



XLIII. The mechanism of radiation

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XLIII. *The Mechanism of Radiation.* By J. H. JEANS, B.A.,
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Introduction.

§ 1. THIS paper attempts to give a consistent interpretation of a certain class of phenomena by referring them all to the same hypothetical view as to the structure of matter. As the result of some work on the kinetic theory of gases the author was led, rightly or wrongly, to the conclusion that the kinetic-theory phenomena of matter compel us to attribute certain definite properties to the molecules of which matter is composed. The range of view as to the structure of matter could, it was found, be still further narrowed by the help of certain optical phenomena. It was then of interest to examine to what extent the view arrived at in this way was capable of giving an account of the remaining phenomena, and how it compared in this respect with other views as to the structure of matter.

To this end, several hypotheses as to the structure of matter were examined by the present writer, and it seemed to him that the one which is put forward in this paper was much more capable of giving an account of the phenomena in question than were any of the others tested by him. For the sake of brevity, it has been thought advisable to remove the scaffolding, by the help of which the theory of the present paper has been formed, and simply to submit for

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judgment the view ultimately arrived at, together with the account of the phenomena of matter to which it leads, in so far as it has been found possible to examine these phenomena.

The theory will not, it is hoped, be judged as an attempt to attain to ultimate truth. At most the author hopes that by attempting a definite and consistent hypothetical interpretation of certain phenomena, some kind of clue may be suggested as to the real significance of these phenomena, and perhaps something of the nature of a foreshadowing of the real truth arrived at.

Analytical Expression for the Radiation from a Gas.

§ 2. It will be best to begin by a consideration of the general question of spectroscopy.

We shall suppose the radiation emitted by a gas to be the aggregate of contributions from a great number of similar vibrators. Each of these vibrators will be supposed to be capable of vibrating with certain definite frequencies of vibration, and the disturbances of the æther which are set up by these vibrations constitute the radiation.

Let us, in the first place, consider only the radiation propagated along a certain line of sight, say the axis of x , and polarized in a certain plane, say that of xy . If the vibrator were at rest in space, this radiation might be represented, so long as the vibrator was undisturbed by collisions, by

$$A \cos (pt + \epsilon),$$

in which A and ϵ would be constants, which would, in general, depend upon the orientation of the vibrator.

If, however, the vibrator is rotating with an angular velocity w about some axis fixed in space, the above expression will no longer represent the radiation in question. This radiation may, however, be represented by

$$A \cos pt + B \sin pt,$$

where A , B are themselves periodic functions of the time, of period $2\pi/w$.

If we expand A and B in Fourier-series, the foregoing expression can be at once expressed as a series of simply harmonic terms of frequencies

$$p, \quad p \pm w, \quad p \pm 2w, \quad \dots \text{ \&c.}$$

Suppose, to take a particular case, that the vibrator is an electrical doublet of strength $A \cos pt$, rotating about a fixed axis with angular velocity w , the axis of the doublet always

making a constant angle with this line. The direction-cosines of the axis of the doublet at time t are each of the form

$$a + b \cos (wt + \eta),$$

so that the component of the doublet along any axis is of the form

$$A (a + b \cos (wt + \eta)) \cos pt,$$

and this may be replaced by three simply harmonic doublets of frequency

$$p-w, \quad p, \quad p+w$$

Hence the radiation in question may be represented by three simple harmonic terms of frequencies

$$p-w, \quad p, \quad p+w.$$

Analysed in a spectroscope, this radiation will show bright lines at the points corresponding to the frequencies p , $p \pm w$, and (in the more general case) $p \pm 2w$, &c. In adding up the radiation from all the vibrators, we must suppose w to vary as we pass from vibrator to vibrator, so that the whole radiation may be supposed to consist of two parts.

(α) A bright line at the point of the spectrum corresponding to the frequency p .

(β) A band of light, symmetrical about the point p , and of which the width depends upon the mean rotation of the vibrators.

§ 3. The complete spectrum is, of course, found by adding up the radiation corresponding to every degree of vibratory freedom. The condition that the resulting spectrum shall be a pure line-spectrum, is that that part of the spectrum which has just been denoted by β shall be imperceptible. This condition can be fulfilled in two different ways:—

(i.) The intensity of the bands of light may be very small in comparison with the intensity of the bright lines.

(ii.) The breadth of these bands may be so small that they are indistinguishable from the lines.

§ 4. Let us begin by the consideration of the former alternative. The aggregate brightness of a band bears to that of a line a ratio comparable with unity except when the radiation emitted by a vibrator is approximately the same in all directions. Now spherical symmetry of this kind would be at variance with the fundamental suppositions of the undulatory theory, for spherical symmetry could only be obtained by supposing the radiation to be specified by a single vector, and this vector to be radial at every point; whereas the undulatory theory is such that two vectors are required

to specify the radiation, and these vectors, being perpendicular to one another, cannot coincide in direction.

§ 5. We fall back, therefore, upon the second alternative, and inquire what is the condition that the bands shall be so narrow as to be indistinguishable from the lines. The condition is obviously that the mean value of w shall be very small in comparison with p .

Now in the case of a molecule of a gas, the mean energy of rotation about a principal axis which is not an axis of symmetry is equal to one-third of the mean energy of translation. If k_1 , w_1 are the radius of gyration and the rotation about such an axis,

$$\kappa_1^2 w_1^2 = \frac{1}{3} c^2,$$

where c is the velocity of translation, and mean values are taken on each side of the equation. We therefore find that the mean value of w is of the order of c/κ . If, in c.g.s. units, we take $c = 5 \times 10^4$, and $2\kappa = 10^{-9}$, we get $w = 10^{14}$.

The value of p is of the order of 3×10^{15} , so that in this case p and w are of the same order of magnitude, and the bands of the spectrum cannot be so narrow as to be indistinguishable from lines. This shows that the vibrator, at any rate in the case of a gas emitting a line-spectrum, is not identical with the molecule.

§ 6. An exception, however, occurs in the case of monatomic gases, and this seems to supply the key to the situation. In a monatomic gas the energy of rotation is known to be very small in comparison with the energy of translation, so that, in our notation, w is small compared with p . We should therefore expect a monatomic gas to emit a pure line-spectrum.

In general, the condition that w shall be small in comparison with p is, that the rotating body shall be so nearly spherical in shape that the rotation never attains to a value comparable with that which the Boltzmann law of the partition of energy would assign to it. In this case, the energy of rotation is proportional to what has been, in a former paper*, designated as a "subsidiary" temperature. This temperature is given by an equation of the form †

$$\tau = \rho f(T),$$

where τ is the subsidiary temperature, proportional to the mean value of w^2 , ρ is the density of the gas, and $f(T)$ is a function of the temperature of the gas, of which the value is very small.

* "Distribution of Molecular Energy," Phil. Trans. cxcvi. p. 397.

† *l. c.* § 30.

§ 7. We are therefore driven to the conclusion that the vibrators by which radiation possessing a line-spectrum is emitted, must behave like the molecules of a monatomic gas. In other words, we are led to suppose that a line-spectrum is emitted only by the dissociated atoms of a gas and not by the complete molecules, and, further, that these dissociated atoms must be spherically symmetrical.

§ 8. On this view, we can see why it is that pure line-spectra are emitted only by elements, and not by compounds. We can also understand why a gas raised to incandescence by mere heating emits a continuous and not a line-spectrum: the vibrations must be those of complete molecules, not of dissociated atoms. The same substance placed in a flame emits its line-spectrum at a temperature lower than that at which it first becomes luminous if merely heated. Hence the dissociation and radiation which occur when a substance is placed in a flame, cannot be merely the result of the temperature of the flame: they must be produced by chemical action, a view originally put forward by Pringsheim*.

The faint continuous spectrum which is often seen to accompany a line-spectrum must be supposed to proceed from undissociated molecules.

We have incidentally found a factor tending to increase the width of the lines, namely, the rotation of the atoms by which these lines are emitted. We must, however, consider this question at greater length in a later section (§ 34).

The Electrical Structure of an Atom.

§ 9. Let us now leave this train of thought altogether, and regard an atom as a collection of negative and positive ions, the negative ions each carrying a charge of electricity of amount $-e$, and the positive ions each carrying a charge $+e$.

The conception of an atom which we are tempted to adopt at first sight, is that of a collection of point charges of positive and negative electricity, these charges repelling or attracting according to the law of the inverse square of the distance. These point charges would be supposed to settle into a position of stable equilibrium, and the oscillations about this position might be supposed to be the vibrations of definite period which result in the emission of a line-spectrum.

Against this very simple conception of an atom there is one fatal objection: Earnshaw's theorem shows that no position

* Wied. *Ann.* xlvi. p. 428; xlix. p. 347. On the luminosity produced by heating, see J. Evershed, *Phil. Mag.* xxxix. p. 460; A. Smithells, *Phil. Mag.* xxxvii. p. 245, and xxxix. p. 122; A. Paschen, *Wied. Ann.* l. p. 409.

of stable equilibrium exists. It is not hard to see that positive and negative charges would rush together and annihilate one another until there would be nothing left to distinguish the point at which a body ought to be from a point in empty space. In fact a consideration of the physical "dimensions" of the quantities concerned, will show that there could be nothing to determine the linear scale of the atom*.

§ 10. An escape from this dilemma is for the moment made possible by supposing the stability of an atom to be kinetic rather than statical, but this seems (to the present author at least) to lead to a new and apparently insurmountable difficulty. There will be an infinite number of steady motions possible, and a different series of vibrations will be possible about each state of steady motion. The periods of the vibrations, then, will not form a spectrum of disconnected lines, but of continuous bands. We cannot suppose the ions in an atom to be oscillating about a state of steady motion which is the same for all atoms, for even if the atoms were once arranged in this special state, they would rapidly depart from it under the influence of collisions. To explain the line-spectrum of an element, it would be necessary to suppose that the vibrations by which it was produced were not vibrations of the ions as rigid bodies, but vibrations internal to the ions, and, moreover, vibrations which do not depend on the configuration of ions in the atom. If this is the true account of the origin of the line-spectrum, it is very hard to see why the spectra of different elements are not all the same. Further, the ratio of the charge of an ion to its mass, which is deduced from the magnitude of the Zeeman effect, on the assumption that the spectral lines arise from bodily vibrations of the negative ions, is in close agreement with the actual value of this ratio; and this fact supplies a powerful argument against supposing that the lines of the visible spectrum arise from vibrations of units smaller than the negative ion.

§ 11. A second way of escape from the dilemma of § 9 is opened by supposing that the ions are not strict point charges, but that in some sense they possess size. In this case the law of force will not be that of the inverse square at all distances. The law of the inverse square will require correction at distances comparable with the size of an ion, so that two ions of opposite charge will not necessarily rush together and annihilate one another, and the objection of § 9 falls through.

For this explanation to hold, it is necessary that two ions should repel one another at very small distances, independently of their sign, and this shows that the force cannot be proportional simply to the product of their charges.

* Cf. Larmor, *Æther and Matter*, § 122.

Instead of supposing the complete potential-function to be

$$\frac{ee'}{r},$$

we are compelled to suppose it to be of the form

$$ee'\psi_1(r) + mm'\psi_2(r),$$

where ee' are the charges, and mm' the masses of the two ions*. When $r=0$, we must have

$$\psi_2(r) = \infty, \quad \text{and} \quad \psi_2(r)/\psi_1(r) = \infty.$$

When r is very great we must have, in the limit,

$$\psi_1(r) = r^{-1}, \quad \psi_2(r) = 0 \dagger.$$

This complete potential-function must necessarily contain a reference to some fixed length or lengths‡, and this will determine the scale of the atom. Let us suppose the potential-function to be such that some stable configurations of ions exist, and examine the consequences of regarding such a configuration of ions as our picture of an atom. Seeing that there are several hundreds of ions in an atom§, we should naturally expect the configuration of stable equilibrium to be such that the shape of the atom is very approximately spherical, and this conclusion agrees with the result already reached in § 7.

The Equations of Small Displacements of the Ideal Atom.

§ 12. To determine the positions of equilibrium and the vibrations about these positions, for a dynamical system consisting of a large number of ions, is obviously impracticable. It is, however, known that the number of ions in an atom is very large, so that we shall attack the problem in the simple case of an "ideal" atom in which the ions are supposed to be so small that the number in an atom may be regarded as infinite. After the investigation it will be shown how it is possible to obtain an approximate knowledge of the spectrum

* For ions such as we are now considering $e = \pm e'$ and $m = m'$. I have, however, stated the law in general terms.

† In an exhaustive treatment of æther-force, $\psi_2(r)$ would probably be identical with the gravitational potential, but for our present purpose gravitational forces may be disregarded.

‡ *E.g.* we might have as the potential-function

$$ee' \frac{1}{r} + mm' \frac{a}{r^2},$$

and a might be referred to as the "size" of the ion.

§ Roughly, 700 in the hydrogen atom, and for other elements in proportion to the atomic weights of the elements. We here suppose the mass of the atom to consist solely of the masses of ions of which it is composed. See J. J. Thomson, *Phil. Mag.* vol. xlvi. p. 547, and earlier papers.

of an atom which consists of a number of ions which is very great but is not infinite.

The ideal atom is to consist of a continuous distribution of electricity of density ρ . The corresponding density of matter is to be σ , so that it will ultimately be necessary to put $\sigma/\rho = \pm m/e$, where m/e is the ratio of the mass to the charge, in the case of the negative ions of the cathode rays. For the present, however, ρ and σ will be regarded as capable of independent variation. To correspond with the condition of spherical symmetry for the actual atom, it will be assumed that the distribution is arranged in spherical symmetry about some centre, so that both ρ and σ will be functions of the single coordinate r , the distance from the centre.

When the atom is at rest, every element is supposed to act on every other element with a force which acts along the line joining the two elements. The mutual potential of two elements at distance r and of volumes $dv dv'$ will be supposed to be

$$\{\rho\rho'\chi_1(r) + \sigma\sigma'\chi_2(r)\}dv dv',$$

and for large values of r this must reduce to $\rho\rho'r^{-1}dv dv'$.

When the atom is executing a small vibration, the forces may be supposed to be the same as if the atom were at rest in the displaced configuration. For in the case of a vibration of infinitesimal amplitude, the electromagnetic forces will vanish in comparison with the electrostatic, and it is easily verified that the velocity of propagation may, without appreciable error, be treated as infinite*.

§ 13. Let the whole atom undergo a small continuous displacement, so that the element of which the spherical polar coordinates before displacement were r, θ, ϕ is moved to $r+u, \theta+v, \phi+w$. In rectangular coordinates, which it will be convenient to use in conjunction with polars, let the element initially at x, y, z be displaced to $x+\xi, y+\eta, z+\zeta$.

Consider, in the first place, the field of force arising from the term $\chi_1(r)$ in the potential-function. The displacement of the element $\rho' dx' dy' dz'$ is equivalent to the creation of a doublet of moment

$$(\xi' \rho' dx' dy' dz', \eta' \rho' dx' dy' dz', \zeta' \rho' dx' dy' dz').$$

Hence the potential per unit charge, upon the element originally at x, y, z , but now at $x+\xi, y+\eta, z+\zeta$, which arises from the displacement of the foregoing element, will be

$$\rho' dx' dy' dz' \left\{ (\xi' - \xi) \frac{\partial}{\partial x'} + (\eta' - \eta) \frac{\partial}{\partial y'} + (\zeta' - \zeta) \frac{\partial}{\partial z'} \right\} \chi_1(R)$$

where $R^2 = (x-x')^2 + (y-y')^2 + (z-z')^2$.

* Larmor, Camb. Phil. Trans. xviii. p. 391.

The potential arising from the displacement of the whole atom will therefore be

$$E = \iiint \left\{ (\xi' - \xi) \frac{\partial}{\partial x'} + (\eta' - \eta) \frac{\partial}{\partial y'} + (\zeta' - \zeta) \frac{\partial}{\partial z'} \right\} \chi_1(\mathbf{R}) \rho' dx' dy' dz'.$$

The integration extends over the whole atom, but it will be convenient to take the integration throughout all space, writing $\rho = 0$ at points outside the atom.

This potential may be at once transformed, so that we obtain

$$E = - \iiint \left\{ \frac{\partial}{\partial x'} (\xi' \rho') + \frac{\partial}{\partial y'} (\eta' \rho') + \frac{\partial}{\partial z'} (\zeta' \rho') \right\} \chi_1(\mathbf{R}) dx' dy' dz',$$

$$+ \left(\xi \frac{\partial}{\partial x} + \eta \frac{\partial}{\partial y} + \zeta \frac{\partial}{\partial z} \right) \iiint \chi_1(\mathbf{R}) \rho' dx' dy' dz'.$$

Returning to polar coordinates, we can write $E = E_1 + E_2$, where

$$E_1 = - \iiint \left\{ \frac{\partial}{r'^2 \partial r'} (r'^2 u' \rho') + \frac{\partial}{\sin \theta' \partial \theta'} (v' \rho' \sin \theta') + \frac{\partial}{\partial \phi'} (w' \rho') \right\} \chi_1(\mathbf{R})$$

$$r'^2 \sin \theta' dr' d\theta' d\phi'.$$

$$E_2 = \left(u \frac{\partial}{\partial r} + v \frac{\partial}{\partial \theta} + w \frac{\partial}{\partial \phi} \right) \iiint \chi_1(\mathbf{R}) \rho' r'^2 \sin \theta' dr' d\theta' d\phi'.$$

For any displacement which is continuous at the poles, $v/\sin \theta$ must be finite at both poles, and we may therefore assume expansions in the form

$$u = \sum \sum \alpha_n^m P_n^m(\mu) e^{im\phi}$$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (v \sin \theta) = \sum \sum \beta_n^m P_n^m(\mu) e^{im\phi},$$

$$w = \sum \sum \gamma_n^m P_n^m(\mu) e^{im\phi} \quad . \quad . \quad . \quad (1)$$

where μ , as usual, stands for $\cos \theta$; n has all values from 0 to ∞ , and m from $-n$ to $+n$, $P_n^{-m}(\mu)$ being taken equal to $P_n^m(\mu)$. The symbols α_n^m , β_n^m , γ_n^m denote functions of r , and the letter m is not an index but is written from analogy with $P_n^m(\mu)$. The expressions on the r.h. sides of (1) are capable of representing the most general displacements which are physically possible.

Substituting these values, E_1 can be written in the form

$$E_1 = - \sum \sum \iiint \left\{ \frac{\partial}{r'^2 \partial r'} (r'^2 \alpha_n^m \rho') + \rho' (\beta_n^m + im \gamma_n^m) \right\} \chi(\mathbf{R})$$

$$P_n^m(\mu') e^{im\phi'} r'^2 \sin \theta' dr' d\theta' d\phi'.$$

If we write γ for the angle between the radii r and r' , so that

$$\cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos (\phi - \phi'),$$

we may expand $\chi_1(R)$ in the form

$$\chi_1(R) = \sum_0^{\infty} \tau_n P_n(\cos \gamma),$$

where τ_n is a function of r , r' and of the coefficients which occur in $\chi_1(R)$. When R is so great that $\chi_1(R)$ becomes the same as R^{-1} , we have

$$\tau_n = r^n/r'^{n+1} \text{ or } r'^n/r^{n+1}, \text{ according as } r < \text{ or } > r'. \quad (2)$$

We can further expand the biaxial harmonic $P_n(\cos \gamma)$ in the usual form, and so obtain

$$\chi_1(R) = \sum_{n=0}^{\infty} \sum_{m=0}^m C_n^m \tau_n P_n^m(\mu) P_n^m(\mu') \cos m(\phi - \phi'),$$

where $C_n^m = 2|n-m|/|n+m|$ or 1, according as m is different from or equal to zero.

If we substitute this value for $\chi_1(R)$ in E_1 , it appears that every term will vanish upon integration, except products of pairs of terms which are such that n and m are numerically the same for each. Performing the remaining integrations, we obtain

$$E_1 = \sum \sum F_n^m P_n^m(\mu) e^{im\phi}, \quad \dots \quad (3)$$

where

$$F_n^m = -\frac{4\pi}{2n+1} \int \left\{ \frac{\partial}{\partial r'} (r'^2 \alpha_n^m \rho') + r'^2 \rho' (\beta_n^m + im\gamma_n^m) \right\} \tau_n dr'. \quad (4)$$

The integral occurring in E_2 is that part of the potential of the whole atom upon a unit charge at the point r , θ , ϕ , which arises from the term $\chi_1(r)$ in the potential-function. This is obviously a function of r only; so that if we denote it by V_1 , we have

$$E_2 = u \frac{\partial V_1}{\partial r}.$$

The remaining part of the potential-function may be treated in a similar way. If we expand $\chi_2(R)$ in the form

$$\chi_2(R) = \sum_0^{\infty} \lambda_n P_n(\cos \gamma),$$

we find for the potential of the whole displacement upon a unit mass initially at r , θ , ϕ the value $E_3 + E_4$, where

$$E_3 = \sum \sum G_n^m P_n^m(\mu) e^{im\phi},$$

where

$$G_n^m = - \frac{4\pi}{2n+1} \left\{ \frac{\partial}{\partial r'} (r'^2 \alpha_n^m \sigma') + r'^2 \sigma' (\beta_n^m + im\gamma_n^m) \right\} \lambda_n dr',$$

and

$$E_4 = u \frac{\partial V_2}{\partial r},$$

where V_2 is that part of the potential of the whole atom upon a unit mass at r, θ, ϕ which arises from the term $\chi_2(r)$ in the potential-function.

§ 14. The potential of the whole displacement upon the element initially occupying the volume $dx dy dz$ at x, y, z has been seen to be

$$\{\rho(E_1 + E_2) + \sigma(E_3 + E_4)\} dx dy dz.$$

Since the distribution of doublets which gives rise to the displacement-potential at x, y, z is of zero strength at x, y, z , the forces arising from the displacement can be calculated by differentiation. The differential operators must, however, act only upon those parts of the displacement-potential which are directly derived from $\chi_1(R)$ and $\chi_2(R)$, so that the term u which occurs in E_2 and E_4 will be exempt from differentiation.

If, for the sake of generality, we admit externally applied forces of amounts L, M, N per unit charge in the directions of r, θ, ϕ increasing, the equations of motion of the element initially at r, θ, ϕ will be

$$\begin{aligned} \sigma \frac{d^2 u}{dt^2} &= -\Sigma \Sigma P_n^m(\mu) e^{im\phi} \left(\rho \frac{dF_n^m}{dr} + \sigma \frac{dG_n^m}{dr} \right) \\ &\quad - u \left(\rho \frac{d^2 V_1}{dr^2} + \sigma \frac{d^2 V_2}{dr^2} \right) + L\rho, \quad \dots \dots (5) \end{aligned}$$

$$\sigma \frac{d^2 v}{dt^2} = -\Sigma \Sigma \frac{dP_n^m(\mu)}{rd\theta} e^{im\phi} (\rho F_n^m + \sigma G_n^m) + M\rho, \quad \dots (6)$$

$$\sigma r \sin \theta \frac{d^2 w}{dt^2} = -\Sigma \Sigma \frac{imP_n^m(\mu)}{r \sin \theta} e^{im\phi} (\rho F_n^m + \sigma G_n^m) + N\rho. \quad \dots (7)$$

The Equations of Free Vibrations.

§ 15. Let us suppose that there is a normal vibration such that the element of which the equilibrium position is at r, θ, ϕ is found at time t at the point

$$r + ue^{ipt}, \quad \theta + ve^{ipt}, \quad \phi + we^{ipt},$$

u, v, w being given by scheme (1).

We write $L=M=N=0$ in equations (5), (6) and (7); replace d^2/dt^2 by $-p^2$, and substitute for u, v, w from scheme (1). The resulting equations must then be identities for all values of $r, \theta,$ and ϕ .

To save printing, we shall write

$$W = \rho \frac{d^2 V_1}{dr^2} + \sigma \frac{d^2 V_2}{dr^2},$$

$$J_n^m = \rho F_n^m + \sigma G_n^m,$$

and

$$\frac{\delta J_n^m}{\delta r} = \rho \frac{dF_n^m}{dr} + \sigma \frac{dG_n^m}{dr}.$$

In this abbreviated notation, the transformed equations (5), (6) and (7) are found to be

$$\sigma p^2 \sum \alpha_n^m P_n^m(\mu) e^{im\phi} = \sum \left(\frac{\delta J_n^m}{\delta r} + \alpha_n^m W \right) P_n^m(\mu) e^{im\phi}, \quad \dots (8)$$

$$\sigma p^2 r^2 \sum \beta_n^m P_n^m(\mu) e^{im\phi} = \sum J_n^m \frac{1}{\sin \theta} \frac{d}{d\theta} \left\{ \sin \theta \frac{dP_n^m(\mu)}{d\theta} \right\} e^{im\phi}, \quad (9)$$

$$\sigma p^2 r^2 \sin^2 \theta \sum \gamma_n^m P_n^m(\mu) e^{im\phi} = \sum J_n^m im P_n^m(\mu) e^{im\phi}. \quad \dots (10)$$

Equation (8) is expanded on both sides in zonal, tesseral, and sectorial harmonics, and is true for all values of θ and ϕ . We may therefore equate the coefficients of the various harmonics, and obtain

$$\sigma p^2 \alpha_n^m = \frac{\delta J_n^m}{\delta r} + \alpha_n^m W. \quad \dots (11)$$

In equations (9) and (10) we may begin by equating the coefficients of $e^{im\phi}$; multiply the equation obtained in this manner from (10) by $im/\sin^2 \theta$ and add the result to the equation obtained by equating coefficients of $e^{im\phi}$ in (9). The result is

$$\begin{aligned} & \sigma p^2 r^2 \sum (\beta_n^m + im\gamma_n^m) P_n^m(\mu) \\ & = \sum J_n^m \left\{ \frac{1}{\sin \theta} \frac{d}{d\theta} \left\{ \sin \theta \frac{dP_n^m(\mu)}{d\theta} \right\} - \frac{m^2 P_n^m(\mu)}{\sin^2 \theta} \right\}. \quad \dots (12) \end{aligned}$$

The right-hand member is equal to

$$-\sum n(n+1) J_n^m P_n^m(\mu),$$

and we are now able to equate coefficients of $P_n^m(\mu)$. The

equation so obtained, and equation (11), may be written

$$(\sigma p^2 - W)\alpha_n^m = \rho \frac{dF_n^m}{dr} + \sigma \frac{dG_n^m}{dr}, \quad (13)$$

$$\sigma p^2 r^2 (\beta_n^m + im\gamma_n^m) = -n(n+1)(\rho F_n^m + \sigma G_n^m), \quad . (14)$$

while we have (*cf.* equation (4), p. 430)

$$F_n^m = -\frac{4\pi}{2n+1} \int \left\{ \frac{d}{dr'} (r'^2 \rho' \alpha_n^m) + r'^2 \rho' (\beta_n^m + im\gamma_n^m) \right\} \tau_n dr', \quad . (15)$$

$$G_n^m = -\frac{4\pi}{2n+1} \int \left\{ \frac{d}{dr'} (r'^2 \sigma' \alpha_n^m) + r'^2 \sigma' (\beta_n^m + im\gamma_n^m) \right\} \lambda_n dr'. \quad (16)$$

Equations (13) to (16) must hold for all values of r , and contain only the four variables $\alpha_n^m, \beta_n^m + im\gamma_n^m, F_n^m$, and G_n^m , each equation being homogeneous and of the first degree in these four variables. It is easily seen that there is no solution of these equations other than

$$\alpha_n^m = 0, \quad \beta_n^m + im\gamma_n^m = 0, \quad F_n^m = 0, \quad G_n^m = 0, \quad . . (17)$$

except only when a special relation is satisfied by the various constants of the equations. Now m has entirely disappeared, so that any such relation may be written in the form

$$f(p^2, n) = 0, \quad (18)$$

where the coefficients which determine the functional form f are constants of the atom and of the potential-function.

Hence the normal vibrations fall into two classes, given by the two equations (17) and (18) respectively. In either class the displacement exists only for single values of n and m .

For a vibration of the first class $\alpha_n^m = 0$, and β_n^m, γ_n^m may have any values such that

$$\beta_n^m + im\gamma_n^m = 0.$$

The displacement is purely tangential, and no forces of restitution are called into play. Hence the frequency is in every case $p=0$ (as is otherwise obvious from equations (9) and (10)), and, strictly speaking, the corresponding normal degrees of freedom do not give rise to vibrations at all.

For a vibration of the second class, the frequency is a root of equation (18), and the functions $\alpha_n^m, \beta_n^m + im\gamma_n^m, F_n^m, G_n^m$ are determined by equations (13) to (16). These functions do not contain m ; to determine β_n^m and γ_n^m separately we must give to m any one of the $(2n+1)$ integral values between n and $-n$, and determine β_n^m, γ_n^m from equations (9) and (10),

in this way obtaining $(2n + 1)$ independent normal vibrations, the frequency of each being the same.

From the manner in which the analysis has been conducted, it will be clear that all possible normal vibrations must have been taken into account.

The Spectrum of the Ideal Atom.

§ 16. For the vibrations of the first class $p=0$; so that these vibrations are not represented in the visible spectrum.

The frequencies of the second class of vibration are all contained in equation (18). Solving for p^2 , this equation can be split up into the separate equations

$$\begin{aligned} p^2 &= f_1(n), \\ p^2 &= f_2(n), \quad \&c. \end{aligned}$$

Any one of these equations gives rise to a simply infinite series of lines in the spectrum, the wave-lengths of the lines in any such series being found by assigning the various positive integral values to n , in a formula in which n alone varies. Such a collection of lines will be referred to as a "spectrum-series." It has accordingly been shown that the visible spectrum of the ideal atom can be sorted out into a collection of spectrum-series; and it has also been shown that the n th line in each series must be regarded as the superposition of $(2n + 1)$ equal free periods.

Heads of Spectrum-Series.

§ 17. It can be shown that every spectrum-series tends to a definite limit corresponding to $n=\infty$, and the position of the line $n=\infty$ will accordingly be referred to as the "head" of the series.

The heads of the various series will be given by (*cf.* equation 18)

$$f(p^2, \infty) = 0, \quad (19)$$

this equation being the result of eliminating the four variables from equations (13) to (16) after putting $n=\infty$.

Let us begin with the consideration of the form assumed by equation (15) when $n=\infty$. We have

$$\chi_1(R) = \sum_0^{\infty} \tau_n P_n(\cos \gamma),$$

where

$$\frac{1}{R} = \frac{1}{\sqrt{r^2 - 2rr' \cos \gamma + r'^2}} = \sum_0^{\infty} \frac{r^n}{r'^{n+1}} P_n(\cos \gamma),$$

in the case in which $r' > r$. Since $\chi_1(R)$ becomes identical with R^{-1} except for small values of r , we may assume

$$\tau_n = \frac{r^n}{r^{n+1}} (1 + \delta_1),$$

when $r' > r$, where δ_1 is a series in descending powers of r' and ascending powers of r , which is very small except near to the value $r' = r$. Similarly we may assume

$$\tau_n = \frac{r'^n}{r^{n+1}} (1 + \epsilon_1),$$

when $r' < r$, where ϵ_1 is a similar series in ascending powers of r' and descending powers of r . At $r = r'$, $(1 + \delta_1)$ and $(1 + \epsilon_1)$ must have a common limit $(1 + \zeta_1)$.

In the identities

$$\int_0^r f_1(r') \frac{r'^n}{r^{n+1}} dr' = \frac{f_1(r)}{n+1} - \frac{1}{n+1} \int_0^r r' \frac{\partial f_1(r')}{\partial r'} \frac{r'^n}{r^{n+1}} dr',$$

$$\int_r^\infty f_2(r') \frac{r'^n}{r^{n+1}} dr' = \frac{f_2(r)}{n} + \frac{1}{n} \int_r^\infty r' \frac{\partial f_2(r')}{\partial r'} \frac{r'^n}{r^{n+1}} dr',$$

put $f_1(r') = \phi(r')(1 + \delta_1)$, $f_2(r') = \phi(r')(1 + \epsilon_1)$ and add. We obtain

$$\int_0^\infty \phi(r') \tau_n dr' = \frac{2n+1}{n(n+1)} \phi(r) (1 + \zeta)$$

+ terms of lower degree in n .

The function λ_n may be treated in the same way as τ_n , except that the principal term r^n/r^{n+1} or r'^n/r^{n+1} is wanting. We therefore assume

$$\lambda_n = \frac{r^n}{r^{n+1}} \delta_2 \text{ between } r' = r \text{ and } \infty,$$

$$\lambda_n = \frac{r'^n}{r^{n+1}} \epsilon_2 \text{ between } r' = 0 \text{ and } r,$$

where δ_2, ϵ_2 are similar to δ_1 and ϵ_1 , and have a common limit ζ_2 at $r = r'$.

Writing Y for α_n^m and Z for $\beta_n^m + im\gamma_n^m$, we are now able to expand equations (15) and (16) in the form

$$F_n^m = - \frac{4\pi\rho}{n(n+1)} \left\{ \frac{d}{dr} (r^2\rho Y) + r^2\rho Z \right\} (1 + \zeta_1)$$

+ terms of lower degree in n, \dots (20)

$$G_n^m = - \frac{4\pi\sigma}{n(n+1)} \left\{ \frac{d}{dr} (r^2\sigma Y) + r^2\sigma Z \right\} \zeta_2$$

+ terms of lower degree in n, \dots (21)

Substituting these values for F_n^m and G_n^m in equations (13) and (14), and putting $n=\infty$, we find as the equivalent of equations (13) to (16) the two equations

$$(\sigma p^2 - W)Y = 0, \dots \dots \dots (22)$$

$$\{\sigma p^2 - 4\pi\rho^2(1 + \xi_1) - 4\pi\sigma^2\xi_2\}Z = 0. \dots \dots (23)$$

§ 18. These equations are not difficult to interpret. Corresponding to any value of n , the displacement-potential at r of the shell of radius r' contains the factor r^n/r'^{n+1} or r'^n/n^{n+1} , according as $r <$ or $> r'$. This shows that in the case of $n=\infty$, the potential created by the displacement of any shell will vanish everywhere except in the immediate neighbourhood of that shell. It is therefore clear that the normal vibrations for which $n=\infty$ will split up into the normal vibrations of the separate shells.

This is the meaning of equations (22) and (23). Corresponding to a given value of p^2 , the second factors of equations (19) or (20) can only vanish over a single isolated shell of ions; hence the first factor must vanish everywhere except over this shell. The corresponding displacement and displacement-potential are limited to the shell in question.

Corresponding to any specified shell, equations (22) and (23) show that there will be two vibrations of order $n=\infty$. For the first of these $Z=0$ and $\sigma p^2 = W$. For the second, $Y=0$ and $\sigma p^2 = 4\pi\{\rho^2(1 + \xi_1) + \sigma^2(1 + \xi_2)\}$. The displacement of the shell is therefore in the former case purely radial; in the latter purely tangential.

§ 19. This concludes the investigation of the frequency-equation for the case of $n=\infty$. Corresponding to each particular solution for the case of $n=\infty$, there will be a general solution for all values of n from 0 to ∞ . Hence the number of spectrum-series will be equal to twice the number of shells in the atom. The frequencies of the heads of the series are, as we have seen, given by

$$p^2 = \frac{W}{\sigma}, \dots \dots \dots (24)$$

$$p^2 = \frac{4\pi}{\sigma} \{\rho^2(1 + \xi_1) + \sigma^2\xi_2\}. \dots \dots (25)$$

§ 20. It is easily verified that all possible degrees of freedom have been accounted for. The $(2n+1)$ degrees represented by the n th line of a spectrum-series may be associated with the $(2n+1)$ independent spherical surface-harmonics of order n ; so that a complete spectrum-series may be associated with the most general function of position on any

spherical surface. Writing Δ for $\frac{1}{\sin \theta} \frac{d}{d\theta} (v \sin \theta) + \frac{dw}{d\phi}$, the tangential dilatation, we see that the two spectrum-series corresponding to any single shell may be associated with the most general distribution of u and Δ which is possible over the surface of the shell in question. Combining the series from all the shells, we find that we can now associate a free-period with every degree of freedom implied in the possibility of giving arbitrary values to u and Δ at every point of every shell. The remaining degrees of freedom can be accounted for by adding to the foregoing distribution of u and Δ a distribution of displacement for which $u=0$ and $\Delta=0$ everywhere. These are the tangential degrees of freedom of the first class, for which $p^2=0$.

Numerical Calculation of the Size of an Atom.

§ 21. From equation (25) we can form an estimate of the size of atom which would be required in order to give vibrations comparable in frequency with those of light.

As regards order of magnitude, we may take $p^2=10^{31}$, $\rho/\sigma = e/m = \pm 10^7$, $\rho^2(1 + \zeta_1) + \sigma^2\zeta_2 = \rho^2$; and these values substituted in (25) give $\rho=10^{23}$, as regards order of magnitude. The charge on a single negative ion is 6×10^{-10} , so that the number of ions per cub. centim. is of the order of 2×10^{32} . In an atom of atomic weight n , the number of ions is of the order of $10^9 n$, so that the radius of the atom will be $n^{\frac{1}{3}} 10^{-9}$ cm.

The Spectrum of a Real Atom.

§ 22. It will be convenient at this stage to examine to what extent it is possible to deduce the spectrum of a real atom (as we are imagining it to be) from the spectrum of the ideal atom which has so far been the subject of investigation.

Let us consider a real atom I consisting of a finite number of ions A, B, C We are going to compare this with an ideal atom I', consisting of a finite number of elements of volume A', B', C' These elements can always be chosen (since the whole structure of I' is, up to the present, at our disposal) so that the total charge in the element A' is all of the same sign, and equal to the charge of the ion A. In this case, since we shall suppose the ratio of the charge to the mass to be numerically equal to the same constant for both atoms, the mass of the element A' will be equal to the mass of the ion A'.

The position of the element A' is as yet undetermined; but the more closely the atom I approaches to spherical symmetry of structure the more nearly will it be possible to arrange the

ideal atom in such a way that, if we imagine the two atoms "superposed" (made to occupy the same space), then the ion A will be near to the element A', B to B', and so on, while at the same time the ideal atom shall satisfy the condition of perfect spherical symmetry.

In order to avoid a discussion of continuity at points at which the electrical density changes sign, we may suppose elements for which ρ is of different sign to be separated by a thin transition-layer of thickness small in comparison with the dimensions of an element.

Imagine the ideal atom subjected successively to a system of displacements finite in number, say

$$u = r^s S_t, \quad \Delta = 0,$$

or
$$u = 0, \quad \Delta = r^s S_t,$$

where Δ , as in § 20, denotes the tangential dilatation, S_t denotes a surface harmonic of order t , and s, t have any number of integral values. For each of these displacements calculate the forces acting upon each of the elements A', B', . . . ; these will be linear functions of C_1, C_2, \dots , the constants which may be supposed to enter in the specification of the law of force in the ideal atom. In order that the forces calculated in this way may be finite, it is necessary and sufficient that the forces between elements at a small distance r shall be of an order not greater than $\frac{1}{r^2}$ in $\left(\frac{1}{r}\right)$.

Imagine the real atom to undergo the same system of displacements, and for each of these displacements calculate the forces acting upon each of the ions in terms of the constants which occur in the actual law of force between ions (supposed known). Now equate the forces acting upon A to the forces acting upon A' in the case of the same displacement. We see in this way that the forces acting on A, B, C . . . can be made identical with the forces acting on A', B', C' . . . for the case of any finite number of displacements (the number being as large as we please so long as it is not infinite) provided that the infinite number of constants C_1, C_2, \dots satisfy a finite number of linear algebraical equations.

Corresponding to any selected system of displacements it will be possible to find C_1, C_2, \dots , so that the forces acting upon corresponding elements and ions may be equal in every case. Cases of failure (cases in which two or more of the equations for C are inconsistent with finite values for C) can always be avoided by slightly altering one or more of the selected displacements. If the displacements are suitably chosen, it will be possible very approximately to expand any

normal displacement of the ideal atom as a sum of these displacements. Hence the forces acting upon any element A' of the ideal atom when this atom undergoes any one of its normal displacements will be very approximately equal to the forces acting upon the ion A when the real atom undergoes the same displacement.

But the ion A is very nearly in the position corresponding to that occupied by the element A' , and the total mass of the element A' is equal to the mass of the ion A . Hence the integral mass-displacement of the element A' is very nearly equal to the mass-displacement of the ion A .

It follows that the free vibrations of the ideal atom I' will be very approximately reproduced, as regards both frequency and displacement, in the real atom I , provided only that we select the imaginary law of force for the ideal atom in the manner indicated above. It is easy to see that this imaginary law of force must approximate at infinite distances to the limit of the real law at infinite distances, namely the ordinary electrostatic law. Hence, so long as we make no assumptions about this imaginary law except that at infinite distances it approximates to the ordinary electrostatic law (the assumption which was made in §§ 12, 17), we shall be justified in supposing that every quantitative result obtained for the free vibrations of the ideal atom will be very approximately a reproduction of a similar result for the real atom.

§ 23. It follows that there must be a line of the real spectrum in the neighbourhood of every line of the ideal spectrum. Confining our attention to the lines of a single spectrum-series of the ideal spectrum, we see that the lines must be approximately reproduced, line for line, in the real spectrum, until we reach such large values of n that the distance between successive lines becomes comparable with the error of our approximation: after this it will be impossible to trace corresponding lines. This last result is, from another point of view, obvious: when the order n of an harmonic becomes comparable with the number of ions on a great circle of an atom, it is impossible to distinguish a displacement of the real atom given by an harmonic of order n from one given by an harmonic of different order.

§ 24. For one kind of spectrum-series which occurs in the ideal spectrum (equation (25), p. 436), the value of p^2 at the head is equal to $(\rho^2(1 + \zeta_1) + \sigma^2\zeta_2)/\sigma$. When the transition-layers are supposed to be infinitely thin, this may be regarded as a continuous function of n . Hence the heads of these series will form a continuous band of light.

This, however, is not true for lines of the spectrum-series other than the head, since it is only for $n = \infty$ that ρ enters

the frequency equation through its square, and expressions which contain odd powers of ρ must not be regarded as continuous functions of r . Hence the lines in the spectrum-series corresponding to values of n other than $n=\infty$, cannot be regarded as forming continuous bands of light*.

It will be seen that such a group of lines may be regarded as forming two striated bands of light. A line will fall into one band or the other according to the sign of ρ for the shell with which it is associated, the dark places in one band corresponding to the bright places in the other.

In the case of the real atom, this will give two separate groups of spectrum-series. Each group will consist of a number of adjacent spectrum-series, and the two groups will have (approximately) a common head. The various series correspond to the various shells of ions in the atom; those in one group correspond to shells of negative ions, those in the other to shells of positive ions. We may imagine the vibrations associated with the innermost shells of ions to be of less energy than those associated with the outer shells, and in this case the lines of a given order (n) in either group will themselves form a series of lines of diminishing brightness, until the lines become so faint as to be invisible.

The spectrum-series of the real atom which correspond to the ideal spectrum-series of which the heads are given by equation (24) will similarly fall into two groups, but the series of any groups will be adjacent only if W varies continuously from ion to ion as we pass inwards from the surface of the atom.

§ 25. It will be at once seen that the arrangement of spectrum-series just found is sufficiently general to describe the arrangement which is known to exist in an actual atom. The adjacent series forming a single group may be supposed to form the series of triplets, double or single lines which occur in observed spectra. The two classes of series corresponding to equations (24) and (25) will be the principal and subordinate (or else subordinate and principal) series of the classification of Kayser and Runge. The two sets of subordinate series (the first and second according to Kayser and Runge; the 'nébuleux' and 'étroit' according to Rydberg) will be the two groups of one of the two classes given by (either) equation (24) or (25). It does not seem possible to identify the various series of our theory with observed series without carrying our theory much further than has been

* Otherwise thus:—The continuity in the ideal spectrum, in the case of every value of n except $n=\infty$, is effected by the vibrations associated with the thin transition-layers, and these have no actual existence.

done at present. But enough has, perhaps, been said to show that the general arrangement of lines in the spectrum which is predicted by our theory is sufficiently general to include that which is observed, while being at the same time sufficiently definite to afford a test of capability of the atom as we are now imagining it to reproduce the phenomena of the natural atom.

§ 26. A comparison between the theoretical and observed spectrum suggests that the actual atom may be regarded as approximately made up of shells of ions of alternate signs, or, still better, of shells of doublets. The same conclusion might have been arrived at from a consideration of the conditions of either equilibrium or stability. The evidence of the Zeeman phenomenon—that the predominating vibrations are those of negative ions, as well as the experimental result that negative ions are dissociated from the atom more readily than positive ions (there being no evidence that these latter can be dissociated at all), leads to the conclusion that the outermost layer of ions is of negative sign.

§ 27. The class of tangential vibrations of frequency $p^2=0$ which was found for the ideal atom (§ 15) will be approximately reproduced in the real atom. The corresponding values of p^2 will not now be actually zero, but will be very small.

Hence, in addition to the spectrum already discussed, which has been shown to consist solely of a collection of spectrum-series, there will be a second spectrum, far removed from the former, and at the infra-red end of it. It is not practicable to investigate the positions or arrangement of the lines of this spectrum, since the whole value of p^2 consists of a correction arising from the discrete structure of the atom. At the same time the existence of this spectrum might throw some light on the phenomenon of "electromagnetic resonance" discovered by Drude. It is found that resonance can be established between matter (in the case of certain substances at least) and electromagnetic waves of which the frequency is only about a millionth part of the frequencies of the visible spectrum*.

The Zeeman Phenomenon.

§ 28. Let us return to the general equations of the ideal atom, found in § 14, and suppose that u , v , w specify a normal vibration under the influence of a magnetic field H ,

* Wied. *Ann.* lviii. p. 1; lix. p. 17; lxiv. p. 131.

parallel to the axis of the molecule. We must in this case write

$$\begin{aligned} L &= Hip r w \sin^2 \theta, \\ M &= Hip r w \sin \theta \cos \theta, \\ N &= -Hip (rv \cos \theta + u \sin \theta). \end{aligned}$$

Writing E for $\rho E_1 + \sigma E_3$ (§ 13) and

$$\delta E / \delta r \text{ for } \rho dE_1 / dr + \sigma dE_3 / dr,$$

the equations of motion will be (*cf.* equations 8, 9, 10, p. 432)

$$\sigma p^2 u = \frac{\delta E}{\delta r} + u W - \rho Hip r w \sin^2 \theta, \quad . . . \quad (26)$$

$$\sigma p^2 r^2 v = \frac{dE}{d\theta} - \rho Hip r^2 w \sin \theta \cos \theta, \quad . . . \quad (27)$$

$$\sigma p^2 r^2 \sin^2 \theta w = \frac{dE}{d\phi} + \rho Hip r \sin \theta (rv \cos \theta + u \sin \theta). \quad . \quad (28)$$

We shall only attempt the solution upon the supposition that H^2 may be neglected, and in this case we obtain from (26) and (28)

$$\sigma p^2 u = \frac{\delta E}{\delta r} + u W - \frac{\rho Hip}{\sigma p^2 r} \frac{dE}{d\phi}.$$

Equating the various harmonics in this, we obtain (*cf.* equation 11, p. 432)

$$\sigma p^2 \alpha_n^m = \frac{\delta J_n^m}{\delta r} + \alpha_n^m W + \frac{\rho H m}{\sigma p r} J_n^m. \quad . . . \quad (29)$$

Similarly we obtain from (27) and (28),

$$\sigma p^2 r^2 v = \frac{dE}{d\theta} - \frac{\rho Hip}{\sigma p^2} \cot \theta \frac{dE}{d\phi}.$$

Equating coefficients of $e^{im\phi}$, multiplying by $\sin \theta$, and operating with $\frac{1}{\sin \theta} \frac{d}{d\theta}$, we get

$$\begin{aligned} \sigma p^2 r^2 \Sigma \beta_n^m P_n^m(\mu) &= \left\{ \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d P_n^m(\mu)}{d\theta} \right) \right. \\ &\quad \left. + \frac{\rho H m}{\sigma p \sin \theta} \frac{d}{d\theta} (\cos \theta \cdot P_n^m(\mu)) \right\} J_n^m. \quad . \quad (30) \end{aligned}$$

From (28), with the help of (26) and (27),

$$\sigma p^2 r^2 \sin^2 \theta w = \frac{dE}{d\phi} + \frac{\rho H i p}{\sigma p^2} \left(\sin \theta \cos \theta \frac{dE}{d\theta} + r \sin^2 \theta \frac{\delta E}{\delta r} \right).$$

Equate coefficients of $e^{im\phi}$, multiply by $im/\sin^2 \theta$, add to (30) and we obtain, after some simplification,

$$\begin{aligned} \sigma p^2 r^2 \Sigma (\beta_n^m + im\gamma_n^m) P_n^m(\mu) \\ = -\Sigma \left(n(n+1) + \frac{\rho H m}{\sigma p} \right) P_n^m(\mu) J_n^m \\ - \frac{\rho H m}{\sigma p} \Sigma r \frac{\delta J_n^m}{\delta r} P_n^m(\mu). \end{aligned}$$

We can now equate coefficients and obtain

$$-\sigma p^2 r^2 (\beta_n^m + im\gamma_n^m) = \left\{ n(n+1) + \frac{\rho H m}{\sigma p} \right\} J_n^m + \frac{\rho H m r}{\sigma p} \frac{\delta J_n^m}{\delta r}. \quad (31)$$

It appears, therefore, that under the influence of a magnetic field, the normal coordinates will fall into the same two classes as before. The frequency of the lines of the visible spectrum is, however, no longer given by equation (18) but by an equation of the form

$$f(p^2, n) + H p m F(p^2, n) = 0. \quad . \quad . \quad . \quad (32)$$

§ 29. We see from this that the effect of the magnetic field is to separate the $(2n+1)$ lines, which, in the absence of a magnetic field, coincide in the n th line of a spectrum-series, in such a way that the line $m=0$ remains in its original position and forms the central one of a group of $(2n+1)$ equidistant lines. Thus the line $n=0$ will be unaffected by a magnetic field, the line $n=1$ separated into a symmetrical triplet, the line $n=2$ into an evenly-spaced quintet, and so on.

§ 30. The lines of the spectrum of the actual atom must be influenced by a magnetic field in a manner approximately the same as that found for the ideal atom. It may, however, happen that some of the side lines will be too faint for observation. It may also happen that the $(2n+1)$ lines did not originally form a single coincident line, but a doublet or even more complex structure. It may thus happen that the number of equal periods represented by any single line is an even number. In this case it is known that the lines must spread symmetrically * so that there will be no middle line left, and the separated line will consist of a doublet, quartet, &c.

* Lorentz, *Astrophys. Journal*, ix. p. 37.

The solution of equation (32) will be of the form

$$p = \phi(n) + H_m \Phi(n),$$

where ϕ and Φ are the same for the same spectrum-series.

The separation is therefore directly proportional to the strength of the field; and we can see reasons for expecting the remaining factor to be intimately dependent upon the spectrum-series to which the line belongs, as well as upon its position in this series.

§ 31. In considering the polarization of the various lines, we shall neglect the ratio of the radius of the atom to the wave-length. In this case the radiation emitted by the atom may be taken to be the same as the radiation emitted by an "equivalent particle," this particle moving so that its displacement multiplied by its charge is equal to the vector-sum of the displacements of the ions of the atom multiplied by their various charges*.

We have seen that the central line of a Zeeman group is emitted by a vibration which is specified by a zonal harmonic, having the direction of magnetic force as axis. The orbits of the ions are therefore in the meridional planes, and are the same in all such planes. The resultant radiation is therefore such as would be emitted by a single particle vibrating along the axis.

The vibrations by which the side lines are emitted may each be regarded as composed of two parts:—

- (α) A vibration parallel to the axis of harmonics.
- (β) A vibration in which every ion describes an orbit parallel to the equatorial plane.

The amount of the former will be different in different meridional planes. Since this amount will, for the line m ,

* The radiation emitted by a vibrating system of ions can be calculated as follows:—Let the displacement arising from a single vibration be such that ξ , η , ζ (the components along three rectangular axes) are the real parts of αe^{ipt} , βe^{ipt} , γe^{ipt} , and introduce a complex vector \mathbf{C} of which the components are α , β , γ . Then the radiation at an external point can be determined from the single vector \mathbf{P} which is the real part of

$$e^{ipt} \iiint \mathbf{R}^{-1} e^{-ipR/V} \rho \mathbf{C} \, dx \, dy \, dz,$$

where R is the distance of the external point from the element $dx \, dy \, dz$. When we neglect the radius of the atom we may take $\mathbf{R}^{-1} e^{-ipR/V}$ outside the integral, and this leads to the rule for the vector composition of displacements. The radiation is given by the equations

$$\mathbf{E} = \frac{1}{V^2} \frac{d^2 \mathbf{P}}{dt^2}, \quad \mathbf{H} = -\frac{1}{V} \frac{d}{dt} (\text{curl } \mathbf{P}).$$

Cf. Larmor, *Æther and Matter*, §§ 151–156.

contain the factor $e^{im\phi}$, we see that the aggregate radiation is *nil*.

The amount of the latter will also be proportional to a factor $e^{im\phi}$, and the radiation will be *nil* except in the case of $m = \pm 1$.

In the case of $m = 1$, the radiation is such as would be emitted by a single particle describing an orbit in the equatorial plane. To investigate this orbit it is only necessary to notice that the values of u , v , w at every point will depend on ϕ and t only through the factor $e^{i(m\phi + pt)}$. Hence the equivalent displacement will depend on ϕ and t through the same factor, and will therefore be that of a particle describing a circle in the equatorial plane, the direction being that of ϕ increasing or decreasing according as m has the value -1 or $+1$.

Hence the polarization of the lines $m = -1, 0, +1$ can be accounted for in the manner in which they have already been accounted for by Larmor upon the supposition that the radiation is emitted by a single ion vibrating in a spherically symmetrical field of force. On the other hand, our theory does not compel us to expect that every line will be separated into a triplet, or that the separation will be of constant amount.

§ 32. It must be remembered that our examination of the polarization is subject to two corrections: one arising from the finite radius of the atom (which was neglected in comparison with the wave-length), and the other from the discrete structure of the actual atom. For this reason we cannot expect the polarization of the lines to be absolutely complete, and the lines for which m has values other than 0 or ± 1 will not actually be invisible, although since the total radiation arises solely from two small corrections, they will probably be very faint.

The polarization of the side-lines of a triplet shows that the equivalent single ion must be supposed to be of negative sign. It is of interest to notice that on the present theory this does not indicate that the light is emitted solely by negative ions, but only that the vibrations of the negative ions contribute more to the radiation of the particular periods in question than do the positive ions (see § 26).

The Influence of the Translation and Rotation of the Atom.

§ 33. There is a purely kinematical result of the translational motion of the atom, which shows itself in the well-known Doppler effect, and consequent broadening of the

spectral lines. In addition to this, the actual periods of vibration of the atom are altered by its velocity in space. It has been shown by Lorentz that the effect of a uniform velocity of translation ($u, 0, 0$) is to decrease the components along the axis of x of all the electrical forces involved, in the ratio $1 : (1 - u^2/V^2)^{\frac{1}{2}}$, where u is the total velocity of the atom relatively to the æther.

The result of this is that the spherical symmetry of the atom is destroyed, and the lines in the spectrum which have been supposed to be superposed and indistinguishable will become separated. It is, however, easily verified that this separation will be much too small to be capable of observation.

The view which we have taken up compels us to suppose that the linear dimensions, not only of atoms, but of complete bodies, depends upon their orientation in space. It has been pointed out by Lorentz*, Larmor†, and Walker‡, that this supplies the only satisfactory explanation of Michelson's aberration experiments.

§ 34. The influence of the rotation of the atoms will, like that of the translation, be two-fold. There is, first, a purely kinematical effect, already discussed in § 2, and, second, a dynamical effect, as follows:—

We can allow for a rotation w , by supposing a force $w^2 r \sin \theta$ to act per unit mass, perpendicular to the axes of the atom. The effect of this, regarded as a steady force, will be to produce a new equilibrium configuration, each element being moved a slight distance from its old position.

The vibrations will now be vibrations about this displaced position of equilibrium, under the influence, partly of the displacement-potential, and partly of the centrifugal force which is supposed to act.

The periodicities will therefore be slightly changed, and the amount of change for every vibration will contain w^2 as a factor.

Remembering that w^2 varies from atom to atom, it appears that the effect upon the spectrum of the whole gas, which is produced by allowing for the rotation of the atoms, will be to change each line into a band. The centre of the band will not coincide with the original line; the position of this line will now be occupied by the extreme edge of the band, corresponding to $w=0$, and since the probability of zero rotation is *nil* for each atom, this line will be of zero intensity.

* Lorentz, *Versuch einer theorie* . . . p. 120.

† Adams Prize Essays, 1900.

We have, however, seen that each "line" of the original line-spectrum ought to be regarded as the superposition of several lines. The rotation of the atom destroys the spherical symmetry, and therefore separates these lines, each one being, at the same time, spread out into a band.

The resulting "band" will therefore be a more complex structure than we have hitherto supposed it to be. It may, for instance, spread to both sides of the original line, and may show several maxima and minima of intensity. But in every case the widening effect ought to remain always similar to itself, the amount being always proportional to \bar{w}^2 , the mean value of w^2 .

Now if the rotation is governed by a subsidiary temperature, \bar{w}^2 will be proportional to the temperature, and therefore to the density (§ 6), so that the shift and the broadening of any line will each be directly proportional to the pressure in a pure gas, and roughly proportional to the total pressure in a mixed gas*.

In any single spectrum-series, not only the periodicity but also the form of the normal function depends solely upon the single parameter n . From this it follows that the amount of shift in a single spectrum-series will depend only on n . There will therefore be a similarity between the shift of the different lines of the same series, such as does not exist between those of different series.

The broadening effect just found must be added to that of § 8. The broadening due to each effect, and therefore also the resultant broadening, will be proportional to the pressure.

§ 35. In the case of complete molecules the rotation will not be governed by a subsidiary temperature, so that the effect of rotation will be much greater than in the case of dissociated atoms. There need therefore be no difficulty in accounting for the continuous spectrum emitted by a solid or a heated gas.

The Structure of Molecules.

§ 36. Let us now pass from the consideration of the phenomena of spectroscopy to the consideration of the other properties of matter which are implied in our provisional view of the structure of an atom.

If an atom consists of n negative and $n+s$ positive ions, the total charge on the atom will be se , and s may, by a slight extension of the usual terminology of chemistry, be referred to as the valency of the atom.

* A Summary of Experimental Knowledge is given by W. J. Humphreys, *Astrophys. Journal*, vi. p. 225.

It is clear that there will be no atom of which the valency s is comparable with n , since such an atom would tend to expel the ions of that sign which was in the majority, although, when s is small compared with n , the corrections which we have seen must be applied to the ordinary electrostatic law may be sufficient to counterbalance this tendency.

An atom of valency s behaves at sufficient distances from its surface like an electrostatic point-charge of electricity se placed at its centre. We may therefore expect that under favourable conditions the atoms will combine into larger systems, namely molecules, a molecule being now defined as a system of ions of which the total charge is zero.

Thus an atom of valency -2 may combine with another atom of valency $+2$, or with two atoms each of valency $+1$, and so on. Or two similar atoms each of valency ± 1 may combine with two ions to form a neutral molecule, though, by hypothesis, a single such atom cannot combine in a stable manner with a single ion. So two atoms of valency ± 1 may combine and form a neutral body, by ejecting the two superfluous ions.

On this view, a molecule of an element cannot be the same as two (or more) atoms, although the molecule of a compound may or may not be a sum of atoms of elements. But it follows from the definition of a molecule, as a system of which the total charge is zero, that no free ions can be liberated by chemical change. It follows further that the force exerted by a complete molecule at external points will fall off very rapidly as we recede from the molecule.

Electrostatic Forces.—Chemical Affinity, Cohesion.

§ 37. We may examine the electrostatic field of force more closely as follows.

With core as origin of coordinates, the potential of an atom upon an ion exterior to it (and at a distance so great that the unknown part of the potential function may be ignored) can be written

$$V = \frac{a_0}{r} + \frac{S_1}{r^2} + \frac{S_2}{r^3} + \dots \quad (33)$$

where S_1, S_2, \dots are spherical surface-harmonics of orders 1, 2, \dots

Now

$$\iint \frac{dV}{dr} r^2 d\theta \sin \theta d\phi = 4\pi \times \text{total convergence of force inside atom,} \\ = -4\pi se.$$

Substituting for V the value given by equation (33), we find that a_0/r is the *chemical force*, a_0 being proportional to the valency of the atom.

Hence between two atoms there will be a chemical attraction or repulsion along the line joining their centres, and also a force (proportional to $1/r^3$ at most) arising from the coarse-grainedness of the ionic structure. Between two molecules the latter force exists alone.

This latter force (force of cohesion) will be vanishingly small in a gas, where the distance between adjacent molecules is small compared with scale of coarse-grainedness of atoms, but may become very large in a solid.

The force consists of a couple and a radial force. From the form of V these are equally likely, if the atoms are placed at random, to be in either direction. But if the atoms (or molecules) are permanently near one another, the couple will turn them into a position in which this potential is a minimum (and therefore, speaking roughly, negative), and the radial force dV/dr is now attractive.

Electrodynamical Forces.—Permanent and Induced Magnetism.

§ 38. In addition to the forces just considered, there will be electro-dynamical forces arising from the motions of the atoms or molecules.

Each molecule of a solid will, in addition to its internal and translational vibrations, possess a rotational vibration in the field of intermolecular force. As we pass to greater amplitudes of this vibration, we shall come to a point at which a vibration through a finite angle gives place to a complete rotation. The rotation is not of uniform velocity, since irregularities are introduced by the field of force. In a rotating atom or molecule we have the rotation of a system of charges of electricity. The net result is therefore equivalent to a circular current of electricity in the direction of rotation.

Hence, in the case of vibration, the result is the emission of electromagnetic waves; but the force on the atom or molecule varies in direction at each half-phase.

In the case of complete rotation the current and forces are of constant direction: *the atom or molecule may be regarded as a permanent magnet* of moment proportional (except for irregularities) to the angular velocity, and of axis coinciding with axis of rotation.

In general, the axes of these molecular magnets will be distributed at random, so that the solid will exhibit no magnetic properties.

If the solid is placed in a magnetic field, there will be a couple acting on each such magnet, tending to turn its axis of rotation parallel to the lines of magnetic force. Two effects can be detected.

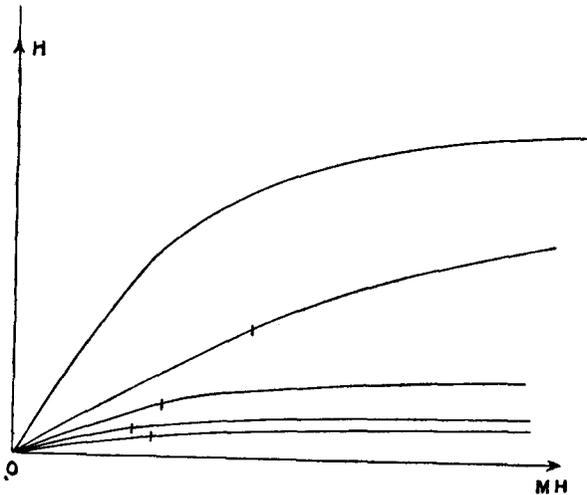
I. The axes of rotation will turn towards the direction of the lines of force. Hence, as in Weber's Theory (Maxwell, § 443), if the axes be a "set," in a particular direction giving the phenomenon of induced magnetism.

Other things being equal, this set will, for sufficiently small values of H , be proportional to H ; it will also depend on the rotation of the molecule being proportional to $1/w$.

It follows that the curve of induced magnetization will be given by the superposition of a number of curves such as that given by Weber.

The discontinuities will occur at different points, so that the resultant curve will be continuous.

Fig. 1.



When the magnetic force is removed, the molecules can neither continue to rotate in their present condition, nor can they return immediately to their original state. An intermediate state will ensue, and the time required for the induced magnetism to disappear will depend on the ease with which energy passed between certain degrees of freedom in the solid. The field of intermolecular force may be such that some molecules retain their set for ever. For it may be that some molecules cannot return to their old positions without passing

through a position in which their motion is opposed by an intermolecular couple greater than the gyrostatic couple caused by their angular rotation. In the former and more general case, we have residual magnetism; in the latter, permanent magnetism.

II. A further effect of the external field H is seen upon considering that the rotation of the molecules gives rise, virtually, to an electric current. If the current were *real*, the addition of the external magnetic force would give rise to an induced current: in the present case it gives rise to a retardation of the angular velocity about the lines of magnetic force, the velocity being regarded as a vector. It may therefore be regarded as giving rise to a system of magnets of which the direction is opposite to that of the magnetic force.

Hence diamagnetism may be accounted for in the manner of Weber (Maxwell, Treatise, § 838).

§ 39. The great range of values which is known to be possible for K , the coefficient of magnetic induction, can easily be accounted for. Suppose (for the sake of simplicity) that the rotation of a molecule is a "normal" degree of freedom. This will be specified by a subsidiary temperature; and if α be the mean energy, the law of distribution may for illustrative purposes be taken to be

$$Ee^{-\frac{E}{\alpha}} d\sqrt{E}$$

where E is the energy of the rotation (proportional to w^2).

Let b be the value of E at which the motion changes from oscillatory vibrations to complete revolutions.

In a field of force H a couple acts on this magnet which is proportional (as regards H and w) to Hw . If θ is the angular displacement produced, the couple is also proportional to θw^2 . Hence θ is proportional to H/w . This displacement may be regarded as the creation of a new magnet, proportional to $(H/w) \times w$, and therefore proportional to H , and independent of w . The total *induction* is therefore proportional to

$$H \int_b^{\infty} Ee^{-\frac{E}{\alpha}} d\sqrt{E};$$

and therefore to the area of the curve

$$y = x^2 e^{-x^2},$$

which is on the right of the ordinate

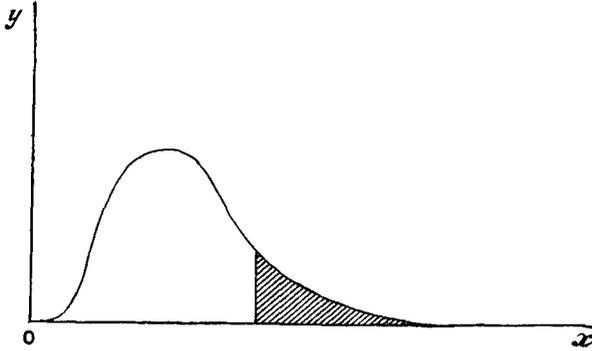
$$x = \sqrt{b/a}.$$

Thus if b is comparable with a , the coefficient k , given by

$$4\pi k = \int_b^\infty E e^{-\frac{E}{a}} d\sqrt{E}$$

will vary rapidly with slow changes in b/a .

Fig. 2.



Since a is the measure of a subsidiary temperature, a may vary enormously from one substance to another.

Calculation of Specific Inductive Capacity.

§ 40. Under a steady field of electric force C every ion at the surface of any atom is in equilibrium under the force, the displacement-potential of the atom to which it belongs, and the potential arising from other atoms. Neglecting the latter, the displacement-potential at every point of the surface of any atom must be Ea ; or if R is the radius of the atom,

$$E_1 R \cos \theta. \quad (34)$$

At all points outside the atom this displacement-potential satisfies Laplace's equation, and it is continuous with (34) at $r=R_1$. The general solution is therefore

$$E \cos \theta R_1^3 / r^2.$$

If there are Ndv such atoms in a small element of volume dv , the total displacement-potential at an external point will be

$$NE \cos \theta R_1^3 dv / r^2 \quad \text{or} \quad ENR_1^3 x / r^3.$$

The specific inductive capacity of a medium composed of such atoms will therefore be given by

$$\frac{k-1}{k+2} = NR_1^3.$$

For a gas this gives

$$k = 1 + 9\theta/4\pi,$$

where θ is the fraction of the total volume which is occupied by atoms.

It is clear that this is of the right order of magnitude. For oxygen, hydrogen, nitrogen at the density of the air the refractive index is roughly 1.00025*, giving

$$k = 1.0005.$$

Substituting this value in the formula just found for k (and neglecting the difference between atoms and molecules, since this will not affect the order of magnitude of the quantities concerned), we get $\theta = .0007$.

Now the density of liquid oxygen, nitrogen, &c., is roughly 1000 times that of air, so that the value of θ just found will be at any rate comparable with the true value.

Dielectrics, Conductors, and Electrolytes.

§ 41. It will be seen that the foregoing theory of the specific inductive capacity of a dielectric is virtually that of Mossotti †. The atoms or molecules must not be regarded as perfect conductors, but they arrange themselves so that their external surfaces are equipotentials, and therefore behave like conductors to all external points.

In a solid body each ion will be in equilibrium under the forces arising from all the ions in the solid. In the case of some substances, the solid may be regarded as a collection of atoms, or molecules, each individual atom retaining its identity; whereas for other substances the body must simply be regarded as a confused mixture of ions which have placed themselves in equilibrium.

The difference is that between a dielectric and a conductor. If the former body is placed in an electric field, the molecules will arrange themselves so that their surfaces are equipotentials, and we have a dielectric of which the theory of Mossotti gives a good account.

When a body of the second sort is placed in an electric field, the ions (possibly all ions, or possibly only the ions of the outermost layer) will be free to move from one molecule to another, and will therefore arrange themselves so that the whole surface of the body is an equipotential. In one half of the body there would be an excess of negative ions, in the other half an excess of positive ions: the former is the so-called "induced charge" of negative electricity, the latter of

* Preston, 'Theory of Light,' p. 137.

† Maxwell, *Elect. and Mag.* § 62.

positive. Before the ions have taken up their equilibrium positions there will be a flow of ions through the body, and this is a "current of electricity."

A third class of body can be imagined in which the ions are closely bound into atoms, but the bond between the various atoms of a molecule is very slight: this is the class of electrolytes. A current in this case involves an actual transfer of atoms through the electrolyte.

Consider, for instance, the electrolysis of hydrochloric acid. The hydrogen atom has a convergence of force equal and opposite to that of a negative ion. Every pair of hydrogen atoms as they arrive at the cathode will combine with two of the negative ions which have been conveying the current through the metal cathode, and will together form a neutral hydrogen molecule. So also at the anode, the pairs of chlorine atoms combine into molecules, and in doing so liberate the ions which are to carry the current away from the anode. Faraday's Laws of electricity follow at once.

Conclusion.

§ 42. This concludes the comparison between the phenomena which are to be expected from our hypothetical matter and those which are observed to occur in nature. It must be left for individual judgments to decide whether the test afforded in this way is sufficiently strict to be worth anything; and if so, to decide what is the measure of probability that our hypothetical matter gives a clue to the structure of actual matter.

§ 43. In conclusion, reference may be made to a question which demands an answer in the case of this, as in the case of every other hypothesis which attempts to place the structure of matter on a purely electrical or æthereal basis. The only difference which the æther-equations of electricity can recognize between a negative and a positive charge of electricity is a mere difference of sign; so that if we regard a negative ion as an æther-structure, we are inevitably led to regard the possibility of positive ions differing from negative ions only by a difference of sign. On the other hand, the predominance of the negative ion in most material phenomena, and in the emission of light (as evidenced by the Zeeman Effect) seems to suggest the view that positive and negative ions differ in something more than mere sign. Any attempt to explain matter in terms of æther must therefore face the problem of reducing what appears to be a difference in quality to a difference in sign only.

We can explain these facts, in terms of our present theory, by supposing (§ 26) that the outermost shell of ions in any

atom consists exclusively of negative ions, but there still remains the question as to why it is that the positive ions rather than the negative are excluded from the outermost shells of the atom; we have not yet removed the essential difference in quality between positive and negative ions.

We cannot suppose that all atoms with positive ions at the surface are unstable; for corresponding to any stable arrangement with negative ions at the surface, there must be a stable arrangement which is exactly the same except that the sign of every ion is changed. If an ordinary atom is referred to as a positive atom, this other kind of atom may be referred to as a negative atom.

Let us refer to the atoms of the various chemical elements as A, B, C, . . . , and let the imaginary corresponding negative atoms be referred to as A', B', C', In order that a system of chemical elements A, B, C, . . . may have a permanent existence it is not only necessary that the individual atoms A, B, C, . . . shall each be statically stable, but also that when any atom A meets another atom B, the atoms A and B shall not lose their identity. Now the forces exerted between A and B when in proximity will arise mainly from that part of the potential-function which represents the divergence of the forces exerted by the ions near the point of closest approach from those calculated on the ordinary electrostatic law, and will possibly depend largely upon the signs of the ions in these outermost shells. Thus if A and B do *not* unite so closely as to lose their separate identity, it is not difficult to imagine that A' and B would be drawn together until a complete rearrangement of ions had been effected and a new atom or atoms formed. If this supposition be accepted it will be clear that a condition that a system of elements should have a permanent existence is that the outermost layers of all the atoms shall be of the same sign. We can imagine a number of positive and negative ions initially scattered at random in space to condense into matter of both kinds, but whenever a collision takes place between two atoms of different kinds, the result is a rearrangement of parts, until finally only one class of matter is left in the field.

This last suggestion is of a very speculative kind; but it may be noticed that if matter is an æther-structure, and if the difference between positive and negative electricity only enters in the æther-equations through a mere difference of sign, then the observed difference between the relations of the two kinds of electricity to material phenomena can only arise from a difference in the initial conditions, such as that just described.