Multipole Polarizabilities and Shielding Factors from Hartree-Fock Wave Functions

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Electric dipole, quadrupole, and octupole polarizabilities and shielding factors are calculated for a large number of two- to twenty-electron S-state atoms and ions. The calculations are carried out within the framework of an uncoupled Hartree-Fock approximation, subject to the proviso that the exchange part of the Fock potential be expressable as a multiplicative function. All zeroth-order functions used are of the anaylitical Hartree-Fock type. The resulting numerical values are found to be strongly sensitive to the quality of the Hartree-Fock function used in the calculation, in agreement with Sternheimer's previous conclusion. This point proves to be of special importance in the case of the negative ions. In addition, it is shown that the variational method pioneered by Das and Bersohn, if carried out under proper orthogonality conditions, is equivalent to the present uncoupled Hartree-Fock approximation. Finally, it is noted that the variational method used in this work is less accurate than the Sternheimer numerical method; however, use of the variational method allows some simplification in the computational procedure.

I. INTRODUCTION

THE distortion suffered by the electronic charge distribution of an atom or ion, in the presence of a perturbing electrostatic field, may be expressed in terms of a series of induced multipole moments. Quantitatively, this distortion is described by the electric multipole polarizabilities. Associated with these induced moments are changes induced in the electric field and its gradients at the nucleus. These changes in the field and its gradients are described by the electric multipole shielding factors. An excellent review article dealing with this subject is available.[1]

Interest in the dipole polarizability has a long history because of its close relationship with the dielectric constant. On the other hand, comparatively little research has been done on the quadrupole and higher order polarizabilities, though they can indeed be observed. One incentive for computing the higher induced multipole moments, in addition to the intrinsic interest in these quantities themselves, lies in the fact that the wave functions obtained in the polarizability calculations can be used directly in computing the multipole shielding factors. In particular, the quadrupole shielding factor often represents a significant correction to the nuclear quadrupole coupling constant.

Sternheimer,[2] in a series of papers, has examined polarization and shielding effects first utilizing the Thomas-Fermi model of the atom and later a numerical integration of the Schrödinger equation. Using a variational procedure, Das and Bersohn,[3] Burns,[4] and others[1] have calculated quadrupole polarizabilities and shielding factors using essentially the same approximation as Sternheimer. Apparent difficulties concerning questions of orthogonality in the variational method have been mentioned by Ingalls.[5] Dalgarno has pointed out that these numerical and variational methods are approximations to what he calls the uncoupled Hartree-Fock method.[6]

Recently, Yoshimine and Hurst[7] have published extensive calculations of dipole polarizabilities utilizing the uncoupled Hartree-Fock approximation. These authors emphasized the marked sensitivity of dipole polarizabilities to the choice of unperturbed Hartree-Fock functions used in the calculation.

In this paper electric dipole, quadrupole, and octupole polarizabilities and shielding factors are calculated in an uncoupled Hartree-Fock approximation. A sensitivity is noted in the resultant polarizabilities and shielding factors to the choice of unperturbed Hartree-Fock function, in essential agreement with Sternheimer's[2] conclusion. This resultant sensitivity of polarizabilities and shielding factors to the choice of unperturbed Hartree-Fock function is of importance in properly interpreting the accuracy and utility of the various approximations used in such calculations.

A particular numerical case in point is the quadrupole shielding factor of the Cl⁻ ion. Recently, Watson and Freeman[8] have calculated this quantity using the self-consistent unrestricted Hartree-Fock procedure. Their result is in substantial disagreement with Sternheimer's[9] result and previous variational calculations.[10]

[1] A. Dalgarno, Advan. Physics 11, 281 (1962).
[2] R. M. Sternheimer, Phys. Rev. 80, 102 (1950); 84, 244 (1951); 102, 731 (1956); 107, 1565 (1957); 115, 1198 (1959); 127, 1220 (1962); 130, 1423 (1963); 132, 1637 (1963).
[3] T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956).
[4] G. Burns, Phys. Rev. 115, 357 (1959).
[5] R. Ingalls, Phys. Rev. 128, 1155 (1962).
[6] A. Dalgarno, Proc. Roy. Soc. (London) A251, 282 (1959).
[7] M. Yoshimine and R. P. Hurst, Phys. Rev. 135, A612 (1964).
[8] R. E. Watson and A. J. Freeman, Phys. Rev. 131, 250 (1963).
[9] R. M. Sternheimer and H. M. Foley, Phys. Rev. 102, 731 (1956).
[10] E. G. Wikner and T. P. Das, Phys. Rev. 109, 360 (1958).

The present uncoupled Hartree-Fock calculation yields a quadrupole shielding factor for Cl⁻ in better agreement with Watson and Freeman's value if Watson and Freeman's[11] unperturbed Hartree-Fock function is used. On the other hand, using a more recent function of Clementi's[12] yields a shielding factor in agreement with both Sternheimer's result and with previous variational calculations. Hence, some of the discrepancy between Watson and Freeman's value and the simpler methods may be ascribed to the choice of unperturbed wave function. As emphasized by Watson and Freeman, part of the discrepancy is also due to the neglect of self-consistancy.

In addition, in the present paper, it is noted that the variational method pioneered by Das and Bersohn,[3] if properly carried out, is equivalent to the uncoupled Hartree-Fock approximation used here.

The quantitative definitions of polarizabilities and shielding factors are presented in Sec. II along with a discussion of the uncoupled Hartree-Fock procedure, some questions concerning the form of perturbation function used in the calculation, and consideration of the orthogonality problem. The numerical results for the polarizabilities and shielding factors for two- to twenty-electron S-state atoms and ions are given in Sec. III. A general discussion of the reliability of these values is presented in Sec. IV.

II. THEORY

A. Polarizability and Shielding

Sternheimer's original papers considered the quadrupole moment induced in a closed-shell electron core by the nuclear quadrupole moment. In a later paper[13] the source of the perturbing field was a distant point charge. This later physical situation is presented here as an expedient for defining the multipole polarizabilities and shielding factors. A detailed discussion may be found in Dalgarno's review article[1] and, hence, the following brief summary is included only for the sake of clarity.

Let the point charge q be located a distance R away from the nucleus along the positive Z axis. The electrostatic interaction between this charge and an atom or ion may be written in atomic units as

$$V = qZ_0/R - \sum_{i=1}^{N} (q/r_i'),\qquad(1)$$

where Z_0 is the nuclear charge and r_i' specifies the position of the ith electron relative to the charge q. The summation on i is over all N electrons. This perturbation may be expressed in terms of electron coordinates r_i centered at the nucleus by using the familiar expansion in Legendre polynomials, valid for $R > r_i$:

$$1/r_i' = \sum_{L=0}^{\infty} (r_i^L/R^{L+1}) P_L(\cos\theta_i).\qquad(2)$$

Then, the interaction potential given by Eq. (1) becomes

$$V = [q(Z_0-N)]/R - q \sum_{L=1}^{\infty} \sum_{i=1}^{N} (r_i^L/R^{L+1}) P_L(\cos\theta_i).\qquad(3)$$

Since the first term on the right side of Eq. (3) is constant, it cannot polarize the electronic charge distribution and need not be considered further here. The nonconstant terms of Eq. (3) allow a convenient definition of the multipole polarizabilities when a single term in the multipole expansion is considered at a time. It is to be emphasized that these terms are considered separately not because the physical situation leading to Eq. (3) gives rise to multipole polarizabilities which are necessarily independent, but rather because by clever arrangement of external charges, the experimentalist can create electric fields resulting in potentials which approximate the individual terms of Eq. (3). Therefore, the individual multipole polarizabilities are of interest. Thus, if one considers the system to be perturbed by a potential containing the Lth Legendre polynomial, a 2^L pole polarizability is induced.

Following this procedure, the perturbing potential is written as

$$V_L = -\lambda \sum_{i=1}^{N} r_i^L P_L(\cos\theta_i),\qquad(4)$$

where $\lambda = q/R^{L+1}$. The total wave function for a nondegenerate atom or ion subjected to this perturbation may be written, to first order in λ, as

$$\phi = \phi^0 + \lambda\phi^1.\qquad(5)$$

It is now possible to complete the definition of polarizabilities and shielding factors.

The 2^L pole polarizability is defined as $(-1)^L L!$ times the ratio of the induced 2^L pole moment to the Lth-order gradient of the perturbing potential. The 2^Lth moment is defined as

$$\mu_{2L} = -\langle\phi| \sum_{i=1}^{N} r_i^L P_L(\cos\theta_i) |\phi\rangle.\qquad(6)$$

Since the Lth-order gradient at the nucleus due to the external point charge is simply $(-1)^L L!\lambda$, to first order in λ the 2^L pole polarizability is given by

$$\alpha_{2L} = -2\langle\phi^1| \sum_{i=1}^{N} r_i^L P_L(\cos\theta_i) |\phi^0\rangle.\qquad(7)$$

The associated 2^L pole shielding factor is defined as the ratio of the change in the Lth-order electric gradient at the nucleus due to the electron charge distribution to

[11] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).
[12] E. C. Clementi, A. D. McLean, P. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).
[13] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).

the Lth-order gradient due to the external charge alone. Physically, the change in gradient at the nucleus when the perturbing charge q is "turned on" is due to the moment induced in the originally spherically symmetric electronic charge distribution. Hence, once the first-order perturbed function ϕ^1 is calculated, both the polarizabilities and shielding factors can be obtained by performing the indicated quadratures. The electrostatic potential at the nucleus due to the electronic charge distribution is simply $-\sum_{i=1}^{N}(1/r_i)$. Taking the necessary derivatives of this quantity and evaluating the Lth-order gradient due to the external charge then gives, to first order in λ, for the 2^L pole shielding factor,

$$\gamma_{2}L = 2\langle\phi^1|\sum_{i=1}^{N}(P_L(\cos\theta_i)/r_i^{L+1})|\phi^0\rangle. \qquad (8)$$

The necessary task at hand then is to obtain the first-order perturbation function ϕ^1, and this is carried out in the present paper through the use of variation-perturbation theory in the uncoupled Hartree-Fock approximation.

B. Variation-Perturbation Theory and the Uncoupled Hartree-Fock Approximation

As discussed in the previous section, the Hamiltonian for an atom or ion subjected to a multipole perturbing potential may be written in the form

$$H = H^0 + V_L = H^0 + \lambda H^1, \qquad (9)$$

where $\lambda = q/R^{L+1}$, H^0 is the unperturbed Hamiltonian, and

$$H^1 = -\sum_{i=1}^{N} r_i^{L} P_L(\cos\theta_i). \qquad (10)$$

Following the usual arguments of perturbation theory[14] a sequence of equations is obtained, the first three of which are

$$(H^0 - E^0)\phi^0 = 0, \qquad (11)$$

$$(H^0 - E^0)\phi^1 + (H^1 - E^1)\phi^0 = 0, \qquad (12)$$

$$(H^0 - E^0)\phi^2 + (H^1 - E^1)\phi^1 = E^2\phi^0. \qquad (13)$$

Equations (12) and (13) yield immediately

$$E^1 = \langle\phi^0|H^1|\phi^0\rangle = 0, \qquad (14)$$

$$E^2 = \langle\phi^1|H^1|\phi^0\rangle. \qquad (15)$$

Equation (12) is solved by considering the functional

$$J(\phi) = \langle\phi|H^0 - E^0|\phi\rangle + 2\langle\phi|H^1|\phi^0\rangle \text{ (ϕ real)}. \qquad (16)$$

The condition that $J(\phi)$ have a stationary value is equivalent to Eq. (12) and that trial function ϕ for which $\delta J = 0$ is the first-order perturbation solution.

Also note that

$$J(\phi^1) = E^2 = -\tfrac{1}{2}\alpha_2 L, \qquad (17)$$

and that the second variation of $J(\phi)$ may be shown to be positive.[15]

The first assumption fundamental to the uncoupled Hartree-Fock approximation is that the exact infinite nuclear mass nonrelativistic Hamiltonian may be replaced by the Hartree-Fock Hamiltonian. That is,

$$H^0 = \sum_{i=1}^{N} h^0(i) - \sum_{i=1}^{N}\sum_{j=i+1}^{N}\langle x_i x_j|(1/r_{ij})(1-P_{ij})|x_i x_j\rangle. \qquad (18)$$

Here $h^0(i)$ is the one-particle Fock operator, P_{ij} permutes the coordinates of the ith and jth spin orbitals before integration, and the x_i are an orthonormal set of spin orbitals satisfying

$$(h^0(i) - \epsilon_i^0)x_i = 0. \qquad (19)$$

The variational procedure is equivalent to the solution of Eq. (12) if the necessary boundary conditions are satisfied and the trial function ϕ is completely flexible. However, the second assumption made is that the first-order perturbation function may be written in the form

$$\phi = \sum_{i=1}^{N} U_i(x_i^1), \qquad (20)$$

where[16]

$$U_i(x_i^1) = (x_1 x_2 \cdots x_i^1 \cdots x_N)$$

$$\equiv \frac{1}{(N!)^{1/2}}
\begin{vmatrix}
x_1(1) & x_1(2) & \cdots & x_1(N) \\
x_2(1) & x_2(2) & \cdots & x_2(N) \\
\vdots & & & \vdots \\
x_i^1(1) & x_i^1(2) & \cdots & x_i^1(N) \\
\vdots & & & \vdots \\
x_N(1) & x_N(2) & \cdots & x_N(N)
\end{vmatrix}. \qquad (21)$$

Here x_i^1 is the ith first-order perturbed spin orbital.

It is to be noted that the first assumption mentioned is not strictly independent of the second since the total unperturbed Hamiltonian may be written as

$$H_{\text{TOTAL}}^0 = H^0 + V_B, \qquad (22)$$

where V_B is the Brillouin perturbation,

$$V_B = -\sum_{i=1}^{N} u(i) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}[(1/r_{ij})$$

$$+ \langle x_i x_j|(1/r_{ij})(1-P_{ij})|x_i x_j\rangle] \qquad (23)$$

and

$$u(i) = \sum_{j=1}^{N}\langle x_j|(1/r_{ij})(1-P_{ij})|x_j\rangle. \qquad (24)$$

Now considering $V_L + V_B$ as a perturbation, the first-

[14] See, for example, H. A. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 122.

[15] M. Karplus and H. J. Kolker, J. Chem. Phys. 38, 1263 (1963).
[16] Notation similar to that used by J. C. Slater, *Quantum Theory of Atomic Structure II* (McGraw-Hill Book Company Inc., 1960), p. 76.

order perturbation equation is

$$(H^0 - E^0)\phi^1 + (V_L + V_B - E^1)\phi^0 = 0, \qquad (25)$$

and the associated functional becomes

$$J'(\phi) = \langle \phi | H^0 - E^0 | \phi \rangle + 2\langle \phi | V_L + V_B - E^1 | \phi^0 \rangle. \qquad (26)$$

However, for a trial function taken in the form of a sum of single excitation functions, Brillouin's theorem[17] assures us that V_B will not affect the form of the x_i^1. Indeed, we see

$$\langle \phi | V_B | \phi^0 \rangle = 0 \qquad (27)$$

for ϕ given by Eq. (20). Notice that this result does not imply that the uncoupled Hartree-Fock approximation is correct to first order in the Brillouin perturbation,[18] but only that the prime assumption in this approximation may be considered to be the chosen form of function Eq. (20). Indeed, ϕ given by Eq. (20) represents a poor trial function for the solution of Eq. (25), although it appears to be a good choice for solution of Eq. (12).

Substituting Eq. (20) into Eq. (16) gives

$$J(\phi) = \sum_{i=1}^{N} J_i(x_i^1), \qquad (28)$$

where

$$J_i(x_i^1) = \langle x_i^1 | h^0 - \epsilon_i^0 | x_i^1 \rangle + 2\langle x_i^1 | h^1 | x_i \rangle$$
$$- \sum_{j=1}^{N} \left[(\epsilon_j^0 - \epsilon_i^0) | \langle x_i^1 | x_j \rangle |^2 + 2\langle x_i^1 | x_j \rangle \langle x_i | h^1 | x_j \rangle \right] \qquad (29)$$

and

$$h^1 = r_i^L P_L(\cos\theta_i). \qquad (30)$$

The total functional $J(\phi)$ may be minimized by minimizing each of the subfunctionals $J_i(x_i^1)$ separately and, hence, the procedure is indeed uncoupled. The equations satisfied by the x_i^1 are seen to be

$$(h^0 - \epsilon_i^0)x_i^1 + h^1 x_i$$
$$= \sum_{j=1}^{N} \left[(\epsilon_j^0 - \epsilon_i^0)\langle x_i^1 | x_j \rangle + \langle x_i | h' | x_j \rangle \right] x_j. \qquad (31)$$

Equations (29) and (31) are obtained subject to no constraints on the functions x_i^1. The demand that the total wave function be normalized to first order may be satisfied by

$$\langle \phi^0 | \phi^0 \rangle = 1, \quad \langle \phi^1 | \phi^0 \rangle = 0. \qquad (32)$$

This condition leads to apparent constraints on the x_i^1 since

$$\langle \phi^1 | \phi^0 \rangle = \sum_{i=1}^{N} \langle x_i^1 | x_i \rangle = 0. \qquad (33)$$

[17] L. Brillouin, Actualitiés sci. ind. No. 71 (1933); No. 159 (1934); C. Moller and M. S. Plesset, Phys. Rev. 46, 618 (1934).
[18] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) A247, 245 (1958).

Equation (33) may be satisfied by setting

$$x_i^1 = x_i' - \langle x_i' | x_i \rangle x_i, \qquad (34)$$

where x_i' is subject to no constraint. The Dalgarno functional $J_i(x_i^1)$, however, is invariant to this substitution and it is easily seen that for x_i^1 given by Eq. (34),

$$J_i(x_i^1) = J_i(x_i'). \qquad (35)$$

In the uncoupled Hartree-Fock approximation, then, the trial first-order perturbed orbitals need not be explicitly orthogonalized to the associated unperturbed functions.

It is interesting to note that the variational method pioneered by Das and Bersohn, based on the functionals

$$J_i^0(x_i^1) = \langle x_i^1 | h^0 - \epsilon_i^0 | x_i^1 \rangle + 2\langle x_i^1 | h^1 - \epsilon_i^1 | x_i \rangle, \qquad (36)$$

is equivalent to the uncoupled Hartree-Fock approximation if the first-order perturbed orbital x_i^1 is properly orthogonalized to all unperturbed orbitals. This is seen by letting

$$x_i^1 = x_i' - \sum_{j=1}^{N} \langle x_i' | x_j \rangle x_j, \qquad (37)$$

where x_i' is unconstrained, and substituting into the functional Eq. (36), yielding

$$J_i^0(x_i^1) = J_i(x_i'). \qquad (38)$$

That is, the functional $J_i^0(x_i^1)$ becomes the Dalgarno functional $J_i(x_i')$ for x_i^1 given by Eq. (37). It is seen then that minimizing the functional $J_i^0(x_i^1)$, with x_i^1 subject to the constraint of being Schmidt orthogonalized to all unperturbed orbitals, is equivalent to minimizing the Dalgarno functionals $J_i(x_i')$ with x_i' unconstrained. This shows that the simple variational method of Das and Bersohn, based on the functionals $J_i^0(x_i^1)$, is identical with this uncoupled Hartree-Fock approximation if the orthogonality specified by Eq. (37) is maintained.

The uncoupled Hartree-Fock approximation leaves no chance at all for inconsistency concerning the manner in which orthogonality is maintained. It is merely necessary to minimize the Dalgarno functionals $J_i(x_i')$ where the trial perturbation orbitals x_i' are subject to no orthogonality constraints whatever. Once the x_i' are obtained, explicit expressions for the polarizability and shielding factor follow from Eqs. (7) and (8) in the form

$$\alpha_2 L = 2 \sum_{i=1}^{N} \left[\langle x_i' | h^1 | x_i \rangle - \sum_{j=1}^{N} \langle x_i | h^1 | x_j \rangle \langle x_i' | x_j \rangle \right], \qquad (39a)$$

$$\gamma_2 L = 2 \sum_{i=1}^{N} \left[\langle x_i' | h'^1 | x_i \rangle - \sum_{j=1}^{N} \langle x_i | h'^1 | x_j \rangle \langle x_i' | x_j \rangle \right], \qquad (39b)$$

where

$$h^1 = r_i^L P_L(\cos\theta_i) \qquad (40a)$$

and

$$h'^1 = P_L(\cos\theta_i)/r_i^{L+1}. \qquad (40b)$$

C. Solution of the One-Particle Equations

The one-particle equations (31) are solved by individually minimizing the associated functionals $J_i(x_i')$. The proper symmetry[19] of the first-order perturbed orbitals has been discussed by Foley *et al.*[13] and Dalgarno.[1] In general, x_i' is expressed as a series of radial functions times spherical harmonics. The terms of contributing symmetry associated with S- and P-unperturbed orbitals are then: for the dipole case, $S \rightarrow P$, $P \rightarrow S+D$; for the quadrupole case, $S \rightarrow D$, $P \rightarrow P+F$; and for the octupole case, $S \rightarrow F$, $P \rightarrow D+G$. Here, the arrow represents a symbolic transition connecting the symmetry of the unperturbed orbital with that of the first-order perturbed orbital.

The radial parts of the first-order perturbed orbitals are written as a polynomial in r times the unperturbed Hartree-Fock radial function for the orbital under consideration. This form has been found to be an adequate representation for polarizability calculations in the past.[7] The convergence of the method is considered in Sec. IV.

In all three calculations, dipole, quadrupole, and octupole, it is possible to write the first-order perturbed orbitals in the form

$$x_i' = h_i x_i. \qquad (41)$$

Explicit forms for the functions h_i for each case in real form are:

(1) Dipole Case
(a) s orbitals

$$h_i = Z \sum_{K=1}^{N_0} C_K{}^i r^{K-1}. \qquad (42a)$$

(b) P_x and P_y orbitals

$$h_i = Z \sum_{K=1}^{N_0} C_K{}^i r^{K-1}. \qquad (42b)$$

(c) P_z orbitals

$$h_i = \sum_{K=1}^{N_0} (r^{K-1}/Z)[D_K{}^i + (3Z^2 - r^2)C_K{}^i]. \qquad (42c)$$

(2) Quadrupole Case
(a) s orbitals

$$h_i = \tfrac{1}{2}(3Z^2 - r^2) \sum_{K=1}^{K_0} C_K{}^i r^{K-1}. \qquad (43a)$$

(b) P_x and P_y orbitals

$$h_i = \sum_{K=1}^{N} r^{K-1}[D_K{}^i r^2 + (5Z^2 - r^2)C_K{}^i]. \qquad (43b)$$

(c) P_z orbitals

$$h_i = \sum_{K=1}^{N_0} r^{K-1}[D_K{}^i r^2 + (5Z^2 - 3r^2)C_K{}^i]. \qquad (43c)$$

(3) Octupole Case
(a) s orbitals

$$h_i = \tfrac{1}{2}(5Z^3 - 3Zr^2) \sum_{K=1}^{N_0} C_K{}^i r^{K-1}. \qquad (44a)$$

(b) P_x and P_y orbitals

$$h_i = \sum_{K=1}^{N_0} r^{K-1}[ZD_K{}^i + (7Z^3 - 3Zr^2)C_K{}^i]. \qquad (44b)$$

(c) P_z orbitals

$$h_i = \sum_{K=1}^{N_0} (r^{K-1}/Z)[(3Z^2 - r^2)D_K{}^i$$
$$+ (35Z^4 - 30Z^2 r^2 + 3r^4)C_K{}^i]. \qquad (44c)$$

These explicit forms are now substituted into the Dalgarno functionals Eq. (29). For the ith orbital the condition $\delta J_i(x_i') = 0$ is equivalent to requiring

$$\partial J_i(x_i')/\partial C_K{}^i = 0,$$
$$\partial J_i(x_i')/\partial D_K{}^i = 0, \quad K = 1, 2, \cdots, N_0. \qquad (45)$$

These conditions give rise to two independent sets of linear equations

$$\sum_{L=1}^{N_0} A_{KL}{}^i C_L{}^i = -B_K{}^i,$$
$$\sum_{L=1}^{N_0} A_{KL}{}^i D_L{}^i = -\dot{B}_K{}^i, \quad K = 1, 2, \cdots, N_0 \qquad (46)$$

in all cases but s orbitals and P_x or P_y orbitals in the dipole case, where only the first set of equations are obtained. Explicit expressions for $A_{KL}{}^i$, $B_K{}^i$, $\dot{A}_{KL}{}^i$, and $\dot{B}_K{}^i$ for all cases are presented in the Appendix. These quantities are essentially sums of various moment integrals over the unperturbed orbitals and offer no special computational problem. Writing the first-order perturbed orbitals in the form given by Eq. (41) allows elimination of all two-electron integrals if it is assumed that the Hartree-Fock potential may be expressed in multiplicative form [cf., Eqs. (144) and (145) in Ref. 1]. The polarization and shielding-factor calculation is completed once the Eqs. (46) are solved for the $C_L{}^i$ and $D_L{}^i$.

III. NUMERICAL RESULTS

A FORTRAN program written by the authors is used on an IBM-7044 computer to carry out the calculation outlined above. In all cases the zeroth-order functions used are of the analytical Hartree-Fock type.[20,21]

Indication of the convergence of the method upon addition of more terms to the polynomial in the perturbed orbital may be seen in Table I. The three inert gases in Table I are used as test cases in a preliminary

[19] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 62.

[20] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).
[21] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), p. 47.

TABLE I. Convergence of the method for inert-gas atoms.

Atom[a]	Number of terms in perturbed orbital[b]	Total polarizability Dipole $(10^{-24}$ cm$^3)$	Total polarizability Quadrupole $(10^{-40}$ cm$^5)$	Total polarizability Octupole $(10^{-56}$ cm$^7)$
He	2	0.2204	0.0979	0.1166
	3	0.2204	0.0979	0.1166
	4	0.2204	0.0979	0.1166
	5	0.2204	0.0979	0.1166
Ne	2	0.3421	0.2575	0.2514
	3	0.3979	0.2576	0.3349
	4	0.4177	0.2577	0.3634
	5	0.4180	0.2577	0.3941
Ar	2	1.988	2.190	4.370
	3	2.355	2.195	5.391
	4	2.460	2.196	5.775
	5	2.461	2.196	6.077

[a] The Hartree-Fock functions used are: He—C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960), Table VI; Ne—L. M. Sachs, Phys. Rev. **124**, 1283 (1961); Ar—E. C. Clementi and D. Raimondi, J. Chem. Phys. **38**, 2686 (1963).
[b] The first-order perturbed orbitals are written in the form $x_i' = h_i x_i$, where h_i contains a polynomial in r with arbitrary coefficients. Convergence is exhibited in this table by observing the diminishing role of added terms.

calculation to determine the best lowest power of r in the perturbing function. The functions so obtained are then used for all other calculations.

Results for dipole polarizabilities are compared with the previous extensive calculation of Yoshimine and

TABLE II. Calculated and experimental values of dipole polarizabilities.

Atom or ion	Reference[a]	Present results	Previous calculation[b]	Experimental values[c]
H⁻	1	16.7	16.7	30.2
He	2	0.220	0.220	0.2068±0.0002
Li⁺	2	0.0304	0.0304	0.025
Be⁺⁺	2	0.00815	0.00815	0.007
B³⁺	2	0.00304	0.00304	0.0033
C⁴⁺	2	0.00138	0.00138	0.0015
Li	2	21.0	21.0	22.0±2
F⁻	3	1.89	1.81	0.99
Ne	4	0.418	0.409	0.398
Na⁺	5	0.165	0.163	0.17
Mg⁺⁺	2	0.0812	0.0801	0.10
Al³⁺	2	0.0453	0.0446	0.053
Si⁴⁺	2	0.0275	0.0271	0.043
Na	6	27.2	27.1, 22.9[d]	21.5±2
Mg	7	19.4	19.4	7.4±1.8
Cl⁻	3	6.61	6.23	3.05
Ar	8	2.44	2.32	1.63
K⁺	7	1.14	1.08	0.80
Ca⁺⁺	7	0.652	0.620	0.54
K	9	59.7	59.6, 44.4[d]	38±4
Ca	9	49.0	48.9	22.5±0.6

[a] References for Hartree-Fock functions are:
1. M. Yoshimine (unpublished).
2. E. C. Clementi, J. Chem. Phys. **38**, 996 (1963).
3. E. C. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964).
4. L. M. Sachs, Phys. Rev. **124**, 1283 (1961).
5. P. Bagus, T. Gilbert, H. D. Cohen, and C. C. J. Roothaan (to be published).
6. E. C. Clementi (unpublished).
7. E. C. Clementi, J. Chem. Phys. **38**, 1001 (1962).
8. P. Bagus (private communication).
9. E. C. Clementi (unpublished).
[b] Values published by M. Yoshimine and R. P. Hurst, Phys. Rev. **135**, A612 (1964). The Hartree-Fock functions used in this previous calculation are the same as those used in the present calculation. Exceptions noted are Sternheimer's results.
[c] Values taken from Dalgarno's review article, Advan. Phys. **11**, 281 (1962).
[d] R. M. Sternheimer, Phys. Rev. **127**, 1220 (1962).

Hurst,[7] and with available experimental values, in Table II. The contributions from each orbital to the quadrupole polarizability and shielding factor are given in Table III for selected ions and atoms. These values are of interest in view of previous calculations available in a number of approximations.

A comparison of present quadrupole polarizabilities and shielding factors with previous results for some ions of interest is presented in Table IV. Table V contains the calculated values of polarizabilities and shielding factors. These results are obtained using five terms in the perturbing polynomial.

IV. DISCUSSION

The convergence exhibited in Table I is seen to be quite satisfactory. A similar behavior is observed for each individual orbital, although convergence is somewhat better in the dipole and quadrupole cases than in the octupole case. The lack of convergence in the $P \to S$ dipole case mentioned by Burns[4] was not observed, substantiating the suggestion of Das[4] that proper orthogonalization is important in this context. In addition, the cancellation of the $S \to P$ and $P \to S$ contributions to the dipole polarizability mentioned by Burns[4] was not obtained in any of the present calculations, both of these quantities being positive. Although detailed convergence tests were not run for every atom or ion, the decreasing nature of the contribution to the polarizability from the third to fifth terms in the five-term polynomial indicated quite good convergence in all cases. It is, of course, naive to assume that the trial perturbed orbitals used $(x_i' = h_i x_i)$ reproduce in exact detail the "true" uncoupled Hartree-Fock perturbed functions. Indeed, Sternheimer[22] has pointed out that functions of this form, in some cases, contain spurious nodes. Dalgarno[1] has suggested these additional nodes should not be expected to affect polarizabilities significantly but that the shielding factors may be somewhat unreliable. Note, however, that Sternheimer's discussion[22] is based on solutions obtained from the approximate form (essentially Hartree perturbation theory) of the uncoupled Hartree-Fock procedure used in his calculation. The actual number of nodes obtained in a numerical integration procedure seems to be sensitive, as shown by Sternheimer, to the details of the procedure. What effect the exchange terms left out of Sternheimer's procedure would have on the actual number of nodes obtained is not clear.

In Table II, the calculated dipole polarizability values are seen to be in substantial agreement with experiment for the lighter atoms, but that agreement for atoms and ions with more than 10 electrons becomes quite poor. This disagreement may be attributed in large measure to the excessively diffuse nature of Hartree-Fock functions, as it is seen that in all cases the calculated dipole polarizabilities tend to be too large. The small differ-

[22] R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).

TABLE III. Orbital contributions to the quadrupole polarizability and shielding factor.[a]

Orbital contribution[b]	Polarizability (10^{-40} cm⁵)	Shielding factor	Polarizability (10^{-40} cm⁵)	Shielding factor
		Li⁺		Be
$1s \rightarrow d$	4.699×10^{-3}	0.2570	6.522×10^{-4}	0.1769
$2s \rightarrow d$			15.09	1.179
Total	4.699×10^{-3}	0.2570	15.10	1.356
		Na⁺		Al³⁺
$1s \rightarrow d$	1.078×10^{-6}	5.872×10^{-2}	3.842×10^{-7}	4.836×10^{-2}
$2s \rightarrow d$	1.007×10^{-2}	0.3720	2.152×10^{-3}	0.3118
$2p \rightarrow p+f$	5.380×10^{-2}	-4.150	6.952×10^{-3}	-2.596
Total	6.387×10^{-2}	-4.497	9.104×10^{-3}	-2.236
		Cl⁻ (1)		Cl⁻ (2)
$1s \rightarrow d$	5.886×10^{-7}	0.1379	8.584×10^{-8}	4.531×10^{-2}
$2s \rightarrow d$	2.743×10^{-4}	0.1924	2.709×10^{-4}	0.2115
$2p \rightarrow p+f$	6.496×10^{-4}	-0.5317	4.993×10^{-4}	-1.006
$3s \rightarrow d$	6.272×10^{-1}	0.7659	5.951×10^{-1}	0.7857
$3p \rightarrow p+f$	18.81	-67.13	11.19	-53.95
Total	19.44	-66.56	11.79	-53.91

[a] Hartree-Fock functions used are: Li⁺ and Al³⁺, E. C. Clementi, J. Chem. Phys. **38**, 996 (1963); Be, C. C. J. Roothan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960), Table VI; Na⁺, P. Bagus, T. Gilbert, H. D. Cohen, and C. C. J. Roothan (to be published); Cl⁻ (1), R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961); Cl⁻ (2), E. C. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).
[b] Contribution from both spins included.

ences between the currently reported dipole polarizability values and those of Yoshimine and Hurst and due to the neglect of $P \rightarrow S$ contribution in the latter calculations. This neglect is seen to be quite negligible in most cases. In this same table are given Sternheimer's[2] results for Na and K. It is of interest to note that his values for these atoms are in much better agreement with experiment than those of the present work.

The results of Table III are in substantial agreement with previous properly orthogonalized variational calculations, except for the case of Cl⁻ using Watson and Freeman's function. Some of the differences between previous variational calculations for the quadrupole shielding factor and Watson and Freeman's[8] more elaborate method may be accounted for by the choice of Hartree-Fock function used. The neglect of self-consistancy in the present work also contributes to this discrepancy. This is shown in Table IV where explicit comparisons are presented.

The results in Table V substantiate the previous conclusions of Sternheimer[2] concerning the sensitivity of polarizabilities and shielding factors to the choice of Hartree-Fock functions. This is especially noticeable in the case of negative ions. Further, from Table V it is of interest to compare Sternheimer's[2] dipole shielding factors for F⁻ and Na⁺ (1.43 and 1.15, respectively) with our results for these same ions (1.72 and 1.27). Since the exact theoretical values are 1.11 and 0.91, respectively, this difference probably reflects the inherent error of the present variational method as compared with Sternheimer's numerical procedure. A similar effect is noted on comparing Sternheimer's[2] quadrupole shielding factor for K⁺ with that presented in this table. Here Sternheimer obtained -17.32 whereas the value we obtain is -12.17. Other previously calculated quadrupole polarizabilities and shielding factors may be found in Ref. (1) while the only extensive theoretical

values of octupole polarizabilities available for comparison seem to be those published by Burns[23] and Stewart.[24]

The dipole shielding factors γ_2 are seen to differ greatly from the known exact values[1,22] (i.e., $\gamma_2 = N/Z_0$ where N is the number of electrons and Z_0 is the nuclear charge). Some of the discrepancies may be due to near nS, nP degeneracy,[7] in which case doubt is cast on the

TABLE IV. Comparison of quadrupole polarizabilities and shielding factors with previous calculations.

Ion	Polarizability (10^{-40} cm⁵) Present results[a]	Previous calculation[b]	Shielding factor Present results[a]	Previous calculation[b]
Na⁺	0.06417 (1)	0.0670²	$-$ 4.514 (1)	$-4.1$¹
	0.06416 (2)	0.0634³	-4.505 (2)	$-4.5$²
	0.06387 (3)	0.0649⁸	-4.497 (3)	$-4.6$³
Al³⁺	0.9104×10^{-2}	1.01×10^{-2} (2)	-2.236	$-2.6$²
		0.915×10^{-2} (9)		
Cl⁻	19.44 (1)	13.8¹⁰	-66.56 (1)	$-56.6$¹
	11.79 (2)	13.1⁴	-53.91 (2)	$-50.1$⁴
				$-49.3$⁵
				$-55.5$⁶
				$-87.5$⁷

[a] The Hartree-Fock functions used are: Al³⁺ and Na⁺ (1), E. C. Clementi, J. Chem. Phys. **38**, 996 (1963); Na⁺ (2), L. M. Sachs, Phys. Rev. **124**, 1283 (1961); Na⁺ (3), P. Bagus, T. Gilbert, H. D. Cohen, and C. C. J. Roothaan (to be published); Cl⁻ (1), R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961); Cl⁻ (2), E. C. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).
[b] Superscripts refer to the following references:
1. R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).
2. T. P. Das and R. Bersohn, Phys. Rev. **102**, 360 (1956).
3. R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).
4. G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961).
5. E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).
6. P. G. Khubchandani, R. R. Sharma, and T. P. Das, Phys. Rev. **126**, 594 (1962).
7. R. E. Watson and A. J. Freeman, Phys. Rev. **131**, 250 (1963).
8. G. Burns, Phys. Rev. **115**, 357 (1959).
9. G. Burns, J. Chem. Phys. **31**, 1253 (1959).
10. R. M. Sternheimer, Phys. Rev. **107**, 1565 (1957).

²³ G. Burns, J. Chem. Phys. **31**, 1253 (1959).
²⁴ A. L. Stewart, Proc. Phys. Soc. (London) **77**, 447 (1961).

TABLE V. Multipole polarizabilities and shielding factors.

Atom or ion	Reference[a]	Dipole Polarizability (10⁻²⁴ cm³)	Dipole Shielding factor[b]	Quadrupole Polarizability (10⁻⁴⁰ cm⁵)	Quadrupole Shielding factor	Octupole Polarizability (10⁻⁵⁶ cm⁷)	Octupole Shielding factor
H⁻	1	8.211	2.695	47.50	1.051	745.3	0.3672
	2	16.68	3.328	94.76	1.149	1487.	0.5317
He	3	0.2204	1.235	0.9790×10^{-1}	0.4189	0.1166	0.2119
	4	0.2203	1.235	0.9806×10^{-1}	0.4145	0.1196	0.1783
	5	0.2204	1.235	0.9795×10^{-1}	0.4183	0.1168	0.2107
Li⁺	4	0.3036×10^{-1}	0.7628	0.4699×10^{-2}	0.2570	0.1940×10^{-2}	0.1288
	5	0.3036×10^{-1}	0.7628	0.4695×10^{-2}	0.2567	0.1931×10^{-2}	0.1285
Be⁺⁺	4	0.8153×10^{-2}	0.5520	0.6424×10^{-3}	0.1857	0.1367×10^{-3}	0.9226×10^{-1}
B³⁺	4	0.3037×10^{-2}	0.4326	0.1435×10^{-3}	0.1453	0.1816×10^{-4}	0.7288×10^{-1}
C⁴⁺	4	0.1377×10^{-2}	0.3556	0.4330×10^{-4}	0.1193	0.3625×10^{-5}	0.5994×10^{-1}
N⁵⁺	4	0.7118×10^{-3}	0.3019	0.1596×10^{-4}	0.1011	0.9487×10^{-6}	0.5078×10^{-1}
Li	3	21.02	4.003	65.19	1.358	493.4	0.7032
	6	20.97	3.608	61.53	1.083	486.1	0.5362
	4	21.00	3.610	62.01	1.079	495.9	0.5079
	5	20.98	3.608	61.64	1.079	488.1	0.5041
Be⁺	4	2.478	2.268	2.308	0.7088	5.779	0.4228
B⁺⁺	4	0.6540	1.669	0.3002	0.5461	0.3679	0.2557
C³⁺	4	0.2448	1.323	0.6713×10^{-1}	0.4508	0.4886×10^{-1}	0.1812
N⁴⁺	4	0.1119	1.096	0.2044×10^{-1}	0.3842	0.9872×10^{-1}	0.1535
O⁵⁺	4	0.5835×10^{-1}	0.9359	0.7613×10^{-2}	0.3340	0.2619×10^{-2}	0.1445
Li⁻	7	289.2	8.767	4754.	2.642	$2188.\times10^{2}$	1.087
Be	3	9.523	4.496	15.10	1.356	66.31	0.5950
	6	9.525	4.496	15.10	1.349	66.25	0.6508
	4	9.541	4.496	15.27	1.355	68.45	0.6042
	5	9.522	4.496	15.08	1.354	66.03	0.6126
B⁺	4	1.957	3.153	1.256	0.9996	2.230	0.4369
C⁺⁺	4	0.6532	2.435	0.2262	0.8021	0.2122	0.3311
N³⁺	4	0.2804	1.987	0.6135×10^{-1}	0.6721	0.3596×10^{-1}	0.2735
O⁴⁺	4	0.1404	1.678	0.2127×10^{-1}	0.5798	0.8581×10^{-2}	0.2351
F⁵⁺	4	0.7809×10^{-1}	1.454	0.8693×10^{-2}	0.5107	0.2567×10^{-2}	0.2061
O⁻⁻	8	65.88	1.712	399.8	−429.4	6842.	−29.30
	9	134.3	1.384	1044.	−950.5	2120.	−88.85
F⁻	10	1.953	1.695	3.457	−23.03	20.47	−3.172
	11	1.904	1.722	2.817	−22.15	12.60	-0.3849×10^{-1}
	5	1.902	1.704	2.818	−22.12	12.61	-0.7624×10^{-1}
	9	1.893	1.723	2.769	−22.00	12.21	0.2011×10^{-1}
Ne	11	0.4733	1.459	0.4611	−9.262	1.494	−1.368
	10	0.4180	1.460	0.2577	−7.810	0.3941	0.9379
	6	0.4236	1.440	0.2698	−7.956	0.4324	0.8667
	4	0.4241	1.478	0.2689	−7.937	0.4306	0.8605
	5	0.4212	1.458	0.2624	−7.872	0.4105	0.8282
Na⁺	4	0.1659	1.313	0.6417×10^{-1}	−4.514	0.5605×10^{-1}	0.9326
	10	0.1654	1.273	0.6416×10^{-1}	−4.505	0.5565×10^{-1}	0.9920
	5	0.1654	1.269	0.6387×10^{-1}	−4.497	0.5527×10^{-1}	0.8638
Mg⁺⁺	4	0.8122×10^{-1}	1.105	0.2188×10^{-1}	−3.038	0.1232×10^{-1}	0.8597
Al³⁺	4	0.4525×10^{-1}	0.9981	0.9104×10^{-2}	−2.236	0.3651×10^{-2}	0.7741
Si⁴⁺	4	0.2746×10^{-1}	0.9060	0.4317×10^{-2}	−1.743	0.1291×10^{-2}	0.6929
P⁵⁺	4	0.1774×10^{-1}	0.8289	0.2247×10^{-2}	−1.412	0.5232×10^{-3}	0.6244
Na	12	27.16	4.119	91.64	−3.835	788.3	1.716
	13	27.17	4.143	89.85	−3.657	751.3	1.262
	12	27.06	4.052	90.24	−3.663	758.1	1.920
Mg⁺	13	5.510	3.150	7.774	−2.472	27.99	1.233
Al⁺⁺	13	2.050	2.603	1.625	−1.787	3.164	1.157
Si³⁺	13	0.9940	2.267	0.5192	−1.353	0.6447	1.043
P⁴⁺	13	0.5558	2.015	0.2085	−1.059	0.1827	0.8665
S⁵⁺	13	0.3402	1.817	0.9735×10^{-1}	−0.8502	0.6375×10^{-1}	0.7112
Na⁻	14	293.7	9.244	3371.	−2.131	92540.	0.9756
Mg	13	19.38	5.607	40.36	−1.776	214.3	1.516
Al⁺	13	5.893	4.440	6.208	−1.270	16.65	1.433
Si⁺⁺	13	2.566	3.757	1.657	−0.8995	2.657	1.101
P³⁺	13	1.347	3.284	0.5975	−0.6502	0.6508	1.038
S⁴⁺	13	0.7919	2.928	0.2589	−0.4783	0.2002	0.9847
Cl⁵⁺	13	0.5021	2.648	0.1269	−0.3567	0.7446×10^{-1}	0.9364
Cl⁻	15	7.772	2.719	19.44	−66.56	163.5	21.03
	14	6.605	2.619	11.79	−53.91	68.15	29.10
Ar	16	1.441	4.775	0.8381	−5.146	1.291	9.356
	12	2.141	4.532	1.662	−19.85	3.791	11.43
	13	2.410	6.884	2.062	−25.22	5.367	17.68
	17	2.461	7.363	2.196	−25.58	6.077	21.53
	18	2.436	6.799	2.178	−25.83	6.000	17.62
	15	2.829	14.15	2.940	−30.19	11.95	−3.724

TABLE V (continued)

Atom or ion	Reference[a]	Dipole Polarizability $(10^{-24}$ cm$^3)$	Dipole Shielding factor[b]	Quadrupole Polarizability $(10^{-40}$ cm$^5)$	Quadrupole Shielding factor	Octupole Polarizability $(10^{-56}$ cm$^7)$	Octupole Shielding factor
K$^+$	13	1.135	2.693	0.7194	-12.17	1.223	12.38
Ca^{++}	13	0.6520	2.354	0.3088	-12.12	0.3706	9.253
Sc^{3+}	13	0.4111	2.130	0.1524	-9.461	0.1375	7.333
Ti^{4+}	13	0.2759	1.958	0.8296×10^{-1}	-7.721	0.5886×10^{-1}	5.969
V^{5+}	13	0.1939	1.812	0.4850×10^{-1}	-6.503	0.2783×10^{-1}	4.952
K	12	59.69	6.031	277.4	-15.70	3005.	12.26
Ca$^+$	12	14.25	4.895	30.14	-11.91	137.7	10.58
K$^-$	12	671.5	12.28	$1351.\times10^1$	-14.33	$6804.\times10^2$	9.891
Ca	12	49.02	7.904	161.3	-11.26	1313.	10.93

[a] References for Hartree-Fock functions used are:
1. C. C. J. Roothan and A. W. Weiss (unpublished).
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[b] The dipole shielding factor γ_2 can be shown to be given exactly by $\gamma_2 = N/Z_0$, where N is the number of electrons and Z_0 is the nuclear charge.

associated quadrupole and octupole values. In addition, as indicated above, the form of the perturbed $3P$-orbital used in the dipole calculation contains a spurious node when compared with Sternheimer's numerical result. This affects the 18-, 19-, and 20-electron dipole calculation.

In view of the generally good convergence observed, it is doubtful that a more general r dependence for the perturbation function would significantly alter the calculated polarizability values. This does not seem to be the case for the dipole shielding factor, however. The numerical results quoted here, then, may be considered to be the uncoupled Hartree-Fock results for dipole, quadrupole, and octupole polarizabilities and for quadrupole and octupole shielding factors. If the experimental values for dipole polarizabilities may be used as a guide, it is evident that the calculated values for the polarizabilities for second and third row atoms are too large by a factor of 1.25 to 1.5, although the first-row atom values are more reliable. These remarks do not apply to those cases where the dipole-shielding factors differ greatly from the known exact values. In these cases, where, as mentioned above, most of the discrepancies are expected to be in large measure due to the inadequate nature of a single configurational zeroth-order function, the calculated polarizability values are probably too large by a factor of 2.0 to 2.5. In addition, for some of the negative ions, in particular O^{--} and Na$^-$, the polarizability values are not reliable in view of the

great difficulty in constructing good Hartree-Fock functions for these systems.

It is felt that the uncoupled Hartree-Fock approximation represents a simple and adequate method for obtaining meaningful atomic parameters and for assessing the quality of zeroth-order Hartree-Fock functions. As yet it is not certain whether a more elaborate self-consistent scheme, such as that being currently pursued by Cohn,[25] will cast serious doubt on the utility of the uncoupled method. The currently reported values for polarizabilities and shielding factors are felt, then, to be adequate for such tasks as estimating term values in the van der Waals force equation,[26] estimating binding energies in ionic substances, interpreting nuclear quadrupole coupling constants,[3] and for discussing nuclear-spin transitions induced by ultrasonic waves[27] and spin-lattice relaxation times.[28]

ACKNOWLEDGMENTS

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APPENDIX

Explicit expressions for the coefficients $A_{KL}{}^i$, $B_K{}^i$, $\dot{A}_{KL}{}^i$, and $\dot{B}_K{}^i$ appearing in Eq. (46) are given here.

1. Dipole Case

(a) s and p_x or p_y orbitals

$$A_{KL}{}^i = \langle x_i | (KL-1)Z^2 r^{K+L-4} + r^{K+L-2} | x_i \rangle - 2 \sum_{j=1}^{N} (\epsilon_j{}^0 - \epsilon_i{}^0) \langle x_i | Z r^{K-1} | x_j \rangle \langle x_i | Z r^{L-1} | x_j \rangle ,$$

$$B_K{}^i = 2 \langle x_i | Z^2 r^{K-1} | x_i \rangle - 2 \sum_{j=1}^{N} \langle x_i | Z r^{K-1} | x_j \rangle \langle x_i | Z | x_j \rangle .$$

(b) p_z orbitals

$$A_{KL}{}^i = \langle x_i | (KL-2)(1/Z^2) r^{K+L} + 6(8-KL) r^{K+L-2} + 9(KL-6) Z^2 r^{K+L-4} | x_i \rangle$$
$$- 2 \sum_{j=1}^{N} (\epsilon_j{}^0 - \epsilon_i{}^0) \langle x_i | (1/Z)(3Z^2 - r^2) r^{K-1} | x_j \rangle \langle x_i | (1/Z)(3Z^2 - r^2) r^{L-1} | x_j \rangle ,$$

$$B_K{}^i = 2 \langle x_i | (3Z^2 - r^2) r^{K-1} | x_i \rangle - 2 \sum_{j=1}^{N} \langle x_i | (1/Z)(3Z^2 - r^2) r^{K-1} | x_j \rangle \langle x_i | Z | x_j \rangle ,$$

$$A_{KL}{}^i = \langle x_i | (KL - 2K - 2L + 2)(1/Z^2) r^{K+L-4} | x_i \rangle - 2 \sum_{j=1}^{N} (\epsilon_j{}^0 - \epsilon_i{}^0) \langle x_i | (1/Z) r^{K-1} | x_j \rangle \langle x_i | (1/Z) r^{L-1} | x_j \rangle ,$$

$$\dot{B}_K{}^i = 2 \langle x_i | r^{K-1} | x_i \rangle - 2 \sum_{j=1}^{N} \langle x_i | (1/Z) r^{K-1} | x_j \rangle \langle x_i | Z | x_j \rangle .$$

2. Quadrupole Case

(a) s orbitals

$$A_{KL}{}^i = \tfrac{1}{4} \langle x_i | (KL+K+L+1) r^{K+L} - 6(KL+K+L-5) Z^2 r^{K+L-2} + 9(KL+K+L-3) Z^4 r^{K+L-4} | x_i \rangle$$
$$- \tfrac{1}{2} \sum_{j=1}^{N} (\epsilon_j{}^0 - \epsilon_i{}^0) \langle x_i | (3Z^2 - r^2) r^{K-1} | x_j \rangle \langle x_i | (3Z^2 - r^2) r^{L-1} | x_j \rangle ,$$

$$B_K{}^i = \tfrac{1}{2} \langle x_i | (3Z^2 - r^2)^2 r^{K-1} | x_i \rangle - \tfrac{1}{2} \sum_{j=1}^{N} \langle x_i | (3Z^2 - r^2) | x_j \rangle \langle x_i | (3Z^2 - r^2) r^{K-1} | x_j \rangle .$$

(b) p_x or p_y orbitals

$$A_{KL}{}^i = \langle x_i | (KL+K+L+1) r^{K+L} - 10(KL+K+L-9) Z^2 r^{K+L-2} + 25(KL+K+L-3) Z^4 r^{K+L-4} | x_i \rangle$$
$$- 2 \sum_{j=1}^{N} (\epsilon_j{}^0 - \epsilon_i{}^0) \langle x_i | (5Z^2 - r^2) r^{K-1} | x_j \rangle \langle x_i | (5Z^2 - r^2) r^{L-1} | x_j \rangle ,$$

$$B_K{}^i = \langle x_i | (3Z^2 - r^2)(5Z^2 - r^2) r^{K-1} | x_i \rangle - \sum_{j=1}^{N} \langle x_i | (5Z^2 - r^2) r^{K-1} | x_j \rangle \langle x_i | 3Z^2 - r^2 | x_j \rangle ,$$

$$A_{KL}{}^i = \langle x_i | (KL+K+L+1) r^{K+L} | x_i \rangle - 2 \sum_{j=1}^{N} (\epsilon_j{}^0 - \epsilon_i{}^0) \langle x_i | r^{K+1} | x_j \rangle \langle x_i | r^{L+1} | x_j \rangle ,$$

$$\dot{B}_K{}^i = \langle x_i | (3Z^2 - r^2) r^{K+1} | x_i \rangle - \sum_{j=1}^{N} \langle x_i | r^{K+1} | x_j \rangle \langle x_i | 3Z^2 - r^2 | x_j \rangle .$$

(c) p_z orbitals

$$A_{KL}{}^i = \langle x_i | 9(KL+K+L+1) r^{K+L} + (70 - 30(KL+K+L)) Z^2 r^{K+L-2} + 25(KL+K+L-3) Z^4 r^{K+L-4} | x_i \rangle$$
$$- 2 \sum_{j=1}^{N} (\epsilon_j{}^0 - \epsilon_i{}^0) \langle x_i | (5Z^2 - 3r^2) r^{K-1} | x_j \rangle \langle x_i | (5Z^2 - 3r^2) r^{L-1} | x_j \rangle ,$$

$$B_K{}^i = \langle x_i | (3Z^2 - r^2)(5Z^2 - 3r^2)r^{K-1} | x_i \rangle - \sum_{j=1}^N \langle x_i | (5Z^2 - 3r^2)r^{K-1} | x_j \rangle \langle x_i | 3Z^2 - r^2 | x_j \rangle,$$

$$A_{KL}{}^i = \langle x_i | (KL + K + L + 1)r^{K+L} | x_i \rangle - 2 \sum_{j=1}^N (\epsilon_j{}^0 - \epsilon_i{}^0)\langle x_i | r^{K+1} | x_j \rangle \langle x_i | r^{L+1} | x_j \rangle,$$

$$\dot{B}_K{}^i = \langle x_i | (3Z^2 - r^2)r^{K+1} | x_i \rangle - \sum_{j=1}^N \langle x_i | r^{K+1} | x_j \rangle \langle x_i | 3Z^2 - r^2 | x_j \rangle.$$

3. Octupole Case

(a) S orbitals

$$A_{KL}{}^i = \tfrac{1}{4}\langle x_i | 9r^{K+L+2} + 9(KL + 2K + 2L - 7)Z^2 r^{K+L} - 30(KL + 2K + 2L - 6.5)Z^4 r^{K+L-2}$$

$$+ 25(KL + 2K + 2L - 5)Z^6 r^{K+L-4} | x_i \rangle - \tfrac{1}{2} \sum_{j=1}^N (\epsilon_j{}^0 - \epsilon_i{}^0)\langle x_i | (5Z^3 - 3Zr^3)r^{K-1} | x_j \rangle \langle x_i | (5Z^3 - 3Zr^2)r^{L-1} | x_j \rangle,$$

$$B_K{}^i = \tfrac{1}{2}\langle x_i | (25Z^6 + 9Z^2 r^4 - 30Z^4 r^2)r^{K-1} | x_i \rangle - \tfrac{1}{2} \sum_{j=1}^N \langle x_i | (5Z^3 - 3Zr^2)r^{K-1} | x_j \rangle \langle x_i | 5Z^3 - 3Zr^2 | x_j \rangle.$$

(b) p_x or p_y orbitals

$$A_{KL}{}^i = \langle x_i | 49(KL + 2K + 2L - 5)Z^6 r^{K+L-4}$$

$$+ (399 - 42(KL + 2K + 2L))Z^4 r^{K+L-2} + 9(KL + 2K + 2L - 11)Z^2 r^{K+L} + 9r^{K+L+2} | x_i \rangle$$

$$- 2 \sum_{j=1}^N (\epsilon_j{}^0 - \epsilon_i{}^0)\langle x_i | (7Z^3 - 3Zr^2)r^{K-1} | x_j \rangle \langle x_i | (7Z^3 - 3Zr^2)r^{L-1} | x_j \rangle,$$

$$B_K{}^i = \langle x_i | (5Z^3 - 3Zr^2)(7Z^3 - 3Zr^2)r^{K-1} | x_i \rangle - \sum_{j=1}^N \langle x_i | (7Z^3 - 3Zr^2)r^{K-1} | x_j \rangle \langle x_i | 5Z^3 - 3Zr^2 | x_j \rangle,$$

$$A_{KL}{}^i = \langle x_i | (KL - 1)Z^2 r^{K+L-4} + r^{K+L-2} | x_i \rangle - 2 \sum_{j=1}^N (\epsilon_j{}^0 - \epsilon_i{}^0)\langle x_i | Zr^{K-1} | x_j \rangle \langle x_i | Zr^{L-1} | x_j \rangle,$$

$$\dot{B}_K{}^i = \langle x_i | (5Z^4 - 3Z^2 r^2)r^{K-1} | x_i \rangle - \sum_{j=1}^N \langle x_i | Zr^{K-1} | x_j \rangle \langle x_i | 5Z^3 - 3Zr^2 | x_j \rangle.$$

(c) p_z orbitals

$$A_{KL}{}^i = \langle x_i | 1225(KL + 2K + 2L - 14)Z^6 r^{K+L-4} + (32\,200 - 2100(KL + 2K + 2L))Z^4 r^{K+L-2}$$

$$+ (1215(KL + 2K + 2L) - 19\,650)Z^2 r^{K+L} + (3240 - 180(KL + 2K + 2L))r^{K+L+2}$$

$$+ (9(KL + 2K + 2L) + 18)(1/Z^2)r^{K+L+4} | x_i \rangle - 2 \sum_{j=1}^N (\epsilon_j{}^0 - \epsilon_i{}^0)$$

$$\times \langle x_i | (35Z^4 - 30Z^2 r^2 + 3r^4)(1/Z)r^{K-1} | x_j \rangle \langle x_i | (35Z^4 - 30Z^2 r^2 + 3r^3)(1/Z)r^{L-1} | x_j \rangle,$$

$$B_K{}^i = \langle x_i | (5Z^2 - 3r^2)(35Z^4 - 30Z^2 r^2 + 3r^4)r^{K-1} | x_i \rangle - \sum_{j=1}^N \langle x_i | (35Z^4 - 30Z^2 r^2 + 3r^4)(1/Z)r^{K-1} | x_j \rangle \langle x_i | 5Z^3 - 3Zr^2 | x_j \rangle,$$

$$A_{KL}{}^i = \langle x_i | 9(KL - 6)Z^2 r^{K+L-4} + (48 - 6KL)r^{K+L-2} + (KL - 2)(1/Z^2)r^{K+L} | x_i \rangle$$

$$- 2 \sum_{j=1}^N (\epsilon_j{}^0 - \epsilon_i{}^0)\langle x_i | (3Z^2 - r^2)(1/Z)r^{K-1} | x_j \rangle \langle x_i | (3Z^2 - r^2)(1/Z)r^{L-1} | x_j \rangle,$$

$$\dot{B}_K{}^i = \langle x_i | (5Z^2 - 3r^2)(3Z^2 - r^2)r^{K-1} | x_i \rangle - \sum_{j=1}^N \langle x_i | (3Z^2 - r^2)(1/Z)r^{K-1} | x_j \rangle \langle x_i | 5Z^3 - 3Zr^2 | x_j \rangle.$$