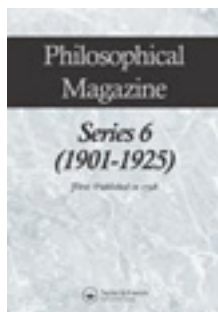


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### XLII. On the Quantum theory of radiation and the structure of the atom

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thickness in an arc. The area of each curve is a function of the number of vibrating centres in the layer and of the amplitude of vibration, while its shape and the position of its maximum ordinate are governed by the combined effect of pressure and the density of the material responsible for the spectrum line; since the latter factor is more important in the central zones than in the outer strata, we have the differences in the shapes of the curves  $a$ ,  $b$ ,  $c$  in the diagram, in which  $a$  represents the effect of the central core and  $b$  and  $c$  the effect of two of the outer envelopes. The position of the maximum ordinate of the resultant composite line (dotted) does not correspond to that of the light emitted by the core, but to some intermediate layer  $b$  in the diagram. Further differences in the shapes of  $a$ ,  $b$ , and  $c$  are occasioned by the scattering of light by the layers outside the one considered. Had the temperature and density gradients and the scattering power been different, it is obvious that the resultant curve would have differed both in its shape and in the position of its maximum ordinate. We consequently see that bright lines as well as reversals are likely to show their dependence upon the density gradients and the scattering power in the various layers in the arc. It becomes increasingly evident that the anomalies which have been encountered in estimating the pressure of the solar atmosphere arise from the fact that the density and temperature gradients in the sun and in the sources of light with which his spectrum has been compared, are different; it is not strictly legitimate, for example, to compare solar displacements with those found when an arc is subjected to external pressure, because the two sources are radically dissimilar in structure.

Physical Laboratory,  
University College, Reading,  
May 19, 1915.

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XLIII. *On the Quantum Theory of Radiation and the Structure of the Atom.* By N. BOHR, *Dr. phil. Copenhagen*; *p. t. Reader in Mathematical Physics at the University of Manchester* \*.

**I**N a series of papers in this periodical † the present writer has attempted to give the outlines of a theory of the constitution of atoms and molecules by help of a certain

\* Communicated by Sir Ernest Rutherford, F.R.S.

† *Phil. Mag.* xxvi. pp. 1, 476, 857 (1913) and xxvii. p. 506 (1914). These papers will be referred to as I., II., III., & IV. respectively.

application of the Quantum theory of radiation to the theory of the nucleus atom. As the theory has been made a subject of criticism, and as experimental evidence of importance bearing on these questions has been obtained in the meantime, an attempt will be made in this paper to consider some points more closely.

### § 1. General assumptions.

According to the theory proposed by Sir Ernest Rutherford, in order to account for the phenomena of scattering of  $\alpha$ -rays, the atom consists of a central 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. From the results of experiments on scattering of alpha rays, Rutherford concluded that the charge on the nucleus corresponds to a number of electrons per atom approximately equal to half the atomic weight. Concordant evidence from a large number of very different phenomena has led to the more definite assumption that the number of electrons per atom is exactly equal to the atomic number, *i. e.*, the number of the corresponding element in the periodic table. This view was first proposed by van den Broek\*. While the nucleus theory has been of great utility in explaining many important properties of the atom †, on the other hand it is evident that it is impossible by its aid to explain many other fundamental properties if we base our considerations on the ordinary electro-dynamical theory; but this can hardly be considered as a valid objection at the present time. It does not seem that there is any escape from the conclusion that it is impossible to account for the phenomena of temperature radiation on ordinary electro-dynamics, and that the modification to be introduced in this theory must be essentially equivalent with the assumptions first used by Planck in the deduction of his radiation formula ‡. These assumptions are known as the Quantum theory. In my previous paper it was attempted to apply the main principles of this theory by introducing the following general assumptions:—

\* van den Broek, *Phys. Zeit.* xiv. p. 32 (1913).

† See Rutherford, *Phil. Mag.* xxvii. p. 488 (1914).

‡ See J. H. Jeans, "Report on Radiation and the Quantum Theory," *Phys. Soc. London*, 1914.

- A. An atomic system possesses a number of states in which no emission of energy radiation takes place, even if the particles are in motion relative to each other, and such an emission is to be expected on ordinary electrodynamics. The states are denoted as the "stationary" states of the system under consideration.
- B. Any emission or absorption of energy radiation will correspond to the transition between two stationary states. The radiation emitted during such a transition is homogeneous and the frequency  $\nu$  is determined by the relation

$$h\nu = A_1 - A_2, \quad . . . . . (1)$$

where  $h$  is Planck's constant and  $A_1$  and  $A_2$  are the energies of the system in the two stationary states.

- C. 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 transition from one state to another.
- D. That the various possible stationary states of a system consisting of an electron rotating round a positive nucleus are determined by the relation

$$T = \frac{1}{2} n h \omega, \quad . . . . . (2)$$

where  $T$  is the mean value of the kinetic energy of the system,  $\omega$  the frequency of rotation, and  $n$  a whole number.

It will be seen that these assumptions are closely analogous to those originally used by Planck about the emission of radiation in quanta, and about the relation between the frequency of an atomic resonator (of constant frequency) and its energy. It can be shown that, for any system containing one electron rotating in a closed orbit, the assumption C and the relation (2) will secure a connexion between the frequency calculated by (1) and that to be expected from ordinary electrodynamics, in the limit where the difference between the frequency of the rotation of the electron in successive stationary states is very small compared with the absolute value of the frequency (see IV. p. 310). On the nucleus theory this occurs in the region of very slow vibrations. If the orbit of the electron is circular, the assumption D is equivalent to the condition that the angular momentum of the system in the stationary states is an integral multiple of  $h/2\pi$ . The possible importance of the

angular momentum in the discussion of atomic systems in relation to Planck's theory was first pointed out by J. W. Nicholson\*.

In paper I. it was shown that the above assumptions lead to an interpretation of the Balmer formula for the hydrogen spectrum, and to a determination of the Rydberg constant which was in close agreement with the measurements. In these considerations it is not necessary to make any assumption about the degree of excentricity of the orbit of the electron, and we shall see in the next section that it cannot be assumed that the orbit is always circular.

So far we have considered systems which contain only one electron, but the general validity of the assumptions A and B seems strongly supported by the fact that they offer a simple interpretation of the general principle of combination of spectral lines (see IV. p. 507). This principle was originally discovered by Ritz to hold for the ordinary series spectra of the elements. It has recently acquired increased interest by Fowler's work on the series spectra of enhanced lines emitted from many elements when subject to a powerful electric discharge. Fowler showed that the principle of combination holds for these spectra although the laws governing the numerical relation between the lines at an important point (see section 3) differed from those of the ordinary series spectra. There is also, as we shall see in section 4, some indication that the principle holds for the high frequency spectra revealed by interference in crystals.

In this connexion it may also be remarked that the assumption A recently has obtained direct support by experiments of A. Einstein and J. W. de Haas †, who have succeeded in detecting and measuring a rotational mechanical effect produced when an iron bar is magnetized. Their results agree very closely with those to be expected on the assumption that the magnetism of iron is due to rotating electrons, and as pointed out by Einstein and Haas, these experiments therefore indicate very strongly that electrons can rotate in atoms without emission of energy radiation.

When we try to apply assumptions, analogous with C and D, to systems containing more than one electron, we meet with difficulties, since in this case the application of ordinary

\* Nicholson, Month. Not. Roy. Astr. Soc. lxxii. p. 679 (1912).

† Einstein and Haas, *Verh. d. D. Phys. Ges.* xvii. p. 152 (1915). That such a mechanical rotational effect was to be expected on the electron theory of magnetism was pointed out several years ago by O. W. Richardson, *Phys. Review*, xxvi. p. 248 (1908). Richardson tried to detect this effect but without decisive results.

mechanics in general does not lead to periodic orbits. An exception to this, however, occurs if the electrons are arranged in rings and rotate in circular orbits, and from simple considerations of analogy the following assumption was proposed (see I. p. 24).

E. In any atomic or 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 each electron round the centre of its orbit will be equal to  $h/2\pi$  in the "normal" state of the system, *i. e.* the state in which the total energy is a minimum.

It was shown that in a number of different cases this assumption led to results in approximate agreement with experimental facts. In general, no stable configuration in which the electrons rotate in circular orbits can exist if the problem of stability is discussed on ordinary mechanics. This is no objection, however, since it is assumed already that the mechanics do not hold for the transition between two stationary states. Simple considerations led to the following condition of stability.

F. A configuration satisfying the condition E is stable if the total energy of the system is less than in any neighbouring configuration satisfying the same condition of angular momentum of the electrons.

As already mentioned, the foundation for the hypothesis E was sought in analogy with the simple system consisting of one electron and one nucleus. Additional support, however, was obtained from a closer consideration of the formation of the systems. It was shown how simple processes could be imagined by which the confluence of different rings of electrons could be effected without any change in the angular momentum of the electrons, if the angular momentum of each electron before the process was the same. Such considerations led to a theory of formation of molecules.

It must be emphasized that only in the case of circular orbits has the angular momentum any connexion with the principles of the Quantum theory. If, therefore, the application of ordinary mechanics to the stationary states of the system does not lead to strictly circular orbits, the assumption E cannot be applied. This case occurs if we consider configurations in which the electrons are arranged in different rings which do not rotate with the same frequency. Such configurations, however, are apparently necessary in order

to explain many characteristic properties of the atoms. In my previous papers an attempt was made in certain cases to overcome this difficulty by assuming, that if a very small alteration of the forces would make circular orbits possible on ordinary mechanics, the configuration and energy of the actual system would only differ very little from that calculated for the altered system. It will be seen that this assumption is most intimately connected with the hypothesis F on the stability of the configurations. Such considerations were used to explain the general appearance of the Rydberg constant in the spectra of the elements, and were also applied in discussing possible configurations of the electrons in the atoms suggested by the observed chemical properties. These calculations have been criticised by Nicholson \*, who has attempted to show that the configurations chosen for the electrons in the atoms are inconsistent with the main principles of the theory, and has also attempted to prove the impossibility of accounting for other spectra by help of assumptions similar to those used in the interpretation of the hydrogen spectrum.

Although I am quite ready to admit that these points involve great and unsolved difficulties, I am unable to agree with Nicholson's conclusions. In the first place, his calculations rest upon a particular application to non-circular orbits of the principle of constancy of angular momentum for each electron, which it does not seem possible to justify either on the Quantum theory or on the ordinary mechanics, and which has no direct connexion with the assumptions used in my papers. It has not been proved that the configurations proposed are inconsistent with the assumption C. But even if it were possible to prove that the unrestricted use of ordinary mechanics to the stationary states is inconsistent with the configurations of the electrons, apparently necessary to explain the observed properties of the elements, this would not constitute a serious objection to the deductions in my papers. It must be remarked that all the applications of ordinary mechanics are essentially connected with the assumption of periodic orbits. As far as the applications are concerned, the first part of the assumption C might just as well have been given the following more cautious form :—

“The relation between the frequency and energy of the particles in the stationary states can be determined by means of the ordinary laws of mechanics if these laws lead to periodic orbits.”

\* Nicholson, *Phil. Mag.* xxvii. p. 541 and xxviii. p. 90 (1914).



The possible necessity for an alteration of this kind in assumption C may perhaps not seem unlikely when it is remembered that the laws of mechanics are only known to hold for certain mean values of the motion of the electrons. In this connexion it should also be remarked that when considering periodic orbits only mean values are essential (comp. I. p. 7). The preliminary and tentative character of the formulation of the general assumptions cannot be too strongly emphasized, and admittedly they are made to suit certain simple applications. For example, it has been already shown in paper IV. that the assumption B needs modification in order to account for the effect of a magnetic field on spectral lines. In the following sections some of the recent experimental evidence on line spectra and characteristic Röntgen rays will be considered, and I shall endeavour to show that it seems to give strong support to the main principles of the theory.

2. *Spectra emitted from systems containing only one electron.*

In the former papers it was shown that the general assumptions led to the following formula for the spectrum emitted by an electron rotating round a positive nucleus

$$\nu = N^2 \frac{2\pi^2 e^4 M m}{h^3 (M+m)} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \dots \dots \dots (3)$$

$Ne$ ,  $-e$ ,  $M$ ,  $m$  are the electric charges and the masses of the nucleus and the electron respectively. The frequency of rotation and the major axis of the relative orbit of the particles in the stationary states are given by

$$\omega_n = N^2 \frac{4\pi^2 e^4 M m}{h^3 (M+m)} \frac{1}{n^3}, \quad 2a_n = \frac{1}{N} \frac{h^2 (M+m)}{2\pi^2 e^2 M m} n^2 \dots \dots (4)$$

The energy necessary to remove the electron to infinite distance from the nucleus is

$$W_n = N^2 \frac{2\pi^2 e^4 M m}{h^2 (M+m)} \frac{1}{n^2} \dots \dots \dots (5)$$

This expression is also equal to the mean value of the kinetic energy of the system. Since  $-W_n$  is equal to the total energy  $A_n$  of the system we get from (4) and (5)

$$\frac{dA_n}{dn} = h\omega_n \dots \dots \dots (6)$$

If we compare (6) with the relation (1), we see that the

connexion with ordinary mechanics in the region of slow vibration, mentioned in the former section, is satisfied.

Putting  $N=1$  in (3) we get the ordinary series spectrum of hydrogen. Putting  $N=2$  we get a spectrum which, on the theory, should be expected to be emitted by an electron rotating round a helium nucleus. The formula is found very closely to represent some series of lines observed by Fowler\* and Evans†. These series correspond to  $n_1=3$  and  $n_1=4$  ‡. The theoretical value for the ratio between the second factor in (3) for this spectrum and for the hydrogen spectrum is 1.000409; the value calculated from Fowler's measurements is 1.000408 §. Some of the lines under consideration have been observed earlier in star spectra, and have been ascribed to hydrogen not only on account of the close numerical relation with the lines of the Balmer series, but also on account of the fact that the lines observed, together with the lines of the Balmer series, constitutes a spectrum which shows a marked analogy with the spectra of the alkali metals. This analogy, however, has been completely disturbed by Fowler's and Evans' observations, that the two new series contain twice as many lines as is to be expected on this analogy. In addition, Evans has succeeded in obtaining the lines in such pure helium that no trace of the ordinary hydrogen lines could be observed ||. The great difference between the conditions for the production of the Balmer series and the series under consideration is also brought out very strikingly by some recent experiments of Rau¶ on the minimum voltage necessary for the production of spectral lines. While about 13 volts was sufficient to excite the lines of the Balmer series, about 80 volts was found necessary to excite the other series. These values agree closely with the values calculated from the assumption E for the energies necessary to remove the electron from the hydrogen atom and to remove both electrons from the helium atom, viz. 13.6 and 81.3 volts respectively. It has recently been argued\*\* that the lines are not so sharp as should be expected from the atomic weight of helium on Lord Rayleigh's theory of the width of spectral lines. This might, however, be explained by the fact that the systems

\* Fowler, Month. Not. Roy. Astr. Soc. lxxiii. Dec. 1912.

† Evans, Nature, xcii. p. 5 (1913); Phil. Mag. xxix. p. 284 (1915).

‡ For  $n_1=2$  we get a series in the extreme ultraviolet of which some lines have recently been observed by Lyman (Nature, xcv. p. 343, 1915).

§ See Nature, xcii. p. 231 (1913).

|| See also Stark, *Verh. d. D. Phys. Ges.* xvi. p. 468 (1914).

¶ Rau, *Sitz. Ber. d. Phys. Med. Ges. Würzburg* (1914).

\*\* Merton, Nature, xcv. p. 65 (1915); Proc. Roy. Soc. A. xci. p. 389 (1915).

emitting the spectrum, in contrast to those emitting the hydrogen spectrum, are supposed to carry an excess positive charge, and therefore must be expected to acquire great velocities in the electric field in the discharge-tube.

In paper IV. an attempt was made on the basis of the present theory to explain the characteristic effect of an electric field on the hydrogen spectrum recently discovered by Stark. This author observed that if luminous hydrogen is placed in an intense electric field, each of the lines of the Balmer series is split up into a number of homogeneous components. These components are situated symmetrically with regard to the original lines, and their distance apart is proportional to the intensity of the external electric field. By spectroscopic observation in a direction perpendicular to the field, the components are linearly polarized, some parallel and some perpendicular to the field. Further experiments have shown that the phenomenon is even more complex than was at first expected. By applying greater dispersion, the number of components observed has been greatly increased, and the numbers as well as the intensities of the components are found to vary in a complex manner from line to line\*. Although the present development of the theory does not allow us to account in detail for the observations, it seems that the considerations in paper IV. offer a simple interpretation of several characteristic features of the phenomenon.

The calculation can be made considerably simpler than in the former paper by an application of Hamilton's principle. Consider a particle moving in a closed orbit in a stationary field. Let  $\omega$  be the frequency of revolution,  $T$  the mean value of the kinetic energy during the revolution, and  $W$  the mean value of the sum of the kinetic energy and the potential energy of the particle relative to the stationary field. We have then for a small arbitrary variation of the orbit

$$\delta W = -2\omega\delta\left(\frac{T}{\omega}\right). \quad \dots \quad (7)$$

This equation was used in paper IV. to prove the equivalence of the formulæ (2) and (6) for any system governed by ordinary mechanics. The equation (7) further shows that if the relations (2) and (6) hold for a system of orbits, they will hold also for any small variation of these orbits for which the value of  $W$  is unaltered. If a hydrogen atom in one of its stationary states is placed in an external electric field and the electron rotates in a closed orbit, we shall therefore expect that  $W$  is not altered by the introduction of the atom in

\* Stark, *Elektrische Spektralanalyse chemischer Atome*, Leipzig, 1914.

the field, and that the only variation of the total energy of the system will be due to the variation of the mean value of the potential energy relative to the external field.

In the former paper it was pointed out that the orbit of the electron will be deformed by the external field. This deformation will in course of time be considerable even if the external electric force is very small compared with the force of attraction between the particles. The orbit of the electron may at any moment be considered as an ellipse with the nucleus in the focus, and the length of the major axis will approximately remain constant, but the effect of the field will consist in a gradual variation of the direction of the major axis as well as the excentricity of the orbit. A detailed investigation of the very complicated motion of the electron was not attempted, but it was simply pointed out that the problem allows of two stationary orbits of the electron, and that these may be taken as representing two possible stationary states. In these orbits the excentricity is equal to 1, and the major axis parallel to the external force; the orbits simply consisting of a straight line through the nucleus parallel to the axis of the field, one on each side of it. It can very simply be shown that the mean value of the potential energy relative to the field for these rectilinear orbits is equal to  $\mp 3/2 aeE$ , where  $E$  is the external electric force and  $2a$  the major axis of the orbit, and the two signs correspond to orbits in which the direction of the major axis from the nucleus is the same or opposite to that of the electric force respectively. Using the formulæ (4) and (5) and neglecting the mass of the electron compared with that of the nucleus, we get, therefore, for the energy of the system in the two states

$$A_n = -N^2 \frac{2\pi^2 e^4 m}{h^2} \frac{1}{n^2} \mp E \frac{3h^2}{8\pi^2 N e m} n^2 \dots \quad (8)$$

respectively. This expression is the same as that deduced in paper IV. by an application of (6) to the expressions for the energy and frequency of the system. Applying the relation (1) and using the same arguments as in paper IV. p. 515, we are therefore led to expect that the hydrogen spectrum in an electric field will contain two components polarized parallel to the field and of a frequency given by

$$\nu = \frac{1}{h} (A_{n_2} - A_{n_1}) = N^2 \frac{2\pi^2 e^4 m}{h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \mp E \frac{3h}{8\pi^2 N e m} (n_2^2 - n_1^2). \quad (9)$$

The table below contains Stark's recent measurements of the frequency difference between the two strong outer components polarized parallel to the field for the five first lines

in the Balmer series\*. The first column gives the values for the numbers  $n_1$  and  $n_2$ . The second and fourth columns give the frequency difference  $\Delta\nu$  corresponding to a field of 28500 and 74000 volts per cm. respectively. The third and fifth columns give the values of

$$\alpha = \Delta\nu \frac{4\pi^2 em}{3Eh(n_2^2 - n_1^2)},$$

where  $\alpha$  should be a constant for all the lines and equal to unity.

$n_1 \quad n_2$		28500 volts. per cm.		74000 volts. per cm.	
		$\Delta\nu \cdot 10^{-12}$	$\alpha$	$\Delta\nu \cdot 10^{-12}$	$\alpha$
2	3	0.46	0.83	...	...
2	4	1.04	0.79	2.86	0.83
2	5	2.06	0.89	5.41	0.90
2	6	3.16	0.90	7.81	0.85
2	7	4.47	0.90	...	...

Considering the difficulties of accurate measurement of the quantities involved, it will be seen that the agreement with regard to the variation of the frequency differences from line to line is very good. The fact that all the observed values are a little smaller than the calculated may be due to a slight over-estimate of the intensity of the fields used in the experiments (see Stark, *loc. cit.* pp. 38 and 118). Besides the two strong outer components polarized parallel to the field, Stark's experiments have revealed a large number of inner weaker components polarized in the same way, and also a number of components polarized perpendicular to the field. This complexity of the phenomenon, however, cannot be considered as inconsistent with the theory. The above simple calculations deal only with the two extreme cases, and we may expect to find a number of stationary states corresponding to orbits of smaller excentricity. In a discussion of such non-periodic orbits, however, the general principles applied are no longer sufficient guidance.

Apart from the agreement with the calculations, Stark's experiments seem to give strong support to the interpretation of the origin of the two outer components. It was found that the two outer components have not always equal intensities; when the spectrum is produced by positive rays, it

\* Stark, *loc. cit.* pp. 51, 54, 55, & 56.

was found that the component of highest frequency is the stronger if the rays travel against the electric field, while if it travels in the direction of the field the component of smallest frequency is the stronger (*loc. cit.* p. 40). This indicates that the components are produced independently of each other—a result to be expected if they correspond to quite different orbits of the electron. That the orbit of the electron in general need not be circular is also very strongly indicated by the observation that the hydrogen lines emitted from positive rays under certain conditions are partly polarized without the presence of a strong external field (*loc. cit.* p. 12). This polarization, as well as the observed intensity differences of the two components, would be explained if we can assume that for some reason, when the atom is in rapid motion, there is a greater probability for the orbit of the electron to lie behind the nucleus rather than in front of it.

§ 3. *Spectra emitted from systems containing more than one electron.*

According to Rydberg and Ritz, the frequency of the lines in the ordinary spectrum of an element is given by

$$\nu = f_r(n_1) - f_s(n_2), \quad . . . . . (11)$$

where  $n_1$  and  $n_2$  are whole numbers and  $f_1, f_2, \dots$  are a series of functions of  $n$  which can be expressed by

$$f_r(n) = \frac{K}{n^2} \phi_r(n), \quad . . . . . (12)$$

where  $K$  is a universal constant and  $\phi$  a function which for large values of  $n$  approaches unity. The complete spectrum is obtained by combining the numbers  $n_1$  and  $n_2$  as well as the functions  $f_1, f_2, \dots$  in every possible way.

On the present theory, this indicates that the system which emits the spectrum possesses a number of series of stationary states for which the energy in the  $n$ th state in the  $r$ th series is given by (see IV. p. 511)

$$A_{n,r} = C - \frac{hK}{n^2} \phi_r(n), \quad . . . . . (13)$$

where  $C$  is an arbitrary constant, the same for the whole system of stationary states. The first factor in the second term is equal to the expression (5) if  $N=1$ .

In the present state of the theory it is not possible to account in detail for the formula (13), but it was pointed

out in my previous papers that a simple interpretation can be given of the fact that in every series  $\phi(n)$  approaches unity for large values of  $n$ . It was assumed that in the stationary states corresponding to such values of  $n$ , one of the electrons in the atom moves at a distance from the nucleus large compared with the distance of the other electrons. If the atom is neutral, the outer electron will be subject to very nearly the same forces as the electron in the hydrogen atom, and the formula (13) indicates the presence of a number of series of stationary states of the atom in which the configuration of the inner electrons is very nearly the same for all states in one series, while the configuration of the outer electron changes from state to state in the series approximately in the same way as the electron in the hydrogen atom. From the considerations in the former sections it will therefore appear that the frequency calculated from the relations (1) and (13) for the radiation emitted during the transition between successive stationary states within each series will approach that to be expected on ordinary electrodynamics in the region of slow vibrations\*.

From (13) it follows that for high values of  $n$  the configuration of the inner electrons possesses the same energy in all the series of stationary states corresponding to the same spectrum (11). The different series of stationary states must therefore correspond to different types of orbits of the outer electron, involving different relations between energy and frequency. In order to fix our ideas, let us for a moment consider the helium atom. This atom contains only two electrons, and in the previous papers it was assumed that in the normal state of the atom the electrons rotate in a circular ring round a nucleus. Now the helium spectrum contains two complete systems of series given by formulæ of

\* On this view we should expect the Rydberg constant in (13) to be not exactly the same for all elements, since the expression (5) depends to a certain extent on the mass of the nucleus. The correction is very small; the difference in passing from hydrogen to an element of high atomic weight being only 0.05 per cent. (see IV. p. 512). In a recent paper (Proc. Roy. Soc. A. xci. p. 255, 1915), Nicholson has concluded that this consequence of the theory is inconsistent with the measurements of the ordinary helium spectrum. It seems doubtful, however, if the measurements are accurate enough for such a conclusion. It must be remembered that it is only for high values of  $n$  that the theory indicates values of  $\phi$  very nearly unity; but for such values of  $n$ , the terms in question are very small, and the relative accuracy in the experimental determination not very high. The only spectra for which a sufficiently accurate determination of  $K$  seems possible at present are the ordinary hydrogen spectrum and the helium spectrum considered in the former section, and in these cases the measurements agree very closely with calculation.

the type (11) and the measurements of Rau mentioned below indicate that the configuration of the inner electron in the two corresponding systems of stationary states possesses the same energy. A simple assumption is therefore that in one of the two systems the orbit of the electron is circular and in the other very flat. For high values of  $n$  the inner electron in the two configurations will act on the outer electron very nearly as a ring of uniformly distributed charge with the nucleus in the centre or as a line charge extending from the nucleus, respectively. In both cases several different types of orbit for the outer electron present themselves, for instance, circular orbits perpendicular to the axis of the system or very flat orbits parallel to this axis. The different configurations of the inner electrons might be due to different ways of removing the electron from the neutral atom: thus, if it is removed by impact perpendicular to the plane of the ring, we might expect the orbit of the remaining electron to be circular, if it is removed by an impact in the plane of the ring we might expect the orbit to be flat. Such considerations may offer a simple explanation of the fact that in contrast with the helium spectrum the lithium spectrum contains only one system of series of the type (11). The neutral lithium atom contains three electrons, and according to the configuration proposed in paper II. the two electrons move in an inner ring and the other electron in an outer orbit; for such a configuration we should expect that the mode of removal of the outer electron would be of no influence on the configuration of the inner electrons. It is unnecessary to point out the hypothetical nature of these considerations, but the intention is only to show that it does not seem impossible to obtain simple interpretations of the spectra observed on the general principles of the theory. However, in a quantitative comparison with the measurements we meet with the difficulties mentioned in the first section of applying assumptions analogous with C and D to systems for which ordinary mechanics do not lead to periodic orbits.

The above interpretation of the formulæ (11) and (12) has recently obtained very strong support by Fowler's work on series of enhanced lines on spark spectra\*. Fowler showed that the frequency of the lines in these spectra, as of the lines in the ordinary spectra, can be represented by the formula (11). The only difference is that the Rydberg constant  $K$  in (12) is replaced by a constant  $4K$ . It will be seen that this is just what we should expect on the present

\* Fowler, *Phil. Trans. Roy. Soc. A.* 214. p. 225 (1914).



theory if the spectra are emitted by atoms which have lost two electrons and are regaining one of them. In this case, the outer electron will rotate round a system of double charge, and we must assume that in the stationary states it will have configurations approximately the same as an electron rotating round a helium nucleus. This view seems in conformity with the general evidence as to the conditions of the excitation of the ordinary spectra and the spectra of enhanced lines. From Fowler's results, it will appear that the helium spectrum given by (3) for  $N=2$  has exactly the same relation to the spectra of enhanced lines of other elements as the hydrogen spectrum has to the ordinary spectra. It may be expected that it will be possible to observe spectra of a new class corresponding to a loss of 3 electrons from the atom, and in which the Rydberg constant  $K$  is replaced by  $9K$ . No definite evidence, however, has so far been obtained of the existence of such spectra\*.

Additional evidence of the essential validity of the interpretation of formula (13) seems also to be derived from the result of Stark's experiments on the effect of electric fields on spectral lines. For other spectra, this effect is even more complex than for the hydrogen spectrum, in some cases not only are a great number of components observed, but the components are generally not symmetrical with regard to the original line, and their distance apart varies from line to line in the same series in a far more irregular way than for the hydrogen lines †. Without attempting to account in detail for any of the electrical effects observed, we shall see that a simple interpretation can be given of the general way in which the magnitude of the effect varies from series to series.

In the theory of the electrical effect on the hydrogen spectrum given in the former section, it was supposed that this effect was due to an alteration of the energy of the systems in the external field, and that this alteration was intimately connected with a considerable deformation of the orbit of the electron. The possibility of this deformation is due to the fact that without the external field every elliptical orbit of the electron in the hydrogen atom is stationary. This condition will only be strictly satisfied if the forces which act upon the electron vary exactly as the inverse square of the distance from the nucleus, but this will not be the case for the outer electron in an atom containing more than one electron. It was pointed

\* Fowler, *loc. cit.* p. 262, see also II. p. 490.

† Stark, *loc. cit.* pp. 67-75.

out in paper IV. that the deviation of the function  $\phi(n)$  from unity gives us an estimate for the deviation of the forces from the inverse square, and that on the theory we can only expect a Stark effect of the same order of magnitude as for the hydrogen lines for those series in which  $\phi$  differs very little from unity.

This conclusion was consistent with Stark's original measurements of the electric effect on the different series in the helium spectrum, and it has since been found to be in complete agreement with the later measurements for a great number of other spectral series. An electric effect of the same order of magnitude as that for hydrogen lines has been observed only for the lines in the two diffuse series of the helium spectrum and the diffuse series of lithium. This corresponds to the observation that for these three series  $\phi$  is very much nearer to unity than for any other series; even for  $n=5$  the deviation of  $\phi$  from 1 is less than one part in a thousand. The distance between the outer components for all three series is smaller than that observed for the hydrogen line corresponding to the same value of  $n$ , but the ratio between this distance and that of the hydrogen lines approaches rapidly to unity as  $n$  increases. This is just what would be expected on the above considerations. The series for which the effect, although much smaller, comes next in magnitude to the three series mentioned, is the principal single line series in the helium spectrum. This corresponds to the fact that the deviation of  $\phi$  from unity, although several times greater than for the three first series, is much smaller for this series than for any other of the series examined by Stark. For all the other series the effect was very small, and in most cases even difficult of detection.

Quite apart from the question of the detailed theoretical interpretation of the formula (13), it seems that it may be possible to test the validity of this formula by direct measurements of the minimum voltages necessary to produce spectral lines. Such measurements have recently been made by Rau\* for the lines in the ordinary helium spectrum. This author found that the different lines within each series appeared for slightly different voltages, higher voltages being necessary to produce the lines corresponding to higher values of  $n$ , and he pointed out that the differences between the voltages observed were of the magnitude to be expected from the differences in the energies of the different stationary states calculated by (13). In addition Rau found that the lines corresponding to high values of  $n$  appeared for

\* Rau, *loc. cit.*

very nearly the same voltages for all the different series in both helium spectra. The absolute values for the voltages could not be determined very accurately with the experimental arrangement, but apparently nearly 30 volts was necessary to produce the lines corresponding to high values of  $n$ . This agrees very closely with the value calculated on the present theory for the energy necessary to remove one electron from the helium atom, viz., 29.3 volts. On the other hand, the later value is considerably larger than the ionization potential in helium (20.5 volts) measured directly by Franck and Hertz\*. This apparent disagreement, however, may possibly be explained by the assumption, that the ionization potential measured does not correspond to the removal of the electron from the atom but only to a transition from the normal state of the atom to some other stationary state where the one electron rotates outside the other, and that the ionization observed is produced by the radiation emitted when the electron falls back to its original position. This radiation would be of a sufficiently high frequency to ionize any impurity which may be present in the helium gas, and also to liberate electrons from the metal part of the apparatus. The frequency of the radiation would be

$$20.5/300 \frac{e}{h} = 5.0 \cdot 10^{15},$$

which is of the same order of magnitude

as the characteristic frequency calculated from experiments on dispersion in helium, viz.,  $5.9 \cdot 10^{15}$  †.

Similar considerations may possibly apply also to the recent remarkable experiments of Franck and Hertz on ionization in mercury vapour ‡. These experiments show strikingly that an electron does not lose energy by collision with a mercury atom if its energy is smaller than a certain value corresponding to 4.9 volts, but as soon as the energy is equal to this value the electron has a great probability of losing all its energy by impact with the atom. It was further shown that the atom, as the result of such an impact, emits a radiation consisting only of the ultraviolet mercury line of wave-length 2536, and it was pointed out that if the frequency of this line is multiplied by Planck's constant, we obtain a value which, within the limit of experimental error, is equal to the energy acquired by an electron by a fall through a potential difference of 4.9 volts. Franck and Hertz assume that 4.9 volts corresponds to the energy necessary to remove an electron from the mercury atom, but it seems that their experiments may possibly be consistent

\* Franck & Hertz, *Verh. d. D. Phys. Ges.* xv. p. 34 (1913).

† Cuthbertson, *Proc. Roy. Soc. A.* lxxxiv. p. 13 (1910).

‡ Franck and Hertz, *Verh. d. D. Phys. Ges.* xvi. pp. 457, 512 (1914).

with the assumption that this voltage corresponds only to the transition from the normal state to some other stationary state of the neutral atom. On the present theory we should expect that the value for the energy necessary to remove an electron from the mercury atom could be calculated from the limit of the single line series of Paschen, 1850, 1403, 1269\*. For since mercury vapour absorbs light of wavelength 1850†, the lines of this series as well as the line 2536 must correspond to a transition from the normal state of the atom to other stationary states of the neutral atom (see I. p. 16). Such a calculation gives 10·5 volts for the ionization potential instead of 4·9 volts‡. If the above considerations are correct it will be seen that Franck and Hertz's measurements give very strong support to the theory considered in this paper. If, on the other hand, the ionization potential of mercury should prove to be as low as assumed by Franck and Hertz, it would constitute a serious difficulty for the above interpretation of the Rydberg constant, at any rate for the mercury spectrum, since this spectrum contains lines of greater frequency than the line 2536.

It will be remarked that it is assumed that all the spectra considered in this section are essentially connected with the displacement of a single electron. This assumption—which is in contrast to the assumptions used by Nicholson in his criticism of the present theory—does not only seem supported by the measurements of the energy necessary to produce the spectra, but it is also strongly advocated by general reasons if we base our considerations on the assumption of stationary states. Thus it may happen that the atom loses several electrons by a violent impact, but the probability that the electrons will be removed to exactly the same distance from the nucleus or will fall back into the atom again at exactly the same time would appear to be very small. For molecules, *i. e.* systems containing more than one nucleus, we have further to take into consideration that if the greater part of the electrons are removed there is nothing to keep the nuclei together, and that we must assume that the molecules in such cases will split up into single atoms (comp. III. p. 858).

\* Paschen, *Ann. d. Phys.* xxxv. p. 860 (1911).

† Stark, *Ann. d. Phys.* xlii. p. 239 (1913).

‡ This value is of the same order of magnitude as the value 12·5 volts recently found by McLennan and Henderson (Proc. Roy. Soc. A. xci. p. 485, 1915) to be the minimum voltage necessary to produce the usual mercury spectrum. The interesting observations of single-lined spectra of zinc and cadmium given in their paper are analogous to Franck and Hertz's results for mercury, and similar considerations may therefore possibly also hold for them.

§ 4. *The high frequency spectra of the elements.*

In paper II. it was shown that the assumption E led to an estimate of the energy necessary to remove an electron from the innermost ring of an atom which was in approximate agreement with Whiddington's measurements of the minimum kinetic energy of cathode rays required to produce the characteristic Röntgen radiation of the K type. The value calculated for this energy was equal to the expression (5) if  $n=1$ . In the calculation the repulsion from the other electrons in the ring was neglected. This must result in making the value a little too large, but on account of the complexity of the problem no attempt at that time was made to obtain a more exact determination of the energy.

These considerations have obtained strong support through Moseley's important researches on the high frequency spectra of the elements\*. Moseley found that the frequency of the strongest lines in these spectra varied in a remarkably simple way with the atomic number of the corresponding element. For the strongest line in the K radiation he found that the frequency for a great number of elements was represented with considerable accuracy by the empirical formula

$$\nu = \frac{3}{4}(N-1)^2K, \dots \dots \dots (14)$$

where K is the Rydberg constant in the hydrogen spectrum. It will be seen that this result is in approximate agreement with the calculation mentioned above if we assume that the radiation is emitted as a quantum  $h\nu$ .

Moseley pointed out the analogy between the formula (14) and the formula (3) in section 2, and remarked that the constant  $3/4$  was equal to the last factor in this formula, if we put  $n_1=1$  and  $n_2=2$ . He therefore proposed the explanation of the formula (14), that the line was emitted during a transition of the innermost ring between two states in which the angular momentum of each electron was equal to  $2 \frac{h}{2\pi}$  and  $\frac{h}{2\pi}$  respectively. From the replacement of  $N^2$  by  $(N-1)^2$  he deduced that the number of electrons in the ring was equal to 4. This view, however, can hardly be maintained. The approximate agreement mentioned above with Whiddington's measurements for the energy necessary to produce the characteristic radiation indicates very strongly that the spectrum is due to a displacement of a single electron, and not to a whole ring. In the latter case the energy

\* Moseley, Phil. Mag. xxvi. p. 1024 (1913); and xxvii. p. 703 (1914).

should be several times larger. It is also pointed out by Nicholson \* that Moseley's explanation would imply the emission of several quanta at the same time; but this assumption is apparently not necessitated for the explanation of other phenomena. At present it seems impossible to obtain a detailed interpretation of Moseley's results, but much light seems to be thrown on the whole problem by some recent interesting considerations by W. Kossel †.

Kossel takes the view of the nucleus atom and assumes that the electrons are arranged in rings, the one outside the other. As in the present theory, it is assumed that any radiation emitted from the atom is due to a transition of the system between two steady states, and that the frequency of the radiation is determined by the relation (1). He considers now the radiation which results from the removal of an electron from one of the rings, assuming that the radiation is emitted when the atom settles down in its original state. The latter process may take place in different ways. The vacant place in the ring may be taken by an electron coming directly from outside the whole system, but it may also be taken by an electron jumping from one of the outer rings. In the latter case a vacant place will be left in that ring to be replaced in turn by another electron, etc. For the sake of brevity, we shall refer to the innermost ring as ring 1, the next one as ring 2, and so on. Kossel now assumes that the K radiation results from the removal of an electron from ring 1, and makes the interesting suggestion that the line denoted by Moseley as  $K_\alpha$  corresponds to the radiation emitted when an electron jumps from ring 2 to ring 1, and that the line  $K_\beta$  corresponds to a jump from ring 3 to ring 1. On this view, we should expect that the K radiation consists of as many lines as there are rings in the atom, the lines forming a series of rapidly increasing intensities. For the L radiation, Kossel makes assumptions analogous to those for the K radiation, with the distinction that the radiation is ascribed to the removal of an electron from ring 2 instead of ring 1. A possible M radiation is ascribed to ring 3, and so on. The interest of these considerations is that they lead to the prediction of some simple relations between the frequencies  $\nu$  of the different lines. Thus it follows as an immediate consequence of the assumption used that we must have

$$\begin{aligned} \nu_{K_\beta} - \nu_{K_\alpha} &= \nu_{L_\alpha} \\ \nu_{K_\gamma} - \nu_{K_\beta} &= \nu_{L_\beta} - \nu_{L_\alpha} = \nu_{M_\alpha} \end{aligned}$$

\* Nicholson, *Phil. Mag.* xxvii. p. 562 (1914).

† Kossel, *Verh. d. Deutsch. Phys. Ges.* xvi. p. 953 (1914).

It will be seen that these relations correspond exactly to the ordinary principle of combination of spectral lines. By using Moseley's measurements for  $K_\alpha$  and  $K_\beta$  and extrapolating for the values of  $L_\alpha$  by the help of Moseley's empirical formula, Kossel showed that the first relation was closely satisfied for the elements from calcium to zinc. Recently T. Malmer \* has measured the wave-length of  $K_\alpha$  and  $K_\beta$  for a number of elements of higher atomic weight, and it is therefore possible to test the relation over a wider range and without extrapolation. The table gives Malmer's values for  $\nu_{K_\beta} - \nu_{K_\alpha}$  and Moseley's values for  $\nu_{L_\alpha}$ , all values being multiplied by  $10^{17}$ .

N.....	40	42	44	46	47	50	51	57
$\nu_{K_\beta} - \nu_{K_\alpha}$ ..	4.6	5.5	6.1	6.6	6.9	8.4	9.0	11.6
$\nu_{L_\alpha}$ .....	4.93	5.53	6.17	6.84	7.19	8.29	8.67	11.21

It is seen that the agreement is close, and probably within the limits of experimental error. A comparison with the second relation is not possible at present, and we meet also here with a difficulty arising from the fact that Moseley observed a greater number of lines in the L radiation than should be expected on Kossel's simple scheme †.

There is another point in connexion with the above considerations which appears to be of interest. In a recent paper W. H. Bragg ‡ has shown that, in order to excite any line of the K radiation of an element, the frequency of the exciting radiation must be greater than the frequency of all the lines in the K radiation. This result, which is in striking contrast to the ordinary phenomena of selective absorption, can be simply explained on Kossel's view. The simple reverse of the process corresponding to the emission of, for instance,  $K_\alpha$  would necessitate the direct transfer of an electron from ring 1 to ring 2, but this will obviously not be possible unless at the beginning of the process there was a vacant place in the latter ring. For the excitation of any line in the K radiation, it is therefore necessary that the electron should be completely removed from the atom. Another consequence of Kossel's view is that it should be impossible to obtain the K series of an element without the simultaneous emission of the L series. This seems to be in

\* Malmer, *Phil. Mag.* xxviii. p. 787 (1914).

† See Kossel, *loc. cit.* p. 960.

‡ Bragg, *Phil. Mag.* xxix. p. 407 (1915).

agreement with some recent experiments of C. G. Barkla \* on the energy involved in the production of characteristic Röntgen radiation. From these examples it will be seen that even if Kossel's considerations will need modification in order to account in detail for the high frequency spectra, they seem to offer a basis for a further development.

As in the former section, it is assumed that the spectra considered above are due to the displacement of a single electron. If, however, several electrons should happen to be removed from one of the rings by a violent impact, the considerations at the end of the former section would not apply, since the electrons removed in this case can be replaced by electrons in the other rings. We might therefore possibly expect that the rearrangement of the electrons, consequent to the removal of more than one electron from a ring, would give rise to spectra of still higher frequency than those considered in this section.

University of Manchester,  
August 1915.

XLIII. *Residual Ionization in Gases.* By Professor J. C. McLENNAN, F.R.S., and C. L. TRELEAVEN, M.A., University of Toronto †.

### I. Introduction.

FROM observations made by Simpson & Wright ‡, McLennan & McLeod §, and others, it is now known that the ionization in air confined in air-tight clean zinc vessels is about 8 or 9 ions per c.c. per second when the observations are made on land where the soil contains only such minute traces of radioactive substances as are found in ordinary clays or loams. It is also known that when the observations are made on the Atlantic, the Indian, or the Antarctic Ocean, or on the surface of large bodies of water such as Lake Ontario, the ionization in air confined in the manner indicated above drops to approximately 4 ions per c.c. per second. Moreover, this reduction in the

\* Barkla, *Nature*, xcv. p. 7 (1915). In this note Barkla proposes an explanation of his experimental results which in some points has great similarity to Kossel's theory.

† Communicated by the Authors; read before the Royal Society of Canada, May 26th, 1915.

‡ Simpson & Wright, *Proc. Roy. Soc., Ser. A*, vol. lxxxv. p. 175 (1911).

§ McLennan & McLeod, *Phil. Mag.*, Oct. 1913, p. 740.