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Magnetic Quadrupole Polarizability of Closed-Shell Atoms*

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The magnetic quadrupole polarizability tensor determines the quadrupole moment induced in an atomic system by a nonuniform external magnetic field. From the analogy to the corresponding electric field case, this quantity is defined and simplified for a spherically symmetric system in an axially symmetric external field. Expressions are presented for the magnetic vector potential corresponding to the first three terms of a Taylor-series expansion for the magnetic field vector, and the Hamiltonian operator is obtained for a many-electron atom in an axially symmetric magnetic field with first-order gradients. Calculations are presented for the magnetic quadrupole polarizability for closed-shell atoms and ions with two to eighteen electrons. These calculations employ the fully coupled Hartree-Fock variation-perturbation procedure. The magnetic quadrupole polarizability shows a rapid decrease with atomic number within each isoelectronic series. Positive values are obtained for all atoms and ions except Li^-, Be, and Na^-.

I. INTRODUCTION

Of late, much interest has centered on the electric and magnetic properties of atoms and molecules in external fields. For example, calculations have recently been made of the electric dipole, quadrupole, and octupole polarizabilities,[1] the magneto-electric susceptibility, and the electric dipole hyperpolarizability[1,2] of atomic systems. Furthermore, calculations of the magnetic susceptibility (magnetic dipole polarizability) have been made from the early days of quantum mechanics.[3] The work reported in this paper represents a logical extension of efforts to understand the influence of large external fields on the electric and magnetic properties of atoms. Specifically considered is the response of an atom to a nonuniform magnetic field.

The advent of very high magnetic fields, e.g., 10^6 G, makes possible the intentional generation of field gradients large enough to cause a significant variation in the magnetic field within the dimensions of an atom or molecule. Thus, the effect of a gradient in the external magnetic field on the energy of a molecule may be measureable. Furthermore, very large magnetic field gradients exist between paramagnetic ions within a crystal, so that the energy of an impurity ion is strongly affected by the gradient. Mattis[4] also suggests that the attraction of noble gases to the surface of ferromagnetic material and the Knight shift in superconductors could be partially explained by the perturbation of the energy of a closed-shell system by an inhomogeneous magnetic field.

In the following sections we present the magnetic multipole expansion, define the magnetic quadrupole polarizability tensor, and simplify it for a spherically symmetric atomic system in an axially symmetric field. The magnetic vector potential and Hamiltonian operator are then obtained and the Hartree-Fock variation-perturbation procedure is described for calculating the second-order energy of an atomic system in a magnetic field gradient. We then describe the method of computation of the magnetic quadrupole polarizability in more detail and present and discuss the calculated values.

II. MAGNETIC MULTIPOLE EXPANSION

The expansion of the energy of a localized distribution of moving charges or currents in an external magnetic field $\vec{H}$ is given in terms of the current-density distribution $\vec{j}$ by

$$W = W_0 + W' + W'' + \cdots , \tag{1}$$

where

$$W_0 = -\vec{H}_0 \cdot \vec{M} , \tag{2}$$

$$W' = -\tfrac{1}{6}\sum_{i,j} \frac{\partial H_i}{\partial x_j}(0) T_{ij} , \tag{3}$$

$$W'' = -\tfrac{1}{24}\sum_{i,j,k} \frac{\partial^2 H_i}{\partial x_j \partial x_k}(0) R_{ijk} . \tag{4}$$

In (2) $\vec{M}$ is the total magnetic dipole moment:

$$\vec{M} \equiv 1/2c \int \vec{r} \times \vec{j}\, d^3x , \tag{5}$$

while in (3) the magnetic quadrupole moment tensor T_{ij} is defined as

$$T_{ij} \equiv \frac{1}{c}\sum_{k,l} \epsilon_{ikl} \int (3x_j x_k - r^2 \delta_{jk}) j_l \, d^3x , \tag{6}$$

where x_j is the jth component of the position vector $\vec{r}$, and r is its magnitude. In addition, the tensor T_{ij} is traceless, i.e.,

$$\textstyle\sum_i T_{ii} = 0 .$$

Similarly, in (4) the magnetic octupole moment tensor R_{ijk} is defined as

$$R_{ijk} \equiv \frac{6}{c}\sum_{l,m} \epsilon_{ilm} \int x_l x_j x_k j_m \, d^3x \quad . \tag{7}$$

III. MAGNETIC QUADRUPOLE POLARIZABILITY FOR SPHERICALLY SYMMETRIC SYSTEMS

When a nonuniform external magnetic field is applied to an atomic system, the gradient in the magnetic field polarizes the system so as to generate a magnetic quadrupole moment proportional to the gradient. Thus, one may define the magnetic quadrupole polarizability tensor γ_{ijkl} so that the quadrupole moment is given by

$$T_{ij} = \sum_{k,l} \gamma_{ijkl} \frac{\partial H_k}{\partial x_l}(0) , \tag{8}$$

or so that the magnetic quadrupole energy term (3) is

$$W' = -\tfrac{1}{6}\sum_{i,j,k,l} \gamma_{ijkl} \frac{\partial H_k}{\partial x_l}(0) \frac{\partial H_i}{\partial x_j}(0) . \tag{9}$$

The magnetic quadrupole polarizability tensor can be simplified (i.e., reduced to fewer components) for the case of spherically symmetric systems by considering the most general form for a fourth-order isotropic tensor[2]:

$$\gamma_{ijkl} = \lambda\, \delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \nu(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) ,$$

and noting that neither λ nor ν contribute to T_{ij} or the energy W'. Hence, taking $\gamma = 2\mu$, one obtains

$$\gamma_{ijkl} = (\gamma/2)(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) , \tag{10}$$

$$T_{ij} = \gamma \frac{\partial H_i}{\partial x_j}(0) , \tag{11}$$

$$W' = -\frac{1}{6}\gamma \sum_{i,j}\left(\frac{\partial H_i}{\partial x_j}(0)\right)^2 . \tag{12}$$

Therefore, for the spherically symmetric system, the fourth-order tensor γ_{ijkl} is determined in terms of a single parameter γ, henceforth called the *magnetic quadrupole polarizability*.

The calculation of γ can be further simplified, without loss of generality, by assuming an external field which is axially symmetric about the z axis. In this case

$$\begin{aligned} &H_1 = -\tfrac{1}{2}H' x_1 = -\tfrac{1}{2}H' x , \\ &H_2 = -\tfrac{1}{2}H' x_2 = -\tfrac{1}{2}H' y , \qquad H_3 = H' x_3 = H' z . \end{aligned} \tag{13}$$

The nonvanishing components of T_{ij} are

$$T_{33} = -2T_{11} = -2T_{22} = \gamma H' , \tag{14}$$

and

$$W' = -\tfrac{1}{4}\gamma H'^2 . \tag{15}$$

In order to determine γ from calculations on an atomic system we equate W' from (15) to the term in H'^2 in the quantum-mechanical perturbation expansion for the energy

$$E = E_0 + H'^2 E_2 + \cdots , \tag{16}$$

and find that

$$\gamma = -4E_2 . \tag{17}$$

In (16) the first-order energy term $H'E_1$ vanishes as explained in a later section.

IV. VECTOR POTENTIAL

The external magnetic field is generated by current distributions, but the atomic system under consideration is far removed from these distributions. Hence, the Cartesian components of $\vec{H}$ satisfy Laplace's equation:

$$\nabla^2 H_i = 0 \ , \quad i = 1, 2, 3 \ . \tag{18}$$

We expand the magnetic field in a Taylor series about the origin, retaining only the first three terms,

$$\vec{H} = \vec{H}_0 + \vec{H}' + \vec{H}'' \ , \tag{19}$$

where

$$H_{0_i} = H_i(0) \ , \tag{20}$$

$$H_i' = \sum_j \frac{\partial H_i}{\partial x_j} (0) x_j \ , \tag{21}$$

$$H_i'' = \sum_{j,k} \frac{1}{2!} \frac{\partial^2 H_i}{\partial x_j \partial x_k} (0) x_j x_k \ , \tag{22}$$

and where

$$H_i(0), \ \frac{\partial H_i}{\partial x_j}(0), \ \frac{\partial^2 H_i}{\partial x_j \partial x_k}(0) \ ,$$

are the field, first gradient, and second partial derivatives, respectively, all evaluated at the origin. The magnetic vector potential is also taken as a sum of terms

$$\vec{A} = \vec{A}_0 + \vec{A}' + \vec{A}'' + \cdots \ , \tag{23}$$

so that

$$\vec{H} = \nabla \times \vec{A}_0 \ , \quad \vec{H}' = \nabla \times \vec{A}' \ , \quad \vec{H}'' = \nabla \times \vec{A}'' \ . \tag{24}$$

Solutions of (24) for the vector potentials, given the magnetic field components [(20)–(22)], are not unique. Therefore, solutions are selected first, to satisfy the Lorentz condition

$$\nabla \cdot \vec{A} = 0 \ , \tag{25}$$

and second, to simplify the Hamiltonian for the atomic system. Thus, we choose

$$\vec{A}_0 = \tfrac{1}{2} \vec{H}_0 \times \vec{r} \ , \tag{26}$$

$$\vec{A}' = \tfrac{1}{3} \vec{H}' \times \vec{r} \ , \tag{27}$$

$$\vec{A}'' = \tfrac{1}{4} \vec{H}'' \times \vec{r} \ . \tag{28}$$

It can easily be verified that (26)–(28) satisfy (24) and (25).

In cylindrical polar coordinates (ρ, φ, z) for an axially symmetric field, the magnetic field and vector potentials take the form

$$\vec{H}_0 = \hat{e}_z H \ , \tag{29}$$

$$\vec{H}' = \hat{e}_\rho(-\tfrac{1}{2}\rho H') + \hat{e}_z(zH') \ , \tag{30}$$

$$\vec{H}'' = \hat{e}_\rho(-\tfrac{1}{2}\rho z H'') + \hat{e}_z(\tfrac{1}{2}(z^2 - \tfrac{1}{2}\rho^2)H'') \ , \tag{31}$$

$$\vec{A}_0 = \hat{e}_\varphi(\tfrac{1}{2}\rho H) \ , \tag{32}$$

$$\vec{A}' = \hat{e}_\varphi(\tfrac{1}{2}\rho z H') \ , \tag{33}$$

$$\vec{A}'' = \hat{e}_\varphi[\tfrac{1}{4}\rho(z^2 - \tfrac{1}{4}\rho^2)H''] \ , \tag{34}$$

where $\hat{e}_\rho$, $\hat{e}_\varphi$, and $\hat{e}_z$ are unit vectors in the ρ, φ, and z directions, respectively, and

$$H = H_z(0) \ , \tag{35}$$

$$H' = \frac{\partial H_z}{\partial z}(0) \ , \tag{36}$$

$$H'' = \frac{\partial^2 H_z}{\partial z^2}(0) \ . \tag{37}$$

V. HAMILTONIAN FOR THE MANY-ELECTRON ATOM

The nonrelativistic Hamiltonian operator for an N-electron atom in an external magnetic field is given by[3]

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{1}{2m} \left(-\hbar\nabla_i + \frac{e}{c} \vec{A}_i \right)^2 + \frac{e}{mc} (\vec{s}_i \cdot \vec{H}_i) \right] + V \ , \tag{38}$$

where

$$V = -Ze^2 \sum_{i=1}^{N} \frac{1}{r_i} + e^2 \sum_{i,j} \text{pairs}\,(i,j) \frac{1}{r_{ij}} \ , \tag{39}$$

and $\vec{A}_i$ is given by (23) and (26)–(28). In what follows we retain only the gradient term $\vec{H}'$, however, extension to combined magnetic and electric fields and their first-order gradients is presented in Ref. 5. Since $\vec{A}$ satisfies the Lorentz condition

$$\mathcal{H} = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 + \frac{e}{mc} (\tfrac{1}{3}\vec{H}' \cdot \vec{L}_i) + \frac{e^2}{2mc} \left| \vec{A}_i \right|^2 + \frac{e}{2mc} (\vec{s}_i \cdot \vec{H}_i) \right) + V \ . \tag{40}$$

Substituting from (30) and (33) and employing the following relations,

$$z = r\cos\theta \ , \quad \rho = r\sin\theta \ ,$$
$$\vec{H}' \cdot \vec{L} = H'(zL_z - \tfrac{1}{2}\rho L_\rho) \ , \quad \vec{H}' \cdot \vec{s} = H'(zs_z - \tfrac{1}{2}\rho s_\rho) \ ,$$
$$L_\rho = -\cot\theta\, L_z \ , \quad s_\rho = \tfrac{1}{2}(e^{-i\varphi}s_+ + e^{i\varphi}s_-) \ , \quad s_\pm = s_x \pm i s_y \ , \tag{41}$$

yields

$$\mathcal{H} = \sum_{i=1}^{N} \left[-\tfrac{1}{2}\nabla_i^2 + \tfrac{1}{2}\alpha H'(\tfrac{4}{3}\pi)^{1/2} r_i \left(Y_{10}(L_{z_i} + H'^{2}_{z_i}) + \frac{1}{\sqrt{2}} Y_{11} s_{-_i} - \frac{1}{\sqrt{2}} Y_{1,-1} s_{+_i} \right) - \frac{\alpha^2}{35} H'^2 (4\pi)^{1/2} r_i^4 \times \left(\tfrac{1}{3} Y_{40} - \frac{\sqrt{5}}{12} Y_{20} - \tfrac{7}{12} Y_{00} \right) \right] + V \ , \tag{42}$$

where the Y_{lm} are spherical harmonics and are understood to have arguments θ_i, φ_i. In (42) we have introduced atomic units according to Hartree[6] wherein the magnetic field is measured in units of e/a_0^3 or 3.2412×10^{-15} Oe/cm. a_0 is the radius of the first Bohr orbit of the hydrogen atom and α is the fine-structure constant $e^2/\hbar c$.

VI. HARTREE-FOCK FORMALISM - ELIMINATION OF SPIN VARIABLES

The Hartree-Fock formalism[7–10] yields the following integrodifferential equations for the spin orbitals ϕ_i:

$$(h_i+v)\phi_i(1)+\textstyle\sum_j\lambda_{ij}\phi_j(1)=0\ , \tag{43}$$

where

$$h_i=h_0+H'V+H'^2W\ , \tag{44}$$

$$h_0=-\tfrac{1}{2}\nabla^2-Z/r\ , \tag{45}$$

and the operators v, V, and W are here defined as

$$V=\frac{\alpha}{2}\left(\frac{4\pi}{3}\right)^{1/2}r\left(Y_{10}(L_z+2s_z)+\frac{1}{\sqrt{2}}\,(Y_{11}s_- - Y_{1,-1}s_+)\right)\ , \tag{46}$$

$$W=\frac{\alpha^2}{35}\,(4\pi)^{1/2}r^4\left(\tfrac{1}{3}Y_{40}-\frac{\sqrt{5}}{12}\,Y_{20}-\tfrac{7}{12}\,Y_{00}\right)\ , \tag{47}$$

$$v=\sum_{j\neq i}\ \langle\phi_j(2)\,|\,Q_{12}\,|\,\phi_j(2)\rangle\ . \tag{48}$$

For brevity we have defined the operator

$$Q_{12}\equiv(1-P_{12})/r_{12}\ , \tag{49}$$

where P_{12} has the effect of interchanging the arguments of the two functions which follow, that is,

$$\langle\phi_i(1)\,\phi_j(2)\,|\,P_{12}/r_{12}\,|\,\phi_j(2)\phi_i(1)\rangle$$
$$=\langle\phi_i(1)\phi_j(2)\,|\,1/r_{12}\,|\,\phi_i(2)\phi_j(1)\rangle\ . \tag{50}$$

The spin variables may be eliminated, leaving only orbital functions, by letting

$$\phi_i=\psi_i(r,\theta,\varphi)\,\overline{\alpha}+\chi_i(r,\theta,\varphi)\,\overline{\beta}\ . \tag{51}$$

It is noted that the operator V in (46) has the effect of mixing the two coordinate functions ψ_i and χ_i in the following manner:

$$V\phi_i=\frac{\alpha}{2}\left(\frac{4\pi}{3}\right)^{1/2}r\left[\left(Y_{10}(L_z+1)\psi_i-\frac{1}{\sqrt{2}}\,Y_{1,-1}\chi_i\right)\overline{\alpha}+\left(Y_{10}(L_z-1)\chi_i+\frac{1}{\sqrt{2}}\,Y_{11}\psi_i\right)\overline{\beta}\right]\ . \tag{52}$$

Substituting (51) into (43) and premultiplying first by $\overline{\alpha}^\dagger$ and then by $\overline{\beta}^\dagger$ yields two simultaneous integrodifferential equations for ψ_i and χ_i,

$$[h_0+H'V_\alpha+H'^2W+v_\alpha+u_\alpha]\ \psi_i+H'U_\alpha\chi_i+\textstyle\sum_j\lambda_{ij}\psi_j=0\ , \tag{53}$$

$$H'U_\beta\psi_i+[h_0+H'V_\beta+H'^2\,W+v_\beta+u_\beta]\ \chi_i+\textstyle\sum_j\lambda_{ij}\chi_j=0\ , \tag{54}$$

where we have made use of the definitions

$$V_\alpha=\frac{\alpha}{2}\left(\frac{4\pi}{3}\right)^{1/2}\ rY_{10}(L_z+1)\ , \tag{55}$$

$$U_\alpha=\frac{\alpha}{2}\left(\frac{4\pi}{3}\right)^{1/2}\left(-\frac{1}{\sqrt{2}}\right)rY_{1,-1}\ , \tag{56}$$

$$v_\alpha=\sum_{j\neq i}\ \langle\psi_j|\,Q_{12}\,|\psi_j\rangle\ , \tag{57}$$

$$u_\alpha=\sum_{j\neq i}\ \langle\chi_j|\,Q_{ij}\,|\chi_j\rangle\ , \tag{58}$$

$$V_\beta=\frac{\alpha}{2}\left(\frac{4\pi}{3}\right)^{1/2}\ rY_{10}(L_z-1)\ , \tag{59}$$

$$U_\beta=\frac{\alpha}{2}\left(\frac{4\pi}{3}\right)^{1/2}\left(\frac{1}{\sqrt{2}}\right)rY_{11}\ , \tag{60}$$

$$v_\beta=\sum_{j\neq i}\ \langle\chi_j|\,Q_{12}\,|\chi_j\rangle\ , \tag{61}$$

$$u_\beta=\sum_{j\neq i}\ \langle\psi_j|\,Q_{ij}\,|\psi_j\rangle\ . \tag{62}$$

In u_α and u_β the operator Q_{ij} has a different effect than the operator Q_{12}. While Q_{12} causes subtraction of a term with the arguments of the orbitals interchanged (i.e., electron exchange terms), the operator Q_{ij} causes subtraction of a term with the orbital numbers exchanged. Specifically, u_α and u_β are defined, such that

$$u_\alpha\psi_i=\sum_{j\neq i}\left(\left\langle\chi_j\left|\frac{1}{r_{12}}\right|\chi_j\right\rangle\psi_i-\left\langle\chi_j\left|\frac{1}{r_{12}}\right|\chi_i\right\rangle\psi_j\right), \tag{63}$$

$$u_\beta\chi_i=\sum_{j\neq i}\left(\left\langle\psi_j\left|\frac{1}{r_{12}}\right|\psi_j\right\rangle\chi_i-\left\langle\psi_j\left|\frac{1}{r_{12}}\right|\psi_i\right\rangle\chi_j\right)\ . \tag{64}$$

The Hartree-Fock energy is given by

$$E=\textstyle\sum_i\langle\phi_i\,|\,h_0+H'V+H'^2\,W\,|\,\phi_i\rangle$$
$$+\tfrac{1}{2}\textstyle\sum_i\langle\phi_i\,|\,v\,|\,\phi_i\rangle\ . \tag{65}$$

Substitution for ϕ_i in terms of ψ_i and χ_i and introduction of the orthonormal property of the spin functions yield, after some simplification,

$$E=-\textstyle\sum_i(\lambda_{ii}+\tfrac{1}{2}\,\langle\psi_i|\,v_\alpha+u_\alpha\,|\psi_i\rangle\ +\tfrac{1}{2}\,\langle\chi_i\,|\,v_\beta+u_\beta\,|\,\chi_i\rangle)\ , \tag{66}$$

where use has been made of (53), (54), and the orthogonality relations

$$\langle\phi_i\,|\,\phi_j\rangle=\langle\psi_i\,|\,\psi_j\rangle+\langle\chi_i\,|\,\chi_j\rangle=\delta_{ij}\ . \tag{67}$$

VII. HARTREE-FOCK PERTURBATION THEORY

We now obtain perturbation equations for the first- and second-order energies, starting from the Hartree-Fock equations (53) and (54). First, we expand ψ_i, χ_i, and λ_{ij} in perturbation series in H', assuming the zero-order matrix of Lagrange multipliers to be diagonal, that is,

$$\lambda_{ij}^0 = -\delta_{ij}\epsilon_i^0 \ . \tag{68}$$

Thus, we have

$$\psi_i = \psi_i^0 + H'\psi_i^1 + H'^2\psi_i^2 + \cdots \ , \tag{69}$$

$$\chi_i = \chi_i^0 + H'\chi_i^1 + H'^2\chi_i^2 + \cdots \ , \tag{70}$$

$$\lambda_{ij} = -\epsilon_i^0\delta_{ij} + H'\lambda_{ij}^1 + H'^2\lambda_{ij}^2 + \cdots \ . \tag{71}$$

Substituting these series into the expressions for u_α, u_β, v_α, and v_β yields

$$u_\alpha = u_\alpha^0 + H'u_\alpha^1 + H'^2u_\alpha^2 + \cdots \ , \tag{72}$$

$$u_\beta = u_\beta^0 + H'u_\beta^1 + H'^2u_\beta^2 + \cdots \ , \tag{73}$$

$$v_\alpha = v_\alpha^0 + H'v_\alpha^1 + H'^2v_\alpha^2 + \cdots \ , \tag{74}$$

and

$$v_\beta = v_\beta^0 + H'v_\beta^1 + H'^2v_\beta^2 + \cdots \ , \tag{75}$$

where

$$v_\alpha^0 = \sum_{j\neq i} \langle\psi_j^0|Q_{12}|\psi_j^0\rangle \ , \tag{76}$$

$$v_\alpha^1 = \sum_{j\neq i} (\langle\psi_j^0|Q_{12}|\psi_j^1\rangle + \langle\psi_j^1|Q_{12}|\psi_j^0\rangle) \ , \tag{77}$$

$$v_\alpha^2 = \sum_{j\neq i} (\langle\psi_j^0|Q_{12}|\psi_j^2\rangle + \langle\psi_j^1|Q_{12}|\psi_j^1\rangle + \langle\psi_j^2|Q_{12}|\psi_j^0\rangle) \ , \tag{78}$$

$$u_\alpha^0 = \sum_{j\neq i} \langle\chi_j^0|Q_{ij}|\chi_j^0\rangle \ , \tag{79}$$

$$u_\alpha^1 = \sum_{j\neq i} (\langle\chi_j^0|Q_{ij}|\chi_j^1\rangle + \langle\chi_j^1|Q_{ij}|\chi_j^0\rangle) \ , \tag{80}$$

$$u_\alpha^2 = \sum_{j\neq i} (\langle\chi_j^0|Q_{ij}|\chi_j^2\rangle + \langle\chi_j^1|Q_{ij}|\chi_j^1\rangle + \langle\chi_j^2|Q_{ij}|\chi_j^0\rangle) \ , \tag{81}$$

$$v_\beta^0 = \sum_{j\neq i} \langle\chi_j^0|Q_{12}|\chi_j^0\rangle \ , \tag{82}$$

$$v_\beta^1 = \sum_{j\neq i} (\langle\chi_j^0|Q_{12}|\chi_j^1\rangle + \langle\chi_j^1|Q_{12}|\chi_j^0\rangle) \ , \tag{83}$$

$$v_\beta^2 = \sum_{j\neq i} (\langle\chi_j^0|Q_{12}|\chi_j^2\rangle + \langle\chi_j^1|Q_{12}|\chi_j^1\rangle + \langle\chi_j^2|Q_{12}|\chi_j^0\rangle) \ , \tag{84}$$

$$u_\beta^0 = \sum_{j\neq i} \langle\psi_j^0|Q_{ij}|\psi_j^0\rangle \ , \tag{85}$$

$$u_\beta^1 = \sum_{j\neq i} (\langle\psi_j^0|Q_{ij}|\psi_j^1\rangle + \langle\psi_j^1|Q_{ij}|\psi_j^0\rangle) \ , \tag{86}$$

$$u_\beta^2 = \sum_{j\neq i} (\langle\psi_j^0|Q_{ij}|\psi_j^2\rangle + \langle\psi_j^1|Q_{ij}|\psi_j^1\rangle + \langle\psi_j^2|Q_{ij}|\psi_j^0\rangle) \ . \tag{87}$$

Next, substitution of the perturbation series (69)–(74) into the Hartree-Fock orbital Eqs. (53) and (54) yields the following perturbation equations:

$$[h_0 + (v_\alpha^0 + u_\alpha^0) - \epsilon_i^0]\psi_i^1 + (V_\alpha + v_\alpha^1 + u_\alpha^1)\,\psi_i^0 + U_\alpha\chi_i^0 + \textstyle\sum_j \lambda_{ij}^1\psi_j^0 = 0 \tag{88}$$

$$[h_0 + (v_\beta^0 + u_\beta^0) - \epsilon_i^0]\chi_i^1 + (V_\beta + v_\beta^1 + u_\beta^1)\,\chi_i^0 + U_\beta\psi_i^0 + \textstyle\sum_j \lambda_{ij}^1\chi_j^0 = 0 \tag{89}$$

$$[h_0 + (v_\alpha^0 + u_\alpha^0) - \epsilon_i^0]\psi_i^2 + (V_\alpha + v_\alpha^1 + u_\alpha^1)\psi_i^1 + (W + v_\alpha^2 + u_\alpha^2)\psi_i^0 + U_\alpha\chi_i^1 + \textstyle\sum_j (\lambda_{ij}^1\psi_j^1 + \lambda_{ij}^2\psi_j^0) = 0 \tag{90}$$

$$[h_0 + (v_\beta^0 + u_\beta^0) - \epsilon_i^0]\chi_i^2 + (V_\beta + v_\beta^1 + u_\beta^1)\,\chi_i^1 + (W + v_\beta^2 + u_\beta^2)\,\chi_i^0 + U_\beta\psi_i^1 + \textstyle\sum_j(\lambda_{ij}^1\chi_j^1 + \lambda_{ij}^2\chi_j^0) = 0 \ . \tag{91}$$

The Hartree-Fock energy from (66) is also expanded in a perturbation series:

$$E = E_0 + H'E_1 + H'^2E_2 + \cdots \ , \tag{92}$$

where, after simplification,[5] one finds that

$$E_1 = \textstyle\sum_i (\langle\psi_i^0|U_\alpha|\chi_i^0\rangle + \langle\chi_i^0|U_\beta|\psi_i^0\rangle + \langle\psi_i^0|V_\alpha|\psi_i^0\rangle + \langle\chi_i^0|V_\beta|\chi_i^0\rangle) \tag{93}$$

and

$$E_2 = \textstyle\sum_i(\langle\chi_i^0|W|\chi_i^0\rangle + \langle\psi_i^0|W|\psi_i^0\rangle + \langle\chi_i^0|V_\beta|\chi_i^1\rangle + \langle\psi_i^0|V_\alpha|\psi_i^1\rangle + \langle\chi_i^0|U_\beta|\psi_i^1\rangle + \langle\psi_i^0|U_\alpha|\chi_i^1\rangle) \ . \tag{94}$$

Furthermore, the first two terms of (93) vanish because χ_i^0 and ψ_i^0 cannot simultaneously be nonzero, and, since V_β and V_α have odd parity, the remaining terms also vanish, leaving

$$E_1 = 0 \ .$$

This result is expected because, to first order in H',

$$E = E_0 + H'E_1 \ ,$$

and a change in the direction of the field, that is, a change in sign of H' cannot change the energy.

The Hartree-Fock perturbation Eqs. (87) and (89) are not in a particularly convenient form for calculation of the first-order wave functions because they do not account for the fact that zero-order spin orbitals occur in orbital pairs. That is,

$$\phi_i^0 = \psi_i^0\overline{\alpha} \ \text{or} \ \chi_i^0\overline{\beta} \ ,$$

and the coordinate functions ψ_i^0 and χ_i^0 are equal for an orbital pair. Thus, we write the zero- and first-order spin orbitals in pairs:

$$\begin{aligned} \varphi_{i\alpha}^0 &= \psi_i^0\,\overline{\alpha}, & \varphi_{i\alpha}^1 &= \psi_{i\alpha}^1\overline{\alpha} + \chi_{i\alpha}^1\overline{\beta} \ , \\ \varphi_{i\beta}^0 &= \psi_i^0\,\overline{\beta}, & \varphi_{i\beta}^1 &= \psi_{i\beta}^1\overline{\alpha} + \chi_{i\beta}^1\overline{\beta} \ , \end{aligned} \tag{95}$$

where the second subscript α denotes that the corresponding zero-order function has an $\overline{\alpha}$ spin function and the subscript β denotes that the zero-order function has a $\overline{\beta}$ spin function.

Use of (95) leads directly to the following four simultaneous integrodifferential equations for the first-order functions of each orbital pair:

$$(h_0-\epsilon_i^0)\psi_{i\alpha}^1+\left\langle \psi_i^0\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_{i\alpha}^1+\sum_{j\neq i}^{N/2}\left\langle \psi_j^0\left|\frac{2-P_{12}}{r_{12}}\right|\psi_j^0\right\rangle \psi_{i\alpha}^1+V_\alpha\psi_i^0+\left\langle \chi_{i\beta}^1\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_i^0+\left\langle \psi_i^0\left|\frac{1}{r_{12}}\right|\chi_{i\beta}^1\right\rangle \psi_i^0$$

$$+\sum_{j\neq i}^{N/2}\left(\left\langle \psi_j^0\left|\frac{1-P_{12}}{r_{12}}\right|\psi_{j\alpha}^1\right\rangle+\left\langle \psi_{j\alpha}^1\left|\frac{1-P_{12}}{r_{12}}\right|\psi_j^0\right\rangle+\left\langle \psi_j^0\left|\frac{1}{r_{12}}\right|\chi_{j\beta}^1\right\rangle+\left\langle \chi_{j\beta}^1\left|\frac{1}{r_{12}}\right|\psi_j^0\right\rangle\right)\psi_i^0+\sum_j^{N/2}\lambda_{ij}^1\psi_j^0=0\ , \tag{96}$$

$$(h_0-\epsilon_i^0)\chi_{i\beta}^1+\left\langle \psi_i^0\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \chi_{i\beta}^1+\sum_{j\neq i}^{N/2}\left\langle \psi_j^0\left|\frac{2-P_{12}}{r_{12}}\right|\psi_j^0\right\rangle \chi_{i\beta}^1+V_\beta\psi_i^0+\left\langle \psi_{i\alpha}^1\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_i^0+\left\langle \psi_i^0\left|\frac{1}{r_{12}}\right|\psi_{i\alpha}^1\right\rangle \psi_i^0$$

$$+\sum_{j\neq i}^{N/2}\left(\left\langle \psi_j^0\left|\frac{1-P_{12}}{r_{12}}\right|\chi_{j\beta}^1\right\rangle+\left\langle \chi_{j\beta}^1\left|\frac{1-P_{12}}{r_{12}}\right|\psi_j^0\right\rangle+\left\langle \psi_j^0\left|\frac{1}{r_{12}}\right|\psi_{j\alpha}^1\right\rangle+\left\langle \psi_{j\alpha}^1\left|\frac{1}{r_{12}}\right|\psi_j^0\right\rangle\right)\psi_i^0+\sum_j^{N/2}\lambda_{ij}^1\psi_j^0=0\ , \tag{97}$$

$$(h_0-\epsilon_i^0)\chi_{i\alpha}^1+\left\langle \psi_i^0\left|\frac{1-P_{12}}{r_{12}}\right|\psi_i^0\right\rangle \chi_{i\alpha}^1+\sum_{j\neq i}^{N/2}\left(\left\langle \psi_j^0\left|\frac{2-P_{12}}{r_{12}}\right|\psi_j^0\right\rangle \chi_{i\alpha}^1-\left\langle \psi_j^0\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \chi_{j\alpha}^1\right)$$

$$+U_\beta\psi_i^0-\left\langle \psi_{i\beta}^1\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_i^0-\sum_{j\neq i}^{N/2}\left\langle \psi_{j\beta}^1\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_j^0+\sum_j^{N/2}\lambda_{ij}^1\psi_j^0=0\ , \tag{98}$$

$$(h_0-\epsilon_i^0)\psi_{i\beta}^1+\left\langle \psi_i^0\left|\frac{1-P_{12}}{r_{12}}\right|\psi_i^0\right\rangle \psi_{i\beta}^1+\sum_{j\neq i}^{N/2}\left(\left\langle \psi_j^0\left|\frac{2-P_{12}}{r_{12}}\right|\psi_j^0\right\rangle \psi_{i\beta}^1-\left\langle \psi_j^0\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_{j\beta}^1\right)+U_\alpha\psi_i^0$$

$$-\left\langle \chi_{i\alpha}^1\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_i^0-\sum_{j\neq i}^{N/2}\left\langle \chi_{j\alpha}^1\left|\frac{1}{r_{12}}\right|\psi_i^0\right\rangle \psi_j^0+\sum_j^{N/2}\lambda_{ij}^1\psi_j^0=0\ . \tag{99}$$

In (96)–(99) the sums over j now correspond to sums over doubly occupied orbitals, not spin orbitals.

It may be noted that Eqs. (96) and (97) do not contain $\psi_{i\beta}^1$ or $\chi_{i\alpha}^1$ nor do (98) and (99) contain $\psi_{i\alpha}^1$ or $\chi_{i\beta}^1$. Hence, there are two sets of two simultaneous integrodifferential equations which may be solved independently for each set. This is precisely the simplification that we sought in treating spin-orbital pairs. Furthermore, it can be shown[5] that the radial parts of $\psi_{i\alpha}^1$ and $\chi_{i\beta}^1$ are equal in magnitude but opposite in sign and that the same is true of $\psi_{i\beta}^1$ and $\chi_{i\alpha}^1$. Hence, Eqs. (96) and (97) may be combined to give a single equation for the radial part of $\psi_{i\alpha}^1$, while (98) and (99) may be combined to yield the radial part of $\chi_{i\alpha}^1$.

In order to determine an expression for the Hartree-Fock second-order energy in terms of sums of orbitals (not spin orbitals), we employ (95) in (94) and obtain

$$E_2=\sum_i^{N/2}\left(\langle\psi_i^0|V_\alpha|\psi_{i\alpha}^1\rangle+\langle\psi_i^0|V_\beta|\chi_{i\beta}^1\rangle\right)+\sum_i^{N/2}\left(\langle\psi_i^0|U_\beta|\psi_{i\beta}^1\rangle+\langle\psi_i^0|U_\alpha|\chi_{i\alpha}^1\rangle\right)+2\sum_i^{N/2}\langle\psi_i^0|W|\psi_i^0\rangle\ , \tag{100}$$

where again the sums are now over doubly occupied orbitals.

VIII. VARIATIONAL METHOD OF SOLUTION OF FIRST-ORDER EQUATIONS

Equations (96)–(99) are fully coupled integrodifferential equations for the first-order functions, perturbed in the magnetic field gradient. They are described as coupled because, for example, the equation for $\psi_{i\alpha}^1$ [(96)] involves the solutions $\psi_{j\alpha}^1$ for all other orbitals. Since closed form analytic solutions for these equations do not exist, resort is made to numerical methods. Variational methods, using wave functions in analytic form with variational parameters, have yielded convergent results in similar calculations of electric dipole and quadrupole polarizabilities.(2, 11–17) Furthermore, numerous accurate analytic Hartree-Fock functions are available for the zero-order wave functions. Accordingly, we employ a variational method by constructing four functionals and requiring that each of them be stationary. For example, the first of these functionals is

$$
\begin{aligned}
J_1(\psi^1_{i\alpha}) = {} & \langle\psi^1_{i\alpha}| h_0 - \epsilon^0_i | \psi^1_{i\alpha}\rangle + \left\langle \psi^1_{i\alpha}(1)\psi^0_i(2) \left| \frac{1}{r_{12}} \right| \psi^0_i(2)\psi^1_{i\alpha}(1) \right\rangle + \sum_{j\neq i} \left\langle \psi^1_{i\alpha}(1)\psi^0_j(2) \left| \frac{2-P_{12}}{r_{12}} \right| \psi^0_j(2)\psi^1_{i\alpha}(1) \right\rangle \\
& + 2\langle\psi^1_{i\alpha}| V_\alpha | \psi^0_i\rangle + 2\left\langle \psi^1_{i\alpha}(1)\chi^1_{i\beta}(2) \left| \frac{1}{r_{12}} \right| \psi^0_i(2)\psi^0_i(1) \right\rangle + 2\left\langle \psi^1_{i\alpha}(1)\psi^0_i(2) \left| \frac{1}{r_{12}} \right| \chi^1_{i\beta}(2)\psi^0_i(1) \right\rangle \\
& + 2\sum_{j\neq i}\Bigg(\left\langle \psi^1_{i\alpha}(1)\psi^0_j(2) \left| \frac{1-P_{12}}{r_{12}} \right| \psi^1_{j\alpha}(2)\psi^0_i(1) \right\rangle + \left\langle \psi^1_{i\alpha}(1)\psi^1_{j\alpha}(2) \left| \frac{1-P_{12}}{r_{12}} \right| \psi^0_j(2)\psi^0_i(1) \right\rangle + \left\langle \psi^1_{i\alpha}(1)\psi^0_j(2) \left| \frac{1}{r_{12}} \right| \chi^1_{j\beta}(2)\psi^0_i(1) \right\rangle \\
& + \left\langle \psi^1_{i\alpha}(1)\chi^1_{j\beta}(2) \left| \frac{1}{r_{12}} \right| \psi^0_j(2)\psi^0_i(1) \right\rangle \Bigg) + \sum_j 2\lambda^1_{ij}\langle\psi^1_{i\alpha}|\psi^0_j\rangle ,
\end{aligned}
\tag{101}
$$

so that imposing the condition

$$\delta J_1(\psi^1_{i\alpha}) = 0 \tag{102}$$

yields Eq. (96).

The functional forms assumed for $\psi^1_{i\alpha}$, $\chi^1_{i\beta}$, etc., are

$$\psi^1_{i\alpha} = \sum_{n=1}^{M} c_n f_n(r, \theta, \varphi), \tag{103}$$

where the f_n are assumed basis functions and the c_n are variational coefficients. The condition of stationarity (102) then requires

$$\frac{\partial J_1}{\partial c_n} = 0, \quad n = 1, 2, 3 \cdots M. \tag{104}$$

Equations (104) are then a set of simultaneous linear algebraic equations for the c_n. However, since the $\lambda^1_{i\alpha}$'s are additional unknowns, more equations are required to determine unique solutions for the c_n. These additional equations are supplied by the orthogonality conditions:

$$\langle\psi^0_i|\psi^1_{j\alpha}\rangle + \langle\psi^1_{i\alpha}|\psi^0_j\rangle = 0, \tag{105}$$

$$\langle\psi^0_i|\chi^1_{j\beta}\rangle + \langle\chi^1_{i\beta}|\psi^0_j\rangle = 0, \tag{106}$$

$$\langle\psi^0_i|\psi^1_{j\beta}\rangle + \langle\chi^1_{i\alpha}|\psi^0_j\rangle = 0, \tag{107}$$

$$\langle\psi^0_i|\chi^1_{j\alpha}\rangle + \langle\psi^1_{i\beta}|\psi^0_j\rangle = 0. \tag{108}$$

We note at this point that had we not retained the off-diagonal Lagrange multipliers λ^1_{ij} from the beginning (i.e., by assuming the λ-matrix diagonal), then the functional (101) would still have been obtained. That is, the terms

$$\textstyle\sum_j 2\lambda^1_{ij}\langle\psi^1_{i\alpha}|\psi^0_j\rangle \tag{109}$$

would have been added to the functional according to the method of undetermined Lagrange multipliers to account properly for the conditions of constraint.

The zero-order functions have been calculated by a number of researchers and are generally in the form of sums of coefficients times Slater orbitals. We have

$$\eta_n(r) = N_n r^n e^{-\zeta r}, \tag{110}$$

where the N_n are normalizing factors. Thus, ψ^0_i takes the form

$$\psi^0_i = [\textstyle\sum_n b^i_n \eta^i_n(r)]\, Y_{l_i m_i}(\theta,\varphi), \tag{111}$$

where the set of basis functions $\eta^i_n(r)$, are taken as the same for all orbitals of given l quantum number (e.g., all S or all P orbitals). Further, because of the degeneracy on the magnetic quantum number, the coefficients b^i_n are the same for all orbitals belonging to the same P shell (e.g., $2P_+$, $2P_-$ and $2P_0$ orbitals).

As a matter of convenience in calculations we take the first-order functions in the same form as the zero-order function, for example,

$$\psi^1_{i\alpha} = \textstyle\sum_j Y_{l_j m_j}(\theta, \varphi) \sum_k c^i_{jk} r^{n^i_{jk}} e^{-\zeta^i_{jk} r}. \tag{112}$$

The values of ζ^i_{jk} are chosen equal to the value ζ^0_j in the zero-order functions. Furthermore, it may be shown[5] that the first-order function should contain spherical harmonics according to the following:

$$
\begin{aligned}
\psi^1_{i\alpha} &\sim V_\alpha \psi^0_i, & \chi^1_{i\alpha} &\sim U_\alpha \psi^0_i, \\
\chi^1_{i\beta} &\sim V_\beta \psi^0_i, & \psi^1_{i\beta} &\sim U_\beta \psi^0_i,
\end{aligned}
\tag{113}
$$

where $\psi^1_{i\alpha} \sim V_\alpha \psi^0_i$ implies that $\psi^1_{i\alpha}$ is to be taken as a sum of terms, each with a radial function multiplied by one of the spherical harmonics contained in $V_\alpha\psi^0_i$. Table I summarizes the forms of the zero- and first-order functions.

In addition, the smallest value of the exponent n^i_{jk} in (112) is selected as indicated by calculations for the hydrogen atom.[5] That is, the lowest power of r is selected as one higher than the power of r multiplying $\exp\{-\zeta^0_{ij} r\}$ in the zero-order function. This choice of lowest power of r is consistent with that of both Lyons[2] and Langhoff[1] for the calculation of the first-order functions required

TABLE I. Functional forms of the zero- and first-order functions.

Orbital type	Zero-order function	$\psi^1_{i\alpha}$	$\chi^1_{i\beta}$	$\chi^1_{i\alpha}$	$\psi^1_{i\beta}$
S	$f_s(r)Y_{00}$	$g_{10}(r)Y_{10}$	$g'_{10}(r)Y_{10}$	$h_{11}(r)Y_{11}$	$h_{1,-1}(r)Y_{1,-1}$
P_+	$f_p(r)Y_{11}$	$g_{21}(r)Y_{21}$	...[a]	$h_{22}(r)Y_{22}$	$h'_{00}(r)Y_{00}$ $+h'_{20}(r)Y_{20}$
P_-	$f_p(r)Y_{1,-1}$	...[a]	$g_{2,-1}(r)Y_{21}$	$h_{00}(r)Y_{00}$ $+h_{20}(r)Y_{20}$	$h_{2,-2}(r)Y_{2,-2}$
P_0	$f_p(r)Y_{10}$	$g_{00}(r)Y_{00}$ $+g_{20}(r)Y_{20}$	$g'_{00}(r)Y_{00}$ $+g'_{20}(r)Y_{20}$	$h_{21}(r)Y_{21}$	$h_{2,-1}(r)Y_{2,-1}$

[a] These functions are zero because $V_\alpha\psi_i^0=0$ or $V_\beta\psi_i^0=0$.

to obtain the electric dipole polarizability. The similarity between the electric dipole and magnetic quadrupole cases occurs because the perturbations that require calculation of the first-order functions (V_α, V_β, U_α, and U_β in the present case) all contain the first power of r.

IX. COMPUTATIONS AND RESULTS

Tables II and III summarize calculations for the two- and four-electron systems, respectively, wherein the number of variation coefficients per value of ζ in (112) is varied from one to three. It may be seen from Table II that, except for the H$^-$ ion, the calculations of γ are identical to five significant figures for two and three coefficients per ζ value. Similarly, Table III indicates convergence to three significant figures with only two coefficients per ζ value.

Table II shows calculations of γ for several He and Li$^+$ zero-order wave functions. When these results are compared for only one coefficient per ζ value, they differ in the third significant figure. However, similar calculations using two coefficients (i.e., twice as many variation parameters) differ only in the fifth significant figure. Similar results also occur for the Be atom as shown on Table III. Hence, comparisons of γ for different zero-order wave functions are meaningful only if enough variation parameters have been used to guarantee convergence. In comparing values of γ for other atoms and ions, therefore, we shall consider differences in the second and third significant figures as indicative of differences in the zero-order functions.

Calculations of the magnetic quadrupole polarizability are summarized in Table IV for atoms and ions in the 2-, 4-, 10-, 12-, and 18-electron systems. Several zero-order wave functions are also available for F$^-$, Ne, Na$^+$, Mg, and Ar, so that comparisons are made of the effect of these

TABLE II. Effect of increasing the number of variation parameters on the magnetic quadrupole polarizability for two-electron systems.

Atom or ion	Refs.[a]	No. of linear variation coefficients[b]	Magnetic quadrupole polarizability (a.u.)
H$^-$	18	5	$0.423\,72\times10^{-2}$
		10	$0.430\,27\times10^{-2}$
		15	$0.430\,28\times10^{-2}$
He	19	4	$0.406\,76\times10^{-4}$
		8	$0.410\,76\times10^{-4}$
		12	$0.410\,76\times10^{-4}$
He	20	12	$0.410\,84\times10^{-4}$
He	21	3	$0.405\,10\times10^{-4}$
		6	$0.410\,81\times10^{-4}$
		9	$0.410\,81\times10^{-4}$
		12	$0.410\,81\times10^{-4}$
He	19	5	$0.410\,07\times10^{-4}$
		10	$0.410\,85\times10^{-4}$
		15	$0.410\,85\times10^{-4}$
Li$^+$	19	4	$0.518\,87\times10^{-5}$
		8	$0.521\,12\times10^{-5}$
		12	$0.521\,12\times10^{-5}$
Li$^+$	21	3	$0.519\,04\times10^{-5}$
		6	$0.521\,19\times10^{-5}$
		9	$0.521\,19\times10^{-5}$
Be^{2+}	19	4	$0.134\,29\times10^{-5}$
		8	$0.134\,47\times10^{-5}$
		12	$0.134\,47\times10^{-5}$
B^{3+}	19	4	$0.490\,25\times10^{-6}$
		8	$0.490\,70\times10^{-6}$
		12	$0.490\,70\times10^{-6}$
C^{4+}	19	4	$0.219\,39\times10^{-6}$
		8	$0.219\,55\times10^{-6}$
		12	$0.219\,55\times10^{-6}$
N^{5+}	19	4	$0.112\,36\times10^{-6}$
		8	$0.112\,44\times10^{-6}$
		12	$0.112\,44\times10^{-6}$

[a] Source of zero-order wave function.

[b] Found in the first-order function.

TABLE III. Effect of increasing the number of variation parameters on the magnetic quadrupole polarizability for four-electron systems.

Atom or ion	Refs.[a]	No. of linear variation parameters[b]	Magnetic quadrupole polarizability (a.u.)
Li^-	19	12	-0.12181×10^0
		24	-0.11959×10^0
		36	-0.11878×10^0
Be	19	10	-0.47374×10^{-1}
		20	-0.39840×10^{-1}
		30	-0.39833×10^{-1}
Be	20	24	-0.39844×10^{-1}
Be	19	12	-0.39952×10^{-1}
		24	-0.39897×10^{-1}
		36	-0.39897×10^{-1}
Be	21	10	-0.41449×10^{-1}
		20	-0.39759×10^{-1}
		30	-0.39758×10^{-1}
B^+	19	10	0.11999×10^{-1}
		20	0.15725×10^{-1}
		30	0.15726×10^{-1}
C^{2+}	19	10	0.24914×10^{-2}
		20	0.27706×10^{-2}
		30	0.27706×10^{-2}
N^{3+}	19	10	0.97399×10^{-3}
		20	0.10336×10^{-2}
		30	0.10336×10^{-2}
O^{4+}	19	10	0.48591×10^{-3}
		20	0.50400×10^{-3}
		30	0.50401×10^{-3}
F^{5+}	19	10	0.27831×10^{-3}
		20	0.28501×10^{-3}
		30	0.28501×10^{-3}

[a] Source of zero-order wave function.
[b] Found in the first-order wave function.

zero-order functions on the magnetic quadrupole polarizability. Differences shown for the F^-, Ne, and Na^+ ions are not expected to be significant compared to errors inherent in using the Hartree-Fock method. This conclusion is based on comparisons between coupled Hartree-Fock calculations of the electric dipole polarizability[14] and corresponding experimental values.

An exception occurs in the case of the neon wave function from Ref. 26 for which γ is considerably lower than the corresponding values for the other five neon wave functions. This difference is attributed to a poorer zero-order wave function as indicated by the higher zero-order energy and by an anomalous electric dipole polarizability as noted by Lyons.[30]

Again for magnesium and argon the differences between calculations for alternate wave functions are not considered significant compared to expected discrepancies with experimental values. An exception, however, occurs in the case of the wave function from Ref. 29 which contains too few basis functions and has a somewhat higher zero-order energy.

Table IV contains calculated values of γ for the H^-, Li^-, F^-, Na^-, and Cl^- negative ions. These results appear consistent with the remaining calculations in the corresponding series, although anomalous values for the electric dipole polarizability have been obtained from calculations using the uncoupled Hartree-Fock method.[1,30] Furthermore, the four values of γ calculated for the F^- ions are quite consistent. Despite these consistencies, one would expect the calculated values of γ for negative ions to be in poor agreement with experiment because of the inherent inability of Hartree-Fock theory to describe negative ions. This occurs because the Hartree-Fock method neglects electron correlation, a defect which is very serious for the outermost electrons wherein the major contributions to γ arise.

Table IV also indicates that the magnetic quadrupole polarizability decreases rapidly with increasing atomic number. As Z becomes large for 2-, 4-, and 12-electron ions, γ approaches a Z^{-4} dependence, however, the values of γ for the 10-electron systems decrease more rapidly than Z^{-4} for large Z.

Negative values of γ are obtained for the Li^- and Na^- ions and the Be atom, wherein the predominant contributions to γ arise from the outer orbitals. Again these calculations are subject to error in the Hartree-Fock approximation because of lack of correlation between the outer two electrons.

One atomic unit of magnetic quadrupole polarizability is $4.48\times10^{-22}\ \mu_B\ \text{cm}^2\text{Oe}^{-1}$. Hence, magnesium in a magnetic field gradient

$$\frac{\partial H_3}{\partial x_3} = 10^7\ \text{Oe/cm}$$

has an induced magnetic quadrupole moment T_{33} of $1.971\times10^{-16}\ \mu_B$ cm.

Within a crystal, at a site between two paramagnetic atoms, the magnetic field gradient approaches 1 a.u. (3.24×10^{15} Oe cm^{-1}). The energy associated with the induced magnetic quadrupole moment (15) may therefore become significant compared to other magnetic energy terms. Hence, it appears likely that the magnetic quadrupole polarizabilities presented here are of interest in the investigation of impurities in paramagnetic and ferromagnetic crystals.

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TABLE IV. Magnetic quadrupole polarizabilities.

Atom or ion	Refs.	Zero-order wave function Number of zero-order basis functions		Energy (a.u.) (E_0)	Magnetic quadrupole polarizability (a.u.) (γ)
		S	P		
H^-	18	5	⋯	$-0.487\,929\,33\times10^{0}$	$0.430\,27\times10^{-2}$
He	19	4	⋯	$-0.286\,167\,85\times10^{1}$	$0.410\,76\times10^{-4}$
He	20	12	⋯	$-0.286\,168\,00\times10^{1}$	$0.410\,84\times10^{-4}$
He	21	3	⋯	$-0.286\,168\,00\times10^{1}$	$0.410\,81\times10^{-4}$
He	19	5	⋯	$-0.286\,167\,99\times10^{1}$	$0.410\,85\times10^{-4}$
Li^+	19	4	⋯	$-0.723\,641\,36\times10^{1}$	$0.521\,12\times10^{-5}$
Li^+	21	3	⋯	$-0.723\,641\,40\times10^{1}$	$0.521\,19\times10^{-5}$
Be^{2+}	19	4	⋯	$-0.136\,112\,56\times10^{2}$	$0.134\,47\times10^{-5}$
B^{3+}	19	4	⋯	$-0.219\,861\,90\times10^{2}$	$0.490\,70\times10^{-6}$
C^{4+}	19	4	⋯	$-0.323\,611\,54\times10^{2}$	$0.219\,55\times10^{-6}$
N^{5+}	19	4	⋯	$-0.447\,361\,33\times10^{2}$	$0.112\,44\times10^{-6}$
Li^-	19	6	⋯	$-0.742\,822\,98\times10^{1}$	$-0.118\,78\times10^{0}$
Be	19	5	⋯	$-0.145\,730\,14\times10^{2}$	$-0.398\,33\times10^{-1}$
Be	20	12	⋯	$-0.145\,730\,20\times10^{2}$	$-0.398\,44\times10^{-1}$
Be	22	6	⋯	$-0.145\,730\,20\times10^{2}$	$-0.398\,97\times10^{-1}$
Be	21	5	⋯	$-0.145\,730\,20\times10^{2}$	$-0.397\,58\times10^{-1}$
B^+	19	5	⋯	$-0.242\,375\,56\times10^{2}$	$0.157\,26\times10^{-1}$
C^{2+}	19	5	⋯	$-0.364\,084\,84\times10^{2}$	$0.277\,06\times10^{-2}$
N^{3+}	19	5	⋯	$-0.510\,823\,09\times10^{2}$	$0.103\,36\times10^{-2}$
O^{4+}	19	5	⋯	$-0.682\,577\,00\times10^{2}$	$0.504\,01\times10^{-3}$
F^{5+}	19	5	⋯	$-0.879\,340\,35\times10^{2}$	$0.285\,01\times10^{-3}$
F^-	23	5	5	$-0.994\,593\,60\times10^{2}$	$0.364\,18\times10^{-3}$
F^-	24	7	6	$-0.994\,592\,10\times10^{2}$	$0.367\,14\times10^{-3}$
F^-	21	5	4	$-0.994\,593\,69\times10^{2}$	$0.354\,75\times10^{-3}$
F^-	25	5	4	$-0.994\,593\,58\times10^{2}$	$0.354\,81\times10^{-3}$
Ne	19	5	4	$-0.128\,546\,98\times10^{3}$	$0.551\,88\times10^{-4}$
Ne	22	6	4	$-0.128\,547\,00\times10^{3}$	$0.550\,70\times10^{-4}$
Ne	24	7	6	$-0.128\,547\,00\times10^{3}$	$0.547\,39\times10^{-4}$
Ne	26	7	5	$-0.128\,543\,18\times10^{3}$	$0.486\,70\times10^{-4}$
Ne	21	5	4	$-0.128\,547\,10\times10^{3}$	$0.538\,93\times10^{-4}$
Na^+	19	5	4	$-0.161\,676\,76\times10^{3}$	$0.149\,23\times10^{-4}$
Na^+	24	7	6	$-0.161\,676\,90\times10^{3}$	$0.149\,33\times10^{-4}$
Na^+	21	5	4	$-0.161\,677\,00\times10^{3}$	$0.146\,60\times10^{-4}$
Mg^{2+}	19	5	4	$-0.198\,830\,51\times10^{3}$	$0.480\,28\times10^{-5}$
Al^{3+}	19	5	4	$-0.240\,000\,01\times10^{3}$	$0.150\,84\times10^{-5}$
Si^{4+}	19	5	4	$-0.285\,180\,58\times10^{3}$	$0.293\,86\times10^{-6}$
P^{5+}	19	5	4	$-0.334\,369\,32\times10^{3}$	$0.170\,05\times10^{-6}$
Na^-	27	7	4	$-0.161\,854\,64\times10^{3}$	$-0.661\,84\times10^{-1}$
Mg	19	7	3	$-0.199\,614\,32\times10^{3}$	$0.435\,03\times10^{-1}$
Mg	19	8	5	$-0.199\,614\,58\times10^{3}$	$0.441\,43\times10^{-1}$
Al^+	19	7	3	$-0.241\,674\,08\times10^{3}$	$0.570\,07\times10^{-2}$
Si^{2+}	19	7	3	$-0.287\,995\,16\times10^{3}$	$0.203\,19\times10^{-2}$
P^{3+}	19	7	3	$-0.338\,562\,63\times10^{3}$	$0.992\,45\times10^{-3}$
S^{4+}	19	7	3	$-0.393\,368\,80\times10^{3}$	$0.569\,23\times10^{-3}$
Cl^{5+}	19	7	3	$-0.452\,409\,13\times10^{3}$	$0.360\,77\times10^{-3}$
Cl^-	27	7	6	$-0.459\,576\,67\times10^{3}$	$0.141\,60\times10^{-2}$
Ar	19	7	5	$-0.526\,817\,06\times10^{3}$	$0.415\,26\times10^{-3}$
Ar	28	6	4	$-0.526\,784\,07\times10^{3}$	$0.401\,22\times10^{-3}$
Ar	29	3	2	$-0.525\,765\,26\times10^{3}$	$0.149\,90\times10^{-3}$
K^+	19	7	5	$-0.599\,017\,11\times10^{3}$	$0.199\,70\times10^{-3}$
Ca^{2+}	19	7	5	$-0.676\,153\,60\times10^{3}$	$0.115\,69\times10^{-3}$
Sc^{3+}	19	7	5	$-0.758\,213\,93\times10^{3}$	$0.747\,39\times10^{-4}$
Ti^{4+}	19	7	5	$-0.845\,189\,77\times10^{3}$	$0.518\,15\times10^{-4}$
Va^{5+}	19	7	5	$-0.937\,075\,40\times10^{3}$	$0.377\,54\times10^{-4}$

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