On the Constitution of Atoms and Molecules

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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 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 appears -- the radius of the positive sphere -- of dimensions 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 &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 often 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. 237 (1904).

** See f. inst., ' Théorie du ravonnement 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 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 2*a* 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

$$\omega = \frac{\sqrt{2}}{\pi} \frac{W^{\frac{3}{2}}}{eE\sqrt{m}}, \quad 2a = \frac{eE}{W}. \quad . \quad . \quad . \quad (1)$$

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 τ*h*ν, 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 bad 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 orbit; then, from Planck's theory, we might expect, that the amount of energy emitted by the process considered is equal to τ*h*ν, 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.

Putting

$$W = \tau h \frac{\omega}{2}, \quad . \quad . \quad . \quad . \qquad (2)$$

we can by help of the formula (1)

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

If in these expressions we give τ different values we get -a series of values for W, ω, and *a* 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 τ = l and E = *e*, and introducing the experimental values

$$e = 4.7 \times 10^{-10}, \; e / m = 5.31 \times 10^{17}, \; h = 6.5 \times 10^{-27}$$

we get

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

$$2a = 1.1 \times 10^{-8} \text{ cm.}, \omega = 6.2 \times 10^{15} \text{ sec}^{-1}, W / e = 13 \text{ volt.}$$

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

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* 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 Sommerfield [*sic*]. 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 quantity which we have denoted above by W. In 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

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* A. E. Haas, *Jahrb. d. Rad. u. El.* vii. p. 261 (1910). See further, A. Schidlof, *Ann. d. Phys.* xxxv. p. 90 (1911); E. Wertheimer, *Phys. Zeitschr*. xii. p. 409 (1911), *Verh. deutsch. Phys. Ges.* 1912, p. 431; 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. 49,130, 677, 693, 729 (1912).

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 Miner 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 further made use

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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 reformation 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,

$$W_\tau = \frac{2\pi^2 m e^4}{h^2 \tau^2}.$$

The amount of energy emitted by the passing of the system from a state corresponding to $\tau = \tau_1$ to one corresponding to $\tau = \tau_2$, is consequently

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

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

$$W_{\tau_2} - W_{\tau_1} = h\nu,$$

* 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

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

We see that this expression accounts for the law connecting lines in the spectrum of hydrogen. If we put $\tau_2 = 2$ and let τ_1 vary, we get the ordinary Balmer series. If we put $\tau_2 = 3$, we get the series in the ultra-red observed by Paschen* and previously suspected by Ritz. If we put $\tau_2 = 1$ and $\tau_2 = 4, 5, \ldots$, 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

$$e = 4.7 \times 10^{-10},\ e / m = 5.31 \times 10^{17},\ h = 6.5 \times 10^{-27}$$

we get

$$\frac{2\pi^2 m e^4}{h^3} = 3{\cdot}1 \,.\, 10^{15}.$$

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

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

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 τ^2. For $\tau = 12$ the diameter is equal to 1.6×10^{-6} cm., or equal to the mean distance between the molecules in a gas at a pressure of about 7 mm. mercury; for $\tau = 33$ the diameter is equal to 1.2×10^{-5} cm., corresponding to the mean distance of the molecules at a pressure of 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. 565 (1908).

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 2*e* and two electrons. Now considering the binding of a single electron by a helium nucleus, we get, putting E = 2*e* in the expressions (3) on page 5, and proceeding in exactly the same way as above,

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

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 $\tau_2 = 5, 6, \ldots$, 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 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 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 those considered. I shall try to show that the 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 call be expressed by

$$\nu = F_r(\tau_1 \text{ minus } F_s(\tau_2),$$

where τ_1 and τ_2 are entire numbers, and F_1, F_2, F_2, ... are functions of τ which approximately are equal to $K / (\tau + a_1)^2$, $K / (\tau + a_2)^2$, ... 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

$$\lim (\tau^2 . F_1 (\tau)) = \lim (\tau^2 . F_2 (\tau)) = ... = 2\pi^2 me^4 / h^3$$

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

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

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

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 -r=-r2 is equal to hν, we get instead of (4)

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

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

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

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

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

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

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* = 1/2. Putting f(τ) = τ / 2, we 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 τ = N and τ = N - n, where n is small compared with N, we get with the same approximation as above putting f(τ) = τ / 2,

$$\nu = n\omega$$

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The possibility of an emission of a radiation of such a frequency may also be interpreted from analogy with the ordinary elecrodynamics, as in 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 $\omega / 2$ 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 th, 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 mechanics. Denoting the angular momentum of the electron round the nucleus by M, we have immediately for a circular orbit $\pi M = T / \omega$ 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

$$M = \tau M_o, \text{ where}$$

$$M_o = h / 2\pi = 1.04 \text{ x } 10^{-27}$$

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 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 hich correspond to those we have used considering the emission. Thus we must assume that a system consisting of a nucleus and in 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.

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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 τ [greater then or equal to] 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 stateswill be constant. Further, there will be perfect continuity between the two kinds of states, as the difference between

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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.* $T = I\nu - W$, 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

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* A. Einstein, *Ann. d. Phys*. xvii. p. 146 (1905).

** R. W. Wood, Physical Optics p. 513 (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 τ 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 tile 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.

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* 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 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 loose 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 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 Le 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 seen, 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).

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£*The permanent State of an Atomic System.*

to be continued