

Faraday Lecture.

(DELIVERED BEFORE THE FELLOWS OF THE CHEMICAL SOCIETY AT THE SALTERS' HALL ON MAY 8TH, 1930.)

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*Chemistry and the Quantum Theory of Atomic Constitution.**

It is with a feeling of deep reverence that I accept the kind invitation of the Chemical Society to deliver this lecture in commemoration of the great genius to whom we owe so large a part of the common foundation on which chemists and physicists build to-day. Indeed, Faraday's work may be taken as a symbol of the intimate relationship of our sciences, between which all sharp distinction is now disappearing on account of the rapid growth of our insight into the atomic constitution of matter. The peculiar feature of the great recent advance in this field is not only the intense mutual fertilisation of chemical and physical investigations; but it will even appear that a fusion of the attitudes of mind by which the study of the laws of nature has been approached by physicists and chemists is essential for the proper appreciation of the situation with which the recent development of atomic theory has faced us. Certainly, a leading idea in physical theory has been to seek the ultimate cause of all natural phenomena in the relative displacements of material bodies; while the proper field of chemistry may be said, I think, to be the study of those transmutations of the substances which defy a simple visualisation in terms of displacements. As is well known, atomic ideas originated just in the endeavour to bridge the gap between these different lines of research. Also, I need not remind you that, in the present epoch of science, the existence of atoms is more than a fruitful hypothesis. A large number of physical and chemical discoveries have given us direct evidence of effects of individual atoms, and we now possess several methods of counting the molecules in a body with great precision. Thanks, above all, to the great English pioneers in intra-atomic research, Sir Joseph Thomson and Lord Rutherford, we have even gained detailed information regarding the structure of atoms, which to a wide extent allows us to interpret the properties of the chemical elements as consequences of general physical laws. At the same time, however, we have in this new field met with a peculiar insufficiency of the ordinary ideas of natural philosophy, for the first disclosure of which

* This article, the publication of which has been delayed owing to unforeseen circumstances, is an elaboration of the author's Faraday Lecture, the plan and substance of which are maintained, while a number of details, omitted at the verbal delivery, are added.

we are indebted to the venerated master of the great German school of theoretical physics, Max Planck. In the lecture I have the honour and pleasure to deliver, I shall attempt to show, in a retrospective survey, how the fundamental ideas regarding the constitution of atoms have logically developed, and how it has gradually been recognised that the very stability of atomic structures, which is essential for our analysis of natural phenomena, imposes an unavoidable limitation of the use of space-time pictures in accounting for atomic reactions. Indeed, we meet here with an illustration of the old truth that our power of analysing a harmony and the width of its perception will always exhibit a mutually exclusive, complementary relationship.

In the scientific literature of the centuries following Newton's great work one often meets the expression "mechanical system of natural philosophy," with reference not only to the masterly explanation of astronomical facts, but also to the kinetic theory of matter which permitted an interpretation on atomic ideas of the laws of thermodynamics so fruitful in the study of chemical reactions. If nowadays a similar comprehensive expression were to be used, we should surely speak of an "electromagnetic description of the world" and should thereby think not only of the imposing structure built on the discoveries of Volta, Ørsted, Faraday, and Maxwell, which has been essential for modern technical development, but just as much of the revolution in our ideas of atomic processes brought about by the creation of the electric theory of matter, for which the discovery of the *elementary quantum of electricity* was fundamental. As was pointed out by Stoney in his British Association Address of 1874, and especially emphasised by Helmholtz in his famous Faraday Lecture of 1881, this discovery may be regarded, from the standpoint of Dalton's atomic theory of chemical combination, as an immediate consequence of Faraday's fundamental work on electrolytic equivalence. Time will not allow me to enter here on the great importance of this discovery for the whole science of electrochemistry and especially for the theory of electrolytic dissociation, on the development of which Arrhenius lectured before this Society in 1914. In electrolysis we follow the motions of the ions through the transport of chemical substance, but a still closer examination of ionic properties has been afforded by discharges in rarefied gases, to the study of which Crookes and Lenard contributed so materially. In fact, the deflection of electric rays in discharge tubes allows us to measure the ratio between the mass and the charge of individual ions, and, as is well known, such measurements led at the close of the last century to the epoch-

making discovery of the *electron* as a universal constituent of matter. This electron carries a negative charge equal to the elementary quantum and exhibits a mass-charge ratio very small compared with that of chemical ions in electrolysis. The incorporation of the idea of the atomic nature of electricity in the general electro-magnetic theory of Maxwell was most successfully performed in those years by Lorentz and Larmor. It is above all Thomson, however, who took a leading part, not only in the establishment of the fundamental experimental evidence but also in the attack on the problem of the electric constitution of matter. His ingenious methods of estimating the number of electrons in atoms, based on the scattering of Röntgen rays and the effects accompanying the penetration of swiftly-moving ions through matter, led him to approximately correct values for this electron number in the different chemical elements. Surely, few achievements have made a greater impression than the attempt to interpret the general relationship between the elements, which Thomson outlined in 1904 on the basis of these results. Indeed, it brought in a most suggestive way to the notice of physicists the wonderful outlooks into the central problems of atomic constitution which were opened up by the recognition of the peculiar periodicity in the chemical properties of the elements when arranged according to atomic weights, of which Mendeleiev spoke with such great enthusiasm and foresight in his Faraday Lecture of 1889.

A more detailed insight into the problem of atomic constitution was at that time hindered by our ignorance of the forces by which the negatively-charged electrons are held in the atoms, or, in other words, of the distribution of *intra-atomic positive electrification*. Decisive progress in this direction, however, was soon made possible through the startling discovery of the radioactivity of certain elements, in the history of which the isolation of radium by Madame Curie forms a conspicuous landmark. This phenomenon, which contrasts markedly with the ordinary physical and chemical properties of matter and at first even threatened to overthrow the general principle of the conservation of energy, found, as is well known, a lucid and complete interpretation in the disintegration theory of Rutherford and Soddy. According to this theory, the radioactivity of the substances in question is due to a spontaneous disintegration of the atoms which follows a simple probability law quite independent of the physical and chemical conditions to which the atoms are subjected. In this audience, I need not spend many words in reminding you of the unparalleled success with which Rutherford and his collaborators pursued this new clue to the problem of atomic constitution. Within the first decade of this century he built up a whole new branch of chemical and physical science which embraces

the remarkable changes in the properties of the radioactive substances accompanying the disintegration of their atoms as well as the nature of the rays emitted by these disintegrations and consisting, as is well known, partly of electromagnetic radiation (γ -rays) and partly of high-speed electrons (β -rays) and positively-charged ions (α -rays). Above all, however, the results of these studies proved to be, in Rutherford's hands, powerful tools for the exploration of intra-atomic structures. Thus, the careful study of the remarkable phenomenon of large-angle scattering of α -rays in passing through matter led him in 1911 to the fundamental discovery that the positive electrification in any atom is confined within the so-called *nucleus*, the dimensions of which are exceedingly small compared with ordinary atomic dimensions, and which is at the same time the seat of practically the whole mass of the atom.

Not least from the chemical point of view Rutherford's discovery was of decisive importance, offering us for the first time an unambiguous distinction between atoms and molecules. In fact, while an atom possesses only one nucleus, a molecule is a structure in which two or more nuclei enter as separate parts. We thus recognise at once the origin of the remarkable stability of the natural elements in contrast to chemical compounds. While a separation and a displacement of the various atomic constituents are sufficient for chemical substitutions, we learned that a realisation of the old aim of the alchemists, namely the *transmutation of elements*, implies a radical change of the atomic nucleus itself. Now, it is just an explosion of the nucleus which we witness in the spontaneous disintegration of radioactive elements. In fact, after the expulsion from the nucleus of an α - or a β -particle, a new atomic nucleus remains, which corresponds to an element of quite different physical and chemical properties. In this connexion, it was also most instructive that Rutherford was able to prove that the helium generated by radium, first observed by Ramsay and Soddy, is a direct product of the neutralisation of the emitted α -rays by capture of two electrons, α -particles thus being identified with helium nuclei. As everyone knows, the first artificial transmutation of elements was achieved about ten years later by Rutherford when he discovered that the penetration of α -rays through matter in certain cases is accompanied by the generation of high-speed, singly-charged, positive ions which proved to be identical with hydrogen nuclei. These are ejected from the nuclei of the atoms bombarded, this process leading to the formation of new nuclei consisting of the remainder of the original nuclei, with which, in some cases, the impinging α -particle may associate itself.

At the end of this lecture we shall discuss the outlook created by

these last achievements which have inaugurated a new epoch in science. To keep to our subject, however, we shall for the moment return to the time when the fundamental ideas of the electric constitution of atoms were taking shape. To everyone who, like myself, had the good fortune to visit the physical laboratories in Cambridge and Manchester about twenty years ago and work under the inspiration of the great leaders it was an unforgettable experience to witness almost every day the disclosure of hitherto hidden features of nature. I remember, as if it were yesterday, the enthusiasm with which the new prospects for the whole of physical and chemical science, opened by the discovery of the atomic nucleus, were discussed in the spring of 1912 among the pupils of Rutherford. Above all, we realised that the localisation of the positive electrification of the atom within a region of practically infinitesimal extension allowed a great simplification in the *classification of the properties of matter*. In fact, it permitted a far-reaching distinction between such atomic properties as are wholly determined by the total charge and mass of the nucleus and those which depend directly on its internal constitution. Radioactivity, which according to all experience is independent of the physical and chemical conditions, is typical of the last class of properties. The ordinary physical and chemical properties of matter, on the other hand, depend in the first place on the total charge and mass of the atom as well as on the electronic configuration round the nucleus, which is responsible for the reaction of the atom to external influences. Moreover, in an isolated atom this electronic configuration must be expected to depend almost entirely on the nuclear charge and very little on its mass, this being so large compared with the electronic mass that the nuclear motion to a first approximation can be neglected in comparison with that of the electrons. These simple deductions from the nuclear atomic model offered, indeed, an immediate explanation of the fact that two elements of different atomic weights and with quite different radioactive properties may be so alike as regards other properties that they are inseparable by chemical methods.

The first evidence of such a case had been obtained a few years earlier by Boltwood's discovery of ionium, which is chemically inseparable from thorium and even possesses an optical spectrum indistinguishable from the thorium spectrum, as was proved just at that time in Rutherford's laboratory by experiments of Russell and Rossi. Two such elements, which evidently have equal nuclear charge, occupy the same place in the periodic table and are appropriately called *isotopes*, according to the proposal of Soddy, through whose extensive investigation of the chemical properties of the radioactive elements in the preceding years the general importance

of isotopy was first recognised. The intimate connexion between the periodic table and the nuclear charge, of which we shall soon speak, led to further expectations regarding the connexion between radioactivity and chemical properties which were confirmed by investigations in Manchester by Hevesy and Russell. A complete co-ordination of the experimental evidence on this question was soon obtained, as is well known, in the formulation of the so-called displacement laws, according to which any α -ray disintegration is accompanied by a descent of the element of two steps in the periodic table, and any β -ray disintegration by an ascent of one step. In accordance with this law an especially instructive case of isotopy is exhibited by two members of a radioactive family between which one α -ray and two β -ray disintegrations take place. In fact, the identity of the nuclear charge of two such elements follows at once, if we realise that in the triple process the nucleus loses two negatively-charged electrons besides the α -particle with its double positive charge. This confirmation of the views in question is all the more interesting because the final empirical establishment of the general displacement law by Fajans and Soddy in 1913 was quite independent of the development of the ideas on atomic structure here discussed. As we now know from Aston's ingenious refinement of the analysis of ionic rays originated by Thomson, the existence of isotopes is not confined to the radioactive elements, but almost all ordinary chemical elements consist of a mixture of isotopes of different atomic masses. The usual atomic weights are thus mean values of secondary importance as regards ordinary chemical properties. Moreover, Aston's discovery that all atomic masses are very close to simple multiples of the atomic mass of hydrogen made it clear that the nucleus of any atom is built up of electrons and hydrogen nuclei. Indeed, we find here an interesting revival of the ideas of Prout, which a hundred years ago caused so much discussion among chemists.

The recognition that the electron and the hydrogen nucleus, generally termed "proton," form the ultimate units of atomic structures places before us the prospect of a purely electric constitution of matter. Still, as we have seen, the interpretation of the bulk of chemical and physical experience is independent of the problem of the internal constitution of atomic nuclei, which presents peculiar aspects to be discussed later. For this interpretation, it is sufficient to consider the nucleus as a charged mass point, and we are solely concerned with the problem of the configuration of the extra-nuclear electrons, the number of which in a neutral atom is, of course, determined by the nuclear charge. Now, the first element in the periodic table, namely hydrogen, contains one electron in the atom, and the second element, helium, contains two extra-

nuclear electrons. From the general ideas of Thomson concerning the relation between electron number and periodic table, it was therefore an unavoidable generalisation that for any element the number of extra-nuclear electrons in the neutral atom is given by the integer, the so-called *atomic number*, which fixes its position in the table, often termed the "natural system of the elements." This view was in obvious conformity with the radioactive displacement law and agreed, within the limits of experimental error, with Rutherford's original estimate of the nuclear charge, derived from the measurements of α -ray scattering by Geiger and Marsden. It has since been directly confirmed by the refined measurements of Chadwick on this phenomenon, as well as by renewed investigations, interpreted by Thomson's famous formula, of the scattering of Röntgen rays by matter. Above all, the experimental evidence regarding this fundamental point has obtained a most extraordinary amplification, as we shall see, through Moseley's brilliant researches on the characteristic Röntgen spectra of the elements. Summarising the situation, we may say that, as regards the co-ordination of all ordinary properties of matter, Rutherford's model of the atom puts before us a task reminiscent of the old dream of philosophers: to reduce the interpretation of the laws of nature to the consideration of pure numbers.

On setting out to work on this attractive programme, however, one was at once confronted with difficulties of a most serious character, which would at first sight even appear to be fatal to the whole conception of the electric constitution of atoms. Indeed, on classical theories no system of charged material points will exhibit a *stability* of the kind which must be attributed to atomic structures in order to account for the chemical and physical properties of matter. Such systems will not possess statical states of stable equilibrium in the ordinary mechanical sense, nor will any dynamical state fulfil the conditions required. Even in the simplest case of an atom consisting of a positive nucleus and one electron, this is quite evident. It is true that, according to Newtonian mechanics, two particles attracting each other with a force, ruled by Coulomb's law, will revolve in Keplerian ellipses round their common centre of gravity. But this solution, which accounts satisfactorily for the stability of planetary motions, does not enable us to understand why, by the combination of an electron and a proton, an atom is formed with properties corresponding to the chemical behaviour and characteristic line-spectrum of hydrogen. Without entering into any speculation regarding the origin of the solar system, it is clear that the dimensions of the earth's orbit and the length of the year are essentially deter-

mined by the initial conditions and may any day be permanently modified by a collision with a meteor. On the other hand, the definiteness of the hydrogen atom under most varied conditions is impressively exhibited by the identification of spectral lines from distant stars with the hydrogen spectrum obtained in ordinary discharge tubes. If we look closer into the origin of this spectrum, the situation becomes even worse. In fact, the very emission of radiative energy from the atom will be accompanied, according to ordinary electromagnetic ideas, by a gradual decrease of the size of the electron orbit and the period of revolution, which process will prevent the appearance of sharp monochromatic spectral lines and ultimately cause the electron to combine with the proton into a neutral system of linear dimensions exceedingly small compared with those of actual atoms. Similar remarks obviously hold for any atomic system of the type under consideration. Indeed, from ordinary mechanics and electrodynamics no argument can be derived which allows us to explain why the electric constituents of the atom do not neutralise each other in a way catastrophic to the stability of material bodies.

Clearly, an entirely new idea was needed before the discoveries regarding the ultimate electric particles could be properly utilised in the interpretation of the general properties of matter. In the search for such an idea, however, one had not to look far: A clue to the solution of the difficulties was offered by Planck's fundamental discovery of the *elementary quantum of action*, which, especially in the hands of Einstein, had already proved so fruitful in co-ordinating physical experience of most varied kinds. Indeed, this discovery had disclosed a novel feature of atomicity in the laws of nature, quite foreign to the classical ideas of physics, and in a certain sense even more so than the atomic nature of electricity. Of course, no explanation based on general electromagnetic theory can be given of the existence of the elementary quantum of electricity and of the specific values of the masses of the electron and of the proton, but it must be remembered that the measurements of the charge and the mass of these particles rest on experimental evidence which permits of an unambiguous interpretation by means of classical ideas. No account of the existence of the quantum of action can be given, however, which does not involve a radical departure from ordinary physical principles. Of course, the determination of Planck's universal constant is also based on measurements classically defined, but in contrast to the case of the electronic charge and mass, no rational interpretation in electromagnetic terms can be given of the derivation of the action quantum from these measurements. The field of unambiguous applicability of classical concepts

is limited to processes where the mechanical action involved is large compared with the quantum, as in the deflection experiments with electric rays; and the insufficiency of these ideas to account for atomic reactions is due just to the fact that a detailed analysis of the intra-atomic motions would involve the consideration of elements of electron paths for which the action is of the same order of magnitude as, and even smaller than, the quantum. Certainly, the two fundamental aspects of atomicity, symbolised by the elementary quanta of electricity and action, are intimately connected, and when we come to the problem of the constitution of atomic nuclei, we shall see that it is no longer possible to use the ideas of electron charge and mass without ambiguity. But, as regards the extra-nuclear electronic configuration, a great simplification arises from the fact that the dimensions of the constituent particles, defined in a classical sense, can be considered as negligibly small compared with those of the whole atom. Indeed, this idealisation, on which the simple classification of atomic properties rests, allows us in the region outside the nucleus to regard the specific properties of the electrons as independent of the quantum of action.

Already in the years preceding the establishing of the nuclear model of the atom, the question of the bearing of Planck's discovery on the problem of atomic constitution had been discussed from various sides, and approximate relationships between atomic constants had been suggested. Previous atomic models, however, constructed from the point of view of mechanical stability, were obviously unsuited to a satisfactory interpretation of the specific properties of the elements, and, as they were in themselves fully determined as regards dimensions and frequencies, the introduction of the action quantum meant no decisive improvement in this respect. The situation was completely changed by Rutherford's discovery. Indeed, the evident insufficiency of simple mechanical ideas as regards the interpretation of atomic stability not only made a radical departure from classical principles inevitable but left at the same time sufficient freedom for the utilisation of the guidance offered by the direct evidence concerning the physical and chemical properties of the elements. A suitable basis for the use of this evidence I found in two simple "postulates." According to the first of these, any well-defined change of state of an atom is to be considered as an elementary process, consisting in a complete transition of the atom from one of its so-called *stationary states* to another of these states. On the one hand, this postulate is no more than a definite formulation of the remarkable stability of atomic structure disclosed by general chemical evidence. On the other hand, it is directly suggested by the existence of the quantum of action.

Not only is the view of the *elementary character of the transition processes* directly related to the essential indivisibility of the quantum, but it permits at once the use of Planck's famous relation between energy and frequency of individual radiation processes as a basis for a simple interpretation of a fundamental law of spectroscopy, the so-called combination principle. This principle, established through the remarkable researches of Balmer, Rydberg, and Ritz, states that the frequency of any spectral line may be written as the difference between two terms belonging to a term-system characteristic of the spectrum under consideration. Assuming that these terms, multiplied by the quantum of action, are numerically equal to the energies of the stationary states of the atom, we see, in fact, that the combination principle is equivalent to the second postulate, according to which the radiation emitted or absorbed during a transition process is essentially *monochromatic* and possesses a frequency equal to the energy difference between the two states divided by Planck's constant.

This view of the origin of spectral lines is in obvious conformity with Einstein's law of photochemical equivalence and brings the conditions for the appearance of spectra into close connexion with the chemical state of the substance in question. Indeed, the apparent capriciousness of the occurrence of lines in emission and absorption spectra is completely accounted for, in accordance with Kirchhoff's law, if it is taken into consideration that the emission of a spectral line corresponding to a given transition between two stationary states implies the presence of the atom in the state of higher energy, whereas the condition for absorption is the presence of the atom in the state of lower energy. The inversion of individual atomic reactions, with which we have here to do, is especially instructive, since the transition processes concerned are essentially elementary and fall outside the scope of ordinary mechanical reversibility. In fact, according to the interpretation of the combination principle, an atom in a stationary state will generally have a choice between a number of different transitions to other stationary states, and the occurrence of these elementary processes is necessarily a question of *a priori probability*. A step of far-reaching importance as regards the formulation of probability laws for radiation processes was taken, as is well known, by Einstein in 1916, when, on the basis of the above-mentioned postulates, he gave a lucid derivation of Planck's law of black-body radiation. A still more direct confirmation of the postulates had been obtained a few years earlier by the well-known experiments of Franck and Hertz on collisions between atoms and free electrons. They found, in complete agreement with the theoretical predictions, that no exchange of energy between the

atom and the electron is possible unless the collision results in a transference of the atom from its normal state to another stationary state of higher energy. The collision processes in question may, indeed, be considered as chemical reactions of a particularly simple type, whereby the atom is brought from its initial inactive state into a so-called activated state, from which, in general, it will fall back to the initial state in one or more steps with emission of radiation. For the theory of chemical reactions, however, it is of special importance that the return of the atom to its normal state can also take place in a radiationless process in which the energy of activation is transferred by a collision to a free electron or to another atom in the form of kinetic or chemical energy. The possible occurrence of such so-called inverse collisions was first pointed out by Klein and Rosseland from the consideration of thermal equilibrium; and the importance of these processes in chemical reactions is shown most instructively by the recent researches of Franck and his collaborators.

The connexion so far discussed between atomic stability and the quantum of action is quite general and is only indirectly related to the atomic model. In view of the conflict between the postulates which underlie our discussion and the ordinary ideas of mechanics and electrodynamics involved in the definition of the charge and the mass of the constituents of the atom, it is clear that these ideas can only offer us limited guidance for a direct attack on the problem of atomic constitution. A proper basis for a detailed treatment of this problem has, in fact, been established only in the last few years through the development of a consistent quantum mechanics in which the two fundamental postulates are rationally incorporated. In direct connexion with the formulation of these postulates, however, it was possible to take a first step towards the realisation of the programme, referred to above, of interpreting the specific properties of the chemical elements and their mutual relationship on the basis of the nuclear atom model. A starting point was offered by the extraordinary simplicity of the *hydrogen spectrum*. According to the well-known formula of Balmer, this spectrum can be derived from a single sequence of terms, each equal to a constant divided by the square of an integer, the so-called term-number. Now, in conformity with the interpretation of the combination principle, each spectral term, multiplied by Planck's constant, may be taken to represent, for the corresponding stationary state of the atom, the work necessary to remove the electron to an infinite distance from the proton. The term-system of hydrogen thus offers valuable information about the formation of the atom by the binding of the electron to the proton through a step-like process. According to

the ideas of ordinary mechanics, the steps in this binding process would be pictured as a sequence of electron orbits, the major axes and the revolution frequencies of which are respectively proportional to the square and the inverse cube of the term-numbers, in accordance with Kepler's laws. The values thus obtained for the orbital dimensions and frequency in the normal state, with term-number 1, are, in fact, of the same order of magnitude as those derived for atomic diameters and frequencies from the classical interpretation of mechanical and optical properties of gases. Still, since this interpretation conflicts with the view of atomic stability under consideration, such a comparison can, of course, only be of an approximate character. A quantitative connexion between the mechanical pictures of the stationary states and the actual properties of the hydrogen atom, however, is offered by the circumstance that the relative differences between successive values of orbital dimensions and frequencies tend to zero for increasing term-numbers. Indeed, we see here how the ordinary mechanical idea of continuous variability of orbital characteristics appears as a limiting case; and we shall expect that the general electromagnetic concepts will gradually gain full justification in this limit, so far as the elementary character of the individual transition processes can be disregarded. From this so-called *correspondence argument*, it follows that the radiation emitted during the limiting stages of the binding process can be quantitatively described by classical ideas. In particular, the spectral frequencies calculated from the possible transition processes on the basis of the postulates must, in these stages, tend to coincide with the frequencies of the harmonic components into which the classical radiation from the revolving electron can be analysed. A simple calculation shows, however, that this condition is equivalent to the existence of a definite relation expressing the constant in Balmer's formula in terms of the charge and the mass of the electron and of Planck's constant. This relation was convincingly supported by the empirical values of these quantities then available and has been fully confirmed by the refined measurements of Millikan, as described, for example, in his Faraday Lecture of 1924.

The establishment of this connexion between the hydrogen spectrum and the model of the atom led directly to the recognition of a *relationship between the spectra of the elements* of a more intimate character than hitherto suspected. In fact, it follows from the calculation just mentioned that the term-system of the spectrum emitted by the binding of an electron to a nucleus of a given charge will only differ from the hydrogen term-system by a factor equal to the square of the ratio between this charge and that of the proton. In other words, the spectrum is given by the Balmer formula, if only the

constant be multiplied by the square of the atomic number. Now a spectral series, which could be represented by this generalised formula for the atomic number 2, had first been observed by Pickering in the spectra of certain stars, and after much labour was also obtained by Fowler in the spectrum emitted from tubes containing a mixture of hydrogen and helium and exposed to condensed electric discharges. Owing to its close numerical relationship with the ordinary hydrogen series, this new spectral series was attributed to hydrogen both by astronomers and by physicists. According to our argument, however, it should originate from helium under such conditions that one electron is totally removed from the atom and the remaining ion transferred to an activated state. This view offered an explanation of the capricious appearance of the series in question in stellar spectra as well as of its excitation under special experimental conditions and was soon confirmed by experiments in the Manchester Laboratory by Evans, who succeeded in exciting the series in helium of such great purity that no trace of hydrogen lines could be detected. A further verification of the generalised Balmer formula has been obtained, in recent years, in Siegbahn's laboratory, where remarkable progress in the spectroscopy of the far ultra-violet region has been achieved. In fact, spectra corresponding to this formula for atomic numbers 3, 4, and 5 were found by Edlén to be emitted from lithium, beryllium, and boron, respectively, when they are exposed to intense electron bombardment.

This intimate relationship between the spectral characteristics of the elements, which so instructively remind us of the extraordinary simplicity of the atomic model, is so far confined to the case of one extra-nuclear electron, and the properties of atoms with several electrons will naturally exhibit a greater complexity. Still, remarkably simple relationships of a general character are disclosed by the study of the spectra. As was first recognised by Rydberg, the constant in Balmer's formula, now generally known as Rydberg's constant, appears quite universally in the numerical representation of the term-systems, often highly complicated, into which the spectra emitted from elements under ordinary conditions can be analysed. In particular, every such term-system was found to include terms closely coinciding with the hydrogen terms. This observation, which was for some time rather puzzling, obtains, however, an immediate interpretation on our view of atomic constitution, if we assume that such hydrogen-like terms correspond to activated states of a neutral atom in which one electron is removed to a distance from the nucleus large compared with the linear dimensions of the configuration of the remaining electrons. In fact, this outer electron will, during its re-binding, be subject to

forces which are nearly the same as those exerted by a proton, and we must therefore expect that the steps of this process will resemble closely the stationary states of the hydrogen atom. This view was soon confirmed in an interesting manner. Indeed, in the course of a discussion in *Nature* in 1913 on the spectrum of ionised helium mentioned before, Fowler pointed out that certain series which he had recently observed in the magnesium spectrum could be united into a simpler series system, if instead of the Rydberg constant a value four times larger were used. Now, this is just what we should expect for activated states of singly-ionised atoms in which one electron is bound at a comparatively large distance from the nucleus. Especially through the researches of Fowler, spectra of this type have since been shown to occur quite generally when elements are subjected to heavy discharges. A further extension of the spectral classification was achieved a few years later by Paschen, who discovered in the aluminium spectrum a series system corresponding to nine times the Rydberg constant, which evidently originates from doubly-ionised atoms. In recent years, a valuable addition to the general spectral evidence regarding atomic constitution has been obtained through Millikan's researches on highly condensed discharges, by which spectra have been found of atoms of a still higher degree of ionisation.

Before we proceed to the closer discussion of the bearing of the optical spectral evidence on the problem of the periodic variation in the chemical properties within the natural system of the elements, we must mention the wonderful support which the general ideas on atomic constitution received through the investigations on *Röntgen ray spectra*. In contrast to the optical spectra, which originate in the binding of electrons in the exterior parts of the atom, these spectra are emitted during the reorganisation of the electronic configuration when electrons bound in the interior of the atom are removed from their normal state. Notwithstanding the intrinsic complexity of this problem, it is characteristic of our atom model that, owing to the predominance of the nuclear attraction over the mutual repulsion of the electrons in the inner region of the atom, we should expect a close resemblance between the Röntgen spectrum of an element and the spectrum emitted by the binding of a single electron to the nucleus. This view was also in conformity with the remarkable regularities disclosed by Barkla's fundamental researches on the characteristic Röntgen radiation of the elements, and, in connexion with the establishing of the generalised Balmer formula, I pointed out that it explained the empirical rule of Whiddington on the velocity of cathode rays necessary to excite this radiation. Only a few months later, moreover, the experimental evidence re-

garding the subject was enormously increased through Moseley's far-reaching researches on the spectral constitution of Röntgen rays, made possible by Laue's discovery of the diffraction of Röntgen rays in crystals and the subsequent fundamental work of the Braggs on crystal structures. Moseley, working in Rutherford's laboratory and endeavouring to put the new ideas to a decisive test, made in an astoundingly short time a number of important discoveries which laid the foundations of high-frequency spectroscopy. Above all, the characteristic Röntgen spectra of the elements were found to vary with increasing atomic number in a way so regular that not only was it evident whenever an element was still missing from the periodic table, but it even became possible to draw unambiguous deductions regarding the number of elements in any period of the natural system. One cannot here refrain from admiring the thoroughness with which chemists have explored their great field, and especially the intuition of Mendeleiev, when one sees that all his predictions regarding missing elements as well as his expectations concerning the proper sequence of such pairs of elements as were inverted when classified according to atomic weight were borne out completely by Moseley's work. It is also interesting that Moseley's deductions regarding the number of elements in the longer periods, for which chemical evidence at Mendeleiev's time was very scanty, agreed entirely with the remarkable rules more or less intuitively predicted by Julius Thomsen from chemical and by Rydberg from spectral evidence.

As we shall see, the quantum interpretation of atomic stability not only enables us to bring out the simple regularities in the relationships between the elements directly suggested by the nuclear atom, but also, in connexion with the atomic model, it has proved to be a clue to the understanding of the more intricate features of those relationships embodied in the periodic table. The remarkable periodicity of the physical and chemical properties of the elements when classified by increasing atomic number evidently originates from the gradual development of a *group structure* of the electron configuration, as had already been convincingly shown in Thomson's pioneer work on the electronic constitution of atoms. This work contains, indeed, an abundance of original and fruitful ideas as regards the interpretation of chemical evidence which have received suggestive amplification especially in the hands of Kossel and Lewis. However, the views of mechanical stability on which Thomson based his discussion of the electron group structure are not directly utilisable in connexion with Rutherford's model of the atom. A suitable basis for the investigation of this group

structure has been found in the recognition of the step-like character of the binding of electrons in atoms, which enables us to utilise for this purpose the general spectral evidence. An important starting point was offered by the closer study of the Röntgen spectra. In fact, the characteristic structure of these spectra can be simply explained, as was first pointed out by Kossel, on the assumption that their lines are emitted by elementary transition processes, in which the place left free in an inner electron group by the removal of an electron from the atom is taken up by a new electron falling from a group where the electrons are more loosely bound. The empty place left in this last group may then, under emission of another Röntgen line, be occupied by an electron coming from a group of electrons bound still more loosely, and so on. According to this view, which is in obvious conformity with the combination principle, each term of the Röntgen spectrum of an element gives us direct information about the work necessary for the removal of an electron from one of the various groups in the normal electron configuration of the atom. Interpreted in this way, the empirical rules, in which Moseley summarised his measurements of the frequencies of the main Röntgen lines, lead, as was first noted by Vegard, to the result that the strength of the binding of each principal electron group is approximately equal to that of some stationary state of the binding of one electron to the nucleus. Thus we see that the term-number appearing in the Balmer formulæ, which in the quantum-theory terminology is called "the principal quantum number," enters directly into the classification of the group structure of the normal electronic configuration. In fact, it is characteristic of the ideas of atomic constitution under discussion that, besides the atomic number, other integers play a fundamental rôle in the account of the relationships between the elements.

The simple classification of the stationary states of the hydrogen atom did not suffice, however, for a closer investigation of the group structure of atoms with several electrons, nor for the detailed interpretation of the complex spectra of such atoms. A great advance in the classification of stationary states and a corresponding refinement of the systematics of quantum numbers was achieved, in the following years, by the extension of the use of mechanical pictures to orbital motions of more complicated type than the simple periodic Keplerian orbits which were sufficient for the derivation of the Rydberg constant. For such orbits of higher degree of periodicity, the so-called rules of quantisation, by which the stationary states are selected from the continuous infinity of mechanically possible motions, involve the use of as many quantum numbers as there are

independent frequencies in the motion. This important advance was introduced in 1915 by Wilson and Sommerfeld, and the formal consistency of the scheme thus obtained was secured to a large extent by Ehrenfest's principle of adiabatic invariance of stationary states. In the following development Sommerfeld, especially, contributed in a most successful way to the disentangling of the extensive spectroscopic material regarding the fine structures exhibited not only by complex spectra, but even by the hydrogen lines when examined with instruments of high resolving power. Notwithstanding the fundamental limitation of mechanical and electromagnetical ideas already emphasised, the essential reality of the results obtained in this way was also confirmed by the explanation of the remarkable selection rules, governing the appearance of spectral lines predicted by the combination principle, which was offered by correspondence arguments of the kind indicated in our discussion of the hydrogen spectrum. Encouraged by this progress, I made in 1921 an attempt to utilise the whole spectroscopic evidence for a comprehensive survey of the electronic constitution of the atoms. Although, of course, many details could at that time not be explained, it was still clear that the principles of quantum theory were in a sufficiently advanced state to enable a number of unambiguous deductions to be drawn regarding the gradual development of the electronic groups with increasing atomic number. The leading idea was to follow the building up of these groups by the successive addition of the electrons, one by one, using the information regarding the binding process of each electron given by the structure of the accompanying spectrum. Corresponding to the appearance, in the classification of the spectral terms, of a so-called subordinate quantum number in addition to the principal quantum number, it was thus possible within each principal electron group in the completed atomic structures to distinguish between a number of *sub-groups* which are gradually filled up as the atomic number increases. In every atom the strength of the electron binding decreases regularly with increasing values of any of the two quantum numbers and will normally be firmer for an electron of lower principal quantum number, irrespective of the value of the subordinate number. During the building-up of the group structures, however, it sometimes happens that electrons in a sub-group with given quantum numbers are more firmly bound than in sub-groups of lower principal number, but higher subordinate number. The former sub-groups therefore appear in the atom before the latter, but with increasing atomic number the normal relationship between the strength of the various types of electron binding is restored, and the groups of lower principal quantum number are filled up

while the development of higher principal groups is brought to a temporary standstill. This accounts for the anomalous positions within the periodic table of such families of elements as the iron and platinum metals and the rare earths which are due to a temporary delay in the regular development of outer electron groups with increasing atomic number, caused by some transitory stage in the development of inner groups. This circumstance, which also explains the singular behaviour of the elements in question regarding their magnetic properties and their characteristic colours, has been especially emphasised by Ladenburg and Bury. According to the theory, all such transitory stages in the regular development of the atomic group structures were now simply accounted for by the addition of new sub-groups to principal electron groups that are only partially completed, and the apparent irregularities in the periodic table appear thus as direct consequences of quite elementary features of the quantum theory.

These conclusions regarding the gradual development of the group structure in atoms soon received instructive support through the great advance in our knowledge of the high-frequency spectra, achieved in those years by Siegbahn and his collaborators. Especially, we owe to Coster a very considerable increase in the empirical material regarding the terms of these spectra and their classification, by means of which it was possible to make a detailed diagrammatic representation of the way in which any of the Röntgen terms varies with increasing atomic number. Now, this diagram disclosed marked deviations from the uniform slope of the Moseley term curve, occurring at all values of the atomic number for which, according to the theory, the beginning or the completion of a new stage in the development of inner electron groups took place. A further important verification of the theoretical ideas was furnished in 1922 by Coster's and Hevesy's discovery, by Röntgen-ray analysis of zirconium minerals, of a new element of atomic number 72. The properties of an element of this atomic number had been the subject of discussions among chemists, and the view was advocated that it should be a member of the rare-earth family. This opinion, however, was in sharp contrast with the theory of group structure in question, according to which the new element should be homologous with titanium and zirconium, as was also definitely indicated in the old diagrammatic representation of the periodic table by Julius Thomsen which has been found so well suited to illustrate the later theoretical views. In fact, the new element, named hafnium, not only showed, as Hevesy's researches proved, an intimate relation with zirconium in all its chemical properties, but in addition it was

found to be contained in considerable percentage in all common zirconium minerals, though hitherto undetected. Indeed, hafnium belongs to the elements which are quite abundant in the earth's crust and differs in this way from the other new elements which have been detected in recent years by means of the powerful tool offered by Moseley's discovery and which have filled up almost all the empty places in the natural system.

Although a definite connexion between the atomic group structure and the general spectral evidence could be traced by the indicated procedure, the underlying principles were admittedly limited in various directions. I am thinking here not only of the fundamental revision of quantum theoretical methods which we shall soon discuss, but also of the many questions concerning finer details which were still left open. Indeed, the table then given of the group distribution of the electrons in the atoms exhibited various hypothetical features which were ameliorated by subsequent developments. In this respect, Landé's analysis, based on the combination principle and the correspondence argument, of the remarkable Zeeman effect patterns of spectral lines became of decisive importance. In fact, the results of this analysis enabled Stoner to extend the systematics of group structure by the use of three quantum numbers for the characterisation of the electron binding instead of the two quantum numbers of the previous group classification. It is interesting that this improvement showed a striking resemblance to the proposal of a division of the sub-groups made by Main Smith on the basis of a comprehensive examination of the chemical evidence. A final contribution to the elucidation of the problem was given in 1925 by Pauli, who, by the introduction of a fourth quantum number, was able to co-ordinate all the evidence concerning the completion of electron groups in a single rule, the so-called *exclusion principle*, which states that two electrons in an atom are never in exactly the same stage of binding, as defined by the four quantum numbers. To the new quantum number Pauli was led by the analysis of the remarkable transformation, known as the Paschen-Back effect, which the Zeeman patterns undergo in magnetic fields of increasing strength as a consequence of the gradual predominance of the external field over the mutual influence of the bound electrons as regards spatial orientation effects. We have here, however, gone beyond the limit of a legitimate use of mechanical pictures; and in this connexion it is important to note that no unambiguous interpretation can be given on classical ideas to the concept of electron spin, by which so fruitful an attempt was made to interpret the fourth quantum number. In fact, it follows from the general arguments to be discussed later that it is impossible to measure

the magnetic moment, ascribed to the electron according to this idea, in a well-defined way similar to the ingenious method of Stern and Gerlach by which the resultant magnetic moments of atoms are measured. In contrast to the charge and the mass of the electron, the spin cannot therefore be said to belong to the classically defined properties of the atomic model. On the other hand, even ordinary spectral evidence forces us to abandon the idealisation of the model according to which the nucleus is considered as a charged material point. Indeed, from the analysis of the so-called hyperfine structure of spectral lines it is possible, as was originally suggested by Pauli and proved especially by Goudsmit, to draw unambiguous and important conclusions regarding the magnetic moments and angular momenta of complex nuclei.

Through the completion of the systematics of electron binding in atoms, which allows us to account for all regularities in the periodic table down to the finest features, a connexion of a comprehensive character has been established between the general chemical evidence and our ideas of atomic constitution. For the detailed account of this evidence, however, the classification of electron binding by means of orbital pictures is a proper guide only in the case of chemical combinations involving *polar bonds*. As stressed especially by Kossel, molecules resulting from such combinations may be considered as agglomerations of ions, each keeping its electrons in the same state of binding as if it were isolated. It is true that, even for isolated ions and atoms, the mechanical picture of the electron binding is unable to account quantitatively for the binding energies, as was most clearly shown in the case of the neutral helium atom where the rules of quantisation of electron orbits are unable to account for the ionisation energy predicted with great accuracy by the analysis of the ultra-violet helium spectrum. While this was no serious drawback in the general description of polar molecules, the failure of mechanical pictures hindered for some time progress in the understanding of such chemical combinations which involve *homopolar bonds*. In a homopolar molecule the binding of the valency electrons differs from that in isolated atoms to such an extent that it is not even possible to distribute them in an unambiguous way between the individual atoms entering the molecule. A typical example is here offered by the hydrogen molecule which consists of two protons held together by two electrons. In connexion with the original discussion of the hydrogen spectrum, I proposed in 1913 a simple model of the hydrogen molecule in which the electrons revolved in a common orbit symmetrically oriented with respect to the protons. Although this model gave values of the right order of magnitude for the heat of dissociation and the

ionisation potential of hydrogen gas, it was unsuited to an exact calculation of these quantities. The limitation of the use of mechanics in picturing stationary states, which thus again confronts us, is all the more serious because here the very classification of these states on the basis of the rules of quantisation loses its uniqueness. Even though, as was shown most instructively by Lewis, the general idea of the sharing of pairs of equivalent electrons by atoms has proved fruitful in symbolising homopolar bonds, especially in the molecular aggregates of organic chemistry, we are here definitely outside the limit of visualisation either by means of statical configurations or by orbital motions. A detailed account of the elementary processes of chemical reactions by means of the ordinary ideas of mechanics is indeed prevented by the conflict between these ideas and the view of atomic stability expressed by the quantum postulates. An adequate basis for this account, however, has in the last few years been afforded by the new symbolic methods properly adapted to the existence of the action quantum.

A fundamental step towards the establishing of a proper *quantum mechanics* was taken in 1925 by Heisenberg who showed how to replace the ordinary kinematical concepts, in the spirit of the correspondence argument, by symbols referring to the elementary processes and the probability of their occurrence. This symbolism may, indeed, be considered as a most ingenious completion of the trend of ideas characterised by Kramers' adaptation of Lorentz' classical theory of the optical dispersion phenomena to the quantum theory of spectra. Above all, this correspondence treatment of dispersion accounts in a natural way for the Raman effect which in recent years has been so important for the elucidation of chemical problems. In fact, this effect, the existence of which was first suggested by Smekal on the basis of the quantum postulates, contrasts most strikingly with the expectations of classical theory, according to which spectral lines should only show normal dispersion, since they are supposed to originate from harmonic oscillators. From a general theoretical standpoint, Heisenberg's symbolism, extended by important contributions especially from Born, Jordan, and Dirac, is quite satisfactory within its scope. A method, however, which is not only most powerful for the treatment of particular problems, but which also greatly illuminates the general principles of quantum mechanics has been developed by Schrödinger. This method is based on the original idea of de Broglie, who in 1924 proposed to associate a wave train with the motion of a material particle, the frequency and wave-length being related to the energy and momentum by Einstein's fundamental formulæ for radiation quanta which have

been so helpful in the explanation of the Compton effect. As is well known, this idea of so-called "matter-waves" offered a complete explanation of Davisson and Germer's and G. P. Thomson's remarkable experiments on diffraction of electron beams by crystals which so strikingly resembles diffraction of Röntgen rays. Corresponding to Debye's ingenious method of structural analysis by Röntgen rays, this electron diffraction has even recently proved of great utility for the exploration of the molecular structure of organic substances. The extreme fertility of wave pictures in accounting for the behaviour of electrons must, however, not make us forget that there is no question of a complete analogy with ordinary wave propagation in material media or with non-substantial energy transmission in electromagnetic waves. Just as in the case of radiation quanta, often termed "photons," we have here to do with symbols helpful in the formulation of the probability laws governing the occurrence of the elementary processes which cannot be further analysed in terms of classical physical ideas. In this sense, phrases such as "the corpuscular nature of light" or "the wave nature of electrons" are ambiguous, since such concepts as corpuscle and wave are only well defined within the scope of classical physics, where, of course, light and electrons are electromagnetic waves and material corpuscles respectively.

As regards its application to chemical problems, the merit of Schrödinger's method lies, above all, in the instructive pictures of stationary states afforded by standing waves, the nodes of which are directly related to the quantum numbers used in the classification of spectral terms. Indeed, it was just a visualisation of quantum numbers of electron orbits by means of vibration nodes which was the original aim of de Broglie. Still, the symbolic aspect of Schrödinger's wave functions appears immediately from the use of a multidimensional co-ordinate space, essential for their representation in the case of atomic systems with several electrons. Far from being a hindrance, just this circumstance permits us to formulate Pauli's exclusion principle in a simple and general way. According to this formulation, the wave function of a system of electrons is never symmetrical both in the space and spin co-ordinates of any two electrons, although all electrons are indistinguishable from one another and in consequence play equivalent parts in the wave-function. The non-visualisable character of Pauli's principle, to which we have already alluded, is also clearly brought out by the rôle which the idea of electron spin plays in this formulation. Indeed, one of the most outstanding contributions to the new developments is Dirac's quantum theory of the electron which accounts for all effects previously attributed to the magnetic moment or angular momentum of

electrons by a symbolic procedure utilising, in addition to the quantum of action, only the concepts of classical relativistic electron theory. Heisenberg, to whom, besides Dirac, we owe the quantum mechanical elucidation of the exclusion principle, showed how it was consistent with the appearance of two non-combining term-systems in the spectrum of the neutral helium atom, corresponding to wave-functions respectively symmetrical and antisymmetrical in the space co-ordinates of the two electrons. Indeed, the existence of these so-called ortho- and para-systems had been a puzzle ever since the frustrated endeavours of chemists to separate helium gas into two hypothetical constituents named ortho- and para-helium. While the normal state of the helium atom belongs to the para-system, the first term of the ortho-system corresponds to the so-called metastable state of the helium atom, the remarkable properties of which were first pointed out by Franck. A very interesting recent contribution to the problem of the constitution of the helium atom is due to Hylleraas who, on the basis of wave mechanics, developed a precision method for the numerical evaluation of wave-functions and derived a value for the ionisation potential of helium which agrees, within the limits of experimental error, with the spectral evidence. Indeed, this result represents the first quantitative derivation of a constant depending on the constitution of an atom with more than one electron. Recently, Hylleraas' calculation has obtained further striking confirmation by Edlén's analysis of the spectra emitted by singly, doubly, and trebly charged ions of beryllium, boron, and carbon, respectively. For atoms and ions with more than two electrons, no exact calculations of spectral terms have hitherto been performed; still, for such atoms also, the wave-functions derived by the approximation method of Hartree have proved helpful, especially in accounting for the spatial electronic distribution in atoms determining the dispersion of Röntgen rays.

The wonderful tool of quantum mechanics, with the incorporation of the exclusion principle, has been not only essential for the detailed treatment of properties of isolated atoms, but also indispensable as regards the problem of molecular constitution. For this problem the study of the so-called *band spectra* plays as fundamental a part as that of series spectra for the constitution of atoms. Just as the latter spectra inform us about the states of binding of the electrons in the atoms, the analysis of band spectra tells us about the electron binding in the molecules, and, in addition, about the vibrations of the nuclei relative to each other and the states of rotation of the whole molecule. The gradual elucidation of this problem gives an interesting illustration of the general development of theoretical spectroscopy. The infra-red absorption bands

of polar molecules had already been satisfactorily accounted for on classical electromagnetic theory, as resulting from vibrations of the constituent ions relative to each other; and, in contrast to the case of spectra resulting from changes in the electron binding, this explanation needs only slight modification in the quantum theory, since the ionic masses are so large that vibrations involving several quanta may still be considered as small harmonic oscillations about equilibrium positions. The expectations of classical theory regarding the influence on spectra of translatory and rotatory motions of an atomic system as a whole were originally discussed by Rayleigh. While his deductions regarding the breadth of spectral lines resulting from the translatory thermal agitation of gas molecules are still valid in investigations of the masses of the emitting systems, the expectations regarding the influence of thermal rotation constituted a fundamental difficulty for the understanding of the observed sharpness of the lines of atomic spectra until the advent of the nuclear model, according to which the essential part of the mass of the atom does not contribute to its moment of inertia. In the case of molecules, however, thermal rotation is essential for the shape of the infra-red absorption bands, as was first recognised by Bjerrum in 1912. His considerations were quite independent of special ideas on atomic constitution, and, in accordance with Einstein's quantum theory of specific heats, he made the important prediction that the bands under consideration should show a fine structure in which each component should correspond to a different number of rotation quanta. On the present view of the origin of spectral lines, this interpretation of the fine structure has to be modified in the sense that each component is not associated with a single rotation state, but originates from a transition process involving a change of rotation as well as of vibration quanta. Nevertheless, on account of the selection rules for such transitions, deduced from the correspondence argument, the resulting fine structures of the infra-red absorption bands are of the general type predicted by Bjerrum and soon verified by observation. The complete analysis of these bands, first made possible by the refined methods of quantum mechanics, allows an unambiguous determination of the moments of inertia of the molecule in its different vibration states, and, in consequence, a detailed insight into the spatial configuration of the nuclei. In the case of the band spectra of the optical region, we have to do with transitions involving an essential modification of the electron binding, responsible for the energy exchanges occurring in chemical reactions, and the analysis of these spectra, based on the combination principle and the correspondence argument, has given us valuable information regarding such reactions. The

methods of quantum mechanics have been here especially helpful for the understanding of the homopolar bonds, as was first shown by Heitler and London. The chemical "bond" thus appears as essentially connected with such aspects of atomic stability as do not allow of an unambiguous visualisation by means of space-time pictures. Although no quantitative results have hitherto been obtained in this field, the underlying ideas are, no doubt, sufficiently advanced to furnish, in connexion with the analysis of band spectra, a trustworthy basis for the discussion of the large amount of material regarding organic compounds, disentangled by chemists with such unflinching intuition.

It is very tempting to enlarge upon this point which would be in itself a suitable subject for a lecture on chemistry and quantum theory, but this would oblige me to enter into details of a more technical character than the plan of the present lecture permits. Before proceeding to other problems, however, we shall briefly discuss the important conclusions which can be drawn from the interpretation of molecular spectra regarding the so-called *quantum statistics* in their relation to the nuclei. A starting point here was found by Heisenberg and Hund in the peculiar alternations in intensity occurring within the rotation bands of the spectra of molecules consisting of two identical atoms. Corresponding to the fact that the rotation of such symmetrical molecules, on classical theory, will not give rise to any radiation of the rotation frequency, but only to radiation of double frequency, the rotation states will, on quantum mechanics, split into two non-combining sets, characterised respectively by even and uneven values of the rotation quantum number. As was shown by Dennison, this result receives a striking confirmation from Eucken's measurements of the specific heat of hydrogen at low temperatures which for a long time had resisted all attempts at an interpretation on quantum theoretical statistics. Indeed, owing to the impossibility of transitions between the two types of rotation state of the hydrogen molecule, there will only be thermal equilibrium, under the conditions of these measurements, within each of the two sets of states, but not between them. Even at the very lowest temperatures, molecules will then be present in rotation states of both sets, which, in analogy with the classification of the stationary states of the helium atom, are called ortho- and para-states. Only under special conditions facilitating the establishment of thermal equilibrium, Bonhöffer and Eucken have recently succeeded in bringing all molecules into the lowest para-state, analogous to the normal helium state. For the quantitative interpretation of these remarkable phenomena, it is necessary to assume that the protons obey the same exclusion

principle as the electrons, in the sense that all wave-functions of a hydrogen molecule are not only antisymmetrical in the space and spin co-ordinates of the electrons, but also in those of the protons, defined in an exactly analogous way. This conclusion is in complete agreement with the intensity variations within the hydrogen rotation bands, the analysis of which has given for the moments of inertia of the molecule values identical with those derived from the theory of specific heat. The study of the helium band spectrum, however, has disclosed a new important feature. In fact, it was found that the wave-functions in this case were symmetrical in the space co-ordinates of the two nuclei, for which no spin had to be taken into account. We meet here with the same kind of statistics as that first introduced by Bose to account for Planck's law of black-body radiation on the basis of the idea of photons. Notwithstanding this formal similarity, the striking departure from classical ideas of statistics with which we have here to do presents, from the point of view of correspondence, an important difference in the cases of photons and of material particles like helium nuclei. In the first case, this departure is connected with the symbolic character of the photon idea, already emphasised; in fact, in the limit where the quantum of action can be neglected, and thus any trace of this idea disappears, the kind of statistics under consideration reduces to the classical treatment of electromagnetic radiation fields. In the case of material particles on the other hand, which are well-defined concepts from the classical point of view, the new quantum statistics find no unambiguous application within the scope of ordinary statistical mechanics in which the existence of the action quantum is neglected and the particles are treated as individual dynamical entities. This situation appears also from the very circumstance that in quantum mechanics we have two radically different kinds of statistics, namely, besides the Bose-statistics, the so-called Fermi-statistics which rest on the exclusion principle. The essentially non-visualisable character of these statistics has been no hindrance, however, to their great fruitfulness in the most varied atomic problems. Thus, in the hands of Sommerfeld, the Fermi-statistics have been fundamental for the understanding of the electric conduction in metals and allied phenomena; and, as was recently shown by Mott, the Bose-statistics are necessary to account for the scattering of α -rays in helium.

In this very cursory account it is impossible to give a proper impression of the beauty and consistency of the new quantum mechanics, in which nobody can take greater delight than those who have followed from the primitive stages the evolution of ideas

which I have tried to sketch in this lecture. It is true that this development has gradually carried us farther away from the ideals which inspired the ancient philosophers of the atomistic school and which have been so immensely fruitful for the development of chemical and physical science. This disillusion, however, has in return led us to a more comprehensive and, I venture to say, more open-minded view regarding natural phenomena. Indeed, we recognise in the existence of the quantum of action an inherent limitation, as regards the problem of atomic constitution, not only of all concepts of classical physics, but even of the ideas underlying our account of every-day experience. In fact, the unambiguous application of such fundamental concepts as space and time is essentially limited on account of the finite interaction between the object and the measuring tools, which, as a consequence of the existence of the elementary quantum, is involved in any measurement. To appreciate this point, we must remember that this interaction cannot be taken fully into account in the description of the phenomena, since the very definition of the space-time frame implies the neglect of the reaction of the object on the measuring instruments. Thus, any attempt to fix the space-time co-ordinates of the constituent particles of an atom would ultimately involve an essentially uncontrollable exchange of energy and momentum with the measuring rods and clocks which prevents an unambiguous correlation of the dynamical behaviour of the atomic particles before the observation with their later behaviour. Inversely, every application of conservation theorems, for instance to the energy balance in atomic reactions, involves an essential renunciation as regards the pursuance in space and time of the individual atomic particles. In other words, the use of the idea of stationary states stands in a mutually exclusive relationship to the applicability of space-time pictures. This situation corresponds exactly to the formalism of quantum mechanics, according to which the numerical values of two dynamical variables cannot in general be simultaneously determined, the limits for their unambiguous evaluation being given by the peculiar reciprocal relations known as the *indeterminacy principle* of Heisenberg. This principle defines the latitude in the application of classical concepts, necessary for the comprehension of the fundamental laws of atomic stability which are beyond the reach of these concepts. The essential indeterminacy in question must therefore not be taken to imply a one-sided departure from the ideal of causality underlying any account of natural phenomena. The use of energy conservation in connexion with the idea of stationary states, for instance, means an upholding of causality particularly striking when we realise that the very

idea of motion, on which the classical definition of kinetic energy rests, has become ambiguous in the field of atomic constitution. As I have stressed by the argumentation mentioned, space time co-ordination and dynamical conservation laws may be considered as *two complementary aspects of ordinary causality* which in this field exclude one another to a certain extent, although neither of them has lost its intrinsic validity. In this sense we recognise, as I mentioned at the beginning of this lecture, in the very attitudes of physicists and chemists respectively two complementary viewpoints equally indispensable for the comprehension of the laws of nature.

To appreciate the rôle of the concept of probability in atomic theory, it is moreover important to remember that the complete control over the course of events aimed at in the classical description of natural phenomena involves the essential assumption of a perfect liberty in the choice of the initial conditions. In such cases, however, as the occurrence of elementary transition processes where we have not even the possibility of defining the initial conditions in the classical sense we must be satisfied to have recourse to probability considerations in the sense of the correspondence argument. Notwithstanding the essentially new situation created by the discovery of the quantum of action, the characteristic feature with which we have here to do is not unfamiliar in atomic theory. A typical example is afforded by the statistical theory of heat, according to which the very concept of temperature stands in an exclusive relation to a detailed description of the behaviour of the atoms in the bodies concerned. It is just this point, implied in Maxwell's law of velocity distribution and especially conspicuous in Gibbs's treatment of statistical thermodynamics, which allows us to solve the apparent contradiction between the law of increase of entropy and the general reversibility of the individual mechanical processes which are involved in Boltzmann's interpretation of entropy in terms of probability. In fact, thermodynamical irreversibility, as exhibited in the levelling of temperatures, does not mean that a reversal of the course of events is impossible, but that the prediction of such a reversal cannot be part of any description involving a knowledge of the temperatures of the various bodies. This situation presents a remarkable analogy with the peculiar irreversibility characteristic of the description of quantum mechanics. Indeed, the reversibility of the classical laws of motion is formally upheld in the quantum symbolism, but the indeterminacy in the use of classical concepts defining the state of a system at a given time implies an essential irreversibility in the physical interpretation of this symbolism. In thermodynamics as well as in quantum

mechanics, the description contains an essential limitation imposed upon our control of the events which is connected with the impossibility of speaking of well-defined phenomena in the ordinary mechanical sense. Of course, this limitation has a quite different origin in the two cases. In fact, in statistical thermodynamics, we have in the first place not to do with a failure of the mechanical concepts in accounting for the details of the events, but with the incompatibility of such a detailed account with a definition of temperature. In quantum mechanics, on the other hand, we are concerned with the essential incompatibility between the elementary laws of atomic stability and the use of the classical mechanical concepts on which all measurements must be interpreted. Indeed, as we have seen, the view-point of "complementarity" in the description of atomic phenomena is forced upon us by the existence of the quantum of action in a similar way as the view-point of relativity in classical physics by the finite propagation of all electromagnetic interactions. In this sense, quantum mechanics may be said to represent the next step in the development of our tools of an adequate description of the natural phenomena.

The scope of the quantum mechanical symbolism is essentially confined, however, to problems where the intrinsic stability of the elementary electrical particles can be left out of consideration in a similar way as in the classical electron theory. In this connexion, it must not be forgotten that the existence of the electron even in classical theory imposes an essential limitation on the applicability of the mechanical and electromagnetic concepts. Indeed, the finite propagation of electromagnetic forces brings with it the existence of a fundamental length, the so-called "electron diameter," defining a lower limit for the extension of the region where the idealisation according to which the electron is considered as a charged material point is justifiable. Not only would a concentration of the charge of the electron within a smaller space result in an essential modification of its mass, but we even meet here with a limitation of the unambiguous use of the idea of inertial mass. In fact, we lose any simple basis for a sharp separation between ponderomotoric forces and radiative reactions when we consider processes in which the electron undergoes a velocity change of the same order as the velocity of light within a length of path equal to the electron diameter. It is true that such considerations lose their significance to a large extent on account of the existence of the quantum of action which imposes an essential limit to the analysis of motion. The fertility of quantum mechanics as applied to the problem of atomic stability lies just in the fact that the linear dimensions of the regions ascribed to even the firmest electron-bindings outside the nucleus are still very large compared

with the classical electron diameter. At the same time the theory of Dirac, already referred to, which represents a most important step towards the adaptation of the symbolism to the point of view of relativistic invariance, has disclosed new aspects of the fundamental difficulties involved in the reconciliation of the intrinsic stability of the electron with the existence of the quantum of action. In fact, Dirac's formalism implies the possibility of transition processes from states corresponding to normal properties of the electron to so-called states of negative energy for which the sign of its mass-charge ratio is reversed, the energy changes involved exceeding the critical value which, from Einstein's well-known relation, corresponds to the inertial mass of the electron. Transitions of this type should, on the theory, occur so frequently that even hydrogen atoms would be instantaneously destroyed with emission of radiation of very high frequency. Dirac himself has made an interesting attempt to overcome these difficulties by an extension of the formalism which permits exclusion of the unwanted transition processes by assuming that all states of negative energy are ordinarily filled up in a similar way as the completed electron groups in atomic structures. Such considerations, however, would seem to trespass the limit of applicability of the correspondence argument, and the difficulties inherent in any symbolism resting on the idealisation of the electron as a charged material point appear also most instructively in the recent attempt of Heisenberg and Pauli to build up a theory of electromagnetic fields on the lines of quantum mechanics. Their formalism leads, in fact, to consequences inconsistent with the finite mass of the electron and the small coupling between atoms and electromagnetic radiation fields, on which rests the interpretation of the empirical evidence regarding spectra, based on the idea of stationary states. Under these circumstances, we are strongly reminded that the whole attack on atomic problems leaning on the correspondence argument is an *essentially approximative procedure*, made possible only by the smallness of the ratio between the square of the elementary unit of electric charge and the product of the velocity of light and the quantum of action which allow us to a large extent to avoid the difficulties of relativistic quantum mechanics in considering the behaviour of extra-nuclear electrons. Like the ratio between the masses of the electron and of the proton, this is a non-dimensional constant fundamental for our whole picture of atomic phenomena, the theoretical derivation of which has been the object of much interesting speculation. Although we must expect that the determination of these constants will be an integral part of a general consistent theory in which the existence of the elementary electric particles and the existence of the quantum of action are both naturally incor-

porated, these problems would appear to be out of reach of the present formulation of quantum theory in which the complete independence of these two fundamental aspects of atomicity is an essential assumption.

This situation must above all be kept in mind when we turn to the problem of the *constitution of atomic nuclei*. The empirical evidence regarding the charges and the masses of these nuclei, as well as the evidence concerning the spontaneous and the excited nuclear disintegrations, leads, as we have seen, to the assumption that all nuclei are built up of protons and electrons. Still, as soon as we inquire more closely into the constitution of even the simplest nuclei, the present formulation of quantum mechanics fails essentially. For instance, it is quite unable to explain why four protons and two electrons hold together to form a stable helium nucleus. Evidently we are here entirely beyond the scope of any formalism based on the assumption of point electrons, as it also appears from the fact that the size of the helium nucleus, as deduced from the scattering of α -rays in helium, is of the same order of magnitude as the classical electron diameter. Just this circumstance suggests that the stability of the helium nucleus is inseparably connected with the limitation imposed on classical electrodynamics by the existence and the stability of the electron itself. This means, however, that no direct attack on this problem, based on the usual correspondence argument, is possible as far as the behaviour of the intra-nuclear electrons is concerned. As regards the behaviour of the protons, the situation is essentially different, since their comparatively large mass permits of an unambiguous use of the idea of space co-ordination even within nuclear dimensions. Of course, in absence of a general consistent theory accounting for the stability of the electron, we cannot make any direct estimate of the forces which hold the protons in the helium nucleus, but it is interesting to note that the energy liberated by the formation of the nucleus, as calculated from the so-called mass-defect by means of Einstein's relation, is in approximate agreement with the binding energy of the protons to be expected on quantum mechanics from the known nuclear dimensions. Indeed, this agreement indicates that the value of the ratio of the masses of the electron and the proton plays a fundamental part in the question of the stability of atomic nuclei. In this respect, the problem of nuclear constitution exhibits a characteristic difference from that of the constitution of the extra-nuclear electron configuration, since the stability of this configuration is essentially independent of the mass-ratio. When we pass from

the helium nucleus to heavier nuclei, the problem of nuclear constitution is, of course, still more complicated, although a certain simplification is afforded by the circumstance that the α -particles can be considered to a large extent to enter as separate entities into the constitution of these nuclei. This is not only suggested by the general facts of radioactivity, but appears also from the smallness of the additional mass defect, expressed by Aston's whole-number rule for the atomic weights of isotopes.

The main source of knowledge regarding the constitution of atomic nuclei is the study of their disintegrations, but important information is also derived from ordinary spectral analysis. As was mentioned, the hyperfine structures of spectral lines allow us to draw conclusions concerning the magnetic moments and angular momenta of the atomic nuclei, and from the intensity variations in band spectra we deduce the statistics obeyed by the nuclei. As might be expected, the interpretation of these results falls largely outside the scope of present quantum mechanics, and, in particular, the idea of spin is found not to be applicable to intra-nuclear electrons, as was first emphasised by Kronig. This situation appears especially clearly from the evidence concerning nuclear statistics. It is true that the fact, already mentioned, that the helium nuclei obey the Bose statistics is just what was to be expected from quantum mechanics for a system composed of an even number of particles which, like the electrons and protons, satisfy Pauli's exclusion principle. But the next nucleus for which data concerning statistics are available, namely the nitrogen nucleus, obeys also the Bose statistics, although it is composed of an uneven number of particles, namely 14 protons and 7 electrons, and thus should obey the Fermi statistics. Indeed, the general experimental evidence concerning this point seems to follow the rule that nuclei containing an even number of protons obey the Bose statistics, while nuclei containing an uneven number of protons obey the Fermi statistics. On the one hand, this remarkable "passivity" of the intra-nuclear electrons in the determination of the statistics is a very direct indication, indeed, of the essential limitation of the idea of separate dynamical entities when applied to electrons. Strictly speaking, we are not even justified in saying that a nucleus contains a definite number of electrons, but only that its negative electrification is equal to a whole number of elementary units, and, in this sense, the expulsion of a β -ray from a nucleus may be regarded as the creation of an electron as a mechanical entity. On the other hand, the rule just mentioned regarding nuclear statistics may be considered, from this point of view, as a support for the essential validity of a quantum mechanical treatment of the behaviour of the α -particles and protons in the nuclei. Actually, such a treatment

has also been very fruitful in accounting for their part in spontaneous and controlled nuclear disintegrations.

In the ten years that have elapsed since Rutherford's fundamental discoveries, a large amount of most valuable material on this subject has been accumulated, owing, above all, to the great exploration work in the new field carried on in the Cavendish Laboratory under his guidance. Now, from the theoretical standpoint, it is one of the most interesting results of the recent development of atomic theory that the use of probability considerations in the formulation of the fundamental *disintegration law*, which for its time was a quite isolated and very bold hypothesis, has been found to fall entirely in line with the general ideas of quantum mechanics. Already at the more primitive stage of the quantum theory, this point was touched upon by Einstein in connexion with his formulation of the probability laws of elementary radiation processes, and was further stressed by Rosseland in his fruitful work on inverse collisions. It is the wave-mechanical symbolism, however, which first offered the basis for a detailed interpretation of radio-active disintegrations, in complete conformity with Rutherford's deduction of nuclear dimensions from the scattering of α -rays. As was pointed out by Condon and Gurney, and independently by Gamow, the wave-formalism leads, in connexion with a simple model of the nucleus, to an instructive explanation of the law of α -ray disintegration as well as of the peculiar relationship, known as the rule of Geiger and Nuttall, between the mean life-time of the parent element and the energy of the α -ray expelled. Gamow, especially, succeeded in extending the quantum mechanical treatment of nuclear problems to a general qualitative account of the relationship between α - and γ -ray-spectra, in which the ideas of stationary states and elementary transition processes play the same part as in the case of ordinary atomic reactions and the emission of optical spectra. In these considerations, the α -particles in the nuclei are treated similarly to the extra-nuclear electrons in the atoms, with the characteristic difference, however, that the α -particles obey the Bose statistics and are kept within the nucleus by their own interaction, while the electrons, obeying the Fermi statistics, are held in the atom by the attraction of the nucleus. This is, among other causes, responsible for the smallness of the rate of energy emission, as γ -radiation, from excited nuclei which is even comparable with the rate of mechanical energy exchange between such nuclei and the surrounding electron clusters, the so-called internal conversion. In fact, in contrast to an atom built up of separate positive and negative particles, a nucleus-like system composed only of α -particles will never possess an electric moment, and, in this respect the additional protons and negative electric-

ation of actual nuclei can hardly be expected to make much difference. Apart from such simple applications of the correspondence argument, our ignorance of the forces acting on the α -particles and protons in the nuclei, which must be assumed to depend essentially on the negative electrification, prevents at present theoretical predictions of a more quantitative character. A promising means of exploring these forces is afforded, however, by the study of controlled disintegrations and allied phenomena. As far as the behaviour of α -particles and protons is concerned, it may therefore be possible to build up gradually, by means of quantum mechanics, a detailed theory of nuclear constitution, from which in turn we may get further information about the new aspects of atomic theory presented by the problem of negative nuclear electrification.

As regards this last question, much theoretical interest has recently been aroused by the peculiar features exhibited by the β -ray expulsions. On the one hand, the parent elements have a definite rate of decay, expressed by a simple probability law, just as in the case of the α -ray disintegrations. On the other hand, the energy liberated in a single β -ray disintegration is found to vary within a wide continuous range, whereas the energy emitted in an α -ray disintegration, when due account is taken of the accompanying electromagnetic radiation and the mechanical energy conversion, appears to be the same for all atoms of the same element. Unless the expulsion of β -rays from atomic nuclei, contrary to expectation, is not a spontaneous process but caused by some external agency, the application of the principle of energy conservation to β -ray disintegrations would accordingly imply that the atoms of any given radioelement would have different energy contents. Although the corresponding variations in mass would be far too small to be detected by the present experimental methods, such definite energy differences between the individual atoms would be very difficult to reconcile with other atomic properties. In the first place, we find no analogy to such variations in the domain of non-radioactive elements. In fact, as far as the investigations of nuclear statistics go, the nuclei of any type, which have the same charge and, within the limits of experimental accuracy, the same mass, are found to obey definite statistics in the quantum mechanical sense, meaning that such nuclei are not to be regarded as approximately equal, but as essentially identical. This conclusion is the more important for our argument, because, in absence of any theory of the intra-nuclear electrons, the identity under consideration is in no way a consequence of quantum mechanics, like the identity of the extra-nuclear electronic configurations of all atoms of an element in a given stationary state, but represents a new fundamental feature of atomic stability. Secondly,

no evidence of an energy variation of the kind in question can be found in the study of the stationary states of the radioactive nuclei involved in the emission of α - and γ -rays from members of a radioactive family preceding or following a β -ray product. Finally, the definite rate of decay, which is a common feature of α - and β -ray disintegrations, points, even for a β -ray product, to an essential similarity of all the parent atoms, in spite of the variation of the energy liberated by the expulsion of the β -ray. In absence of a general consistent theory embracing the relationship between the intrinsic stability of electrons and protons and the existence of the elementary quanta of electricity and action, it is very difficult to arrive at a definite conclusion in this matter. At the present stage of atomic theory, however, we may say that we have no argument, either empirical or theoretical, for upholding the energy principle in the case of β -ray disintegrations, and are even led to complications and difficulties in trying to do so. Of course, a radical departure from this principle would imply strange consequences, in case such a process could be reversed. Indeed, if, in a collision process, an electron could attach itself to a nucleus with loss of its mechanical individuality, and subsequently be recreated as a β -ray, we should find that the energy of this β -ray would generally differ from that of the original electron. Still, just as the account of those aspects of atomic constitution essential for the explanation of the ordinary physical and chemical properties of matter implies a renunciation of the classical ideal of causality, the features of atomic stability, still deeper-lying, responsible for the existence and the properties of atomic nuclei, may force us to renounce the very idea of energy balance. I shall not enter further into such speculations and their possible bearing on the much debated question of the source of stellar energy. I have touched upon them here mainly to emphasise that in atomic theory, notwithstanding all the recent progress, we must still be prepared for new surprises.

In judging the present situation of atomic theory, it is essential to recognise that the whole classical description of natural phenomena depends on the intrinsic stability of ordinary material bodies, and that therefore we must not be too much surprised when in that part of science where this stability itself is the object of investigation we shall meet with new aspects of natural philosophy. In striving with the unsolved difficulties involved in this situation, we are above all encouraged by the example of men like Faraday who in their wandering on untrodden paths knew how to find reliable guidance to the disclosure of Nature's secrets in Nature herself. The unfamiliar character of the views to which

such endeavours lead will naturally often appear mysterious, but, as Helmholtz so forcefully emphasised, just Faraday's general scientific method allowed him more than anybody else to contribute to the great aim "to purify science from the last remnants of metaphysics." In concluding this lecture, I may be allowed to express the hope that modern endeavours in atomic theory have not in this respect betrayed the great example which Faraday has set us, and that the new aspects of natural philosophy, which tend to harmonise the knowledge collected by chemists and physicists in their respective fields, far from involving any mysticism foreign to the spirit of science will be found to have contributed to the great common aim.
