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RELATIVISTIC EVALUATION OF INTERNAL DIAMAGNETIC FIELDS FOR ATOMS AND IONS*

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Diamagnetic shielding factors for a number of atoms and ions are evaluated using relativistic electron theory in the Hartree-Fock-Slater approximation. The results agree well with previous nonrelativistic values for light atoms but include relativistic corrections which rise to 62% for Hg.

The interaction energy of a nucleus of magnetic moment $\vec{\mu}$ with a weak external magnetic field $\vec{B}$ is given by $E=-\vec{\mu}\cdot\vec{B}(1-\sigma)$, where the diamagnetic shielding factor σ arises from induced magnetic fields at the nucleus. Using relativistic Hartree-Fock-Slater (RHFS) wave functions to describe the atomic electrons, the diamagnetic shielding factor is found to be[1]

$$\sigma=-\tfrac{1}{3}\alpha\sum_{n\kappa}(2j+1)\sum_{\kappa'}(2j'+1)\times(\kappa+\kappa')^2\Lambda_{j1j'}J_{n\kappa\kappa'}, \qquad (1)$$

where

$$J_{n\kappa\kappa'}=\int_R^\infty \frac{dr}{r^2}[S_{n\kappa\kappa'}F_{n\kappa}+T_{n\kappa\kappa'}G_{n\kappa}]. \qquad (2)$$

The intermediate-state functions $S_{n\kappa\kappa'}$ and $T_{n\kappa\kappa'}$ are determined from inhomogeneous radial Dirac equations

$$\left(\frac{d}{dr}+\frac{\kappa'}{r}\right)S_{n\kappa\kappa'}+(2+W_{n\kappa}-V)T_{n\kappa\kappa'}=rG_{n\kappa}+C_{n\kappa}F_{n\kappa}\delta_{\kappa\kappa'},$$

$$\left(\frac{d}{dr}-\frac{\kappa'}{r}\right)T_{n\kappa\kappa'}+(V-W_{n\kappa})S_{n\kappa\kappa'}=rF_{n\kappa}-C_{n\kappa}G_{n\kappa}\delta_{\kappa\kappa'}. \qquad (3)$$

The coefficients

$$C_{n\kappa}=2\int_0^\infty dr\, rG_{n\kappa}F_{n\kappa} \qquad (4)$$

assure that the intermediate state is orthogonal to the ground state for $\kappa=\kappa'$. The ground-state Dirac wave functions are denoted by $G_{n\kappa}$ and $F_{n\kappa}$ where n is the principal quantum number and κ the angular quantum number $[\kappa=\mp(j+\frac{1}{2})$ for $j=l\pm\frac{1}{2}]$; the atomic binding energies are $W_{n\kappa}$, and V is the self-consistent atomic potential. The coefficients $\Lambda_{j1j'}$ which contain the magnetic selection rules $(\kappa'=\kappa, -\kappa\pm1)$ are defined by

$$\Lambda_{j1j}=C^2(j1j';\tfrac{1}{2}0)/(2j'+1) \text{ for } \kappa'=\kappa\pm1,$$
$$=0 \text{ otherwise}.$$

The lower limit in Eq. (2) results from using an extreme single-particle shell model for the nucleus where the magnetic moment is due to an unpaired nucleon concentrated in a spherical shell at the nuclear radius R. This surface-current model leads to the Schmidt values for the magnetic moments of even-odd nuclei.[2] A correction of the form

$$\delta J_{n\kappa\kappa'}\approx-\frac{1}{2R^3}\int_0^R rdr[S_{n\kappa\kappa'}F_{n\kappa}+T_{n\kappa\kappa'}G_{n\kappa}]$$

Table I. Magnetic shielding factors for closed-shell atoms and ions: Z = atomic number, I = degree of ionization. Elements grouped according to electron configuration.

	Z	I	$10^2\sigma$	$10^2\sigma_{NR}$		Z	I	10^2 0	$10^2\sigma_{NR}$
H	1	0	0.00178	0.00178	Kr	36	0	0.3622	0.3355
					Sr	38	2	0.3923	0.3606
He	2	0	0.00599	0.00599	Zr	40	4	0.4233	0.3857
Li	3	1	0.00955	0.00954	Mo	42	6	0.4551	0.4109
Be	4	2	0.01312	0.01310	Ru	44	8	0.4879	0.4364
B	5	3	0.01670	0.01665					
C	6	4	0.02030	0.02021	Pd	46	0	0.536	0.476
					Cd	48	2	0.574	0.505
Be	4	0	0.01531	0.01527	Sn	50	4	0.613	0.533
B	5	1	0.01979	0.01973	Te	52	6	0.654	0.562
C	6	2	0.02428	0.02419					
N	7	3	0.02880	0.02864	Xe	54	0	0.704	0.600
O	8	4	0.03333	0.03310	Cs	55	1	0.727	0.615
F	9	5	0.03790	0.03756	Ba	56	2	0.750	0.631
					La	57	3	0.773	0.646
Ne	10	0	0.05690	0.05640	Ce	58	4	0.797	0.662
Mg	12	2	0.07165	0.07078					
Si	14	4	0.08652	0.08516	Yb	70	2	1.168	0.891
S	16	6	0.10161	0.09957	Hf	72	4	1.240	0.930
					W	74	6	1.316	0.969
A	18	0	0.1292	0.1262	Re	75	7	1.356	0.989
Ca	20	2	0.1483	0.1441	Ir	77	9	1.439	1.029
Ti	22	4	0.1675	0.1620	Au	79	11	1.528	1.070
Cr	24	6	0.1872	0.1799					
Fe	26	8	0.2072	0.1980	Au	79	1	1.542	1.083
Ni	28	10	0.2278	0.2161	Hg	80	2	1.585	1.105
					Tl	81	3	1.634	1.127
Cu	29	1	0.2597	0.2463	Pb	82	4	1.684	1.149
Ga	31	3	0.2855	0.2690	Bi	83	5	1.737	1.172
As	33	5	0.3117	0.2916					
Br	35	7	0.3385	0.3144	Hg	80	0	1.587	1.106
					Tl	81	1	1.636	1.129
					Pb	82	2	1.686	1.151
					Bi	83	3	1.739	1.174

arising from finite nuclear size is found to be completely negligible, for all but the heavier nuclei, giving a contribution of about −0.25% of the uncorrected value in the case of Hg.

It should be noted that Eq. (1) applies only to atoms and ions with closed electron subshells. The open-subshell problem is complicated by contributions to the interaction energy which are independent of the applied field.

If the nuclear moment is assumed to be at the origin, the nonrelativistic limits of Eqs. (1)-(3) reduce to the formula of Lamb,[3]

$$\sigma_{NR} = \tfrac{1}{3} e v(0)/mc^2, \qquad (5)$$

where

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

is the electron potential at the origin.

The atomic electron wave functions and binding energies, as well as the self-consistent potential are obtained by solving the RHFS equations numerically, using a procedure similar to that of Lieberman, Waber and Cromer.[4] The resulting wave functions give bulk magnetic susceptibilities for the noble gases which agree within experimental errors with the measured values.[1] The RHFS wave functions were used as input to Eqs. (3), which were in turn integrated numerically and used to determine $J_{n\kappa\kappa'}$. Results for the corrected magnetic shielding factor are presented in Table I. For comparison the "nonrelativistic" values σ_{NR} obtained by evaluating Eq. (5) using relativistic wave functions are included in Table I. It should be noticed that even these nonrelativistic values disagree with the previous nonrelativistic calculations of Dickinson[5] for heavy elements. This discrepancy has its origin in the relativistic contraction of the inner electron orbits. In addition to the "contraction" effect there is an "intrinsic" relativistic effect which arises from the use of the Dirac current, rather than the Schrödinger current in determining the internal fields.

Comparison of the results with Dickinson's value for Hg ($\sigma = 0.00965$ for $Z = 80$) shows a 14% discrepancy due to contraction and an even more striking 38% "intrinsic" effect. Relativistic corrections thus increase the shielding factor for Hg by 62% over the previous nonrelativistic value.

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[1]The derivation of Eqs. (1)-(3) is similar to the treatment of magnetic susceptibilities given by the authors: W. R. Johnson and F. D. Feiock, Phys. Rev. 168, 22 (1968).

[2]R. R. Roy and B. P. Nigam, Nuclear Physics (John Wiley & Sons, Inc. New York, 1967), p.42.

[3]W. E. Lamb, Jr., Phys. Rev. 60, 817 (1941).

[4]D. Lieberman, J. T. Waber, and D. T. Cromer, Phys. Rev. 137, A27 (1965).

[5]W. C. Dickinson, Phys. Rev. 80, 563 (1950).