Variational Calculations of Dipole Polarizabilities of Helium-Like Ions*

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The dipole polarizabilities of a number of helium-like ions are calculated by a variational procedure, using the analytic ground state wave functions calculated for these ions by Green, Mulder, Lewis, and Woll. Our values agree well with those obtained by Sternheimer by a numerical solution of the first-order Schrödinger equation in the presence of an electric field. The basis for the convergence of our variational procedure is discussed along with its advantages and disadvantages relative to Sternheimer's procedure. Comparison is also made with experimental values of the polarizabilities. For helium, our value (0.218 A^3) is within 7% of the experimental value (0.204 A^3). For the ions Li$^+$, Be^{++}, B^{+++}, the agreement is only fair. The diamagnetic susceptibilities are also calculated in order to test the accuracy of the ground state wave functions. The agreement of our values here with the experimental ones is very good.

INTRODUCTION

DIPOLE polarizabilities of free atoms and ions have been determined by a variety of methods pertaining to the gaseous, liquid and solid states. A brief but adequate review of the various methods has been made recently by Sternheimer.[1] Tessman, Kahn, and Shockley[2] have obtained values of polarizabilities for a large number of ions in ionic crystals from refractive index data in solid state. Values of polarizabilities deduced from data on solid and liquid states cannot be considered as representative of free ions by virtue of the presence of water of hydration molecules around the ions in solution, and the possibility of some covalent binding between the cations and the anions in the ionic crystals. Theoretical values of the polarizabilities of the free ions are therefore best compared with the values obtained from spectroscopic term defect data. This procedure for estimating polarizabilities of ions was first proposed by Born and Heisenberg[3] and later used by Mayer and Mayer[4] for a number of ions. Sternheimer[1] has recently made a recalculation of the dipole polarizabilities of some of these ions taking into consideration the effects of the quadrupole polarizabilities of the ions.

Among the earlier theoretical procedures employed in the calculation of the polarizabilities is the variational procedure used by Hasse[5] and Atanasoff[6] for the helium atom. These authors used, for the ground state of the helium atom, a Hylleraas wave function $u_0(r_1,r_2,r_{12})$, where r_1 and r_2 are the distances of the two electrons from the nucleus and r_{12} is the interelectron distance.

They used perturbed wave functions of the form

$$u_0(r_1,r_2,r_{12})\{1+E[Z_1 f(r_1,r_2,r_{12})+Z_2 f(r_1,r_2,r_{12})]\},$$

where E is the applied field, Z_1 and Z_2 are effective charge parameters involved in the Hylleraas[7] wave functions and $f(r_1,r_2,r_{12})$ is an analytic expression involving parameters which are obtained by minimizing the perturbation energy to the second power in E. Atanasoff obtained a value of the polarizability within 5% of the experimental value by this method.

Sternheimer[1] has obtained the dipole polarizabilities (denoted henceforth by α_d) of the helium-like ions by solving the first-order Schrödinger equation involving the perturbation due to an electric field. For the ground state wave functions, he used analytic Löwdin functions which differ little from those of Green et al.[8] which we use. However, in his earlier work, in order to avoid excessive calculations, he made use of an approximation which briefly is the following. Since the Löwdin wave functions involve the sum of a number of hydrogenic terms, an analytic solution is no longer possible for the perturbed Schrödinger equation. Sternheimer assumed the solution of the perturbed equation to be the sum of the analytic solutions obtained by using separately the various hydrogenic terms in the ground state wave functions. Recently he has recalculated the polarizabilities without his earlier approximation, i.e., by solving the perturbed Schrödinger equation numerically. For Be^{++} and B^{+++}, he finds the value of α_d to be nearly the same by both procedures. For Li$^+$ the approximate method gives a result about 5% larger than the detailed numerical solution, while for He and H$^-$, the α_d are about 6% and 20% larger, respectively, than the values obtained by the numerical solution.

In our calculations we adopt a variational procedure which resembles that of Hasse,[5] Atanasoff,[6] and Buckingham[9] and is identical with the procedure employed recently by Bersohn[10] to calculate shielding (and

[1] R. M. Sternheimer, Phys. Rev. 96, 951 (1954); Sternheimer has informed us of his more recent calculations in a private communication.
[2] Tessman, Kahn, and Shockley, Phys. Rev. 92, 890 (1953).
[3] M. Born and W. Heisenberg, Z. Physik 23, 388 (1924).
[4] J. E. Mayer and M. G. Mayer, Phys. Rev. 43, 605 (1933).
[5] H. R. Hasse, Proc. Cambridge Phil. Soc. 26, 542 (1930); 27, 66 (1931).
[6] J. V. Atanasoff, Phys. Rev. 36, 1232 (1930).
[7] E. A. Hylleraas, Z. Physik 54, 347 (1929).
[8] Green, Mulder, Lewis, and Woll, Phys. Rev. 93, 757 (1954).
[9] R. A. Buckingham, Proc. Roy. Soc. (London) A160, 94 (1935).
[10] T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956); henceforth referred to as Paper I.

antishielding) of nuclear quadrupole moments of ions in crystals. Thus the perturbed wave function employed for each electron is taken to be of the form

$$u_0 + u_0 H_1(\alpha + \beta r + \gamma r^2),$$

where H_1 is the perturbation Hamiltonian for each electron in the electric field and r is the electron distance from the nucleus. The quantities α, β, γ are variation parameters obtained by minimizing the energy to the second power in the field. The motivation for these calculations was twofold. First, we wanted to test the convergence and accuracy of Bersohn's[10] variational procedure when applied to the dipole polarizabilities. Secondly, we wanted to compare the results of the variational calculation with Sternheimer's[2] results. Further, since Sternheimer's recent values were then not available, we wanted to calculate α_d without the earlier approximation made by Sternheimer by a procedure which would not require any extensive computational effort. It is gratifying that our values agree quite well with Sternheimer's revised values.

I. VARIATIONAL PROCEDURE

As mentioned in the introduction, the procedure used is analogous to that employed in the calculation of the shielding of nuclear quadrupole moments by core electrons in ions. The net Hamiltonian for an atomic electron, in the presence of the electric field due to a unit positive point charge at a distance R from the nucleus, may be written as

$$H = H_0 + H_1, \tag{1}$$

where

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

and

$$H_1 = -2r \cos\theta / R^2. \tag{3}$$

Atomic units are used throughout the calculations. The polar coordinates r, θ of the core electron are taken with respect to the nucleus as origin, and the line joining the neighboring charge and the nucleus is taken as the z axis ($\theta = 0$). V_0 refers to the zero-order self-consistent atomic potential, in which the electron moves and H_1 is the perturbation term. Denoting by ψ_0 the ground state wave function for the electron and by ψ_1 the perturbed wave function, then by the usual first-order perturbation theory, one obtains

$$(H_0 - E_0)\psi_1 = -(H_1 - E_1)\psi_0, \tag{4}$$

where E_0 is the ground state energy and E_1 is the first-order perturbation energy,

$$E_1 = \langle \psi_0 | H_1 | \psi_0 \rangle. \tag{5}$$

Sternheimer obtained ψ_1 by solving Eq. (4). We calculate ψ_1 by a variational procedure by taking

$$\psi_1 = -\psi_0 H_1 f(r), \tag{6}$$

where $f(r)$ is a variational function which must be adjusted to give a minimum value for the energy. When the ground state is an S state, we have $\psi_0 = \psi_0'/\sqrt{2}$, where

$$\psi_0' = Nr(e^{-Zr} + Ce^{-kZr}) \tag{7}$$

is a function of r only. The quantities Z, k, and C have been tabulated by Green, Mulder, Lewis, and Woll.[8] N is the normalization factor. One may then write

$$\psi_1 = \psi_1' \cos\theta / R^2,$$

where

$$\psi_1' = (1/\sqrt{2})\psi_0' r f(r). \tag{8}$$

We must now choose a suitable $f(r)$. Equation (8) may also be written

$$\sqrt{2}\psi_1' / r\psi_0' = f(r).$$

Thus we want to find a function $f(r)$ which resembles the quotient function $\sqrt{2}\psi_1'/r\psi_0'$ as closely as possible. In general, then, we write

$$\sqrt{2}\psi_1' / r\psi_0' = \sum_i C_i \phi_i, \tag{9}$$

where the ϕ_i are a complete set of functions[11] and the C_i are parameters to be adjusted, using the variation principle. As pointed out by Shull and Löwdin[12] the functions $L_i(r)e^{-r/2}$, where the $L_i(r)$ are Laguerre polynomials, form a complete "discrete" set of functions. We therefore use the expansion

$$\sqrt{2}\psi_1'/r\psi_0'e^{+r/2} = \sum_i C_i L_i(r)e^{-r/2}, \tag{10}$$

which can be rewritten as

$$\psi_1' = (\psi_0'/\sqrt{2})r \sum_i C_i L_i(r). \tag{11}$$

Now the Laguerre functions[13] are actually polynomials in powers of r, so, in place of (11), we use the following form for ψ_1':

$$\psi_1' = (1/\sqrt{2})\psi_0' r(\alpha + \beta r + \gamma r^2 + \cdots), \tag{12}$$

where α, β, γ, etc., are variation parameters to be adjusted to give a minimum energy in the presence of the electric field. To make use of a complete set of functions, we should rigorously have an infinite number of terms in Eqs. (11) and (12), but it has been found that terms beyond γr^2 may be excluded, since these terms produce a negligible change in the energy, and hence in the polarizability.

It is clear from Eqs. (4), (6), and (12) that the s-electron can be excited only to the p-state by the perturbation H_1. The perturbed energy to second order in the field (i.e., involving no powers of $1/R$ higher

[11] P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, New York, 1956), third edition.

[12] H. Shull and P. O. Löwdin, J. Chem. Phys. **23**, 1362 (1955).

[13] The authors are grateful to Professor R. Bersohn for pointing out the relation between our variation procedure and the procedure employed by Shull and Löwdin (reference 12) in obtaining a convergent series expansion for helium atom orbitals.

TABLE I. Results of variational calculation of dipole polarizabilities of He-like ions.

Ion	α	β	γ	Polarizability α_d(A^3) (This work)	(Sternheimer)[a]	(Experimental)
H⁻	3.04667			10.99		
	0.81887	0.67159		14.88		
	0.72737	0.72478	−0.0055758	14.88	13.4	
He	0.393925			0.184		
	0.16360	0.18642		0.218		
	0.16146	0.18984	−0.0010555	0.218	0.224	0.204
Li⁺	0.148757			0.0262		
	0.066399	0.10781		0.0305		
	0.066238	0.10822	−0.0002103	0.0305	0.0307	0.0235
Be⁺⁺	0.077268			0.00707		
	0.035701	0.075281		0.00812		
	0.035585	0.075697	−0.00029527	0.00813	0.00825	0.0059
B⁺⁺⁺	0.047297			0.00265		
	0.022243	0.057907		0.00303		
	0.022176	0.058213	−0.00027814	0.00303	0.00306	0.0029

[a] Recent revised values obtained by R. Sternheimer (private communication).

than $1/R^4$) is given by

$$E=E_0+\langle\psi_0|H_1\psi_0\rangle+2\langle\psi_0|H_1|\psi_1\rangle+\langle\psi_1|H_0-E_0|\psi_1\rangle. \quad (13)$$

It may be seen from Eqs. (3) and (7) that

$$\langle\psi_0|H_1|\psi_0\rangle=0.$$

Also, since E_0 does not involve α, β, or γ when minimizing the net energy E with respect to α, β, and γ, one need only consider the second order terms

$$E_2=2\langle\psi_0|H_1|\psi_1\rangle+\langle\psi_1|H_0-E_0|\psi_1\rangle. \quad (14)$$

By using Eqs. (2), (3), (6), and (7), it may be shown that

$$E_2=\frac{8}{3R^4}[\tfrac{3}{2}\alpha^2+4\alpha\beta\langle r\rangle+5\alpha\gamma\langle r^2\rangle+8\beta\gamma\langle r^3\rangle+3\beta^2\langle r^2\rangle$$
$$+(11/2)\gamma^2\langle r^4\rangle-\alpha\langle r^2\rangle-\beta\langle r^3\rangle-\gamma\langle r^4\rangle], \quad (15)$$

where

$$\langle r^n\rangle=\int \psi_0'^2 r^n r^2 dr. \quad (16)$$

Minimizing E_2 with respect to α, β, and γ successively, one obtains three simultaneous linear equations in α, β and γ. The coefficients in these equations involve expectation values of r^n over the radial parts of the ground state function. Using Eq. (7) for ψ_0', one obtains

$$\langle r^n\rangle=N^2\left\{\frac{(n+2)!}{(2z)^{n+3}}+\frac{c^2(n+2)!}{(2kz)^{n+3}}+\frac{2c(n+2)!}{[(k+1)z]^{n+3}}\right\}. \quad (17)$$

The values of $\langle r^n\rangle$ for the various He-like ions are calculated from this expression using values of c, k, and z tabulated by Green, Mulder, Lewis, and Woll.[8] The solutions of the requisite simultaneous equations then yield α, β, γ, which, when substituted into Eq. (14), give E_2 in terms of $1/R^4$. Since there are two electrons in the $1s$ state in the ground state configuration of

He-like ions, the net perturbation energy for the ion is equal to $2E_2$. Equating this to $\alpha_d E^2$,[14] where $E=1/R^2$ is the field due to the point charge at the position of the nucleus, the polarizability α_d is then given by

$$\alpha_d=2E_2R^4, \quad (18)$$

where E_2 is given by (15). The quantity α_d, as given by Eq. (18), is in atomic units and the conversion factor $(0.529)^3$ is necessary to convert to A^3. To test the convergence of the variational calculations, values of α_d were obtained by using one, two, and three parameters in (12), starting with α.

II. RESULTS AND DISCUSSION

The results of our calculations are tabulated in Table I. For comparison, experimental values and Sternheimer's calculated values are also included. The experimental values for Li⁺, Be⁺⁺, and B⁺⁺⁺ are those obtained by Sternheimer from spectroscopic term defect data; for helium the value is that of Herzfeld and Wolf,[15] as obtained from their optical refractivity measurements on helium gas after extrapolation of their measurements down to zero frequency.

Several points are to be noted in Table I:

1. The convergence of the variational calculation is excellent for all ions. The introduction of two parameters α, β causes a considerable change from the value of α_d, using a single parameter α alone, but the use of the additional parameter γ causes very little change in α_d. A similar behavior was noted in I for quadrupole polarizabilities. The very good convergence of the variational calculation shows that a reliable value of α_d

[14] The energy of the atom in the electric field is taken as $\alpha_d E^2$ and not $\alpha_d E^2/2$, because the unit of energy in atomic units is a Rydberg ($=e^2/2a_0$, $a_0=$Bohr radius).

[15] K. F. Herzfeld and K. L. Wolf, Ann. Physik 76, 71 and 567 (1925).

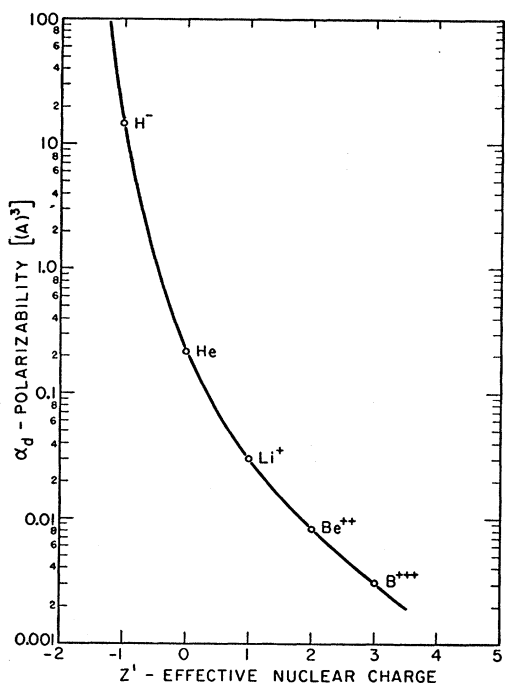FIG. 1. Polarizability α_d versus effective nuclear charge Z'.

may be obtained provided the ground state wave function is correctly known.

2. The agreement between our calculated values and those of Sternheimer is quite good except for the H$^-$ ion, where there is a difference of about 10%. Since both his and our methods have been used for extensive calculations on dipole and quadrupole polarizabilities of ions,[16] it would be meaningful to discuss here the relative merits of the two procedures. In our calculations we use in (12) a variational function of the form of (6) for u_1', which directly involves the ground state wave function u_0'. Our calculated u_1', and hence α_d, will therefore include the error present in the approximate ground state wave function used. In Sternheimer's procedure, the ground state wave function occurs on the right hand side of the differential equation[17] he solves for u_1'. It probably will not be as dependent on the accuracy of u_0' therefore, and most likely would lead to a more accurate result. Our procedure involves only a knowledge of the expectation values of different powers of r over the ground state wave function and once these are known, one need only solve a set of linear equations in α, β, and γ to obtain the polarizabilities. Also these same expectation values may be used for an estimation of quadrupole polarizabilities and Sternheimer antishielding factors, γ_∞, for nuclear quadrupole moments, as discussed in Sec. I. Sternheimer's procedure requires the numerical solution of a

differential equation for each ion. Apart from the longer computational efforts necessary, his method also is susceptible to cumulative errors due to rounding off and due to the use of finite intervals in the process of solving the differential equation. This could be the reason that our value of α_d is somewhat nearer the experimental value than his for the helium atom. However, by using high-speed computing machines, errors due to rounding off can be reduced to a great extent, and then Sternheimer's method would be inherently more accurate than ours.

The agreement between our results and the experimental ones for positive ions is not very good, as seen in Table I. These experimental values, however, are estimated from spectroscopic term-defect data and not as much reliance should be placed on them as the directly measured value for the helium atom. Atanasoff[6] has calculated the value of α_d for helium, using the Hylleraas ground state wave function and a complicated variational function mentioned in the introduction. He obtained a value within 5% of experiment. Since he included r_{12} terms both in the ground state and the perturbed state wave function, his procedure took direct account of spatial correlation effects between the electrons. But since our value, using a simpler wave function without spatial correlations, is within 7% of experiment, it may be concluded that these effects do not lead to any large error in α_d for helium. For the positive ions, Li$^+$, Be^{++}, and B^{+++}, the spatial correlation effects would be expected to be smaller and therefore more reliance may be placed on these calculated values of α_d than on the experimental values tabulated in Table I. For each of the positive ions, the values of α_d shown are the mean of a fairly wide range of values obtained by Sternheimer from spectral term-defect data for various states of a valence electron outside the closed shell. For the H$^-$ ion, on the other hand, the correlation effects are likely to be more important. There is no experimental value available to confirm this. Shull and Löwdin[18] have recently proposed a set of ground state wave functions for the helium-like ions where spatial correlation is included by making the two electrons move in two separate hydrogenic orbitals with different Z factors. It would be interesting to investigate the change in the values of α_d for these ions using the Shull and Löwdin ground state wave functions.

3. To obtain additional information on the correctness of Green, Mulder, Lewis, and Wolls' wave functions, which were employed in our calculations, they were used to estimate the diamagnetic susceptibilities of the He-like ions. Van Vleck[19] gives the following expression for the molar diamagnetic susceptibility, viz.,

$$\chi_{mol} = -5.664 \times 10^{10} \langle r^2 \rangle,$$

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[16] Quadrupole polarizability calculations for other ions than those in I will soon be completed.

[17] Refer to Eq. (15) in reference 1.

[18] H. Shull and P. O. Löwdin, J. Chem. Phys. **25**, 1035 (1956).

[19] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 206.

where $\langle r^2 \rangle$ is in cm². The values of χ_{mol} obtained from this equation are tabulated in Table II. In the third column of this table are shown the values of χ_{mol} calculated by Pauling, using screened hydrogen-like wave functions. In the fourth column, the experimental values of χ_{mol} for He and Li⁺ are listed. Hector and Wills obtained the value for He by direct measurement on helium gas which may be considered accurate, while the wide range of values of χ_{mol} for Li⁺, obtained by various authors, are from susceptibility measurements on Li salts and salt solutions. Our value of χ_{mol} for He agrees very well with Hector and Wills' experimental value, but Pauling's value is somewhat smaller. There is a better agreement between Pauling's values and ours for the positive ions, indicating the validity of Pauling's approximation of screened hydrogen-like orbitals for these ions, and its poor validity for the helium atom and H⁻ ion. In addition, it is to be noted that the evaluation of χ_{mol} involves the ground state wave functions only, whereas in calculating the dipole polarizability, use is also made of the perturbed wave function in the presence of the electric field. If the departure of our value of α_d from experiment be mainly ascribed to the neglect of correlation effects, then the very good agreement with experiment (within 2%) of the calculated value of χ_{mol} for helium, as compared to the less satisfactory result for α_d (7% difference), indicates that correlation effects are more important in

TABLE II. Calculated values of χ_{mol} compared with those of Pauling's and the experimental values.

| Ion | $10^6 \times \chi_{mol}$ | | |
	Our results	Pauling's value	Experimental values
H⁻	−14.49	−8	
He	− 1.873	−1.54	−1.88
Li⁺	− 0.7073	−0.63	−0.2 to −1.3
Be⁺⁺	− 0.3674	−0.34	
B⁺⁺⁺	− 0.2249	−0.21	

the perturbed state than in the ground state of the helium atom.

4. One final conclusion may be drawn from our calculations. In Fig. 1 are plotted the values of α_d as a function of the effective charge Z' on the ions. The very rapid alteration in α_d with change in Z' indicates that the electronic polarizabilities in ionic crystals will depend very sensitively on the presence of any covalent bonding between adjacent ions. Since the presence of covalency decreases the effective positive charge on the cations, the electronic polarizabilities of cations would be smaller in the solid than in the free state. The opposite would be expected for anions.