

Atomic Dipole Polarizabilities from the Uncoupled Hartree-Fock Approximation

M. YOSHIMINE

IBM Research Laboratory, San Jose, California

AND

R. P. HURST*

Department of Physics, State University of New York at Buffalo, Buffalo, New York

(Received 19 December 1963; revised manuscript received 1 April 1964)

Electric dipole polarizabilities are computed for a large number of 2-, 3-, 4-, 10-, 11-, 12-, 18-, 19-, and 20-electron atoms and ions. These results are all obtained within the framework of the uncoupled Hartree-Fock approximation. All calculations are made using analytical Hartree-Fock wave functions. For the lighter atoms and positive ions the results of these calculations are in fairly good agreement with the experimental and other more accurate theoretical values. However, for the heavier atoms and ions the results are too large. It is also found that great care must be exerted in selecting self-consistent functions for use in making polarizability calculations.

I. INTRODUCTION

THE polarizability is a property of atoms which is dependent primarily on the behavior of the outermost electrons in an external electric field. Since there is also an effect which depends upon the field gradient we will define the property of interest here. Thus, if an atom is placed in a uniform external electric field F it becomes polarized and receives an induced electric dipole moment $\mu = \alpha F$. Then, assuming the atom has no permanent moment and that the ground electronic state is nondegenerate the energy E in the field is given by¹

$$E = E_0 - \frac{1}{2}\alpha F^2 + \dots \quad (1)$$

Here E_0 is the free atom energy and α is the dipole polarizability and is the subject of this paper.

Since the greatest contribution to α comes from the most loosely bound, outer electrons, which contribute very little to the total energy, studies of computed polarizabilities enable one to infer qualitative information concerning the accuracy of various approximate wave functions at large radial distances. This offers an independent means of assessing wave functions as the computed free atom energies give information mostly concerning the accuracy of the wave function near the nucleus. More specifically, in the polarizability calculations presented here it is shown that use of poor solutions to the Hartree-Fock equations can change the polarizability by a factor of 2 while the free atom energies differ by ≈ 0.0005 a.u.

In this paper the atomic dipole polarizabilities have all been computed from analytical Hartree-Fock wave functions using the uncoupled Hartree-Fock approximation. Since two comprehensive review papers on polariz-

abilities have recently appeared^{2,3} the next section on the theory will be greatly abridged to include only details necessary for clarity.

II. THEORY

A. Variation-Perturbation Theory

The Hamiltonian H for an atom in a uniform electric field is given in atomic units by⁴

$$H = H_0 + H_1 = H_0 + \mathbf{F} \cdot \mathbf{r}. \quad (2)$$

Here H_0 is the usual atomic Hamiltonian in the absence of the external field. For simplicity, the origin of the coordinate system for the radius vector \mathbf{r} is chosen at the nucleus.

For the applications considered here one can assume, without loss of generality, that the electric field is along the z axis so that Eq. (2) reduces to

$$H = H_0 + F \sum_{i=1}^N z_i \quad (\text{summed over all electrons}). \quad (3)$$

We approximate the solution to the Schrödinger equation, which results from Eq. (3), using perturbation theory. Thus, following the usual arguments⁵ one finds that the zeroth-, first-, and second-order functions, i.e., ψ_0 , ψ_1 , and ψ_2 must satisfy

$$H_0\psi_0 - E_0\psi_0 = 0, \quad (4)$$

$$H_0\psi_1 + H_1\psi_0 - E_0\psi_1 - E_1\psi_0 = 0, \quad (5)$$

$$H_0\psi_2 + H_1\psi_1 - E_0\psi_2 - E_1\psi_1 - E_2\psi_0 = 0. \quad (6)$$

² A. Dalgarno, *Advan. Phys.* **11**, 281 (1962).

³ K. S. Pitzer in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. 2, p. 59.

⁴ E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), p. 380.

⁵ H. A. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 122.

* Work supported in part by U. S. Air Force Office of Scientific Research Grant No. AF-AFOSR=191-63.

¹ L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 226.

In addition, from Eqs. (4)–(6) one finds that the first- and second-order energies are obtained from

$$E_1 = \int \psi_0 H_1 \psi_0 d\tau \quad (7)$$

$$E_2 = \int \psi_0 H_2 \psi_0 d\tau, \quad (8)$$

respectively. Provided the ground state is nondegenerate one can show by direct substitution, for atoms, that $E_1=0$.

From Eq. (8) it is clear that the principal problem in obtaining polarizabilities, assuming ψ_0 is known, lies in solving Eq. (5) for the first order function ψ_1 . Perhaps the most successful of the methods proposed for solving Eq. (5) are the Sternheimer numerical integration scheme⁶ and the variational method.⁵ In this work we use the latter approach.

Consider the functional

$$J[\psi_1'] = \int \psi_1' H_0 \psi_1' d\tau - E_0 \int \psi_1' \psi_1' d\tau + 2 \int \psi_1' H_1 \psi_0 d\tau. \quad (9)$$

The condition that $J[\psi_1']$ have a stationary value, i.e., $\delta J[\psi_1']=0$ reduces to Eq. (5) since $E_1=0$. Thus, that function ψ_1' for which $\delta J[\psi_1']=0$ has the property

$$J[\psi_1'] = J[\psi_1] = E_2 = \int \psi_0 H_2 \psi_0 d\tau.$$

In addition, as Karplus and Kolker observe,⁷ the second variation $\delta^2 J[\psi_1']$ is positive so that $J[\psi_1']$ must be a minimum. Essentially, then the variational procedure usually followed in approximating ψ_1 consists in constructing a trial function ψ_1' which contains a number of parameters with respect to which $J[\psi_1']$ is minimized. Once $J[\psi_1']$ is minimized α is obtained from

$$\alpha = -(2/F^2)E_2 = -(2/F^2)J[\psi_1]. \quad (10)$$

B. Uncoupled Hartree-Fock Approximation

The field-independent Hartree-Fock wave function for atoms, having only closed shells, has the form⁸

$$\psi_0 = \begin{pmatrix} x_1 & x_1 & x_2 & x_2 & \cdots & x_n & x_n \\ \alpha & \beta & \alpha & \beta & \cdots & \alpha & \beta \end{pmatrix}. \quad (11)$$

Since this function is not an eigenfunction of H_0 the perturbation Eqs. (4)–(9) are not consistent. Thus,

⁶ R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).
⁷ M. Karplus and H. J. Kolker, J. Chem. Phys. **38**, 1263 (1963).
⁸ Notation similar to that used by H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1954), p. 232.

several assumptions are made in applying the theory of the previous section. These are:

(1) The external field free Hamiltonian H_0 can be replaced by the corresponding Hartree-Fock Hamiltonian H_0' and the corresponding energy E_0 by E_0' where

$$H_0' = \sum_{i=1}^{2n} H_i - \sum_{i<k} \sum \int \int \frac{|x_i(\mathbf{r}_i)|^2 |x_k(\mathbf{r}_k)|^2}{r_{ik}} d\tau_i d\tau_k + \sum_{i<k} \sum \int \int \frac{x_i(\mathbf{r}_i) x_k(\mathbf{r}_i) x_i(\mathbf{r}_k) x_k(\mathbf{r}_k)}{r_{ik}} d\tau_i d\tau_k \quad (12)$$

and

$$E_0' = \sum_{i=1}^{2n} \epsilon_i^0 - \sum_{i<k} \sum \int \int \frac{|x_i(\mathbf{r}_i)|^2 |x_k(\mathbf{r}_k)|^2}{r_{ik}} d\tau_i d\tau_k + \sum_{i<k} \sum \int \int \frac{x_i(\mathbf{r}_i) x_k(\mathbf{r}_i) x_i(\mathbf{r}_k) x_k(\mathbf{r}_k)}{r_{ik}} d\tau_i d\tau_k. \quad (13)$$

(2) Although the Hartree-Fock wave functions ψ_0 are analytical functions of the Roothaan type,^{9,10} ψ_0 is nevertheless assumed to be an exact eigenfunction of H_0' .

The first assumption is the fundamental approximation made in what Dalgarno² calls the uncoupled Hartree-Fock method. It would, of course, have been preferable to use solutions to the Hartree-Fock equations which minimize the total energy in the external field (coupled Hartree-Fock approximation); however, this approach is more laborious and it has successfully been carried out only for the helium sequence.¹¹

C. Choice for First-Order Wave Function

Some insight into a suitable form to choose for the first-order wave function can be gained from a study of the hydrogen-like atom polarizability. Hence we will briefly consider this problem.

First it is clear that when considering forms for ψ_1' for this problem, that since the second-order energy E_2 is obtained from

$$E_2 = \int \psi_1 H_1 \psi_0 d\tau, \quad (14)$$

one can restrict choices of the trial first-order function ψ_1' to functions for which $\int \psi_1' H_1 \psi_0 d\tau$ is nonzero. One possible such choice is

$$\psi_1' = \psi_1 h, \quad (15)$$

where

$$h = F(C_0 z + C_1 z r + C_2 z r^2 + C_3 z r^3 + \cdots). \quad (16)$$

After substituting this form into the functional, Eq. (9),

⁹ C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

¹⁰ C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

¹¹ A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 289 (1959).

one finds on requiring that

$$\frac{\partial J[\psi_1']}{\partial C_i} = 0 \quad i=0, 1, 2, 3, \dots \quad (17)$$

that

$$C_0 = -\frac{1}{Z^2}, \quad C_1 = -\frac{1}{2Z}, \quad C_2 = C_3 = C_4 = \dots = 0 \quad (18)$$

(Z =atomic number).

It can be shown² that Eq. (15) with the coefficients specified by Eqs. (18) is the exact first-order function for the hydrogen-like atom problem. This result suggests a form the perturbed orbitals can take.

Next, since we restrict ψ_0 to a single determinant antisymmetrical atomic orbital product function, it would seem consistent and convenient to assume also a first-order function to be of the orbital product form. Thus, proceeding from these considerations we can choose ψ_1' to be of the form

$$\psi_1' = \sum_{k=1}^n U_k, \quad (19)$$

where

$$U_k = \begin{pmatrix} x_1 & x_1 & x_2 & x_2 & \dots & x_k & h_k & x_k & \dots & x_n & x_n \\ \alpha & \beta & \alpha & \beta & \dots & \alpha & \beta & \dots & \alpha & \beta \end{pmatrix} + \begin{pmatrix} x_1 & x_1 & x_2 & x_2 & \dots & x_k & h_k & \dots & x_n & x_n \\ \alpha & \beta & \alpha & \beta & \dots & \alpha & \beta & \dots & \alpha & \beta \end{pmatrix} \quad (20)$$

and

$$h_k = Fz(C_0^k + C_1^k r + C_2^k r^2 + C_3^k r^3 + \dots). \quad (21)$$

This choice for ψ_1' seems to have first been proposed by Buckingham.¹² Use of a more general form for the perturbation function would be indicated if convergence were slow. Thus, for example, one might argue that negative or even nonintegral powers of r should be included in such event. Indeed, Pople and Schofield¹³ have used a numerical function for the r dependence. More careful consideration of this point will be deferred to the discussion of the numerical results.

D. Formulation

The formulas from which actual computations are made are obtained by substituting the Hartree-Fock Hamiltonian and energy, Eqs. (12) and (13), and the wave function, Eqs. (11), (19), (20), and (21) into the functional as given by Eq. (9). Once this has been done the functional can be reduced by straightforward means so that one obtains

$$J[\psi_1'] = \sum_{k=1}^n J_k(U_k), \quad (22)$$

where

$$J_k(U_k) = \langle x_k | \nabla h_k \cdot \nabla h_k | x_k \rangle + 4 \langle x_k | F h_k z | x_k \rangle - 2 \sum_{j=1}^n \{ (\epsilon_k - \epsilon_j) \langle x_j | h_k | x_k \rangle \langle x_k | h_k | x_j \rangle + 2 \langle x_k | h_k | x_j \rangle \langle x_k | F z | x_j \rangle \}. \quad (23)$$

Because of the form $J[\psi_1']$ takes in Eq. (22) the condition

$$\delta J[\psi_1'] = 0 \quad (24)$$

leads to $\delta J_k(U_k) = 0$ for each orbital x_k separately. Since the only adjustable parameters in h_k are coefficients [see Eq. (21)] the condition $\delta J_k(U_k) = 0$ is equivalent to requiring

$$\partial J_k(U_k) / \partial C_i^k = 0, \quad i=0, 1, 2, 3, 4, \dots \quad (25)$$

Here the k superscript denotes the orbital and the i denotes the power of r in the polynomial in r .

The conditions listed as Eqs. (25) lead to the set of linear equations

$$\sum_p A_{ip}^k C_p^k = -B_i^k, \quad (26)$$

where

$$A_{ip}^k = \langle x_k | r^{p+i} + (p+i+p!) z^2 r^{p+i-2} | x_k \rangle - 2 \sum_{j=1}^n (\epsilon_k - \epsilon_j) \langle x_j | z r^i | x_k \rangle \langle x_k | z r^p | x_j \rangle \quad (27)$$

and

$$B_i^k = 2 \langle x_k | z r^i | x_k \rangle - 2 \sum_{j=1}^n \langle x_j | z r^i | x_k \rangle \langle x_k | z | x_j \rangle. \quad (28)$$

After the coefficients C_p^k of Eqs. (26) are found for each orbital the contribution to the polarizability from the k th orbital is obtained from [cf. Eqs. (8) and (10)].

$$-2 \sum_p C_p^k B_p^k. \quad (29)$$

The total polarizability is obtained by summing the contribution of each orbital so that

$$\alpha = -2 \sum_k \sum_p C_p^k B_p^k. \quad (30)$$

Finally, in cgs units we have

$$\alpha = -2a_0^3 \sum_k \sum_p C_p^k B_p^k, \quad (31)$$

where a_0 is the atomic unit of length and the B_p^k are given by Eq. (28).

III. RESULTS

Using the method outlined in Eqs. (26)–(31) the polarizability calculations are performed on an IBM 7090 computer. In each case the analytical Hartree-

¹² R. A. Buckingham, Proc. Roy. Soc. (London) **160**, 94 (1937).

¹³ J. A. Pople and P. Schofield, Phil. Mag. **2**, 591 (1957).

TABLE I. Calculated and experimental values of dipole polarizabilities.

Atom or ion	Dipole polarizability (10 ⁻²⁴ cm ³)		
	This paper ^a	Other calculations ^b	Experimental
H ⁻	16.7 ^o	13.4-31.4	30.2 ^k
He	0.220 ^d	0.196-0.224	0.2068±0.0002 ^l
Li ⁺	0.0304 ^d	0.024-0.08	0.025 ^m
Be ²⁺	0.00815 ^d	0.007-0.04	0.007 ^m
B ³⁺	0.00304 ^d	0.00288-0.02	0.0033 ^m
C ⁴⁺	0.00138 ^d	0.0013-0.00139	0.0015 ^m
N ⁵⁺	0.000712 ^d		
Li	21.0 ^d	20-25.1	22±2 ⁿ
Be ⁺	2.48 ^d	3.65	
B ²⁺	0.654 ^d	1.16	
C ³⁺	0.245 ^d	0.509	
N ⁴⁺	0.112 ^d	0.267	
O ⁵⁺	0.0586 ^d	0.157	
Be	9.53 ^d	4.5-9.6	
B ⁺	1.96 ^d		
C ²⁺	0.653 ^d		
N ³⁺	0.280 ^d		
O ⁴⁺	0.140 ^d		
F ⁵⁺	0.0781 ^d		
F ⁻	1.81 ^o	1.2-1.9	0.99 ^o
Ne	0.409 ^f	0.367-0.62	0.398 ^p
Na ⁺	0.163 ^g	0.145-0.26	0.17 ^m
Mg ²⁺	0.0801 ^d	0.072-0.10	0.10 ^m
Al ³⁺	0.0446 ^d	0.045-0.050	0.053 ^m
Si ⁴⁺	0.0271 ^d	0.027	0.043 ^o
P ⁵⁺	0.0175 ^d		
Na	27.1 ^h	22.9-24.6	21.5±2 ⁿ
Mg ⁺	5.51 ⁱ		
Al ²⁺	2.05 ⁱ		
Si ³⁺	0.994 ⁱ		
P ⁴⁺	0.556 ⁱ		
S ⁵⁺	0.340 ⁱ		
Mg	19.4 ⁱ		7.0±1.8-7.4±1.8 ^q
Al ⁺	5.89 ⁱ		
Si ²⁺	2.57 ⁱ		
P ³⁺	1.35 ⁱ		
S ⁴⁺	0.792 ⁱ		
Cl ⁵⁺	0.502 ⁱ		
Cl ⁻	6.23 ^o	7.19	3.05 ^o
Ar	2.32 ^j	2.40	1.63 ^p
K ⁺	1.08 ^j	1.24-0.83	0.80 ^m
Ca ²⁺	0.620 ⁱ	0.73	0.54 ^m
SC ³⁺	0.391 ⁱ	0.286-0.35	
Ti ⁴⁺	0.263 ⁱ		
V ⁵⁺	0.185 ⁱ		
K	59.6 ^k	41.6-44.4	38±4 ⁿ
Ca ⁺	14.3 ^h		
Ca	48.9 ^h		19.7±0.6-22.5±0.6 ^q

^a Superscripts in this column indicate the sources of the zeroth-order wave functions used.

^b Taken from Dalgarno's review paper, *Advan. Phys.* **11**, 281 (1962) except Lithium isoelectronic series for which the values are taken from M. R. Flannery and A. L. Stewart, *Proc. Phys. Soc. (London)* **82**, 188 (1963).

^c M. Yoshimine (unpublished).
^d E. Clementi, *J. Chem. Phys.* **38**, 996 (1963).
^e E. Clementi and A. D. McLean, *Phys. Rev.* **133**, A419 (1964).
^f L. M. Sachs, *Phys. Rev.* **124**, 1283 (1961).
^g P. Bagus, T. Gilbert, H. D. Cohen, and C. C. J. Roothaan (to be published).
^h E. C. Clementi (unpublished).
ⁱ E. C. Clementi, *J. Chem. Phys.* **38**, 1001 (1962).
^j P. Bagus (private communication).
^k S. Geltman, *Astrophys. J.* **136**, 935 (1962).
^l D. R. Johnston, G. J. Oudemans, and R. H. Cole, *J. Chem. Phys.* **33**, 1310 (1960).
^m J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933).
ⁿ G. E. Chamberlain and J. C. Zorn, *Phys. Rev.* **129**, 677 (1963).
^o M. Born and W. Heisenberg, *Z. Physik* **23**, 407 (1924).
^p Landolt Bornstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik*, Atome und Ionen (Springer-Verlag, Berlin, 1950), Vol. 1, Part 1.
^q P. L. Altick, *J. Chem. Phys.* **40**, 238 (1964).

Fock orbitals are of the general form

$$x_k = \sum_i a_i \phi_i, \tag{32}$$

where

$$\phi_i = N_i r^{n_i} e^{-\zeta_i r} Y_{l,m}(\theta, \phi). \tag{33}$$

These results are presented in Table I for a number of atoms and ions together with the results of other

TABLE II. Dependence of dipole polarizabilities on zeroth order wave functions.

Atom or ions	ψ_0	No. of basis functions used		Total energy of unperturbed state (a. u.)	Orbital energy of the outmost orbital	Polarizability (10 ⁻²⁴ cm ³)
		s	p			
H ⁻	a	5		-0.48793		8.211
	b	5		-0.4879293	-0.04622	16.67
He	c	11		-2.861680	-0.917956	0.2204
	d	4		-2.861679	-0.91795	0.2203
	e	3		-2.861680	-0.91795	0.2204
Li ⁺	d	4		-7.2364136	-2.79234	0.03036
	e	3		-7.236414	-2.79236	0.03036
Li	c	12		-7.432727	-0.196323	21.02
	f	6		-7.432726	-0.19632	20.97
	d	5		-7.432726	-0.19632	21.00
	e	5		-7.432726	-0.19632	20.98
Be	c	12		-14.57302	-0.309270	9.523
	f	6		-14.57302	-0.30927	9.525
	d	5		-14.57301	-0.30927	9.541
	e	5		-14.57302	-0.30927	9.522
O ⁻⁻	g	5	4	-74.48032	0.14478	52.33
	h	5	5	-74.48442	0.12547	99.42
F ⁻	i	7	6	-99.45921	-0.1810072	1.865
	g	5	4	-99.45936	-0.18087	1.818
	e	5	4	-99.45937	-0.18083	1.816
	h	5	5	-99.45936	-0.18079	1.808
Ne	j	7	5	-128.54318	-0.84615	0.4621
	i	7	6	-128.5470	-0.8501921	0.4086
	f	6	4	-128.5470	-0.85048	0.4140
	d	5	4	-128.54698	-0.85020	0.4149
	e	5	4	-128.5471	-0.85034	0.4118
Na ⁺	d	5	4	-161.6768	-1.79629	0.1633
	i	7	6	-161.6769	-1.797188	0.1626
	e	5	4	-161.6770	-1.79718	0.1626
Na	k	8	5	-161.8589	-0.18211	27.15
	l	7	3	-161.8586	-0.18199	27.17
	k	7	4	-161.8587	-0.18210	27.06
Cl ⁻	m	9	7	-459.5750	-0.1518	7.305
	n	7	6	-459.5767	-0.14988	6.227
Ar	o	3	2	-525.7653	-0.50633	1.365
	k	6	4	-526.7841	-0.5840	2.039
	l	7	5	-526.8171	-0.59071	2.293
	p	8	8	-526.8173	-0.59125	2.344
	q	7	7	-526.8174	-0.59093	2.320
	m	9	7	-526.814	-0.589	2.699

^a C. C. J. Roothaan and A. W. Weiss, *Rev. Mod. Phys.* **32**, 194 (1960).
^b M. Yoshimine (unpublished).
^c C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960), Table VI.
^d E. Clementi, *J. Chem. Phys.* **38**, 996 (1963).
^e P. Bagus, T. Gilbert, H. D. Cohen, and C. C. J. Roothaan (to be published).
^f E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1962).
^g A. D. McLean (unpublished).
^h E. Clementi and A. D. McLean, *Phys. Rev.* (to be published).
ⁱ L. M. Sachs, *Phys. Rev.* **124**, 1283 (1961).
^j L. G. Allen, *J. Chem. Phys.* **34**, 1156 (1961).
^k E. C. Clementi (unpublished).
^l E. C. Clementi, *J. Chem. Phys.* **38**, 1001 (1962).
^m R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 521 (1961).
ⁿ E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, *Phys. Rev.* **133**, A1274 (1964).
^o E. Clementi and D. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).
^p G. L. Malli (private communication).
^q P. Bagus (private communication).

TABLE III. Expansion coefficients and orbital contributions in polarizability calculations for inert gas atoms.

Helium ^a						
Coefficients ^b in h_k						
Orbital	1	2	3	4	5	α (a.u.)
$x_1=1s$	-0.33290	-0.35258	-0.01960	-0.00603	-0.00063	1.4865
Neon ^a						
Coefficients ^b in h_k						
Orbital	1	2	3	4	5	α (a.u.)
$x_1=1s$	-0.01193	-0.03088	-0.09637	0.12242	-0.00282	0.00081
$x_2=2s$	-0.09590	-0.08338	-0.04529	0.01282	-0.00102	0.06997
$x_3=2p_x$	-0.13843	-0.22481	-0.08058	0.01755	-0.00127	0.63783 ^c
$x_5=2p_z$	-0.13808	-0.07939	-0.21237	0.04825	-0.00360	1.41120
						Total $\alpha=2.75764$
Argon ^a						
Coefficients ^b in h_k						
Orbital	1	2	3	4	5	$\Delta\alpha$ (a.u.)
$x_1=1s$	-0.00352	-0.04763	0.14864	-0.75458	0.24633	0.00005
$x_2=2s$	-0.00777	-0.08075	0.09173	-0.15854	0.10019	0.00324
$x_3=2p_x$	-0.02767	-0.08884	-0.01029	0.00444	-0.00203	0.01118 ^c
$x_5=2p_z$	-0.03551	-0.04951	-0.02603	-0.00882	-0.00526	0.01579
$x_6=3s$	-13.95020	5.70761	-1.66368	0.07700	0.00735	1.04939
$x_7=3p_x$	-0.69269	-0.41923	0.12105	-0.03820	0.00312	3.81443 ^c
$x_9=3p_z$	-0.71437	0.16057	-0.21969	0.02816	-0.00121	6.93559
						Total $\alpha=15.6553$

^a For the wave function used see Table I.

^b The coefficients correspond to those in Eq. (21) of the text.

^c The contribution of the $2p_x$ orbital equals that from the $2p_y$ orbital. Similarly, that from the $3p_x$ equals that of the $3p_y$.

calculations and the experimental values whenever they are available. Except for lithium isoelectronic sequence the values of "other calculations" are taken from the review paper by Dalgarno.² Lithium values are taken from Flannery and Stewart.¹⁴ For some atoms and ions we calculated the polarizabilities with several wave functions of different degrees of accuracy in order to find out how the polarizability depends on the zeroth order wave function. These results are presented in Table II. In this table the column headed " ψ_0 " gives references to the sources of the wave functions used in the calculations and the column headed "No. of Basis Functions" give the number of ϕ_i 's used in constructing the orbitals x_k . Since the polarizability depends primarily on the behavior of the outmost electrons, the orbital energies of the outmost orbitals are also given. To further illustrate the dependence of the polarizability on the outer electrons the expansion coefficients and orbital contributions for the inert gas atoms are given in Table III.

For the calculations presented in Tables I and II five terms are included in the perturbation polynomial, Eq. (21). In each case the polarizabilities have converged at least to the first three figures though generally the convergence is much better.

A word of explanation seems appropriate for the case of the three-, eleven- and nineteen-electron systems

presented here. The theory developed in the previous section is specific to problems where all orbitals are doubly occupied. However, these systems each contain one singly occupied orbital. On carrying out the analysis in the same way as previously described one finds no change in the procedure as outlined is required except that only half the contribution the doubly occupied orbital would normally have, were it full, is taken in summing Eq. (31) to obtain α .

A very comprehensive review of previous theoretical and experimental polarizability results has been recently given by Dalgarno.² Hence this will be omitted here.

IV. DISCUSSION

Comparison of calculated dipole polarizabilities α_d with experimental values shows that, although reasonable agreements are obtained for lighter atoms, agreements become progressively worse for heavier atoms. We note that calculated α_d for atoms of the first row of the periodic table (except the beryllium sequence) are in reasonable agreement with experimental values whereas calculated α_d for atoms of the second and third rows are too large by a factor of 1.25 to 1.5. These results indicate that the uncoupled Hartree-Fock method with the Hartree-Fock wave functions as the zero-order functions fails to give accurate values of α_d for heavier atoms. This failure is largely due to the fact that the electron in the Hartree-Fock approximation are not held as tightly as is actually the case, due to

¹⁴ M. R. Flannery and A. L. Stewart, Proc. Phys. Soc. (London) 82, 188 (1963).

the neglect of electron correlation effects and to a small extent of relativistic effects. For heavier atoms and ions the effect of neglect of electron correlation is to make the calculated wave functions too diffuse, so that the associated charge cloud becomes more expanded than is the experimental situation, an effect which is clearly associated with the high calculated values of α_d .

For alkaline earths the situation is even worse. The results of the present calculations for Mg and Ca differ from the experimental values by a factor of 2.5; although there is no experimental value for Be, it is reasonable to assume that the calculated α_d for Be is also too large perhaps by a factor of 2. These large discrepancies may be due in part to an incorrect choice of the zero-order functions in which the near ns , np degeneracy has been neglected.^{15,16} For example, the correct zero-order function of the beryllium sequence is not $\Psi_0(1s^2 2s^2)^1S$ as assumed in the Hartree-Fock approximation but the linear combination of

$$\Psi_0 = a\Psi_0(1s^2 2s^2)^1S + b\Psi_0(1s^2 2p^2)^1S$$

which diagonalizes the Hamiltonian matrix. A similar argument applies also for the cases of Mg and Ca.

For negative ions the computed results are not reliable. In the first place it is more difficult to obtain Hartree-Fock solutions for negative ions than for neutral atoms, and even if we do obtain them, they may be very far from the exact wave functions, especially for the outer electrons. For this reason the result for O^{--} is not listed in Table I although two values are listed in Table II.

As Goodings¹⁷ pointed out, there is a difficulty

¹⁵ D. Layzer, *Ann. Phys. (N. Y.)* **8**, 271 (1959).

¹⁶ J. Linderberg and H. Shull, *J. Mol. Spectry.* **5**, 1 (1960).

¹⁷ D. A. Goodings, *Phys. Rev.* **123**, 1706 (1961).

associated with the analytical method used in this study, and that is the difficulty of choosing optimum sets of basis functions and assessing the error resulting from the limited size of these basis sets. In regard to this difficulty we can see from Table II that if unperturbed wave functions constructed from different sets of carefully optimized basis functions are used, then the same results are obtained for dipole polarizabilities. But we must clearly emphasize the importance of careful choice of the self-consistent field wave function for use in polarizability calculations. It is necessary to use a sufficient number of basis functions in constructing the orbitals, and the linear and nonlinear parameters must be well optimized. A comparison of the various neon and argon calculations suggests that it is as important to evaluate the parameters carefully as it is to use an adequate number of basis functions.

For all calculations reported in this work a five term perturbation polynomial [Eq. (21)] is adequate for insuring convergence to three or more figures in the polarizability. We suggest, on the basis of these results, that use of a more general r dependence in Eq. (21) would not significantly alter the computed dipole polarizabilities. Indeed, in most cases three or four terms in the r polynomial would have been sufficient.

ACKNOWLEDGMENTS

It is a pleasure for the authors to thank Professor Martin Karplus, Dr. H. J. Kolker, and Dr. Enrico Clementi for a number of helpful discussions and for their encouragement. In addition, we wish to thank T. W. Sidwell for his help in the initial stages of this work.