If we assume that the active size is $r=10^{-4}$ cm., then

$$T=300\left(\frac{24}{25}\right)=284^{\circ},$$

i.e., at this temperature, or with a supercooling of 16° C., the solution would crystallize spontaneously.

The theory now described therefore leads to the following properties of supersaturated solutions:—

(1) It is possible for a solution to contain more solute than corresponds with equilibrium in contact with a plane surface of solid solute (*i. e.* large crystals of the latter).

(2) Such a “supersaturated” solution can be in equilibrium with particles of solid of a definite size. Smaller particles dissolve in the solution, larger particles bring about its crystallization.

(3) According as the solid dissolves in its nearly saturated solution with absorption or evolution of heat, the size of “active” particles of solid, *i.e.* such as induce crystallization in a given solution, decreases with fall of temperature, or rise of temperature respectively.

(4) The solution may, at a sufficiently low or high temperature, respectively, crystallize spontaneously.

*V. The Magnetic Field of an Atom in Relation to Theories of Spectral Series. By H. STANLEY ALLEN, M.A., D.Sc.**

IN the course of a discussion on the structure of the atom it was pointed out by the present writer† that it may be necessary to take into account not only the electrostatic, but also the magnetic forces in the neighbourhood of the atom. It was suggested‡ that the atom might be regarded as a central core, carrying an electric charge and producing a magnetic field similar to that due to an elementary magnet, the core being surrounded by electrons in orbital motion. Such a magnetic core might arise from a spherical volume distribution of electricity rotating about a diameter with a specified angular velocity.

One of the most important questions to be considered in connexion with any atomic model is the possibility of explaining the lines in the spectra of the elements, and in particular the relations between the frequencies of the lines

* Communicated by the Author.

† ‘Nature,’ vol. xcii. p. 630 (1914).

‡ ‘Nature,’ vol. xcii. p. 713 (1914). Discussion on the Structure of the Atom, Royal Society, p. 17, March 19, 1914.

in spectral series. Nicholson* has been successful in calculating the frequencies of the lines in the nebular and coronal spectra by employing Rutherford's model involving only electrostatic forces. In these cases, however, only a *simple* nucleus is dealt with. The theory put forward by Bohr† is confessedly not dependent on the usual dynamical laws, although it involves the calculation by ordinary mechanics of the steady motion of the electron in the electrostatic field of the positive nucleus. All the relations that have been obtained between the lines in a spectrum involve the frequency of the vibration. Lord Rayleigh‡ has pointed out that in the case of vibrations under electric or elastic forces it is the square of the frequency that is involved. If, however, the vibrations take place under the action of magnetic forces, the acceleration, instead of being proportional to the displacement, is proportional to the velocity of the moving electrified particle, and relations involving the frequency of the vibration may be obtained. A theory based on this consideration has been put forward by Ritz§. He assumes the existence of molecular magnets, and supposes that the electron is describing a circular orbit in a fixed plane perpendicular to the axis of the magnet. The elementary magnets are the same for all elements. To get the different lines of a series he supposes that a number of the elementary magnets are placed end to end, so that the magnetic field is due to two poles whose distance apart is always some multiple of the length of the elementary magnet. It is a characteristic feature of the theory of Ritz that every spectral line is brought about by the difference of two actions.

Empirical Formulæ for Spectral Series ||.

It will be convenient to summarize here the empirical formulæ that have been suggested to represent the distribution of the lines in a spectral series.

If N denote the wave number (*i. e.* the number of waves in 1 cm.) Balmer's series for hydrogen may be written

$$N = N_0 \left(\frac{1}{4} - \frac{1}{m^2} \right),$$

where N_0 is Rydberg's "universal" constant (usually taken as 109675) and m is a positive integer, 3, 4, 5 ...

* Nicholson, Monthly Notices R. A. S., 1912-1914.

† Bohr, Phil. Mag. xxvi. pp. 1, 476 (1913).

‡ Rayleigh, Phil. Mag. xlv. p. 536 (1897).

§ Ritz, *Ann. der Physik*, xxv. p. 660 (1908).

|| See Baly's 'Spectroscopy,' Chapter xvii., 1912.

If ν denote the frequency of vibration, $\nu = Nc$, where c is the velocity of light, and the formula may be written

$$\nu = \nu_0 \left(\frac{1}{4} - \frac{1}{m^2} \right),$$

where ν_0 has the value 3.29×10^{15} sec.⁻¹. Bohr's theory identifies ν_0 with $2\pi^2 me^4/h^3$, the numerical agreement between the two quantities being remarkable.

In the case of elements other than hydrogen*, more complicated formulæ have been proposed. The typical Rydberg series is of the form

$$N = N_0 \left\{ \frac{1}{(1 + \mu_0)^2} - \frac{1}{(m + \mu)^2} \right\},$$

where μ_0 and μ are fractions. This may conveniently be written

$$N = N_0 \left\{ \frac{1}{D_0^2} - \frac{1}{D^2} \right\}.$$

Rydberg states that the true formula should be given by writing for D some function of $m + \mu$, say $m + \mu + \frac{\alpha}{m + \mu}$. In commenting on this Hicks makes the following significant statement:—

“If a series is represented by $D = m + \mu + \frac{\alpha}{m + \mu}$ a slight alteration will represent it equally well by putting D a continued fraction, viz.

$$D = m + \mu + \frac{\alpha}{m + \mu + \frac{\alpha}{m + \mu + \dots}},$$

in other words,

$$\frac{N_0}{D^2} - \frac{N_0}{\alpha^2} \left[\sqrt{\left\{ \left(\frac{m + \mu}{2} \right)^2 + \alpha \right\}} - \frac{m + \mu}{2} \right]^2,$$

or
$$N = A - B \{ \sqrt{(m^2 + 2am + b)} - (m + a) \}^2,$$

which looks quite different, and points to the frequencies depending on the roots of a quadratic”†.

* Curtis (Proc. Roy. Soc. vol. xc. p. 605, 1914) finds that the results for hydrogen may be represented by a modified Rydberg formula.

† Hicks, Phil. Trans. vol. ccx. p. 85 (1910). The notation of the original has been slightly modified.

Ritz* has obtained remarkable agreement between the observed and the calculated results by taking

$$D = m + \mu + \beta/m^2 \quad \text{or} \quad D = m + \mu + \frac{\beta}{(m + \mu)^2}.$$

Several investigators have made use of the form suggested by Moggendorf and Hicks, in which

$$D = m + \mu + \alpha/m.$$

The value of the expression N_0/D^2 for integral values of m has been called a sequence. Four sequences exist, and it has been shown by Hicks, van Lohuizen†, and others that the majority of the lines in spectral series can be determined by the difference between two sequences.

*The Magnetic Field of the Atom in the Quantum
Theory of Spectral Series.*

In a letter to 'Nature' (vol. xcii. p. 630, 1914) I have drawn attention to the important work of Professor Carl Størmer on the path of an electron in the magnetic field of an elementary magnet. He has investigated the motion of an electron when it is subject to the action of a central force varying inversely as the square of the distance from the centre of the magnet. Such a case would arise if the atom consisted of a magnetic core, electrically charged and surrounded by one or more electrons. Størmer finds certain remarkable periodic trajectories in the form of a circle whose plane is perpendicular to the axis of the magnet, and whose centre is at some point on that axis. If this point coincide with the centre of the magnet we obtain circular orbits in the equatorial plane of the magnet. Further there are other trajectories which never get outside closed toroidal spaces, in the case of stability, or which approach asymptotically the circle in question in the case of instability.

Let the magnetic moment of the core, considered as an elementary magnet, be M and its positive charge be E , electrostatic units being employed throughout. The equation of motion of an electron (charge e , mass m) moving, with angular velocity ω , in a circular orbit of radius r in the equatorial plane is

$$m r^3 \omega^2 = M e \omega + E e. \quad . \quad . \quad . \quad . \quad (1)$$

It must be noticed that there are two possible directions

* Ritz, *Phys. Zeitschr.* vol. iv. p. 406 (1903); vol. ix. pp. 244, 521 (1908).

† van Lohuizen, *Science Abstracts*, vol. xvi. no. 179 (1913).

of motion of the electron in its circular path, in the one the mechanical force due to the movement in the magnetic field is directed towards the centre, in the other away from it. These may both be included in the formula by supposing that M may be either positive or negative, the positive sign being taken when the mechanical force is directed towards the centre.

This equation is not in itself sufficient to specify the motion completely. "There is but one equation of motion, the radial one, while there are two independent variables, the speed and the radius of the orbit" (Schott, 'Electromagnetic Radiation'). In order to obtain a second equation we assume that the angular momentum can be expressed in the form

$$mr^2\omega = \tau h/2\pi, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where h is Planck's constant, and τ is a coefficient whose value is not for the present specified.

On eliminating r by means of equations (1) and (2) we obtain a quadratic equation for ω , which may be written

$$(M\omega + E)^2 = A\omega,$$

$$\text{or} \quad M^2\omega^2 - \omega(A - 2ME) + E^2 = 0, \quad . \quad . \quad . \quad (3)$$

where $A = \frac{\tau^3 h^3}{8\pi^3 m e^2}$.

Remembering that M may be either positive or negative, we see that there are in general four possible values for ω and four corresponding frequencies ν , since $\omega = 2\pi\nu$.

If we divide equation (1) by the square of equation (2) we obtain the value of $\frac{1}{r}$ in the form

$$\frac{1}{r} = \frac{4\pi^2 m}{\tau^2 h^2} (M\omega + Ee),$$

or approximately, when the effect of the magnetic field is neglected,

$$\frac{1}{r} = \frac{4\pi^2 m Ee}{\tau^2 h^2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As in Bohr's theory we consider next the work that is required to move the electron from its orbit to a position of rest at infinity. Denoting this quantity by W , we find, assuming the mass of the core large and the effect of other electrons negligible,

$$W = \frac{Ee}{r} - \frac{1}{2}mr^2\omega^2. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In Bohr's theory W is capable of being expressed by the equation

$$W = \frac{\sigma h \omega}{4\pi},$$

where σ is an integer.

Let us now put

$$\begin{aligned} U &= W + \frac{Me\omega}{r} \quad . \quad . \quad . \quad . \quad . \quad (6) \\ &= \frac{Ee}{r} - \frac{1}{2}mr^2\omega^2 + \frac{Me\omega}{r}. \end{aligned}$$

Then by means of (1) we find that U reduces to $\frac{1}{2}mr^2\omega^2$, which is the kinetic energy of the electron.

Making use of (2) we see that

$$U = \frac{\tau h \omega}{4\pi} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

When there is no magnetic field present τ and σ become identical and $U = W$. In the presence of the magnetic field we have to take into account the small term $Me\omega/r$. We proceed to find the approximate relation between τ and σ in this case.

Combining (6) and (7) we find

$$\begin{aligned} \frac{\tau h \omega}{4\pi} &= \frac{\sigma h \omega}{4\pi} + \frac{Me\omega}{r} \\ &= \frac{\sigma h \omega}{4\pi} + \frac{4\pi^2 m M E e^2 \omega}{\tau^2 h^2}. \end{aligned}$$

Hence

$$\tau = \sigma + \frac{16\pi^3 m M E e^2}{\tau^2 h^3}, \quad . \quad . \quad . \quad . \quad (8)$$

or, approximately,

$$\begin{aligned} \tau &= \sigma + \frac{16\pi^3 m M E e^2}{\sigma^2 h^3} \\ &= \sigma + \frac{\delta}{\sigma^2}, \quad . \quad . \quad . \quad . \quad . \quad (9) \end{aligned}$$

where

$$\delta = \frac{16\pi^3 m M E e^2}{h^3}.$$

The value of W may be expressed in a form more convenient for our purpose as follows :

$$\begin{aligned} W &= \frac{\sigma h \omega}{4\pi} \\ &= \frac{\sigma h}{4\pi A} (M\omega + E)^2 \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

Substituting the value of ω derived from the quadratic equation (3) we find

$$W = \frac{2\pi^2 me^2 E^2 \sigma}{\tau^3 h^2} \left[\frac{A}{2ME} \pm \sqrt{\left(\frac{A}{2ME}\right)^2 - \frac{A}{ME}} \right]^2. \quad (11)$$

We now proceed to express the quantity inside the square bracket, which may be denoted by x , as a continued fraction of the form $x = \frac{1}{a + \frac{1}{b + \frac{1}{a + \dots}}}$.

Since $x = \frac{1}{a + \frac{1}{b + x}}$, x is the root of the quadratic equation $ax^2 + abx - b = 0$, and therefore

$$x = -\frac{b}{2a} \pm \sqrt{\left(\frac{b}{2a}\right)^2 + \frac{b}{a}}.$$

So we find $a = 1$ and $b = -\frac{A}{ME}$.

Hence

$$W = \frac{2\pi^2 me^2 E^2 \sigma}{\tau^3 h^2} \frac{1}{\left[1 + \frac{1}{-\frac{A}{ME} + \dots} \right]^2}, \quad (12)$$

or approximately

$$W = \frac{2\pi^2 me^2 E^2 \sigma}{\tau^3 h^2} \frac{1}{\left[1 - \frac{ME}{A} \right]^2} \dots \dots \dots (13)$$

An examination of the numerical magnitude of the quantities involved in the term ME/A shows that in general the value of this term must be less than unity.

In Bohr's theory monochromatic radiation is supposed to be emitted during the passage from one steady state of motion of the electron to another. How this change takes place is left undetermined, but it is assumed that the amount of energy radiated, that is the difference between the energy in the first orbit and that in the second, is exactly one quantum. That is

$$h\nu = \delta W = W_2 - W_1. \quad (14)$$

The frequency of the radiation is therefore given by

$$\nu = \frac{2\pi^2 me^2 E^2}{h^3} \left\{ \frac{\sigma_2 x_2^2}{\tau_2^3} - \frac{\sigma_1 x_1^2}{\tau_1^3} \right\}, \quad (15)$$

or approximately

$$\nu = \frac{2\pi^2 me^2 E^2}{h^3} \left\{ \frac{\sigma_2}{\tau_2^3 \left[1 - \frac{ME}{A_2} \right]^2} - \frac{\sigma_1}{\tau_1^3 \left[1 - \frac{ME}{A_1} \right]^2} \right\}. \quad (16)$$

Substituting the value of τ in terms of σ previously obtained, we find that the frequency is given by the approximate formula

$$\nu = \frac{2\pi^2 me^2 E^2}{h^3} \left\{ \frac{1}{\left[\sigma_2 + \frac{B}{\sigma_2^2} \right]^2} - \frac{1}{\left[\sigma_1 + \frac{B}{\sigma_1^2} \right]^2} \right\}, \quad (17)$$

where

$$B = -\frac{8\pi^3 m M E e^2}{h^3} + \frac{3\delta}{2} = \frac{16\pi^3 m M E e^2}{h^3} = \delta.$$

We may note that equation (17) is equivalent to

$$\nu = \frac{2\pi^2 me^2 E^2}{h^3} \left\{ \frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right\}. \quad (18)$$

The formula proposed by Ritz to represent spectral series may be written

$$\nu = \nu_0 \left\{ \frac{1}{D_2^2} - \frac{1}{D_1^2} \right\}, \quad (19)$$

where D is of the form $m + \mu + \beta/m^2$ or $m + \mu + \beta/(m + \mu)^2$, and ν_0 is the frequency corresponding to Rydberg's constant.

When $E = e$, that is when the core carries a charge equivalent to the loss of one electron, the factor outside the bracket in equation (17) reduces to $2\pi^2 me^4/h^3$, which Bohr identifies with ν_0 . The bracket becomes identical in form with that in the formula of Ritz if we take $\sigma = m + \mu$ and $\delta = \beta$.

This implies that σ , instead of being an exact integer (m), as in Bohr's theory, is equal to an integer plus a certain fractional quantity μ , which depends on the element and on the particular series considered. The presence of this fractional part must be assumed; it is not explained by the action of magnetic forces.

We conclude that, on the assumptions stated, we can account for the existence of four sequences in spectral series, the denominator of each sequence being of the form proposed by Ritz, and we can determine the lines in a spectral series by the difference between two sequences.

When, however, we examine the numerical value of the constant β as given by Ritz, we find that the values obtained for the magnetic moment M by identifying Ritz's constant with the δ of our analysis are many times too large to be possible. Thus taking for illustration the case of lithium, Ritz gives for β in the principal series the value 0.0257, which would correspond with $M = 4.5 \times 10^{-18}$ E.M.U. The magnetic moment of the magneton is 1.854×10^{-21} E.M.U.

Thus the core of the lithium atom would have to be equivalent to about 2500 magnetons ! We are forced to the conclusion that the magnetic field can be responsible for only a small part of the term in question. The assumptions that we have been compelled to make as to the constitution of the atom, namely, that the magnetic field may be regarded as equivalent to that set up by an elementary magnet and that the electrostatic field may be treated as varying inversely as the square of the distance from the centre, involve so much simplification that we can hardly expect the result to do more than point the way towards the correct form for the expression D in the denominator of a sequence. If, for example, we treat the core of the atom as a positive nucleus surrounded by a continuous ring of negative electricity, analysis shows that the electrostatic field gives rise to a term in the expression D of the same form as δ/σ^2 . Thus in the case of an element containing a large number of electrons, it may be possible to obtain an approximate formula which would agree with that proposed by Ritz (or perhaps that proposed by Hicks), but in the case of elements like helium and lithium, which contain only a few electrons, the difficulties in the way of Bohr's theory put forward by Nicholson* still remain serious if not insuperable.

The general conclusion that may be drawn from the present work is that the magnetic forces set up by the atom, though they may play a part in controlling and perhaps stabilising the motion of the electrons, are insufficient to account for more than a small fraction of the effect that would be necessary to give the observed distribution of lines in spectral series.

Summary.

It is shown that a formula, similar to that of Ritz, representing the distribution of lines in spectral series can be deduced from the assumptions following :—

(1) The core of an atom gives rise not only to an electrostatic field varying inversely as the square of the distance from the centre, but also to a magnetic field such as would be set up by an elementary magnet.

(2) The steady states of motion of an electron in the field of the atom are determined by the ordinary laws of electrodynamics, combined with specified assumptions as to the angular momentum and the energy of the electron.

(3) The energy of the radiation, as in Bohr's theory, is

* Nicholson, *Phil. Mag.* vol. xxviii. p. 90 (1914).

given out in quanta, which represent the differences between the energies in two steady states of motion.

When, however, the numerical value of the appropriate constants in the formula of Ritz is considered, it is found that the magnetic forces set up by the atom are not in themselves sufficient to account for more than a small fraction of the effect that would be necessary to give the observed distribution of lines in spectral series.

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VI. *On the Motion of the Lorentz Electron.* By G. A. SCHOTT, B.A., D.Sc., Professor of Applied Mathematics, University College of Wales, Aberystwyth*.

DURING a theoretical investigation of the origin of X-rays I found it necessary to take into account the effect on the motion of the electron of the reaction due to its own radiation, and from this point of view examined some simple cases of motion in order to gain a clear idea of the result to be expected. The following communication includes these preliminary studies, but is also intended to serve as an introduction to a more complete investigation to be published later.

The Equations of Motion and Energy of the Electron.

1. The vector-equation of motion of the electron may be written in the following form†

$$\dot{\mathbf{G}} - \mathbf{K} = \mathbf{F} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$G = \frac{mV}{\sqrt{(1-\beta^2)}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathbf{K} = \frac{2e^2 \ddot{\mathbf{v}}}{3c(c^2 - v^2)} + \frac{2e^2 (\mathbf{v} \ddot{\mathbf{v}}) \mathbf{v}}{3c(c^2 - v^2)^2} + \frac{2e^2 (\mathbf{v} \dot{\mathbf{v}}) \dot{\mathbf{v}}}{c(c^2 - v^2)^2} + \frac{2e^2 (\mathbf{v} \dot{\mathbf{v}})^2 \mathbf{v}}{c(c^2 - v^2)^3}. \quad (3)$$

$\mathbf{G}$ denotes the electromagnetic momentum of the electron in the form due to Lorentz, $\mathbf{K}$ the reaction due to radiation, *i. e.* the radiation pressure in the form due to Abraham[†], and $\mathbf{F}$ the external mechanical force. If we accept the Principle of Relativity for accelerated as well as for uniform

* Communicated by the Author.

† Schott, 'Electromagnetic Radiation,' pp. 175, 176, 246 (quoted below as E. R.).

† Abraham, *Theorie der Elektrizität*, ii. p. 123.