$\frac{3}{2}$. It is impossible to confirm this from the structure observed in any line.

Further work is being done on samples enriched in the isotopes 174 and 176 in order to determine the shifts 174–176 and 176–178. The interference systems on hand at this writing do not warrant even qualitative conclusions, however.

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Electronic Polarizabilities of Ions from the Hartree-Fock Wave Functions*†

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The electronic polarizability α has been calculated for several ions by obtaining the perturbation of the wave functions by an external field from a numerical solution of the differential equation satisfied by the perturbation. For the helium-like ions an analytic solution was obtained by using the wave functions of Löwdin. The calculated values of α are, in general, between 1 and 1.5 times the observed values. For several ions values have been calculated for the quadrupole polarizability which measures the quadrupole moment induced in the ion by an external charge. The effect of the dipole moment induced in the ion on the electric field at the nucleus is discussed.

I. INTRODUCTION

THE electronic polarizability of ions has been determined by a number of different methods. The polarizability can be obtained from the index of refraction of the ion in solutions or in crystals. An independent method consists in a consideration of the Rydberg-Ritz correction for the spectral series of atoms. Following Born and Heisenberg,[1] the deviation of the spectral terms of the alkalis from hydrogenic levels is attributed to the polarization of the core by the valence electron. This procedure to obtain the polarizability was also used by Mayer and Mayer.[2] The determination of the polarizability from the index of refraction of solutions was first carried out by Heydweiller[3] and by Fajans and Joos.[4] While the present work was in progress, there appeared a paper by Tessman, Kahn, and Shockley[5] who made a determination of the ionic polarizabilities from the experimental refraction data of crystals containing the ions considered.[6]

In contrast to the variety of experimental determinations of the polarizability α, there exist comparatively few theoretical treatments which attempt to explain the values of α in terms of the electronic structure of the ion. Pauling[7] derived an analytic expression for α for electrons which move in a pure Coulomb field (hydrogenic wave functions). He used this expression with appropriate screening constants for the helium-like ions and obtained good agreement with the observed values of α. This method is not expected to give accurate results for medium and heavy ions since the electronic wave functions are very different from hydrogenic wave functions in this case. Buckingham[8] obtained an expression relating α to the average values of r^2 for the various electron shells, where r is the distance between the nucleus and an electron of the core. This expression was derived from a variational calculation in which the perturbed wave function for each shell was taken as a preassigned function times a parameter which was varied to minimize the energy. Although different parameters were used for the different subshells, this procedure probably does not always give a good approximation to the actual perturbed function, because only a single parameter for each subshell is available in the variational calculation.

In the present paper, values of α are obtained for nine ions from F^- to Cs^+ by means of a numerical solution of the differential equation for the perturbation of the electronic wave functions for the various shells. For the unperturbed wave functions, the Hartree-Fock functions of the ions are used. For the helium-like ions an approximate analytic solution for the perturbation based on the wave functions of Löwdin[9] will be employed. The calculated values of α lie, in general, between 1 and 1.5 times the experimental values. Thus the calculations are in reasonable agreement with ex-

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† A preliminary account of this work was presented at the April 29–May 1, 1954 Meeting of the American Physical Society in Washington, D. C. [Phys. Rev. **95**, 594 (1954)].

[1] M. Born and W. Heisenberg, Z. Physik **23**, 388 (1924).

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[5] Tessman, Kahn, and Shockley, Phys. Rev. **92**, 890 (1953).

[6] An extensive discussion of the work on polarizabilities is given by J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), first edition, Chap. VIII.

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[9] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

periment. The tendency for the calculated values to be somewhat too large is probably due to the fact that the Hartree-Fock wave functions give less binding and are more external than the actual wave functions. An increase of the binding would be accompanied by a decrease of α. The agreement of the present values of α with experiment is on the whole better than that obtained by Buckingham.[8]

Besides the dipole polarizability α, it is of interest to consider the quadrupole polarizability which will be defined as the ratio of the quadrupole moment induced in the ion by the field of an external charge to the field gradient at the nucleus produced by the charge. The quadrupole polarizability α_q was first introduced by Mayer and Mayer.[2] In the present paper, values of α_q have been calculated analytically for the helium-like ions and numerically for the Na$^+$ and Cs$^+$ ions. The last section of this paper gives a discussion of the electric field at the nucleus due to the dipole moment induced in the ion by the field of an external charge.

II. EXPRESSION FOR THE POLARIZABILITY

Assume that the electric field is produced by a unit charge $+e$ at a large distance R from the nucleus along the positive X axis. If R is in units of the Bohr radius a_H, the dipole part of the potential energy (in Rydberg units) is given by

$$H_1=-(2/R^2)r\cos\theta, \tag{1}$$

where θ is the angle between the X axis and the radius vector (of length r) from the nucleus to an electron in the core. The unperturbed wave function times r for a core electron will be denoted by u_0. Let u_1 denote r times the perturbation of the wave function due to H_1, and let E_1 by the first-order perturbation of the energy. H_0 and E_0 will denote the unperturbed Hamiltonian and energy, respectively. The Schrödinger equation to the first order in H_1 is given by

$$(H_0+H_1)(u_0+u_1)=(E_0+E_1)(u_0+u_1). \tag{2}$$

E_1 is given by

$$E_1=\int_0^\infty\int_0^\pi\int_0^{2\pi} H_1u_0^2dr\,\sin\theta d\theta d\varphi, \tag{3}$$

where φ is the azimuthal angle. Since H_1 is linear in $\cos\theta$ while u_0^2 is an even function of $\cos\theta$, the integral over θ vanishes, so that $E_1=0$. By subtracting from Eq. (2) the unperturbed Schrödinger equation,

$$H_0u_0=E_0u_0, \tag{4}$$

one obtains the equation for u_1:

$$(H_0-E_0)u_1=-H_1u_0. \tag{5}$$

In the following, u_0 will be normalized according to

$$\int_0^\infty\int_0^\pi\int_0^{2\pi} u_0^2dr\,\sin\theta d\theta d\varphi=1. \tag{6}$$

u_0 will be written

$$u_0=(2\pi)^{-\frac{1}{2}}u'_0\Theta_l^m\exp(im\varphi), \tag{7}$$

where u'_0 is the radial wave function (times r), l=azimuthal quantum number, m=magnetic quantum number, Θ_l^m is the angular eigenfunction with the choice of phases as given in Condon and Shortley.[10] u_0' and Θ_l^m are normalized according to

$$\int_0^\infty u'^2_0dr=\int_0^\pi |\Theta_l^m|^2\sin\theta d\theta=1. \tag{8}$$

The first-order perturbation of the density $[(u_0+u_1)^2]$ is given by $2u_0u_1$ for each core electron. Hence, the induced dipole moment which will be called $p_{\text{ind},X}$ is given by

$$p_{\text{ind},X}=-2e\sum_{nlm}\int_0^\infty\int_0^\pi\int_0^{2\pi}(u_0u_1)_{nlm}r\times\cos\theta dr\,\sin\theta d\theta d\varphi, \tag{9}$$

where n is the principal quantum number, and the sum extends over all electrons of the core. Since the density $2u_0u_1$ depends on n, l, and m, it has been labeled $2(u_0u_1)_{nlm}$. The field E_X is $-e/R^2$, so that the polarizability is given by

$$\alpha=p_{\text{ind},X}/E_X=2R^2\sum_{nlm}\int_0^\infty\int_0^\pi\int_0^{2\pi}(u_0u_1)_{nlm}r\times\cos\theta dr\,\sin\theta d\theta d\varphi. \tag{10}$$

We will now obtain an expression for α in terms of the radial functions by integrating over θ and φ, and performing the sum over the magnetic quantum numbers m for each shell.

The contribution of the s shells will be considered first. Since $\Theta_0^0=2^{-\frac{1}{2}}$, u_0 can be written

$$u_0=(2\pi)^{-\frac{1}{2}}2^{-\frac{1}{2}}u'_0. \tag{11}$$

Thus the right hand side of (5) becomes in view of (1),

$$-H_1u_0=(2\pi)^{-\frac{1}{2}}2^{\frac{1}{2}}R^{-2}u'_0r\cos\theta. \tag{12}$$

If Rydberg units are used, H_0 is given by

$$H_0=-\nabla^2+V_0, \tag{13}$$

where V_0 is the unperturbed potential in which the electron moves. Equation (12) shows that u_1 is a p wave. u_1 can be written

$$u_1=(2\pi)^{-\frac{1}{2}}2^{\frac{1}{2}}R^{-2}u'_{1,0\to1}\cos\theta, \tag{14}$$

where $u'_{1,0\to1}$ is the radial function which is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{2}{r^2}+V_0-E_0\right)u'_{1,0\to1}=u'_0r. \tag{15}$$

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[10] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Macmillan Company, New York, 1935), p. 52.

Here and in the following the notation $u'_{1,\,l\to l'}$ denotes the radial function for the excitation of a state with azimuthal quantum number l into states with azimuthal quantum number l'. Upon inserting Eqs. (11) and (14) into Eq. (10) one obtains for the contribution of both ns electrons to α:

$$\alpha(ns\to p)=4R^2\int_0^\infty\int_0^\pi\int_0^{2\pi} u_0u_1r\cos\theta dr\sin\theta d\theta d\varphi$$
$$=(8/3)\int_0^\infty u'_0u'_{1,\,0\to1}rdr. \quad (16)$$

The procedure of the numerical solution of Eq. (15) will be described in Sec. III. Here we note that for the $1s$ shell, if u'_0 is assumed to be a hydrogenic wave function, Eq. (15) has an exact solution, as was shown previously.[11] Thus if the unperturbed function is taken as

$$u'_0=2Z^{\frac{3}{2}}r\exp(-Zr) \quad (17)$$

with an appropriate value of the effective atomic number Z (including screening), then $u'_{1,\,0\to1}$ is given by

$$u'_{1,\,0\to1}=Z^{-\frac{1}{2}}r^2\exp(-Zr)[1+(Z/2)r], \quad (18)$$

as can be verified by substitution in Eq. (15). Upon inserting (17) and (18) into (16), one obtains

$$\alpha(1s\to p)=(9/Z^4)a_{\mathrm{H}}^3. \quad (19)$$

This is a well-known result which has been derived previously by Pauling[7] and others.[6]

The contribution of the p shells to α will now be obtained. The electrons with $m=0$ will be considered first. The unperturbed function is given by

$$u_0^{(0)}=(2\pi)^{-\frac{1}{2}}(3/2)^{\frac{1}{2}}u'_0\cos\theta. \quad (20)$$

Here and in the following the superscript of $u_0^{(m)}$ indicates the magnetic quantum number. In view of Eqs. (1) and (20), $-H_1u_0^{(0)}$ is given by

$$-H_1u_0^{(0)}=(2\pi)^{-\frac{1}{2}}(2/3)^{\frac{1}{2}}R^{-2}u'_0[(3\cos^2\theta-1)+1], \quad (21)$$

where the square bracket is written as the sum of a d function and an s function; these terms give rise to excited d waves and s waves, respectively. The $np\to d$ excitation will be considered first. In view of (5) and (13), the excited wave function is given by

$$u_{1,\,1\to2}^{(0)}=(2\pi)^{-\frac{1}{2}}(2/3)^{\frac{1}{2}}R^{-2}u'_{1,\,1\to2}(3\cos^2\theta-1), \quad (22)$$

where the radial function $u'_{1,\,1\to2}$ is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{6}{r^2}+V_0-E_0\right)u'_{1,\,1\to2}=u'_0r. \quad (23)$$

In Eq. (22) and in the following, $u_{1,\,l\to l'}^{(m)}$ denotes r times the wave function for the excitation of an electron with azimuthal quantum number l and magnetic quantum number m into states with azimuthal quantum number l'. The details of the numerical solution of Eq. (23) are given in Sec. III. Upon inserting Eqs. (20) and (22) into (10), one obtains for the contribution of both $m=0$ electrons to α,

$$\alpha^{(0)}(np\to d)=4R^2\int_0^\infty\int_0^\pi\int_0^{2\pi} u_0^{(0)}u_{1,\,1\to2}^{(0)}r$$
$$\times\cos\theta dr\sin\theta d\theta d\varphi \quad (24)$$
$$=(32/15)\int_0^\infty u'_0u'_{1,\,1\to2}rdr.$$

The np states with $m=\pm1$ will now be considered. The unperturbed function is given by

$$u_0^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}(3^{\frac{1}{2}}/2)u'_0\sin\theta\exp(\pm i\varphi). \quad (25)$$

We have

$$-H_1u_0^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}3^{\frac{1}{2}}R^{-2}u'_0\sin\theta\cos\theta\exp(\pm i\varphi). \quad (26)$$

Since the right hand side of (26) is a pure d function, the $m=\pm1$ electrons do not contribute to the $np\to s$ excitation. The perturbation is given by

$$u_{1,\,1\to2}^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}3^{\frac{1}{2}}R^{-2}u'_{1,\,1\to2}\sin\theta\cos\theta\exp(\pm i\varphi). \quad (27)$$

Upon inserting (26) and (27) into (10), one obtains for the contribution of the four $m=\pm1$ electrons to α,

$$\alpha^{(\pm1)}(np\to d)=8R^2\int_0^\infty\int_0^\pi\int_0^{2\pi} u_0^{(\pm1)}u_{1,\,1\to2}^{(\pm1)}r$$
$$\times\cos\theta dr\sin\theta d\theta d\varphi \quad (28)$$
$$=(16/5)\int_0^\infty u'_0u'_{1,\,1\to2}rdr.$$

In view of (24) and (28), the $np\to d$ contribution of the complete p shell to α is given by

$$\alpha(np\to d)=(16/3)\int_0^\infty u'_0u'_{1,\,1\to2}rdr. \quad (29)$$

The $np\to s$ term due to the $m=0$ electrons is obtained in the same manner as $np\to d$. From (21) one finds for the perturbation,

$$u_{1,\,1\to0}^{(0)}=(2\pi)^{-\frac{1}{2}}(2/3)^{\frac{1}{2}}R^{-2}u'_{1,\,1\to0}, \quad (30)$$

where the radial function $u'_{1,\,1\to0}$ is determined by

$$\left(-\frac{d^2}{dr^2}+V_0-E_0\right)u'_{1,\,1\to0}=u'_0r. \quad (31)$$

Upon inserting (20) and (31) into (10) one obtains for both $m=0$ electrons,

$$\alpha(np\to s)=(8/3)\int_0^\infty u'_0u'_{1,\,1\to0}rdr. \quad (32)$$

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[11] Foley, Sternheimer, and Tycko, Phys. Rev. 93, 734 (1954).

Here and in the following, $\alpha(nl\rightarrow l')$ denotes the contribution to α of the complete subshell nl.

The contributions of the d shells to α can be found in the same manner as for np. The d electrons are excited into p and f states. The complete derivation will not be given here, but the various excited wave functions will be listed together with the final results. The $nd\rightarrow f$ waves will be considered presently. The excited wave functions are given by

$$u_{1,\,2\rightarrow3}^{(0)}=(2\pi)^{-\frac{1}{2}}(3/10^{\frac{1}{2}})R^{-2}u'_{1,\,2\rightarrow3}(5\cos^3\theta-3\cos\theta), \tag{33}$$

$$u_{1,\,2\rightarrow3}^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}(3/5)^{\frac{1}{2}}R^{-2}u'_{1,\,2\rightarrow3}\times(5\sin\theta\cos^2\theta-\sin\theta)\exp(\pm i\varphi), \tag{34}$$

$$u_{1,\,2\rightarrow3}^{(\pm2)}=(2\pi)^{-\frac{1}{2}}(15^{\frac{1}{2}}/2)R^{-2}u'_{1,\,2\rightarrow3}\sin^2\theta\times\cos\theta\exp(\pm2i\varphi), \tag{35}$$

for the $m=0$, ±1, and ±2 electrons, respectively. Similarly to Eqs. (15), (23), and (31), the radial function $u'_{1,\,2\rightarrow3}$ is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0-E_0\right)u'_{1,\,l\rightarrow l'}=u'_0r, \tag{36}$$

in which $l=2$, $l'=3$, and u'_0 is the unperturbed radial nd function. Upon inserting Eqs. (7) and (33)–(35) into (10), one obtains

$$\alpha(nd\rightarrow f)=8\int_0^\infty u'_0u'_{1,\,2\rightarrow3}rdr. \tag{37}$$

The $nd\rightarrow p$ excited wave functions are given by

$$u_{1,\,2\rightarrow1}^{(0)}=(2\pi)^{-\frac{1}{2}}(8/5)^{\frac{1}{2}}R^{-2}u'_{1,\,2\rightarrow1}\cos\theta, \tag{38}$$

$$u_{1,\,2\rightarrow1}^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}(3/5)^{\frac{1}{2}}R^{-2}u'_{1,\,2\rightarrow1}\times\sin\theta\exp(\pm i\varphi), \tag{39}$$

and $u_{1,\,2\rightarrow1}^{(\pm2)}=0$. The radial function $u'_{1,\,2\rightarrow1}$ is determined by Eq. (36) with $l=2$ and $l'=1$. From Eqs. (10), (38), and (39), one obtains

$$\alpha(nd\rightarrow p)=(16/3)\int_0^\infty u'_0u'_{1,\,2\rightarrow1}rdr. \tag{40}$$

The f electrons are excited into d and g states. The excited wave functions for $nf\rightarrow g$ are given by

$$u_{1,\,3\rightarrow4}^{(0)}=(2\pi)^{-\frac{1}{2}}14^{-\frac{1}{2}}R^{-2}u'_{1,\,3\rightarrow4}\times(35\cos^4\theta-30\cos^2\theta+3), \tag{41}$$

$$u_{1,\,3\rightarrow4}^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}(75/56)^{\frac{1}{2}}R^{-2}u'_{1,\,3\rightarrow4}\times(7\sin\theta\cos^3\theta-3\sin\theta\cos\theta)\exp(\pm i\varphi), \tag{42}$$

$$u_{1,\,3\rightarrow4}^{(\pm2)}=(2\pi)^{-\frac{1}{2}}(15/28)^{\frac{1}{2}}R^{-2}u'_{1,\,3\rightarrow4}\times(7\sin^2\theta\cos^2\theta-\sin^2\theta)\exp(\pm2i\varphi), \tag{43}$$

$$u_{1,\,3\rightarrow4}^{(\pm3)}=\mp(2\pi)^{-\frac{1}{2}}(35/8)^{\frac{1}{2}}R^{-2}u'_{1,\,3\rightarrow4}\times\sin^3\theta\cos\theta\exp(\pm3i\varphi), \tag{44}$$

where $u'_{1,\,3\rightarrow4}$ is determined by Eq. (36) with $l=3$, $l'=4$, and u'_0 taken as the unperturbed f function. From Eqs. (10) and (41)–(44), one obtains

$$\alpha(nf\rightarrow g)=(32/3)\int_0^\infty u'_0u'_{1,\,3\rightarrow4}rdr. \tag{45}$$

The excited wave functions for $nf\rightarrow d$ are as follows,

$$u_{1,\,3\rightarrow2}^{(0)}=(2\pi)^{-\frac{1}{2}}(3/14^{\frac{1}{2}})R^{-2}u'_{1,\,3\rightarrow2}(3\cos^2\theta-1), \tag{46}$$

$$u_{1,\,3\rightarrow2}^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}(24/7)^{\frac{1}{2}}R^{-2}u'_{1,\,3\rightarrow2}\times\sin\theta\cos\theta\exp(\pm i\varphi), \tag{47}$$

$$u_{1,\,3\rightarrow2}^{(\pm2)}=(2\pi)^{-\frac{1}{2}}(15/28)^{\frac{1}{2}}R^{-2}u'_{1,\,3\rightarrow2}\times\sin^2\theta\exp(\pm2i\varphi), \tag{48}$$

where $u'_{1,\,3\rightarrow2}$ is determined by Eq. (36) with $l=3$, $l'=2$. From Eqs. (10) and (46)–(48), one finds

$$\alpha(nf\rightarrow d)=8\int_0^\infty u'_0u'_{1,\,3\rightarrow2}rdr. \tag{49}$$

From Eqs. (16), (29), (32), (37), (40), (45), and (49), one obtains the following expression for α,

$$\alpha=\sum_n\left(\frac{8}{3}I_{0\rightarrow1}\right)_{ns}+\sum_n\left(\frac{8}{3}I_{1\rightarrow0}+\frac{16}{3}I_{1\rightarrow2}\right)_{np}+\sum_n\left(\frac{16}{3}I_{2\rightarrow1}+8I_{2\rightarrow3}\right)_{nd}+\sum_n\left(8I_{3\rightarrow2}+\frac{32}{3}I_{3\rightarrow4}\right)_{nf}, \tag{50}$$

where the sums extend over the occupied s, p, d, and f shells, and $I_{l\rightarrow l'}$ is defined as

$$I_{l\rightarrow l'}\equiv\int_0^\infty u'_0u'_{1,\,l\rightarrow l'}rdr, \tag{51}$$

where $u'_{1,\,l\rightarrow l'}$ is the perturbation considered. It may be noted that the coefficients of $I_{l\rightarrow l'}$ and $I_{l'\rightarrow l}$ in Eq. (50) are equal. This was expected because the transition from nlm to $n'l'm$ (n' = principal quantum number of excited state) has the same matrix element as the transition from $n'l'm$ to nlm. Since the angular factors do not depend on n and n', the equality of the coefficients of the $I_{l\rightarrow l'}$ follows. We note that Eq. (50) gives α in units $a_H{}^3$ and must be multiplied by a factor $0.529^3=0.148$ to obtain α in units A^3.

III. CALCULATIONS OF THE POLARIZABILITY

In this section the calculation of the radial functions $u'_{1,\,l\rightarrow l'}$ is described and the resulting values of α, as obtained from Eq. (50), are compared with experiment.

The $u'_{1,\,l\rightarrow l'}$ are determined by Eq. (36), of which Eqs. (15) for $ns\rightarrow p$, (23) for $np\rightarrow d$, and (31) for $np\rightarrow s$ are special cases. The calculations of α for the helium-like ions, which were done analytically, will be discussed below. In the numerical calculations for the medium and heavy ions, the unperturbed functions u'_0, were taken as the Hartree-Fock or Hartree wave functions. For Na^+, Cl^-, K^+, Ca^{++}, and Cu^+, the Hartree-Fock functions[12–16] (including exchange) were used, while for F^-, Al^{3+}, Rb^+, and Cs^+ only Hartree functions[17–18] (without exchange) are available. The function on the left hand side of Eq. (36) was obtained directly from the tabulated Hartree-Fock functions, in the manner shown previously.[11] Thus, let $P(r)$ be defined as

$$P(r) \equiv [l(l+1)/r^2] + V_0(r) - E_0, \tag{52}$$

where l is the azimuthal quantum number for the unperturbed state. If r_n is a selected radius and δ is the interval at which u'_0 is tabulated, $P(r_n)$ is given by

$$P(r_n) = [u'_0(r_n+\delta) - 2u'_0(r_n) + u'_0(r_n-\delta)]/[\delta^2 u'_0(r_n)]. \tag{53}$$

The function which appears on the left hand side of Eq. (36) is

$$P'(r) \equiv P(r) + [l'(l'+1) - l(l+1)]/r^2. \tag{54}$$

If I denotes the inhomogeneity $I = u'_0 r$, the equation used for the numerical integration with the same interval δ is given by

$$u'_1(r_n+\delta) = u'_1(r_n)\{2 + \delta^2[P'(r_n) - I(r_n)/u'_1(r_n)]\} - u'_1(r_n-\delta). \tag{55}$$

Equation (55) is appropriate for outward integration starting near $r=0$. The equation for inward integration is obtained from (55) by reversing the sign of δ.

For $ns \rightarrow p$ and $np \rightarrow s$, Eq. (36) was integrated outward with starting values obtained as follows. Near $r=0$, the $ns \rightarrow p$ function $u'_{1,0\rightarrow 1}(ns)$ is approximately proportional to the unperturbed np function $u'_0(np)$ for the same n, as will now be shown. Here and in the following $u'_0(nl)$ denotes the unperturbed function for nl, and $u'_{1,l\rightarrow l'}(nl)$ denotes the perturbation of the state nl. From Eq. (15) it is seen that the inhomogeneity $u'_0 r$ acts in the same manner as an additional potential $\delta V = -u'_0 r/u'_{1,0\rightarrow 1}$. Near $r=0$, $u'_0(ns) \propto r$, $u'_{1,0\rightarrow 1}(ns) \propto r^2$, so that δV is constant and therefore much smaller than the terms $2/r^2$ and V_0. Thus the right hand side of (15) can be neglected near $r=0$ and the equation for $u'_{1,0\rightarrow 1}(ns)$ is the same as the equation for $u'_0(np)$, except for the small difference between the unperturbed energies E_0 for ns and for np. However, the term E_0 plays a negligible role near $r=0$, so that $u'_{1,0\rightarrow 1}(ns)$ is approximately proportional to $u'_0(np)$. The integration [Eq. (55)] was started at two values of r near $r=0.05a_H$; the starting values $u'_1(r_n)$ and $u'_1(r_n+\delta)$ were taken proportional to the values of $u'_0(np)$ at these radii. Thus $u'_1 = \beta_1 u'_0(np)$, where β_1 is a proportionality constant to be determined. The integrations were carried out with several values of β_1. The correct β_1 is that for which the resulting $u'_{1,0\rightarrow 1}$ is well behaved (i.e., exponentially decreasing) at infinity. In practice, β_1 and $u'_{1,0\rightarrow 1}$ were found by interpolation. For two choices of β_1 which enclose the correct value, the functions diverge slowly, the one to positive values, the other to negative values as $r \rightarrow \infty$. However, they agree quite well (in general within ~ 15 percent) in the region of importance for α, between $r \sim 1a_H$ and $r \sim 3a_H$, where the outermost maximum of u'_0 occurs. Figure 1 shows the $3s \rightarrow p$ function $u'_{1,0\rightarrow 1}$ for Cl^-, together with twice the unperturbed $3s$ function $2u'_0$.

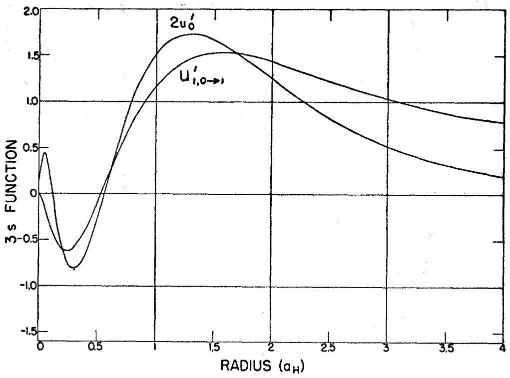

FIG. 1. $3s$ function u'_0 and $3s \rightarrow p$ perturbation $u'_{1,0\rightarrow 1}$ for Cl^-.

For the $np \rightarrow s$ excitation essentially the same procedure was used as for $ns \rightarrow p$. Near $r=0$, the perturbation $u'_{1,1\rightarrow 0}(np)$ is proportional to $u'_0(ns)$ since the extra potential $\delta V = -u'_0(np)r/u'_{1,1\rightarrow 0}(np)$ which corresponds to the inhomogeneity of Eq. (31) is negligible near the nucleus. This follows from the fact that $u'_0(np) \propto r^2$, $u'_{1,1\rightarrow 0}(np) \propto r$, so that $\delta V \propto r^2$ near $r=0$, in contrast to V_0 which goes as $1/r$. The difference between the values of E_0 for ns and for np can also be neglected, so that Eq. (31) is approximately the same as the equation for $u'_0(ns)$. The numerical integration [Eq. (55)] was started near $r=0.05a_H$, using for $u'_{1,1\rightarrow 0}$ the values of $\beta_2 u'_0(ns)$ where β_2 is a proportionality constant. Similarly to $ns \rightarrow p$, the integrations were carried out for several values of β_2 until a value was found by interpolation for which the resulting $u'_{1,1\rightarrow 0}$ is well behaved at $r=\infty$. Figure 2 shows the $3p \rightarrow s$ perturbation $u'_{1,1\rightarrow 0}$ for Cl^-, together with twice the unperturbed $3p$ function $2u'_0$.

For $np \rightarrow d$, an inward method of integration was used in most cases, starting at a large radius r_1. For this purpose, Eq. (23) was written as follows,

$$d^2u'_{1,1\rightarrow 2}/dr^2 = Nu'_{1,1\rightarrow 2}, \tag{56}$$

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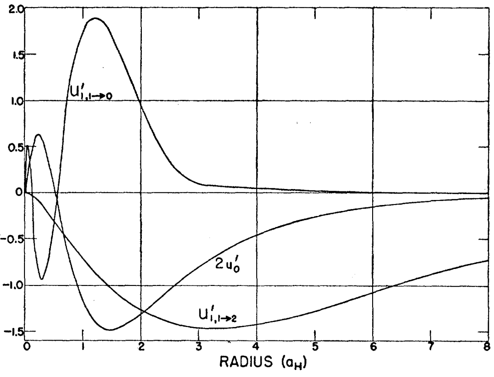

FIG. 2. $3p$ function u'_0, $3p\to s$ perturbation $u'_{1,1\to0}$, and $3p\to d$ perturbation $u'_{1,1\to2}$ for Cl$^-$.

where N is given by [see Eqs. (52) and (54)]:

$$N=P'-[u'_0r/u'_{1,1\to2}]. \tag{57}$$

Note that for large r, N is constant and given by $-E_0$. Several integrations were carried out with different starting values $u'_{1,1\to2}(r_1)$. It was assumed that N is constant for $r>r_1$; for a given $u'_{1,1\to2}(r_1)$, $N(r_1)$ is calculated from (57), and $u'_{1,1\to2}(r_1+\delta)$ is obtained from

$$u'_{1,1\to2}(r_1+\delta)=u'_{1,1\to2}(r_1)\exp\{-[N(r_1)]^{\frac{1}{2}}\delta\}. \tag{58}$$

The numerical integration is then started with the values $u'_{1,1\to2}(r_1)$ and $u'_{1,1\to2}(r_1+\delta)$. The correct value of $u'_{1,1\to2}(r_1)$ is that for which the resulting $u'_{1,1\to2}$ is zero at $r=0$. This requirement is appropriate since the actual perturbation goes as r^3 near $r=0$. In practice, the actual $u'_{1,1\to2}(r_1)$ and the solution were found by interpolation. For two choices of $u'_{1,1\to2}(r_1)$ which enclose the correct value, the solutions $u'_{1,1\to2}(r)$ diverge slowly, the one to positive values, the other to negative values, near $r=0$. However, they agree closely (in general within 15 percent) in the region of importance for $\alpha(r\sim1a_H-3a_H)$. Figure 2 shows the $3p\to d$ perturbation $u'_{1,1\to2}$ for Cl$^-$. The contribution to α is determined by $(16/3)u'_0u'_{1,1\to2}r$ [see Eq. (29)]. Since $u'_{1,1\to2}$ and u'_0 have the same sign for $r>0.55a_H$, the contribution to $\alpha(3p\to d)$ from this region is positive. For $r<0.55a_H$, $u'_{1,1\to2}$ and u'_0 have opposite sign because of the node of u'_0, so that the region inside $0.55a_H$ makes a negative contribution to $\alpha(3p\to d)$. However, this contribution is negligible compared to that made by $r>0.55a_H$, because the values of u'_0, $u'_{1,1\to2}$, and r are considerably smaller than in the region[19] $r>0.55a_H$. The sign of the terms of α due to $3s\to p$ and $3p\to s$ is discussed below.

For Cu$^+$, $3d\to f$, and inward method of integration was used, similar to that for $np\to d$, while the $3d\to p$ wave of Cu$^+$ was obtained by outward integration, similar to $ns\to p$ and $np\to s$.

After the $u'_{1,l\to l'}$ are obtained, the integrals $I_{l\to l'}$ [Eq. (51)] are evaluated and α is calculated from Eq. (50). It is estimated that the inaccuracy of the values of α due to the interpolation procedure to obtain the $u'_{1,l\to l'}$ is less than ±20 percent. In many cases the values of $\alpha(nl\to l')$ are probably accurate to ±10–15 percent.

It was found that the polarizability α is almost entirely due to the outermost shell whose principal quantum number will be called n_0. The contribution of the shells with $n<n_0$ is negligible in all cases. This result was already obtained by Pauling[7] from the hydrogenic wave functions and by Buckingham.[8] The results of the calculations are presented in Table I. The first five rows list the term $\alpha(n_0l\to l')$ due to the various modes of excitation of the outermost shell. The last two rows give the resulting calculated value of α and the experimental values. The fact that the inner shells $(n<n_0)$ make a negligible contribution to α was established by calculating $\alpha(2p\to d)$ for Cl$^-$, $\alpha(3d\to f)$ for Rb$^+$, and $\alpha(4d\to f)$ for Cs$^+$. These represent the largest terms for the shell with $n=n_0-1$, and were found to be 0.01A^3, 0.03A^3, and 0.16A^3, respectively. Even for Cs$^+$, this term represents only 3 percent of the contribution due to $n_0=5$, and is therefore appreciably smaller than the uncertainty of the calculations. The reason why the inner shells make only a negligible contribution is that both the right hand side of Eq. (36) for $u'_{1,l\to l'}$ and the integrand of $I_{l\to l'}$ [Eq. (51)] contain a factor r, so that the contribution to α depends essentially on the average value of r^2 for the shell considered.[8] Since $\langle r^2\rangle_{nl}$ decreases very considerably as n is decreased by 1, only the outermost shell contributes effectively to α.

The experimental values α(exp) given in the last row of Table I correspond to the values obtained by Born and Heisenberg,[1] Mayer and Mayer,[2] Fajans and Joos,[4] Pauling,[7] and Tessman, Kahn, and Shockley.[5] The range of α(exp) is due to the fact that different experimental methods give appreciably different values of α in some instances. These discrepancies can probably be attributed to uncertainties in corrections which enter into the determination of α from the experimental data. As an example of these corrections, the quadrupole polarizability and the effect of penetration of the core enter into the spectral level method.[2] Similarly, the values of α obtained from the index of refraction of

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[19] While the contribution of $r<0.55a_H$ is negligible for the polarizability, it may be important for properties which depend strongly on the region of the electron cloud near the nucleus. Thus as shown below (Sec. V) the induced charge distribution contributes to the electric field at the nucleus. The term in the electric field due to $3p\to d$ is given by $(16e/3R^2)\int_0^\infty u'_0u'_{1,1\to2}r^{-2}dr$. The fact that the dependence on r is r^{-2} rather than r as for the polarizability results in a strong dependence on the values of $u'_0u'_{1,1\to2}$ near the nucleus. It may also be noted that the antishielding correction to the nuclear quadrupole coupling (reference 11) is an effect similar to the one discussed here. In this case, the perturbed wave functions are such as to shield the atom from the electric field gradient of the external charge in the vicinity of that charge, i.e., in the region of the outermost maximum of the atomic wave functions. However, near the nucleus, the effect is in some cases an antishielding because of nodes and changes of sign of the unperturbed and perturbed wave functions.

crystals[1,5] may be affected by distortion of the ion by interatomic forces.[6]

Table I shows that $\alpha(n_0s\rightarrow p)$ and $\alpha(n_0p\rightarrow s)$ cancel each other approximately, so that $\alpha(n_0p\rightarrow d)$ makes the major contribution to α for the cases where n_0p is the outermost subshell. A similar near-cancellation takes place for $3p\rightarrow d$ and $3d\rightarrow p$ of Cu^+, so that the $3d$ subshell through $\alpha(3d\rightarrow f)$ makes the largest contribution to α for Cu^+. This cancellation will now be explained for the case of $n_0s\rightarrow p$ and $n_0p\rightarrow s$. For this purpose, Eq. (15) for $u'_{1,0\rightarrow 1}$ and Eq. (31) for $u'_{1,1\rightarrow 0}$ will be solved in terms of eigenfunctions. We expand $u'_{1,0\rightarrow 1}$ in terms of the np eigenfunctions for the potential V_0. Thus

$$u'_{1,0\rightarrow 1}=\sum\nolimits_n a_n u'_0(np), \tag{59}$$

where a_n is a coefficient and $u'_0(np)$ is the normalized solution of

$$\left[-\frac{d^2}{dr^2}+\frac{2}{r^2}+V_0-E_0(np)\right]u'_0(np)=0, \tag{60}$$

where $E_0(np)$ is the energy eigen value for np. In (59) the sum extends over all of the discrete states allowed by (60) and over the continuum states with $E_0(np)>0$. In Eq. (15) E_0 will be written more explicitly as $E_0(n_0s)$ and u'_0 will be written as $u'_0(n_0s)$. Upon inserting (59) into (15), one obtains

$$\left[-\frac{d^2}{dr^2}+\frac{2}{r^2}+V_0-E_0(n_0s)\right]\sum_n a_n u'_0(np)=u'_0(n_0s)r. \tag{61}$$

In view of (60), Eq. (61) becomes

$$\sum\nolimits_n[E_0(np)-E_0(n_0s)]a_n u_0'(np)=u_0'(n_0s)r. \tag{62}$$

Upon multiplying both sides of (62) by $u'_0(np)$ and integrating over r, one obtains

$$a_n=\left[\int_0^\infty u'_0(n_0s)ru'_0(np)dr\right]\bigg/[E_0(np)-E_0(n_0s)]. \tag{63}$$

Since the energy denominator is smallest for $n=n_0$, the largest a_n is expected to be a_{n0}, so that $u'_{1,0\rightarrow 1}$ is approximately given by $a_{n0}u'_0(n_0p)$. As a result,

$$I_{0\rightarrow 1}\sim a_{n0}\int_0^\infty u'_0(n_0s)ru'_0(n_0p)dr. \tag{64}$$

In a similar manner, the $np\rightarrow s$ perturbation $u'_{1,1\rightarrow 0}$ will be expanded in terms of the ns eigenfunctions $u'_0(ns)$ which are the normalized solutions of

$$\left[-\frac{d^2}{dr^2}+V_0-E_0(ns)\right]u'_0(ns)=0. \tag{65}$$

Thus,

$$u'_{1,1\rightarrow 0}=\sum\nolimits_n b_n u'_0(ns), \tag{66}$$

where b_n is a coefficient. In Eq. (31) E_0 will be written more explicitly as $E_0(np_0)$ and u'_0 as $u'_0(n_0p)$. Upon inserting (66) into (31) and using (65), one obtains

$$\sum\nolimits_n[E_0(ns)-E_0(n_0p)]b_n u'_0(ns)=u'_0(n_0p)r. \tag{67}$$

Upon multiplying both sides of (67) by $u'_0(ns)$ and integrating over r, one finds

$$b_n=\left[\int_0^\infty u'_0(n_0p)ru'_0(ns)dr\right]\bigg/[E_0(ns)-E_0(n_0p)]. \tag{68}$$

Again the smallest energy denominator is obtained for $n=n_0$, and a comparison of (63) and (68) shows that $b_{n0}=-a_{n0}$. In the approximation in which the terms $n\neq n_0$ are neglected, we have

$$I_{1\rightarrow 0}\sim -a_{n0}\int_0^\infty u'_0(n_0s)ru'_0(n_0p)dr, \tag{69}$$

so that $I_{0\rightarrow 1}$ and $I_{1\rightarrow 0}$ would exactly cancel each other.

These results have a simple physical interpretation. In the absence of the Pauli principle, the major part of the $n_0s\rightarrow p$ excitation would be n_0p, and the major part of the $n_0p\rightarrow s$ excitation would be n_0s. However, since both the n_0s and n_0p shells are filled, the two terms just cancel each other, so that only excitations of n_0s into higher p states ($n>n_0$) and excitations of n_0p into higher s states ($n>n_0$) are possible. This leaves $n_0p\rightarrow d$

TABLE I. Calculated and experimental values of the polarizability α. The rows above α(calc) list the contributions to α of the various modes of excitation of the (outermost) shell with highest principal quantum number n_0. All values are in units A^3.

Ion	F^-	Na^+	Al^{3+}	Cl^-	K^+	Ca^{++}	Cu^+	Rb^+	Cs^+
$\alpha(n_0s\rightarrow p)$	0.39	0.125	0.061	1.33	0.57	0.40	0.077	0.98	2.15
$\alpha(n_0p\rightarrow s)$	−0.30	−0.101	−0.054	−0.97	−0.44	−0.36	−0.069	−0.89	−1.71
$\alpha(n_0p\rightarrow d)$	3.11	0.121	0.043	5.28	1.13	0.69	0.096	2.61	4.43
$\alpha(n_0d\rightarrow p)$							−0.084		
$\alpha(n_0d\rightarrow f)$							0.450		
α(calc)	3.20	0.145	0.050	5.65[a]	1.26	0.73	0.470	2.73[b]	5.03[c]
α(exp)	0.76–1.04	0.17–0.26	0.052–0.067	2.97–3.66	0.80–1.20	0.47–1.1	1.6	1.4–1.8	2.35–3.14

[a] Includes a term $0.01\mathrm{A}^3$ due to $2p\rightarrow d$.
[b] Includes a term $0.03\mathrm{A}^3$ due to $3d\rightarrow f$.
[c] Includes a term $0.16\mathrm{A}^3$ due to $4d\rightarrow f$.

as the major contribution to α, since the energy difference between n_0p and n_0d is fairly small and the n_0d states are unoccupied. A similar explanation applies to the approximate cancellation of the $3p \rightarrow d$ and $3d \rightarrow p$ terms for Cu$^+$ and the predominance of the $3d \rightarrow f$ term, involving the excitation into the unoccupied f states.

The preceding results are illustrated by Figs. 1 and 2. Figure 1 shows that the $3s \rightarrow p$ excitation $u'_{1,0\rightarrow1}$ of Cl$^-$ and the $3s$ function $u'_0(3s)$ have the same sign throughout most of the range of r (for $r > 0.12a_H$), resulting in a positive contribution to α since $u'_0u'_{1,0\rightarrow1} > 0$ [see Eq. (16)]. By contrast the $3p \rightarrow s$ wave $u'_{1,1\rightarrow0}$ and the $3p$ function have in general opposite sign (see Fig. 2) so that $\alpha(3p \rightarrow s)$ is negative. It is also seen that $u'_{1,0\rightarrow1}$ for $3s \rightarrow p$ has the same node as $u'_0(3p)$ at $r = 0.55a_H$ and is approximately proportional to $u'_0(3p)$ inside $r = 2a_H$. Similarly, $u'_{1,1\rightarrow0}(3p \rightarrow s)$ and $u'_0(3s)$ have the same nodes and are approximately proportional for $r < 2a_H$.

From Table I it is seen that the calculated values of α are, in general, between 1 and 1.5 times the experimental values. As mentioned above, a discrepancy in this direction is expected because the Hartree-Fock functions provide less binding than the actual wave functions and should, therefore, tend to give values of α which are too large. For Cl$^-$, Rb$^+$, and Cs$^+$, the disagreement is a factor of $\sim$1.5. However, for K$^+$, the calculated α is barely above the experimental range, and for Na$^+$, Al^{3+}, and Ca^{++}, the calculated α is either within the experimental range or slightly below the experimental values. This agreement can be understood by virtue of the fact that for small positive ions or ions with net charge greater than 1, the wave functions of the outermost electrons have a relatively strong binding, and the calculated polarizability should be insensitive to small inaccuracies of the potential for the external electrons and of the zero-order wave functions. The fact that for Na$^+$, $\alpha(\text{calc}) = 0.145\text{A}^3$ is below the experimental values is somewhat disturbing. A difference in this direction has already been noted by Buckingham.[8] However, it should be pointed out that the experimental values are subject to uncertainties, and the discrepancy $(0.17 - 0.145 = 0.025\text{A}^3)$ is smaller than the difference between the experimental values $(0.26 - 0.17 = 0.09\text{A}^3)$. We also note that the value of α derived in Sec. IV from the spectral term defect including the quadrupole polarizability is 0.138A^3 which is smaller than α(calc). For F$^-$, α(calc) is larger than α(exp) by a factor of 3. This disagreement is probably due to the fact that only Hartree functions[17] were available for the calculation. Since F$^-$ is a negative ion, the binding of the $2p$ electrons is very sensitive to small changes of the potential in which these electrons move. Since the wave function was obtained from the Hartree equations,[17] the exchange correlation which would provide additional binding is not included. Thus, the rather large discrepancy is not surprising. The fact that there is better agreement for Cl$^-$ than for F$^-$ is probably due to the use of Hartree-Fock functions[13] for Cl$^-$. For Cu$^+$, Table I shows that $\alpha(\text{calc}) = 0.47\text{A}^3$ is appreciably smaller than $\alpha(\text{exp}) = 1.6\text{A}^3$. The experimental value was obtained by Tessman, Kahn, and Shockley[5] from the index of refraction of CuCl, CuBr, and CuI for the wavelength λ_D of the sodium D line. While the values of α obtained from the 3 compounds agree quite well (1.47, 1.67, and 1.71A^3) it is likely that α for infinite wavelength $\lambda = \infty$ is appreciably smaller than α for $\lambda = \lambda_D$. This trend is shown by all of the positive ions investigated by Tessman *et al.*[5] However, it seems unlikely that it can account for all of the discrepancy. Thus for Rb$^+$, $\alpha(\lambda_D) - \alpha(\infty)$ is 0.182A^3. For Ca^{++} and Ba^{++} the difference between $\alpha(\lambda_D)$ determined by Tessman *et al.*[5] and the largest value of α obtained by the other authors[1–4] is 0.59A^3 and 0.82A^3. Hence it cannot be excluded that the difference $\alpha(\text{exp}) - \alpha(\text{calc})$ is due to the inaccuracy of the experimental determination and the fact that α(exp) pertains to λ_D rather than $\lambda = \infty$. Another possible explanation is that part of the discrepancy is due to the use of a single radial wave function for the $3d$ electrons of Cu$^+$. This wave function was obtained by Hartree[16] from the Hartree-Fock method which treats the ten $3d$ electrons as a single group. It is possible that in a more accurate treatment the $3d$ electrons would fall into two groups, some being closer to the nucleus than predicted by the Hartree-Fock function, while the remainder would be more loosely bound since they are shielded more effectively from the nucleus. Such a distribution of two $3d$ groups could have a lower total energy, because of the presence of the tightly bound group of electrons, and at the same time, the distribution could have a larger polarizability because of the loosely bound electrons, each of which may give a considerably larger contribution than an electron which is described by the Hartree-Fock function.

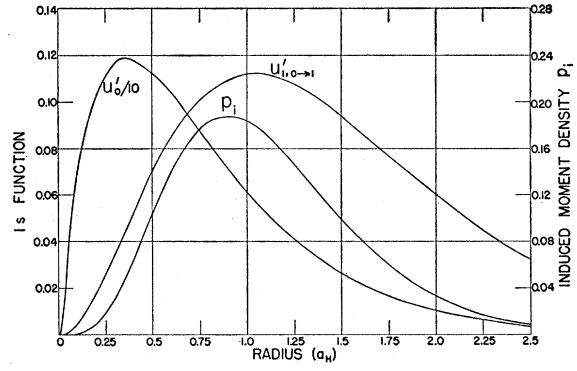

FIG. 3. $1s$ function u'_0, $1s \rightarrow p$ perturbation $u'_{1,0\rightarrow1}$, and induced moment density $p_i = (8/3)u'_0u'_{1,0\rightarrow1}r$ for Li$^+$.

It can be concluded that with the exception of F$^-$ and Cu$^+$, the calculated values of α are in reasonable agreement with experiment. In 4 out of 9 cases, α(calc) is essentially within the range of the observed values. In 3 other cases, α(calc) exceeds α(exp) by a factor of order 1.5.

The calculations for the helium-like ions will now be described. For the unperturbed 1s functions we used the Slater-type functions of Löwdin[9] which can be written as follows,

$$u'_0=c_1[2Z_1^{3/2}r\exp(-Z_1r)]+c_2[2Z_2^{3/2}r\exp(-Z_2r)], \quad (70)$$

where Z_1 and Z_2 are two effective values of the atomic number Z; c_1 and c_2 are coefficients. If there were no overlap between the two functions in square brackets, we would have $c_1^2+c_2^2=1$. In Sec. II, the $1s\rightarrow p$ perturbed function $u'_{1,0\rightarrow1}$ was obtained for an arbitrary Z [Eq. (18)]. Therefore, it seems reasonable to use for the perturbation corresponding to (70) the following expression,

$$u'_{1,0\rightarrow1}=c_1\{Z_1^{-\frac{1}{2}}r^2[1+(Z_1/2)r]\exp(-Z_1r)\} \\ +c_2\{Z_2^{-\frac{1}{2}}r^2[1+(Z_2/2)r]\exp(-Z_2r)\}. \quad (71)$$

Thus the polarizability (in units a_H^3) is given by

$$\alpha=(8/3)\int_0^\infty u'_0u'_{1,0\rightarrow1}rdr, \quad (16)$$

in which u'_0 and $u'_{1,0\rightarrow1}$ are given by Eqs. (70) and (71), respectively.

It may be noted that the expression of Eq. (71) is not exact, because it assumes that the 1s electrons are in a superposition of two states in which they experience slightly different potentials. Thus if the energy is E_0, the potential pertaining to Z_1 which is implied by Eq. (71) is

$$V_1=-(2Z_1/r)+Z_1^2+E_0, \quad (72)$$

while the potential pertaining to Z_2 is

$$V_2=-(2Z_2/r)+Z_2^2+E_0, \quad (73)$$

both in Rydberg units. However, the error made by this approximation is very small, as was verified by a calculation for Li$^+$. Thus the exact perturbed function can be found by solving Eq. (15) numerically by means of the function P [Eq. (52)] which can be obtained directly from the Löwdin function u'_0 according to Eq. (53). For the case of Li$^+$ the function $u'_{1,0\rightarrow1}$ obtained numerically was found to differ from (71) by less than 6 percent throughout the range of r, and the resulting value of α is 0.0306A^3 as compared to 0.0316A^3 obtained from (70) and (71). This difference is probably well within the uncertainty which arises from the inaccuracy of the Löwdin wave function u'_0 due to neglect of the correlation between the 1s electrons. Figure 3 shows the perturbed wave function $u'_{1,0\rightarrow1}$ for Li$^+$, as calculated from (71), together with the unperturbed 1s function [Eq. (70)], and the density of induced moment $p_i=(8/3)u'_0u'_{1,0\rightarrow1}r$, i.e., the integrand of α [see Eq. (16)]. The constants c_i and Z_i for Li$^+$ as obtained from Löwdin's[9] work, are:

$$Z_1=2.435, \quad Z_2=4.425,$$
$$c_1=6.664/(2Z_1^{3/2})=0.877, \quad c_2=2.562/(2Z_2^{3/2})=0.138.$$

TABLE II. Calculated and experimental values of α for helium and the helium-like ions. The calculated values were obtained from the Löwdin wave functions. All values are in units A^3.

Ion	α(calc)	α(exp)
H$^-$	16.1	
He	0.236	0.203
Li$^+$	0.0316	0.025–0.08
Be^{++}	0.0083	0.007–0.04
B^{3+}	0.00308	0.003–0.02
C^{4+}	0.00139	0.0013–0.012

Table II gives the calculated values of α for helium and the helium-like ions from H$^-$ to C^{4+}. The experimental values are also listed.[1–5] It is seen that the calculated values are generally in good agreement with experiment. This agreement was expected for the positive ions, since for these ions the 1s electrons have a relatively strong binding, and hence α should be insensitive to small inaccuracies of the potential and of the zero-order Löwdin wave functions, in the same manner as was discussed above for Na$^+$, Al^{3+}, and Ca^{++}.

IV. QUADRUPOLE POLARIZABILITY

When an ion is placed in the field of an external charge, the quadrupole part of the field of the charge induces a quadrupole moment in the charge distribution of the ion. The quadrupole field is closely connected with the electric field gradient at the nucleus. If the external charge is at $X=R$, the term in the potential energy is given by

$$V_q=-(r^2/R^3)(3\cos^2\theta-1), \quad (74)$$

in Rydberg units. Equation (74) is valid for $r<R$. The field gradient at the nucleus in the X direction is

$$\partial E_X/\partial X=-2e/R^3. \quad (75)$$

The induced quadrupole moment Q_{ind} is given by

$$Q_{\text{ind}}=\int\rho_{\text{ind},q}r^2(3\cos^2\theta-1)dV, \quad (76)$$

where dV=volume element, and $\rho_{\text{ind},q}$ is the density induced in the ion by the potential V_q. It is convenient to define the quadrupole polarizability as follows,

$$\alpha_q=\frac{-eQ_{\text{ind}}}{\partial E_X/\partial X}. \quad (77)$$

The quadrupole polarizability was first discussed by Mayer and Mayer[2] in their calculations on the spectral term defect of the alkalis. A problem related to α_q was also treated by Foley, Sternheimer, and Tycko[11] who calculated the perturbation of the electric field gradient at the nucleus produced by the density $\rho_{\text{ind},q}$ due to an external charge. In view of (76) and (77) α_q is given by

$$\alpha_q=(R^3/2)\int\rho_{\text{ind},q}r^2(3\cos^2\theta-1)dV. \quad (78)$$

We now obtain an expression for α_q similar to Eq. (50) for the dipole polarizability α. The derivation follows closely the same lines as for α. The results of Foley, Sternheimer, and Tycko[11] will be used. These authors showed that V_q results in an excitation of s electrons into excited d states, and of p electrons into p and f states. Similarly the d electrons are excited into s, d, and g states. The $ns\rightarrow d$ wave will now be considered. If the zero-order ns function (times r) is denoted by u_0, and if u_1 denotes r times the $ns\rightarrow d$ perturbation, then u_1 is determined by Eq. (2) in which H_1 is now defined as V_q and E_1 is the first-order perturbation of the energy due to H_1. By subtracting Eq. (4) from Eq. (2), one obtains

$$(H_0-E_0)u_1=(E_1-H_1)u_0. \tag{79}$$

E_1 is zero for s states. Upon inserting Eq. (11) for u_0 and Eq. (74) for H_1 into (79), one obtains

$$(H_0-E_0)u_{1,\,0\rightarrow 2}=(2\pi)^{-\frac{1}{2}}2^{-\frac{1}{2}}R^{-3}u'_0r^2(3\cos^2\theta-1). \tag{80}$$

Here and in the following $u_{1,\,l\rightarrow l'}$ denotes the wave function for the quadrupole excitation of a state with azimuthal quantum number l into states with azimuthal quantum number l'. Upon inserting (13) into (80), one obtains

$$u_{1,\,0\rightarrow 2}=(2\pi)^{-\frac{1}{2}}2^{-\frac{1}{2}}R^{-3}u'_{1,\,0\rightarrow 2}(3\cos^2\theta-1), \tag{81}$$

where the radial function $u'_{1,\,0\rightarrow 2}$ is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{6}{r^2}+V_0-E_0\right)u'_{1,\,0\rightarrow 2}=u'_0r^2. \tag{82}$$

Here and in the following the subscript notation for $u'_{1,\,l\rightarrow l'}$ is the same as for $u_{1,\,l\rightarrow l'}$. In view of (78) the contribution to α_q from the $ns\rightarrow d$ wave is given by

$$\alpha_q(ns\rightarrow d)=4(R^3/2)\int_0^\infty\int_0^\pi\int_0^{2\pi}u_0u_{1,\,0\rightarrow 2}r^2 \times(3\cos^2\theta-1)dr\,\sin\theta d\theta d\varphi, \tag{83}$$

where the factor 4 arises from the fact that the perturbed density $\rho_{\mathrm{ind},\,q}$ is $2u_0u_{1,\,0\rightarrow 2}$ for each ns electron. Upon inserting Eqs. (11) and (81) into (83) and performing the integrations over θ and φ, one obtains

$$\alpha_q(ns\rightarrow d)=(8/5)\int_0^\infty u'_0u'_{1,\,0\rightarrow 2}r^2dr. \tag{84}$$

We will next consider the excitation of p electrons into p states. For the states with $m=0$ the perturbation energy E_1 is given by

$$E_1=-R^{-3}\int_0^\infty\int_0^\pi\int_0^{2\pi}[u_0^{(0)}]^2r^2 \times(3\cos^2\theta-1)dr\,\sin\theta d\theta d\varphi, \tag{85}$$

where $u_0^{(0)}$ is the unperturbed np function as given by Eq. (20). Upon substituting this expression in (85), one obtains

$$E_1=-(4/5)\langle r^2\rangle_{nl}R^{-3}, \tag{86}$$

where $\langle r^2\rangle_{nl}$ is the average value of r^2 over the radial function u'_0:

$$\langle r^2\rangle_{nl}=\int_0^\infty u'^2_0r^2dr. \tag{87}$$

Upon inserting Eqs. (20), (74), and (86) into Eq. (79), one obtains

$$(H_0-E_0)u_1^{(0)}=-(2\pi)^{-\frac{1}{2}}\frac{4}{5}\left(\frac{3}{2}\right)^{\frac{1}{2}}\frac{\langle r^2\rangle_{nl}}{R^3}u_0\cos\theta +(2\pi)^{-\frac{1}{2}}\left(\frac{3}{2}\right)^{\frac{1}{2}}\frac{r^2}{R^3}u'_0\left[\frac{4}{5}\cos\theta +\left(3\cos^3\theta-\frac{9}{5}\cos\theta\right)\right], \tag{88}$$

where the angular factor in the square brackets has been written as the sum of a p and a f function. The p part contributes to the excited p wave function $u_{1,\,1\rightarrow 1}^{(0)}$ which can be written

$$u_{1,\,1\rightarrow 1}^{(0)}=(2\pi)^{-\frac{1}{2}}(24/25)^{\frac{1}{2}}R^{-3}u'_{1,\,1\rightarrow 1}\cos\theta, \tag{89}$$

where the radial function $u'_{1,\,1\rightarrow 1}$ is determined by the following equation,

$$\left(-\frac{d^2}{dr^2}+\frac{2}{r^2}+V_0-E_0\right)u'_{1,\,1\rightarrow 1}=u'_0(r^2-\langle r^2\rangle_{nl}). \tag{90}$$

The contribution to α_q due to the excitation of the $m=0$ electrons is given by

$$\alpha_q^{(0)}(np\rightarrow p)=4(R^3/2)\int_0^\infty\int_0^\pi\int_0^{2\pi}u_0^{(0)}u_{1,\,1\rightarrow 1}^{(0)} \times r^2(3\cos^2\theta-1)dr\,\sin\theta d\theta d\varphi \tag{91}$$
$$=(32/25)\int_0^\infty u'_0u'_{1,\,1\rightarrow 1}r^2dr,$$

where the factor 4 has the same origin as in Eq. (83).

For the np electrons with $m=\pm 1$, E_1 is given by

$$E_1=\int_0^\infty\int_0^\pi\int_0^{2\pi}[u_0^{(\pm 1)}]^2V_qdr\,\sin\theta d\theta d\varphi =(2/5)\langle r^2\rangle_{nl}R^{-3}, \tag{92}$$

where Eq. (25) for $u_0^{(\pm 1)}$ has been used. Upon inserting Eqs. (25), (74), and (92) into Eq. (79), one obtains

$$(H_0-E_0)u_1^{(\pm 1)}=\pm(2\pi)^{-\frac{1}{2}}\left(\frac{3^{\frac{1}{2}}}{5}\right)\frac{\langle r^2\rangle_{nl}}{R^3}u'_0\sin\theta \times\exp(\pm i\varphi)\pm(2\pi)^{-\frac{1}{2}}\left(\frac{3^{\frac{1}{2}}}{2}\right)\frac{r^2}{R^3}u'_0\left[-\tfrac{2}{5}\sin\theta +(3\cos^2\theta\sin\theta-\tfrac{3}{5}\sin\theta)\right]\exp(\pm i\varphi). \tag{93}$$

The square bracket has been written as a sum of *p* and *f* functions. Upon using the *p* part, one obtains the following expression for the perturbed *p* wave,

$$u_{1,\,1\to1}{}^{(\pm1)}=\mp(2\pi)^{-\frac{1}{2}}(3^{\frac{1}{2}}/5)R^{-3}u'_{1,\,1\to1}\times\sin\theta\exp(\pm i\varphi),\quad(94)$$

where $u'_{1,\,1\to1}$ is determined by Eq. (90). The contribution to α_q from the four electrons with $m=\pm1$ is given by

$$\alpha_q{}^{(\pm1)}(np\to p)=8(R^3/2)\int_0^\infty\int_0^\pi\int_0^{2\pi}u_0{}^{(\pm1)}\times u_{1,\,1\to1}{}^{(\pm1)}r^2(3\cos^2\theta-1)dr\,\sin\theta d\theta d\varphi\quad(95)$$
$$=(16/25)\int_0^\infty u'_0u'_{1,\,1\to1}r^2dr.$$

From Eqs. (91) and (95) one obtains for the complete *np* shell,

$$\alpha_q(np\to p)=(48/25)\int_0^\infty u'_0u'_{1,\,1\to1}r^2dr.\quad(96)$$

In order to obtain the terms of α_q for the excitation of *np* electrons into *f* states and the excitation of the *d* electrons, we make use of the results previously derived[11] for the perturbation of the electric field gradient at the nucleus. This quantity, which will be called $\Delta(\partial E_X/\partial X)$, is given by

$$\Delta(\partial E_X/\partial X)=e\int\rho_{\mathrm{ind},\,q}r^{-3}(3\cos^2\theta-1)dV.\quad(97)$$

Results were obtained for the ratio of $-\Delta(\partial E_X/\partial X)$ to the field gradient $-2e/R^2$ produced by the external charge. In view of Eq. (97), this ratio which was called γ_∞ is given by

$$\gamma_\infty=(R^3/2)\int\rho_{\mathrm{ind},\,q}r^{-3}(3\cos^2\theta-1)dV.\quad(98)$$

By comparing (78) with (98), it is seen that α_q differs from γ_∞ only by having r^2 instead of r^{-3} in the integrand. Thus the integration over θ and φ, and the summation over the magnetic substates in Eq. (78) give the same coefficients as for γ_∞.

The radial wave functions $u'_{1,\,l\to l'}$ are determined by the following equation similar to Eq. (14) of reference 11,

$$\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0-E_0\right]u'_{1,\,l\to l'}=u'_0(r^2-\langle r^2\rangle_{nl}\delta_{ll'}),\quad(99)$$

where $\langle r^2\rangle_{nl}$ is given by Eq. (87). Obviously, Eqs. (82) and (90) are special cases of (99). The term $\langle r^2\rangle_{nl}\delta_{ll'}$ arises from the E_1u_0 term of Eq. (79) [see Eqs. (88) and (93)]. For the case $l=l'$ that solution $u'_{1,\,l\to l}$ of Eq. (99) must be chosen which is orthogonal to u'_0.

As is seen from Eqs. (84) and (96), $\alpha_q(nl\to l')$ involves the integral.

$$J_{l\to l'}\equiv\int_0^\infty u'_0u'_{1,\,l\to l'}r^2dr.\quad(100)$$

The coefficients of the $J_{l\to l'}$ can be obtained from the expression for γ_∞, as was mentioned above. For this purpose, we note that γ_∞ also occurs in the calculation of the quadrupole moment $Q_{\mathrm{ind},\,Q}$ induced in the core by the nuclear quadrupole moment[20] Q. γ_∞ is equal to this induced moment expressed in units of Q. Thus the coefficients of the $J_{l\to l'}$ must be proportional to the coefficients which occur in the expression for $Q_{\mathrm{ind},\,Q}$ as given by Eqs. (3) and (7) of reference 20. In fact, with the present normalization of the radial wave functions $u'_{1,\,l\to l'}$ [Eq. (99)] the coefficients for $Q_{\mathrm{ind},\,Q}$ and for α_q turn out to be equal; e.g., the contribution to $Q_{\mathrm{ind},\,Q}$ from $ns\to d$ is given by $(8/5)Q\int_0^\infty u'_0u'_{1,\,Q}r^2dr$, where $u'_{1,\,Q}$ is the appropriate perturbation; the coefficient 8/5 is equal to that which appears in Eq. (84) for $\alpha_q(ns\to d)$. Hence the coefficients of the $J_{l\to l'}$ can be obtained directly from Eqs. (3) and (7) of reference 20. One finds

$$\alpha_q=\sum_n\left(\frac{8}{5}J_{0\to2}\right)_{ns}+\sum_n\left(\frac{48}{25}J_{1\to1}+\frac{72}{25}J_{1\to3}\right)_{np}+\sum_n\left(\frac{8}{5}J_{2\to0}+\frac{16}{7}J_{2\to2}+\frac{144}{35}J_{2\to4}\right)_{nd},\quad(101)$$

where the sums extend over the occupied *s*, *p*, and *d* shells, respectively. The terms $J_{1\to1}$ and $J_{1\to3}$ for *np* pertain to the $np\to p$ and $np\to f$ excitations, respectively. The terms for *nd* pertain to the $nd\to s$, $nd\to d$, and $nd\to g$ waves. Equation (101) gives α_q in units $a_{\mathrm{H}}{}^5$ and must be multiplied by $0.529^5=0.0415$ to obtain α_q in units A^5.

For $1s\to d$, it is easily verified that if u'_0 is a hydrogenic wave function Eq. (82) has an exact solution which is given by

$$u'_{1,\,0\to2}=(Z^{-\frac{1}{2}}/2)r^3[1+\tfrac{2}{3}Zr]\exp(-Zr).\quad(102)$$

Upon inserting (17) and (102) into (84) one finds for both 1*s* electrons,

$$\alpha_q(1s\to d)=(30/Z^6)a_{\mathrm{H}}{}^5.\quad(103)$$

Thus for the hydrogen atom, $\alpha_q=15a_{\mathrm{H}}{}^5=0.622$A^5.

In order to obtain values of α_q for helium and the helium-like ions, the Löwdin[9] wave functions will again be used [Eq. (70)]. For the perturbation $u'_{1,\,0\to2}$ we will use an expression similar to Eq. (71) for the $1s\to p$ perturbation. In view of (102), $u'_{1,\,0\to2}$ will be taken as follows,

$$u'_{1,\,0\to2}=c_1\{(Z_1{}^{-\frac{1}{2}}/2)r^3[1+\tfrac{2}{3}Z_1r]\exp(-Z_1r)\}+c_2\{(Z_2{}^{-\frac{1}{2}}/2)r^3[1+\tfrac{2}{3}Z_2r]\exp(-Z_2r)\}.\quad(104)$$

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[20] R. M. Sternheimer, Phys. Rev. **95**, 736 (1954).

By inserting Eqs. (70) and (104) into (84) one obtains the values of α_q listed in Table III.

Besides the calculations for the helium-like ions, values of α_q were obtained for the cases of Na^+ and Cs^+ by numerical integration of Eq. (99). The results are listed in Table III. For Na^+, the contributions to $\alpha_q(=0.058A^5)$ are as follows: $0.013A^5$ from $2s\rightarrow d$, $0.020A^5$ from $2p\rightarrow p$, and $0.025A^5$ from $2p\rightarrow f$. The unperturbed functions u'_0 used in these calculations are the Hartree-Fock functions obtained by Fock and Petrashen.[12] As an illustration of the numerical procedure, in order to obtain the $2p\rightarrow p$ wave, $\langle r^2\rangle_{2p}$ is calculated from $u'_0(2p)$ and the resulting value $0.78a_H{}^2$ is inserted in Eq. (99) in which l and l' are taken as 1. $P(r_n)$ is obtained from the tabulated values of[12] u'_0 by means of (53), and $u'_{1,1\rightarrow 1}$ is calculated by outward integration by means of (55) in which

$$I(r)=u'_0(r^2-\langle r^2\rangle_{2p}).$$

After a function $u'_{1,1\rightarrow 1}$ is thus obtained, a suitable multiple of u'_0 is subtracted, so as to make the resulting function orthogonal to u'_0. From Eq. (103) the $1s\rightarrow d$ term for Na^+ is $0.0415\times(30/Z^6)\approx 0.8\times 10^{-6}A^5$ which is negligible.

For Cs^+ the wave functions obtained by Hartree[19] were used. The terms of $\alpha_q(=7.62A^5)$ are as follows: $0.90A^5$ for $5s\rightarrow d$, $1.56A^5$ for $5p\rightarrow p$, and $5.16A^5$ for $5p\rightarrow f$. The largest term is due to the $5p\rightarrow f$ waves, because the overlap of $5p$ with the $5p\rightarrow f$ function $u'_{1,1\rightarrow 3}$ is greatest for large values of r which in turn make large contributions to $J_{1\rightarrow 3}$ through the factor r^2 [see Eq. (100)]. The contribution of the inner shells is expected to be negligible because of the relatively small values of $\langle r^2\rangle_{nl}$ for these shells. This was verified by calculating the $4d\rightarrow g$ wave which gives one of the largest $n=4$ terms. The result was $\alpha_q(4d\rightarrow g)=0.019A^5$ which is negligible compared to the $n_0=5$ terms. Note that r^2 enters twice, namely in Eq. (99) for $u'_{1,l\rightarrow l'}$ and in the integral $J_{l\rightarrow l'}$. Since $\langle r^2\rangle_{nl}$ decreases rapidly as n is decreased, this explains why only the outermost shell contributes to α_q. The situation is similar to that for the dipole polarizability α. In fact, the relative contribution of the inner shells is even smaller for α_q than for α, because α_q depends essentially on $[\langle r^2\rangle_{nl}]^2$ as compared to the dependence of α on $\langle r^2\rangle_{nl}$.

TABLE III. Calculated values of the quadrupole polarizability (in units A^5).

Ion	α_q
H^-	71.1
He	0.101
Li^+	4.77×10^{-3}
Be^{++}	6.40×10^{-4}
B^{3+}	1.40×10^{-4}
C^{4+}	4.31×10^{-5}
Na^+	0.058
Cs^+	7.62

As was first shown by Mayer and Mayer,[2] the values of α_q enter into the term defect of the energy levels of the valence electron in the alkalis and the alkali-like atoms. The term defect ΔT is defined as the difference between the energy E of the level and the corresponding hydrogenic value which is $E_H=-R_AZ^2/n^2$, where R_A is the value of the Rydberg constant for the atom considered, Z is the net charge of the ion in whose field the valence electron moves, and n is the principal quantum number. Thus

$$\Delta T=E_H-E. \tag{105}$$

As is well known, ΔT has been interpreted by Born and Heisenberg[1] as due to the dipole moment induced in the electron core by the series electron. However, as pointed out by Mayer and Mayer,[2] the induced quadrupole moment makes an additional contribution to ΔT. The dipole part ΔT_d of ΔT is given by $\alpha\langle r^{-4}\rangle$ Rydberg, where α is the polarizability in units $a_H{}^3$ and $\langle r^{-4}\rangle$ is the average value of r^{-4} over the valence wave function, where r is in units a_H. The quadrupole part ΔT_q of ΔT is obtained in the same manner as[1,2] ΔT_d. For the following derivation we assume that all lengths are in cm. When the valence electron is at a distance r, the electric field gradient at the nucleus is $2e/r^3$, and hence the induced quadrupole moment is given by

$$Q_{\rm ind}=2\alpha_q/r^3. \tag{106}$$

$Q_{\rm ind}$ gives rise to the following potential at the position of the valence electron,

$$\bar{V}_q=Q_{\rm ind}e/(2r^3). \tag{107}$$

The resulting field is given by

$$E_q=-\partial\bar{V}_q/\partial r=3Q_{\rm ind}e/(2r^4)=3\alpha_q e/r^7, \tag{108}$$

where the last equality follows from (106). From (108) one obtains for the potential due to E_q,

$$\delta V_q=e\int_r^\infty E_q dr'=-\alpha_q e^2/(2r^6). \tag{109}$$

Hence δV_q equals $-\alpha_q/r^6$ rydbergs, if α_q and r are units $a_H{}^5$ and a_H, respectively. Thus

$$\Delta T_q=\alpha_q\langle r^{-6}\rangle R_A, \tag{110}$$

where $\langle r^{-6}\rangle$ is the average of r^{-6} over the valence wave function.

It was shown by Mayer and Mayer[2] that the observed ΔT includes, besides ΔT_d and ΔT_q, a term $\Delta T_{\rm pen}$ which is due to the penetration of the core by the series electron. The zero-order (spherical) part of the potential is larger than $2Z/r$ when the series electron is inside the core. $\Delta T_{\rm pen}$ has been calculated by Mayer and Mayer.[2] Thus we have

$$\Delta T-\Delta T_{\rm pen}=R_A[\alpha\langle r^{-4}\rangle+\alpha_q\langle r^{-6}\rangle]. \tag{111}$$

Mayer and Mayer[2] have made a study of the term defects by means of Eq. (111) in order to obtain values of α. In this treatment, they used estimates of α_q based on an expansion of the quadrupole perturbation of the core in terms of eigenfunctions of the unperturbed problem [similar to Eqs. (59)–(69) of Sec. III]. It was assumed that all of the excitations have the same energy denominator, so that the completeness properties of the eigenfunctions could be used. The expectation value of r^4 for the core electrons which enters into the resulting expression for α_q was not calculated directly, but was estimated from the values of $\langle r^2\rangle_{nl}$. The present values of α_q lead to a quadrupole term ΔT_q of the order of twice as large as that obtained by Mayer and Mayer.[2] It therefore seems worth while to repeat their calculations using the values of α_q of Table III. The discrepancy of the α_q is probably due in part to the approximations made by Mayer and Mayer.[2] On the other hand, the present values of α_q are subject to uncertainties, because α_q is rather sensitive to the zero-order wave functions, since it depends on the external part of the ion core through the factor r^2 in $J_{l\rightarrow l'}$. However, this reservation probably does not apply to the α_q for Be^{++}, B^{3+}, and C^{4+} because of the large binding of the $1s$ electrons for these ions.

Following Mayer and Mayer,[2] Eq. (111) will be written as follows,

$$\Delta T-\Delta T_{\mathrm{pen}}=R_A\alpha_0\langle r^{-4}\rangle=R_A\alpha C_q\langle r^{-4}\rangle, \tag{111a}$$

where α_0 and C_q are constants; in view of (111), C_q is given by

$$C_q=1+\alpha_q\langle r^{-6}\rangle/(\alpha\langle r^{-4}\rangle). \tag{112}$$

In order to calculate C_q, $\langle r^{-4}\rangle$ is obtained from the formula of Waller[21] and $\langle r^{-6}\rangle$ is obtained from the work of Van Vleck.[22] For convenience the values of $\langle r^{-6}\rangle/\langle r^{-4}\rangle$ will be listed here; they are $0.222Z^2$, $0.271Z^2$, $0.291Z^2$ for $3d$, $4d$, $5d$, respectively; and $0.0208Z^2$, $0.0267Z^2$, $0.0295Z^2$ for $4f$, $5f$, $6f$, respectively. As has been mentioned previously by several authors,[1] [2] $\langle r^{-6}\rangle/\langle r^{-4}\rangle$ and hence C_q-1 is approximately constant within a given series, but is considerably smaller for nf than for nd. For the p electrons $\langle r^{-6}\rangle$ diverges so that the present treatment is inapplicable.[2] C_q is obtained from the above $\langle r^{-6}\rangle/\langle r^{-4}\rangle$ together with values of α_q obtained from Table III and of α from Tables I and II. Note that α_q and α must be expressed in units $a_{\mathrm{H}}{}^5$ and $a_{\mathrm{H}}{}^3$, respectiively, for use in Eq. (112). The resulting values of C_q are listed in Table IV. The third column in this table lists the values of α_0 as obtained by Mayer and Mayer$_2$ from $\Delta T-\Delta T_{\mathrm{pen}}$. The last column gives the resulting dipole polarizability $\alpha=\alpha_0/C_q$. By comparing Table IV with the results of Mayer and Mayer,[2] it is seen that the present values of C_q are appreciably larger. As a result, the values of α of Table VI are about 10–20 percent smaller than those given in reference 2.

TABLE IV. Values of the polarizability α as obtained from spectral term defects. The second column gives the state of the valence electron in the field of the ion. The values of the constant α_0 were calculated by Mayer and Mayer.[2] C_q is the factor which corrects for the quadrupole polarizability. α and α_0 are in units A^3.

Ion	State	α_0	C_q	α
Li^+	$3d$	0.0258	1.12	0.0230
	$4d$	0.0273	1.14	0.0239
	$5d$	0.005	1.16	0.0043
Be^{++}	$3d$	0.00841	1.24	0.00678
	$4d$	0.00746	1.30	0.00574
	$5d$	0.00696	1.32	0.00527
B^{3+}	$3d$	0.00361	1.32	0.00273
	$4d$	0.00405	1.40	0.00289
	$5d$	0.00421	1.43	0.00294
C^{4+}	$3d$	0.00185	1.40	0.00132
	$4d$	0.00193	1.48	0.00130
	$5d$	0.00198	1.52	0.00130
Na^+	$3d$	0.184	1.32	0.139
	$4d$	0.192	1.39	0.138
	$5d$	0.194	1.42	0.137
Cs^+	$4f$	2.58	1.11	2.32
	$5f$	2.61	1.14	2.29
	$6f$	2.56	1.16	2.21

In Table IV, values are given only for the d series, except for Cs, where the d levels are too strongly penetrating so that the f series must be used to calculate α. The "best" values of α as obtained by averaging the values[23] of Table IV are (in units A^3):

$$\alpha(\mathrm{Li}^+)=0.0235,\quad \alpha(\mathrm{Be}^{++})=0.0059,\quad \alpha(\mathrm{B}^{3+})=0.0029,$$
$$\alpha(\mathrm{C}^{4+})=0.0013,\quad \alpha(\mathrm{Na}^+)=0.138,\quad \text{and}\quad \alpha(\mathrm{Cs}^+)=2.27.$$

It is of interest that all of these values are somewhat smaller than those calculated from the perturbed wave functions, as was expected from the discussion of Sec. III.

V. ELECTRIC FIELD AT THE NUCLEUS

It was pointed out by Foley[24] that the electric field at the nucleus of an ion in the presence of an external electric field is known and can therefore be used as an additional test of the perturbed wave functions u_1. Taking first the example of a neutral atom, the total electric field at the nucleus $\mathbf{E}_{\mathrm{tot}}(0)$ must be zero since the nucleus does not move. This means that the induced density must give rise to a field at the nucleus $\mathbf{E}_{\mathrm{ind}}(0)$ which just cancels the external field. In the present discussion it is assumed that the external field is weak enough so that it does not cause ionization; this, of course, is implied in the assumption that $u_1 \ll u_0$ so that first-order perturbation theory can be used. The external field will again be considered as due to a unit positive external charge $+e$ at a distance $X=R$ from the

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[21] I. Waller, Z. Phys. 38, 635 (1926).

[22] J. H. Van Vleck, Proc. Roy. Soc. (London) A143, 679 (1934). The values of $\langle 1/r^6\rangle$ for nd states as given in this paper are too large by a factor of 10.

[23] The $5d$ level of Li will be excluded because the Li nd series is strongly perturbed starting with $5d$, as can be seen from the fact that for $6d-9d$, $E_{\mathrm{H}}-E$ is negative, i.e., the valence electron is bound less strongly than for a hydrogenic level [see R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932), first edition, p. 265].

[24] Professor H. M. Foley (private communication).

nucleus. For an ion of net charge qe, $E_{\text{tot},X}(0)$ must be $-qe/(ZR^2)$ since the force on the nucleus in the X direction is $-qe^2/R^2$. Thus the field due to the induced density is given by

$$E_{\text{ind},X}(0)=-\frac{qe}{ZR^2}+\frac{e}{R^2}=\frac{e}{R^2}\left(1-\frac{q}{Z}\right), \tag{113}$$

where the term e/R^2 in the first equality is minus the external field. By calculating $E_{\text{ind},X}(0)$ from the perturbed wave functions u_1 and comparing with Eq. (113) one obtains an additional check on the u_1. It may be noted that the preceding considerations can also be used for the total force on the electrons in the presence of an external field. Since the acceleration of the electrons is the same as that of the nucleus, the force must be smaller by a factor of order m/M, where m and M are the mass of the electron and of the proton, respectively.[25] In the present approximation this means that the total force on the electrons must be zero both for neutral atoms and ions, i.e., the force due to the induced distribution cancels the effect of the external field e/R^2.

If Eq. (113) is satisfied, then it follows that the total force F_X on the electrons is zero, so that the condition $F_X=0$ does not lead to a further test of the perturbed wave functions u_1. In order to prove this result, we note that $E_{\text{ind},X}(0)$ is given by

$$E_{\text{ind},X}(0)=e\int\rho_{\text{ind}}r^{-2}\cos\theta dV, \tag{114}$$

where ρ_{ind} is the electron density induced by the field e/R^2 of the external charge $+e$ at $X=R$. The force on the electrons F_X consists of two parts: (1) the force $F_{\text{ext},X}$ due to the external charge which is

$$F_{\text{ext},X}=(Z-q)e^2/R^2, \tag{115}$$

since there are $Z-q$ electrons; (2) the force $F_{\text{ind},X}$ due to the electric field of the nucleus acting on ρ_{ind}. Since the component of electric field along X is $Ze\cos\theta/r^2$, $F_{\text{ind},X}$ is given by

$$F_{\text{ind},X}=-Ze^2\int\rho_{\text{ind}}r^{-2}\cos\theta dV=-ZeE_{\text{ind},X}(0), \tag{116}$$

where the last equality follows from Eq. (114). Thus in order that $F_X=0$, we must have

$$F_{\text{ext},X}+F_{\text{ind},X}=-Ze\left[E_{\text{ind},X}(0)-\left(1-\frac{q}{Z}\right)\frac{e}{R^2}\right]=0, \tag{117}$$

which leads to the condition of Eq. (113) for $E_{\text{ind},X}(0)$.

In order to obtain an expression for $E_{\text{ind},X}(0)$ in terms of the u_0 and u_1, we note that the induced dipole moment is given by

$$\alpha e/R^2=e\int\rho_{\text{ind}}r\cos\theta dV. \tag{118}$$

Since (114) and (118) involve the same angular factor, the integration over θ and φ, and the summation over the magnetic substates give the same coefficients as for α, and hence $E_{\text{ind},X}(0)$ is given by the following expression similar to Eqs. (50) and (51),

$$\begin{aligned}E_{\text{ind},X}(0)=\frac{e}{R^2}\Bigg\{&\sum_n\left(\frac{8}{3}K_{0\to1}\right)_{ns}\\&+\sum_n\left(\frac{8}{3}K_{1\to0}+\frac{16}{3}K_{1\to2}\right)_{np}\\&+\sum_n\left(\frac{16}{3}K_{2\to1}+8K_{2\to3}\right)_{nd}\\&+\sum_n\left(8K_{3\to2}+\frac{32}{3}K_{3\to4}\right)_{nf}\Bigg\},\end{aligned} \tag{119}$$

where $K_{l\to l'}$ is defined by

$$K_{l\to l'}\equiv\int_0^\infty u'_0u'_{1,l\to l'}r^{-2}dr. \tag{120}$$

The sums of Eq. (119) extend over the filled s, p, d, and f shells. Before proceeding to the calculations for the helium-like ions by means of the Löwdin wave functions, we note the result of Eq. (119) for the $1s$ electrons when the hydrogenic wave functions of Eqs. (17) and (18) are used. If one considers an ion with a single $1s$ electron (e.g., He$^+$, Li^{++}, etc.) one obtains for the field due to ρ_{ind} by substituting (17) and (18) into (119):

$$E_{\text{ind},X}(0)=(4/3)(e/R^2)K_{0\to1}=e/(ZR^2). \tag{121}$$

This agrees with Eq. (113) since $q=Z-1$ when only one $1s$ electron is present.

In obtaining $E_{\text{ind},X}(0)$ for the helium-like ions using the Löwdin[9] wave functions, $K_{0\to1}$ [Eq. (120)] was evaluated using Eq. (70) for u'_0 and Eq. (71) for $u'_{1,0\to1}$. The results are given in the second column of Table V. The values listed are $E_{\text{ind},X}(0)/(e/R^2)$ which will be denoted by $\bar{E}_{\text{ind},X}(0)$. Thus $\bar{E}_{\text{ind},X}(0)$ was calculated from

$$\bar{E}_{\text{ind},X}(0)=(8/3)\int_0^\infty u'_0u'_{1,0\to1}r^{-2}dr. \tag{119a}$$

The third column gives the actual values of $\bar{E}_{\text{ind},X}(0)$, i.e., $1-q/Z$ [see Eq. (113)]. The fourth column gives the ratio ρ of the calculated to the actual values. It is seen that ρ is always larger than 1, as was expected from the similar result for the polarizability α. Thus since the calculated wave functions give too little

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[25] If the mass of the electrons is not neglected, $-qe/ZR^2$ in Eq. (113) is replaced by $-(qe/ZR^2)(1-M_e/M_i)$, where M_e=mass of all electrons and M_i=mass of ion. The force on the electrons is then $F_X=-(qe^2/R^2)(M_e/M_i)$.

binding, they are expected to give values for the induced density which are too large, and hence an overestimate of $\bar{E}_{\text{ind},X}(0)$. ρ decreases with increasing state of ionization in passing from H^- to C^{4+}. This result can be explained as follows. As the field due to the nucleus becomes relatively more important in comparison with the repulsion between the electrons, the wave function becomes less sensitive to small inaccuracies of the binding, and hence the calculated $E_{\text{ind},X}(0)$ should become closer to the actual value.

Besides the calculations for the helium-like ions, $E_{\text{ind},X}(0)$ was also calculated numerically from the perturbed wave functions $u'_{1,l\rightarrow l'}$ for the cases of F^-, Na^+ and Al^{3+}. The integrals involved in (120) were carried out numerically, using the functions $u'_{1,l\rightarrow l'}$ obtained in Sec. III. However, the $2p\rightarrow d$ wave functions $u'_{1,1\rightarrow 2}$ for Na^+ and Al^{3+} were recalculated by outward integration starting with a power series near $r=0$, so that accurate values could be obtained near the nucleus which is the region of importance for $E_{\text{ind},X}(0)$, because of the $1/r^2$ factor in $K_{1\rightarrow 2}$. This recalculation was necessary because the function $u'_{1,1\rightarrow 2}$ determined in Sec. III for the calculation of α was obtained by inward integration starting from a large r. This procedure does not give reliable values of $u'_{1,1\rightarrow 2}$ near the nucleus. For F^-, the function $u'_{1,1\rightarrow 2}$ determined in Sec. III to calculate α had been obtained by outward integration from the nucleus so that a recalculation was not necessary. The resulting values of $\bar{E}_{\text{ind},X}(0)$ are listed in Table V. The contributions to $\bar{E}_{\text{ind},X}(0)$ from $1s\rightarrow p$, $2s\rightarrow p$, $2p\rightarrow s$, and $2p\rightarrow d$ are as follows for F^-: 0.23, 1.42, -1.29, and 1.91, respectively. For Na^+ the contributions in the same order are: 0.19, 1.06, -0.95, and 1.05. For Al^{3+} the corresponding terms are 0.16, 0.82, -0.74, and 0.80. We note that for the $1s$ shells a numerical calculation was not carried out, since the term of $\bar{E}_{\text{ind},X}(0)$ is given to a good approximation by $2/Z_{\text{eff}}$ [see Eq. (121)] where Z_{eff} is an effective Z obtained by subtracting from the atomic number a correction for shielding of 0.30 as obtained from Slater's[26] screening constants. We note that the $2s\rightarrow p$ and $2p\rightarrow s$ terms nearly cancel each other, as was expected in view of the behavior of the wave functions $u'_{1,0\rightarrow 1}$ and $u'_{1,1\rightarrow 0}$ and of the corresponding terms for α. The values of ρ again decrease with increasing binding in going from F^- to Al^{3+}. The large value of ρ for F^- arises for the same reason as the similar discrepancy for α (see Table I), namely the use of Hartree wave functions (without exchange) which give considerably too little binding for $2p$. We note, however, that the discrepancy $\rho=2.05$ is less than the corresponding discrepancy for α, presumably because the wave functions are less sensitive to binding near $r=0$ than in the region of large r which is of importance for α.

The values of ρ are of interest in connection with previous calculations of the electric field gradient at the nucleus due to the charge distribution induced in the core by an external charge or valence electron.[11,20] This effect is of importance in the determination of nuclear quadrupole moments, since it enters into the nuclear quadrupole coupling q. An estimate of the reliability of this calculated correction Δq to q can be obtained from the accuracy of $E_{\text{ind},X}(0)$, i.e., from the values of ρ. The calculation of $E_{\text{ind},X}(0)$ should be better suited for this estimate than the calculated α, since the integrand of $K_{l\rightarrow l'}$ for $E_{\text{ind},X}(0)$ has a factor $1/r^2$ and involves therefore the region near the nucleus in a manner similar to Δq [$=\Delta(\partial E_X/\partial X)$, see Eq. (97)] which involves $1/r^3$, and in contrast to α for which the integrand of $I_{l\rightarrow l'}$ has a factor r and depends essentially on the behavior of the wave functions at large r. We may conclude that the calculated Δq is probably overestimated by ~10–50 percent, except possibly for negative ions, where the overestimate may be larger if the calculations are based on Hartree wave functions (without exchange). This estimate of the accuracy of Δq is actually not very different from that which would have been obtained from a comparison of the calculated values of α with the experimental values. However, it should be noted that the values of the overestimate given above neglect two differences between Δq and $E_{\text{ind},X}(0)$. $E_{\text{ind},X}(0)$ was calculated for the field of an external charge, whereas Δq is determined by the field of the valence electron which penetrates the core during an appreciable part of the time. This fact reduces Δq considerably and may tend to make the error for Δq smaller than that for $E_{\text{ind},X}(0)$ since the region near the nucleus (which is insensitive to binding) becomes more emphasized. The second difference is that Δq involves a different perturbation than $E_{\text{ind},X}(0)$, namely a perturbation in which l changes by 0 or 2 units, whereas $E_{\text{ind},X}(0)$ involves $\Delta l=\pm 1$. The perturbation which gives rise to $E_{\text{ind},X}(0)$ is probably more related to the modes of excitation with $\Delta l=\pm 2$ (shielding modes) for Δq than to those with $\Delta l=0$ (radial or antishielding modes).[20]

TABLE V. Values of the field at the nucleus due to the induced charge distribution. $\bar{E}_{\text{ind},X}(0)$ is the induced field (in units of e/R^2) as obtained from wave function calculations. $1-q/Z$ is the actual value of $\bar{E}_{\text{ind},X}(0)$, and ρ is the ratio of the calculated to the actual value.

Ion	$\bar{E}_{\text{ind},X}(0)$	$1-q/Z$	ρ
H^-	3.81	2	1.91
He	1.32	1	1.32
Li^+	0.792	0.667	1.19
Be^{++}	0.566	0.5	1.13
B^{3+}	0.441	0.4	1.10
C^{4+}	0.361	0.333	1.08
F^-	2.27	1.11	2.05
Na^+	1.35	0.909	1.49
Al^{3+}	1.04	0.769	1.35

It seems of interest to calculate $E_{\text{ind},X}(0)$ from the Thomas-Fermi model, in order to compare with the wave function results. The calculation follows the same

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[26] J. C. Slater, Phys. Rev. **36**, 57 (1930).

lines as the Thomas-Fermi calculation[27] of Δq. The momentum p of an electron in the presence of an external charge $+e$ at $X=R$ is given by

$$\frac{p^2}{2m}=\frac{Z\chi e^2}{r}+\frac{e^2 r\cos\theta}{R^2}, \tag{122}$$

where χ is the Thomas-Fermi function. If p_0 denotes the momentum in the absence of the external charge, and $\Delta p=p-p_0$, we have

$$p_0\Delta p=me^2 r\cos\theta/R^2, \tag{123}$$

$$p_0=(2mZ\chi e^2/r)^{\frac{1}{2}}. \tag{124}$$

The change of density $\Delta\rho$ corresponding to Δp is given by

$$\Delta\rho=8\pi p_0^2\Delta p/h^3. \tag{125}$$

The field at the nucleus produced by $\Delta\rho$ is

$$E_{\mathrm{ind},\,X}(0)=2\pi e\int_0^\infty\int_0^\pi \Delta\rho\cos\theta dr\sin\theta d\theta. \tag{126}$$

Upon inserting Eqs. (123), (124), and (125) into (126) and integrating over θ one obtains

$$E_{\mathrm{ind},\,X}(0)=\frac{e}{R^2}\left[\frac{32\pi^2 2^{\frac{1}{2}}m^{\frac{3}{2}}Z^{\frac{1}{3}}e^3}{3h^3}\int_0^\infty(\chi r)^{\frac{1}{2}}dr\right]. \tag{127}$$

Upon using the Thomas-Fermi variable

$$x=2Z^{\frac{1}{3}}r(3\pi/4)^{-\frac{2}{3}}a_{\mathrm{H}}^{-1},$$

one finds

$$E_{\mathrm{ind},\,X}(0)=(e/2R^2)\int_0^\infty(\chi x)^{\frac{1}{2}}dx. \tag{128}$$

The integral over $(\chi x)^{\frac{1}{2}}$ diverges logarithmically at the upper limit, because χ falls off only as $1/x^3$ for large x, instead of exponentially, as required by the wave functions. This result is associated with the inadequacy of the statistical model for large x. Thus we can conclude that the Thomas-Fermi model (without exchange) cannot be used to discuss the distribution induced by an external charge.[28]

In contrast to the function χ, the Thomas-Fermi-Dirac potential χ_{exch} which includes exchange vanishes for large x. Since the difficulties encountered above are associated with this region, it appears possible that the Thomas-Fermi-Dirac potential will give reasonable results for $E_{\mathrm{ind},\,X}(0)$. A derivation of $E_{\mathrm{ind},\,X}(0)$ using the potential χ_{exch} will now be given.

The maximum momentum p_0 in the Thomas-Fermi-Dirac model is determined by[29]

$$\frac{p_0^2}{2m}-\frac{2e^2p_0}{h}+e(E_0-V_0)=0, \tag{129}$$

where E_0 is the maximum energy of the electrons, and V_0 is the electrostatic potential; the second term $-2e^2p_0/h$ takes into account the exchange. If V_0 is varied by an amount

$$\Delta V=er\cos\theta/R^2, \tag{130}$$

the resulting change of p_0 called Δp is determined by

$$\frac{p_0\Delta p}{m}-\frac{2e^2\Delta p}{h}-e\Delta V=0, \tag{131}$$

which gives

$$\Delta p=e\Delta V\Big/\left(\frac{p_0}{m}-\frac{2e^2}{h}\right). \tag{132}$$

The solution of Eq. (129) for p_0 is given by[29]

$$p_0=\frac{2e^2m}{h}+\left[\frac{4e^4m^2}{h^2}+2em(V_0-E_0)\right]^{\frac{1}{2}}. \tag{133}$$

The change of the density $\Delta\rho$ is again given by Eq. (125). Upon using the definition of χ_{exch} given by Slater and Krutter,[29]

$$Z\chi_{\mathrm{exch}}e/r=V_0-E_0+2me^3/h^2, \tag{134}$$

p_0 can be written as follows,

$$p_0=4(4\pi^2/3)^{\frac{1}{3}}me^2h^{-1}[\epsilon+(\chi_{\mathrm{exch}}/x)^{\frac{1}{2}}], \tag{135}$$

where $\epsilon=0.2118Z^{-\frac{2}{3}}$ and x is the Thomas-Fermi variable defined after Eq. (127). We also have

$$\frac{p_0}{m}-\frac{2e^2}{h}=\frac{me^2}{h}\left(\frac{\chi_{\mathrm{exch}}}{x}\right)^{\frac{1}{2}}. \tag{136}$$

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[27] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950).

[28] The same integral over $(\chi x)^{\frac{1}{2}}$ also occurs in the expression for the quadrupole moment induced by the nuclear quadrupole moment Q. The total induced quadrupole moment is given by

$$Q_{\mathrm{ind},\,QT}=(3/10)Q\int_0^\infty(\chi x)^{\frac{1}{2}}dx, \tag{128a}$$

and its sign is such as to shield the nuclear Q. [Note that the factor 0.2998 in Eq. (8) of reference 27 should be 3/10.] The divergence of the integral for large x does not affect the calculation of Δq for atomic ground states since Δq depends only on the values of $(\chi x)^{\frac{1}{2}}$ near the nucleus [see reference 20 and discussion at the end of this section]. From Eq. (128a) one can also conclude that the electric field gradient at the nucleus produced by an external charge is changed by an amount

$$\Delta\left(\frac{\partial Ex}{\partial x}\right)=\frac{2e}{R^3}\left[\frac{3}{10}\int_0^\infty(\chi x)^{\frac{1}{2}}dx\right], \tag{128b}$$

due to the perturbation of the core by the external change [R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953)]. Thus the Thomas-Fermi model is inadequate both for the electric field and the electric field gradient at the nucleus due to an external charge.

[29] J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935).

The rest of the derivation is identical with that given in Eqs. (126)–(129) for the Thomas-Fermi model. From Eqs. (132), (135), and (136), one obtains

$$E_{\mathrm{ind},X}(0)=(e/2R^2)\int_0^{x_0}[\epsilon+(\chi_{\mathrm{exch}}/x)^{\frac{1}{2}}]^2 \times(\chi_{\mathrm{exch}}/x)^{-\frac{1}{2}}x\,dx, \qquad (137)$$

where x_0 is the value of x beyond which $\chi_{\mathrm{exch}}=0$. Equation (137) differs from (128) only through the replacement of χ by χ_{exch} and the presence of ϵ.

Values of χ_{exch} throughout the range of Z have been obtained by Metropolis and Reitz.[30] We have carried out calculations of $E_{\mathrm{ind},X}(0)$ using the tabulated χ_{exch} for $Z=18$ and 57, to correspond approximately to the cases of Cl and Cs, respectively. For each value of Z, Metropolis and Reitz[30] have calculated several functions χ_{exch} which are obtained by using different slopes at $x=0$ and lead to different values of x_0. Solutions with a relatively large downward slope at $x=0$ become zero at a finite $x=x_0$ and correspond to positive ions. Solutions with a less negative slope at $x=0$ go through a minimum at large x and correspond to neutral atoms; they are cut off at the value of $x=x_0$ for which

$$\left(\frac{d\chi_{\mathrm{exch}}}{dx}\right)_{x=x_0}=\left(\frac{\chi_{\mathrm{exch}}}{x}\right)_{x=x_0}.$$

Equation (137) was evaluated for nine cases. The results are given in Table VI. The first two columns list the value of Z and the number labeling the function χ_{exch} as given by Metropolis and Reitz[30] (e.g., $Z=18$, 1 is "case 1" for $Z=18$ in their paper). The third column lists the values of x_0; the unit of x is $0.338a_{\mathrm{H}}$ for $Z=18$ and $0.230a_{\mathrm{H}}$ for $Z=57$. The fourth column gives the net charge $Z_i(=q)$ of the ion if the solution is ionic; the other cases where no value is listed correspond to neutral atoms of various radii. The next column gives $\bar{E}_{\mathrm{ind},X}(0)$ which is one-half the integral of Eq. (137), while the last column lists the values of $\bar{E}_{\mathrm{ind},X}(0)/x_0$. It may be noted that for ionic solutions where χ_{exch} becomes zero at x_0, the integrand of (137) has a singularity at $x=x_0$. However, since the integrand goes as $(x_0-x)^{-\frac{1}{2}}$ near x_0, the integral is finite, and in fact, the region near x_0 makes only a very small contribution.

TABLE VI. Values of $\bar{E}_{\mathrm{ind},X}(0)$ from the Thomas-Fermi-Dirac model.

Z	Case	x_0	Z_i	$\bar{E}_{\mathrm{ind},X}(0)$	$\bar{E}_{\mathrm{ind},X}(0)/x_0$
18	1	6.00	3.047	2.19	0.365
18	2	9.20	0.976	3.99	0.434
18	3	7.25		2.98	0.411
18	4	6.66		2.73	0.409
18	5	5.46		2.22	0.406
57	1	5.17	14.80	1.59	0.306
57	3	12.80	2.303	4.41	0.345
57	4	9.66		3.50	0.362
57	7	3.81		1.47	0.385

It is seen that the calculated $\bar{E}_{\mathrm{ind},X}(0)$ are considerably too large, since the actual value is 1 for neutral atoms and $1-Z_i/Z$ for ions [see Eq. (113)]. Except for $Z=57$, case 7, the disagreement is by a factor larger than 2 with values ranging up to 4.6 for $Z=57$, case 3. These values of ρ may be compared with those obtained from the wave function calculations (see Table V) which are generally in the range 1–1.5. It may be noted that the values of $\bar{E}_{\mathrm{ind},X}(0)/x_0$ are nearly constant. Thus the Thomas-Fermi-Dirac values of $\bar{E}_{\mathrm{ind},X}(0)$ depend primarily on the radius x_0. For ions the general decrease of $\bar{E}_{\mathrm{ind},X}(0)$ with increasing Z_i and decreasing x_0 is in the right direction, but the values of $\bar{E}_{\mathrm{ind},X}(0)$ for the small Z_i of interest are too large. For neutral atoms one could obtain a value of $\bar{E}_{\mathrm{ind},X}(0)$ close to 1 by assuming a small value for the radius x_0. However, as is shown by the example of $Z=57$, case 7, the required x_0 would be unreasonably small, since $x_0=3.81$ for $Z=57$, case 7, corresponds to a radius of $3.81\times0.230=0.88a_{\mathrm{H}}$, which is considerably smaller than the radius of the outermost maximum of the $5p$ distribution which occurs at $r=1.9a_{\mathrm{H}}$.

It should be emphasized that the preceding discussion of the inadequacy of the statistical model for the field at the nucleus produced by an external charge does not apply to the correction Δq to the quadrupole coupling for atomic states. Δq can be regarded as due to the interaction of the valence electron with the quadrupole moment $Q_{\mathrm{ind},Q}$ induced in the core by the nuclear Q. The Thomas-Fermi expression for the density of induced moment is[27,28]

$$Q_{\mathrm{ind},Q}dr=(3/10)Q(\chi x)^{\frac{1}{2}}(x/r)dr. \qquad (138)$$

For the atomic ground states and first excited states the statistical model can be used to calculate the shielding because the result depends only on the values of $(\chi x)^{\frac{1}{2}}$ near the nucleus, by virtue of the penetration of the valence electron. Thus in the expression[27] for Δq, $(\chi x)^{\frac{1}{2}}$ is essentially multiplied by v^2, where v is r times the valence wave function. As a result of the exponential decrease of v^2 at large r, the contribution of this region to Δq becomes negligible. As was shown in reference 20, the Thomas-Fermi values of Δq divided by 1.5 give a good estimate of the contribution of the shielding modes of excitation of the core to the quadrupole coupling. The factor 1.5 by which the Thomas-Fermi model overestimates these shielding terms arises primarily because $Q_{\mathrm{ind},Q}$ is too large near the nucleus.

In the same manner as in the derivation of (137), one can show that the density of induced moment according to the Thomas-Fermi-Dirac model is given by

$$Q_{\mathrm{ind},Q}dr=(3/10)Q\{[\epsilon+(\chi_{\mathrm{exch}}/x)^{\frac{1}{2}}]^2 \times(\chi_{\mathrm{exch}}/x)^{-\frac{1}{2}}x\}(x/r)dr. \qquad (139)$$

The previous calculations[20] of Δq from the statistical

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[30] N. Metropolis and J. R. Reitz, J. Chem. Phys. **19**, 555 (1951).

model were carried out using the Thomas-Fermi expression (138). However, the values given by (139) differ from (138) by less than 12 percent (for $Z \geqq 18$) in the region of importance near the nucleus (i.e., for $x \lesssim 2$). Thus at $x=2$, the curly bracket of (139) which replaces $(\chi x)^{\frac{1}{2}}$ in Eq. (138) has the value 0.779 for $Z=18$ and 0.732 for $Z=57$, as compared to $(\chi x)^{\frac{1}{2}}=0.698$. These differences are even smaller for $x<2$ and vanish as $x \to 0$. Hence the previous conclusions[20] about the Thomas-Fermi values of Δq are essentially unaffected by the inclusion of exchange in the statistical model.

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Rotational Spectra of RbCl by the Molecular Beam Electric Resonance Method*

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The rotational transitions for which $J=0\to 1$ were studied by the molecular beam electric resonance method for the first three vibrational states, $v=0$, 1, 2, of $Rb^{85}Cl^{35}$ and the ground vibrational state, $v=0$, of $Rb^{87}Cl^{35}$. The molecular constants are:

	$Rb^{85}Cl^{35}$	$Rb^{87}Cl^{35}$
Y_{01} (Mc/sec)	2627.394 ±0.002	2609.779±0.003
$-Y_{11}\approx\alpha_e$ (Mc/sec)	13.601 ±0.005	13.464±0.005
$Y_{21}\approx\gamma_e$ (Mc/sec)	0.021 ±0.002	0.021±0.002
B_e (Mc/sec)	2627.414 ±0.010	
r_e (A)	2.78670±0.00006	

The quadrupole (eqQ) and spin-rotation (c) interaction constants of $Rb^{85}Cl^{35}$ are:

	$v=0$	$v=1$	$v=2$
$(eqQ)_{Rb}$ (Mc/sec)	−52.675±0.005	−52.306±0.030	−51.903±0.040
$(eqQ)_{Cl}$ (Mc/sec)	+ 0.774±0.009	+ 0.612±0.013	+ 0.470±0.017
c_{Rb} (kc/sec)	+ 0.3 ±0.3		
c_{Cl} (kc/sec)	0.0 ±0.8		

For the $v=0$ state of $Rb^{87}Cl^{35}$, $(eqQ)_{Rb}=-25.485\pm0.006$ Mc/sec. The ratio of the Rb quadrupole moments is $Q_{85}/Q_{87}=2.0669\pm0.0005$. The mass ratio of the Rb isotopes is $M_{85}/M_{87}=0.9770163\pm0.0000045$.

I. INTRODUCTION

THROUGH their studies of KCl and KBr Carlson, Fabricand, Lee, and Rabi[1,2] initiated an investigation by the molecular beam electric resonance method[1,3] of the rotational spectra of the alkali halide molecules in their ground $^1\Sigma$ electronic states. We have continued this work by studying the $J=0\to 1$ transitions of $Rb^{85}Cl^{35}$ in its three lowest vibrational states and of $Rb^{87}Cl^{35}$ in its ground vibrational state.

We selected RbCl in order to clarify further the nature of the Cl quadrupole interaction which shows unusual variations with vibration in KCl.[2] Also, at the outset of our work, the mass ratio of the Rb isotopes had not been determined with the accuracy made possible by the electric resonance method. Since then Honig, Mandel, and Townes, using microwave absorption measurements of the rotational spectra of RbBr and RbI, have obtained this mass ratio with an accuracy equal to ours,[4] while Collins, Johnson, and Nier have made mass spectrometric measurements which give a mass ratio of much greater accuracy.[5]

The hyperfine structure of the spectra yielded the Rb and Cl quadrupole and spin-rotation interaction constants, the ratio of the quadrupole moments of the Rb isotopes and the frequencies of the unperturbed rotational lines. The last-named frequencies gave the first three rotational constants of the molecules, the equilibrium internuclear distance and the mass ratio of the Rb isotopes. Of the above quantities the following have been measured by other methods: the magnitudes of the quadrupole and spin-rotation interactions of Rb^{87} in $Rb^{87}Cl$,[6] the ratio of the quadrupole moments of the Rb isotopes,[7] the internuclear distance,[8] and the mass ratio of the Rb isotopes.[4,5] These constants, with the

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