Atomic Susceptibilities and Shielding Factors*

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A calculation of electric and magnetic susceptibilities and shielding factors for closed-shell atomic systems based on relativistic Hartree-Fock-Slater (RHFS) electron theory is presented. Numerical results are given for the electric dipole and quadrupole, and for the magnetic dipole and octupole cases for closed-shell atoms and ions from $Z=2$ to $Z=92$. Comparison is made with previous nonrelativistic uncoupled Hartree-Fock calculations and with experiment.

I. INTRODUCTION

An applied electric or magnetic multipole field induces an electric or magnetic multipole moment in a closed-shell atom or ion. This induced moment is proportional to the applied field, for weak fields; the proportionality constant being the electric or magnetic susceptibility.[1] The induced electric or magnetic moment gives rise to a secondary field which has the spatial symmetry of the applied field. Thus, at the nucleus of a closed-shell atom or ion, the applied multipole field is shielded (or enhanced) by a factor characteristic of the atom or ion.[2]

It is the purpose of this paper to study these atomic susceptibilities and shielding factors from the point of view of relativistic electron theory. The importance of relativity in this study is twofold; to account automatically for atomic fine structure and to allow for the rapid motion of the inner electrons of heavy atoms. A useful consequence of the relativistic approach is that electric and magnetic effects can be treated in parallel; thereby simplifying the theoretical discussion.

We describe the external applied field by a scalar potential or by a (Coulomb gauge) vector potential[3]

$$\phi_J(\vec{r}) = C_J r^J Y_{JO}(\hat{r}),$$
$$\vec{A}_J(\vec{r}) = a_J r^J \vec{Y}_{JJO}(\hat{r}). \tag{1}$$

Because of the assumed spherical symmetry of the atom or ion, it is sufficient to consider the $M=0$ component of the applied field. At large distances from the atom, the induced field behaves as follows:

$$\phi_J^{\,1} \to -\alpha_J C_J Y_{JO}(\hat{r})/r^{J+1}, \quad \text{as } r\to\infty;$$
$$\vec{A}_J^{\,1} \to [(J+1)/J]\chi_J a_J \vec{Y}_{JJO}(\hat{r})/r^{J+1}, \quad \text{as } r\to\infty. \tag{2}$$

The constants α_J and χ_J are the electric and magnetic susceptibilities[4]; they have dimensions of length to the $(2J+1)$ power.

Near the nucleus, the induced field reduces to

$$\phi_J^{\,1} \to -\gamma_J \phi_J, \quad \text{as } r\to 0;$$
$$\vec{A}_J^{\,1} \to -\sigma_J \vec{A}_J, \quad \text{as } r\to 0. \tag{3}$$

The dimensionless proportionality constants γ_J and σ_J are the electric and magnetic shielding factors.[5] A negative value of either constant represents an antishielding effect.

We describe the atom or ion by a relativistic Hartree-Fock-Slater (RHFS) product wave function. The unperturbed Hamiltonian is a sum of single-electron terms of the form[6]

$$H^0 = \vec{\alpha}\cdot\vec{p} + \beta m + V(r), \tag{4}$$

where $\vec{r}$ and $\vec{p}$ are the electron coordinate and momentum vectors, and $\vec{\alpha}$ and β are the usual Dirac matrices, $V(r)$ is a self-consistent potential constructed using a Slater average for the exchange interaction.

Single-electron orbitals are designated by a principle quantum number n, an angular momentum quantum number $\kappa = \mp(j\pm\frac{1}{2})$ for $j = l\pm\frac{1}{2}$ and an angular momentum projection quantum number m. These orbitals satisfy a central-field Dirac equation

$$H^0\psi_{n\kappa m}^{\,0} = E_{n\kappa}^{\,0}\psi_{n\kappa m}^{\,0}. \tag{5}$$

In the presence of an external field, H^0 is modified by the addition of a term $H^1 = e(\phi_J - \vec{\alpha}\cdot\vec{A}_J)$,

where e is the specific electronic charge, and ϕ_J and $\vec{A}_J$ are the multipole potentials given in Eq. (1). Replacing $\psi_{n\kappa m}{}^0 \to \psi_{n\kappa m}{}^0 + \psi_{n\kappa m}{}^1$, $E_{n\kappa}{}^0 \to E_{n\kappa}{}^0 + E_{n\kappa m}{}^1$, we find to first order in the perturbation

$$(H^0 - E_{n\kappa}{}^0)\psi_{n\kappa m}{}^1 = -(H^1 - E_{n\kappa m}{}^1)\psi_{n\kappa m}{}^0, \quad (6)$$

where $E_{n\kappa m}{}^1 = (\psi_{n\kappa m}{}^0, H^1\psi_{n\kappa m}{}^0)$.

Here we are neglecting any effect on the self-consistent potential which arises because of distortion of the orbitals. It is this approximation which leads to the relatively simple uncoupled Eq. (6) above.

In the presence of the external field, the charge density of the atomic subshell n, κ is given by $\rho_{n\kappa} = \rho_{n\kappa}{}^0 + \rho_{n\kappa}{}^1$, where $\rho_{n\kappa}{}^1$, the induced charged density, is given by

$$\rho_{n\kappa}{}^1 = e\sum_m \psi_{n\kappa m}{}^{0\dagger}\psi_{n\kappa m}{}^1 + \text{c. c.} \quad (7)$$

The current density of a closed subshell vanishes in the absence of an external field. In the presence of an external field, the induced current density for the shell n, κ is given by

$$\vec{j}_{n\kappa}{}^1 = e\sum_m \psi_{n\kappa m}{}^{0\dagger}\vec{\alpha}\psi_{n\kappa m}{}^1 + \text{c. c.} \quad (8)$$

These induced charge-current densities serve as the sources of induced electric and magnetic fields.

In Sec. II, the functions $\psi_{n\kappa m}{}^1$ are decomposed into angular momentum eigenstates and the inhomogeneous Dirac equations (6), thereby reduced to radial differential equations suitable for numerical integration. The corresponding decomposition and integration of the homogeneous equations (5) have been described previously by Lieberman, Waber, and Cromer.[7]

The induced charge and current densities of Eqs. (7) and (8) are used to find the induced fields $\phi_J{}^1$ and $\vec{A}_J{}^1$. Examination of these induced fields in the asymptotic region leads to expressions for susceptibilities while the behavior of the induced fields near the origin determines the electric and magnetic shielding factors.

II. ANGULAR DECOMPOSITION

The unperturbed single-electron states can be written

$$\psi_{n\kappa m}{}^0(\vec{r}) = \frac{1}{r}\begin{pmatrix} iG_{n\kappa}(r)\Omega_{\kappa m}(\hat{r}) \\ F_{n\kappa}(r)\Omega_{-\kappa m}(\hat{r}) \end{pmatrix}, \quad (9)$$

where $\Omega_{\kappa m}(\hat{r})$ are angular momentum eigenstates given by[8]

$$\Omega_{\kappa m}(\hat{r}) = \sum_\mu C(l\tfrac{1}{2}j; m-\mu, \mu)\chi_\mu Y_{l\,m-\mu}(\hat{r}). \quad (10)$$

Using the angular decomposition (9), the homogenous Dirac equations (5) for the unperturbed orbitals reduce to radial differential equations

$$\begin{aligned} (m + V - E_{n\kappa}{}^0)G_{n\kappa} + \left(\frac{d}{dr} - \frac{\kappa}{r}\right)F_{n\kappa} = 0, \\ \left(\frac{d}{dr} + \frac{\kappa}{r}\right)G_{n\kappa} + (m - V + E_{n\kappa}{}^0)F_{n\kappa} = 0. \end{aligned} \quad (11)$$

These equations are solved numerically for the self-consistent potential $V(r)$, the binding energies $E_{n\kappa}{}^0$, and for the radial functions $G_{n\kappa}(r)$ and $F_{n\kappa}(r)$ using numerical procedures similar to those described in Ref. 7.

A. Electric Fields

Given an applied electric field described by the scalar potential of Eq. (1), one finds, using Eq. (6), a first-order energy shift

$$E_{n\kappa m}{}^1 = eC_J I_{\kappa m \kappa m JO}\int_0^\infty dr\, r^J (G_{n\kappa}{}^2 + F_{n\kappa}{}^2), \quad (12)$$

where

$$I_{\kappa m \kappa' m' JM} = (-1)^{J+j'-j}\left(\frac{(2J+1)(2j'+1)}{4\pi(2j+1)}\right)^{1/2} \times C(j'Jj;\tfrac{1}{2}0)C(j'Jj;m'Mm)\Pi_{lJl'}, \quad (13)$$

with $\Pi_{lJl'} = \begin{cases} 1, & l+l'+J \text{ even} \\ 0, & l+l'+J \text{ odd} \end{cases}$ (14)

Clearly Π_{lJl} together with the first-order energy shift vanishes unless J is even. The integral appearing in Eq. (13) is the expectation value of r^J in the state $\psi_{n\kappa m}{}^0$ and is denoted by $\langle r^J \rangle_{n\kappa}$. Assuming a first-order wave function

$$\psi_{n\kappa m}{}^1(\vec{r}) = eC_J\sum_{\kappa'} I_{\kappa' m \kappa m JO} \times \frac{1}{r}\begin{pmatrix} iS_{n\kappa\kappa'}(r)\Omega_{\kappa' m}(\hat{r}) \\ T_{n\kappa\kappa'}(r)\Omega_{-\kappa' m}(\hat{r}) \end{pmatrix}, \quad (15)$$

One may reduce the inhomogeneous first-order

equations (6) to radial equations

$$(m+V-E_{n\kappa}{}^{0})S_{n\kappa\kappa'}+\left(\frac{d}{dr}-\frac{\kappa'}{r}\right)T_{n\kappa\kappa'}=K_{n\kappa\kappa'J},$$
$$\left(\frac{d}{dr}+\frac{\kappa'}{r}\right)S_{n\kappa\kappa'}+(m-V+E_{n\kappa}{}^{0})T_{n\kappa\kappa'}=-L_{n\kappa\kappa'J}, \tag{16}$$

where

$$K_{n\kappa\kappa'J}=(\langle r^{J}\rangle_{n\kappa}\delta_{\kappa\kappa'}-r^{J})G_{n\kappa},$$
$$L_{n\kappa\kappa'}=(\langle r^{J}\rangle_{n\kappa}\delta_{\kappa\kappa'}-r^{J})F_{n\kappa}. \tag{17}$$

Equations (16) are solved numerically for $S_{n\kappa\kappa'}$ and $T_{n\kappa\kappa'}$, for those values of κ' allowed by the selection rules in Eq. (13).

One easily proves that the induced current density $\vec{j}_{n\kappa}{}^{1}(\vec{r})$ (and therefore the induced magnetic field) vanishes. The induced charge density $\rho_{n\kappa}{}^{1}(\vec{r})$ of Eq. (7) simplifies to

$$\rho_{n\kappa}{}^{1}(\vec{r})=C_{J}(2J+1)U_{n\kappa}(r)Y_{J\,0}(\hat{r})/r^{2},$$

with

$$U_{n\kappa}(r)=\frac{2\alpha}{2J+1}\sum_{\kappa'}(2j+1)(2j'+1)\Lambda_{jJj'}\Pi_{lJl'}$$
$$\times(G_{n\kappa}S_{n\kappa\kappa'}+F_{n\kappa}T_{n\kappa\kappa'}). \tag{18}$$

The multipole selection rules limiting κ' are contained in the factors $\Pi_{lJl'}$ and in

$$\Lambda_{jJj'}=C^{2}(jJj';\tfrac{1}{2}0)/(2j'+1). \tag{19}$$

Summing over subshells, one obtains an expression for the induced charge density of the entire atom or ion.

$$\rho^{1}(\vec{r})=C_{J}(2J+1)U(r)Y_{JO}(\hat{r})/r^{2}, \tag{20}$$

with $U(r)=\sum_{n\kappa}U_{n\kappa}(r)$.

The induced charge density gives rise to an induced electric field with scalar potential

$$\phi_{JO}{}^{1}(\vec{r})=C_{J}Y_{JO}(\hat{r})[r^{-J-1}\int_{0}^{r}r'^{J}U(r')dr'$$
$$+r^{J}\int_{r}^{\infty}r'^{-J-1}U(r')dr'], \tag{21}$$

which has the angular behavior of the applied potential.

As $r\to\infty$, the second term in the bracket of Eq. (21) vanishes; comparing the first term with the definition of the electric susceptibility given in Eq. (2), one finds

$$\alpha_{J}=-\int_{0}^{\infty}dr\,r^{J}U(r). \tag{22}$$

For sufficiently small values of r, the first term in Eq. (21) is negligible. Comparing Eq. (21) with Eq. (3) in the $r\to 0$ limit, one finds the electric shielding factor

$$\gamma_{J}=-\int_{0}^{\infty}dr\,r^{-J-1}U(r). \tag{23}$$

Calculations of α_J and γ_J are identical except for the weight factors r^J or r^{-J-1} occurring in the integrals in Eqs. (22) and (23).

B. Magnetic Fields

In the case of an applied magnetic multipole field of order J, the first-order energy shift is given by

$$E_{n\kappa m}{}^{1}=-ie\,a_{J}I_{-\kappa m\,\kappa m JO}\frac{4\kappa}{[J(J+1)]^{1/2}}$$
$$\times\int_{0}^{\infty}dr\,r^{J}G_{n\kappa}F_{n\kappa}. \tag{24}$$

The amplitude factor a_J occurring in Eqs. (1) and (24) is imaginary; the energy shift is therefore real. For even-order magnetic multipoles, the parity factor occurring in $I_{-\kappa m\,\kappa m JO}$ causes the energy shift to vanish.

Expanding the first-order wave function as

$$\psi_{n\kappa m}{}^{1}(\vec{r})=iea_{J}\sum_{\kappa'}\frac{\kappa+\kappa'}{[J(J+1)]^{1/2}}I_{-\kappa' m\,\kappa m JO}$$
$$\times\frac{1}{r}\begin{pmatrix}iS_{n\kappa\kappa'}\Omega_{\kappa' m}\\ T_{n\kappa\kappa'}\Omega_{-\kappa' m}\end{pmatrix}, \tag{25}$$

one reduces the inhomogeneous equations (6) to a set of radial equations of precisely the form given in Eq. (16); the driving terms are now given by

$$K_{n\kappa\kappa'J}=r^{J}F_{n\kappa}-(r^{J})_{n\kappa}\delta_{\kappa\kappa'}G_{n\kappa}, \tag{26}$$

$$L_{n\kappa\kappa' J} = r^J G_{n\kappa} - (r^J)_{n\kappa}\delta_{\kappa\kappa'} F_{n\kappa},$$

where we have introduced the notation

$$(r^J)_{n\kappa} = 2\int_0^\infty dr\, r^J G_{n\kappa} F_{n\kappa}. \tag{27}$$

One may now evaluate the induced charge and current densities. It is easily established that the induced charge density vanishes. The induced current density can be obtained from Eq. (8). Summing over closed subshells one arrives at

$$\vec{j}^1(\vec{r}) = a_J(2J+1)S(r)\vec{Y}_{JJO}(\hat{r})/r^2, \tag{28}$$

where

$$S(r) = \frac{2\alpha}{2J+1}\sum_{n\kappa\kappa'}{}' (2j+1)(2j'+1)\frac{(\kappa+\kappa')^2}{J(J+1)} \times \Lambda_{jJj'}\Pi_{lJ+1l'}(G_{n\kappa}T_{n\kappa\kappa'} + F_{n\kappa}S_{n\kappa\kappa'}).$$

The vector potential derived from the induced current density of Eq. (28) is

$$\vec{A}_J^{\,1} = a_J\vec{Y}_{JJO}(\hat{r})[r^{-J-1}\int_0^r r'^J S(r')dr' + r^J\int_r^\infty r'^{-J-1}S(r')dr']. \tag{29}$$

Comparing Eq. (29) with the definitions of magnetic susceptibility and shielding factor given in Eq. (2) and Eq. (3), we see that

$$\chi_J = \frac{J}{J+1}\int_0^\infty dr\, r^J S(r), \tag{30}$$

and

$$\sigma_J = -\int_0^\infty dr\, r^{-J-1}S(r). \tag{31}$$

III. NONRELATIVISTIC LIMIT

The nonrelativistic limit of the frequency dependent electromagnetic susceptibilities has been discussed previously for the dipole ($J=1$) case.[4] It was shown that calculations of magnetic susceptibilities could be reduced to evaluation of matrix elements of powers of r; the corresponding nonrelativistic calculation of electric susceptibilities was found to be nontrivial even in the dipole case.

It is interesting to examine the nonrelativistic limit of static susceptibilities and shielding factors for magnetic multipoles of order $J \geq 1$. We again find that the dipole case is essentially trivial; whereas, for $J > 1$, no simple nonrelativistic limit occurs.

The limit is to be taken of integrals of the form

$$J_{n\kappa\kappa'} = \int_0^\infty dr\, r^a(G_{n\kappa}T_{n\kappa\kappa'} + F_{n\kappa}S_{n\kappa\kappa'}), \tag{32}$$

where

$$a = \begin{cases} J, & \text{for the susceptibility} \\ -J-1, & \text{for the shielding factor.} \end{cases}$$

Using the Pauli approximation to Eqs. (11) for $F_{n\kappa}$ and $G_{n\kappa}$, one easily shows

$$(r^J)_{n\kappa} \approx \frac{1}{2m}(J-2\kappa)\langle r^{J-1}\rangle_{n\kappa}. \tag{33}$$

The same approximation applied to the inhomogeneous equations (16) gives

$$T_{n\kappa\kappa'} \approx -\frac{1}{2m}\left[\left(\frac{d}{dr} + \frac{\kappa'}{r}\right)S_{n\kappa\kappa'} + L_{n\kappa\kappa'}\right], \tag{34}$$

where $S_{n\kappa\kappa'}$ satisfies

$$\left[(m - V - E_{n\kappa}{}^0) - \frac{1}{2m}\left(\frac{d^2}{dr^2} - \frac{\kappa'(\kappa'+1)}{r^2}\right)\right]S_{n\kappa\kappa'} = \frac{J-\kappa-\kappa'}{2m}\left(r^{J-1} - \delta_{\kappa\kappa'}\langle r^{J-1}\rangle_{n\kappa}\right)G_{n\kappa}. \tag{35}$$

Evaluation of $J_{n\kappa\kappa'}$ using these Pauli-approximation wave functions gives

$$J_{n\kappa\kappa'} \approx -\frac{1}{2m}\langle r^{a+1}\rangle_{n\kappa} + \frac{a-\kappa-\kappa'}{2m} \times \int_0^\infty dr\, r^{a-1}G_{n\kappa}S_{n\kappa\kappa'}. \tag{36}$$

The inhomogeneous Schrödinger equation (35) has simple solutions only in the dipole case $J=1$. For a magnetic dipole the selection rules give $\kappa' = \kappa, -\kappa \pm 1$, and we have two distinct cases:

(i) If $\kappa' = \kappa$ or $\kappa' = -\kappa + 1$, the driving term of Eq. (35), vanishes, and the solution is trivial $S_{n\kappa\kappa'} = 0$; from Eq. (36) we, therefore, find

$$J_{n\kappa\kappa'} \approx -\frac{1}{2m}\langle r^{a+1}\rangle_{n\kappa}. \tag{37}$$

(ii) When $\kappa' = -\kappa - 1$, the driving term of Eq. (35) is simply $G_{n\kappa}/m$. If we set $E_{n\kappa}{}^0 - E_{n\kappa'}{}^0 = \Delta_{n\kappa\kappa'}$ (the fine-structure separation), then

$$S_{n\kappa\kappa'} = G_{n\kappa}/(m\Delta_{n\kappa\kappa'}). \tag{38}$$

Using this result in Eq. (36), we find

$$J_{n\kappa\kappa'} = -\frac{1}{2m}\langle r^{a+1}\rangle_{n\kappa} + \frac{a+1}{2m^2\Delta_{n\kappa\kappa'}} \times \langle r^{a-1}\rangle_{n\kappa}. \tag{39}$$

The states n, κ and $n, -\kappa - 1$ have the same l and are degenerate in the nonrelativistic limit. If these subshells are both filled, the second term of Eq. (39) gives no contribution on summing over

κ and κ', since $\Delta_{n\kappa\kappa'} = -\Delta_{n\kappa'\kappa}$ and the rest of the summand is symmetric in κ and κ'. For atoms and ions with filled nonrelativistic subshells the contribution of the integral $J_{n\kappa\kappa'}$ is $-\langle r^{a+1}\rangle_{n\kappa}/2m$ for all allowed values of κ'. Using the fact that

$$\tfrac{1}{2}\sum_{\kappa'}(2j'+1)(\kappa+\kappa')^2\Lambda_{j_1 j'} = 1, \tag{40}$$

it is easily verified that the nonrelativistic limit of the magnetic dipole susceptibility is given by the Van Vleck equation[1]

$$\chi_{NR} = -\frac{\alpha}{6m}\sum_{n\kappa}(2j+1)\langle r^2\rangle_{n\kappa}. \tag{41}$$

In a similar way, the magnetic dipole shielding factor reduces to the formula of Lamb[2]

$$\sigma_{NR} = \tfrac{1}{3}e\frac{V(0)}{mc^2}, \tag{42}$$

where $V(0) = e\sum_{n\kappa}(2j+1)\langle\frac{1}{r}\rangle_{n\kappa}$

is the electron potential at the origin.

For an atom or ion, which has a filled subshell n, κ but no electrons in the subshell n, $-\kappa-1$, the second terms of Eq. (39) gives an additional contribution to the susceptibility

$$\Delta\chi_{n\kappa} = \frac{\alpha}{6m}\frac{(2j+1)(2j+3)}{4(j+1)m\Delta_{n,\kappa,-\kappa-1}} \tag{43}$$

The shielding factor in this case is corrected by

$$\Delta\sigma_{n\kappa} = \frac{\alpha}{6m}\frac{(2j+1)(2j+3)}{4(j+1)m\Delta_{n,\kappa,-\kappa-1}}\langle\frac{1}{r^3}\rangle_{n\kappa}. \tag{44}$$

These contributions are quite large, in general, because of the small size of the fine-structure separation $\Delta_{n,\kappa,-\kappa-1}$ in outer subshells.

IV. FINITE NUCLEAR SIZE

Interest in atomic shielding factors results from their effect of reducing the apparent coupling of of nuclear multipoles with external applied fields. The magnetic dipole is of particular interest in this regard since measurements of nuclear magnetic moments are sufficiently precise to warrant inclusion of shielding corrections. Experiments to measure nuclear magnetic moments involve the interaction energy of the applied field with the nuclear magnetic moment. For a nucleus described by a state function $\Psi(\vec{r}_1,\ldots,\vec{r}_A)$ in a magnetic field $\vec{B}(\vec{r})$, the interaction energy is

$$E_I = -\mu_N\int d^3r_1\cdots d^3r_A\,\Psi^\dagger(\vec{r}_1,\ldots,\vec{r}_A) \times\sum_{i=1}^{A}[g_l(i)\vec{l}_i + g_s(i)\vec{s}_i]\cdot\vec{B}(\vec{r}_i)\Psi(\vec{r}_1,\ldots,\vec{r}_A), \tag{45}$$

where $\mu_N = e\hbar/2Mc$ is the nuclear Bohr magneton. The summation is over nucleons; $g_s(i)$ is the gyromagnetic ratio of nucleon i, and $g_l(i)$ is one for protons and zero for neutrons; $\vec{l}_i$ is the orbital angular momentum, and $\vec{s}_i$ is the spin. The interaction energy is considerably simplified in the extreme single-particle model for even-odd nuclei where the magnetic moment is due to a single unpaired nucleon. In this approximation

$$E_I = -\mu_N\int d^3r\,\psi^\dagger(\vec{r})[g_l\vec{l} + g_s\vec{s}]\cdot\vec{B}(\vec{r})\psi(\vec{r}), \tag{46}$$

where $\psi(\vec{r}) = u(r)\Omega_{\kappa m}(\hat{r})/r$

is the single-particle state of the unpaired nucleon. The magnetic field is the sum of an external dipole field $\vec{B}^0$ and an induced field $\vec{B}^1(\vec{r})$ determined from Eq. (29). One finds

$$\vec{B}^1(\vec{r}) = -a(r)\vec{B}^0 - b(r)(\hat{r}\cdot\vec{B}^0)\hat{r}, \tag{47}$$

where

$$a(r) = \int_r^\infty\frac{dr'}{r'}S(r') - \frac{1}{2r^3}\int_0^r dr'r'S(r'),$$

$$b(r) = \frac{3}{2r}\int_0^r dr'r'S(r'). \tag{48}$$

Taking $\vec{B}^0$ along the z axis and noting that $\vec{r}\cdot\vec{l} = 0$, the interaction energy becomes

$$E_I = -\mu_N B^0\int d^3r\psi^\dagger(\vec{r})[g_l l_z + g_s s_z] \times[1-a(r)]\psi(\vec{r}) + \mu_N B^0\int d^3r\psi^\dagger(\vec{r})g_s \times\hat{s}\cdot\hat{r}P_1(\cos\theta)b(r)\psi(r). \tag{49}$$

Using the states described in Eq. (46) the first term is easily evaluated to give

$$E_{Ia} = -\vec{\mu}\cdot\vec{B}^0[1-\textstyle\int_0^\infty dr\,u^2(r)a(r)], \tag{50}$$

where $\vec{\mu} = \mu_N g_N\vec{I}$ is the Schmidt value for the nuclear moment,[9] g_N is the nuclear g factor, and $\vec{I} = \vec{l} + \vec{s}$ is the nuclear spin. The second term may be written

$$E_{Ib} = \vec{\mu}\cdot\vec{B}^0\frac{g_s}{g_N}\frac{1}{4I(I+1)}\int_0^\infty dr\,u^2(r)b(r). \tag{51}$$

For a surface-current model which assumes the odd nucleon at the nuclear surafce $[u^2(r) = \delta \times(r-R)$, where R is the nuclear radius] the interaction energy becomes

$$E_I = -\vec{\mu}\cdot\vec{B}^0\left[1 - \int_R^\infty\frac{dr}{r^3}S(r) + \left(\frac{1}{2} + \frac{g_s}{g_N}\frac{3}{8I(I+1)}\right)\frac{1}{R^3}\int_0^R dr\,rS(r)\right]. \tag{52}$$

It is convenient to consider the dipole shielding factor as a sum of a major contribution σ and a small correction $\delta\sigma$. Writing $E_I = -\vec{\mu}\cdot\vec{B}^0(1-\sigma-\delta\sigma)$, one can make the identification

$$\sigma = \int_R^\infty \frac{dr}{r^2} S(r), \tag{53}$$

and $$\delta\sigma \approx -\frac{1}{2R^3}\int_0^R dr\, r S(r).$$

Results of numerical calculations using these equations for the magnetic dipole shielding factor are given for several atoms and ions in Sec. V. Similar equations can be developed for finite nuclear size corrections to higher-order shielding factors. These corrections are small, however, compared to other inaccuracies for higher-order multipoles.

V. RESULTS AND CONCLUSIONS

In this section, we present numerical values of the susceptibilities and shielding factors for a number of closed-shell atoms and ions. Table I gives these results for the magnetic and electric dipole, the electric quadrupole, and the magnetic octupole.

Values of the magnetic dipole shielding factor computed using Eq. (53) are given in the first column of Table I. As noted previously,[5] the finite nuclear size correction is negligible for light elements. For example, the $\delta\sigma$ contribution to $10^2\,\sigma$ is -0.86×10^{-7} (which is negligible) for Ne, and -0.0039 for Hg (or about -0.25% of the uncorrected value).

The second column of Table I gives the nonrelativistic values of the shielding factor (σ_{NR}) computed with the Lamb formula Eq. (42) but using relativistic wave functions in evaluating the expectation values. These nonrelativistic values agree fairly well with the completely nonrelativistic results of Dickinson[10] for low atomic numbers but show an increasing discrepancy with increasing Z. The origin of this discrepancy is the relativistic contraction of the inner electron orbits which give large contributions to the shielding factor. In addition to the "contraction" effect, there is a "current" effect which arises from the use of the Dirac current rather than the Schrödinger current as a source of the internal fields. As an example, comparison of the results of Table I with Dickinson's value for $U(\sigma = 1.16$ for $Z = 92)$ shows a 20% correction due to contraction and an even larger 66% current effect. Relativistic corrections thus increase the shielding factor of U by 100% over the nonrelativistic value. Similarly, comparison of the values of χ and χ_{NR} [computed using the Van Vleck formula Eq. (41)] shows that the current effect increases with atomic number in susceptibility calculations, also.

A nonrelativistic computation of magnetic dipole shielding factors, which takes electron-electron correlation into account by using Hylleraas-type wave functions in the Lamb formula, has been given by Glick[11] for heliumlike atoms and ions. Comparison of his results for He ($\sigma = 5.9935\times10^{-5}$) and Li^+ ($\sigma = 9.5459\times10^{-5}$) with Table I shows that relativistic corrections are of the same order of magnitude and sign as correlation effects for these low Z elements.

It should be mentioned that for the helium sequence, relativistic Hartree wave functions, rather than RHFS, have been used, since computations with the Slater average exchange term seriously underestimate the helium binding energy. Even with this modification the computed binding energy of the negative hydrogen ion of 1.258 eV is rather poor. However, the shielding factor does not appear to be too sensitive to this since the value given in Table I is in fair agreement with that of Glick, H^- ($\sigma = 2.4670\times10^{-5}$).

The magnetic dipole shielding factors and susceptibilities, column three of Table I, for several sequences, e.g., that beginning with un-ionized carbon, appear to be abnormally large. These sequences have closed relativistic subshells which are open in the nonrelativistic limit; in carbon, for example, the $2p_{1/2}$ ($\kappa = 1$) state is filled, but the $2p_{3/2}$ ($\kappa = -2$) state is empty. The large contribution comes from the terms given in Eqs. (43) and (44). The accuracy of these contributions depend on how accurately the fine-structure separation is determined numerically. Since this separation may not be determined accurately for the outer atomic electrons these values may be unreliable; they are included only as an indication of the large contributions of such subshells.

The magnetic dipole susceptibility has been measured for the noble gases.[12] The experimental values corresponding to the theoretical values given in Table I are He (3.35 ± 0.13), Ne (11.56 ± 0.231), Ar (32.08 unweighted), Kr (48.15 ± 0.66), and Xe (75.62 ± 1.16). The two sets agree within experimental error except in the case of He.

The nonrelativistic values of the magnetic dipole susceptibility χ_{NR} are computed using the Van Vleck formula, Eq. (41), but evaluating the matrix elements using relativistic wave functions. The close agreement between the fully relativistic and these nonrelativistic values indicates that the susceptibility is due to the outer subshells which are nonrelativistic. The individual subshell contributions given in Table II confirm this conclusion, since 92% of the susceptibility of Hg is due to electrons bound by less than 10 eV.

The electric dipole shielding factor is of little experimental interest since the nucleus has no permanent electric dipole moment. However, on general theoretical grounds,[13] one has

TABLE I. Electric and magnetic shielding factors, polarizabilities, and susceptibilities for closed-shell atoms and ions: Z = atomic number, N = number of electronic subshells, and I = degree of ionization. Polarizabilities and susceptibilities are given in angstrom units raised to the appropriate power.

				Magnetic dipole				Electric dipole		Electric quadrupole		Magnetic octupole	
*	Z	N	I	$10^2\,\sigma$	$10^2\,\sigma_{NR}$	$10^6\,\chi$	$10^6\,\chi_{NR}$	β	α	γ	α_2	$10^2\,\sigma_3$	$10^6\,\chi_3$
H	1	1	0	0.001775	0.001775	3.956	3.956	1.0000	0.6687	0.3333	0.6253	−0.002282	−14.01
H	1	1	−1	0.002435	0.002434	24.82	24.82	3.339	16.86	1.185	99.47	−0.004727	−2007
He	2	1	0	0.005994	0.005990	3.125	3.125	1.236	0.2210	0.4206	0.09835	−0.009040	−2.137
Li	3	1	1	0.009553	0.009542	1.174	1.174	0.7632	0.03044	0.2575	0.004712	−0.01356	−0.1037
Be	4	1	2	0.01312	0.01310	0.6109	0.6113	0.5522	0.008165	0.1856	0.0006373	−0.01810	−0.01410
B	5	1	3	0.01670	0.01665	0.3737	0.3740	0.4326	0.003041	0.1451	0.0001427	−0.02266	−0.003165
C	6	1	4	0.02030	0.02021	0.2519	0.2522	0.3557	0.001378	0.1191	0.00004314	−0.02722	−0.0009588
Be	4	2	0	0.01531	0.01527	22.43	22.43	4.024	11.83	1.041	15.50	0.01347	−367.3
B	5	2	1	0.01979	0.01973	10.25	10.25	2.793	2.889	0.6797	1.213	0.02154	−29.98
C	6	2	2	0.02428	0.02419	5.980	5.981	2.159	1.136	0.5069	0.2204	0.02963	−5.570
N	7	2	3	0.02880	0.02864	3.940	3.941	1.764	0.5611	0.4046	0.06001	0.03771	−1.538
O	8	2	4	0.03333	0.03310	2.799	2.799	1.493	0.3176	0.3367	0.02082	0.04577	−0.5388
F	9	2	5	0.03790	0.03756	2.093	2.093	1.294	0.1968	0.2884	0.008515	0.05383	−0.2219
C	6	3	0	5.882		−4327		2.390	2.607	6275	521.1	0.02729	15.60
N	7	3	1	5.743		−1933		1.923	0.7685	2996	55.79	0.03465	−0.9710
O	8	3	2	4.216		−772.9		1.607	0.3485	1344	8.430	0.04236	−0.5599
F	9	4	−1	0.04951	0.04914	21.32	21.33	1.579	2.916	−42.19	7.843	10.19	−202.6
Ne	10	4	0	0.05690	0.05640	11.79	11.79	1.378	0.4162	−9.550	0.2953	3.191	−6.746
Na	11	4	1	0.06426	0.06360	8.049	8.051	1.215	0.1544	−5.072	0.06325	2.244	−1.389
Mg	12	4	2	0.07165	0.07078	5.937	5.940	1.083	0.07498	−3.350	0.02100	1.899	−0.4546
Al	13	4	3	0.07907	0.07797	4.588	4.591	0.9771	0.04185	−2.462	0.008671	1.740	−0.1868
Si	14	4	4	0.08652	0.08516	3.663	3.666	0.8897	0.02550	−1.927	0.004102	1.663	−0.08836
S	16	4	6	0.1016	0.09957	2.499	2.502	0.7546	0.01124	−1.323	0.001192	1.620	−0.02577
Cl	17	4	7	0.1092	0.1068	2.117	2.120	0.7105	0.007926	−1.139	0.0007038	1.628	−0.01527
S	16	5	4	0.1049	0.1028	8.836	8.839	2.671	0.9811	−1.046	0.2454	0.6831	−7.446
Cl	17	5	5	0.1129	0.1105	7.177	7.180	2.412	0.6602	−0.9099	0.1253	0.4973	−3.919
S	16	6	2	2.102		−344.8		2.789	1.649	1863	33.55	0.8211	−5.302
Cl	17	6	3	2.080		−228.3		2.505	0.9896	1354	12.21	0.6596	−3.411
Cl	17	7	−1	0.1198	0.1173	47.71	47.71	2.748	7.541	−83.50	19.46	86.46	−438.8
A	18	7	0	0.1292	0.1262	31.82	31.83	2.488	2.243	−30.72	2.041	36.22	−39.67
K	19	7	1	0.1387	0.1352	23.99	24.00	2.270	1.140	−19.16	0.6375	25.52	−12.22
Ca	20	7	2	0.1483	0.1441	19.05	19.05	2.087	0.6893	−13.95	0.2722	20.76	−5.303
Ti	22	7	4	0.1675	0.1620	13.09	13.10	1.800	0.3212	−9.006	0.07532	16.29	−1.545
Cr	24	7	6	0.1872	0.1799	9.653	9.659	1.584	0.1785	−6.636	0.02799	14.17	−0.6038
Fe	26	7	8	0.2072	0.1980	7.448	7.453	1.414	0.1099	−5.244	0.01234	12.92	−0.2782

TABLE I. (*Con't.*)

				Magnetic dipole				Electric dipole		Electric quadrupole		Magnetic octupole	
*	Z	N	I	$10^2\,\sigma$	$10^2\,\sigma_{NR}$	$10^6\,\chi$	$10^6\,\chi_{NR}$	β	α	γ	α_2	$10^2\,\sigma_3$	$10^6\,\chi_3$
Ni	28	7	10	0.2278	0.2161	5.935	5.940	1.278	0.07249	−4.333	0.006099	12.08	−0.1430
Cu	29	9	1	0.2597	0.2463	23.37	23.38	1.350	1.115	−17.37	1.529	150.2	−75.61
Zn	30	9	2	0.2725	0.2577	18.47	18.48	1.290	0.4186	−12.31	0.2834	74.40	−12.32
Ga	31	9	3	0.2855	0.2690	15.39	15.40	1.235	0.2130	−9.905	0.09594	56.24	−3.781
Ge	32	9	4	0.2985	0.2803	13.18	13.19	1.185	0.1269	−8.397	0.04259	48.22	−1.538
As	33	9	5	0.3117	0.2916	11.50	11.51	1.137	0.08327	−7.322	0.02214	43.67	−0.7384
Br	35	9	7	0.3385	0.3144	9.070	9.082	1.053	0.04263	−5.855	0.007916	38.70	−0.2302
As	33	10	3	0.3142	0.2940	20.52	20.53	3.352	1.572	−7.415	0.5720	4.315	−14.65
Br	35	10	5	0.3416	0.3173	15.42	15.43	2.898	0.8054	−5.914	0.1892	3.783	−5.098
Br	35	11	3	1.243		−35.21		2.977	1.271	834.6	5.766	3.854	−3.577
Br	35	12	−1	0.3474	0.3230	65.46	65.50	3.295	10.44	−210.0	28.99	1075	−716.4
Kr	36	12	0	0.3622	0.3355	47.84	47.86	3.069	3.483	−84.15	3.774	426.2	−72.86
Rb	37	12	1	0.3772	0.3480	38.68	38.69	2.877	1.910	−54.97	1.376	286.6	−25.54
Sr	38	12	2	0.3923	0.3606	32.57	32.59	2.711	1.229	−41.35	0.6692	223.1	−12.50
Zr	40	12	4	0.4233	0.3857	24.66	24.67	2.440	0.6376	−28.09	0.2310	162.9	−4.529
Mo	42	12	6	0.4551	0.4110	19.63	19.65	2.223	0.3860	−21.43	0.1027	133.2	−2.124
Ru	44	12	8	0.4879	0.4364	16.13	16.14	2.045	0.2551	−17.39	0.05257	115.4	−1.143
Pd	46	14	0	0.5360	0.4759	53.14	53.17	2.086	4.928	−51.56	13.25	1944	−712.7
Ag	47	14	1	0.5549	0.4902	42.62	42.64	2.000	1.856	−35.82	2.053	752.6	−91.64
Cd	48	14	2	0.5741	0.5046	36.26	36.28	1.928	1.012	−29.27	0.7060	523.2	−28.05
Sn	50	14	4	0.6133	0.5334	28.21	28.23	1.803	0.4530	−22.34	0.1783	371.8	−5.932
Te	52	14	6	0.6540	0.5624	23.05	23.08	1.694	0.2594	−18.32	0.06952	311.9	−2.021
I	53	14	7	0.6746	0.5770	21.07	21.10	1.645	0.2062	−16.84	0.04729	293.3	−1.301
I	53	15	5	0.6771	0.5793	30.07	30.09	3.708	1.449	−18.24	0.4367	19.68	−10.05
I	53	17	−1	0.6820	0.5841	96.03	96.17	4.304	15.84	−396.1	49.84	5190	−1321
Xe	54	17	0	0.7042	0.5996	74.72	74.79	4.033	6.010	−177.1	8.192	2112	−166.1
Cs	55	17	1	0.7268	0.6151	62.96	63.00	3.816	3.528	−121.3	3.443	1429	−69.83
Ba	56	17	2	0.7497	0.6307	54.76	54.81	3.629	2.385	−94.23	1.892	1113	−41.42
La	57	17	3	0.7733	0.6463	48.56	48.60	3.465	1.739	−77.88	1.214	931	−30.34
Ce	58	17	4	0.7973	0.6621	43.62	43.66	3.320	1.329	−66.79	0.9129	814.6	−28.68
Yb	70	19	2	1.168	0.8908	44.21	44.28	2.789	1.718	−92.95	0.5465		
Hf	72	19	4	1.240	0.9296	35.87	35.93	2.596	0.7504	−68.12	0.1978	1306	−3.475
W	74	19	6	1.316	0.9688	30.30	30.36	2.435	0.4603	−54.73	0.1019	1074	−1.588
Re	75	19	7	1.356	0.9887	28.10	28.16	2.363	0.3772	−50.11	0.07987	999.1	−1.255
Ir	77	19	9	1.439	1.029	24.49	24.54	2.231	0.2668	−43.11	0.04714	880.7	−0.7629
Au	79	19	11	1.528	1.070	21.62	21.67	2.115	0.1979	−38.14	0.03037	800.9	−0.5009

TABLE I. (*Con't.*)

*	Z	N	I	Magnetic dipole $10^2\sigma$	$10^2\sigma_{NR}$	$10^6\chi$	$10^6\chi_{NR}$	Electric dipole β	α	Electric quadrupole γ	α_2	Magnetic octupole $10^2\sigma_3$	$10^6\chi_3$
Au	79	21	1	1.542	1.083	59.02	59.11	2.469	2.792	−65.58	4.487	11099	−252.1
Hg	80	21	2	1.585	1.105	51.86	51.93	2.378	1.615	−60.20	1.546	6140	−74.67
Tl	81	21	3	1.634	1.127	46.60	46.67	2.304	1.074	−55.17	0.7423	4511	−32.35
Pb	82	21	4	1.684	1.149	42.46	42.52	2.240	0.7750	−50.88	0.4206	3706	−16.91
Bi	83	21	5	1.737	1.172	39.05	39.12	2.182	0.5898	−47.24	0.2636	3222	−9.911
Hg	80	22	0	1.587	1.106	75.37	75.46	5.364	9.129	−88.73	10.06	−708.4	−184.7
Tl	81	22	1	1.636	1.129	64.48	64.55	4.879	5.187	−75.21	3.528	−193.3	−61.68
Pb	82	22	2	1.686	1.151	57.07	57.15	4.539	3.439	−66.82	1.739	12.55	−29.34
Bi	83	22	3	1.739	1.174	51.47	51.54	4.274	2.470	−60.78	1.006	113.9	−16.57
Pb	82	23	0	2.055		58.06		4.507	10.10	1367	54.72	−140.0	178.3
Bi	83	23	1	2.103		54.06		4.222	4.616	926.6	14.72	14.16	14.93
Po	84	23	2	2.153		50.29		3.986	2.898	720.0	6.525	103.1	−2.362
At	85	23	3	2.205		46.88		3.785	2.043	591.4	3.532	155.3	−5.079
Rn	86	24	0	1.914	1.248	93.71	94.05	4.546	7.906	−438.8	12.25	14602	−285.0
Ra	88	24	2	2.038	1.297	71.96	72.14	4.101	3.095	−242.4	2.840	7429	−65.66
Th	90	24	4	2.173	1.347	59.50	59.64	3.786	1.750	−177.5	1.303	5341	−36.31
U	92	24	6	2.319	1.399	50.89	51.00	3.534	1.141	−143.9	0.8569	4374	−32.21

$$\beta = \gamma_1 = (Z - I)/Z, \tag{54}$$

where I is the degree of ionization, and Z is the nuclear charge. The computed values given in Table I are not generally in agreement with the theoretical values. This is an unfortunate consequence of the use of the uncoupled equations, which the present relativistic calculation shares with previous uncoupled nonrelativistic calculations.

The He-sequence results presented here for the electric dipole and electric quadrupole shielding factors and susceptibilities are in good agreement with the previous uncoupled nonrelativistic calculations summarized by Dalgarno.[14] Furthermore, the values given in Table I are in fair agreement with the results of previous authors for the electric dipole and quadrupole susceptibilities, and the electric quadrupole shielding factors of many heavier atoms and ions. Previous calculations which used Hartree orbitals gave similar values for shielding factors but the susceptibilities tended to be considerably higher than the values reported here. For negative ions, however, the values quoted in Table I are considerably larger than the corresponding nonrelativistic values given by Sternheimer[15]; F^- (− 22.53), Cl^- (− 56.6), Br^- (− 123.0), and I^- (− 138.4). Examination of Table II shows that over 97% of the electric dipole susceptibility, and 99% of the quadrupole susceptibility is due to the last three subshells which are bound by less than 1.25 Ry. It is also these subshells which are computed least accurately. The electric dipole susceptibilities of the noble gases have been measured by Cuthbertson and Cuthbertson[16]; He (0.6055), Ne (0.3963), Ar (1.646), Kr (2.486), and Xe (4.049) in the units of Table I.

The magnetic octupole shielding factors and susceptibilities are given in the last two columns of Tables I and II. Negative shielding factors indicate antishielding or an increase of the field at the nucleus due to the electron cloud. The octupole shielding factor tends to increase with atomic number. The Hg sequence shows a change of sign between Tl and Pb. This is because the contributions of the inner orbits remain approximately constant while the two outer orbits give contributions of opposite sign which shift in magnitude. Examination of Table II shows that the contributions of the inner orbits to the octupole shielding factor of Hg are important whereas only the last three orbitals contribute appreciably to the octupole susceptibility.

We summarize with the following comments: (i) RFHS wave functions give magnetic dipole susceptibilities for the noble gases above He which agree with experiment. Relativistic corrections are small and even for the heavier elements it suffices to use relativistic wave functions in the Van Vleck formula. (ii) In the evaluation of magnetic dipole shielding factors, current corrections are more

TABLE II. Energy eigenvalues and subshell contributions to magnetic and electric susceptibilities and shielding factors for the neutral Hg atom: n=principal quantum number, $\kappa=\mp(j+\frac{1}{2})$ for $j=l\pm\frac{1}{2}$. Susceptibilities are in Å.

		Energy	Magnetic dipole		Electric dipole		Electric quadrupole		Magnetic octupole	
n	κ	(Ry)	$10^2\sigma$	$10^6\chi$	β	α_1	γ	α_2	$10^2\sigma_3$	$10^6\chi_3$
1	−1	6126.096	0.7119	0.0007	0.025	0.20×10^{-7}	0.007	0.29×10^{-11}	−0.42	-0.68×10^{-10}
2	−1	1089.699	0.1389	0.0147	0.059	0.18×10^{-4}	0.021	0.39×10^{-8}	1.10	-0.10×10^{-6}
2	1	1047.689	0.1034	0.0103	0.040	-0.10×10^{-4}	−0.050	0.13×10^{-8}	−0.0002	0.16×10^{-7}
2	−2	903.018	0.1433	0.0258	0.043	-0.26×10^{-5}	−0.137	0.56×10^{-8}	6.13	-0.18×10^{-6}
3	−1	260.004	0.0458	0.0969	0.152	0.38×10^{-3}	−0.026	0.11×10^{-5}	−13.41	-0.38×10^{-4}
3	1	240.682	0.0451	0.0880	−0.016	-0.92×10^{-4}	−0.275	0.34×10^{-6}	0.041	0.32×10^{-5}
3	−2	208.503	0.0463	0.2083	0.087	0.23×10^{-3}	−0.899	0.12×10^{-5}	36.49	-0.34×10^{-4}
3	2	176.015	0.0549	0.1593	0.025	-0.66×10^{-4}	0.048	0.32×10^{-6}	0.41	0.14×10^{-4}
3	−3	169.076	0.0789	0.2500	0.019	-0.20×10^{-3}	−0.099	0.67×10^{-6}	27.98	-0.19×10^{-4}
4	−1	57.9098	0.0184	0.4683	0.366	0.52×10^{-2}	−0.249	0.87×10^{-4}	−75.58	-0.27×10^{-4}
4	1	49.5115	0.0262	0.4746	−0.038	-0.36×10^{-3}	−1.314	0.46×10^{-4}	−0.13	0.15×10^{-3}
4	−2	41.6902	0.0123	1.115	0.167	0.43×10^{-2}	−4.779	0.17×10^{-3}	185.15	−0.0051
4	2	27.8051	0.0230	1.165	0.049	0.26×10^{-2}	0.191	0.17×10^{-3}	2.89	0.0038
4	−3	26.3319	0.0315	1.833	0.031	0.27×10^{-2}	−0.821	0.31×10^{-3}	189.60	−0.0156
4	3	8.3320	0.0285	2.085	0.011	0.61×10^{-2}	−0.450	0.0030	7.49	0.0138
4	−4	8.0058	0.0372	2.852	0.007	0.81×10^{-2}	−0.538	0.0031	4.60	−0.416
5	−1	9.2520	0.0055	2.348	0.902	0.093	−1.246	0.0087	−359.85	−0.210
5	1	6.4291	0.0185	2.715	−0.070	0.013	−9.056	0.0054	−4.90	0.272
5	−2	5.0218	−0.0036	6.566	0.329	0.125	−33.452	0.0301	1297.52	−0.529
5	2	1.1746	0.0085	11.979	0.165	0.698	8.002	0.7743	53.00	7.990
5	−3	1.0234	0.0085	19.666	0.086	1.192	−18.995	1.9760	7062.18	−156.134
6	−1	0.7025	0.0022	21.253	2.962	6.981	−24.610	7.2566	−9128.63	−35.708
Total			1.587	75.37	5.364	9.129	−88.73	10.06	−708.4	−184.7

important than the relativistic contraction of the orbits. Total corrections are as much as 100% for uranium and are as important as correlation effects for helium. (iii) The uncoupled theory used here is too simple to give good values of the electric dipole shielding factors and susceptibilities. A similar statement probably holds for the electric quadrupole results also. The results presented are generally in good agreement with previous uncoupled calculations and have the virtue that all values were computed in the same manner using RHFS wave functions. (iv) No comparison of the magnetic octupole results is made, either with experiment or with previous calculations since no measurements of the shielding factors or susceptibilities or previous calculations of these quantities are known to the authors.

VI. NUMERICAL PROCEDURE

In presenting results such as those given in Sec. V, it is perhaps appropriate to comment on the numerical techniques[17] used and on the accuracy of these techniques.

In outline, the numerical procedure involved the following steps: (i) Solve the unperturbed Hartree-Fock problem using numerical methods analogous to those described in Ref. 7. The solution consists of a set of unperturbed wave functions $F_{n\kappa}$ and $G_{n\kappa}$ and a binding energy $E_{n\kappa}{}^0$ for each electron together with a RHFS potential $V(r)$. (ii) Generate the driving terms $K_{n\kappa\kappa' J}$ and $L_{n\kappa\kappa' J}$ for the inhomogeneous first-order equation (16) using the results of (i) in Eqs. (17) or (26). (iii) Determine the first-order wave functions $S_{n\kappa\kappa'}$ and $T_{n\kappa\kappa'}$ by solving the inhomogeneous differential equations (16). (iv) Evaluate the integrals

$$\int_0^\infty r^a (G_{n\kappa} S_{n\kappa\kappa'} + F_{n\kappa} T_{n\kappa\kappa'}) dr,$$

in the electric case or

$$\int_0^\infty r^a (G_{n\kappa} T_{n\kappa\kappa'} + F_{n\kappa} S_{n\kappa\kappa'}) dr,$$

in the magnetic case, where $a = J$ or $-J-1$. From these integrals the subshell contributions to the susceptibilities and shielding factors can be evaluated as detailed in Sec. II. (v) Accumulate the partial contribution for each subshell to give the susceptibility or screening factor for an entire atom. (vi) Repeat steps (ii)–(v) for each separate multipole J, electric or magnetic.

The equations of Sec. II are modified slightly in the magnetic dipole case because of the following numerical problem. Large contributions to the shielding factors and susceptibilities for the filled subshell (n, κ) are almost entirely canceled by contributions from the closed subshell with the same l, $(n, -\kappa-1)$. These cancellations, of course, cause a loss of numerical accuracy. These large terms were already apparent in the nonrelativistic calculations of Sec. III. Examining the nonrelativistic limit calculations, we are led to write

$$\begin{aligned} S_{n\kappa\kappa'} &= \tilde{S}_{n\kappa\kappa'} + G_{n\kappa'}/\Delta_{n\kappa\kappa'}, \\ T_{n\kappa\kappa'} &= \tilde{T}_{n\kappa\kappa'} + F_{n\kappa'}/\Delta_{n\kappa\kappa'}, \end{aligned} \tag{55}$$

whenever $\kappa' = -\kappa - 1$; $\Delta_{n\kappa\kappa'}$ being the fine-structure separation. The functions $\tilde{S}_{n\kappa\kappa'}$ and $\tilde{T}_{n\kappa\kappa'}$ satisfy Eqs. (16) with the driving terms replaced by

$$\begin{aligned} \tilde{K}_{n\kappa\kappa' 1} &= K_{n\kappa\kappa' 1} + G_{n\kappa'}/m, \\ \tilde{L}_{n\kappa\kappa' 1} &= L_{n\kappa\kappa' 1} + F_{n\kappa'}/m. \end{aligned} \tag{56}$$

The contributions from $G_{n\kappa'}/\Delta_{n\kappa\kappa'}$ and $F_{n\kappa'}/\Delta_{n\kappa\kappa'}$ give the large contributions to the susceptibilities mentioned above. The contributions from these terms cancel on summing over κ and $-\kappa-1$. That we are left with small residual values from $\tilde{S}_{n\kappa\kappa'}$ and $\tilde{T}_{n\kappa\kappa'}$ which do not cancel significantly can be seen by inspecting the magnetic dipole columns of Table II. A similar modification is made in the electric quadrupole and magnetic octupole cases.

As a practical measure of the numerical accuracy of techniques used we solve a special case analytically and compare the results with the corresponding numerical computations. The particular case considered is the magnetic dipole with $n = 1$, $\kappa = \kappa' = -1$ for a Coulomb potential $V(r) = -\alpha Z/r$. Analytically, one has the following partial contributions to σ and χ:

$$\begin{aligned} \sigma &= 2\alpha^2 Z(4 - \gamma - 2\gamma^2)/9\gamma(2\gamma - 1), \\ \chi &= (4\gamma^2 - 1)(1 + \gamma)/18\alpha Z^2 m^3, \end{aligned} \tag{57}$$

where $\gamma = [1 - (\alpha Z)^2]^{1/2}$. The results of this calculation are presented as the exact values given in Table III. The corresponding results generated following steps (i)–(iv) above for $Z = 1$, 10, 54, and 80 are presented in the numerical columns of Table III.

On comparing the numerical and exact values, it should be noted that integrand of the integral for the shielding factor has an algebraic singularity at the origin, behaving as $r^{2\gamma-2}$. The singularity is integrable for physical values of Z but becomes more severe as Z increases. For $\gamma < \frac{1}{2}$ ($Z > 118.68$), the integral does not exist. The singularity accounts for the declining accuracy of the numerical

TABLE III. Comparisons of exact and numerical results for the $\kappa = \kappa' = -1$ contribution to the magnetic dipole shielding factors and susceptibilities for some H-like ions.

		$10^2\,\sigma$	$10^2\,\sigma_{NR}$	$10^6\,\chi$	$10^6\,\chi_{NR}$
H	Exact	0.0011836172	0.0011833966	2.6374821	2.6376226
	numerical	0.0011836155	0.0011833965	2.6374820	2.6376226
Ne	Exact	0.012087744	0.011865285	0.026154850	0.026295062
	numerical	0.012087731	0.011865284	0.026154850	0.026295061
Xe	Exact	0.11542485	0.069527470	0.00068826146	0.00082114612
	numerical	0.11542391	0.069527462	0.00068826152	0.00082114610
Hg	Exact	0.34948198	0.11660124	0.00020371189	0.00032656009
	numerical	0.34940287	0.11660124	0.00020371187	0.00032656003

values of the integration as Z increases. The singularity is not present for a finite nucleus since the exponent $2\gamma - 2$ is replaced by $2|\kappa| - 2 \geq 0$ for all κ.

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