The Theoretical Prediction of the Physical Properties of Many-Electron Atoms and Ions. Mole Refraction,* Diamagnetic Susceptibility, and Extension in Space.

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I.—*Introduction.*

It is customary to express the empirical data concerning term values in the X-ray region by introducing an effective nuclear charge $Z_{eff.}e$ in the place of the true nuclear charge Ze in an equation theoretically applicable only to a hydrogen-like atom. Often a screening constant S is used, defined by the equation

$$Z_{eff.} = Z - S;$$

and this screening constant is qualitatively explained as due to the action of electrons which are nearer the nucleus than the electron under consideration, and which in effect partially neutralise the nuclear field. Thus the relativistic or magnetic doublet separation may be represented by the equation

$$\Delta \nu = \frac{R\alpha^2}{n^3 k (k-1)} (Z - s_0)^4 + \dots .$$

This equation, including succeeding terms, was obtained originally by Sommerfeld from relativistic considerations with the old quantum theory; the first term, except for the screening constant s_0, has now been derived by Heisenberg and Jordan† with the use of the quantum mechanics and the idea of the spinning electron. The value of the screening constant is known for a number of doublets, and it is found empirically not to vary with Z.

It has been found possible to evaluate s_0 theoretically by means of the following treatment : (1) Each electron shell within the atom is idealised as a uniform surface charge of electricity of amount $-z_i e$ on a sphere whose radius is equal to the average value of the electron-nucleus distance of the electrons in the shell. (2) The motion of the electron under consideration is then determined by the use of the old quantum theory, the azimuthal quantum number being chosen so as to produce the closest approximation to the quantum

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* The phrase "mole refraction" will be used in this paper in place of "coefficient of refraction" or "molal coefficient of refraction," in conformity with the use of the German word Molrefraktion.

† 'Z. f. Physik,' vol. 37, p. 263 (1926).

mechanics. (3) Since s_0 does not depend on Z, it is evaluated for large values of Z, by expanding in powers of z_i/Z and neglecting powers higher than the first, and then comparing the expansion with that of the expression containing $Z - s_0$ in powers of s_0/Z. The values of s_0 obtained in this way* are in satisfactory agreement with the empirical ones, the agreement being excellent in the case of orbits of large excentricity, for which the idealisation of the electron shells would be expected to introduce only a small error.

The important problem of the theoretical evaluation of the properties of many-electron atoms and ions has so far received little attention, compared with that devoted to spectral term values. The wave mechanics of Schrödinger provides an atomic model which suggests that the method of treatment given s_0 can be used in deriving theoretical values of screening constants to be used in the equations representing the mole refraction or polarisability, diamagnetic susceptibility, extension in space, and other properties of atoms and monatomic ions. This procedure is followed in this paper, the assumption being made that the nuclear charge is large in comparison with the charge of an electron shell. This requirement is not well fulfilled by actual atoms and ions. However, from a comparison with the accurately known experimental values of the mole refraction of the rare gases and of some ions in aqueous solution it is found that the calculated values of the mole refraction screening constant are not greatly in error. The indicated corrections are made ; so that, with the aid of this one empirical change, theoretical values are obtained for the mole refraction and the diamagnetic susceptibility of a large number of atoms and ions. A third screening constant is also evaluated, which permits the calculation of the electron distribution in atoms and ions and the estimation of interatomic distances. In this connection it is shown that the investigation of the diffraction of X-rays by crystals provides a method for the direct experimental verification of the form of Schrödinger's eigenfunctions.

II.—*The Wave Mechanics of the Hydrogen Atom and the Idealisation of an Electron Shell.*

In the wave mechanics of Schrödinger† a conservative Newtonian dynamical system is represented by a wave function or amplitude function ψ, obtained from the partial differential equation

$$\text{div. grad. } \psi + \frac{8\pi^2}{h^2}(W - V(q_x))\,\psi = 0,$$

* Pauling, ' Z. f. Physik,' vol. 40, p. 344 (1926).

† Schrödinger, ' Ann. d. Physik,' vol. 79, p. 361 (1926) ; vol. 79, p. 489 ; vol. 80, p. 437 ; vol. 81, p. 109 ; cited hereafter as I, II, III, IV.

with the conditions that ψ be everywhere continuous, single-valued, and bounded. W and $V(q_\kappa)$ are the energy constant and the potential energy ; and the indicated operations are with respect to co-ordinates whose line element is given by

$$ds^2 = 2\mathrm{T}\,(q_\kappa, \dot{q}_\kappa)\,dt^2,$$

in which T is the kinetic energy expressed as a function of the velocities. Only certain functions (called eigenfunctions) satisfy these requirements in any given case ; correspondingly there are certain characteristic values of the energy constant W. For the hydrogen-like atom with fixed nucleus the potential energy is $-e^2 Z/r$; on writing for the eigenfunctions

$$\Psi_{nlm} = \mathrm{X}_{nl}(r)\,\mathrm{Y}_{lm}(\vartheta)\,\mathrm{Z}_m(\phi), \tag{1}$$

the wave equation can be resolved into three total differential equations, with the solutions*

$$
\begin{aligned}
\mathrm{X}_{nl}(r) &= \left\{ \left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)\,!}{2n\,[(n+l)\,!]^3} \right\}^{\frac{1}{2}} e^{-\xi/2}\,\xi^l\,\mathrm{L}_{n+l}^{(2l+1)}(\xi) \\[2mm]
&\quad \text{with } \xi = \frac{2Z}{a_0 \cdot n} \cdot r \\[2mm]
\mathrm{Y}_{lm}(\vartheta) &= \left\{ (l+\tfrac{1}{2}) \frac{(l-m)\,!}{(l+m)\,!} \right\}^{\frac{1}{2}} \mathrm{P}_l^{\,m}(\cos\vartheta) \\[2mm]
\mathrm{Z}_m(\phi) &= \frac{1}{\sqrt{2\pi}}\,e^{im\phi}
\end{aligned}
\right\} \tag{2}
$$

$\mathrm{L}_{n+l}^{(2l+1)}(\xi)$ represents the $(2l+1)$th derivative of the $(n+l)$th Laguerre polynomial ; and $\mathrm{P}_l^{\,m}(\cos\vartheta)$ is Ferrer's associated Legendre function of the first kind, of degree l and order m. $\mathrm{Y}_{lm}\,\mathrm{Z}_m$ thus constitutes a surface harmonic. The Ψ's are in this form orthogonal and normalised with respect to unity, so that they fulfil the conditions

$$\int \Psi_{nlm}\,\Psi_{n'l'm'}\,d\mathrm{V} = \begin{cases} 1 \text{ for } n=n',\, l=l',\, m=m' \\ 0 \text{ otherwise.} \end{cases}$$

The parameter n can assume the values 1, 2, 3, ..., and is to be identified with the principal quantum number characterising the energy of the atom ; l can assume the values 0, 1, 2, ... $n-1$, and is to be identified with $k-1$, k being the azimuthal quantum number of the old quantum theory ; while m, the magnetic quantum number, can assume the values 0, ± 1, ± 2, ... $\pm l$.

Schrödinger (IV) has interpreted $\Psi\,\overline{\Psi}$ ($\overline{\Psi}$ being the conjugate complex of Ψ) as giving the weight or probability to be assigned to the corresponding micro-

* See Schrödinger I ; Waller, 'Z. f. Physik,' vol. 38, p. 635 (1926).

scopic state of the system ; in the hydrogen-like atom $\Psi \overline{\Psi}$ would then give the *electron density* as a function of r, ϑ, and ϕ, the electron being considered as distributed through space in accordance with this expression (following Schrödinger), or as achieving this distribution through a time average of its instantaneous positions. Unsöld* has shown that this conception provides a simple explanation of Schrödinger's perturbation theory, to the effect that it gives the interaction of the perturbing field and this distribution of electricity. Thus it can easily be shown that the first-order Stark effect energy given by the wave mechanics (Schrödinger, III) is just the field energy of the electric dipole corresponding to such an electron density (the wave equation being separated in parabolic co-ordinates in this case). Accepting these views, the fractional number of electrons in a spherical shell of unit thickness at the distance r from the nucleus is

$$D = 4\pi r^2 \, \Psi \overline{\Psi} = r^2 \, X_{nl}^2 \, (r). \tag{3}$$

An atom in the S state, with $l = m = 0$, has $Y_{00}^2 (\vartheta) \, Z_0^2 (\phi) = 1/4\pi$, so that Ψ_{n00} is spherically symmetrical. Unsöld has further shown that the sum of the quantities $\Psi \overline{\Psi}$ for the electrons of a completed sub-group (n and l constant, $m = -l, -l+1, \ldots 0, \ldots +l$) is not dependent on ϑ and ϕ. Accordingly the electron distribution in an atom in the S state or containing only completed sub-groups† is spherically symmetrical, and a function of r alone.

The dependence on r of several eigenfunctions is shown by the following equations, and by fig. 1, in which $- X_{nl} (r) \cdot Z^{-3/2} \cdot 10^{-12}$ is plotted as a function of ξ.

$$X_{10} (r) = - 2 \left(\frac{Z}{a_0} \right)^{3/2} \cdot e^{-\xi/2},$$

$$X_{20} (r) = \frac{2}{2^{5/2}} \left(\frac{Z}{a_0} \right)^{3/2} \cdot e^{-\xi/2} (\xi - 2),$$

$$X_{30} (r) = - \frac{2}{3^{5/2} \, 2!} \left(\frac{Z}{a_0} \right)^{3/2} \cdot e^{-\xi/2} (\xi^2 - 6\xi + 6),$$

$$X_{40} (r) = \frac{2}{4^{5/2} \, 3!} \left(\frac{Z}{a_0} \right)^{3/2} \cdot e^{-\xi/2} (\xi^3 - 12\xi^2 + 36\xi - 24),$$

$$X_{50} (r) = - \frac{2}{5^{5/2} \, 4!} \left(\frac{Z}{a_0} \right)^{3/2} \cdot e^{-\xi/2} (\xi^4 - 20\xi^3 + 120\xi^2 - 240\xi + 120),$$

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* ' Dissertation,' Munich, 1927.

† The sub-groups for which this theorem is derived are not the Stoner sub-groups. However, it is highly probable that the inclusion of the spinning electron in the theory will lead to the result that the theorem is actually true for the Stoner sub-groups.

$$X_{21}(r) = -\frac{2}{2^2\sqrt{3!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2} \cdot \xi,$$

$$X_{31}(r) = \frac{2}{3^2\sqrt{4!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2} \cdot \xi(\xi-4),$$

$$X_{41}(r) = -\frac{2}{4^2\sqrt{5!\cdot2!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2} \cdot \xi(\xi^2-10\xi+20),$$

$$X_{51}(r) = \frac{2}{5^2\sqrt{6!\cdot3!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2} \cdot \xi(\xi^3-18\xi^2+90\xi-120).$$
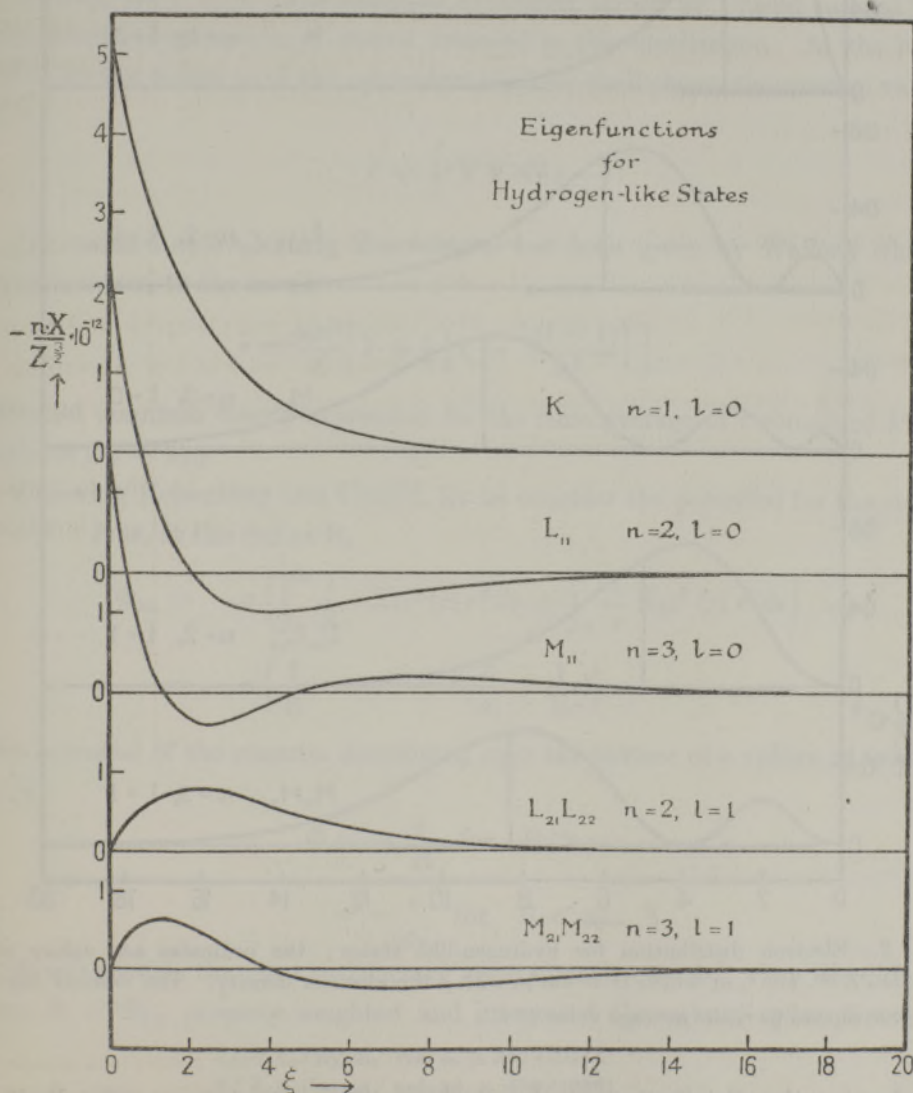

Fig. 1.—Eigenfunctions for hydrogen-like states; as ordinates are shown values of $-nX_{nl}(\xi) \cdot Z^{-3/2} \cdot 10^{-12}$ with values of ξ as abscissæ.

It will be observed that the function differs appreciably from zero only within a radius of the order of magnitude of the major axis of the corresponding ellipses of the old quantum theory; namely, $r = 2a_0 n^2/Z$, or $\xi = 4n$, as was remarked by Schrödinger (I). In fig. 2 are given values of D as a function of

Electron Distribution
for
Hydrogen-like States

K   n = 1,   l = 0

L_{11} n = 2,   l = 0

M_{11} n = 3,   l = 0

$L_{21}L_{22}$ n = 2,   l = 1

$M_{21}M_{22}$ n = 3,   l = 1
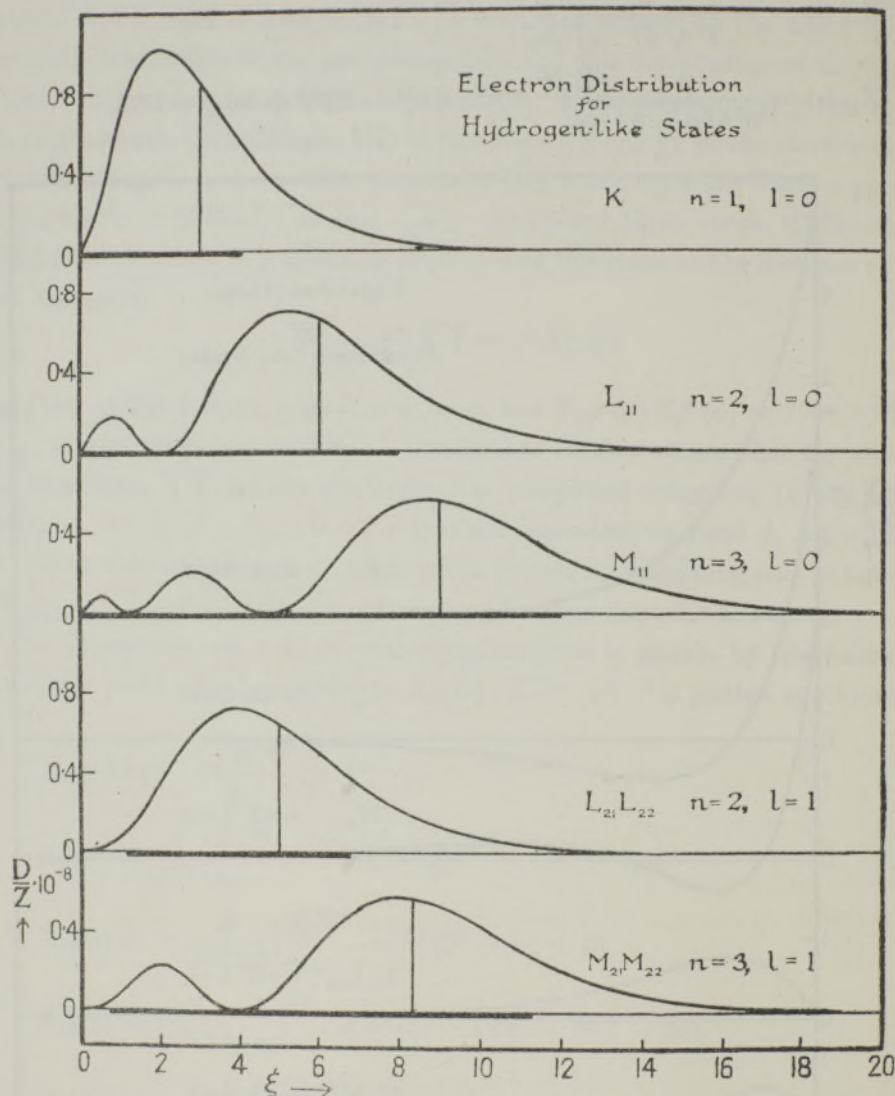
$\frac{D}{Z}\cdot 10^{-8}$

FIG. 2.—Electron distribution for hydrogen-like states; the ordinates are values of $D \cdot Z^{-1} \cdot 10^{-8}$, in which $D = 4\pi r^2 \rho$, with ρ the electron density. The vertical lines correspond to $\bar{r}$, the average value of r.

ξ, showing the distribution of the electron with respect to r. The limits indicated on the ξ-axis correspond to the electron-nucleus distances at aphelion

and perihelion given by the old quantum theory with k^2 placed equal to $l(l+1)$.

The idealisation of an electron shell as a uniform distribution of electricity on the surface of a sphere was innovated by Schrödinger,* who calculated the term-values of penetrating orbits by this method, with the old quantum theory. It was pointed out by Heisenberg† and Unsöld‡ that the same idealisation is permitted by the wave mechanics, the potential of the $e\Psi\overline{\Psi}$ distribution of electricity approximating $- e^2/r$ for large values of r, and being equal to $- e^2 Z/a_0 n^2$ for $r = 0$. The spherical symmetry shown by Unsöld to hold for completed sub-groups is, of course, retained in this idealisation. As the best value for the radius ρ_0 of the equivalent shell we shall choose the average value of r,

$$\bar{r} = \int r \Psi \overline{\Psi}\, dV.$$

The method of evaluating this integral has been given by Waller,§ whose equations lead to the result

$$\bar{r} = \frac{a_0 n^2}{Z}\left[1 + \tfrac{1}{2}\left\{1 - \frac{l(l+1)}{n^2}\right\}\right]. \tag{4}$$

(The old quantum theory expression for the time average of r contained k^2 in place of $l(l+1)$.)

Following Heisenberg and Unsöld, let us consider the potential for the state $n = 1$. It is, at the radius R,

$$\Phi_{10} = - e\left\{\int_0^R \frac{1}{R}\cdot X_{10}^2(r)\, r^2\, dr + \int_R^\infty \frac{1}{r} X_{10}^2(r)\, r^2\, dr\right\}$$

$$= - e\left\{\frac{1}{R} - e^{-(2Z/a_0)R}\left(\frac{Z}{a_0} + \frac{1}{R}\right)\right\}.$$

The potential of the electron distributed over the surface of a sphere of radius ρ_0 is

$$\Phi = - \frac{e}{R} \quad\text{for}\quad R > \rho_0$$

$$= - \frac{e}{\rho_0} \quad\text{for}\quad R < \rho_0.$$

Φ will provide the most satisfactory approximation to Φ_{10} when the difference $\Phi - \Phi_{10}$, properly weighted and integrated throughout space, is zero.

* 'Z. f. Physik,' vol. 4, p. 347 (1921).
† 'Z. f. Physik,' vol. 39, p. 499 (1926).
‡ Dissertation,' Munich, 1927.
§ Waller, 'Z. f. Physik,' vol. 38, p. 635 (1926).

Reference to fig. 2 shows that for small values of r, for which Φ and Φ_{10} differ appreciably, the dependence of D on r is roughly linear for all states, which we may consider to represent other electrons which interact with the electron in the state $n = 1$. Hence the weight may be taken as linear in r, and we obtain

$$\int_0^\infty (\Phi - \Phi_{10})\, r\, dr = \text{const.} \left(3 - \frac{2Z}{a_0}\, \rho_0\right),$$

which vanishes for

$$\rho_0 = \tfrac{3}{2} \frac{a_0}{Z}\,;$$

that is, for exactly the value $\bar{r}$ as given by equation (4). It is probable that the explicit consideration of further cases would lead to similar conclusions. The ξ values corresponding to $r = \bar{r}$ are shown in fig. 2.

In the following discussion we shall use m_i to denote the principal quantum number of the ith shell, $i.e.$, instead of n. We shall introduce for convenience the numerical factor γ_i, such that

$$\bar{r} = \gamma_i \frac{a_0 m_i^2}{Z}\,. \tag{5}$$

From equations (4) and (5) we accordingly obtain for an electron with the quantum numbers m_i and l_i the expression

$$\gamma_i = 1 + \tfrac{1}{2} \left\{ 1 - \frac{l_i(l_i + 1)}{m_i^2} \right\}. \tag{6}$$

It has been found that no significant error is introduced by combining the sub-groups of an entire shell, using an average value of γ for the entire K, L, M, ... shell. With the Stoner distribution of electrons among the levels, this average value is

$$\gamma(m_i) = 1 + \frac{1}{2m_i} + \frac{(m_i - 1)^2}{4m_i^2} \tag{7A}$$

for completed shells,

$$\gamma(m_i) = \tfrac{3}{2} - \frac{3}{4m_i^2} \tag{7B}$$

for eight-shells (octets), and

$$\gamma(m_i) = \tfrac{3}{2} - \frac{2}{m_i^2} \tag{7C}$$

for eighteen-shells.

It might be thought that these values of γ are not correct because of the fact that the electron shells actually do not consist of hydrogen-like electrons, but rather themselves of " penetrating " electrons. However, as Z increases the " penetrating orbits " become more and more hydrogen-like ; and these

values of γ can accordingly be used in our later treatment, which postulates that Z is large, the error introduced being quadratic in z/Z, and so negligible.

III.—*The Quantisation of Penetrating Orbits.*

Let us now consider an electron orbit n_k (in which $k = k_1$, in the X-ray nomenclature of Sommerfeld), which penetrates a number of electron shells. We shall determine the orbit with the methods of classical mechanics, quantising with the rules of the old quantum theory ; values of the azimuthal quantum number k will later be chosen in such a way as to cause our formulas to approximate as closely as possible to the quantum mechanics. In accordance with the previous discussion, the ith electron shell is idealised as a homogeneous surface charge of amount $-z_i e$ on a sphere of radius $\rho_i = \bar{r}_i$. We shall let $Z_i e$ be the effective nuclear charge in the ith region, which is the region between the radii ρ_{i-1} and ρ_i ; accordingly $Z_{i+1} = Z_i - z_i$, and $Z_1 = Z - z$, in which Z is the atomic number of the atom and z the number of electrons entirely within the orbit under consideration. With the use of Newtonian dynamics, *i.e.*, neglecting the relativistic effect and the perturbations due to the spinning electron, the motion of the electron is described by the Hamiltonian equation

$$\frac{1}{2m}\left(p_r{}^2 + \frac{p_\phi{}^2}{r^2}\right) + V(r) = W, \tag{8}$$

in which W is the energy constant and

$$V(r) = V_i(r) = -\frac{Z_i e^2}{r} - \frac{z_i e^2}{\rho_i} - \frac{z_{i+1} e^2}{\rho_{i+1}} - \quad \cdots \tag{9}$$

in the ith region. Since ϕ is cyclic, the quantum rules require

$$p_\phi = \frac{kh}{2\pi}.$$

Let us now define for the ith region a radial quantum number n_i', which we shall call the *segmentary* radial quantum number, by means of the equation

$$n_i' h = \oint \sqrt{2m\left\{W - V_i(r)\right\} - \frac{k^2 h^2}{4\pi^2}\cdot\frac{1}{r^2}}\, dr. \tag{10}$$

n_i' is thus the radial quantum number which would characterise the orbit if the ith region were large enough to include the entire orbit. The true radial quantum number, on the other hand, is given by the equation

$$n' h = \sum_{i=1}^{j} \int_{i\text{th region}} \sqrt{2m\left\{W - V(r)\right\} - \frac{k^2 h^2}{4\pi^2}\cdot\frac{1}{r^2}}\, dr. \tag{11}$$

From equations (8), (9) and (10) it is evident that the path of the electron in the ith region is a segment of the Kepler ellipse defined by the segmentary radial and the azimuthal quantum numbers n_i' and k, so that it can be described by the known equations

$$r = \frac{a_0 k^2}{Z_i} \cdot \frac{1}{(1 - \varepsilon_i \cos \phi)} = \frac{a_0 n_i^2}{Z_i} (1 + \varepsilon_i \cos u)$$

$$t = \frac{n_i^3}{4\pi R Z_i^2} (u + \varepsilon_i \sin u).$$

In these equations ϕ and u are the segmentary true anomaly and excentric anomaly, respectively, measured from aphelion; while n_i and ε_i are the segmentary principal quantum number and excentricity, given by the equations

$$n_i = n_i' + k, \qquad \varepsilon_i = \sqrt{1 - \frac{k^2}{n_i^2}}.$$

To evaluate the segmentary quantum numbers we observe from a comparison of equations (9) and (10) with the corresponding ones for a hydrogen-like orbit that

$$W = -\frac{e^2}{2a_0} \cdot \frac{Z_i^2}{n_i^2} + \frac{z_i e^2}{\rho_i} + \frac{z_{i+1} e^2}{\rho_{i+1}} + \dots = -\frac{e^2}{2a_0} \cdot \frac{Z_{i+1}^2}{n_{i+1}^2} + \frac{z_{i+1} e^2}{\rho_{i+1}} + \dots = \text{const.} \tag{12}$$

From this there is obtained, neglecting powers of z_i/Z higher than the first, the expression

$$n_{i+1} = n_i\left(1 + \frac{z_i}{Z} \cdot \beta_i\right), \quad \text{with} \quad \beta_i = \frac{n^2}{\gamma_i m_i^2} - 1. \tag{13}$$

On carrying out the integrations in equation (11), it becomes

$$n' = n_1\{F(\pi) - F(u_1)\} + n_2\{F(u_2') - F(u_2)\} + \dots + n_j\{F(u_j') - F(0)\}, \tag{14}$$

in which

$$F(u_i)$$

$$= \frac{1}{\pi}\left[u_i - \varepsilon_i \sin u_i - \sqrt{1 - \varepsilon_i^2} \arcsin\left\{\frac{\sqrt{1 - \varepsilon_i^2} \sin u_i}{1 + \varepsilon_i \cos u_i}\right\} - \pi(1 - \sqrt{1 - \varepsilon_i^2})\right], \tag{15}$$

the initial and final values u_i and u_i' of the excentric anomaly in the ith region being given by the equations

$$1 + \varepsilon_i \cos u_i = \frac{\rho_i Z_i}{a_0 n_i^2}, \qquad 1 + \varepsilon_{i+1} \cos u'_{i+1} = \frac{\rho_i Z_{i+1}}{a_0 n_{i+1}^2}. \tag{16}$$

From this, with the use of equation (13), and again neglecting powers of z_i/Z

higher than the first, there is derived the following relation between n_1 and the true quantum number n :

$$n_1 = n \left[1 - \sum_{i=1}^{j} \cdot \frac{1}{\pi} \cdot \frac{z_i}{Z} \{ \beta_i u_i + (1 + \beta_i) \varepsilon \sin u_i \} \right]. \tag{17}$$

The equation connecting ε_i and ε is easily obtained from the definition of ε_i with the use of equations (13) and (17).

In order to approximate as closely as possible to the quantum mechanics we shall use throughout for k^2 the quantity $l(l+1)$; for often in the quantum mechanics $l(l+1)$ occupies the place formerly given to k^2, as we have seen in the case of $\bar{r}$.

The use of these expressions describing the penetrating orbit in predicting the physical properties of many-electron atoms will be exemplified in the following sections.

IV.—*The Theoretical Determination of the Mole Refraction.*

A simple consideration involving a slow mechanical transformation* shows that if the energy quantity corresponding to the second-order Stark effect of a system is

$$\Delta E = - \tfrac{1}{2} \alpha F^2, \tag{18}$$

then the electric moment induced in the system is

$$\bar{\mu} = \alpha F. \tag{19}$$

The polarisation in unit volume can be expressed in terms of the index of refraction n as

$$P = \frac{N}{V} \bar{\mu} = \frac{N}{V} \alpha F = \frac{3}{4\pi} \frac{n^2 - 1}{n^2 + 2} . F \tag{20}$$

in which N is Avogadro's number and V the volume occupied by one mole of the molecules under consideration, α referring to one molecule. The mole refraction R is defined by the equation

$$R = V . \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N}{3} . \alpha. \tag{21}$$

Wentzel,† Waller‡ and Epstein§ have derived a formula for the second-order

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* Jones, ' Roy. Soc. Proc.,' A, vol. 105, p. 650 (1924). The first attempt to calculate the mole refraction from the quadratic Stark effect formula was made by Lennard-Jones (Jones), with the old quantum theory.

† ' Z. f. Physik,' vol. 38, p. 518 (1926).

‡ ' Z. f. Physik,' vol. 38, p. 635 (1926).

§ Epstein, ' Nature,' vol. 118, p. 444 (1926), ' Phys. Rev.,' vol. 28, p. 695 (1926).

Stark effect of a hydrogen-like atom, using the Schrödinger wave mechanics.
Their equation, obtained independently and by different methods, is

$$\Delta E = -\frac{h^6}{16\,(2\pi)^6\,m^3 e^6 Z^4}\,n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19)\,.\,F^2, \qquad (22)$$

which gives

$$R = \frac{N\,.\,h^6}{12\,(2\pi)^5\,m^3 e^6 Z^4}\,n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19), \qquad (23\text{A})$$

or, introducing for the physical constants their accepted values,

$$R = \frac{0\cdot0470}{Z^4}\,n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19). \qquad (23\text{B})$$

Here n is the principal quantum number, and m and n_3 are given by the equations

$$m = n_2 - n_1, \qquad n_3 = n - 1 - n_1 - n_2.$$

The quantum numbers n_1 and n_2 have the integral values

$$0 \leqq n_1 \leqq n - 1, \qquad 0 \leqq n_2 \leqq n - 1.$$

These conditions suffice to determine the possible values of m and n_3. As was
shown by Pauli,[*] they are compatible with the experimental evidence, and
explain many previously difficultly explicable facts involving the exclusion of
certain quantum states.[†]

The electrons within the atom are actually not quantised in parabolic co-
ordinates, but instead, on account of the central field of the atom core, in polar
co-ordinates. It would, then, not be logical to attempt to select favoured values
of m and n_3. Instead, we shall calculate the quantity

$$n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19)$$

for each set of values of the quantum numbers, and then average the result.
This procedure is justified to a considerable extent by the fact that the polarisa-
tion does not depend largely on the subsidiary quantum numbers, but is a
function mainly of the principal quantum number, which is not changed by
quantisation in a central field. On averaging over all values of m^2 and n_3^2,

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[*] 'Z. f. Physik,' vol. 36, p. 336 (1926).

[†] Equation 22 differs from that derived by Epstein with the old quantum theory
only in the inclusion of the number 19, and in the values given to n_3 (previously
$n_3 = n - n_1 - n_2$). Wentzel and Waller have shown that the new equation is in some-
what better agreement with the best experimental data than the old one.

assigning equal weight to each set of values of n_1 and n_2, there is obtained the result $\overline{m^2} = \overline{n_3^2} = \frac{1}{6}(n^2 - 1)$, which on substitution in equation (23) gives

$$R = 0.0470 . n^4 (15n^2 + 21) . \sum_\kappa \frac{1}{(Z - S_{R_\kappa})^4}, \tag{24}$$

in which the summation is to be taken over all electrons in the nth shell.* S_R is called the mole refraction screening constant.

We shall now predict values of S_R for ions for which z_i/Z is small, *i.e.*, for Z large. If this screening constant is constant, and does not depend on Z, these values hold for all atoms and ions with the structures considered. The nature of the agreement between the theoretical and the experimental values of R or of S_R will show to what extent this is true.

From equation (24) it is seen that, except for a small additive term in $n^4 Z^{-4}$, the mole refraction of a hydrogen-like electron is proportional to $n^6 Z^{-4}$. Now most of the polarisation occurs in the outermost part of the orbit, for here the externally applied field has its greatest value relative to the nuclear field. Accordingly we shall assume that the polarisation produced in a penetrating orbit is equal to that produced in a hydrogen-like orbit having the same parameters as those effective in the outermost (jth) region. This assumption is reasonable in view of the fact that in every case nearly the entire outer half of the orbit lies in this region. We accordingly write

$$R = \text{const. } n_j^6 Z_j^{-4} = \text{const. } n^6 (Z - S_R)^{-4}, \tag{25}$$

and from this determine S_R.

For generality let us consider a property proportional to $n^r Z^{-t}$, so that we have

$$\text{const. } n_j^r Z_j^{-t} = \text{const. } n^r (Z - S)^{-t}.$$

On expanding the left hand expression in powers of z_i/Z, using equations (13) and (17), and comparing the first term of the expansion with the corresponding term in the expansion of the right-hand expression in powers of S/Z, it is found that

$$S = z + \sum_i z_i - \frac{r}{t} \sum_i z_i D_i, \tag{26A}$$

in which D_i, which we shall call the unit screening defect for an electron in the ith shell, is given by the equation

$$D_i = \frac{1}{\pi} \beta_i u_i + (1 + \beta_i) \varepsilon \sin u_i\} - \beta_i \tag{26B}$$

with

$$1 + \varepsilon \cos u_i = \frac{\gamma_i m_i^2}{n^2}. \tag{27}$$

* This equation is, of course, rigorously true for H, He$^+$, etc., for which S_R is zero.

Internal shells are thus seen to screen completely, and the screening effects of penetrated shells are additive. Moreover, it is seen that for properties proportional to different powers of n and Z the total screening defect varies directly with r/t.

For the mole refraction screening constant we accordingly have

$$S_{R\infty} = z + \sum_i z_i - \tfrac{3}{2} \sum_i z_i D_i. \qquad (28)$$

Table I.—The Mole Refraction Screening Constant.

	Z_0		$S_{R\infty}.$	$S_{R_0}.$	$S_{R_0} - S_{R\infty}.$	$\Delta S_R.$
He	2	K	0·391	0·397		0
Ne	10	L_{11}	4·45	4·31	−0·14	0
		$L_{21} L_{22}$	5·64	5·50		
Ar	18	M_{11}	9·70	11·11	1·41	0·05
		$M_{21} M_{22}$	10·99	12·40		
Kr	36	N_{11}	21·28	26·69	5·41	0·19
		$N_{21} N_{22}$	22·92	28·33		
Xe	54	O_{11}	34·29	42·26	7·97	0·29
		$O_{21} O_{22}$	36·63	44·60		
$[Cu^+]_0$	28	M_{11}	14·4	14·9	0·5	0·02
		$M_{21} M_{22}$	16·1	16·6		
		$M_{32} M_{33}$	19·5	20·0		
$[Ag^+]_0$	46	N_{11}	25·7	32·15	6·5	0·23
		$N_{21} N_{22}$	27·5	33·95		
		$N_{32} N_{33}$	31·1	37·55		
$[Au^+]_0$	78	O_{11}	46·0	59·9	13·9	0·50
		$O_{21} O_{22}$	48·1	62·0		
		$O_{32} O_{33}$	52·4	66·3		

In column 4 of Table I are given the values of $S_{R\infty}$ obtained by the application of this equation to the structures included. (We have written $S_{R\infty}$ because the values are derived for very large values of Z.) The symbols $[Cu^+]_0$, $[Ag^+]_0$, and $[Au^+]_0$ denote atoms with the corresponding structures and the atomic numbers 28, 46, and 78. In column 5 are given values of S_R obtained from the experimental values of R (for light of infinite wave-length) shown in Table II by the following procedure. It is assumed that the differences in S_R for different sub-levels within a shell are those given by the theory ; the solution of equation (24), with R given its experimental values, then gives the " experimental " values, S_{R_0}.

Table II.—Experimental Values of the Mole Refraction.*

—	R.	—	R.
He	0·513	Zn^{++}	0·72
Ne	0·995	Cd^{++}	2·74
Ar	4·132	Hg^{++}	3·14
Kr	6·25	Ag^{+}	4·33
Xe	10·16		

* The experimental values for the rare gases are those of C. and M. Cuthbertson (' Roy. Soc. Proc.,' A, vol. 84, p. 13 (1911)) extrapolated to infinite wave-length by Born and Heisenberg (' Z. f. Physik,' vol. 23, p. 388 (1924)). The silver ion value is obtained from the solution value given by Heydweiller (' Phys. Z.,' vol. 26, p. 526 (1925)) by taking 2·17 for the potassium ion. The cadmium ion value was calculated from this by the methods in the text, and the zinc and mercury ion values obtained from Heydweiller's by correcting by the difference between his cadmium value and ours ; this procedure being adopted to correct for the effect of hydration of these highly charged ions.

The agreement between the theoretical and the experimental values of S_R is most encouraging. It is seen that for elements with only a few electrons the agreement is complete, and that it becomes less satisfactory as the electron number of the structure increases, the difference $S_{R_0} - S_{R_\infty}$ showing a uniform increase. We can hence draw the conclusions that for light atoms all of the assumptions involved in the derivation of equations (24) and (28) are justified, that for these atoms the theoretical treatment of the electron orbits proposed in this paper is in general acceptable, and that it is permissible, in addition, to suppose the screening constants to be constant, and not to vary with Z. For heavier atoms the theoretical derivation of screening constants (valid for Z large) is only approximate, and the assumption that the screening constants are independent of Z is only approximately true, for they approach the theoretical values as Z becomes large. Evidence tending to show the fundamental correctness of our theoretical procedure, other than the good agreement of theory and experiment for light atoms, is provided by the regularity in the increase of $S_{R_0} - S_{R_\infty}$ as the electron number of the structure increases, and by the similarity in the values of $S_{R_0} - S_{R_\infty}$ for corresponding eight-shell and eighteen-shell structures.

It is of interest to note that on introducing the theoretical value of S_{R_∞} for helium in equation (24), the result R $= 0·506$ is obtained. The experimental data of C. and M. Cuthbertson were extrapolated to 0·513 for light of infinite wave-length by Born and Heisenberg, and to 0·518 by Heydweiller ; so that our *entirely theoretically derived* value agrees with experiment within the limit of error of the extrapolation.

By introducing in equation (24) the values of S_{R_0} given in Table I we obtain

tentative predicted values for the mole refraction of univalent ions with the structures considered (Table III). These values apply only to free ions

Table III.—Mole Refraction of Univalent Ions.

Ion.	R predicted.	R solution.	R crystal.
Na^+	0·457	0·11	0·04 to −0·55
K^+	2·17	(2·17)	(2·17)
Rb^+	3·88	3·56	3·77 to 4·10
Cs^+	6·82	6·17	6·23 to 6·42
$F-$	2·65	2·71	2·96
$Cl-$	8·92	8·76	8·04 to 8·48
$Br-$	10·75	12·14	11·06 to 11·80
$I-$	15·71	18·07	16·24 to 17·02

in the gaseous state. It is difficult to say *a priori* whether measurements made on alkali halide crystals or those made on dilute aqueous solutions of the alkali halides would give mole refraction values in the better agreement with those holding for the gaseous ions. Previous investigators, in attempting to derive values of the polarisabilities of gaseous ions from experimental data for salts, have decided differently; Born and Heisenberg[*] chose to use crystals, while Fajans and Joos[†] and Heydweiller[‡] used dilute aqueous solutions. One fact showing that the perturbing effects in crystals are large is the large deviation from additivity exhibited by their mole refraction, amounting to as much as 1·5 units for the alkali halides.[§] Our predicted values for gaseous ions show that ions in solution are indeed more similar to gaseous ions than are ions in crystals, as far as the mole refraction is concerned. In column 3 of Table III are given experimental values of R for ions in dilute solution, obtained from Heydweiller's tables by assuming the value 2·17 for potassium ion to be correct; and in column 4 values of R for the ions in the alkali halide crystals, calculated from the data given by Born and Heisenberg by again assuming the same value for potassium ion. Only the sodium, fluoride, and chloride ions can be compared

[*] Born and Heisenberg, ' Z. f. Physik,' vol. 23, p. 388 (1924); for criticism of their derivation of polarisabilities from spectral term values see Hartree, ' Proc. Camb. Phil. Soc.,' vol. 22, p. 409 (1924); ' Roy. Soc. Proc.,' A, vol. 106, p. 552 (1924); and Schrödinger ' Ann. d. Physik,' (4), vol. 77, p. 43 (1925).

[†] Fajans and Joos, ' Z. f. Physik,' vol. 23, p. 1 (1924). These authors also discussed the data for crystals, and showed that the mole refraction values for ions in solution are usually only slightly different from those for gaseous ions.

[‡] Heydweiller, ' Phys. Z.,' vol. 26, p. 526 (1925); for a discussion of the experimental and previous theoretical work on mole refraction see the two preceding papers.

[§] Fajans and Joos; also Spangenberg, ' Z. f. Krist.,' vol. 53, p. 499 (1923).

with the theoretical results, for only in these cases have we shown S_R to be practically independent of Z. In each of these three cases the solution results agree better with the theoretical values than do the crystal results, so that the conclusion can be safely drawn that in general ions in solution resemble gaseous ions more closely than do ions in crystals. The agreement between the solution values and the theoretical ones is good for the fluoride and chloride ions ; the solution value for the sodium ion is low, without doubt on account of the action of this very small ion on the surrounding water molecules, which has previously been estimated by Fajans and Joos to cause a decrease of about $0 \cdot 3$ in R.

We are now led to introduce a second empirical correction into our calculations. The theoretical values for the rubidium, cæsium, bromide, and iodide ions in Table III resulted from the assumption that S_R is independent of Z, which is known not to be true for these structures, on account of the difference between S_{R_0} and S_{R_∞}. The solution values of R, which we may assume to hold also for gaseous ions in these cases, also show that the screening constant for the negative ions should be larger and for the positive ions smaller than that used ; that is, as Z increases S_R decreases, presumably approaching our theoretical values for Z large. We shall assume that S_R is a linear function of Z in this region, and evaluate the parameters of the function with the use of the solution values for the bromide and iodide ions. If we write

$$S_R = S_{R_0} - (Z - Z_0) \Delta S_R, \qquad (29)$$

within a range of values of Z not too far removed from Z_0 (the electron number of the structure), then ΔS_R is found to be $0 \cdot 19$ and $0 \cdot 29$ for the krypton and xenon structures respectively. These values are approximately proportional to $S_{R_0} - S_{R_\infty}$; hence we may safely accept $0 \cdot 23$ and $0 \cdot 50$ for the silver and aurous ion structures, respectively ; and for consistency the corresponding values $0 \cdot 05$ and $0 \cdot 02$ will be used for the argon and cuprous ion structures also.

In Table IV are given values* of the mole refraction of gaseous ions calculated from equations (24) and (29) with the use of the values found above for S_{R_0} and ΔS_R. Values for hydrogen-like atoms and ions are also included ; these are, of course, accurate, since no screening constant is needed. Table IV is

* Throughout we have considered only the portion of the mole refraction produced in the outermost shell. In the case of xenon one finds by our methods that as much as 4 per cent. of the total mole refraction is due to the N shell ; accordingly our values of S_R for the O electrons would be decreased by about $0 \cdot 1$ on making this correction. The values of R for ions would in most cases not be changed materially by the explicit consideration of the polarisation of inner shells, and so the less complicated treatment of this paper has been adopted.

Table IV.—The Mole Refraction and Diamagnetic Susceptibility of Atoms and Ions.

In each cell: ion symbol, mole refraction $R \cdot 10^{6}$, and $-\chi \cdot 10^{6}$.

series	-4	-3	-2	-1	0	$+1$	$+2$	$+3$	$+4$	$+5$	$+6$	$+7$
1 e					H 1·691 2·415	He^{+} 0·1058 0·604	Li^{++} 0·0209 0·268					
He core				H^{-} 25·65 8	He 0·513 1·54	Li^{+} 0·074 0·63	Be^{+2} 0·020 0·34	B^{+3} 0·0076 0·21	C^{+4} 0·0034 0·15	N^{+5} 0·0018 0·11		
Ne core	C^{-4} 5400 50	N^{-3} 72·6 22	O^{-2} 9·88 12·6	F^{-} 2·65 8·1	Ne 0·995 5·7	Na^{+} 0·457 4·2	Mg^{+2} 0·238 3·2	Al^{+3} 0·136 2·5	Si^{+4} 0·084 2·1	P^{+5} 0·054 1·7	S^{+6} 0·036 1·4	Cl^{+7} 0·025 1·2
Ar core	Si^{-4} 950 110	P^{-3} 105 65	S^{-2} 26·0 40	Cl^{-} 9·30 29	Ar 4·13 21·5	K^{+} 2·12 16·7	Ca^{+2} 1·19 13·3	Sc^{+3} 0·73 10·9	Ti^{+4} 0·47 9·0	V^{+5} 0·31 7·7	Cr^{+6} 0·22 6·6	Mn^{+7} 0·16 5·7
Cu^{+} core						Cu^{+} 1·08 13	Zn^{+2} 0·72 11	Ga^{+3} 0·50 9·5	Ge^{+4} 0·36 8·5	As^{+5} 0·26 7·5	Se^{+6} 0·19 6·5	Br^{+7} 0·15 6·0
Kr core	Ge^{-4} 276 140	As^{-3} 72·6 95	Se^{-2} 26·8 70	Br^{-} 12·14 54	Kr 6·26 42	Rb^{+} 3·57 35	Sr^{+2} 2·18 28	Y^{+3} 1·41 24	Zr^{+4} 0·95 20	Nb^{+5} 0·66 17	Mo^{+6} 0·48 15	
Ag^{+} core						Ag^{+} 4·33 44	Cd^{+2} 2·74 37	In^{+3} 1·84 32	Sn^{+4} 1·26 28	Sb^{+5} 0·91 24	Te^{+6} 0·66 20	I^{+7} 0·49 17
Xe core	Sn^{-4} 228 180	Sb^{-3} 80·6 130	Te^{-2} 35·6 105	I^{-} 18·07 80	Xe 10·16 66	Cs^{+} 6·15 55	Ba^{+2} 3·94 46	La^{+3} 2·64 38	Ce^{+4} 1·86 33			
Au^{+} core						Au^{+} 4·75 65	Hg^{+2} 3·14 55	Tl^{+3} 2·19 48	Pb^{+4} 1·56 42	Bi^{+5} 1·15 37		

Row labels on original: $R \cdot 10^{6} =$ and $-\chi \cdot 10^{6} =$.

made complete because it is often desirable to have even approximate values of R for ions, even for those which are not capable of existence in solution. Thus, for example, they may be compared with core polarisabilities deduced from the energy levels of non-penetrating alkali-like electron states in order to test the spectral theory used in the deduction. Moreover, the deviation of the observed mole refraction from the calculated value for a crystal or complex ion can be considered as a measure of the deformation experienced by the individual ions composing the crystal or ion, as was especially emphasised by Fajans and Joos. For example, they give for $PO_4^{\equiv}$, $SO_4^{=}$, and ClO_4^{-} the values $16 \cdot 3$, $14 \cdot 6$, and $13 \cdot 3$ respectively; from Table IV we obtain $39 \cdot 5$ in each case, assuming the complex ion to consist of undeformed monatomic ions. They give also for $CO_3^{=}$ $12 \cdot 3$ and for NO_3^{-} $11 \cdot 0$; our values are $29 \cdot 6$ in each case.* The reasonable conclusion can hence be drawn that in each series the deforming influence of the central ion increases with its electrical charge.†

No extensive comparison with experiment to test the values in Table IV will be made. The close agreement between the purely theoretical and the experimental results in the case of helium and neon allows one to place confidence in the R values for ions with these structures; and the same remark applies with less force in the case of the argon structure, where only a small empirical correction was introduced. It is interesting to note that the theoretical values $3 \cdot 57$ and $6 \cdot 15$ for the rubidium and the cæsium ion agree very well with the experimental ones, $3 \cdot 56$ and $6 \cdot 17$ (Table III), which were not used at all in the evaluation of the empirical corrections for these structures. Finally, we may mention that our values agree in general with those of Fajans and Wulff,‡ obtained by them from the experimental R values for salt solutions by the application of only the simplest theoretical considerations.

* The experimental values are for the sodium D-lines, but are only slightly changed on extrapolation to infinite wave-length.

† For other uses of the ionic polarisability reference may be made to its rôle in the theoretical discussion of the structures of molecules (Heisenberg, ' Z. f. Physik,' vol. 26, p. 196 (1924); Kornfeld, *ibid.*, vol. 26, p. 205 (1924); Hund, *ibid.*, vol. 31, p. 81 (1925); vol. 32, p. 1 (1925); and in simple thermodynamic quantities such as the heat of vaporisation of crystals (Born and Heisenberg), and the heat of ionisation (into H^+ and X^-) of the hydrogen halides (Kemble, ' Journ. Opt. Soc. Am.,' vol. 12, p. 1 (1926)).

‡ Fajans and Wulff, not yet published. Their ionic refraction values for light of infinite wave-length are found by the methods applied by Fajans and Joos to the refraction for the sodium D-lines.

V.—*Diamagnetic Susceptibility.*

According to the classical theory, the effect of a magnetic field on a system composed of electrons in motion about a fixed nucleus is equivalent to the first order of approximation to the imposition on the system of a uniform rotation about the field direction (the Larmor precession) with the angular velocity $2\pi\omega_H = He/2mc$. This rotation of electrons produces a magnetic moment opposed to the field, such that the molal diamagnetic susceptibility is

$$\chi = -\frac{Ne^2}{4mc^2} \cdot \sum_{\kappa} \overline{r_{\kappa}^2 \sin^2 \vartheta_{\kappa}},$$

in which $r_{\kappa} \sin \vartheta_{\kappa}$ is the projection normal to the field direction of the distance r_{κ} of the κth electron from the nucleus; $\overline{r_{\kappa}^2 \sin^2 \vartheta_{\kappa}}$ denotes the time average of $r_{\kappa}^2 \sin^2 \vartheta_{\kappa}$. For S states and for completed groups and sub-groups the new quantum mechanics gives $\overline{r_{\kappa}^2 \sin^2 \vartheta_{\kappa}} = \tfrac{2}{3}\overline{r_{\kappa}^2}$, so that we obtain

$$\chi = -\frac{Ne^2}{6mc^2} \cdot \sum_{\kappa} \overline{r_{\kappa}^2}. \tag{30}$$

Adhering to our general method of treatment, we shall now evaluate a screening constant S_M valid in the case of Z large. Taking the time average of r^2 in the various regions traversed, we write

$$\overline{r^2} = \frac{\sum\limits_{i=1}^{j} \int\limits_{i\text{th region}} r^2\, dt}{\sum\limits_{i=1}^{j} \int\limits_{i\text{th region}} dt},$$

which gives, on evaluating the integrals,

$$\overline{r^2} = a_0^2 \frac{\sum\limits_{i=1}^{j} n_i^7 Z_i^{-4}\{U(u_i') - U(u_i)\}}{\sum\limits_{i=1}^{j} n_i^3 Z_i^{-2}\{(u_i' + \varepsilon_i \sin u_i') - (u_i + \varepsilon_i \sin u_i)\}},$$

in which

$$U(u_i) = u_i(1 + \tfrac{3}{2}\varepsilon_i^2) + 3\varepsilon_i \sin u_i + \tfrac{3}{2}\varepsilon_i^2 \sin u_i \cos u_i + \varepsilon_i^3 \sin u_i - \tfrac{1}{3}\varepsilon_i^3 \sin^3 u_i,$$

and u_i and u_i' are given by equation (16). On expanding this in powers of z_i/Z, with the use of equations (13) and (17) and neglecting terms other than linear, and comparing the expansion with that of

$$\overline{r^2} = a_0^2 \frac{n^4}{(Z - S_{M\infty})^2}(1 + \tfrac{3}{2}\varepsilon^2), \tag{31}$$

in powers of S_{M_∞}/Z, there is obtained for S_{M_x} the value

$$S_{M\infty} = z + \sum_i S_{Mi} = z + \sum_i z_i - \sum_i D_{Mi} \qquad (32\text{A})$$

with
$$S_{Mi} = \frac{z_i}{\pi} \left\{ u_i + \frac{\varepsilon \sin u_i \left(\frac{3}{4} - \frac{7}{4}\varepsilon^2 - \varepsilon\cos u_i + \frac{1}{12}\varepsilon^2\sin^2 u_i\right)}{(1+\frac{3}{2}\varepsilon^2)(1+\varepsilon\cos u_i)} \right\} \qquad (32\text{B})$$

with u_i as given in equation (27).

In column 4 of Table V are given values of S_{M_∞} calculated by means of equation (32). The mole refraction results show that we may expect the

Table V.—The Diamagnetism Screening Constant.

	$Z_0.$		$S_{M\infty}.$	$S_{M_0}.$	$\Delta S_M.$
He	2	K	0·228	0·228	0
Ne	10	L_{11}	3·26	3·26	0
		$L_{21} L_{22}$	4·11	4·11	
Ar	18	M_{11}	7·57	9·40	0·07
		$M_{21} M_{22}$	8·68	10·63	
Kr	36	N_{11}	17·19	24·21	0·25
		$N_{21} N_{22}$	18·94	26·13	
Xe	54	O_{11}	27·34	38·28	0·39
		$O_{21} O_{22}$	29·38	40·87	
$[Cu^+]_0$	28	M_{11}	10·8	11·45	0·03
		$M_{21} M_{22}$	12·2	12·9	
		$M_{32} M_{33}$	14·4	15·25	
$[Ag^+]_0$	46	N_{11}	20·0	28·35	0·31
		$N_{21} N_{22}$	21·8	30·35	
		$N_{32} N_{33}$	25·0	34·3	
$[Au^+]_0$	78	O_{11}	36·7	54·8	0·65
		$O_{21} O_{22}$	39·1	57·35	
		$O_{32} O_{33}$	43·3	62·35	

theoretical values to be correct in the case of the helium and neon structures, and to show an increasing error with increasing electron number for the other structures. The form of equation (26), which gives the screening constant for a property proportional to $n^r Z^{-t}$, immediately suggests a method for correction by means of the empirical changes introduced in the mole refraction screening constant S_R; namely, with the assumption that the various screening constants (for various physical properties) of an atom or ion deviate from their values calculated for Z large in such a way as to keep constant the ratios of the corresponding screening defects of the penetrated shells. Thus we would assume that D_M/D_R for argon, krypton, etc., has the values holding for Z large;

and from this ratio and the empirical D_R values D_M and hence S_{M_0} and ΔS_M can be found. The results are given in Table V, which accordingly contains theoretical values of the diamagnetism screening constant, corrected for all structures but helium and neon by the empirical mole refraction data. For each ion S_M is obtained by an equation of the form of equation (29).

The quantum mechanics treatment of diamagnetism has not been published.[*] It seems probable, however, that Larmor's theorem will be retained essentially, in view of the marked similarity between the results of the quantum mechanics and those of the classical theory in related problems, such as the polarisation due to permanent electric dipoles and the paramagnetic susceptibility.[†] Thus we are led to use equation (30), introducing for $\overline{r_\kappa^2}$ the quantum mechanics value

$$\overline{r_{nlm}^2} = \int r^2 \Psi_{nlm} \overline{\Psi}_{nlm} \, dV = a_0^2 \cdot \frac{n^4}{(Z - S_M)^2}\left[1 + \frac{3}{2}\left\{1 - \frac{l(l+1) - \frac{1}{3}}{n^2}\right\}\right], \quad (33)$$

differing from the value of the old quantum theory in the number $\frac{1}{3}$, and in having $l(l+1)$ instead of k^2. Substituting this in equation (30), and introducing the numerical values of the physical constants, there results

$$\chi = -2\cdot010 . 10^{-6} . \sum_\kappa \frac{n_\kappa^4}{(Z - S_{M_\kappa})^2}\left[1 - \frac{\{3l_\kappa(l_\kappa+1) - 1\}}{5n_\kappa^2}\right], \quad (34)$$

in which the summation over κ denotes over all the electrons in the atom.

The molal diamagnetic susceptibilities of rare gas atoms and a number of monatomic ions obtained by the use of equation (34) are given in Table IV. The values for the hydrogen-like atoms and ions are accurate, since here the screening constant is zero. It was found necessary to take into consideration in all cases except the neon (and helium) structure not only the outermost electron shell but also the next inner shell, whose contribution is for argon 5 per cent., for krypton 12 per cent., and for xenon 20 per cent. of the total.

The available experimental data, because of their paucity and their inaccuracy, do not permit the extensive testing of these figures. The directly determined susceptibilities for helium, neon, and argon are in gratifying agreement with the theoretical ones (Table VI). From the mole refraction results we may expect ions in solution to have values of χ near those for gaseous ions. Koenigsberger[‡] has made determinations of χ for seven alkali halides in aqueous solution, in

[*] Schrödinger (IV) has tentatively advanced a form of the wave equation in which magnetic fields are considered.

[†] Mensing and Pauli, 'Phys. Z.,' vol. 27, p. 509 (1926) ; Van Vleck, 'Nature,' vol. 118, p. 226 (1926).

[‡] Koenigsberger, quoted in Landolt-Börnstein.

Table VI.—Diamagnetic Susceptibilities of the Rare Gases.

———	$-\chi \cdot 10^6$ Calculated.	Observed.*	From salt solutions.
He	1·54	1·88	1·8
Ne	5·7	6·7	9
Ar	21·5	18·1, 20·3	18
Kr	42		37
Xe	66		59

* The three numbers in the first column are from Hector, ' Phys. Rev.,' vol. 24, p. 418 (1924); the second value for argon is from Lehrer, ' Ann. d. Physik, vol. 81, p. 229 (1926).

each case obtaining a specific susceptibility of $-0\cdot45 \cdot 10^{-6}$ units per gram. Assuming this rule to hold in general, one obtains the rare gas susceptibilities given in the last column of Table VI, in satisfactory agreement with those calculated. He also gives for the halides of calcium, barium, and strontium specific susceptibilities somewhat lower, about $-0\cdot41 \cdot 10^{-6}$, corresponding satisfactorily with the decrease observed in Table IV on going from a univalent to the adjoining divalent cation.

The experimental specific susceptibilities of solid salts obtained by different investigators (quoted in Landolt-Börnstein) show wide variations, but in general agree roughly with those from solutions. Thus for sodium chloride five investigators report five values, varying from $-0\cdot38$ to $-0\cdot58 \cdot 10^{-6}$. Of these the most trustworthy seems to be that of Ishiwara, $-0\cdot498 \cdot 10^{-6}$. This corresponds to $\chi = -29\cdot2 \cdot 10^{-6}$, in satisfactory agreement with our value $-33 \cdot 10^{-6}$. Pascal has also made extensive experimental investigations, from which he deduced a set of atomic susceptibilities,* choosing them in such a way as to give agreement with those for the elementary substances in a number of cases. These values are of little use to us because of lack of information regarding the nature of the compounds studied.† Pascal‡ has later reported the susceptibilities of several salts of each of the alkali and alkali earth metals, from which ionic susceptibilities can be derived after the choice of one as a starting point. We shall take for $-\chi \cdot 10^6$ for sodium ion 5·2 and for potassium ion 14·5 (compatible values), which are 4 smaller than those chosen by Pascal ; in this way the " experimental " values in Table VII are obtained. For helium-, neon- and argon-like ions, as well as for the cuprous ion, the agreement with our

* ' C. R.,' vol. 158, p. 1895 (1914).

† Despite the improbability that these atomic susceptibilities correspond at all with true ionic susceptibilities, they have been made the basis of a theoretical discussion by Cabrera, ' Journ. de physique et le radium,' VI, vol. 6, p. 241 (1925).

‡ ' C. R.,' vol. 158, p. 37 (1914) ; vol. 159, p. 429 (1914) ; vol. 173, p. 144 (1921).

Table VII.—Ionic Susceptibilities, from Pascal.

——	$-\chi \cdot 10^6$ Experiment.	Theory.	——	$-\chi \cdot 10^6$ Experiment.	Theory.
Li$^+$	0·2	0·6			
Na$^+$	5·2	4·2	F$^-$	10·3	8·1
K$^+$	14·5	16·7	Cl$^-$	24·1	29
Rb$^+$	23·2	35	Br$^-$	34·6	54
Cs$^+$	37·0	55	I$^-$	48·6	80
Be^{++}	0·2	0·3	CO$_3^=$	30·2	38
Mg^{++}	3·3	3·2	NO$_3^-$	18·2	38
Ca^{++}	7·8	13·3	PO$_4^{\equiv}$	47·1	52
Sr^{++}	16·5	28	SO$_4^=$	41·6	51
Ba^{++}	29·8	46	OH$^-$	11·5	12·6
Cu$^+$	ca. 14	13			
Ag$^+$	27	44			

predicted values is satisfactory ; but for the more complicated ions the experimental values are low. It is impossible to give with certainty the explanation of this difference. The experimental values from solutions indicate that our predicted values are at least approximately correct for isolated ions, so that probably the differences are real, and are to be attributed to the mutual action of the ions in crystals. In regard to this effect of mutual action it is significant that the crystals show deviations from additivity (as in the case of the mole refraction), amounting, however, to only a few per cent.

We can draw conclusions regarding deformation of ions from observations of the diamagnetic susceptibility just as from those of the mole refraction. Thus in the series CO$_3^=$, NO$_3^-$ and PO$_4^{\equiv}$, SO$_4^=$ the experimental values of χ show successively greater deviations from the theoretical ones (assuming undeformed O$^=$ ions) with increasing electrical charge of the central ion.*

We may accordingly conclude that our theoretical values of the diamagnetic susceptibility of atoms and ions are not incompatible with the experimental data.

VI.—*The Electron Distribution in Atoms and Ions. Atomic Sizes.*

According to the discussion in Section II, the quantity $\Psi\overline{\Psi}$ represents the electron density about the nucleus in a hydrogen-like atom. The electron

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* Larmor's Theorem is, of course, valid only for systems of electrons and one nucleus, so that complexes of atoms presumably do not permit the usual treatment. It seems probable, however, that the introduction of a hydrogen nucleus into an ion would cause a diminution in the susceptibility (in absolute value). The value of $-\chi \cdot 10^6$ for water, 13·0, suggests that 12·6 for O$^=$ is low, in agreement with the fact that the value 5·7 for neon is smaller than Hector's 6·7.

density corresponding to a " penetrating orbit " could be found by the solution of the boundary problem resulting on giving the potential energy V in the wave equation the value shown in equation (4). An approximation to this result is obtained by the introduction of a screening constant S_S, which we shall call the size screening constant, the shape of the distribution curve being considered to remain unaltered.

To evaluate this screening constant, we observe that in the penetrating orbits of the old quantum theory the electron remains for most of its period in the outer half of its orbit, *i.e.*, in the outermost or *j*th region. Hence we may consider that the entire orbit corresponds to one characterised by the segmentary quantum number n_j of the outermost region. It is desirable to evaluate S_S' in such a way as to give the correct value to $\bar{r}$, the average distance of the electron from the nucleus. This distance is given by equation (4). Omitting for simplicity the factor $1 + \frac{1}{2}\left\{1 - \frac{l(l+1)}{n^2}\right\}$, which is of little significance in the result obtained, we then write

$$a_0 \cdot \frac{n_j^2}{Z_j} = a_0 \cdot \frac{n^2}{(Z - S_{S_\infty})} \cdot$$

The value of the size screening constant S_{S_∞} is accordingly given by equation (26), r/t being replaced by 2.

As before, we may expect the values of S_{S_∞} calculated for Z large to be valid for actual ions with the helium and neon structures. For the other structures we introduce the empirical corrections based upon those used for the mole refraction screening constant, with the aid of the principle of the constancy of the ratios of corresponding screening defects, already used for the diamagnetism screening constant. In this way the values of S_{S_0} and ΔS_S given in Table VIII are obtained. An equation similar to equation (29) is to be used to find individual values of S_S.

The most instructive method of representing the electron distribution is by a graph showing it as a function of the distance *r* from the nucleus ; that is, by the use of $D = 4\pi r^2 \rho$, where ρ is the electron density. Such a graph is shown in fig. 3, in which is represented the total value of D for the sodium ion and the chloride ion, the D values being calculated as in Section II, but with the use of the appropriate effective atomic numbers $Z - S_S$. The vertical line for each shell is drawn at the average position $\bar{r}$ of the electrons in that shell, and its height gives the contribution of these electrons to D at this point. The distribution curves of the individual shells are those of fig. 2, with the scale

Table VIII.—The Size Screening Constant.

Z_0		S_{S_0}	ΔS_S
He	2	K	0·188	0
Ne	10	L_{11} L_{21} L_{22}	2·84 4·52	0
Ar	18	M_{11} M_{21} M_{22}	9·15 10·87	0·07
Kr	36	N_{11} N_{21} N_{22}	23·91 26·83	0·25
Xe	54	O_{11} O_{21} O_{22}	38·68 41·80	0·49
$[Cu^+]_0$	28	M_{11} M_{21} M_{22} M_{32} M_{33}	10·9 13·15 17·7	0·03
$[Ag^+]_0$	46	N_{11} N_{21} N_{22} N_{32} N_{33}	27·9 30·3 35·1	0·31
$[Au^+]_0$	78	O_{11} O_{21} O_{22} O_{32} O_{33}	54·2 57·0 62·7	0·67

varied as indicated by the positions and heights of the corresponding vertical lines.*

We are thus led to the following picture of atoms and ions containing only completed sub-groups of electrons ; the chloride ion, for example. The electron distribution about the nucleus is spherically symmetrical. The two K electrons in the chloride ion form a ball about the nucleus extending to the radius of about 0·1 Å, the electron density ρ decreasing monotonically as r increases. (This meaning will be implied by the word "ball." See fig. 1, in which the ordinates are proportional to $\pm \sqrt{\rho}$, to find the electron density.) The two L_{11} electrons provide a small ball extending to 0·07 Å, and then a thick shell, of maximum density at a distance of about 0·15 Å. The six L_{21} L_{22} electrons form one shell only, its density increasing from zero at $r = 0$ to a maximum at $r = 0·1$ Å, and then decreasing. A small portion (1 per cent.) of the two M_{11} electrons forms a ball about the nucleus, extending to 0·13 Å ; from this distance to 0·48 Å extends a shell containing about 10 per cent. of

* In fig. 3 L_1 represents L_{11}, L_2 represents L_{21} L_{22}, &c. Through a mistake the L_1 and L_2 vertical lines for the chloride ion are drawn to the wrong heights ; the L_2 line should have the height shown for the L_1 line, and vice versa.

the two electrons, of maximum density at about 0·2 Å, and the remainder forms still another shell of maximum density at 0·8 Å. The six M_{21} M_{22} electrons
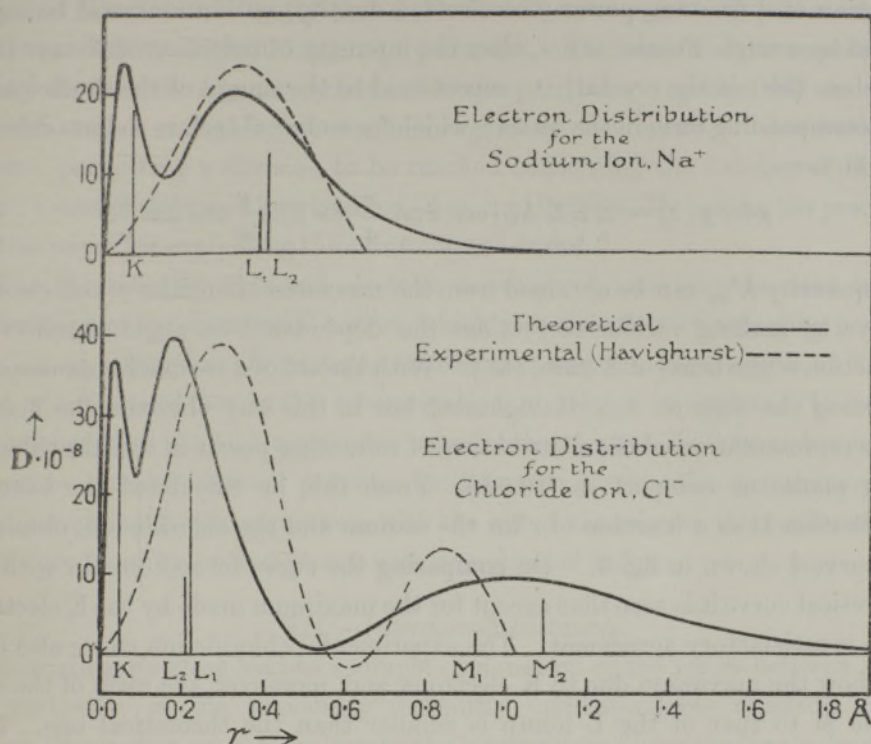

Fig. 3.—The theoretical and the experimental electron distribution (as a function of the distance from the nucleus) for the sodium and the chloride ion.

form two shells, one, containing about 10 per cent. of the electrons, having its maximum density at 0·13 Å, and the other with maximum density at 0·9 Å.*

We may accordingly say that an atom is composed of a nucleus embedded in a ball of electricity (the two K electrons with small contributions from other shells), which in turn is surrounded by more or less distinctly demarcated thick concentric shells, containing essentially the L, M, N, etc., electrons.†

Of particular interest is the result that for a radius of around 0·55 Å the electron density in the chloride ion falls nearly to zero ; for this conclusion has

* The details of this description would be changed slightly, but not essentially, by the introduction of the spinning electron into the theory.

† The experiments of Davisson and Kunsman, ' Phys. Rev.,' vol. 22, p. 242 (1923), on the distribution in angle of electrons scattered by metals provide some experimental verification of this layer structure of atoms ; for the investigators remark that their results are explicable by the atomic model involving the surface layer idealisation of electron shells.

been previously drawn from the experimental intensities of reflection of X-rays from sodium chloride crystals. It was remarked by Duane* that if the distribution of diffracting power (the electron density) within a crystal be represented by a triple Fourier series, then the intensity of reflection of X-rays from the plane (hkl) of the crystal† is proportional to the square of the coefficient of the corresponding term in the series; which for a crystal such as sodium chloride has the form,

$$\rho(x, y, z) \sim \sum_h \sum_k \sum_l A_{hkl} \cos 2\pi h \frac{x}{a} \cos 2\pi k \frac{y}{a} \cos 2\pi l \frac{z}{a}. \qquad (35)$$

The quantity A^2_{hkl} can be obtained from the measured intensities of reflection of X-rays by making various corrections (for dependence on angle of reflection, extinction of the beam of X-rays, etc.). With the aid of a reasonable assumption regarding the sign of A_{hkl}, Havighurst‡ has in this way obtained the Fourier series representation of the distribution of refracting power in sodium chloride, using planes as complex as (10.0.0). From this he calculated the electron distribution D as a function of r for the sodium and the chloride ion, obtaining the curves§ shown in fig. 3. On comparing the curve for sodium ion with the theoretical curve it is seen that except for the maximum made by the K electrons there is satisfactory agreement. The experimental chloride ion curve also does not show the maximum due to K electrons, and, moreover, the ratio of the area of the M to that of the L hump is smaller than the theoretical one. It is gratifying, however, to observe the experimental verification of the existence of the M shell, and of the minimum in the electron density in the region at 0·6 Å from the nucleus. In explanation of the small size of the M hump found by Havighurst we observe that the densities ρ in this region as given by equation (35) are very small, not much larger than the random fluctuations shown by the series, so that this portion of the curve may be in considerable error. The non-appearance of the K maxima may be attributed to several co-operating causes. In order for the Fourier series to be sensitive enough to show such sharp maxima, accurate values of the coefficients A_{hkl} for a large number of planes with indices of the order of 15 would be required. Furthermore, it is probable that

* ' Proc. Nat. Acad. Amer.,' vol. 11, p. 489 (1925).

† (hkl) represents here the Miller indices multiplied by the order of reflection.

‡ ' Proc. Nat. Acad. Amer.,' vol. 11, p. 502 (1925). Havighurst used the intensity measurements of W. L. Bragg, James, and Bosanquet, ' Phil. Mag.,' vol. 41, p. 309 (1921); vol. 42, p. 1 (1921).

§ A somewhat similar but not identical electron distribution for these ions has been derived by A. H. Compton, ' Phys. Rev.,' vol. 27, p. 510 (1926), from the same experimental data.

thermal motion of the ions in the crystal at ordinary temperatures would smooth the curve somewhat, and displace it towards larger values of r. It is also possible that for the tightly bound K electrons the reflecting power and the electron density are no longer proportional. The careful determination of many coefficients A_{hkl} for sodium chloride and other crystals will no doubt provide much valuable information regarding the electron distribution in atoms, permitting a decision to be reached concerning the validity of Schrödinger's interpretation of his eigenfunctions, and incidentally testing the procedure of this paper for evaluating the screening constants.

The theoretically obtained electron densities of ions may be used for the calculation of the so-called F curves, which give the effective reflecting power of the ion as a function of the angle of reflection and the wave-length of X-rays, and which are of use in the determination of crystal structures. It may be mentioned that the high maximum value of the electron density at the nucleus given by our calculations provides considerable justification for the method[*] of determining crystal structures with the aid of the relative intensities of Laue spots produced by crystal planes with complicated indices.

VII.—*Interatomic Distances.*

Schrödinger's ideas lead to a simple explanation of the forces between atoms, in particular of the previously difficultly understandable repulsive force.[†] As an illustration we shall calculate the internuclear distances for the hydrogen halides.

For simplicity we shall assume the fluoride ion to consist of the nucleus, two K electrons very close to it, and eight $L_{21} L_{22}$ electrons ; for as can be seen from the representation of the sodium ion in fig. 3 the L_{11} electrons show nearly the same distribution along r as the $L_{21} L_{22}$ electrons. The potential energy of a hydrogen nucleus at the distance R from the fluorine nucleus is then

$$\Phi = \frac{7e^2}{R} - 8e^2 \left\{ \int_0^R X_{21}{}^2(r) \frac{r^2}{R} \, dr + \int_R^\infty X_{21}{}^2(r) \frac{r^2}{r} \, dr \right\}, \qquad (36)$$

assuming that the fluoride ion is not deformed by the hydrogen ion. The first term in Φ is due to the nucleus and the K electrons, with a charge of $7e$, and the second term to the eight L electrons. For equilibrium we have the condition

$$\left(\frac{d\Phi}{dR} \right)_{R = R_0} = - \frac{7e^2}{R_0{}^2} + \frac{8e^2}{R_0{}^2} \int_0^{R_0} X_{21}{}^2(r) \, r^2 \, dr = 0, \qquad (37)$$

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[*] Used principally in the United States, by Wyckoff, Dickinson, etc.

[†] This was remarked by Unsöld, ' Dissertation,' Munich, 1927.

with the simple interpretation that the number of electrons within the radius R_0 is Z, so that the repulsive force of the nucleus on the hydrogen ion just balances the attractive force of an equivalent number of electrons.

The solution of this equation is $R_0 = 0 \cdot 91$ Å, in deceptively good agreement with the band spectra value given in Table IX. For there are two important

Table IX.—Internuclear Distances in the Hydrogen Halides.

——	Theoretical.	Experimental.*
	Å	Å
HF	0·91	0·92
HCl	1·55	1·265, 1·28
HBr	2·12	1·407

* The experimental figures, with one exception, were obtained from oscillation-rotation spectra with the use of integral rotational quantum numbers by Kratzer, ' Z. f. Physik,' vol. 3, p. 289 (1920). The second figure for hydrogen chloride was calculated by Colby, ' Astrophys. Journ.,' vol. 58, p. 303 (1923), from the same data, with the use of half quantum numbers, and by Czerny, ' Z. f. Physik,' vol. 34, p. 227 (1925), from pure rotation spectra with half quantum numbers.

considerations which must be introduced in the more detailed treatment of interatomic forces, and which in this case apparently effectively neutralise each other. Our evaluation of the electron distribution provides only an approximation to that corresponding to a " penetrating orbit," so that the average electron-nucleus distance $\bar{r}$ is correctly given, but for large values of r the electron density is given a smaller value than the actual one. This effect, if taken into consideration, would increase the repulsive force at large values of R, and would tend to give a larger value of R_0. But the deforming action of the hydrogen ion on the fluoride ion must also be taken into account. This can be thought of as the polarisation of the fluoride ion in the field of the positive ion, resulting in an attractive force between the two ions of amount $2\alpha e^2/R_0^5$, if the polarisability α be assumed constant. The potential of this term, introduced in equation (37), would tend to decrease the value of R_0. The higher order effects, induced quadrupole, etc., moments, also in reality are of importance.

The values of R_0 similarly calculated for hydrogen chloride and hydrogen bromide, with the substitution of $X_{31}(r)$ and $X_{41}(r)$ for $X_{21}(r)$ in equation (37), are somewhat larger than the experimental ones. This indicates that the deforming effect of the hydrogen ion on the halide ions is of greater relative importance for these ions than for the fluoride ion.

A similar procedure can be used in predicting interatomic distances in ionic crystals, by evaluating the potential energy of a three-dimensional array of

undeformed ions, and determining the condition that this be a minimum. Such a procedure leads to interatomic distances of the order of magnitude of the actual ones ; because of the approximate nature of our determination of the electron distribution it is not worth while to carry out accurately the lengthy calculations involved.

VIII.—*Conclusion.*

The general method followed in this paper is capable of refinements which should make possible the accurate prediction of the properties of any atom or ion. The most obvious one is the use of the wave mechanics in determining the state of an electron under the influence of a positive nucleus and several idealised electron shells. Explicit expressions for the properties of an electron in such a state may then be derived, eliminating the necessity of the more or less inaccurate adaptation of the equations obtained for hydrogen-like atoms. Further progress may also be made in approximating an electron shell more closely than is possible with a spherical surface charge. All of these refinements will greatly complicate the treatment, however ; and while without doubt they will sooner or later be introduced, the relatively simple, if less exact, procedure which we have used suffices to show the general applicability of the method, and to provide approximate values of the physical properties of ions which may not exist under conditions permitting experimental investigation. The usefulness of these values in the consideration of the structure of molecules and of crystals will be illustrated elsewhere.

[*Added February* 10, 1927.—J. H. Van Vleck in ' Proc. Nat. Acad. America,' vol. 12, p. 662 (December, 1926), has discussed the mole refraction and the diamagnetic susceptibility of hydrogen-like atoms with the use of the wave mechanics, obtaining results identical with our equations (24) and (34). He also considered the effect of the relativity corrections (which is equivalent to the effect of a central field) and concluded that equation (24), derived by the use of parabolic instead of spherical co-ordinates, is not invalidated.]