Diamagnetism of Atoms and Molecules with Unpaired Electrons

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Abstract: The magnetic shielding constant, σ, and the magnetic susceptibility, χ, are investigated for an atom and a molecule with unpaired electrons. It is found that the only situation affected by the electron spin is the expression for σ for molecules with unpaired electrons. Coupling between electron spin and other degrees of freedom has been ignored.

Although present experimental methods cannot determine the magnetic susceptibility, χ, or the magnetic shielding constant, σ, of a species with unpaired electrons, there is still a desire by theoreticians to calculate the magnetic properties for such paramagnetic species. Recent workers[1-3] have investigated these properties for paramagnetic species. In this brief article we are concerned with the effect that the spin will have on these properties.

For ^1S atoms it has been shown[4] that the susceptibility per mole, χ, is

$$\chi = \chi_0 \left\langle 0 \left| \sum_{j=1}^{N} r_{aj}^2 \right| 0 \right\rangle \tag{1}$$

where $\chi_0 = -(e^2 a_0^2 N_0/6mc^2) = -0.79199 \times 10^{-6}$, N is the number of electrons, r_{aj} is the distance from nucleus a to electron j, and the wave function, 0, in the Dirac brackets is the ground-state atomic wave function in the absence of a magnetic field. Also, for ^1S atoms it has been shown[5,6] that the magnetic shielding constant, σ, is

$$\sigma = \sigma_0 \left\langle 0 \left| \sum_{j=1}^{N} r_{aj}^{-1} \right| 0 \right\rangle \tag{2}$$

where $\sigma_0 = (e^2/3mc^2 a_0) = 1.77504 \times 10^{-5}$.

For $^1\Sigma$ linear polyatomic molecules the results are the following: the susceptibility[4] is

$$\chi = \chi_0 \left[\left\langle 0 \left| \sum_{j=1}^{N} r_j^2 \right| 0 \right\rangle - \sum_{k=1}^{\infty} (E_k - E_0)^{-1} \times \{\langle 0|\mathbf{M}|k\rangle \cdot \langle k|\mathbf{M}|0\rangle\} \right] \tag{3}$$

where $\mathbf{M}$ is the total orbital angular momentum.

$$\mathbf{M} = M_x\hat{\imath} + M_y\hat{\jmath} + M_z\hat{k} \tag{4}$$

with

$$M_x = \frac{\hbar}{i} \sum_{j=1}^{N} \left\{ y_j \frac{\partial}{\partial z_j} - z_j \frac{\partial}{\partial y_j} \right\} \tag{5}$$

and cyclic (the wave functions, l, in the Dirac brackets represent the eigenfunctions of the Hamiltonian in the absence of a magnetic field); the shielding[7] is

$$\sigma = \sigma_0 \left[\left\langle 0 \left| \sum_{j=1}^{N} r_j^{-1} \right| 0 \right\rangle - \sum_{k=1}^{\infty} (E_k - E_0)^{-1} \{\langle 0|\mathbf{M}|k\rangle \cdot \langle k|\mathbf{L}_a|0\rangle + \langle 0|\mathbf{L}_a|k\rangle \cdot \langle k|\mathbf{M}|0\rangle\} \right] \tag{6}$$

where

$$\mathbf{L}_a = L_{xa}\hat{\imath} + L_{ya}\hat{\jmath} + L_{za}\hat{k} \tag{7}$$

with

$$L_{xa} = \frac{\hbar}{i} \sum_{j=1}^{N} \frac{1}{r_{aj}^3} \left(y_{aj} \frac{\partial}{\partial z_j} - z_{aj} \frac{\partial}{\partial y_j} \right) \tag{8}$$

and cyclic.

The problem we consider is how these results will be altered, if at all, for species with unpaired electrons.

Derivation of General Results

Let us assume that the Hamiltonian in the absence of a homogeneous magnetic field, $\mathbf{H}$, is $\mathcal{H}^0$ and that the allowed wave functions are Ψ_n with corresponding eigenvalues E_n. In the presence of $\mathbf{H}$ the Hamiltonian (considering only terms which would contribute an H_α factor or a magnetic dipole component, $\mu_{a\alpha}$ factor) is[8]

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}_{\text{ext}} + \mathcal{H}_{\text{spin}} \tag{9}$$

where

$$\mathcal{H}_{\text{ext}} = \sum_{j=1}^{N} \left\{ \frac{e\hbar}{mci} \mathbf{A}_j \cdot \nabla_j + \frac{e^2}{2mc^2} A_j^2 \right\} \tag{10}$$

and

$$\mathcal{H}_{\text{spin}} = \frac{e}{mc} \sum_{j=1}^{N} \mathbf{S}_j \cdot \mathbf{H} + \frac{e}{mc} \sum_{j=1}^{N} \times \left\{ \frac{(\mathbf{S}_j \cdot \boldsymbol{\mu}_a) r_{aj}^2 - 3(\mathbf{S}_j \cdot \mathbf{r}_{aj})(\boldsymbol{\mu}_a \cdot \mathbf{r}_{aj})}{r_{aj}^5} - \frac{8\pi}{3} (\mathbf{S}_j \cdot \boldsymbol{\mu}_a) \delta(\mathbf{r}_{aj}) \right\} \tag{11}$$

We should note that an analogous expression to eq 11 involving the nuclear spin should be included. However, since these terms involve the reciprocal of the mass of the nucleus, their contributions would be relatively small compared to the other effects. For a simultaneous calculation of χ and σ we can take

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(1) G. Malli and S. Fraga, *Theor. Chim Acta*, **5**, 275, 284 (1966).

(2) G. Malli and C. Froese, *Intern. J. Quantum Chem.*, **S1**, 95, 99 (1967); K. M. S. Saxena and P. T. Narasimhan, *ibid.*, **1**, 731 (1967).

(3) R. W. Silbey in a private communication has indicated that he has performed a calculation of the susceptibility for H_2^+.

(4) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932.

(5) E. Hylleraas and S. Skavlem, *Phys. Rev.*, **79**, 117 (1950).

(6) W. C. Dickinson, *ibid.*, **80**, 563 (1950).

(7) N. F. Ramsey, *ibid.*, **77**, 567 (1950); **78**, 699 (1950); *Physica*, **17**, 303 (1951).

(8) H. F. Hameka, "Advanced Quantum Chemistry," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965, pp 58–59.

$$\mathbf{A}_j = {}^1\!/_2(\mathbf{H} \times \mathbf{r}_j) + \frac{\boldsymbol{\mu} \times \mathbf{r}_{aj}}{r_{aj}^{\,3}} \tag{12}$$

Employing the variational perturbation technique,[9] we can determine the expansion of the energy up to terms in μ_a^2, H^2, or $\mu_a H$. We find from this treatment that the lowest eigenvalue of $\mathcal{H}$, ϵ_0, is

$$\epsilon_0 = H_{00}S^{-1} - \sum_{k=1}^{\infty}(E_k - E_0)^{-1} \times (H_{0,k} - S_{0,k}E_0)(H_{k,0} - S_{k,0}E_0) \tag{13}$$

where

$$H_{l,k} = \langle \Psi_e | \mathcal{H} | \Psi_k \rangle \equiv \langle l | \mathcal{H} | k \rangle$$

$$S_{l,k} = \langle \Psi_e | \Psi_k \rangle \equiv \langle l | k \rangle \tag{14}$$

The term in ϵ_0 proportional to H^2 is

$$\epsilon_{0,\mathrm{H}^2} = \frac{e^2}{8mc^2}\left\langle 0 \left| \sum_{j=1}^{N} \left\{ H^2 r_j^{\,2} - (\mathbf{H}\cdot\mathbf{r}_j)^2 \right\} \right| 0 \right\rangle - \left(\frac{e}{2mc}\right)^2 \sum_{k=1}^{\infty}(E_k - E_0)^{-1} \times \{\langle 0 | \mathbf{H}\cdot(\mathbf{M} + 2\mathbf{S}) | k \rangle \langle k | \mathbf{H}\cdot(\mathbf{M} + 2\mathbf{S}) | 0 \rangle\} \tag{15}$$

where

$$\mathbf{M} = \sum_{j=1}^{N} \mathbf{M}_j$$

and

$$\mathbf{S} = \sum_{j=1}^{N} \mathbf{S}_j$$

The term in ϵ_0 proportional to $\mu_a H$ is

$$\epsilon_{0,\mu\mathrm{H}} = \frac{e^2}{2mc^2}\left\langle 0 \left| \sum_{j=1}^{N} r_{aj}^{-3} \{ (\boldsymbol{\mu}_a \cdot \mathbf{H})(\mathbf{r}_j \cdot \mathbf{r}_{aj}) - (\boldsymbol{\mu}_a \cdot \mathbf{r}_j)(\mathbf{H} \cdot \mathbf{r}_{aj}) \} \right| 0 \right\rangle - \frac{e^2}{2mc^2c^2}\sum_{k=1}^{\infty}(E_k - E_0)^{-1} \times [\langle 0 | \mathbf{H}\cdot(\mathbf{M} + 2\mathbf{S}) | k \rangle \langle k | \boldsymbol{\mu}_a \cdot (\mathbf{L}_a + \mathbf{F}_a) | 0 \rangle + \langle 0 | \boldsymbol{\mu}_a \cdot (\mathbf{L}_a + \mathbf{F}_a) | k \rangle \langle k | \mathbf{H}\cdot(\mathbf{M} + 2\mathbf{S}) | 0 \rangle] \tag{16}$$

where

$$\mathbf{F}_a = \sum_{j=1}^{N} \left\lfloor r_{aj}^{-5}\{ r_{aj}^{\,2}\mathbf{S}_j - 3(\mathbf{S}_j \cdot \mathbf{r}_{aj})\mathbf{r}_{aj} \} - \frac{8\pi}{3}\, \mathbf{S}_j \delta(\mathbf{r}_{aj}) \right] \tag{17}$$

Susceptibility

The susceptibility components, $\chi_{\alpha,\beta}$, can now be rapidly determined from eq 15 and

$$\chi_{\alpha\beta} = \frac{\partial^2}{\partial H_\alpha \partial H_\beta}\, \epsilon_{0,\mathrm{H}^2} \tag{18}$$

For both atoms and molecules we observe that the matrix elements involving the spin will vanish because of the orthogonality of the orbital parts of the wave functions. The average susceptibility

$$\langle \chi \rangle = {}^1\!/_3\{ \chi_{xx} + \chi_{yy} + \chi_{zz} \} \tag{19}$$

is then found to be identical with the results given by eq 1 for a diamagnetic or paramagnetic atom and eq 3 for a diamagnetic or paramagnetic molecule.

Shielding

The shielding components, $\sigma_{\alpha\beta}$ can be determined from eq 16 and

$$\sigma_{\alpha\beta} = \frac{\partial^2}{\partial \mu_\alpha \partial H_\beta}\, \epsilon_{0,\mu\mathrm{H}} \tag{20}$$

For both an atom and a molecule the term involving the spin which is linear in the field does not contribute in the infinite series because of orbital orthogonality. For an atom, if we would choose the origin of our coordinate system to be the nucleus, then the wave functions will also be eigenfunctions of **M** and the matrix elements involving the angular momentum will vanish. The result will be identical with eq 2. For a molecule with a closed shell, the term involving the spin that is linear in μ_a will yield matrix elements that are zero. The S_{xj} and S_{yj} terms do not contribute because of spin orthogonality; the S_{zj} terms contribute but the contribution is cancelled by another electron in the same orbital but with opposite spin. Also, the term involving the Dirac δ function is zero since we usually deal with wave functions which vanish at the origin. The result for σ will be identical with eq 6. For a molecule with an open shell our results are

$$\sigma_{xx} = \frac{e^2}{2mc^2}\left\langle 0 \left| \sum_{j=1}^{N} r_{aj}^{-3}\{ \mathbf{r}_{aj}\cdot\mathbf{r}_j - x_{aj}x_j \} \right| 0 \right\rangle - \frac{e^2}{2mc^2c^2}\sum_{k=1}^{\infty}(E_k - E_0)^{-1} \times \left[\langle 0 | M_x | k \rangle \left\langle k \left| L_x - 3\sum_{j=1}^{N} \frac{S_{zj}z_{aj}x_{aj}}{r_{aj}^{\,5}} \right| 0 \right\rangle + \left\langle 0 \left| L_x - 3\sum_{j=1}^{N} \frac{S_{zj}z_{aj}x_{aj}}{r_{aj}^{\,5}} \right| k \right\rangle \langle k | M_x | 0 \rangle \right] \tag{21}$$

and

$$\sigma_{zz} = \frac{e^2}{2mc^2}\left\langle 0 \left| \sum_{j=1}^{N} r_{aj}^{-3}\{ \mathbf{r}_{aj}\mathbf{r}_j - x_{aj}x_j \} \right| 0 \right\rangle - \frac{e^2}{2m^2c^2}\sum_{k=1}^{\infty}(E_k - E_0)^{-1}\left[\langle 0 | M_z | k \rangle \left\langle k \left| L_z + \sum_{j=1}^{N} S_{zj}\left(\frac{r_{aj}^{\,2} - 3z_{aj}^{\,2}}{r_{aj}^{\,5}}\right) \right| 0 \right\rangle + \left\langle 0 \left| L_z + \sum_{j=1}^{N} S_{zj}\left(\frac{r_{aj}^{\,2} - 3z_{aj}^{\,2}}{r_{aj}^{\,5}}\right) \right| k \right\rangle \langle k | M_z | 0 \rangle \right] \tag{22}$$

The average σ, $\langle \sigma \rangle$, will then be determined from

$$\langle \sigma \rangle = {}^1\!/_3\{ \sigma_{xx} + \sigma_{yy} + \sigma_{zz} \} \tag{23}$$

Discussion

It is found that the diamagnetic susceptibility (temperature independent magnetic susceptibility) of a diamagnetic or paramagnetic atom or molecule is independent of the electron spin. The magnetic shielding constant of a diamagnetic or paramagnetic atom is found to be independent of spin while σ for a paramagnetic molecule is found to have a spin dependence. It is currently believed that this spin dependence, due to the interaction of the electron spin and the magnetic dipole, is small. Calculations on the hydrogen molecule ion are in progress to determine the order of magnitude of this spin contribution. Also, calculations considering the coupling between electron spin and other degrees of freedom are in progress.

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(9) Reference 8, pp 72–75.