Dirac–Fock calculations of magnetic shielding constants: hydrogen molecule and hydrogen halides

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Abstract

Proton magnetic shielding constants of HX (X = H, F, Cl, Br, I) are calculated based on the Dirac–Fock finite perturbation (DF-FP) method. The results are in good agreement with experiments: the halogen dependence of the proton chemical shifts is well reproduced. The Gordon decomposition for the magnetic shielding constant gives results closely parallel to the lowest-order (c^{-2}) terms in the traditional quasi-relativistic theories; the so-called diamagnetic, paramagnetic, spin–dipolar, and Fermi-contact terms. This decomposition shows that the Fermi-contact term is the most important origin of the relativistic effect on the chemical shift, as is well known in the quasi-relativistic theories. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The importance of relativistic effects in the theory of magnetic shielding constants of molecules containing heavy elements has been suggested for many years [1–5]; however, no accurate relativistic calculations were carried out until we performed spin–orbit calculations of NMR chemical shifts [6–8]. Thereafter, a number of relativistic calculations of magnetic shieldings have been published at various levels of relativistic methods [9–19].

We have presented a series of studies about the relativistic effects of nuclear magnetic shielding constants. First we have proposed a method for computing magnetic shielding constants under the influence of spin–orbit (SO) interaction using the unrestricted Hartree–Fock (UHF) wavefunctions with the finite perturbation (FP) method. We call this approach the SO-UHF method [6]. This method has been applied to the H, C [6], Ga, In [7], Si [8], Al [9], Sn [10], Nb and Ti [11] chemical shifts of various halogen-containing compounds. We have shown that the experimental chemical shifts in these compounds are well reproduced only when the SO interaction is included and thus the importance of the SO effect has been amply demonstrated. Other spin-free relativistic (SFR) terms of the c^{-2} order, like the so-called mass-velocity and Darwin terms, have been incorpo-

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rated into the SO–UHF method [12] and applied to H [12], Hg [13], and W [14] chemical shifts of halide and oxide compounds. These SFR terms are shown to strongly couple with the SO term, affecting significantly the chemical shifts of heavy elements.

Since the relativistic effects on magnetic shielding constants are critically important [6–19], it may be necessary to apply a 'fully' relativistic method. In our previous Letter, we proposed the use of the matrix Dirac–Fock finite perturbation (DF-FP) theory [20]: we explicitly dealt with the four-component Dirac–Coulomb–Breit many-body Hamiltonian within the Dirac–Fock approximation. Since the DF-FP method avoids the problem of negative-energy states as arising in the sum-over-states methods [3–5], this method gave numerically stable results.

However, recently we found a defect in the previous treatment. Therefore, in this Letter we present again a series of calculations of proton magnetic shielding constants using the DF-FP method. Calculations are carried out for HX molecules with X = H, F, Cl, Br, and I.

2. Theory

As the detailed formulation has already been presented in a previous communication [20], we present here only a few important working equations. The relativistic many-body Hamiltonian used is the so-called no-pair Dirac–Coulomb (DC) Hamiltonian prescribed by Sucher and Mittleman [21,22]. In the presence of the magnetic vector potential, the effective many-body Hamiltonian is given by

$$H_+^{DC}(\boldsymbol{B}_0) = \sum_i \left[c\boldsymbol{\alpha} \cdot (\boldsymbol{P}_i + \boldsymbol{A}_i) + \beta' c^2 + \sum_n V_n(i) \right]$$
$$+ L_+ \left[\frac{1}{2} \sum_{i \neq j} 1/r_{ij} \right] L_+ , \qquad (1)$$

where c is the speed of light, $\boldsymbol{\alpha}$ and β' are 4×4 Dirac matrices, V_n is the nuclear attraction term due to the nucleus n, $L_+ = \Lambda_+(1)\Lambda_+(2)\ldots\Lambda_+(N)$ with Λ_+ denoting the projection operator onto the space spanned by the positive-energy eigenfunctions of the

matrix DF equation [21,22]. As the two-electron term, the non-relativistic Coulomb repulsion $1/r_{ij}$ without the Breit interaction is used in the present calculations. The effect of the Breit interaction was shown to be small for the present systems [20].

The vector potential $\boldsymbol{A}_i$ arising from a uniform external magnetic field $\boldsymbol{B}_0$ and the nuclear magnetic moment of the nth nucleus μ_n is given by

$$\boldsymbol{A}_i = \frac{1}{2}\boldsymbol{B}_0 \times (\boldsymbol{r}_i - \boldsymbol{d}) + \sum_n c^{-2}\mu_n \times \boldsymbol{r}_{ni}/r^{-3}, \quad (2)$$

where r_{ni} is the distance between the electron i and the nucleus n and $\boldsymbol{d}$ denotes the gauge origin. The finite nucleus model reported in Ref. [20] is not adopted in Eq. (2), since the present calculations are carried out only for the proton magnetic shieldings.

The magnetic shielding constant $\sigma_{n,tu}$ $(t, u = x, y, z)$ on the nucleus n is given by a single term as

$$\sigma_{n,tu} = \frac{\partial}{\partial B_{0t}} \left[\langle \Phi^{DF}(B_{0t}) | H_{nu}^{(0,1)} | \Phi^{DF}(B_{0t}) \rangle \right]_{B_{0t}=0}, \qquad (3)$$

where $\Phi^{DF}(B_{0t})$ is here the total N-electron DF wavefunction, and $H_{nu}^{(0,1)}$ is the first-order term of μ_{nu} in the expansion of the DC Hamiltonian in Eq. (1) as

$$H_{nt}^{(0,1)} = \frac{1}{c} \sum_i (\boldsymbol{r}_{ni} \times \boldsymbol{\alpha}_i)_t/r^{-3}. \qquad (4)$$

Eq. (3) is evaluated by the finite perturbation (FP) method using Eqs. (1) and (2) with $\boldsymbol{\mu}_n = 0$. The DF-FP method avoids the treatment of negative-energy states in contrast to the sum-over-states method. For the perturbed wavefunction $\Phi^{DF}(B_{0t})$, one must use the general unrestricted Kramers' spinor pairs in the DF calculations in order to take the effects of B_0 correctly into account. On the other hand, the restricted Kramers' spinor pairs are automatically obtained in the unperturbed wavefunction $\Phi^{DF}(B_{0t} = 0)$. This was not done completely in Ref. [20] but is done in the present Letter. The differences between

Table 1
Calculated and experimental proton magnetic shielding constants (ppm) for HX (X = H, F, Cl, Br, I)

Molecule	Dirac–Fock (present)	Quasi-relativistic[a] (SO-UHF)[b]	Exptl.
H_2	26.62(left)[c]		26.69
H_2	26.48(right)[c]		26.69
HF	27.14[d]	28.00[d]	29.20
HCl	29.82[d]	30.80[d]	31.78
HBr	32.05[d]	34.99[d]	35.63
HI	37.85[d]	44.43[d]	44.54

[a] Spin–orbit interaction, mass-velocity, and Darwin terms are included. The basis set for hydrogen is (4s4p), and for halogen double-zeta plus FOBFs for the valence p functions (Ref. [12]).
[b] See Ref. [6].
[c] The terms 'left' and 'right' specify the nuclei on which the gauge origin is located. The resonant nucleus is located on the 'left'.
[d] The gauge origin is located on the halogen atom.

the present and previous results are mainly due to this correction.

3. Computation

The Dirac–Fock calculations were carried out by using the modified MOLFDIR program [23]. The bond distances used for HX (X = H, F, Cl, Br, I) were taken from Ref. [6]. The large-component basis sets of halogen atoms F, Cl, Br, I were the uncontracted gaussian functions (6s3p), (9s6p), (14s11p6d), and (15s12p7d), respectively, which are taken from Tables 9.10.1, 17.5.1, 35.5.1, and 53.1.1 of Ref. [24]. The p and d primitive functions for Br and I were slightly modified in order to reduce the number of the small-component basis functions. The basis sets for the halogen atoms are better in quality than those used in Ref. [20], though they gave essentially the same results as the previous ones. For hydrogen, the uncontracted Huzinaga–Dunning (4s) functions plus their first-order basis functions (FOBFs) [25] were used. In the small-component basis, the first derivatives of the large-component basis functions were included so as to satisfy the condition of 'kinetic balance' [23,26].

For evaluating Eq. (3) by the finite perturbation (FP) method, we used 0.001 a.u. as the magnetic field strength B_{0t} ($t = x, y, z$). This perturbation did not affect the Dirac–Fock SCF convergence in the present calculations.

4. Results and discussions

The calculated and experimental ^{1}H magnetic shielding constants of HX are shown in Table 1. In the hydrogen molecule, the calculated proton magnetic shielding constants agree well with the experiment. Two different gauge origins were used; one located on the left hydrogen and the other on the right one, the resonant proton being on the left-hand side. The gauge origin dependence is small, showing that the FOBFs reduces the gauge origin dependence also in the present relativistic calculations as confirmed in the non-relativistic calculations [25]. For hydrogen halides, the gauge origin was always located on the halogen atom, since the halogen atom is much heavier than the hydrogen atom. The calculated proton shielding constants agree fairly well with the experimental values, though they are underestimated especially for HBr and HI. The halogen dependence, the so-called normal halogen dependence [27], of the proton chemical shifts in HX, which is not reproduced by the non-relativistic methods [6,12], is reproduced as shown in Fig. 1. Note that the proton chemical shifts of HX obtained by the non-relativistic method are almost constant among
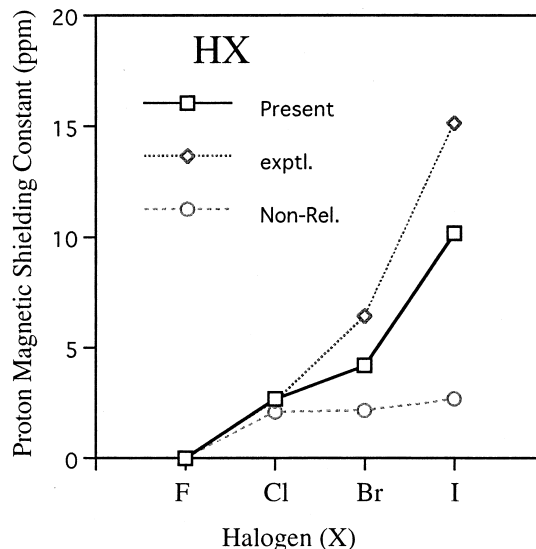

Fig. 1. Proton magnetic shielding constants (ppm) in HX (X = F, Cl, Br, I) by the Dirac–Fock (□), the non-relativistic RHF (○) and the experiments (◇). The non-relativistic values are taken from Table 2 of Ref. [12].

Table 2
The Gordon decomposition and quasi-relativistic terms of the proton magnetic shielding constants (ppm) for HX (X = H, F, Cl, Br, I)

Molecule	Gordon decomposition (Dirac–Fock)						Quasi-relativistic[a]					Exptl.
	σ^{dia}	σ^{para}	σ^{SD}	σ^{FC}	$\sigma(G)$[c]	$\sigma(DF)$[d]	σ^{dia}	σ^{para}	σ^{SD}	σ^{FC}	$\sigma(QR)$[e]	
H_2(left)[b]	32.31	−5.68	0.00	−0.01	26.63	26.62						26.69
H_2(right)[b]	19.48	7.00	0.00	0.01	26.49	26.48						26.69
HF	16.65	10.41	0.02	0.14	27.22	27.14	15.90	11.92	0.01	0.16	28.00	29.20
HCl	17.45	11.91	0.08	0.85	30.28	29.82	16.80	13.09	0.04	0.86	30.80	31.78
HBr	17.21	12.15	0.37	5.01	34.74	32.05	16.71	13.23	0.17	4.87	34.99	35.63
HI	17.90	12.48	0.86	14.07	45.31	37.85	17.12	13.26	0.35	13.69	44.43	44.54

[a] The SO-UHF method are used. Spin–orbit interaction, mass-velocity, and Darwin terms are included. The basis set for hydrogen is (4s4p), and for halogen double-zeta plus FOBFs for the valence p functions (Ref. [12]).
[b] The terms 'left' and 'right' specify the nuclei on which the gauge origin is located. The resonant nucleus is located on the 'left'.
[c] $\sigma(G)$ is the sum of the four terms ($\sigma(G) = \sigma^{dia} + \sigma^{para} + \sigma^{SD} + \sigma^{FC}$) in the Gordon decomposition.
[d] $\sigma(DF)$ is the single term value given by Eq. (3) of the text.
[e] $\sigma(QR)$ is the sum of the quasi-relativistic terms.

X = Cl, Br, and I. The chemical shifts of HX are due essentially to the relativistic effect.

The Gordon decomposition of the magnetic shielding constant was proposed by Pyper [3] for the first time. The explicit formulas are shown in Eq. (12) of Ref. [3]. Using this decomposition, a single relativistic term given by Eq. (3) is converted identically to the four terms corresponding to the diamagnetic, paramagnetic, spin–dipolar, and Fermi-contact terms, which are the leading (c^{-2}) terms in the traditional quasi-relativistic theories. This decomposition is exact only when the basis set used is complete. Pyper's Gordon decomposition for the present results is shown in Table 2. The trends of the decomposed diamagnetic and paramagnetic terms are essentially the same as those in the quasi-relativistic method reported previously [12]. As expected, each decomposed term is strongly gauge-origin dependent, though the sum of these terms is almost independent of the position of the gauge origin. The Fermi-contact term is quite small in HF and HCl, while it gradually increases in HBr and HI. This result shows that the total halogen dependence (more-shielding in heavier halogen) is due to the Fermi-contact term. Table 2 shows that Pyper's Gordon decomposition numerically parallels the quasi-relativistic analysis: it is useful as an analysis method for the magnetic shielding constants calculated by the four-component DF method.

We note here about the disagreement in Table 2 between the sum of the decomposed terms and the single term given by Eq. (3). This is due to basis set incompleteness. The decomposed terms are generated from the couplings within the large components (L–L) and within the small components (S–S), while the single term of Eq. (3) is due to the coupling between the large and small components (L–S). Since the S–S coupling is quite small even in HI, the decomposed terms are essentially due to the L–L coupling. Further, $\sigma(G)$ in Table 2 is very close to the quasi-relativistic term $\sigma(QR)$, while only $\sigma(DF)$ deviates from both $\sigma(G)$ and $\sigma(QR)$.

5. Conclusions

Fully relativistic calculations of the proton magnetic shielding constants of HX (H = H, F, Cl, Br, I) based on the four-component no-pair DFC theory are presented. This method is free from the nightmare of positron-like states, and the calculated values are numerically stable. The calculated proton magnetic shielding constants agree well with experiments. The normal halogen dependence in HX (more-shielded in heavier halogen) is well reproduced. The FOBF works to reduce the gauge origin dependence even in the DFC calculations.

We have confirmed numerically that Pyper's Gordon decomposition closely parallels the quasi-relativistic concept of diamagnetic, paramagnetic, spin–dipolar, and Fermi-contact terms, which is valuable for analysing and interpreting the results obtained by the

four-component relativistic methods. The halogen dependence is mainly due to the Fermi-contact term as shown previously [2,6,12].

Acknowledgements

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