Finite Perturbation Studies of Magnetic Susceptibility and Shielding with GIAO

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The magnetic susceptibility tensor and proton and fluorine magnetic shielding tensors are calculated for F_2 and $(FHF)^-$ using an ab initio finite perturbation method with gauge-invariant atomic orbitals (GIAO). The discussion of the basis set deficiency shows that the calculated values for the susceptibilities are reliable. Simple additivity (Pascal rule) for the susceptibility is confirmed.

Introduction

Developments of experimental techniques for determining both magnetic susceptibility and magnetic shielding tensors have resulted in recent years in the collection of a large body of precise data[1]. Significant advances have been made also in theoretical methods for the study of magnetic shielding. Ditchfield has developed a theory which utilizes gauge-invariant atomic orbitals (GIAO) within the perturbed Hartree-Fock framework[2] and gives extremely good results for magnetic shieldings[3]. He has shown that even using a minimal Gaussian type orbital basis set of GIAO one obtains results which are in better agreement with experiment than the moderately extended to extended sets of other authors[1]. This is due to the use of the complex modulating factor on each basis function which ensures that the circulatory motion of electrons, induced by an external magnetic field, is fully included even though the basis set is not enlarged to describe it. It is reasonable that the GIAO basis set would have to be at least as good for calculating magnetic susceptibilities as it is for magnetic shieldings.

Recently we have developed a finite perturbation procedure for the calculation of the magnetic susceptibility by means of GIAO and tested it on HF[4]. The purpose of this work is to examine the performance of this method for the calculation of the magnetic susceptibility of F_2 and $(FHF)^-$ and to compare the results with those for HF and F^-. With the wavefunctions obtained from the SCF procedure also the magnetic shieldings of proton and fluorine are calculated. We also present some details about the calculation procedure.

Method and Calculation

The method used is a finite perturbation self consistent field theory. Molecular wavefunction is approximated by a single determinant of molecular orbitals. Each molecular orbital is expanded over gauge invariant Gaussian orbitals. Since the basis functions are explicitly dependent on external magnetic fields, all the matrix elements in the Roothaan equations are also field dependent. The integrals are calculated analytically[5]. Nuclear attraction and electron repulsion integrals are evaluated in terms of incomplete gamma functions of complex arguments. In the Appendix it is shown how this auxiliary function can be efficiently calculated with the required accuracy.

The Roothaan equations were solved for various magnetic field directions and finite magnitudes and the total energies were deduced. The magnetic susceptibility was calculated by a numerical differentiation of the energy[6, 7]. As the chosen magnetic field strength was small enough, the calculation at a single value of magnetic field component was sufficient to evaluate the derivatives of the energy. Thus the susceptibility was obtained simply through the relation $\chi_t = -2\,\Delta E/H_t^2$ where ΔE means the difference of the molecular energy in the presence and absence of the magnetic field (with a component H_t in the t direction). Knowing the density matrix $P_{\mu\nu}(H)$ we calculated magnetic shieldings of all nuclei in a molecule using Ditchfield's expression[2]. The derivate $\partial P_{\mu\nu}(H_t)/\partial H_t$ was substituted by $[P_{\mu\nu}(H_t) - P_{\mu\nu}(0)]/H_t$, which means actually the imaginary part of $P_{\mu\nu}(H_t)$ divided by H_t.

All calculations were done with STO-3G basis set[8]. The intermolecular distances taken were 2.68, 1.733 and 4.2 a.u. for F_2, HF and FHF^-, respectively. The magnitude 100 T was chosen for the

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magnetic field strength for each principal component. For this value of the magnetic field the energy difference was of the order 10^{-6} a. u. All the integrals were calculated with accuracy 10^{-10}. With a given basis set the magnetic susceptibility, calculated only through the first difference, is accurate up to three significant numbers.

Results and Discussion

The susceptibilities are given in Table 1. At the bottom of this table available experimental or calculated results are given for comparison. Our STO-3G results are systematically lower than experimental ones or those calculated with extended basis sets. The greatest difference is for the susceptibility of F^- and the lowest one is for F_2, where it differs only by 2% from the isotropic value. Previous calculations[4] showed that the STO-3G susceptibility of HF is 15% lower than the one calculated with extended Dunning's set. It is surprising how accurately the susceptibility components are additive: $\chi_\perp$, $\chi_{||}$ and χ_{iso} for $(FHF)^-$ are the sum of equivalent values of HF and F^-. The contribution of the H – F bond in HF to the total susceptibility is small (in accordance with Pascal's rule), and since the hydrogen bonds in $(FHF)^-$ are weaker than the H – F bond their contributions are even smaller.

Calculated magnetic shieldings are given in Table 2. Our calculation together with the recent Ditchfield's one[11] shows a large dependence of fluorine magnetic shieldings upon the basis set. It is smaller for isotropic values and larger for anisotropies. An exception is F_2 where the minimum basis set is completely insufficient. There is a substantial discrepancy between the calculated fluorine chemical shift in $(FHF)^-$ without regard to the basis set and the experimental values[12] deduced from NMR studies of crystal KHF_2. Comparing the values of σ_{iso} for fluorine in HF, $(FHF)^-$ and F^- we can conclude that the electronic structure of the fluorine atom in $(FHF)^-$ is not much different from that of F^-, since the σ_{iso} of both are nearly equal. In HF the paramagnetic contribution of the bond is more significant and σ_{iso} is much smaller than that

Table 1. Calculated magnetic susceptibility tensors and anisotropies (cgs — ppm).

Molecule	Total energy	$\chi_\perp$	$\chi_{\|\|}$	χ_{iso} [a]	$\Delta\chi$ [b]
F_2	−195.965755	−7.28	−13.87	−9.48	−6.59
HF	−98.570784	−8.9	−8.17	−8.7	0.7
$(FHF)^-$	−196.359611	−16.60	−15.67	−16.29	0.93
F^-	−97.613311			−7.47	0
F_2 expt. (Ref. [1])		−6.0	−17.0	−9.7	−11.0
HF expt. (Ref. [1])		−10.4	−10.1	−10.3	0.3
$(FHF)^-$ calc. (Ref. [9])				−28.6	
F^- calc. (Ref. [10])				−12.6	

[a] $\chi_{\text{iso}} = \frac{1}{3}(2\chi_\perp + \chi_{||})$. [b] $\Delta\chi = \chi_{||} - \chi_\perp$ ($\chi_{||}$ along symmetry axis).

Table 2. Calculated magnetic shielding tensors and anisotropies (ppm).

Molecule	Nucleus	$\sigma_\perp$	$\sigma_{\|\|}$	σ_{iso} [a]	$\Delta\sigma$ [b]
F_2		−124.21	480.91	77.50	605.12
HF	F	383.37	478.45	415.07	95.08
	H	30.08	44.41	34.86	14.33
$(FHF)^-$	F	504.71	485.39	498.27	−19.32
	H	12.89	50.89	25.56	38.00
F^-				487.48	0
F_2 expt. (Ref. [1])	F	−560	490	−210	1050
HF expt. (Ref. [1])	F	380	482	414	102
	H			29.2	
KHF_2 expt. (Ref. [12])	F		385	329	84
	H		39.5	16.6	44.8

[a] $\sigma_{\text{iso}} = \frac{1}{3}(2\sigma_\perp + \sigma_{||})$. [b] $\Delta\sigma = \sigma_{||} - \sigma_\perp$ ($\sigma_{||}$ along symmetry axis).

of F^-. Proton magnetic shielding is not so sensitive to the basis set used in calculations. Our results are in accordance with those of Ditchfield[11] and agree qualitatively with the experiment[12, 1].

It is not surprising that the STO-3G values for shieldings at least for hydrogens are in better agreement with experiment than the STO-3G susceptibilities. The greatest contribution to the susceptibility is from the outer electrons, while to the shielding it is from the inner ones. The STO-3G basis set, optimized to minimize the energy, describes thus better inner electrons than outer ones. Previous calculations show[13] that the coupled Hartree-Fock procedure completely fails in predicting the susceptibility of $(FHF)^-$, while the uncoupled Hartree-Fock procedure[9] predicts it only with moderate accuracy not better than ours with the minimum basis set. Though the absolute values of the susceptibility are too low, the STO-3G calculations are thus still meaningful. They can predict relative susceptibilities (confirming Pascal's rule) and give qualitatively anisotropies.

Appendix

Nuclear attraction and electron repulsion integrals over GIAO can be expressed in terms of auxiliary functions $F_m(z)$, a reduced form of the incomplete gamma function of complex argument. The necessary formulae for computing $F_m(x)$, where the argument is real, can be found in Shavitt's paper[14]. While the complex functions

$$F_m(z) = \int_0^1 r^{2m} \exp\{-z\,r^2\}\,\mathrm{d}r\,,$$

$$m = 0, 1, \ldots, \quad z = x + i\,y\,,$$

are analytic for all values of $|z| < \infty$, all Shavitt's formulae for real functions can be used without modifications substituting a real argument with a complex one.

The computation of the functions $F_m(z)$ depends on the range of the argument z, on the required accuracy and the required sequence of orders. For the magnetic fields of about 100 T the imaginary parts of the arguments are small enough to use the expansion

$$F_m(x + i\,y) = \sum_{n=0}^{\infty} \frac{(-i\,y)^n}{n!} F_{m+n}(x)\,. \qquad (1)$$

A sequence of real functions $F_m(x)$ is all one needs in such a case. Let us show how the sequence of real functions $F_m(x)$ was computed with the accuracy $1 \cdot 10^{-10}$. In the interval $0 \leqq x \leqq 5$ the recurrence relation

$$F_m(x) = (2\,m+1)^{-1}\,[2\,x\,F_{m+1}(x) + \exp\{-x\}] \qquad (2)$$

provides the best way for computing $F_m(x)$. It is easy to see that assuming $F_{27}(x) = 0$ the sequence $F_m(x)$ for $0 \leqq m \leqq 10$ satisfies the required accuracy. In the intermediate range $5 < x < 10.3$ the fastest way is the use of the series expansion

$$F_m(x) = \tfrac{1}{2}\,\Gamma(m+\tfrac{1}{2})\,\exp\{-x\} \sum_{i=0}^{\infty} \frac{x^i}{\Gamma(m+i+\frac{3}{2})} \qquad (3)$$

for $F_0(x)$. By means of (3) one has to compute the value of the function for integer and half integer values of x, between these values one can use the expansion

$$F_0(x + \Delta x) = \sum_{n=0}^{\infty} \frac{(-\Delta x)^n}{n!} F_n(x)\,. \qquad (4)$$

The required accuracy is satisfied with the first nine terms in (4) for $|\Delta x| \leqq 0.25$. Higher orders $F_m(x)$ can be obtained from $F_0(x)$ using (2) for values $0 < m \leqq 13$ in this interval. The asymptotic expansion

$$F_m(x) = \frac{\Gamma(m+\frac{1}{2})}{2\,x^{m+\frac{1}{2}}} - \Gamma(m+\tfrac{1}{2})\,\frac{\exp\{-x\}}{2\,x} \sum_{i=0}^{[N]} \frac{1}{x^i\,\Gamma(m-i+\frac{1}{2})} \qquad (5)$$

provides the best chance for $x \geqq 10.3$. The notation $[N]$ for the upper limit implies that the summation should not extend beyond the smallest term[14]. The accuracy 10^{-10} is achieved by the ten first terms in the summation (5) (for $x \geqq 19.4$ the first term is enough). The sequence $F_m(x)$ can be obtained from $F_0(x)$ using (2) up to order $m = 27$ for $x \geqq 10.3$.

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