

For gold the number of deflexions was observed up to  $\phi = 150^\circ$  and found to be correct. Taking  $e$  as 100 times the electronic charge and  $V = 2 \times 10^9$  cm. per sec., this gives as the closest approach of nucleus and  $\alpha$  particle  $3.5 \times 10^{-12}$  cm.

The closest possible approach of all is between an  $\alpha$  particle and a hydrogen nucleus in a straight-on collision. With  $V = 2 \times 10^9$  this gives a distance  $1.7 \times 10^{-13}$  cm. If it can be verified that the distribution of H particles is as predicted in this paper, then we may conclude that the radii of the nuclei of hydrogen and helium are certainly less than  $10^{-13}$  cm.

LIX. *On the Effect of Electric and Magnetic Fields on Spectral Lines.* By N. BOHR, *Dr. phil. Copenhagen* \*.

IN a previous paper † the writer has shown that an explanation of some of the laws of line spectra may be obtained by applying Planck's theory of black radiation to Rutherford's theory of the structure of atoms. In the present paper these considerations will be further developed, and it will be shown that it seems possible on the theory to account for some of the characteristic features of the recent discovery by Stark ‡ of the effect of an electric field on spectral lines, as well as of the effect of a magnetic field first discovered by Zeeman. It will also be shown that the theory seems to offer an explanation of the appearance of ordinary double spectral lines §.

§ 1. *The Emission of a Line Spectrum.*

The theory put forward by the writer to explain the emission of a line-spectrum may be summarized as follows:—

The principal assumption of Planck's theory is that the

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

† *Phil. Mag.* vol. xxvi. pp. 1, 476, 857 (1913).

‡ *Sitzungsb. d. Kgl. Akad. d. Wiss. Berlin*, 1913, p. 932.

§ While this paper was in course of preparation, a theoretical paper dealing with the same subject was published by E. Warburg (*Verh. d. deutsch. Phys. Ges.* xv. p. 1259 (1913)). The latter finds that the effect of electric and magnetic fields to be expected on my theory of the hydrogen spectrum is of the same order of magnitude as determined by experiment. However, contrary to the conclusions of the present paper, Warburg concludes that it does not seem possible on the theory to account in detail for the experimental results. In his opinion the theory leads to a broadening of the hydrogen lines in an electric field, instead of the appearance of the homogeneous components observed by Stark. He also calculates that the Zeeman effect should vary from line to line in a manner inconsistent with experiment.

energy of a system of vibrating electrified particles cannot be transferred into radiation, and *vice versa*, in the continuous way assumed in the ordinary electrodynamics, but only in finite quanta of the amount  $h\nu$ , where  $h$  is a universal constant and  $\nu$  the frequency of the radiation\*. Applying this assumption to the emission of a line-spectrum, and assuming that a certain spectral line of frequency  $\nu$  corresponds to a radiation emitted during the transition of an elementary system from a state in which its energy is  $A_1$  to one in which it is  $A_2$ , we have

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

According to Balmer, Rydberg, and Ritz the frequency of the lines in the line-spectrum of an element can be expressed by the formula

$$\nu = f_r(n_1) - f_s(n_2), \quad \dots \dots \dots (2)$$

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

$$f_r(n) = \frac{K}{n^2} \phi_r(n), \quad \dots \dots \dots (3)$$

where  $K$  is a universal constant and  $\phi$  a function which for large values of  $n$  approaches the value 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 above view this can be interpreted by assuming:

(1) That every line in the spectrum corresponds to a radiation emitted by a certain elementary system during its passage between two states in which the energy, omitting an arbitrary constant, is given by  $-hf_s(n_2)$  and  $-hf_r(n_1)$  respectively;

(2) That the system can pass between any two such states during emission of a homogeneous radiation.

The states in question will be denoted as "stationary states."

\* In Planck's original theory certain other assumptions about the properties of the vibrating systems were used. However, Debye (*Ann. d. Phys.* xxxiii. p. 1427 (1910)) has shown that it is possible to deduce Planck's formula of radiation without using any assumption about the vibrators, if it be supposed that energy can be transferred between them and the radiation, only in finite quanta  $h\nu$ . It may further be remarked that Poincaré (*Journ. d. Physique*, ii. p. 5 (1912)) has deduced the necessity of assuming that the transference of energy takes place in quanta  $h\nu$  in order to explain the experimental laws of black radiation.

The spectrum of hydrogen observed in ordinary vacuum-tubes\* is represented by (2) and (3) by putting

$$\phi_1(n) = \phi_2(n) = \dots = 1. \quad (4)$$

Accordingly we shall assume that this spectrum is emitted by a system possessing a series of stationary states in which, corresponding to the  $n$ th state, the energy, omitting the arbitrary constant, is given by

$$A_n = -h \frac{K}{n^2}. \quad (5)$$

According to Rutherford's theory, the atom of an element consists of a central positive nucleus surrounded by electrons rotating in closed orbits. Concordant evidence, obtained in very different ways, indicates that the number of electrons in the neutral atom is equal to the number of the corresponding element in the periodic table †.

On this theory the structure of the neutral hydrogen atom is of extreme simplicity; it consists of an electron rotating round a positive nucleus of opposite charge. In such a system we get on the ordinary mechanics the following equations for the frequency of revolution  $\omega$  and the major axis  $2a$  of the relative orbit of the particles

$$\omega^2 = \frac{2W^3(M+m)}{\pi^2 e^4 m M}, \quad 2a = \frac{e^2}{W}, \quad (6)$$

where  $e$  and  $-e$  are the charges,  $M$  and  $m$  the masses of the nucleus and the electron respectively, and where  $W$  is the amount of energy to be transferred to the system in order to remove the electron to an infinite distance from the nucleus. It may be noticed that the expressions are independent of the degree of eccentricity of the orbits.

In order to obtain a mechanical interpretation of the above-mentioned stationary states, let us now in (6) put  $W_n = -A_n$ . This gives

$$W_n = \frac{hK}{n^2}, \quad \omega_n^2 = \frac{2h^3 K^3 (M+m)}{\pi^2 e^4 m M n^6}, \quad 2a_n = \frac{e^2 n^2}{hK}. \quad (7)$$

According to this view, a line of the hydrogen spectrum is emitted during the passage of the atom between two

\* A series of lines, first observed by Pickering in stellar spectra and recently by Fowler in vacuum-tubes containing a mixture of hydrogen and helium, is generally also ascribed to hydrogen. These lines, however, can be accounted for on the present theory, if we ascribe them to helium. (Phil. Mag. *loc. cit.* p. 10; comp. also 'Nature,' xcii. p. 231 (1913).)

† Comp. A. v. d. Broek, *Phys. Zeitschr.* xiv. p. 32 (1913), comp. also several recent contributions to 'Nature.'

stationary states corresponding to different values for  $n$ . We must assume that the mechanism of emission cannot be described in detail on the basis of the ordinary electrodynamics. However, it is known that it is possible on the latter theory to account satisfactorily for the phenomena of radiation in the region of slow vibrations. If our point of view is sound, we should therefore expect to find in this region some connexion between the present theory and the ordinary ideas of electrodynamics.

From (7) we see that  $\omega_n$  vanishes for large values of  $n$ , and that at the same time the ratio  $\omega_n/\omega_{n+1}$  tends to unity. On the present theory the frequency of the radiation emitted by the transition from the  $(n+1)$ th to the  $n$ th stationary state is equal to  $\frac{1}{h}(A_{n+1} - A_n)$ . When  $n$  is large, this

approaches to  $\frac{1}{h} \frac{dA_n}{dn}$ . On the ordinary electrodynamics we should expect the frequency of the radiation to be equal to the frequency of revolution, and consequently it is to be anticipated that for large values of  $n$

$$\frac{dA_n}{dn} = h\omega_n. \quad (8)$$

Introducing the values for  $A_n$  and  $\omega_n$  given by (5) and (7), we see that  $n$  disappears from this equation, and that the condition of identity is

$$K = \frac{2\pi^2 e^4 m M}{h^3 (M+m)}. \quad (9)$$

From direct observations we have  $K = 3 \cdot 290 \cdot 10^{15}$ . Introducing recent values for  $e$ ,  $m$ , and  $h^*$ , we get for the expression on the right side of (9)  $3 \cdot 26 \cdot 10^{15}$ . The agreement is inside the limit of experimental errors in the determination of  $e$ ,  $m$ , and  $h$ ; and we may therefore conclude that the connexion sought between the present considerations and the ordinary electrodynamics actually exists.

From (7) and (9) we get

$$W_n = \frac{2\pi^2 e^4 m M}{n^2 h^2 (M+m)}, \quad \omega_n = \frac{4\pi^2 e^4 m M}{n^3 h^3 (M+m)}, \quad 2a_n = \frac{n^2 h^2 (M+m)}{2\pi^2 e^2 m M}. \quad (10)$$

For  $n=1$ , corresponding to the normal state of the atom, we get  $2a = 1 \cdot 1 \cdot 10^{-8}$ ; a value of the same order of magnitude as the values for the diameters of atoms calculated on

\* Phil. Mag. *loc. cit.* p. 487.



the kinetic theory of gases. For higher values of  $n$ , however,  $2a$  is great compared with the values of ordinary atomic dimensions. As I pointed out in my former paper, this result may be connected with the non-appearance in vacuum-tubes of hydrogen lines corresponding to high numbers in Balmer's formula and observed in the spectra of stars. Further, it will appear from the considerations of the next section that the large diameter of the orbits offers an explanation of the surprisingly great magnitude of the Stark effect.

From (10) it appears that the condition (8) holds, not only for large values of  $n$  but for all values of  $n$ . In addition, for a stationary orbit  $W$  is equal to the mean value of the total kinetic energy  $T$  of the particles; from (10) we therefore get

$$T_n = \frac{1}{2}nh\omega_n. \quad \dots \quad (11)$$

In using the expressions (6) we have assumed that the motion of the particles in the stationary states of the system can be determined by help of the ordinary mechanics. On this assumption it can be shown generally that the conditions (8) and (11) are equivalent. 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 a 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. Applying Hamilton's principle, we get for a small variation of the orbit

$$\delta W = -2\omega \delta \left( \frac{T}{\omega} \right). \quad \dots \quad (12)$$

If the new orbit is also one of dynamical equilibrium, we get  $\delta A = -\delta W$ , where  $A$  is the total energy of the system, and it will be seen that the equivalence of (8) and (11) follows immediately from (12).

In these deductions we have made no assumptions about the degree of eccentricity of the orbits. If the orbits are circular (11) is equivalent to the simple condition that the angular momentum of the system in the stationary states is equal to an entire multiple of  $\frac{h}{2\pi}$ \*

In Planck's vibrators the particles are held by quasi-elastic forces, and the mean value of the kinetic energy is

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

equal to the mean value of the potential energy due to the displacements. Consequently (11) forms a complete analogy to Planck's original relation

$$U = nh\nu$$

between the energy  $U$  of a monochromatic vibrator and its frequency  $\nu$ . This analogy offers another way of representing the present theory—a way more similar to that used in my former paper\*. Considering, however, the widely different assumptions underlying the relation (11) and Planck's relation, it may seem more adequate not to seek the basis of our considerations in the formal analogy in question, but directly in the principal condition (1) and in the laws of the line-spectra.

In dealing with the more complicated structure of the spectra of other elements, we must assume that the atoms of such elements possess several different series of stationary states. This complexity of the system of stationary states, compared with that of the hydrogen atom, might naturally be anticipated from the greater number of electrons in the heavier atoms, which render possible several different types of configurations of the particles.

According to (1), (2), and (3) the energy of the  $n$ th state in the  $r$ th series is, omitting the arbitrary constant, given by

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

The present theory is not sufficiently developed to account in detail for the expression (13). However, a simple interpretation may be obtained of the fact that in every series  $\phi_r(n)$  approaches unity for large values of  $n$ .

Suppose that in the stationary states one of the electrons moves at a distance from the nucleus which is 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. Consequently, the expression (13) may be interpreted as indicating the presence of a number of series of stationary states of the

\* Note added during the proof.—In the *Phys. Zeitschr.* of Feb. 1, E. Gehrcke has attempted to represent the theory of the hydrogen spectrum in a way somewhat different from that in my former paper. Like the procedure in my paper, Gehrcke does not attempt to give a mechanical explanation of Planck's relation between the frequency of the radiation and the amount of energy emitted; but he does also not try to give a mechanical interpretation of the dynamical equilibrium of the atom in its possible stationary states, or to obtain a connexion to ordinary mechanics in the region of slow vibrations.



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 in the hydrogen atom.

It will appear that these considerations offer a possible simple explanation of the appearance of the Rydberg constant in the formula for the spectral series of every element. In this connexion, however, it may be noticed that on this point of view the Rydberg constant is not exactly the same for every element, since the expression (8) for  $K$  depends on the mass of the central nucleus. The correction due to the finite value of  $M$  is very small for elements of high atomic weight, but is comparatively large for hydrogen. It may therefore not be permissible to calculate the Rydberg constant directly from the hydrogen spectrum. Instead of the value 109675 generally assumed, the theoretical value for a heavy atom is 109735.

### § 2. The Effect of an Electric Field.

As mentioned above, J. Stark has recently discovered that the presence of an external electric field produces a characteristic effect on the line-spectrum of an element. The effect was observed for hydrogen and helium. By spectroscopic observation in a direction perpendicular to the field, each of the lines of the hydrogen spectrum was broken up into five homogeneous components situated very nearly symmetrically with regard to the original line. The three inner components were of feeble intensity and polarized with electric vector perpendicular to the field, while the two outer stronger components were polarized with electric vector parallel to the field. The distance between the components was found to be proportional to the electric force within the limits of experimental errors. With a field of 13,000 volt per cm. the observed difference in the wave-length of the two outer components was  $3.6 \times 10^{-8}$  cm. and  $5.2 \times 10^{-8}$  cm. for  $H_\beta$  and  $H_\gamma$  respectively. For both systems of lines emitted by helium, Stark observed an effect on the lines of the Diffuse series which was of the same order of magnitude as that observed for the hydrogen lines, but of a different type. Thus the components were situated unsymmetrically with regard to the original line, and were also not polarized relative to the field. The effect of the field on the lines of the Principal series and the Sharp series was very small and hardly distinguishable.

On the theory of this paper the effect of an external field

on the lines of a spectrum may be due to two different causes:—

(1) The field may influence the stationary states of the emitting system, and thereby the energy possessed by the system in these states.

(2) It may influence the mechanism of transition between the stationary states, and thereby the relation between the frequency of the radiation and the amount of energy emitted.

Considering an external *electric* field we shall not expect an effect of the second kind. Having assumed the atoms to be systems of particles governed by electrostatic forces, we may consider the presence of the field simply as a complication of the original system; but on the interpretation given in the former section of the general principle of Ritz of combination of spectral lines, we may expect that the relation (1) will hold for every system of electrified particles.

It appears that a necessary condition for the correctness of this view is that the frequencies of the components of spectral lines produced by the electric field can be expressed by a formula of the type (2). As we shall see, this seems to be consistent with Stark's experiments.

Let us first consider the effect of an electric field on the hydrogen spectrum. In order to find the effect of the field on the energy of the atom in the different stationary states, we shall seek for its influence on the relation between the energy and the frequency of the system. In this calculation we shall make use of the ordinary mechanics, from analogy with the considerations of the former section.

For simplicity, let us suppose that the mass of the nucleus is infinitely great in comparison with that of the electron. Consider an electron originally moving in a circular orbit round the nucleus. Through the effect of an external electric field the orbit will be deformed. If the force is not accurately perpendicular to the plane of the orbit, this deformation will in course of time be considerable, even if the external electric force is very small compared with the attraction between the particles. In this case, the orbit may at every moment be considered as an ellipse with the nucleus in the focus, and the effect of the field will consist in a gradual variation of the direction of the major-axis as well as of the eccentricity. During this variation, the length of the major-axis will approximately remain constant and equal to the diameter of the original circular orbit. A detailed investigation of the motion of the electron may be

very complicated; but it can be simply shown that the problem only allows of two stationary orbits of the electron. In these, the eccentricity is equal to 1 and the major-axis parallel to the axis of the external field; the orbits simply consist of a straight line through the nucleus parallel to the axis of the field, one on each side of it. It can also be shown that orbits which are very near to these limiting cases will be very nearly stationary.

Neglecting quantities proportional to the square of the magnitude of the external electric force, we get for the rectilinear orbits in question

$$\omega^2 = \frac{e^2}{4\pi^2 m a^3} \left(1 \mp 3E \frac{a^2}{e}\right), \quad \dots \quad (14)$$

where  $\omega$  is the frequency of vibration and  $2a$  the amplitude of the orbit.  $E$  is the external electric force, 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. For the total energy of the system we have

$$A = C - \frac{e^2}{2a} \mp 2aeE, \quad \dots \quad (15)$$

where  $C$  is an arbitrary constant. The mean value of the kinetic energy of the electron during the vibration is

$$T = \frac{e^2}{2a} \left(1 \mp 2E \frac{a^2}{e}\right). \quad \dots \quad (16)$$

Leaving aside for a moment the discussion of the possibility of such orbits, let us investigate what series of stationary states may be expected from the expressions (14) and (15). In order to determine the stationary states we shall, as in the former section, seek a connexion with ordinary electrodynamics in the region of slow vibrations. Proceeding as on page 509, suppose when  $n$  is large

$$\frac{dA_n}{dn} = h\omega_n,$$

where  $A_n$  and  $\omega_n$  denote the energy and the frequency in the  $n$ th state. By help of (14) and (15) we get

$$\frac{dn}{da} = \frac{\pi e \sqrt{m}}{h \sqrt{a}} \left(1 \mp \frac{5}{2} E \frac{a^2}{e}\right).$$

This gives  $n = \frac{2\pi e \sqrt{m}}{h} \sqrt{a} \left(1 \mp \frac{1}{2} E \frac{a^2}{e}\right)$ ,

or  $2a_n = \frac{n^2 h^2}{2\pi^2 e^2 m} \left(1 \pm E \frac{h^4 n^4}{16\pi^4 e^5 m^2}\right). \quad \dots \quad (17)$

Introducing this in (14), (15), and (16) we get

$$\omega_n = \frac{4\pi^2 e^4 m}{h^3 n^3} \left(1 \mp E \frac{3h^4 n^4}{16\pi^4 e^5 m^2}\right), \quad \dots \quad (18)$$

and

$$A_n = C - \frac{2\pi^2 e^4 m}{n^2 h^2} \left(1 \pm E \frac{3h^4 n^4}{16\pi^4 e^5 m^2}\right), \quad \dots \quad (19)$$

$$T_n = \frac{2\pi^2 e^4 m}{n^2 h^2} \left(1 \mp E \frac{3h^4 n^4}{16\pi^4 e^5 m^2}\right). \quad \dots \quad (20)$$

It should be remembered that these deductions hold only for large values of  $n$ . For the mechanical interpretation of the calculations we need therefore only assume that the eccentricity is very nearly unity for the large orbits. On the other hand, it appears from (17), (18), and (19) that the principal terms in the expressions for  $2a_n$ ,  $\omega_n$ , and  $A_n$  are the same as those deduced in the former section directly from the Balmer formula. If we therefore suppose that these quantities in the presence of an electric field can be expressed by a series of terms involving ascending powers of  $E \frac{a^2}{e}$ , we

may regard the above deduction as a determination of the coefficient of the second term in this series, and may expect the validity of the expressions for every value of  $n$ . It may be considered, in support of this conclusion, that we obtain the same simple relation (11) between the frequency of revolution and the mean value of the kinetic energy as was found without the field, *cf.* p. 510.

In the presence of an electric field we shall therefore assume the existence of two series of stationary states of the hydrogen atom, in which the energy is given by (19). In order to obtain the continuity necessary for a connexion with ordinary electrodynamics, we have assumed that the system can pass only between the different states in each series. On this assumption we get for the frequency of the radiation emitted by a transition between two states corresponding to  $n_2$  and  $n_1$  respectively:

$$\nu = \frac{1}{h} (A_{n_2} - A_{n_1}) = \frac{2\pi^2 e^4 m}{h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \left(1 \mp E \frac{3h^4}{16\pi^4 e^5 m^2} n_1^2 n_2^2\right). \quad \dots \quad (21)$$



This formula gives for every hydrogen line two components situated symmetrically with regard to the original line. Their difference in frequency is proportional to the electric force and equal to \*

$$\Delta\nu = \frac{3}{4\pi^2} \frac{h}{em} E (n_2^2 - n_1^2). \quad (22)$$

According to the deduction of (21) we may expect that for high values of  $n$  the radiation corresponds to vibrations parallel to the electric force. From analogy with the above considerations and in order to obtain agreement with Stark's result we shall assume that this polarization holds also for small values of  $n$ .

Introducing in (21) the experimental values for  $e$ ,  $m$ , and  $h$ , and putting  $E = 43.3$  corresponding to an electric force of 13,000 volt per cm., we obtain for the distance between the components of  $H_\beta$  ( $n_1 = 2$ ;  $n_2 = 4$ ) and  $H_\gamma$  ( $n_1 = 2$ ;  $n_2 = 5$ ),  $4.77 \cdot 10^{-8}$  and  $6.65 \cdot 10^{-8}$  cm. respectively. We see that these values are of the same order of magnitude as the distance observed by Stark between the two components polarized parallel to the electric force, viz.  $3.6 \cdot 10^{-8}$  and  $5.2 \cdot 10^{-8}$  cm. The values calculated are somewhat higher than those observed; the difference, however, might possibly be due to the difficulties, mentioned in Stark's paper, of the determination of the magnitude of the electric force in his preliminary experimental arrangement.

For the ratio between the displacements of  $H_\beta$  and  $H_\gamma$  we get from (21) 0.7168, independent of the magnitude of the electric force. It will be seen that this value agrees closely with that observed, viz.  $3.6/5.2$  or 0.69. In this connexion it may be noticed that the value calculated for the ratio in question is independent of the value of the numerical factor in the expression (21), and consequently of the detailed assumptions used in deducing this expression. The value for the ratio can be derived directly from the assumption of the existence of a series of stationary states, in which the energy can be expressed in terms corresponding to ascending powers of  $E \frac{a^2}{e}$ .

A possible origin of the feeble components polarized perpendicular to the field, which were observed by Stark, may

\* Note added during the proof.—In the *Phys. Zeitschr.* of Feb. 1, A. Garbasso and E. Gehrcke (cf. note, p. 511) have deduced expressions for  $\Delta\nu$  which differ from (22) only by a numerical factor of 2 and 4/3 respectively. The arguments of Garbasso are stated very briefly, but seem of a type similar to those of the present paper. The line of arguments of Gehrcke differs essentially from that used here.

be found when a closer examination is made of the effect of the electric field on the motion of the electron\*. This problem, however, will not be considered further at this stage.

The problem of the influence of an electric field on the spectra of other elements is naturally far more complicated than for hydrogen, and cannot be discussed in detail until the theory for such spectra is further developed. It seems, however, possible on the present theory to obtain a simple explanation of the characteristic difference, observed by Stark, in the effect of the field on the lines of the different series of the helium spectrum.

According to the last section, the different series of lines in the spectrum of an element correspond to different series of stationary states of the atom in which one of the electrons moves in an orbit outside the others. For any high value of  $n$  this orbit is approximately the same as that of the electron in a hydrogen atom. In the discussion we assumed that the effect of an electric field on the energy of the stationary states of the hydrogen atom, is connected with a considerable variation in the position and eccentricity of the orbit of the electron in the presence of the field. The possibility of such a variation is due to the fact that without the field every elliptical orbit is stationary. When, however, there are perturbing forces from the inner electrons the latter condition is not satisfied, and thus the effect of an external electric field on the stationary states may be expected to be much smaller than for the corresponding states of the hydrogen atom.

A measure of this effect of the inner electrons on the motion of the outer may be obtained by considering the function  $\phi_r(n)$ . The nearer this function approaches unity the smaller is the disturbance due to the inner electrons, and the more the motion of the outer approaches to that of the electron in the hydrogen atom. Now for the elements of low atomic weight, such as helium and lithium,  $\phi_r(n)$  has a value very nearly unity for the Diffuse series, while for the Sharp series or the Principal series, the value is not at all as close. On our theory we should, therefore, expect a much greater influence of an electric field on the first series than

\* Note added during the proof.—In *Verh. d. Deutsch. Phys. Ges.* 1914, p. 20, K. Schwarzschild has discussed the problem of the effect of the field on the motion of the electron in some detail. In contrast to the above considerations he attempts to apply the results on the explanation of the Stark effect without leaving ordinary electrostatics.



on the other two series. This is in agreement with Stark's experiments\*.

On the present point of view a line of the Diffuse series of the helium spectrum corresponds to a transition between two stationary states, one of which is affected by the presence of an electric field, and the other not: while for the hydrogen lines both states were assumed to be affected by the field. This circumstance may afford an explanation of the fact observed by Stark, viz. that the components of the helium lines were not polarized relatively to the field like the hydrogen lines.

### § 3. The Effect of a Magnetic Field.

An effect of a magnetic field on the line-spectrum of an element was discovered by Zeeman in 1896. By spectroscopic observation in a direction perpendicular to the field the lines are resolved, in the simplest case, into symmetrical triplets of which the central components have the same position as the original line and are polarized with electric vector parallel to the field, while the outer components are polarized with electric vector perpendicular to the magnetic field.

As is well known, Lorentz succeeded in explaining this result on the basis of the classical electron theory. According to his calculation, which was found to agree with Zeeman's observation within the limit of experimental error, the difference in frequency between the outer and the inner components is the same for every spectral line, and equal to

$$\tau = \frac{1}{4\pi} \frac{e}{cm} H, \quad \dots \dots \dots (23)$$

where  $H$  is the magnetic force and  $c$  the velocity of light.

Later more complicated types of magnetic effect on spectral lines have been observed. In most cases, however, simple numerical relations are found to exist between the distance † of the components observed and that calculated by Lorentz. Further, the recent experiments by Paschen and Back ‡ on the magnetic effect on double lines, which will be mentioned in the next section, indicate that the complicated types of Zeeman effect are intimately connected with complication

\* Since the value of  $\phi_r(n)$  differs widely from unity for all series of lines in the spectra of the heavier elements, it is to be expected that the electric effect should be very small, or undetectable for such elements.

† See C. Runge, *Phys. Zeitschr.* viii. p. 232 (1907).

‡ *Ann. d. Phys.* xxxix. p. 897 (1912), xl. p. 960 (1913).

of structure in the undisplaced lines. Theoretical explanations of these results have been proposed by Voigt\* and Sommerfeld †.

Since in the presence of a magnetic field the spectrum of an element cannot be expressed by a formula of the type (2), it follows that the effect of the field cannot be explained by considerations analogous to those employed in section 2 in considering the effect of an electric field. If we retain the principal assumption of stationary states, we must assume that a magnetic field exerts an influence on the mechanism of transition between the stationary states, and thereby on the relation between the frequency of the radiation and the amount of energy emitted (cf. p. 513). In order to investigate this problem we shall seek a connexion with ordinary mechanics in the region of slow vibrations, from analogy with the procedure of the former sections.

Consider an electron rotating round a positive nucleus of infinite mass. In the stationary states of the system the motion of the electron without any field will be an ellipse with the nucleus in the focus. Similarly, suppose that in the presence of a magnetic field the motion of the electron in the stationary states can be calculated in the ordinary way; then, according to a general theorem of Larmor ‡, the orbit of the electron in the field will be a superposition of an elliptical orbit and a uniform rotation round an axis through the nucleus parallel to the magnetic force. This implies a neglect of terms proportional to the square of the magnetic force. The frequency of rotation is equal to  $\tau$  in (23). According to ordinary electrodynamics the radiation emitted by the rotating system will correspond to a Zeeman triplet, the central component of which has the same frequency as the frequency of revolution in the elliptical orbit. In addition, Langevin § has shown that the total energy of the system is not altered by the rotation, since a possible gain in the kinetic energy of the electrons may be considered as balanced

\* *Ann. d. Phys.* xl. p. 368, xli. p. 403, xlii. p. 210 (1913).

† *Ann. d. Phys.* xl. p. 748 (1913).

‡ 'Ether and Matter,' Cambridge, 1900, p. 341.

§ *Ann. de Chim. et de Phys.* v. p. 70 (1905). In this connexion it may be remarked that on the present theory the rotation will give rise to diamagnetism only, since the kinetic energy of the electrons in the stationary states cannot be transferred into heat motion such as is supposed by Langevin in his theory of magnetism. This conclusion seems consistent with experiments which show that the monatomic gases helium and argon are diamagnetic (see P. Tänzler, *Ann. d. Phys.* xxiv. p. 931 (1907)), although the structure of these atoms, proposed in my former paper, was of a type which on Langevin's theory should show paramagnetism.



by a corresponding loss of potential energy of the whole system relative to the field.

In order, therefore, to obtain the connexion with the ordinary mechanics and at the same time to be in agreement with experiment\*, we are led to assume that the effect of a magnetic field on the stationary states of the hydrogen atom consists simply in a superposed rotation of frequency  $\tau$  round the axis of the field, and that the radiation emitted by the transition between two stationary states is changed by the field so as to have the polarization and frequencies of a Zeeman triplet. It will be seen that this assumption is equivalent to supposing that the energy of the hydrogen atom in its stationary states is not altered by the presence of the field, but that the relation (1) in case of vibrations perpendicular to the field is replaced by the relation

$$A_1 - A_2 = h(\nu \mp \tau). \quad \dots \quad (24)$$

The essential difference between these assumptions and those employed in explaining the effect of an electric field will be noticed †.

From the analogy between the explanation of the hydrogen spectrum and that of spectral series of other elements given in the first section, we may naturally assume that similar assumptions will hold for the stationary states of other atoms. A possible explanation on this basis of the complex Zeeman effect of double lines will be indicated in the next section.

#### § 4. Double Spectral Lines.

According to the considerations used in sections 1 and 2, each series of lines in the spectrum of an element corresponds to a series of stationary states of the atom, in which one of the electrons moves outside the others. The configuration of the inner electrons is assumed to be very nearly the same in each series, while that of the outer electron changes from

\* See Fr. Croze, *Journ. de Phys.* iii. p. 882 (1913).

† Note added during the proof.—In *Phys. Zeitschr.* of Feb. 15, K. Herzfeld has discussed in detail the different possibilities of the effect of a magnetic field which might be expected on the theory of the hydrogen spectrum proposed by the writer. His conclusions are equivalent with those obtained above. In addition he considers the effect of terms proportional to the square of the magnetic force and shows that in a strong magnetic field these terms may be expected to have an appreciable influence on the magnetic resolution of the hydrogen lines corresponding to high numbers in the Balmer series. This is a consequence of the large orbits of the electron in the stationary states corresponding to high values of  $n$ .

state to state approximately in the same way as that of the electron in the stationary states of the hydrogen atom.

On this interpretation we may naturally assume that the appearance of double lines in the spectra of many elements\* is due to small perturbing forces originating in the configuration of the inner electrons and having a different effect on the motion of the outer electron according to different positions of its orbits. From the fact that the frequency of the components of double lines can be expressed by a formula of the type (2), we may conclude, on the considerations of section 2 and 3, that the perturbing forces in question are of electrostatic and not of electromagnetic origin. As we shall see, this view seems to offer a simple explanation of the laws observed for the variation of the distances between the components in a series of double lines.

At a distance from the centre of the atom, great in comparison with the distances of the inner electrons, the total force due to the nucleus and the inner electrons will be very nearly equal to that from a nucleus of a single positive charge. At a distance  $r$  the force may be expressed by

$$\frac{e}{r^2} + \frac{P}{r^3} + \frac{Q}{r^4} + \dots, \quad \dots \quad (25)$$

where  $P, Q, \dots$  may vary with the direction of the line from the nucleus to the outer electron, as well as with the time. The second term in (25) corresponds to a configuration of the inner electrons and the nucleus equivalent to an electric doublet. In case of such a configuration it will appear that the condition of dissymmetry necessary for a different effect on different orbits of the outer electron is satisfied. For configurations more symmetrical, in which the centre of gravity of the inner electrons coincides with that of the

\* The lines of the ordinary hydrogen spectrum from a vacuum-tube also appear as close doublets with high dispersion. Considering, however, the want of sharpness of the lines and the discrepancies between the distance of components found by different observers, it seems probable that the lines are not true doublets, but are due to an effect of the electric field in the discharge. This is also indicated by the fact that the distance between the components observed increases with the number of the line, contrary to the behaviour of ordinary double lines. The distance between the components observed by Paschen and Back (*loc. cit.*) was  $0.20 \cdot 10^{-8}$  cm. and  $0.24 \cdot 10^{-8}$  cm. for  $H_\alpha$  and  $H_\beta$  respectively. According to Stark's experiments on  $H_\beta$  this corresponds to a resolution produced by an electric force of about 900 volt per cm. The ratio between an electric resolution of  $H_\alpha$  and  $H_\beta$  should, according to the calculations of section 2, be 0.76; the ratio between the components observed is 20/24 or 0.83.



nucleus,  $P$  will be zero and the perturbing forces will be given by the higher terms in (25).

Let us now assume that for a certain series of stationary states  $P$  is different from zero. According to our considerations, the major-axis of the orbit of the outer electron is approximately equal to that in the stationary states of the hydrogen atom. The major-axis will therefore be approximately proportional to  $n^2$ . Accordingly the quantity corresponding to  $E$  in the equation (19) and due to the second term in (25) will vary approximately as  $n^{-6}$ . The difference in the energy of the two stationary states corresponding to (19) may therefore be expected to vary approximately as  $n^{-4}$ . This corresponds to the variation observed for the distances between the components of the double lines in the spectra of the alkali metals.

The visible spectra of the alkali metals consist of three series of double lines. The difference in frequency of the components of the lines of the Sharp series and the Diffuse series is the same for every line. For the Principal series the difference diminishes rapidly with the number of the line in the series, the difference being approximately proportional to the inverse fourth power of this number. It will appear that this spectrum can be interpreted on the assumption of three series of stationary states of the atom, corresponding to different configurations of the inner electrons; viz.: two single series I. and II., and a double series III. representing for every  $n$  two stationary states for which the difference in energy varies in proportion to  $n^{-4}$ . The Principal series of doublets corresponds to a transition from a pair of the states III. to the first state of I., while the Sharp and Diffuse series correspond to transitions respectively from states I. and II. to the first pair of state III.

I shall not here try to develop these considerations in further detail, but confine myself to show that the view adopted seems to indicate a possible explanation of the results of the experiments by Paschen and Back on the effect of a magnetic field on spectral lines of complicated structure. The characteristic result of these experiments is the great difference between the effect of a weak and a strong magnetic field. In the presence of a weak magnetic field the components of a double line are resolved in a complicated way. If the field increases, the distances between the sub-components at first increase regularly with the strength of the field. When, however, the distances are of the same order of magnitude as the distance between the components of the original double line, the aspect of the system of lines

gradually alters. The single lines get diffuse and grow together; and when the field is increased still more the whole system of lines tends to shrink into three homogeneous components, with the same relative positions as the components of a simple Zeeman triplet.

An analogy to these results is obtained by considering the simultaneous effect of an electric and a magnetic field on a system consisting of an electron rotating round a nucleus of infinite mass. In section 2 we assumed that the effect of an external electric field is to increase the eccentricity of the orbit of the electron and to direct the major-axis parallel to the electric force. According to section 3, the effect of a magnetic field is to superpose a rotation of uniform frequency on the orbit of the electron. To consider the simultaneous effect of electric and magnetic fields the axes of which are perpendicular to each other, let us first suppose that the effect of the electric force is large compared with the effect of the magnetic force. In this case, the directing effect of the electric force will oppose the rotatory effect of the magnetic force, and the result may be the appearance of a number of stationary orbits close to the orbits to be expected when the electric field acts alone. If, on the other hand, the effect of the magnetic field is large compared with that of the electric field, the directing effect of the latter cannot prevent the general rotation of the system, and it is easily seen that the case will be very similar to that due to the magnetic field alone. The necessary condition for the application of this analogy to the case of the magnetic effect on double lines, is that the configuration of the inner electrons does not rotate in the field with the same frequency as the orbits of the outer electrons. It may be noticed that these considerations bear an analogy to the theory of Sommerfeld (*cf.* p. 519), which corresponds to the analogy between the considerations of the former section and the theory of Lorentz.

#### *Concluding Remarks.*

In the deductions of this paper the following general assumptions are used:—

1. That an elementary system containing rotating electrons will not emit energy radiation in the continuous way assumed in ordinary electrodynamics, but that radiation is only emitted during the passing of the system between a certain number of stationary states.

2. That the dynamical equilibrium of the system in the



stationary states is governed by the ordinary laws of mechanics, while these laws do not hold for the passing of the system between the different stationary states.

3. That the radiation emitted during the passing of the system between two stationary states is homogeneous; and that only in the region of slow vibrations does the frequency approach that to be expected on ordinary electrodynamics, while in general the frequency  $\nu$  is determined by the relation  $E = h \cdot \nu$ , where  $E$  is the total amount of energy emitted and  $h$  Planck's constant.

It has been attempted to show that, applying these assumptions to Rutherford's theory of the structure of atoms, it seems possible to obtain an explanation of the laws of line-spectra discovered by Balmer, Rydberg, and Ritz.

It has further been attempted to show that it seems possible to account for some of the general features of the effect of magnetic and electric fields on spectral lines discovered by Zeeman and Stark. In the case of an electric field it is assumed that no alterations in the above assumptions take place. In the case of a magnetic field, however, it is found necessary to modify the third assumption in order to retain the connexion with ordinary electrodynamics in the region of slow vibrations.

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LX. *Separation of Close Spectrum Lines for Monochromatic Illumination.* By R. W. WOOD, Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University\*.

[Plate VII.]

**I**N many branches of research in physical optics it often becomes necessary, for one reason or another, to separate two or more close spectrum lines, utilizing the light of one only.

For example, in experiments upon the monochromatic excitation of resonance spectra, the line utilized for the illumination of the fluorescing vapour must be isolated either by absorbing screens or by a spectroscope, used as a monochromator.

If the latter method is employed the illumination is much restricted by the necessity of employing a slit, or rather two slits; and in the case of close spectrum lines, such as the D lines of sodium, the necessity of employing very fine slits makes it very nearly impossible to accomplish anything in

\* Communicated by the Author.

this way. Even in the case of the three green copper lines, I found the greatest difficulty in getting sufficient illumination with a single line isolated by means of a very large monochromator of 1.5 metres focus.

In the present paper I shall give a method which enables us to utilize a source of light of large size, say  $1 \times 3$  cm., and remove one or more lines from it with *practically no loss of light*.

For example, we can form two images of a sodium flame by means of a condenser having an effective aperture equal to  $f^2$ , one image containing only the light of wave-length 5890, the other only light of wave-length 5896, both images being very nearly as intense (with respect to *one* sodium line) as if the condenser had been employed without the separating apparatus.

The method is an improvement upon one which I used many years ago in the study of the dispersion of sodium vapour and described briefly at that time. It is a polarization method, and may be described briefly as follows.

If plane-polarized monochromatic light is passed through a plate of some doubly refracting crystal with its direction of vibration making an angle of  $45^\circ$  with the axis, it will emerge plane-polarized parallel to the original plane for certain thicknesses of the plate, and plane-polarized at a right angle to this plane for other thicknesses. For intermediate thicknesses it will be elliptically or circularly polarized.

If we employ a plate of quartz 30 mm. thick the emergent waves of  $D_1$  and  $D_2$  of sodium will be plane-polarized at right angles to each other, and either can be quenched by a nicol suitably oriented. If white light is used, and analysed by a spectroscope, the spectrum will be furrowed by dark bands, the distance between a bright and a dark band being, in the yellow region, 6 Ångström units, the distance between the D lines.

As it was desired to utilize this principle for the separation of the D lines for the purpose of exciting the resonance radiation of sodium vapour by the light of  $D_1$  and  $D_2$  separately, by which means we may determine whether the mechanisms which give rise to the radiations are coupled together, an investigation which is being carried to a successful conclusion in collaboration with L. Dunoyer at the present time, it became necessary to bring the method up to the highest possible efficiency. As it is necessary to employ a large condenser and work with very divergent and convergent cones of light, a block of quartz of very large size