

Relativistic One-Electron Calculations of Shielded Atomic Hyperfine Constants*[†]

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(Received 1 June 1970)

Core shielding effects in atomic hyperfine structure are examined within the framework of relativistic electron theory in the Hartree-Fock-Slater approximation. Expressions are developed for shielding factors pertaining to electric and magnetic hyperfine constants of arbitrary order. Known values of the nuclear magnetic moments for alkali and halogen atoms are used to obtain theoretical predictions of the dipole hyperfine constant "a" with shielding effects included. These theoretical values of *a* are then compared with experiment as a test of the atomic model. Experimental values of the quadrupole and octupole hyperfine constants "b" and "c" for various halogen atoms are analyzed using the model to give revised values for nuclear quadrupole moments, as well as new values for octupole moments of Cl, Br, and I, including screening corrections.

I. INTRODUCTION

We reexamine the effects of core shielding¹⁻³ on electric and magnetic hyperfine constants of arbitrary multipolarity for the alkali and halogen atoms. The point of view of relativistic electron theory is adopted to obviate the Pauli-type corrections for heavier atoms,⁴ and to permit a parallel treatment of electric and magnetic hyperfine constants.

For computational simplicity we adopt the relativistic Hartree-Fock-Slater⁵ (RHFS) approximation to describe the unperturbed atom; the formal results for the shielding factors apply with obvious modifications to the relativistic Hartree-Fock (RHF) atom as well.

We derive lowest-order corrections to the various hyperfine constants computed using the RHFS model, and calculate the shielded dipole hyperfine constant "a" making use of known values of nuclear magnetic moments. These theoretical hyperfine constants are found to agree with experimentally determined hyperfine constants to a few percent; the order of agreement serves as a measure of the validity of the techniques employed to analyze hyperfine data.

Experimentally determined hyperfine constants "b" and "c" are used to obtain values for the nuclear quadrupole and octupole moments including effects of shielding. The results presented for the octupole moments of the halogens Cl, Br, and I are of particular interest, since the rather sizable shielding effects have been neglected previously in the literature.

The phenomenology of hyperfine structure is well understood and has been worked out within a relativistic framework for all orders of multipolarity by Schwartz.⁶ From Schwartz's work, we obtain the following expressions relating the various hyperfine constants to the corresponding nuclear

multipoles:

$$a = \frac{-|e|\mu\kappa_J}{IJ(J+1)} \left\langle \frac{1}{r^2} \right\rangle_{n_J\kappa_J}, \quad (1a)$$

$$b = \pm |e|Q \frac{(2J-1)}{2(J+1)} \left\langle \frac{1}{r^3} \right\rangle_{n_J\kappa_J}, \quad (1b)$$

$$c = -|e|\Omega\kappa_J \frac{(2J-1)}{4(J+2)(J+1)} \left\langle \frac{1}{r^4} \right\rangle_{n_J\kappa_J}. \quad (1c)$$

The upper sign refers to alkali atoms and the lower to the halogens. The quantities *a*, *b*, and *c* are the dipole, quadrupole, and octupole atomic hyperfine constants; μ , *Q*, and Ω are the corresponding nuclear multipole moments; *I* and *J* are the total nuclear angular momentum and the total atomic angular momentum; the quantum numbers *n_J* and κ_J refer to the valence state; *e* is the specific electronic charge. The matrix elements are defined as follows:

$$\left\langle \frac{1}{r^{k+1}} \right\rangle_{n\kappa} = 2 \int dr \frac{F_{n\kappa} G_{n\kappa}}{r^{k+1}}, \quad (2)$$

$$\left\langle \frac{1}{r^{k+1}} \right\rangle_{n\kappa} = \int dr \frac{[F_{n\kappa}^2 + G_{n\kappa}^2]}{r^{k+1}}, \quad (3)$$

where $\kappa = \mp(j + \frac{1}{2})$ for $j = l \pm \frac{1}{2}$ and *G* and *F* are, for our purposes, solutions to the RHFS equations. We shall see a little more detail on this below. Such simple one-electron formulas occur whenever using a central-field approximation. In the spherically averaged HFS potential, the radial wave functions do not depend on the projection quantum number *m*. Hence, sums over closed shells vanish. In fact, the nuclear multipoles distort the electron orbitals, inducing a distributed multipole field in the atom. These distortions are incorporated in shielding corrections or shielding factors. It is important to realize that, in a HFS self-consistent

field calculation, an electron moves in a potential calculated from the wave functions of all the electrons including itself. Therefore, shielding corrections ought to involve not only distortions of the core electrons, but of the valence electrons as well. This last point shows up explicitly in our later formulas.

II. EVALUATION OF THE SHIELDING FACTORS

We now proceed to evaluate the effect of these distortions from spherical symmetry. We describe the unperturbed atom with the Hamiltonian

$$H^0 = \sum_{i=1}^N H_0(i) + \frac{1}{2} e^2 \sum_{i,j} \frac{1}{r_{ij}}, \quad (4)$$

where

$$H_0(i) = \vec{\alpha}_i \cdot \vec{p}_i + \beta_i m - e^2 Z / r_i, \quad (5)$$

and where $\vec{\alpha}$ and β are the usual Dirac matrices. The double sum contains the mutual Coulomb interactions of the electrons among themselves. Mutual magnetic interactions among the electrons have been neglected. The perturbing Hamiltonian is

$$H_1 = \sum_{i=1}^N e \left(c_k \frac{1}{r_i^{k+1}} Y_{k0} - a_k \frac{1}{r_i^{k+1}} \vec{Y}_{k0}^{(0)} \cdot \vec{\alpha}_i \right). \quad (6)$$

The quantities Y_{k0} and $\vec{Y}_{k0}^{(0)}$ are spherical harmonics and magnetic vector spherical harmonics, respectively, and c_k and a_k are proportional to the electric and magnetic multipole moments of order k , respectively. To first order, the energy shift due to turning on the nuclear multipole fields is

$$\begin{aligned} E^1 = & \sum_{\kappa} [(u_0^{\kappa}, H_1 u_0^{\kappa}) + (u_1^{\kappa}, H_0 u_0^{\kappa}) + (u_0^{\kappa}, H_0 u_1^{\kappa})] \\ & + e^2 \sum_{\kappa, L} \int \frac{d^3 r' d^3 r}{|\vec{r} - \vec{r}'|} [(u_1^{\kappa \dagger} u_0^{\kappa}) (u_0^L \dagger u_0^L)' \\ & + (u_0^{\kappa \dagger} u_1^{\kappa}) (u_0^L \dagger u_0^L)' - (u_1^{\kappa \dagger} u_0^L) (u_0^L \dagger u_0^{\kappa})' \\ & - (u_0^{\kappa \dagger} u_1^L) (u_0^L \dagger u_0^{\kappa})'] . \end{aligned} \quad (7)$$

The zero-order wave functions u_0 are solutions of the HFS equations

$$(H_0 + V_{\text{HFS}}) u_0^K = \epsilon_0^K u_0^K . \quad (8)$$

The first-order wave functions u_1 are solutions to the equation

$$(H_0 + V_{\text{HFS}} - \epsilon_0^K) u_1^K = (\epsilon_1^K - H_1) u_0^K , \quad (9)$$

where

$$V_{\text{HFS}} = (\alpha/r) \sum_L Y_0(L, L, r) - \bar{V}^E(r),$$

\bar{V}^E is the Slater⁷ or Kohn-Sham⁸ averaged exchange potential, and

$$Y_k(A, B, r) = r \int dr' \frac{r'^k}{r'^{k+1}} (G_A G_B + F_A F_B)' . \quad (10)$$

We have neglected first-order distortions of the potential V_{HFS} in writing down Eq. (9).

Neglecting the distortions of V_{HFS} has the effect of reducing the coupled integrodifferential equations for u_1 to the more tractable form (9). This approximate uncoupled treatment of the perturbed orbitals has its parallel in the theory of atomic susceptibilities and gives rise to somewhat larger values of the electric polarizabilities of closed-shell atoms than the more exact coupled treatment. We expect correspondingly increased values of this electric shielding factor to occur in the numerical results presented below.

The unperturbed wave functions are assumed to have the spherically symmetric form

$$u_0^K = u_0^{n\kappa m} = \frac{1}{r} \begin{pmatrix} iG_{n\kappa}(r) & \Omega_{\kappa m} \\ F_{n\kappa}(r) & \Omega_{-\kappa m} \end{pmatrix}, \quad (11)$$

with

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

The quantity χ_{μ} is a two-component Pauli spinor and l and j are defined in the usual manner. To investigate the form of the perturbation u_1 , we break up the perturbing Hamiltonian H_1 into its electric part and its magnetic part and deal with each part separately. This is possible since only one or the other ever contributes to any order of multipolarity. We first consider the effect of an electric multipole of order k .

A. Electric Multipoles

The first-order perturbation takes the form

$$u_1^{n\kappa m} = e c_k \sum_{\kappa'} I_{\kappa', m \kappa m k 0} \frac{1}{r} \begin{pmatrix} iS_{n\kappa\kappa'} & \Omega_{\kappa' m} \\ T_{n\kappa\kappa'} & \Omega_{-\kappa' m} \end{pmatrix}, \quad (12)$$

where $S_{n\kappa\kappa'}$ and $T_{n\kappa\kappa'}$ satisfy the radial equations

$$\begin{aligned} (m + V - \epsilon_0) S_{n\kappa\kappa'} + \left(\frac{d}{dr} - \frac{\kappa'}{r} \right) T_{n\kappa\kappa'} &= K_{n\kappa\kappa' k}, \\ \left(\frac{d}{dr} + \frac{\kappa'}{r} \right) S_{n\kappa\kappa'} + (m - V + \epsilon_0) T_{n\kappa\kappa'} &= -L_{n\kappa\kappa' k}, \end{aligned} \quad (13)$$

with

$$V = V_{\text{HFS}} - Z e^2 / r ,$$

$$K_{n\kappa\kappa' k} = -G_{n\kappa} / r^{k+1} + \delta_{\kappa\kappa'} \langle 1 / r^{k+1} \rangle_{n\kappa} G_{n\kappa},$$

$$L_{n\kappa\kappa' k} = -F_{n\kappa} / r^{k+1} + \delta_{\kappa\kappa'} \langle 1 / r^{k+1} \rangle_{n\kappa} F_{n\kappa}, \quad (14)$$

$$\begin{aligned} I_{\kappa m \kappa' m' k M} &= \int d\Omega \Omega_{\kappa m}^{\dagger} Y_{k M} \Omega_{\kappa' m'} \\ &= (-1)^{k+j'-j} \left(\frac{(2k+1)(2j'+1)}{4\pi(2j+1)} \right)^{1/2} \end{aligned}$$

$\times C(j'kj; m'Mm) C(j'kj, \frac{1}{2}0\frac{1}{2}) \pi_{l',kl}$.
The parity factor $\pi_{l',kl}$ is 1 or 0 as the sum of l' ,

k , and l is even or odd. Substituting the above expression for u_1 into Eq. (7) we obtain explicitly

$$E_1 = \pm c_{k0} I_{\kappa_J m_J \kappa_J m_J k0} \left\langle \frac{1}{r^{k+1}} \right\rangle_{n_J \kappa_J} \left[1 + \frac{1}{\langle 1/r^{k+1} \rangle_{n_J \kappa_J}} \left(-2 \int dr \bar{V}^E (G_{n_J \kappa_J} S_{n_J \kappa_J \kappa_J} + F_{n_J \kappa_J} T_{n_J \kappa_J \kappa_J}) \right) \right] \quad (15a)$$

$$+ 2 e^2 \int dr (S_{n_J \kappa_J \kappa_J} G_{n_J \kappa_J} + T_{n_J \kappa_J \kappa_J} F_{n_J \kappa_J}) \frac{1}{r} Y_0(\kappa_J, \kappa_J, r) \quad (15b)$$

$$+ 2 e^2 \sum_{n\kappa, (\text{closed})} \sum_{\kappa'} \frac{(2j+1)(2j'+1)}{(2k+1)} \Lambda_{\kappa' n\kappa} \int dr (S_{n\kappa \kappa'} G_{n\kappa} + T_{n\kappa \kappa'} F_{n\kappa}) \frac{1}{r} Y_k(\kappa_J, \kappa_J, r) \quad (15c)$$

$$- 2 e^2 \sum_{n\kappa, (\text{closed})} \sum_{\kappa' l} V(\kappa_J \kappa; \kappa_J \kappa'; l\kappa) \int dr (S_{n\kappa \kappa'} G_{n_J \kappa_J} + T_{n\kappa \kappa'} F_{n_J \kappa_J}) \frac{1}{r} Y_l(\kappa, \kappa, r) \quad (15d)$$

$$- 2 e^2 \sum_{n\kappa, (\text{closed})} \sum_i (2j+1) \Lambda_{\kappa i \kappa_J} \int dr (S_{n_J \kappa_J \kappa_J} G_{n_J \kappa_J} + T_{n_J \kappa_J \kappa_J} F_{n_J \kappa_J}) \frac{1}{r} Y_i(\kappa, \kappa_J, r) \quad (15e)$$

where

$$\Lambda_{\kappa_K l \kappa_L} = [C^2(j_K l j_L, \frac{1}{2}0\frac{1}{2}) / (2j_L + 1)] \pi_{l_K l l_L}, \quad (16)$$

and

$$V(\kappa_L \kappa_K; \kappa_L \kappa_K'; l\kappa) = (-1)^{j_L + j_K' - l} W(j_L j_K j_L' j_K'; l\kappa) \\ \times (2j_L' + 1)^{1/2} (2j_K + 1)^{1/2} C(j_L l j_K', \frac{1}{2}0\frac{1}{2}) \\ \times C(j_L' l j_K', \frac{1}{2}0\frac{1}{2}) C(j_K j_K', \frac{1}{2}0\frac{1}{2}) \\ \times C^{-1}(j_L j_L', \frac{1}{2}0\frac{1}{2}) \pi_{l_L l l_K} \pi_{l_K l l_L} \pi_{l_K' l_K'}. \quad (17)$$

The quantity in the large brackets is the correction factor $(1+R_k)$ which will multiply the zeroth-order matrix elements of electric nuclear multipoles of order k in Eq. (1b). The quantum numbers with the subscript J refer to the valence electron or hole. The upper sign is used for a valence electron outside of closed shells as with the alkalis and the lower sign is used with a valence hole in a closed shell as with the halogens. The term (c) in Eq. (15) is a distortion of the core caused by the direct electron mutual interactions and (d) is a similar term due to the exchange interaction. These terms are the core distortions and represent a relativistic

generalization of the terms used by Sternheimer to evaluate electric quadrupole shielding.^{3a} The remaining terms have no counterparts in the Sternheimer theory of shielding. They all represent distortions of the valence state from spherical symmetry. The terms (a) and (c) are exchange effects and (b) is a direct term.

B. Magnetic Multipoles

We now turn on the magnetic perturbation and turn off the electric perturbation. The perturbed wave function u_1 assumes the form

$$u_1^{n\kappa m}(r) = i e a_n \sum_{\kappa'} \frac{(\kappa + \kappa')}{[k(k+1)]^{1/2}} \\ \times I_{-\kappa' m \kappa m k0} \frac{1}{r} \begin{pmatrix} i S_{n\kappa \kappa'} & \Omega_{\kappa' m} \\ T_{n\kappa \kappa'} & \Omega_{-\kappa' m} \end{pmatrix}. \quad (18)$$

This expansion leads to radial equations identical to Eq. (13) except that now

$$K_{n\kappa \kappa' k} = F_{n\kappa} / r^{k+1} - (1/r^{k+1})_{n\kappa} G_{n\kappa} \delta_{\kappa \kappa'}, \\ L_{n\kappa \kappa' k} = G_{n\kappa} / r^{k+1} - (1/r^{k+1})_{n\kappa} F_{n\kappa} \delta_{\kappa \kappa'}. \quad (19)$$

Using these expressions, Eq. (7) becomes for a magnetic multipole perturbation

$$E_1 = - \frac{i e a_{k0}}{[k(k+1)]^{1/2}} I_{-\kappa_J m_J \kappa_J m_J k0} (2\kappa_J) \left\langle \frac{1}{r^{k+1}} \right\rangle_{n_J \kappa_J} \left[1 + \frac{1}{\langle 1/r^{k+1} \rangle_{n_J \kappa_J}} \left(2 \int dr (S_{n_J \kappa_J \kappa_J} G_{n_J \kappa_J} + T_{n_J \kappa_J \kappa_J} F_{n_J \kappa_J}) \right) \bar{V}^E \right] \quad (20a)$$

$$+ 2 e^2 \int dr (S_{n_J \kappa_J \kappa_J} G_{n_J \kappa_J} + T_{n_J \kappa_J \kappa_J} F_{n_J \kappa_J}) \frac{1}{r} Y_0(\kappa_J, \kappa_J, r) \quad (20b)$$

$$+ 2 e^2 \sum_{n\kappa, (\text{closed})} \sum_i (2j+1) \Lambda_{\kappa i \kappa_J} \int dr (S_{n_J \kappa_J \kappa_J} G_{n\kappa} + T_{n_J \kappa_J \kappa_J} F_{n\kappa}) \frac{1}{r} Y(\kappa_J, \kappa, r) \quad (20c)$$

$$+ 2e^2 \int_{n\kappa, (\text{closed})} \sum_{i\kappa'} \frac{(\kappa + \kappa')}{(2\kappa_J)} V(\kappa_J \kappa, -\kappa_J - \kappa', lk) \int dr' (S_{n\kappa\kappa'} G_{n_J \kappa_J} + T_{n\kappa\kappa'} F_{n_J \kappa_J}) \frac{1}{r} Y_l(\kappa_J, \kappa, r) \Bigg]. \quad (20d)$$

The expression in large brackets represents the correction factor $(1 + R_k)$ for a magnetic nuclear multipole of order k . As before, the upper sign refers to a valence electron and the lower sign to a valence hole. A term of the type (d) occurs in the work of Sternheimer^{3b} on dipole shielding as well as in the work of Das *et al.*⁹ Only s states contribute in these nonrelativistic calculations of dipole-core shielding. Our work indicates that other states contribute in a relativistic calculation, but numerical results show that s states do, in fact, dominate in the magnetic dipole calculation. The other terms occurring in Eq. (20) constitute distortions of the valence state. Terms (a), (c), and (d) are exchange effects and (b) is a direct effect.

III. EXPERIMENTAL COMPARISONS

In addition to evaluating the shielding factors expressed in Eqs. (15) and (20), we also evaluate the relativistic generalization of Sternheimers' core-polarization shielding factors by omitting those terms in (15) and (20) which involved the distortions of the valence orbitals. In the remainder of this paper, we will denote these generalizations by the use of a prime and call them *standard shielding factors*.

In Table I, we have listed the zero-order results for the alkali hyperfine constants a_0 together with the corrected values a_1 and a_1' . The prime indicates corrections obtained by means of the standard shielding factors. The two types of shielding factors are also

TABLE I. Magnetic dipole hyperfine constants for the alkali elements. Unprimed quantities refer to theoretical results including valence orbital distortions, primed quantities are calculated without valence distortions.

	νE	a_{expt} (MHz)	$(1 + R_1)$	$(1 + R_1')$	a_0 (MHz)	a_1 (MHz)	a_1' (MHz)
${}_3\text{Li}^7$	KS ^a	401.75 ^b	1.061	1.336	362.6	384.7	484.5
$S_{1/2}$	S ^c	401.75	0.998	1.917	374.0	373.4	716.9
${}_{11}\text{Na}^{23}$	KS	885.8 ^d	1.082	1.237	750.3	812.2	928.4
$S_{1/2}$	S	885.8	0.724	1.218	912.5	660.9	1112.0
${}_{19}\text{K}^{39}$	KS	230.9 ^e	1.154	1.252	172.1	198.6	215.4
$S_{1/2}$	S	230.9	0.602	1.231	226.9	136.6	279.2
${}_{37}\text{Rb}^{85}$	KS	1011.9 ^f	1.216	1.232	727.6	884.9	896.4
$S_{1/2}$	S	1011.9	0.519	1.213	1013.5	525.8	1129.4
${}_{55}\text{Cs}^{133}$	KS	2298.0 ^g	1.277	1.227	1570.0	2004.0	1927.0
$S_{1/2}$	S	2298.0	0.474	1.209	2272.0	1076.0	2748.0
${}_3\text{Li}^{7*}$	KS	-3.073 ^h	-0.601	-0.619	6.577	-3.856	-4.069
$2P_{3/2}$							
${}_3\text{Li}^{7*}$	KS	-0.965 ⁱ	-0.848	-0.543	2.6398	-2.239	-1.434
$3P_{3/2}$							
${}_3\text{Li}^{7*}$	KS	-0.41 ^j	-0.945	-0.512	1.277	-1.207	-0.65
$4P_{3/2}$							
${}_{19}\text{K}^{39*}$	KS	6.0 ^j	1.090	1.565	4.99	5.45	7.82
$4P_{3/2}$							

^aDenotes Kohn-Sham treatment of exchange potential.

^bR. G. Schlecht and D. W. McColm, Phys. Rev. **142**, 11 (1966).

^cDenotes Slater's treatment.

^dJ. A. Nolen, Ph.D. thesis, Princeton University, 1965 (unpublished); reported by Y. W. Chan *et al.*, Phys. Rev. **150**, 933 (1966).

^eReported by P. A. Vanden Bout *et al.*, Phys. Rev. **165**, 88 (1969) from a private communication by S. Penselin.

^fS. Penselin *et al.*, Phys. Rev. **127**, 524 (1962).

^gP. A. Vanden Bout *et al.*, Phys. Rev. **165**, 88 (1968).

^hJ. D. Lyons and R. K. Nesbet, Phys. Rev. Letters **24**, 434 (1970).

ⁱR. C. Isler, S. Marcus, and R. Novick, Phys. Rev. **187**, 76 (1969).

^jR. W. Schmieder *et al.*, Phys. Rev. **173**, 76 (1968).

listed. These values were obtained using the treatment of the exchange potential proposed by Kohn and Sham.¹⁰ Slater's average exchange potential gave good results for the zero order in the alkali family. However, the corrected values were quite poor. The results for the halogens using the Slater potential were poor both before and after employing the shielding corrections. We note that the values of a_1 obtained using the Kohn-Sham exchange potential are all better than the zero-order values a_0 . However, they systematically fall short of the experimental value a_{expt} . It seems that R_1 is underestimated by roughly a factor of 2. Since using Kohn and Sham's average exchange produces more reliable results than using Slater's average, we will confine our discussion to the former unless otherwise stated. It is to be noted that the shielding factors $(1+R)$ are closer to unity than the factors $(1+R')$. This is due to an inter-cancellation between the terms due to the distortion of the valence orbitals from spherical symmetry and the other contributions.

Except for cesium, where our corrections and standard core-shielding corrections happen to be virtually identical, the standard core-shielding corrections for the ground states of the alkali are always larger than ours. Because of this, coupled with the fact that our correction factors are underestimated, the standard core-shielding corrections seem better than ours for Na, K, and Rb. We believe that this is an accident and that our type of correction is more meaningful. There are several reasons for this belief. When we look at the halogens, we will see that our corrections are slightly overestimated and that the standard-type corrections are grossly overestimated. Furthermore, the following simple check was made on the results for the alkali family. We can consider an alkali as possessing either a single electron outside of closed shells or as being one electron short of closed shells, since the valence electron is in an $s_{1/2}$ state which is twofold degenerate. Although it is not obvious that the resulting shielding factors evaluated from these two points of view will be the same from Eq. (20), it can be shown analytically that these two approaches yield identical results. This provides a further check on the result both from an analytic standpoint and from a conceptual one since the standard core-shielding corrections do not have this s -electron- s -hole symmetry. For example, we obtained the results given in Table II for lithium.

We further note that when the hyperfine constants a'_1 are calculated treating the $s_{1/2}$ electron as an $s_{1/2}$ hole, they are grossly overestimated. Thus, the apparently better agreement found in some cases in Table I for the standard-type corrections is illusory.

The various values of the dipole-hyperfine constants a for the halogens are listed in Table III. Here again the Slater average for the exchange potential produces poor results. Therefore, we again devote our attention to the results obtained using the average exchange potential of Kohn and Sham. Note that, except for fluorine, our corrections are always in the right direction, but that they overshoot the experimental values. The value for R_1 now seems to be overestimated by a factor of approximately 2. The standard-type shielding factors are consistently too large and they "correct" in the wrong direction as often as not.

In the above paragraphs, we have shown that our standard shielding factors are unsatisfactory. On the other hand, the calculations including valence distortions are symmetric with respect to s -hole- s -electron interchange and generally give corrected values of the dipole hyperfine constants in closer agreement with experiment. For these reasons, we will consider only the shielding factors calculated using the entire expressions (15) and (20) in analyzing the higher-order multipoles.

Before turning to these higher-order moments, it is entertaining to make a few comparisons of our results with previous theoretical predictions. The quantities R_1 and R_2 for chlorine were calculated by Sternheimer.¹¹ His values are 0.358 and 0.42, respectively. These agree well with our corresponding results for standard shielding factors. We obtained 0.384 and 0.425, respectively. Sternheimer also reported a value of R_2 for lithium. His value of -0.11 and our standard value of -0.117 again agree. Das⁹ reports values of about 0.23 for R_1 for the alkali family. This agrees well with our standard shielding factors in Table I. In view of this agreement, we believe our standard shielding factors are a valid relativistic generalization of Sternheimer's shielding factors.

We now wish to apply the above theory of hyperfine shielding to the analysis of the quadrupole and octupole moments of the halogens. For this purpose, we adopt the suggestion of Schwartz,¹² and express the quadrupole moment in terms of the dipole moment

TABLE II. S -electron- S -hole symmetry for lithium $2S_{1/2}$.

Exchange potential	Point of view	$(1+R)$	$(1+R')$
Slater's average	Hole	0.998	1.917
	Electron	0.998	1.296
Kohn-Sham's average	Hole	1.061	1.948
	Electron	1.061	1.336

TABLE III. Zero- and first-order magnetic dipole hyperfine constants for the halogen family of elements.

$\bar{\nu} E$	$a_{\text{exp}}^{\text{tot}}$ (MHz)	$(1 + R_1')$	$(1 + R_1')$	a_0 (MHz)	a_1 (MHz)	a_1' (MHz)	
${}^9\text{F}^{19}$	KS ^a	2010 ^b	1.124	1.478	2012	2260	2974
	S ^c	2010	0.734	1.360	2343	1720	3286
${}^{17}\text{Cl}^{35}$	KS	205.2 ^d	1.044	1.384	199.3	208.1	275.8
	S	205.2	0.682	1.317	234.0	159.5	308.2
${}^{35}\text{Br}^{79}$	KS	884.8 ^e	0.938	1.250	912.3	855.7	1140.4
	S	884.8	0.533	1.212	1094	583.1	1326
${}^{54}\text{I}^{127}$	KS	827.3 ^f	0.814	1.087	899.2	732.3	977.2
	S	827.3	0.399	1.084	1102.7	440.3	1195.3

^aDenotes Kohn-Sham treatment of exchange potential.

^bH. E. Radford *et al.*, Phys. Rev. **130**, 1441 (1963).

^cDenotes Slater's treatment.

^dL. Davis *et al.*, Phys. Rev. **76**, 1076 (1949).

^eH. H. Brown *et al.*, Phys. Rev. **142**, 53 (1966).

^fV. Jaccarino *et al.*, Phys. Rev. **94**, 1798 (1954).

$$Q_1 = \frac{\mp 2\kappa_J}{IJ(2J-1)} \frac{b\mu}{a} \frac{(1/\gamma^2)_{n_J\kappa_J}}{\langle 1/\gamma^3 \rangle_{n_J\kappa_J}} \frac{(1+R_1)}{(1+R_2)}. \quad (21)$$

The shielding factor R_1 is computed from Eq. (20) as described above, and R_2 is determined from Eq. (15). The numerical results for the shielded quadrupole moment Q_1 together with unshielded values Q_0 obtained from Eq. (21) using $R_1 = R_2 = 0$ are presented in Table IV.

Finally, we present corrected values for the nuclear octupole moments. As in the quadrupole case, we follow Schwartz's suggestion and make use of the following expression:

$$\Omega_1 = \frac{4(J+2)}{IJ(2J-1)} \frac{c}{a} \frac{(1/\gamma^2)_{n_J\kappa_J}}{\langle 1/\gamma^4 \rangle_{n_J\kappa_J}} \frac{(1+R_1)}{(1+R_3)}. \quad (22)$$

The results also appear in Table IV together with values of Ω_0 given by Eq. (22) with $R_1 = R_3 = 0$.

In the above calculations we have included many-body effects approximately in shielding corrections $(1+R_k)$ to one-electron matrix elements. Recently, rather detailed nonrelativistic Brueckner-Goldstone calculations¹³⁻¹⁵ have appeared for several of the systems treated here - Li, Li*, and Na. For Li and Li* (where relativistic effects are negligible) these many-body calculations are in excellent agreement with experiment, while for Na the discrepancy between the theoretical value of the dipole hyperfine constant (857.0 MHz) and experiment (885.8 MHz) is presumably due to the neglect of relativistic effects.

One could, in principle, redo these rather in-

TABLE IV. Quadrupole and octupole moments.^a

	$(1 + R_2)$	b (MHz)	Q_0^b	Q_1^b	$(1 + R_3)$	c (Hz)	Ω_0^c	Ω_1^c
${}^{17}\text{Cl}^{35}$	1.085	54.9	-0.108	-0.104	1.211	-7.015	-0.0188	-0.0162
${}^{35}\text{Br}^{79}$	1.114	-385	0.445	0.367	1.245	393	0.123	0.0928
${}^{53}\text{I}^{127}$	1.192	1146	-1.097	-0.750	1.292	2602	0.265	0.167
${}^3\text{Li}^{7*}$ ^d $2P_{3/2}$	0.900				1.345			
${}^3\text{Li}^{7*}$ $3P_{3/2}$	0.609	-0.019	0.00073	-0.0013	0.839			
${}^{19}\text{K}^{37*}$ $P_{3/2}$	1.145	2.9	-0.337	-0.321	0.895			

^aFor references to experimental data, see Tables I and III and the Appendix.

^bIn units of barns.

^cIn units of nuclear magneton barns.

^dAsterisk denotes excited state.

TABLE V. Dipole, quadrupole, and octupole atomic hyperfine constants corrected to second order.^a

	<i>a</i> (Hz)	<i>b</i> (Hz)	<i>c</i> (Hz)
¹⁷ Cl ³⁵	205 046 860	54 872 934	- 7.015
³⁵ Br ⁷⁹	884 809 720	- 384 882 900	393
⁵³ I ¹²⁷	827 265 020	1146 359 200	2602

^aSee Table III for the references for the data.

volved many-body calculations for Na, including the more important relativistic effects, by replacing the usual Schrödinger Hamiltonian by the Dirac Hamiltonian of Eqs. (4)–(6).

Before attempting such an ambitious program it would be worthwhile to investigate the hyperfine constants in the framework of a coupled Dirac-Hartree-Fock theory. Such a calculation would be the best one could do within the Hartree-Fock framework and would provide the basis for more complete many-body studies of the type mentioned

above.

ACKNOWLEDGMENTS

The authors wish to thank Professor J. Zorn for calling to their attention the question of octupole-shielding constants which motivated this work. Thanks are also due to Professor T. P. Das for useful comments on the mechanism of shielding. Finally, the authors owe a debt of gratitude to Dr. F. D. Feiock for the use of routines for solving the inhomogeneous Dirac equations and for other invaluable advice on the numerical phase of the problem.

APPENDIX

Following Schwartz,¹² the experimental data for the $P_{3/2}$ states were corrected for second-order effects. We have used RHFS wave functions to evaluate the required matrix elements. For completeness, we list in Table V the values of the hyperfine constants corrected for second-order effects that we have employed in this paper.

*Research supported in part by the U.S. AEC under Contract No. AT(11-1)-427.

†Work based in part on a thesis submitted by one of the authors (M. J. A.) to the Graduate School of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics.

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