whole, the two electrons shared one orbit, with a phase relationship such that one electron was near the one nucleus when the other electron was near the other

* See Chapter XVI.

nucleus. Shared orbits being excluded on our present views we must suppose two different orbits, but some kind of a phase relationship must exist between the two electrons in them.

Accepting, without too close a scrutiny, the binding by two shared electrons, it is clear that a saturated molecule such as NH_3, or the equivalent—for co-ordination compounds —H_2O, must contribute two electrons to the metal atom, since itself it is incapable of disposing of extra electrons. On the other hand, an atom such as the chlorine atom has one electron missing from the inert gas form towards which it tends, and readily takes up one electron : sharing one electron belonging to the metal atom it contributes only one itself to the binding pair. The chief chemical argument to this effect (*i.e.* to show that a saturated molecule must contribute two electrons to the metal atom, an electronegative element, such as a chlorine, one) is that when an NH_3 in a complex ion is replaced by a chlorine the charge on the ion changes by one, increasing if negative and decreasing if positive, as exemplified by Werner's series of platinic compounds. Further, if the whole complex is combined as an ion with one or more acid Cl atoms, say, we must subtract an electron from the metal atom for every Cl. Thus in such a compound as $[CoNO_2(NH_3)_5]Cl_2$ the five (NH_3)'s contribute two electrons each, the NO_2 (which is equivalent to a Cl in that it has an unsaturated valency) contributes one, while the acid Cl_2 subtracts two : the cobalt atom has 9 more electrons than its normal 27. The same argument applied to $[PtNH_3Cl_5]K$ gives 8 extra electrons to the platinum atom.

Sidgwick, having calculated the number of extra electrons for various components, pointed out that in the 6-co-ordinated complex salts the transition elements, such as Co, seemed to tend to take up sufficient electrons to bring the number up to that of the next higher inert gas : thus Co in these compounds has $27 + 9 = 36$, or the krypton number. This he attributed to a tendency of the cobalt to complete the M_{II} and M_{III} subgroups, which on Bohr's original theory each contained 6 electrons, the M_I group being already completed. With these elements the ordinary valency electrons belong, of course, not to the M but to the N group. One electron of each of the two

sub-groups of the M group was supposed to be shared in each co-valency. Sidgwick supported his argument by many chemical instances, and deduced a co-valency of 8 for certain elements of the rubidium-xenon period. While there seems to be no doubt that electrons of the inner incompleted groups (whose total quantum number is less than that of the true valency electrons) are involved in the co-ordination compounds, and, in general, in compounds where the element shows irregular valency, the details of Sidgwick's interpretation have been criticised, especially by Main Smith in view of his sub-division of the n_k levels. The Stoner—Main. Smith scheme does not admit within a group two n_k sub-groups containing the same number of electrons. For the cobalt elements the numbers in the M_I, M_{II}, M_{III} sub-groups are 2, 6 and 10, divided into 2 ; 2, 4 ; 4, 6. It is therefore difficult to connect Sidgwick's co-valency rules with details of the scheme of atomic structure which is now accepted by physicists. Sidgwick's hypothesis, which is, in essence, that the maximum co-valency is 2 for hydrogen, 4 for the elements of the first short period, 6 for the elements of the second short period, and 8 for all subsequent periods, is, of course, based on chemical evidence, and not on considerations of atomic structure, and, if its application is in fact generally satisfactory—a point which it is for the chemists to decide—it must stand as an empirical rule, and its interpretation in terms of the quantum scheme must be postponed. In short the question must go for the present on the list of unsolved problems.

This brief and hazardous excursion into the realms of chemistry has been undertaken with the object of indicating the kind of way in which the atomic model has been applied to chemical problems rather than with the hope of exhibiting any very clear-cut results. A certain indefiniteness in the conclusions is, perhaps, a feature of these attempts, which are always supported by a wealth of isolated instances against which opponents seem able to adduce an equal number of other isolated instances. The conflicts of certain organic chemists, to which I have not alluded, are best watched from a distance. I have no doubt that, as in the case of quarrels between man and wife, the participants are not

dismayed by the fact that no result is ever reached, and that under all the noise and banging there exists a genuine mutual regard. At any rate wise men know what happens to the well-meaning party who, without any very clear understanding of the cause of the dispute, should attempt to interfere in such a fray. I have no desire to demonstrate his fate, or, if I may change the metaphor, die like a second Tarpeia under a shower of benzene rings.

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See also references Chapter XVI.

CHAPTER XV

Introductory. The question of multiplet structure and the question of the anomalous Zeeman effect are closely connected, since the anomalous effect is shown by all component lines of multiplets, and the type of Zeeman resolution exhibited by such a component line depends upon the multiplicity with which it is associated. We have seen that the quantum theory of multiply periodic systems, founded on a definite mechanical picture of the atomic system as a core and an optical electron either penetrating or not penetrating within this core, can give a good representation of the general series systems, neglecting multiplet structure, and that in the case of the lighter alkali metals, where the doublets are very close, a tolerable numerical representation can be obtained by working out the mechanics of such a core + electron system, the core being regarded as exerting a spherically symmetrical conservative field of force in which the electron moves. The normal Zeeman effect was also calculated on the basis of the quantum theory of a multiply periodic system, and an exact result obtained. Matters were taken a little further when we considered a polarisation of the core by the electron. When, however, we come to treat of the doublet structure of either X-ray or optical spectra, we find that the conception of a rigid core and a circulating electron, exerting forces on one another according to the laws of classical dynamics, cannot be made to act as a satisfactory model. The problem of the theoretical significance of the doublets is not yet convincingly solved, but from our present point of view it seems clear that for the explanation some non-mechanical *ad hoc* principle must be invoked.

When we turn to multiplets in general, of which the doublets are a particularly simple case, and to the anomalous Zeeman effect, there are general arguments, which will be discussed later, to show that the method which we have used in the building up of atoms by addition óf electrons is insufficient to account for the experimental facts unless special hypotheses are introduced. It is clear that a much more complicated interrelationship between core and electron exists than is contemplated in our model. Nevertheless, it is convenient at first to use this type of model, and to express the result in terms of it, invoking such subsidiary assumptions as may be necessary, and afterwards to use the mode of expression to embody the paradoxes with which we shall be confronted. The services and insufficiences of the model are so best revealed. Before even this is attempted, however, we shall describe the empirical regularities which have been established, since these will be needed whatever turn the theory may subsequently take. The quantum theory has emphasised one great simplification, due to Ritz, namely the discussion of the problem through the medium of terms rather than of lines : this alone represents a great advance, and substantially reduces the number of entities needed to express the results found. A further feature of the quantum theory which lies at the basis of this recent work of ordering the multiplets and their associated Zeeman effect is the selection principle, fixing the possible transitions between states determined by different quantum numbers. In all attempts to solve the general spectral problem the arithmetical character of the quantum theory has maintained its validity.

Quantum Description of Empirical Results on Multiplets. We have already drawn attention to the fact that systems of given multiplicity are characteristic of neutral atoms of elements in a given column in the periodic table, as singlets and triplets for the neutral alkaline earths, doublets and quartets for the neutral elements óf Column III, and so on. The question now arises as to how the observed series of multiplet lines can most simply be expressed, and our previous experience in the description of spectra leads us to look for simple relations among terms, by differences of which these lines may be expressed.

The model described in Chapter XII. consisted of a core, with a given moment of momentum determined by quantum laws, and a circulating electron with its own moment of momentum : the total moment of momentum, obtained by compounding vectorially that of the core and of the electron, was also subject to quantum restrictions. We let the moment of momentum of the core be $rh/2\pi$, that of the electron be $kh/2\pi$, and the total moment of momentum compounded of these two be $jh/2\pi$. In addition there is a principal quantum number n, existing independently of k by virtue of the fact that the total action of the electron contains a radial component which does not contribute to the moment of momentum, as discussed in Chapter XI. We require to describe the multiplet as far as possible in terms of these four quantum numbers.

We take as fundamental for our quantum description the selection rules which we have already derived from application to the correspondence principle, namely :

(a) j changes by 0 or $+1$ or -1 $\left\{\begin{array}{l}\text{the combination } j=0 \\ \text{with } j=0 \text{ being ex-} \\ \text{cluded.}\end{array}\right.$

(b) k changes by $+1$ or -1

Let us consider first the odd multiplicities, namely, singlets, triplets, quintets, and so on, and, for simplicity, let us take of these the triplet system to begin with. To analyse such a system empirically into terms, it is found necessary to take the S term as single, as it is found with all systems, the P term as triple, and, in general,* the D term and F term as triple also. (Cf. the analysis of the Sr_I spectrum in Fowler's *Report*.) The principal series, S-P, will then consist of triplets, as observed. The sharp series, P-S, will similarly consist of triplets. It would appear, at first sight, that the diffuse series, P-D, should consist of groups of nine lines if this analysis were correct, since both P and D have three different values. However, the selection principle excludes certain combinations.

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* In general, because the diffuse and fundamental series have not in all cases been sufficiently resolved to render triple values of the D and F terms necessary.

We must allot values of j to the terms. Suppose that for the P term we take $j = 2$, 1, 0, and for the D term $j = 3$, 2, 1, regarding this merely as a guess at present. (We have said nothing about the value of r, so that, although we know the value of k —$k = 2$ for P; $k = 3$ for D terms—and that j is found by compounding k and r vectorially in the different possible ways, we cannot fix j.) Taking these values for j, we can write the terms in our notation : $^3P_0$, $^3P_1$, $^3P_2$; $^3D_1$, $^3D_2$, $^3D_3$. Then, as far as k is concerned, all combinations of P and D with one another are possible, since Δk always $= \pm 1$, but the j rule limits us to $^3P_0 \sim {}^3D_1$, $^3P_1 \sim {}^3D_1$, $^3P_1 \sim {}^3D_2$, $^3P_2 \sim {}^3D_1$, $^3P_2 \sim {}^3D_2$, $^3P_2 \sim {}^3D_3$, and we expect only six lines, if our allotment is correct. Now this is what is found empirically (cf. again Sr1 in Fowler's *Report*). The experimenters who first ordered triplet spectra referred to such a group of six lines in the diffuse series, for instance, as a triplet with satellites, three lines being regarded as the chief lines, and the other three as satellites on account of their smaller intensities. It was realised that the satellites, although measured only for certain triplet spectra, might be of general occurrence ; for instance, A. Fowler wrote : " It is quite possible that satellites are a normal feature of the diffuse series of doublets and triplets, and that their apparent absence in some cases may be due to their small separation from the chief lines," as we now feel sure to be the case.

The structure of a P-D triplet with satellites may be made clear by the following example, which is the Ca_I triplet

CALCIUM$_1$: PD TRIPLET SCHEME.

			Term.	Term value.
(Forbidden)	(Forbidden)	(25) 4425·43 **22590·4**	1^3P_0	34146·9
(Forbidden)	(54) 4434·95 **22542·0**	(19) 4435·67 **22538·3**	1^3P_1	34094·6
(100) 4454·77 **22441·7**	(18) 4455·88 **22436·1**	(1) 4456·61 **22432·4**	1^3P_2	33988·7
Term - Term value	2^3D_3 11547·0	2^3D_2 11552·6	2^3D_1 11556·4	

PLATE VII
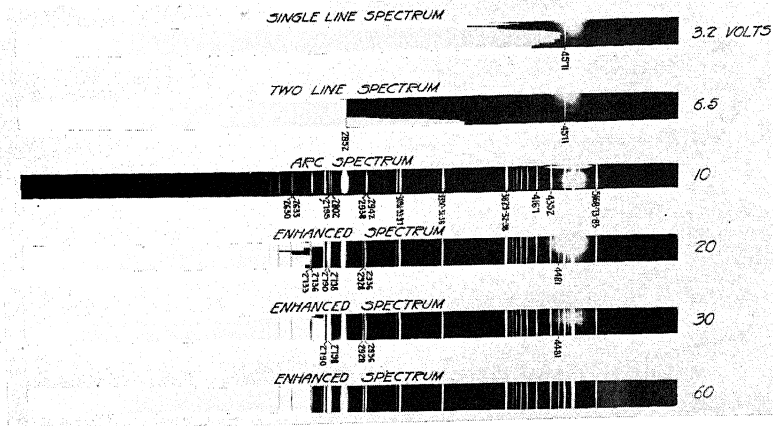
FIG. 1. Excitation of Magnesium Spectra by Stages. (Foote, Meggers and Mohler.)
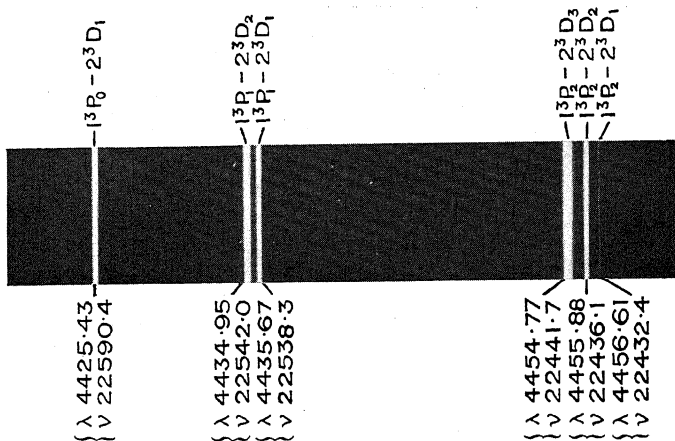
FIG. 2. The 1 P – 2 D Triplet of Neutral Calcium. (Jevons.)

(a)　　　　(b)　　　　(c)　　　　(d)　　　　(e)
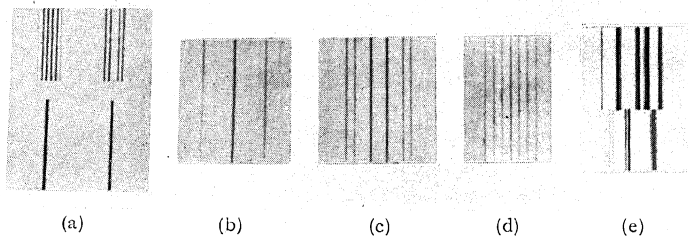
FIG. 3. Anomalous Zeeman Resolutions. (E. Back.)

$1^3P_j - 2^3D_j$. The values of the P terms are written in the vertical column on the right, the values of the D terms in the horizontal row underneath, and the values of the combination, *i.e.* of the line, at the intersection of the corresponding row and column. Above the wave-number value (in vacuo) of the line is written the wave-length (I.A. in air), and, in brackets, the number giving the intensity of the line : this is not needed for our present discussion, but is given for the sake of completeness, and will receive reference later.

Fig. 3, Plate VII, shows a photograph of this triplet, specially taken for me by Dr. W. Jevons with the 8-foot grating at the Artillery College. The lines originally called the chief lines are $\lambda\lambda\, 4425\cdot43$, $4434\cdot95$, $4454\cdot77$; the others are the satellites.

It is found, then, that all the features of a triplet series can be represented by a sequence of single S terms, and sequences of triple P, D and F terms, the observed restrictions in combination of these terms being adequately given by the allotment of values for j, the inner quantum number, obeying the rule $\Delta j = 0$ or ± 1. Now other series of odd multiplicity exist, *e.g.* quintet and septet series, as rendered evident by the investigations of Catalán, Laporte, Gieseler, Walters, Meggers and Kiess, and others on elements of the higher columns in the periodic table. Many lengthy investigations have been made with the object of representing the observed facts by quantum numbers. It is found that the S term is single, the P term triple, and the D and F terms five-fold for the quintets, while for the septets the S, P and D terms have the same multiple character as for the quintets, but the F term is seven-fold. This gives us a general rule, that in the case of odd multiplicities the numbers of terms in the different sequences, S, P, D, F, G . . . are odd, always beginning at 1 for the S term, and increasing to the next odd number, as we proceed from sequence to sequence in this order until the full number of the multiplicity in question is reached, after which there is no further increase. This attainment of a fixed value, equal to the multiplicity of the series, is referred to as the *permanence* of multiplicity, and the number itself is often called the permanence number or maximum multiplicity (*Permanenzzahl*).

STRUCTURE OF THE ATOM

This rule, together with the actual allotment of the j's, is well represented, after Sommerfeld, by the following scheme :

		Singlet	Triplet	Quintet	Septet
		$j = 0$	$j = 1$	$j = 2$	$j = 3$
$k = 1$	S	0			
2	P	1	2 1 0	3 2 1	4 3 2
3	D	2	3 2 1	4 3 2 1 0	5 4 3 2 1
4	F	3	4 3 2	5 4 3 2 1	6 5 4 3 2 1 0
5	G	4	5 4 3	6 5 4 3 2	7 6 5 4 3 2 1
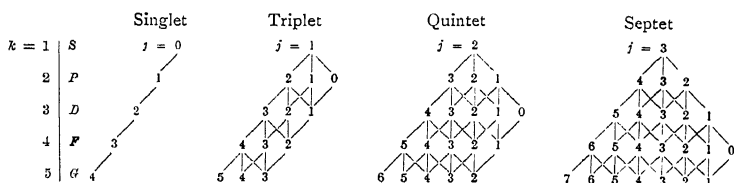
It will be observed that all numbers vertically under one another are equal, and that, starting with $j = 0$, 1, 2, 3 . . for singlets, triplets, quintets . . ., the scheme is extended symmetrically in both directions until the number 0 is reached, which corresponds to the attainment of the permanence number. After this the scheme is extended to the left only, the number of terms being permanent. These values of j give, by the selection rules, a very good representation of the permitted combinations, but, of course, this alone only fixes the values of j within an additive constant, since differences alone are concerned. Deciding always to abide by the selection rule, which has been so successful in representing experimental fact, we have a further guide as to the j's furnished by the intercombinations between terms of different systems. To take a simple example, in the spectrum of neutral mercury, which we have already discussed more than once as an illustration, combinations between the singlet and the triplet terms are known, and the j values must be allotted so as to permit the observed combinations. Fortunately it has been found possible to do this, as already illustrated in Fig. 50. That this can be done is sufficiently remarkable, and a good illustration of what has been referred to as the arithmetical character of the quantum theory.

Now we can represent this scheme on the assumption that j (multiplied, of course, by $h/2\pi$) gives the total moment of momentum of the atom, compounded of the momentum of the core and that of the series electron ; that is, we can represent it formally, although, as we shall see later, this simple mechanical scheme cannot maintain its validity in the face of certain facts. That, however, does not destroy the value of our

scheme as a pictorial representation of a limited number of experimental observations, if we remember this limitation. Temporarily we take j to be necessarily a whole number, although subsequently we shall have to remove this restriction. For the moment of momentum of the series electron we have $kh/2\pi$. Unfortunately, however, we cannot get the right number of terms by compounding this with a vector taken to represent the moment of momentum of the core, as will be seen when our vector scheme is completed. We take instead an arbitrary vector denoted by $j_a = k - 1$. We then have to select a vector s to take the place of the moment of momentum of the core : this, if chosen so as to give the number of terms in agreement with experiment, turns out to be given by $r = 2s + 1$, where r is the maximum multiplicity. That is, in place of r we take $\frac{1}{2}(r - 1)$, which is the value of j for the atom in the S state of the system under consideration, as can be seen by consulting the scheme on p. 506 : in place of k we take the value of j for the given sequence of the singlet system. For this reason Sommerfeld originally denoted by j_s the quantity here called s. There is at this stage no definite theoretical reason why these quantities should be chosen in place of r and k; it has simply been found empirically that with them we can make a simple machine for giving the right number of terms.

Fig. 90 shows the way in which the number of terms can be derived from this vector scheme (a) for a triplet system, for which $s = \frac{1}{2}(3 - 1) = 1$; (b) for a quintet system, for which $s = \frac{1}{2}(5 - 1) = 2$. Fig. 90 (c) shows the method: AO is the vector s and the vector j_a is laid off from A in all positions that make j a whole number. The way in which this is done with circles in Fig. 90 (a) and (b) should be obvious. In each case there are two vectors j collinear with s, representing $s + j_a$ and $s - j_a$: in (a), representing the triplet sequences, where $s = 1$, there is a single additional vector for each sequence, that is, for each value of j_a, so that we have three possible values of j for all values of j_a except 0, i.e. for all values of k except 1. For $j_a = 0$ $(k = 1)$ there is only one vector, which is s itself, by definition of s. In (b) it will be seen that, in addition to the one value of j for $j_a = 0$, there are three values for $j_a = 2$, five for $j_a = 3$, $j_a = 4$, and

higher values. Thus the diagram represents correctly the number of terms in each sequence.

It is obvious, from considerations of symmetry, that on any scheme where s and j_a have whole number values the number of values of j obtained by compounding s and j_a in the above way must be odd. It appears, then, that we shall have difficulties when we turn to the so-called even multiplicities, where
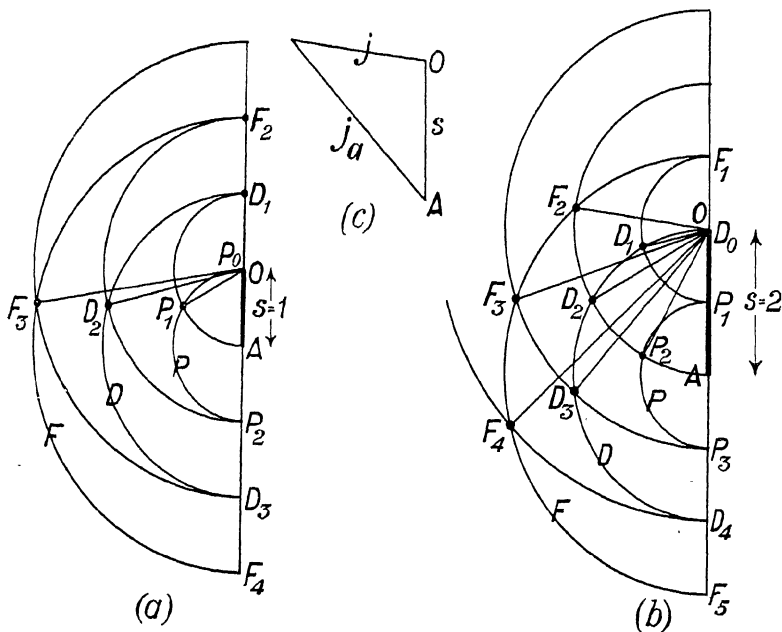
FIG. 90.
Sommerfeld's vector scheme for multiplet terms : (a) triplet system, (b) quintet system.

the permanence number is even. Thus in the simplest case, the doublet system, it is a familiar fact that the S terms are single and all the other terms double. In the quartet system the S terms are single, the P terms triple, and the D and higher terms quadruple. In the sextet system the D terms are five-fold, and the F and higher terms six-fold. These are empirical facts. In general, then, the number of terms increases from 1, with the S sequence, to the next odd number as we progress from sequence to sequence, until the odd number just

before the permanence number (which is, of course, even) is reached. Thus the following scheme expresses the multiplicity of the terms in each sequence:

	Doublet.	Quartet.	Sextet.	Octet.
S	I	I	I	I
P	2	3	3	3
D	2	4	5	5
F	2	4	6	7
G	2	4	6	8

If we desire to express this number-scheme by a vector scheme, as with the odd multiplicities, we are forced to abandon whole
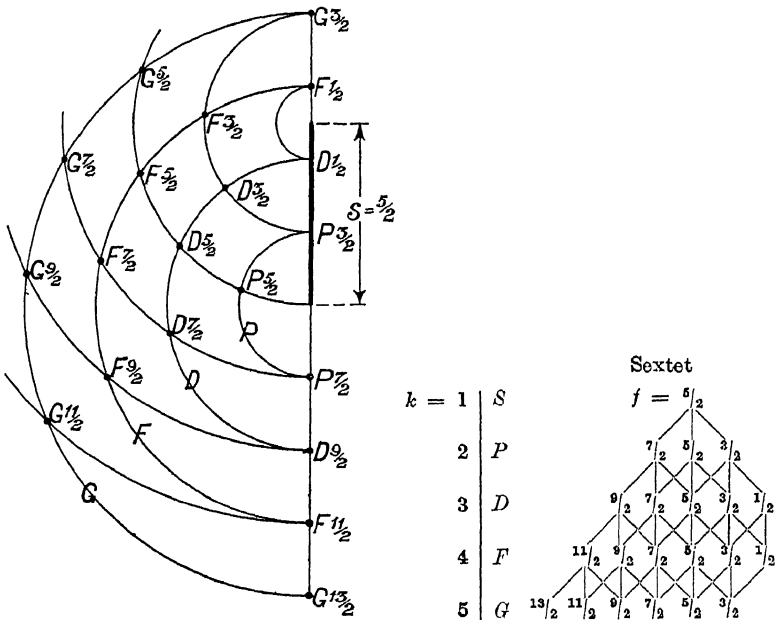
FIG. 91.

Vector and quantum number scheme for sextet system.

number values for the vectors. For which choice of vectors we do this appears at first sight immaterial. Sommerfeld

chooses half-odd-integer values for s and j, retaining integer values for k, and consequently for j_a. The way in which the scheme then works may be illustrated by the sextet system, for which vector scheme and equivalent numerical scheme are shown in Fig. 91. Here $s = \frac{1}{2}(6-1) = \frac{5}{2}$. The terminal points alone are shown, since drawing all the vectors in full would confuse the diagram.

So far we have described an allotment of quantum numbers which (1) gives an adequate description of the possible inter-combinations, if the ordinary selection rule be observed, (2) allows a simple scheme by which two vectors, j_a and s, one representative in some obscure way of the moment of momentum of the series electron, and the other of the moment of the core, may be made to indicate the multiplicity of the term in each sequence, and, in particular, the attainment of a permanence number. As a descriptive scheme this allotment of inner quantum numbers has proved most effective, and by it the arithmetical, as distinct from dynamical, character of the quantum theory of spectra has received further strong support. The adoption of half-integers * as quantum numbers, which, from the point of view of the quantum theory here adopted,† is a grave and repulsive step, seems inevitable ; the anomalous Zeeman effect, as will be seen, necessitates this.

Apart from the general necessity of adopting half quantum numbers, the scheme, due to Sommerfeld, just expounded, is not rigid, and, in fact, Landé has a different allotment. He denotes the integral quantum numbers expressing the moment of momentum of series electrons, of the core, and of the atom as a whole, by k, r, j ; r is equal to the maximum multiplicity of the system in question. He introduces new numbers defined as follows :

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* We shall have, in the following, frequent occasion to refer to quantum numbers which are integers, and others which are half-odd-integers. For brevity we shall call the former *integer values*, the latter *half-integer values*, and correspondingly speak of *whole quantum numbers* and *half quantum numbers*.

† Since this chapter was written a new quantum mechanics has been developed by Heisenberg, Born and Jordan, and others, which is based on the use of the theory of matrices. There has not been time to give any account of this new mechanics here, but according to it the occurrence of half integral values of j is natural. An alternative, still more fundamental development has been initiated by Schrödinger, which leads to the same result.

$R = r/2$, *i.e.* $R = \frac{1}{2}$, 1, $\frac{3}{2}$, 2 . . . for singlet, doublet, triplet, quartet . . . systems

$K = k - \frac{1}{2}$, *i.e.* $K = \frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ . . . for S, P, D sequences.

J, obtained by compounding R and K vectorially, is half integral for odd multiplets, integral for even multiplets.

The selection rules are unaffected, since k and j are only changed by additive constants. A vector scheme of R and K
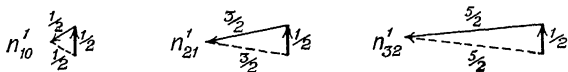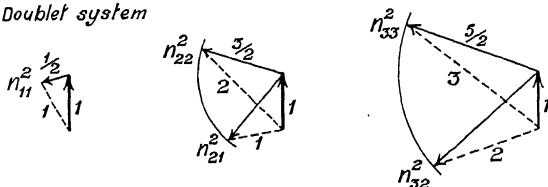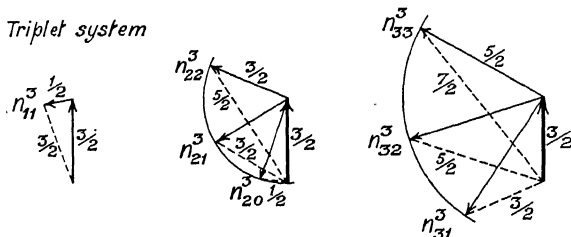
FIG. 92.

Landé's scheme for compounding R and K.

compounding to J, similar to Sommerfeld's, can be made up, giving exactly the same number of terms of each sequence as does Sommerfeld's: however, the case of R and K collinear is forbidden on Landé's scheme, since when R is integer, J is integer, and when R is half-integer, J is half-integer, while K is always a half-integer. This implicit denial of the possibility that the core and electron can set themselves so that their moments of momentum fall in one line seems an unnecessary complication

but Landé's scheme has been widely adopted, and proves extremely useful for many purposes. It is important to note, then, on either scheme, or any scheme so far suggested, (1) half quantum numbers must be introduced, so that we may as well accept them, and ascribe their occurrence to features of the mechanism of the interaction between core and electron which we do not understand. Their existence has been made a source of satisfaction by Heisenberg in his duplicity scheme (see page 546) ; (2) the quantum numbers chosen for compounding according to a vector scheme are not the simple r, k, j of our childhood's dreams, but numbers related to them. Landé's scheme for singlets, doublets and triplets is represented in Fig. 92. The notation originally proposed by him, by which the n, r, k, j belonging to a term are written n_{kj}^r, is shown in the diagram. In this symbol for a term only integers are used, for convenience of printing, k being the nearest integer greater than K, and j the nearest integer less than J when J is half-integer.

The schemes may be summarised as follows :

Bohr's original scheme.

$$\text{Moment of momentum of core} \quad = rh/2\pi.$$
$$\text{Moment of momentum of electron} \quad = kh/2\pi.$$
$$\text{Moment of momentum of whole atom} = jh/2\pi.$$
$$\text{Maximum value of } j = j_{max} = r + k.$$

For S, P, D, F ... sequences $k = 1, 2, 3, 4 \ldots$.

Landé.

$$R = r/2, \ K = k - \tfrac{1}{2}, \ J_{max} = R + K - \tfrac{1}{2}.$$

This forbids R and K to be collinear.

Sommerfeld.

$$s = r/2 - \tfrac{1}{2}, \ j_a = k - 1, \ j_{max} = s + j_a.$$

This allows s and j_a to be collinear.

Obviously s plays the role of R, j_a that of K.*

$$s = R - \tfrac{1}{2}, \ j_a = K - \tfrac{1}{2}, \ j_{max} = J_{max} - \tfrac{1}{2}.$$

* It may be contended that the writer should adopt one notation, but as this book is intended to put the reader in the position to read the original papers easily, and follow current work, for which both notations are required, both notations are introduced. This policy also has the merit of emphasising the element of arbitrariness which exists.

A word is perhaps needed as to the values of j adopted in writing a given spectral term in the ^rT_j notation. To avoid writing half-integers for j in the symbol the following rule is adopted : integer values of j are written unchanged in ^rT_j, but to values of j which are actually half-integers $\frac{1}{2}$ is added before they are written into ^rT_j. Or, as above, the J values may be taken, and $\frac{1}{2}$ subtracted from the half-integer values, the integer values being left unchanged.

Anomalous Zeeman Effect. It has been already mentioned that all component lines of a multiplet, but not singlet lines, show an anomalous Zeeman effect, that is, in a magnetic field of moderate strength they split up into a group of lines, the complexity of which depends upon the character of the multiplet to which the line in question belongs. We say " of moderate strength," because in a very strong field the whole group of lines belonging to a multiplet behaves as if it were a singlet line, and becomes in a sense a normal Zeeman triplet. This effect is known as the Paschen-Back effect, and will have to be mentioned later, when a word will be said as to the meaning of a " strong " field in this connection. Confining ourselves for the moment to fields of moderate strength, the anomalous Zeeman effect has proved to be of great importance for the question with which we are concerned— namely, the nature of the interaction or coupling between core and series electron—because the quantum analysis of the effect gives us a direct means of determining the number of different stationary states to which a given state of the undisturbed atom can give rise, which is obviously connected with the interaction between core and electron. It also throws light upon the general problem of the allotment of j's to a given atomic state. Consideration of this effect has also shown that certain difficulties which have arisen in considering the magneto-mechanical effect discussed in Chapter XVI are of fundamental significance, while it has not solved them.

Within a few years of Zeeman's original discovery, Preston made a discovery which proved very useful in sorting out the lines belonging to different series, namely, that while most lines showed anomalous effects, among which different types could

be distinguished, all analogous * lines of the same series showed the same type of anomalous Zeeman effect. In terms of our quantum theory the nature of the Zeeman resolution is independent of n, but depends upon both k and j. As regards the types themselves, we may say that the higher the degree of multiplicity to which the line belongs, the richer in lines is the Zeeman pattern produced. It is generally but not universally true that this Zeeman pattern is subject to a rule due to Runge, namely, that the displacement of any component from the position of the unresolved line is a rational multiple of the Lorentz separation shown by the normal triplet. This implies, of course, that the displacement of a given component line is proportional to the magnetic field, since this is the case with the normal triplet.

The anomalous effect contains components polarised both parallel to † (π components) and normal to (σ components) the magnetic field. There is, of course, both a longitudinal and a transverse effect, just as with the normal effect, but, again as with the normal effect, the transverse effect is inclusive, showing all the components, of which certain ones, namely, those corresponding to a vibration along the lines of magnetic force, are invisible for the longitudinal position. The transverse effect will therefore always be considered, and the longitudinal effect not mentioned again.

To consider the type of resolution a little more closely, Runge's rule may be mathematically expressed by the formula :

$$\Delta v = \frac{q}{p} \cdot \frac{e}{m} \frac{H}{4\pi c}, \quad \dotfill (\text{I})$$

$\dfrac{e}{m} \dfrac{H}{4\pi c}$ being the normal Lorentz separation, and q and p being whole numbers which never have a very large value for the simpler spectra, investigation of which established the rule.‡

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* *I.e.* in the case of multiplet series, lines occupying corresponding positions in the multiplet, or, in the notation of to-day, lines of identical j values.

† We say a line is polarised in the plane containing the electric vector and the direction of propagation.

‡ For some terms of the more complicated spectra recently investigated large values of p and q are indicated. In such cases measurement of the separation cannot distinguish between chosen values and values slightly different, *e.g.* between $q/p = 63/78$ and $q/p = 62/77$.

Thus p, which is called the Runge denominator, does not exceed 15 in practice for the simpler spectra. Further, the pattern is always symmetrical about the undisturbed position of the line, unless the field exceeds the values which we are at present considering.

As a simple example we may take the resolution of lines of a principal doublet series, for instance the D lines of sodium, for which a photograph of the actual pattern, without polarising prism (*i.e.* π and σ components shown together) is given in Plate VII, Fig. 2 (*a*). (In this photograph the doublet without field is shown below, the Zeeman resolution above.) This is diagrammatically represented in Fig. 93 (*a*), the π and σ components being here distinguished, the former by short verticals
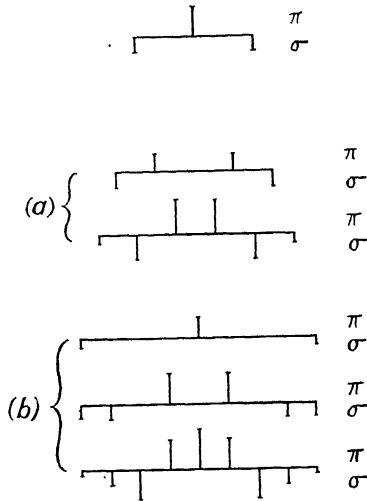
FIG. 93.

Zeeman resolution : (*a*) *SP* doublet ; $^2S_1 - {}^2P_1$ above, $^2S_1 - {}^2P_2$ below. (*b*) *SP* triplet ; $^3P_0 - {}^3S_1$, $^3P_1 - {}^3S_1$, $^3P_2 - {}^3S_1$, in this order from above to below. At the top of the diagram the normal Zeeman effect.

above, the latter by short verticals below, the horizontal line. The Zeeman pattern for lines of a principal triplet is shown diagrammatically in Fig. 93 (*b*). The relative intensities of the components are quantitatively indicated by the length of the vertical lines in the diagram. Experiment has shown these intensities to be simple multiples of a common factor.

Plate VII, Fig. 2 (b), (c), (d), is an actual photograph of the effect for the three lines of the Zinc PS triplet, $\lambda\lambda\, 4680 \cdot 38$, $4772 \cdot 34$, $4810 \cdot 71$, π and σ components being shown together. The three lines for $^3P_0 - {}^3S_1$ and the six for $^3P_1 - {}^3S_1$ are very clear : of the nine for $^3P_2 - {}^3S_1$, indicated in Fig. 93 (b), only seven are shown in the plate, the two outermost lines being too faint to appear in reproduction. These excellent photographs are due to Back.

There is a very simple notation for writing the empirically observed Zeeman resolution of any line. Since the resolution in the cases now under consideration is always symmetrical, it suffices to describe one half of the pattern. The Runge denominator is written under a horizontal line, and above are placed the numerators, which specify the displacement of the various lines, separated by commas. The π components are distinguished by being enclosed in brackets, the σ components being left unbracketed. Thus the resolutions of the lines of a principal doublet may be written $\pm\dfrac{(2),\, 4}{3}$ and $\pm\dfrac{(1),\, 3,\, 5}{3}$ respectively, and those of the lines of a principal triplet

$$\pm\frac{(0),\, 4}{2},\quad \pm\frac{(1),\, 3,\, 4}{2},\quad \pm\frac{(0),\, (1),\, 2,\, 3,\, 4}{2}$$

respectively (compare Fig. 93).

Of primary importance is the fact that it is possible to represent the Zeeman resolution of all multiplet lines by assigning groups of *terms* into which each *term* of the undisturbed spectrum splits up in the magnetic field. That is, the combination principle of Ritz is satisfied by the Zeeman components. Further, we can allot to each term a special quantum number m which satisfies the correspondence and selection principle in the sense that the application of these rules to the numbers allotted gives the experimentally observed lines, and the correct polarisation of these lines. Even if a satisfactory mechanical model cannot be found to exemplify all features of the quantum theory, the quantum numbers have their justification so long as they introduce this great descriptive principle. We now proceed to discuss briefly the way in which the quantum number m is attributed to the terms.

Since, in order to satisfy our general quantum principles, including the correspondence principle, the quantum numbers allotted to a given set of terms must differ from one another successively by 1, it is clear that where an even number of m terms is attributable to a given spectral term the values of m must be half-integer values, if the effect is to be symmetrical, whereas in the case of an odd number of m terms integral values are needed. Examples of this will appear below. It may be mentioned that Hicks has proposed to do away with half-integer numbers by taking, for the case of an odd number of m terms, even number values for m, starting at 0, and, for the case of an even number of m terms, odd number values for m, starting at 1. Thus we should have for the magnetic resolution of any term successive values of m differing by 2 instead of by 1. Hicks claims certain advantages for this method, but the fact that it necessitates such drastic changes of the selection rule as to invalidate the correspondence principle in its present form seems to deprive it of any great value.

We can allot selection rules for m by invoking the arguments used in Chapter X. in discussing the normal Zeeman effect. It was pointed out there that the number expressing the effect of the magnetic field (n_H in equation (28), p. 253) changes by ± 1 for a σ component, by 0 for a π component, and we may take this rule to apply to the m's which we are now using. As an example of the allotment of the m's, the principal doublet and triplet already used in Fig. 93 may be taken. To the $^2P_2$ term we give values of m $-\frac{3}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, $\frac{3}{2}$; to $^2P_1$ values $-\frac{1}{2}$, $\frac{1}{2}$; to $^2S_1$ $-\frac{1}{2}$, $\frac{1}{2}$, and we write our scheme as follows :

Zeeman resolution of principal doublet lines : m values.
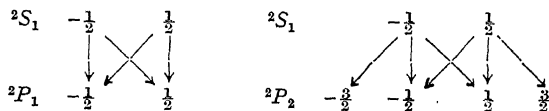
The arrows indicate possible transitions : our polarisation rule, on this scheme, is that vertical arrows denote π components, oblique arrows σ components. We see at once that this scheme indicates four σ and two π components for the line $^2S_1 - {}^2P_2$.

and two σ and two π components for $^2S_1 - {}^2P_1$, as observed, For the principal triplet lines we write :
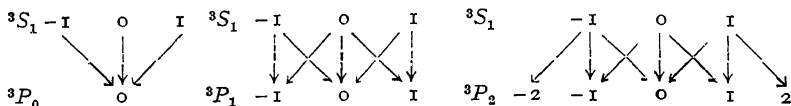
which will be found to give the number and polarisation of the observed lines as shown in Fig. 93.* These examples illustrate what is an essential feature of any quantum scheme, that the quantum numbers allotted to a term are a feature of that term, no matter into what combinations it enters. Thus $^3S_1$ has the same m values, -1, 0, 1, in its combination with all three ^3P_j terms : similarly, the values allotted to the ^3P_j terms give the correct selections and polarisations when we consider the combination of these ^3P_j terms with ^3D_j terms. It is this fact, of course, which constitutes the combination principle. Particular attention is drawn to this, lest the significance of the fact that we can attribute quantum numbers in this way should be underrated.

There are certain general empirical rules for the relative intensities of the Zeeman component lines. When we are dealing with two terms which have the same number of Zeeman component terms (such as $^3S_1$ and $^3P_1$ above, which each have three), then of the π components those which correspond to transitions at the edges of the arrow scheme are strongest, while of the σ components those which correspond to transitions at the middle of the arrow scheme are strongest. If we are dealing with two terms which have unequal numbers of Zeeman components (such as $^3S_1$ and $^3P_2$ above, with three and five respectively), then the rules are reversed, the strong π components corresponding to transitions in the middle of the scheme, and the strong σ components to transitions at the edge. Sommerfeld and Heisenberg have shown how these rules can be derived in a quantitative form by applying the correspondence principle.

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* Except that in $^3P_1 - {}^3S_1$ the theoretical scheme indicates an additional undisplaced π component, not observed. There is, however, no contradiction here, as consideration of the correspondence principle shows that this component (due to the transition $m = 0 \rightarrow m = 0$, while $\Delta J = 0$ as well) must be of intensity zero.

Thanks to the labours of Landé and others groups of quantum numbers m, such as we have indicated above, can be attached to each of the various types of term of ordered spectra. Any satisfactory quantum scheme, however, must give the *magnitude* of the displacement of the component lines as well as their number and polarisation. On the basis of our usual quantum theory, developed in connection with the normal Zeeman effect, we should expect the *magnitude* of the terms to be simply $mh \cdot \dfrac{eH}{4\pi m^* c}$: a glance at the above examples forces us to admit that this consideration is not valid in the present case, or else *e.g.* the displacement of the π terms should be zero in all cases.* Neither will any one fixed multiple of m, applied to all m's indiscriminately, no matter to what k and j they pertain, give the observed displacements.

We can, however, allot *another* set of numbers to the various Zeeman terms, one to each value of m, which will then give the

m	$-\tfrac{3}{2}$	$-\tfrac{1}{2}$	$\tfrac{1}{2}$	$\tfrac{3}{2}$
$^2S_1$		$-\tfrac{1}{1}$	$\tfrac{1}{1}$	
$^2P_1$		$-\tfrac{1}{3}$	$\tfrac{1}{3}$	
$^2S_1 - {}^2P_1$ resolution		$\pm\dfrac{(2),\,4}{3}$		
$^2S_1$		$-\tfrac{1}{1}$	$\tfrac{1}{1}$	
$^2P_2$	$-\tfrac{6}{3}$	$-\tfrac{2}{3}$	$\tfrac{2}{3}$	$\tfrac{6}{3}$
$^2S_1 - {}^2P_2$ resolution		$\pm\dfrac{(1),\,3,\,5}{3}$		

displacements. Once more, the significance of this is that a given number belongs to a given term, no matter what combination it enters : this takes away the reproach that such an allotment is purely *ad hoc*, and without significance, in each

* Where the quantum number m enters into the formula we write m^* for the mass of the electron, to avoid confusion. This device seems to do least violence to the current notation.

case. These numbers (multiplied by the value of the displacement in the normal effect, viz. $\omega_H h = \dfrac{eh}{4\pi m^* c} H$)* give the magnitude of the terms, while the m's determine the combinations and polarisations. Taking our principal doublets again, we have the numbers tabulated on p. 519, which give the various term values as multiples of $\omega_H h$.

It will be seen that to get the value of the term, in multiples of $\omega_H h$, we have to multiply m by a value which is *constant* for each type of multiplet term, *i.e.* by 2 in the case of the $^2S_1$ term, by $\frac{2}{3}$ in the case of the $^2P_1$ term, and by $\frac{4}{3}$ in the case of the $^2P_2$ term. This is a general feature of the anomalous Zeeman effect of all multiplet lines : to each undisturbed term ^rT_j a series of sub-terms can be. allotted which give by combination with the sub-terms of another multiplet term $^rT_{j'}$ the correct Zeeman resolution of the line $^rT_j - {}^rT_{j'}$, and these terms can be derived by multiplying the m values (allotted so as to give selection and polarisation) by a constant. This constant is the so-called splitting factor g.

To describe in full the anomalous Zeeman effect it therefore suffices to attribute to each type of term ^rT_j two numbers : (1) $m_{\max}$, the maximum value of m, which implies all the others, since m will then have the values $\pm m_{\max}$, $\pm(m_{\max}-1)$, $\pm(m_{\max}-2)$, ..., the final value being $\pm\frac{1}{2}$ or 0 according as $m_{\max}$ is integer or half-integer. (2) A number g, such that the magnitude of the terms $^rT_j{}^z$ (the z indicates Zeeman terms corresponding to the undisturbed term ^rT_j) is given by mg. Thus all the information embodied in the table just given can be expressed in short in the following table, which contains, for ready reference, the g, $m_{\max}$ and J values for singlet, doublet and triplet S, P, D terms.

Term ^rT_j	$^1S_0$	$^1P_1$	$^1D_2$	$^2S_1$	$^2P_1$	$^2P_2$	$^2D_2$	$^2D_3$	$^3S_1$	$^3P_0$	$^3P_1$	$^3P_2$	$^3D_1$	$^3D_2$	$^3D_3$
g	$\frac{0}{0}$	1	1	$\frac{2}{1}$	$\frac{2}{3}$	$\frac{4}{5}$	$\frac{4}{5}$	$\frac{6}{5}$	$\frac{2}{1}$	0	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{7}{6}$	$\frac{4}{3}$
$m_{\max}$	0	1	2	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	1	0	1	2	1	2	3
J	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	1	1	2	2	3	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$

* See Chapter X., page 250 *et· seq.*

The number of terms into which the term is resolved is at once obtained by multiplying the J value in question by 2.

The magnitude of g depends upon the particular term of the particular multiplet in question, that is, upon R, K and J. Landé has shown that there is a comparatively simple general empirical formula giving g in terms of these quantum numbers, viz. :

$$g = \tfrac{3}{2} + \frac{R^2 - K^2}{2(J^2 - \tfrac{1}{4})}.$$

This can be written in a symmetrical form :

$$g = 1 + \frac{(J+\tfrac{1}{2})(J-\tfrac{1}{2}) + (R+\tfrac{1}{2})(R-\tfrac{1}{2}) - (K+\tfrac{1}{2})(K-\tfrac{1}{2})}{2(J+\tfrac{1}{2})(J-\tfrac{1}{2})} \quad \ldots (2)$$

The occurrence of the two values $J \pm \tfrac{1}{2}$, $R \pm \tfrac{1}{2}$, $K \pm \tfrac{1}{2}$ in place of J, R, K is particularly to be noted. If, for convenience, we write

$$(J+\tfrac{1}{2})(J-\tfrac{1}{2}) = \overset{\ast}{J}{}^2, \ (R+\tfrac{1}{2})(R-\tfrac{1}{2}) = \overset{\ast}{R}{}^2, \ (K+\tfrac{1}{2})(K-\tfrac{1}{2}) = \overset{\ast}{K}{}^2,$$

i.e. take $\overset{\ast}{J}$ as the geometric mean between $J + \tfrac{1}{2}$ and $J - \tfrac{1}{2}$, and so for the other quantities, then the formula becomes

$$g = 1 + \frac{\overset{\ast}{J}{}^2 + \overset{\ast}{R}{}^2 - \overset{\ast}{K}{}^2}{2\overset{\ast}{J}{}^2}. \qquad \ldots \ldots \ldots \ldots \ldots \ldots (2a)$$

Since Sommerfeld's $s = R - \tfrac{1}{2}$, $j_a = K - \tfrac{1}{2}$, $j = J - \tfrac{1}{2}$, we have on his notation

$$g = 1 + \frac{j(j+1) + s(s+1) - j_a(j_a+1)}{2j(j+1)}. \qquad \ldots \ldots \ldots \ldots (2b)$$

The theoretical significance of the empirical regularities so far described will be considered further on in this chapter.

Paschen-Back Effect. We have seen that the anomalous Zeeman effect can be expressed by a splitting of a given term into several terms on the application of a magnetic field, the number and position of the new terms depending on K and J. The dependence on J means that the type of resolution in one sequence is different for different terms of the same multiplet. The effect of increasing the strength of the magnetic field is at first merely to increase proportionally the displacement of all the lines in the Zeeman pattern from the undisturbed position of the line, which can also be expressed by saying

that, for fields below a certain strength, the term values may be taken as proportional to H, as expressed in formula (1). If this feature of the anomalous Zeeman effect were to hold true for fields of any strength, the effect of a very strong field on a close multiplet would be that each line of the multiplet would be transformed into its characteristic pattern, well spread out, and the patterns would overlap, magnetic component lines corresponding to different multiplet lines being intermixed. Thus, even if the lines of an alkali metal P doublet were too close for resolution, the application of a very strong field should, if the effect were a magnification of the weak field effect, give rise to ten lines, six from one doublet line, and four from the other (cf. the discussion of the sodium doublet), and, similarly, a close triplet would give rise to a still more numerous complex of lines.

Actually the symmetrical magnification of the pattern due to a given multiplet line does not continue indefinitely with increasing field. As soon as the field becomes strong enough for Zeeman components due to the different lines of the same multiplet to approach one another, the patterns lose their symmetry, and behave, in fact, somewhat as if the various Zeeman components of the different lines were exerting forces of repulsion or attraction on one another. This effect is well shown in Fig. 3 (e), Plate VII, which is a photograph of the SP triplet $\lambda\lambda$ 5204·67, 5206·20, 5208·58 of the chromium quintet system in a strong field, the upper part of the photograph representing σ components, the lower part π components. The asymmetry of the pattern belonging to each line is clearly visible.

As the field is still further increased a great simplification takes place : the complex of all the lines due to the multiplet simplifies into three lines, constituting a normal Zeeman triplet, *i.e.* the lines are equally spaced, separated by a wavenumber gap proportional to the field, and polarised according to the Lorentz rule. The central line of the triplet (π line) appears at the " optical centre of gravity " of the multiplet, by which is meant the centre of gravity obtained by giving the individual lines weights proportional to their intensities. This appearance of a normal triplet in very strong fields is called

the Paschen-Back effect, having been first obtained by these experimenters in 1912.

When discussing this effect, we mean by a strong field not a field of a given number of Gauss, but a field strong enough to produce displacements greater than the normal separation of the multiplet lines : a field is weak if the Zeeman displacements are still small compared to the separations of the undisturbed multiplet lines. Hence whether a field is weak or strong in this sense depends upon the multiplet in question : for instance, for the close oxygen PS triplet $\lambda\lambda\,3947\cdot33$, $3947\cdot51$, $3947\cdot61$ a field of 30,000 Gauss is strong, while for the sodium SP doublet $\lambda\lambda\,5889\cdot96$, $5895\cdot93$ the same field is considered weak. A field of the order of 200,000 Gauss would be required to obtain something like the complete Paschen-Back effect with this doublet. Fields of this order are now feasible, having been produced by Kapitza, although only for brief intervals of time, of the order of one hundredth second.

To obtain greater definiteness we should, however, consider the terms, and not the lines. It would be more correct to say that a field is strong when ω_H (which is the $\Delta\nu_T$ of the term in the normal effect) is large compared to the frequency separation of the components of a given multiplet term. The frequency separation of the components of the initial multiplet term may, however, be quite different from that of the components of the final multiplet term involved in a quantum switch. If the field is sufficiently large to be strong for the more widely spread multiplet terms we have the Paschen-Back effect as described above, but if it is large for the narrow multiplet term, and weak for the wide term, we have an intermediate effect which is called the partial Paschen-Back effect. This partial effect will not be discussed in detail.

Voigt, in the days before the quantum theory, succeeded in giving a formal mechanical description of the Paschen-Back effect for a doublet, but as he treated the frequencies of the lines, and not of the terms, his theory needs considerable modification to bring it into accord with modern ideas. Sommerfeld has replaced Voigt's theory by a quantum expression for the terms, and Landé has somewhat modified this expression. The work which we shall now discuss is in the

main a formal expression of the transformation of the pattern in a strong field, though an attempt is made to connect it up with the model.

Taking first of all the fieldless * multiplet, we may consider this as a kind of Zeeman effect produced by the internal magnetic field of the atom itself on what would, in the absence of this field, be a single line. It may be assumed (and the assumption can be supported by general arguments) that this single line would be at the centre of gravity of the multiplet, as defined above, and if this assumption be made, it is clear that we should express the fieldless multiplet in terms of separation of the component lines from the centre of gravity, to which a wave-number ν_S is attributed. This separation Landé takes as being a multiple of a quantity Ω, which for a doublet is the difference of wave-number of the two components. He writes for the term

$$\nu = \nu_S + \gamma\Omega,$$

γ having a different value for each term of the multiplet. For higher multiplicities, even when ν_S is ascertained, we can derive experimentally only $\gamma\Omega$, so that there is a certain arbitrariness, within a constant multiple, as to the values taken by γ and Ω independently. The choice is dictated by considerations of analogy with the doublet case, which are relatively unimportant, and need not be here discussed. γ depends, of course, on R, K and J only, and not on n. It bears a formal analogy to the splitting factor g in the true Zeeman effect, and Landé has expressed it in terms of R, K and J by a formula similar to that for g.† Ω then bears a formal analogy to the Larmor constant ω_H.

On this basis we can express the anomalous Zeeman effect (weak field) by the formula

$$\nu = \nu_S + \gamma\Omega + mg\omega_H,$$

the values of γ and g being determinable by analysis of the

---

* The German term is so convenient that I venture to introduce it, with apologies to any who may feel hurt.

† The formula for g in a weak field has been already given on page 521.

The corresponding formula for γ in a weak field is $\gamma_w = \dfrac{\vec{J}^2 - \vec{R}^2 - \vec{K}^2}{2RK}$.

experimental values with the limits of arbitrariness indicated. Thus γ and g can be tabulated for given R, K and J.

The effect of a strong field is expressed by a change in the values of both γ and g. In the case of the doublets the nature of this change is given by a formula derived by Sommerfeld from Voigt's theory. In the general case the derivation of the values of γ and g for a strong field (which we can write γ_s and g_s, γ_w and g_w being similarly the values for a weak field) is somewhat more complicated. Whereas g_w and γ_w belong to a given fieldless term (they are fixed by R, K, J), and therefore by their nature are the same for all magnetic components of the term, g_s and γ_s depend upon the value of m. However, the g's and γ's are subject to a simple law referred to as the " permanence of the g-sums " or " permanence of the γ-sums " respectively, which states that a sum of certain g's or γ's is unaffected by change in the magnetic field. This sum is to be formed in the following way : for a given multiplet system (R fixed) and a given sequence within the multiplet (K fixed) a value of m is selected. For this m value g (and γ) will have a different value for each value of J (there being, e.g., three values of J for all triplet sequences except S ; three values of J for P sequences, and four values of J for D and higher sequences in quartets ; and so on, as expressed in the schemes on pp. 506 and 509). If, then, the g's for all the different J's be summed, it is found that this value is the same for strong fields as for weak fields, and, incidentally, it is the same for intermediate fields. Symbolically expressed :

$$\left.\begin{array}{l} \sum_J g_w = \sum_J g_s \ (= \sum_J g \text{ any field}) \\ \sum_J \gamma_w = \sum_J \gamma_w (= \sum_J \gamma \text{ any field}) \end{array}\right\} \text{for fixed } m, R \text{ and } K.$$

Thus, turning to the table on p. 527, which gives the very simple form of a P doublet, we take as an example $K = \frac{3}{2}(P \text{ terms})$, $m = -\frac{1}{2}$: for $J = 2$, $mg_w = -\frac{2}{3}$, $mg_s = 0$: for $J = 1$, $mg_w = -\frac{1}{3}$. $mg_s = -1$. Hence

$$\sum_J mg_w = -\tfrac{2}{3} - \tfrac{1}{3} = -1, \quad \sum_J mg_s = 0 - 1 = -1,$$

which, m being constant, accords with the above rule. The γ rule can be illustrated from the same table. Of course, if

J has only one value, as for $K = \frac{1}{2}$, then g and γ must be unchanged by the passage from strong to weak field, in accordance with this rule. The reader can easily check the rule for more complicated cases by using the full table of mg and γ values given on pp. 528, 529.

Further, Pauli has given rules for deriving mg_s and γ_s from J, K and R, which, of course, express a dependence on m. He takes $m = m_R + m_K$, m_R pertaining in some way to the core, and m_K to the electron. m_R and m_K are given individually by the following expressions:

$$
\begin{aligned}
m_R &= J - K, & m_K &= m - (J - K) \text{ for } m \geq R - K \\
m_R &= m - (R - J), & m_K &= R - J \quad\quad \text{ for } m \leq R - K
\end{aligned} \right\} \quad \dots(3)
$$

Then
$$
mg_s = m_K + 2m_R,
$$

and
$$
\gamma_s = \frac{m_R}{R} \cdot \frac{m_K}{K}.
$$

These rules can be used to describe correctly the Paschen-Back effect. Their interpretation in terms of the model will be briefly considered in the next section. The combination of the terms is limited by the rule that only terms can combine for which m_R, namely, the m belonging to the core, remains the same, $i.e.$ $\Delta m_R = 0$. As the rules are rather complicated, they will now be illustrated by a full consideration of the P doublet terms.

For a P doublet the line $^2S_1 - {}^2P_2$ is exactly twice as intense as $^2S_1 - {}^2P_1$. The $^2P_2$ term has double the weight of the $^2P_1$ term, so that $\gamma_1 = -2\gamma_2$ in a weak field. Since Ω is the separation between the two terms (or lines), $\gamma = \frac{1}{3}$ for $^2P_2$ and $\gamma = -\frac{2}{3}$ for $^2P_1$. The values for mg_w have already been discussed. For $^2P_1$: $R = 1$, $K = \frac{3}{2}$, $J = 1$; for $^2P_2$: $R = 1$, $K = \frac{3}{2}$, $J = 2$. Hence from formula (3):

	$m \geq -\frac{1}{2}$.	$m \leq -\frac{1}{2}$.
m_R for $^2P_1$	$-\frac{1}{2}$	m
$^2P_2$	$+\frac{1}{2}$	$m + 1$
m_K for $^2P_1$	$m + \frac{1}{2}$	0
$^2P_2$	$m - \frac{1}{2}$	-1

It will be seen that for $m = -\frac{1}{2}$ both columns give identical values, as they should.

From these values the following table can be constructed. The values for the S term can be put in at once from the above considerations. For a given m a pair of values of mg, and of γ are given, connected with an arrow. The first of the pair is the value for a weak field, the second is for a strong field, the arrow indicating that as the field increases there is a continuous transition. The values of m_R are given again for convenience, as they are wanted for the $\Delta m_R = 0$ rule.

Doublet Terms. $R=1$.

K	J	m $-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	
$\frac{1}{2}$	1		$-1 \to -1$	$1 \to 1$		mg
			$0 \to 0$	$0 \to 0$		γ
			$-\frac{1}{2}$	$\frac{1}{2}$		m_R
$\frac{3}{2}$	2	$-2 \to -2$	$-\frac{2}{3} \to 0$	$\frac{2}{3} \to 1$	$2 \to 2$	mg
		$\frac{1}{3} \to \frac{1}{3}$	$\frac{1}{3} \to -\frac{1}{3}$	$\frac{1}{3} \to 0$	$\frac{1}{3} \to \frac{1}{3}$	γ
		$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	m_R
	1		$-\frac{1}{3} \to -1$	$\frac{1}{3} \to 0$		mg
			$-\frac{2}{3} \to 0$	$-\frac{2}{3} \to -\frac{1}{3}$		γ
			$-\frac{1}{2}$	$-\frac{1}{2}$		m_R

We then have, as the scheme for the actual components in a strong field, omitting transitions for which $\Delta m_R \neq 0$,

$$
\begin{array}{lcc}
^2S_1 & -\omega_H & \omega_H \\
 & \downarrow & \searrow \\
^2P_1 & -\omega_H & -\tfrac{1}{3}\Omega
\end{array}
$$

$$
\begin{array}{lcccc}
^2S_1 & & -\omega_H & \omega_H & \\
 & \swarrow & \swarrow\ \downarrow & \searrow & \\
^2P_2 & -\tfrac{1}{3}\Omega - 2\omega_H & -\tfrac{1}{3}\Omega & \omega_H & \tfrac{1}{3}\Omega + 2\omega_H
\end{array}
$$
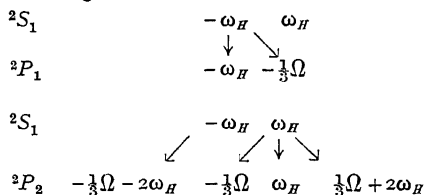
Remembering that vertical arrows give π components, oblique arrows σ components, we have finally, for the whole doublet,

$$
\begin{array}{ll}
\pi \text{ components at} & \nu_S + 0 \\
\sigma \text{ components at} & \nu_S + \omega_H \pm \tfrac{1}{3}\Omega, \quad \nu_S - \omega_H \pm \tfrac{1}{3}\Omega
\end{array}
$$

This represents a normal triplet with its centre at ν_S, except

The values of mg are in every case printed above, the values of γ below, strong field on the right.

Singlet Terms $R = \frac{1}{2}$

KJ \\ m	-2	-1	0	1	2
$\frac{1}{2}\ \frac{1}{2}$			$0\to0$ $(0\to0)$		
$\frac{3}{2}\ \frac{3}{2}$		$-1\to-1$ $(0\to0)$	$0\to0$ $(0\to0)$	$1\to1$ $(0\to0)$	
$\frac{5}{2}\ \frac{5}{2}$	$-2\to-2$ $(0\to0)$	$-1\to-1$ $(0\to0)$	$0\to0$ $(0\to0)$	$1\to1$ $(0\to0)$	$2\to2$ $(0\to0)$

Quartet Terms $R = \frac{4}{2}$

KJ \\ m	$-\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$
$\frac{1}{2}\ 2$			$-3\to-3$ $(0\to0)$	$-1\to-1$ $(0\to0)$	$1\to1$ $(0\to0)$	$3\to3$ $(0\to0)$		
$\frac{3}{2}\ \{\ 3$		$-4\to-4$ $\left(\frac{1}{2}\to\frac{1}{2}\right)$	$-\frac{12}{5}\to-2$ $\left(\frac{1}{2}\to\frac{1}{6}\right)$	$-\frac{4}{5}\to0$ $\left(\frac{1}{2}\to-\frac{1}{6}\right)$	$\frac{4}{5}\to2$ $\left(\frac{1}{2}\to-\frac{1}{2}\right)$	$\frac{12}{5}\to3$ $\left(\frac{1}{2}\to0\right)$	$4\to4$ $\left(\frac{1}{2}\to\frac{1}{2}\right)$	
$\quad 2$			$-\frac{39}{15}\to-3$ $\left(-\frac{1}{3}\to0\right)$	$-\frac{13}{15}\to-1$ $\left(-\frac{1}{3}\to0\right)$	$\frac{13}{15}\to1$ $\left(-\frac{1}{3}\to0\right)$	$\frac{39}{15}\to2$ $\left(-\frac{1}{3}\to\frac{1}{6}\right)$		
$\quad 1$				$-\frac{4}{3}\to-2$ $\left(-\frac{5}{6}\to-\frac{1}{2}\right)$	$\frac{4}{3}\to0$ $\left(-\frac{5}{6}\to-\frac{1}{6}\right)$			
$\frac{5}{2}\ \{\ 4$	$-5\to-5$ $\left(\frac{3}{5}\to\frac{3}{5}\right)$	$-\frac{25}{7}\to-3$ $\left(\frac{3}{5}\to\frac{1}{5}\right)$	$-\frac{15}{7}\to-1$ $\left(\frac{3}{5}\to-\frac{1}{5}\right)$	$-\frac{5}{7}\to1$ $\left(\frac{3}{5}\to-\frac{3}{5}\right)$	$\frac{5}{7}\to2$ $\left(\frac{3}{5}\to-\frac{3}{10}\right)$	$\frac{15}{7}\to3$ $\left(\frac{3}{5}\to0\right)$	$\frac{25}{7}\to4$ $\left(\frac{3}{5}\to\frac{3}{10}\right)$	$5\to5$ $\left(\frac{3}{5}\to\frac{3}{5}\right)$
$\quad 3$		$-\frac{120}{35}\to-4$ $\left(-\frac{1}{10}\to\frac{3}{10}\right)$	$-\frac{72}{35}\to-2$ $\left(-\frac{1}{10}\to\frac{1}{10}\right)$	$-\frac{24}{35}\to0$ $\left(-\frac{1}{10}\to-\frac{1}{10}\right)$	$\frac{24}{35}\to1$ $\left(-\frac{1}{10}\to0\right)$	$\frac{72}{35}\to2$ $\left(-\frac{1}{10}\to\frac{1}{10}\right)$	$\frac{120}{35}\to3$ $\left(-\frac{1}{10}\to\frac{1}{5}\right)$	
$\quad 2$			$-\frac{9}{5}\to-3$ $\left(-\frac{3}{5}\to0\right)$	$-\frac{3}{5}\to-1$ $\left(-\frac{3}{5}\to0\right)$	$\frac{3}{5}\to0$ $\left(-\frac{3}{5}\to-\frac{1}{10}\right)$	$\frac{9}{5}\to1$ $\left(-\frac{3}{5}\to-\frac{1}{5}\right)$		
$\quad 1$				$0\to-2$ $\left(-\frac{9}{10}\to\frac{3}{10}\right)$	$0\to-1$ $\left(-\frac{9}{10}\to\frac{3}{5}\right)$			

enclosed in brackets. The value for the weak field is on the left, for the ·

Doublet Terms $R=\dfrac{2}{2}$

KJ \ m		$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$
$\frac{1}{2}$	1			$-1\to-1$ $(0\to0)$	$1\to1$ $(0\to0)$		
$\frac{3}{2}$	2		$-2\to-2$ $\left(\frac{1}{3}\to\frac{1}{3}\right)$	$-\frac{2}{3}\to0$ $\left(\frac{1}{3}\to-\frac{1}{3}\right)$	$\frac{2}{3}\to1$ $\left(\frac{1}{3}\to0\right)$	$2\to2$ $\left(\frac{1}{3}\to\frac{1}{3}\right)$	
	1			$-\frac{1}{3}\to-1$ $\left(-\frac{2}{3}\to0\right)$	$\frac{1}{3}\to0$ $\left(-\frac{2}{3}\to-\frac{1}{3}\right)$		
$\frac{5}{2}$	3	$-3\to-3$ $\left(\frac{2}{5}\to\frac{2}{5}\right)$	$-\frac{9}{5}\to-1$ $\left(\frac{2}{5}\to-\frac{2}{5}\right)$	$-\frac{3}{5}\to0$ $\left(\frac{2}{5}\to-\frac{1}{5}\right)$	$\frac{3}{5}\to1$ $\left(\frac{2}{5}\to0\right)$	$\frac{9}{5}\to2$ $\left(\frac{2}{5}\to\frac{1}{5}\right)$	$3\to3$ $\left(\frac{2}{5}\to\frac{2}{5}\right)$
	2		$-\frac{6}{5}\to-2$ $\left(-\frac{3}{5}\to\frac{1}{5}\right)$	$-\frac{2}{5}\to-1$ $\left(-\frac{3}{5}\to0\right)$	$\frac{2}{5}\to0$ $\left(-\frac{3}{5}\to-\frac{1}{5}\right)$	$\frac{6}{5}\to1$ $\left(-\frac{3}{5}\to-\frac{2}{5}\right)$	

Triplet Terms $R=\dfrac{3}{2}$

KJ \ m		-3	-2	-1	0	1	2	3
$\frac{1}{2}$	$\frac{3}{2}$			$-2\to-2$ $(0\to0)$	$0\to0$ $(0\to0)$	$2\to2$ $(0\to0)$		
$\frac{3}{2}$	$\frac{5}{2}$		$-3\to-3$ $\left(\frac{4}{9}\to\frac{4}{9}\right)$	$-\frac{3}{2}\to-1$ $\left(\frac{4}{9}\to0\right)$	$0\to1$ $\left(\frac{4}{9}\to-\frac{4}{9}\right)$	$\frac{3}{2}\to2$ $\left(\frac{4}{9}\to0\right)$	$3\to3$ $\left(\frac{4}{9}\to\frac{4}{9}\right)$	
	$\frac{3}{2}$			$-\frac{3}{2}\to-2$ $\left(-\frac{4}{9}\to0\right)$	$0\to0$ $\left(-\frac{4}{9}\to0\right)$	$\frac{3}{2}\to1$ $\left(-\frac{4}{9}\to0\right)$		
	$\frac{1}{2}$				$0\to-1$ $\left(-\frac{8}{9}\to-\frac{4}{9}\right)$			
$\frac{5}{2}$	$\frac{7}{2}$	$-4\to-4$ $\left(\frac{8}{15}\to\frac{8}{15}\right)$	$-\frac{8}{3}\to-2$ $\left(\frac{8}{15}\to0\right)$	$-\frac{4}{3}\to0$ $\left(\frac{8}{15}\to-\frac{8}{15}\right)$	$0\to1$ $\left(\frac{8}{15}\to-\frac{4}{15}\right)$	$\frac{4}{3}\to2$ $\left(\frac{8}{15}\to0\right)$	$\frac{8}{3}\to3$ $\left(\frac{8}{15}\to\frac{4}{15}\right)$	$4\to4$ $\left(\frac{8}{15}\to\frac{8}{15}\right)$
	$\frac{5}{2}$		$-\frac{14}{6}\to-3$ $\left(-\frac{4}{15}\to\frac{4}{15}\right)$	$-\frac{7}{6}\to-1$ $\left(-\frac{4}{15}\to0\right)$	$0\to0$ $\left(-\frac{4}{15}\to0\right)$	$\frac{7}{6}\to1$ $\left(-\frac{4}{15}\to0\right)$	$\frac{14}{6}\to2$ $\left(-\frac{4}{15}\to0\right)$	
	$\frac{3}{2}$			$-\frac{1}{2}\to-2$ $\left(-\frac{12}{15}\to0\right)$	$0\to-1$ $\left(-\frac{12}{15}\to-\frac{4}{15}\right)$	$\frac{1}{2}\to0$ $\left(-\frac{12}{15}\to-\frac{8}{15}\right)$		

that the σ components are represented each by two lines, displaced by $\frac{1}{3}\Omega$ to either side of the normal position of the σ components.

Landé's formula leads, in general, to each line of the normal triplet being represented by a close group of lines, whose separation is of the order of the separation of the original multiplet. Thus, proceeding in a manner similar to the above, we get for a P triplet :

$$\pi \text{ components at} \quad \nu_s + 0$$
$$\sigma \text{ components at} \quad \nu_s \pm \omega_H, \qquad \nu_s \pm \omega_H \pm \tfrac{4}{3}\Omega,$$

while for a D triplet (six lines ; see p. 504) we get :

$$\pi \text{ components at} \quad \nu_s + 0, \qquad \nu_s + 0 \pm \tfrac{24}{135}\Omega,$$
$$\sigma \text{ components at} \quad \nu_s \pm \omega_H, \qquad \nu_s \pm \omega_H \pm \tfrac{12}{135}\Omega,$$
$$\nu_s \pm \omega_H \pm \tfrac{4}{15}\Omega, \qquad \nu_s \pm \omega_H \pm \tfrac{4}{3}\Omega$$

This feature of the theoretical description has not yet been either definitely confirmed or contradicted experimentally. In order to obtain the Paschen-Back effect a very close multiplet is always chosen, so that the field may be strong in the sense defined : this does not, of course, render it doubtful whether the effect takes place or not, since the separations produced by the strong field are considerable, and, if each line of the multiplet, however close, produced its weak field type of pattern, a large number of well separated lines would, generally speaking, be visible. It does, however, render it · doubtful whether the wing components of the triplet which actually results are single lines, or complexes of lines separated by distances which are fractions of the width of the original multiplet. Thus the experimental result of applying a strong field to the oxygen PS triplet quoted on p. 523, whose total width is ·28 A.U., is to produce a strong and definite π component, but weak and washy σ components, which may well consist of close lines. In the field used, 32,000 Gauss, the distance of the wing components from the centre component is almost exactly the width of the original triplet.

Experiments carried out by Kent some years ago illustrate the nature of the Paschen-Back effect very well. He worked with the lithium doublets, which are very close, the difference of wave-length for the SP doublet λ 6708, on which the main

work was done, being about ·15 A.U.   In a weak field the two lines showed a magnetic resolution exactly similar to that of the sodium D doublet, while in very strong fields a normal triplet appeared, the separation of the two σ components being about 1·85 A.U. for 44,200 Gauss and 1·52 A.U. for 36,220 Gauss, which is that given by the Lorentz formula.*   These distances are greatly in excess of the width of the fieldless doublet.   A point of great interest is that the effect of a gradually increasing field on the individual components of the weak field pattern was followed, and found to correspond closely to the details of the theory, which are illustrated by Fig. 94, prepared by Sommerfeld for the sodium D lines.†
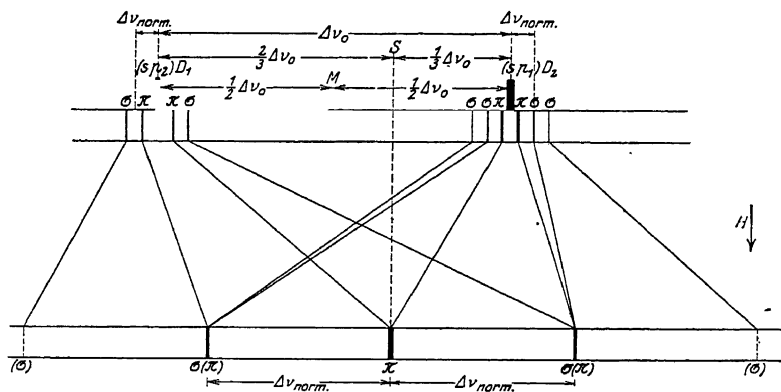
FIG. 94.

Paschen-Back effect for a principal doublet.

The oblique lines illustrate the way in which the weak field components blend and disappear to give a triplet.   Thus experimentally the enhancement of the inner components and the decrease in intensity of the outer components, the crossing over of the inner σ components, the symmetry of the final triplet about the optical centre of gravity S of the doublet, and other features exhibited in the figure were all established.

* $\Delta \nu = 4 \cdot 7 \times 10^{-5} H$ cm.$^{-1}$ or $\Delta \lambda = \lambda^2 \times 4 \cdot 7 \times 10^{-5} H$ cms., if λ be expressed in cms., and H in Gauss. $\Delta \lambda = \lambda^2 \times 4 \cdot 7 \times 10^{-13} H$ A.U. if λ be expressed in A.U.

† The Paschen-Back effect has not been experimentally obtained with the sodium doublet, on account of the very high field required.   See p. 523.

The Quasi-Mechanical Model. We have seen how it is possible to describe a large number of experimental results connected with the multiplet structure, and, in particular, the effect of a magnetic field on the multiplet lines, in terms of the quantum theory. In obedience to a fundamental postulate of that theory we have throughout based our considerations on term frequencies rather than line frequencies, and it has, in fact, been possible to express the wave-numbers of the components by the use of a restricted number of terms, in the case both of an external magnetic field and of no magnetic field. The attribution of quantum numbers to the terms, and a provisional mechanical scheme of rotations, enabled us to apply the correspondence principle, and the selection rules so obtained give good agreement with experiment. The correspondence principle has also given satisfactory results as regards intensities in simple cases. The time has now come to take a general look at the problem of representing these results in terms of a mechanical model, or, in the generally accepted sense, explaining them theoretically. Although, as will soon be seen, the model which has so far been devised is not satisfactory, in that arbitrary and unmechanical rules are frequently invoked to help over the chasms which cross the road, it has very useful functions as a mnemonic. It does give some kind of a meaning to many rules, and often it was by using such a model that rules were discovered. For many minds even a bad model is better than no model at all, which is the alternative to which some are turning.

Bohr's original model, based upon the theory of multiply periodic orbits, has been briefly described in Chapter XI. The principal quantum number n involves a radial quantum number: since at present we are concerned with moments only, we shall not need to refer to n further. The atom is considered to consist of a rigid core, exerting an axially symmetrical force, and an optical electron, each having its own moment of momentum, expressed by r and k respectively : these can be vectorially compounded to give j, the total moment of momentum of the atom. Throughout we express moments of momentum in terms of $h/2\pi$ as unity, to avoid unnecessary writing of symbols. According to the ordinary laws of

mechanics, in the absence of external forces, j must have a fixed direction in space, the vector framework of r and k revolving round this direction. Thus, since the plane of the orbit of the optical electron is normal to the vector k, there is a uniform precession of the plane of the orbit, bringing in a periodicity additional to the two periodicities considered in the theory of the plane orbit. The three periodicities give, by the theory of multiply periodic orbits, n, k and j. The model introduces four quantum numbers : n, k, r and j, but, the core being assumed rigid, the quantum number r—or, rather, its associated frequency—is not involved in the Fourier series for the electric moment of the atom. The number r serves to explain why k and j are not equal, and to limit the possible values of j, all quantum numbers being, of course, on this simple theory, integers. The correspondence principle can be at once applied to this straightforward scheme, and gives $\Delta k = \pm 1$, $\Delta j = 0$ or ± 1, as explained in Chapter XI. On this model the correspondence principle recognises only switches for which $\Delta r = 0$, although experimentally a very large number of combinations between terms of different systems are known (cf. Hg_I, with combinations for which $\Delta r = 2$.)

This model, in its original form, has proved unable to give a description of the properties revealed by the Zeeman effect. To preserve the selection rules, we have had to attribute half-integer values to certain of the quantum numbers. Again, the number of components which a given n_k orbit shows in the magnetic field is not consistent with the simple core-electron model. If we have a system consisting of a core acting, in the simple way assumed, on an electron, the number of stationary states in a magnetic field must clearly be equal to the number of stationary states of the core multiplied by the number of possible different stationary states of the electron in the field. Now for an alkali metal atom the core is of inert gas form : according to Bohr in the absence of any coupling forces the core takes one position only in the magnetic field, namely, with its moment set across the field, the K * group having, on the crossed orbit model, unit moment, and the other closed L, M groups no

* Not to be confused with the quantum number K.

moment.* The electron, of moment k, can, in the absence of coupling forces, take up $2k+1$ positions in the field, namely, every position of the vector k for which its projection on the direction of the magnetic field H is a whole number. Bohr, by whom these considerations were first put forward, excludes, for certain reasons, the direction across the field, so that he takes $2k$ states, but whether $2k+1$ or $2k$ be taken is a minor point. With the one state of the core, this gives $2k$ states for the whole atom. From the experimentally observed anomalous Zeeman effect, however, it appears that there are $4k-2$ states in all for an alkali metal atom in a magnetic field. Expressed in Landé's notation, the number of states (terms) for a given J is $2J$,† and, for a given k, J has two values, k and $k-1$, since $J = K + \frac{1}{2}$, $K - \frac{1}{2}$, and $K = k - \frac{1}{2}$. Expressed in Sommerfeld's notation, the number of states is $2j+1$ and j has the two values $k - \frac{3}{2}$, $k - \frac{1}{2}$, which likewise gives $4k-2$ as the total number of states, as, indeed, it must, since both Landé's and Sommerfeld's schemes are in this case a direct formulation of experimental results. Hence the original Bohr scheme is insufficient to account for the number of states observed, which is nearly double that which it predicts. The coupling between core and electron cannot be of the same nature as the action of an external field of force, but rather there must exist some additional constraint (or *Zwang*, as Bohr calls it) due to a non-mechanical stability of the atom, probably the same feature which finds expression in the postulate of the invariance and permanence of the quantum numbers. One way of picturing the action of this constraint is to say that it leads to two positions of the core when it is part of an atom, whereas when it is without accompanying electrons, it only has one.‡

* Bohr's explanation of the lack of paramagnetic properties of the inert gases is that they have unit magnetic moment, as demanded by the K group orbits, but that the moment sets with its axis across the direction of the field H, as assumed above. Since all directions of moment in the xy plane (the direction of the field being along the z axis) are possible, there is no moment for a large assemblage of atoms. Cf. Chapter XIV.

† See page 521.

‡ See, however, the discussion of Pauli's hypothesis of the electron with four quantum numbers, and the note on the spinning electron, later on in the chapter.

There are many other anomalies which are, no doubt, all expressions of the same fundamental difficulty as leads to the disagreement over the number of terms.   On the simple theory r and k are integers, which means that j, the resultant, must, if restricted to an integer, always have an odd number of values. This would allow only odd number multiplets, and hence we conclude that half-integer values must be permitted.   Again, if the Larmor theorem held, *i.e.* if the moment of momentum in a magnetic field were given by the classical relations expressed in the formula $\omega_H = \dfrac{eH}{4\pi m^* c}$, then the magnitude of the terms in the anomalous Zeeman effect would be given by the values of m alone, and g would be 1 in all cases, instead of having a different value for each j and k.   Further anomalies will appear when the occurrence of different spectral systems for the same atom is discussed.

It will now be as well to show what can be achieved by applying to the old model new assumptions, which unfortunately often contradict laws hitherto accepted. Desperate positions demand desperate devices, and some of the suggestions which will have to be discussed may justly be so called.   On occasions it has been deemed necessary to sacrifice classical mechanics, on other occasions to sacrifice classical electro-dynamics ; if, further, a sacrifice of logic be demanded we must not be distressed.   We are groping our way in a very dark and difficult region, and if we can, at any rate, obtain regularities, it may help towards the light.

Fig. 95.

Vector scheme for quasi-mechanical model.

Using Landé's notation we take R, K, J for the model in place of r, k, j, J being the vector resultant of R and K, and we assume that a special coupling force exerted between core and electron, *i.e.* between R and K, keeps this framework rigid in a magnetic field that

does not exceed moderate strength : the weak field does not control R and K separately, but acts upon J.

In Fig. 95 OM is the direction of the magnetic field H, and OA, OB, BA are J, R and K respectively, the plane of OBA not lying, in general, in the plane MOA. The effect of the field is, by assumption, to leave the magnitude of J unaffected, but to change its direction, so that it describes a cone of half angle θ about the direction of H, the angular velocity being given by Larmor's formula $\omega_H = \dfrac{eH}{4\pi m^* c}$. On classical theory the additional kinetic energy due to the rotation is

$$\Delta E = 2\pi \omega_H \cos \theta \cdot J, \quad \text{.......................(4)}$$

as follows at once from the ordinary laws of mechanics, remembering that the additional angular velocity, due to the magnetic field, about the axis of J is $2\pi \omega_H \cos \theta$. If ω_H, which is $\Delta \omega$, should be large, a term in $\omega_H{}^2$ must, of course, be added to the above expression, but we are not concerned with such cases.

We can quantise the direction of the total angular momentum by restricting the resolved part of J along H to be a whole number m times $h/2\pi$ or

$$J \cos \theta = \frac{mh}{2\pi}, \quad \cos \theta = \frac{mh}{2\pi J} \ .$$

(4) becomes

$$\Delta E = \omega_H mh,$$

or

$$\Delta \nu = \frac{\omega_H m}{c} \ . \quad \text{.........................(5)}$$

If the selection principle, $\Delta m = 0$ or ± 1, as deduced in Chapter X. be used, this gives the normal Zeeman effect. $\Delta m = 0$ corresponds to a polarisation parallel to the field, and $\Delta m = \pm 1$ corresponds to circularly polarised emissions which appear as linear polarisation normal to the field for transverse observation. It should be noted that the quantum number m gives the resolved part of the *mechanical* angular momentum along H, this mechanical momentum being that derived by applying Larmor's theorem. The anomalous Zeeman effect shows, however, that this reasoning will not give the correct change in energy due to the magnetic field.

We now consider the extension of the model to the anomalous effect. The magnetic quantum number m must retain its meaning, expressed in (5) : in particular $\Delta m = 0$ must give π components, $\Delta m = \pm 1$ must give σ components. The preservation of the selection and polarisation rule is the main object of allotting to a given term, ^rT_j, values of m which differ successively by unity. The magnitude of the energy change ΔE due to the magnetic field is, however, no longer given by $m\omega_H h$, but by $gm\omega_H h$, the value of g depending upon K and J, and the values of m are half-integer for even multiplets. One experimental fact, to which the splitting factor g gives expression, is that the terms no longer have their magnitude fixed by the value of m alone, as in the case of the normal effect, but J, K and R are also involved. The analysis of experimental results leads to a given number of terms for a given J (or j), which number is clearly $2m_{max} + 1$. Turning to the model, it is obvious that if the resultant moment J (expressed in terms $h/2\pi$ as unity) can place itself parallel to the field, then $m_{max} = J$, whereas if, as on Landé's scheme, half-integer m's are allotted to sequences for which J has integer values, and integer m's to sequences for which J has half-integer values, then m_{max} must always be less than J by $\frac{1}{2}$, or

$$\left| J - \tfrac{1}{2} \right| \geqq m \geqq - \left| J - \tfrac{1}{2} \right| .$$

Hence on Landé's scheme the total number of terms which the magnetic field produces for a term of given J is $2J$. On Sommerfeld's scheme, which allows the total moment of momentum to set parallel to H, m and j are integer or half-integer together, and the total number of terms is $2j + 1$. The number of terms obtained for a given fieldless term by analysis of the anomalous Zeeman patterns gives in many cases the surest way of fixing the value of J (or j).

To explain the appearance of the splitting factor g we are forced to appeal to some non-mechanical relation between core and electron, or to some non-mechanical property of the core, or of the electron, rendered evident by the magnetic field. It may be said that the precession is given by $g\omega_H$ instead of by Larmor's ω_H. Or we may refer the effect back to the core, as will be seen.

Landé's expression of empirical fact is

$$g = 1 + \frac{(J + \frac{1}{2})(J - \frac{1}{2}) + (R + \frac{1}{2})(R - \frac{1}{2}) - (K + \frac{1}{2})(K - \frac{1}{2})}{2(J + \frac{1}{2})(J - \frac{1}{2})} , \quad \ldots(2)$$

two values each for J, R and K, differing by unity, appearing in a formula which gives g for one value of J, R and K. This has also been expressed in the form *

$$g = 1 + \frac{\overset{\approx}{J}{}^2 + \overset{\approx}{R}{}^2 - \overset{\approx}{K}{}^2}{2\overset{\approx}{J}{}^2} . \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2a)$$

Driven by geometrical desire, we take in Fig. 95, $\overset{\approx}{J}$, $\overset{\approx}{R}$, $\overset{\approx}{K}$ in place of J, R, K; then

$$g = 1 + \frac{\overset{\approx}{R} \cos \psi}{\overset{\approx}{J}}.$$

Using

$$\frac{m}{\overset{\approx}{J}} = \cos \theta,$$

then

$$mg = \overset{\approx}{J} \cos \theta + \overset{\approx}{R} \cos \theta . \cos \psi.$$

θ and ψ are constant throughout the motion, but H, J, R are not, in general, coplanar. $\overset{\approx}{R}$ and $\overset{\approx}{K}$ precess uniformly round $\overset{\approx}{J}$. From this the average value of $\cos(\overset{\approx}{R}H)$ over a cycle is $\cos \theta . \cos \psi$, as can easily be seen by writing down direction cosines for H and R with respect to $\overset{\approx}{J}$ and associated axes. Therefore $mg = \overset{\approx}{J} \cos \theta + \overset{\approx}{R} \cos \theta . \cos \psi$

$$= \overset{\approx}{R} \overline{\cos (\overset{\approx}{R}H)} + \overset{\approx}{K} \overline{\cos (\overset{\approx}{K}H)} + \overset{\approx}{R} \overline{\cos \overset{\approx}{R}H)}$$

$$= \overset{\approx}{K} \overline{\cos (\overset{\approx}{K}H)} + 2\overset{\approx}{R} \overline{\cos \overset{\approx}{R}H}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

the bars denoting average values over complete cycles. On the other hand, if in the magnetic field $\overset{\approx}{K}$ and $\overset{\approx}{R}$ were to obey Larmor's formula we should have m simply equal to the sum of the resolved parts of $\overset{\approx}{K}$ and $\overset{\approx}{R}$ along H, averaged over a cycle, or

$$m = \overset{\approx}{K} \overline{\cos \overset{\approx}{K}H} + \overset{\approx}{R} \overline{\cos (\overset{\approx}{R}H)}. \quad \ldots\ldots\ldots\ldots\ldots(7)$$

* See page 521.

Comparison of (7) and (6) shows that the existence of a splitting factor g whose value is given by ($2a$) may be explained by attributing to the core a moment due to the field which is twice that to be expected, *i.e.* $2\omega_H \vec{R}$ instead of $\omega_H \vec{R}$. It should be noted, however, that to derive this it has been necessary to make two modifications, of obscure import, in Bohr's original scheme : (a) to introduce R and K instead of r and k ; (b) to replace R by $\sqrt{(R+\tfrac{1}{2})(R-\tfrac{1}{2})}$ and to modify K and J in a similar way, making the expression for g depend upon two values, differing by unity, for R, K and J. It may be remarked that this point seems to be so fundamental a feature of the newer quantum theory that Heisenberg has modified the formal rules of the theory in order to account for it.*

So far no explanation has been found as to why the core possesses a double magnetic moment. Experiments in the so-called magneto-mechanical effect, described in Chapter XVI, have, however, also indicated the necessity of ascribing to the atom an anomalous magnetic moment.

Intervals and Intensities. The model can be used to obtain other relations which accord with observation. We will first consider the intervals between the lines forming fieldless multiplets. Our assumption has been that the energy of the atom as a whole consists of (a) the energy of the core, (b) the energy of the series electron, (c) the energy of interaction between core and electron, due to the coupling forces between the two, of the nature of a potential energy. To the existence of these coupling forces the quantisation of the possible inclinations of the orbit with respect to the core must be attributed. Landé makes the reasonable assumption that this energy of inter-action (c), due to a force which tends to make the direction of the moment of the core and of the electron coincide, is pro-portional to the cosine of the angle α between R and K. If this be allowed, then for a given sequence, *i.e.* fixed value of R and K, the differences between terms will be proportional to the differences between permitted values of $\cos \alpha$. The permitted values are those that make J an integer or half-integer, as the case may be.

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* The new mechanics of Heisenberg, Born and Jordan automatically introduces this modification.

Thus, if C be a constant of proportionality, and $\Delta\nu_{ab}$ be the interval between two terms, characterised by J_a and J_b respectively, of same R and K ;

$$C\Delta\nu_{ab} = \cos_a (RK) - \cos_b (RK)$$

$$= \frac{J_a^2 - K^2 - R^2}{2KR} - \frac{J_b^2 - K^2 - R^2}{2KR}$$

$$= \frac{J_a^2 - J_b^2}{2KR} ;$$

or, within a group of terms belonging to a given multiplet sequence, $\Delta\nu_{ab}$ is proportional to $(J_b + J_a)(J_b - J_a)$.

On Landé's scheme J has integer values for even multiplets, half-integer values for odd multiplets. We must give J values 1, 2, 3 ... in the former, values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ ... in the latter case: this gives the intervals between successive terms—

for even multiplets $3 : 5 : 7 : 9 : ...$
for odd   multiplets $2 : 4 : 6 : 8 : ...$

Thus when the three terms of a P triplet sequence combine with a single term of another sequence the interval between the three resulting lines, taken in pairs, should be as $1 : 2$, since the values of J are $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$.   When the three terms of a D triplet sequence combine with a common term the intervals should be as $2 : 3$, since the values of J are $\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$.   This is approximately true : for instance, in the Ca$_I$ triplet $1\ {}^3P_{0, 1, 2} - 2\ {}^3D_{1, 2, 3}$ quoted on p. 504,

$$\Delta {}^3P_{01} : \Delta {}^3P_{12} = 52 \cdot 1 : 105 \cdot 9 = 1 : 2 \cdot 03 ;$$

while

$$\Delta {}^3D_{12} : \Delta {}^3D_{23} = 3 \cdot 7 : 5 \cdot 6 = 2 : 3 \cdot 03.$$

Many other spacings can be brought forward to support the scheme of term intervals just derived.   Hicks has criticised the rule, and found many cases which do not fall into line with it. Nevertheless, it enjoys a significant degree of success.

The intensities of the lines of a multiplet are also instructive, from the point of view of the weights of the terms.   If we regard each of the positions in the magnetic field as representing an equally probable state, then $2J$ will give the *a priori* probability of a term of quantum number J where there is no field, since $2J$ is the number of sub-terms, and an adiabatic

transformation does not change the *a priori* probability. If we consider the lines arising from combinations of the terms of a group of given J with a common term, then it is reasonable to suppose that the intensity of the different resulting lines should be proportional to the weights of the corresponding different terms. Thus the SP doublet terms of the alkali metals arise from a combination of $^2P_1$ and $^2P_2$ with $^2S_1$. For $^2P_1$ we have $J = 1$; for $^2P_2$ we have $J = 2$, and hence the weights are as 1 to 2; or the ratio of the intensity of the line $1\ ^2S_1 - n^2P_1$ to that of $1\ ^2S_1 - n^2P_2$ (the ratio of D_1 to D_2 in the sodium doublet) should be as 1 to 2. In the case of the triplet arising from a combination of the three ^3P terms with a given single term, since $J = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, the intensities should be as $5 : 3 : 1$. Now Burger and Dorgelo in Ornstein's laboratory have used the methods worked out by Moll and Ornstein to measure the relative intensities of lines of several types of multiplets, and have found experimentally the simple relationships just deduced from the J values for doublets, and for triplets arising from the combination of a group of triplet terms with a single term. The J rule has been further confirmed for a variety of types of multiplet terms combining with a single (or a very close multiple) term. This shows that the attribution of a space-quantisation meaning to J has a wider scope than might be expected.

Further success, however, has been obtained in interpreting the relative intensities in terms of the J's, for a scheme has been devised which includes satisfactorily the lines resulting from combination of a multiplet term with a multiplet term. In the case of a compound multiplet there will be a certain number of lines for all of which one of the two terms involved in each line is the same. If the intensities of these lines be added together, and the same be done for all groups of lines having a common term, then these sums will be proportional to the weights of the corresponding common terms. This is known as the intensity summation rule, and will now be illustrated by examples. We take first the case of a compound doublet, *i.e.* a doublet in which both terms have been resolved into two, and, to particularise, let it be a $^2P - ^2D$ doublet of the alkali metals. For the two ^2P terms J is respectively 1 and 2:

for the two ^2D terms J is 3 and 2, and the weights, being $2J$, are proportional to these numbers. Three lines arise from the two pairs of terms, the fourth being forbidden by the J selection principle, viz. $^2P_1 - {}^2D_2$, $^2P_2 - {}^2D_2$, $^2P_2 - {}^2D_3$. To satisfy the summation rule it will be found that we must attribute to these lines intensities in the ratio $5 : 1 : 9$, and we exhibit the result in the following way :

Sums	9	6	
5	0	5	$^2P_1$
10	9	1	$^2P_2$
	$^2D_3$	$^2D_2$	Terms

In the column to the extreme right are written the P terms, in the row at the bottom the D terms. In the square in the middle are written numbers proportional to the intensities of the lines, a given intensity being placed at the intersection of the row and column through the two terms involved. (Thus intensity 9 belongs to the line $^2P_2 - {}^2D_3$.) Intensity 0 represents, of course, the forbidden transition $^2P_1 - {}^2D_3$, for which $\Delta J = 2$. Above are written the sums of the intensities added in columns : to the left the sums of the intensities added in rows, and it will be seen that the numbers so obtained are proportional to the weights of the terms written opposite, the J's for which are given by the suffixes. Thus $9 : 6 = 3 : 2$ (D terms) while $5 : 10 = 1 : 2$ (P terms). Actually the intensities can, in this simple case, be calculated so as to give the right sums, and there is no element of arbitrariness in the ratio of the intensities, once the summation rule is assumed. The intensities have been measured for such a doublet, e.g. for a caesium $1\ ^2P_j - 2\ ^2D_j$ doublet, in Ornstein's laboratory, and the ratio $5 : 1 : 9$ accurately confirmed, and further measurements have been made by Dorgelo and by Frerichs which confirm the summation rule.

The summation rule has also been applied with success to compound triplets. In this case, however, the rule does not suffice to fix mathematically all the intensities from given J's, although measured intensities will fix the J's. We may

illustrate this by the case of a $^3P - {}^3D$ triplet.   For the ^3P terms $J = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$: for the ^3D terms $J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$.   From these J's the intensities can be calculated as given in the following scheme :

Sums	63	45	27		$(2J)$
15			15	$^3P_0$	1
45		$45 - x$	x	$^3P_1$	3
75	63	x	$12 - x$	$^3P_2$	5
	$^3D_3$	$^3D_2$	$^3D_1$	Terms	
$(2J)$	7	5	3		

Here, again, it will be seen that the sums of the columns are in the ratio $7 : 5 : 3$ of the weights, $2J (= 2j + 1)$, of the ^3D terms, and the sum of the rows in the ratio $1 : 3 : 5$ of the weights of the ^3P terms.   There is, however, an unknown x involved in the intensities.   If we put $x = 11$, so as to make the intensity of the weakest line 1, we have for the intensities :

		15
	34	11
63	11	1

which are in the same ratio as

		24
	54	17·5
100	17·5	1·6

as against the experimental values

		25
	54	19
100	18	1

This is the case of the calcium 1 $^3P_j - 2\ ^3D_j$ triplet given on page 504.   A large number of measurements on compound triplets have confirmed the validity of the summation rule in these cases.

The rule just discussed includes an earlier intensity rule due to Sommerfeld, which is very useful for qualitative application. This states that in a given multiplet those lines are strongest for which k and j (or, of course, K and J) change in the same sense, while for the weakest lines k and j change in opposite senses. This rough rule can easily be checked on the above example.

It has been seen that for triplets and higher multiplets there is an element of arbitrariness in the prediction of intensities by the summation rule, since the values of the J's do not suffice to determine all the intensities, *i.e.* an unknown x has to be

introduced. Attempts have been made to arrive at more comprehensive results by invoking the correspondence principle. By its essence the principle provides exact results only when the change of quantum number involved in a quantum jump is small compared to the quantum numbers themselves, which is not generally the case with the multiplets in question. In other words, we are confronted with the problem as to whether to use the initial or final J, or a compromise. It would seem, therefore, that ordinary considerations of the correspondence principle cannot replace the summation rules, but, by determining the order of the intensity ratios when the initial and final quantum numbers are both large, can provide a general scheme to be supplemented by the summation rule. Such generalisations have been made by Sommerfeld and Hönl, and by Kronig. R. H. Fowler has since shown that by a refined application of the correspondence principle a theoretical meaning may be attached to the summation rules, so that in a certain sense the correspondence principle may be said to include these rules.

The chief point which we wish to emphasise by quoting these rules is that not only the Zeeman splitting, but also the intervals and intensities, go to demonstrate that J has a real meaning, and that its allotment is not so arbitrary as might at first appear. When arguments are being based on the value of J it is well that this should be borne in mind.

Theory of Paschen-Back Effect. Duplicity Scheme. On the core + electron model, the Paschen-Back effect is explained by assuming that in a very strong external field the interaction between core and electron is overcome, the field, as it were, taking complete control, so that both core and electron set themselves independently in such a way as to make the projection of the moment of momentum in the direction of the field an integer or half-integer, as the case may be. Instead of allotting a single quantum number m to give the projection of J in the direction of H, we must, when K and R behave independently, allot two quantum numbers, m_R to give the projection of R, and m_K to give the projection of K,

$$\cos(KH) = \frac{m_K}{K}, \qquad \cos(RH) = \frac{m_R}{R}.$$

In the case of a weak field, the coupling between R and K is the controlling factor, and the vector triangle RKJ behaves as a rigid framework, the angle between R and K remaining constant with the time as the whole rotates about J, J itself rotating so as to make a constant angle with H, and thus describing a cone. The frequency of rotation is given by $g\omega_H$, which, as we have seen, is, on the hypothesis stated, equivalent to giving to the electron its normal magnetic moment, but to the core a double moment. In the case of a strong field the " natural " coupling forces are negligible, and it is to be supposed that the core rotates with a double frequency, the electron with a normal frequency : J then varies with the time, since R and K no longer keep in the same plane, the forces that tend to make them do so being now negligible.* Hence in this case J is no longer an action variable at. all, and so is incapable of quantisation. The energy of interaction will still be given by the cosine of the inclination of R and K, which inclination is governed by the external field, and must be assumed, on our ordinary quantum basis, to be fixed by the time mean of cos (RK) over a whole cycle. This energy of interaction is what we have expressed by γ : in a weak field this γ expresses the energy due to the fixed angle of inclination, so that, as we saw, in the case of a doublet term

$$\nu = \nu_S + \gamma\Omega. \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots(8)$$

In a strong field $\gamma =$ mean value of cos (KR)

$$= \cos (KH) \cdot \cos (RH),$$

just as, in deducing the g value for the weak field, the mean value of cos $(\overset{\leftrightarrow}{R}H)$ was cos $\theta \cdot \cos \psi$, so that

$$\gamma_s = \frac{m_R}{R} \cdot \frac{m_K}{K}. \quad\dots\dots\dots\dots\dots\dots\dots\dots(9)$$

As regards the g value for the strong field, by definition the additional energy in the field is given by $mg\omega_H$. The energy

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* The effect of a weak field may also be expressed by saying that, in this case, the forces of interaction being the controlling feature, the frequency of rotation of J is a kind of compromise between that of the core and of the electron.

of the electron in the magnetic field is given by $\omega_H m_K$, and of the core is $2\omega_H m_R$, so that

$$mg_s\omega_H = \omega_H(m_K + 2m_R),$$

or $$mg_s = m_K + 2m_R. \dots\dots\dots\dots\dots\dots\dots\dots\dots(10)$$

(9) and (10) are the formulae given on p. 526 in discussing the Paschen-Back effect. The values for m_R and m_K in terms of R, J and K, given in that discussion, have been deduced by Pauli from this model, but the calculation is very intricate. That $m_K = m - m_R$ as implied by the formulae, is obvious from Fig. 95, and is, of course, an immediate consequence of the adiabatic invariance of the moment of momentum of the atom about H.

There are, of course, certain grave imperfections in the mechanical model. We have, for example, to consider the difficulties connected with the choice of k for the orbits, which has to be taken sometimes as an integer, sometimes as a half-integer. Sufficient stress has already been laid upon the difficulties presented by the simultaneous existence of the relativity and the shielding doublet, both for optical and for X-ray spectra. In addition to n we require two quantum numbers to represent the doublets, k_1 and k_2 (or k and j). If we take k_1, the ordinary azimuthal quantum number, to give the sequences (putting $k_1 = 1, 2, 3, 4 \dots$ for $S, P, D, F \dots$), then we shall have k_1 the same for both terms of the relativity doublet. We are thus at a loss to explain why the relativity formula, based upon the energy differences of orbits of the same n, but different k, should hold. If we take the differences of k_1 to give the relativity doublet, that is, if we take different values of k for one and the same sequence, the whole periodicity scheme, with its correspondence and selection rules, is imperilled. The predicament is grave.

Heisenberg has made a determined attempt to devise a scheme which shall accept the duplicity of behaviour to which we have so often directed attention, and make it a fundamental feature of the quantum theory. He definitely abandons any attempt at a mechanical or quasi-mechanical model as far as the dilemma in question is concerned, and this makes it somewhat difficult to get accustomed to his method of presentation. It is by no means certain that the scheme put forward will retain

a place in the quantum theory : it seems likely that the very difficult ideas involved will be replaced by others at the same time more general and more precise. However, a brief description of Heisenberg's suggestions may help to classify and emphasize the existing difficulties, and so pave the way for the inclusive theory that is to come.

We consider first of all the doublet system, given by an inert gas core and one electron, postponing the general question of the multiplet systems. Heisenberg divides the energy of the atom into three parts, that of the electron itself, that of the core itself, and an energy of interaction. This energy of interaction does not exist on the original Bohr scheme : it originates in the constraint (*Zwang*) to which reference has already been made. It depends upon some forces of a mysterious non-mechanical nature. He then assumes a kind of reciprocal duplicity : that is, with a given· stationary state of core and of electron not one, but two, possible energies of interaction are compatible, and, conversely, compatible with any one value of the energy of interaction are two, not one, stationary states of the atom as a whole. This demands the simultaneous existence of two azimuthal quantum numbers, one an integer and the other a half-integer, which we denote by k and K as before, although these symbols no longer necessarily retain in all cases their precise former significance.

There are two ways in which the duplicity may be supposed to occur : either the electron acts on the core in some occult way so that to each stationary state of the electron correspond two stationary states of the core, or the core may act on the electron, so that to one stationary state of the core there correspond two stationary states of the electron. These two schemes, called by Heisenberg Scheme I. and Scheme II. respectively, are not mutually contradictory, but complementary. One explains one set of facts, the other another set, and both must be taken together to get a satisfactorily complete representation of experimental fact. The two values of the electron energy obviously correspond to the relativity doublet theory : the two states of the core correspond, as will be seen later, to the case of Landé's inclination hypothesis, by which the different systems are due

to different cores. The two schemes are a formal rearrange-ment of the known facts, and are to be regarded as such.

Taking Scheme II. first, the inherent energy of the electron E_0 (" own " energy) is a function of n and k. A sequence of integer values is chosen for this k, while K, for which half-integer values are chosen, represents the energy of inter-action E_i. To give the duplicity, we then have the following scheme :

For E_0: $\quad k =$

$\qquad \text{I} \qquad\qquad\qquad 2 \qquad\qquad\qquad 3 \qquad\qquad\qquad 4$

$\qquad\qquad {}^2S_1 \ {}^2P_1 \qquad {}^2P_2 \ {}^2D_2 \qquad {}^2D_3 \ {}^2F_3 \qquad {}^2F_4$

For E_i ; $\quad K = \frac{1}{2} \qquad\qquad\qquad \frac{3}{2} \qquad\qquad\qquad \frac{5}{2} \qquad\qquad\qquad \frac{7}{2}$
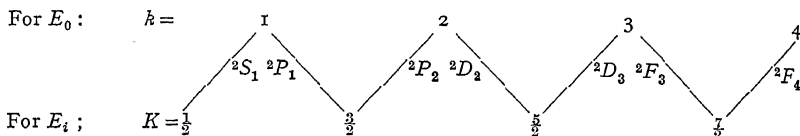
To understand the scheme it should be noted that to every value of the interaction energy except the first $(K = \frac{1}{2})$ corre-spond two values of the inherent energy, while to every value of the inherent energy correspond two interaction energies. If we regard the K's as fixing the sequences $S, P, D, F \ldots$, as on Landé's scheme, then corresponding to each sequence (except S) we have two integer k's for the energy of the electron itself. Two different integer k's give a relativity doublet, viz. I and 2 for the P doublet, 2 and 3 for the D doublet, and so on. This scheme, then, expresses the relativity regularities, and shows in a neat form the necessity of invoking both integer and half-integer values of the azimuthal quantum number. It cannot, however, give any account of the corre-spondence and selection principles, since these are based upon an electron moving in a periodic orbit characterised by a single k (in addition, of course, to n).

To express the valuable results deducible from the electron in a periodic orbit Scheme I. must be considered, where the electron energy has a single value corresponding to one inter-action energy, but the core energy has two values. The doublets are given by the hypothesis that different inclinations of the electron orbit with respect to the core give different energies for the atom as a whole, the number of possible inclinations being $2R$, where R is the core quantum number, as on Landé's scheme. Actually, as the doublet system is the only system for the alkali metals, only one value of the core energy, $R = I$,

is needed. For formal reasons connected with the branching rule which will soon appear the two possible values $R=0$ and $R=1$ are assumed for the core, $R=0$ having no physical meaning (a system of zero multiplicity). The sequences are given by $K=\frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ldots$, as far as the interaction energy, the compounding with R, is concerned, since Landé's R is adopted. For the electron orbit itself, as concerned in the correspondence and selection principle, integer values of k can be taken : the electron has a single inherent energy. On this scheme the two whole numbers written down as corresponding to each different value of K (1 and 2 for $K=\frac{3}{2}$, 2 and 3 for $K=\frac{5}{2}$, and so on) represent the J values for the doublets. Scheme I. is an expression of the inclination hypothesis analogous to the representation of the relativity hypothesis given by Scheme II. On both schemes the energy of interaction is given by half-integer K's, while integer values of k are adopted to allow the results of the theory of periodic orbits to be included.

Heisenberg extended his duplicity considerations to the magnetic properties of the atom. We will content ourselves with mentioning that he connected the anomalous magnetic properties with the inherent energy of the electron, since this leads to an interesting way of deriving straightway the values of g for the case of doublets. g expresses, from the definition, the ratio of the actual magnetic energy to the energy to be expected on mechanical grounds, if the Larmor theorem held. Now, strikingly enough, the result of dividing an integer k by a half-integer K connected with it is to give the g value for the term belonging to these particular values of k. This is clearly expressed in the following scheme which is given as a mnemonic :

For E_0 : $\quad k \qquad 1 \qquad\qquad 2 \qquad\qquad 3$

$$g=2 \diagup \searrow g=\tfrac{2}{3} \quad g=\tfrac{4}{3} \diagup \searrow g=\tfrac{4}{5} \quad g=\tfrac{6}{5} \diagup$$
$$\diagup {}^2S_1\ {}^2P_1 \searrow \qquad\qquad \diagup {}^2P_2\ {}^2D_2 \searrow \qquad\qquad \diagup {}^2D_3$$

For E_i : $\quad K\ \tfrac{1}{2} \qquad\qquad\qquad \tfrac{3}{2} \qquad\qquad\qquad \tfrac{5}{2}$
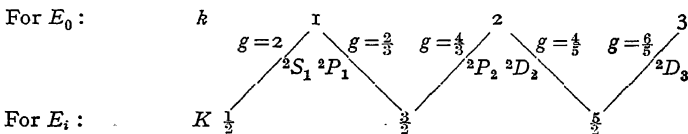
The question of the j's or J's is most simply settled by defining j, which gives the total moment of momentum of the atom, as the total number of permitted positions of the axis of total momentum in the magnetic field. We have seen that on Sommerfeld's scheme this number $N=2j+1$ or $j=(N-1)/2$.

According to Landé's scheme $J = N/2$. This defines J or j uniquely. However, Heisenberg, basing himself on the fact that the g formula has indicated not one, but two values of J to determine the enigmatic coupling between core and electron (in the formula for g the expression $(J + \frac{1}{2})(J - \frac{1}{2})$ occurs where we should expect J^2 from the mechanical model), has shown how the quantum conditions may be made to depend on two values of J, not one. In this connection, it should be remembered that when an electron is added to an atom of atomic number Z, inner quantum number J, making an atom of atomic number $Z + 1$, we do not get J as the moment of the core, as we should expect, but two values $J + \frac{1}{2}$, $J - \frac{1}{2}$, as expressed in the branching rule to which reference is made in the following pages.

To introduce the two J values Heisenberg defines an integral invariant $F = \int H \, dJ$, H being the Hamiltonian function, expressing the energy of coupling, determined by the moment of momentum J. Then obviously $H = \dfrac{\partial F}{\partial J}$ on the ordinary theory. Instead, however, of a differential coefficient in this last expression, Heisenberg suggests taking a ratio of finite differences : for the infinitesimal ∂J we are to take

$$\Delta J = (J + \tfrac{1}{2}) - (J - \tfrac{1}{2}),$$

and correspondingly ∂F becomes $F(J + \frac{1}{2}) - F(J - \frac{1}{2})$. That is, the different values of the energy corresponding to a fixed n and k are determined not by a single quantum number J, but by two J's, differing by unity. The coupling energy of electron (or, in the case of many electrons taken together, of electrons) and kernel demands a pair of quantum numbers for its expression. This is a new conception in the quantum theory, and the advantage claimed for it is that the innovation, difficult as it is to provide it with a physical meaning, seems to give a suggestive expression of the difficulties to which Bohr's principle of successive additions led, namely, the fact that the weights derived from the principle do not agree with the facts of the anomalous Zeeman effect. Further, it can be made to explain the permanence of the g sums, and allows us to see how the

multiplicities observed for elements of different columns in the periodic table arose. The permanence of the g sums is obtained by Heisenberg by applying the Hamiltonian method to the new quantum principle. The scheme for multiplicities can be simply expressed as follows :

Taking Landé's R and K, we have for doublets, since each of Landé's J's now becomes $J \pm \frac{1}{2}$,

R		1			1				1	
K		$\frac{1}{2}$			$\frac{3}{2}$				$\frac{5}{2}$	
J (Landé)		1		2		1		3		2
J (Heisenberg)	$\frac{3}{2}$	$\frac{1}{2}$		$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{7}{2}$		$\frac{5}{2}$	$\frac{3}{2}$
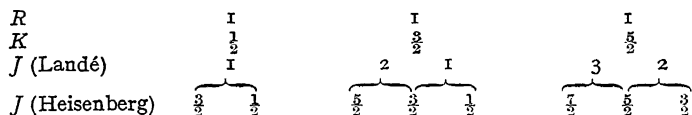
The rule $K + R \geq J \geq |K - R|$ is clearly obeyed, allowing K and R to be parallel to one another as extreme cases, which seems natural, but which is excluded on Landé's original scheme, where the J's are whole numbers for doublets. It is true that the parallel position is allowed on Sommerfeld's scheme, but there the moment of the S state has to be taken for R, and j_a for K. The scheme of two values of J corresponding to one value of R leads also to a general expression for the multiplets (*i.e.* an expression of the branching rule) as a consequence of the principle of successive additions. If the S term state becomes the core for the atom of the next higher atomic number, then the J of the first atom becomes the R of the next atom, and we have both $R = \frac{3}{2}$ and $R = \frac{1}{2}$; $R = \frac{3}{2}$ giving a triplet system, and $R = \frac{1}{2}$ giving a singlet system. For the S state when $R = \frac{3}{2}$ we have $J = 2$ or 1; when $R = \frac{1}{2}$ we have $J = 1$ or 0, *i.e.* for the whole second atom $J = 2, 1$ or 0. This in turn leads to quartets and doublets for the next higher atom, since $R = 0$ has no physical significance. The scheme can be expressed as follows :

Potassium$_I$ (^2S state normal)	R		1			
			(Doublets)			
	J		$\frac{3}{2}$		$\frac{1}{2}$	
			↓		↓	
Calcium$_I$	R		$\frac{3}{2}$		$\frac{1}{2}$	
			(Triplets)		(Singlets)·	
	J	2	1	1		0
		↓	↓	↓		↓
Scandium$_I$	R	2	1	1		0
		(Quartets)	(Doublets)			(Nothing)
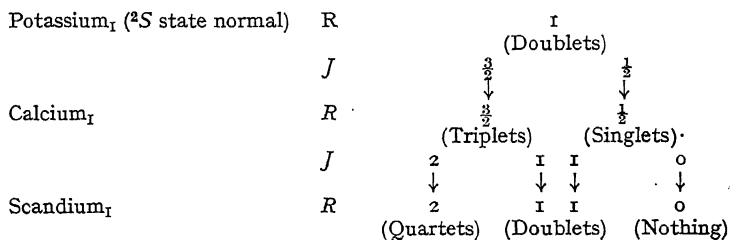
This attribution of multiplicities is in accordance with the analysis of experimental data.

The change of J is, in general, expressed in Heisenberg and Landé's branching rule (*Verzweigungsprinzip*). Consider an atom A, of atomic number Z, which is succeeded in the periodic table by an atom B, of atomic number $Z + 1$, formed from A by the addition of an electron. The branching rule lays down that if the x states of A are characterised by values of J which are $J_1, J_2 \ldots J_x$, then, the atom B possesses S terms characterised by values of J which are $J_1 \pm \frac{1}{2}, J_2 \pm \frac{1}{2}, \ldots J_x \pm \frac{1}{2}$. The multiplicities expressed in the tables on page 435 obviously follow from this.

Delegation of Anomalies to Electron. The atom can be considered to consist of a closed, inert gas structure, which we have called the kernel, and certain outer electrons, the valence electrons : alternatively we can consider it as consisting of a core, comprising all the electrons but one, and an optical electron. In all cases but the alkali metals, where core and kernel are the same, the core will consist of the kernel and certain other electrons : in general, it is the singly charged positive ion of the atom in question.

Heisenberg, Russell and Saunders, and, following them, Hund, have obtained valuable results by considering the kernel plus valence electrons scheme, and take all the outer electrons as possessing together a moment of momentum characterised by a quantum number l : this moment of momentum can have more than one value for a fixed number of electrons, such electrons possessing each a fixed k, according to the various possible ways in which the orbits of the electrons can be spatially quantised with respect to one another. It is clear, without considering details, that the more outer electrons there are, the greater the number of possible values of l, so that we have here an indication of the way in which the many different systems of spectral terms can occur. On this scheme, the interaction of l, as a whole, with the kernel has to be considered. It is equivalent to the assumption that the interaction of the outer electrons with one another is large compared to the interaction of the single electrons with the core. We may refer to it as the kernel scheme.

On the other hand, it is often possible to reach very important results by considering all the outer electrons but one, taken with the kernel, as forming the core : this corresponds more directly to Bohr's principle of successive additions, each whole atom acting as the core of the next atom in order of Z. In this case we have various possibilities for the core, according to the way in which the core electrons are arranged about the kernel. Physically this separation of the atom into a core and a single electron, which we may call the core scheme, implies that there is one single electron much more loosely coupled to the other outer electrons than any other, so that these outer core electrons are coupled to the kernel more tightly than to the single electron. The Landé-Heisenberg branching rule is consonant with this scheme. Which of the two methods, the core or the kernel scheme, better corresponds to the fact clearly depends upon the atom under consideration. For certain problems the simpler scheme of the single privileged electron suffices, but for others, more particularly the term structure of the complex spectra, the interaction of all the outer electrons must be taken into account. Even with one atom it is possible for the deeper terms to correspond to one scheme, the remoter terms to the other, since the interaction of the electrons with one another may vary, as compared to that of the electrons and the kernel, according to the orbits occupied.

We proceed to consider attempts which have been made to state the observed regularities in simple arithmetic form. Of explanation in the normal sense of a valid mechanical model, there is hardly any question, since the laws both of mechanics and of the original Bohr theory are freely broken in the hypotheses by which the struggle forward is supported. The immediate problem is to find cookery receipts, rather than physical principles, for compounding and selecting and combining quantum numbers.

Pauli has obtained significant results by a method which falls under Heisenberg's Scheme II.* He is particularly anxious to retain the principle of successive additions, and troubles little

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* Pauli's paper was written before Heisenberg's classification was published, so that he does not make use of Heisenberg's nomenclature.

about the theory of multiple periodicities and the correspondence principle, and hence Scheme II., with its duplicity of the inherent energy of the optical electron is indicated : he throws the anomalies upon the electron itself. He is mainly concerned with the deduction of the number of possible states for atoms with different numbers of outer electrons, and relies on the invariance, during an adiabatic transformation, of the statistical weights of the various quantum states to derive the number of fieldless states from the case of the strong external field, which introduces a certain simplicity.

We start with the alkali metals, which form the jumping-off place for all such considerations, since they are the simplest case which exemplifies the fundamental difficulties which we have already discussed in connection with the duplicity scheme. The core, being of inert gas form, has no moment, as we have argued in Chapter XIV., so that the whole moment must be attributed to the optical electron. We characterise this by three quantum numbers, n, K and k, where K, which determines the sequence, corresponds to the interaction energy on Heisenberg's Scheme II., and k, which determines (for definiteness, say by the relativity effect) the doublet nature of the terms, is the k corresponding to the inherent energy on that scheme. Whether we use the language of Heisenberg's scheme is immaterial : in any case K has the value $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ . . . for the ^2S, ^2P, ^2D . . . sequences, while k is 1 for the ^2S sequence, 2 or 1 for the ^2P sequence, 3 or 2 for the ^2D sequence, and so on, or $k = K \pm \frac{1}{2}$. The number k therefore has the same values as J on Landé's scheme, but, as we are considering an inherent duplicity in the electron, it seems better to use k as the symbol. These three quantum numbers n, K, and k do not, however, fully determine an orbit, for in the presence of an external field various positions of the orbit are possible, which require a fourth quantum number for their determination. Since this quantum number remains the same as the field is progressively weakened, we can suppose that even in the normal atom there is an orbit corresponding to each of the possible orbits in the field (n, K and k being, of course, left unchanged). A quantum number m will specify, as we know, the number of possible positions in a magnetic field, or, more precisely, the projection of the

mechanical moment on the direction of the field. Hence n, K, k, m specify uniquely an electron orbit, and the fact that four quantum numbers are required to specify an orbit of three degrees of freedom is a fresh way of expressing the fundamental difficulties which meet any attempt to apply the theory of multiple periodicities in detail to the atomic system.* If we take a very strong magnetic field producing the complete Paschen-Back effect, we have, as we have seen, a magnetic quantum number m_K to attribute to the electron itself, expressing its own magnetic moment, as distinct from the mechanical moment given by m. If m_K is specified, k is not necessary, since in the very strong field differences of k (or differences of J) have no significance. The four values n, K, m, m_K may be used in place of n, K, k, m to specify the orbit, as may be seen from formulae (3). In general, when the core itself has a moment, we can use the number mg_s, expressing the energy of the atom in a strong field, $i.e.$ the moment resolved parallel to the field, in place of m_K, one being deducible from the other.

Now the number of possible orientations of the electron orbit in a magnetic field which, in the case of the alkali metals with the kernel as core, is the same thing as the number of possible states of the atom, is $2J = 2k$. Hence for both doublet components, $i.e.$ for a given K, the total number of terms is $2(K - \frac{1}{2}) + 2(K + \frac{1}{2}) = 4K$. This is a direct expression of experimental results.

* A suggestive hypothesis, which gives a mechanical interpretation of the necessity for four quantum numbers, has been recently put forward by Uhlenbeck and Goudsmit. (*Nature*, 117, 264, 1926.) They assume that the electron spins about an axis through its figure with a moment of momentum which can be quantised. There are the four quantum numbers—n, K, J and a quantum number giving the spin of the electron. Different possible orientations of the spin axis with respect to the orbital plane correspond to different states of the atom. When the electron has a one-quantum spin there are two possible orientations for the axis of the electron moving in a nuclear electric field, $i.e.$ in the field produced by an electric charge without magnetic moment, and calculation shows that the difference of energy between the two possible states is proportional to the fourth power of the nuclear charge. In the case of the alkali metals the core has no magnetic moment, and the doublets can, then, clearly be explained as due to the spin of the electron. In the case of atoms in which the kernel is accompanied by two or more electrons the problem is complicated by the magnetic field produced by the electrons. The quantum theory of an atom in which the electrons possess quantised spins has not yet been developed, but the new conception seems very promising, and has received the approbation of Bohr.

Passing to the alkaline earths, the analysis of experimental data gives $8K$ as the permanent number of stationary states corresponding to a given sequence number K in a magnetic field, namely, $2K$ for the singlet and $6K$ for the triplet sequence. For example, for the ^3D sequence, $K = \frac{5}{2}$, the terms $^3D_1$, $^3D_2$, $^3D_3$ are resolved respectively into 3, 5 and 7 terms, while $^1D_2$ is resolved into 5 terms, making 20 terms in all. (Cf. table on pp. 528, 529.) These are explained on the inclination hypothesis by supposing that in a strong field the series electron can take up $2K$ positions in the field, while to each position of the electron orbit corresponds one position of the core for the singlet, three positions of the core for the triplet system. This violates the principle of successive additions, for on the same inclination hypothesis the alkaline earth *core* system of electrons, when it is associated with a nucleus of one lower atomic number to form an alkali metal *atom*, can only take up two positions in the field, so that the quantum numbers of the old electron would have been changed by the addition of a new electron. Pauli, however, takes the singlet and triplet terms together to give a group of $8K$ states. If we allow the alkaline earth core the two positions which it should have if regarded as the S state of an alkali metal atom ($K = \frac{1}{2}$, $k = 1$, $m = \pm\frac{1}{2}$), and allow the electron the $4K$ positions which, on Pauli's hypothesis, it must always possess in virtue of its duplicity, then we get in all $2 \times 4K = 8K$ states, as required.

Pauli's scheme leads not only to the number of states, but also to a calculation of the j values for atoms with more than one valence electron, and the value of the energy proportional to the field in the case of strong fields, *i.e.* the value of mg_s. By the principle of successive addition, as interpreted by Pauli, we give to each electron the various possible values of m and mg_s which it would have independent of the other electrons, *i.e.* the value which it would have for the alkali metals, and, assuming a strong field, add the m's and the mg_s's, taking one value at a time for each electron, to give values for the whole atom. We form

$$\bar{m} = \Sigma m, \quad \overline{mg_s} = \Sigma mg_s$$

where the summation sign includes one value for each electron,

and every possible selection of m's gives an $\overline{m}$, and similarly with the mg_s's. The $\overline{m}$'s so obtained hold for a weak, or zero, field as well, and tell us what the j's will be for the whole atom, since $\overline{j} \geqslant \overline{m} \geqslant -\overline{j}$. Thus, as a simple example, consider the S terms, $^1S_0$ and $^3S_1$ of an alkaline earth. There are two electrons in addition to the closed inert gas structure : for each of these $m = \pm\frac{1}{2}$, while $mg_s = \pm 1$. The mg_s values can be taken from the tables on pp. 528, 529, or calculated from formula (3). Then we have as possible values :

$$
\begin{aligned}
\overline{m} &= -\tfrac{1}{2}-\tfrac{1}{2} = -1 & \overline{mg_s} &= -1-1 = -2 \\
&= -\tfrac{1}{2}+\tfrac{1}{2} = 0 & &= -1+1 = 0 \\
&= \tfrac{1}{2}-\tfrac{1}{2} = 0 & &= 1-1 = 0 \\
&= \tfrac{1}{2}+\tfrac{1}{2} = 1 & &= 1+1 = 2
\end{aligned}
$$

The $\overline{m}$ values are the values of m for the atom with two electrons, and give for the atom as a whole, $\overline{j} = 1$, corresponding to $\overline{m} = \pm 1, 0$; and $\overline{j} = 0$, corresponding to $m = 0$. The $\overline{j} = 1$ belongs to the term $^3S_1$, the $\overline{j} = 0$ to $^1S_0$. The $\overline{mg_s}$ values give the possible values of the energy due to the strong field for the whole atom.

The delegation of the anomalies to the electron and consequent specification of the orbit by four quantum numbers has led to a very important generalisation of Stoner's scheme. On this scheme the electron orbits are grouped firstly according to their n's : the group belonging to one n is divided into subgroups distinguished by different values of k_1, and these subgroups are further divided into grouplets, distinguished by values of k_2, k_2 being k_1 or $k_1 - 1$. (See Chapter XIV.) The number of electrons in an $n_{k_1k_2}$ group is $2k_2$. In this notation k_1 is our present $K + \frac{1}{2}$, since k_1 has the values 1, 2, 3, 4 . . . , while $k_2(=k_1$ or $k_1 - 1) = K \pm \frac{1}{2}$ is our present k. Now we have seen that the total number of states for a single electron in a magnetic field is $2k$. In agreement with this Pauli makes the hypothesis that an atom can never contain more than one electron having a given set of values for the four quantum numbers n, K, k, m (or n, K, m, m_K), or, *in other words, if one electron occupies an orbit fixed by four given numbers n, K, k, m, this type of orbit is no longer available for a second electron.*

This hypothesis of the *uniqueness* of an orbit determined by four quantum numbers is capable of a wide range of application, and seems likely to become an established feature of atomic theory. It is proving of the greatest importance for the analysis of complex spectra. It gives, of course, the number of electrons in each closed inert gas system, since it is an expression of Stoner's scheme. Certain features of the spectra of atoms with two outer electrons follow at once from the hypothesis. Consider, for example, the case of the S terms of the alkaline earths just treated. For both electrons $K = \frac{1}{2}$, $k = 1$, $m = \pm \frac{1}{2}$. In the particular case where n is the same for both electrons the principle of uniqueness says that they cannot both have the same value of m as well as of K and k, so that, in this particular case, $m = \frac{1}{2}$ for one electron, $m = -\frac{1}{2}$ for the other electron. In a strong field, therefore, $\overline{m} = \frac{1}{2} - \frac{1}{2} = 0$, which means that $\bar{j} = 0$ for the atom as a whole ; this must also be true for a weak, or zero, field. There is, then, only one possible case if both electrons are bound in orbits of equivalent K, k and n, namely the atomic state having $j = 0$, corresponding to the $^1S_0$ term. For the deepest triplet $^3S_1$ term n must be greater for one electron than for the other. In other words, for the neutral alkaline earths the basic $^1S_0$ term corresponds to the two electrons normally bound, while $^3S_1$ does not. More elaborate applications of the hypothesis will be discussed later.

Pauli's scheme leads further to a kind of conjugate relationship which is very suggestive. The characteristic of a completed group or sub-group is that $\bar{j} = 0$, or $\overline{m}$ for the whole group or sub-group is zero in a strong field.* In such a completed grouping of, say, r electrons, equal positive and negative values of m are possible, and, on Pauli's hypothesis, each possible value of m must be represented by one electron. Suppose p electrons to be abstracted from the grouping ; then $\sum\limits_{p} m$ has a given value, which must be equal and opposite to $\sum\limits_{r-p} m$, since $\sum\limits_{r} m = 0$. This reciprocal relation leads to a kind of analogy between atoms at the beginning and atoms at the

* Since j is usually reserved for a single electron, $\bar{j}$ is written for the quantum number giving the resultant moment of a specified number of electrons taken together.

end of a closed grouping. Two atoms which occupy positions symmetrical about the centre of the grouping will have the same possible values for j and the same number of terms corresponding to each value of j. To give examples of this from general optical spectra would occupy too much space, and, as the spectra of the elements of the higher columns of the periodic table, e.g. carbon and oxygen in the 2_{22} grouping, have not been worked out in full it is not easy to confirm the results of the rule in detail.* However, the particular example of the reciprocal relation offered by the X-ray spectrum is simple and illuminating. Here the excited atom has one electron missing from a normally completed group, say, for precision, the L group. Seven electrons are left, which, as far as the j's are concerned, is the same as if the L group contained one electron, having the same azimuthal quantum numbers and m as the missing electron. The resemblance between the X-ray spectra and the spectra of the neutral atoms of the alkali metals is thus explained.

All through Pauli's work the electrons are considered first of all to be in a strong field, so that their interaction may be neglected, and the field is then considered to be reduced to a vanishingly weak state. The quantum states are supposed to be unaffected by this. His work, therefore, is based upon the adiabatic invariance of the quantum weights, and takes no account of the correspondence principle.

Stoner has likewise invoked a strong field, with its uncoupling action, to simplify the consideration of the effect of different numbers of outer electrons, since it allows these effects to be added, the interaction being disregarded. The other core electrons are supposed to be more firmly bound to the kernel than the series electron. He lets Sommerfeld's s and j_a represent the magnetic moment of the core and the series electron respectively, the core consisting, of course, of the kernel plus all the outer electrons but one. Sommerfeld's notation being used, k now represents the integer which fixes the sequence. If the vectors corresponding to s and j_a are collinear, and in the same sense, then we have the maximum moment, given by $j = s + j_a$, independent of the coupling between core and electron,

* Cf., however, F. Hund, *Zeitschrift für Physik*, **33**, 353 *et seq.*, 1925.

and of the strength of the field : it is a property of the atom. From Landé's formula for the splitting factor g we can calculate the term energy mg corresponding to a magnetic quantum number m. The mg value is independent of the strength of the field for the particular case of the maximum value of m corresponding to a given k, which we shall be considering, so that the weak field formula can be used. (Cf. p. 526, or the tables on pp. 528, 529.) It seems reasonable to assume that the abnormal term energy (abnormal as compared to that derived from the simple consideration of the Larmor precession) is due to the magnetic moment of the atom having the abnormal value $gmh/2\pi$ instead of $mh/2\pi$. It might be argued that when we know merely that the ratio magnetic moment/mechanical moment is abnormal we should be equally justified in attributing the abnormal value of the term energy to an abnormal value of the mechanical moment, but definite evidence in favour of the former assumption is afforded by the experiments of Gerlach and Stern.*

Consider now, for example, a D term of a sextet. For the D sequence $k=3$, so that $j_a=k-1=2$. Also

$$s=\tfrac{1}{2}r-\tfrac{1}{2}=\tfrac{6}{2}-\tfrac{1}{2}=\tfrac{5}{2}.$$

Hence $j_{\max}=s+j_a=\tfrac{9}{2}=m.$

Further, from equation $(2b)$,

$$g=\tfrac{3}{2}+\frac{\tfrac{5}{2}\times\tfrac{7}{2}-2\times3}{9\times1\tfrac{1}{2}}=1\tfrac{4}{9},$$

so that $mg=7$. Calculating the various mg's in this manner we derive the following table.

Maximum magnetic moment $=\mu_{\max}$.

Multiplicity r		1	2	3	4	5	6	7
Term type	$S(k=1)$	0	1	2	3	4	5	6
	$P(k=2)$	1	2	3	4	5	6	7
	$D(k=3)$	2	3	4	5	6	7	8

It may be assumed that the magnetic moment of the series electron is normal, that is, given by k : this supposes that

* See Chapter XVI.

$j_a = k - 1$, for which we have no physical meaning, is introduced only for the sake of the g formula, which expresses empirical results. If we took j_a as giving the magnetic moment it would be zero for $k = 1$. On the above assumption we get at once the magnetic moment of core, which, from the above table, comes out the same for a given multiplicity, no matter what sequence be considered, a fact which constitutes the essence of the scheme. A glance at the table shows that

$$\mu_{\max} = r + k - 2,$$

or moment of core $= \mu_c = r - 2$.

The core of the alkali metal atoms has, on this scheme, the value $\mu_c = 0$, which agrees with our view that the inert gas form has, in virtue of its symmetry, no magnetic moment. The core of the alkaline earth atoms consists of an inert gas structure together with a single electron in its most stable (^1S) orbit, and the magnetic moment of the core, $\mu_c = 1$, must be due to this electron. According as the series electron circulates in the same or in the opposite sense to this core electron we have for $\mu_{\max}$ two values differing by 2. Thus, if $k = 1$, $\mu_{\max} = 0$ or 2. This explains the existence of the two systems, for which the multiplicity differs by 2, since $r = \mu_c + 2$ and $\mu_c = \pm 1$. The inclination hypothesis is, of course, implicitly assumed as the cause of the multiplicity. The whole scheme is based on the anomalous Zeeman effect, invoked by the introduction of g. Incidentally it may be noted that the systems given by an atom are made to depend solely on the number of outer electrons, as required by the Kossel-Sommerfeld displacement rule.

This scheme of Stoner's can be extended to give certain general features of the spectra of atoms of the higher columns of the table. Thus if, in addition to the series electron, there is more than one outer electron, these electrons are associated with the core, and any one of them may be considered as having a possibility of either sense of rotation, the change of magnetic moment associated with a change of sense being 2 for each electron. This involves a change of r by 2, and gives an explanation of the fact that, when there are several systems for a given atom or a given ion, the multiplicities of the different systems differ by 2, r having either the values 1, 3, 5 ..., or

2, 4, 6 .... Further, the more the outer electrons, the more systems possible.

These simple considerations are based upon the assumption that the maximum contribution of a single core electron to the magnetic moment is 1. They supply only a rough qualitative explanation of the general features of multiplet systems, but have a particular interest because of the simple physical features underlying them, namely, the possibility of either sense of circulation for a single electron. The mystery of the four quantum numbers remains, of course, unsolved.

Simultaneous Displacement of Two Electrons. When the arc spectra of alkaline earths, *e.g.* calcium, strontium and barium, are ordered according to the ordinary Rydberg or Ritz formulae, a majority, but not a large majority, of the lines are found to fall into the singlet and triplet systems to which reference has so often been made. There are, however, many lines which long defied attempts at classification, not because they showed slight deviations from the values computed from the formulae, but because they fall right outside the systems. Such lines have been recently very successfully ordered by H. N. Russell and F. A. Saunders, following earlier empirical work by Rydberg himself and by Popow and Götze. They have found laws which are of very great theoretical significance, and throw much light on the validity of the schemes which have been discussed.

The lines not included in the ordinary series have been classified by the allotment of terms, the essential feature of the combination principle, namely, that a single term appears in several combinations giving observed lines, being preserved. Many of the lines are expressed as combinations of known (*i.e.* regular) triplet terms with new terms, known as dashed terms, or primed terms, since they are expressed by placing a dash over, or a prime (or accent) on, the ordinary symbols. Thus there are primed triplet terms $^3P'_0$, $^3P'_1$, $^3P'_2$, which combine with the already known triplet terms $^3P_0$, $^3P_1$, $^3P_2$ according to the j selection rules, giving six lines for which the j changes are :

$$0 \to 1, \quad 1 \overset{\nearrow 0}{\underset{\searrow 2}{\to}} 1, \quad 2 \overset{\nearrow 1}{\underset{\searrow 2}{}}, \quad 0 \to 0 \text{ being forbidden.}$$

and similar dashed D terms have been found, giving rise to seven lines of a $^3D - {}^3D'$ combination (no $0 \to 0$ transition involved). The terms can be represented by a formula of Ritz type to which a constant has been added. For example, there are five *lines* of the series $1^3P_2 - n\ ^3P'_2$ which can be represented by the formula

$$\nu = 47950 - R/\{n + \cdot 1798 + 3\cdot 75 \times 10^{-5}(47950 - \nu)\}^2 \ldots (11)$$

Now the term 1^3P_2 is $33988\cdot7$, whence the $n\ ^3P'_2$ term is

$$R/\{n + \cdot 1798 + 3\cdot 75 \times 10^{-5}(47950 - \nu)\}^2 - 13961\cdot3. \ldots (12)$$

From this a remarkable feature of the primed terms can be seen at once, namely, that it is possible for them to have negative values. Thus the term value for $3^3P'_2$ comes out to be $-4999\cdot8$, and the higher values of this sequence obviously have still smaller (algebraic) values, the limiting value being $-13961\cdot3$. The existence of negative terms seems to have been first established by R. Götze.

To explain the existence of negative terms we must suppose that an atom can, in an excited state corresponding to the emission of optical lines not belonging to the regular arc series, possess energy greater than the normal ionisation potential. Since this latter corresponds to the complete removal of the optical electron we must either assume that an electron removed is not the most loosely bound of the electrons in the normal atom, but proceeds from a deeper level than the ordinary optical electron, or else that more than one electron is displaced at the same time, and that the energy corresponding to both electrons together is radiated as a frequency given by the ordinary quantum law. The latter hypothesis has proved able to account quantitatively for the lines involving primed terms, and, according to Wenzel, who has himself developed it to apply to the alkaline earth spectra, was first put forward by Bohr, in lectures still unpublished, to account for features of the neon spectrum. The newly classified lines ordered by Russell and Saunders fall within the scope of this hypothesis.

If for the primed terms the excited state is one in which two electrons are displaced, then we should be able to find a quantitative relation between the arc and the spark spectrum.

Consider for simplicity that the one electron always occupies a level, higher than the normal level, of fixed quantum number, while the second may occupy various levels, all distinguished, however, by one value of k for a given sequence. In the case where this second electron occupies a level of high total quantum number, or to proceed to the limit, where it is completely removed, we have an ionised atom which is also an excited ion, on account of the position of the other displaced electron. Hence, if we can represent the new anomalous terms by a Ritz formula from which a constant is subtracted, then this constant should equal the energy required to displace an electron to a given orbit in an atom from which one electron has already been removed, *i.e.* when expressed in volts it should equal a resonance potential of the ionised atom. This is found to be the case. Thus for the $1^3P_2 - n^3P'_2$ series represented by formula (11), the limiting value is -13961 cm.$^{-1}$, which agrees (within experimental error, which is fairly large for this somewhat irregular series) with the first resonance potential of the ionised calcium atom 13711 cm.$^{-1} = 1.69$ volts. This resonance potential corresponds to the transition $1^2S_1 - 2^2D_2$, 1^2S_1 being the basic state and 2^2D_2 the next lowest in the ionised atom. A direct transition from 2^2D_2 to 1^2S_1 is forbidden by the k selection principle, so that the ion with an electron in a 2^2D_2 orbit is in a metastable state, which, as we have seen, endures on the average for a comparatively long time. Hence an ion in this state has a good opportunity of catching a second electron. When the atom has two outer electrons it is apparently no longer in the metastable state as was the ion, and both electrons can move simultaneously to orbits of lower energy, the change of energy of the whole atom being radiated with a frequency given by the ordinary quantum relation.

Russell and Saunders find that with all three elements, calcium, strontium and barium, the primed terms receive a natural explanation on the assumption that they are due to an atom returning in one step to a state in the regular spectrum of the neutral atom from an excited state in which one electron is in a level corresponding to the first metastable state of the ionised atom, while a second electron is in any one of the many

possible higher levels. Thus, if the wave number corresponding to the difference of energy between normal and metastable state (13711 for ionised calcium, 14837 for ionised strontium, 12567 for ionised barium) be added to the experimentally found primed term values, and the values so obtained be expressed by a Rydberg formula, then the Rydberg denominators (*i.e.* the effective quantum numbers) are nearly the same for all three atoms, as is to be expected, in view of their similarity of structure. Simultaneous jumps of two electrons may be taken, then, to be well established in the particular cases described, and further work, to be mentioned later, show that such two electron jumps are a feature of complicated spectra in general.

As a further illustration a particular example of two electron jumps may be quoted from the work of Millikan and Bowen on stripped atoms. They find the existence of negative terms in the spectrum of Al_I corresponding to certain lines in the extreme ultra-violet. These lines occur in characteristic groups, four lines symmetrically arranged for three-valence-electron ions, such as Si_{II}, P_{III}, S_{IV}, and so on, and five nearly equally spaced lines for two-valence-electron ions such as Mg_I, Al_{II}, Si_{III}, and so on. The wave-number of the lines of these groups show the linear increase of wave-number with atomic number which is characteristic of the screening doublets, and hence the electron jumps must take place between levels of the same principal total quantum number. The explanation of the origin of these peculiar groups of four or five lines may be illustrated by the groups given by three-valence-electron ions. Normally, in such an atom as Al_I, of the three outer electrons two are in ^2S orbits, and one is in a $^2P_1$ orbit, and these are the only orbits of principal quantum number 3, and hence the only ones involved if the principal quantum number is not to change in the transitions considered. The normal $^2S_1$ orbit is, of course, not one concerned in the ordinary S series, but the next deeper $^2S_1$ orbit, corresponding to an electron more firmly bound than one in the basic $^2P_1$ orbit. This accounts for the term value being greater than that corresponding to ionisation, which is the removal of the P electron. When, in consequence of the exciting influence, one electron goes from the $^2S_1$ orbit to one of the P orbits, say, $^2P_1$, then the energy corresponding to the P levels changes,

owing to the fact that now there is only one electron in the $^2S_1$ level. When now one of the $^2P_1$ electrons returns to $^2S_1$, the other must be supposed to find itself again in either of the old ^2P levels. The two jumps are simultaneous. This gives two possible lines, according as $^2P_1$ or $^2P_2$ is chosen by the electron. As in the excitation the $^2S_1$ electron may pass to either $^2P_2$ or $^2P_1$, and in emission the other electron may find itself in either $^2P_2$ or $^2P_1$, we have four possible lines, and a group of four is actually observed. If there are two outer electrons instead of three, e.g. Al_{II}, there are three P levels, and hence six possible lines. We must suppose, to get the five observed, that the two central lines of this six overlap, a supposition which is made reasonable by the fact that, whereas for the group of four the lines are about equally intense, for the group of five the central line has double the intensity of the others.

The explanation of the neon spectrum requires, as do the spectra just discussed, both the extraction of an electron from more than one sub-group and the possibility of the simultaneous jumping of two electrons. The experimental facts are that Paschen has succeeded in ordering the neon spectrum into a large number of term sequences : four S sequences, ten P sequences, twelve D sequences. These sequences can be divided into two families, each including some of the S, P and D sequences : the sequences of one family can be expressed by a Ritz formula, while the sequences of the other family can only be expressed by a Ritz formula if a constant is first added to all the terms (the constant being 782 cm.$^{-1}$). This recalls the primed terms just discussed.

Now the neon atom contains in its L group ($n=2$) the following sub-groups, according to Stoner : two L_{11} electrons, two L_{21} electrons, four L_{22} electrons, the first suffix denoting the value of the k, the second the value of j. As has been already pointed out, the L_{21} group must, in general, correspond to the $^2P_1$ term, the L_{22} group to the $^2P_2$ term in an optical doublet. To account for the two families we can assume, as originally suggested by Grotrian, that the one family corresponds to the removal of an L_{21} electron to various higher levels ; this should give the spectrum characteristic of an atom with two outer

electrons, one of which is removed, *i.e.* of an atom of alkaline earth column in the periodic table. $J = 1$ for the core, and by the branching rule this gives rise to S terms for which $J = \frac{1}{2}$, $J = \frac{3}{2}$ on the addition of an electron. The selection of an L_{21} electron to play the part of an optical electron should, then, give a singlet and a triplet system. The other family of sequences we must suppose to correspond to the removal of an L_{22} electron, which is one of a closed sub-group of four electrons. This family of sequences should, therefore, not only differ from the other family by a constant in the limit where the variable Ritz term vanishes (or in other words, when the electron is completely removed), but should also give the system of triplets and quintets, since $J = 2$ for the core. We may summarise this by saying that we might anticipate one complete spectrum, consisting of systems, built on the neon ion with an L_{21} (or $^2P_1$) electron missing, and another complete spectrum built on the neon ion with an L_{22} (or $^2P_2$) electron missing. The L_{21} electrons being more firmly bound than the L_{22}, the complete removal of such an electron leaves the atom with positive energy as compared with the arbitrary zero energy when an L_{22} electron is completely removed. Hence the group corresponding to shifting an L_{21} electron must be the one which requires a constant added to the Ritz formula.

All this agrees excellently with observation. The sequences for which 782 cm.$^{-1}$ must be added to the terms before they can be represented by a Ritz formula are, in fact, exactly those required to give a regular singlet-triplet spectrum : there are two S sequences, four P sequences, four D sequences in all, divided into one singlet sequence each of ^1S, ^1P, and ^1D terms, and one triplet ^3S sequence, and three each of triplet ^3P and ^3D sequences. The sequences which are represented by ordinary Ritz formulae give triplets and quintets. The actual combinations between terms which are found can be expressed, as Landé showed, by an allotment of inner quantum numbers J, and these J's obey the branching rule as expressed in the table on the following page.

Thus the two groups are satisfactorily explained by the possibility of plucking either a $^2P_1$ electron or a $^2P_2$ electron

out of an atom, leaving a different core in either case, the two cores not differing, however, much in energy, for 782 cm.$^{-1}$ is less than a tenth of a volt. When terms of the Ritz family combine with terms of the non-Ritz family, we must suppose that there is interchange of an electron between the L_{21} and the L_{22} grouplet, as well as the passage of the "optical" electron

	Non-Ritz family	Ritz family
Neon ion $\{$	$^2P_1$ term $\quad J=1$	$^2P_2$ term $\quad J=2$
Neon atom		

$$\text{Non-Ritz family} \quad {}^2P_1 \text{ term} \quad J=1 \qquad \text{Ritz family} \quad {}^2P_2 \text{ term} \quad J=2$$

$$
\begin{array}{l|ccc|ccc}
S & \frac{1}{2} & \nearrow\searrow & \frac{3}{2} & \frac{3}{2}\nearrow\searrow\frac{5}{2} \\
P & \frac{3}{2} & \frac{1}{2}\,\frac{3}{2}\,\frac{5}{2} & & \frac{1}{2}\,\frac{3}{2}\,\frac{5}{2} & \frac{3}{2}\,\frac{5}{2}\,\frac{7}{2} \\
D & \frac{5}{2} & \frac{3}{2}\,\frac{5}{2}\,\frac{7}{2} & & \frac{3}{2}\,\frac{5}{2}\,\frac{7}{2} & \frac{1}{2}\,\frac{3}{2}\,\frac{5}{2}\,\frac{7}{2}\,\frac{9}{2} \\
F & \frac{7}{2} & \frac{5}{2}\,\frac{7}{2}\,\frac{9}{2} & & \frac{5}{2}\,\frac{7}{2}\,\frac{9}{2} & \frac{3}{2}\,\frac{5}{2}\,\frac{7}{2}\,\frac{9}{2}\,\frac{11}{2}
\end{array}
$$
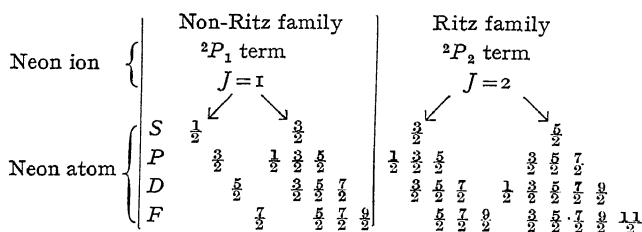
from one level to another. Before the radiation one of the L_2 grouplets is imperfect by one electron, and the electron which is missing from the L_2 sub-group both before and after executes (simultaneously with the L electron switch) some quantum switch in outer orbits. This is another example of the two electron jumps.

The neon spectrum occupies a peculiar position in the complicated spectra, in that the core is so compact that, even when the electron removed (the series electron) occupies low orbits the interaction between it and the other electrons is small compared with the interaction of these electrons among themselves. The seven L electrons are not outer electrons in the same way as the electrons additional to a completed group are in atoms other than those of the inert gases. Hence the series properties of the alkaline earths and the earths are imitated, and the spectrum can be ordered in the same way as that of the simpler structures discussed in other chapters. This will be made clearer in the next section, when the theory of complicated spectra is discussed.

The ordering of the neon spectrum, with its twenty-six sequences, is one of the triumphs of modern spectroscopy. The fact that this ordering can find expression in terms of the quantum theory is comforting, even if we are met by the apparently inevitable half-quantum numbers and branching. The attack on the complicated spectra, such as those of the

elements of the fourth and fifth columns of the periodic table, proceeds with vigour, and Hund, in particular, has had success in applying to such spectra the scheme of Russell and Saunders, and of Heisenberg, on which the moments of momentum of the outer electrons are compounded, and the resultant allowed to interact with the inert gas kernel. Not the least difficulty in following and expounding the most recent work is the difference of notation, since every writer uses his own system, and, what is worse, different writers use the same symbols with different meanings.*

We now proceed to give a slight sketch of the general theory of complex spectra.

General Scheme for Complex Spectra. The treatment of the general case of complex spectra, such as those of the elements from scandium to nickel, originated largely in the work of Russell and Saunders, to which reference has so frequently been made. They emphasised that many of the difficulties of ordering the whole spectrum of neutral calcium could be crystallised in a recognition of the fact that the combination properties of the primed terms and the inner quantum number properties of the primed terms do not give consistent results as to the sequence to which given terms belong, and they worked out a scheme by means of which this could be explained. The inner quantum number properties—or internal properties, as we may call them for short—are the Zeeman effect, the multiplet structure, and the relative intensities of lines in a multiplet. We have discussed at some length how, by a study of some or all of these features, J and K may be allotted to terms. A given term will therefore have a K corresponding to its internal properties. In the case of the alkali metals, or the earths, we can allot a K to the terms from their combination properties, using the rule $\Delta K = \pm 1$, and in the case of these simple spectra (as distinct from the complex spectra of such elements as iron), the K so allotted is

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* A discussion at Dantzig in September, 1925, between some of the most celebrated workers in the field of quantum analysis of spectra, at which the writer had the pleasure of being present, foundered, if the expression may be used, on the question of notation, none of the speakers being able to understand the notation of the others, and each having also, apparently, difficulties with his own.

identical with the K required for the internal properties. In all these simple cases we are dealing with a single privileged, or optical, electron, which makes the quantum jump, for although in the case of the earths there are three outer electrons, two of them form a closed grouplet. When we turn to the primed terms of the calcium spectrum, which we have discussed, two electrons jump simultaneously, one electron (which we will call the first electron) occupying in the excited state various orbits, while the second electron occupies a $^2D_2$ orbit. The first electron would seem to play a privileged rôle, and, if we regard it as an ordinary series electron, we can allot a K value to the various primed terms from the combination properties. However, this K is not the K given by the internal properties. For example, the P' terms discussed by Russell and Saunders have internal properties of P terms $(K = \frac{3}{2})$, but combining properties of D terms $(K = \frac{5}{2})$. The letter (sequence) notation is fixed by Russell and Saunders from the internal properties, and not the combination properties. This rule is generally followed in ordering the terms of complex spectra.*

The fundamental theoretical idea introduced by Russell and Saunders, and generalised by Heisenberg, is that in the case of more than one outer electron, where the interaction of the electrons plays a part, the angular momenta of the different electrons must be compounded to give an angular momentum which characterises the internal properties of the atom. It is assumed, in fact, that the inclination of the angular momenta of the various electrons to one another can be quantised just as is that of the momenta of core and electron on Landé's inclination hypothesis ; this implies, of course, that the interaction between kernel and electrons is small compared to that between the two (or more) outer electrons. Taking two electrons for simplicity, for which K' and K'' are the azimuthal quantum numbers giving the individual angular momenta, K' and K'' must be compounded vectorially in the various possible ways to make the resultant (which gives the angular momentum of both electrons together) a half-integer. The resultant quantum

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* In the case of simple spectra, the ambiguity of notation does not, of course, arise.

number is called l.*   The number l can then have the various values governed by the inequality $K' + K'' > l > |K' - K''|$.   The values adopted for K are the half-integer values, according to the scheme $K = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2} \ldots$ for S, P, D, $F \ldots$ sequences in simple spectra.   The number l so obtained gives the internal properties of the term to which it applies, and, in all cases where the interaction of the electrons, of which it gives an account, is predominant the sequences are named from the l values, viz. S, P, D, $F \ldots$ for the $l = \frac{1}{2}, \frac{3}{2}, \frac{5}{7}, \frac{7}{2} \ldots$.   For neon, of course, where the interaction between what may justly be called the series electron and the L group ($n = 2$) electrons is negligible except possibly for the very lowest terms, the compounding is not justified, and the spectrum is ordered by the K value of a single electron.

The new scheme of outer electrons acting as a single system can be expressed in terms of Heisenberg's general duplicity scheme : he called it Scheme III., and it is a modification of Scheme I. to include the case of several valence electrons.   It is a convenient expression of the empirical rules which must be followed in order to describe the spectra in question.

The core is given a duplicity which in the case of two valence electrons is expressed by putting $R = \frac{1}{2}$, $R = \frac{3}{2}$, arising from the value $R = 1$ (or 0), which it has in the case of a single electron, by the branching rule.   For more than two valence electrons the values of R are found from the branching rule, each value of R becoming $R \pm \frac{1}{2}$ when a fresh electron is added, the maximum value of R being $\frac{1}{2}(N + 1)$, where N is the number of valence electrons.   This merely expresses the multiplicity of the systems as laid down in Laporte's original empirical scheme. The l values found for the systems of outer electrons are compounded with the core, thus endowed with R values, according to the inclination scheme.   The values of K from which l is obtained by compounding are half-integers, which in the case

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* Here, again, the notation displays a pleasing diversity.   Russell and Saunders call the individual angular momenta L_1 and L_2, and the resultant angular momentum K, but the notation here adopted is more consonant with that previously used, since k has always been restricted to the angular momentum of single electrons.   I have used K' and K'' in preference to k_1 and k_2 (Hund's notation), since k_1 and k_2 have often been used (as by Bohr and Coster) as the two azimuthal quantum numbers required in general for a single electron.

of two electrons gives integral values for l, but, just as in Scheme I., agreement with experiment can only be obtained by taking half-integer values of l for the interaction energy. We therefore have a duplicity scheme as before :

$$l_0 \qquad 1 \qquad 2 \qquad 3 \qquad 4 \qquad 5 \cdots$$
$$l \qquad \tfrac{3}{2} \quad \tfrac{5}{2} \quad \tfrac{7}{2} \quad \tfrac{9}{2} \quad \cdots$$
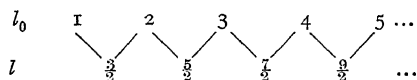
the lower line giving the values of l actually taken for compounding with the kernel. This is another expression of the rule $K' + K'' > l > |K' - K''|$ already quoted. Taking, as an example, $K' = \tfrac{3}{2}, K'' = \tfrac{5}{2}$, we have: maximum value of $l_0 = \dfrac{3+5}{2} = 4$, minimum value $\dfrac{5-3}{2} = 1$, and $l = \tfrac{3}{2}, \tfrac{5}{2}, \tfrac{7}{2}$ from the above scheme. This is merely throwing what we have already done into Heisenberg's notation.

In the case of the alkaline earths, therefore, where $R = \tfrac{1}{2}$ or $\tfrac{3}{2}$, we should expect, corresponding to one electron in a D orbit ($K = \tfrac{5}{2}$) and the other in a P orbit ($K = \tfrac{3}{2}$), three triple terms and three singlet terms, with the inner quantum number properties of P, D, F terms ($l = \tfrac{3}{2}, \tfrac{5}{2}, \tfrac{7}{2}$). The electron which has a large choice of orbits, called for convenience the first electron, having the $K = \tfrac{3}{2}$ orbit in the above example (for the second electron is, as we have seen in discussing the experiments, always in one particular D orbit when the atom is in the excited state), these terms should all have the combining properties of P terms. Hence the l scheme leads us to suppose that we can have triple terms with the internal properties of F, D and P terms respectively, but all having the combining properties of P terms. This is exactly what Russell and Saunders found for the primed terms involved in the three familiar multiplets in the less refrangible part of the spectra of calcium, strontium and barium.

The above is a very elementary example introduced, perhaps, rather out of place in order to illustrate the meaning of the scheme. We shall return to this case after a further review of the rules.

In the general case of atoms with many outer electrons we cannot select any one electron to play the part of the optical electron, since, for the lower terms, at any rate, the outer electrons

do not differ much among themselves in strength of binding. The number l thus becomes of supreme importance, while no individual K has any claim to pre-eminence. In such a case the internal properties may become clear, and the ordering into multiplets be comparatively straightforward, but no series properties will appear. For the higher terms, however, one electron may be much more loosely bound than the others, and the ordinary series properties become evident. Clearly as the terms progress along a sequence a limit is approached which is the energy of the positive ion in a given state, there being more than one such state involved in the spectrum. Thus in the case of neon we have seen that the spectrum can be explained as built on two possible states of the positive ion, but neon is peculiar in that owing to the fact that the single optical electron is very loosely bound, even in low orbits, compared to the electrons of the positive ion, the series properties persist down to the deep terms, and the ordering is simplified. With other complicated spectra the tracing of series relationships is a difficult task, and we are faced with the problem : to which of the series limits, *i.e.* basic terms of the ion, do the lower multiplets belong. This involves, of course, the determination of the basic states of the ion. We also want to know the basic term of the spectrum of the neutral atom.

Before the combination possibilities and the existence of given terms can be satisfactorily discussed, certain general rules which have been recently elaborated must be considered. In the first place, there are certain selection rules to be applied both to the l's and to the individual K's. For possible changes in l during a quantum switch we have Laporte's empirical rule, that $\Delta l = 0$ or ± 1 or ± 2. The different classes of transitions covered by the rule are used to divide the terms into two classes, to facilitate comparison with empirical data. With calcium we have seen that the terms are divided into primed and unprimed, the unprimed terms combining with the primed terms of the same sequence letter (*i.e.* same l) and with unprimed terms for which $\Delta l\ (=\Delta K) = \pm 1$. In general the distinction between primed and unprimed terms has no physical significance, since in the more complicated spectra there is not

a set of, as it were, privileged ordinary terms, such as existed with calcium on account of the easy ordering into series of the terms due to one electron jump. Nevertheless, a classification into primed and unprimed terms has been retained, but it is purely arbitrary, and defined by the following rule :

For combinations between primed and primed, or between unprimed and unprimed terms (" like " combinations) $\Delta l = \pm 1$.*

For combinations between primed and unprimed terms (" unlike " combinations) $\Delta l = 0$ or ± 2.

Thus when a given term has been arbitrarily defined as primed or unprimed the class of other terms combining with it can be fixed.

In the case of even the most complicated spectra the present indications are that only two, and not more, electrons can jump simultaneously. Heisenberg has put forward the following rule, based on considerations of the correspondence principle : when two electrons jump at once, for one of which the azimuthal quantum number is K', for the other K'', then

$$\Delta K' = \pm 1, \quad \Delta K'' = 0 \text{ or } \pm 2.$$

A further rule which is invoked in building up a scheme of possible terms deals with the result of adding an electron to an ion of known properties, and embodies formally relations which have already been implied. If we have an ion for which $R = R_a$, $l = l_a$ (the suffixes have no significance except to distinguish special values of R and l) and add to it a new electron of given K, then the multiplicity $2R$ splits up into the two neighbouring multiplicities (R becomes $R \pm \frac{1}{2}$), and the new l is obtained by compounding K with l_a in the way already laid down for the compounding of different K's.

The method by which the basic terms are derived is to start by calculating the various possible values of l for a given number of electrons of known azimuthal quantum numbers, and hence to find all possible terms due to these electrons. Two of the electrons can be first considered, and the other electrons added one by one, use being made of the rule just given. From the general theory of atomic structure discussed in Chapter XIV., the other quantum numbers, besides K, of

* Combinations for which $\Delta l = \pm 3$ have been found by Catalán for nickel.

the electrons in incomplete grouplets are known, and these quantum numbers have to be used to limit the number of these terms which occur for the atom in the normal state. We know by Pauli's principle of uniqueness of electron orbits that if two electrons have the same n and K, they must not also have the same value of m and mg_s.* This, therefore, will exclude a certain number of possibilities when we are dealing with two or more electrons of the same n and K. If in an ion a type of term given by R_a, l_a is forbidden, then all terms which could be derived from it by adding an electron are forbidden in the spectrum of the atom : if the term type R_a, l_a be present in the ion, and a further electron be added of the same n and K as one already present in the ion, certain terms are again to be excluded. To decide precisely which terms are to be excluded the possible values of m, mg_s corresponding to R, J (or k), K must be calculated for each electron by Pauli's formulae (3). We then form $\overline{m} = \Sigma m$, $\overline{mg_s} = \Sigma mg_s$, there being, of course, various possibilities for two electrons of the same K and k, since there is more than one value of m (and mg_s) corresponding to a given K and k, and these must be selected in all possible pairs, one from each electron. Now if the $\overline{m}$ and $\overline{mg_s}$ of the atom be regarded just as if they were the m, mg_s of a single electron, we can find by Pauli's work, conveniently summarised, as far as we are now concerned, in the tables on pp. 528 and 529, exactly which values of R, J, K will cover a given group of $\overline{m}$, $\overline{mg_s}$ values, and so can attribute given terms to given K and k. Merely compounding the K's to form l tells us which multiplet terms as a whole belong to a given pair of K's : it does not tell us, however, which individual terms of a multiplet, such as a triplet P, belong to which pairs of k's, or, in other words, which values of J are to be attributed to which series limit. Writing down the $\overline{m}$'s and $\overline{mg_s}$'s enables us not only to attribute the individual terms, such as ${}^3P_1$, to a given pair of k values, but also to decide which terms will drop out when both electrons have the same n as well as the same k. Hund was the first to apply the method in detail to complex spectra.

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* Or else they must not have the same value of k, m. As has been pointed out, only four of the five quantum numbers n, K, k, m, mg_s are independent.

The method will be illustrated by an example. Suppose both electrons are in $K = \frac{3}{2}$ orbits. Then by our compounding rule the possible values of l are $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, while for two electrons the possible values of R are $\frac{1}{2}$, $\frac{3}{2}$. Accordingly we expect ^1S, ^1P, ^1D, ^3S, ^3P, ^3D terms in the general case. To examine which terms belong to which series limit, and which drop out when both electrons have the same n (as they do in the normal state of an atom) we have to consider the magnetic states. $k(=J)$ may be either 1 or 2; corresponding to $k = 1$, we have two values of m, viz. $\pm \frac{1}{2}$, and corresponding to $k = 2$ four values, viz. $\pm \frac{1}{2}$, $\pm \frac{3}{2}$. There are therefore six magnetic states of each electron, or thirty-six possible values of $\overline{m}$ (and of $\overline{mg_s}$) for the two taken together. These are written down in the table on the opposite page : the m's and mg_s's may be calculated by Pauli's formulae, or taken direct from the table on pp. 528 and 529. Corresponding to these $\overline{m}$'s and $\overline{mg_s}$'s we know that there must be certain terms for which $R = \frac{3}{2}$ or $\frac{1}{2}$, while $l = \frac{1}{2}$, $\frac{3}{2}$ or $\frac{5}{2} = \frac{1}{2}$, $\frac{3}{2}$ or $\frac{5}{2}$.* We have to select terms, some belonging to states in which the one (say the first) electron has $k = 1$, and others belonging to states in which this electron has $k = 2$: if n for this electron has the value of the incomplete group of the atom, and the other electron be completely removed, we have the $^2P_1$ and $^2P_2$ state of the ion. Hence the terms which correspond to the $k = 1$ state for the first electron pertain to one series limit, those which correspond to the $k = 2$ state pertain to the other series limit. They can be allotted by noting that the terms selected have to cover all the possible $\overline{m}$ states. It will be found, as shown in the table, that $^3P_0$, $^3P_1$, $^3D_1$, $^3D_2$ belong to the one series limit, and the other terms to the other series limit. The $\overline{J}$'s for the whole atom, given in the column headed $J - \frac{1}{2}$, can be found by noting $\overline{J - \frac{1}{2}} \geqslant \overline{m} \geqslant -|\overline{J - \frac{1}{2}}|$, so that, e.g. $\overline{J - \frac{1}{2}} = 2$ corresponds to $\overline{m} = \pm 2, \pm 1, 0$. This shows how the new scheme helps to order the complicated spectra.

To derive the basic terms of the normal atom we must take the n of both electrons the same. K for both electrons is already the same : by Pauli's principle we cannot then have

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* The l for the whole atom plays the part of the K for a single electron.

two electrons for which m and mg_s (or k and m) are also the same. This excludes straightway all the cases marked with a u (uniqueness). Further, n being the same for both electrons,

K	$k(=J)$	m		mg_s		$\overline{m}$	$\overline{mg_s}$		$\overline{J-\tfrac{1}{2}}$	Terms
$\tfrac{3}{2}\quad\tfrac{3}{2}$	1	1	$\frac{1}{2}$	$\frac{1}{2}$	0	0	1	0	u		
		$\frac{1}{2}$	$-\frac{1}{2}$	0	-1	0	-1	u'		
		$-\frac{1}{2}$	$\frac{1}{2}$	-1	0	0	-1			
		$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	-1	-2	u		
	1	2	$\frac{1}{2}$	$\frac{3}{2}$	0	2	2	2	u'	0, 1	$^3P_0, \,^3D_1$
		$\frac{1}{2}$	$\frac{1}{2}$	0	1	1	1	u'	1, 2	$^3P_1, \,^3D_2$
		$\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	u'		
		$\frac{1}{2}$	$-\frac{3}{2}$	0	-2	-1	-2	u'		
		$-\frac{1}{2}$	$\frac{3}{2}$	-1	2	1	1	u'		
		$-\frac{1}{2}$	$\frac{1}{2}$	-1	1	0	0	u'		
		$-\frac{1}{2}$	$-\frac{1}{2}$	-1	0	-1	-1	u'		
		$-\frac{1}{2}$	$-\frac{3}{2}$	-1	-2	-2	-3	u'		
	2	1	$\frac{3}{2}$	$\frac{1}{2}$	2	0	2	2			
		$\frac{3}{2}$	$-\frac{1}{2}$	2	-1	1	1			
		$\frac{1}{2}$	$\frac{1}{2}$	1	0	1	1			
		$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	0	0			
		$-\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0			
		$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	-1	-1			
		$-\frac{3}{2}$	$\frac{1}{2}$	-2	0	-1	-2			
		$-\frac{3}{2}$	$-\frac{1}{2}$	-2	-1	-2	-3			
	2	2	$\frac{3}{2}$	$\frac{3}{2}$	2	2	3	4	u	0, 1, 1	$^1S_0, \,^3S_1,$
		$\frac{3}{2}$	$\frac{1}{2}$	2	1	2	3	u'	2, 2, 3	$^1P_1, \,^3P_2$
		$\frac{3}{2}$	$-\frac{1}{2}$	2	0	1	2	u'		$^1D_2, \,^3D_3$
		$\frac{3}{2}$	$-\frac{3}{2}$	2	-2	0	0	u'		
		$\frac{1}{2}$	$\frac{3}{2}$	1	2	2	3			
		$\frac{1}{2}$	$\frac{1}{2}$	1	1	1	2	u		
		$\frac{1}{2}$	$-\frac{1}{2}$	1	0	0	1	u'		
		$\frac{1}{2}$	$-\frac{3}{2}$	1	-2	-1	-1	u'		
		$-\frac{1}{2}$	$\frac{3}{2}$	0	2	1	2			
		$-\frac{1}{2}$	$\frac{1}{2}$	0	1	0	1			
		$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	-1	0	u		
		$-\frac{1}{2}$	$-\frac{3}{2}$	0	-2	-2	-2	u'		
		$-\frac{3}{2}$	$\frac{3}{2}$	-2	2	0	0			
		$-\frac{3}{2}$	$\frac{1}{2}$	-2	1	-1	-1			
		$-\frac{3}{2}$	$-\frac{1}{2}$	-2	0	-2	-2			
		$-\frac{3}{2}$	$-\frac{3}{2}$	-2	-2	-3	-4	u		

cases which differ from another case (retained) merely by interchange of the rôles played by each of the two electrons, must vanish : these are marked with a u'. In all twenty-one of the thirty-six states thus disappear : the fifteen pairs of

values of $\overline{m}$, $\overline{mg_s}$ which remain correspond to ^3P, ^1S, ^1D.* We thus conclude that these are the basic states for an atom containing two P electrons in its normal state, and Fowler and Hartree have, for instance, shown that the spectrum of O^+ (for which the ion O^{++} has two 1_1 and two 2_1 electrons in complete sub-groups, and two 2_2 electrons) is built upon the three ^3P states, and the ^1D and ^1S states. It is worked out by adding an electron to this ion, using the rules already expounded.

It is hoped that this example may do something to indicate the way in which the new principles are being applied : it is impossible to give a full account within the limitations imposed by the general scope of the book. To conclude, we may glance again at the calcium spectrum in the light of the general work which has just been described. For Ca_{II} the basic term is a ^2S term, with $K' = \frac{1}{2}$, and, if the core be in this state, with a single electron in an S orbit, the orbits of the second, or optical, electron for which $K'' = \frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ . . . will give S, P, D . . . sequences with both combining properties and internal properties determined by the value of K''. These are the ordinary, or old terms, as distinct from the " new " terms. The term next above the basic term in the Ca_{II} spectrum is a ^3D term, for which $K' = \frac{5}{2}$. If we add an electron to this core we shall have various possibilities according to the K'' of the added electron. For example, consider the case in which the added electron has $K'' = \frac{3}{2}$, while n is greater than the value for the incompleted group in the atom, *i.e.* greater than 3. Corresponding to $K' = \frac{5}{2}$, $K'' = \frac{3}{2}$ we have $l = \frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$. This gives three triple terms if $R = \frac{3}{2}$, three singlet terms if $R = \frac{1}{2}$. The l values show that these terms have internal properties of P, D, and

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* For the ^3P terms the pairs of values of $\overline{m}$, $\overline{mg_s}$ are $^3P_0$: 0, -1 ; $^3P_1$: -1, -2 ; 0, 0 ; 1, 1 ; $^3P_2$: -2, -3 ; -1, -1 ; 0, 1 ; 1, 2 ; 2, 3. For $^1S_0$: 0, 0. For $^1D_2$: -2, -2 ; -1, -1 ; 0, 0 ; 1, 1 ; 2, 2. The reader must not be disconcerted that in the upper section of the table only values corresponding to $^3P_0$ have been left unmarked by u or u', while $^3P_1$ appears in that section, and is yet said to be retained. When n is the same for both electrons the allotment of the terms to the different states of the ion ceases to be significant ; it has a meaning only when one n is large. Which one of two equivalent arrangements is marked with u', and which one retained is, of course, purely arbitrary. All the u''s possible have, in the table, been put in the top section, for convenience of checking, but the reader can, if desired, transfer the u''s from -1, -2 ; 0, 0 ; 1, 1 to the equivalent arrangements in the upper part of the lower section.

F terms, and hence are to be denoted by these letters. In a two electron jump, if K' goes from $\frac{5}{2}$ to the normal value $\frac{1}{2}$, $\Delta K' = 2$, and therefore, by Heisenberg's rule, $\Delta K''$ must be ± 1. The possible combinations are therefore with an ordinary S term ($K' = \frac{1}{2}$, $K'' = \frac{1}{2}$), or with an ordinary D term ($K' = \frac{1}{2}$, $K'' = \frac{5}{2}$). Hence the P and F terms corresponding to $K' = \frac{5}{2}$, $K'' = \frac{3}{2}$ are normal in their combining properties, although not ordinary P and F terms, since both electrons jump, while for ordinary terms one is fixed in the basic orbit. Such P and F terms were found by Russell and Saunders, and denoted as double primed terms,* P'' and F''. On the other hand, the D terms corresponding to $K' = \frac{5}{2}$, $K'' = \frac{3}{2}$ combine with an ordinary D term, with $\Delta l = 0$, and are therefore D' terms, by our definition.

If the second electron has $K'' = \frac{5}{2}$, instead of $K'' = \frac{3}{2}$, the l values are $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, $\frac{9}{2}$, corresponding to S, P, D, F, G terms. Of these the P term, $l = \frac{3}{2}$, combines with the ordinary P term ($K' = \frac{1}{2}$, $K'' = \frac{3}{2}$) since for such a quantum jump $\Delta K' = 2$, $\Delta K'' = 1$. Having thus the internal properties of a P term, but not the combining properties of an unprimed term, since $\Delta l = 0$; it is a P' term. These illustrations may, perhaps, serve to make clear the general rules.

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* The primes on the terms have, of course, nothing to do with the primes on the K's, which are merely used to distinguish the K of one electron from the K of the other. Unused symbols are scarce.

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CHAPTER XVI

MAGNETIC PROPERTIES AND ATOMIC STRUCTURE

Introductory. Investigation of the magnetic properties of bodies cannot be said to have given so far any very precise information as to the structure of the atom, but, at the same time, magnetism is a physical property of such fundamental significance that it can scarcely be left out of any discussion of the subject. The very fact that the study of magnetism has hitherto yielded comparatively few important generalisations suggests that we have here, possibly, the direction from which the next advance may come. At present the subject seems to be awaiting some radically new theory to order the immense amount of rather incoherent, and occasionally contradictory, information which has been accumulated. The investigations of the anomalous Zeeman effect, and of the magnetic properties of atomic rays by Gerlach and Stern have already shown how information can be obtained as to the magnetic properties of single atoms, but have not so far received any simple interpretation.

All theorists who have busied themselves with the problem of the general modifications of atomic structure which take place as elements of increasing atomic number are built up by the binding of successive electrons cite the periodic changes of magnetic properties, which is one of the most striking results of recent experimental investigation of magnetism. Reference to this has been made in Chapter XIV. Fig. 96, embodying the results of the extension investigations of Honda, represents the specific susceptibility * χ of the elements plotted against

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* Notation. Throughout this chapter $\kappa = I/H$ denotes the magnetic susceptibility, where I is the magnetic moment per unit volume and H is the magnetic force : $\chi = \kappa/d$, where d is the density, is the specific susceptibility,

the atomic number Z, positive values of χ corresponding, of course, to paramagnetic elements, and negative values to
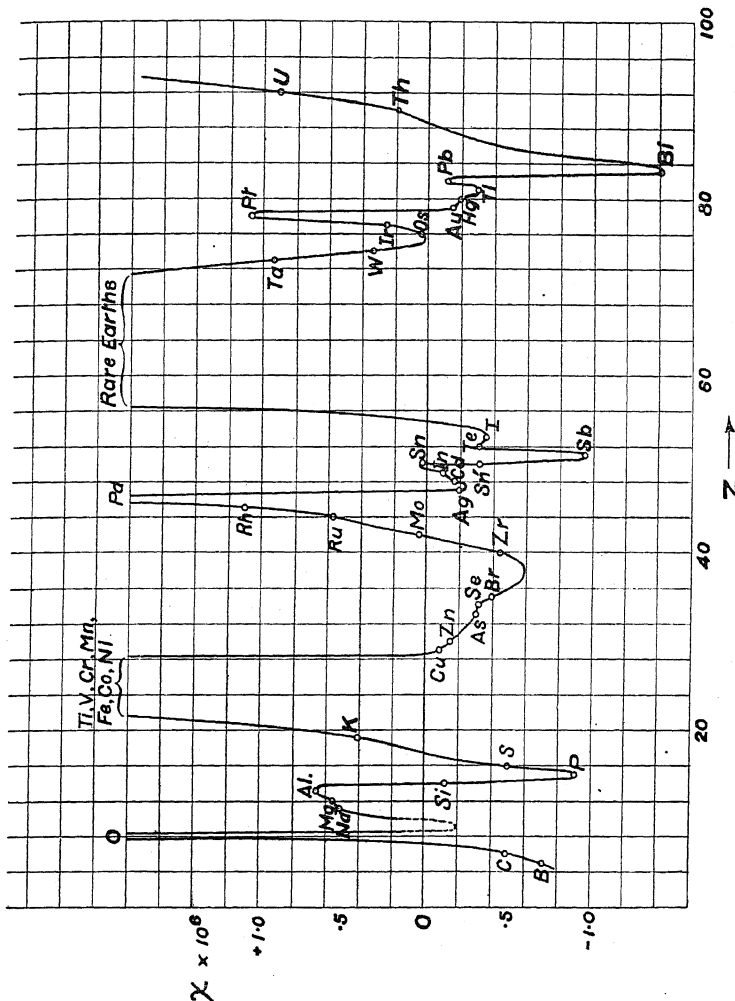
Fig. 96.

Specific susceptibility χ of the elements, plotted against atomic number.

diamagnetic elements. It will be seen at once how in the middle of the long periods the elements have abnormally high susceptibilities, while the inert gases have low values. It must

i.e. the susceptibility per unit mass; and $\chi_m = \kappa W/d$, where W is the molecular weight, is the susceptibility per gram molecule, the so-called coefficient of molecular magnetism.

be remembered that the susceptibility of even pure elementary solids varies with changes in the nature of the solid structure, such as are involved in changes of crystalline state or allotropic modifications.* Again, paramagnetic susceptibility varies with the temperature. The diagram refers to elements at room temperature, but only a rough general significance can be attached to it, such as pertains to the curve of atomic volumes.

These results, while useful for indicating a break in the regularity of structure in the middle of the long periods, are capable of a very general interpretation only : they do not afford any precise information as to the origin of the magnetic behaviour of the elements. When we seek for greater definiteness we find that variety rather than simplicity is characteristic of what is offered. Many reasons may be given to account for our comparative ignorance of the origin of magnetic properties. We could not, until recently, do as we have done in the case of other phenomena, and deal with single atoms or molecules, or even with small numbers of them. Even now, when Stern and Gerlach have shown how isolated atoms may be studied, as will be described later, the method has been applied to only a few elements. We cannot isolate the magnetic element from matter, as we can the electrical element, the electron. The magnetic susceptibility of most substances is very small, and, in the case of solids, liable to be markedly affected by the smallest traces of iron : it cannot be measured with high accuracy. Above all, we have the difficulty that magnetism is not, in general, an atomic property. It is true that in solutions of metallic salts the susceptibility is the sum of the susceptibilities of the ions present, and that, for instance, in halogen compounds of many metals the susceptibility is roughly independent of the particular halogen combined with the metal, but it varies with the different valencies which the metallic ion has in different salts. Thus Townsend has shown that a given amount of iron in solution as any ferric salt has a fixed susceptibility, while the same amount of iron in solution as a ferrous salt has a different susceptibility : the ferricyanides, again, are

* For example, crystalline tin is feebly paramagnetic, grey tin, at the same temperature, is markedly diamagnetic. The former is indicated on the diagram as Sn, the latter as Sn'.

different, having zero susceptibility. This feature has, however, found a rational interpretation. With solids, the general result of chemical combination is that an additive law, according to which the susceptibility of the compound would be equal to the sum of the susceptibilities of the component atoms, breaks down completely. To take some extreme cases, iron carbonyl and nickel carbonyl are diamagnetic ; again, while oxygen (at any rate in the molecular form, for which alone measurements have been made) is strongly paramagnetic, yet the oxides of a series of paramagnetic metals, such as aluminium, magnesium, thorium and uranium, are diamagnetic. In these cases magnetism may be said to be a molecular property. But in still other cases the magnetic properties seem to be determined by aggregates larger than molecules, in the ordinary sense : thus sudden changes in the susceptibility occur on fusion of a metal, even if it be a diamagnetic one, such as bismuth. Further, *abrupt* changes of susceptibility of elements in solid form occur at certain definite temperatures, corresponding probably to modifications in the solid structure. Tin may be either diamagnetic or paramagnetic, according to temperature. The remarkable Heusler bronzes, which, although consisting exclusively of elements of very small susceptibility (manganese, copper and aluminium ; sometimes also tin and other metals), have magnetic properties which approach in intensity those of iron, depend for their efficacy on heat treatment, which introduces modifications of structure visible under the microscope. The complexity of the problem is very great, especially for the ferromagnetic and paramagnetic substances. The diamagnetics are somewhat simpler, since in many cases, but by no means always, an additive law holds roughly when diamagnetic atoms combine to form a diamagnetic molecule. It may be said in general, however, that little has been done to elucidate the diversity of behaviour of magnetic substances, and that the substances selected for verification of theories are of a very limited class, called of normal behaviour rather because they agree with the theories than because they represent a numerical majority.

General Theory of Diamagnetism and Paramagnetism. Having indicated the difficulties which confront any attempt to

refer the magnetic properties of substances to a particular feature of atomic structure, we may consider in outline the prevailing general theories of magnetism, which postulate electrons circulating in closed orbits to act as the elementary magnets which all bodies are supposed to contain. These theories have been guided mainly by laws experimentally established by P. Curie, and generally known by his name. The first law states that the susceptibility of diamagnetic substances is independent of the temperature : the second that the susceptibility of paramagnetic substances is inversely as the absolute temperature. In the case of the first law the changes of structure which take place at definite temperature with accompanying changes of diamagnetism must be excluded from the scope of the law. Even then there are marked exceptions to the law, for substances are known whose diamagnetic susceptibility decreases with rise of temperature, and others for which it increases : whereas the latter case can be explained by the presence of a slight paramagnetism, which decreases with rise of temperature, the former remains anomalous. As regards the second law, it breaks down for many substances at low temperature.

On classical electrodynamic theory an electron rotating uniformly in a circular orbit is equivalent to a magnet of moment $M = \dfrac{eS}{\tau}$, whose direction coincides with the axis of rotation of the electron : here S is the area of the orbit, τ the period of revolution, e the electronic charge in electromagnetic units. The accepted theories assume such electrons as magnetic elements. Taking first the theory of diamagnetism, it is assumed that the various orbits present in the atom are of such magnitude, sense of description and orientation that, on the whole, the atom possesses no magnetic moment. A simple instance of such an arrangement would be afforded by an even number of symmetrically arranged orbits, in half of which the electrons are rotating right-handedly, while in the other half they rotate left-handedly. The planes of the orbits are considered to be fixed, so that a magnetic field has no tendency to rotate them when its direction is not normal to the planes. The effect of the establishment of the magnetic field is, by the

ordinary laws of electromagnetism, to produce an electric force E tangential to the orbit, which will cause a change in the moment of momentum of the electron : this change will produce changes of magnetic force normal to the plane of the orbit, the sense of which will be opposed to the external field, whichever the sense of the rotation of the electron in the orbit, as follows at once from Lenz's law. It can be shown that the external field will not produce a change in the area of the orbit, except in the special case where the central force holding the electron in the orbit varies as the inverse cube of the distance, and further, that the change ΔM of magnetic moment M produced by the field H is given by

$$\frac{\Delta M}{M} = -\frac{e\tau H \cos\theta}{4\pi m},$$

where θ is the angle which the normal to the plane of the orbit makes with H.* Now $M = \dfrac{eS}{\tau}$, so that

$$\Delta M = -\frac{e^2 S}{4\pi m} H \cos\theta.$$

To arrive at the susceptibility this has to be resolved in the direction of H, and averaged for all values of θ, taken as equally probable. A simple calculation shows that, if there are N' molecules per gram,

$$\chi = -\frac{N'e^2}{6\pi m}\Sigma S = -\frac{N'e^2}{6m}\Sigma \bar{r}^2, \quad\dots\dots\dots\dots\dots(1)$$

where the summation sign refers to different orbits in the same molecule and $\bar{r}^2$ is the mean value of r^2 for a single orbit, so that $\pi\bar{\bar{r}}^2 = \bar{S}$. No temperature effect has been considered, so the susceptibility is independent of the temperature. This cannot be regarded as a confirmation of the theory : it is

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* This follows at once from Larmor's theorem (see p. 250), which states that

$$\omega_H = \Delta\frac{1}{\tau} = \frac{e H \cos\theta}{4\pi m} \ (e \text{ in } e.m.u.),$$

so that

$$\frac{\Delta M}{M} = -\frac{\Delta\tau}{\tau} = -\frac{\tau e H \cos\theta}{4\pi m}.$$

rather equivalent to the assumption on which the theory is based. Confirmation of the theory is offered by the fact that the susceptibility of diamagnetic elements which can be deduced from it is of the right order, *i.e.* formula (1) can be used to deduce from the experimentally found value of χ a value of ΣS which turns out to be reasonable. This may be exhibited by dividing ΣS so found by the number of electrons in the atom or molecule in question (assuming in the case of molecules that χ obeys a simple additive law, and is the sum of the χ's for the component atoms), and so getting an average area of an electron orbit for the whole atom, from which an average r^2 can be derived if desired. The following table shows the results of such a calculation. The value of χ for the ion cited is that derived by Joos from a consideration of the diamagnetism of solutions of salts of the alkali metals. We may assume, as an approximation, that in units of similar electronic structure, such as Cl^-, A, K^+, the areas of the orbits are inversely as the squares of the nuclear charges (as they are in a hydrogen-like atom), and on this assumption we can divide the molecular susceptibility of a dilute solution of KCl, say, between the two kinds of ions. In this way Joos calculated diamagnetic susceptibilities for K^+, Cl^-, Na^+, F^-, Br^-, I^- and some other ions. The values for the inert gases are those of Hector : some of the earlier determinations were more than ten times as great. χ_a denotes the atomic χ, *i.e.* $\chi_a = \dfrac{\kappa}{d} A$, where d is the density and A the atomic weight.

Numerically we have from formula (1) :

$$-\chi_a = \frac{Ne^2}{6\pi m}\Sigma S = \cdot 907 \times 10^{10}\Sigma S,$$

e being in electromagnetic units, and N being Avogadro's constant ;

or

$$\Sigma \bar{r}^2 = \frac{-\chi_a}{\pi \times \cdot 907 \times 10^{10}}.$$

It will be seen that the average area of the orbit is much the same for all the atoms and ions cited, hydrogen showing the

greatest departure, as would be expected.* This average area has no very precise significance, since the areas of the orbits of different groups differ so markedly : *e.g.* the areas of the K orbits will be negligible for the heavier atoms. It is, in

Element	Number of electrons $=n$	$-\chi_a \times 10^6$	$\frac{1}{n}\sum\bar{r}^2$	$\sqrt{\bar{r}^2}$
H -	1	1·98	·69 $\times 10^{-16}$	·83 $\times 10^{-8}$
He -	2	1·87	·33	·57
C -	6	6·6	·38	·62
Cl⁻ -	18	19·5	·38	·62
F⁻ -	10	11·5	·40	·63
Br⁻ -	36	39·5	·39	·62
I⁻ -	54	60·5	·39	·62
A -	18	18·0	·35	·59
Br -	35	33	·33	·57
I -	53	49	·32	·57
Sr⁺⁺ -	36	24	·23	·48
Ba⁺⁺ -	54	43	·28	·53
Zn⁺⁺ -	28	29	·37	·61
Cd⁺⁺ -	46	53	·40	·63
Ne -	10	6·6	·232	·48
Na⁺ -	10	6·5	·23	·48

fact, rather surprising that the values derived from the different elements agree so well. The point which is to be emphasised is that this average value is of the right order, since atomic radii are in general small multiples of 10^{-8} cm. (see Fig. 79) and the average value of $\sqrt{\bar{r}^2}$ would be expected to be somewhat less than this, as the size of the atom is the size of the largest orbits. In the case of the neon-like structures Na⁺, Ne, F⁻, rather more precision can be reached. These consist of two K electrons and eight L electrons, and the area of the K orbits is negligible, as can be demonstrated either by calculating the size of circular 1_1 orbits for $Z = 10$, or by diminishing the susceptibility for helium in the inverse ratio of Z^2 to get the susceptibility due to the K group in neon. If the K orbits be neglected, we have eight L orbits among which to share the value for ΣS, and, assuming each to have an equal area (admittedly a rough assumption), we can

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* This value of the susceptibility was found, of course, for the hydrogen molecule H_2, and so little is known of the structure of this molecule that it is hardly worth while to discuss the value of $\bar{r}$ which can be derived from this.

calculate a radius for the ions. The results so obtained are given in the following table.

Element	$\bar{r}$ for L orbits from diamagnetism	r from crystal measurement
Na$^+$ - -	$\cdot54 \times 10^{-8}$ cm.	$\cdot63 \times 10^{-8}$ cm.
Ne - -	$\cdot54$	—
F$^-$ - -	$\cdot71$	$\cdot75$
K$^+$ - -	$\cdot75 - \cdot8o^*$	$\cdot79$
A - -	$\cdot84 - \cdot89$	—
Cl$^-$ - -	$\cdot87 - \cdot92$	$\cdot95$

It will be seen that the sizes of these ions calculated from the theory of diamagnetism which has been discussed agree excellently with the values obtained from considerations of crystal structure. The assumption that every electronic orbit is acted upon by the magnetic field in the sense of change of velocity of the electron, and so takes part in the diamagnetic effect, appears to be well founded, or, in other words, diamagnetism is a universal property, which in the case of strongly paramagnetic bodies is hidden by the superposition of the much greater paramagnetic susceptibility. Certain substances, such as glass or porcelain, which may be feebly paramagnetic at ordinary temperatures, become diamagnetic at higher temperatures, owing to the diminution of paramagnetism with increasing temperature.; † in other cases diamagnetic bodies become more strongly diamagnetic at high temperatures, which is likewise to be attributed, not to a true change in the diamagnetic element, but to the diminution of a very small superimposed paramagnetism. In the case of the paramagnetics platinum and palladium, Foex has shown that a small diamagnetism, independent of the temperature, must be allowed for if these substances are to obey the paramagnetic law $\chi(T - \theta) = C$, which is discussed later on.

The belief that all the electrons contribute to the diamagnetism of the atom is further confirmed by a consideration of

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* The two values here are an upper and a lower limit, according as we attribute all the effect to the electrons of the M group, or estimate for the K and L group by using the value for neon, reduced in the ratio of the squares of the nuclear charge.

† The effect may be due to traces of iron in the substance in question.

the effect of chemical combination. The inner electrons of an atom are indifferent to chemical combination and thermal agitation : their contribution should therefore be independent of the nature of the molecule when the atoms are combined. The outer electrons, or some of them, are certainly affected by chemical combination, and their orbits modified. We should therefore expect diamagnetism to be an atomic property as far as the inner part of the atom is concerned, and the heavier the atom the more marked will be the atomic nature : on the other hand, since the outside electrons also contribute to the diamagnetic susceptibility, we expect chemical combination to have some small effect on the diamagnetism, the more marked the lighter the atom. This general argument finds support in observations on the susceptibility of molecules, and especially in Pascal's law for diamagnetic organic compounds, which states that if χ_m is the molecular susceptibility of the compound, χ_a the atomic susceptibility of a constituent atom of the compound, then

$$\chi_m = \Sigma\chi_a + \lambda,$$

where λ is a constant which has a fixed value for each type of molecular compound.

To explain paramagnetism, it is assumed that the arrangement and magnitude of the orbits is such that the atom possesses a resultant magnetic moment, and tends to turn so as to set the axis of this moment parallel to the magnetic field, and so increase the intensity of magnetisation of the substance. An opposing force of some kind must also be assumed, or saturation would be obtained with the smallest fields. In the case of solids this may be attributed to the forces which lead to cohesion, which are probably of electrostatic nature : in the case of gases and liquids Langevin, to whom this theory of magnetism is due, assumes that it is supplied by the thermal agitation which tends to make all orientations equally likely. We may consider as an analogy the case of an atmosphere subjected to gravitation : the tendency of the gravitational field is to cause all the molecules to pile themselves close together on the ground, and it is resisted by the sharing of velocities among the molecules due to gas-kinetic impact.

For all substances in which a turning of the elementary magnets —but no hysteresis—is assumed, it can be shown, by general thermodynamic reasoning, that the intensity of magnetisation I is a function of $\frac{H}{T}$, or $I=f\left(\frac{H}{T}\right)$, where T is the absolute temperature. Since for paramagnetic substances subjected to fields not too large I is proportional to H, we have $I=\frac{C}{T}\cdot H$, which is Curie's equation for paramagnetics, or susceptibility$=\kappa=\frac{I}{H}=\frac{C}{T}$.

If we express this in terms of the coefficient of molecular magnetism, or susceptibility per gram molecule, χ_m, defined by the equation $\chi_m=\frac{\kappa}{d}W$, where d is the density and W the molecular weight, we have $\chi_m T=C_m$, where C_m is called Curie's molecular constant.

This is general. Applying his particular theory to the case of a paramagnetic gas Langevin was able to express the magnetic intensity in terms of the field for fields of any strength. The equation deduced is

$$\frac{I_m}{I_{m_0}}=\coth a-\frac{1}{a}, \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

where $I_m=\frac{IW}{d}$ is the magnetic moment of the gram molecule; I_{m_0} the saturation value of I_m, attained when all the elementary moments are oriented parallel to the field ; and a is written for $\frac{I_{m_0}H}{RT}$, R being the gas constant referred to the gram molecule. This equation is fundamental for the work of Weiss on the magneton, which is a much discussed feature of modern magnetic theory. The calculation can easily be carried out, by applying Boltzmann's theorem. If μ is the magnetic moment of the molecule, whose axis makes an angle θ with the direction of H, the potential energy is $-\mu H \cos \theta$, and the exponent in Boltzmann's expression $e^{-\frac{E}{kT}}$ is

$$\frac{\mu H \cos \theta}{kT}=\frac{N\mu \cdot H \cos \theta}{Nk \cdot T}=\frac{I_{m_0}H}{RT}\cos \theta = a \cos \theta,$$

where N is the number of molecules in a gram molecule. The number of molecules with inclinations between θ and $\theta + d\theta$ is

$$dn = 2\pi A e^{\alpha \cos \theta} \sin \theta \, d\theta,$$

where A is a constant which can be fixed by considering the total number of molecules

$$N = \int dn = 2\pi A \int_0^\pi e^{\alpha \cos \theta} d \cos \theta = 2\pi A \frac{1}{\alpha} (e^\alpha - e^{-\alpha}),$$

so that

$$dn = \frac{N\alpha}{e^\alpha - e^{-\alpha}} e^{\alpha \cos \theta} \sin \theta \, d\theta.$$

$$\frac{\cos n \, \alpha}{\sinh \alpha} - \frac{1}{\alpha}$$
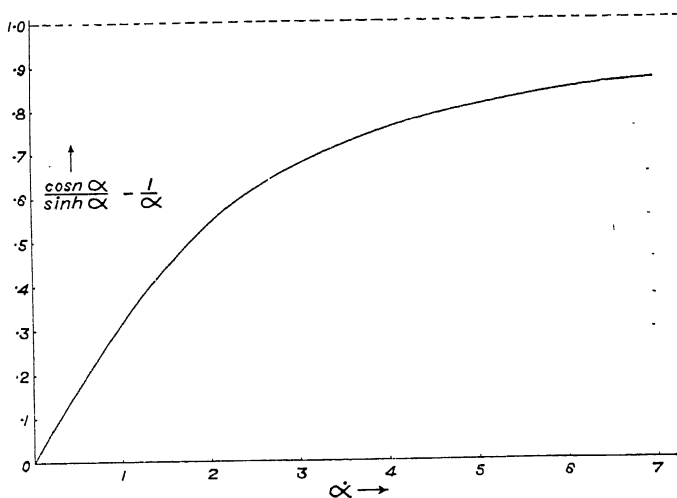
FIG. 97.

Langevin's function $\coth \alpha - \dfrac{1}{\alpha}$.

The resultant intensity must, from considerations of symmetry, be obtained by resolving the moments in the direction of H, so that

$$I_m = \mu \int \cos \theta \, dn = \frac{\mu N \alpha}{e^\alpha - e^{-\alpha}} \int_0^\pi e^{\alpha \cos \theta} \cos \theta \sin \theta \, d\theta$$

$$= \mu N \left(\coth \alpha - \frac{1}{\alpha} \right),$$

which is equation (2), since $\mu N = I_{m_0}$.

Fig. 97 shows the function $\coth a - \dfrac{1}{a}$ plotted against a, which is equivalent to plotting against H. It will be seen that as a increases, $\coth a - \dfrac{1}{a}$ tends to the value 1, whereas for small values of a the curve approximates to a straight line making a finite angle with the axis. For values of H not exceeding a certain value we have a constant susceptibility; for extremely large values of H, we have saturation. For paramagnetic substances at ordinary temperature sufficiently large values of H to give saturation cannot be obtained in the laboratory—the range corresponds to the initial part of the curve, where the susceptibility is constant. By going to very low temperatures, however, saturation can be approached, since $\dfrac{I_m}{I_{m_0}}$ is a function of $\dfrac{H}{T}$.

To find the slope of the curve in the neighbourhood of the origin, where the susceptibility is constant, we note that, if a is small

$$\coth a - \frac{1}{a} = \frac{a}{3},$$

as can easily be verified by expansion.

Hence
$$\frac{I_m}{I_{m_0}} = \frac{a}{3} = \frac{I_{m_0} H}{3RT}$$

or
$$\chi_m = \frac{I_m}{H} = \frac{I_{m_0}^2}{3RT} = \frac{C_m}{T}. \quad \dots\dots\dots\dots\dots\dots\dots\dots (3)$$

We have here the very important result that for a paramagnetic substance which rigidly obeys Curie's law a single determination of χ_m gives the saturation value I_{m_0}.

It is to be noted that the approximation for small values of H can also be obtained by putting a small in the expression where the intensity is averaged, when we have

$$I_m = \frac{\mu N a}{2a} \int_0^\pi (1 + a \cos\theta) \cos\theta \, d\cos\theta = \frac{\mu N a}{2} \left[\frac{\cos^3\theta}{3} \right]_0^\pi = \frac{I_{m_0} a}{3},$$

or the constant $\frac{1}{3}$ is obtained by averaging $\cos^2\theta$ over all values of $\cos\theta$. Langevin's formula is, of course, based on classical statistics, in that all values of θ are taken into account, while

on the quantum theory, as we shall see later, this is no longer permissible.

This theory of paramagnetism, deduced originally for gases, can be easily extended to paramagnetic salts in solution : the close analogy between dissolved substances and gases has been realised since the days of van't Hoff. Weiss has also applied Langevin's general reasoning to the molecules in a crystal, and has shown that, if we use a crystalline powder, so that all directions of crystalline axes are equally likely, then Langevin's formula holds for a solid.

Weiss has extended Langevin's theory of paramagnetism to cover ferromagnetic bodies, which can possess a permanent magnetism, and has derived a formula somewhat more general than the Curie formula $\chi T = C$, which often fits cases not covered by the Curie formula. He assumes that within a magnetic body there can exist a molecular field, produced at any point by all the molecules in the neighbourhood of that point. This field is assumed proportional to the intensity of magnetisation, or

$$H_{mol} = \lambda I_m,$$

while the total field H', made up of the molecular field and the external field H, is

$$H' = H + H_{mol}.$$

We may write
$$a_i = \frac{I_{m_0} H_{mol}}{RT} = \frac{I_{m_0} \lambda}{RT} I_m,$$

which gives a straight line relation between I_m and a_i. If we consider the case of no external field, then $a_i = a$, and we can plot this straight line, passing through the origin, on Langevin's diagram, Fig. 97. Where it intersects Langevin's curve we have a value of I_m which is permanent when there is no field, being maintained by the molecular field. In this way permanent magnetism is explained. Now suppose that there is a temperature θ at which permanent magnetism disappears : this is the so-called critical temperature, or Curie point. If the Langevin diagram be drawn for this temperature, the straight line $\frac{I_{m_0} \lambda}{RT} I_m = a_i$ must be tangential to the Langevin curve at

the origin, so as to give for the permanent I_m the value zero. We know that, at the origin, the slope of the curve I_m/I_{m_0} against a is $\frac{1}{3}$, and therefore

$$\frac{R\theta}{\lambda I_{m_0}^2} = \frac{1}{3},$$

or

$$\theta = \frac{\lambda I_{m_0}^2}{3R}.$$

Considering both external and molecular field, we have

$$\frac{I_m}{I_{m_0}} = \frac{I_{m_0}}{3RT}(H + \lambda I_m) = \frac{I_{m_0}}{3RT}H + \frac{I_m\theta}{I_{m_0}T}$$

and

$$I_m = \chi_m H,$$

whence

$$\chi_m(T - \theta) = \frac{I_{m_0}^2}{3R} = C_m. \quad\dots\dots\dots\dots\dots(4)$$

The law expressed by this formula is sometimes designated as Curie's generalised law, but as it is not due to Curie at all it is more correct to call it Weiss's law. In a sense it bears the same relation to Curie's law as van der Waals' law does to Boyle's law. Langevin's deduction, like the simple kinetic theory of perfect gases, takes no account of the forces exerted by the molecules on one another, while Weiss has introduced the conception of a molecular field, to be added to the external field, just as van der Waals introduced an internal pressure to be added to the external pressure.

On Weiss's law, as with Curie's law, $1/\chi$ is linear with T, but the straight line does not go through the origin. Not only do ferromagnetic substances above the critical point obey this law over certain temperature ranges, as established by Weiss and Foex, but many solid salts obey it over a large temperature range, as shown by Honda and his collaborator Ishiwara, and by Theodorides. For example, $1/\chi$ plotted against T gives good straight lines for $FeSO_4$ and $CuSO_4$ from $-180°$ to $600°$. Foex has found that for very concentrated solutions Curie's law must in some cases be replaced by Weiss's law, showing that in such solutions the molecules are able to give rise to a molecular field.

Direct Evidence for Electron Theory of Magnetism. Langevin and, following him, Weiss have, then, been able to account for the general properties of certain diamagnetic and paramagnetic substances by assuming as elementary magnets electrons circulating in closed orbits, the planes of which, in the case of para- and ferro-magnetism, are oriented by the magnetic field. Evidence in favour of a rotation of the magnetic elements was deduced by Swinburne from certain experiments in which the magnetisation of iron was reversed by a strong rotating field, instead of by abrupt reversal of field. When the direction of the field is steadily rotated the orbits, if they follow the field, should pass from one position to the other without passing through any unstable states, and there should be no hysteresis losses. This prediction has been experimentally confirmed. The argument is interesting, but not conclusive.

Attempts have been made to obtain more direct evidence in favour of the fundamental hypothesis of paramagnetism. O. W. Richardson pointed out some years ago that if, as a result of the application of the magnetic field, there is a rotation of the planes of the electron orbits, then there will be a change of the moment of momentum of the electrons about a line parallel to the direction of the magnetising field. The creation of a magnetic intensity in a given direction is equivalent to the creation of a moment of momentum about that direction. The moment of momentum per unit volume, U_z, is connected with the magnetic moment per unit volume by the simple expression *

$$U_z = 2\,\frac{m}{e}\,I_z$$

$$= 1 \cdot 13 \times 10^{-7} I_z. \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(5)$$

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* A simple, but not very thorough, method of deriving this expression is to consider a single circular electron orbit, of radius r, in which the electron revolves with angular velocity ω. Let μ and u be, respectively, the magnetic moment and moment of momentum pertaining to this single orbit. Then

$$\mu = \frac{e\pi r^2 \omega}{2\pi} = \tfrac{1}{2}er^2\omega\,; \quad u = mr^2\omega.$$

Hence
$$\frac{u}{\mu} = 2\,\frac{m}{e}.$$

Hence, if an unmagnetised rod (for which $I_z=0$) be suddenly magnetised to intensity I_z a moment of momentum about the z axis will be established, which, if the electron orbits react upon the matter which contains them, demands the creation of an equal moment of the matter as a whole about the same axis. In other words, unless the atoms, or parts of the atoms, are free to turn without influencing the neighbouring matter, there will be a mechanical rotation of the rod about its axis of magnetisation, the magnitude of which is of measurable order. It is to be noted that the calculation depends only upon the assumption that the planes of the orbits do rotate, and does not consider the nature of the force that makes them rotate—whether the external field, or an internal molecular field, or both—so that it holds equally for para- and ferro-magnetic substances. The latter are, of course, used in experiment because of the large magnetic intensity realisable with them.

Various experimenters have looked for this effect. Einstein and de Haas were the first to measure it, by making use of a resonance method to increase the angular deflection on magnetisation. A thin cylindrical iron rod is suspended vertically in a magnetising solenoid, and the period of torsional oscillation adjusted to be equal to that of an alternating current passed through the solenoid. In this way an oscillation of the rod is worked up, from the amplitude of which the increase of angular momentum due to magnetisation can be calculated. J. Q. Stewart has carried out experiments on the same subject, with a like arrangement of a rod suspended vertically in a solenoid, the rotation of the rod about its axis being measured by means of the ballistic throw on magnetisation. Very accurate experiments are due to Chattock and Bates, who make use of a method similar to that of Stewart. They have worked with three specimens of iron, and one of nickel : the spurious moments due to any lack of symmetry in the suspension are

Since for any given orbit u and μ are codirectional

$$\frac{U_z}{I_z}=\frac{\Sigma u}{\Sigma \mu}=\frac{u}{\mu}=2\frac{m}{e}.$$

A more satisfying proof is given in O. W. Richardson's *Electron Theory of Matter* (page 395, second edition, 1916), where it is easily shown that the moment of momentum is the same about any line parallel to the direction of magnetisation.

carefully eliminated. While Einstein and de Haas found a moment of momentum agreeing within 2 per cent. with that given by equation (4), the later experimenters find about half this value. Thus for

$$\frac{U_z}{I_z} \times \frac{1}{1 \cdot 13 \times 10^{-7}}$$

Chattock and Bates find an average value of ·503 instead of 1. Sucksmith and Bates have since repeated the experiment by a null method, and find for iron ·503, for nickel ·501, and for a Heusler alloy ·501. The inverse magnetomechanical effect, *i.e.* the production of magnetism by mechanical rotation, has been established and investigated by J. S. Barnett, who likewise finds a value ·5 instead of 1 for the above expression.

These measurements of the magnetomechanical effect lead, then, to a ratio of magnetic moment to mechanical moment twice as great as we should expect on classical theory. This cannot be satisfactorily explained on classical mechanics, but it no longer stands as an isolated fact, for, as we have seen in Chapter XV., the study of the anomalous Zeeman effect shows that the magnetic effect associated with a given mechanical moment of the atom is not, in general, that which we should expect if Larmor's theorem, exemplifying classical mechanics, held, but g times this. Accordingly the experiments under discussion have been interpreted as meaning that for the atoms of the substances investigated g is 2, or that the atoms, or ions, are in the S state. There seems, however, little point in pushing things so far, since we know that ferromagnetism is not an atomic property, as evidenced particularly clearly by the Heusler alloys, and therefore the orbits concerned cannot be orbits of the atoms as we know them when emitting line spectra, but must be governed by forces of crystallisation, or, to be quite general, by the influence of neighbouring atoms. We know nothing of the outer atomic orbits in such cases. It is, perhaps, remarkable that the three ferromagnetic substances so far investigated all give the same value for the ratio.

Although the magnitude of the effect disagrees with the theory to the extent indicated, it may be said that these experiments have shown that paramagnetism (using the term to

include ferromagnetism) is accompanied by the production of a mechanical moment of momentum of the order to be expected if the magnetisation is due to electrons rotating in closed orbits which can be oriented by the field.

Another method by which the question of nature and orientation of the electronic orbits may be explored has been adopted by A. H. Compton and O. Rognley, who have carried out experiments to see if the intensity of a beam of X-rays reflected from a crystal of magnetite changes on magnetisation of the crystal. If the atom is the ultimate magnetic particle, or even if the atom contains certain electron orbits of Bohr type, the orientation of whose planes can be changed by the field without changing the orientation of the atom as a whole, such change of intensity is to be anticipated. It was not, however, detected, although a very sensitive null method was employed.

From this the experimenters deduce that neither the atom nor the molecule is the ultimate magnetic particle, since the supposition that the electron distribution in the atom is so nearly isotropic that rotation of the whole system leaves the arrangement of electrons in space much as it was is rendered untenable by general considerations. They consider that the electron itself must be the ultimate particle, and, further, that the electrons to which paramagnetism is due cannot circulate about the nucleus (in which case a change of orientation of the plane of the orbit would markedly affect the average space distribution of the electrons), but must circulate about certain fixed points on the surface of the atom in orbits whose dimensions are small compared to the size of the atom, say of order 1×10^{-9} cms. or less. Such orbits are equivalent to Parson's "ring electrons," and represent a point of view which has been adopted by Oxley and others. It is clear that if the orbit is of such restricted size a rotation of its plane will not affect the general distribution of electrons sufficiently to modify measurably the intensity of X-ray reflection, but it is not so clear that there are not other ways of explaining the result than this assumption, which is so much in conflict with our general views of atomic structure as to stand little chance of general adoption. If only one or two of the orbits per atom take part in the paramagnetic mechanism (for which arguments can be

deduced if Bohr's value of the magneton be considered; see later) it is possible that the effect of a partial rotation would not be measurable. This, however, supposes that in some obscure way the heat agitation communicates itself to these selected orbits.

In connection with these experiments we may mention an attempt of Ehrenfest's to explain paramagnetism without any changes of orientation of the magnetic element in the atom. It is somewhat difficult to see how in a crystal such change of orientation can take place, for on Langevin's theory the heat agitation of the atom or molecule is the controlling factor which tends to make all orientations equally likely : the crystal molecule cannot very well rotate without upsetting the crystal structure, and, if it were the atom which rotated, it would involve the atom having a thermal energy of rotation, which, on the theory of equipartition, approximately valid at ordinary temperatures, would lead to too high a value of the specific heat. Ehrenfest, basing himself upon general considerations due to Weiss, Stern, and Lenz, assumes that in a crystal the magnetic element consists of an electron circulating in an orbit, for the axis of which a given direction is fixed with reference to the crystal lattice : in the absence of a magnetic field a circulation in either sense is assumed to be equally likely, or to every electron moving in one sense there is one moving in the opposite sense. The crystal as a whole, therefore, shows no permanent magnetism. When, however, a field is applied the potential energy of the individual magnetic element has opposite signs for electrons moving in opposite senses, so that by Boltzmann's theorem the probability of the two states is no longer the same. If we want to envisage a definite mechanism we must suppose that a certain number of orbits turn over with a snap, so that the circulation of the electron is reversed.

The crystal then acquires a magnetic intensity. By Boltzmann's theorem the number of electrons circulating in the one sense is to the number circulating in the opposite sense as $e^{\alpha \cos \theta}$ is to $e^{-\alpha \cos \theta}$, and the mean moment contributed by the elementary magnet is

$$\bar{\mu} = \mu \cos \theta \, \frac{e^{\alpha \cos \theta} - e^{-\alpha \cos \theta}}{e^{\alpha \cos \theta} + e^{-\alpha \cos \theta}}$$

$$= \mu \cos \theta \tanh (\alpha \cos \theta).$$

θ is the angle between H and the direction of μ, the elementary magnetic moment, assumed to be fixed in the crystal lattice. If a crystal powder be used all directions of μ are equally likely, and we must integrate over the half sphere. We get

$$\frac{I_m}{I_{m_0}} = \frac{\overline{\mu}}{\mu} = \int_0^1 x \tanh ax \,.\, dx.$$

Instead of assuming a fixed direction for the elementary magnet we can, if we choose, adopt a quantised direction with respect to H, retaining Ehrenfest's elementary magnets consisting of electrons circulating in opposite sense which are equally probable in the absence of a field. This leads to a somewhat more complicated formula. A check on these formulae can be derived by considering the saturation value I_{m_0}, which is determined as a multiple of the Curie constant, the multiple depending upon the nature of the function expressing $\overline{\mu}/\mu$.* Now gadolinium sulphate obeys Curie's laws down to very low temperatures, and a saturation of 84 per cent. is attained, from which Curie's constant can be determined. The value so found invalidates Ehrenfest's formula : how far it can be fitted by a quantum formula admitting a discrete number of inclinations remains to be determined.

It cannot, in short, be said that there is any direct decisive proof that magnetic phenomena are ultimately due to electrons circulating in orbits, and producing the magnetic force to be calculated from classical theory. There is, however, a strong body of indirect evidence to show that magnetic phenomena are amenable to the methods of the quantum theory of spectra, and that a completer knowledge of the properties of the orbits towards which a study of the complex spectra is leading will clear up many of the magnetic problems.

The Magneton. As regards the question how the ultimate magnetic particle, be it what it may, varies from element to element, Weiss, as is well known, has obtained evidence for the hypothesis that a certain elementary magnet—or its equivalent —of fixed moment $18 \cdot 5 \times 10^{-22}$ gauss cms. is a constituent of all magnetic matter : this elementary magnet he calls a

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* If $\overline{\mu}/\mu = f(a)$, then $I_{m_0}^2 = \dfrac{f^2(\infty)}{f'(0)} RC_m$. See Debye, *Handbuch der Radiologie,* vol. vi. p. 714.

magneton. Weiss's contention may be formally stated as follows :—whenever we can determine, directly or indirectly, the magnetic moment of an atom, this moment is found to be a whole multiple of a single elementary moment, the magneton. The elementary moment per gram molecule, one magneton being attributed to each molecule, is 1123·5 gauss cms.* If Avogadro's number be taken as $6·06 \times 10^{23}$, this gives the above value for the magneton.

We can calculate from experiment the magnetic moment per atom if we have saturation conditions, since in that case every atom will be contributing its full magnetic moment to the intensity, or moment per unit volume, I. There are, however, ways of estimating the magnetic moment of the atom without reaching saturation conditions, which are hard to attain with paramagnetic substances. The methods of deriving it experimentally may, in fact, be divided into four classes, which will be briefly considered.

Firstly, we may use paramagnetic metals at very low temperatures. The magnetic behaviour depends upon the ratio $\frac{H}{T}$, so that whereas enormous fields may be necessary to produce saturation at normal room temperature, fields practically obtainable suffice to produce an approach to saturation when T is small. Secondly, we may experiment with ferro-magnetic materials at temperatures above the Curie point, where the behaviour becomes, in a sense, paramagnetic : at such temperatures we have Weiss's equation,

$$\chi_m = \frac{C_m}{T - \theta} ,$$

as a good representation of experimental fact. We are here, of course, far from saturation : in fact, the validity of the formula depends upon $a = \frac{I_{m_0} H}{RT}$ being small. Thirdly, we may consider solutions of paramagnetic salts, for which extensive series of measurements have been made by Pascal, and Cabrera and Moles. Here again we can work far from saturation, and Langevin's theory applies (or, for very concentrated

* Weiss has recently amended this value to 1126 gauss cms.

solutions, Weiss's equation). Hence to find the saturation value I_{m_0} the formula

$$C_m = \frac{I_{m_0}^2}{3R}$$

can be applied, the value of C_m being found from Curie's law $\chi_m = \dfrac{C_m}{T}$ by a single determination of χ_m at a given temperature. Fourthly, the saturation value can be obtained by working with certain paramagnetic compounds which in the solid state obey closely Curie's law. Such bodies are called normal paramagnetic bodies, but complete normality among paramagnetics seems to be as rare as it is among humanity. Gadolinium sulphate is, for instance, one of the few substances which obey Curie's law down to very low temperatures. However, certain solid paramagnetic salts obey Weiss's law over a large range of temperatures, as established by Honda, alone and in collaboration with Ishiwara, and by Theodorides. Reference to substances for which this behaviour has been demonstrated was made on p. 596.

It is very remarkable that gadolinium sulphate should obey Langevin's law $I_m/I_{m_0} = \coth a - \dfrac{1}{a}$ even down to practically the lowest attainable temperature of 1·31 absolute, as it does ; at this temperature a saturation of 84 per cent. of the theoretical maximum is reached. Not only is the substance a solid, so that a rotation of the elementary magnets is, as already explained, hard to understand, but at these extremely low temperatures the law of equipartition would be expected to break down, and it is implicitly assumed in Langevin's theory. Ehrenfest's theory was constructed to meet such cases, but, as already pointed out, it is not altogether satisfactory. What is satisfactory is that the saturation value for gadolinium sulphate has also been calculated from the Curie constant, and the value so determined agrees with that obtained directly. This substance is so far unique in having its atomic moment fixed by these two independent methods.

The results of the four methods of investigation mentioned above have been adduced by Weiss to prove the existence of his magneton. It must not be thought, however, that they

are sufficiently simple to permit the hypothesis that a fixed number of magnetons is invariably associated with an atom of a given element. Consider, for example, the experiments on ferromagnetism above the Curie point. When $\frac{1}{\chi}$ is plotted against T, instead of the single straight line to be expected we have a curve consisting of a series of approximately straight lines of different slopes connected by comparatively sharp elbows, *i.e.* over a given range of temperature there will be a line of given slope, which is succeeded by a line of a different slope for another range of temperature. If the existence of the magneton be admitted, this can only mean that the number of magnetons associated with a given kind of atom changes abruptly at certain temperatures, presumably due to modifications in the outer orbits. Again, in the case of solutions, the number of magnetons associated with a given atom depends upon the valency of the dissolved salt, and is often different from the value associated with the same atom combined in a solid compound. Other examples of varying number of magnetons might be given. To take the ferromagnetic metals as an example, metallic nickel has 3 magnetons in the neighbourhood of absolute zero, but 8 for temperatures between 500° and 900° C. Above 900° C. it has 9. When combined as a salt it can have either 15 or 16 in the solid state, while in solutions it has 16 magnetons. The variability of magneton number is equally remarkable for iron and cobalt.

The type of evidence on which the magneton is based has been briefly described ; a more detailed discussion of some of the measurements is given in the next section. It may be said at once that the existence of the Weiss magneton as a fundamental unit is certainly not established beyond controversy. It is always difficult to establish a whole number rule, especially when the experimental data are not measured with a high degree of accuracy, and the whole numbers involved as multipliers may be large. (Integers greater than 30 are frequently in question as magneton numbers.) Small differences from integers are always explained as due to experimental error—for instance, Kamerlingh Onnes obtained

for the atomic magnet of gadolinium 39·2 magnetons, which, he says, is 39 within experimental error. Bigger variations from the whole number are often found—the recent measurements of Theodorides give fractions of a magneton in the case of cobalt and nickel chlorides, while Cabrera gives 29·43 magnetons for dissolved $MnCl_2$, and 28·45 for solid $MnCl_2$ and solid MnO. If the magneton is indeed a universal constant, it is, of course, of the greatest importance for considerations of atomic structure, whatever speculations may be made as to the nature of the elementary magnet. It is, however, clear from what has already been said that the evidence in favour of the Weiss magneton leaves something to be desired.

It is natural to try to connect the magneton with the accepted universal constants ; any simple and reasonable expression of this elementary magnetic moment in terms of these would greatly strengthen its position.* Bohr's simple theory has connected the moment of momentum of an electron in an orbit with Planck's constant h, so that we can easily calculate the value of the magneton on the assumption used in the theory of the hydrogen spectrum. The magnetic moment is

$$\mu = \frac{eS}{\tau} = \tfrac{1}{2} e \omega r^2 \qquad \text{\textasteriskcentered}$$

and by the quantum hypothesis

$$m \omega r^2 = \frac{nh}{2\pi}$$

whence

$$\mu = \frac{e}{m} \cdot \frac{nh}{4\pi},$$

or, taking $n=1$, to give the magneton,

$$\mu = \frac{e}{m} \cdot \frac{h}{4\pi} \times 6 \cdot 06 \times 10^{23} \text{ per gram molecule,}$$

attributing one magneton to each molecule.

The numerical value of this is 5589 gauss cm., which is almost exactly five times (actually 4·97 times) the Weiss magneton. In the light of this result the Weiss magneton has been critically

* Just as Bohr's expression of Rydberg's constant in terms of universal constants won immediate support for his theory.

examined from the point of view of the quantum theory, especial enquiry being made as to how far, if at all, experiment speaks against the Bohr magneton.

At first sight the fact that the numbers of magnetons found experimentally for different atoms are but seldom multiples of 5, and are in certain cases actually less than 5, would appear to rule out the Bohr magneton. It is to be noted, however, that a number of magnetons less than 5 is rare, and is only found, in fact, for ferro-magnetic solids at very low temperatures. The crystalline forces in the solid may well prevent complete orientation of all the orbits (it is, in fact, astonishing that Langevin's theory holds as well as it does), and, again, in the neighbourhood of the absolute zero we must be prepared for departures from any law which is based on the supposition that all atoms have the same fixed number of quanta of action for their orbits. As regards the infrequent occurrence of multiples of 5 Weiss magnetons, W. Pauli has indicated how this can be explained on the quantum theory. He confines himself to the case of paramagnetic gases, since for solutions the question is complicated by the electric field of the water molecules and the formation of various hydrates, while for solids the crystalline forces cause difficulties. His theory has, however, been extended to apply to solutions and to solid salts. His arguments will now be given in outline.

Suppose, then, we have a gas in which the molecules possess resultant magnetic moments tending to set themselves parallel to the magnetic field. Whereas on classical theory any orientation of an elementary moment is possible, on the quantum theory only certain angles with the direction of the magnetic field are permitted, since the presence of the field gives a reference line for quantising the directions of the moments in space. We are dealing, in the case of gases, with the susceptibility as determined by the formula

$$\chi_m T = C_m = \frac{I_{m_0}^2}{R} \cdot \frac{1}{3} \quad \dots\dots\dots\dots\dots\dots(3)$$

or, in general,

$$\chi_m T = C_m = \frac{I_{m_0}^2}{R} \cdot K. \quad \dots\dots\dots\dots\dots(6)$$

We are so far from saturation that the directing influence of the magnetic field is negligible for this discussion. On Langevin's theory the value of K in (6) is $\frac{1}{3}$: this, as we have seen, is the result of taking an average value of $\cos^2 \theta$, where the angle θ between the magnetic moment and the magnetic field is distributed at random in three dimensions, *i.e.* we adopt classical statistics. When we turn to the quantum theory only a limited number of determinate values of θ are admitted as possible : for a quantum number n, there are n different, equally probable, angles. Instead of averaging $\cos^2 \theta$ over all values of θ distributed at random we have to take the mean value of $\cos^2 \theta$ for a discrete number of values of θ, given by space quantisation. The result of this is that for every different quantum number we get a different constant K in formula (6) instead of $\frac{1}{3}$, the value $\frac{1}{3}$ being the limit reached as n tends to ∞. The formula which Pauli derives is

$$\overline{\cos^2 \theta} = \frac{1}{3} \frac{(n+1)(2n+1)}{2n^2}, \quad \dots\dots\dots\dots\dots(7)$$

when the bar denotes average value, and n is the number of units (Bohr magnetons) in the elementary magnet. Pauli more or less arbitrarily excludes the case where the elementary magnet sets with its moment across the field. For example, if $n=1$, all the moments are parallel to field ; $\theta=0$ and $K=1$. If $n=2$, $\theta=0$ or $60°$, both directions being equally probable, and calculation shows that $K=\frac{5}{8}$. If $n=3$, θ has three possible values, and $K=\frac{14}{27}$, and so on. The consequence is that the number of Bohr magnetons in a given molecule is not a whole number, as it would be if all directions were admitted for the magnetic moments, but is a fractional number whose value depends upon the number of quanta allotted to the orbit. Thus, if $n=1$, which corresponds to $K=1$, the value of the elementary magnetic moment should be $5\sqrt{3}=8.7$ times a Weiss magneton.* If $n=2$ the value should be $5\sqrt{3}/\sqrt{\frac{8}{5}}$ times 2 Weiss magnetons, *i.e.* $10\sqrt{\frac{1.5}{8}}=13.7$ times a Weiss magneton.

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* The formula used by Weiss is $I^2_{m_0}=3RTX$, whereas, on the quantum theory, $I^2_{m_0}=RTX$ when $n=1$. Hence the ratio of the two magnetons is increased by $\sqrt{3}$.

Now the only two paramagnetic gases for which satisfactory measurements of susceptibility have been made are O_2 and NO,* for which the number of Weiss magnetons has been found to be about 9 and 14 respectively. It is astonishing that these numbers should be so near those calculated for 1 and 2 quantum orbits on the theory just indicated. We know so little of the dynamic model of molecules, especially of molecules containing a fair number of electrons, that it is useless to speculate as to how the one and two quantum electrons circulate in the O_2 and NO molecules.

Pauli's theory has been modified by later workers, to take into account the anomalous magnetic behaviour of the general atom which finds expression in the anomalous Zeeman effect. Pauli assumed that the elementary magnet behaves as if it were a hydrogen atom, or, in other words, as if the splitting factor g, discussed in Chapter XV, were 1. Now we know that, in general, g is not 1, and that the magnetic moment resolved in the direction of the field is mg units (Bohr magnetons), where m can take the values $\pm j$, $\pm(j-1)$, $\pm(j-2)\ldots$. We therefore replace the expression

$$\frac{I_{m_0}H}{RT}\cos\theta,$$

deduced for the case where θ could have any value, by

$$\frac{Njg\mu_B H}{RT} \cdot \frac{m}{j} = \frac{mg\mu_B H}{kT},$$

where μ_B is the Bohr magneton. Following the line of argument used in deducing Langevin's formula, $Ae^{\frac{mg\mu_B H}{kT}}$ is the number of molecules whose moment resolved parallel to the field is $mg\mu_B$, and to determine A we have

$$N = \sum_{-j}^{j} Ae^{\frac{mg\mu_B H}{kT}}$$

$$= A\sum_{-j}^{j}\left(1 + \frac{g\mu_B H}{kT}m\right), \text{ if } \frac{g\mu_B H}{kT}m \text{ is small,}$$

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* It may be noted that in Kaye and Laby's tables N_2 is given as paramagnetic, whereas it is now known to be diamagnetic : this is an example of the uncertainties of magnetic measurements.

where the summation has to be carried out over all values of m from $+j$ to $-j$ inclusive. $\sum_{-j}^{j} m = 0$, and $\sum_{-j}^{j} 1 = 2j+1$ since the number of states is $2j+1$. Hence

$$A = N \frac{1}{2j+1},$$

and the total moment is

$$I_m = N \frac{1}{2j+1} \sum_{-j}^{j} \left(1 + \frac{g\mu_B H}{kT} m\right) m g \mu_B$$

$$= N \frac{1}{2j+1} \frac{(g\mu_B)^2 H}{kT} \sum_{-j}^{j} m^2$$

$$= N \frac{(g\mu_B)^2 H}{kT} \cdot \frac{j(j+1)}{3},$$

since

$$\sum_{0}^{n} x^2 = \frac{n}{3}(n+1)(n+\tfrac{1}{2}).$$

Hence $$\chi_m = \frac{1}{3} \frac{N(g\mu_B)^2}{kT} j(j+1) = \frac{1}{3} \frac{N(jg\mu_B)^2}{kT} \cdot \frac{j+1}{j}. \quad \ldots\ldots\ldots(8)$$

Now the experimenters usually express their results in terms of Weiss magnetons, using Langevin's formula

$$\chi_m = \frac{1}{3} \frac{I_{m_0}^2}{RT} = \frac{1}{3} \frac{N\mu^2}{kT}$$

to determine the elementary moment μ from the experimentally found χ. Suppose, then, that μ_W be the Weiss magneton, and n_W the number of Weiss magnetons, we have

$$\frac{1}{3} \frac{N(n_W \mu_W)^2}{kT} = \chi_m = \frac{1}{3} \frac{N(jg\mu_B)^2}{kT} \cdot \frac{j+1}{j},$$

or $$n_W^2 = \left(\frac{jg\mu_B}{\mu_W}\right)^2 \frac{j+1}{j}.$$

Hence $$n_W = jg \times \sqrt{\frac{j+1}{j}} \, 4\cdot97,$$

since we know that $\mu_B/\mu_W = 4\cdot97$. This shows us how to find the number of Weiss magnetons to be anticipated for a given

atom or ion if the above theory is correct : find the value of j and g for the atom or ion, and multiply the product by

$$4 \cdot 97 \sqrt{\frac{j+1}{j}}.$$

Sommerfeld was the first to take into account the anomalous magnetic behaviour : he assumed that in the case of the ions of the iron group we are dealing with the S state, so that $g=2$. In this case

$$\chi_m = \frac{1}{3} \frac{N^2 n^2 \mu_B{}^2}{NkT} \cdot \frac{n+2}{n}$$

$$= \frac{I_{m_0}^2}{RT} \frac{1}{3} \frac{n+2}{n}, \quad \dots\dots\dots\dots\dots\dots\dots(9)$$

where $n=2j$ is the number of Bohr magnetons in the elementary magnetic moment. Hence, on Sommerfeld's hypothesis,

$$\overline{\cos^2 \theta} = \frac{1}{3} \frac{n+2}{n}, \quad \dots\dots\dots\dots\dots\dots(9a)$$

as contrasted with Pauli's original value

$$\overline{\cos^2 \theta} = \frac{1}{3} \frac{(n+1)(2n+1)}{2n^2}. \quad \dots\dots\dots\dots\dots(7)$$

As n tends to ∞, $\overline{\cos^2 \theta}$ tends to $\frac{1}{3}$ in both cases, which is necessary, since Langevin's value must appear when all values of θ are admitted.*

In discussing the paramagnetic ions later in this chapter we shall see that Hund has applied the general formula (8) to the rare earths, while Sommerfeld has applied (9) to the interpolated elements of the first long period. As different workers have made use of Pauli's and Sommerfeld's methods, a little table showing the number of Weiss magnetons corresponding to integral numbers of Bohr magnetons is appended. n is the

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* A difficulty of Pauli's theory, both in its original form and as modified, is that at high temperatures the formula for the susceptibility does not, in the general case, go over into the classical form deduced by Langevin, as on the general conceptions of the quantum theory we should expect it to do. I hear, as the book goes to press, that this difficulty has been satisfactorily settled by application of the new mechanics to the problem.

number of Bohr magnetons, and n_W the equivalent number of Weiss magnetons.

n - - -	1	2	3	4	5	6	7	8	9
n_W (Pauli) - -	8·7	13·7	18·7	23·7	28·7	33·7	38·7	43·7	48·7
n_W (Sommerfeld) -	8·7	14·1	19·3	24·5	29·6	34·6	39·7	44·7	49·7

The Paramagnetic Atoms. We now turn to a more detailed consideration of the marked paramagnetic properties exhibited by atoms possessing certain electronic groupings. We know that strong paramagnetism is connected with the building up of a sub-group temporarily passed over in the scheme of atomic structure—thus for the elements scandium to nickel the 3_3 sub-group is built up, although 4_1 orbits are already occupied for calcium, and continue to be so for heavier elements. A sub-group consists of two grouplets, and the completion of a grouplet corresponds, we believe, to zero moment. Hence if the grouplets are built up successively, one being completed before the other is started, we should expect a minimum (zero) moment within the group of paramagnetics, but if the two grouplets are built up by some kind of alternative additions to the one and the other we cannot, of course, make any such prediction. It will be seen later that the rare earth elements lanthanum to lutecium (cassiopeium) show such a minimum moment within the group, while the scandium to nickel elements do not.

Before attempting a discussion of the paramagnetic suscepti- bilities it may be well to add something to what has been already said as to the experimental determinations. These determinations generally refer to ions, since they are carried out either with solutions of salts or with solid salts of the metals. If we suppose the susceptibility of a solution of a paramagnetic salt to be proportional to the concentration (which is rigorously true of solutions of nickel salts, for instance), we can attribute a certain susceptibility per unit mass to the dissolved salt. A correction must be made for the diamag- netism of the solvent. In the case of the salts under con-

sideration the susceptibility of the paramagnetic ion is large compared to that of the diamagnetic radical combined with it in the salt, and so a correction for the radical can be made with accuracy, the value obtained for the paramagnetism of the metallic ion being found to be the same when different salts are used. We have already seen that all atoms are essentially diamagnetic, the paramagnetism being superimposed, but a rough calculation shows that the subjacent diamagnetism is negligible for the ions in question. We can, then, obtain from measurements made with solutions a value for the atomic (or, rather, the ionic) susceptibility of the metallic elements. Now, in general, solutions obey Curie's law,

$$\chi T = C, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

although, as Foex has shown, for high concentrations it may be necessary to use Weiss's modification,

$$\chi (T - \theta) = C. \quad \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

In either case the value of C can be found from the experimental data, and hence the saturation value I_{m_0}, and the elementary magnetic moment.

While, as stated above, for some salts, notably nickel sulphate, chloride, and nitrate, the value found for the susceptibility per ion is independent of the concentration, in general there is a certain definite, although not large, variation with the concentration. We can take the value obtained by extrapolation for infinitely dilute solutions, or, on the other hand, we can suppose with Weiss that ions of two different adjacent magneton values are present, the equilibrium between which changes with the concentration, and assume that both these values represent possible states of the ion. This is to suppose that the fractional magneton values are due to ions of integral magneton values present in different proportions, just as fractional atomic weights are due to mixtures of isotopes of whole number masses. These features of the measurements are mentioned to indicate that, in spite of the accuracy of a measurement made with a given solution, there is a certain element of doubt as to the exact value of the elementary magnetic moment to be attributed to some of the ions.

The measurements of paramagnetism made with solid salts by Honda and his collaborator Ishiwara, and others, may also be invoked. Many of these salts obey Wiess's law over a large range of temperature, as exhibited by plotting $1/\chi$ against T. From the slope of the straight line a value of Curie's constant can be obtained, which agrees in general with that obtained from solutions.

The atomic susceptibility χ_a ($\chi_a = \frac{\kappa}{d} A$, where A is the atomic weight) of a metallic ion depends upon the valency which it exhibits or, in other words, upon the charge which it carries.
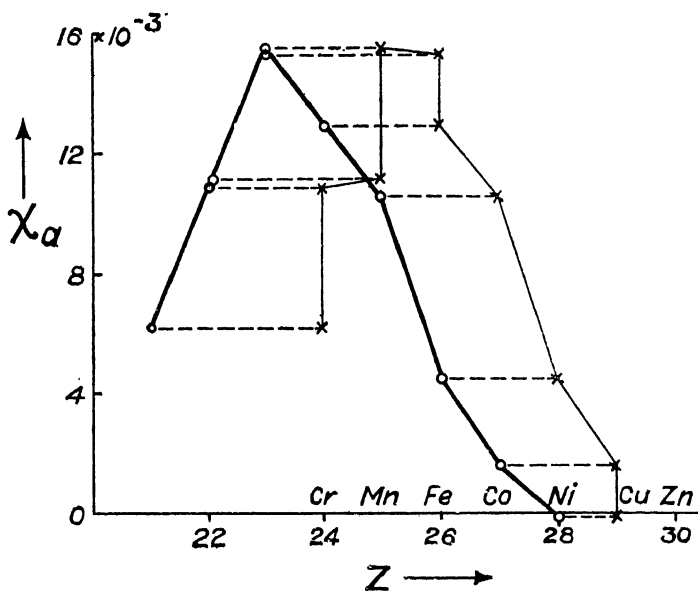
FIG. 98.

Influence of valency on paramagnetic susceptibility of elements from chromium to copper.

It has, for instance, already been mentioned that it is different for ferrous or ferric, or for cuprous and cupric ions. Hence there can be no single-valued functional relationship between atomic magnetism and atomic number. Kossel was the first to point out an elegant relationship which considerably simplifies the discussion. If we consider not the atomic number, but the number N of extranuclear electrons actually

present in the ion we find that a given atomic susceptibility corresponds to a given number of electrons, no matter what the nuclear charge may be. This is exemplified in Fig. 98. The crosses represent the measured atomic susceptibility of the ions plotted against the atomic number Z : for the same Z there are, in most cases, two values of χ_a. If, however, the crosses be displaced to the left by a number corresponding to the valency of the ion in question (for instance, the value for ferrous iron is displaced two places to the left, that for ferric iron three places), a one-valued relationship for χ_a is obtained, represented by the heavy line in the figure. Ions with the same number of electrons have the same susceptibility. This recalls the Kossel-Sommerfeld displacement law in spectra.

Weiss and the other experimenters who have determined the magnetic moments of the ions have, in general, expressed their results in terms of the Weiss magneton. Frequently, as in the case of nickel, for which the value is 16·06, the number of Weiss magnetons is very nearly an integer, but in other cases the departure from integral value is considerable. It has already been mentioned that Weiss invokes, among other things, the existence side by side of ions of different magnetic moments to account for this. Epstein and Gerlach, however, independently applied Pauli's theory of the Bohr magneton to the measurements made with solutions of paramagnetic salts, and obtained very interesting results, although the departures in certain cases from integral multiples of the Bohr magneton were as marked as those in other cases from integral multiples of the Weiss magneton. As far as exact integral values are concerned, supporters of the Weiss magneton can hold their ground. It must be remembered, however, that the integral numbers involved in the case of the Bohr magneton are very small, while in the case of the Weiss magneton we are dealing with integers in the neighbourhood of 20. There is one very striking argument for the Bohr magneton furnished by the experiments in question. Even allowing the numbers to be rounded off so as to be integral multiples of the Weiss magneton, only certain multiples are found, namely, 9 (Ti^{+++} and Cu^{++}), 16 (Ni^{++}), 19 (Cr^{+++}), 24 (Cr^{++}) and 25 (Co^{++}), and 29 (Mn^{++} and Fe^{+++}). Now it seems strange that, in the first place, the

smallest number of magnetons should be 9, and, in the second place, that even after 9 there are large gaps in the integer series. Referring, however, to the table on p. 612, we see that on the Pauli theory (or Sommerfeld's modification of it) there are only five possibilities for values of the Weiss magneton below 30, viz. 8·7, 14·1, 19·3, 24·5, 29·6 (Sommerfeld's values).
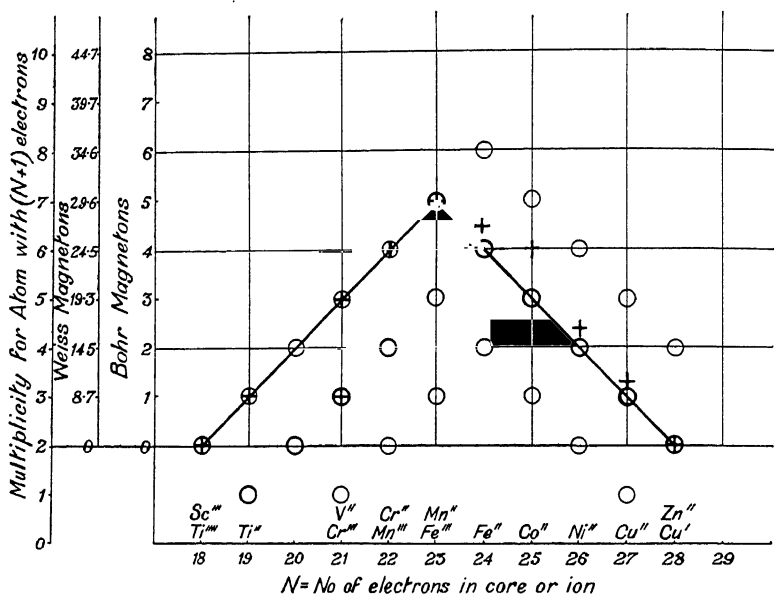
FIG. 99.

Magnetic moments of paramagnetic ions of first long period.
Values derived from paramagnetism of solutions +
Magnetic moments of core (Stoner) ⊙

The five values found experimentally are just in the neighbour-hood of these numbers. The lack of exact agreement between experiment and magneton numbers, which is found in certain cases on both theories, must be attributed to secondary features of the mechanism : if fractional values of g be allowed, fractional values of the Bohr magneton will, in general, appear.

Fig. 99 shows the results obtained by a study of the para-magnetism of solutions, the magnetic moment of the ion, indicated by a cross, being expressed as a multiple of the Bohr magneton. (In Fig. 98 the values are expressed in absolute

units.) Sommerfeld's values, given on p. 612, are used to convert Weiss magneton values, in which the results are given by the experimenters. It will be seen that while for ions containing 18, 19, 21, 22, 23, 25 and 28 electrons the multiple of the Bohr magneton is approximately an integer, for ions of 24, 26 and 27 electrons the integral rule is far from being obeyed. We can, of course, assume that ions of two different integral magneton values are present in such cases. The chief interest of the diagram is that, as indicated by the heavy line, the assumption that the number of Bohr magnetons increases from 0 to 5 by steps of unity as we pass from $N=18$ to $Al=23$, and then decreases by steps of unity to 0 at $N=28$ agrees fairly well with the experimental data. It may be noted that at $N=21$ there are two possible values for the magneton number, viz. 1 for V^{++}, and 3 for Cr^{+++}. This indicates two possible stable arrangements of 21 electrons according as the nuclear charge is 23 or 24. Now Hund has deduced from spectral evidence that the number of electrons in 3_3 orbits is 3 for vanadium, but 5 for chromium, the value 4 not occurring. The above fact may be connected with this peculiarity.

Fig. 99 also shows the magnetic moment of the core of the atoms, as deduced by Stoner on his assumption that the magnetic moment of the atom can be made up of that of the core and of a single optical electron. He finds

$$\mu_c = \gamma - 2,$$

where μ_c is the moment of the core, and γ is the multiplicity. This gives, of course, three values of μ_c for the middle elements, since they have three spectral systems of different multiplicity. The values of μ_c are indicated by circles, the value corresponding to the deepest term of all the spectral systems being indicated by a heavier circle. It will be seen that there is a kind of general correspondence between the values so obtained and those deduced from the magnetic data, everything going to show a maximum moment in the middle of the family. The diagram also indicates that there are plenty of irregularities still to be cleared up.

The elements of the rubidium-xenon period have not been sufficiently investigated for general conclusions to be formed, although much work has been done on individual elements,

notably palladium. In the period of thirty-two the rare earths have been studied in detail, especially by Cabrera and St. Meyer, the solid salts being used. Fig. 100 shows the values
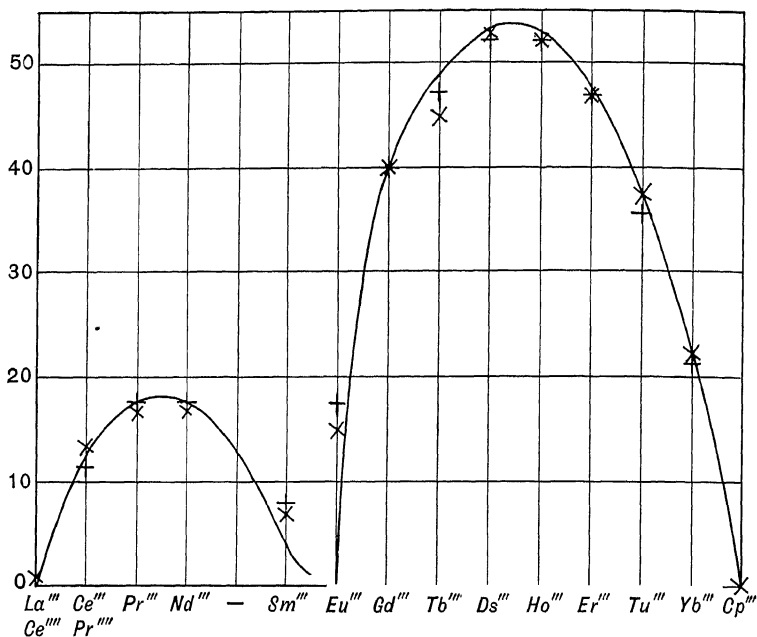
Magnetic moments of rare earths
(× = St. Meyer's measurements ; + = Cabrera's measurements).

obtained by both these workers, expressed in terms of the Weiss magneton, and it will be seen that there is very clear evidence for the division of the rare earths into two groupings. On Stoner's theory the rare earths correspond to the building up of a sub-group of fourteen 4_4 electrons, consisting of six 4_{43} and eight 4_{44} electrons. In the case of the ions considered we are not troubled with electrons of an incomplete grouplet for which $n = 6$, since the maximum number of electrons of the $n = 6$ group is two for neutral atoms of the rare earths, and the ions with which we deal are always triply or quadruply charged. Hund has derived satisfactory values for the magnetic moments of the different ions from the basic terms of the spectra, which in the case of the rare earths are not

known experimentally, but can be deduced from certain general rules derived from a consideration of known complex spectra. The basic terms being calculated, not only as regards the multiplicity but also as regards the value of j, we can find the value of g from Landé's formula given in Chapter XV. The moment is then given by jg (which will not, in general, be an integer) in terms of the Bohr magneton, and to get the value in terms of the Weiss magneton we have to multiply by $4 \cdot 97 \sqrt{\dfrac{j+1}{j}}$, as explained in the preceding section. The values so calculated by Hund are shown by the curve in Fig. 100. The experimental points, indicated by crosses, lie astonishingly close to it. The method, however, has no success with the elements scandium to nickel, where Sommerfeld's earlier treatment gives better results.

Experiments with Atomic Rays. Gerlach and Stern have succeeded in finding the magnetic moment of single atoms, in the state of a highly rarefied gas, when they are far removed from the influence of other atoms. Their experiments are of the greatest importance, as they not only yield a direct estimate of the magnetic moment which speaks in favour of the Bohr magneton, but they also afford the most direct proof of a quantisation of the direction of the moment of the atom in space with respect to the direction of the magnetic field.

The metal to be investigated is obtained in the form of a beam of uncharged atoms moving in a space evacuated so highly that the atoms traverse it without a collision. Such an "atomic beam" (*Atomstrahl*) can be obtained by vaporising a metal in a very high vacuum; the atoms, shot off with a velocity which can be deduced by the kinetic theory of gases from the temperature of vaporisation, pass through suitable slits, which isolate a narrow pencil. If necessary the space in which the vaporisation takes place can be separated from the main body of the vessel by a narrow slit, and a lower pressure maintained in the latter than in the former. Such atomic beams were first investigated in detail by Dunoyer.* It is of

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* For a general account of the work which has been done on atomic beams, see W. Gerlach, Atomstrahlen, *Ergebnisse der exacten Wissenschaften*, iii. 182, 1924.

interest for the present discussion to note that the velocity of the flying atoms has been directly measured by Stern, whose results agree with the estimates which are made from the kinetic theory.

The theory of the experiments of Gerlach and Stern is simple. According to the theory of quantisation of direction, an atom which possesses a resultant moment of momentum must orient itself in a magnetic field so that the component of the moment in the direction of the field is an integral multiple of the unit $h/2\pi$. In particular an atom of unit moment must set itself with its axis of momentum either parallel to, or antiparallel to the field. If such an atom, equivalent to a minute bar magnet, finds itself in a uniform magnetic field, there will be no tendency for it to move either towards the one magnetic pole or the other, but if the field be inhomogeneous the atoms whose axes are parallel to the field will tend in the one direction, the atoms whose axes are antiparallel will tend to move in the opposite direction. The qualitative result of this is that if a beam of atoms be sent through an inhomogeneous magnetic field, in which the direction of the gradient of magnetic force is normal to the beam, it will be split into two discrete beams, while, on the other hand, if all directions of the atomic moment in the magnetic field be admitted, as on the classical theory,* the beam will merely be broadened. If, then, the deflection of the atomic beam can be observed, experiment will afford a decision for or against space quantisation. If the magnetic moment is unity we shall have the splitting into two. To consider the general case, and express ourselves in terms of the spectral theory, the number of parts into which the beam is split will be $2j + 1$, where j is Sommerfeld's j for the basic term of the spectrum of the neutral atom in question. Thus for an atom of Column I, for which the S state is basic, with $j = \frac{1}{2}$, and for which we have unit magnetic moment, there should be the two beams which we have considered. If the basic term is a ^6S term,

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* On the classical theory if an atomic magnet, whose axis is in a given direction, enter a magnetic field, the elementary axis will maintain its inclination to the field, but execute a motion of precession round the direction of the lines of force.

$j = \frac{5}{2}$, there should be a splitting into six. To get the magnitude of the separation we must consider the g value, since the magnetic moment is mg. Neighbouring beams will differ by unity in the value of m, in all cases, and therefore the separation will be simply proportional to g. Thus for thallium, which we shall have to mention later, the basic term is a $^2P_1$ term, $j = \frac{1}{2}$; whereas for ^2S terms $g = 2$, for $^2P_1$ terms $g = \frac{2}{3}$. Therefore with thallium we should expect a splitting into two, but a separation only one-third of that of sodium, say.

What is actually observed is the displacement X of the beam normal to its direction. To obtain a quantitative theoretical value for this displacement, let μ be the moment of the atomic magnet, H the field strength, and $\frac{\partial H}{\partial x}$ the field gradient which is in the same direction as H, and normal to the path of the atom. Then the force acting on the elementary magnet is $\pm\mu\frac{\partial H}{\partial x}$, the sign depending upon whether μ is parallel to or antiparallel to $\frac{\partial H}{\partial x}$. If the flying atom has velocity v, mass M, and traverses a path of length l at every point of which $\frac{\partial H}{\partial x}$ has the same value, elementary considerations show that

$$\pm X = \frac{1}{2}\frac{\mu}{M}\frac{\partial H}{\partial x}\left(\frac{l}{v}\right)^2.$$

If as unit moment the Bohr magneton be assumed, and if $N\mu_B$ be the value of the Bohr magneton per gram molecule, W the molecular weight of the element in question,

$$\pm X = \frac{1}{2}\frac{N\mu_B}{W}\frac{\partial H}{\partial x}\left(\frac{l}{v}\right)^2 \quad\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

It has been assumed that the atoms all have the same velocity. Actually, if obtained by evaporation, they will, of course, have the Maxwellian distribution of velocity. This will lead to a broadening out of each of the discrete beams, as shown in Fig. 101, a, b, c, which represent diagrammatically the

trace of the beam on a plane normal to its direction.   Fig. 101(d) shows the general form of trace to be expected with the actual experimental disposition, where $\dfrac{\partial H}{\partial x}$ diminishes symmetrically on either side of a mid line horizontal in the diagram.   At
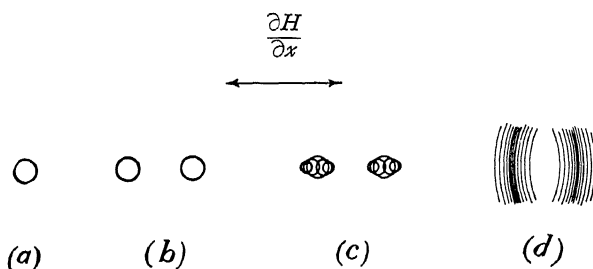
FIG. 101.

Diagrammatic trace of atomic beam on plane normal to its direction. (a) No field. (b) Field: uniform velocity. (c) Field: Maxwellian distribution of velocities. (d) General appearance with type of field experimentally produced.

some distance from this line, where the field becomes practically homogeneous, the two parts of the beam will come together.

The apparatus used is represented in Fig. 102. F is the miniature furnace (about 1 cm. long) in which the metal M is
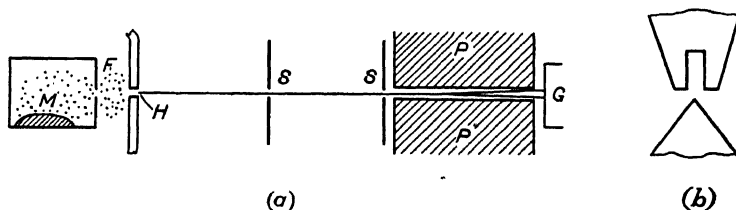
FIG. 102.

Gerlach and Stern's apparatus for investigating the magnetic behaviour of atomic rays. (a) General scheme of experiment. (b) Pole pieces as seen looking along atomic beam.

vaporised. This furnace is contained in a separate vessel communicating with the rest of the apparatus by the slit H through which the metal atoms issue, and the furnace vessel is exhausted by its own pumping system. SS are diaphragms pierced with small holes, to limit the beam. PP are the poles

PLATE VIII
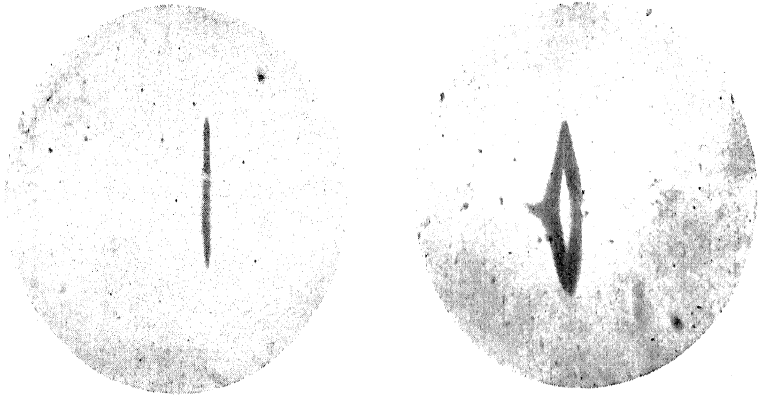
(a)   (b)

Fig. 1.
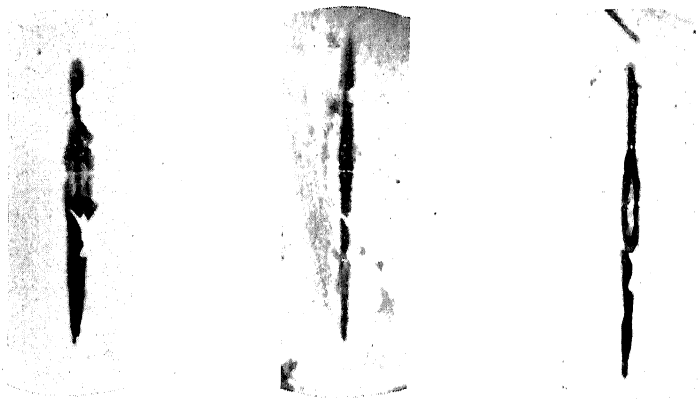
(a)   (b)   (c)

Fig. 2.

Atomic Rays in Inhomogeneous Magnetic Field.   (Gerlach and Stern.)

Fig. 1.   Silver : (a) without field, (b) with field.
Fig. 2.   Nickel : (a) with field, (b) without field, (c) control experiment with silver

of the magnet, producing a field which is inhomogeneous, varying strongly in the vertical direction, but uniform at all points of a given horizontal line in the diagram. G is a glass plate, which can be cooled if necessary, exposed to the atomic beam : the atoms form a deposit where they strike, which is generally too faint to be seen, but can be developed to good visibility by means of a special technique described by Gerlach and Stern. The whole apparatus of diaphragms and magnetic poles is enclosed in a vessel which is very highly exhausted. Fig. 102 (b) shows the form of pole-pieces used to produce the inhomogeneous field, as seen looking along the direction of the beam. The distance between the knife edge and the plane of the slotted pole-piece is about 1 mm. The field so produced was quantitatively investigated by means of a small diamagnetic wire, the repulsion at various points being measured. The inhomogeneity is, of course, strongest in the vertical line through the knife edge, and falls off to left and right, so that an atomic beam of unit moment, split into two if the anticipations of the quantum theory are valid, would be most widely separated in this line, the separation diminishing to either side until a place is reached where the gradient is not sufficiently strong to produce a resolution of the beam. It may be said at once that in many cases a splitting into two of the beam was observed, the middle part of the trace having the form shown in Fig. 101 (d), in accordance with the above explanation.

Plate VIII., Fig. 1, shows the result of an experiment with silver : on the left is the trace of the ray without field, on the right with field. The direction of $\frac{\partial H}{\partial x}$ is horizontal in these photographs. The projection on the left hand side of the trace obtained with the field is due to the very strong gradient of magnetic force in the immediate neighbourhood of the knife edge. The length of path in the magnetic field was about 3 cms., and the field gradient about 120,000 gauss/cm. Plate VIII., Fig. 2, shows the result of an experiment with nickel : on the left we have nickel with a field gradient of 200,000 gauss/cm. : in the middle nickel without field, and on the right a control experiment with silver in the same

apparatus with the same field.   It will be seen that with nickel there is an undeflected beam which is absent with silver.

From the particularly good records obtained with silver a value for the Bohr magneton may be calculated from equation (10), since all the quantities are known except μ_B.   Four experiments with silver give for $N\mu_B$ the value 5400-5700 gauss cm./mol., the theoretical value being, as we have seen, 5589 gauss cm./mol.   The agreement is excellent, considering the very difficult nature of the experiment.   The Gerlach-Stern method may, then, be said to have given a direct proof that both the Bohr magneton and space quantisation have a real existence.

As regards the magnetic moment of individual elements, the following results have been obtained from the study of the atomic beam.   Copper, silver and gold have in the normal state a magnetic moment of one Bohr magneton ; zinc, cadmium and mercury have no magnetic moment ; tin and lead have likewise no magnetic moment.   Thallium has a small moment, not exactly determined, but round about one-third of a Bohr magneton.   Nickel shows a very peculiar behaviour ; as can be clearly seen from Plate VIII., Fig. 2, there are both deflected and undeflected atoms present, or, in other words, some atoms have no magnetic moment, while others have a moment.   The moment corresponding to the deviated atom works out to be not one Bohr magneton but two.   Iron has been investigated, but so far no magnetic effect has been established ; the traces obtained show the undeflected beam only, but the iron experiments are not regarded as final.

These results are in excellent agreement with our general views on the structure of the atom.   The diamagnetism of the inert gases indicates, as we have before had occasion to emphasise, that for these symmetrical systems there is no resultant magnetic moment : we have discussed the bearing of this on the model for neutral helium.   We have further been led to assume that the electrons added to an inert gas system try to arrange themselves within the grouplets as far as possible so that there shall be no resultant moment of momentum or magnetic moment.   For a neutral atom of an

element of Column I, where there is only one " outer " electron, we should expect unit magnetic moment : this has been proved by the atomic beam experiments to be the case with all the elements so far tested, namely, copper, silver, and gold. Further, the experiments on the paramagnetism of solutions have shown that the Ti^{+++} ion, which should have the structure of potassium has unit moment. For elements of Column II there are two outermost electrons, which can clearly arrange themselves with opposite senses of rotation so that there is no resultant moment. To support the view that elements of this column have no magnetic moment, we have, besides the Gerlach-Stern experiments for zinc, cadmium and mercury, the fact that mercury vapour is diamagnetic. Spectral evidence shows that the basic term in the case of all these elements is a singlet $^1S_0$ term with $j = 0$. For elements of Column III the only element which has been investigated by Gerlach is thallium. Spectroscopic evidence shows that the basic term for thallium is a $^2P_1$ term (cf. Grotrian's experiments on the absorption of thallium vapour) for which $m = \pm \frac{1}{2}$, $g = \frac{2}{3}$: this agrees with the value found by Gerlach as far as the approximate nature of the atomic beam measurement allows. For elements of Column IV we have Gerlach's measurements for tin and lead, giving zero moment. The basic term of the lead spectrum is a $^3P_0$ term, and Sponer has recently shown that the basic term of the tin spectrum likewise has $j = 0$. The case of nickel is more troublesome, and too little has been done in the way of term analysis for the spectrum to be reconciled with the atomic beam results. On the whole we can clearly say that the determination of atomic moment made by Gerlach and Stern agrees excellently with the deductions made from both spectroscopic and chemical evidence as regards the moments of atoms in their normal states.

There are, however, plenty of problems still awaiting solution in the realms of magnetism. The magnetic beam experiments show that the atoms must certainly take up the quantised positions within the first half centimetre of their path in the field, or else the separation of the beam into two would not be as distinct as it is. This means that they must take up their quantised positions in less than 10^{-5} sec., and

Einstein and Ehrenfest have shown that such a rapid settling down into position offers grave difficulties from the point of view of either quantum or classical mechanics. The point can merely be mentioned here : for details the reader is referred to the original paper.* There are further difficulties in interpreting certain magneto-optical experiments, such as the quenching of the fluorescence of iodine vapour (molecular) by a magnetic field, but we know so little about the behaviour of molecules that it is difficult to draw definite conclusions from this observation.

Whittaker's Magnetic Atom Model. The following brief account of a model devised by E. T. Whittaker on the basis of the classical theory is inserted here, since, although it is not especially adapted to give an account of magnetic properties, it assumes a magnetic element in the atom. The model is very artificial, even in comparison with other atom models, and so far has a very restricted scope, but it is of interest as showing how the older theory may be made to yield a quantum result.

We have emphasised, in discussing the question of resonance and ionisation potential, that whereas an electron whose energy exceeds a certain number of volts can excite the emission of a spectral line by the atoms through which it passes, an electron of lesser energy cannot do so, but is in this case, in contradistinction to the first, gas-kinetically reflected from the struck atom without loss of energy. The energy of motion required for the excitation of a given line of frequency ν_T is determined by the quantum equation

$$\text{kinetic energy} = h\nu_T, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

and if the kinetic energy of the electron is greater than this it sacrifices only the amount $h\nu_T$, and passes on with the balance.

The relation (11) is accepted by the disciples of the quantum theory as fundamental, without any attempt being made to devise a mechanism to account for it. Whittaker, however, has indicated how classical electrodynamics can be made to supply a model atom which has the property that an electron approaching it is either repelled without loss of kinetic energy,

* E. Einstein and P. Ehrenfest, *Zeitschr. f. Phys.* **11**, 31, 1922.

or is allowed to pass on with the sacrifice of a finite amount of energy. It is supposed that the electron, as it approaches along a direction which, for definiteness, we take as the x axis, induces within the atom what may be called a "magnetic current," by analogy with the electric current which an approaching magnetic pole would induce. To explain this magnetic current there is postulated within the atom a magnetic pole P, of strength μ, and mass M, rigidly attached in some unknown way to a centre O, about which it can rotate in a circular orbit of radius a. Suppose that it is free to rotate in the yz plane, and that the angle which it makes at time t with the axis of y is ψ. Then the magnetic force which the electron exerts at P is

$$\frac{ea\dot{x}}{(a^2+x^2)^{\frac{3}{2}}},$$

and hence

$$A\ddot{\psi}-\frac{\mu ea^2\dot{x}}{(a^2+x^2)^{\frac{3}{2}}}=0, \quad \dots\dots\dots\dots\dots\dots(12)$$

where $A=a^2M$. In order to produce a resultant force always directed along the axis several magnetic poles can be arranged symmetrically in the circle: μ and M must then be the total pole strength and total mass respectively of all the poles. The rotating poles set up an electric force $\dfrac{\mu a^2\dot{\psi}}{(a^2+x^2)^{\frac{3}{2}}}$ at x, along the axis of x, so that for the motion of the electron we have

$$m\ddot{x}+\frac{\mu ea^2\dot{\psi}}{(a^2+x^2)^{\frac{3}{2}}}=0 \quad \dots\dots\dots\dots\dots\dots(13)$$

If the electron be projected from rest at $-\infty$ with velocity u, and if the magnetic structure were initially at rest we get, by integrating (12),

$$A\dot{\psi}-\frac{\mu ex}{(a^2+x^2)^{\frac{1}{2}}}=\mu e; \quad \dots\dots\dots\dots\dots(14)$$

and from (12) and (13), $A\dot{\psi}\ddot{\psi}+m\dot{x}\ddot{x}=0$.

$$\tfrac{1}{2}A\dot{\psi}^2+\tfrac{1}{2}m\dot{x}^2=\tfrac{1}{2}mu^2, \quad \dots\dots\dots\dots\dots(15)$$

which expresses the conservation of energy.

When the electron approaches the "magnetic wheel" its velocity diminishes, since its energy of motion is being transformed into rotational energy of the magnetic poles. If all its energy is so used up before it reaches the plane of the wheel, then, at its nearest distance d, $\dot{x}=0$ and $\frac{1}{2}A\dot{\psi}^2=\frac{1}{2}mu^2$, and, from (14), we have for d,

$$-\frac{\mu e d}{(a^2+d^2)^{\frac{1}{2}}}=\mu e-\sqrt{Am}\,.\,u. \quad\quad\dots\dots\dots\dots\dots(16)$$

After approaching within the distance d the electron retraces its path, and the energy of rotation of the magnetic wheel is re-transformed into kinetic energy of the electron. In other words, the rotation of the magnetic wheel is accelerated by the approach of the electron, which ultimately comes to rest when it has given up all its kinetic energy : after this the magnetic wheel, which continues to rotate on account of its postulated inertia, gives back its energy to the electron, and ultimately comes to rest again. This is the case if u is less than $\dfrac{\mu e}{\sqrt{Am}}$, as can be seen from (16).

If, however, u is greater than $\dfrac{\mu e}{\sqrt{Am}}$, the electron can pass through the plane of the wheel, and the reversal point is on the far side of the wheel. If u is greater than $\dfrac{2\mu e}{\sqrt{Am}}$, it not only passes through, but escapes from the influence of the wheel, and goes to $+\infty$. In this case we see, from (14) and (15) respectively, that $A\omega=2e\mu$ and $\frac{1}{2}A\omega^2=\frac{1}{2}m(u^2-v^2)$, where ω is the final value of $\dot{\psi}$, v is the final velocity of the electron at $+\infty$. The electron has sacrificed a definite amount of energy which remains as energy of rotation in the magnetic wheel.

This is the essential feature of Whittaker's device : if the initial energy of the electron is less than a quantity $U=\dfrac{2e^2\mu^2}{A}$, it is sent back along its path without loss of energy—gas-kinetically reflected ; if it is greater than U it gives up a definite quantum of energy U, and passes on with the balance. By

considering circuits of wire of self-inductance L, within the atom, Whittaker is able to transfer his energy of rotation of the magnetic wheel into radiant energy of frequency $v_T = \dfrac{\mu}{\pi\sqrt{LA}}$, so that if $\mu e^2 \sqrt{\dfrac{L}{A}} = \dfrac{h}{2\pi}$, then $U = h v_T$. It has thus been shown possible, using only the ordinary laws of electrodynamics, to devise a machine giving the quantum relation concerned in the ionisation potential, and consequent radiation. The supply of materials called for, however, exceeds considerably that usually allowed to the atom builder : rigid rods and coils of wire can scarcely be supposed to have any very close counterparts in the actual atom. An isolated magnetic pole is itself a convenient fiction rather than an experimentally established entity. The theory is important rather as showing that it is possible to account for a quantum mechanism on classical lines, and so encouraging us to hope that we shall ultimately find some means of reconciling the quantum theory and the wave theory, than as offering anything which appeals to the physicist as an approach to reality, using that word in the sense in which it is understood by physicists.

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CHAPTER XVII

STATIC ATOM MODELS

Introductory. We have seen how the dynamic atom model has had a considerable measure of success in giving a quantitative account of many branches of spectroscopic observation. When, however, we turn to the question of chemical combination, we find that no fully satisfactory model of even the simplest *molecule*, that of hydrogen, has so far been constructed. Bohr originally suggested that the nuclei of the two hydrogen atoms lie on an axis round which the two electrons revolve in a circular orbit, the plane of which is normal to the axis, and midway between the nuclei, the electrons always lying at opposite ends of a diameter. Preliminary investigation appeared to show that this arrangement was stable, but it has been shown that if both electrons be struck simultaneously in the same direction with forces lying in the plane of the orbit and normal to the diameter joining the electrons, then they leave the orbit. For certain disturbances, then, the model is unstable. But even if this objection be passed over, in view of the fact that the model can be made to yield certain properties of molecular hydrogen, such as the variation of refractive index with wave-length (dispersion) and the magnetic rotation of the plane of polarisation, there are other serious criticisms to be considered. The work required to separate the molecule into its component atoms—the heat of dissociation— is calculated from the model to be 61,000 calories, while Langmuir's experimental value is 84,000 calories.* Again, the magnetic properties of such a molecule are not in accord with experiment, for whereas the model indicates paramagnetism,

* Other observations are :—Isnardi, 95,000 calories ; Franck, Knipping and Krüger, 81,000 ± 5700 calories.

molecular hydrogen is actually diamagnetic. The dynamic models for nitrogen and oxygen molecules devised by Sommerfeld and by Pauer have likewise been unable to withstand the criticism directed against them. So far, then, the molecule, even of the simplest type, has not been adequately represented in terms of moving electrons, on the lines of Bohr's atom model. It may be noted, however, that recent theoretical work on the analysis of molecular (band) spectra is yielding information on the moments of inertia and the internuclear distances of many diatomic molecules, as well as the values of electronic energy levels, and it seems likely that in the near future dynamic models may be constructed on the basis of this work.

Being, then, at the present moment, unable to construct a model of the molecule which shall give satisfactory quantitative results, we may set ourselves the simpler task of describing in general terms the formation of the molecule, making some kind of provisional picture which shall serve to represent chemical combinations until some more satisfactory and generally valid model shall be devised. The dynamic atom is not, at present, very well adapted for general descriptive purposes, for, in spite of Bohr's recent work, it is not easy to form a precise mental picture of two atoms, each of which is surrounded by a complicated system of electronic orbits, combining to form a molecule. We can, of course, devise representations of molecules consisting of atoms with electronic orbits encircling two or more nuclei, and may well believe that some such mechanism actually exists, but so far no empirical control for hypotheses as to intramolecular electronic motion has been found. As long as this is so, as long as we are not in a position to consider in detail the dynamical consequences, the modifications of orbital motion, which attend chemical combination, then it is simpler to consider merely fixed electrons, which may be done without loss of generality. To offer an analogy from another branch of physics, so long as we are not able to discuss in detail the forces between two approaching molecules, we may, in the kinetic theory of gases, treat them as elastic impenetrable spheres, or, more generally, ellipsoids, while realising that this is in contradiction to our modern knowledge. So long as we

cannot calculate the effect of the details of structure of the molecule, but can only take into account those properties which make it equivalent to a hard elastic solid, there is no point in using what we know to be the more correct, and more complicated, model.

Considerations of chemical combinations have been based mainly on atomic models in which the electrons are at rest. Without discussing further, for the moment, the relation which the dynamical and statical models bear to one another, let us consider how far the nucleus atom model with fixed electrons can be advantageously used to represent chemical properties.

The General Valency Problem. At the root of all problems of chemical combination is the conception of valency, or perhaps rather the word valency.* In the older school of chemical thought there was attributed to each element a certain power of combining with hydrogen, or, in other words, the power to bind to itself a definite number of hydrogen atoms, or chemically equivalent atoms. This number was spoken of as the negative valency of the atom in question: atoms which combined with those of negative valency were said to have positive valency. The power of combining with one hydrogen was represented by a single valency bond, to which, in stereochemistry, a definite direction was attributed. The bond was little more than a hook on which to hang a hydrogen atom, yet there gradually arose around the valency bonds a semi-mystical philosophy,† which, as it grew less and less able to respond to the questions put to it for solution, became the more diffuse and dogmatic. The one atom with which the older theory of valency worked moderately satisfactorily was the carbon atom, and for the sake of this one atom the theory was imposed on all inorganic compounds. But the carbon atom is anything but a typical atom, a fact which is well expressed in the form of periodic table given on p. 473. It occupies a central position among the seven elements between

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* " Denn eben wo Begriffe fehlen
    Da stellt ein Wort zur rechten Zeit sich ein."—Goethe's *Faust*.

† " Our knowledge of valency cannot be expressed in a few symbols or in a few formal statements."—H. E. ARMSTRONG.

the inert gases helium and neon, and, judging from the three elements which precede it, we should expect it to be positively quadrivalent, but approaching it from the end of the period we should anticipate negative quadrivalence. It combines equally freely with oxygen and with hydrogen, in a way that leads to series of compounds of a kind peculiar to the chemistry of carbon. The only other atom which occupies the middle position in a short period is silicon, which, as is well known, has some of the characteristic properties of carbon. Carbon is, then, an extremely unsuitable element on which to base general theories of valency : by stressing its properties we are starting on the problem from a very difficult point of approach. One has only to try to follow the discussions of the organic chemists—for example, the discussion at the British Association in 1925 in which Flürscheim, Lapworth, Robinson, Lowry and Ingold took part —to realise that there is little common ground among the recognised authorities, and it may, perhaps, be said that the time is not yet ripe for profitable application of general electronic theories to organic chemistry. So far, in fact, this application has been more apparent than real, in that there has rather been a translation of known results into a different language than the introduction of a new and fertile point of view. There has been a remarkable lack of predictions capable of experimental verification or contradiction.

One of the standard difficulties for theories of chemical combination is, as pointed out in Chap. XIV., to explain the so-called molecular compounds of which the ammonium salts give a simple type. Nitrogen is tervalent to hydrogen, when hydrogen alone is present, forming NH_3, yet in the presence of chlorine it takes up another hydrogen, and forms NH_4Cl, with a complex radicle NH_4. As regards this problem, we may quote the words of an eminent chemist, H. E. Armstrong, " Kekulé took the further important step of dividing compounds into two classes—that of atomic compounds, such as ammonia and hydrogen chloride, in which the components are held together by atomic affinities : and that of molecular compounds, such as ammonium chloride, containing atomic compounds held together by molecular affinities : but Kekulé

never gave any very clear explanation of the difference. Notwithstanding Brereton Baker's observations, the question remains with us to-day (1911), the only difference being that we have substituted the more precise term 'residual affinity' for Kekulé's term 'molecular affinity.'" Other difficulties will be described as the newer theories are developed.

The general atom can take part in a variety of compounds in which it exhibits a range of valencies. Thus chlorine, which has a negative valency of 1 in HCl, has a positive valency of 5 in Cl_2O_5, and 7 in Cl_2O_7 : phosphorus has a negative valency of 3 in PH_3 and a positive valency of 3 in PCl_3, 4 in P_2O_4 and 5 in P_2O_5. To every atom can be allotted a greatest positive and a greatest negative valency, and one of the most important generalisations for guiding chemical speculation as to atomic structure was made by Abegg when he enunciated the rule that the sum of the greatest positive and greatest negative valency which an atom can exhibit is, in general, 8.

We shall also make use of Abegg's terminology of homœopolar and heteropolar compounds. Atoms which possess definitely different electrochemical character may be said to form molecules of definite polarity, one part of the molecule tending naturally to have a positive charge, and the other part a negative charge—these are the heteropolar compounds, exemplified in all salts, such as NaCl, K_2SO_4, and so on. On the other hand, there are many molecules in which the component atoms have exactly the same electrochemical character, being, in fact, all of the same kind. Examples of such homœopolar molecules which readily occur are the diatomic gases, such as N_2, O_2, H_2 : another example is IBr : the numerous organic compounds in which there are chains of carbon atoms directly connected together offer further instances. While heteropolar compounds yield ions on solution, homœopolar compounds do not. To explain the formation of homœopolar compounds is one of the chief tasks of any valency theory.

Kossel's Theory. Fundamental for all recent attempts at devising a model to represent chemical combination is the separation of extra-nuclear electrons into two classes. There are certain electrons which have a privileged exterior position, forming what is variously called an external shell, layer, ring or

group : these, which are often called the valency electrons, are more immediately concerned in the re-groupings and sharings of electrons which accompany chemical action.   The remaining electrons, together with the nucleus, tend to act more or less as a positively charged whole, the positive charge, of course, being equal to the number of external electrons in the neutral atom : they form a group which is often called the kernel of the atom. On Kossel's theory the electrical attraction of this kernel holds the valency electrons in place, and may be taken as acting in all directions, just as does the attractive force of a positively charged sphere ; the external electrons are considered to be in equilibrium under this central force, their mutual repulsion, and, if they are rotating, the forces consequent on their accelerations.   If they are not rotating, special forces must be assumed, since equilibrium of stationary electrons is impossible round a centre of Coulombian force.   For our present general purposes we need not consider in detail the nature of the forces which maintain the equilibrium, nor even whether the electrons are in motion or not.   On the Lewis-Langmuir theory, the positions of the electrons (which are stationary) in the outside layer of the kernel affect the positions of the external electrons, as we shall see, but the central attraction still exercises a prevailing influence.

A cardinal feature of all accepted theories is the tendency for the atom to gain or lose electrons until the external group has a certain number of electrons, the same for several near elements, which represents a very stable state.   This stable form is the inert gas form, as discussed in Chapter XIV., and illustrated by means of Kossel's diagram, Fig. 77.   The formation of heteropolar compounds between atoms which tend to gain and atoms which tend to lose electrons can then be considered in two steps : firstly, the interchange of electrons between the combining atoms, which gives them opposite charges, and secondly, the juxtaposition of the ions so formed.   It is important to note that we have, in the case of certain simple molecules, direct experimental evidence provided by modern methods of investigating crystal structure that the combined atoms are not in their normal neutral, but in an ionised state. Working in this field Debye and Scherrer examined the intensity

of reflexion of homogeneous X-rays from halogen salts of the alkali metals, which crystallise in simple cubical form. In Chapter VI. it has been pointed out, in connection with the experiments of W. L. Bragg, that the scattering of X-rays is produced by the electrons in the atoms, and that the intensities of the homogeneous beams reflected from various crystal planes are governed by interference of the waves scattered from the separate electrons, and so give evidence as to the number and position of the electrons For reflexion from certain crystal planes the waves reflected from the metal atoms will be in opposite phases to those from the halogen atoms. If the metal and the halogen atoms contain the same number of electrons there should be complete cancellation, and no reflexion from these planes should be detected. If, on the other hand, the atoms contain different numbers of electrons, the reflected beam will have a measurable intensity. Debye and Scherrer chose sodium fluoride for their experiments : the neutral sodium atom contains 11 electrons, the neutral fluorine 9. The experimental results prove that in the crystal the number of electrons associated with fluorine planes is the same as that associated with sodium planes : both fluorine and sodium ions must hold 10 electrons each. In the crystal of sodium fluoride, then, every sodium atom has given up one electron, which has become attached to a fluorine atom. A similar deduction can be made from W. H. Bragg's earlier experiments on sylvine, which indicate that both potassium and chlorine ions hold 18 . electrons.* Reference has already been made in Chapter XIV. to the evidence which residual rays offer to the same effect.

In order to combine, then, atoms of marked electropositive or electronegative character ionise themselves by interchange of an electron or electrons, and take on the external form of the inert gases : the atoms are then held together by electric forces. In this way the simple heteropolar compounds are formed. For many of them the old theory of valency was moderately satisfactory. Kossel, however, has made a great step forward by indicating how the formation of complex

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* Debye and Scherrer consider that in W. H. Bragg's experiments the sensitiveness was not great enough to render the conclusion inevitable, and carried out their experiments to establish it with greater certainty.

compounds (such as, to take the simplest case, NH_4Cl) can be explained. For such compounds the conception of valency bonds, single directed forces which can each hold one hydrogen, fails completely, if nitrogen has a negative valency of three. Werner, who has done so much work on complex salts, has emphasised that their behaviour indicates rather that the atom is surrounded by a continuous field of force, and Kossel has given a certain precision to this suggestion.

An atom can only take away, or give up, a definite maximum number of electrons, determined by the incompleteness of its outside layer as compared with that of the nearest inert gas. This does not mean that the whole field of force of the positively charged kernel has then been annulled. The force of attraction for negative charges extends all round the kernel, and it can still attract charged atoms, if they are presented to it ready charged, with a force which is proportional to the charge on the kernel, and greater for small atoms than for large ones, since we assume the kernel to behave like a charged sphere. The *numerical* condition is that, as a whole, the molecule formed must be uncharged. Consider, for example, the case of the ammonium compounds, for definiteness ammonium chloride. Nitrogen can take up only three electrons, assuming the stable form of neon : these electrons are taken from hydrogen atoms, the nuclei of which become thus attached to the nitrogen. Hydrogen combines with chlorine, the chlorine taking up a single electron to complete its stable, argon-like form. In the HCl the hydrogen is now ready charged with a single positive charge, and can be firmly bound by the strongly charged nitrogen. We have the compound NH_4Cl, in which, on account of the greater charge on the nitrogen kernel, the hydrogen last added is more strongly held to the nitrogen than to the chlorine. NH_4Cl therefore dissociates into $(NH_4)^+$ and Cl^- ions in solution. Similar considerations apply to such compounds as $AuCl_4H$.

Kossel has discussed in some detail, on this theory, a great number of the heteropolar compounds of inorganic chemistry. We will give only one example of the roughly quantitative results which can be obtained. It has been pointed out that the force of binding must increase with the charge on the

binding atom, and with decreasing size of the binding atom. Small atoms of high charge should be the best complex builders. The following table indicates a verification of the general rule just indicated with a range of compounds with hydrogen formed by the elements at the end of periods.

NH_3	OH_2	FH	Strong hold
PH_3	SH_2	ClH	
AsH_3	SeH_2	BrH	↓
SbH_3	TeH_2	IH	Weak hold

Strong hold.   →   Weak hold.

Taking the horizontal rows, the bodies on the right, with a weak hold for hydrogen, are strong acids in the presence of water : those on the left, with a strong hold for hydrogen, are basic in the presence of water. Taking the vertical columns, the bodies above, whose main atom is small, are weaker acids than those below, whose main atom is large. Thus, the O^{--} ion in the OH_2, occupying the position at the top of the middle column, has a stronger hold for an H^+ ion than any of the elements combined with H in the right-hand column, or in the remainder of the middle column. Hence on solution in water all the compounds in these parts of the table give up an H^+ ion, which forms complexes with water groups, while the negative ion remaining will form salts with metallic ions, if any such be present. The NH_3 can, however, take an H^+ ion from water, forming $(NH_4)^+$ on solution, just as it can from HCl in the example quoted above.

For heteropolar compounds and complex compounds Kossel's theory has had considerable success in indicating a way out of the main difficulties of the theory of valency bonds. It is very general : it makes no essential assumption as to the state of motion or arrangement of the external electrons. It does not deal, as do the considerations sketched in Chapter XIV., with the function of the different groups of electrons, nor give any precise explanation of the co-ordination number of the different atoms. For the carbon atom it contents itself with pointing out that four spheres drawn in by a strong central force will have a tetrahedral arrangement. There is nothing to indicate why the two short periods are succeeded by long periods, although the corresponding valency properties of the.

elements at the beginning and the end of every period are well represented.

The formation of homœopolar molecules requires a knowledge of the structure of the field, since they can only be supposed to be formed by local excesses of positive and negative electricity on two exactly similar atoms attracting each other, head to tail. A definite scheme of structural arrangement of the external electrons, which is very useful in dealing with these problems, was proposed by G. N. Lewis ; in his model the electrons are explicitly assumed to be at rest. An account of the development of this theory will be found in Lewis's book, quoted in the references at the end of the chapter. Langmuir, making use of Lewis's work, has very much elaborated the fundamental conceptions of the statical atom, with a success which is variously estimated by various men. It is true that if the eleven postulates, on which Langmuir's theory is founded, are granted, and a certain freedom of interpretation allowed, a great body of chemical observation is covered by this theory, but it must be observed that the postulates have very much an *ad hoc* character, often paying little attention to any previously established laws of electromagnetism. The theory will now be discussed.

Lewis-Langmuir Atom Model. This model was devised to account for chemical properties, a fact which must be borne in mind when considering it. The electrons are assumed to be stationary,* but no serious attempt is made to explain how the stability is attained. It is, of course, clear that the inverse square law must be abandoned to reach this end. The eleven postulates of Langmuir need not be given at length: we shall restrict ourselves here to certain main features of the model.

Not only are the electrons stationary, but certain cells are postulated in which they must be located. In planning this housing scheme account is taken of the fact that the number of elements in the successive periods of the periodic table is 2, 8, 8, 18, 18 and 32, which can be expressed by what

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* Langmuir allows that they may circulate around fixed positions in comparatively limited orbits, not enclosing the nucleus ; but this does not help the model appreciably, except, perhaps, that it makes the magnetic properties a little more comprehensible.

Sommerfeld calls the "somewhat cabalistic formula" $2 \times m^2$, where m is a whole number; thus

$$2 = 2 \times 1^2; \quad 8 = 2 \times 2^2; \quad 18 = 2 \times 3^2; \quad 32 = 2 \times 4^2.$$

To correspond to this it is assumed that the electrons in the atoms of the inert gases, which represent the completion of their respective periods, are arranged in concentric spherical shells of equal thickness, the mean radii of the successive shells being as $1 : 2 : 3 : 4$. The surfaces of spheres of these radii are as $1 : 2^2 : 3^2 : 4^2$, or are as the numbers of electrons in (i) the first group (hydrogen and helium), (ii) the short groups of 8, (iii) the long groups of 18, and (iv) the final group of 32. If each shell be divided into cells of equal floor space, and each cell, except the two of the first period, be divided into two storys, so that the shells consist of two layers each, we have, as each layer is completed by putting an electron in every cell, the atoms of the inert gases. The layers may be indicated by the numbers I; IIa, IIb; IIIa, IIIb; and IVa. This gives our cabalistic formula a geometrical expression, but does little more.

Now, to account for the properties of the elements of the long groups further assumptions are made as to the action of electrons on one another. These interactions vary essentially according to the positions of the electrons. It is assumed, for instance, that, while electrons in the same cell (one in each story) are almost without effect on one another, the electrons in the outside layer tend to repel one another (which is, exceptionally enough, in accord with ordinary theory), but at the same time tend to line up radially with those in the underlying cells. Langmuir makes great use of these assumptions in discussing the chemical properties of elements such as iron, cobalt and nickel, which occur in the middle of long groups. It is scarcely necessary to insist on the artificiality of this picture, and we shall not here lay very much stress on it. The electrons in the Langmuir atom have, in fact, so few of the known properties of electrons that it is not immediately clear why they are called electrons at all.

To take first of all the structure of the atoms of the rare gases in a little more detail, in helium the two electrons are assumed to be arranged symmetrically on either side of the

nucleus. This pair is present in all heavier atoms, and determines an axis which may be called the polar axis. In neon the 8 additional electrons, which form a very stable system, are arranged at the corners of a cube, two parallel faces of which are normal to the polar axis; the arrangement is symmetrical about this axis, and about the meridian plane. The electrons occupy the 8 cells of layer IIa. In argon this system persists, but 8 additional electrons are arranged at corners of a second cube, situated similarly to the first cube : they occupy the cells of layer IIb. These octets are a very essential feature of the Lewis-Langmuir atom, and their importance will be considered later. Of the additional 18 electrons of krypton, two are situated on the polar axis, while the other sixteen are distributed symmetrically in layer IIIa. The 18 further electrons of xenon are arranged in a like manner in layer IIIb. The structure postulated for radon need not be considered here.

It is to be noted that a feature of Langmuir's theory is that no layer can contain an electron or electrons before the layer underneath it is completed ; or, in other words, once a layer contains sufficient electrons for an external layer to be begun, the layer first named persists in the same form as a feature of the structure of all subsequent atoms. This is in direct contradiction of Bohr's and Bury's views, and is almost certainly wrong.

Langmuir attributes the anomalous behaviour of the elements in the middle of the long periods to the conflict between (i) the postulated tendency of the electrons to place themselves over those in the under shell, and (ii) the tendency of the electrostatic repulsion between the electrons in the outer shell to force them from this position, a tendency which is pronounced when the number of electrons in the shell becomes large. The reasoning is of a very general nature, and it is not proposed to attempt to expound it here, especially as Bury has offered what seems to be a better solution of the problem.

Bury supposes that the electrons are arranged in spherical shells of radii 1, 2, 3, 4, ···, but drops the invention of cells, with its accompanying hypothesis of two electrons in one cell for all outer shells. Instead he assumes that the

maximum number of electrons which can occur in each shell is proportional to the area, *i.e.* the successive shells can contain as a maximum number 2, 8, 18, 32, and (if there were enough elements) 50 electrons. Groups of 8 or 18 electrons in a shell are assumed to be of particular stability, even when the shell can contain more electrons. There is an additional hypothesis, which is the essence of Bury's scheme, and forms a link between his ideas and those of Bohr. It is postulated that the maximum number of electrons in the outermost shell is always 8; more than 8 electrons can coexist in a shell only if the shell exterior to it already contains electrons. Thus, considering the successive building up of atoms of increasing atomic number, when sufficient electrons have been added to complete an outer shell (which we will call shell R^*) of 8, the electrons next added go to form a shell S exterior to shell R, but, after a certain number have been put in S, further electrons can be placed in R. Corresponding to the change in shell R from a stable group of 8 to the other stable group of 18, we have formed transition elements, which can have more than one structure. On this theory the groupings for the inert gases are as follows: He 2; Ne 2, 8; A 2, 8, 8; Kr 2, 8, 18, 8; Xe 2, 8, 18, 18, 8; Rn 2, 8, 18, 32, 18, 8, which is the same as that adopted by Bohr, if we substitute for the number of electrons in a shell, in Bury's terminology, the number having a given principal quantum number in Bohr's theory. The chemical properties of the elements in the long periods find a more direct explanation on this comparatively simple scheme than on the Langmuir postulates.

The exact point at which the transition in the long periods takes place must be determined by consideration of the chemical properties. It appears that after 4 electrons have accumulated in the outermost shell, the next electron added goes to the shell immediately interior : with 3 electrons already in the outermost shell the tendency of the next electron added to go to this interior shell is less, but it can do so alternatively to adding itself to the other 3 in the outermost shell; while when there are only 2 in the

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* This naming of shells as R and S shells is merely for convenience of discussion. It has no connection with the notation of X-ray spectra.

outermost shell the next electron added nearly always adds itself to the 2, having only a very small tendency to go to the inner shell. Consider, for example, the first long period (potassium to krypton). In accordance with what has been said, arrangements of electrons in successive shells of 2, 8, 10, 2 ; 2, 8, 11, 2 ; and 2, 8, 12, 2 will be very unstable. These numbers of electrons correspond to neutral titanium, vanadium and chromium, with 2 electrons in the outermost shell, and the inner group of 8 on its way to the stable 18. The divalent salts of these metals are very unstable, while salts in which higher valencies are exhibited are more stable. Other possible arrangements for titanium are 2, 8, 9, 3, and 2, 8, 8, 4, giving tri- and quadrivalent salts respectively.

When the group of 8 has been once destroyed by addition of an electron the resistance to further additions in the R shell is diminished, and electrons pass into it comparatively easily until the group of 18 is formed. The arrangement 2, 8, 18, 1 represents copper, which forms monovalent salts. For cobalt ($Z=27$), nickel ($Z=28$) and copper ($Z=29$) the stable group of 8 in the R layer is definitely impossible, for it would involve a group of more than 8 in the outermost layer—for example, an arrangement, for cobalt, of 2, 8, 8, 9. For all the elements between titanium and copper it is supposed that, for the same element, different distributions in the R and S layers, of different degrees of stability, are possible. Thus, in the case of manganese, the arrangements 2, 8, 8, 7 ; 2, 8, 9, 6 ; and 2, 8, 11, 4 are all supposed to exist, the outer shell of 7 occurring when the metal is combined to form permanganates, the outer shell of 6 for manganates, and the outer shell of 4 for the dioxide. In short, chemical properties would appear to call for more than one possible structure of this element, and its neighbours, and this diversity of structure is provided by the theory.

There is not space here to discuss the chemical properties of the elements in the other long groups. Suffice it to say that Bury's scheme seems to represent chemical fact very well without imposing too many arbitrary conditions, although, of course, arbitrary conditions are there, and are bound to be present in any scheme until our knowledge has advanced much beyond its present state. The theory, in its most general

aspect—as far, that is, as it calls for the completion of inner groups after outer groups have been started—falls into line with Bohr's scheme, described in Chapter XIV., which was largely based on the consideration of optical and X-ray spectra. The modifications introduced by Stoner and Main Smith naturally apply with the same force to Bury's scheme as they do to Bohr's scheme.

The Octet Theory of Valency. The great service of the Lewis theory, which essentially founded the static atom, and the extensions made by Langmuir, is the elaboration of the octet theory of valency, with its new conception of the sharing of electrons between atoms in combination. The octet theory was applied by Langmuir to the two short periods, for both of which the number of electrons in the outermost shell is 8. If more than 8 electrons be allowed in the outermost shell, as assumed by Langmuir himself for the long periods, then the theory can only be applied with considerable additional complication. If, on the other hand, Bury's assumption of a maximum number of 8 for the outermost shell of all elements be accepted, then the octet theory can be applied to all atoms, once the division of electrons between what we have called the R and S shells has been fixed.

We consider, then, the elements of the two short periods. The greatest number of electrons which any element can have in the outermost shell is 8 ; elements which have less than 8 tend to give up, or to take up, electrons until the shell of 8 is completed. This is merely a re-expression of Kossel's interpretation of Abegg's rule. The essential novelty of Lewis's presentation is that he assumes that it is possible for atoms to hold pairs of electrons—but not single electrons—in common, which pairs are generally called duplets.* These pairs of electrons form part of the outer octets of both the atoms considered to hold them. A single octet may share one or may share two duplets with another single octet, or it may share

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* The credit for the conception of electron-sharing between cubic atomic structure, which seems to constitute one of the biggest advances yet made in the study of valency, is due exclusively to G. N. Lewis, as far as I can ascertain from a necessarily hurried study of the literature. Single shared electrons play a large part in the earlier, and very interesting, molecular models of Stark. (*Prinzipien der Atomdynamik*. 1910. Hirzel.)

each of its duplets with a different octet, for instance, but it cannot share a duplet with more than one other atom.

The simplest representation of this is given by supposing that the electrons of the outer shell are arranged at the corners of a cube. Electron-sharing can then take place between two cubes which have either (a) an edge in common, or (b) one complete side in common. The two types of sharing are shown in Fig. 103. This sharing of electrons enables atoms, which have between them in their outermost shells insufficient electrons to make a whole number of separate octets, to complete their shells on combination.

Langmuir distinguishes, then, three types of valency :

> (1) positive valency, which is determined by the number of electrons which an atom gives up ;
> (2) negative valency, which is determined by the number of electrons which an atom takes up ;
> (3) covalency, which is determined by the number of duplets which an atom shares with its neighbours.

(1) and (2) together are spoken of as electro-valency. The type (3) is often spoken of as a two-electron bond.

The number of covalencies is given by the simple expression

$$\Sigma e = \Sigma s - 2B,$$

where e is the number of electrons in the outer shell of a neutral atom, s is the number of electrons in the outer shell of the atom after combination has taken place, and B is the number of duplets shared, the summation being taken over all the atoms combined.

We have now, if the assumptions of the octet theory be accepted, the further information as to the distribution of electricity which is required to account for the formation of homœopolar compounds. Thus the oxygen atom has 6 electrons in its outer shell, and two oxygen atoms, by sharing two duplets, can complete their outer shells, as indicated in Fig. 103 (b). The fluorine atom has 7 electrons in its outer shell, and two fluorine atoms can complete their octets by sharing one duplet, as indicated in Fig. 103 (a), which also represents the combination of two chlorine atoms. The nitrogen molecule offers greater difficulties, the atom having 5 electrons in the outer shell, so that two atoms have between them 10 outer

electrons, which is 2 too many. Langmuir considers that 8 go to form a single cube, within which lie both nuclei, each with its closely bound inner pair of electrons, as in helium. The remaining 2 of the outer electrons are also considered to have passed within the cube: the arrangement is indicated in
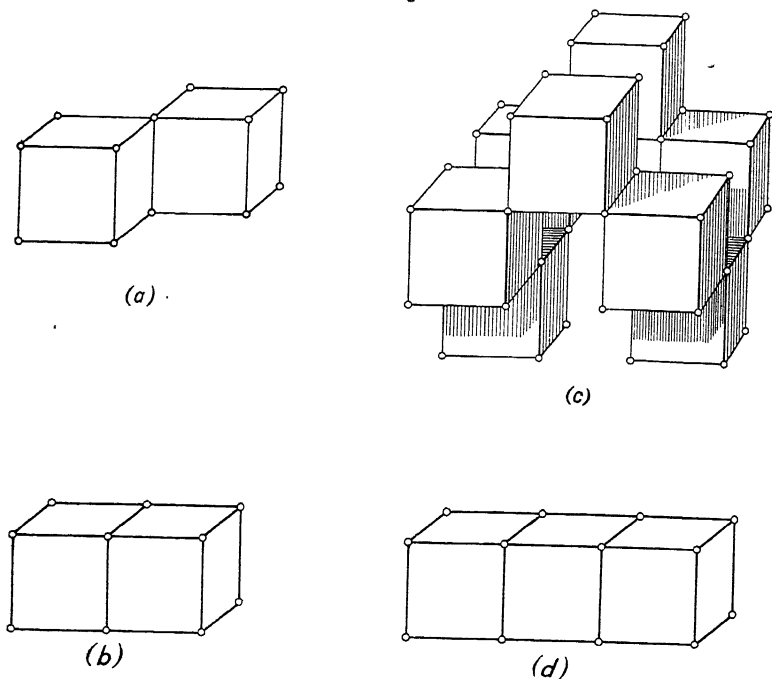
Fig. 103.
Models of molecules on the cube theory.
(a) Fluorine molecule.   (c) Sulphur molecule.
(b) Oxygen molecule.   (d) Carbon dioxide molecule.

Fig. 104. This structure is said to account for the stability of the nitrogen molecule, which does not dissociate into its atoms, even at a temperature of 3300° C., and also for the low boiling point of the liquid form and the chemical inertness of the gas. The sulphur molecule, S_8, is represented in Fig. 103 (c) as an example of molecule building on the octet theory.

For carbon compounds the results of this theory are much the same as those of the older valency theory of organic

chemistry, for each pair of electrons held in common corresponds to a bond. The peculiar case of carbon monoxide, however, receives special interpretation on the octet theory. A carbon and an oxygen atom have between them the same number of external electrons as two nitrogen atoms, namely, 10, and the physical properties of CO and N_2 are very similar. The chemical inertness claimed for CO, which on the older theory is hard to explain, since the carbon should be unsaturated, is accounted for by giving to the CO molecule a structure similar to that of the N_2 molecule, taking both nuclei, and 2 electrons from the external 10, inside the octet. The oxides of nitrogen are well described in the octet theory. Thus the molecule of N_2O is similar in structure to CO_2, the total number of external electrons being 16 in each case, which can be made to give 3 complete octets if the three cubes are placed in a line, face to face, as shown in Fig. 103 (d). These two
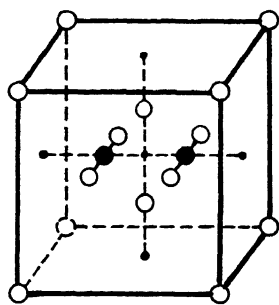
Fig. 104.
Langmuir's model of the nitrogen molecule.

compounds are very similar in physical properties: their critical constants differ but little, and the viscosities and magnetic susceptibilities of the gaseous form, the refractive indices and dielectric constants of the liquid form, and certain other constants, are very nearly the same for N_2O and CO_2.

The other oxides of nitrogen can be built up out of cubes, some sharing two duplets, and others one, with adjoining cubes. In general, the conception of the sharing of pairs of electrons has simplified certain chemical problems.

The cubical atom model is by no means of universal application. It does not allow two atoms to share more than two duplets, while the chemical facts which, to use the language of everyday chemistry, call for a " triple bond " would seem to call for the sharing of three duplets between two atoms. This is allowed by G. N. Lewis, who is prepared in certain circumstances to allow the two electrons of a duplet to be drawn close together by certain unspecified forces—of the type so freely invoked in this branch of the subject—so as to deform the cube

into a structure of general tetragonal form. This permits the sharing of three duplets, since we then have triangular faces with a duplet at each corner. But further difficulties, to which T. M. Lowry has drawn attention, are offered by the fact that in the hydrides of boron *four* duplets must be shared, while further, in $Mo(CO)_6$ and $K_3CoC_6N_6$ *six* duplets are shared by the metal and the attached radicals. To meet such points modifications of the cubical atom will have to be made, but the nature of these modifications is a matter of dispute. It may be added that the postulate of covalency has been freely and frequently criticised by Main Smith.

An interesting case is presented by the hydrogen atom in combination with other atoms. Whereas in the general case there is a clear distinction between electrovalence and covalence —exemplified, in the case of chlorine, for instance, by NaCl and ClCl respectively—in the case of hydrogen compounds, such as HCl, say, it is not easy to decide if the hydrogen has given up its electron to complete the chlorine octet, the rest of the hydrogen atom, the proton, remaining definitely separated from the chlorine, but bound by the electric force between the negatively charged chlorine and the positively charged proton ; or whether the electron is shared between chlorine and hydrogen atom, an arrangement which would presumably involve a closer combination of the hydrogen with the chlorine than the ionic mechanism. Lowry has published some important speculations on this point, in which, making use of a suggestion of W. H. Bragg's, he supposes that in the case of ionisation the proton, or hydrogen ion, can attach itself to any one of the twelve edges of the cube, whereas in the case of the hydrogen radical—the covalence case—the proton is specifically attached to one duplet of the octet. The hydrogen ion has, therefore, a certain mobility, as it is equally at home in any one of a large number of positions, whereas the radical is definitely bound to a particular part of the atom. This point of view has interesting applications both to crystal structure and to the problems of organic chemistry.

Physical Applications of the Static Atom. Langmuir has endeavoured to show that many of the physico-chemical properties of compounds can be explained in terms of his

atom, and in the case of boiling points, critical constants and solubilities of certain groups of gases has indicated that similar values of the constants are associated with what on his theory is similar structure.   He has satisfied himself that the magnetic properties of the elements are also explained on his theory, but the handling of this question, and that of the formation of coloured salts, is not sufficiently precise to carry conviction. Most unconvincing of all is Langmuir's attempt to show that his atom will give all the spectral results of the Bohr atom. He assumes that the expression derived for the kinetic energy of the electron in Bohr's theory really represents a form of potential energy " dependent upon certain quantum changes in the electron."   Naturally, if it be assumed that the electron is subject to a Coulombian force $F_c = \dfrac{Ze^2}{r^2}$, and in addition to a hypermysterious " repulsive quantum force,"

$$F_q = \frac{1}{mr^3}\left(\frac{nh}{2\pi}\right)^2$$

(which is, be it noted, independent of the charge on the nucleus), then Bohr's simplest results follow from the equilibrium condition, if the equation $h\nu = E_1 - E_2$ be assumed.   But this is not all.   If F_q is assumed to be $= \left(\dfrac{nh}{2\pi}\right)^2 \dfrac{\frac{1}{m} + \frac{1}{M}}{r^3}$, then the effect of the mass of the nucleus can also be calculated.   And, further, if we write down the formula deduced for the relativity correction, but say that they are due to unknown static forces, *mirabile dictu* all the results of Sommerfeld and his school follow for a static atom.   This outline of Langmuir's explanation is given because there is * an impression in some quarters that the Langmuir atom can do as much to explain spectral observation as the Bohr atom.

More serious application of the static atom to physical problems has, however, been made.   Born, alone and in conjunction with Landé, has carried out a series of important investigations on the physical and physico-chemical properties of crystals, in the course of which he invokes the conception

* Or rather was, when the first edition of this book appeared.

of the cubic atom.   A static atom has to be used, to render the calculations possible.   Since the forces considered are those outside, although not very far outside, the atom, *i.e.* are of the nature of the forces evident in chemical combination, it is understandable that this yields valid results.   The method adopted is essentially unable to yield any information as to details of atomic structure, which are the main object of study in this book, and therefore only a thin outline of the work will be given, in spite of its inherent interest.

Crystals are particularly suitable for the study of the forces between atoms, since in them the conditions are perfectly definite, as opposed to the conditions in solutions, where the ions may interact with the water molecules in a complicated way.   We consider for simplicity a crystal of a simple salt, such as NaCl, where the structure is cubic, and every atom of the one kind is at the centre of an octahedron of atoms of the other kind.   Many reasons have already been adduced for believing that the atoms actually exist in the crystal in the form of ions, the metal atom having given up an electron to the halogen atom.   If we know the law of force existing between the atoms, it then becomes a task for the mathematician to calculate the compressibility of the salt, which is a matter of the difficulty of pushing the ions closer together, or the heat of formation of the crystal from the ions in gaseous form, which is the energy required to take all the ions to infinity against the forces which they exert on one another. Actually we assume a general law of force, and discuss what precise form it must take for the calculated properties to agree with experimental measurements, and then what deductions can be made from this form as to general atomic structure.

In order to work out a theory of electrostatic cohesion the assumption which we make as to the law of interatomic force must clearly lead to a stable equilibrium position for an atom in a crystal.   Two oppositely charged ions, each carrying unit charge e, will at large distances, when the ions can be treated as charged points, attract one another according to Coulomb's law, with a force $\dfrac{e^2}{r^2}$, but when they come close to one another a repulsive force must come into play, or else the ions would

approach indefinitely.* Physically the existence of this repulsion can easily be explained as due to the close proximity of the peripheries of the ions, which consist in both cases entirely of negative charges. Born assumes that the potential of the repulsive force can be represented by an inverse power law β/r^n, so that the total potential, including the Newtonian part corresponding to the inverse square law, is

$$\varphi = -e^2/r + \beta/r^n. \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots(\text{I})$$

The potential of a single chosen ion in a crystal is, of course, the resultant of a very large number of expressions of form (I), due to all the other ions, the sign of the first term being reversed when we are considering ions of the same sign as the chosen ion. The resultant potential must be of the form

$$\Phi = \Sigma\left(-\frac{e^2}{r} + \frac{\beta}{r^n}\right) = -\frac{A}{d} + \frac{B}{d^n},$$

where d is the shortest distance from one ion to the next ion of the same kind, *i.e.* the grating constant. There are mathematical difficulties in carrying out the summation, due to slow convergence, which were successfully overcome by Madelung, who has shown how to calculate the electrical field in a system of regularly arranged point charges exerting Coulombian forces, whether all the charges are of one kind, or alternately positive and negative, as in the case under consideration. The constant A, sometimes known as Madelung's constant, can therefore be found in terms of the charge on the ions ; for the simple type of lattice which we have chosen for discussion it has the value $13 \cdot 94e^2$. B depends upon the unknown constant β. However, if the crystal be subject to no external forces, the force on an ion in equilibrium must be zero, and therefore

$$\frac{\partial \Phi}{\partial r} = \frac{A}{r^2} - \frac{nB}{r^{n+1}} = 0 \text{ when } r = d$$

or
$$B = \frac{A}{n} d^{n-1}, \quad\dots\dots\dots\dots\dots\dots\dots\dots(\text{I}a)$$

---

* It is interesting to note that Boscovich, in the eighteenth century, developed this argument, and actually gave curves representing the supposed variation of interatomic force with the distance, showing reversals. See Boscovich, *Theoria Philosophiae Naturalis*, Venetiis, MDCCLXIII, of which an English translation has been published by the Open Court Publishing Company.

where d is known, but n is unknown. We have, however, an experimental criterion to determine the value of n. The compressibility depends upon the force of repulsion which the ions exert on one another when the distance between them is diminished, and so involves the form of the potential as given in (1), and hence n. Born and Landé have succeeded in calculating the compressibility $\varkappa$ in terms of n, and have deduced the formula

$$\varkappa = \frac{9d^4}{A(n-1)} = \frac{9d^4}{13\cdot94e^2(n-1)}$$

in the case under consideration. If d_0 be the distance between the (100) planes, so that $d_0 = \frac{1}{2}d$, this becomes

$$\varkappa = \frac{9d_0^4}{\cdot873e^2(n-1)} \; .$$

Also $\rho N d_0^3 = \dfrac{A_1 + A_2}{2} = \dfrac{M}{2}$, where N is Avogadro's constant and A_1, A_2 are the atomic weights of the different elements involved, or M is the molecular weight of the compound, so that, substituting for d_0, we have

$$\varkappa = \frac{9}{\cdot873e^2(2N)^{\frac{4}{3}}} \left(\frac{M}{\rho}\right)^{\frac{4}{3}} \frac{1}{n-1}$$

$$= 3\cdot5 \times 10^{-13} \left(\frac{M}{\rho}\right)^{\frac{4}{3}} \frac{1}{n-1} \; . \quad \dots\dots\dots\dots\dots\dots(2)$$

If we can find n theoretically as a result of assumptions about the general form of the atom we can obtain a value for $\varkappa$, to be compared with the experimental value, or, of course, what is the same thing, we can find a value for n by putting the experimental value for $\varkappa$ in (2), and discuss what general form of atom will lead to this value for n.

Born and Landé took up first Bohr's old ring model, to see if it would yield satisfactory results in the case of halogen salts of the alkali metals. On this model the ions consist of a nucleus, with which the two innermost electrons may be associated, and concentric rings of eight electrons. The basis of the lattice was assumed to consist of eight ring atoms (ions) with their axes parallel to the cube diagonal. The potential due to such

a distribution of electricity was developed in inverse powers of r, and the final result was that the index of the second term in (1) was 5, *i.e.* the second term in the energy is in d^{-5}. At the same time the equilibrium distance was calculated, and found to agree well with the known value of d, with certain subsidiary assumptions. However, when the value $n = 5$ was put into the expression for the compressibility (2) the resulting value of $\varkappa$ was nearly double that found from experiment. This attempt is mentioned to show that it is not the case that any model will do.

Born then calculated the energy on the assumption that the ions had a cubic electronic structure instead of a ring structure, in accordance with Kossel's views. He took, for example, for the alkali metal ion and the halogen ion, eight electrons at the corners of a cube, having at its centre a positive kernel with nine unit charges in the former case, and seven in the latter case. The formula obtained when all the cubes are arranged with their edges parallel is

$$\varphi = -\frac{e^2}{r} + \frac{e^2(a^4 - a'^4)}{r^5}f_5 + \frac{e^2a^4a'^4}{r^9}f_9 + \dots, \quad \dots\dots\dots(3)$$

where a and a' are the radii of the spheres described about the cubic ions of the two different kinds respectively, and r is the distance apart of their centres, while the f's are functions of the inclination of the line of centres. If a is approximately equal to a', we have

$$\varphi = -\frac{e^2}{r} + \frac{e^2a^8}{r^9}f_9$$

or the index n in (1) is 9. If $n = 9$ be put into equation (2), values are obtained for $\varkappa$ which agree very well with those experimentally found. Or, putting it from the other point of view, if the experimental values of $\varkappa$ be put into equation (2) the following values of n are obtained for the salts given.

Salt	NaCl	NaBr	NaI	KCl	KBr	KI
n	7·84	8·61	8·45	8·86	9·78	9·31

These approximate to 9 as closely as we have any right to expect.

Various extensions have been made of the theory, but what has been said will suffice to show the way in which it has confirmed the hypothesis that the atoms in crystalline salts, at any rate of the simple type considered, exist in the ionised state, and have a cubic structure.

J. J. Thomson has applied the static model to the question of the compressibility of elementary substances, where the binding must be homœopolar. He makes no assumption as to the mechanism of combination in such cases, but divides the body into equal cells which fill all space, for which one of the following four types must be employed : (1) cubes, (2) hexagonal prisms, (3) rhombic dodecahedra, (4) cubo octahedra. If a positive charge be put at the centre of each cell, and an electron at each corner, a brief consideration shows that we shall have : in case (1) one electron to each atom, in case (2) two electrons, in case (3) three electrons, and in case (4) six electrons to each atom. The electrons in question must be considered to belong to the outside layer only, the other electrons, constituting the kernel, being taken with the nucleus. Certain other regular arrangements provide for four, five and seven electrons per atom, so that this scheme gives a rough method of representing elements of valencies from one to seven. J. J. Thomson does not use Madelung's result, so that the series which he uses are very slowly convergent, and lead to rough values, and he assumes for the potential energy the very simple form

$$\varphi = -\frac{e^2}{r}\left(1 - \frac{c}{r}\right),$$

i.e. he takes $n=2$ in equation (1). The formula which he deduces for the compressibility is

$$\varkappa = \frac{9}{3 \cdot 65 e^2 N^{\frac{4}{3}}}\left(\frac{A}{\rho}\right)^{\frac{4}{3}},$$

where A is the atomic weight, for the monovalent class, for which the cells are such that there is one electron per atom. Similar formulae, differing only in the numerical coefficient, are obtained for bivalent and tervalent elements. In spite of

the rough nature of the assumptions fair agreement with experimental results is obtained in many cases. A more elaborate theory has been put forward by Landé.

Another instructive quantitative application of the lattice theory to physico-chemical problems has been initiated by Born. We know, using (1a), that

$$-\Phi = \frac{A}{d} - \frac{B}{d^n} = \frac{A}{d}\left(1 - \frac{1}{n}\right),$$

where Φ is the energy per volume d^3, if the value $13\cdot94e^2$ be taken for A. Each volume d^3 contains eight ions in the case of substances such as rocksalt, once more considered for simplicity, or four molecules, so that the energy per gram

molecule $= U = \dfrac{N}{4}\Phi = \dfrac{NA}{4d}\left(1 - \dfrac{1}{n}\right).$

Using the fact that $N\rho d^3 = 4M$, where M is the molecular weight, we have

$$U = \left(\frac{N}{4}\right)^{\frac{1}{3}} A\left(1 - \frac{1}{n}\right)\left(\frac{\rho}{M}\right)^{\frac{1}{3}} \text{ ergs}$$

$$= \left(\frac{N}{4}\right)^{\frac{1}{3}} \frac{13\cdot94e^2}{4\cdot2 \times 10^{10}} \frac{8}{9}\left(\frac{\rho}{M}\right)^{\frac{1}{3}} \text{ kilogram calories,}$$

putting $n = 9$, and $A = 13\cdot94e^2$, or

$$U = 545\left(\frac{\rho}{M}\right)^{\frac{1}{3}} \text{ kilogram calories per gram molecule}$$

for the rocksalt type of crystal. Similar formulae with a different value for the constant term have been worked out for other types of crystals. This gives the energy of the crystal, *i.e.* the work required to take the ions to infinity, or, in other words, the heat of formation of the crystal from ionic gas. While this cannot be measured directly, Born has shown how it can be deduced from known measurements by means of a cyclic process, sometimes called a Born cycle. The cycle is expressed in the following scheme, where the solid state is indicated by enclosing the symbol in a bracket, while

for the gaseous state the symbol is not enclosed. M denotes a metal atom, X a halogen atom.

$$[M], \tfrac{1}{2}X_2 \xrightarrow{\quad Q_{MX} \quad} [MX]$$

$$S_M \Big\uparrow D_X \qquad\qquad\qquad\qquad \Big\downarrow -U_{MX}$$

$$M, X \xleftarrow[\quad -E_X \quad]{\quad I_M \quad} M^+, X^-$$
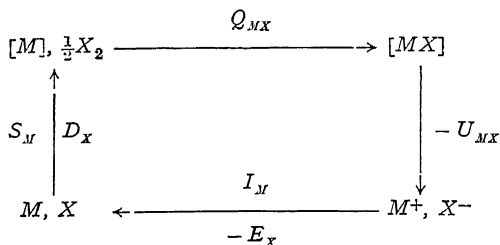
The meaning of the symbols is as follows :

Q_{MX} is the heat of formation of the solid salt from solid metal and gaseous (molecular) halogen, and can be determined calorimetrically.

S_M is the heat of sublimation of the metal, and can be determined calorimetrically, or by measuring the pressure of sublimation as a function of the temperature, and using Clapeyron's equation.

I_M is the energy required to ionise the metal, or ionisation potential discussed in Chapter XII.

D_X is the heat of dissociation of the halogen, obtained by measuring the dissociation constant as a function of the temperature, and using van 't Hoff's equation.

E_X is the energy required to remove the extra electron from the halogen ion X^-, and can be found by investigation of a particular region in the absorption spectrum, which need not be discussed in detail here.

U_{MX} is the heat of formation of the crystal from ions in the gaseous state, which is required.

We have from the cycle :

$$Q_{MX} - U_{MX} + (I_M + S_M) + (D_X - E_X) = 0,$$

so that, all the quantities discussed being known separately, U_{MX} can be found.   Excellent agreement between the values of U_{MX} so derived and those calculated from the energy of the lattice has been found for a series of halogen salts of the alkali metals.

This method of Born's is likely to come into extensive use. Grimm and Sommerfeld have, for instance, applied a Born

cycle to show why, on energetic grounds, the diatomic molecule of chlorine must be a homœopolar gas, and not a hypothetical solid salt Cl^+Cl^-, by showing that if the salt could exist its transformation to the gas would be accompanied by an emission of 100 kilogram calories, and so would take place at once.

We return to our discussion of physical applications of the cubic static model, from which we have somewhat strayed. A. O. Rankine has applied the structure arrived at by the hypothesis of electron sharing to the theoretical consideration of the viscosity of polyatomic gases. It is well known that the viscosity of a gas depends on the cross-section of the molecule presented as a target to other molecules, as exemplified in the familiar Maxwellian formula $\eta = \dfrac{\cdot 44\rho u}{\sqrt{2} \cdot n 4\pi\sigma^2}$, where η is the coefficient of viscosity, ρ the density of the gas, u the mean velocity of the molecule, n the number of molecules per unit volume, and σ the radius of the molecule. Recently Chapman has worked out an improved formula which takes account of the mutual attraction existing between the molecules : according to this formula

$$4\pi\sigma^2 = \frac{\cdot 491\rho u}{\sqrt{2} \cdot \eta n \left(1 + \dfrac{S}{T}\right)}$$

where S is Sutherland's constant and T the absolute temperature. The molecules are hard attracting spheres, for which $\pi\sigma^2$ represents the cross-sectional area. This applies well for the monatomic gases, but obviously a CO_2 molecule, for instance, cannot be considered to be spherical in shape. If the molecule is not spherical, then $\pi\sigma^2$ must be taken as the *average area* presented by the molecule as a target to other molecules for all angles of approach. By making assumptions as to the shape of the molecule this average can be calculated.

Rankine has considered, with Langmuir, that the molecules Cl_2, Br_2, I_2, for instance, are made up of chlorine, bromine and iodine atoms sharing two electrons, and so taking on the external form of double atoms of argon, krypton and xenon respectively. By comparison of the dimensions of the monatomic gases—

spherical molecules—as obtained from the viscosity measurements with those obtained from the crystal measurements of W. L. Bragg,* it is found that the gas-kinetic diameter is bigger than the crystal diameter, which latter represents the distance between the centres of combined atoms. Round the centre of each atom Rankine draws a sphere representing the gas kinetic size of the inert gas in question, and places the two atoms at the distance apart indicated for combined atoms: the two spheres overlap as shown in Fig. 105, which represents the molecule of a halogen gas. The average cross-section
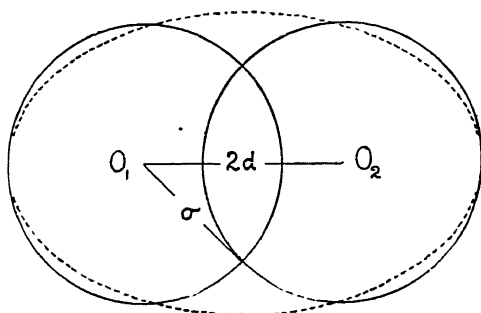
Fig. 105.

Representation of a molecule of a halogen gas for the purpose of gas-kinetic calculations.

presented by such a molecule in different directions can be calculated without much difficulty. Rankine considers that it is better to take the atom as an ellipsoid of the form indicated by the dotted line, as it is probable that the field of force which determines the effective gas kinetic dimensions is rounded off when the atoms combine. With this model he calculates, by making use of the known dimensions of the atoms of the inert gases, good values for the viscosity of the gases O_2, Cl_2, Br_2, I_2. He has extended his work to the triatomic molecules of CO_2 and N_2O, represented in Fig. 106 (compare Fig. 103 (d)), which have the same structure on Langmuir's theory, as has been

* Of course, the dimensions of the atoms of the inert gases cannot be obtained directly from crystal measurements, since they do not combine and form crystals, but they can be deduced from the dimensions of the neighbouring atoms in the periodic arrangement, it having been shown by W. L. Bragg that the atomic diameters of the elements of each period approach a limit as the heavy end of the period is approached. Cf. Fig. 79.

pointed out already. Satisfactory results have been obtained with them, and with still more complex molecules. It may be noted that the special structure claimed for the nitrogen molecule, and illustrated in Fig. 104 is, in a sense, confirmed by the viscosity considerations, for if it be represented as two
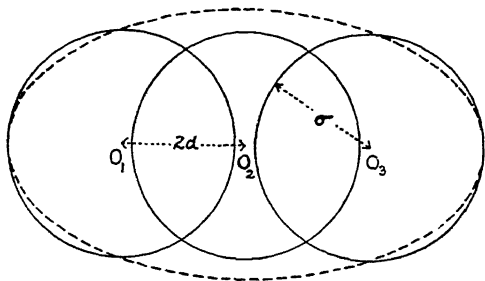
FIG. 106.

Representation of CO_2 or N_2O molecule for the purpose of gas-kinetic calculations.

linked neons, by extension of the successful work on the oxygen and chlorine molecule, results are obtained which do not agree with experiment. The nitrogen molecule does not resemble the oxygen molecule in its formation.

Considerations of the electrical conductivities of metals have also been based upon the static atom model. The ordinary electron theory of conductivity assumes that the current is carried by a swarm of free electrons which exist in the metal in the interstices between the atoms, these electrons being supposed to behave exactly like a gas, *i.e.* to be subject to the laws of the kinetic theory of gases, and, in general, to have the same energy per electron as a gas molecule at the same temperature. This theory has had certain successes in representing isolated features of electrical and thermal conductivity, but meets with the great difficulty that, if the equipartition of energy be admitted, the electrons must be responsible for the greater part of the heat energy of the metal, since the theory indicates about three times as many free electrons as atoms. This can scarcely be reconciled with the general validity of Dulong and Petit's law for metals as well as metalloids, nor with the fact that at very low temperatures the conductivity

is extraordinarily high and the specific heat very low. If the law of equipartition of energy be abandoned fresh difficulties arise, as has been emphasised by F. A. Lindemann.

Both Lindemann and J. J. Thomson have proposed to get round the difficulty by making the " free " electrons, which carry the current, form a space lattice, and move in rigid lines along the lines of the lattice under the influence of an electric force. J. J. Thomson's theory can best be exemplified by considering the case of a simple cubical space lattice : the atoms occupy the central space of the cubes, and the conduction or valency electrons are at each corner. It is then assumed that a chain of electrons lying along a straight line in the lattice, such as A, A', A'', A''' (Fig. 107), moves as a whole, carrying

FIG. 107.

Simple lattice illustrating chain theory of electrical conduction.

electricity from one part of the metal crystal to another part. An electron in this chain is not independent of its neighbours in the chain, but acts as if rigidly connected to them, so that the whole chain has only one degree of freedom, instead of three degrees of freedom *per electron*, as in the old theory. The variation of electrical resistance with temperature, including the super-conductivity at low temperature, has been accounted for on the basis of this new conception, which seems to offer in any case a way out of the difficulties and contradictions in which the kinetic theory of electrons has become involved.

In this connection reference must be made to an interesting paper by Höjendahl, who has applied the general conception of penetrating orbits, with large rotation of perihelion, to the problem of metallic conductivity. He supposes that in a solid such a penetrating orbit, having made an " inner loop " round the nucleus (see Chapter XIV.) and emerged, is liable to be drawn into the sphere of influence of a neighbouring atom, and to execute an inner loop round its nucleus, and so on for successive atoms, the outer loop never being completed, but existing (as far as it can be said to exist) merely as a connecting path between two inner loops about different nuclei, instead of, as in a gaseous atom, as a connection between two inner

loops about the same nucleus. At very low temperature, when the heat motion of the atoms is negligible, the electron will then describe a zigzag path, swinging from atom to atom, its path embracing each nucleus as shown in Fig. 108. This gives us the free passage of an electron right through the crystal as demanded by the superconductivity at low temperatures, and is equivalent to the chain of electrons supposed by Thomson and by Lindemann. At higher temperatures, however, when the atoms cannot be regarded as stationary, the path is liable to be broken by the heat vibration of an atom. The path can also be broken by irregularities in the crystal, or by the presence of an atom of another kind, as in alloys. The unbroken length of the regular path of the type illustrated is equivalent to the mean free path of the electron on the old Drude theory of electronic conduction. Höjendahl has obtained satisfactory quantitative results, and the method seems very promising.
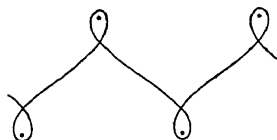
FIG. 108.
To illustrate Höjendahl's hypothesis.

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CHAPTER XVIII

WAVE THEORY AND QUANTUM THEORY

Introductory. The difficulties of reconciling the wave theory with the quantum theory are well known, and have been discussed at length by physicists of the calibre of H. A. Lorentz and J. H. Jeans without any very compelling solution being obtained. The wave theory gives an excellent account of the reflexion, refraction, diffraction and (but for the matter of the calculation of the constant in the dispersion formula) dispersion of light of all wave-lengths. In all these phenomena we have an interaction of radiation with matter, but no transformation of the energy of radiation into energy of other forms, nor yet a transformation of radiant energy of one frequency into radiant energy of another frequency, such as takes place in the phenomena of fluorescence. On the other hand, all phenomena which involve a transformation of the radiant energy into energy of the electrons bound in matter, in one manifestation or another, are explained by the quantum theory, and the larger part of this book has been devoted to phenomena susceptible of a quantum explanation. It will be remembered that the quantum theory originated in Planck's investigations on the theory of black body radiation, which involve, of course, the transformation of radiant energy into atomic energy and the reverse process. Each within its own sphere, both quantum theory and wave theory render excellent service, but when we come to try to extend either the one or the other theory to cover all the phenomena, we are met by difficulties which so far have proved insuperable. It is true that Bohr's correspondence principle has given us a method for incorporating certain results of the wave theory in the quantum theory, but

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it is, in a sense, merely a useful device, and does not in any way reconcile the two theories. It is an extension of the general fact that if the quantum be made small enough, *i.e.* the wave-length be made long enough, all quantum results must agree with the results of the wave theory.

The immediate problem is, then, less that of the fundamental reconciliation of the two theories than that of deciding exactly how far each can be employed in dealing with particular phenomena. Accordingly, with this more modest end in view, we shall in this chapter merely discuss certain cases in which the relative validity of quantum and wave theory have been and are the subject of peculiar interest. As a preliminary, it may, however, be well to allude very briefly to the fundamental difficulties before relegating them to the skeleton cupboard.

The wave theory supposes that when an elementary oscillator—an atom or molecule—emits light, this light spreads out, in a homogeneous medium, in spherical waves. To explain interference with monochromatic light, it is necessary to suppose that there is a regular succession of waves extending over a distance at least equal to that of the path difference in the particular case under observation, or, in other words, that the emitter shall continue vibrating regularly and uninterruptedly for a time equal to that needed for the light to travel through the path difference. Further, although it cannot be directly concluded from experiment that a complete elementary spherical wave is emitted, the elementary wave front must extend at least far enough to cover the two slits, or their equivalent, of the interference apparatus.* Now interference fringes have been obtained with a path difference of more than a million waves, so that the length of the regular train of waves in the direction of propagation must be of the order of 50 centimetres or greater. In the Michelson interferometer attached to the Hooker telescope to measure the diameter of a star by the interference method, the mirrors which receive the light are twenty feet apart, and the interference effects

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* There is, on the classical theory, no way of explaining the emission of a portion of a spherical wave only, but if such a partly directed emission would satisfy all our needs, as indicated by experiment, it might be assumed *ad hoc.*

produced are in accordance with classical theory, so that the unbroken wave front must have this extent.   Hence, unless there is a coherence between the light emitted by different atoms of a source which is controlled by their mutual positions (a supposition which is hard to support), each elementary emitter must send out a disturbance of regular waves which extends at least 50 cms. in the direction of propagation and 600 cms. normally to the direction of propagation.

If, then, light be emitted in quanta, unless a single elementary emitter send out several successive quanta in phase with one another, the extent of the quantum in space must be of the order just given.   All the facts of photoelectricity, however, demand a strictly localised quantum of energy, since the whole energy of the quantum is transferred to the electron, whose velocity of ejection depends only upon the frequency of the incident radiation, and not at all upon the intensity, *i.e.* not upon the number of quanta which reach the photoelectric surface in unit time.   It is difficult to think of an atom catching a quantum unless the quantum is something like a minute atom of radiation.   The quantum theory of absorption of radiation seems similarly to demand a strictly localised light quantum.   An extended quantum, considered for simplicity as an isolated train of spherical waves, can be admitted if we are allowed to suppose that when an absorbing system, namely an atom which happens to be in some particular (let us say phase) relationship to the incident train of radiation is reached by the train, the whole train collapses instantaneously on to the atom, as a pricked soap bubble collapses, and its energy is transferred to the atom.   This would demand an instantaneous velocity of the energy in the wave front itself, but not necessarily in the direction of propagation of the wave, since the atom might be allowed the time necessary for a wave to travel 60 cms. (*i.e.* 2×10^{-9} secs.) to absorb the energy.   The hypothesis seems fantastic, but it may be better than nothing.   An objection which Jeans has raised to any extension of the quantum over a length measured in centimetres, namely that every camera shutter or Fizeau toothed wheel would cut some of them in half, may be urged, but we know so little about the properties of quanta, and have already swallowed such hypo-

theses, that it does not seem excessive to ask the faithful to believe that if the head of the quantum has got through unabsorbed, it cannot be absorbed by matter, and will drag its tail after it, so to speak. The quantum, considered as a long train of strictly localised waves, has been called an eel-like quantum by reputable physicists, and an eel is not easily cut in half. An interesting experiment of G. P. Thomson's, carried out with canal rays as emitters and an ingenious arrangement of slits, shows that normal visual and photographic effects are still produced when the particles travel so fast past the slits that there is not time for a complete quantum train to pass through them. Here, again, if we are to assume an extended quantum of the kind needed for interference phenomena, the head must drag the tail through; the tail must take no notice of matter at all. I should hesitate to use such loose language about so grave a matter as a quantum were it not that its irregular behaviour seems to justify irregular analogies. After all, the assumption that unless the head of the train finds an atom ready to interact with it the whole train gets through, is merely the expression of the observed fact and its associated difficulties. It is not offered as an explanation, but merely as a concise expression.

A final argument for the extended quantum, and one for the localised quantum, or light dart, may be cited. When we consider interference on the wave theory, we should expect the same pattern, no matter how feeble the light may be. For instance, in the case of the diffraction image of a star formed by a telescope, the waves fill the whole aperture of the lens, and the pattern can be calculated. On the theory of localised quanta, or light darts, as they may be called (the *Nadelstrahlung* of Einstein), we should have to suppose the effect a statistical one in any case, before we could attempt to deal with other difficulties : a given part of the pattern would be due to the influence on one another of quanta striking within a very small distance in a very small time interval. But if this were so, then if the light were made exceedingly feeble, so that only an occasional quantum entered the telescope or other apparatus, we should expect no pattern to be found. It is found, however, that the same pattern is formed, no matter how much the

intensity of the light be reduced.   G. I. Taylor showed that even when the illumination was so feeble that 2000 hours were required to obtain a photograph of the diffraction fringes of a needle the normal effect was obtained.   This is another argument for the wave theory, or, at any rate, the extended quantum which behaves as a long train of waves with a wide wave front.

On the other hand, Einstein, in the investigations which led to his derivation of Planck's formula from the theory of stationary states, argued that to maintain the Maxwellian distribution of energies in a collection of Bohr atoms in equilibrium with radiation it is necessary to assume that the radiation is emitted in darts of energy.   For the purposes of his deductions, the radiation is considered as possessing momentum $h\nu/c$ * (the kinetic energy being, on Einstein's theory, mc^2, and the velocity c), and as being fired off in a random direction like a bullet, with a consequent recoil of the atomic gun.   The argument has been criticised, notably by Breit, and the criticisms answered by Einstein : on the whole Einstein's interpretation seems less strained than any other leading to the required results.

The linearly and unidirectionally emitted light dart, and the spherical wave of radiation are, then, at present, conceptions of which the physicist makes use at his convenience, while awaiting a reasonable substitute which shall be inclusive and have the properties of the one and the other according to circumstances.   It may be mentioned that various more or less fantastic attempts have been made to derive a cross-sectional area for the linear quantum, which all lead to different results, although, as might be expected, all give a value of the order λ^2.

Dispersion.   We will start by giving a brief summary of the classical electromagnetic theory of dispersion.   This is based upon the assumption that atoms contain linear harmonic oscillators, consisting of electrons bound to equilibrium positions by quasi-elastic forces.   These oscillators therefore have a definite free frequency ν_0 : when a monochromatic radiation of frequency ν is incident upon them they are set into forced

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* Since in this chapter there is no need to mention wave number as distinct from frequency, the symbol ν, and not ν_T, will be used to denote frequency, to simplify the notation.

vibrations of frequency ν,* whose amplitude depends upon the relation of ν to ν_0 in the familiar way described in the standard text-books.† The result of these forced vibrations is a modification of the velocity of the electromagnetic wave to an extent depending upon the frequency of the incident wave, and so we get dispersion. If there were no damping of the oscillators the theoretical amplitude of the forced vibration would be infinite if the incident wave were to have frequency ν_0, and the wave would not penetrate at all. To obtain finite absorption and finite refractive index in the neighbourhood of an absorption line a damping constant is introduced. If we are considering the dispersion at some distance from an absorption line, the assumption of damping makes little difference, but in the immediate neighbourhood of a line it is very important. Of course, in general, the presence of various classes of oscillators, of different frequencies ν_0, $\nu_0{}'$, $\nu_0{}''$ . . . must be assumed, to correspond to different absorption lines, and the dispersion not in the immediate neighbourhood of any one line is the sum of the effects of all the lines. In the immediate neighbourhood of one line, the effect of that line is overwhelming, and the effect of the others may be neglected.

We now review the chief formulae deduced on the classical theory of dispersion. The displacement of the electron with reference to the rest of the atom under the influence of the periodic electric force gives rise to an electric polarisation (electric moment per unit volume) of the medium which is periodic in both space and time, like the force. In the case of a liquid or a gas, where the distribution of molecules is irregular, the polarisation **P** must be calculated by choosing as unit volume a sphere large enough to contain a very large number of molecules, but small compared to the wave-length, so that the electric force is uniform in the space considered. Owing to

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* Of course when the disturbed motion first begins there is a motion of frequency ν_0 as well as the motion of frequency ν—the complementary functions as well as the particular integral—but the slightest damping reduces this to nothing in a very short time, on account of the high frequency.

† For the classical theory of dispersion consult, *e.g.*, O. W. Richardson, *The Electron Theory of Matter*, or A. Schuster, *The Theory of Optics*. The summary here given is provided in order to lead up to the so-called quantum theory of dispersion, and is intended merely as a guide for those wishing to revise their classical theory.

the polarisation of the medium there will be a force on any chosen electron which is additional to the electric force $\mathbf{E}$ acting in the absence of all other molecules, to the elastic restoring force which gives the electron its free period, and to any hypothetical damping force, or resistance. If we lay a small sphere round the chosen molecule the force due to the polarisation of all molecules lying outside the sphere can be shown to be $\dfrac{4\pi}{3}\mathbf{P}$, while the force due to the molecules inside the sphere is negligible.* The force $\mathbf{E'}$ acting on the electron is therefore

$$\mathbf{E'}=\mathbf{E}+\frac{4\pi}{3}\mathbf{P}.$$

The polarisation $\mathbf{P}$ is determined by $\mathbf{E}$; it expresses the amplitude of the vibrating electron. Let $\mathbf{E}=Ee^{ipt}$. We may write

$$\mathbf{P}=\frac{\alpha}{4\pi}\mathbf{E}, \quad\dotfill(\mathrm{I})$$

or
$$\mathbf{P}=\frac{\mathrm{I}}{4\pi}\,\frac{\alpha}{\mathrm{I}+\frac{1}{3}\alpha}\mathbf{E'}=\alpha'\mathbf{E'}. \quad\dotfill(\mathrm{I}a)$$

If a damping constant γ be assumed,† without enquiry as to the mechanism by which the damping takes place, $\mathbf{P}$ is the real part of $\dfrac{\alpha}{4\pi}\mathbf{E}$, where α is the complex quantity

$$\alpha=\frac{\mathrm{I}}{\dfrac{\pi m}{Ne^2}(v_0{}^2-v^2)-\frac{1}{3}+i\dfrac{mv}{2Ne^2}\gamma},$$

N being the number of oscillators of free period v_0 per unit volume. There is a phase difference between $\mathbf{E}$ and $\mathbf{P}$ which

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* If the molecules have a regular cubical arrangement this force is zero : if they are irregularly arranged, as in a gas, there is a small resultant force due to the molecules inside the sphere, which we neglect above. See H. A. Lorentz, *The Theory of Electrons*, pp. 138 and 303 *et seq.* The reader should note that in this book Lorentz is using Heaviside units, and also that what Lorentz calls " the frequency *n* " is the number of radians per second, *i.e.* $2\pi v$, or he will get into trouble with 4π's, and condemn the formulae here given.

† That is, $\mathbf{E}=\mathbf{E_0}e^{-\gamma t}$. The damping constant is often expressed by the time τ which is required for the amplitude to fall to I/eth of its value, or $\tau=\mathrm{I}/\gamma$.

depends upon γ. If the damping be neglected (the case of dispersion in a transparent medium) we have

$$a = \frac{1}{\dfrac{\pi m}{N e^2}(\nu_0{}^2 - \nu^2) - \tfrac{1}{3}} . \qquad \dots\dots\dots\dots\dots\dots(2)$$

It can be further shown that, if v is the velocity of the radiation through the system of molecules, then

$$\frac{c^2}{v^2} = \mu^2 = 1 + a,$$

so that $\mu^2 - 1 = a$ where μ is the refractive index. This gives the expression

$$\frac{\mu^2 - 1}{\mu^2 + 2} = \frac{a}{a + 3} = \frac{1}{\dfrac{3\pi m}{N e^2}(\nu_0{}^2 - \nu^2)}, \qquad \dots\dots\dots\dots\dots(3)$$

first deduced theoretically by Lorentz. It is convenient to express these results in terms of a', since they are often quoted in this form by writers who are concentrating attention on the electric force $\mathbf{E}'$, which includes the contribution of the polarisation. We have, then, the following formulae to represent dispersion in a transparent medium:

$$\mathbf{P} = a'\mathbf{E}', \qquad \dots\dots\dots\dots\dots\dots\dots\dots(1a)$$

$$a' = \frac{1}{4\pi} \frac{a}{1 + \tfrac{1}{3}a} = \frac{N e^2 / m}{4\pi^2(\nu_0{}^2 - \nu^2)} \qquad \dots\dots\dots\dots(2a)$$

and

$$\frac{\mu^2 - 1}{\mu^2 + 2} = \frac{4\pi}{3} a'.$$

So far we have considered only one class of oscillator, with free frequency ν_0, *i.e.* we have taken only one absorption line into account. If there are different classes of oscillators we have to replace $(2a)$ by

$$a' = \sum \frac{N e^2 / m}{4\pi^2(\nu_0{}^2 - \nu^2)}, \qquad \dots\dots\dots\dots\dots(4)$$

where N is the number per unit volume of oscillators of charge e, mass m and free frequency ν_0, and the summation is taken for every kind of oscillator present.

Now in the earlier theories of dispersion the electric force contributed by the polarisation of the medium was neglected: if this be done,

$$a' = \frac{a}{4\pi} = \frac{1}{4\pi}(\mu^2 - 1)$$

and

$$\mu^2 - 1 = \sum \frac{Ne^2/m}{\pi(\nu_0{}^2 - \nu^2)}. \quad \dots\dots\dots\dots\dots(4a)$$

Clearly at some distance from an absorption frequency, where μ is small, and the polarisation small, $(4a)$ may be used in place of the more rigorous formula : this can be seen at once by considering (3) and observing that when μ is small

$$\frac{\mu^2 - 1}{\mu^2 + 2} = \tfrac{1}{3}(\mu^2 - 1) \text{ approximately.}$$

In the equation considered N is an unknown constant, concerning which experimental evidence may be obtained by discussing the dispersion in the case where it is almost entirely due to one absorption frequency, so that the summation in (4) or $(4a)$ reduces to one term. It is found that N is not the number of molecules per unit volume. For vibrations in the ultra-violet,* if e and m be given the electronic values, N turns out to be a few times the number of molecules present.† Drude called N the number of dispersion electrons of the given frequency. It is a very important constant for our subsequent discussion.

Now it has been shown, notably by Planck, that the results of the classical theory of dispersion which we have just summarised can be obtained by considering as the sole means of interaction between the molecules electromagnetic waves, originating in the vibrations of the bound electrons, propagated in the free vacuum between the molecules. This is a point of view which concerns us intimately in discussing modern developments. Each oscillator, assumed to be at rest as a whole and vanishingly small compared to the distance between

* In the infra-red, with which we are not concerned, e and m must have the values pertaining to the material ions.

† For the inert gases, for instance, Cuthbertson finds the following values for q, where $N = qN'$, N' being the number of molecules per unit volume : helium 1·113, neon 2·385, argon 4·330, krypton 4·906, xenon 5·619.

the molecules, becomes the centre of a spherical wave, and, the phases of the oscillators being governed by the incident wave, these spherical wavelets are coherent. They interfere with one another and with the incident radiation, producing a modification of phase velocity within the medium. The change of velocity depends upon the amplitude of the spherical waves, so that from the amplitude of the oscillator we can calculate the dispersion formula. If the frequency of the incident radiation agrees with that of the oscillators themselves the phase of the incident waves bears such a relationship to that of the induced wavelets that relatively large energies are abstracted from the forward direction of the primary beam by interference : if the frequency of the incident waves is markedly different the phase relationship is modified and the energy influence turns out to be negligible, although the influence on the velocity of the wave is still important. All the results for dispersion in a transparent medium can be expressed in this way. To get absorption Planck assumed that the damping was caused by the radiation itself : the damping force due to the loss of energy by radiation was shown by Lorentz to be

$$\frac{2}{3}\frac{e^2}{c^3}\frac{\partial^3 x}{\partial t^3},$$

where x is the displacement. This leads in the case of a harmonic vibration $Ae^{i p t}$ to a damping force

$$-\frac{2}{3}\frac{e^2 p^2}{c^3}\frac{\partial x}{\partial t} = -\frac{8\pi^2 e^2 \nu^2}{3c^3}\frac{\partial x}{\partial t},$$

i.e. a frictional force of the ordinary type proportional to the velocity. If τ be the time for the amplitude to fall to $1/e$th of its value, then $\tau = \dfrac{3mc^3}{8\pi^2 e^2 \nu^2}$, an expression which we shall need later. This damping by radiation turns out to be too small to account for the absorption in any but very transparent bodies. H. A. Lorentz has elaborated a theory in which true absorption, *i.e.* transformation of the incident radiation into heat, takes place by means of molecular impacts, calculated from the kinetic theory. It is supposed that when a molecule in which the oscillator has been set in motion by light collides

with another molecule, the regular vibration is destroyed, and its energy transformed into translatory molecular motion, or heat. This recalls the quantum collision of the second kind. Lorentz calculated the absorption in terms of the mean life t of an oscillator in a state undisturbed by impacts, but found that the value obtained by applying his theory to experiment gave a value for t very much smaller than that given by the kinetic theory, or, in other words, the number of collisions optically required is a large multiple of the gas kinetic number of collisions. There is, then, no fully satisfactory explanation of absorption on the classical theory. The theory of damping by collisions can be essentially transferred into the quantum theory.

In spite of minor difficulties, then, the classical theory has had a considerable measure of success in explaining the facts of dispersion, and the physical assumptions on which this success is based are, firstly, that the atom contains oscillators whose free periods are those of the incident light most strongly absorbed ; secondly, that these oscillators give rise to spherical waves ; and thirdly, that these waves are coherent. In attempting to explain dispersion on the quantum theory, we have either to abandon the wave theory completely, or else to admit that, as far as interference, dispersion, and such like phenomena are concerned, we must for a quantitative description still suppose that atoms emit spherical waves with the ordinary interference properties, or, in other words, that while the quantum theory governs interaction between radiation and matter, the wave theory still gives a correct account of the phenomena outside matter.

Ornstein and Burger have adopted the former method, and consider a light quantum as a spherical volume of electromagnetic energy, whose linear dimensions are of the order of the wave-length of the light. In passing through matter this quantum makes collisions with the atoms, which lead to a retardation : the ordinary formula for probability of collision, supported by sufficient subsidiary hypotheses, leads to the classical formula for the refractive index for long waves. Scattering also takes place, and Rayleigh's formula for the scattering in terms of the wave-lengths of light can also be

found. Further, if the atoms be supposed to contain oscillators, consisting of charges with inertia, a dispersion formula can be derived which agrees with the classical formula to a first approximation. However, the assumptions necessary for these deductions are such that the results are more or less inevitable, and there is little real advance. There is no indication as to how the arbitrary constants may be calculated, and, while the attempt is interesting, it does not seem at present that this method is likely to lead to new results.

When we turn to the other method, and assume that the atoms emit spherical waves, we have to devise some method to account for the way in which the atoms are excited to radiate by the incident light. It is clear that we cannot simply treat the electrons in their quantised orbits as oscillators which can be set into forced vibrations, for if this were the case the resonance frequencies would be those of the electron in its various orbits, which are quite different from the frequencies of the emitted light, given by $h\nu = E - E'$. Experiment leaves no doubt, however, that it is the latter which are the absorption frequencies significant for the anomalous dispersion, as evidenced by the success of the classical theory. If this difficulty can be surmounted, we still have to make some assumption which will make the spherical waves coherent, and not emitted at random, as they would be on the pure quantum theory. One of the early attempts to get over the fundamental difficulty of the period of the resonator was made by C. G. Darwin, who put forward the assumption that the atoms subjected to incident radiation possess a certain probability of emitting a quantum of radiation, in the form of a damped wave whose frequency ν_0 is given by quantum conditions (*i.e.* determined by the nature of the atom), and is consequently different in general from that of the incident wave. The probability of the emission of such a wave by the atom between time t and $t + dt$ is assumed by Darwin to be proportional to $\dfrac{\partial \mathbf{E}}{\partial t} \cdot dt$, where $\mathbf{E} = E \cos 2\pi\nu(t - z/c)$ represents the incident radiation. This introduces the frequency of the incident wave into the expression for the scattered wave. It is further assumed that the damped radiation emitted by the atom has a certain phase

relationship at the start. When the effect of all the atoms in the body, emitting damped waves, is taken into account by integrating, the frequency of the atom itself, as given by the quantum theory, is found to average out, and we are left with a resultant disturbance which has the frequency of the incident wave, but an amplitude involving $\dfrac{1}{\nu_0{}^2 - \nu^2}$ in the classical way. By adjusting the constants Darwin's expression for the scattered energy, and hence for the dispersion formula, can be made to agree exactly with the classical expression. The constants in Darwin's formula cannot be calculated, any more than those of the classical formula, and the mechanism of the conversion of radiant energy into heat remains obscure. The theory has the peculiar feature that the law of conservation of energy holds statistically only, and not for individual processes, a conception which will receive mention again when the theory of Bohr, Kramers and Slater is discussed. Darwin's theory has been criticised by Bohr and others on the ground that for very feeble incident light the atoms emitting energy discontinuously in the way assumed would not produce enough wave trains to interfere regularly : the statistical machinery would break down, whereas experiment has shown that the dispersion phenomena are quite independent of the intensity, just as are interference phenomena. The theory is briefly described here to show how an attempt has been made to retain the quantum machinery of emission in dispersion theory.

This standpoint failing, it has been found necessary to make still further concessions to the wave theory, retaining of the quantum mechanism only certain considerations of the probability of transitions between stationary states. To preserve the features in which the wave theory is successful, we must so far assimilate the quantum theory of dispersion to the wave theory as to suppose that the atoms give rise to a " virtual " field of radiation, which has the frequency determined by the quantum relation $h\nu = E - E'$ and not the frequency of the electron in its orbit, but is continuous, and not spasmodic like a true quantum field. The assimilation of the field to that prevailing on the wave theory implies that the atom contains a virtual or substitute oscillator (Ersatzoscillator) correspond-

ing to each transition from an occupied orbit to another orbit permitted by the selection principle : there is, of course, associated with a given atom no virtual oscillator corresponding to transitions from an unoccupied orbit, since there can be no absorption line of frequency corresponding to such a transition. The substitute oscillator has the properties of a classical oscillator, consisting of a vibrating charge which possesses inertia, but, if one oscillator of each kind be considered attached to an atom, the charge and the mass have not the electronic charge and mass, or, in particular, the value of e^2/m which enters into the formula has not the value which it has for an electron. Alternatively we may let e^2/m have the electronic value, but assume an arbitrary number of oscillators, since Ne^2/m is the arbitrary factor in the equation.

Of course, if the substitute oscillator which continuously emits waves capable of interference has exactly the same properties as a classical oscillator all the dispersion results which follow for the classical oscillator will follow for the substitute, since the dispersion is the result of the interaction of the spherical waves proceeding from the atoms. On the classical theory the dispersion formula contains, as we have seen, an unknown constant N, which has not been theoretically connected with the general properties of the atom : we have therefore the opportunity to introduce specific features of the quantum theory in trying to deduce the constant. The constant is connected with the amplitude of the wave emitted by the atom, and hence, if we adopt the quantum theory in so far as we suppose the frequency determined by a passage from one stationary state to another, we shall have to express this constant in terms of the Einstein factor $A_{k \to i}$, which expresses the probability of a transition from a state k to a state i of lesser energy ; this takes the place of the amplitude of the oscillator on the classical theory. We have a possibility of connecting the dispersion constant of gases with the intensities of spectral lines. Once the amplitude is obtained we have an expression for a in equation (1), which is connected with the refractive index by the classical expressions (3) or (4), since, on the theory of the virtual oscillator, outside the atom wave conditions prevail.

Ladenburg's method is to equate the total absorption of N_{cl} harmonic oscillators, as calculated on the classical theory, to that of N virtual oscillators, calculated on the quantum theory by introduction of the Einstein coefficient. It can be shown * that N_{cl} similar classical oscillators, of free frequency ν, bound isotropically in space, absorb by scattering an amount of energy $N_{cl} \dfrac{\pi e^2}{m} I_\nu$ per unit time, where $I_\nu d\nu$ is the density of incident radiation of frequency ν to $\nu + d\nu$. Now the quantum absorption is

$$A_{qu} = h\nu_0(N_i B_{i\to k} - N_k B_{k\to i})I_{\nu_0}, \quad \dots\dots\dots\dots\dots(5)$$

where $B_{i\to k}$, $B_{k\to i}$ are the Einstein coefficients for transitions from state i to k, and state k to i under the influence of radiation, N_i and N_k are the numbers of atoms in states i and k respectively, and $h\nu_0$ is, of course, the energy absorbed or emitted in the $i\to k$ and $k\leftarrow i$ transitions respectively. From the considerations of Einstein's development of Planck's formula (see p. 355, *et seq.*), we have

$$q_i B_{i\to k} = q_k B_{k\to i}; \quad \dots\dots\dots\dots\dots\dots\dots(6)$$

and further, using this relation, we have from equation (6), Chapter XII.,

$$B_{i\to k} = \frac{q_k}{q_i} \frac{c^3}{8\pi h\nu_0^3} A_{k\to i}, \quad \dots\dots\dots\dots\dots(7)$$

since the constant C introduced on p. 355 has the value $8\pi h/c^3$. Using these relations (5) becomes

$$A_{qu} = h\nu_0 I_{\nu_0} N_i B_{i\to k} \frac{\text{I}}{\text{I} + \dfrac{c^3}{8\pi h\nu_0^3} I_{\nu_0}}.$$

If I_{ν_0} is not too large, $\dfrac{c^3}{8\pi h\nu_0^3} I_{\nu_0}$ can be neglected in comparison with I, and

$$A_{qu} = h\nu_0 I_{\nu_0} N_i B_{i\to k}.$$

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* Planck, *Wärmestrahlung*, Fourth Edition, formulae (159) and (260). The expressions given by Planck apply to the linear oscillator, and must be multiplied by 3 to give the result for an isotropically bound oscillator.

Now on the classical theory the absorption of N_{cl} oscillators isotropically bound is

$$A_{cl} = \frac{\pi e^2}{m} N_{cl} I_{\nu_0}.$$

Equating the classical and the quantum expressions, we have

$$N_{cl} = N_i \frac{mh\nu_0}{\pi e^2} B_{i \to k} = N_i \frac{q_k}{q_i} \frac{mc^3}{8\pi^2 e^2 \nu_0^2} A_{k \to i} = N_i \frac{q_k}{q_i} A_{k \to i} \frac{\tau}{3}, \quad ...(8)$$

τ having the value already given on p. 674.

Now N_{cl} is the dispersion constant in the classical formula which we have already given, so that (8).gives the dispersion constant in terms of the Einstein probability $A_{k \to i}$, which is the probability of a spontaneous transition from state k to state i. We can express the inequality of N_{cl} and N_i either by supposing that each quantum atom reacting to the incident radiation is replaced by x classical oscillators of electronic charge e, and mass m, where $x = N_{cl}/N_i$, or we may say that each quantum atom is replaced by a classical oscillator of charge xe, mass xm, so that e^2/m has x times its value for an electronic oscillator. The weights q and the probability coefficients $A_{k \to i}$ can be calculated approximately in certain simple cases, where the machinery of the electronic orbits is susceptible of quantitative treatment. Simple confirmation of the formula has been reached by Ladenburg with hydrogen, and Thomas (whose calculations of the electronic orbits have been mentioned in Chapter XI.) with sodium. Of course, in the case of absorption by unexcited vapour, N_i may be taken as the total number of atoms.

Kramers has shown how to apply the correspondence principle in general. The reaction of the atom to the incident wave is, on the theory of the virtual oscillator, conditioned by the amplitude of the harmonic component corresponding to the quantum switch which gives the frequency in question. The correspondence principle does not allow a rigorous solution, but Kramers has considered the region of small frequency, where the stationary states are close to one another, or, in other words, the case of large quantum numbers. Since we have here an initial state which is not a normal state of the

atom, we must consider the Einstein coefficient both for jumps in which the state considered is the initial state, and in which it is the final state. Assuming all statistical weights to be the same, *i.e.* $q_k = q_i$, Kramers finds

$$\mathbf{P} = \mathbf{E} \sum_k A_{k \to i} \tau_{ki} \frac{e^2}{m} \frac{\text{I}}{4\pi^2(\nu_{ki}^2 - \nu^2)} - \mathbf{E} \sum_j A_{i \to j} \tau_{ij} \frac{e^2}{m} \frac{\text{I}}{4\pi^2(\nu_{ij}^2 - \nu^2)},$$

where $k > i > j$, so that the first summation refers to transitions in which energy is emitted, and the second summation to transitions in which energy is absorbed. The τ's and the ν's correspond to these transitions, so that

$$\tau_{ki} = \frac{3mc^3}{8\pi^2 e^2 \nu_{ki}^2} \quad \text{and} \quad \tau_{ij} = \frac{3mc^3}{8\pi^2 e^2 \nu_{ij}^2}.$$

The first summation is, in effect, the expression which we have already considered, and represents the reaction to radiation of a classical harmonic oscillator with charge xe and mass me, such that *

$$\left(\frac{e^2}{m}\right)_{\text{effective}} = x\frac{e^2}{m} = A_{k \to i} \tau_{ki} \frac{c^2}{m}. \quad \ldots\ldots\ldots\ldots\ldots(9)$$

The second summation, however, corresponds to a virtual oscillator for which

$$\left(\frac{e^2}{m}\right)_{\text{effective}} = -A_{i \to j} \tau_{ij} \frac{e^2}{m},$$

and so has a negative value. This negative virtual oscillator is a somewhat troublesome conception. It represents a negative dispersion which bears a close analogy to Einstein's "negative absorption." There are two kinds of virtual oscillators.

As already pointed out, the relation of $\mathbf{P}$ to $\mathbf{E}$ is sufficient to give the dispersion formula, if the wave theory be considered as valid outside the atom, so the actual dispersion formula need not be written down. The formula given by Kramers applies only to regions for which ν is outside the absorption lines which contribute, in effect, the different terms in the summation. This is clear from ordinary classical considerations.

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* No q's appear in (9), since it is assumed that all statistical weights are the same. Whether $\tau/3$ or τ appears depends upon whether we consider a linear oscillator or a spatial oscillator.

An important point is that Kramers has shown that his formula merges into the classical formula for the polarisation of the medium when the quantum numbers tend to infinity, just as all quantum processes should do.   This is in favour of the formula, which further contains only quantities which have by themselves a definite physical meaning, once the general postulates of the quantum theory are accepted.   So far no very important applications have been made of the formula, on account of the difficulties of calculating the quantities involved, but it has been accepted as a distinct advance in many quarters.   It is given here to indicate the direction in which the attempts are being made, but the virtual oscillator is clearly a provisional assumption made for want of a proper understanding of the true mechanism which, as experimental results demand, must lead to so many features peculiar to the wave theory.

On the whole, it must be admitted that the quantum theory has done little in the way of elucidating the problems of dispersion which meet the experimental physicist who wants to explain his results.

The Theory of Bohr, Kramers and Slater.   In reviewing briefly the quantum theory of dispersion we have seen how the hypothesis of virtual oscillators, giving out energy steadily and continuously, whatever the quantum history of the atom with which they are associated, has been introduced.   This hypothesis implicitly denies that the conservation of energy and momentum hold for the atomic scattering process, for if an atom is put in a given stationary state, on the quantum theory it has a fixed energy until the stationary state changes abruptly, but if it is radiating spherical waves all the time it must, apparently, be losing energy.   The suggestion that the conservation of energy and momentum break down for atomic interchanges of certain kinds is not new : O. W. Richardson in 1916 tentatively suggested, for example, that the energy of the photoelectric electrons was not derived directly from the incident radiation, but represented a condition which determined the disruption of matter under the stimulus of incident radiation.   Sommerfeld, in discussing the general relation between wave theory and quantum theory, has also suggested

abandoning the conservation of energy for individual elementary radiation processes, and Darwin, in his theory of dispersion, was also led to assume that the law held statistically only. Experiment leaves no doubt that, when we handle matter in bulk, the conservation of energy and momentum holds, but it is open to us to assume, if we think fit, that the law is, like the second law of thermodynamics, a macroscopic manifestation.

Bohr, Kramers and Slater have put forward a general theory which definitely dissociates the energy of the field of radiation from the energy of the atom, as far as a single atom is concerned, and treats the conservation of energy and momentum as statistical effects. They make the assumption, first put forward by Slater, that an atom in a given stationary state can communicate energy effects to a distant atom by virtue of a field of radiation before it experiences a quantum switch, in contradistinction to the original hypothesis of the quantum theory, which asserts that an atom ejects radiant energy, in quanta, only when a switch takes place. They require, of course, the field of radiation, which they call a virtual field (presumably to soften the contradiction to all accepted principles which it expresses), to give the classical wave properties of interference and the allied phenomena : as has been emphasised, if we have atoms giving out spherical waves under the influence of an incident radiation, all the accepted consequences of the wave theory can be made to follow.

The essence of the new theory is as follows : when an atom is put into a given excited stationary state it is to be considered as immediately starting to emit a steady train of spherical waves, and as continuing to do so until its stationary state changes. As far as this radiation is concerned, then, the atom is replaced by a virtual harmonic oscillator. The frequencies of these waves are the frequencies which correspond, by the fundamental relation $h\nu = E - E'$, to all the possible quantum jumps from that state : thus if the atom is in the state corresponding to the first resonance potential it will emit a single monochromatic radiation, but if it is in a higher state it will emit as many monochromatic radiations as there are possible transitions. When the quantum jump takes place the emission of one set of monochromatic radiations ceases, and the emission

of another set begins, unless the state to which the jump takes place be the basic state. The continuous emission from an atom which is in a stationary state violates the conservation of energy. The conservation is preserved as a statistical effect by introducing considerations of the probability of a quantum switch, for, taking a single monochromatic radiation of frequency v, if N be the (very large) number of jumps from a state n to a state n' in a given time, then Nhv, the loss of energy, must equal the total energy of frequency v radiated in the virtual field by all the atoms in that time. There must, for a single atom, be a certain probability qdt, which is independent of the time, that a jump takes place within the time dt, and this must be so adjusted that the energy of frequency v radiated continuously during the mean duration of the atom in a given stationary state n is equal to the product of hv into the fraction of atoms which execute the jump n to n', where $v = E_n - E_{n'}$. That is, $s = qhv$, where s is the energy given out continuously as virtual radiation in unit time. Where several monochromatic radiations are possible the individual atoms, on the virtual field theory, are emitting simultaneously and continuously the various frequencies, whereas a single atom can only perform one quantum jump : the probability of a particular jump will be the greater the more intense the corresponding virtual radiation. With a given atom it is a matter of chance which particular quantum jump occurs, just as for a particular radioactive atom it is, firstly, a matter of chance when a disintegration takes place, and, secondly, as far as we know, when there is a branching it is a matter of chance which disintegration takes place.

On the original quantum theory there was a causal connection between the radiation transformations in distant atoms. A given atom would change its stationary state and emit a quantum of energy, which would eventually be absorbed by another atom, causing a quantum switch to a higher energy state in that atom. On the hypothesis of Bohr, Kramers and Slater there is no causal connection between the jump in one atom and that in another. An atom in a stationary state is accompanied by an emission of virtual radiation, which contributes to the creation of a field of radiation in the neigh-

bourhood of a second atom, and, as considered by Einstein, the probability of a quantum jump to a higher state in this second atom will be conditioned by the density of this field, but the jump takes place at a time which is not connected with the jumps in other atoms, and merely because the other atoms are in an excited stationary state, and not because they happen to be undergoing quantum changes. The two processes of radiation and of quantum switches are taking place side by side, the field of virtual radiation looking after the classical wave-theory effects, and the quantum switches governing the frequency and the energy interchanges. The flow of energy and momentum by which the atoms produce all the interference phenomena is considered to arise from the virtual oscillators, while the discontinuous phenomena of the type of the photo-electric effect are still governed by the accepted quantum theory. The radiation is continuous, but the gain and loss of energy by the atoms is discontinuous. The theory is scarcely an explanation of the difficulties which arise from the conflicting claims of the wave theory and the quantum theory, but rather a particular way of classifying those difficulties, which was already adumbrated in our discussion of dispersion.

The failure of the conservation of energy for atomic interchanges is a conception which is repugnant, and the question must be asked as to whether the freedom which it gives for speculative theorising compensates for the loss of a principle which has proved of such use even in considering single atomic processes. The conservation of energy and of momentum have proved adequate to describe the collision of nuclei, where Blackett's experiments provide a drastic check. The experiments on the impact of electrons on atoms which have established the existence of elastic collisions, unaccompanied by radiation of any kind, when the energy of the incident electron is below a certain value, and of sharp resonance and ionisation potentials, indicate that here again we have very definite stationary states which can only be changed by the addition or loss of determined quantities of energy. Everything, then, goes to show that the method of interaction by virtual field postulated by Bohr, Kramers and Slater can only apply, if at all, to atoms at comparatively large distances from one another,

such as are contemplated in the classical theory of dispersion. We shall see later that experiment has indicated still further limits to the possible validity of the hypothesis.

We can now very briefly refer again to dispersion.   When the incident radiation has a frequency equal to that corresponding to a transition involving the actual stationary state of the atom we have, on the theory of the virtual oscillator, to consider that there is a weakening of the primary beam due to the secondary waves originating in these oscillators, which, in this case, have large amplitude and a phase differing by $\pi/2$ from that of the primary wave, just as in the classical theory.*   Correlated with this loss of energy we have a gain of energy of the atoms due to their passage to higher stationary states, but the energy is not conserved for single atoms, but only for the process as a whole, the average energy abstracted from the primary beam being equal to the average gain of energy of the atoms.   When the frequency of the incident wave differs appreciably from that of the primary wave the frequency of the virtual oscillation is still that of the primary wave, but, owing to the phase difference which exists in this case, the energy loss of the primary beam is negligible, although a change of phase velocity takes place. (Dispersion in transparent substance.)   The conservation of momentum implies that when an atom absorbs energy and undergoes a quantum switch it must also acquire momentum, and receive a small push.   The theory of Bohr, Kramers and Slater insists that the conservation of momentum is also a matter of averages, so that the momentum acquired by the atoms in discrete amounts during quantum changes averages out to equal the momentum lost by the incident radiation.   As long as only atoms as a whole are considered, passing from one stationary state to another, the energy involved in the small impulses is negligible, owing to the large mass of the atom.   Suppose, however, that we consider ionisation.   If the incident frequency is the ionisation frequency, the weakening of the primary beam through the

* On the general theory of transitions due to Einstein there might be a reinforcing as well as a weakening, according as the induced transition is in the direction of a decrease or an increase of energy of the atom.   As in actual cases the great majority of the atoms is in the basic state the reinforcing is not observed.   Compare Kramers' dispersion formula.

mechanism of the virtual oscillators takes place as above, and there is a probability of ionisation, which looks after the energy balance.   If, however, the $h\nu$ of the primary beam exceeds the work of ionisation, then there must be a chance of the electron liberated acquiring a high velocity.   In fact, if $h\nu$ is very large compared to the energy of ionisation, there must be a chance of the electron acquiring all the momentum $h\nu/c$ of the primary radiation.   The view which Bohr, Kramers and Slater take of the interaction between radiation and free electrons is best considered after the discussion of the Compton effect, since the experimental observations involved in the effect are what any theory has to fit.

The natural breadth of the spectral lines, *i.e.* the minute range of frequencies which is covered by a single line even when the broadening effects due to pressure and Doppler effect are eliminated, finds a ready expression in terms of the theory under consideration.   The emission of the classical wavelet lasts for a finite time only, namely, the duration of the excited stationary state, so that a train of a finite number of waves, with a beginning and an end, must actually be considered. Since the duration of the stationary state is of the order 10^{-8} second, the wave-train for visible light comprises some five million wave-lengths.   To represent such a finite train by Fourier's series a small range of frequencies is required, the range being of the order of the reciprocal of the duration of the stationary state.   The sudden initiation and interruption of the virtual emission which is postulated leads, then, to a finite breadth of the spectral line.   It is, however, possible to account for the finite breadth on general grounds, without the characteristic assumptions of the Bohr, Kramers, Slater theory.   The quantum conditions which we have considered in Chapter X. apply to motions which are multiply periodic, and unless the motions are steady for an infinite time the quantum conditions are not really fulfilled.   Now the interruption of the orbital motions is a feature of the quantum theory, and consequently the energies of the stationary states cannot really be determined with the sharpness which has been assumed.   The question of the so-called weak quantisation, which prevails when the orbital motion is not strictly periodic, has been

treated by Ehrenfest and Breit with the help of the correspondence principle, which clearly demands a small range of frequencies when an orbital motion has a beginning and an end, to replace each single frequency when the orbital motion is of infinite duration. Ehrenfest, Tolman and Slater have considered the problem in further detail.

The Compton . Effect. We have seen that the so-called quantum theory of dispersion involves the assumption of virtual oscillators emitting what are actually classical waves. We still have, then, to rely upon the wave theory for a quantitative description of many properties of radiation. For other purposes, however, it is more convenient to consider radiation as consisting of directed bundles of energy $h\nu$, or light darts. Einstein's relation between mass and energy *. states that mass $\times c^2 =$ energy, so that, since the energy is projected with velocity c, the momentum of the light dart, or light quant, is $h\nu/c$. It is considered as being fired off like a bullet from the atomic gun, which recoils. Reference to Einstein's arguments in favour of this conception from equilibrium radiation has been made at the beginning of the chapter. The light dart hypothesis is supported by photoelectric facts, while, further, during the last few years a very striking new phenomenon has been discovered which is strongly in its favour. This is the Compton effect, named after A. H. Compton, to which casual reference has been made earlier in the book. It is an experimental observation which has received an easy interpretation on the light dart hypothesis, but, whatever the fate of the latter, if the validity of the effect be admitted (as, after many criticisms, it seems to be to-day), it constitutes an important addition to our stock of observational knowledge.

The simple idea underlying the experiments is that, if a light quant be considered as a localised lump possessing energy $h\nu$ and momentum $h\nu/c$, when it strikes an electron it must interact with it according to laws analogous to those governing the collision of elastic bodies, the result of the interaction being that the electron acquires a velocity, while the light quant proceeds with diminished energy, and so corresponds to a wave of lesser frequency. To be precise, the conservation of

* Cf. Chapter VII.

energy demands that the energy of the quant before collision shall equal the energy acquired by the electron plus the energy of the quant after collision, while the conservation of momentum demands (a) that the momenta of the incident quant, of the struck electron, and of the resulting quant shall lie in one plane, (b) that the momentum of the electron shall make an angle φ, the momentum of the resulting quant an
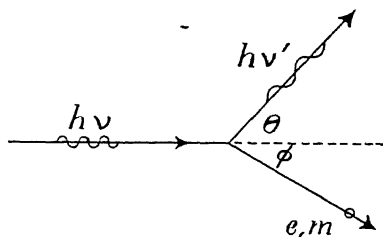
FIG. 109.

Diagrammatic representation of the Compton effect.

angle θ with the direction of the incident quant, such that the added momenta of electron and resulting quant, resolved in the direction of the incident quant, shall equal the momentum of the incident quant, while the added momenta resolved normally to this incident quant shall be zero. Making use of the relativistic expressions for the mass and the kinetic energy of a particle, given on p. 245, the energy equation is

$$h\nu = m_0 c^2 \left(\frac{1}{(1 - \beta^2)^{\frac{1}{2}}} - 1 \right) + h\nu' \quad \dots \dots \dots \dots \dots (10)$$

where ν' is the frequency of the scattered radiation, while the equations of momentum are

$$\frac{h\nu}{c} = \frac{m_0 v}{(1 - \beta^2)^{\frac{1}{2}}} \cos \varphi + \frac{h\nu'}{c} \cos \theta, \quad \dots \dots \dots \dots (11)$$

$$0 = \frac{m_0 v}{(1 - \beta^2)^{\frac{1}{2}}} \sin \varphi - \frac{h\nu'}{c} \sin \theta, \quad \dots \dots \dots \dots (12)$$

where v is the velocity of the electron after impact.

We have here only three equations to determine the four quantities v, ν', θ, φ, so that they are not all fixed : any angle θ

of scattering is possible, according to the impact parameter, whatever that may be for a light quant. We can obtain a relation between ν', the frequency of the scattered quant, and θ, the angle through which it is scattered, which is what we require. Let $M = \dfrac{m_0 c^2}{h}$. From (10) we get, by simple manipulation,

$$\left(1 - \frac{\nu'}{\nu} + \frac{M}{\nu}\right)^2 - \left(\frac{M}{\nu}\right)^2 = \frac{\beta^2}{1 - \beta^2}\left(\frac{M}{\nu}\right)^2, \quad \dots\dots\dots(13)$$

while from (11) and (12), by squaring and adding, we have

$$1 + \left(\frac{\nu'}{\nu}\right)^2 - 2\frac{\nu'}{\nu}\cos\theta = \frac{\beta^2}{1 - \beta^2}\left(\frac{M}{\nu}\right)^2. \quad \dots\dots\dots(14)$$

Equating the left-hand sides of (13) and (14),

$$\frac{\nu'}{\nu} = \frac{1}{1 + \dfrac{2\nu}{M}\sin^2\dfrac{\theta}{2}}; \quad \dots\dots\dots\dots(15)$$

or if $\nu - \nu' = \Delta\nu$ is small, so that $\dfrac{\Delta\nu}{\nu}$ is small compared with 1,

$$\Delta\nu = \frac{2\nu^2}{M}\sin^2\theta/2$$

or,

$$\Delta\lambda = 2\lambda_0\sin^2\theta/2, \quad \dots\dots\dots\dots(16)$$

where

$$\lambda_0 = \frac{c}{M} = \frac{h}{m_0 c} = \cdot 0243 \ A.U.$$

This equation gives the change in wave-length in terms of the angle of scattering. It further shows that, for a fixed angle, the change in wave-length is independent of the incident wavelength, or that the percentage change in wave-length is inversely as the wave-length. For very long wave-lengths the change is therefore negligible, or the classical theory holds, which is what we should expect for any quantum effect. The shorter the wave-length the more easily should the effect be detected. X-rays or γ-rays are, then, indicated as the radiation best suited to furnish an experimental test of the theory.

Long before the quantum theory of scattering was discussed (*i.e.* in 1904) Eve observed that scattered γ-rays were softer than the primary beam, and later Florance confirmed this, and showed that the scattered radiation becomes gradually less penetrating, as measured by its absorption in lead, the greater the angle which the direction of scattering makes with the primary beam.   He further showed that whether carbon, aluminium, or zinc were used as scattering body the effect was much the same, and Gray obtained results which emphasised the fact that the quality of the scattered radiation is approximately independent of the nature of the radiator.   When in 1922 Compton set out to detect experimentally the effect which he had predicted, he used as primary beam the radiation from an X-ray tube with a molybdenum anticathode, scattered it with graphite powder, and found that the scattered rays were more easily absorbed than the primary rays.   He followed up these preliminary experiments by more accurate ones, in which the wave-length was measured by means of crystal reflexion, with the ordinary technique of X-ray spectroscopy. The arrangement is shown in Fig. 110.   Radiation from the
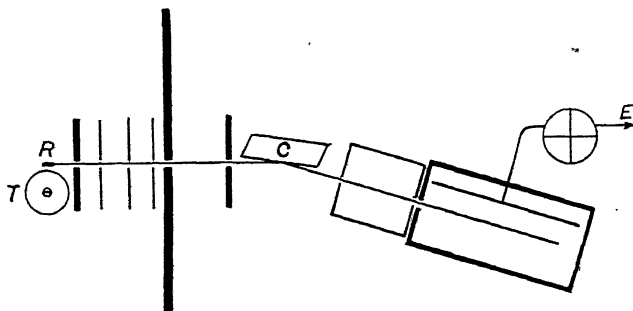
FIG. 110.

Compton's experimental disposition.

tube T falls on the scattering body R, which is placed as close as possible to the anticathode, since one of the experimental difficulties is the low intensity of the scattered radiation.   A narrow beam of radiation scattered in a given direction is isolated by a suitable system of lead slits, and falls on the crystal C of the X-ray spectrometer.   The reflected beam is

detected by the ionisation chamber. The same X-ray spectrometer is used to measure the wave-length of the primary radiation. With this arrangement Compton found that in the scattered radiation the $K\alpha$ line of molybdenum ($\lambda = \cdot708$ A.) was slightly displaced in the direction of increasing wavelength, and when the angle of scattering was 90°, as in Fig. 110, the magnitude of the displacement proved to be $\cdot022$ A., which agrees with equation (16), since $2 \sin^2 \theta/2$ is 1 in this case.

Compton and Ross have carried out independently experiments upon the variation of the Compton shift with angle of scattering θ, and verified the formula in this respect. Ross was the first to replace the ionisation chamber by the photographic plate and obtain successful pictures of the Compton effect, and he was followed by Müller, who used the $K\alpha$ radiation of silver, molybdenum and copper as primary radiation. A shift of the correct magnitude was found in all cases. The chief difficulty in obtaining photographs of the shift is due to the feebleness of the scattered radiation, which necessitates exposures of five hours or more, even with expert disposal of the apparatus. Certain doubt was at one time thrown upon the reality of the Compton effect by Duane and others, but further experiment has led to the withdrawal of the criticisms, and it may be definitely said that to-day there is no doubt as to the existence of the effect as an experimental fact.

According to the theory the Compton displacement should be independent of the nature of the scattering substance, since it is assumed to be due to interaction of the incident radiation with free * electrons. The following table, due to Ross, shows that this independence is an experimental fact, as has been also demonstrated by Müller, who used paraffin, glass and aluminium as scatterers. The table also contains one or two measurements which confirm the dependence of the displacement on angle given by formula (16).

θ is the angle of scattering, $\Delta\lambda$ obs. the Compton displacement experimentally observed, $\Delta\lambda$ calc. is the theoretical value given by formula (16), i.e. is $2\lambda_0 \sin^2 \theta/2$. The quantity R in the last column will receive attention a little later on.

* Or very loosely bound. See p. 693.

COMPTON EFFECT FOR VARIOUS SCATTERING SUBSTANCES.

Scatterer	Primary Radiation λ in cms. × 10⁻¹¹	θ	Δλ obs. in cms. × 10⁻¹¹	Δλ calc. in cms. × 10⁻¹¹	R
Graphite - -		$30°$	3 ± 1	$3 \cdot 2$	$\cdot 2$
Graphite - -		$60°$	$12 \cdot 0 \pm \cdot 1$	$12 \cdot 2$	$\cdot 95$
Graphite - -	MoKα, $\lambda = 708$	$90°$	$23 \cdot 6 \pm \cdot 3$	$24 \cdot 3$	$1 \cdot 7$
Aluminium - -		$90°$	$24 \cdot 4 \pm \cdot 1$	$24 \cdot 3$	$\cdot 7$
Aluminium - -	MoKβ, $\lambda = 630$	$90°$	$24 \cdot 2 \pm \cdot 1$	$24 \cdot 3$	$1 \cdot 0$
Sulphur - -		$90°$	$24 \cdot 0 \pm \cdot 5$	$24 \cdot 3$	$\cdot 29$
Copper - -		$90°$	$24 \cdot 4 \pm \cdot 2$	$24 \cdot 3$	$\cdot 32$
Silver - -	MoKα, $\lambda = 708$	$90°$	$23 \cdot 8 \pm \cdot 2$	$24 \cdot 3$	$\cdot 21$
Lead - -		$90°$	$24 \cdot 0 \pm \cdot 2$	$24 \cdot 3^{*}$	$\cdot 024$

The scattered radiation which shows the Compton softening is always accompanied by scattered radiation of the same frequency as the primary radiation, *i.e.* scattered radiation of the frequency to be anticipated on the classical theory. This might at first sight appear hard to reconcile with the simple theory of the Compton effect, but an explanation is not far to seek. In deducing the formula we considered the interaction of incident radiation with a free electron, by which we mean that the energy required to free the electron from any binding forces to which it may be subjected is very small compared to the energy of the incident radiation. When X radiation, for which $h\nu$ is large, is used for the primary beam there must always be a large number of electrons for which this is true, and so we get the Compton effect. There are also, however, very firmly bound electrons in the inner parts of the atom, and when the incident radiation interacts with these its energy is insufficient to free them. In this case the electron is, then, bound up as one with the atom, and m_0 in the formula for $\Delta\lambda$ must mean not the mass of the electron, but the mass of the atom. This is so great that only a vanishingly small energy is communicated to the atom-electron system, and the radiation is scattered without change of wave-length, or if for m_0 be substituted a mass some thousands of times that of the electron, $\Delta\lambda$ becomes imperceptible. This accounts for the sharp line of unchanged frequency. Jauncey and others have modified the original theory in various ways, but there seems little doubt that some such explanation as that just offered is needed to account for the experimental facts.

If this explanation be accepted it is clear that the softer the primary radiation, and the heavier the scattering atom, the greater must be the intensity of the undisplaced line compared to the displaced line, since the number of electrons firmly bound with reference to the incident radiation is increased. In the table on p. 693 R denotes the ratio of the intensity of displaced line to undisplaced line, and it will be seen that, with a given incident radiation Mo$K\alpha$, the heavier the scattering atom the less marked is the intensity of the scattered radiation showing the Compton displacement compared to the intensity of scattered radiation of primary frequency. Further, taking a given kind of scattering atom, aluminium, for which measurements with both Mo$K\alpha$ and Mo$K\beta$ are shown, the harder the incident radiation the more pronounced the intensity of the radiation showing the Compton effect.

A further example of this general behaviour is given by experiments carried out by Ross with visible light. Although the Compton change of wave-length is small for measurements in the visible region, *i.e.* ·024 A., it is well within the limits of observation with the refinements of modern spectroscopy, Ross scattered visible light with a substance containing atoms of low atomic number, viz. paraffin-wax, but was unable to detect the slightest change of wave-length, and, indeed, if such an effect had existed it is very unlikely that it would not have forced itself into the notice of the professional spectroscopists. On the theory just outlined the absence of effect is explained by the length of the waves, for which $h\nu$ is so small that even the weakest bound electrons can no longer be regarded as free, so that we must substitute the mass of the atom for the mass of the struck electron, and $\Delta\lambda$, as given by (16), is of the order 10^{-5} A., and so imperceptible.

On the theory of the Compton effect, when a quantum of radiation strikes an electron the frequency of the scattered radiation is changed by virtue of the fact that energy of translation is communicated to the electron—we have what is called a recoil electron. The theory is strongly supported by the fact that such recoil electrons have been detected, and, to a certain extent, quantitatively investigated. They were identified by C. T. R. Wilson and by Bothe on photographs of the ionisation

produced by a narrow beam of X-rays, taken by the Wilson method of the expansion chamber. Such photographs show not only long, irregularly curved tracks starting from the path of the beam, but also, in the path of the beam itself, certain very short tracks, which appear either as small dots or else as dots with a small tail. C. T. R. Wilson refers to them as " sphere," " comma," and " fish " tracks, according to the length of the small tail, the " fish " tracks being so called because, when the dots have a pronounced tail, and a number of them appear on the plate with their tails pointing in the same direction, they resemble, to a fanciful eye, a shoal of small fishes. The tail of the fish is directed towards the source.

The long tracks can be attributed without hesitation to photo-electrons, which leave the atom with practically the full energy $h\nu$, since the work needed to free the electron from the atom is negligible : their range agrees well with this attribution, as shown by C. T. R. Wilson. Now the recoil electrons must always have an energy markedly less than $h\nu$. Taking, for instance, hard X-rays whose wave-length is $10\lambda_0 = \cdot243$ A., or frequency is $\nu = \frac{1}{10}\frac{m_0c^2}{h}$, we have, from equation (15), $\frac{\nu'}{\nu} = \frac{10}{11}$ if the radiation is scattered at right angles to the primary beam, or the energy communicated to the electron $= h(\nu - \nu') = \frac{1}{11}h\nu$. If $\varphi = 0$ and $\theta = 180$, i.e. if the electrons are thrown straight forward, the energy of the recoil electron is $\frac{1}{8}h\nu$. Now the range is roughly proportional to the fourth power of the velocity, or the square of the kinetic energy, so the range of the recoil electron must be very much smaller than that of the photoelectron, and must be greater when the electron is thrown straight forward than when it is thrown aside at a smaller angle to the primary beam. Good qualitative agreement with theory can, then, be obtained by attributing sphere, comma, and fish tracks to the recoil electrons : the fish, which are the longest of the short tracks, have their tails towards the source of radiation, and so represent recoil electrons which have been thrown on in the forward direction. The large head of the fish is due to the fact that the ionisation increases as the velocity diminishes. The spheres represent electrons with very low initial velocity, thrown off at right angles, say, and the

commas are intermediate cases. Quantitative agreement with the theory has also been obtained by careful investigation of photographs taken by the Wilson method. A. H. Compton and A. W. Simon, who call the long photoelectron tracks P tracks, and the short recoil tracks R tracks, have, by measuring the R tracks, roughly confirmed the theoretical relation between range and angle at which the recoil electron is discharged. Further, using as primary beam homogeneous radiation, whose wave-length varied in different experiments from ·13 to ·71 A , they have shown that the ratio of the number of R to the number of P tracks increases rapidly as the wave-length is diminished, which is just what we should expect from the theory of the Compton effect here expounded. Other quantitative confirmation of the Compton theory of recoil electrons has been furnished by Bothe, who devised an ionisation method of measuring the maximum component of the range of recoil electrons normal to the primary beam. The velocity deduced from the range so measured agreed well with the theoretical values. There is, then, a large body of experimental evidence, firstly to show that the scattered radiation is softened and loses energy in the way deduced in the simple impact theory, and secondly to show that the struck electron gains energy as predicted by the theory, the variation of the effect with angle, with scattering substance, and with wave-length all agreeing well with the theoretical arguments. The light quant does, then, in this class of phenomenon, behave as if it were a little localised lump of energy travelling in a straight line.

It is, however, possible to give an account of the Compton effect on the hypothesis of Bohr, Kramers and Slater, and as the explanation offered has been made the occasion of a critical experimental test of the hypothesis it is of some importance to consider it. On the classical theory of the Doppler effect, we have for a source of radiation moving with a velocity $v = \beta c$,

$$\nu_0 = \nu' \frac{\mathrm{I} - \beta \cos \theta}{(\mathrm{I} - \beta^2)^{\frac{1}{2}}},$$

where ν_0 is the true frequency of the source, as measured by an observer moving with it, and ν' is the frequency of the radiation (as seen by an observer at rest) proceeding in a direction making

an angle θ with the path of the source.   If ν is the frequency as seen by an observer at rest situated in the line of motion of the source,

$$\nu_0 = \nu \frac{1-\beta}{(1-\beta^2)^{\frac{1}{2}}}.$$

Hence
$$\frac{\nu'}{\nu} = \frac{1-\beta}{1-\beta\cos\theta} = \frac{1}{1+\dfrac{\beta}{1-\beta}2\sin^2\dfrac{\theta}{2}}. \quad \ldots\ldots\ldots\ldots(17)$$

Equation (15) gives the ratio of the frequencies as seen by an observer looking obliquely at an angle θ and looking along the direction of propagation of the incident radiation respectively, as deduced from the light dart hypothesis.   It agrees with (17) if

$$\frac{\beta}{1-\beta} = \frac{\nu}{M} = \frac{h\nu}{m_0c^2},$$

whence
$$v = \beta c = \frac{h\nu/c}{h\nu/c^2 + m_0}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(18)$$

A source of radiation moving with the velocity v will give exactly the same diminished frequency for an observer looking at an angle θ to the direction of travel, as compared to an observer looking straight at the source along the line of travel, as does the light dart hypothesis.

Bohr, Kramers and Slater assume that the scattering of the incident radiation by " free " electrons takes place continuously, every electron emitting coherent spherical wavelets.   These wavelets behave classically as if emitted by an electron moving in the direction of the primary radiation with velocity v, depending on the frequency of the primary wave in the way given by equation (18), and hence the softening of the scattered radiation will agree with that experimentally found by Compton.   There is, however, no suggestion that the free electron actually moves forward with the velocity v : rather we are asked to make the assumption that the virtual oscillator emitting the classical wavelets can be in a different place from the electron with which it originated.*   Associated with the

* Presumably if incident radiation from more than one direction falls on a free electron the virtual oscillator can also be in several places at once, none of them that of the electron !

scattering of the radiation is a certain probability that the real electron will acquire a momentum in a given direction, there being no causal connection in this case any more than in the general theory of Bohr, Kramers and Slater. We assume a statistical, but not an atomic, conservation of momentum. There is no continuous transfer of momentum from the radiation to the electron, nor is there a sudden transference of momentum from a light quant to an electron, but there is a continuous classical scattering of a paradoxical type, accompanied by a probability, which can be calculated, that an electron shall acquire a momentum in a given direction θ.

Now Bothe and Geiger pointed out that this aspect of the theory was capable of an experimental test, which they subsequently carried out. If there is a causal connection between the scattering of a quant of radiation of modified frequency and the communication of momentum to an electron, and if the scattered radiation be allowed to fall upon matter, producing a photoelectron, then the emission of this photoelectron will occur simultaneously with the recoil of the free electron. On the theory of Bohr, Kramers and Slater, however, the scattered radiation is emitted continuously, and if it fall upon matter it will produce photoelectrons, the number of which is on the average the same as on the causal theory, but there will be no relation in time between the emission of the recoil electron in the primary beam, and the emission of the photoelectron. The two processes will occur independently of one another. Hence if it be experimentally possible to detect the moment at which the electrons of the two kinds are emitted we have a crucial test.

Now the ionisation produced by the passage of a single electron can be detected by a needle-point counter, of the type originally devised by Rutherford and Geiger for counting α particles. Bothe and Geiger passed a narrow beam of X-rays through hydrogen, and employed two point counters, one adapted to detect the passage of the recoil electron, and the other to detect the scattered radiation. The apparatus is represented in Fig. III. The primary beam is indicated by $h\nu$: it passes between the two point counters, one of which is open on the side turned towards the beam, while the other is

closed with a platinum foil 0·02 mm. thick.   This latter counter
is therefore protected from recoil electrons, but detects photo-
electrons liberated by the scattered radiation from the inner
side of the foil, and is therefore called the $h\nu'$ counter : the
open counter detects recoil electrons.   We cannot, of course,
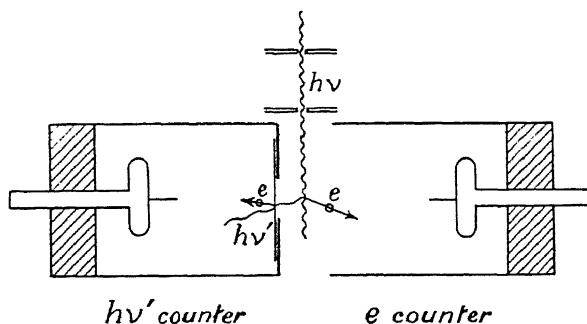
FIG. III.
Bothe and Geiger's apparatus.

expect as many throws in the electrometer connected with the
$h\nu'$ counter as with the e counter, since only a small fraction
of the scattered radiation releases photoelectrons.   The point
of the experiment is to determine whether the observed $h\nu'$
throws coincide with e throws, or whether there is no correlation
between the two phenomena.

Bothe and Geiger found that every eleventh $h\nu'$ throw
coincided with (i.e. occurred within a small arbitrary time
interval of) an e throw.   Calculation showed that a very much
smaller number of such coincidences was to be expected if
there were no correlation, as demanded by the hypothesis of
Bohr, Kramers and Slater, while, if the inevitable imperfections
of the recording conditions be taken into account, the agree-
ment with the hypothesis that scattered quant and recoil
electrons are causally connected is satisfactory.

A. H. Compton and Simon have investigated the same
question with the Wilson cloud chamber, and obtained coinci-
dences between recoil tracks and secondary β ray tracks
produced by the scattered radiation in such numbers that the
probability of their being due to chance was about 1/250.   We

may say, then, that the Bohr, Kramers, Slater theory of the Compton effect seems to be definitely put out of court by experiment, and with it the whole statistical view of radiation and quantum changes is seriously compromised. On the other hand, the theory of the light quant, on which the considerations given at the beginning of this section were founded, seems to be satisfactory as far as its applications in this limited field are concerned.

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CHAPTER XIX

CONCLUDING REMARKS

THE advances of knowledge which we have attempted to describe are the direct result of a series of remarkable developments of experimental technique. The future historian of science will probably record as one of the outstanding features of the period in which we live the ability, so rapidly acquired during the last decade or so, to deal with single atoms and small numbers of atoms. The methods of α-ray counting, of α-ray scattering and of α-ray analysis developed by Rutherford and his school, the ionisation tracks of C. T. R. Wilson, the mass ray technique devised by Aston represent a fundamentally new class of investigations. At the same time, the analysis of X-ray spectra by the crystal diffraction grating, initiated by Laue and immediately turned to account by W. H. and W. L. Bragg and by Moseley, has provided a powerful instrument for the investigation of the inner structure of the atom. The rapid improvement in methods of measuring the critical potentials, the importance of which was first emphasised by Lenard, has afforded essential information as to the forces by which the outer electrons are held, and definitely proved the existence of stationary states. The developments of high vacuum technique have rendered practicable the study of the behaviour of atoms when traversing long paths uninterrupted by collisions. The physicist who looks back fifteen years cannot but be impressed by the confidence with which we now attack problems then scarcely put forward as capable of solution. We should not be depressed by a limited success in certain branches of a subject in which, at a period within the lifetime of the youngest investigator, any success at all would have been unexpected.

From the theoretical standpoint the enunciation and rapid development of the quantum theory has played a leading part. Since the day when it was originally propounded by Planck it has shown a perhaps unexpected power of expressing the energy relations which govern the transformation of radiations of all frequencies. In particular the fundamental hypothesis expressed by the formula $E=h\nu$ has been experimentally confirmed over a very wide range, both as regards the energy imparted to an electron by a radiation of given frequency, and, *vice versa*, the frequency of the radiation excited by an electron of given energy. It holds for the ordinary photoelectric effect, where the electron has a velocity of a few volts, and, through a range of intermediate velocities, also for the electrons liberated by the γ rays, where the velocities are of the order of a hundred thousand volts. In this general field it commands such confidence that it is now used for measuring frequencies. Bohr's extension of the quantum relationship to connect a frequency of radiation with a transition between stationary states of the atom dominates the modern theory of spectra. Together with the theory of relativity, which is also involved in the theory of spectra, the quantum theory represents that departure from classical electrodynamics which characterises the recent attacks on the complex problems connected with the different aspects of radiation, but, whereas the theory of relativity, although born of experiment, can be argued as a matter of logical necessity, the quantum theory has no justification but its success, and actually cannot be reconciled with certain wave phenomena, such as interference. It represents a postulate beyond which, at present, we cannot see ; and all we can do is to be profoundly thankful that so far the elephantine philosophers have not offered to help us hatch out our quantic egg.

The book has been divided into two parts, the first dealing with the nuclear theory in general, and the second with the more particular problem of the arrangement of the extranuclear electrons. The experimental work described in Chapters II. to VI. has given results as to the interpretation of which there is little divergence of opinion. The calculations involved are, for the most part, of a comparatively simple nature, and based

upon the familiar laws of classical mechanics and electro-dynamics. It is particularly to be remarked, in view of the persistency with which the validity of all these laws is questioned where subatomic phenomena are concerned, that the inverse square law has been abundantly proved to hold for the repulsive force between nuclei, except they be very close. As the result of the work in question it is established as firmly as most of the conclusions in physics that the atom has a nuclear structure ; that the net positive charge of the nucleus is equal to the atomic number, and determines the chemical and optical properties of the atom ; that the mass is concentrated in the nucleus, and may be changed without alteration of the charge, while the charge can be changed without appreciably altering the mass. The conception of isotopes and isobares introduced in this connection has cleared up the question of fractional atomic weights, and brought with it far-reaching simplifications, especially in connection with the radioactive elements. However, experimental work now in progress both on the close collisions between nuclei and on the non-integral mass numbers of certain isotopes may show that the simple laws of the nucleus expounded in this book require drastic modification if they are to account for these phenomena.

The nuclear theory has made such progress, and the nucleus itself is so well established an entity that, as we have seen, investigations and speculations as to its structure are already plentiful. The size of the nucleus has been determined by Rutherford and his school in a variety of experiments which lead to consistent results. We know that the nucleus contains protons and electrons, and can estimate the number of each in a given nucleus ; that the helium nucleus, consisting of four protons and two electrons, forms a particularly stable group, which probably takes part as a whole in the structure of the nucleus ; and, further, that there are comparatively loosely-held protons which can be struck off from the nucleus of the atom of certain elements by swift α particles. The question, however, of the arrangement and conditions of motion of these nuclear components is bound up with immense difficulties. Whereas in the discussion of extranuclear phenomena it is possible to treat nucleus and electrons as point charges, owing

to the very open structure of the atom, we are confronted with the seeming paradox that, while the general nucleus contains some tens of electrons, its size is of the same order as that of a single electron. In this connection it must always be remembered that neither the size of the nucleus nor the size of an electron is as definite a quantity as the size of, say, a billiard ball.   There is a tendency to think of the size of the electron as the more certain of the two, because we have been talking about it longer, but, if we are to institute a comparison, the reverse is probably true.   Size is usually estimated by a sphere of impenetrability : thus the size of the billiard ball is measured as the size of a sphere impenetrable to the callipers,* and the size of a gas molecule as the sphere impenetrable to another gas molecule.   In other words, there is an abrupt change in the law of force between the test body and the body to be measured which takes place when the distance between the two is reduced to a certain magnitude : when this change takes place we say that the bodies are touching, and measure the size accordingly.   Now the size of the nucleus has been measured as the distance within which a very swift α particle can approach it without deforming the shape of the nucleus, or, to use the other method of expression, which corresponds more closely to what is actually observed in this case, the distance within which it can approach without causing marked departure from the inverse square law.   This determination falls into line with other determinations of size.   The size of the electron, however, has been taken as the size of the sphere on which the electric charge must be concentrated in order to give the observed mass electromagnetically † : we have no experimental evidence as to the way in which the force close to the electron varies with distance, or, in other words, as to the distance at which an electron ceases to act as a point charge. Our estimate of its size is, then, much more artificial than that

* By great pressure the points of the callipers may be brought closer together: the sphere is then said to be deformed.   Cf. the case of the α particle and nucleus.

† The size varies according to the distribution assumed for the charge : thus that deduced on the supposition that the charge is uniformly distributed over the surface (Lorentz electron) differs from that deduced on the assumption of a volume charge (Abraham electron).   For our point of view, however, the difference is insignificant.

made for the nucleus, since, in reaching it, we make assumptions which can resemble the physical truth only very remotely. It is true that this comparison does not take us much further, but it may serve to emphasise the fact that we know absolutely nothing of the behaviour of electrons when very close to one another. As to the size of the proton, if we determine it in the same way as that of the electron it comes out two thousand times smaller than the electron. We have, then, in a heavy nucleus a very large number of mobile centres of force acting on one another according to an unknown law of force, of which the most definite thing that we can say is that it is extremely unlikely to be the inverse square law. All that we can attempt at present with such a system is to obtain some rough general laws by extending our experimental knowledge. This we may well hope to do by examining more closely the a rays, and those particular β and γ rays which come from the nucleus itself ; but unfortunately the only atoms from which we get a nuclear radiation are the very heavy, and so most complex, ones. A first step has been made by Ellis, who has shown that the frequencies of the very penetrating γ rays can be expressed as the differences of terms, which, if the quantum law $E=h\nu$ holds within the nucleus, can be interpreted in terms of energy levels. At present, however, we know far too little of the behaviour of elementary charges in such close proximity, of the conditions for stability, and the connection between motion and radiation to hope to make a model of very definite structure. The only rules which have been put forward to account for the relative nuclear stabilities of the lighter atoms are tentative generalisations from the relative stabilities of the different radioactive atoms.

The radiations of the nucleus are spontaneous, and cannot be influenced by laboratory agents. When we turn to the extranuclear structure we enter a region which is much more accessible to experiment. The radiations from it undergo abrupt changes with different intensities of excitation : they are, in the optical case, modified in a continuous fashion by steady external electric and magnetic fields : we have further the behaviour of the atom under very rapidly alternating electric fields, as exemplified in optical dispersion, to consider.

There is available a vast body of empirical results by which to control any theory. Bohr's theory of orbits which obey the laws of classical mechanics, although the frequency of the radiation is derived from them by a formula which constitutes a denial of all classical laws, has, during the past twelve years, been searchingly investigated from all points of view by a body of brilliant mathematicians, especially of the German school, with the object of discovering how far it can describe the facts of optical and X-ray radiation. The theory has satisfactorily accounted for the line spectrum of hydrogen and of ionised helium, and for the Stark effect in such atoms (the normal Zeeman effect has also been satisfactorily covered, but was already described by the old theory), but even with these simple structures the problem of steady electric and magnetic field of different directions simultaneously applied, the so-called problem of crossed fields, has given rise to grave difficulties, which led Heisenberg to suggest that the methods of classical mechanics are not applicable to the calculation of orbits in this case. As regards the problem of the general atom, we have seen that Bohr has successfully derived the Rydberg and Ritz formulae from the general orbital theory, and has elaborated a half empirical scheme, which is intuitive rather than mathematical, to connect the general chemical and physical periodic properties with the spectra of the atomic radiations. The services of Stoner and Main Smith in extending this scheme have been noted. A brilliant confirmation of the theory, as far as the existence of stationary states is concerned, has been furnished by the experiments on critical potentials, and the general theory of stationary states has been utilised by Einstein for statistical considerations leading to Planck's radiation formula. The quantum theory of orbits has, however, signally failed to give an accurate quantitative description of the spectrum of neutral helium, and of all heavier atoms, although a satisfactory numerical representation of the broad features of certain simple spectra, notably those of the alkali metals, has been worked out.

Against this we have to set Sommerfeld's calculation of the relativity doublet, which, in spite of the obstacles in the way of reconciling it with other features of the orbital

scheme, gives so detailed a quantitative agreement that it still seems strange to believe that it can be founded on illusion, as appears from the standpoint of the new mechanics. The difficulties summarised in the conflict between inclination hypothesis and relativity hypothesis as an explanation of features of the multiplet structure are, however, merely characteristic of the troubles in which we find ourselves as soon as we attempt to explain the finer features of general spectra, among which the anomalous Zeeman effect and the Paschen-Back effect occupy a prominent place.   Non-integral quantum numbers, quantum numbers whose significance in the orbit model is ambiguous, four quantum numbers to characterise an electron with three degrees of freedom have all forced themselves upon us.   The truly mechanical features of the orbit scheme (speaking from the standpoint of classical mechanics) have retreated further and further into the background, and the willingness of the theoretical physicists to sacrifice dynamical sanity for the temporary description of an empirical rule has been occasionally bewildering.   The quantum theory has become, in its higher branches, a collection of numerical receipts, to which a superficial resemblance to a coherent mathematical theory has been given to hide their *ad hoc* character.   The difficulty of understanding them is not mathematical, but fundamental. Some of the rules recall irresistibly the teaching of the alchemists, or the witches' kitchen in *Faust*.

The quantum theory of spectra as originally formulated by Bohr concerned itself solely with frequencies of line spectra, and did not attempt to describe intensities or polarisations. It may, perhaps, even be said that the theory is due to the accident that we have long been able to measure frequencies very accurately, while the measurement of intensities is a technique of recent growth, which is still far from approaching the precision of frequency measurements.   There is nothing in the empirical intensities which can count as a confirmation of the fundamental features of the quantum theory.   They have been brought within its scope by the correspondence principle, which shows · how the classical theory—which connects intensities very simply with the electric moment of the electron

in its orbit—can be made to agree with the quantum theory in a limiting case, and then extending the results to the general case. In dealing with intensities, then, we lean heavily upon the classical theory, but, as we have seen in the preceding chapter, in dealing with dispersion we have to lean still more heavily.' Historically we may say that the first instinctive revulsion at the unreasonable character of the quantum theory of spectra, with its non-radiating orbits, the first incredulity, was followed by a belief in the infallibility of the theory as a method of attacking all spectral problems. The accumulation of facts which can only be explained by fanciful distortions is, however, leading to a conclusion that some at least of the fundamental postulates must be abandoned or drastically changed.

While, then, the theory of orbits governed by mechanical laws has led to many striking quantitative results which it would be ungrateful to minimise, it has in the end brought us into a wilderness which, in spite of the most assiduous cultivation, has failed to yield the anticipated crop of fruitful relations. The theory of stationary states, and the frequency rule $h\nu = E - E'$ have, however, retained their validity throughout. They are, in fact, expressions of relations which are capable of direct experimental verification, and which have actually been confirmed in many directions. The orbit hypothesis, however, designed to enable the energy of the stationary states to be calculated, is in a different class, for so far no one has been able even to suggest a way in which it might be experimentally tested. It demands an electron executing a multiply periodic motion under the influence of the laws of classical mechanics, and, now that we know its insufficiency, we may say that it would have been astonishing if it had proved of universal application, considering that the frequency conditions with which it is involved represent so definite a break with classical mechanics. The stationary states and the frequency condition are compatible with any mechanism for determining the energy of the stationary states, and by no means inevitably demand the Bohr orbits. Recently, therefore, the question has arisen as to whether we cannot get rid of the orbits altogether, and devise some other method for deriving the frequencies, and also

the intensities and polarisations, which on Bohr's theory are deduced from the orbital motion itself by application of the correspondence principle. A plan for doing this has been put forward in the " new " quantum mechanics of Heisenberg, to which incidental reference has been made in the latter part of this book. It has been extended by Born and Jordan, and by Dirac, and has paved the way for new developments which are likely to exercise a profound influence on atomic theory. It appeared too recently for a proper discussion to be included in the body of the book, but it can hardly be passed over in these concluding remarks without a word as to its scope and significance.

The plan with which Heisenberg started out was to avoid the use of conceptions which are not subject to direct experimental control, such as position, phase and period of a circulating electron. The general standpoint adopted may be illustrated by a reference to the nature of thermodynamic theory. In thermodynamics we make no appeal to atomic machinery, but deal only with quantities which can be experimentally observed, such as energy, pressure, temperature and volume. In the early days of the science it might well have been argued (and was, in fact, maintained by Ostwald as late as the beginning of the present century) that we could never possibly get any direct experimental evidence of the existence of atoms, and that therefore we should dispense with the atomic hypothesis and throw back everything upon considerations of energy, which is an experimental quantity. Again, in the theory of relativity, Einstein renounced all the machinery of a hypothetical ether with mechanical properties which no experiment could detect, and the intuitive conception of simultaneity, and reduced everything to quantities capable, in their nature, of direct measurement. We see, then, that the revolt from a machinery out of range of experimental control, constructed to afford relations between quantities which are measurable, has taken place before in the history of science, and has led to powerful methods which are of general application. The example of thermodynamics should warn us, however, against asserting too confidently that the mechanism of electron orbits is essentially outside the range of direct observa-

tion, for the atomic mechanism with which it dispensed has, since the days when the theory was built up, been directly verified by such experiments as those on the Brownian movement.

Heisenberg is, then, concerned to discover a mathematical machinery which shall connect with one another the empirical quantities, such as frequencies, intensities, and energies of stationary states, without making use of electron orbits. He employs, in effect, the conception of virtual oscillators, which we discussed in the preceding chapter, each one of which has a frequency conditioned by two quantum numbers pertaining to stationary states, given by the Bohr relation $h\nu(m, n) = E_n - E_m$. The frequencies of the collection of oscillators corresponding to a series of values of m and n are not, in consequence, harmonics (*i.e.* integral multiples of a fundamental frequency), but obey the combination law of Ritz. Corresponding to a quantum oscillator will be a whole battery—or orchestra, to use a more melodious term—of virtual oscillators which are collected together as a manifold expressing all possible states of the given atomic system, and rules have to be found for manipulating these manifolds. In the form given to the theory by Born, Heisenberg and Jordan these manifolds are matrices which obey the addition and multiplication laws of such arrays. The commutative law of multiplication does not hold for these quantities, and this fact is utilised in introducing the quantum constant h into the formulae. The problem is to find the energies of the stationary states without using any mechanical model to give a dynamical picture corresponding to our classical orchestra. A matrix **p** and another matrix **q** are formed from the collection of classical oscillators, and a special mechanism, made as analogous as possible to that of ordinary Hamiltonian mechanics, is devised for the calculation of the energies. The correspondence principle is not a supplementary concept to the new quantum theory, but is, rather, embodied in it. These few words can, of course, give no satisfactory idea of the new theory, but may, perhaps, suffice to indicate both its strength and its weakness. Its strength is that it operates with manifolds which represent directly the observed radiation, and not with p's and q's which belong to hypothetical electron orbits,

and that the quantum conditions are an organic part of the mechanics, and not limitations added as an afterthought, as it were. Its weakness is that we have no geometrical or mechanical picture of what is going on to make the problem resemble those to which we are accustomed, and that the mathematical machinery is very difficult to operate, at any rate for those who, like the present writer, are new to it. We can only rely on custom to reconcile us to what now appears awkward and strange. The quantum condition $h\nu = E - E'$, which we now handle so freely and which is heard from the lips of babes, seemed strange, if not revolting, at first, and we think that we understand it now only because time has rendered it familiar.

The new quantum theory is still on its trial, but it has started off with considerable achievements, just as did the old. The difficulties of the half integral quantum numbers do not occur with it : the theory decides of itself, and rightly, whether a quantum number is to be integral or half integral. The dispersion theory of Kramers falls naturally within its scope, as even the little that has been said here would indicate. Pauli has succeeded in deducing the formula for the Balmer series, the Stark effect, and the fine structure from the new theory. As regards the anomalous Zeeman effect and multiplet structure, nothing can be done as long as the electron is considered as having only three degrees of freedom. If, however, the spinning electron of Uhlenbeck and Goudsmit be introduced, possessing itself mechanical and magnetic moment, the ratio of which is double as great as it is for the atom itself, then the new mechanics can give an account of the features just cited. Much may be hoped from the combination of spinning electron and new mechanics, but so far the spectrum of neutral helium awaits calculation.

Still more recently Schrödinger has put forward a theory of atomic mechanics which is based on ideas of L. de Broglie's concerning the theory of groups of waves. It is far too difficult to be discussed at this stage, but those few who profess to be conversant with it seem to hold high hopes of its future performance.

As regards the problems of chemical combination, it is satisfactory to note that the modified Bohr scheme of grouping electrons into assemblies characterised by three quantum numbers, which was derived by Main Smith from chemical considerations, agrees exactly with that deduced by Stoner from evidence mainly of a physical character. We have further noted Sidgwick's attempt to explain co-ordination compounds in terms of the incompleted inner groups of Bohr's scheme. Consideration of the facts of chemical combination has, however, failed to throw light on details of atomic structure, as distinct from the general ordering of electrons into different classes. Two rival schemes of atomic structure have been used to discuss chemical problems, which are generally spoken of as the static and the dynamic model, but as long as arguments are simply based on the numbers of electrons in different classes of sub-groups, and the stage of atomic development at which given sub-groups are initiated and completed, it is clearly a matter of indifference whether the electrons be thought of as moving or at rest, provided that certain combining properties are associated with certain stages of group development. When the static atom of Lewis and Langmuir was first put forward it was hailed with enthusiasm by the chemists : its placid and unchanging external cubical faces seemed to promise a solution of their troubles. The fact that it could be cut out of cardboard was a source of solid comfort. The conception of electron sharing, to which it so readily lent itself, certainly worked well for many simple inorganic salts, but it can scarcely be claimed to apply to the majority of inorganic compounds. The organic chemists do not appear to have found in it that unifying principle which is so much to be desired. Incidentally, electron sharing in itself does not necessarily imply a static model ; as long as it is merely a qualitative conception we can think instead of an electron orbit embracing two nuclei in some way or other, or simply speak of shared electrons without defining how they are shared. There can, in fact, be no real conflict between the static and the dynamic model until the two different theories are in a position to make predictions which are different in the two cases, and no decision until such predictions can be put to an experimental test. At present

neither theory (nor any of the various modified theories of the organic chemists) seems to be able to make any definite decision as to what combination phenomena are to be expected unless the result is known beforehand, and when this is the case all theories seem, in the hands of their supporters, equally successful in predicting it.   What has recommended the dynamic atom to the physicist is its quantitative achievement, which is definite though limited in scope.   As long as we cannot calculate orbits for an atom disturbed by the near presence of another atom, with another nucleus, little is to be expected from it in the way of description of chemical combination. The electron theory of chemistry, it must be confessed, has not so far had any striking successes of the first order to record.

We have noted that it looks as if the conception of electron orbits is to assume less importance in the future quantum theory of spectra.   The energy of the stationary states retains, however, its fundamental importance.   It is possible that in the chemistry of the future we shall not lay much stress upon the positions of the electrons, but operate with the energies of stationary states, and reduce all questions of chemical combination to a branch of thermodynamics.   The work of Grimm and Sommerfeld offers an early example of a way in which this may be done.

The study of the structure of the atom is in its first youth, a period of vigorous achievement, when too much introspection is unhealthy.   While fresh knowledge is being so rapidly won by repeated experiment, both in the laboratory and the study —for the mathematician is experimenting just as much as the practical physicist ; the disciple of the quantum theory has to discover his principles empirically, and justify them by trial— we should not be too much disturbed by a certain lack of logic, a certain hastiness and enthusiastic dogmatism which characterises the views put forward in some quarters.   We may well, in our rapid advance, leave behind us unsolved difficulties, to be dealt with at leisure.   After the ebullient activity of the present time will come a period of comparative rest and reflection, when the results won will be more carefully ordered than is now possible, and will receive that certificate of respectability which is conferred, late in life, by the text-book writer, with

his *ne varietur*. Some difficulties will be explained away, others we shall think of as explained, because we have become reconciled to their continued existence. Whatever may be the fate of the theories which have been so inadequately exposed in this book, whatever modifications or mishaps they may meet, the experimental facts which led to their formation, and those others to whose discovery they in their turn gave rise, will remain as definite knowledge, to form a lasting ornament to an age otherwise rich in manifold disaster and variety of evil change.

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L. DE BROGLIE. Recherches sur la théorie des quanta. Thèse presentée à la faculté des sciences de l'université de Paris. 1924. Also *Ann. de Physique*, **3**, 22, 1925.

E. SCHRÖDINGER. Quantisierung als Eigenwert problem. *Ann. d. Phys.*, **79**, 361, 489, 1926; **80**, 437, 1926; **81**, 109, 1926.

—— Über das Verhältniss der Heisenberg-Born-Jordanschen Quantenmechanik zu der meinen. *Ann. d. Phys.*, **79**, 734, 1926.

An excellent summary of the work of Heisenberg, Born and Jordan is given in :

BORN. Probleme der Atommechanik. 1926. Springer.

APPENDIX I

ABSORPTION AND DIMINUTION OF VELOCITY OF CATHODE RAYS.

SINCE there is sometimes confusion on the subject of absorption and diminution of velocity of cathode rays passing through a given thickness of matter, a series of curves (Figs. 112, 113 and 114) is here offered which expresses (1) the reduction of intensity (intensity being defined as the number of electrons per second which fall on unit area set normal to the direction of the rays) which takes place on passage through various thicknesses of aluminium, and (2) the reduction of velocity.

Each separate curve starts at the top of the diagram with a value of the intensity arbitrarily taken as 1, and a velocity indicated by a value of v. The reduction of intensity to a fraction of its initial value of 1 is given by the course of the curve, the reduction of velocity by the short cross lines on the curve itself, each with a value of the velocity attached. When the value of the ordinate becomes too small for convenient reading a fresh curve is started. The diagrams cover all velocities from ·99 c. to ·255 c.

The curves have been copied from a publication of P. Lenard's (*Quantitatives über Kathodenstrahlen aller Geschwindigkeiten.* Heidelberger Akademie der Wissenschaften, 1918), which is not generally accessible in England. They are calculated from smoothed values of the absorption coefficient, and from smoothed curves giving the value of $\frac{dv}{dx}$. The broken curves give the intensity as measured by the conductivity produced in air.
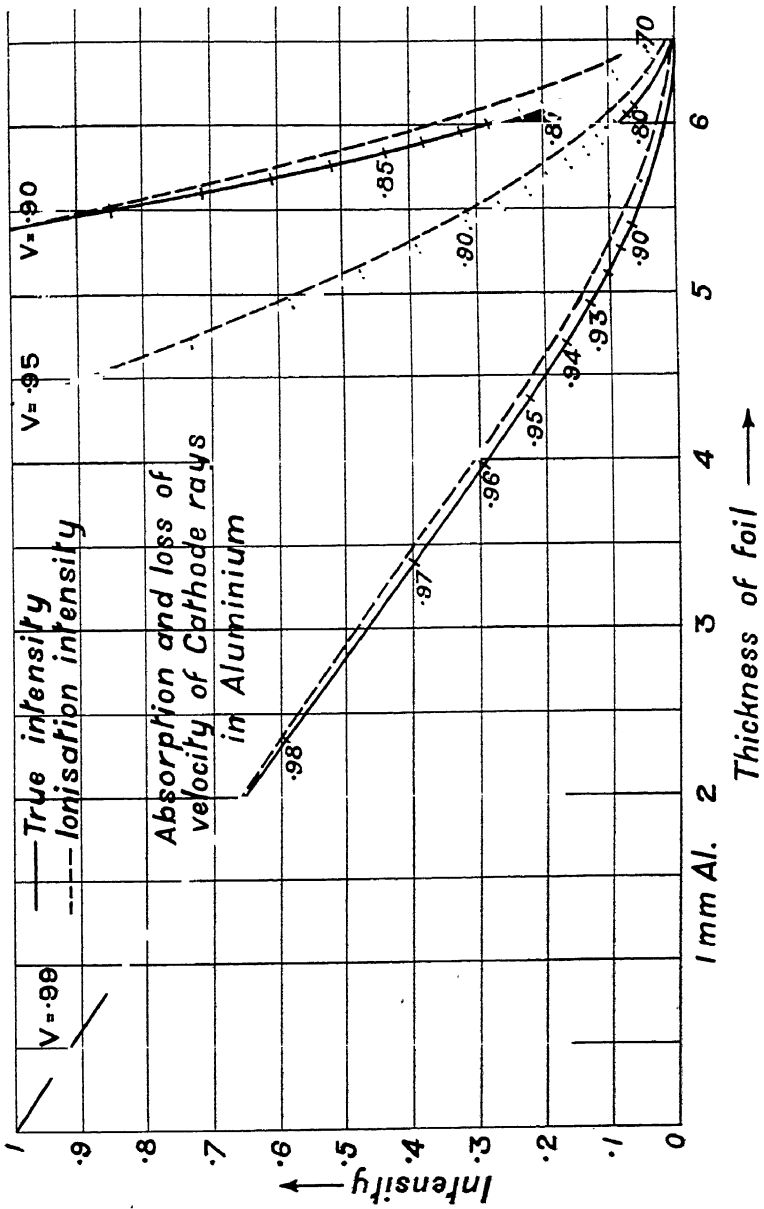
FIG. 112.
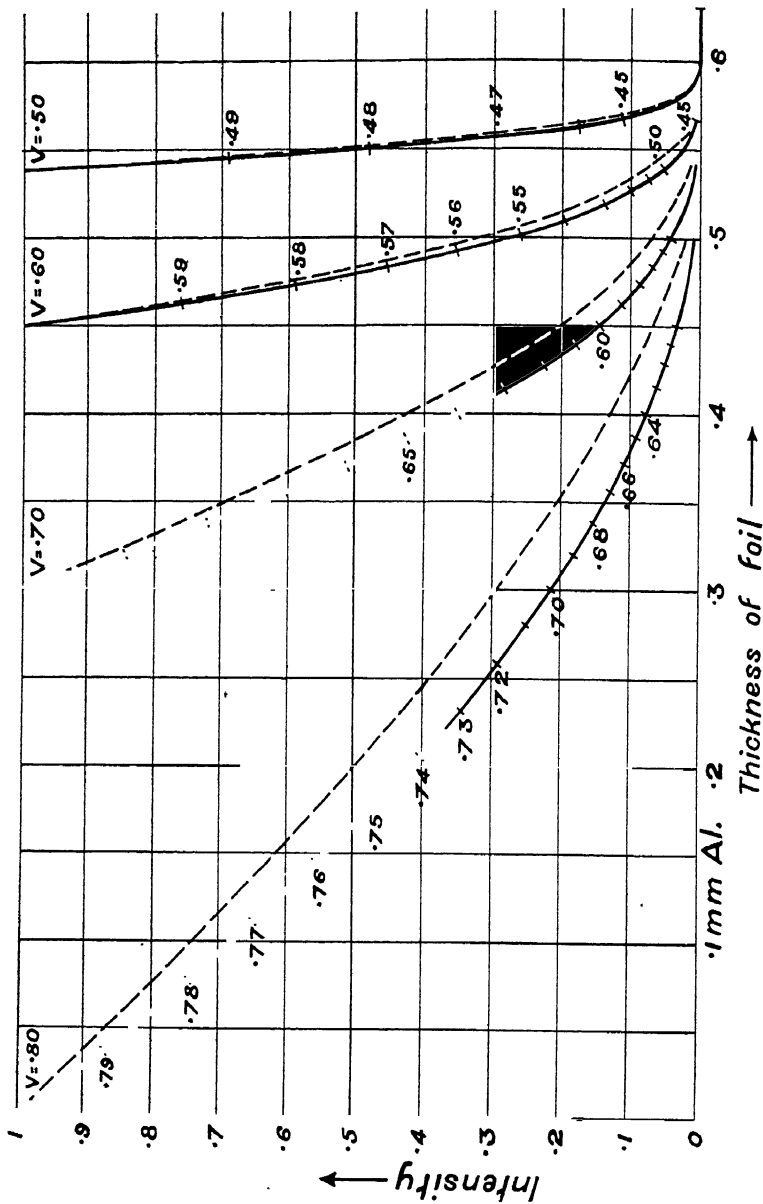
FIG. 113.
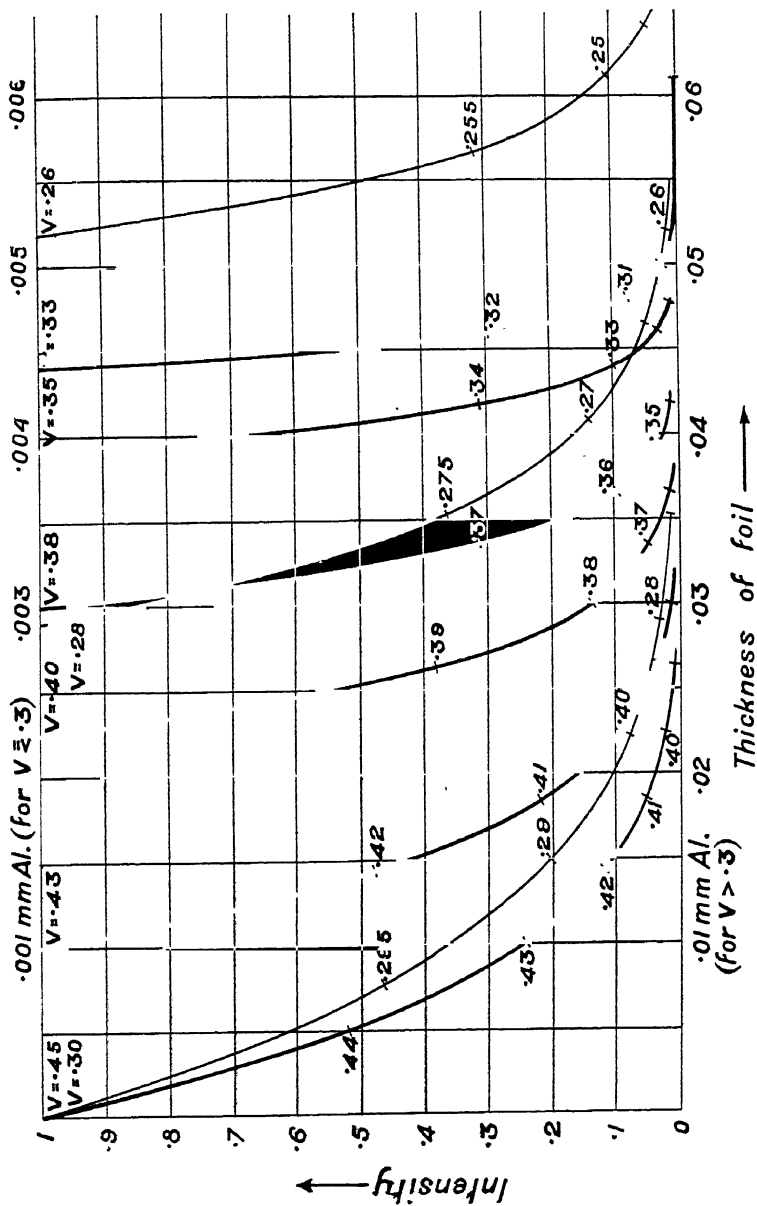
Fig. 114.

APPENDIX II

THE following table is calculated from Einstein's formula for the kinetic energy of an electron :

$$\text{kinetic energy} = m_0 c^2 \left(\frac{1}{\sqrt{1-\beta^2}} - 1 \right) = \frac{1}{300} \, Ve,$$

where m_0 is the rest mass of the electron, c the velocity of light, β the velocity of the electron expressed as a fraction of c, V the velocity in volts, and e the charge on the electron in electrostatic units. The following values of the constants have been adopted :

$$e = 4 \cdot 774 \times 10^{-10} \text{ E.S.U.},$$

$$\frac{e}{m_0} = 1 \cdot 760 \times 10^7 \text{ E.M.U.},$$

which gives

$$m_0 = 9 \cdot 042 \times 10^{-28} \text{ grams},$$

$$c = 3 \times 10^{10} \text{ cm./sec.}$$

We then have

$$V = 5 \cdot 11 \times 10^5 \left(\frac{1}{\sqrt{1-\beta^2}} - 1 \right).$$

β	V	β	V	β	V
·005	6·37 volts	·5	79·1 × 10³	·88	5·65 × 10⁵
·01	25·55	·55	101·0	·89	6·10
·02	102·2	·6	127·8	·90	6·62
·03	230·0	·65	161·4	·91	7·22
·04	409	·7	204·6	·92	7·93
·05	637	·75	261·5	·93	8·79
·1	2·56 × 10³	·8	341	·94	9·86
·15	5·84	·81	3·61 × 10⁵	·95	11·25
·2	10·54	·82	3·82	·96	13·10
·25	16·76	·83	4·05	·97	15·91
·3	24·68	·84	4·31	·98	20·57
·35	34·5	·85	4·59	·99	31·1
·4	46·5	·86	4·90	·995	46·0
·45	61·2	·87	5·25	·998	75·7

APPENDIX III

ATOMIC NUMBERS OF THE ELEMENTS.

PERIOD I.
1. Hydrogen.
2. Helium.

PERIOD II.
3. Lithium.
4. Beryllium.
5. Boron.
6. Carbon.
7. Nitrogen.
8. Oxygen.
9. Fluorine.
10. Neon.

PERIOD III.
11. Sodium.
12. Magnesium.
13. Aluminium.
14. Silicon.
15. Phosphorus.
16. Sulphur.
17. Chlorine.
18. Argon.

PERIOD IV.
19. Potassium.
20. Calcium.
21. Scandium.
22. Titanium.
23. Vanadium.
24. Chromium.
25. Manganese.
26. Iron.
27. Cobalt.
28. Nickel.
29. Copper.
30. Zinc.
31. Gallium.
32. Germanium.
33. Arsenic.
34. Selenium.
35. Bromine.
36. Krypton.

PERIOD V.
37. Rubidium.
38. Strontium.
39. Yttrium.
40. Zirconium.
41. Niobium.
42. Molybdenum.
43. Masurium.
44. Ruthenium.
45. Rhodium.
46. Palladium.
47. Silver.
48. Cadmium.
49. Indium.
50. Tin.
51. Antimony.
52. Tellurium.
53. Iodine.
54. Xenon.

PERIOD VI.
55. Caesium.
56. Barium.
57. Lanthanum.
58. Cerium.
59. Praseodymium.
60. Neodymium.
61. Illinium.
62. Samarium.
63. Europium.
64. Gadolinium.
65. Terbium.
66. Dysprosium.
67. Holmium.
68. Erbium.
69. Thulium.
70. Ytterbium.

71. Lutecium.
72. Hafnium.
73. Tantalum.
74. Tungsten.
75. Rhenium.
76. Osmium.
77. Iridium.
78. Platinum.

79. Gold.
80. Mercury.
81. Thallium.
82. Lead.
83. Bismuth.
84. Polonium.
85. ——
86. Radon.

PERIOD VII.

87. ——
88. Radium.
89. Actinium.
90. Thorium.
91. Protoactinium.
92. Uranium.

APPENDIX IV

Velocity of Light $=c$ $=2\cdot9986 \times 10^{10}$ cm./sec.

Electronic charge $=e$ $=(4\cdot774 \pm \cdot005) \times 10^{-10}$ E.S.U.

whence

Energy of Electron falling
   through 1 Volt $=(1\cdot591 \pm \cdot002) \times 10^{-12}$ ergs.

$\dfrac{\text{Electronic charge}}{\text{Electronic mass}}$ $=\dfrac{e}{m_0}$ $=(1\cdot760 \pm \cdot008) \times 10^{7}$ E.M.U.

whence

Electronic mass $=m_0$ $=(9\cdot042 \pm \cdot009) \times 10^{-28}$ grams.

Planck's Constant $=h$ $=(6\cdot545 \pm \cdot009) \times 10^{-27}$ erg sec.

Rydberg's Constant :
        for Hydrogen $=R_H$ $=109677\cdot70 \pm \cdot04,$
         for Helium $=R_{He}$ $=109722\cdot14 \pm \cdot04,$
for infinitely heavy nucleus $=R_\infty$ $=109737\cdot11 \pm \cdot06.$

Avogadro's Constant $=N$ $=(6\cdot062 \pm \cdot006) \times 10^{23}$ mols.
                                   per gram-mol.

Loschmidt's Number $=n$ $=(2\cdot705 \pm \cdot003) \times 10^{19}$ mols.
                                   per c.c.

Kinetic Energy of Trans-
   lation of one Molecule
   at 0° C. $=E_0$ $=(5\cdot621 \pm \cdot006) \times 10^{-14}$ ergs.

Mass of Hydrogen Atom $=(1\cdot662 \pm \cdot002) \times 10^{-24}$ grams.

APPENDIX V

THE following table is taken from a paper on " Atomic States
and Spectral Terms," by J. C. McLennan, A. B. McLay, and
H. G. Smith, which has just been published (*Proceedings of the
Royal Society*, 112, 76, August 1926). It shows the distribu-
tion of the extra-nuclear electrons among the n_k orbits originally
contemplated by Bohr,—the subdivision of the n_k sub-groups
into grouplets, invoked by Stoner and by Main Smith, being
disregarded. The authors refer to a paper by P. D. Foote
(*Transactions of the American Institute of Mining and Metal-
lurgical Engineers*, No. 1547 D, p. 1), which is not accessible to
me, where the subdivision into grouplets is discussed.

As regards the basic terms, the S, P, D, F, G... terms
correspond to values 1, 2, 3, 4, 5... for l (see Chapter XV.).
The various possible values for j are given in the usual j position,
the value of j predicted to correspond to the lowest term being
printed in clarendon. Thus for carbon, $^3P_{012}$ indicates that
the basic term is a triplet P term, the values of j for the three
components being 0, 1, 2, of which the $^3P_0$ term is the lowest.

TABLE I

Element.	At. No.	Atomic Weight.	EXTRA-NUCLEAR ELECTRONIC CONFIGURATIONS.							Basic Spectral Term.
			K 1_1	L 2_1 2_2	M 3_1 3_2 3_3	N 4_1 4_2 4_3 4_4	O 5_1 5_2 5_3 5_4 5_5	P 6_1 6_2 6_3 6_4 6_5 6_6	Q 7_1 7_2 7_3	
H	1	1·008	1							$^2S_1$
He	2	3·99	2							$^1S_0$
Li	3	6·94	2	1						$^2S_1$
Be	4	9·1	2	2						$^1S_0$
B	5	10·9	2	2 1						$^2P_{12}$
C	6	12·0	2	2 2						$^3P_{012}$
N	7	14·01	2	2 3						$^4S_2$
O	8	16·0	2	2 4						$^3P_{012}$

TABLE I—*(continued)*

Element.	At. No.	Atomic Weight.	EXTRA-NUCLEAR ELECTRONIC CONFIGURATIONS.							Basic Spectral Term.
			K 1_1	L $2_1\ 2_2$	M $3_1\ 3_2\ 3_3$	N $4_1\ 4_2\ 4_3\ 4_4$	O $5_1\ 5_2\ 5_3\ 5_4\ 5_5$	P $6_1\ 6_2\ 6_3\ 6_4\ 6_5\ 6_6$	Q $7_1\ 7_2\ 7_3$	
F	9	19·0	2	2 5						$^2P_{12}$
Ne	10	20·2	2	2 6						$^1S_0$
Na	11	23·0	2	2 6	1					$^2S_1$
Mg	12	24·32	2	2 6	2					$^1S_0$
Al	13	27·1	2	2 6	2 1					$^2P_{12}$
Si	14	28·3	2	2 6	2 2					$^3P_{012}$
P	15	31·04	2	2 6	2 3					$^4S_2$
S	16	32·06	2	2 6	2 4					$^3P_{012}$
Cl	17	35·46	2	2 6	2 5					$^2P_{12}$
A	18	39·88	2	2 6	2 6					$^1S_0$
K	19	39·1	2	2 6	2 6	1				$^2S_1$
Ca	20	40·07	2	2 6	2 6	2				$^1S_0$
Sc	21	44·1	2	2 6	2 6 1	2				$^2D_{23}$
Ti	22	48·1	2	2 6	2 6 2	2				$^3F_{234}$
V	23	51·06	2	2 6	2 6 3	2				$^4F_{2345}$
Cr	24	52·0	2	2 6	2 6 5	1				$^7S_3$
Mn	25	54·93	2	2 6	2 6 5	2				$^6S_3$
Fe	26	55·84	2	2 6	2 6 6	2				$^5D_{01234}$
Co	27	58·97	2	2 6	2 6 7	2				$^4F_{2345}$
Ni	28	58·68	2	2 6	2 6 8	2				$^3F_{234}$
Cu	29	63·57	2	2 6	2 6 10	1				$^2S_1$
Zn	30	65·37	2	2 6	2 6 10	2				$^1S_0$
Ga	31	69·9	2	2 6	2 6 10	2 1				$^2P_{12}$
Ge	32	72·5	2	2 6	2 6 10	2 2				$^3P_{012}$
As	33	74·96	2	2 6	2 6 10	2 3				$^4S_2$
Se	34	79·2	2	2 6	2 6 10	3 4				$^3P_{012}$
Br	35	79·92	2	2 6	2 6 10	2 5				$^2P_{12}$
Kr	36	82·92	2	2 6	2 6 10	2 6				$^1S_1$
Rb	37	85·45	2	2 6	2 6 10	2 6	1			$^2S_1$
Sr	38	87·63	2	2 6	2 6 10	2 6	2		·	$^1S_0$
Y	39	89·0	2	2 6	2 6 10	2 6 1	2			$^2D_{23}$
Zr	40	90·6	2	2 6	2 6 10	2 6 2	2			$^3F_{234}$
Cb	41	93·5	2	2 6	2 6 10	2 6 4	1			$^6D_{12345}$
Mo	42	96·0	2	2 6	2 6 10	2 6 5	1			$^7S_3$
Ma	43		2	2 6	2 6 10	2 6 6	1			$^6D_{12345}$
Ru	44	101·7	2	2 6	2 6 10	2 6 7	1			$^5F_{12345}$

TABLE I—(continued)

Element	At. No.	Atomic Weight	K 1_1	L $2_1\ 2_2$	M $3_1\ 3_2\ 3_3$	N $4_1\ 4_2\ 4_3\ 4_4$	O $5_1\ 5_2\ 5_3\ 5_4\ 5_5$	P $6_1\ 6_2\ 6_3\ 6_4\ 6_5\ 6_6$	Q $7_1\ 7_2\ 7_3$	Basic Spectral Term
Rh	45	102·9	2	2 6	2 6 10	2 6 8	1			$^4F_{2345}$
Pd	46	106·7	2	2 6	2 6 10	2 6 10				$^1S_0$
Ag	47	107·88	2	2 6	2 6 10	2 6 10	1			$^2S_1$
Cd	48	112·40	2	2 6	2 6 10	2 6 10	2			$^1S_0$
In	49	114·8	2	2 6	2 6 10	2 6 10	2 1			$^2P_{12}$
Sn	50	118·7	2	2 6	2 6 10	2 6 10	2 2			$^3P_{012}$
Sb	51	120·2	2	2 6	2 6 10	2 6 10	2 3			$^4S_2$
Te	52	127·5	2	2 6	2 6 10	2 6 10	2 4			$^3P_{012}$
I	53	126·92	2	2 6	2 6 10	2 6 10	2 5			$^2P_{12}$
Xe	54	130·32	2	2 6	2 6 10	2 6 10	2 6			$^1S_0$
Cs	55	132·81	2	2 6	2 6 10	2 6 10	2 6	1		$^2S_1$
Ba	56	137·37	2	2 6	2 6 10	2 6 10	2 6	2		$^1S_0$
La	57	139·0	2	2 6	2 6 10	2 6 10	2 6 1	2		$^2D_{23}$
Ce	58	140·25	2	2 6	2 6 10	2 6 10 1	2 6 1	2		$^3H_{456}$
Pr	59	140·6	2	2 6	2 6 10	2 6 10 2	2 6 1	2		$^4K_{6789}$?
Nd	60	144·3	2	2 6	2 6 10	2 6 10 3	2 6 1	2		$^5L_{678910}$
Il	61		2	2 6	2 6 10	2 6 10 4	2 6 1	2		$^6L_{5678910}$
Sm	62	150·4	2	2 6	2 6 10	2 6 10 5	2 6 1	2		$^7K_{45678910}$
Eu	63	152·0	2	2 6	2 6 10	2 6 10 6	2 6 1	2		$^8H_{23456789}$
Gd	64	157·3	2	2 6	2 6 10	2 6 10 7	2 6 1	2		$^9D_{23456}$
Tb	65	159·2	2	2 6	2 6 10	2 6 10 8	2 6 1	2		$^8H_{23456789}$
Dy	66	162·5	2	2 6	2 6 10	2 6 10 9	2 6 1	2		$^7K_{45678910}$
Ho	67	163·5	2	2 6	2 6 10	2 6 10 10	2 6 1	2		$^6L_{5678910}$
Er	68	167·4	2	2 6	2 6 10	2 6 10 11	2 6 1	2		$^5L_{678910}$
Tm	69	168·5	2	2 6	2 6 10	2 6 10 12	2 6 1	2		$^4K_{6789}$
Yb	70	173·5	2	2 6	2 6 10	2 6 10 13	2 6 1	2		$^3H_{456}$
Lu	71	175·0	2	2 6	2 6 10	2 6 10 14	2 6 1	2		$^2D_{23}$
Hf	72	178·0	2	2 6	2 6 10	2 6 10 14	2 6 2	2		$^3F_{234}$
Ta	73	181·5	2	2 6	2 6 10	2 6 10 14	2 6 3	2		$^4F_{2345}$
W	74	184·0	2	2 6	2 6 10	2 6 10 14	2 6 4	2		$^5D_{01234}$
Re	75		2	2 6	2 6 10	2 6 10 14	2 6 5	2		$^6S_3$
Re	75		2	2 6	2 6 10	2 6 10 14	2 6 6	1		$^6D_{12345}$
Os	76	190·9	2	2 6	2 6 10	2 6 10 14	2 6 6	2		$^5D_{01234}$
Os	76		2	2 6	2 6 10	2 6 10 14	2 6 7	1		$^5F_{12345}$
Ir	77	193·1	2	2 6	2 6 10	2 6 10 14	2 6 7	2		$^4F_{2345}$
Ir	77		2	2 6	2 6 10	2 6 10 14	2 6 8	1		$^4F_{2345}$
Pt	78	195·2	2	2 6	2 6 10	2 6 10 14	2 6 8	2		$^3F_{234}$
Pt	78		2	2 6	2 6 10	2 6 10 14	2 6 9	1		$^3D_{123}$
Pt	78		2	2 6	2 6 10	2 6 10 14	2 6 10			$^1S_0$
Au	79	197·2	2	2 6	2 6 10	2 6 10 14	2 6 10	1		$^2S_1$
Hg	80	200·6	2	2 6	2 6 10	2 6 10 14	2 6 10	2		$^1S_0$

TABLE I—*(continued)*

Element.	At. No.	Atomic Weight.	EXTRA-NUCLEAR ELECTRONIC CONFIGURATIONS.							Basic Spectral Term.
			K 1_1	L $2_1\ 2_2$	M $3_1\ 3_2\ 3_3$	N $4_1\ 4_2\ 4_3\ 4_4$	O $5_1\ 5_2\ 5_3\ 5_4\ 5_5$	P $6_1\ 6_2\ 6_3\ 6_4\ 6_5\ 6_6$	Q $7_1\ 7_2\ 7_3$	
Tl	81	204·0	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1		$^2P_{12}$
Pb	82	207·2	2	2 6	2 6 10	2 6 10 14	2 6 10	2 2		$^3P_{012}$
Bi	83	208·0	2	2 6	2 6 10	2 6 10 14	2 6 10	2 3		$^4S_2$
Po	84	210·0	2	2 6	2 6 10	2 6 10 14	2 6 10	2 4		$^3P_{012}$
Eka-I.	85		2	2 6	2 6 10	2 6 10 14	2 6 10	2 5		$^2P_{12}$
Rn	86	222·0	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6		$^1S_0$
Eka-Cs.	87		2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1	$^2S_1$
Ra	88	226·0	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2	$^1S_0$
Ac	89	227·0	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2	$^2D_{23}$
Th	90	232·15	2	2 6	2 6 10	2 6 10 14	2 6 10 1	2 6 1	2	$^3H_{456}$
Th	90		2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 2	2	$^3F_{234}$
Pa	91	230·0	2	2 6	2 6 10	2 6 10 14	2 6 10 2	2 6 1	2	$^4K_{6789}$
Pa	91		2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 3	2	$^4F_{2345}$
U	92	238·2	2	2 6	2 6 10	2 6 10 14	2 6 10 3	2 6 1	2	$^5L_{678910}$
U	92		2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 4	2	$^5D_{01234}$
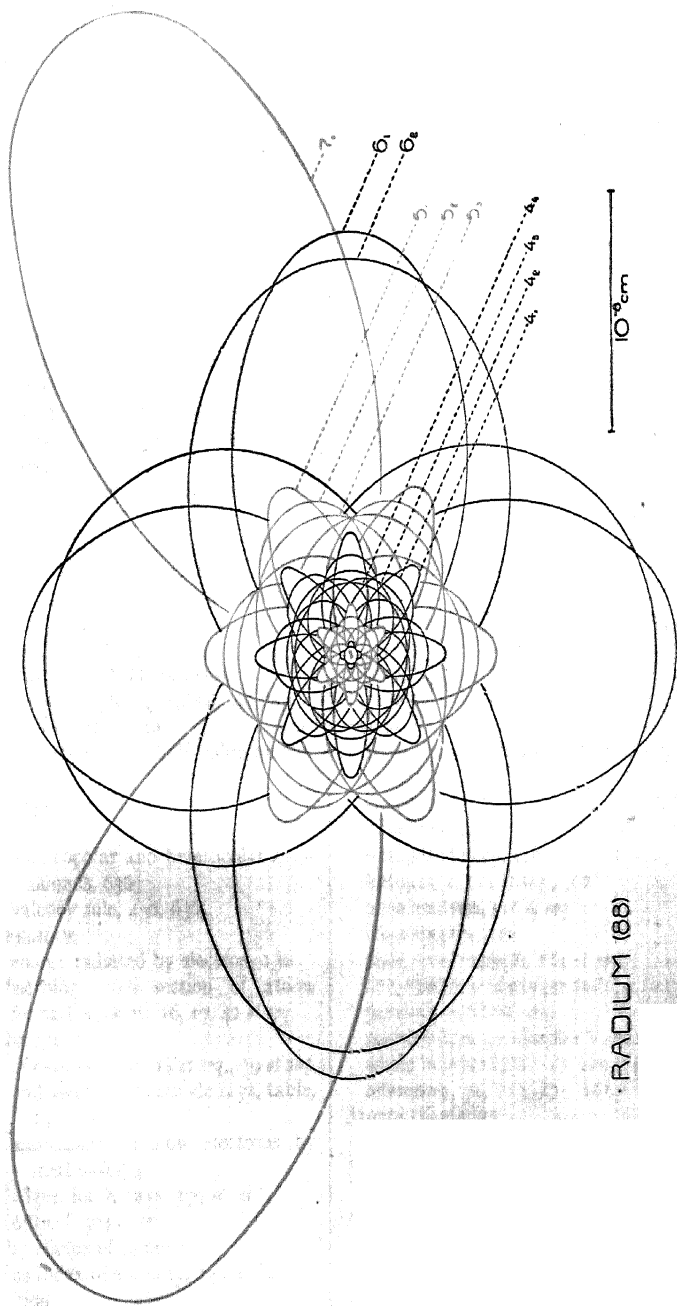
RADIUM (88)

STRUCTURE OF THE RADIUM ATOM

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