$(p-\alpha)z = P$ 

which reduces to zero at t=0. And on evaluating this solution, we obtain \*

 $z = \frac{1}{a} (e^{at} - 1) P.$  . . . (36)

Substituting in (35) from (36), we now see that

$$\frac{F(p)}{\Delta(p)} P = \sum_{\alpha} \frac{A}{\alpha} (e^{\alpha t} - 1) P. \qquad (37)$$

Further, since (35) is an algebraic identity, we may write p=0, which gives

 $-\sum_{\alpha} \frac{A}{\alpha} = \frac{F(0)}{\Delta(0)} = N_0. \quad (38)$ 

On combining (37) and (38), we obtain the formula

$$\frac{F(p)}{\Delta(p)} P = P \left\{ N_0 + \sum_{\alpha} \frac{1}{\alpha} \frac{F(\alpha)}{\Delta'(\alpha)} e^{\alpha t} \right\},\,$$

which is Heaviside's equation as quoted in equation (4) above.

To deduce equation (2) we integrate the last result with respect to t and obtain

$$\frac{\mathbf{F}(p)}{\Delta(p)}\mathbf{G}t = \mathbf{G}\left\{\mathbf{N}_{0}t + \sum_{\alpha} \frac{\mathbf{A}}{\alpha^{2}}\left(e^{\alpha t} - 1\right)\right\}, \qquad (39)$$

where the arbitrary constant of integration has been adjusted so as to make the solution zero at t=0.

Now returning to the identity (35), we see on expanding powers of p, that

powers of 
$$p$$
, that
$$N_0 + N_1 p + N_2 p^2 + \dots = -\sum_{\alpha} \frac{A}{\alpha} \left( 1 + \frac{p}{\alpha} + \frac{p^2}{\alpha^2} + \dots \right);$$
so that
$$N_1 = -\sum_{\alpha} \frac{A}{\alpha^2}. \qquad (40)$$

\* It should be noted that we may also write

$$\frac{1}{p-a}P = \left(\frac{1}{p} + \frac{a}{p^2} + \frac{a^2}{p^3} + \dots\right)P = \left(t + \frac{at^2}{2!} + \frac{a^2t^3}{3!} + \dots\right)P,$$

leading to the same result. But this process is less convincing than that given in the text.

Combining (39) and (40), we deduce that

$$\frac{F(p)}{\Delta(p)}Gt = G(N_0t + N_1 + \sum_{\alpha} \frac{A}{\alpha^2} e^{\alpha t}),$$

which is the same as equation (4) of § 1.

It will be noticed that in § 1 the equation (2) has been used with more general types of function taking the place of the polynomials F(p),  $\Delta(p)$ . It is natural to suppose that the equation (2) still remains valid; but formal proofs are more troublesome, as might be expected \*.

### XXXVI. On the Origin of Spectra and Planck's Law. By Sir J. J. Thomson, O.M., P.R.S.

THE results of investigations on the number of electrons in the atoms of the various elements show that the structure of these atoms, if expressed in terms of electrical charges, is in some cases of a very simple character. The atom of hydrogen, for example, is believed to contain only one electron and one unit positive charge. The question arises whether, if we regard the electrons and the positive charge as centres of forces varying inversely as the square of the distance, we have the potentiality of explaining by mechanical principles the properties of the atom. The explanation of some of these properties such as, for example, the specific inductive capacity of the gas, the formation of molecules by union with other atoms, whether of hydrogen or of some other element, seems to be within the scope of this very simple system; there are, however, other properties of which this cannot be said. Prominent among these is the spectrum emitted by the gas. Hydrogen, as is well known, can emit several spectra. We need, however, for our purpose only refer to the best known ones: the second spectrum, which is a spectrum containing an exceedingly large number of lines and extending far into the ultra-violet, and the so-called four-line spectrum, which contains, we have reason to believe, an infinite number of lines, the frequencies of which are connected by a simple numerical relation discovered by Balmer. The vibrations which would

† Communicated by the Author.

<sup>\*</sup> This problem has been considered with the aid of complex integrals in my paper on "Normal Coordinates in Dynamical Systems" already quoted (Proc. Lond. Math. Soc. vol. xv.); the sections §§ 4, 5, 8 have special bearing on this question. Short summaries are also given in the "Abstracts" of the Proceedings (vol. xiii. ser. 2, 1914, p. xxvii, and vol. xviii. January 1919).

be emitted by a single electron placed near a unit positive charge would not be of this character. Assuming the usual law of force for two charges, if the atom is to be in a steady condition the electron must describe an orbit round the positive charge. The time of rotation of the electron will depend on its distance from this charge, and if this varies continuously the times of rotation will do so also, and the spectrum whose frequencies are determined by these times would be a continuous one. If the charges are regarded merely as centres of inverse square forces there are no reasons for retaining some of these orbits as possible and neglecting the others. Mr. Bohr, in his theory of spectra, supposes that the only orbits which are possible are those where the ratio of the energy of the electron to its angular velocity is an integral multiple of a definite unit. This, however, is not the consequence of dynamical considerations; it is arithmetical rather than dynamical, and if it is true it must be the result of the action of forces whose existence has not been demonstrated. The investigation of such forces would be a problem of the highest interest and importance.

By the use of this principle and a further one, that when an electron passes from one orbit to another it gives out radiation whose frequency is proportional to the difference of the energy of the electron in the two orbits, Mr. Bohr obtains an expression which gives with quite remarkable accuracy the frequencies of the lines in the four-line spectrum of hydrogen. It is, I think, however, not unfair to say that to many minds the arithmetical basis of the theory seems much more satisfactory than the physical.

The vibrations which give rise to the spectrum do not on this theory correspond in frequency with any rotation or vibration in the atom when in the steady and normal state. That in the normal atom there is something which can vibrate with the frequency of the lines, or at any rate with that of some of the lines in the spectrum, seems to be proved almost irresistibly by the experiments of Professor Wood and Mr. Bevan on the absorption spectra of the vapours of the alkali metals. These vapours give as absorption spectra fine well-defined black lines coinciding in position with the lines in the principal series of the spectrum of the metal. Thus, for example, Professor Wood obtained 48 of these lines in the absorption spectrum of sodium vapour, and Mr. Bevan 24 for potassium, 30 for rubidium, 24 for cæsium. The sharpness and intensity of these absorption lines produced by comparatively cold vapour are so great that it is very difficult to believe that they are not due to a resonance

effect caused by systems in the normal atom having periods of vibration identical with those of the lines absorbed, and that there are in the normal atom vibrators with the same period as some of those in the luminous atom. There are, however, lines in the subordinate series in the emission spectrum which do not appear in the absorption one: thus it would appear that some of the atoms in the luminous gas differ from those in the normal gas inasmuch as the electrons vibrate with different periods in the two cases. The absorption spectrum is, however, sufficiently complicated to prove that it cannot be represented by the vibrations of a few electrons under the influence of their own repulsions and the attraction exerted upon them by a positive charge, if these attractions and repulsions follow the simple law of the inverse square.

Though it is natural in any investigation of the equilibrium of electrons and positive charges to begin by assuming that the attraction between the positive and negative charges varies inversely as the square of the distance, we must bear in mind that we have no direct evidence from experiment that this law holds at distances comparable with those which separate the electrons and the positive charges in a molecule. The measurements and the phenomena which furnish the evidence for the inverse square law relate to distances which are enormous compared with atomic distances. If  $c_1$ ,  $c_2$ ,  $c_3$  are of the order of atomic distances, there are no experiments yet made which would distinguish between a force of  $1/r^2$  and one of

$$\frac{1}{r^2} \left( 1 - \frac{c_1}{r} \right) \left( 1 - \frac{c_2}{r} \right) \left( 1 - \frac{c_3}{r} \right),$$

and yet at atomic distances the two forces are quite dissimilar, the second changing from attraction to repulsion and back to attraction again as r passes through the values  $c_1, c_2, c_3, &c.$ 

If the positive part of the atom is built up of distinct units the repulsion between them cannot continue down to distances such as those which occur in this part of the atom, otherwise an atom containing several of these units would explode.

I shall, therefore, consider the consequences of supposing that the field of force round the positive charge, although varying inversely as the square of the distance at large distances from the atom, yet in the atom itself changes backwards and forwards between attraction and repulsion. To fix our ideas let us suppose that the expression for the

force contains the factor  $\frac{\sin cu}{cu}$  where u=1/r, and r is the

distance from the centre. When r is great compared with c,  $\sin cu/cu$  is unity, so that this factor does not affect the force at great distances. Inside the atom, if atomic dimensions are comparable with c, there will be a series of positions of equilibrium determined by  $cu=n\pi$  or  $r=c/n\pi$  where n is an integer. Thus even if there is only one positive charge and one electron there may be a single infinite series of atoms with the electron at distances from the centre represented

by  $r = \frac{c}{n\pi}$ ; the times of vibrations of the electrons about

these positions would be different, so that a collection of such atoms could give rise to an infinite number of lines both in the absorption and emission spectra. Each line would arise from a different kind of atom; the brightness of the line would depend, along with other things, on the number of atoms of the kind giving out the particular line. The theory of dispersion enables us, if we know the connexion between the refractive index and the wave-length, to calculate the number of systems which vibrate in any particular period. Bevan applied this method to find the number of atoms in sodium vapour which could vibrate in unison with the different lines in the principal series of this metal. He found that the number of atoms which can give out or absorb the D line is about one twelfth of the total number of atoms, while only about one in 1000 can give out the pair 3303, and about one in 5500 the pair 2852.

Thus the number of atoms corresponding to a line in the principal series diminishes very rapidly as the number which represents the position of the line in the series increases, and though different kinds of atoms may exist, the great

majority of them are of one kind.

It is remarkable that only about 9 per cent. of the Sodium atoms are of the type giving lines in the visible part of the principal series. This suggests that perhaps the strongest line in the series may be a line in the infra red. An atom of one kind may, by physical or chemical processes, be transformed to one of another kind. Thus, if an atom with the electron at P were ionized, it would be positively electrified and would attract an electron from outside; this electron might, however, settle at another point of equilibrium Q, giving rise to a different type of atom.

It would seem that these different types of atoms would differ in other respects than the period of vibration of the

electrons. They would, for example, differ in their specific inductive capacities so that the proportion of the different kinds would be different at different places in a rapidly varying electric field. Again, the atoms of one kind might more readily combine with an atom of a different element than those of another. So that if the gas in a spectroscopic tube were gradually absorbed by chemical means, as, for example, when oxygen is absorbed by sodium, the relative intensity of the lines at the end of the process might not be the same as at the beginning; or, again, when the spectrum of an element is obtained by decomposing a compound, as, for example, when the spectra of the alkali metals are obtained by putting one or other of their salts in a Bunsen flame, the relative intensity of the lines might depend upon the character of the salt. Bevan's experiment, already alluded to, indicated that the number of atoms giving the lines of shorter wave-length in the principal series increased with the temperature of the sodium vapour. I pointed out many years ago, that the magnitude of the refractive index of helium showed that only a small fraction of the helium atoms could vibrate with the frequency of any particular line in the helium spectrum. Many instances of the variability of the relative intensity of different lines in the same spectrum are given in Kayser's 'Spectroscopie.' Since the processes which make the gas luminous also ionize the gas and thus enable an atom of one kind to be converted into one of another, it does not seem probable that by any process of fractionation we should be able to obtain a gas containing nothing but atoms of one kind, and therefore giving out a spectrum consisting of a single line under all conditions of excitation.

The electric field inside an atom consists, according to the view we have just taken, of alternate shells of attractive and repulsive forces, the places of transition from attraction to repulsion being places where the force vanishes and where an electron could be in equilibrium; the distances of these places of equilibrium from the centre being in harmonic progression.

We now pass on to consider the nature of the forces which act upon the electron and cause it to vibrate in the frequencies of the spectral lines. It is possible, as we shall see, to postulate an infinite number of laws of electric force which could give rise to a sequence of vibrations represented by Rydberg's law.

We may also imagine that in addition to the electric field inside the atom there is also a magnetic one, and that

the frequencies of the vibrations of the electrons are determined by the magnetic and not by the electric forces. An electron, when in a magnetic field, describes a spiral round a line of magnetic force completing a revolution in a time  $2\pi/\frac{\mathrm{H}e}{m}$ , where H is the magnetic force, e the charge, and m the mass of the electron; it thus gives out radiant energy whose frequency is  $\frac{\mathrm{H}}{2\pi}\frac{e}{m}$ , which is independent of the energy of the electron. As this energy diminishes, the radius of the spiral described by the electron diminishes, but the frequency of the vibration is unchanged. Thus, if the magnetic force were predominant in determining the vibrations of electrons, the frequencies of the vibrations given out by the different kinds of atom would be

$$\frac{\mathrm{H_1}}{2\pi}\frac{e}{m}$$
,  $\frac{\mathrm{H_2}}{2\pi}\frac{e}{m}$ ,  $\frac{\mathrm{H_3}}{2\pi}\frac{e}{m}$ ,

where  $H_1$ ,  $H_2$ ,  $H_3$  are the values of the magnetic induction at the various places of equilibrium. Suppose, now, that the value of H at a point of equilibrium at a distance r from the centre were equal to  $\mu(a^2-r^2)$ , a distribution of magnetic force which a priori is not improbable, as it is that inside a sphere uniformly charged with electricity and rotating like a rigid body.

Since the positions of equilibrium are given by  $\sin c/r = 0$ , i. e., by  $\frac{c}{r} = n\pi$  or  $r = c/n\pi$ , where n is an integer, the value of the magnetic force at the positions of equilibrium, and therefore the frequencies of vibration in these positions, would be proportional to

$$a^2 - \frac{c^2}{n^2 \pi^2}$$
 to  $\frac{c^2}{\pi^2} \left( \frac{a^2 \pi}{c^2} - \frac{1}{n^2} \right)$ ,

and would thus form a series of the Balmer type. If, in addition, the place r=a, where the magnetic force vanishes, is also a place where the electric force vanishes,  $\frac{c}{a}=m\pi$  where m is an integer, and the expression for the frequency becomes  $C\left(\frac{1}{m^2}-\frac{1}{n^2}\right)$ , where C is a constant and m and n integers.

Before proceeding to discuss this expression in detail, we

shall consider the type of atom which is required to satisfy the assumption we have made in the preceding investigation. This atom consists of a field of electric force which may be regarded as made up of a series of shells of attractive and repulsive force following one another alternately, the radii of the boundary of these shells, which are places where an electron would be in equilibrium, being in harmonical progression. Superposed on the field of electric force is a field of magnetic force, also arranged in shells, the outer boundary of the magnetic field coinciding with a place where the electric force vanishes. I contemplate that when the atom is exposed to such conditions as may arise in strong electric discharges or other methods of producing spectra, the outer layers of this magnetic field may get detached and the boundary of the magnetic field come close up to the centre, that, in fact, there is what might be called a magnetic ionization of the atom, and that the atom resumes its normal magnetic state when the electric discharge, &c., ceases. The atoms in a luminous gas thus possess a double manifoldness, one arising from the different positions of the electrons in the atom, the other from the variations in the magnetic boundary of the atom. The first manifoldness would give rise to different lines in the same series, the second to a number of different series most of which would only be emitted by the special type of atoms produced when an electric discharge passes through the gas.

So far we have only considered the case when only one electron was in the atom, so that a position of equilibrium was a place where the force due to the positive charge vanishes. If there are more electrons than one, the position of equilibrium will not be where the force due to the positive charge vanishes, but where this force at any electron balances the repulsion due to the other electrons. This will displace the position of equilibrium, and instead of these being given by  $\sin cu = 0$ , or  $cu = n\pi$ , they will be given by  $cu = \pi(n+\delta)$ , where  $\delta$  is a quantity depending on the repulsion of the electrons and perhaps also on n.

As the frequencies of the vibrations are proportional to  $a^2 - r^2$  they will now be proportional to

$$\frac{1}{(m+\delta')^2}-\frac{1}{(n+\delta)^2}.$$

Let us now consider the various types of series that could arise on this view.

427

Principal Series.

If the magnetic boundary is constant and fixed by the parameter m, and the different lines are due to the vibration of electrons in the positions of equilibrium inside the magnetic boundary, the series will be expressed by

$$C\left(\frac{1}{(m+\delta')^2} - \frac{1}{(n+\delta)^2}\right), \qquad (1)$$

When the boundary is that corresponding to the majority of the normal atoms and the number of electrons is the full number proper to the atom, this will be the principal series; as the atoms are in the normal state, the atoms of the cold vapour will contain electrons able to vibrate in these periods, so that the vapour will be able to give this series of lines as an absorption spectrum.

If the atoms were ionized so that the number of electrons inside were diminished, this would alter the positions of equilibrium and therefore  $\delta$ , so that the series of lines given out by the atoms would be represented by

$$C\left(\frac{1}{(m+\delta')^2}-\frac{1}{(n+\delta'')^2}\right), \quad . \quad (2)$$

a series with the same limiting frequency as the preceding.

Inasmuch as these lines proceed from ionized atoms, their frequencies do not correspond to the vibrations of electrons in a normal atom, and so this series would not appear as an absorption spectrum of the cold vapour; it would not then be a principal series, as the reversibility of the lines is the characteristic of this type of series.

Let us now take the case when the magnetic boundary is not the same as in the last case, but now corresponds to the parameter m' instead of m. The series of lines will now be given by

$$C\left(\frac{1}{m_1+\delta_1)^2}-\frac{1}{(n+\delta_2)^2}\right), \quad . \quad (3)$$

where n has the successive integral values and  $m_1$  is a constant integer. This series has a different limit from the preceding. If the new magnetic boundary, which by hypothesis is a position of equilibrium for electrons, were to be the position of equilibrium next nearer the centre than the one for the atoms giving the series (1), then the electron in the gravest mode of vibration of the atoms in (1) would be

on the magnetic boundary of the atoms in (2). In other words,

$$\frac{1}{(m_1+\delta_1)^2} = \frac{1}{(1+\delta)^2},$$

so that the series (3) could be written in the form

$$C\left(\frac{1}{(1+\delta)^2} - \frac{1}{(n+\delta_2)^2}\right). \qquad (4)$$

The difference between the limiting frequencies of the series (1) and (4) is thus

$$C\left(\frac{1}{(m+\delta')^2}-\frac{1}{(1+\delta)^2}\right)$$

and this, as we see from (1), is the gravest frequency of the principal series.

Comparing this result with the Rydberg-Schuster law that the gravest frequency of the principal series is equal to the difference in the limits of the principal and first subordinate series, we infer that the series (4) represents the first subordinate series. Just as in the previous case we may have atoms which are neutral, i. e. which contain the normal number of electrons, and also atoms which have lost one electron and thus have unit positive charge. The positions of equilibrium for these are not the same as for the neutral atom, and the frequencies will therefore be represented by

$$C\left(\frac{1}{(1+\delta)^2} - \frac{1}{(n+\delta_3)^2}\right). \qquad (5)$$

This has the same limit as (4), and therefore corresponds to the second subordinate series. If there are atoms which have two positive charges there would be another series with the same limits as (5), but with a different step between the various lines; or, again, if instead of being positively charged the atom were negatively charged, i. e., had got one more electron than the normal, and in some gases (such as, for example, hydrogen and the electronegative gases oxygen, chlorine, and iodine) these, as Positive Ray Analysis shows, are plentiful, there might yet be another series again with the same limit but with a different step from any of the preceding series. Thus, on this view, one of the subordinate series, the one connected with the principal series, would be emitted by uncharged atoms, while other subordinate series would be emitted by charged ones.

Pairs and Triplets.

A common feature in spectra is that the series consists not of single lines, but of a series of pairs, or triplets.

These are not confined to any particular type of series but occur in the principal as well as the subordinate series, though the law of difference of frequencies is different; in the principal series the frequency difference between the constituents of the pair diminishes as the wave-length diminishes, while in the subordinate series the frequency difference is constant.

The two constituents of a pair arise from different electrons; for Wood has shown that one of the D lines of sodium can be excited without the other and, again, the Zeeman effect for one line of a pair is quite different from that of the other.

We should expect to get pairs or triplets when instead of a single electron we had a ring of electrons or a number arranged at the corners of a polyhedron, if the distribution were not perfectly symmetrical about the centre. Thus, for example, if we had a ring of four electrons, arranged not at the corners of a square, but at those of a rectangle whose diagonals were of slightly different lengths; two of the electrons would be at a greater distance from the centre than the other two, so that the magnetic force, and therefore the frequency, would be smaller for the first than for the second pair of electrons, and since the variable part of the magnetic field, being proportional to  $r^2$ , would vanish at the centre, the limiting frequency which corresponds to the vibrations of electrons close to the centre would be the same for each pair of electrons. We should thus get a series of pairs behaving like those in the principal series.

We have seen reason for ascribing the first subordinate series to the vibrations of the electron in an atom in which the magnetic boundary has crept up to the position occupied by the outer ring of electrons in an atom of the type of that emitting the principal series. If the configuration of the ring is slightly unsymmetrical, that of the magnetic boundary for the atoms giving out the first subordinate series may be expected to be so also.

If this is so, the term in the magnetic force which does not depend on r would be different in different directions, and therefore the value of the first term in the bracket in

the expression for the frequency

$$C\left(\frac{1}{(m+\delta')^2}-\frac{1}{(n+\delta)^2}\right)$$

would be different for electrons lying on different radii drawn from the centre of the atoms, the limiting frequency of electrons lying along these radii would be different, and the lines of the pair would not close up as the wave-length diminished.

Again, the directions in which the electrons giving the principal series bulged out, and along which the vibrations had the smaller frequency, would be the directions where the magnetic boundary bulged out in the atoms giving the first subordinate series. The directions where the magnetic boundary bulges out correspond to places where the constant term inside the bracket is a maximum and therefore to directions along which the frequency is a maximum.

The line of longer wave-length in a pair in the principal series is thus analogous to that of shorter wave-length in one in the first subordinate series. This is in accordance with the behavour of the pairs in the spectra of the alkali metals, for when the more refrangible line of a pair is the stronger in the principal series, in the first subordinate series the more refrangible line is the weaker, while the Zeeman effect for the more refrangible lines in the principal series is analogous to that of the less refrangible one in the first subordinate series.

In the spectra of the alkali metals the terms  $1/(n+\mu)^2$ ,  $1/(m+\mu)^2$ , which occur in the expression for the series approximate to  $1/(n+\frac{1}{2})^2$  in some cases and to  $1/n^2$  in others where n is an integer. This would occur if the positions where the electrons are in equilibrium were given by the equation  $\sin 2x = 0$  rather than by  $\sin x = 0$ , for then the solution of the equation would be  $2x=p\pi$ , where p is an integer. If p is an even integer this may be written  $x=n\pi$ , and if p is an odd one  $x = (n + \frac{1}{2})\pi$  where n is an integer. Thus, if we call the former the "S" solutions and the latter the "C" ones and suppose that the magnetic boundary of the atom may coincide with either a C or an S solution, we can have the following types of series. I call the constant term inside the bracket in Rydberg's expression the limit of the series, and denote it by Ls or Lc according as it corresponds to an S or C solution; the steps, the variable part, will be denoted by S<sub>s</sub> or S<sub>c</sub> according as the electrons giving out the vibrations are in the position of equilibrium corresponding to the S or C solution respectively.

Sir J. J. Thomson on the Origin of

The series may be represented as

(1) 
$$L_s - S_s = C\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$
,

(2) 
$$L_s - S_c = C\left(\frac{1}{m^2} - \frac{1}{(n+5)^2}\right)$$
,

(3) 
$$L_c - S_c = C\left(\frac{1}{(m+5)^2} - \frac{1}{(n+5)^2}\right)$$

(4) 
$$L_c - S_s = C\left(\frac{1}{(m+5)^2} - \frac{1}{n^2}\right),$$

where L<sub>s</sub> and L<sub>c</sub> may have different values corresponding to different positions of the magnetic boundary.

We see from this that the difference in the frequencies of two lines in a series of types (1) or (3) will be the frequency of a line in another series of the same type.

The differences between the frequencies of any two lines in a series of type (2) will be the frequency of a line in another series of type (3).

The difference between the frequencies of any two lines in a series of type (4) will be the frequency of a line in another series of type (1).

Thus, if we take the lines belonging to any one series, the complete spectrum of the gas will contain a line whose frequency is the difference of the frequencies of the two lines in the series.

It must be remembered that the two lines must be selected from the same series, if the two lines are selected at random from the spectrum there need not be a line whose frequency is the difference in frequency of the two lines.

#### Planck's Law.

The view that the vibrations which give rise to radiation are determined by the magnetic forces, leads, if we assume a simple relation between the electric and magnetic forces, to Planck's law, and gives a physical concept for the Quantum Theory.

For suppose that an electric field is accompanied by a magnetic one, the magnetic induction B being in the direction of the electric force R and connected with it by the relation

$$\mathbf{B} = \frac{2\pi m}{h} \int p \frac{d}{ds} (\omega \mathbf{R}) ds,$$

where ds is an element of a line of electric force,  $\omega$  the cross-section of a tube of force, m the mass of an electron, h Planck's

constant, and p determined by the equation  $\frac{dp}{ds} = -\frac{1}{\omega}$ .

When the force is due to a single positive charge we may put p=1/r,  $\omega=r^2$ , where r is the distance from the charge.

We notice that when the law of force reduces to the inverse square law,  $\omega R$  is constant and B vanishes.

Integrating by parts we have

$$\mathbf{B} = \frac{2\pi m}{h} \left[ p\omega \mathbf{R} + \int \mathbf{R} \, ds \right]. \qquad (1)$$

Hence, if B<sub>1</sub>, B<sub>2</sub> be the values of B at two places of equilibrium where R vanishes,

$$B_{1}-B_{2}=\frac{2\pi m}{\hbar}\int_{s_{1}}^{s_{2}}R\ ds,$$

or if w be the work done on an electron in moving from one place to another,

$$\mathbf{B}_1 - \mathbf{B}_2 = \frac{2\pi m}{eh} w.$$

If  $n_1, n_2$  are the frequencies of the vibrations of an electron at the two places

$$n_1 = \frac{1}{2\pi} \frac{e}{m} B_1$$
;  $n_2 = \frac{1}{2\pi} \frac{e}{m} B_2$ .

Hence

$$n_1 - n_2 = \frac{w}{h}.$$

Thus, if an electron falls from a place where the magnetic force vanishes to another position of equilibrium, the frequency of the vibration is equal to w/h, where w is the energy converted into radiation. Thus the transference from potential energy to energy of radiation is in accordance with Planck's law.

Assuming the relation between the electric and magnetic force given in the preceding investigations, it is easy to find laws of electric force such that the frequencies of the vibrations of electrons would be connected by a relation similar to that expressed by a Rydberg series.

Thus, for example, suppose that the force R exerted by

the positive charge on an electron is given by the equation

$$R = \frac{Qx^2}{c^2} \frac{d}{dx} \left\{ \frac{\sin^2 x}{x^2} + \sin x \cos^2 x \right\},\,$$

where x=c/r, when x is small, i.e. when r is large, this expression reduces to

 $\mathbf{R} = \frac{\mathbf{Q}}{r^2}$ 

so that it gives the right value of the force at a great distance from the atom. Again, when x is considerable, the positions of equilibrium are given by

$$\cos x = 0$$
, or  $x = (2p+1)\frac{\pi}{2}$ ,

where p is an integer.

Since

$$\int R \, dr = -c \int \frac{R \, dx}{x^2} = \frac{2Q}{c} \left\{ \frac{\sin^2 x}{x^2} + \sin x \cos^2 x \right\} . \tag{2}$$

At a position of equilibrium we see from equation (1), since  $\sin^2 x = 1$ ,

$${
m B} = rac{4\pi {
m Q}}{ch} \, m \, \left\{ eta - rac{4}{\pi^2 (2p+1)^2} 
ight\} \, ,$$

where  $\beta$  is a constant, if the magnetic induction vanishes at the point of equilibrium where  $p=p_0$ ,

$$\beta = \frac{4}{\{\pi(2p_0+1)\}^2}.$$

Hence n, the frequency of the vibrations, is given by the equation

 $n = \frac{2Qe}{ch} \left\{ \beta - \frac{1}{\pi^2 (p + \frac{1}{2})^2} \right\},\,$ 

which may be written in the form

$$n = \frac{2Qe}{\pi^2 ch} \left\{ \frac{1}{(p_0 + \frac{1}{2})^2} - \frac{1}{(p + \frac{1}{2})^2} \right\},\,$$

a series of the Rydberg type.

If 
$$\frac{cQ}{Q} = \frac{4}{\pi^4} \frac{h^2}{em}.$$

the coefficient of the variable term is the same as in Bohr's theory.

The lines in the spectrum only give information about the value of the magnetic force at a number of isolated points;

they cannot, even when combined with the condition that at great distances the electric force must be expressed by  $Qe/r^2$ , afford sufficient data to determine uniquely the law of force, and, in fact, we can find, without difficulty, different expression for R which would yet give the same series of spectral lines.

The quantity c, which occurs in the expressions for R and B inside the atom, is of the dimensions of a length, and if it were a universal constant, i. e., the same for all atoms, there would be some standard length occurring either in all the atoms or in the medium surrounding them. In this case, since c would not vary from atom to atom, the frequency of the vibration would be proportional to Q, the positive charge in the atom. Moseley's experiments on the wave-length of the characteristic Röntgen radiation given out by the different elements, if taken in conjunction with the assumption that the positive charge is proportional to the atomic number, show that the frequencies are proportional to the square, and not to the first power of the positive charge. For this reason we must suppose that Q/c is proportional to  $Q^2$ , so that c = c'/Q where c' and not c is a universal constant.

Since c' is of the dimensions of a length multiplied by a charge of electricity, it represents the moment of an electric doublet, and if it is taken as a universal constant we must suppose that electrical doublets with constant moments form a part either of the atoms of all the elements or else of the medium which surrounds them.

We can calculate the value of c or c' if we know the amount of work required to move an electron from one of its positions of equilibrium to an infinite distance from the atom. For we see by equation (2) that if the position of equilibrium of the electron is that corresponding to  $x=\pi/2$ , this work is equal to

$$\left(1-rac{4}{\pi^2}
ight)rac{\mathrm{Q}e}{c},$$

or if the work is expressed as Ve, where V is the potential through which the charge e must fall to acquire this amount of energy,

$$\mathbf{V} = \left(1 - \frac{4}{\pi^2}\right) \frac{\mathbf{Q}}{c}.$$

If we take the ionizing potential as the measure of V, then for the atom of hydrogen V=11 volts, and Q=e, we find, putting  $e=4.7 \times 10^{-10}$ , V=11/300,

$$c = 7.7 \times 10^{-9}$$

and  $c' = c \times Q = 3.6 \times 10^{-18}$ .

Phil. Mag. S. 6. Vol. 37. No. 220. April 1919. 2 H

If we calculate c' from the relation

$$c'=\frac{4}{\pi^4}\,\frac{h^2}{em},$$

we find

$$c' = 3.97 \times 10^{-18};$$

this differs by about 10 per cent. from that calculated from the ionizing potential. The determinations of this potential for the hydrogen atom are hardly definite enough to exclude the possibility of an error of 10 per cent., so that the value  $3.97 \times 10^{-18}$  for c' is admissible. This value would make the numerical constants in the series relation agree with those given by Bohr's theory which give values for the frequencies agreeing with observation.

The ionizing potential is usually measured by the potential difference through which cathode rays must fall to enable

them to ionize the gas.

When, however, the atom is, as we have supposed, the seat of intense magnetic forces, it is possible that the energy which the cathode rays must possess to be able to ionize the gas may not measure the energy which the cathode rays have to give up to an electron to enable it to escape from the atom, but rather the energy which the cathode rays must possess if they are to penetrate far enough into the atom to reach that electron which has to be liberated.

Again, in many cases of ionization by cathode rays, the electrons are ejected with a finite amount of kinetic energy which is independent of that of the cathode rays; when this is so, the ionizing potential is greater than the line integral of the electric force from the initial to the final position of the electron.

When the spectrum of a gas is excited by the impact of cathode rays, the first process which goes on is the ejection of electrons from the atom; this does not, on our view, give rise to radiation corresponding to the series lines in the spectrum. This is due to a second process, the return of electrons to the ionized gas to replace those which have been ejected; these electrons are not the high speed cathode rays but slow speed electrons produced by the ionization of the atoms, and the energy which is converted into radiation is that which these electrons acquire when falling into the positions of equilibrium. From some experiments I have made on the radiation produced by the bombardment of substances by cathode rays, I conclude that by far the larger part of the radiant energy is concentrated in radiation of definite wavelength, for I found that when the energy of the cathode rays was gradually measured the character of the radiation did

not at some stages alter appreciably, while at other stages an increase in the energy of the cathode rays produced considerable increase in the hardness of the radiation. This is what would happen if this radiation were a mixture of definite types (a, b, c, d) .....) of characteristic radiations from the target struck by the cathode rays. The type a not being excited unless the energy of the cathode rays exceeded  $e_1$ , b not being excited unless the energy exceeded  $e_2$ , and so on. Thus, when the energy of the cathode rays was between  $e_1$ and  $e_2$ , the radiation would be confined to the  $\alpha$  type, it would be a mixture of the a and b types as soon as the energy of the cathode rays exceeded  $e_2$ , when it exceeded  $e_3$ the c type of radiation would be added, and so on.

# Number of Waves in a Train of Waves.

When an electron falls into a position of equilibrium and rotates round the lines of magnetic force, the energy it acquires by the fall is gradually converted into radiant energy, and the electron gradually comes to rest.

If f is the acceleration of an electron, the rate at which it

emits energy is

$$\frac{2}{3} \frac{e^2 f^2}{V_0}$$
,

where e is the charge on the electron and  $V_0$  the velocity of light.

If H is the magnetic force, v the velocity of the electron, then when the orbit is at right angles to the magnetic force

$$f = \frac{Hev}{m} = 2\pi nv,$$

where n is the frequency of the vibration of the electrons, when this is governed by the magnetic force. Substituting this value for f, we find that the rate at which energy is emitted from the electron is equal to

$$\frac{8\pi^2}{3V_0}e^2n^2v^2 = \frac{16\pi^2}{3V_0}\frac{e^2n^2}{m}E,$$

where E is the kinetic energy of the electron; hence when the loss of energy by the electron is entirely due to the radiation, we have

$$\frac{d\mathbf{E}}{dt} = \frac{-16\pi^2}{3\mathbf{V}_0} \frac{e^2}{m} n^2 \mathbf{E} = -k\mathbf{E}, \text{ say.}$$

Thus

$$\mathbf{E} = c \boldsymbol{\epsilon}^{-kt}$$
.

Now  $\frac{e}{m} = 1.78 \times 10^{7},$   $e = 1.6 \times 10^{-20},$   $k = 5 \times 10^{-22} n^{2},$ 

hence

and the time taken for the energy to fall to  $1/\epsilon$  of its initial value is  $10^{22}/5n^2$ .

Thus, if the vibrations have the frequency  $5.1 \times 10^{14}$  of the D line in the sodium spectrum, this time is equal to  $7.7 \times 10^{-9}$  seconds, and the length of the train emitted in this time would be about 4 million wave-lengths. If the wavelengths were  $10^{-8}$  cm., about that usually given for the L characteristic Röntgen radiation from platinum, the time

would be  $\frac{1}{4.5 \times 10^{15}}$ , and the train emitted would contain

about 660 wave-lengths. Thus, if the spectral lines arise from the effect of magnetic forces, they may be expected to consist of trains containing a very large number of wave-lengths, the number of wave-lengths being inversely proportional to the frequency of the vibrations.

# Transference of Radiant Energy into Potential or Kinetic Energy.

Let us consider a stream of radiant energy passing through a piece of metal. In consequence of the magnetic fields due to the atoms, there will be in the metal magnetic forces reaching very high values in certain places, and falling to quite low ones in others; and between very wide limits of the magnetic force it will be possible to find places where the magnetic force has any assigned value, if at all such places an electron could be found, a piece of metal would be a system containing vibrators of every possible period within very wide limits.

In a metal it seems very probable that the electrons are not all contained within the atoms themselves, but that some of them are detached, helping by the forces they exert to make the atoms cohere and form a solid body. Unless, then, the position of these detached electrons were exactly coordinated with the intensity of the magnetic field, the effect would be much the same as if these electrons were distributed at random through the magnetic field; and we might expect to find some electrons in places where the magnetic force had, within wide limits, any specified value. A piece of metal would then be a system of the kind we are

considering, possessing vibrators able to respond to any vibrations within a wide range of frequency. Thus, if light of any frequency between these limits were to fall on the metal it would find some electrons whose frequency under the magnetic force at the place where they were situated was the same as its own; these would acquire a high velocity. If an electron is to get free, it must get to a place where the magnetic force vanishes, because, as we can easily prove, the effect of the magnetic field on an electron displaced from a position of equilibrium, is the same as if there were an attraction on the electron to the point equal to Be/m times the displacement of the electron. Suppose that P is a place where the magnetic induction vanishes, and where consequently an electron can get free. Suppose that Q is the place from which the electron to be liberated at P starts. To enable it to get from Q to P it must acquire an amount of energy equal to w, where w is the work required to move an electron against the electric field from Q to P. If it is to acquire this by radiation, it must be by resonance, so that the radiant energy from which it gets it must have the frequency of the free vibrations of the electron at Q. Since the magnetic force vanishes at P this frequency is, by equation (2), equal to w/h. Thus the electron at Q, by absorbing energy of frequency n, can be liberated at P with an amount of Potential Energy equal to hn.

This would produce the well-known photoelectric effects. If Q were to absorb a smaller amount than w of energy from the radiation, it would not get liberated. After the radiation had passed over it this energy would be again radiated by the electron at Q vibrating under the magnetic force at Q with the frequency n. Thus the absorbed radiation would be again radiated as radiation of the same frequency, and there would not be any transformation of energy. For the energy to be transformed, energy equal to w must be given to Q; and since w=hn, we get the result given by the quantum theory that the transference from radiant to potential or kinetic energy takes place by definite quanta each equal to hn.

The explanation of the photoelectric effect assumes the possibility of finding in the metal an electron with a natural frequency n, where n may be any assigned number within a wide range of values. In a complex system like a metal this seems probable; and it is noteworthy that the photoelectric effects are on quite a different scale in metals from what they are in gases; thus Hughes found no trace of ionization when ultra-violet light was totally absorbed by the vapour of zinc ethyl, though when the same light fell on a zinc plate

it excited a stream of electrons a million times greater than that which could have been detected if any had emerged from the vapour. Ultra-violet light of very small wave-length does undoubtedly produce ionization in gases, while one of the most characteristic properties of the Röntgen rays is their power of ionizing gases. We must remember, however, that as the absorption-bands in the ultra-violet of gases like CO<sub>2</sub> and O<sub>2</sub> show, gases may in many regions of the ultraviolet light spectrum be able to give out a spectrum which is continuous over many frequencies, and presumably, therefore, possesses electrons able to vibrate freely over a wide range of frequencies. Again, it is important to remember that the number of atoms ionized is an exceedingly small fraction of the number of atoms in the gas. The number varies, of course, with the intensity of the ionizing radiation; but under ordinary conditions of laboratory work the number of atoms ionized per second is much less than 1/1012 of the number of atoms exposed to the radiation; or, to put it another way, an individual atom would not be ionized nearly so often as once in one hundred thousand years.

Now, in a gas the atoms come into collision and may form temporary associations, and while in this state the natural frequencies are changed by an amount which will vary from one pair of atoms or molecules to another; hence, if we take these pairs into account we shall find in the gas, electrons whose natural frequencies are not merely those of the free atom, but extend continuously over the range of frequencies to be found in the pairs. Thus, as far as range of frequencies of the electron goes, the gas will be on an equality with a piece of metal. It is true that in the gas the number of electrons which can vibrate in what we may call these abnormal frequencies is an exceedingly small fraction of the whole number of electrons; but we have seen that if the electron gets into this state once in a hundred thousand years it will be able to do more than its full share of the ionization in the gas. The effect of proximity of the atoms in increasing the range of frequencies is shown by the enormous broadening of some lines when the pressure of the gas is increased. If we accept the view that in a gas we may expect to find electrons with frequencies varying continuously over a wide range, though the number which have frequencies differing from the normal natural frequencies may be exceedingly small, we may apply to gases the reasoning that we use for the photoelectric effect in metals, and assume, as the result, that the energy in the ejected electron will be proportional to the frequency of the radiation which supplied it with

energy. In other words, that the energy in the corpuscular radiation will be proportional to the frequency of the primary Röntgen radiation; the experiments hitherto made on the expulsion of electrons by Röntgen rays are consistent with this law.

An atom from which an electron has been expelled will be an electron short when it gets free from the atom with which it was temporarily associated, and will be in a condition to give out radiation when an electron falls into it to replace the one that was lost; the atom is now free, so that the vibration it will emit will have the normal frequency, whatever may have been the frequency of the radiation which supplied the energy to eject the electron. Thus the character of the Röntgen radiation excited by the primary radiation will not depend on the nature of the radiation, but solely on the nature of the atom; on the other hand, the nature of the corpuscular radiation will depend solely on the nature of the primary radiation, and not upon the nature of the atom. These conclusions are in accordance with known properties of Röntgen radiation.

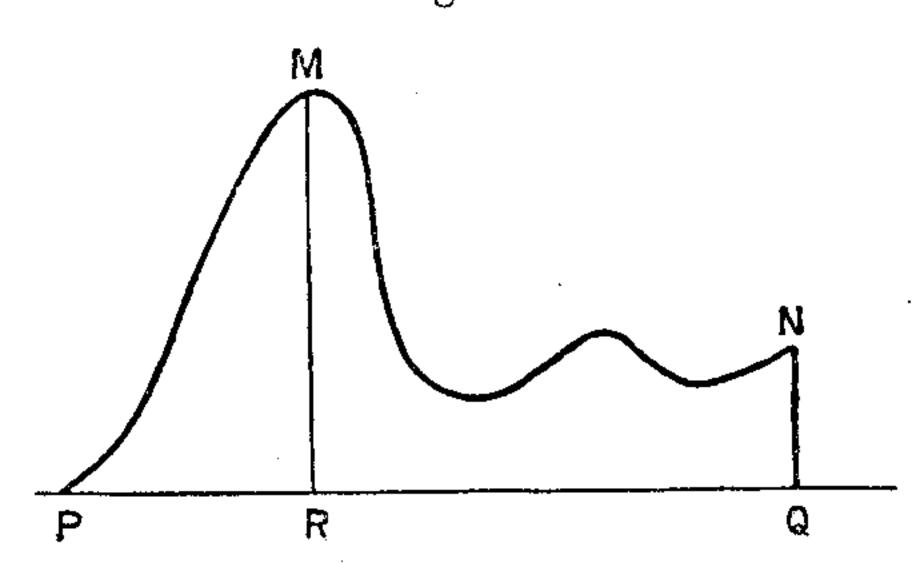
Again, we see that each electron ejected will correspond to one unit of energy of the characteristic radiation of the atom; this will be given out when an electron falls into the atom to replace the one that has been ejected. Thus whatever the energy in the ejected electron, the energy in the corresponding characteristic radiation will be constant.

Now, the energy in the ejected electron increases with the frequency of the rays; hence the ratio of the energy in the corpuscular radiation to that in the characteristic radiation will increase with the hardness of the primary Röntgen radiation. We see, too, that when the frequency of the primary Röntgen radiation is the same as that of the characteristic radiation, the energy in the corpuscular radiation will be equal to that in the characteristic.

We have, in the preceding discussion, neglected the possibility of the high-speed electrons ejected by the Röntgen rays exciting by their impact with the atoms the characteristic radiation of the substance. The justification for this is that in some experiments which I made on the excitation of Röntgen rays by cathode rays I found that the energy of the Röntgen radiation was concentrated in a very soft type of radiation, and that only an exceedingly small fraction of the energy of the cathode rays was transformed into a type of radiation comparable in hardness with that which would excite corpuscular radiation comparable in velocity with that of the cathode rays which produced it.

When the electric force changes from plus to minus, as we have supposed it to do inside the atom, the amount of energy which must be communicated to an electron to enable it to get from one place P to another Q may be greatly in excess of  $\int_{P}^{Q} R ds$ , where R is the force on an electron and ds an element of its path. For the potential distribution may then be represented by a curve such as that in fig. 1, when an electron could not get from P to Q

Fig. 1.



unless it surmounted the peak R. To do this it must receive energy represented by RM, which may be much greater than  $\int_{P}^{Q} R \, ds$ , which is represented by QN. In such a case as this the electron ejected from P will arrive at Q with a finite amount of kinetic energy, measured by the difference between RM and QN.

In a periodically varying electric field of the type we are considering we might expect the maximum value of RM to be approximately twice QN. For the work done between two places of equilibrium is equal to  $B_1-B_2$  when  $B_1$  and  $B_2$  are the values of the magnetic induction at the two places.

Now, if the numerical value of the magnetic force at P is not less than that at any other point nearer the surface of the atom, the greatest possible negative value of B<sub>2</sub> will be —B<sub>1</sub>, and since B<sub>1</sub>, to a rough approximation, varies harmonically, B<sub>2</sub> may be expected to approach this value. Thus B<sub>1</sub>—B<sub>2</sub> will have as its maximum value 2B<sub>1</sub>, i. e. the energy which must be communicated to the electron to enable it to surmount an obstacle like the peak at R is twice the increase in potential energy it gains by going to Q, where B<sub>2</sub> is assumed to vanish. Thus the electron will possess, when it emerges from the atom at Q, kinetic energy equal to half the energy communicated to it at P.

Let us suppose that the atom is being ionized by radiation whose frequency is n, where n is also the frequency of the characteristic radiation of the atom. The ejected electron begins by absorbing an amount of energy equal to 2hn, of this, when it is liberated, it retains as kinetic energy hn—this energy appears as the energy of corpuscular radiation; the other half of the energy appears subsequently as characteristic radiation when an electron drops into the atom to take the place of the one displaced. In this case the energy in the corpuscular radiation is equal to that in the characteristic.

Next suppose that the frequency  $n_1$  of the incident radiation is not the same as n, that of the characteristic radiation. The absorption of energy will take place when the atom has formed a temporary alliance with another atom, of such a kind that the forces between the atoms have altered the frequency of the electron from n to  $n_1$ . The absorption of energy by the electron is now  $2hn_1$ , of this  $hn_1$  appears as the energy of corpuscular radiation, the atom recovering an electron after it has again become free will give out hn units of characteristic radiation; the difference

$$2hn_1 - h(n + n_1) = h(n_1 - n)$$

will be given up to the atoms, making them separate with more energy than they had before they came together, a fraction  $\beta$  of this energy might be converted into slow corpuscular or soft Röntgen radiation.

Thus the ejection of a high-speed electron will be accom-

panied by the following energy effects:

Energy in corpuscular radiation  $=hn_1$ . Energy in characteristic radiation =hn. Energy in soft Röntgen radiation  $=\beta h(n_1-n)$ .

The corpuscular radiation will bear to the characteristic radiation the proportion of  $n_1$  to n and will thus increase indefinitely as  $n_1$  increases. If we include the soft Röntgen radiation with the corpuscular, and in many experiments they would not be distinguished, the ratio of the corpuscular energy to the characteristic energy would be

$$\frac{n_1+\beta(n_1-n)}{n}.$$

The view that when an electron absorbs radiant energy it is a constituent of a system in which it vibrates in unison with the radiation, is not without difficulties. It requires, for example, concentration of the energy of the light-wave in certain places instead of uniform distribution

over the wave front. It has, however, the great advantage that it accounts for the electrical effects produced by light without introducing changes in our conception of light which give rise to difficulties in connexion with ordinary optical effects such as interference or scattering. These would not be affected by the resonance hypothesis.

In favour of this hypothesis may be urged:—

1. That it is an exceedingly minute fraction of the number of atoms or molecules of a substance which plays any part in the electrical effect. Even what is regarded as very intense ionization by Röntgen rays would be produced if on an average each atom got ionized once in some hundred thousand years. So that if each atom were to form a part of a suitable system once in this period it would be all that is required.

2. The number of lines in the spectrum of a substance which are theoretically possible is very large; the electrons have a large number of possible frequencies, each of which would be disturbed by the electric and magnetic forces exerted by a neighbouring atom, so that the frequencies continuously covered by the

system would extend over a wide range. 3. The difficulty of supposing that the influence of two neighbouring atoms of a light element could be so great that the frequency of an electron in one of the atoms could rise to that of the K radiation of a heavy element has been very greatly lessened by some recent researches. Barkla (Phil. Trans. vol. 217. p. 315) has shown that the lighter elements give out a type of radiation much harder than the types previously detected, and that this new type is comparable in hardness with the K type given out by the heavier elements. Again, Shearer (Phil. Mag. xxx. p. 644), who has investigated the ionization of hydrogen by hard Röntgen rays, has shown that the amount of it is, at most, surprisingly small, even when the density of hydrogen is taken into account, and that it is doubtful whether even this small amount is a genuine ionization of hydrogen; the experiments seem to suggest that it was due to a trace of some heavier gas. This is an exceedingly important result, because it shows that the impact of Röntgen rays against an electron does not necessarily communicate very much energy to it, even though there may be a large amount of energy in the rays; it differentiates the action of Röntgen rays from that of either cathode or a-rays.

We have supposed, hitherto, that resonance is obtained by the free periods of the electrons in one atom getting modified by the proximity of another. It is conceivable, however, that the same result might be obtained by processes localized in the atom itself and independent of neighbouring atoms. For the atoms of every substance except hydrogen contain more than one unit positive charge, and if the mass of each positive charge is equal to that of the atom of hydrogen, the number of positive charges will be equal to the atomic weight. If the atom is electrically neutral there must be, somewhere or other inside it, an equal number of electrons; experiment shows, however, that only about half of these are free to exercise any independent effects, the other half must be bound up with the positive charges. If, at long intervals, changes occurred among these positive charges analogous, though on a very much reduced scale, to those which occur in radioactive substances, electrons might be temporarily detached from these charges, though not as in radioactive substances, with such energy as to drive them out of the atom in the form of high-speed \(\beta\)-rays. The displacement of the electrons in the non-radioactive substances would, however, modify the frequency of the vibrations of the electrons in the atom, and would furnish a small supply of atoms whose frequencies differ irregularly from those in the normal atom and which would resonate to vibrations to which the ordinary atom would not respond.

We have supposed that the periods of the oscillations of the electrons are determined solely by the magnetic forces, but even when those forces are predominant the electric forces which accompany them will modify, to some extent, the periods, and may make what, if these are neglected, would correspond to a single line become several lines

separated by very small intervals.

It may, perhaps, be worth pointing out that one objection, often raised against the oscillations being due to electrostatic forces alone, viz. that under such forces, what is primarily given by the equations of motion is the square of the frequency, while the relations given by the series laws relate to the frequency itself and not to its square, does not apply to all types of electrostatic force. If, for example, the force of the positive charge on an electron were represented by  $Ce\frac{d\phi^2}{dr}$ , where C is a constant and  $\phi$  a function of r, then one set of positions of equilibrium would be determined by  $\phi=0$ , and if  $\xi$  is the displacement from one of these positions

the equation of motion is

$$m \frac{d^2 \xi}{dt^2} = -2 \operatorname{Ce} \left\{ \frac{d\phi}{dr} \right\}^2 \xi,$$

where  $\left\{\frac{d\phi}{dr}\right\}$  is the value of  $\frac{d\phi}{dr}$  at the equilibrium position.

The frequency of the oscillation represented by this equation is equal to

$$\left\{\frac{2Ce}{m}\right\}^{\frac{1}{2}}\frac{d\phi}{dr}$$

so that the case resembles that where the oscillations are determined by the magnetic force, inasmuch as the first power of the frequency is given by a simple expression without square roots in the variable part. By taking appropriate values of  $\phi$  we can get series for the frequencies

of the Rydberg type.

When an electron in a magnetic field is acted upon by an electric force, the magnetic forces will deflect it as soon as it gets set in motion, and it will not move along the direction of the electric force. Thus if a plane polarized beam of light in which the electric force is parallel to the axis of xfalls upon the electron, it will originate accelerations parallel to y and z as well as to x. The accelerations parallel to y and z will give rise to scattered waves which will not vanish along the axis of x; now we know that with either visible light or Röntgen rays the light scattered in this direction is in normal cases exceedingly small, so that it is necessary to see if this result is consistent with the existence of strong magnetic forces inside the atom.

Let the electric force in the wave be parallel to x and equal to  $E \cos pt$ . Let  $\xi$ , n,  $\zeta$  be the displacements of an electron parallel to x, y, z and a, b, c the components of the magnetic induction inside the atom; then the equations of motion, if we include an electric restoring force proportional

to the displacement, are

$$\begin{split} \frac{md^2\xi}{dt^2} &= \mathrm{E}e\cos pt - \mu\xi + \frac{ce\ln}{dt} - \frac{bed\zeta}{dt}, \\ \frac{md^2\eta}{dt^2} &= -\mu\eta + \frac{aed\zeta}{dt} - \frac{ced\xi}{dt}, \\ \frac{md^2\zeta}{dt^2} &= -\mu\zeta + \frac{bed\xi}{dt} - \frac{acd\eta}{dt}; \end{split}$$

the solution of these equations when  $\xi$ ,  $\eta$ ,  $\zeta$  vary as  $\epsilon^{pt}$  is

$$\xi = \frac{\text{E}e\cos pt}{\Delta} \{ (\mu - mp^2)^2 - a^2e^2p^2 \},$$

$$\eta = \frac{\text{E}e\cos pt}{\Delta} \{ -abe^2p^2 - \iota cp(\mu - mp^2) \},$$

$$\zeta = \frac{\text{E}e\cos pt}{\Delta} \{ -ace^2p^2 + ibp(\mu - mp^2) \},$$

$$\Delta = (\mu - mp^2)^3 + (\mu - mp^2)e^2(a^2 + b^2 + c^2).$$

where

 $\Delta = (\mu - mp^2)^3 + (\mu - mp^2)e^2(a^2 + b^2 + c^2).$ 

We see from this that the displacements of the electron are not wholly in the direction of the electric force; but from the form of the equations we see that if  $mp^2$  is either very small or very large compared with  $\mu$ , the displacement across the direction of the force is infinitesimal in comparison with that along it. In the theory of scattering of visible light  $mp^2$  is assumed to be small compared with  $\mu$ , while for Röntgen rays it is assumed to be large, so that the magnetic forces would not appreciably affect these types of radiation.

If there are several electrons with their centre of figure at the centre of the atoms, and if the axis of x is a principal axis, then  $\Sigma ab$ ,  $\Sigma ac$ ,  $\Sigma c$ , and  $\Sigma b$  vanish, and the scattered radiation will be in the same direction as that given by the ordinary theory for the non-magnetic atom. The effect of the transverse displacements, if the electrons in one atom were arranged unsymmetrically, so that  $\Sigma ab$ , etc. did not all vanish, would, if all the different atoms were orientated in exactly the same way, produce a rotation of the plane of polarization when plane polarized light passed through the collection of atoms. This effect would, however, disappear if the atoms were orientated at random.

There does not, therefore, appear to be anything in the scattering of light by the atoms of a gas or in the rotation of the plane of polarization of light inconsistent with the existence of a strong magnetic field inside the atom.

#### Scattering of Cathode particles by the Atom.

If the dominant forces inside the atom were magnetic, a charged particle moving through the atom would be deflected, but inasmuch as the force on a moving particle due to its magnetic field is always at right angles to the direction of motion of the particle, the particle would neither lose nor gain energy. The collisions would be what are often called elastic to distinguish them from those in which there is a loss of energy, which are called inelastic.

## 446 Prof. S. D. Wicksell on the Normal Correlation

The experiments of Franck and Hertz show that in some cases, for example, argon and nitrogen, an electron may collide with a very large number of atoms without losing energy, and in cases where the electrons cannot make many collisions before being captured and attached to an atom, the effects seem to be reconcilable with the view that such collisions as occur are elastic, and that the alternatives are capture or escape with undiminished energy.

Since the frequency of vibrations of an electron is proportional to the magnetic force it is evident that it would be affected by an external magnetic field; it would also be affected by an external electric field, since this would displace the position of equilibrium. The consideration of these effects must, however, be left for another occasion.

XXXVII. A General Formula for the Moments of the Normal Correlation Function of any Number of Variates. By S. D. Wicksell, Lund, Sweden\*.

IF  $x_1, x_2, \ldots x_n$  be n variates reckoned from their respective dispersions as units, and  $r_{pq}$  is the coefficient of correlation of  $x_p$  and  $x_q$ , the normal correlation function is given by

$$\phi(x_1, x_2, \dots, x_n) = \frac{1}{(2\pi)^{n/2} \sqrt{S}} e^{-\frac{1}{2S} \Sigma \Sigma S_{pq} x_p x_q}, \qquad (1)$$

where

and

$$S_{pq} = \frac{\partial S}{\partial r_{pq}}.$$

The function  $\phi(x_1, x_2, \ldots, x_n)$  may also be written in the form of a certain multiple integral which will be

Function of any Number of Variates.

447

found to be very useful in discussing the mathematical properties of the function. Indeed we have

$$\phi(x_1, x_2, \dots x_n) = \frac{1}{(2\pi)^n} \int_{-\infty}^{\infty} dw_1 \int_{-\infty}^{\infty} dw_2 \dots$$

$$\int_{-\infty}^{\infty} dw_n e^{-\frac{1}{2}\sum \sum r_{pq} w_p w_q} e^{-i\sum x_p w_p}. \quad (2)$$

This integral, which for n=1 reduces to the well-known integral of Laplace, has been given by Charlier for the special case of n=2. A proof of the theorem for any value of n will be given in the Appendix.

By partial integration it is further easily verified that

$$i^{k_{1}+k_{2}+\cdots+k_{n}} x_{1}^{k_{1}} x_{2}^{k_{2}} \cdots x_{n}^{k_{n}} \phi(x_{1}, x_{2}, \dots x_{n}) = \frac{1}{(2\pi)^{n}} \int_{-\infty}^{\infty} dw_{1} \int_{-\infty}^{\infty} dw_{2} \cdots \int_{-\infty}^{\infty} dw_{n} \frac{\partial^{k_{1}+k_{2}+\cdots+k_{n}} e^{-\frac{1}{2}\sum \sum r_{pq}w_{p}w_{q}}}{\partial w_{1}^{k_{1}} \partial w_{2}^{k_{2}} \cdots \partial w_{n}^{k_{n}}} e^{-i\sum x_{p}^{w} p}.$$
(3)

Hence by the theorem of Fourier we have

$$i^{k_1+k_2+\cdots+k_n} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_n x_1^{k_1} x_2^{k_2} \cdots x_n^{k_n} \phi(x_1, x_2, \dots, x_n) =$$

$$= \left[ \frac{\partial^{k_1+k_2+\cdots+k_n} e^{-\frac{1}{2}\sum \sum r_p q w_p w_q}}{\partial w_1^{k_1} \partial w_2^{k_2} \cdots \partial w_n^{k_n}} \right]_{w_1 = w_2 = \cdots = w_n = 0}$$

Putting

$$\frac{\partial^{k_1+k_2+\dots k_n}e^{-\frac{1}{2}\Sigma\Sigma r_{pq}w_pw_q}}{\partial w_1^{k_1}\partial w_2^{k_2}\dots\partial w_n^{k_n}} = \prod_{\substack{k_1,k_2,\dots k_n \\ k_1,k_2,\dots k_n}} (w_1, w_2, \dots w_n) e^{-\frac{1}{2}\Sigma\Sigma r_{pq}w_pw_q},$$

we find, as

$$\mathbf{H}_{k_1 k_2 \dots k_n}^{(0, 0, \dots, 0)} = 0$$

when  $k_1+k_2+\ldots+k_n$  is an odd number, for the moments of any order of  $\phi(x_1, x_2, \ldots, x_n)$  the formula

$$\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \dots \int_{-\infty}^{\infty} dx_n \, x_1^{k_1} \, x_2^{k_2} \dots \, x_n^{k_n} \, \phi(x_1, x_2, \dots x_n)$$

$$= (-1)^{\frac{k_1 + k_2 + \dots + k_n}{2}} \prod_{k_1 k_2 + \dots + k_n} (0, 0, \dots 0). (4)$$

<sup>\*</sup> Communicated by the Author.