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STATISTICAL THEORY OF THE POLARIZABILITY OF ATOMS AND IONS

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It is shown that the potential and electron density distribution inside an atom or ion placed in a uniform electric field satisfy the equation obtained by linearizing the Thomas-Fermi equation. A universal dependence of the polarizability of atoms and ions on their radius is constructed with the aid of the numerical solution of this equation. The results of the computation is in good agreement with the available experimental data on the polarizability of atoms and ions with closed shells.

THE statistical Thomas-Fermi model has been used to compute the dipole and quadrupole polarizabilities of atoms and ions in[1-3]. However, the authors of these papers made a number of assumptions not related to the basic theses of the statistical model. The object of the present paper is to determine the polarizing potential and the polarizability of an atom, remaining within the framework of statistical theory and without recourse to further approximations. The equation for the statistical polarizing potential is derived in Sec. 1. In Sec. 2 an analytical expression is obtained for the polarizability of highly charged ions. In Sec. 3 the results of numerical computations of the polarizability of atoms and ions are compared with the available experimental data.

1. EQUATION FOR THE POLARIZING POTENTIAL

In the statistical Thomas-Fermi model atomic electrons are considered as a degenerate Fermi gas in the Coulomb field of the atomic nucleus (see, for example,[4]). The potential of the electric field inside the atom satisfies the Poisson equation[1)]

$$\Delta\varphi(\mathbf{r}) = (4/3\pi)p^3(\mathbf{r}), \tag{1}$$

where $p(\mathbf{r})$ is the Fermi momentum, which is determined from the condition of constancy of the Fermi energy $\mathscr{E}$ inside the atom

$$\tfrac{1}{2}p^2(\mathbf{r}) - \varphi(\mathbf{r}) = \mathscr{E}. \tag{2}$$

Equations (1) and (2) describe both an isolated atom and an atom in an external field.

To the isolated atom corresponds the spherically symmetric solution $\varphi(r)$ of Eqs. (1) and (2). The Fermi energy is then equal to the potential of the atom at the boundary: $\mathscr{E} = -(Z-N)/r_0$, and $\varphi(r)$ satisfies the following boundary conditions:

$$\varphi(r)\big|_{r\to 0} \sim \frac{Z}{r}, \quad \varphi(r)\big|_{r=r_0} = \frac{Z-N}{r_0}, \quad \frac{d\varphi}{dr}\bigg|_{r=r_0} = -\frac{Z-N}{r_0^2}, \tag{3}$$

where Z is the charge of the nucleus, N is the number of electrons, and r_0 is the radius of the atom[2)].

Let the atom be now placed in a uniform external electric field **E**. If the field is sufficiently weak, then the potential of the isolated atom $\varphi_0(r)$ changes by a small amount $\varphi_1(\mathbf{r})$. It is clear that the electron Fermi energy does not change to within quantities of the order of E^2. Therefore, setting $\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) + \varphi_1(\mathbf{r})$ and linearizing (1) and (2) with respect to $\varphi_1(\mathbf{r})$, we obtain for $\varphi_1(\mathbf{r})$ the equation

$$\Delta\varphi_1(\mathbf{r}) = \frac{4\sqrt{2}}{\pi}\left(\varphi_0(r) - \frac{Z-N}{r_0}\right)^{1/2}\varphi_1(\mathbf{r}), \quad r < r_0. \tag{4}$$

Outside the atom the potential $\varphi_1(\mathbf{r})$ is equal to the sum of the potentials of the external field and the atomic dipole induced by the field:

$$\varphi_1(\mathbf{r}) = -\mathbf{E}\mathbf{r} + \alpha\mathbf{E}\mathbf{r}/r^3, \quad r > r_0, \tag{5}$$

where α is the polarizability of the atom. To find $\varphi_1(\mathbf{r})$ and α, we must match at the boundary of the atom (at $r = r_0$) the solution of Eq. (4) which is finite at the origin with the potential (5) outside the atom. Performing the matching and taking account of the fact that $\varphi_1(\mathbf{r}) = \varphi_1(r)\cos\theta$ (where θ is the angle between the vectors **E** and **r**), we obtain

$$\alpha = r_0^3\frac{1 - a/r_0}{1 + 2a/r_0}, \quad a = \left[\frac{\varphi_1'(r)}{\varphi_1(r)}\bigg|_{r=r_0}\right]^{-1}. \tag{6}$$

It is convenient for what follows to introduce the reduced length x and the functions $\chi(x)$ and $u(x)$[4]:

$$r = xbZ^{-1/3}, \quad b = \tfrac{1}{2}(3\pi/4)^{2/3} \approx 0.8853,$$

$$\varphi_0(r) - \frac{Z-N}{r_0} = \frac{Z}{r}\chi(x), \quad \varphi_1(r) = u(x)r. \tag{7}$$

Substituting (7) in (1)–(4), we easily obtain the equations for $\chi(x)$ and $u(x)$:

$$\sqrt{x}\chi'' = \chi^{3/2}, \; \chi(0) = 1, \; \chi(x_0) = 0,$$

$$\chi'(x_0) = -(Z-N)/Zx_0, \; x_0 = r_0Z^{1/3}/b, \tag{8}$$

$$u'' + \frac{4}{x}u' - \frac{3}{2}\left(\frac{\chi}{x}\right)^{1/2}u = 0, \quad u(0) = 1. \tag{9}$$

Knowing the Thomas-Fermi potential $\chi(x)$, we can find from Eq. (9) the change in the intratomic potential $u(x)$ for an atom placed in an external field. The polarizability α is, according to (6) and (7), equal to

$$\alpha = b^3x_0^3\Big/Z\left[1 + \frac{3u(x_0)}{x_0u'(x_0)}\right]. \tag{10}$$

[1)] Atomic units are used in the paper.

[2)] The term "atom" will be used for both neutral atoms, Z = N, and positive ions, Z > N.

2. POLARIZABILITY OF HIGHLY CHARGED IONS

If the charge of an atom is sufficiently high ($Z \gg N$), then the intratomic potential is close to the Coulomb field of the nucleus. Under these conditions the radius r_0 of the ion can be determined by substituting $\varphi_0(r) \approx Z/r$ into the expression for the total number of electrons:

$$N = 4\pi \int_0^{r_0} n_0(r) r^2\, dr \approx \frac{4}{3\pi} \int_0^{r_0} \left[2\left(\frac{Z}{r} - \frac{Z}{r_0} \right) \right]^{3/2} r^2\, dr, \qquad (11)$$

where $n_0(r)$ is the electron density:

$$n_0(r) = p_0^3(r) / 3\pi^2. \qquad (12)$$

After simple rearrangements we find from (11)

$$r_0 = (3\sqrt{2}N)^{2/3} / Z. \qquad (13)$$

In a highly charged ion, the electrons attracted by the strong Coulomb field of the nucleus screen off slightly the external uniform field. Therefore, perturbation theory can be used to compute the polarizability. The change in the electron density $n_1(\mathbf{r})$ due to the field is, according to (2) and (12), equal to

$$n_1(\mathbf{r}) = \pi^{-2} p_0^2(r) p_1(\mathbf{r}) = \pi^{-2} p_0(r) \varphi_1(\mathbf{r}). \qquad (14)$$

Setting in the first approximation

$$\varphi_1(\mathbf{r}) \sim -\mathbf{Er}, \qquad p_0(r) \approx [2(Z/r - Z/r_0)]^{1/2}, \qquad (15)$$

we calculate with the aid of (14) the dipole moment $\mathbf{d} = \alpha\mathbf{E} = -\int n_1(\mathbf{r})\mathbf{r}d\mathbf{r}$ of the atom induced by the field. Whence, taking account of (13) and (15), we easily determine the polarizability

$$\alpha = \frac{1}{\pi^2} \int \left[2\left(\frac{Z}{r} - \frac{Z}{r_0} \right) \right]^{1/2} r^2 \cos^2\theta\, d\mathbf{r} = \frac{63}{16} \frac{N^3}{Z^4}. \qquad (16)$$

Thus, when $Z \gg N$ the polarizability of an ion in the Thomas-Fermi model decreases as Z^{-4}. The same dependence follows from quantum theory for ions with closed electron shells. If, however, the outer shell is not filled, then the main contribution to the polarizability ($\sim Z^{-3}$) is made by the excitation of a transition in which the principal quantum number is not changed[5].

The approximation (15) was also used in[2] to compute the quadrupole polarizability of atoms. Practically, this means that in the determination of the potential acting on an atomic electron in an external field, the polarizing influence of the rest of the electrons is neglected. In the general case, $\varphi_1(\mathbf{r})$ in (14) should be understood to be not the potential of the external field, but the solution of the self-consistent Eq. (4). This remark is especially important for neutral atoms and ions of low ionization multiplicity, when the radius r_0 is large and the interelectronic and electron-nucleus interactions are of the same order of magnitude. In the case of highly charged ions, on the other hand, the electrons are tightly bound to the atomic nucleus, their polarization distorts slightly the potential of the external field, and the approximation (15) can be used.

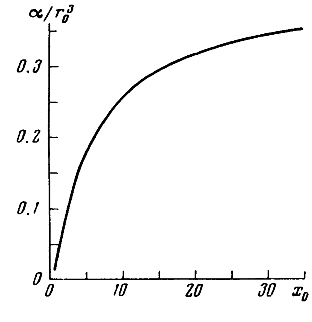
A somewhat different approximation was used in[1], where the change in the electron density in the external field was sought in the form $n_1(\mathbf{r}) = \lambda(\mathbf{E} \cdot \mathbf{r}) n_0^{1/3}$, and the parameter λ was found from a variational principle. For a more consistent and a more exact computation of the polarizability, Eq. (4) must be solved numerically.

3. NUMERICAL COMPUTATIONS AND COMPARISON WITH EXPERIMENT

The ratio $q = (Z - N)/Z$ is the only quantity that determines the properties of an atom in the statistical Thomas-Fermi model. By assigning q and solving Eqs. (8)–(10), we can determine in the framework of the Thomas-Fermi model the radius r_0 and the polarizability α for any atom or ion. However, such calculations yield a value for α that is 5–6 times higher than the experimental values. Such a discrepancy is not surprising. It is well known that the statistical theory describes satisfactorily the electron density distribution within the atom only when the exchange and quantum corrections are taken into account[1,6]. The corrections are especially important at large distances from the nucleus and, consequently, for the value of the radius r_0 of the ion. Since the polarizability is proportional to r_0^3, the effect of the corrections on the polarizability will obviously also be quite substantial.

The dependence of α/r_0^3 on x_0, constructed as a result of the numerical integration of Eq. (9), is shown in the figure. Knowing the reduced boundary radius x_0, we can determine the polarizability of any atom or ion with the aid of this curve. As the boundary radius x_0 we must use in such a calculation the values obtained in the Thomas-Fermi-Dirac model with allowance for the exchange correction (see, for example,[1]). Such a method allows us to phenomenologically take into account the change in the radius x_0 of the ion connected with the exchange effects. The results of the computation are compared in the table with available experimental data and the results of other theoretical investigations. In[8] the measurements of the polarizabilities were carried out in gases and aqueous salt solutions; in[9], in crystals. The results of the quantum-mechanical computations were taken from the review paper[7]. In the third column of the table are values obtained by a variational-statistical method in[1] (see Sec. 2). As can be seen in the table, the values of the polarizabilities computed in the present paper are in good agreement with the experimental data for all atoms and ions heavier than argon. In the case of the lighter, neon-like atoms and ions, the conditions of applicability of the Thomas-Fermi model are violated, and the best results are given by the quantum-mechanical calculations.

Besides the usual applications—the determination of the refractive index of gases and the constant of interaction of atoms with neutral and charged particles—knowledge of the polarizability is necessary for the computation of a number of other atomic characteristics. Thus, for example, it has been shown in[11-13] that, generally



Dependence of the quantity α/r_0^3 on the reduced radius x_0 of an atom or ion.

Polarizabilities α in units of Å^3 for atoms and ions with closed shells

Ion	Quantum-mechanical method [7]	Statistical method		Experiment	
		variational [1]	present work	gas [8]	crystal [9]
Ne	0.4	2.01	1.21	0.39	—
Na^+	0.145	0.850	0.55	0.20	0.26
Mg^{+2}	0.082	0.40	0.27	0.12	—
Al^{+3}	0.045	—	0.16	0.07	—
Si^{+4}	0.027	—	0.093	0.04	0.04
Ar	2.40	2.88	2.00	1.65	—
K^+	1.24	1.36	1.03	0.88	1.2
Ca^{+2}	0,73	0,72	0,56	0,54	—
Cu^+	0.98	—	1,60	—	1.6
Zn^{+2}	—	—	0.75	—	0.8
Kr	—	4.00	3,15	2.48	—
Rb^+	2,020*	2,14	1.76	1,56	1.8
Sr^{+2}	—	1.30	1.11	0.86	1.6
Xe	—	4,61	3.78	4.10	—
Cs^+	3,76 *	2.66	2.27	2.56	3.1
Ba^{+2}	—	1.70	1,51	1.68	2.5

*The values of α for Rb^+ and Cs^+ were taken from the more recent paper [10].

speaking, the polarization of an atomic core under the action of a photoelectron affects the transition probabilities in the discrete and continuous spectra. This effect is especially important for the principal series of the alkali atoms and alkali-like ions. In this connection future measurement of the polarizabilities of different atoms and ions and the comparison of them with the results of the statistical model will be of interest.

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