



## I. The fundamental constant of atomic vibration and the nature of dielectric capacity

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- I. *The Fundamental Constant of Atomic Vibration and the Nature of Dielectric Capacity.* By WILLIAM SUTHERLAND\*.

FROM the many beautiful theoretical discussions of the Zeeman effect it appears that for some purposes the vibrator of atomic radiation can be schematically simplified to a negative electron whose motion is simple harmonic about a central position of equilibrium. The theories have been summarized up to 1900 by Lorentz (*Congr. Internat. de Phys.* Paris, 1900), and since then the more complicated cases of the effect have been discussed by W. Voigt (*Ann. der Phys.* xxiv. 1907, p. 193). It now appears that the orbit of a single electron moving under a force towards a centre and proportional to radius vector gives the generalized essence of the effect of a magnetic field on the lines of spectra, but that there are also complicated conditions yet to be unravelled. Probably these are of a kinematical nature to be added to the several instances of kinematical conditions given in "The Cause of the Structure of Spectra" (*Phil. Mag.* [6] ii. 1901, p. 245). But the nature of the field of force causing the harmonic motion has not yet been investigated in relation to existing knowledge of molecular fields of force. My papers on molecular attraction have led to the general conception of the atom as an electrized sphere analogous to the Earth as a magnetized sphere. In the electron theory of

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matter, if we imagine the electrons associated in pairs consisting of one negative and one positive electron revolving around one another in such a way that each pair has an average electric moment, then if these moments are similarly directed, the atom as a whole will have an electric moment, and can be investigated as a uniformly electrized sphere. From the laws of molecular attraction we find that there are definite broad principles giving the types of external electric field belonging to different classes of atoms. It will be shown in the present paper that the corresponding internal electric fields cause atomic vibrations in much the same way as the Earth's gravitational field causes the oscillations of pendulums, and its magnetic field causes the oscillations of galvanometer needles. Just as the compound pendulum for many purposes can be schematically reduced to the simple equivalent pendulum, so the real atomic vibrator can be reduced to the single electron of the theory of the Zeeman effect, although it is much more complex. The matters to be discussed will be taken under the headings: 1. The Fundamental Constant of Atomic Vibration. 2. A Theory of Dielectric Capacity. 3. A Kinematical Analysis of Balmer's Formula. 4. Summary.

### 1. *The Fundamental Constant of Atomic Vibration.*

The most notable general fact yet brought out concerning spectra is that for the elements they all depend upon one constant which first made its appearance in the formula of Balmer for wave-length in the hydrogen spectrum. This appears as  $b$  in Rydberg's extension of Balmer's formula, namely

$$n = n_0 - b/(m + \mu)^2,$$

where  $n$  is the number of wave-lengths in a cm. belonging to a line in a series,  $m$  is an integer, and  $\mu$  like  $n_0$  is a parameter characteristic of the series. Rydberg, having discovered that  $b$  has nearly the same value for other elements as for hydrogen, assumed it to be an absolute constant of Nature. Others have found empirical convenience in allowing  $b$  to vary from one element to another; for instance, in "The Cause of the Structure of Spectra" (*loc. cit.*) in the Li family of metals  $b$  ranges from 108800 for Rb to 113950 for Cs. For 11 other elements it ranges from 100000 to 110100, so that for 16 elements it ranges from 100000 to 113950. But for Sr it appears to be 96232, and for Ba 89540, the value for Ca being 100000 and for Mg 104320. Even if these variations of  $b$  are genuine, and not merely the acci-

dental results of imperfections in the empirical formula, it is evident that  $b$  tends to a limiting value which is a fundamental constant. In the paper cited I have suggested that with  $V$  for the velocity of light in vacuum  $Vb$  is to be regarded as a frequency of vibration or rotation which is nearly the same in all atoms. In "The Electric Origin of Molecular Attraction" (Phil. Mag. [6] iv. 1902, p. 625) at section 4 an attempt was made to show that the frequency of rotation of a pair of electrons in the Na atom is identical with this fundamental  $Vb$ , whose value is  $33 \times 10^{14}$ . But that attempt gave better numerical agreement than it ought, because the best available estimates of molecular diameters at that date were too small, and introduced a compensating error which masked the incompleteness of the theory then sketched. But by means of the conception of the internal electric field of the atom we can make the discussion of  $Vb$  more definite, and then test it by more definite molecular data.

From the theory of the text-books for a uniformly magnetized sphere (*e. g.* J. J. Thomson's Elements of El. and Magn.) we can specify the field of force of a uniformly electrized sphere of moment  $es$  as that due to a potential  $\psi = (es \cos \theta)/r^2$  at a point  $r, \theta$ , outside the sphere, while inside the sphere the electric intensity has the constant value  $es/a^3$  parallel to the direction of electrization, the radius of the sphere being  $a$ . This constant internal field is very important. Even when the electrization is not uniform and the intensity not constant, for a first approximation we can assume a uniform electrization equal to the average value of the actual and associate with it a constant average intensity.

Evidently in the atom we have a region of electric force suitable for maintaining simple harmonic motion of electrons. Consider a negative electron  $\flat$  and a positive  $\sharp$  in positions of static equilibrium within the sphere, the charge of each being  $e$ . As a pair they will be at rest in unstable equilibrium anywhere within the sphere so long as the line joining them is parallel to the electrization, and of such a length  $z$  that  $e^2/z^2 = e^2s/a^3$ , and the moment  $ez$  is oppositely directed to  $es$ . This pair floats in the internal electric field of the sphere just as a magnet would float in a cavity in a gravitationless Earth, and if suitably constrained it can vibrate as the magnet would. It differs from the magnet inasmuch as its length is also determined by the strength of the electric field. Let us take the pair of electrons to such a position that their midpoint is at the centre of the sphere, and each

is at distance  $r$  from it on the axis of electrization. Let the one electron be displaced through the small distance  $x$  at right angles to the axis and the other through  $-x$ , then if  $i$  is the inertia of each, the equation of motion is

$$i \frac{d^2 x}{dt^2} = - \frac{e^2 s}{a^3} \cdot \frac{x}{r},$$

with frequency  $(e^2 s / a^3 r i)^{\frac{1}{2}} / 2\pi$ .

The instability requiring constraint takes the significance from this case, which is mentioned only in preparation for the following. Imagine with Kelvin the positive electron uniformly distributed through a sphere of radius  $R$ . The same effect would be produced if the positive electron moved at random with a sufficiently high velocity within a sphere of radius  $R$ . Then if the negative electron is within the same sphere of radius  $R$ , but at distance  $r$  from its centre, the force which it experiences from the positive electron is  $(e^2 / r^2) (r^3 / R^3) = e^2 r / R^3$ . In the atom the negative electron comes to rest at distance  $r$  given by

$$\frac{e^2 r}{R^3} = \frac{e^2 s}{a^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and now the equilibrium is stable, given that the positive electron is constrained as stipulated. For simplicity let us make the centre of this sphere of radius  $R$  coincide with that of the atom of radius  $a$ . Then for small displacement  $x$  of the negative electron at right angles to  $r$ , which is parallel to the electrization of the atom, the equation of motion is

$$i d^2 x / dt^2 = - (e^2 r / R^3) x / r = - e^2 x / R^3$$

with frequency  $f = (e^2 / R^3 i)^{\frac{1}{2}} / 2\pi$ .

Again, for a small displacement  $z$  of the negative electron parallel to the electrization the equation of motion is

$$i d^2 z / dt^2 = - e^2 z / R^3,$$

with again the same frequency. In each of the three degrees of freedom of the negative electron the period of vibration is the same. If  $R$  is an absolute constant, this frequency is the same for all atoms.

The first thing to do then is to see whether the equation

$$Vb = 33 \times 10^{14} = (e^2 / R^3 i)^{\frac{1}{2}} / 2\pi \quad . \quad . \quad . \quad . \quad (2)$$

leads to a possible and probable value of  $R$ . The quantity about which there is most uncertainty is  $i$ , its average value

being about  $10^{-27}$ , the values in J. J. Thomson's list ranging from 0.639 to 1.865 times this. According to Rutherford  $e=4.65 \times 10^{-10}$ , and to Planck  $e=4.69 \times 10^{-10}$ . Using the former we get  $R=0.795 \times 10^{-8}$ . Now in a short note following I have recalculated the molecular diameters of Phil. Mag. [6] xvii. 1909, p. 320, on the basis of the value of  $e$  just used, and these values will be used elsewhere in the present paper.

The diameter of the hydrogen molecule is  $2.17 \times 10^{-8}$ , and the radius of the hydrogen atom is this divided by  $2^{4/3}$ , and is  $0.861 \times 10^{-8}$ . Thus  $R$  is smaller than the smallest radius ascertained by the kinetic theory. But there are smaller atoms than that of hydrogen, for the volume of a gramme-atom of Li in its compounds is about 2 and of Be is about 1, whereas according to the value given above for  $a$  in the hydrogen atom with  $2.77 \times 10^{19}$  for the number of molecules in a c.c. of hydrogen under standard conditions the volume of a gramme-atom of H is

$$(2 \times 0.861 \times 10^{-8})^3 \times 2 \times 2.77 \times 10^{19} = 3.176.$$

Hence  $a$  for Li is  $(2/3.176)^{1/3}$  times that for H and is  $0.739 \times 10^{-8}$ , and for Be  $a=0.586 \times 10^{-8}$ . These values for the two smallest known atoms are less than  $R$  as calculated above. These two exceptions show that we cannot stipulate for  $R$  being less than  $a$ , and that the constraining power of the atom over the positive electron may extend beyond the atom of combined Li or Be. However, the fact that  $R$  is of the order of magnitude of atomic radii is encouraging.

If we now consider (1) more closely we see that it has some important bearings. The rigidity of the atom due to its electrization is

$$W = \frac{2\pi}{3} \frac{e^2 s^2}{(2a)^6} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(Phil. Mag. [6] vii. 1904, p. 417), this being the electric energy per unit volume of the atom. So (1) informs us that the electric energy of the atom per unit volume or its rigidity is equal to the electric energy of the special pair of electrons per unit volume of the sphere of radius  $R$  or the rigidity of that sphere due to the presence of the electrons. In "Further Studies on Molecular Force" (Phil. Mag. [5] xxxix. 1895, p. 1) it is shown that for non-metals in compounds  $(M^2l)^{\frac{1}{2}}$ , which is proportional to  $es$ , is proportional to  $a^3$  nearly. Hence from (1) if  $R$  is constant,  $r$  is also nearly constant. In the non-metals then the central atomic vibrator is nearly the same in the different elements. The internal electric

fields in the atoms of different non-metals are of nearly the same strength, so that the atomic vibrators have not only the same periods but nearly the same lengths  $r$ . From (1) also we get that the intensity of electrization throughout the sphere of radius  $R$  due to  $er$  is equal and opposite to that of the atom due to  $es$ .

With the atoms of metals in their compounds the conditions are different. It is proved in "The El. Or. of Mol. Attr." (*loc. cit.*) that in the Li family  $(M^2l)^{\frac{1}{2}}/10^6 = es/h10^6 = 1.2$  (2, 3, 4, 5, 6), where  $h$  is the mass of the hydrogen atom. It is mentioned there too that the volume  $B$  of a gramme-atom of the combined metal is given by  $2 + 2.7(n-1)n$  where  $n$  has successive integral values from 1. But a still simpler relation holds, namely, that  $B^{1/3} = 0.65$  (2, 3, 4, 5, 6), as the following comparison shows:—

TABLE I.

	Li.	Na.	K.	Rb.	Cs.
B.....	2	7.4	18.6	34.4	(56)
$B^{1/3}$ .....	1.26	1.95	2.60	3.25	3.82
$B^{1/3}$ calc.....	1.30	1.95	2.60	3.25	3.90

In this family  $es$  is proportional to  $a$ , and in the next section a similar result is proved for the Be family. In the atoms of metals of the same family  $es/a^3$  is not constant as in the non-metals, thus in the Li family it falls for Cs to  $(2/6)^2$  or  $1/9$  of the value for Li. Yet by virtue of (1)  $r$  is reduced in the same proportion, the larger atom has the shorter vibrator and the frequency of all the vibrators remains the same. We shall see later that in the characteristically non-metal families where  $a^3$  is proportional to  $es$  there is a strong tendency for  $a^3$  in a family to form a series 1, 2, 3, 4, just as we have seen in the characteristically metal families where  $a$  is proportional to  $es$  there is a tendency for  $a$  to form such a series as 2, 3, 4, 5, 6. Electric moment is a controlling factor in the architecture of the atoms. These conceptions of the structure of the atom and of the chief vibrating mechanism in the atom ought to furnish a definite quantitative theory of the nature of dielectric capacity, which will now be investigated.

One other matter requires consideration before we leave this section, namely, the magnitude of  $r$ . In "The Ions of Gases" (Phil. Mag. Sept. 1909) it was stated that this is of the order  $0.05 \times 10^{-8}$ , but when worked out with the molecular data used in this paper it is smaller. We have  $er/R^3 = es/a^3 = (M^2l)^{\frac{1}{2}}/B$ . For non-metallic elements in their

compounds  $B/(M^2l)^{\frac{1}{2}} = 10^{-5}$ , and for the element gases it has double this value. Since  $R$  is constant,  $r$  is constant in both cases, though for the element gases it seems to have only half the value for these substances in their compounds. Let us take the case of hydrogen as element with  $R = 0.795 \times 10^{-8}$  and  $e = 4.65 \times 10^{-10}$ , then  $r = 0.0054 \times 10^{-8}$ . In that paper it was shown that in  $H_2$ , He,  $N_2$ , and  $O_2$  an ion in contact with a molecule has with it potential energy due to the electron of the ion at its centre and a pair of electrons in the molecule which are at the same distance apart in these four cases. For hydrogen this distance was estimated as being  $0.0352 \times 10^{-8}$ . But with the molecular data used in this paper and with the concept of a vibrator for each atom that estimate requires some alteration. With  $N = 4 \times 10^{19}$  the potential energy of hydrogen ion and hydrogen molecule in contact was given as  $916 \times 10^{-16}$ , which ought to have been  $967 \times 10^{-16}$ , if allowance had been made in the numerical reductions for the difference between  $15^\circ$  C. and  $0^\circ$  C. If  $N = 2.77 \times 10^{19}$  to go with the value of  $e$  given above, this potential energy becomes  $1396 \times 10^{-16}$ . If this is  $e^2/x(2a)^2$  where  $a$  is the radius of the hydrogen atom, taken here to be  $0.861 \times 10^{-8}$ , then  $x = 0.0192 \times 10^{-8}$ , which is 3.54 times  $r$ . According to this computation  $x$  and  $r$  are not so nearly equal as I stated them to be in "The Ions of Gases." Probably they will be found to be equal or both to be simply derived from the same length, when we know more about the details of contact between ion and molecule.

## 2. A Theory of Dielectric Capacity.

In an atom within the sphere of absolutely constant radius  $R$  there are two electrons of special importance. The one is uniformly distributed through this sphere, or on account of its rapid random motion within the sphere behaves in certain respects as if so distributed. The other may be treated as a point electron at distance  $r$  from the centre of the sphere. Suppose the atom placed in an electric field of intensity  $F$  with whose direction the electric axis  $r$  makes an angle  $\theta$ . Then for all values of  $\theta$  the average projection of  $r$  on an axis at right angles to  $F$  is  $r/2$ . So we place an electron at the centre of the sphere of radius  $R$  and an opposite electron at distance  $r/2$  from the centre along any radius which is at right angles to  $F$ , and treat this electron pair as representing an average case. The electrons experience two opposite forces of amount  $eF$  in the direction of  $F$ . These may be regarded as tractive forces over the average sectional area



of the sphere of radius  $R$ , which is  $2\pi R^2/3$ . If the sphere is regarded as having a rigidity  $W$ , the angle through which the sphere of radius  $R$  is sheared is  $3eF/2\pi R^2W$ . This displaces one electron relatively to the other by the amount  $3eFr/4\pi R^2W$ , and therefore  $3e^2Fr/4\pi R^2W$  is the electric moment in the direction of  $F$  which  $F$  has produced in the pair of electrons. This gives in an atom an average intensity of electrization, analogous to intensity of magnetization, of amount  $3e^2Fr/4\pi^2R^2Wa^3$ , where  $a$  is the radius of the atom. The corresponding average electric intensity in the atom is  $4\pi/3$  times this, and may be denoted by  $F'$ . This produces induced electrization  $F'(K-1)/4\pi$ , where  $K$  is the dielectric capacity of the atom, and the electric intensity due to this is  $F'(K-1)$ . This is the intensity which acts upon the constitutive electron pairs of the atom. With a typical pair of these constitutive electrons in this field of electric force derived from the special inner pair of electrons we proceed just as we have done with that special pair in the field  $F$ . Let there be  $n$  of these constitutive pairs of electrons in the atom, each of electric moment  $e\sigma$ . The domain of each, or its share of the volume of the atom, is  $4\pi a^3/3n$ . Let  $w$  be the rigidity of each pair of constitutive electrons. This is different from  $W$  because we cannot assume that all the constitutive pairs are directed in the same way. Indeed, within the atom similar considerations apply to those which I have pointed out in the theory of the electric origin of cohesion. In each pair of constitutive electrons the opposite forces are  $eF'$ , which may be assumed to act over area  $2\pi\sigma^2/3$ , so the angle through which the pair is sheared is  $3eF'/2\pi\sigma^2w$ , and so the average distance through which each electron of the pair is displaced is  $3eF'\sigma/4\pi\sigma^2w$ , giving electric moment  $3e^2F'\sigma/4\pi\sigma^2w$ . For the  $n$  pairs the total moment will be  $n$  times this. For the whole electric moment generated in the atom by  $F$  we have

$$\frac{3e^2Fr}{4\pi R^2W} \left( 1 + \frac{3(K-1)ne^2\sigma}{4\pi\sigma^2wa^3} \right). \quad \dots \quad (4)$$

To carry this farther we must express  $W$  and  $w$  by means of the formula given in "The Electric Origin of Rigidity and Consequences" (Phil. Mag. [6] vii. p. 417), with  $K=1$ , namely,

$$W = \frac{2\pi}{3} \frac{e^2s^2}{(2a)^6}, \quad w = \frac{2\pi}{3} \frac{e^2\sigma^2n^2}{(2a)^6} \quad \dots \quad (4a)$$

Let  $v$  be the domain of the atom, that is, the  $n$ th part of the volume through which  $n$  atoms are distributed, then the

average intensity throughout  $v$  due to the induced moment (4) is that moment divided by  $v$ . Now the average intensity of the electrization induced by  $F$  is  $F(K'-1)/4\pi$ , where  $K'$  is the dielectric capacity caused on the average throughout  $v$  by the presence of the atom, to be distinguished from  $K$  the average dielectric capacity through the volume  $4\pi a^3/3$  of the atom. Consider the case where the atoms form a gas whose index of refraction  $N'$  is connected with  $K'$  by the law of Maxwell  $K'=N'^2$ , then since  $K'$  and  $N'$  differ little from 1, we have  $K'-1=2(N'-1)$ . But if  $N$  is the index of refraction of the atom, so that  $K=N^2$ , we have by the chief law of molecular refraction  $(N'-1)v=(N-1)4\pi a^3/3$ , so that  $F(K'-1)/4\pi$  becomes  $2F(N-1)a^3/3v$ , which, when equated to (4) divided by  $v$ , gives the desired relation

$$2(N-1)a^3/3 = \frac{3e^2r}{4\pi R^3W} \left(1 + \frac{3(K-1)ne^2\sigma}{4\pi\sigma^2wa^3}\right). \quad (5)$$

In comparing the results of this equation with the experimental ones we shall have to consider the metallic elements in one group and the non-metallic in another. In the metals it appears that  $\sigma$  is constant in a natural family. Since  $2i$  is the mass of a pair of constitutive electrons, then  $2in=m$  the mass of the atom, and  $2in/(2a)^3$  is the density of the atom, which may be denoted by  $\rho$ . By (1) we have  $r/R^3=s/a^3$ . It has been shown above that in the Li family  $s$  is proportional to  $a$ ,  $=ca$  say, and since  $v$  is the same for all atoms compared under the same conditions of pressure and temperature, and may be replaced by  $V$  for a gramme-atom, (5) for the atoms of metals in their compounds takes the form

$$(N'-1)V=(N-1)B=CB^{\frac{2}{3}}+DB^{\frac{1}{3}}(N^2-1)/\rho, \quad (6)$$

where  $C=2Ra^2/B^{\frac{2}{3}}c$  and  $D=iC/2\sigma^3$ ,

$C$  and  $D$  being parameters characteristic of the family, and  $B$  the volume of a gramme-atom taking the place of  $(2a)^3$ , the actual volume of the smallest cube containing an atom. Table II. contains the data for testing (6) in the Li family of metals in their compounds, the values of  $B$  being already given in Table I. The values of  $\rho$  are obtained by dividing atomic weight by  $B$ . The refraction equivalents  $(N-1)B$  are taken from Gladstone's latest list (Proc. Roy. Soc. 1896). From these by means of  $B$  the values of  $N$  have been calculated, those of  $K=N^2$  being added for completeness. From these data I find that in (6)  $C=0.835$  and  $D=0.735$ . The values of  $N$  yielded by (6) with these values of  $C$  and  $D$  are given in the table as  $\bar{N}$  calc.

TABLE II.

	Li.	Na.	K.	Rb.	Cs.
(N-1)B .....	3.6	4.65	8.00	11.4	15.6
$\rho$ .....	3.5	3.11	2.10	2.485	2.375
N .....	2.80	1.628	1.430	1.331	1.2785
N calc. ....	2.85	1.63	1.47	1.32	1.26
K .....	7.84	2.65	2.045	1.77	1.635

In the case of the Be family of metals there are special circumstances to consider, the chief being the effect of their divalency upon  $es$  for the atom of the metal in its compounds. In "Further Studies on Molecular Force" (Phil. Mag. [5] xxxix. p. 1)  $es/h$  for molecules is investigated under the symbol  $(M^2l)^{\frac{1}{2}}$ , and it is shown that in binary compounds of the metals of the form  $RS_n$  where R is an  $n$ -valent atom of a metal and S is a halogen acting monovalently,  $(M^2l)^{\frac{1}{2}}/n^{\frac{1}{2}}$  is of the form  $F_r/n + F_s$ , whereas on the principle of additive parameters for chemical equivalents the law would be that  $(M^2l)^{\frac{1}{2}}/n$  should be of the form  $F_r/n + F_s$ , where  $F_r$  and  $F_s$  are the parameters characteristic of the elements R and S, and are proportional to  $es$  for the atoms of R and S respectively. In "The Electric Origin of Molecular Attraction" (Phil. Mag. [6] iv. p. 625) I have suggested that this remarkable result is derived from the symmetrical arrangement with regard to the centre of the atom of the  $n$  electric fields in an  $n$ -valent atom. For the metals Be, Mg, Ca, Sr, and Ba the values of  $F_r/2$  are given by 0.53 (4, 5, 6, 7, 8) with a maximum error of 2 per cent. and an average error of 1 per cent. (Phil. Mag. [6] iv. p. 642). For this family of metals the values of B are reproduced in Table III. from Phil. Mag. [5] xxxix. p. 26, along with the derived values of  $B^{1/3}$  to be compared with those furnished by the empirical formula  $B^{1/3}=0.32$  (4, 5, 6, 7, 8).

TABLE III.

	Be.	Mg.	Ca.	Sr.	Ba.
B .....	1.0	5.6	8.6	10.6	16.6
$B^{1/3}$ .....	1.0	1.78	2.05	2.20	2.55
$B^{1/3}$ calc. ....	1.28	1.60	1.92	2.24	2.56

The value of B for Be is very uncertain on account of its smallness and the fewness of the suitable compounds whose density has been measured. For the other metals of the family the liability to error in the value of B is considerable, for example the volume of a gramme-molecule of  $MgCl_2$  is 43.6, which with 38 for  $Cl_2$ , yields 5.6 for Mg, with danger

that any minor error in 43.6 becomes relatively large when all accumulated on the residual 5.6. For this reason then the values of B and of  $B^{1/3}$  in Table III. are to be taken as only rough approximations. In view of the proportionality between  $\epsilon_s$  and  $B^{1/3}$  in the Li family, both giving the series 2, 3, 4, 5, 6, and the sharpness with which  $F_r/2$  or  $\epsilon_s$  in the Be family gives the series 4, 5, 6, 7, 8, I think it is the best course to take B in this family as given by the formula  $B^{1/3}=0.32$  (4, 5, 6, 7, 8). The values of B thus obtained are given in Table IV. as B calc., and are used for the study of (6) with  $C=2.31$ ,  $D=0.456$  in the Be family of metals in their compounds as set forth in Table IV.

TABLE IV.

	Be.	Mg.	Ca.	Sr.	Ba.
B calc. ....	2.097	4.096	7.077	11.24	16.77
(N-1)B .....	6.6	6.9	10.1	13.3	16.1
$\rho$ .....	4.29	5.86	5.65	7.80	8.19
N .....	4.147	2.685	2.427	2.184	1.960
N calc. ....	4.15	2.77	2.40	2.11	1.97
K .....	17.2	7.21	5.89	4.77	3.84

From this Table and II. it appears that (6) gives a satisfactory account of N, and therefore of K, for these two families of metals in their compounds. In the other families of metals the data are imperfect, but when obtained they will show how the transition to the case of non-metals occurs. A comparison of C in these two families of metals is important, and also a comparison of D. The ratio of the two values of C is  $2.31/0.835=2.77$ . Now on the simplest theoretical grounds we should expect this ratio to be 2, for, if we turn back to the reasoning by which (5) was established, we see that two pairs of special electrons in the atom will cause C to have double the value due to one. Moreover, C in the Be family is to C in the Li family as  $0.53/0.32$  is to  $1.20/0.65$ , that is as 1 to 1.114. On these two accounts then C in the Be family ought to be  $2 \times 1.114=2.23$  times C in the Li family. This theoretical 2.23 falls short of the actual 2.77 just found from the data. Perhaps the two special electron pairs in the Be family exercise a mutual influence which should be included in the theory. As regards D we see that  $D/C=i/2\sigma^3$ , and in the Be family has the value  $0.456/2.31$ , in the Li family  $0.735/0.835$ , which bear to one another the ratio 1 to 4.46. But if  $i$  the inertia of an electron is the same in both families, this result implies that  $\sigma^3$  in the Be family is 4.46 times  $\sigma^3$  in the Li family. It is only acci-

dental that this 4.46 is exactly double the 2.23 calculated just above in connexion with C. It appears then that the electric moment of a constitutive electron pair in the atoms of the Be family is 1.64 times that of those of the Li family.

When we proceed to develop for the non-metals formulas like (5) and (6) we find complete similarity in principle, but a most instructive contrast in detail. In the case of the atoms of the metals in their compounds we found that external electric intensity acts first upon the special pair of electrons, and through these upon the constitutive electrons. In the atoms of non-metals, on the other hand, we shall see immediately that an external electric intensity acts first upon the constitutive electrons, and through these upon the special pair of electrons. The most marked electric distinction between the atoms of metals and non-metals, both in the combined state, is that  $es$  in the metals is proportional to  $a$ , and in the non-metals to  $a^3$ . It appears that in the atom of metal the special pair of electrons separating from one another to a distance proportional to  $a$  control the whole electric moment of the atom so that it is proportional to  $a$ . But in the atom of non-metal, on the other hand, as  $es$  is proportional to  $a^3$ , the intensity of electrization  $es/(4\pi a^3/3)$  is constant, a result which makes it appear that in the atom of non-metal the pairs of constitutive electrons are so arranged that they dominate the special electron pair, and make the average intensity of electrization uniform in an atom and nearly constant from the atom of one non-metal to that of another. We shall proceed, therefore, on the assumption that in order to reach the special pair of electrons with an external electric intensity  $F$  we must first act upon the  $n$  pairs of constitutive electrons. To find the electric moment imparted by  $F$  to one of these we need only replace in our calculation for the moment imparted to  $er$  in an atom of metal  $er$  by  $e\sigma$ , and  $R$  by  $a/n^{1/3}$  and  $W$  by  $w$ , obtaining  $3e^2F\sigma/4\pi(a/n^{1/3})^2w$ . In the atom of metal I was led to use  $\sigma$  where  $a/n^{1/3}$  occurs here, an important difference. The electric intensity due to  $n$  such moments in the atom is  $F' = 3ne^2F\sigma/4\pi(a/n^{1/3})^2wa^3$ . Under this the whole atom is strained so that its moment  $es$  is given in the direction of  $F$  an electric moment  $3e^2F's/4\pi a^2W$ , with which is associated the electric intensity  $F'' = 3e^2F's/4\pi a^2Wa^3$ .

It is important to notice the "dimensions" of this intensity. If  $W = 2\pi e^2s^2/3(2a)^6$  and  $es$  is proportional to  $a^3$ , the coefficient of  $F'$  is of dimensions  $-2$  in  $a$ . It will appear immediately that in each natural family of the non-metals,

as for instance in the halogens, if  $a^3$  is used here for the first member, fluorine,  $a^3/2$  is to be used for Cl,  $a^3/3$  for Br, and  $a^3/4$  for I, that is to say, that in  $F''$  the coefficient of  $F'$  is proportional to  $(a^3/u)^{-2/3}$ , where  $u$  has the values 1, 2, 3, 4. It appears then that in the Cl atom two halves are strained separately, in the Br atom three equal parts are strained separately, and in the I atom four equal parts, and similarly with other families of non-metals. In order to draw attention to this phenomenon it is advisable to replace an  $a^2$  in  $F''$  by  $a'^2$ , thus  $F'' = 3e^2F's/4\pi a'^2Wa^3$ .

This intensity acting upon the special pair of electrons imparts to it in the direction of  $F$  a moment  $3e^2F'r/4\pi a^2W'$ , in which  $W'$  is the rigidity due to  $er$ . But as the electric intensity  $F$  is acting in a region of dielectric capacity  $K$ , it will produce a moment  $K$  times as great as that just calculated without reference to dielectric capacity. Thus we get the following equation like (5)

$$2(N-1)a^3/3 = \frac{3Ke^2r}{4\pi a^2W'} \cdot \frac{3e^2s}{4\pi a'^2Wa^3} \cdot \frac{3ne^2\sigma}{4\pi(a/n^{1/3})^2wa^3}, \quad (7)$$

in which  $W' = 2\pi e^2r^2/3(2a)^6$  and  $w = 2\pi e^2\sigma^2n^2/3(2a)^6$ .

It is to be noticed that the right-hand side of (7) is obtained by acting on  $F$  with three successive operators of the form  $3e^2x/4\pi a^2w$ . Moreover, when we have derived  $F'$  from  $F$ , we do not call the intensity  $F' + F$ , but simply  $F'$ . The intensity  $F$  is intensified three times in succession, the final result being independent of the order in which the intensifications are applied. The whole affair recalls the intensification of an ordinary force by a system of levers.

In simplifying (7) we must remember that  $r$  is constant because in (1) when applied to the non-metals  $es$  is proportional to  $a^3$  and  $R$  is constant. If then, as in the atoms of metals,  $\sigma$  is the same for all non-metals, and since  $2in = m$  and  $\rho = m/(2a)^3$ , we have, like (6),

$$(N'-1)V = (N-1)B = EKB^{2/3}u^{2/3}/\rho^{1/3}, \quad \dots \quad (8)$$

where  $E$  is the constant  $3^7 2^2 (2i/h)^{1/3} / \pi^5 k r \sigma$ , where  $ka^3 = s$  and  $h$  is the mass of an atom of hydrogen. The most suitable way to test this relation is to use the values of  $N'-1$  for the non-metals as elements in the gaseous state investigated by Cuthbertson since 1902 ('Nature,' Phil. Trans., and Proc. Roy. Soc.). The data for  $0^\circ$  C. and 1 atmo. (2 atmos. for the monatomic gases of the inert He family) are collected by Cuthbertson and Metcalfe (Phil. Trans. ccvii. A. 1908,

p. 135). Cuthbertson found first in the He family that  $10^6(N'-1)=141$  ( $\frac{1}{2}$ , 1, 4, 6, 10), the corresponding result for the halogens being 192 (1, 4, 6, 10). For the first two members of the oxygen and nitrogen families the values are 275 (1, 4) and 299 (1, 4), but for the higher members of these families the values are not expressed accurately enough by the integers 6 and 10. The elements of the carbon family have not yet been examined in the gaseous state for  $N'-1$ , so for these I shall use the relation  $(N'-1)V=(N-1)B$ , which will be assumed to be the same as the refraction equivalent or atomic refraction of these elements in their compounds. On account of the attention which has been given to atomic refraction in the past it will be convenient to multiply  $N'-1$  by 11215 to get the values tabulated as  $(N'-1)V$ .

Next as to the values of  $B$  to be used in testing (8). If the experimental data were complete enough, the best way to get values of  $B$ , the limiting volume of a gramme-atom of each gas, would be to derive it from  $(2a)^3$ , calculating  $a$  by the principles of the kinetic theory. But on account of many gaps in the data we are compelled to make provisional approximate estimates of some values of  $B$  in the following way. Molecular diameters for a certain number of gases according to the kinetic theory with the best data available are given in a note appended. For the halogen atoms, both in their organic and inorganic compounds, the values of  $B$  are F 9, Cl 19, Br 26, and I 36, which are nearly 9 (1, 2, 3, 4) (Phil. Mag. [5] xxxix. p. 1). Now for the gramme-atom of Cl as an element gas the kinetic theory gives  $B=2.77 \times 10^{19} \times 11215(2a)^3=16.5$ . Again the density of solid iodine, namely, 4.94, gives  $B=127/4.94=25.6$ , which is different from 36 in compounds and not double 16.5. Yet for the halogens in the state of elements I shall assume  $B=6.6$  (1, 2, 3, 4), giving greatest weight to the result for solid iodine and to the law 1, 2, 3, 4. Concerning  $B$  we must give to the inert gases of the helium family a more detailed study. In the first place we must investigate their virial parameters, which have not been calculated in any of my papers on molecular attraction. Let  $T_c$  and  $p_c$  denote the critical temperature and pressure of a substance, then for both compounds and elements  $l$ , the parameter of the virial of the attractive forces for a gramme, is proportional to  $R^2T_c^2/p_c$ , where  $RM$  is the usual gas constant. The constant of proportionality is different for compounds from that for elements. In the absence of knowledge to the contrary I shall assume that the formula for such diatomic gases as

H<sub>2</sub> and O<sub>2</sub> applies to the monatomic inert gases. It is given under "Fourth method of finding the virial constant," on p. 247 of "The Laws of Molecular Force" (Phil. Mag. [5] xxxv. 1893), namely,  $l = 27R^2T_c^2/64p_c$ , for in this case  $l$  is identical with  $a$  of Van der Waals, so that  $M^2l$  depends only upon  $T_c^2/p_c$ . The values of  $10^{-6}(M^2l)^{\frac{1}{2}}$  with the dyne as unit of force are given for three of the inert gases in the last row of the following table :—

	A.	Kr.	X.
$T_c$ abs. ....	156	210	288
$p_c$ atmos.....	52.9	54.3	57.2
	1.15	1.53	2.05

These values of  $10^{-6}(M^2l)^{\frac{1}{2}}$  stand to one another nearly as 3 to 4 to 5. According to the theory of corresponding states the critical volumes of substances are proportional to  $T_c/p_c$ , if the molecules of the substances form similar dynamical systems, but the constant of proportionality for elements is different from that for compounds, and it varies somewhat in compounds according to type. The values of  $T_c/p_c$  from the above table are 2.94, 3.88, and 5.03, which are again nearly as 3 to 4 to 5. If both  $(M^2l)^{\frac{1}{2}}$  and the critical volume were strictly as 3 to 4 to 5,  $p_c$  would need to be the same for the three gases, as it nearly is. According to the equation of Van der Waals the critical volume is proportional to the limiting volume of the molecules. But even though that equation is not of general application, it gives valuable approximate generalizations like those concerning corresponding states. So we shall assume the limiting volumes in A, Kr, and X to be as 3 to 4 to 5. But the diameter of the molecule of A is  $2.66 \times 10^{-8}$  cm., whence

$$B = 2.77 \times 10^{10} \times 2 \times 11215 (2.66 \times 10^{-8})^3 = 11.7.$$

Now for He  $2a = 1.92 \times 10^{-8}$ , whence  $B = 4.42$ . Since 4.42 is to 11.7 nearly as 1 to 3, I shall assume that for the family  $B = 4.0$  (1, 2, 3, 4, 5). To complete the knowledge of  $(M^2l)^{\frac{1}{2}}$  obtainable from existing data we can use the result (Phil. Mag. [5] xxxvi. 1893, p. 507) that  $C$  in the formula for the viscosity of a gas is connected with  $M^2l$  by the relation that  $M^2l$  is proportional to  $CB$ . Now for He and A the values of  $C$  are 76 and 160, so that the values of  $(M^2l)^{\frac{1}{2}}$  are as  $(76 \times 1)^{\frac{1}{2}}$  to  $(160 \times 3)^{\frac{1}{2}} = 1$  to 2.5.

I shall assume that the relation is 1 to 3, and that the last table can be extended to give the formula  $10^{-6}(M^2l)^{\frac{1}{2}} = 0.4(1, 2, 3, 4, 5)$ . One of the assumptions used above would lead to an absurdity if applied directly to the case of helium.



We found that  $p_c$  would have to be constant for the whole family, as the last table shows that it nearly is for A, Kr, and X at about 50 atmos. But  $p_c$  for He is about 2.5 atmos. It looks as if the assumption that critical volume is proportional to limiting volume and also to  $T_c/p_c$  cannot be extended to the extreme case of He in this family. The ratio of B to  $10^{-6}(M^2l)^{\frac{1}{2}}$  in this family is constant, namely  $4.0/0.4=10$ , the same ratio for ordinary atoms in compounds having a value about 10, and for the element gases  $H_2$ ,  $O_2$ , and  $N_2$  a value about 20. In this family then we have  $s=ka^3$ , as in the other chief non-metals. The atomic weights of these elements will be taken to be those given by their densities, namely, He 3.968, Ne 19.96, A 39.96, Kr 83.2, and X 131, though they could equally well be taken at the nearest whole number.

In the families of oxygen and nitrogen B can be obtained for all but the first member of each from the density of the solid element, with a small amount of uncertainty on account of different allotropic forms. For oxygen the kinetic theory gives  $B=6.16$ , and for nitrogen 8.00. When we pass to the carbon family we find that allotropy causes considerable uncertainty in the case of carbon itself, for  $B=3.6$  in the diamond, and 5.58 in graphite, and about 8 in the compounds of carbon. I shall take the smallest of these as the one to be used in testing (8). The data and derived quantities are collected in the following table leading to the values of  $(N'-1)V\rho^{1/3}/KB^{2/3}u^{2/3}$  in the last row, which by (8) is to be constant. It is to be remembered that K is got from  $N'-1$  and B by the relations  $(N'-1)V=(N-1)B$  and  $K=N^2$ .

TABLE V.

	He.	Ne.	A.	Kr.	X.
$u$ .....	$\frac{1}{2}?$	1	2	3	4
$(N'-1)V$ .....	0.8074	1.537	6.369	9.532	15.45
B .....	4	8	12	16	20
N .....	1.202	1.192	1.531	1.597	1.773
K .....	1.444	1.421	2.344	2.551	3.144
$\rho$ .....	0.992	2.496	3.331	5.200	6.551
	.3511	.3667	.4877	.4903	.4955

	F.	Cl.	Br.	I.
$u$ .....	1	2	3	4
$(N'-1)V$ .....	2.153	8.614	12.62	21.53
B .....	6.6	13.2	19.8	26.4
N .....	1.326	1.652	1.637	1.816
K .....	1.758	2.729	2.679	3.298
$\rho$ .....	2.879	2.681	4.040	4.810
	.4953	.4946	.4926	.4933

TABLE V. (continued).

	O.	S.	Se.	Te.
$u$ .....	1	2	3	4
$(N'-1)V$ .....	3.023	12.35	17.55	27.93
B .....	6.16	15.7	17.1	20.2
N .....	1.492	1.787	2.027	2.385
K .....	2.226	3.195	4.109	5.689
$\rho$ .....	2.597	2.038	4.619	6.237
	.5564	.4925	.5151	.4844

	N.	P.	As.	C.	Si.
$u$ .....	1	2	3	1	2
$(N'-1)V$ .....	3.332	13.43	17.38	5	7.5
B .....	8.00	13.5	13.2	3.6	11.2
N .....	1.416	1.995	2.317	2.391	1.67
K .....	2.004	3.981	5.367	5.718	2.789
$\rho$ .....	1.750	2.297	5.682	3.333	2.50
	.5007	.4944	.4974	.5562	.4594

In this table the data for the halogens are probably the best, and in this family the mean value of the ratio is 0.49395, from which the average departure is only 0.2 per cent. and the maximum departure 0.3 per cent. In this family there is the special relation that both B and  $u$  have values as 1, 2, 3, 4. In the He family I have put for He  $u = \frac{1}{2}$  ? to indicate that there is no sure guidance as to what the value of  $u$  should be. A fractional value of  $u$  presents some difficulty of interpretation. If for He  $u = 1/3$  the ratio would be 0.460 in close agreement with the results for A, Kr, and X. As the table stands, the results for He and Ne are a good deal too small. In the table as a whole it will be noticed that those elements which have definitely ascertained values of B from the density in the solid state show a good approach to constancy in the ratio. For O the value of the ratio is large. For C and Si the available data allow only a rough determination of the ratio. On the whole the table shows that the theory gives a good account of dielectric capacity in the non-metals. The interesting questions of the transition from metal to non-metal, and of the action of an element electrically positive in some compounds and negative in others have not been discussed, as they would lead into further complications hardly ready for discussion.

The data for hydrogen should be considered here, namely,  $(N'-1)V = 1.559$  and  $B = 3.18$  from the kinetic theory, which make  $N = 1.490$ ,  $K = 2.22$ ,  $\rho = 0.3145$ , and with  $u = \frac{1}{2}$  the ratio  $(N'-1)V\rho^{1/3}/KB^{2/3}u^{2/3}$  is 0.3504, and with  $u = 1/3$  it is

*Phil. Mag.* S. 6. Vol. 19. No. 109. Jan. 1910. C

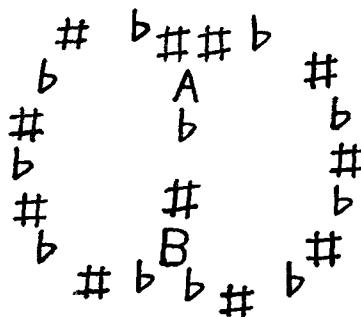
0.4592. These results for H are very like those for He. It may be mentioned that for oxygen if  $B=8.29$  instead of 6.16, the ratio would become 0.4941. The evidence as to B for O and N in their compounds is on the whole towards making its value larger than that given by the kinetic theory. It is rather remarkable that the valency of the non-metallic elements does not influence their dielectric capacity. The order of the element in its family asserts itself by the appearance of  $u$  in (8), but the valency of the family does not appear. If in (8) we put  $\rho=M/B$  and  $(N'-1)V=(N-1)B$ , we get the simple result that  $(N-1)/N^2=EM^{1/3}u^{2/3}$ . That is to say, that the index of refraction or the dielectric capacity of the stuff of an atom of non-metal is a function of only its atomic mass (weight) and  $u$ . In "The Dielectric Capacity of Atoms" (Phil. Mag. [6] vii. p. 402) it is shown that if  $K$  is derived according to certain assumptions from the atomic conductivity of the atoms as ions in aqueous solution, then  $KB^{1/2}/V$  is nearly constant for both metals and non-metals,  $V$  being valency. But in "Ionization in Solutions and Two New Types of Viscosity" (Phil. Mag. [6] xiv. 1907, p. 1) it appears that  $K$  thus derived in the case of the halogens is very different from  $N^2$ , and must be interpreted as  $K$  for slow electric alternations, while  $N^2$  is  $K$  for rapid alternations. The matter requires further investigation. At present we are dealing with  $K$  only as it appears in the electric alternations of light.

In this section then it has been shown that dielectric capacity, both in atoms of combined metal and of non-metal, can be explained by means of internal electric fields in the atoms corresponding with the external electric fields which produce cohesive force, otherwise called molecular attraction. The broad laws that the atom of metal is electrized so that its moment is proportional to its radius, while the atom of non-metal is electrized so as to have its electric moment proportional to its volume, have been found to be fundamental in determining the relations of dielectric capacity in the two classes of atoms. It is also profoundly significant that the radii of the atoms of combined metals should show simple numerical relationships like 2, 3, 4, 5, 6 in the Li family, while the volumes of the atoms of non-metals show a tendency to similar simple relationships like 1, 2, 3, 4 in the halogens. It is evident then that electric conditions largely determine the architecture of atoms.

The cohesion of the constitutive pairs of electrons with the aid of the special pair to form the atom demands investigation. The pair of electrons is to the atom what the molecule

is to an ordinary piece of matter, it is a unit of structure. In "The Electric Origin of Molecular Attraction" (Phil. Mag. [6] xvii. 1909, p. 657) it is suggested, with the aid of diagrams, that in matter contiguous molecules adjust their axes so that these form axial lines, along each of which the axes are similarly directed, while the axial lines are alternately oppositely electrized. This arrangement is one of minimum electric potential energy and causes each molecule to attract its six nearest neighbours with repulsions and attractions beyond these six tending towards an average null effect. At the same time it gives no electric moment to any ordinary piece of matter, the sum of the electric moments of all the molecules being nothing. In the atom the chief difference from this state of affairs is that the cohering constitutive pairs have their electric axes similarly directed to the extent required to give the whole atom its characteristic electric moment  $es$ . This leads naturally to the conception of chains of pairs of electrons, the electric axes of all the pairs being similarly directed along the chain. Let us make a diagram of two such chains symmetrically situated with

Fig. 1.



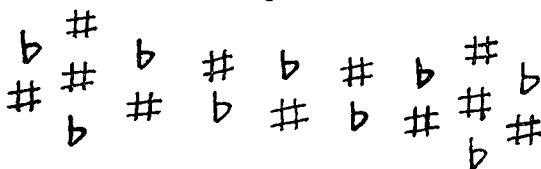
regard to the electric axis of the whole atom, this axis being denoted by AB. The two chains being electrized in the same direction, on the average that of AB, repel one another. It seems to be the function of the special electron pair placed at AB to attract both of these repelling chains and to hold them in position. The special pair acts like a keystone to all the arches of the constitutive pairs of electrons.

It appears then that the cohesion of the molecules of an ordinary piece of matter is the result of the action at more distant range of the same electric forces which cause the

constitutive pairs of electrons to cohere in each chain. One of the effects of atomic disintegration must be the liberation of one of these chains, which, when free, will behave in many respects like the moving steel chain in gyroscopic experiments. If a chain is broken into its separate electron pairs each will form the pair which I have proposed to call a neutron, which seems to be a necessary constituent of the luminiferous æther to enable it to transmit electric and magnetic actions.

Theoretically, then, there is reason to look for the free pair of electrons as a physical agent as it appears in Bragg's hypothesis for the gamma and the Röntgen rays. If Rutherford's view of the alpha particle is correct, namely, that it is an atom of helium carrying two positive electrons, I would suggest for it the structure shown in the diagram, where a

Fig. 2.



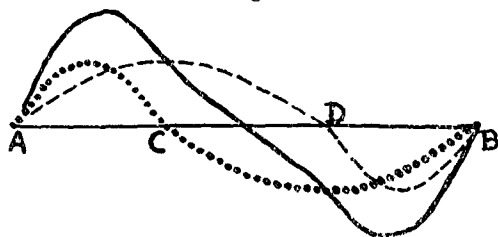
circular ring of electrons has collapsed into the form of two parallel cohering straight chains enclosing a positive electron at each end. These by their repulsion tend to keep the chains straight. If such a structure breaks away in the disintegration of radium with a velocity nearly that of light, it will have many of the properties of an alpha particle. When the two positive electrons are removed the structure rearranges itself in the form of the He atom. It ought to throw much light upon the internal structure of the atom if the reason is discovered for Bragg's remarkable law that the stopping power of the atom of an element for the alpha particle varies as the square root of the atomic mass.

It should be noted that each pair of electrons may be rotating round the average position of its electric axis, and may thus have a magnetic moment parallel to the electric. Each pair by virtue of its inertia has the properties of a gyrost. Each pair is a vibrating system whose period can be calculated on the principles here discussed. The idea of the electric gyrost has already been used in a theory of the electric conductivity of metals in "The Electric Origin of Rigidity and Consequences."

### 3. A Kinematical Analysis of Balmer's Formula.

Under this title in section 3 of "The Cause of the Structure of Spectra" an attempt was made to trace Balmer's formula to certain simple effects of relative motion. In that paper quite a number of numerical laws or indications of such laws are shown to imply the prominence of kinematical considerations. Yet since Rayleigh suggested in 1897 that Balmer's formula points to kinematic, rather than dynamic, relations, many elaborate attempts have been made to find a dynamical explanation of the relations amongst the lines in a spectral series. To follow up the dynamical theory here advanced for the fundamental constant of atomic vibration in Balmer's formula it seems desirable to make my former kinematical analysis of Balmer's formula more definite in the following way. Consider a vibrating circle one point of which is constrained to be a node. The circumference of the circle is half a wave-length. The stationary wave is the resultant of two trains of waves which are travelling in opposite directions round the circle, and are always being reflected at the node. Let the angular velocity of each train be  $\omega$ . Suppose now that the node A is caused to move with angular

Fig. 3.



velocity  $\Omega$  because the constraint producing it so moves. Then relatively to A the one train is moving with angular velocity  $\omega - \Omega$ , and the other with  $-\omega - \Omega$ . Thus the constraint will be met by the one train after time  $2\pi/(\omega - \Omega)$ , and by the other after time  $2\pi/(\omega + \Omega)$ , that is to say, the half wave-length of the one train which was originally  $2\pi c$  is changed to  $2\pi c\omega/(\omega + \Omega)$ , and that of the other to  $2\pi c\omega/(\omega - \Omega)$ . But upon reflexion each of these altered half waves is followed by the other. Thus each whole wave  $\lambda$  of one train is replaced by two parts  $\lambda\omega/2(\omega + \Omega)$  and  $\lambda\omega/2(\omega - \Omega)$ . The state of affairs is represented graphically in the diagram where  $AB = AC + CB$  and represents part of the circumference of the circle developed as an infinite

straight line.  $AC = BD = 2\pi c\omega/(\omega + \Omega)$ ;  $CB = DA = 2\pi c\omega/(\omega - \Omega)$ . With  $x$  as abscissa measured from A the curve in dots is composed as far as C of  $y = \sin \pi x/AC$ , and from C to B of  $y = \sin \pi x/CB$ , while the curve of dashes consists from A to D of  $y = \sin \pi x/DA$ , and from D to B of  $y = \sin \pi x/BD$ . The full curve is got by summing the ordinates of these two. It represents a periodic, but not simple harmonic, function of wave-length

$$AB = 2\pi c\omega \{1/(\omega + \Omega) + 1/(\omega - \Omega)\} = 4\pi c\omega^2/(\omega^2 - \Omega^2)$$

derived from the original wave-length  $4\pi c$ . With  $n = 1/\lambda$  Rydberg's extension of Balmer's formula is  $n = n_0 - b/(m + \mu)^2$ , reducing to Balmer's when  $\mu = 0$ . If we compare this with the formula just derived for wave-length we get, if  $V$  is velocity of light and  $v$  that of disturbance in atom,

$$n_0 = V/4\pi cv \quad \text{and} \quad (b/n_0)^{\frac{1}{2}}/(m + \mu) = \Omega/\omega. \quad (9)$$

Let us suppose that this disturbance travelling with angular velocities  $\omega$  and  $-\omega$  is a deformation caused in the stuff of the atom, that is in the medium formed by the constitutive pairs of electrons, and that the circle of radius  $c$  is the equator of the spherical atom whose poles are the ends of its electric axis, or a small circle parallel to the equator, giving  $\omega > \Omega$ . This deformation is caused by a displacement of the special pair of electrons which brings its negative electron nearer to the most deformed part of the spherical surface of radius  $R$ . This negative electron is the cause of the disturbance and also determines the node, so that its angular velocity is  $\Omega$ . Since  $v$  is the velocity of propagation of the disturbance through the stuff of the atom, then  $v = c\omega$ . Next consider the small circle parallel to the equator whose radius is  $c/m$ , where we shall first suppose  $m$  to be an integer. Then a disturbance travelling round this circle with velocity  $v$  will have angular velocities  $m\omega$  and  $-m\omega$ . In this way by considering the special pair of electrons as cause of elastic disturbance in the atom, and as controlling the position of nodes in the circles of radii  $c/m$ , we can give a simple kinematical account of Balmer's formula. To pass to Rydberg's form we would need to find a kinematical reason for angular velocities which are proportional to  $m + \mu$ , where  $\mu$  is a fraction characteristic of a spectral series. In my previous paper I have shown that  $m$  may take the form  $m + 1/n$  where  $n$  is an integer, and even  $m + p/q$  where  $p$  and  $q$  are integers. But for the present we shall confine our attention to the essentials as they appear in the formula of Balmer. We have a funda-

mental standing wave of length  $4\pi c$  in the atom, which becomes  $4\pi cV/v$  or  $\lambda$  in free æther. This gives an important relation between a linear dimension of the atom and the wave-length of its light. We can test this relation in the following way. We have

$$v = (W/\rho)^{\frac{1}{2}} = (2\pi/3)^{\frac{1}{2}} (es/(2a)^3 \rho^{\frac{1}{2}}) = (2\pi/3)^{\frac{1}{2}} (M^2 l/B^2 \rho)^{\frac{1}{2}}.$$

Now in the non-metals we have  $B = 10^{-5} (M^2 l)^{\frac{1}{2}}$  nearly, and  $\rho$  of the same order of magnitude as  $2\pi/3$ , so that  $v$  is of the order  $10^5$ , and  $V/v$  is of the order  $3 \times 10^5$ . In the visible part of the spectrum  $\lambda$  is of the order  $6 \times 10^{-5}$  and  $c$  at its maximum will be  $R$ , but  $R$  is of the order  $8 \times 10^{-9}$ , so that  $\lambda/4\pi R$  is of the order 600. To make  $\lambda/4\pi c$  of the same order as  $V/v$  we should need to take  $c$  to be only about  $1/500$  of  $R$ . In the combined metals of the Li family we have

$$v = (2\pi/3)^{\frac{1}{2}} \{1 \cdot 2^2/0 \cdot 65^3 (2, 3, 4, 5, 6) M\}^{\frac{1}{2}},$$

with a value whose order ranges from  $10^6$  for Li to  $10^5$  for Cs, so that  $c$  in Li would need to be about  $1/50$  of  $R$ , and for Cs it would need to be about  $1/500$  of  $R$ . If further investigation bears out this view of the kinematical origin of Balmer's formula there will be special interest in seeking for the simplest kinematical conditions that will lead to Rydberg's law of the relations between the principal and usual series in the spectra of the alkalis.

#### 4. *Summary.*

The central cause of the spectrum of an atom is a special pair of electrons situated within the atom on its electric axis. The atom is electrized, or electrically polarized, because it is formed of constitutive pairs of electrons which have their electric axes similarly directed so as to give the atom electric properties analogous to the magnetic ones of a uniformly magnetized sphere. The internal electric field of the atom corresponds with the external field which produces cohesion, and has been investigated in several papers on the laws of molecular attraction. The special electron pair consists of a positive electron which acts as though uniformly distributed through a sphere of radius  $R = 0 \cdot 795 \times 10^{-8}$ , which is the same for all atoms. This action may be due to the rapid random motion of a small positive electron through this sphere of constant size. The negative electron is situated at distance  $r$  along the electric axis of the atom from the centre of the sphere of radius  $R$ . As regards outside action the positive electron may be supposed altogether at the centre of



the sphere, so that the special pair of electrons has an electric moment  $er$  oppositely directed to that of the whole atom, which is denoted by  $es$ . This electric moment  $es$  produces the external electric field of cohesion, and it produces the internal field in which the special pair of electrons vibrates. The special negative electron is attracted by the positive with a force  $(e^2/r^2)(r^3/R^3) = e^2r/R^3$ , and comes to rest in the internal field at the distance defined by the equation  $r/R^3 = s/a^3$ , where  $a$  is radius of atom. If displaced in any direction at right angles to  $r$  the negative electron of inertia  $i$  oscillates with a frequency  $(e^2/R^3i)^{1/2}/2\pi$ . If displaced in the direction of  $r$  it oscillates with the same frequency. Thus the negative electron has three degrees of freedom in which its frequency is the same. Moreover, this frequency is the same for all atoms, if  $R$  is the same for all, and that is why it is stipulated above that  $R$  is to be an absolute constant. It is assumed that there is a fundamental period of vibration the same for all atoms, because in the Balmer-Rydberg formula  $1/\lambda = n = n_0 - b/(m + \mu)^2$  the parameter  $b$  has nearly the same value for many series of spectral lines in many elements. The frequency  $bV$  ( $V$  = velocity of light) is a fundamental constant of Nature, such that  $1/Vb$  might yet furnish a natural unit of time,  $R$  being an associated natural unit of length. In the non-metals there is a tendency for  $es$  to be proportional to  $a^3$ , so that if the frequency is constant and  $R$  also, then  $r$  is nearly constant in the non-metals. In the metals of the Li and Be families  $es$  is proportional to  $a$ , so that  $r$  is inversely proportional to  $a^2$ , yet the fundamental frequency is constant.

By means of the constitutive pairs of electrons and the special pair in the atom a theory of dielectric capacity is reached in the following way. The electric axes of the pairs in matter free from external electric action are distributed at random as regards their direction. Thus an average direction for a single representative pair when an electric intensity is applied to the matter is that at right angles to the intensity. The average pair of electrons is subjected to a shearing stress by the action of the external electric intensity, so also is the special pair, and also the atom as a whole. If in each case we introduce the corresponding rigidity we derive the associated strain which gives the whole electric displacement caused by the external electric intensity. In this way we obtain the dielectric capacity of any atom. For the atom of a metal in its compounds the result obtained is (6), namely,

$$(N' - 1)V = (N - 1)B = CB^{2/3} + DB^{2/3}(N^2 - 1)/\rho,$$

where  $N'$  is the index of refraction of the medium formed by a collection of the atoms as a gas such that a gramme-atom occupies volume  $V$ , and  $N$  is the index of the collection of atoms when reduced to the limiting volume  $B$  per gramme-atom, and  $K$  the dielectric capacity of the atom  $=N^2$ .  $C$  and  $D$  are parameters characteristic of each family of metals, while  $\rho$  is the density of the atom. This formula is verified by the experimental data for the metals of the Li and Be families. For the non-metals the relation deduced is (8)

$$(N' - 1)V = (N - 1)B = EKB^{2/3} u^{2/3} / \rho^{1/3},$$

where  $E$  is an absolute constant and  $u$  is a number having the values 1, 2, 3, 4 for the halogens from F to I and for the elements in other families corresponding with these halogens. These results are obtained by assuming that the internal electric fields of atoms are the counterpart of their external fields as ascertained in studies on cohesion. Thus the laws of molecular attraction are strongly confirmed by the present inquiry, while a very definite conception is obtained of the mechanism which is at the basis of radiation. This is as simple as a pendulum, or a galvanometer needle, or a piano string, but the complex of constitutive pairs of electrons associated with it must be very elaborate. From consideration of the cohesion of the parts of the atom certain conceptions as to the structure of the atom are indicated. The kinematical interpretation of Balmer's formula is stated more definitely on the supposition that the vibrating special pair of electrons causes certain standing waves in the atom and controls the positions of their nodes.

Melbourne, October 1909.

## II. *Molecular Diameters.* By WILLIAM SUTHERLAND\*.

**A**LREADY improvements in the fundamental data make it necessary to revise the list of molecular diameters given in the Phil. Mag. [6] xvii. 1909, Feb. p. 320. That list was derived from one calculated by Jeans (Phil. Mag. [6] viii. 1904, p. 692) who took for  $N$ , the number of molecules in a  $\text{cm}^3$  of gas under standard conditions, the value  $4 \times 10^{19}$ , which was the best obtainable at that date. As he had made no allowance for the effects of cohesive force, I applied that refinement to his calculations. But now from the study of the alpha particle Rutherford finds  $N = 2.77 \times 10^{19}$ , in close agreement with  $2.80 \times 10^{19}$  found by Planck from

\* Communicated by the Author.