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“On the Constitution of Atoms and Molecules”

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On the Constitution of Atoms and Molecules.
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Introduction.

IN order to explain the results of experiments on scattering of α rays by matter Prof. Rutherford† has given a theory of the structure of atoms. According to this theory, the atoms consist of a positively charged nucleus surrounded by a system of electrons kept together by attractive forces from the nucleus; the total negative charge of the electrons is equal to the positive charge of the nucleus. Further, the nucleus is assumed to be the seat of the essential part of the mass of the atom, and to have linear dimensions exceedingly small compared with the linear dimensions of the whole atom. The number of electrons in an atom is deduced to be approximately equal to half the atomic weight. Great interest is to be attributed to this atom-model; for, as Rutherford has shown, the assumption of the existence of nuclei, as those in question, seems to be necessary in order to account for the results of the experiments on large angle scattering of the α rays†.

In an attempt to explain some of the properties of matter on the basis of this atom-model we meet, however, with difficulties of a serious nature arising from the apparent

* Communicated by Prof. E. Rutherford, F.R.S.

† E. Rutherford, *Phil. Mag.* xxi. p. 669 (1911).

‡ See also Geiger and Marsden, *Phil. Mag.* April 1913.

instability of the system of electrons: difficulties purposely avoided in atom-models previously considered, for instance, in the one proposed by Sir J. J. Thomson*. According to the theory of the latter the atom consists of a sphere of uniform positive electrification, inside which the electrons move in circular orbits.

The principal difference between the atom-models proposed by Thomson and Rutherford consists in the circumstance that the forces acting on the electrons in the atom-model of Thomson allow of certain configurations and motions of the electrons for which the system is in a stable equilibrium; such configurations, however, apparently do not exist for the second atom-model. The nature of the difference in question will perhaps be most clearly seen by noticing that among the quantities characterizing the first atom a quantity of a length and of the same order of magnitude as the linear extension of the atom, while such a length does not appear among the quantities characterizing the second atom, viz. the charges and masses of the electrons and the positive nucleus; nor can it be determined solely by help of the latter quantities.

The way of considering a problem of this kind has, however, undergone essential alterations in recent years owing to the development of the theory of the energy radiation, and the direct affirmation of the new assumptions introduced in this theory, found by experiments on very different phenomena such as specific heats, photoelectric effect, Röntgen-rays, &c. The result of the discussion of these questions seems to be a general acknowledgment of the inadequacy of the classical electrodynamics in describing the behaviour of systems of atomic size†. Whatever the alteration in the laws of motion of the electrons may be, it seems necessary to introduce in the laws in question a quantity foreign to the classical electrodynamics, *i. e.* Planck's constant, or as it is called the elementary quantum of action. By the introduction of this quantity the question of the stable configuration of the electrons in the atoms is essentially changed, as this constant is of such dimensions and magnitude that it, together with the mass and charge of the particles, can determine a length of the order of magnitude required.

This paper is an attempt to show that the application of the above ideas to Rutherford's atom-model affords a basis

* J. J. Thomson, Phil. Mag. vii, p. 287 (1904).

† See *f. inst.*, 'Théorie du rayonnement et les quanta,' Rapports de la réunion à Bruxelles, Nov. 1911. Paris, 1912.

for a theory of the constitution of atoms. It will further be shown that from this theory we are led to a theory of the constitution of molecules.

In the present first part of the paper the mechanism of the binding of electrons by a positive nucleus is discussed in relation to Planck's theory. It will be shown that it is possible from the point of view taken to account in a simple way for the law of the line spectrum of hydrogen. Further, reasons are given for a principal hypothesis on which the considerations contained in the following parts are based.

I wish here to express my thanks to Prof. Rutherford for his kind and encouraging interest in this work.

PART I.—BINDING OF ELECTRONS BY POSITIVE NUCLEI.

§ 1. General Considerations.

The inadequacy of the classical electrodynamics in accounting for the properties of atoms from an atom-model as Rutherford's, will appear very clearly if we consider a simple system consisting of a positively charged nucleus of very small dimensions and an electron describing closed orbits around it. For simplicity, let us assume that the mass of the electron is negligibly small in comparison with that of the nucleus, and further, that the velocity of the electron is small compared with that of light.

Let us at first assume that there is no energy radiation. In this case the electron will describe stationary elliptical orbits. The frequency of revolution ω and the major-axis of the orbit $2a$ will depend on the amount of energy W which must be transferred to the system in order to remove the electron to an infinitely great distance apart from the nucleus. Denoting the charge of the electron and of the nucleus by $-e$ and E respectively and the mass of the electron by m , we thus get

$$\omega = \frac{\sqrt{2}}{\pi} \frac{W^{\frac{1}{2}}}{eE\sqrt{m}}, \quad 2a = \frac{eE}{W}. \quad \dots \quad (1)$$

Further, it can easily be shown that the mean value of the kinetic energy of the electron taken for a whole revolution is equal to W . We see that if the value of W is not given, there will be no values of ω and a characteristic for the system in question.

Let us now, however, take the effect of the energy radiation into account, calculated in the ordinary way from the acceleration of the electron. In this case the electron will

no longer describe stationary orbits. W will continuously increase, and the electron will approach the nucleus describing orbits of smaller and smaller dimensions, and with greater and greater frequency; the electron on the average gaining in kinetic energy at the same time as the whole system loses energy. This process will go on until the dimensions of the orbit are of the same order of magnitude as the dimensions of the electron or those of the nucleus. A simple calculation shows that the energy radiated out during the process considered will be enormously great compared with that radiated out by ordinary molecular processes.

It is obvious that the behaviour of such a system will be very different from that of an atomic system occurring in nature. In the first place, the actual atoms in their permanent state seem to have absolutely fixed dimensions and frequencies. Further, if we consider any molecular process, the result seems always to be that after a certain amount of energy characteristic for the systems in question is radiated out, the systems will again settle down in a stable state of equilibrium, in which the distances apart of the particles are of the same order of magnitude as before the process.

Now the essential point in Planck's theory of radiation is that the energy radiation from an atomic system does not take place in the continuous way assumed in the ordinary electrodynamics, but that it, on the contrary, takes place in distinctly separated emissions, the amount of energy radiated out from an atomic vibrator of frequency ν in a single emission being equal to $h\nu$, where τ is an entire number, and h is a universal constant*.

Returning to the simple case of an electron and a positive nucleus considered above, let us assume that the electron at the beginning of the interaction with the nucleus was at a great distance apart from the nucleus, and had no sensible velocity relative to the latter. Let us further assume that the electron after the interaction has taken place has settled down in a stationary orbit around the nucleus. We shall, for reasons referred to later, assume that the orbit in question is circular; this assumption will, however, make no alteration in the calculations for systems containing only a single electron.

Let us now assume that, during the binding of the electron, a homogeneous radiation is emitted of a frequency ν , equal to half the frequency of revolution of the electron in its final

* See f. inst., M. Planck, *Ann. d. Phys.* xxii, p. 758 (1910); xxviii, p. 642 (1912); *Verh. deutsch. Phys. Ges.* 1911, p. 138.

orbit; then, from Planck's theory, we might expect that the amount of energy emitted by the process considered is equal to $h\nu$, where h is Planck's constant and τ an entire number. If we assume that the radiation emitted is homogeneous, the second assumption concerning the frequency of the radiation suggests itself, since the frequency of revolution of the electron at the beginning of the emission is 0. The question, however, of the rigorous validity of both assumptions, and also of the application made of Planck's theory, will be more closely discussed in § 3.

$$\text{Putting } W = \tau h \frac{\omega}{2}, \quad \dots \dots \dots (2)$$

we get by help of the formula (1)

$$W = \frac{2\pi^2 m e^2 E^2}{\tau^2 h^2}, \quad \omega = \frac{4\pi^2 m e^2 E^2}{\tau^2 h^2}, \quad 2\alpha = \frac{\tau^2 h^2}{2\pi^2 m e^2 E^2} \dots \dots (3)$$

If in these expressions we give τ different values, we get a series of values for W , ω , and α corresponding to a series of configurations of the system. According to the above considerations, we are led to assume that these configurations will correspond to states of the system in which there is no radiation of energy; states which consequently will be stationary as long as the system is not disturbed from outside. We see that the value of W is greatest if τ has its smallest value 1. This case will therefore correspond to the most stable state of the system, i. e. will correspond to the binding of the electron for the breaking up of which the greatest amount of energy is required.

Putting in the above expressions $\tau = 1$ and $E = e$, and introducing the experimental values

$$e = 4.7 \cdot 10^{-10}, \quad \frac{e}{m} = 5.31 \cdot 10^{17}, \quad h = 6.5 \cdot 10^{-27},$$

we get

$$2\alpha = 1.1 \cdot 10^{-8} \text{ cm.}, \quad \omega = 6.2 \cdot 10^{15} \frac{1}{\text{sec.}}, \quad \frac{W}{e} = 13 \text{ volt.}$$

We see that these values are of the same order of magnitude as the linear dimensions of the atoms, the optical frequencies, and the ionization-potentials.

The general importance of Planck's theory for the discussion of the behaviour of atomic systems was originally pointed out by Einstein*. The considerations of Einstein

* A. Einstein, *Ann. d. Phys.* xvii, p. 132 (1905); xx, p. 199 (1906); xxii, p. 180 (1907).

have been developed and applied on a number of different phenomena, especially by Stark, Nernst, and Sommerfeld. The agreement as to the order of magnitude between values observed for the frequencies and dimensions of the atoms, and values for these quantities calculated by considerations similar to those given above, has been the subject of much discussion. It was first pointed out by Haas*, in an attempt to explain the meaning and the value of Planck's constant on the basis of J. J. Thomson's atom-model, by help of the linear dimensions and frequency of an hydrogen atom.

Systems of the kind considered in this paper, in which the forces between the particles vary inversely as the square of the distance, are discussed in relation to Planck's theory by J. W. Nicholson†. In a series of papers this author has shown that it seems to be possible to account for lines of hitherto unknown origin in the spectra of the stellar nebulae and that of the solar corona, by assuming the presence in these bodies of certain hypothetical elements of exactly indicated constitution. The atoms of these elements are supposed to consist simply of a ring of a few electrons surrounding a positive nucleus of negligibly small dimensions. The ratios between the frequencies corresponding to the lines in question are compared with the ratios between the frequencies corresponding to different modes of vibration of the ring of electrons. Nicholson has obtained a relation to Planck's theory showing that the ratios between the wave-length of different sets of lines of the coronal spectrum can be accounted for with great accuracy by assuming that the ratio between the energy of the system and the frequency of rotation of the ring is equal to an entire multiple of Planck's constant. The quantity Nicholson refers to as the energy is equal to twice the latest paper cited Nicholson has found it necessary to give the theory a more complicated form, still, however, representing the ratio of energy to frequency by a simple function of whole numbers.

The excellent agreement between the calculated and observed values of the ratios between the wave-lengths in question seems a strong argument in favour of the validity of the foundation of Nicholson's calculations. Serious

* A. E. Haas, *Jahrb. d. Rad. u. El.* vii. p. 261 (1910). See further, *Zeitschr. xii.* p. 408 (1911); *Verh. deutsch. Phys. Ges.* 1912, p. 481; F. A. Lindemann, *Verh. deutsch. Phys. Ges.* 1911, pp. 482, 1107; F. Haber, *Verh. deutsch. Phys. Ges.* 1911, p. 1117.
† J. W. Nicholson, *Month. Not. Roy. Astr. Soc. Lxxii.* pp. 49, 180, 677, 688, 729 (1912).

objections, however, may be raised against the theory. These objections are intimately connected with the problem of the homogeneity of the radiation emitted. In Nicholson's calculations the frequency of lines in a line-spectrum is identified with the frequency of vibration of a mechanical system in a distinctly indicated state of equilibrium. As a relation from Planck's theory is used, we might expect that the radiation is sent out in quanta; but systems like those considered, in which the frequency is a function of the energy, cannot emit a finite amount of a homogeneous radiation; for, as soon as the emission of radiation is started, the energy and also the frequency of the system are altered. Further, according to the calculation of Nicholson, the systems are unstable for some modes of vibration. Apart from such objections—which may be only formal (see p. 23)—it must be remarked, that the theory in the form given does not seem to be able to account for the well-known laws of Balmer and Rydberg connecting the frequencies of the lines in the line-spectra of the ordinary elements.

It will now be attempted to show that the difficulties in question disappear if we consider the problems from the point of view taken in this paper. Before proceeding it may be useful to restate briefly the ideas characterizing the calculations on p. 5. The principal assumptions used are:

- (1) That the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary mechanics, while the passing of the systems between different stationary states cannot be treated on that basis.

- (2) That the latter process is followed by the emission of a homogeneous radiation, for which the relation between the frequency and the amount of energy emitted is the one given by Planck's theory.

The first assumption seems to present itself; for it is known that the ordinary mechanics cannot have an absolute validity, but will only hold in calculations of certain mean values of the motion of the electrons. On the other hand, in the calculations of the dynamical equilibrium in a stationary state in which there is no relative displacement of the particles, we need not distinguish between the actual motions and their mean values. The second assumption is in obvious contrast to the ordinary ideas of electrodynamics, but appears to be necessary in order to account for experimental facts.

In the calculations on page 5 we have further made use

of the more special assumptions, viz. that the different stationary states correspond to the emission of a different number of Planck's energy-quanta, and that the frequency of the radiation emitted during the passing of the system from a state in which no energy is yet radiated out to one of the stationary states, is equal to half the frequency of revolution of the electron in the latter state. We can, however (see § 3), also arrive at the expressions (3) for the stationary states by using assumptions of somewhat different form. We shall, therefore, postpone the discussion of the special assumptions, and first show how by the help of the above principal assumptions, and of the expressions (3) for the stationary states, we can account for the line-spectrum of hydrogen.

§ 2. Emission of Line-spectra.

Spectrum of Hydrogen.—General evidence indicates that an atom of hydrogen consists simply of a single electron rotating round a positive nucleus of charge e^* . The re-formation of a hydrogen atom, when the electron has been removed to great distances away from the nucleus—*e. g.* by the effect of electrical discharge in a vacuum tube—will accordingly correspond to the binding of an electron by a positive nucleus considered on p. 5. If in (3) we put $E=e$, we get for the total amount of energy radiated out by the formation of one of the stationary states,

$$W_r = \frac{2\pi^2 m e^4}{h^2 r^2}.$$

The amount of energy emitted by the passing of the system from a state corresponding to $r=r_1$ to one corresponding to $r=r_2$, is consequently

$$W_{r_2} - W_{r_1} = \frac{2\pi^2 m e^4}{h^2} \left(\frac{1}{r_2^2} - \frac{1}{r_1^2} \right).$$

If now we suppose that the radiation in question is homogeneous, and that the amount of energy emitted is equal to $h\nu$, where ν is the frequency of the radiation, we get

$$W_{r_2} - W_{r_1} = h\nu,$$

* See *f. inst.* N. Bohr, *Phil. Mag.* xxv. p. 24 (1913). The conclusion drawn in the paper cited is strongly supported by the fact that hydrogen, in the experiments on positive rays of Sir J. J. Thomson, is the only element which never occurs with a positive charge corresponding to the loss of more than one electron (comp. *Phil. Mag.* xxiv. p. 672 (1912)).

and from this

$$\nu = \frac{2\pi^2 m e^4}{h^3} \left(\frac{1}{r_2^2} - \frac{1}{r_1^2} \right) \dots \dots \dots (4)$$

We see that this expression accounts for the law connecting the lines in the spectrum of hydrogen. If we put $r_2=2$ and let r_1 vary, we get the ordinary Balmer series. If we put $r_2=3$, we get the series in the ultra-red observed by Paschen* and previously suspected by Ritz. If we put $r_2=1$ and $r_1=4, 5, \dots$ we get series respectively in the extreme ultra-violet and the extreme ultra-red, which are not observed, but the existence of which may be expected.

The agreement in question is quantitative as well as qualitative. Putting

$$e = 4.7 \cdot 10^{-10}, \quad \frac{e}{m} = 5.31 \cdot 10^{17}, \quad \text{and} \quad h = 6.5 \cdot 10^{-27},$$

we get

$$\frac{2\pi^2 m e^4}{h^3} = 3.1 \cdot 10^{15}.$$

The observed value for the factor outside the bracket in the formula (4) is

$$3.290 \cdot 10^{15}.$$

The agreement between the theoretical and observed values is inside the uncertainty due to experimental errors in the constants entering in the expression for the theoretical value. We shall in § 3 return to consider the possible importance of the agreement in question.

It may be remarked that the fact, that it has not been possible to observe more than 12 lines of the Balmer series in experiments with vacuum tubes, while 33 lines are observed in the spectra of some celestial bodies, is just what we should expect from the above theory. According to the equation (3) the diameter of the orbit of the electron in the different stationary states is proportional to r^2 . For $r=12$ the diameter is equal to $1.6 \cdot 10^{-6}$ cm., or equal to the mean distance between the molecules in a gas at a pressure of about 7 mm. mercury; for $r=33$ the diameter is equal to $1.2 \cdot 10^{-5}$ cm., corresponding to about 0.02 mm. mercury. According to the theory the necessary condition for the appearance of a great number of lines is therefore a very small density of the gas; for simultaneously to obtain an

* F. Paschen, *Ann. d. Phys.* xxvii. p. 566 (1906).

intensity sufficient for observation the space filled with the gas must be very great. If the theory is right, we may therefore never expect to be able in experiments with vacuum tubes to observe the lines corresponding to high numbers of the Balmer series of the emission spectrum of hydrogen; it might, however, be possible to observe the lines by investigation of the absorption spectrum of this gas (see § 4).

It will be observed that we in the above way do not obtain other series of lines, generally ascribed to hydrogen; for instance, the series first observed by Pickering* in the spectrum of the star ζ Puppis, and the set of series recently found by Fowler† by experiments with vacuum tubes containing a mixture of hydrogen and helium. We shall, however, see that, by help of the above theory, we can account naturally for these series of lines if we ascribe them to helium.

A neutral atom of the latter element consists, according to Rutherford's theory, of a positive nucleus of charge $2e$ and two electrons. Now considering the binding of a single electron by a helium nucleus, we get, putting $E=2e$ in the expressions (3) on page 5, and proceeding in exactly the same way as above,

$$\nu = \frac{8\pi^2 m e^4}{h^3} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right) = \frac{2\pi^2 m e^4}{h^3} \left(\left(\frac{\tau_2}{2} \right)^2 - \left(\frac{\tau_1}{2} \right)^2 \right).$$

If we in this formula put $\tau_2=1$ or $\tau_2=2$, we get series of lines in the extreme ultra-violet. If we put $\tau_2=3$, and let τ_1 vary, we get a series which includes 2 of the series observed by Fowler, and denoted by him as the first and second principal series of the hydrogen spectrum. If we put $\tau_2=4$, we get the series observed by Pickering in the spectrum of ζ Puppis. Every second of the lines in this series is identical with a line in the Balmer series of the hydrogen spectrum; the presence of hydrogen in the star in question may therefore account for the fact that these lines are of a greater intensity than the rest of the lines in the series. The series is also observed in the experiments of Fowler, and denoted in his paper as the Sharp series of the hydrogen spectrum. If we finally in the above formula put $\tau_2=5, 6, \dots$ we get series, the strong lines of which are to be expected in the ultra-red.

The reason why the spectrum considered is not observed in

* E. C. Pickering, *Astrophys. J.* iv. p. 369 (1896); v. p. 92 (1897).
† A. Fowler, *Month. Not. Roy. Astr. Soc.* lxxiii. Dec. 1912.

ordinary helium tubes may be that in such tubes the ionization of helium is not so complete as in the star considered or in the experiments of Fowler, where a strong discharge was sent through a mixture of hydrogen and helium. The condition for the appearance of the spectrum is, according to the above theory, that helium atoms are present in a state in which they have lost both their electrons. Now we must assume that the amount of energy to be used in removing the second electron from a helium atom is much greater than that to be used in removing the first. Further, it is known from experiments on positive rays, that hydrogen atoms can acquire a negative charge; therefore the presence of hydrogen in the experiments of Fowler may effect that more electrons are removed from some of the helium atoms than would be the case if only helium were present.

Spectra of other substances.—In case of systems containing more electrons we must—in conformity with the result of experiments—expect more complicated laws for the line-spectra than those considered. I shall try to show that the point of view taken above allows, at any rate, a certain understanding of the laws observed.

According to Rydberg's theory—with the generalization given by Ritz*—the frequency corresponding to the lines of the spectrum of an element can be expressed by

$$\nu = F_1(\tau_1) - F_s(\tau_2),$$

where τ_1 and τ_2 are entire numbers, and F_1, F_2, F_3, \dots are functions of τ which approximately are equal to $\frac{K}{(\tau + a_1)^2}, \frac{K}{(\tau + a_2)^2}, \dots$. K is a universal constant, equal to the factor outside the bracket in the formula (4) for the spectrum of hydrogen. The different series appear if we put τ_1 or τ_2 equal to a fixed number and let the other vary.

The circumstance that the frequency can be written as a difference between two functions of entire numbers suggests an origin of the lines in the spectra in question similar to the one we have assumed for hydrogen; i. e. that the lines correspond to a radiation emitted during the passing of the system between two different stationary states. For systems containing more than one electron the detailed discussion may be very complicated, as there will be many different configurations of the electrons which can be taken into consideration as stationary states. This may account for the different sets of series in the line spectra emitted from the

* W. Ritz, *Phys. Zeitschr.* ix. p. 521 (1908).

substances in question. Here I shall only try to show how, by help of the theory, it can be simply explained that the constant K entering in Rydberg's formula is the same for all substances.

Let us assume that the spectrum in question corresponds to the radiation emitted during the binding of an electron; and let us further assume that the system including the electron considered is neutral. The force on the electron, when at a great distance apart from the nucleus and the electrons previously bound, will be very nearly the same as in the above case of the binding of an electron by a hydrogen nucleus. The energy corresponding to one of the stationary states will therefore for τ great be very nearly equal to that given by the expression (3) on p. 5, if we put $E=e$. For τ great we consequently get

$$\lim (\tau^2 \cdot F_1(\tau)) = \lim (\tau^2 \cdot F_2(\tau)) = \dots = \frac{2\pi^2 m e^4}{h^3},$$

in conformity with Rydberg's theory.

§ 3. General Considerations continued.

We shall now return to the discussion (see p. 7) of the special assumptions used in deducing the expressions (3) on p. 5 for the stationary states of a system consisting of an electron rotating round a nucleus.

For one, we have assumed that the different stationary states correspond to an emission of a different number of energy-quanta. Considering systems in which the frequency is a function of the energy, this assumption, however, may be regarded as improbable; for as soon as one quantum is sent out the frequency is altered. We shall now see that we can leave the assumption used and still retain the equation (2) on p. 5, and thereby the formal analogy with Planck's theory.

Firstly, it will be observed that it has not been necessary, in order to account for the law of the spectra by help of the expressions (3) for the stationary states, to assume that in any case a radiation is sent out corresponding to more than a single energy-quantum, $h\nu$. Further information on the frequency of the radiation may be obtained by comparing calculations of the energy radiation in the region of slow vibrations based on the above assumptions with calculations based on the ordinary mechanics. As is known, calculations on the latter basis are in agreement with experiments on the energy radiation in the named region.

Let us assume that the ratio between the total amount of

energy emitted and the frequency of revolution of the electron for the different stationary states is given by the equation $W=f(\tau) \cdot h\nu$, instead of by the equation (2). Proceeding in the same way as above, we get in this case instead of (3)

$$W = \frac{\pi^2 m e^2 E^2}{2 h^2 f^2(\tau)}, \quad \omega = \frac{\pi^2 m e^2 E^2}{2 h^2 f^2(\tau)}.$$

Assuming as above that the amount of energy emitted during the passing of the system from a state corresponding to $\tau=\tau_1$ to one for which $\tau=\tau_2$ is equal to $h\nu$, we get instead of (4)

$$\nu = \frac{\pi^2 m e^2 E^2}{2 h^3} \left(\frac{1}{f^2(\tau_2)} - \frac{1}{f^2(\tau_1)} \right).$$

We see that in order to get an expression of the same form as the Balmer series we must put $f(\tau)=c\tau$.

In order to determine c let us now consider the passing of the system between two successive stationary states corresponding to $\tau=N$ and $\tau=N-1$; introducing $f(\tau)=c\tau$, we get for the frequency of the radiation emitted

$$\nu = \frac{\pi^2 m e^2 E^2}{2 c^2 h^3} \cdot \frac{2N-1}{N^2(N-1)^2}.$$

For the frequency of revolution of the electron before and after the emission we have

$$\omega_N = \frac{\pi^2 m e^2 E^2}{2 c^2 h^3 N^3} \quad \text{and} \quad \omega_{N-1} = \frac{\pi^2 m e^2 E^2}{2 c^2 h^3 (N-1)^3}.$$

If N is great the ratio between the frequency before and after the emission will be very near equal to 1; and according to the ordinary electrodynamics we should therefore expect that the ratio between the frequency of radiation and the frequency of revolution also is very nearly equal to 1. This condition will only be satisfied if $c=\frac{1}{2}$. Putting $f(\tau)=\frac{\tau}{2}$, ω , however, again arrive at the equation (2) and consequently at the expression (3) for the stationary states.

If we consider the passing of the system between two states corresponding to $\tau=N$ and $\tau=N-n$, where n is small compared with N , we get with the same approximation as above, putting $f(\tau)=\frac{\tau}{2}$,

$$\nu = n\omega.$$

The possibility of an emission of a radiation of such a frequency may also be interpreted from analogy with the ordinary electrodynamics, as an electron rotating round a nucleus in an elliptical orbit will emit a radiation which according to Fourier's theorem can be resolved into homogeneous components, the frequencies of which are $n\omega$, if ω is the frequency of revolution of the electron.

We are thus led to assume that the interpretation of the equation (2) is not that the different stationary states correspond to an emission of different numbers of energy-quanta, but that the frequency of the energy emitted during the passing of the system from a state in which no energy is yet radiated out to one of the different stationary states, is equal

to different multiples of $\frac{\omega}{2}$, where ω is the frequency of revolution of the electron in the state considered. From this assumption we get exactly the same expressions as before for the stationary states, and from these by help of the principal assumptions on p. 7 the same expression for the law of the hydrogen spectrum. Consequently we may regard our preliminary considerations on p. 5 only as a simple form of representing the results of the theory.

Before we leave the discussion of this question, we shall for a moment return to the question of the significance of the agreement between the observed and calculated values of the constant entering in the expressions (4) for the Balmer series of the hydrogen spectrum. From the above consideration it will follow that, taking the starting-point in the form of the law of the hydrogen spectrum and assuming that the different lines correspond to a homogeneous radiation emitted during the passing between different stationary states, we shall arrive at exactly the same expression for the constant in question as that given by (4), if we only assume (1) that the radiation is sent out in quanta $h\nu$, and (2) that the frequency of the radiation emitted during the passing of the system between successive stationary states will coincide with the frequency of revolution of the electron in the region of slow vibrations.

As all the assumptions used in this latter way of representing the theory are of what we may call a qualitative character, we are justified in expecting—if the whole way of considering is a sound one—an absolute agreement between the values calculated and observed for the constant in question, and not only an approximate agreement. The formula (4) may therefore be of value in the discussion of the results of experimental determinations of the constants e , m , and h .

While there obviously can be no question of a mechanical foundation of the calculations given in this paper, it is, however, possible to give a very simple interpretation of the result of the calculation on p. 5 by help of symbols taken from the ordinary mechanics. Denoting the angular momentum of the electron round the nucleus by M , we have immediately for a circular orbit $\pi M = \frac{T}{\omega}$ where ω is the frequency of revolution and T the kinetic energy of the electron; for a circular orbit we further have $T = W$ (see p. 3) and from (2), p. 5, we consequently get

$$M = \tau M_0,$$

where

$$M_0 = \frac{h}{2\pi} = 1.04 \times 10^{-27}.$$

If we therefore assume that the orbit of the electron in the stationary states is circular, the result of the calculation on p. 5 can be expressed by the simple condition: that the angular momentum of the electron round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value, independent of the charge on the nucleus. The possible importance of the angular momentum in the discussion of atomic systems in relation to Planck's theory is emphasized by Nicholson*.

The great number of different stationary states we do not observe except by investigation of the emission and absorption of radiation. In most of the other physical phenomena, however, we only observe the atoms of the matter in a single distinct state, i. e. the state of the atoms at low temperature. From the preceding considerations we are immediately led to the assumption that the "permanent" state is the one among the stationary states during the formation of which the greatest amount of energy is emitted. According to the equation (3) on p. 5, this state is the one which corresponds to $\tau = 1$.

§ 4. Absorption of Radiation.

In order to account for Kirchhoff's law it is necessary to introduce assumptions on the mechanism of absorption of radiation which correspond to those we have used considering the emission. Thus we must assume that a system consisting of a nucleus and an electron rotating round it under certain circumstances can absorb a radiation of a frequency equal to the frequency of the homogeneous radiation emitted during

* J. W. Nicholson, *loc. cit.* p. 679.

the passing of the system between different stationary states. Let us consider the radiation emitted during the passing of the system between two stationary states A_1 and A_2 corresponding to values for τ equal to τ_1 and τ_2 , $\tau_1 > \tau_2$. As the necessary condition for an emission of the radiation in question was the presence of systems in the state A_1 , we must assume that the necessary condition for an absorption of the radiation is the presence of systems in the state A_2 .

These considerations seem to be in conformity with experiments on absorption in gases. In hydrogen gas at ordinary conditions for instance there is no absorption of a radiation of a frequency corresponding to the line-spectrum of this gas; such an absorption is only observed in hydrogen gas in a luminous state. This is what we should expect according to the above. We have on p. 9 assumed that the radiation in question was emitted during the passing of the systems between stationary states corresponding to $\tau > 2$. The state of the atoms in hydrogen gas at ordinary conditions should, however, correspond to $\tau = 1$; furthermore, hydrogen atoms at ordinary conditions combine into molecules, *i. e.* into systems in which the electrons have frequencies different from those in the atoms (see Part III.). From the circumstance that certain substances in a non-luminous state, as, for instance, sodium vapour, absorb radiation corresponding to lines in the line-spectra of the substances, we may, on the other hand, conclude that the lines in question are emitted during the passing of the system between two states, one of which is the permanent state.

How much the above considerations differ from an interpretation based on the ordinary electrodynamics is perhaps most clearly shown by the fact that we have been forced to assume that a system of electrons will absorb a radiation of a frequency different from the frequency of vibration of the electrons calculated in the ordinary way. It may in this connexion be of interest to mention a generalization of the considerations to which we are led by experiments on the photo-electric effect, and which may be able to throw some light on the problem in question. Let us consider a state of the system in which the electron is free, *i. e.* in which the electron possesses kinetic energy sufficient to remove to infinite distances from the nucleus. If we assume that the motion of the electron is governed by the ordinary mechanics and that there is no (sensible) energy radiation, the total energy of the system—as in the above considered stationary states—will be constant. Further, there will be perfect continuity between the two kinds of states, as the difference between

frequency and dimensions of the systems in successive stationary states will diminish without limit if τ increases. In the following considerations we shall for the sake of brevity refer to the two kinds of states in question as “mechanical” states; by this notation only emphasizing the assumption that the motion of the electron in both cases can be accounted for by the ordinary mechanics.

Tracing the analogy between the two kinds of mechanical states, we might now expect the possibility of an absorption of radiation, not only corresponding to the passing of the system between two different stationary states, but also corresponding to the passing between one of the stationary states and a state in which the electron is free; and as above, we might expect that the frequency of this radiation was determined by the equation $E = h\nu$, where E is the difference between the total energy of the system in the two states. As it will be seen, such an absorption of radiation is just what is observed in experiments on ionization by ultra-violet light and by Röntgen rays. Obviously, we get in this way the same expression for the kinetic energy of an electron ejected from an atom by photo-electric effect as that deduced by Einstein*, *i. e.* $T = h\nu - W$, where T is the kinetic energy of the electron ejected, and W the total amount of energy emitted during the original binding of the electron.

The above considerations may further account for the result of some experiments of R. W. Wood† on absorption of light by sodium vapour. In these experiments, an absorption corresponding to a very great number of lines in the principal series of the sodium spectrum is observed, and in addition a continuous absorption which begins at the head of the series and extends to the extreme ultra-violet. This is exactly what we should expect according to the analogy in question, and, as we shall see, a closer consideration of the above experiments allows us to trace the analogy still further. As mentioned on p. 9 the radii of the orbits of the electrons will for stationary states corresponding to high values for τ be very great compared with ordinary atomic dimensions. This circumstance was used as an explanation of the non-appearance in experiments with vacuum-tubes of lines corresponding to the higher numbers in the Balmer series of the hydrogen spectrum. This is also in conformity with experiments on the emission spectrum of sodium; in the principal series of the emission spectrum of this substance

* A. Einstein, *Ann. d. Phys.* xvii. p. 146 (1906).

† R. W. Wood, *Physical Optics*, p. 613 (1911).

rather few lines are observed. Now in Wood's experiments the pressure was not very low, and the states corresponding to high values for r could therefore not appear; yet in the absorption spectrum about 50 lines were detected. In the experiments in question we consequently observe an absorption of radiation which is not accompanied by a complete transition between two different stationary states. According to the present theory we must assume that this absorption is followed by an emission of energy during which the systems pass back to the original stationary state. If there are no collisions between the different systems this energy will be emitted as a radiation of the same frequency as that absorbed, and there will be no true absorption but only a scattering of the original radiation; a true absorption will not occur unless the energy in question is transformed by collisions into kinetic energy of free particles. In analogy we may now from the above experiments conclude that a bound electron—also in cases in which there is no ionization—will have an absorbing (scattering) influence on a homogeneous radiation, as soon as the frequency of the radiation is greater than W/h , where W is the total amount of energy emitted during the binding of the electron. This would be highly in favour of a theory of absorption as the one sketched above, as there can in such a case be no question of a coincidence of the frequency of the radiation and a characteristic frequency of vibration of the electron. It will further be seen that the assumption, that there will be an absorption (scattering) of any radiation corresponding to a transition between two different mechanical states, is in perfect analogy with the assumption generally used that a free electron will have an absorbing (scattering) influence on light of any frequency. Corresponding considerations will hold for the emission of radiation.

In analogy to the assumption used in this paper that the emission of line-spectra is due to the re-formation of atoms after one or more of the lightly bound electrons are removed, we may assume that the homogeneous Röntgen radiation is emitted during the settling down of the systems after one of the firmly bound electrons escapes, *e.g.* by impact of cathode particles*. In the next part of this paper, dealing with the constitution of atoms, we shall consider the question more closely and try to show that a calculation based on this assumption is in quantitative agreement with the results of experiments: here we shall only mention briefly a problem with which we meet in such a calculation.

* Compare J. J. Thomson, *Phil. Mag.* xxiii. p. 456 (1912).

Experiments on the phenomena of X-rays suggest that not only the emission and absorption of radiation cannot be treated by the help of the ordinary electrodynamics, but not even the result of a collision between two electrons of which the one is bound in an atom. This is perhaps most clearly shown by some very instructive calculations on the energy of β -particles emitted from radioactive substances recently published by Rutherford*. These calculations strongly suggest that an electron of great velocity in passing through an atom and colliding with the electrons bound will lose energy in distinct finite quanta. As is immediately seen, this is very different from what we might expect if the result of the collisions was governed by the usual mechanical laws. The failure of the classical mechanics in such a problem might also be expected beforehand from the absence of anything like equipartition of kinetic energy between free electrons and electrons bound in atoms. From the point of view of the "mechanical" states we see, however, that the following assumption—which is in accord with the above analogy—might be able to account for the result of Rutherford's calculation and for the absence of equipartition of kinetic energy: two colliding electrons, bound or free, will, after the collision as well as before, be in mechanical states. Obviously, the introduction of such an assumption would not make any alteration necessary in the classical treatment of a collision between two free particles. But, considering a collision between a free and a bound electron, it would follow that the bound electron by the collision could not acquire a less amount of energy than the difference in energy corresponding to successive stationary states, and consequently that the free electron which collides with it could not lose a less amount.

The preliminary and hypothetical character of the above considerations needs not to be emphasized. The intention, however, has been to show that the sketched generalization of the theory of the stationary states possibly may afford a simple basis of representing a number of experimental facts which cannot be explained by help of the ordinary electrodynamics, and that the assumptions used do not seem to be inconsistent with experiments on phenomena for which a satisfactory explanation has been given by the classical dynamics and the wave theory of light.

* E. Rutherford, *Phil. Mag.* xxiv. pp. 453 & 893 (1912).

§ 5. *The permanent State of an Atomic System.*

We shall now return to the main object of this paper—the discussion of the “permanent” state of a system consisting of nuclei and bound electrons. For a system consisting of a nucleus and an electron rotating round it, this state is, according to the above, determined by the condition that the angular momentum of the electron round the nucleus is equal to $\frac{h}{2\pi}$.

On the theory of this paper the only neutral atom which contains a single electron is the hydrogen atom. The permanent state of this atom should correspond to the values of α and ω calculated on p. 5. Unfortunately, however, we know very little of the behaviour of hydrogen atoms on account of the small dissociation of hydrogen molecules at ordinary temperatures. In order to get a closer comparison with experiments, it is necessary to consider more complicated systems.

Considering systems in which more electrons are bound by a positive nucleus, a configuration of the electrons which presents itself as a permanent state is one in which the electrons are arranged in a ring round the nucleus. In the discussion of this problem on the basis of the ordinary electrodynamics, we meet—apart from the question of the energy radiation—with new difficulties due to the question of the stability of the ring. Disregarding for a moment this latter difficulty, we shall first consider the dimensions and frequency of the systems in relation to Planck's theory of radiation.

Let us consider a ring consisting of n electrons rotating round a nucleus of charge E , the electrons being arranged at equal angular intervals around the circumference of a circle of radius a .

The total potential energy of the system consisting of the electrons and the nucleus is

$$P = -\frac{ne}{a} (E - es_n),$$

where

$$s_n = \frac{1}{4} \sum_{s=1}^{s=n-1} \operatorname{cosec} \frac{s\pi}{n}.$$

For the radial force exerted on an electron by the nucleus and the other electrons we get

$$F = -\frac{1}{n} \frac{dP}{da} = -\frac{e}{a^2} (E - es_n).$$

Denoting the kinetic energy of an electron by T and neglecting the electromagnetic forces due to the motion of the electrons (see Part II.), we get, putting the centrifugal force on an electron equal to the radial force,

$$\frac{2T}{a} = \frac{e}{a^2} (E - es_n),$$

or

$$T = \frac{e}{2a} (E - es_n).$$

From this we get for the frequency of revolution

$$\omega = \frac{1}{2\pi} \sqrt{\frac{e(E - es_n)}{ma^3}}.$$

The total amount of energy W necessary transferred to the system in order to remove the electrons to infinite distances apart from the nucleus and from each other is

$$W = -P - nT = \frac{ne}{2a} (E - es_n) = nT,$$

equal to the total kinetic energy of the electrons.

We see that the only difference in the above formula and those holding for the motion of a single electron in a circular orbit round a nucleus is the exchange of E for $E - es_n$. It is also immediately seen that corresponding to the motion of an electron in an elliptical orbit round a nucleus, there will be a motion of the n electrons in which each rotates in an elliptical orbit with the nucleus in the focus, and the n electrons at any moment are situated at equal angular intervals on a circle with the nucleus as the centre. The major axis and frequency of the orbit of the single electrons will for this motion be given by the expressions (1) on p. 3 if we replace E by $E - es_n$ and W by $\frac{W}{n}$.

Let us now suppose that the system of n electrons rotating in a ring round a nucleus is formed in a way analogous to the one assumed for a single electron rotating round a nucleus. It will thus be assumed that the electrons, before the binding by the nucleus, were at a great distance apart from the latter and possessed no sensible velocities, and also that during the binding a homogeneous radiation is emitted. As in the case of a single electron, we have here that the total amount of energy emitted during the formation of the system is equal to the final kinetic energy of the electrons. If we now suppose that during the

formation of the system the electrons at any moment are situated at equal angular intervals on the circumference of a circle with the nucleus in the centre, from analogy with the considerations on p. 5 we are here led to assume the existence of a series of stationary configurations in which the kinetic energy per electron is equal to $\tau \frac{1}{2} \frac{\omega}{\tau}$, where τ is an entire number, h Planck's constant, and ω the frequency of revolution. The configuration in which the greatest amount of energy is emitted is, as before, the one in which $\tau=1$. This configuration we shall assume to be the permanent state of the system if the electrons in this state are arranged in a single ring. As for the case of a single electron we get that the angular momentum of each of the electrons is equal to $\frac{h}{2\pi}$. It may be remarked that instead of considering the single electrons we might have considered the ring as an entity. This would, however, lead to the same result, for in this case the frequency of revolution ω will be replaced by the frequency $n\omega$ of the radiation from the whole ring calculated from the ordinary electrodynamics, and Γ by the total kinetic energy $n\Gamma$.

There may be many other stationary states corresponding to other ways of forming the system. The assumption of the existence of such states seems necessary in order to account for the line-spectra of systems containing more than one electron (p. 11); it is also suggested by the theory of Nicholson mentioned on p. 6, to which we shall return in a moment. The consideration of the existence of stationary states in which all the electrons are arranged in a ring and which correspond to greater values for the total energy emitted than the one we above have assumed to be the permanent state.

Further, there may be stationary configurations of a system of n electrons and a nucleus of charge E in which all the electrons are not arranged in a single ring. The question, however, of the existence of such stationary configurations is not essential for our determination of the permanent state, as long as we assume that the electrons in this state of the system are arranged in a single ring. Systems corresponding to more complicated configurations will be discussed on p. 24.

Using the relation $\Gamma = \frac{h}{2} \frac{\omega}{\tau}$ we get, by help of the above expressions for Γ and ω , values for α and ω corresponding to

the permanent state of the system which only differ from those given by the equations (3) on p. 5, by exchange of E for $E - e\phi_{\text{ext}}$.

The question of stability of a ring of electrons rotating round a positive charge is discussed in great detail by Sir J. J. Thomson*. An adaption of Thomson's analysis for the case here considered of a ring rotating round a nucleus of negligibly small linear dimensions is given by Nicholson†. The investigation of the problem in question naturally divides in two parts: one concerning the stability for displacements of the electrons in the plane of the ring; one concerning calculations perpendicular to this plane. As Nicholson's calculations show, the answer to the question of stability differs very much in the two cases in question. While the ring for the latter displacements in general is stable if the number of electrons is not great; the ring is in no case considered by Nicholson stable for displacements of the first kind.

According, however, to the point of view taken in this paper, the question of stability for displacements of the electrons in the plane of the ring is most intimately connected with the question of the mechanism of the binding of the electrons, and like the latter cannot be treated on the basis of the ordinary dynamics. The hypothesis of which we shall make use in the following is that the stability of a ring of electrons rotating round a nucleus is secured through the above condition of the universal constancy of the angular momentum, together with the further condition that the configuration of the particles is the one by the formation of which the greatest amount of energy is emitted. As will be shown, this hypothesis is, concerning the question of stability for a displacement of the electrons perpendicular to the plane of the ring, equivalent to that used in ordinary mechanical calculations.

Returning to the theory of Nicholson on the origin of lines observed in the spectrum of the solar corona, we shall now see that the difficulties mentioned on p. 7 may be only formal. In the first place, from the point of view considered above the objection as to the instability of the systems for displacements of the electrons in the plane of the ring may not be valid. Further, the objection as to the emission of the radiation in quanta will not have reference to the calculations in question, if we assume that in the coronal spectrum we are not dealing with a true emission but only with a scattering of radiation. This assumption seems probable if we consider

* *Loc. cit.*

† *Loc. cit.*

the conditions in the celestial body in question; for on account of the enormous rarefaction of the matter there may be comparatively few collisions to disturb the stationary states and to cause a true emission of light corresponding to the transition between different stationary states; on the other hand there will in the solar corona be intense illumination of light of all frequencies which may excite the natural vibrations of the systems in the different stationary states. If the above assumption is correct, we immediately understand the entirely different form for the laws connecting the lines discussed by Nicholson and those connecting the ordinary line-spectra considered in this paper.

Proceeding to consider systems of a more complicated constitution, we shall make use of the following theorem, which can be very simply proved:—

“In every system consisting of electrons and positive nuclei, in which the nuclei are at rest and the electrons move in circular orbits with a velocity small compared with the velocity of light, the kinetic energy will be numerically equal to half the potential energy.”

By help of this theorem we get—as in the previous cases of a single electron or of a ring rotating round a nucleus—that the total amount of energy emitted, by the formation of the systems from a configuration in which the distances apart of the particles are infinitely great and in which the particles have no velocities relative to each other, is equal to the kinetic energy of the electrons in the final configuration.

In analogy with the case of a single ring we are here led to assume that corresponding to any configuration of equilibrium a series of geometrically similar, stationary configurations of the system will exist in which the kinetic energy of every electron is equal to the frequency of revolution multiplied by $\frac{\tau}{2}h$, where τ is an entire number and h

Planck's constant. In any such series of stationary configurations the one corresponding to the greatest amount of energy emitted will be the one in which τ for every electron is equal to 1. Considering that the ratio of kinetic energy to frequency for a particle rotating in a circular orbit is equal to π times the angular momentum round the centre of the orbit, we are therefore led to the following simple generalization of the hypotheses mentioned on pp. 15 and 22.

“In any molecular system consisting of positive nuclei and electrons in which the nuclei are at rest relative to each other and the electrons move in circular orbits, the angular momentum

of every electron round the centre of its orbit will in the permanent state of the system be equal to $\frac{h}{2\pi}$, where h is Planck's constant”.*

In analogy with the considerations on p. 23, we shall assume that a configuration satisfying this condition is stable if the total energy of the system is less than in any neighbouring configuration satisfying the same condition of the angular momentum of the electrons.

As mentioned in the introduction, the above hypothesis will be used in a following communication as a basis for a theory of the constitution of atoms and molecules. It will be shown that it leads to results which seem to be in conformity with experiments on a number of different phenomena.

The foundation of the hypothesis has been sought entirely in its relation with Planck's theory of radiation; by help of considerations given later it will be attempted to throw some further light on the foundation of it from another point of view.

April 5, 1913.

* In the considerations leading to this hypothesis we have assumed that the velocity of the electrons is small compared with the velocity of light. The limits of the validity of this assumption will be discussed in Part II.

On the Constitution of Atoms and Molecules.
By N. BOHR, *Dr. phil. Copenhagen* *.

PART II.—SYSTEMS CONTAINING ONLY A SINGLE NUCLEUS †.

§ 1. *General Assumptions.*

FOLLOWING the theory of Rutherford, we shall assume that the atoms of the elements consist of a positively charged nucleus surrounded by a cluster of electrons. The nucleus is the seat of the essential part of the mass of the atom, and has linear dimensions exceedingly small compared with the distances apart of the electrons in the surrounding cluster.

As in the previous paper, we shall assume that the cluster of electrons is formed by the successive binding by the nucleus of electrons initially nearly at rest, energy at the same time being radiated away. This will go on until, when the total negative charge on the bound electrons is numerically equal to the positive charge on the nucleus, the system will be neutral and no longer able to exert sensible forces on electrons at distances from the nucleus great in comparison with the dimensions of the orbits of the bound electrons. We may regard the formation of helium from α rays as an

* Communicated by Prof. E. Rutherford, F.R.S.

† Part I. was published in *Phil. Mag.* xxvi. p. 1 (1913).

observed example of a process of this kind, an α particle on this view being identical with the nucleus of a helium atom.

On account of the small dimensions of the nucleus, its internal structure will not be of sensible influence on the constitution of the cluster of electrons, and consequently will have no effect on the ordinary physical and chemical properties of the atom. The latter properties on this theory will depend entirely on the total charge and mass of the nucleus; the internal structure of the nucleus will be of influence only on the phenomena of radioactivity.

From the result of experiments on large-angle scattering of α -rays, Rutherford * found an electric charge on the nucleus corresponding per atom to a number of electrons approximately equal to half the atomic weight. This result seems to be in agreement with the number of electrons per atom calculated from experiments on scattering of Röntgen radiation †. The total experimental evidence supports the hypothesis ‡ that the actual number of electrons in a neutral atom with a few exceptions is equal to the number which indicates the position of the corresponding element in the series of elements arranged in order of increasing atomic weight. For example on this view, the atom of oxygen which is the eighth element of the series has eight electrons and a nucleus carrying eight unit-charges.

We shall assume that the electrons are arranged at equal angular intervals in coaxial rings rotating round the nucleus. In order to determine the frequency and dimensions of the rings we shall use the main hypothesis of the first paper, viz.: that in the permanent state of an atom the angular momentum of every electron round the centre of its orbit is equal to the universal value $\frac{h}{2\pi}$, where h is Planck's constant.

We shall take as a condition of stability, that the total energy of the system in the configuration in question is less than in any neighbouring configuration satisfying the same condition of the angular momentum of the electrons.

If the charge on the nucleus and the number of electrons in the different rings is known, the condition in regard to the angular momentum of the electrons will, as shown in § 2, completely determine the configuration of the system, i.e., the frequency of revolution and the linear dimensions of the rings. Corresponding to different distributions of the

* Comp. also Geiger and Marsden, *Phil. Mag.* xxv. p. 604 (1913).

† Comp. C. G. Barkla, *Phil. Mag.* xxi. p. 643 (1911).

‡ Comp. A. v. d. Broek, *Phys. Zeitschr.* xiv. p. 32 (1913).

electrons in the rings, however, there will, in general, be more than one configuration which will satisfy the condition of the angular momentum together with the condition of stability.

In § 3 and § 4 it will be shown that, on the general view of the formation of the atoms, we are led to indications of the arrangement of the electrons in the rings which are consistent with those suggested by the chemical properties of the corresponding element.

In § 5 it will be shown that it is possible from the theory to calculate the minimum velocity of cathode rays necessary to produce the characteristic Röntgen radiation from the element, and that this is in approximate agreement with the experimental values.

In § 6 the phenomena of radioactivity will be briefly considered in relation to the theory.

§ 2. Configuration and Stability of the Systems.

Let us consider an electron of charge e and mass m which moves in a circular orbit of radius a with a velocity v small compared with the velocity of light. Let us denote the radial force acting on the electrons by $\frac{e^2}{a^2} F$; F will in general be dependent on a . The condition of dynamical equilibrium gives

$$\frac{mv^2}{a} = \frac{e^2}{a^2} F.$$

Introducing the condition of universal constancy of the angular momentum of the electron, we have

$$mva = \frac{h}{2\pi}.$$

From these two conditions we now get

$$a = \frac{h^2}{4\pi^2 e^2 m} F^{-1} \quad \text{and} \quad v = \frac{2\pi e^2}{h} F; \quad \dots \quad (1)$$

and for the frequency of revolution ω consequently

$$\omega = \frac{4\pi^2 e^4 m}{h^3} F^2. \quad \dots \quad (2)$$

If F is known, the dimensions and frequency of the corresponding orbits are simply determined by (1) and (2). For a

ring of n electrons rotating round a nucleus of charge Ne we have (comp. Part I., p. 20)

$$F = N - s_n \quad \text{where} \quad s_n = \frac{1}{4} \sum_{i=1}^{n-1} \frac{s\tau}{\cos \frac{\pi i}{n}}.$$

The values for s_n from $n=1$ to $n=16$ are given in the table on p. 482.

For systems consisting of nuclei and electrons in which the first are at rest and the latter move in circular orbits with a velocity small compared with the velocity of light, we have shown (see Part I., p. 24) that the total kinetic energy of the electrons is equal to the total amount of energy emitted during the formation of the system from an original configuration in which all the particles are at rest and at infinite distances from each other. Denoting this amount of energy by W , we consequently get

$$W = \sum \frac{1}{2} m v^2 = \frac{2\pi^2 e^4 m}{h^2} \sum F^2. \quad \dots \quad (3)$$

Putting in (1), (2), and (3) $e=4.7 \cdot 10^{-10}$, $\frac{e}{m}=5.31 \cdot 10^{17}$, and $h=6.5 \cdot 10^{-27}$ we get

$$\left. \begin{aligned} a &= 0.55 \cdot 10^{-8} F^{-1}, \quad v = 2.1 \cdot 10^8 F, \quad \omega = 6.2 \cdot 10^{15} F^2 \\ \text{and} \quad W &= 2.0 \cdot 10^{-11} \sum F^2. \end{aligned} \right\} \quad (4)$$

In neglecting the magnetic forces due to the motion of the electrons we have in Part I. assumed that the velocities of the particles are small compared with the velocity of light. The above calculations show that for this to hold, F must be small compared with 150. As will be seen, the latter condition will be satisfied for all the electrons in the atoms of elements of low atomic weight and for a greater part of the electrons contained in the atoms of the other elements.

If the velocity of the electrons is not small compared with the velocity of light, the constancy of the angular momentum no longer involves a constant ratio between the energy and the frequency of revolution. Without introducing new assumptions, we cannot therefore in this case determine the configuration of the systems on the basis of the considerations in Part I. Considerations given later suggest, however, that the constancy of the angular momentum is the principal condition. Applying this condition for velocities

not small compared with the velocity of light, we get the same expression for v as that given by (1), while the quantity m in the expressions for α and ω is replaced by $\frac{m}{\sqrt{(1-v^2/c^2)}}$ and in the expression for W by

$$m \cdot 2 \frac{c^2}{v^2} \left(1 - \sqrt{1 - \frac{v^2}{c^2}} \right).$$

As stated in Part I., a calculation based on the ordinary mechanics gives the result, that a ring of electrons rotating round a positive nucleus in general is unstable for displacements of the electrons in the plane of the ring. In order to escape from this difficulty, we have assumed that the ordinary principles of mechanics cannot be used in the discussion of the problem in question, any more than in the discussion of the connected problem of the mechanism of binding of electrons. We have also assumed that the stability for such displacements is secured through the introduction of the hypothesis of the universal constancy of the angular momentum of the electrons.

As is easily shown, the latter assumption is included in the condition of stability in § 1. Consider a ring of electrons rotating round a nucleus, and assume that the system is in dynamical equilibrium and that the radius of the ring is a_0 , the velocity of the electrons v_0 , the total kinetic energy T_0 , and the potential energy P_0 . As shown in Part I. (p. 21) we have $P_0 = -2T_0$. Next consider a configuration of the system in which the electrons, under influence of extraneous forces, rotate with the same angular momentum round the nucleus in a ring of radius $a = \alpha a_0$. In this case we have $P = \frac{1}{\alpha} P_0$, and on account of the uniformity of the angular momentum $v = \frac{1}{\alpha} v_0$ and $T = \frac{1}{\alpha^2} T_0$. Using the relation $P_0 = -2T_0$, we get

$$P + T = \frac{1}{\alpha} P_0 + \frac{1}{\alpha^2} T_0 = P_0 + T_0 + T_0 \left(1 - \frac{1}{\alpha} \right)^2.$$

We see that the total energy of the new configuration is greater than in the original. According to the condition of stability in § 1 the system is consequently stable for the displacement considered. In this connexion, it may be remarked that in Part I. we have assumed that the frequency of radiation emitted or absorbed by the systems cannot be determined from the frequencies of vibration of the electrons in the plane of the orbits, calculated by help of the ordinary

mechanics. We have, on the contrary, assumed that the frequency of the radiation is determined by the condition $h\nu = E$, where ν is the frequency, h Planck's constant, and E the difference in energy corresponding to two different "stationary" states of the system.

In considering the stability of a ring of electrons rotating round a nucleus for displacements of the electrons perpendicular to the plane of the ring, imagine a configuration of the system in which the electrons are displaced by $\delta z_1, \delta z_2, \dots, \delta z_n$, respectively, and suppose that the electrons, under influence of extraneous forces, rotate in circular orbits parallel to the original plane with the same radii and the same angular momentum round the axis of the system as before. The kinetic energy is unaltered by the displacement, and neglecting powers of the quantities $\delta z_1, \dots, \delta z_n$ higher than the second, the increase of the potential energy of the system is given by

$$\frac{1}{2} \frac{e^2}{a^3} N \sum (\delta z)^2 - \frac{1}{32} \frac{e^2}{a^3} \sum \sum \left| \operatorname{cosec} \frac{\pi(\gamma - s)}{n} \right| (\delta z_\gamma - \delta z_s)^2,$$

where a is the radius of the ring, N the charge on the nucleus, and n the number of electrons. According to the condition of stability in § 1 the system is stable for the displacements considered, if the above expression is positive for arbitrary values of $\delta z_1, \dots, \delta z_n$. By a simple calculation it can be shown that the latter condition is equivalent to the condition

$$N > p_{n,0} - p_{n,m}, \dots \dots \dots (5)$$

where m denotes the whole number (smaller than n) for which

$$p_{n,k} = \sum_{s=1}^{1+n-k-1} \cos 2k \frac{s\pi}{n} \operatorname{cosec}^3 \frac{s\pi}{n}$$

has its smallest value. This condition is identical with the condition of stability for displacements of the electrons perpendicular to the plane of the ring, deduced by help of ordinary mechanical considerations*.

A suggestive illustration is obtained by imagining that the displacements considered are produced by the effect of extraneous forces acting on the electrons in a direction parallel to the axis of the ring. If the displacements are produced infinitely slowly the motion of the electrons will at any moment be parallel to the original plane of the ring, and the angular momentum of each of the electrons round

* Comp. J. W. Nicholson, Month. Not. Roy. Astr. Soc. 72, p. 52 (1912).

the centre of its orbit will obviously be equal to its original value; the increase in the potential energy of the system will be equal to the work done by the extraneous forces during the displacements. From such considerations we are led to assume that the ordinary mechanics can be used in calculating the vibrations of the electrons perpendicular to the plane of the ring—contrary to the case of vibrations in the plane of the ring. This assumption is supported by the apparent agreement with observations obtained by Nicholson in his theory of the origin of lines in the spectra of the solar corona and stellar nebulae (see Part I. pp. 6 & 23). In addition it will be shown later that the assumption seems to be in agreement with experiments on dispersion.

The following table gives the values of s_n and $p_{n,o} - p_{n,m}$ from $n=1$ to $n=16$.

n	s_n	$p_{n,o} - p_{n,m}$	n	s_n	$p_{n,o} - p_{n,m}$
1	0	0	9	3.328	13.14
2	0.25	0.25	10	3.863	18.13
3	0.577	0.58	11	4.416	23.60
4	0.957	1.41	12	4.984	30.80
5	1.377	2.43	13	5.565	38.57
6	1.828	4.25	14	6.159	48.38
7	2.305	6.35	15	6.764	58.83
8	2.805	9.56	16	7.379	71.65

We see from the table that the number of electrons which can rotate in a single ring round a nucleus of charge N increases only very slowly for increasing N ; for $N=20$ the maximum value is $n=10$; for $N=40$, $n=13$; for $N=60$, $n=15$. We see, further, that a ring of n electrons cannot rotate in a single ring round a nucleus of charge ne unless $n < 8$.

In the above we have supposed that the electrons move under the influence of a stationary radial force and that their orbits are exactly circular. The first condition will not be satisfied if we consider a system containing several rings of electrons which rotate with different frequencies. If, however, the distance between the rings is not small in comparison with their radii, and if the ratio between their frequencies is not near to unity, the deviation from circular orbits may be very small and the motion of the electrons to a close approximation may be identical with that obtained on the assumption that the charge on the electrons is uniformly distributed along the circumference of the rings. If the ratio between the radii of the rings is not

near to unity, the conditions of stability obtained on this assumption may also be considered as sufficient.

We have assumed in § 1 that the electrons in the atoms rotate in coaxial rings. The calculation indicates that only in the case of systems containing a great number of electrons will the planes of the rings separate; in the case of systems containing a moderate number of electrons, all the rings will be situated in a single plane through the nucleus. For the sake of brevity, we shall therefore here only consider the latter case.

Let us consider an electric charge E uniformly distributed along the circumference of a circle of radius a .

At a point distant z from the plane of the ring, and at a distance r from the axis of the ring, the electrostatic potential is given by

$$U = -\frac{1}{\pi} E \int_0^\pi \frac{ds}{\sqrt{(a^2 + r^2 + z^2 - 2ar \cos s)}}.$$

Putting in this expression $z=0$ and $\frac{r}{a} = \tan^2 \alpha$, and using the notation

$$K(\alpha) = \int_0^{\frac{\pi}{2}} \frac{ds}{\sqrt{1 - \sin^2 \alpha \cos^2 s}},$$

we get for the radial force exerted on an electron in a point in the plane of the ring

$$\frac{\partial U}{\partial r} = \frac{Ee}{r^2} Q(\alpha),$$

where

$$Q(\alpha) = \frac{2}{\pi} \sin^4 \alpha (K(2\alpha) - \cot \alpha K'(2\alpha)).$$

The corresponding force perpendicular to the plane of the ring at a distance r from the centre of the ring and at a small distance δz from its plane is given by

$$\frac{\partial U}{\partial z} = \frac{Ee \delta z}{r^3} R(\alpha),$$

where

$$R(\alpha) = \frac{2}{\pi} \sin^6 \alpha (K(2\alpha) + \tan(2\alpha) K'(2\alpha));$$

A short table of the functions $Q(\alpha)$ and $R(\alpha)$ is given on p. 485.

Next consider a system consisting of a number of concentric

rings of electrons which rotate in the same plane round a nucleus of charge Ne . Let the radii of the rings be $a_1, a_2, \dots, a_n, \dots$ and the number of electrons on the different rings $n_1, n_2, \dots, n_n, \dots$.

Putting $\frac{a_r}{a_s} = \tan^2(\alpha_{r,s})$, we get for the radial force acting on an electron in the r th ring $\frac{e^2}{a_r^2} \bar{F}_r$, where

$$\bar{F}_r = N - n_s - \sum n_s Q(\alpha_{r,s});$$

the summation is to be taken over all the rings except the one considered.

If we know the distribution of the electrons in the different rings, from the relation (1) on p. 478, we can, by help of the above, determine a_1, a_2, \dots . The calculation can be made by successive approximations, starting from a set of values for the a 's, and from them calculating the F 's, and then redetermining the α 's by the relation (1) which gives $\frac{F_r}{F_s} = \frac{a_r}{a_s} = \tan^2(\alpha_{r,s})$, and so on.

As in the case of a single ring it is supposed that the systems are stable for displacements of the electrons in the plane of their orbits. In a calculation such as that on p. 480, the interaction of the rings ought strictly to be taken into account. This interaction will involve that the quantities F are not constant, as for a single ring rotating round a nucleus, but will vary with the radii of the rings; the variation in F , however, if the ratio between the radii of the rings is not very near to unity, will be too small to be of influence on the result of the calculation.

Considering the stability of the systems for a displacement of the electrons perpendicular to the plane of the rings, it is necessary to distinguish between displacements in which the centres of gravity of the electrons in the single rings are unaltered, and displacements in which all the electrons inside the same ring are displaced in the same direction. The condition of stability for the first kind of displacements is given by the condition (5) on p. 481, if for every ring we replace N by a quantity G_r determined by the condition that $\frac{e^2}{a_r^3} G_r \delta z$ is equal to the component perpendicular to the plane of the ring of the force—due to the nucleus and the electrons in the other rings—acting on one of the electrons if it has received a small displacement δz . Using the same notation as above, we get

$$G_r = N - \sum n_s R(\alpha_{r,s}).$$

If all the electrons in one of the rings are displaced in the same direction by help of extraneous forces, the displacement will produce corresponding displacements of the electrons in the other rings; and this interaction will be of influence on the stability. For example, consider a system of n concentric rings rotating in a plane round a nucleus of charge Ne , and let us assume that the electrons in the different rings are displaced perpendicular to the plane by $\delta z_1, \delta z_2, \dots, \delta z_n$ respectively. With the above notation the increase in the potential energy of the system is given by

$$\frac{1}{2} N \sum n_r \frac{e^2}{a_r^3} (\delta z_r)^2 - \frac{1}{16} \sum \sum n_r n_s \frac{e^2}{a_r a_s} R(\alpha_{r,s}) (\delta z_r - \delta z_s)^2.$$

The condition of stability is that this expression is positive for arbitrary values of $\delta z_1, \dots, \delta z_n$. This condition can be worked out simply in the usual way. It is not of sensible influence compared with the condition of stability for the displacements considered above, except in cases where the system contains several rings of few electrons.

The following Table, containing the values of $Q(\alpha)$ and $R(\alpha)$ for every fifth degree from $\alpha = 20^\circ$ to $\alpha = 70^\circ$, gives an estimate of the order of magnitude of these functions:—

α .	$\tan^2 \alpha$.	$Q(\alpha)$.	$R(\alpha)$.
20	0.132	0.001	0.002
25	0.217	0.005	0.011
30	0.333	0.021	0.048
35	0.490	0.080	0.217
40	0.704	0.373	1.549
45	1.000
50	1.420	1.708	4.488
55	2.040	1.238	1.839
60	3.000	1.083	1.301
65	4.589	1.087	1.115
70	7.548	1.013	1.041

$\tan^2 \alpha$ indicates the ratio between the radii of the rings $\left(\tan^2(\alpha_{r,s}) = \frac{a_r}{a_s} \right)$. The values of $Q(\alpha)$ show that unless the ratio of the radii of the rings is nearly unity the effect of outer rings on the dimensions of inner rings is very small, and that the corresponding effect of inner rings on outer is

to neutralize approximately the effect of a part of the charge on the nucleus corresponding to the number of electrons on the ring. The values of $R(z)$ show that the effect of outer rings on the stability of inner—though greater than the effect on the dimensions—is small, but that unless the ratio between the radii is very great, the effect of inner rings on the stability of outer is considerably greater than to neutralize a corresponding part of the charge of the nucleus.

The maximum number of electrons which the innermost ring can contain without being unstable is approximately equal to that calculated on p. 482 for a single ring rotating round a nucleus. For the outer rings, however, we get considerably smaller numbers than those determined by the condition (5) if we replace Ne by the total charge on the nucleus and on the electrons of inner rings.

If a system of rings rotating round a nucleus in a single plane is stable for small displacements of the electrons perpendicular to this plane, there will in general be no stable configurations of the rings, satisfying the condition of the constancy of the angular momentum of the electrons, in which all the rings are not situated in the plane. An exception occurs in the special case of two rings containing equal numbers of electrons; in this case there may be a stable configuration in which the two rings have equal radii and rotate in parallel planes at equal distances from the nucleus, the electrons in the one ring being situated just opposite the intervals between the electrons in the other ring. The latter configuration, however, is unstable if the configuration in which all the electrons in the two rings are arranged in a single ring is stable.

§ 3. Constitution of Atoms containing very few Electrons.

As stated in § 1, the condition of the universal constancy of the angular momentum of the electrons, together with the condition of stability, is in most cases not sufficient to determine completely the constitution of the system. On the general view of formation of atoms, however, and by making use of the knowledge of the properties of the corresponding elements, it will be attempted, in this section and the next, to obtain indications of what configurations of the electrons may be expected to occur in the atoms. In these considerations we shall assume that the number of electrons in the atom is equal to the number which indicates the position of the corresponding element in the series of elements arranged in order of increasing atomic weight.

Exceptions to this rule will be supposed to occur only at such places in the series where deviation from the periodic law of the chemical properties of the elements are observed. In order to show clearly the principles used we shall first consider with some detail those atoms containing very few electrons.

For sake of brevity we shall, by the symbol $N(n_1, n_2, \dots)$, refer to a plane system of rings of electrons rotating round a nucleus of charge Ne , satisfying the condition of the angular momentum of the electrons with the approximation used in § 2. n_1, n_2, \dots are the numbers of electrons in the rings, starting from inside. By a_1, a_2, \dots and $\omega_1, \omega_2, \dots$ we shall denote the radii and frequency of the rings taken in the same order. The total amount of energy W emitted by the formation of the system shall simply be denoted by $W[N(n_1, n_2, \dots)]$.

$N=1$.

Hydrogen.

In Part I. we have considered the binding of an electron by a positive nucleus of charge e , and have shown that it is possible to account for the Balmer spectrum of hydrogen on the assumption of the existence of a series of stationary states in which the angular momentum of the electron round the nucleus is equal to entire multiples of the value $\frac{h}{2\pi}$, where h is Planck's constant. The formula found for the frequencies of the spectrum was

$$\nu = \frac{2\pi^2 e^4 m}{h^3} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right),$$

where τ_1 and τ_2 are entire numbers. Introducing the values for e, m , and h used on p. 479, we get for the factor before the bracket $3.1 \cdot 10^{15}$; the value observed for the constant in the Balmer spectrum is $3.290 \cdot 10^{15}$.

* This value is that calculated in the first part of the paper. Using the values $e=4.78 \cdot 10^{-10}$ (see R. A. Millikan, Brit. Assoc. Rep. 1912, p. 410), $\frac{e}{m}=5.31 \cdot 10^{17}$ (see P. Gmelin, *Ann. d. Phys.* xxviii. p. 1086 (1909) and A. H. Bucherer, *Ann. d. Phys.* xxxvii. p. 597 (1912)), and $\frac{h}{2\pi}=7.27 \cdot 10^{-27}$ (calculated by Planck's theory from the experiments of E. Warburg, G. Leitnauer, E. Hupke, and C. Müller, *Ann. d. Phys.* xl. p. 611 (1913)) we get $\frac{2\pi^2 e^4 m}{h^3}=3.26 \cdot 10^{15}$ in very close agreement with observations.

For the permanent state of a neutral hydrogen atom we get from the formula (1) and (2) in § 2, putting $F=1$,

$$1(1) \quad a = \frac{h^2}{4\pi^2 e^2 m} = 0.55 \cdot 10^{-8}, \quad \omega = \frac{4\pi^2 e^2 m}{h^3} = 6.2 \cdot 10^{15}, \\ W = \frac{2\pi^2 e^2 m}{h^2} = 2.0 \cdot 10^{-11}.$$

These values are of the order of magnitude to be expected.

For $\frac{W}{e}$ we get 0.043, which corresponds to 13 volts; the value for the ionizing potential of a hydrogen atom, calculated by Sir J. J. Thomson from experiments on positive rays, is 11 volts*. No other definite data, however, are available for hydrogen atoms. For sake of brevity, we shall in the following denote the values for a , ω , and W corresponding to the configuration 1(1) by a_0 , ω_0 and W_0 .

At distances from the nucleus, great in comparison with a_0 , the system 1(1) will not exert sensible forces on free electrons. Since, however, the configuration:

$$1(2) \quad a = 1.33 a_0, \quad \omega = 0.563 \omega_0, \quad W = 1.13 W_0$$

corresponds to a greater value for W than the configuration 1(1), we may expect that a hydrogen atom under certain conditions can acquire a negative charge. This is in agreement with experiments on positive rays. Since $W[1(3)]$ is only 0.54, a hydrogen atom cannot be expected to be able to acquire a double negative charge.

$N=2$.

Helium.

As shown in Part I., using the same assumptions as for hydrogen, we must expect that during the binding of an electron by a nucleus of charge $2e$, a spectrum is emitted, expressed by

$$\nu = \frac{2\pi^2 m e^4}{h^3} \left(\frac{1}{\left(\frac{T_2}{2}\right)^2} - \frac{1}{\left(\frac{T_1}{2}\right)^2} \right),$$

This spectrum includes the spectrum observed by Pickering in the star ξ Puppis and the spectra recently observed by Fowler in experiments with vacuum tubes filled with a mixture of hydrogen and helium. These spectra are generally ascribed to hydrogen.

For the permanent state of a positively charged helium atom, we get

$$2(1) \quad a = \frac{1}{2} a_0, \quad \omega = 4\omega_0, \quad W = 4W_0.$$

* J. J. Thomson, Phil. Mag. xxiv. p. 218 (1912).

At distances from the nucleus great compared with the radius of the bound electron, the system 2(1) will, to a close approximation, act on an electron as a simple nucleus of charge e . For a system consisting of two electrons and a nucleus of charge $2e$, we may therefore assume the existence of a series of stationary states in which the electron most lightly bound moves approximately in the same way as the electron in the stationary states of a hydrogen atom. Such an assumption has already been used in Part I. in an attempt to explain the appearance of Rydberg's constant in the formula for the line-spectrum of any element. We can, however, hardly assume the existence of a stable configuration in which the two electrons have the same angular momentum round the nucleus and move in different orbits, the one outside the other. In such a configuration the electrons would be so near to each other that the deviations from circular orbits would be very great. For the permanent state of a neutral helium atom, we shall therefore adopt the configuration

$$2(2) \quad a = 0.571 a_0, \quad \omega = 3.06 \omega_0, \quad W = 6.13 W_0.$$

Since

$$W[2(2)] - W[2(1)] = 2.13 W_0,$$

we see that both electrons in a neutral helium atom are more firmly bound than the electron in a hydrogen atom. Using the values on p. 488, we get

$$2.13 \cdot \frac{W_0}{e} = 27 \text{ volts and } 2.13 \frac{W_0}{h} = 6.6 \cdot 10^{15} \frac{1}{\text{sec.}}$$

these values are of the same order of magnitude as the value observed for the ionization potential in helium, 20.5 volt*, and the value for the frequency of the ultra-violet absorption in helium determined by experiments on dispersion $5.9 \cdot 10^{15} \frac{1}{\text{sec.}}$ †.

The frequency in question may be regarded as corresponding to vibrations in the plane of the ring (see p. 480). The frequency of vibration of the whole ring perpendicular to the plane, calculated in the ordinary way (see p. 482), is

* J. Franck u. G. Hertz, *Verh. d. Deutsch. Phys. Ges.* xv. p. 34 (1913).
† O. and M. Cuthbertson, *Proc. Roy. Soc. A*, lxxiv. p. 13 (1910). (In a previous paper (Phil. Mag. Jan. 1913) the author took the values for the refractive index in helium, given by M. and O. Cuthbertson, as corresponding to atmospheric pressure; these values, however, refer to double atmospheric pressure. Consequently the value there given for the number of electrons in a helium atom calculated from Drude's theory has to be divided by 2.)

given by $\nu = 3.27 \omega_0$. The fact that the latter frequency is great compared with that observed might explain that the number of electrons in a helium atom, calculated by help of Drude's theory from the experiments on dispersion, is only about two-thirds of the number to be expected. (Using $\frac{e}{m} = 5.31 \cdot 10^{17}$ the value calculated is 1.2.)

For a configuration of a helium nucleus and three electrons, we get

$$2(3) \quad a = 0.703 a_0, \quad \omega = 2.02 \omega_0, \quad W = 6.07 W_0.$$

Since W for this configuration is smaller than for the configuration $2(2)$, the theory indicates that a helium atom cannot acquire a negative charge. This is in agreement with experimental evidence, which shows that helium atoms have no "affinity" for free electrons*.

In a later paper it will be shown that the theory offers a simple explanation of the marked difference in the tendency of hydrogen and helium atoms to combine into molecules.

$N = 3.$

Lithium.

In analogy with the cases of hydrogen and helium we must expect that during the binding of an electron by a nucleus of charge $3e$, a spectrum is emitted, given by

$$\nu = \frac{2\pi^2 m e^4}{h^3} \left(\frac{1}{\left(\frac{T_3}{3}\right)^2} - \frac{1}{\left(\frac{T_1}{3}\right)^2} \right).$$

On account of the great energy to be spent in removing all the electrons bound in a lithium atom (see below) the spectrum considered can only be expected to be observed in extraordinary cases.

In a recent note Nicholson† has drawn attention to the fact that in the spectra of certain stars, which show the Pickering spectrum with special brightness, some lines occur the frequencies of which to a close approximation can be expressed by the formula

$$\nu = K \left(\frac{1}{4} - \frac{1}{(m \pm \frac{1}{2})^2} \right),$$

where K is the same constant as in the Balmer spectrum of hydrogen. From analogy with the Balmer- and Pickering-spectra, Nicholson has suggested that the lines in question are due to hydrogen.

* See J. Franck, *Verh. d. Deutsch. Phys. Ges.* xii, p. 613 (1910).
† J. W. Nicholson, *Month. Not. Roy. Astr. Soc.* lxxiii, p. 382 (1913).

It is seen that the lines discussed by Nicholson are given by the above formula if we put $\tau_3 = 6$. The lines in question correspond to $\tau_1 = 10, 13$, and 14 ; if we for $\tau_2 = 6$ put $\tau_1 = 9, 12$ and 15 , we get lines coinciding with lines of the ordinary Balmer-spectrum of hydrogen. If we in the above formula put $\tau = 1, 2$, and 3 , we get series of lines in the ultra-violet. If we put $\tau_3 = 4$ we get only a single line in visible spectrum, viz.: for $\tau_1 = 5$ which gives $\nu = 6.652 \cdot 10^{14}$, or a wave-length $\lambda = 4503.10^{-8}$ cm. closely coinciding with the wave-length 4504.10^{-8} cm. of one of the lines of unknown origin in the table quoted by Nicholson. In this table, however, no lines occur corresponding to $\tau_2 = 5$.

For the permanent state of a lithium atom with two positive charges we get a configuration

$$3(1) \quad a = \frac{1}{3} a_0, \quad \omega = 9 \omega_0, \quad W = 9 W_0.$$

The probability of a permanent configuration in which two electrons move in different orbits around each other must for lithium be considered still less probable than for helium, as the ratio between the radii of the orbits would be still nearer to unity. For a lithium atom with a single positive charge we shall, therefore, adopt the configuration:

$$3(2) \quad a = 0.364 a_0, \quad \omega = 7.56 \omega_0, \quad W = 15.13 W_0.$$

Since $W[3(2)] - W[3(1)] = 6.13 W_0$, we see that the first two electrons in a lithium atom are very strongly bound compared with the electron in a hydrogen atom; they are still more rigidly bound than the electrons in a helium atom.

From a consideration of the chemical properties we should expect the following configuration for the electrons in a neutral lithium atom:

$$3(2, 1) \quad a_1 = 0.362 a_0, \quad \omega_1 = 7.65 \omega_0, \quad W = 16.02 W_0 \\ a_2 = 1.182 a_0, \quad \omega_2 = 0.716 \omega_0$$

This configuration may be considered as highly probable also from a dynamical point of view. The deviation of the outermost electron from a circular orbit will be very small, partly on account of the great values of the ratio between the radii, and of the ratio between the frequencies of the orbits of the inner and outer electrons, partly also on account of the symmetrical arrangement of the inner electrons. Accordingly, it appears probable that the three electrons

will not arrange themselves in a single ring and form the system :

$$3(3) \quad a=0.413 a_0, \quad \omega=5.87 \omega_0, \quad W=17.61 W_0,$$

although W for this configuration is greater than for $3(2,1)$.

Since $W[3(2,1)] - W[3(2)] = 0.89 W_0$, we see that the outer electron in the configuration $3(2,1)$ is bound even more lightly than the electron in a hydrogen atom. The difference in the firmness of the binding corresponds to a difference of 1.4 volts in the ionization potential. A marked difference between the electron in hydrogen and the outermost electron in lithium lies also in the greater tendency of the latter electron to leave the plane of the orbits. The quantity G considered in § 2, which gives a kind of measure for the stability for displacements perpendicular to this plane, is thus for the outer electron in lithium only 0.55, while for hydrogen it is 1. This may have a bearing on the explanation of the apparent tendency of lithium atoms to take a positive charge in chemical combinations with other elements.

For a possible negatively charged lithium atom we may expect the configuration :

$$3(2,2) \quad a=0.362 a_0, \quad \omega=7.64 \omega_0, \quad W=16.16 W_0, \\ a=1.516 a_0, \quad \omega=0.436 \omega_0$$

It should be remarked that we have no detailed knowledge of the properties in the atomic state, either for lithium or hydrogen, or for most of the elements considered below.

N=4.

Beryllium.

For reasons analogous to those considered for helium and lithium we may for the formation of a neutral beryllium atom assume the following stages :

$$4(1) \quad a=0.25 a_0, \quad \omega=16 \omega_0, \quad W=16 W_0, \\ 4(2) \quad a=0.267 a_0, \quad \omega=14.06 \omega_0, \quad W=28.13 W_0, \\ 4(2,1) \quad a_1=0.263 a_0, \quad \omega_1=14.46 \omega_0, \quad W=31.65 W_0, \\ a_2=0.605 a_0, \quad \omega_2=2.74 \omega_0 \\ 4(2,2) \quad a_1=0.262 a_0, \quad \omega_1=14.60 \omega_0, \quad W=33.61 W_0, \\ a_2=0.673 a_0, \quad \omega_2=2.21 \omega_0$$

although the configurations :

$$4(3) \quad a=0.292 a_0, \quad \omega=11.71 \omega_0, \quad W=35.14 W_0, \\ 4(4) \quad a=0.329 a_0, \quad \omega=9.26 \omega_0, \quad W=37.04 W_0,$$

correspond to less values for the total energy than the configurations $4(2,1)$ and $4(2,2)$.

From analogy we get further for the configuration of a possible negatively charged atom,

$$4(2,3) \quad a_1=0.263 a_0, \quad \omega_1=14.51 \omega_0, \quad W=33.66 W_0, \\ a_2=0.803 a_0, \quad \omega_2=1.55 \omega_0$$

Comparing the outer ring of the atom considered with the ring of a helium atom, we see that the presence of the inner ring of two electrons in the beryllium atom markedly changes the properties of the outer ring; partly because the outer electrons in the configuration adopted for a neutral beryllium atom are more lightly bound than the electrons in a helium atom, and partly because the quantity G , which for helium is equal to 2, for the outer ring in the configuration $4(2,2)$ is only equal to 1.12.

Since $W[4(2,3)] - W[4(2,2)] = 0.05 W_0$, the beryllium atom will further have a definite, although very small affinity for free electrons.

§ 4. Atoms containing greater numbers of electrons.

From the examples discussed in the former section it will appear that the problem of the arrangement of the electrons in the atoms is intimately connected with the question of the confluence of two rings of electrons rotating round a nucleus outside each other, and satisfying the condition of the universal constancy of the angular momentum. Apart from the necessary conditions of stability for displacements of the electrons perpendicular to the plane of the orbits, the present theory gives very little information on this problem. It seems, however, possible by the help of simple considerations to throw some light on the question.

Let us consider two rings rotating round a nucleus in a single plane, the one outside the other. Let us assume that the electrons in the one ring act upon the electrons in the other as if the electric charge were uniformly distributed along the circumference of the ring, and that the rings with this approximation satisfy the condition of the angular momentum of the electrons and of stability for displacements perpendicular to their plane.

Now suppose that, by help of suitable imaginary extraneous forces acting parallel to the axis of the rings, we pull the inner ring slowly to one side. During this process, on account of the repulsion from the inner ring, the outer will move to the opposite side of the original plane of the rings.

During the displacements of the rings the angular momentum of the electrons round the axis of the system will remain constant, and the diameter of the inner ring will increase while that of the outer will diminish. At the beginning of the displacement the magnitude of the extraneous forces to be applied to the original inner ring will increase but thereafter decrease, and at a certain distance between the plane of the rings the system will be in a configuration of equilibrium. This equilibrium, however, will not be stable. If we let the rings slowly return they will either reach their original position, or they will arrive at a position in which the ring, which originally was the outer, is now the inner, and *vice versa*.

If the charge of the electrons were uniformly distributed along the circumference of the rings, we could by the process considered at most obtain an interchange of the rings, but obviously not a junction of them. Taking, however, the discrete distribution of the electrons into account, it can be shown that, in the special case when the number of electrons on the two rings are equal, and when the rings rotate in the same direction, the rings will unite by the process, provided that the final configuration is stable. In this case the radii and the frequencies of the rings will be equal in the unstable configuration of equilibrium mentioned above. In reaching this configuration the electrons in the one ring will further be situated just opposite the intervals between the electrons in the other, since such an arrangement will correspond to the smallest total energy. If now we let the rings return to their original plane, the electrons in the one ring will pass into the intervals between the electrons in the other, and form a single ring. Obviously the ring thus formed will satisfy the same condition of the angular momentum of the electrons as the original rings.

If the two rings contain unequal numbers of electrons the system will during a process such as that considered behave very differently, and, contrary to the former case, we cannot expect that the rings will flow together, if by help of extraneous forces acting parallel to the axis of the system they are displaced slowly from their original plane. It may in this connexion be noticed that the characteristic for the displacements considered is not the special assumption about the extraneous forces, but only the invariance of the angular momentum of the electrons round the centre of the rings; displacements of this kind take in the present theory a similar position to arbitrary displacements in the ordinary mechanics.

The above considerations may be taken as an indication that there is a greater tendency for the confluence of two rings when each contains the same number of electrons. Considering the successive binding of electrons by a positive nucleus, we conclude from this that, unless the charge on the nucleus is very great, rings of electrons will only join together if they contain equal numbers of electrons; and that accordingly the numbers of electrons on inner rings will only be 2, 4, 8, ... If the charge of the nucleus is very great the rings of electrons first bound, if few in number, will be very close together, and we must expect that the configuration will be very unstable, and that a gradual interchange of electrons between the rings will be greatly facilitated.

This assumption in regard to the number of electrons in the rings is strongly supported by the fact that the chemical properties of the elements of low atomic weight vary with a period of 8. Further, it follows that the number of electrons on the outermost ring will always be odd or even, according as the total number of electrons in the atom is odd or even. This has a suggestive relation to the fact that the valency of an element of low atomic weight always is odd or even according as the number of the element in the periodic series is odd or even.

For the atoms of the elements considered in the former section we have assumed that the two electrons first bound are arranged in a single ring, and, further, that the two next electrons are arranged in another ring. If $N \geq 4$ the configuration $N(4)$ will correspond to a smaller value for the total energy than the configuration $N(2,2)$. The greater the value of N the closer will the ratio between the radii of the rings in the configuration $N(2,2)$ approach unity, and the greater will be the energy emitted by an eventual confluence of the rings. The particular member of the series of the elements for which the four innermost electrons will be arranged for the first time in a single ring cannot be determined from the theory. From a consideration of the chemical properties we can hardly expect that it will have taken place before boron ($N=5$) or carbon ($N=6$), on account of the observed trivalency and tetravalency respectively of these elements; on the other hand, the periodic system of the elements strongly suggests that already in neon ($N=10$) an inner ring of eight electrons will occur. Unless $N \geq 14$ the configuration $N(4,4)$ corresponds to a smaller value for the total energy than the configuration $N(8)$; already

for $N \geq 10$ the latter configuration, however, will be stable for displacements of the electrons perpendicular to the plane of their orbits. A ring of 16 electrons will not be stable unless N is very great; but in such a case the simple considerations mentioned above do not apply.

The confluence of two rings of equal number of electrons, which rotate round a nucleus of charge Ne outside a ring of n electrons already bound, must be expected to take place more easily than the confluence of two similar rings rotating round a nucleus of charge $(N-n)e$; for the stability of the rings for a displacement perpendicular to their plane will (see § 2) be smaller in the first than in the latter case. This tendency for stability to decrease for displacements perpendicular to the plane of the ring will be especially marked for the outer rings of electrons of a neutral atom. In the latter case we must expect the confluence of rings to be greatly facilitated, and in certain cases it may even happen that the number of electrons in the outer ring may be greater than in the next, and that the outer ring may show deviations from the assumption of 1, 2, 4, 8 electrons in the rings, e.g. the configurations 5(2,3) and 6(2,4) instead of the configurations 5(2,2,1) and 6(2,2,2). We shall here not discuss further the intricate question of the arrangement of the electrons in the outer ring. In the scheme given below the number of electrons in this ring is arbitrarily put equal to the normal valency of the corresponding element; i.e. for electronegative and electropositive elements respectively the number of hydrogen atoms and twice the number of oxygen atoms with which one atom of the element combines.

Such an arrangement of the outer electrons is suggested by considerations of atomic volumes. As is well known, the atomic volume of the elements is a periodic function of the atomic weights. If arranged in the usual way according to the periodic system, the elements inside the same column have approximately the same atomic volume, while this volume changes considerably from one column to another, being greatest for columns corresponding to the smallest valency 1 and smallest for the greatest valency 4. An approximate estimate of the radius of the outer ring of a neutral atom can be obtained by assuming that the total force due to the nucleus and the inner electrons is equal to that from a nucleus of charge ne , where n is the number of electrons in the ring. Putting $F = n - s$, in the equation (1) on p. 478, and denoting the value of a for $n=1$ by a_0 , we get for $n=2$, $a = 0.57a_0$; for $n=3$, $a = 0.41a_0$; and for $n=4$, $a = 0.33a_0$. Accordingly the arrangement chosen

for the electrons will involve a variation in the dimensions of the outer ring similar to the variation in the atomic volumes of the corresponding elements. It must, however, be borne in mind that the experimental determinations of atomic volumes in most cases are deduced from consideration of molecules rather than atoms.

From the above we are led to the following possible scheme for the arrangement of the electrons in light atoms:—

1 (1)	9 (4, 4, 1)	17 (8, 4, 4, 1)
2 (2)	10 (8, 2)	18 (8, 8, 2)
3 (2, 1)	11 (8, 2, 1)	19 (8, 8, 2, 1)
4 (2, 2)	12 (8, 2, 2)	20 (8, 8, 2, 2)
5 (2, 3)	13 (8, 2, 3)	21 (8, 8, 2, 3)
6 (2, 4)	14 (8, 2, 4)	22 (8, 8, 2, 4)
7 (4, 3)	15 (8, 4, 3)	23 (8, 8, 4, 3)
8 (4, 2, 2)	16 (8, 4, 2, 2)	24 (8, 8, 4, 2, 2)

Without any fuller discussion it seems not unlikely that this constitution of the atoms will correspond to properties of the elements similar with those observed.

In the first place there will be a marked periodicity with a period of 8. Further, the binding of the outer electrons in every horizontal series of the above scheme will become weaker with increasing number of electrons per atom, corresponding to the observed increase of the electropositive character for an increase of atomic weight of the elements in every single group of the periodic system. A corresponding agreement holds for the variation of the atomic volumes.

In the case of atoms of higher atomic weight the simple assumptions used do not apply. A few indications, however, are suggested from consideration of the variations in the chemical properties of the elements. At the end of the 3rd period of 8 elements we meet with the iron-group. This group takes a particular position in the system of the elements, since it is the first time that elements of neighbouring atomic weights show similar chemical properties. This circumstance indicates that the configurations of the electrons in the elements of this group differ only in the arrangement of the inner electrons. The fact that the period in the chemical properties of the elements after the iron-group is no longer 8, but 18, suggests that elements of higher atomic weight contain a recurrent configuration of 18 electrons in the innermost rings. The deviation from

2, 4, 8, 16 may be due to a gradual interchange of electrons between the rings, such as is indicated on p. 495. Since a ring of 18 electrons will not be stable the electrons may be arranged in two parallel rings (see p. 486). Such a configuration of the inner electrons will act upon the outer electrons in very nearly the same way as a nucleus of charge $(N-18)e$. It might therefore be possible that with increase of N another configuration of the same type will be formed outside the first, such as is suggested by the presence of a second period of 18 elements.

On the same lines, the presence of the group of the rare earths indicates that for still greater values of N another gradual alteration of the innermost rings will take place. Since, however, for elements of higher atomic weight than those of this group, the laws connecting the variation of the chemical properties with the atomic weight are similar to those between the elements of low atomic weight, we may conclude that the configuration of the innermost electrons will be again repeated. The theory, however, is not sufficiently complete to give a definite answer to such problems.

§ 5. Characteristic Röntgen Radiation.

According to the theory of emission of radiation given in Part I., the ordinary line-spectrum of an element is emitted during the reformation of an atom when one or more of the electrons in the outer rings are removed. In analogy it may be supposed that the characteristic Röntgen radiation is sent out during the settling down of the system if electrons in inner rings are removed by some agency, *e.g.* by impact of cathode particles. This view of the origin of the characteristic Röntgen radiation has been proposed by Sir J. J. Thomson*.

Without any special assumption in regard to the constitution of the radiation, we can from this view determine the minimum velocity of the cathode rays necessary to produce the characteristic Röntgen radiation of a special type by calculating the energy necessary to remove one of the electrons from the different rings. Even if we knew the numbers of electrons in the rings, a rigorous calculation of this minimum energy might still be complicated, and the result largely dependent on the assumptions used; for, as mentioned in Part I., p. 19, the calculation cannot be performed entirely on the basis of the ordinary mechanics. We can, however, obtain very simply an approximate comparison

* Comp. J. J. Thomson, Phil. Mag. xliii. p. 456 (1912).

with experiments if we consider the innermost ring and as a first approximation neglect the repulsion from the electrons in comparison with the attraction of the nucleus. Let us consider a simple system consisting of a bound electron rotating in a circular orbit round a positive nucleus of charge Ne . From the expressions (1) on p. 478 we get for the velocity of the electron, putting $F = N$,

$$v = \frac{2\pi e^2}{\lambda} N = 2 \cdot 1 \cdot 10^8 N.$$

The total energy to be transferred to the system in order to remove the electron to an infinite distance from the nucleus is equal to the kinetic energy of the bound electron. If, therefore, the electron is removed to a great distance from the nucleus by impact of another rapidly moving electron, the smallest kinetic energy possessed by the latter when at a great distance from the nucleus must necessarily be equal to the kinetic energy of the bound electron before the collision. The velocity of the free electron therefore must be at least equal to v .

According to Whiddington's experiments* the velocity of cathode rays just able to produce the characteristic Röntgen radiation of the so-called K-type—the hardest type of radiation observed—from an element of atomic weight A is for elements from Al to Se approximately equal to $A \cdot 10^8$ cm./sec. As seen this is equal to the above calculated value for v , if we put $N = \frac{A}{2}$.

Since we have obtained approximate agreement with experiment by ascribing the characteristic Röntgen radiation of the K-type to the innermost ring, it is to be expected that no harder type of characteristic radiation will exist. This is strongly indicated by observations of the penetrating power of γ rays†.

It is worthy of remark that the theory gives not only nearly the right value for the energy required to remove an electron from the outer ring, but also the energy required to remove an electron from the innermost ring. The approximate agreement between the calculated and experimental values is all the more striking when it is recalled that the energies required in the two cases for an element of atomic weight 70 differ by a ratio of 1000.

In connexion with this it should be emphasized that the

* R. Whiddington, Proc. Roy. Soc. A. lxxxy. p. 323 (1911).

† Comp. E. Rutherford, Phil. Mag. xxiv. p. 453 (1912).

remarkable homogeneity of the characteristic Röntgen radiation—indicated by experiments on absorption of the rays, as well as by the interference observed in recent experiments on diffraction of Röntgen rays in crystals—is in agreement with the main assumption used in Part I. (see p. 7) in considering the emission of line-spectra, viz. that the radiation emitted during the passing of the systems between different stationary states is homogeneous.

Putting in (4) $F=N$, we get for the diameter of the innermost ring approximately $2a = \frac{1}{N} \cdot 10^{-8}$ cm. For $N=100$ this gives $2a = 10^{-10}$ cm., a value which is very small in comparison with ordinary atomic dimensions but still very great compared with the dimensions to be expected for the nucleus. According to Rutherford's calculation the dimensions of the latter are of the same order of magnitude as 10^{-12} cm.

§ 6. Radiactive Phenomena.

According to the present theory the cluster of electrons surrounding the nucleus is formed with emission of energy, and the configuration is determined by the condition that the energy emitted is a maximum. The stability involved by these assumptions seems to be in agreement with the general properties of matter. It is, however, in striking opposition to the phenomena of radioactivity, and according to the theory the origin of the latter phenomena may therefore be sought elsewhere than in the electronic distribution round the nucleus.

A necessary consequence of Rutherford's theory of the structure of atoms is that the α -particles have their origin in the nucleus. On the present theory it seems also necessary that the nucleus is the seat of the expulsion of the high-speed β -particles. In the first place, the spontaneous expulsion of a β -particle from the cluster of electrons surrounding the nucleus would be something quite foreign to the assumed properties of the system. Further, the expulsion of an α -particle can hardly be expected to produce a lasting effect on the stability of the cluster of electrons. The effect of the expulsion will be of two different kinds. Partly the particle may collide with the bound electrons during its passing through the atom. This effect will be analogous to that produced by bombardment of atoms of other substances by α -rays and cannot be expected to give rise to a subsequent expulsion of β -rays. Partly the expulsion of the particle

will involve an alteration in the configuration of the bound electrons, since the charge remaining on the nucleus is different from the original. In order to consider the latter effect let us regard a single ring of electrons rotating round a nucleus of charge Ne , and let us assume that an α -particle is expelled from the nucleus in a direction perpendicular to the plane of the ring. The expulsion of the particle will obviously not produce any alteration in the angular momentum of the electrons; and if the velocity of the α -particle is small compared with the velocity of the electrons—as it will be if we consider inner rings of an atom of high atomic weight—the ring during the expulsion will expand continuously, and after the expulsion will take the position claimed by the theory for a stable ring rotating round a nucleus of charge $(N-2)e$. The consideration of this simple case strongly indicates that the expulsion of an α -particle will not have a lasting effect on the stability of the internal rings of electrons in the residual atom.

The question of the origin of β -particles may also be considered from another point of view, based on a consideration of the chemical and physical properties of the radioactive substances. As is well known, several of these substances have very similar chemical properties and have hitherto resisted every attempt to separate them by chemical means. There is also some evidence that the substances in question show the same line-spectrum*. It has been suggested by several writers that the substances are different only in radio-active properties and atomic weight but identical in all other physical and chemical respects. According to the theory, this would mean that the charge on the nucleus, as well as the configuration of the surrounding electrons, was identical in some of the elements, the only difference being the mass and the internal constitution of the nucleus. From the considerations of § 4 this assumption is already strongly suggested by the fact that the number of radioactive substances is greater than the number of places at our disposal in the periodic system. If, however, the assumption is right, the fact that two apparently identical elements emit β -particles of different velocities, shows that the β -rays as well as the α -rays have their origin in the nucleus.

This view of the origin of α - and β -particles explains very simply the way in which the change in the chemical properties of the radioactive substances is connected with the

* See A. S. Russell and R. Rossi, Proc. Roy. Soc. A. lxxxvii. p. 478 (1912).

nature of the particles emitted. The results of experiments are expressed in the two rules * :—

1. Whenever an α -particle is expelled the group in the periodic system to which the resultant product belongs is two units less than that to which the parent body belongs.

2. Whenever a β -particle is expelled the group of the resultant body is 1 unit greater than that of the parent.

As will be seen this is exactly what is to be expected according to the considerations of § 4.

In escaping from the nucleus, the β -rays may be expected to collide with the bound electrons in the inner rings. This will give rise to an emission of a characteristic radiation of the same type as the characteristic Röntgen radiation emitted from elements of lower atomic weight by impact of cathode-rays. The assumption that the emission of γ -rays is due to collisions of β -rays with bound electrons is proposed by Rutherford † in order to account for the numerous groups of homogeneous β -rays expelled from certain radioactive substances.

In the present paper it has been attempted to show that the application of Planck's theory of radiation to Rutherford's atom-model through the introduction of the hypothesis of the universal constancy of the angular momentum of the bound electrons, leads to results which seem to be in agreement with experiments.

In a later paper the theory will be applied to systems containing more than one nucleus.

* See A. S. Russell, Chem. News, cvii. p. 49 (1913); G. V. Hevesy, *Phys. Zeitscher.* xiv. p. 49 (1913); K. Fajans, *Phys. Zeitscher.* xiv. pp. 131 & 136 (1913); *Verh. d. deutsch. Phys. Ges.* xv. p. 240 (1913); F. Soddy, Chem. News, cvii. p. 97 (1913).

† E. Rutherford, Phil. Mag. xiv. pp. 453 & 893 (1912).

On the Constitution of Atoms and Molecules.

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PART III.—SYSTEMS CONTAINING SEVERAL NUCLEI †.

§ 1. *Preliminary.*

ACCORDING to Rutherford's theory of the structure of atoms, the difference between an atom of an element and a molecule of a chemical combination is that the first consists of a cluster of electrons surrounding a single positive nucleus of exceedingly small dimensions and of a mass great in comparison with that of the electrons, while the latter contains at least two nuclei at distances from each other comparable with the distances apart of the electrons in the surrounding cluster.

The leading idea used in the former papers was that the atoms were formed through the successive binding by the nucleus of a number of electrons initially nearly at rest.

* Communicated by Prof. E. Rutherford, F.R.S.

† Part I. and Part II. were published in Phil. Mag. xxvi. p. 1 & p. 476 (1913).

Such a conception, however, cannot be utilized in considering the formation of a system containing more than a single nucleus; for in the latter case there will be nothing to keep the nuclei together during the binding of the electrons. In this connexion it may be noticed that while a single nucleus carrying a large positive charge is able to bind a small number of electrons, on the contrary, two nuclei highly charged obviously cannot be kept together by the help of a few electrons. We must therefore assume that configurations containing several nuclei are formed by the interaction of systems—each containing a single nucleus—which already have bound a number of electrons.

§ 2 deals with the configuration and stability of a system already formed. We shall consider only the simple case of a system consisting of two nuclei and of a ring of electrons rotating round the line connecting them; the result of the calculation, however, gives indication of what configurations are to be expected in more complicated cases. As in the former papers, we shall assume that the conditions of equilibrium can be deduced by help of the ordinary mechanics. In determining the absolute dimensions and the stability of the systems, however, we shall use the main hypothesis of Part I. According to this, the angular momentum of every electron round the centre of its orbit is equal to a universal value $\frac{h}{2\pi}$, where h is Planck's constant; further, the stability is determined by the condition that the total energy of the system is less than in any neighbouring configuration satisfying the same condition of the angular momentum of the electrons.

In § 3 the configuration to be expected for a hydrogen molecule is discussed in some detail.

§ 4 deals with the mode of formation of the systems. A simple method of procedure is indicated, by which it is possible to follow, step by step, the combination of two atoms to form a molecule. The configuration obtained will be shown to satisfy the conditions used in § 2. The part played in the considerations by the angular momentum of the electrons strongly supports the validity of the main hypothesis.

§ 5 contains a few indications of the configurations to be expected for systems containing a greater number of electrons.

§ 2. Configurations and Stability of the Systems.

Let us consider a system consisting of two positive nuclei of equal charges and a ring of electrons rotating round the line connecting them. Let the number of electrons in the ring be n , the charge of an electron $-e$, and the charge on each nucleus Ne . As can be simply shown, the system will be in equilibrium if the nuclei are the same distance apart from the plane of the ring and if the ratio between the diameter of the ring $2a$ and the distance apart of the nuclei $2b$ is given by

$$b = a \left(\left(\frac{4n}{N} \right)^{\frac{2}{3}} - 1 \right)^{-\frac{1}{2}}. \quad \dots \quad (1)$$

provided that the frequency of revolution ω is of a magnitude such that for each of the electrons the centrifugal force balances the radial force due to the attraction of the nuclei and the repulsion of the other electrons. Denoting this force by $\frac{e^2}{a^2}F$, we get from the condition of the universal constancy of the angular momentum of the electrons, as shown in Part II. p. 478,

$$a = \frac{h^2}{4\pi^2 e^2 m} F^{-1} \quad \text{and} \quad \omega = \frac{4\pi^2 e^2 m}{h^3} F^2. \quad \dots \quad (2)$$

The total energy necessary to remove all the charged particles to infinite distances from each other is equal to the total kinetic energy of the electrons and is given by

$$W = \frac{2\pi^2 e^4 m}{h^2} \Sigma F^2. \quad \dots \quad (3)$$

For the system in question we have

$$F = \frac{N^2}{2a} \left(\left(\frac{4n}{N} \right)^{\frac{2}{3}} - 1 \right)^{\frac{3}{2}} - s_n. \quad \dots \quad (4)$$

where

$$s_n = \sum_{s=1}^{n-1} \operatorname{cosec} \frac{s\pi}{n};$$

a table of s_n is given in Part II. on p. 482.

To test the stability of the system we have to consider displacements of the orbits of the electrons relative to the nuclei, and also displacements of the latter relative to each other.

A calculation based on the ordinary mechanics gives that

the systems are unstable for displacements of the electrons in the plane of the ring. As for the systems considered in Part II, we shall, however, assume that the ordinary principles of mechanics cannot be used in discussing the problem in question, and that the stability of the systems for the displacements considered is secured through the introduction of the hypothesis of the universal constancy of the angular momentum of the electrons. This assumption is included in the condition of stability stated in § 1. It should be noticed that in Part II, the quantity F was taken as a constant, while for the systems considered here, F , for fixed positions of the nuclei, varies with the radius of the ring. A simple calculation, however, similar to that given in Part II, on p. 480, shows that the increase in the total energy of the system for a variation of the radius of the ring from a to $a + \delta a$, neglecting powers of δa greater than the second, is given by

$$\delta(P + T) = T \left(1 + \frac{a}{F} \frac{\partial F}{\partial a} \right) (\delta a)^2,$$

where T is the total kinetic energy and P the potential energy of the system. Since for fixed positions of the nuclei F increases for increasing a ($F = 0$ for $a = 0$; $F = 2N - s_n$ for $a = \infty$), the term dependent on the variation of F will be positive, and the system will consequently be stable for the displacement in question.

From considerations exactly corresponding to those given in Part II, on p. 481, we get for the condition of stability for displacements of the electrons perpendicular to the plane of the ring

$$G > p_{n,o} - p_{n,m} \quad \dots \dots \dots (5)$$

where $p_{n,o} - p_{n,m}$ has the same significance as in Part II, and $\frac{e^2}{a^3} G \delta z$ denotes the component, perpendicular to the plane of the ring, of the force due to the nuclei, which acts upon one of the electrons in the ring when it has suffered a small displacement δz perpendicular to the plane of the ring. As for the systems considered in Part II, the displacements can be imagined to be produced by the effect of extraneous forces acting upon the electrons in direction parallel to the axis of the system.

For a system of two nuclei each of charge Ne and with a ring of n electrons, we find

$$G = \frac{N^2}{2n} \left(\left(\frac{4n}{N} \right)^{\frac{2}{3}} - 1 \right)^{\frac{2}{3}} \left(1 - 3 \left(\frac{N}{4n} \right)^{\frac{2}{3}} \right) \dots \dots (6)$$

By help of this expression and using the table for $p_{n,o} - p_{n,m}$ given on p. 482 in Part II, it can be simply shown that the system in question will not be stable unless $N = 1$ and n equal to 2 or 3.

In considering the stability of the systems for a displacement of the nuclei relative to each other, we shall assume that the motions of the nuclei are so slow that the state of motion of the electrons at any moment will not differ sensibly from that calculated on the assumption that the nuclei are at rest. This assumption is permissible on account of the great mass of the nuclei compared with that of the electrons, which involves that the vibrations resulting from a displacement of the nuclei are very slow compared with those due to a displacement of the electrons. For a system consisting of a ring of electrons and two nuclei of equal charge, we shall thus assume that the electrons at any moment during the displacement of the nuclei move in circular orbits in the plane of symmetry of the latter.

Let us now imagine that, by help of extraneous forces acting on the nuclei, we slowly vary the distance between them. During the displacement the radius of the ring of electrons will vary in consequence of the alteration of the radial force due to the attraction of the nuclei. During this variation the angular momentum of each of the electrons round the line connecting the nuclei will remain constant. If the distance apart of the nuclei increases, the radius of the ring will obviously also increase; the radius, however, will increase at a slower rate than the distance between the nuclei. For example, imagine a displacement in which the distance as well as the radius are both increased to α times their original value. In the new configuration the radial force acting on an electron from the nuclei and the other electrons is $\frac{1}{\alpha^3}$ times that in the original configuration. From the constancy of the angular momentum of the electrons during the displacement, it further follows that the velocity of the electrons in the new configuration is $\frac{1}{\alpha}$ times, and the centrifugal force $\frac{1}{\alpha^3}$ times that in the original. Consequently, the radial force is greater than the centrifugal force.

On account of the distance between the nuclei increasing faster than the radius of the ring, the attraction on one of the nuclei due to the ring will be greater than the repulsion from the other nucleus. The work done during the displacement by the extraneous forces acting on the nuclei will therefore

be positive, and the system will be stable for the displacement. Obviously the same result will hold in the case of the distance between the nuclei diminishing. It may be noticed that in the above considerations we have not made use of any new assumption on the dynamics of the electrons, but have only used the principle of the invariance of the angular momentum, which is common both for the ordinary mechanics and for the main hypothesis of § 1.

For a system consisting of a ring of electrons and two nuclei of unequal charge, the investigation of the stability is more complicated. As before, we find that the systems are always stable for displacements of the electrons in the plane of the ring; also an expression corresponding to (5) will hold for the condition of stability for displacements perpendicular to the plane of the ring. This condition, however, will not be sufficient to secure the stability of the system. For a displacement of the electrons perpendicular to the plane of the ring, the variation of the radial force due to the nuclei will be of the same order of magnitude as the displacement; therefore, in the new configuration the radial force will not be in equilibrium with the centrifugal force, and, if the radius of the orbits is varied until the radial equilibrium is restored, the energy of the system will decrease. This circumstance must be taken into account in applying the condition of stability of § 1. Similar complications arise in the calculation of stability for displacements of the nuclei. For a variation of the distance apart of the nuclei not only will the radius of the ring vary but also the ratio in which the plane of the ring divides the line connecting the nuclei. As a consequence, the full discussion of the general case is rather lengthy; an approximate numerical calculation, however, shows that the systems, as in the former case, will be unstable unless the charges on the nuclei are small and the ring contains very few electrons.

The above considerations suggest configurations of systems, consisting of two positive nuclei and a number of electrons, which are consistent with the arrangement of the electrons to be expected in molecules of chemical combinations. If we thus consider a neutral system containing two nuclei with great charges, it follows that in a stable configuration the greater part of the electrons must be arranged around each nucleus approximately as if the other nucleus were absent; and that only a few of the outer electrons will be arranged differently rotating in a ring round the line connecting the nuclei. The latter ring, which keeps the system together, represents the chemical "bond."

A first rough approximation of the possible configuration of such a ring can be obtained by considering simple systems consisting of a single ring rotating round the line connecting two nuclei of minute dimensions. A detailed discussion, however, of the configuration of systems containing a greater number of electrons, taking the effect of inner rings into account, involves elaborate numerical calculations. Apart from a few indications given in § 5, we shall in this paper confine ourselves to systems containing very few electrons.

§ 3. Systems containing few Electrons. The Hydrogen Molecule.

Among the systems considered in § 2 and found to be stable the system formed of a ring of two electrons and of two nuclei of charge e is of special interest, as it, according to the theory, may be expected to represent a neutral hydrogen molecule.

Denoting the radius of the ring by a and the distances apart of the nuclei from the plane of the ring by b , we get from (1), putting $N=1$ and $n=2$,

$$b = \frac{1}{\sqrt{3}} a;$$

from (4) we further get

$$F = \frac{3\sqrt{3}-1}{4} = 1.049.$$

From (2) and (3) we get, denoting as in Part II. the values of α , ω , and W for a system consisting of a single electron rotating round a nucleus of charge e (a hydrogen atom) by α_0 , ω_0 , and W_0 ,

$$\alpha = 0.95 \alpha_0, \quad \omega = 1.10 \omega_0, \quad W = 2.20 W_0.$$

Since $W > 2W_0$, it follows that two hydrogen atoms combine into a molecule with emission of energy*. Putting $W_0 = 2.0 \cdot 10^{-11}$ erg (comp. Part II. p. 488) and $N = 6.2 \cdot 10^{23}$, where N is the number of molecules in a gram-molecule, we get for the energy emitted during the formation of a gram-molecule of hydrogen from hydrogen atoms ($W - 2W_0$) $N = 2.5 \cdot 10^{12}$, which corresponds to $6.0 \cdot 10^4$ cal. This value is of the right order of magnitude; it is, however, considerably less than the value $13 \cdot 10^4$ cal. found by Langmuir* by measuring the heat conduction through the gas from an incandescent wire in hydrogen. On account of the indirect

* I. Langmuir, Journ. Amer. Chem. Soc. xxxiv. p. 860 (1912).

method employed it seems difficult to estimate the accuracy to be ascribed to the latter value. In order to bring the theoretical value in agreement with Langmuir's value, the magnitude of the angular momentum of the electrons should be only $2/3$ of that adopted; this seems, however, difficult to reconcile with the agreement obtained on other points.

From (6) we get $G = \frac{3\sqrt{3}}{16} = 0.325$. For the frequency of vibration of the whole ring in the direction parallel to the axis of the system we get

$$\nu = \omega_0 \sqrt{\frac{G^2 \omega_0^3}{\omega_0^3}} = 0.61 \omega_0 = 3.8 \cdot 10^{15} \text{ 1/sec.}$$

We have assumed in Part I. and Part II. that the frequency of radiation absorbed by the system and corresponding to vibrations of the electrons in the plane of the ring cannot be calculated from the ordinary mechanics, but is determined by the relation $h\nu = E$, where h is Planck's constant, and E the difference in energy between two different stationary states of the system. Since we have seen in § 2 that a configuration consisting of two nuclei and a single electron rotating round the line between them is unstable, we may assume that the removing of one of the electrons will lead to the breaking up of the molecule into a single nucleus and a hydrogen atom. If we consider the latter state as one of the stationary states in question we get

$$E = W - W_0 = 1.20 W_0 \quad \text{and} \quad \nu = 1.2 \frac{W_0}{h} = 3.7 \cdot 10^{15} \text{ 1/sec.}$$

The value for the frequency of the ultra-violet absorption line in hydrogen calculated from experiments on dispersion is $\nu = 3.5 \cdot 10^{15}$ 1/sec.* Further, a calculation from such experiments based on Drude's theory gives a value near two for the number of electrons in a hydrogen molecule. The latter result might have connexion with the fact that the frequencies calculated above for the radiation absorbed corresponding to vibrations parallel and perpendicular to the plane of the ring are nearly equal. As mentioned in Part II., the number of electrons in a helium atom calculated from experiments on dispersion is only about $2/3$ of the number of electrons to be expected in the atom, viz. two. For a helium atom, as for a hydrogen molecule, the frequency determined by the relation $\nu \cdot h = E$ agrees closely with the frequency observed from dispersion; in the helium system, however, the frequency

* C. and M. Cutberrison, Proc. Roy. Soc. lxxxiii. p. 151 (1910).

corresponding to vibrations perpendicular to the plane of the ring is more than three times as great as the frequency in question, and consequently of negligible influence on the dispersion.

In order to determine the frequency of vibration of the system corresponding to displacement of the nuclei relative to each other, let us consider a configuration in which the radius of the ring is equal to y , and the distance apart of the nuclei $2x$. The radial force acting on one of the electrons and due to the attraction from the nuclei and the repulsion from the other electron is

$$R = \frac{2e^2 y}{(y^2 + x^2)^{3/2}} - \frac{e^2}{4y^3}.$$

Let us now consider a slow displacement of the system during which the radial force balances the centrifugal force due to the rotation of the electrons, and the angular momentum of the latter remains constant. Putting $R = \frac{e^2}{y^2} F$, we have seen on p. 859 that the radius of the ring is inversely proportional to F . Therefore, during the displacement considered, Ry^3 remains constant. This gives by differentiation

$$(3y^2 + 32y^3 x^2 - (x^2 + y^2)^3) dy - 24xy^4 dx = 0.$$

Introducing $x = b$ and $y = a$, we get

$$\frac{dy}{dx} = \frac{27}{21\sqrt{3}-4} = 0.834.$$

The force acting on one of the nuclei due to the attraction from the ring and the repulsion from the other nucleus is

$$Q = \frac{2e^2 x}{(x^2 + y^2)^{3/2}} - \frac{e^2}{4x^2}.$$

For $x = b$, $y = a$ this force is equal to 0.

Corresponding to a small displacement of the system for which $x = a + \delta x$ we get, using the above value for $\frac{dy}{dx}$ and putting $Q = \frac{e^2}{a^3} H \delta x$,

$$H = \frac{27}{16} \left(\sqrt{3} - \frac{dy}{dx} \right) = 1.515.$$

For the frequency of vibration corresponding to the displacement in question we get, denoting the mass of one of

$$\nu = \omega_0 \sqrt{\frac{m}{M}} \frac{H}{a^3} = 1.32\omega_0 \sqrt{\frac{m}{M}}.$$

Putting $\frac{M}{m} = 1835$ and $\omega_0 = 6.2 \cdot 10^{15}$, we get
 $\nu = 1.91 \cdot 10^{14}$.

This frequency is of the same order of magnitude as that calculated by Einstein's theory from the variation of the specific heat of hydrogen gas with temperature*. On the other hand, no absorption of radiation in hydrogen gas corresponding to this frequency is observed. This is, however, just what we should expect on account of the symmetrical structure of the system and the great ratio between the frequencies corresponding to displacements of the electrons and of the nuclei. The complete absence of infra-red absorption in hydrogen gas might be considered as a strong argument in support of a constitution of a hydrogen molecule like that adopted here, compared with model-molecules in which the chemical bond is assumed to have its origin in an opposite charge of the entering atoms.

As will be shown in § 5, the frequency calculated above can be used to estimate the frequency of vibration of more complicated systems for which an infra-red absorption is observed.

The configuration of two nuclei of charge e and a ring of three electrons rotating between them will, as mentioned in § 2, also be stable for displacements of the electrons perpendicular to the plane of the ring. A calculation gives

$$\frac{b}{a} = 0.486, \quad G = 0.623, \quad \text{and} \quad F = 0.879;$$

and further,

$$\alpha = 1.14\omega_0, \quad \omega = 0.77\omega_0, \quad W = 2.32W_0.$$

Since W is greater than for the system consisting of two nuclei and two electrons, the system in question may be considered as representing a negatively charged hydrogen molecule. Proof of the existence of such a system has been obtained by Sir J. J. Thomson in his experiments on positive rays†.

A system consisting of two nuclei of charge e and a single

* See N. Bierrum, *Zeitschr. f. Elektrochem.* xvii. p. 781 (1911); xviii. p. 101 (1912).
 † J. J. Thomson, *Phil. Mag.* xxiv. p. 253 (1912).

electron rotating in a circular orbit round the line connecting the nuclei, is unstable for a displacement of the electron perpendicular to its orbit, since in the configuration of equilibrium $G < 0$. The explanation of the appearance of positively charged hydrogen molecules in experiments on positive rays may therefore at first sight be considered as a serious difficulty for the present theory. A possible explanation, however, might be sought in the special conditions under which the systems are observed. We are probably dealing in such a case not with the formation of a stationary system by a regular interaction of systems containing single nuclei (see the next section), but rather with a delay in the breaking up of a configuration brought about by the sudden removal of one of the electrons by impact of a single particle. Another stable configuration containing a few electrons is one consisting of a ring of three electrons and two nuclei of charges e and $2e$. A numerical calculation gives

$$\frac{b_1}{a} = 1.446, \quad \frac{b_2}{a} = 0.137, \quad F = 1.552,$$

where a is the radius of the ring and b_1 and b_2 the distances apart of the nuclei from the plane of the ring. By help of (2) and (3) we further get

$$\alpha = 0.644\omega_0, \quad \omega = 2.41\omega_0, \quad W = 7.22W_0,$$

where ω is the frequency of revolution and W the total energy necessary to remove the particles to infinite distances from each other. In spite of the fact that W is greater than the sum of the values of W for a hydrogen and a helium atom ($W_0 + 6.13W_0$; comp. Part II. p. 489), the configuration in question cannot, as will be shown in the next section, be considered to represent a possible molecule of hydrogen and helium.

The vibration of the system corresponding to a displacement of the nuclei relative to each other shows features different from the system considered above of two nuclei of charge e and two electrons. If, for example, the distance between the nuclei is increased, the ring of electrons will approach the nucleus of charge $2e$. Consequently, the vibration must be expected to be connected with an absorption of radiation.

§ 4. Formation of the Systems.

As mentioned in § 1, we cannot assume that systems containing more than one nucleus are formed by successive binding of electrons, such as we have assumed for the

systems considered in Part II. We must assume that the systems are formed by the interaction of others, containing single nuclei, which already have bound electrons. We shall now consider this problem more closely, starting with the simplest possible case, viz., the combination of two hydrogen atoms to form a molecule.

Consider two hydrogen atoms at a distance apart great in comparison with the linear dimensions of the orbits of the electrons, and imagine that by help of extraneous forces acting on the nuclei, we make these approach each other; the displacements, however, being so slow that the dynamical equilibrium of the electrons for every position of the nuclei is the same as if the latter were at rest.

Suppose that the electrons originally rotate in parallel planes perpendicular to the straight line connecting the nuclei, and that the direction of rotation is the same and the difference in phase equal to half a revolution. During the approach of the nuclei, the direction of the planes of the orbits of the electrons and the difference in phase will be unaltered. The planes of the orbits, however, will at the beginning of the process approach each other at a higher rate than do the nuclei. By the continued displacement of the latter the planes of the orbits of the electrons will approach each other more and more, until finally for a certain distance apart of the nuclei the planes will coincide, the electrons being arranged in a single ring rotating in the plane of symmetry of the nuclei. During the further approach of the nuclei the ratio between the diameter of the ring of electrons and the distance apart of the nuclei will increase, and the system will pass through a configuration in which it will be in equilibrium without the application of extraneous forces on the nuclei.

By help of a calculation similar to that indicated in § 2, it can be simply shown that at any moment during this process the configuration of the electrons is stable for a displacement perpendicular to the plane of the orbits. In addition, during the whole operation the angular momentum of each of the electrons round the line connecting the nuclei will remain constant, and the configuration of equilibrium obtained will therefore be identical with the one adopted in § 3 for a hydrogen molecule. As there shown, the configuration will correspond to a smaller value for the total energy than the one corresponding to two isolated atoms. During the process, the forces between the particles of the system will therefore have done work against the extraneous forces acting on the nuclei; this fact may be expressed by

saying that the atoms have "attracted" each other during the combination. A closer calculation shows that for any distance apart of the nuclei greater than that corresponding to the configuration of equilibrium, the forces acting on the nuclei, due to the particles of the system, will be in such a direction as to diminish the distance between the nuclei; while for any smaller distance the forces will have the opposite direction.

By means of these considerations, a possible process is indicated for the combination of two hydrogen atoms to form a molecule. This operation can be followed step by step without introducing any new assumption on the dynamics of the electrons, and leads to the same configuration adopted in § 3 for a hydrogen molecule. It may be recalled that the latter configuration was deduced directly by help of the principal hypothesis of the universal constancy of the angular momentum of the electrons. These considerations also offer an explanation of the "affinity" of two atoms. It may be remarked that the assumption in regard to the slowness of the motion of the nuclei relative to those of the electrons is satisfied to a high degree of approximation in a collision between two atoms of a gas at ordinary temperatures. In assuming a special arrangement of the electrons at the beginning of the process, very little information, however, is obtained by this method on the chance of combination due to an arbitrary collision between two atoms.

Another way in which a neutral hydrogen molecule may be formed is by the combination of a positively and a negatively charged atom. According to the theory a positively charged hydrogen atom is simply a nucleus of vanishing dimensions and of charge e , while a negatively charged atom is a system consisting of a nucleus surrounded by a ring of two electrons. As shown in Part II., the latter system may be considered as possible, since the energy emitted by the formation of it is greater than the corresponding energy for a neutral hydrogen atom. Let us now imagine that, by a slow displacement of the nuclei, as before, a negatively and a positively charged atom combine. We must assume that, when the nuclei have approached a distance equal to that in the configuration adopted for a hydrogen molecule, the electrons will be arranged in the same way, since this is the only stable configuration for this distance in which the angular momentum of the electrons has the value prescribed by the theory. The state of motion of the electrons will, however, not vary in a continuous way with the displacement

of the nuclei as in the combination of two neutral atoms. For a certain distance apart of the nuclei the configuration of the electrons will be unstable and suddenly change by a finite amount; this is immediately deduced from the fact that the motion of the electrons by the combination of two neutral hydrogen atoms considered above, passes through an uninterrupted series of stable configurations. The work done by the system against the extraneous forces acting on the nuclei will therefore, in the case of the combination of a negatively and a positively charged atom, not be equal to the difference in energy between the original and the final configuration; but in passing through the unstable configurations a radiation of energy must be emitted, corresponding to that emitted during the binding of electrons by a single nucleus and considered in Parts I. and II.

On the above view, it follows that in the breaking up of a hydrogen molecule by slowly increasing the distance apart of the nuclei, we obtain two *neutral* hydrogen atoms and not a positively and a negatively charged one. This is in agreement with deductions drawn from experiments on positive rays*.

Next imagine that instead of two hydrogen atoms we consider two helium atoms, *i. e.* systems consisting of a nucleus of charge $2e$ surrounded by a ring of two electrons, and go through a similar process to that considered on p. 868. Assume that the helium atoms at the beginning of the operation are orientated relatively to each other like the hydrogen atoms, but with the exception that the phases of the electrons in the helium atoms differ by one quarter of a revolution instead of one half revolution as in the case of hydrogen. By the displacement of the nuclei, the planes of the rings of electrons will, as in the former case, approach each other at a higher rate than the nuclei, and for a certain position of the latter the planes will coincide. During the further approach of the nuclei, the electrons will be arranged at equal angular intervals in a single ring. As in the former case, it can be shown that at any moment during this operation the system will be stable for a displacement of the electrons perpendicular to the plane of the rings. Contrary, however, to what took place in the case of hydrogen, the extraneous forces to be applied to the nuclei in order to keep the system in equilibrium will always be in a direction to diminish the distance apart of the nuclei, and the system will never pass through a configuration of equilibrium; the helium atoms

* Comp. J. J. Thomson, Phil. Mag. xxiv. p. 248 (1912).

will, during the process, "repel" each other. The consideration offers an explanation of the refusal of helium atoms to combine into molecules by a close approach of the atoms.

Instead of two hydrogen or two helium atoms, next consider a hydrogen and a helium atom, and let us slowly approach the nuclei to each other in a similar way. In this case, contrary to the former cases, the electrons will have no tendency to flow together in a single ring. On account of the great difference in the radii of the orbits of the electrons in hydrogen and helium, the electron of the hydrogen atom must be expected to rotate always outside the helium ring, and if the nuclei are brought very close together, the configuration of the electrons will coincide with that adopted in Part II. for a lithium atom. Further, the extraneous forces to be applied to the nuclei during the process will be in such a direction as to diminish the distance apart. In this way, therefore, we cannot obtain a combination of the atoms.

The stable configuration considered in § 3, consisting of a ring of three electrons and two nuclei of charge e and $2e$, cannot be expected to be formed by such a process, unless the ring of electrons were bound originally by one of the nuclei. Neither a hydrogen nor a helium nucleus will, however, be able to bind a ring of three electrons, since such a configuration would correspond to a greater total energy than the one in which the nucleus has bound two electrons (comp. Part II. pp. 488 and 490). As mentioned in § 3, such a configuration cannot therefore be considered as representing a possible combination of hydrogen and helium, in spite of the fact that the value of W is greater than the sum of the values of W for a hydrogen and a helium atom. As we shall see in the next section, the configuration may, however, give indications of the possible structure of the molecules of a certain class of chemical combinations.

§ 5. Systems containing a greater number of Electrons.

From the considerations of the former section we are led to indications of the configuration of the electrons in systems containing a greater number of electrons, consistent with those obtained in § 2.

Let us imagine that, in a similar way to that considered on p. 868 for two hydrogen atoms, we make two atoms containing a large number of electrons approach each other. During the beginning of the process the effect on the configuration of the inner rings will be very small compared with the effect on the electrons in the outer rings, and the

final result will mainly depend on the number of electrons in these rings. If, for example, the outer ring in both atoms contains only one electron, we may expect that during the approach these two electrons will form a single ring as in the case of hydrogen. By a further approach of the nuclei, the system will arrive at a state of equilibrium before the distance apart of the nuclei is comparable with the radii of the inner rings of electrons. If the distance be decreased still further, the repulsion of the nuclei will predominate and tend to prevent an approach of the systems.

In this way we are led to a possible configuration of a molecule of a combination of two monovalent substance—such as $H(1)$ —in which the ring of electrons representing the chemical bond is arranged in a similar way to that assumed for a hydrogen molecule. Since, however, as in the case of hydrogen, the energy emitted by a combination of the atoms is only a small part of the kinetic energy of the outer electrons, we may expect that small differences in the configuration of the ring, due to the presence of inner rings of electrons in the atoms, will be of great influence on the heat of combination and consequently on the affinity of the substances. As mentioned in § 2, a detailed discussion of these questions involves elaborate numerical calculations. We may, however, make an approximate comparison of the theory with experiment, by considering the frequency of vibration of the two atoms in the molecule relative to each other. In § 3, p. 866, we have calculated this frequency for a hydrogen molecule. Since now the binding of the atoms is assumed to be similar to that in hydrogen, the frequency of another molecule can be simply calculated if we know the ratio of the mass of the nuclei to be that of a hydrogen nucleus. Denoting the frequency of a hydrogen molecule by ν_0 and the atomic weights of the substances entering in the combination in question by A_1 and A_2 respectively, we get for the frequency

$$\nu = \nu_0 \sqrt{\frac{A_1 + A_2}{2 A_1 A_2}}.$$

If the two atoms are identical the molecule will be exactly symmetrical, and we cannot expect an absorption of radiation corresponding to the frequency in question (comp. p. 866). For HCl gas an infra-red absorption band corresponding to a frequency of about $8.5 \cdot 10^{13}$ is observed*. Putting in the above formula $A_1 = 1$ and $A_2 = 35$ and using the value for ν_0

* See H. Kayser, *Handb. d. Spectr.* iii. p. 366 (1905).

on p. 866, we get $\nu = 13.7 \cdot 10^{13}$. On account of the approximation introduced the agreement may be considered as satisfactory.

The molecules in question may also be formed by the combination of a positively and a negatively charged atom. As in the case of hydrogen, however, we shall expect to obtain two *neutral* atoms by the breaking up of the molecule. There may be another type of molecule, for which this does not hold, viz., molecules which are formed in a manner analogous to the system consisting of a ring of three electrons and two nuclei of charges e and $2e$, mentioned in the former section. As we have seen, the necessary condition for the formation of a configuration of this kind is that one of the atoms in the molecule is able to bind three electrons in the outer ring. According to the theory, this condition is not satisfied for a hydrogen or a helium atom, but is for an oxygen atom. With the symbols used in Part II. the configuration suggested for the oxygen atom was given by $8(4, 2, 2)$. From a calculation, as that indicated in Part II., we get for this configuration $W = 228.07 W_0$, while for the configuration $8(4, 2, 3)$ we get $W = 228.18 W_0$. Since the latter value for W is greater than the first, the configuration $8(4, 2, 3)$ may be considered as possible and as representing an oxygen atom with a single negative charge. If now a hydrogen nucleus approaches the system $8(4, 2, 3)$, we may expect a stable configuration to be formed in which the outer electrons will be arranged approximately as in the system mentioned above. In a breaking up of this configuration the ring of three electrons will remain with the oxygen atom.

Such considerations suggest a possible configuration for a water molecule, consisting of an oxygen nucleus surrounded by a small ring of 4 electrons and 2 hydrogen nuclei situated on the axis of the ring at equal distances apart from the first nucleus and kept in equilibrium by help of two rings of greater radius each containing three electrons; the latter rotate in parallel planes round the axis of the system, and are situated relatively to each other so that the electrons in the one ring are placed just opposite the interval between the electrons in the other. If we imagine that such a system is broken up by slowly removing the hydrogen nuclei—we should obtain two positively charged hydrogen atoms and an oxygen atom with a double negative charge, in which the outermost electrons will be arranged in two rings of three electrons each, rotating in parallel planes. The assumption of such a configuration for a water molecule offers a possible explanation of the great absorption of water for rays in the

infra-red and for the high value of its specific inductive capacity.

In the preceding we have only considered systems which possess an axis of symmetry around which the electrons are assumed to rotate in circular orbits. In systems such as the molecule CH_4 , we cannot, however, assume the existence of an axis of symmetry, and consequently we must in such cases omit the assumption of exactly circular orbits. The configuration suggested by the theory for a molecule of CH_4 is of the ordinary tetrahedron type; the carbon nucleus surrounded by a very small ring of two electrons being situated in the centre, and a hydrogen nucleus in every corner. The chemical bonds are represented by 4 rings of 2 electrons each rotating round the lines connecting the centre and the corners. The closer discussion of such questions, however, is far out of the range of the present theory.

Concluding remarks.

In the present paper an attempt has been made to develop a theory of the constitution of atoms and molecules on the basis of the ideas introduced by Planck in order to account for the radiation from a black body, and the theory of the structure of atoms proposed by Rutherford in order to explain the scattering of α -particles by matter.

Planck's theory deals with the emission and absorption of radiation from an atomic vibrator of a constant frequency, independent of the amount of energy possessed by the system in the moment considered. The assumption of such vibrators, however, involves the assumption of quasi-elastic forces and is inconsistent with Rutherford's theory, according to which all the forces between the particles of an atomic system vary inversely as the square of the distance apart. In order to apply the main results obtained by Planck it is therefore necessary to introduce new assumptions as to the emission and absorption of radiation by an atomic system.

The main assumptions used in the present paper are:—

1. That energy radiation is not emitted (or absorbed) in the continuous way assumed in the ordinary electrodynamics, but only during the passing of the systems between different "stationary" states.
2. That the dynamical equilibrium of the systems in the stationary states is governed by the ordinary laws of mechanics, while these laws do not hold for the passing of the systems between the different stationary states.

3. That the radiation emitted during the transition of a system between two stationary states is homogeneous, and that the relation between the frequency ν and the total amount of energy emitted E is given by $E = h\nu$, where h is Planck's constant.

4. That the different stationary states of a simple system consisting of an electron rotating round a positive nucleus are determined by the condition that the ratio between the total energy, emitted during the formation of the configuration, and the frequency of revolution of the electron is an entire multiple of $\frac{h}{2}$. Assuming that the orbit of the electron is circular, this assumption is equivalent with the assumption that the angular momentum of the electron round the nucleus is equal to an entire multiple of $\frac{h}{2\pi}$.

5. That the "permanent" state of any atomic system—i.e., the state in which the energy emitted is maximum—is determined by the condition that the angular momentum of every electron round the centre of its orbit is equal to $\frac{h}{2\pi}$.

It is shown that, applying these assumptions to Rutherford's atom model, it is possible to account for the laws of Balmer and Rydberg connecting the frequency of the different lines in the line-spectrum of an element. Further, outlines are given of a theory of the constitution of the atoms of the elements and of the formation of molecules of chemical combinations, which on several points is shown to be in approximate agreement with experiments.

The intimate connexion between the present theory and modern theories of the radiation from a black body and of specific heat is evident; again, since on the ordinary electrodynamics the magnetic moment due to an electron rotating in a circular orbit is proportional to the angular momentum, we shall expect a close relation to the theory of magnets proposed by Weiss. The development of a detailed theory of heat radiation and of magnetism on the basis of the present theory claims, however, the introduction of additional assumptions about the behaviour of bound electrons in an electromagnetic field. The writer hopes to return to these questions later.