An Estimate of Mean Diamagnetic Properties

B. M. Ludwig and J. Voitländer

Sektion Physik und Physikalisch-Chemisches Institut
der Universität München

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Approximate closed expressions for the mean values of nuclear shielding constants and the diamagnetic susceptibility of $^1\Sigma$ molecules are given which apply if a density matrix constructed over a set of pure Gaussian functions, is known.

In the treatment of the second order magnetic properties[1] of molecules some use has been made of quantities termed "gauge independent atomic orbitals"[2]. The idea behind this modification of atomic orbitals is equivalent to applying Larmor's theorem irrespectively of the in general not spherically symmetric nature of the molecular potentials. For any electronic density made up from pure Gaussian functions closed formulas may be obtained that shall be quoted here.

Consider a one electron function Φ which is assumed to be a linear combination of Gauss functions centered at $\boldsymbol{R}_i$:

$$\Phi = \sum c_i \chi_i(\boldsymbol{R}_i), \quad \chi_i = \left(\frac{2\eta_i}{\pi}\right)^{3/4} \exp[-\eta_i(\boldsymbol{r}-\boldsymbol{R}_i)^2] \qquad (1)$$

with

$$\| \Phi \| = \| \chi_i \| = 1 .$$

The charge density

$$n(\boldsymbol{r}) = e\,|\,\Phi\,|^2 = e \sum_{i,j} n_{ij} = e \sum_{i,j} A_{ij}\,\chi_i\,\chi_j\,, \quad \boldsymbol{A}_{ij} = c_i\,c_j\,, \qquad (2)$$

e, m the electronic charge and mass,

is a superposition of spherical symmetric parts.

Let there be present a homogeneous external field $\boldsymbol{B}$ described by a vectorpotential

$$\boldsymbol{A}(\boldsymbol{r}) = \tfrac{1}{2}\,\boldsymbol{B} \times (\boldsymbol{r} - \boldsymbol{R}_0), \qquad (3)$$

$\boldsymbol{R}_0$ being an arbitrary vector.

The induced current density $\boldsymbol{j}[\boldsymbol{B}]$ may, applying Larmor's theorem to the individual charge contributions, be approximated by

$$\boldsymbol{j}(\boldsymbol{r}) = \sum_{i,j} \boldsymbol{j}_{ij} = \frac{e^2}{m} \sum n_{ij}\, \boldsymbol{B} \times (\boldsymbol{r} - \boldsymbol{R}_{ij}) \qquad (4)$$

with

$$\boldsymbol{R}_{ij} = (\eta_i \boldsymbol{R}_i + \eta_i \boldsymbol{R}_j) / (\eta_i + \eta_j) .$$

Integrating the classical relations

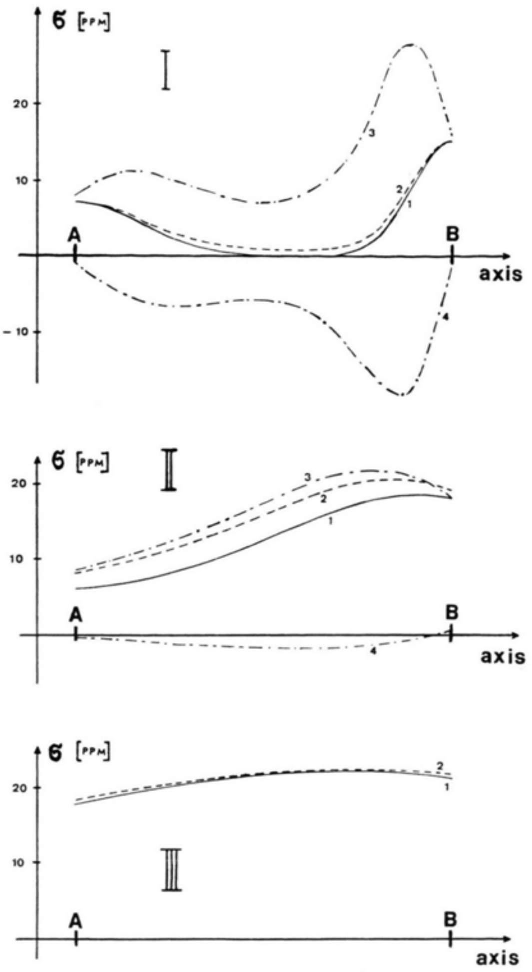
$$\boldsymbol{M} = \tfrac{1}{2} \int \mathrm{d}\tau\, \boldsymbol{j} \times \boldsymbol{r}$$

$$\boldsymbol{B}_1(\boldsymbol{r}') = \frac{\mu_0}{4\pi} \int \mathrm{d}\tau\, \frac{\boldsymbol{j} \times (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3} \qquad (5)$$

μ_0 the vacuum permeability (Giorgi units),

for the current moment $\boldsymbol{M}$ and the secondary field $\boldsymbol{B}_1$ leads after directional averaging to

$$\bar{\sigma}_{\mathrm{a}}(\boldsymbol{R}) = \frac{e^2}{6\,m} \frac{\mu_0}{a_0} \sum_{i,j} \frac{Z_{ij}}{\eta_i + \eta_j} \exp[-(\eta_i + \eta_j)(\boldsymbol{R} - \boldsymbol{R}_{ij})^2] \qquad (6\,\mathrm{a})$$



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$\overline{AB}$	(a. u.)	5	1.5	0.5
Variational:				
χ	$(10^{-11}\ \mathrm{m}^3/\mathrm{mole})$	-1.698	-1.643	-1.398
σ_{A}	(ppm)	15.71	19.36	22.20
σ_{B}	(ppm)	6.96	8.04	18.13
Approximate:				
χ	$(10^{-11}\ \mathrm{m}^3/\mathrm{mole})$	-1.525	-1.405	-1.367
σ_{A}	(ppm)	15.62	18.11	21.97
σ_{B}	(ppm)	6.93	6.15	17.45

Fig. 1. Mean shielding contributions for model density [Eq. (8)] along the central axis. 1: Approximate values, 2: Variational values, 3: "Diamagnetic" part, 4: "Paramagnetic" part. Parameters are: $c_{\mathrm{A}}/c_{\mathrm{B}} = 0.9$, $\eta_{\mathrm{A}} = 0.3$, $\eta_{\mathrm{B}} = 1$ (a. u.).

Reprints request to B. M. Ludwig Phys.-Chem. Institut der Universität München, *D-8000 München*, Sophienstraße 11.

[1] D. W. Davies, Theory of Electric and Magnetic Properties of Molecules, John Wiley & Sons, London, New York 1967.

[2] H. F. Hameka, Advanced Quantum Chemistry, Addison Wesley Publishing Comp., Reading, Mass. 1965; F. London, J. Physique Rad. **8**, 397 [1937].

[3] H. Preuss, Z. Naturforsch. **20 a**, 17 [1965].

for the shielding and

$$\bar{\chi}_{\mathrm{a}} = \sum_{i,j} \chi_{ij} = -\frac{e^2 \mu_0 L}{4\, m} \sum \frac{Z_{ij}}{(\eta_i + \eta_j)^{5/2}} \qquad (6\,\mathrm{b})$$

for the molar susceptibility. L means Avogadros number and a_0 the Bohr radius. Z_{ij} is defined as

$$Z_{ij} = A_{ij} \exp\left\{ -\frac{\eta_i \eta_j}{\eta_i + \eta_j} (\boldsymbol{R}_i - \boldsymbol{R}_j)^2 \right\} \left(\frac{2}{\pi} \right)^{3/2} (\eta_i \eta_j)^{3/4}. \qquad (7)$$

The expressions (6) apply as well if Eq. (2) is the diagonal element of a general density matrix (but $A_{ij} \neq c_i c_j$ then) built up from an arbitrary number – not limited to a determinantal picture – of molecular orbitals. They converge towards the exact answer if the charge globes are either well separated or become concentric.

For the hydrogen molecule a near Hartree-Fock wavefunction [3] gives $\bar{\sigma}_{\mathrm{a}} = 24.5$ ppm, $\bar{\chi}_{\mathrm{a}} = -0.45\ \mathrm{m}^3/\mathrm{mole}$, the experimental values [4] being 26.6 ± 0.5 and -0.5 ± 0.01.

These values are both low; besides the approximation involved the overcontracted form and the absence of a cusp are thought to be responsible.

The behaviour of the approximation has been examined more closely for a model density constructed from two atomic orbitals only:

$$\Phi = c_{\mathrm{A}}\, \chi_{\mathrm{A}} + c_{\mathrm{B}}\, \chi_{\mathrm{B}}\,, \qquad \| \Phi \| = 1\,. \qquad (8)$$

A variational calculation [4] for the induced part of this orbital has been done including up to 30 parameters for the f-function $[\Phi \rightarrow \Phi \cdot (1 + i \cdot f)]$, which should be of reasonable accuracy. Results for different typical situations are displayed in Fig. 1. The origin for the vectorpotential is taken at the electronic centroid, which is the best gauge of the restricted type, Eq. (3), so that the definition of the "diamagnetic" shielding differs somewhat from the usual one (correcting in the right sense). In case I a check is provided for the variational calculation, as here the charges do have negligible overlap and Eqs. (6) are almost exact. The errors are usually less than 10%. No situation has been found with discrepancies exceeding 20%.

Since no effectively working procedure is known to compute diamagnetic properties from first principles for not very small electron numbers the present approximation may sometimes be useful to obtain estimates of the mean values of the susceptibility and shielding tensors. The treatment gives expressions for the tensor elements too, but these are thought to be rather insignificant [5]; for the susceptibility no anisottropy whatsoever is predicted. Isomers will have different χ's. The shielding approximation will not work for nuclei other than protons, since then the nodal structure of π-electrons plays the dominant role [5]. Hydrogen chemical shifts are expected to be portrayed to some extend.

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[5] B. M. Ludwig, to be published.

[4] B. M. Ludwig u. J. Voitländer, Mol. Phys. **16**, 405 [1969] and Z. Naturforsch. **24 a**, 471 [1969].