Dirac–Fock calculations of the magnetic shielding constants of protons and heavy nuclei in XH_2 (X = O, S, Se, and Te): a comparison with quasi-relativistic calculations

Masahiko Hada, Ryoichi Fukuda, Hiroshi Nakatsuji [*]

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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Abstract

Calculations of magnetic shielding constants of protons and heavy elements in HX_2 molecules (X = O, S, Se, and Te) are presented based on the Dirac–Fock (DF) method in the presence of a finite magnetic field. The calculated magnetic shielding constants agree fairly well with experiments. The so-called diamagnetic, paramagnetic, Fermi-contact, and spin–dipolar terms are also presented by applying the Gordon decomposition method. The results are compared with those calculated by the quasi-relativistic (QR) method, and we found that the difference between the DF and QR methods is significant for TeH_2. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is fairly sensitive to chemical environments around resonant nuclei. The nuclear magnetic shielding constants, measured as NMR chemical shifts, have a substantial contribution from orbital and spin angular momenta in atomic core region of valence orbitals [1,2]. Thus, in molecules containing heavy elements, the relativistic effects become substantial and are observed by the NMR spectroscopy. Such importance of the relativistic effect has been suggested for many years [3–7], and confirmed unambiguously by our laboratory [8–16].

We have presented a series of studies about the relativistic effects on the nuclear magnetic shielding constants [8–16]. We have proposed a method for computing the magnetic shielding constants under the influence of the spin–orbit (SO) interaction using the unrestricted Hartree–Fock (UHF) wavefunctions including magnetic field as a finite perturbation [8]. This method called SO–UHF has been applied to H, C [8], Ga, In [9], Si [10], Al [11], Sn [12], Nb and Ti [13] chemical shifts of various halogen-containing compounds. These results have demonstrated the importance of the SO effect. Further, including other c^{-2}-order spin-free relativistic (SFR) terms, like the so-called mass-velocity and Darwin terms, together with the SO interaction, we have carried out calculations of H [14], Hg [15], and W [16] chemical shifts in some halide and oxide compounds. These SFR terms were shown to strongly couple with the SO

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[*] Corresponding author. Fax: +81-75-753-5910; e-mail: hiroshi@sbchem.kyoto-u.ac.jp

term, affecting significantly the chemical shifts of the heavy elements.

Ab-initio fully relativistic four-component calculations of magnetic shielding constants have not appear before our recent calculations [17,18], though some pioneering theoretical works existed [5,6]. Those of nuclear spin–spin coupling constants was also reported very recently [19]. On the other hand, a number of ab-initio quasi-relativistic (QR) calculations have been reported [8–16,20,17], since the computational labours involved are less than the four-component Dirac–Fock (DF) one and the underlying concepts are the extensions of the non-relativistic ones. The density functional theories also have been applied to calculations of magnetic shielding constants [21–25]. Since any QR theories are, in nature, approximate ones derived from a fully relativistic four-component theory, a comparison between these two methods is necessary particularly when they are applied to really heavy elements.

In our recent communications [17,18], we proposed a use of the matrix DF finite perturbation theory for magnetic shielding constants: we explicitly dealt with the four-component Dirac–Coulomb–Breit Hamiltonian with the DF approximation. We have presented the calculations of the proton magnetic shielding constants of H_2 and hydrogen halides [17,18], and the shielding constants of the inert atoms, He to Xe [17].

This communication has two objectives. One is to apply the ab-initio four-component DF method to the calculations of the magnetic shielding constants of heavy resonant nuclei, which is actually first in the world, and the other is to compare the results with those by a standard QR method and discuss the differences. Molecules selected here are XH_2 (X = O, S, Se, and Te). The ^{1}H and X shielding constants in these molecules are calculated by the DF method, and for comparison, they are calculated by the QR Douglas–Kroll (DK) method.

2. Computational details

2.1. Relativistic theory

The matrix DF method are utilized with the no-pair Dirac–Coulomb (DC) Hamiltonian described by

Sucher and Mittleman [26,27] to obtain fully relativistic wavefunctions. The vector potentials arising from external uniform magnetic field and nuclear magnetic moment are added to the no-pair DC Hamiltonian.

To make a comparison between the DF and QR methods, the relativistic Hamiltonian generated from the second-order DK *trans*-formation and the generalized unrestricted Hartree–Fock (GUHF) method are used, evaluating the matrix elements over the basis functions by the matrix-transformation method proposed by Hess [28]. The DC Hamiltonian including magnetic vector potentials were block-diagonalized by the DK transformation which is important for heavy element NMR [29]. One-electron SO term was included in the form generated from the DK transformation, and two-electron SO term was added in the Breit–Pauli form.

2.2. Magnetic shielding constant

In the DF method with no-pair DC Hamiltonian, the magnetic shielding constant σ_{tu} $(t,u = x,y,z)$ is given by a single term as

$$
\sigma_{n,tu}^{\mathrm{DF}}
$$

$$
= \frac{\partial}{\partial B_{0t}} \left[\left\langle \Phi^{\mathrm{DF}}(B_{0t}) \left| \sum_i \frac{(r_{ni} \times \alpha_i)_u}{r_{ni}^3} \right. \right. \right.
$$

$$
\left. \left. \left. \times \Phi^{\mathrm{DF}}(B_{0t}) \right\rangle \right] \right]_{B_{0t}=0}
\tag{1}
$$

where $\Phi^{\mathrm{DF}}(B_{0t})$ is the four-component DF wavefunction in the presence of a uniform external magnetic field $B_{0t}(t = x,y,z)$, α_i are 4×4 standard Dirac matrices, and r_{ni} is a coordinate of electron i from the nucleus n. The derivation of Eq. (1) has been reported in some detail in the previous report [17]. The point nucleus model is used in Eq. (1), since we have found that the finite nucleus model does not affect much the calculated values [29].

Pyper [5] reported that, when the Gordon decomposition is applied to Eq. (1), the DF magnetic

shielding constant is divided into four terms as follows,

$$
\begin{aligned}
&\sigma_{n,tu}^{GD} \\
&= \left\langle \Phi^{DF}(0) \left| \frac{1}{2c^2} \beta \sum_i \frac{(\mathbf{r}_i - \mathbf{d}) \cdot \mathbf{r}_{ni} \delta_{tu} - (r_{it} - d_t) r_{ni,u}}{r_{ni}^3} \right| \Phi^{DF}(0) \right\rangle \\
&\quad + \frac{\partial}{\partial B_{0t}} \left\langle \Phi^{DF}(B_{0t}) \left| \frac{1}{c} \beta \sum_i \frac{(\mathbf{r}_{ni} \times \hat{\mathbf{P}}_i)_u}{r_{ni}^3} \right| \Phi^{DF}(B_{0t}) \right\rangle_{B_{0t}=0} \\
&\quad + \frac{\partial}{\partial B_{0t}} \left\langle \Phi^{DF}(B_{0t}) \left| \frac{8}{3} \pi \beta \sum_i \delta(\mathbf{r}_{ni}) \sigma_u \right| \Phi^{DF}(B_{0t}) \right\rangle_{B_{0t}=0} \\
&\quad + \frac{\partial}{\partial B_{0t}} \left\langle \Phi^{DF}(B_{0t}) \left| \frac{1}{c} \beta \sum_i \frac{3(r_{ni})_u (\boldsymbol{\sigma} \cdot \mathbf{r}_{ni}) - \sigma_u r_{ni}^2}{r_{ni}^5} \right| \Phi^{DF}(B_{0t}) \right\rangle_{B_{0t}=0},
\end{aligned}
\tag{2}
$$

where σ is the Pauli matrix, and β is a 4×4 matrix defined as,

$$
\beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix},
\tag{3}
$$

and I is a 2×2 unit matrix. The first and second terms in Eq. (2) are spin-independent, and the third and fourth terms spin-dependent. Eq. (2) is formally equivalent to Eq. (1), though a non-zero deviation occurs when we use finite basis function expansion. If this deviation is small enough, we can use Eq. (2) as a useful analysis method. The four terms in Eq. (2) are quite similar to the lowest-order (c^{-2}) terms in the traditional QR theories [8], namely diamagnetic term, paramagnetic term, Fermi-contact (FC) term, and spin–dipolar (SD) term. We have reported that, for light elements, these four terms in Eq. (2) numerically parallel to those of the QR theory [18].

As seen from the form of β, Eq. (2) is divided into large- and small-component contributions, corresponding to the fact that the four-component DF wavefunction consists of the so-called large- and small-components. On the other hand, in Eq. (1), the cross-coupling term between large and small components is essential.

The derivative operators $\partial/\partial B_{0t}$ in Eqs. (1) and (2) are approximated by the finite perturbation method in the present calculations. The magnetic shielding constants are averaged over all directions of given molecular axes, x, y, and z.

The detailed formulation for the QR theory of the magnetic shielding constants used here will be published elsewhere in near future [29].

2.3. Basis sets and molecular geometries

The Gaussian basis sets used for large-component wavefunctions in our calculations are as follows.

O	(13s 8p 2d)
S	(15s 10p 2d)
Se	(26s 20p 15d)
Te	(28s 23p 17d)
H	(6s 3p)

We used these primitive functions without contraction. For Te and Se, they are the Huzinaga's well-tempered sets [30], whose exponent ranges of s-orbitals are $104930899.977 - 0.0416$ for Te, and $97106338.742 - 0.0580$ for Se. These ranges of exponents are wide enough in comparison with the universal Gaussian basis sets proposed for carrying

Table 1
Calculated and experimental proton magnetic shielding constants in XH_2 (X = O, S, Se, and Te) and their analysis (ppm)

Molecule	Dirac–Fock[a]							
	σ^{DF}	σ (dia)	σ (para)	σ (FC)	σ (SD)	σ^{GD}	Δ	Exptl.
OH_2	29.66	21.24	8.28	0.07	0.01	29.60	−0.06	30.05
SH_2	30.24	20.82	8.89	0.42	0.07	30.20	−0.04	31.26
SeH_2	31.68	20.41	8.79	2.18	0.10	31.48	−0.20	32.81
TeH_2	34.52	20.42	8.39	5.61	0.22	34.64	−0.12	

Molecule	Douglas–Kroll quasi-relativistic GUHF[b]					
	σ (dia)	σ (para)	σ (FC)	σ (SD)	σ^{DK}	Exptl.
OH_2	21.22	8.28	0.08	0.01	29.59	30.05
SH_2	20.82	8.89	0.62	0.03	30.37	31.26
SeH_2	20.42	8.78	3.24	0.13	32.58	32.81
TeH_2	20.40	8.36	8.74	0.33	37.84	

Molecule	Non-relativistic RHF[c]			
	σ (dia)	σ (para)	σ^{NR}	Exptl.
OH_2	21.23	8.28	29.51	30.05
SH_2	20.83	8.89	29.72	31.26
SeH_2	20.48	8.77	29.26	32.81
TeH_2	20.60	8.42	29.02	

[a] σ^{DF} and σ^{GD} are defined by Eqs. (1) and (2), respectively, and $\sigma^{GD} = \sigma(\text{dia}) + \sigma(\text{para}) + \sigma(\text{FC}) + \sigma(\text{SD})$. Δ is defined as $\Delta = \sigma^{GD} - \sigma^{DF}$.
[b] $\sigma^{DK} = \sigma(\text{dia}) + \sigma(\text{para}) + \sigma(\text{FC}) + \sigma(\text{SD})$.
[c] $\sigma^{NR} = \sigma(\text{dia}) + \sigma(\text{para})$.

out accurate matrix DF calculations [31]. The basis sets for O and S are taken from Huzinaga et al. [32], and for H from Huzinaga and Klobukowski [33]. Two polarization d-functions are added for O [32], and three p-functions whose exponents are taken from the outer three of (6s) are added for H.

For the basis sets used for small-component wavefunctions, the kinetically balanced basis functions $\{\nabla\chi\}$ were used, which are generated from the large-component basis functions $\{\chi\}$.

The XH distances and the HXH angles (X = O, S, Se, and Te) are taken from Ref. [20]. The molecular symmetry is C_{2v} in all molecules. The gauge origin of the external magnetic field is commonly located on the X atom (X = O, S, Se, and Te) for both $\sigma(H)$ and $\sigma(X)$.

3. Results and discussions

3.1. Proton magnetic shielding constants

Table 1 shows the results of the proton magnetic shielding constants $\sigma(H)$ in XH_2 (X = O, S, Se, and Te). The proton magnetic shielding constants calculated by both the DF method (σ^{DF}) and the QR

method (σ^{QR}) agree well with the experimental ones, while those calculated by the non-relativistic restricted Hartree–Fock (RHF) method do not show correct trend. The diamagnetic and paramagnetic terms are almost constant, and the SD terms are commonly small in all methods, and therefore only the FC term is the origin of the proton chemical shifts of XH_2 (X = O, S, Se, and Te).

The differences (Δ) between σ^{DF} and σ^{GD}, which are defined by Eqs. (1) and (2), respectively, are smaller than 0.2 ppm for all molecules (see Table 1). These Δ values are negligibly small in comparison with the proton chemical shifts, suggesting that this decomposition analysis is quantitatively reliable.

The DF method and the QR method give fairly close results for the paramagnetic term, the diamagnetic term, and the SD term. Only the FC terms of σ^{QR} are larger by a few ppm than those of σ^{DF} in SeH_2 and TeH_2, and this deviation is not negligible in terms of the ^fH chemical shifts of XH_2 (X = O, S, Se, and Te).

3.2. Magnetic shielding constants of heavy elements

Table 2 shows the results of the X magnetic shielding constants $\sigma(X)$ in XH_2 (X = O, S, Se, and

Table 2
Calculated and experimental magnetic shielding constants of X in XH_2 (X = O, S, Se, and Te) and their analysis (ppm)
For (a), (b), and (c), see footnotes of Table 1

Molecule	Dirac–Fock[a]							
	σ^{DF}	σ(dia)	σ(para)	σ(FC)	σ(SD)	σ^{GD}	Δ	Exptl.
OH_2	329.7	416.1	−90.2	4.3	−0.5	329.7	0.0	324
SH_2	750.0	1066.1	−348.8	36.8	−4.4	749.4	−0.6	726
SeH_2	2422.0	3021.7	−1028.2	520.6	−97.4	2416.7	−5.3	2401
TeH_2	4769.4	5420.9	−2800.0	2870.4	−753.7	4737.6	−31.8	4954

Molecule	Douglas–Kroll quasi-relativistic GUHF[b]					
	σ(dia)	σ(para)	σ(FC)	σ(SD)	σ^{DK}	Exptl.
OH_2	414.4	−88.7	6.1	0.0	331.8	324
SH_2	1053.1	−338.2	46.6	0.1	761.6	726
SeH_2	2917.4	−859.0	483.1	0.7	2542.2	2401
TeH_2	5098.9	−1738.3	1886.1	12.7	5259.4	4954

Molecule	Non-relativistic RHF[c]			
	σ(dia)	σ(para)	σ^{NR}	Exptl.
OH_2	416.0	−88.8	327.2	324
SH_2	1065.1	−337.3	728.8	726
SeH_2	3011.5	−844.9	2166.6	2401
TeH_2	5373.2	−1650.4	3722.8	4954

Te). The total $\sigma(X)$ values are plotted in Fig. 1 to visualize the overall trends of the calculated and experimental values. The experimental $\sigma(X)$ values are excellently reproduced by the DF method, suggesting that the present method is valid for the third- and fourth-row elements of the periodic table. The DK method also gives reasonable results, though it slightly overestimates the shieldings of Se and Te. We note here that the magnetic shielding operator generated from the DK transformation [29] is different from those in the traditional NR and QR methods, while the magnetic shielding operator in the traditional QR method is the same as the large-component operator in the Gordon decomposition. This difference in the operator may cause a small numerical deviation between the DK method and the other methods even for light elements.

As seen from Fig. 1, with going down on the periodic table as $X = O \rightarrow S \rightarrow Se \rightarrow Te$, the $\sigma(X)$ values increase dramatically in all present methods, though the non-relativistic RHF method underesti-
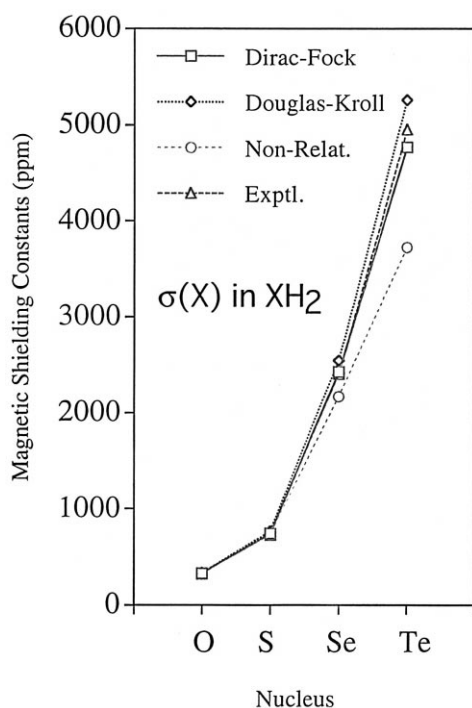

Fig. 1. Magnetic shielding constants of X in XH_2 ($X = O$, S, Se, and Te) calculated by the relativistic DF method, the quasi-relativistic DK method, and the non-relativistic RHF method, and experimentally proposed values.

mates significantly the experiments in SeH_2 and TeH_2. We note here that some of the experimental values in Table 2 are the sum of the observed spin rotation data and the calculated diamagnetic terms with relativistic corrections, and therefore they may have a small deviation from the real magnetic shielding constants. For detailed comments on the experimental values (see Vaara et al. [20] and the references cited therein). The calculated values of $\sigma(Te)$ were reported to be 3496.60 and 3676.86 ppm by the SCF and CAS methods, respectively, considering the higher-order SO contributions [20]. These values are about 1000 ppm smaller than those by the present DF and QR methods, and we guess that this underestimation is due to the lack of the SFR terms. It is true that the SO effect significantly couples with the SFR effect in heavy elements [15].

As shown in Table 2, the deviation Δ between σ^{DF} and σ^{GD} is 0.0–31.8 ppm, the maximum being for TeH_2. Since these Δ values are negligibly small in comparison with the absolute values of $\sigma(X)$ and their shifts, the Gordon decomposition is a meaningful analysis method even for the heavy elements, like Se and Te. The $\sigma(para)$ is much modified by the relativistic effect, and the $\sigma(dia)$ which is calculated from the zeroth-order wavefunction is also slightly modified. The FC and the SD terms are apparently different between the DF and QR methods; however, these deviations may be due to the difference in the definition of the FC and SD operators in the DF and QR methods, as mentioned above. When we define the spin-dependent term as $\sigma(FC) + \sigma(SD)$, this term is not so different between the DF and QR methods. For examples, in TeH_2, $\sigma(FC) + \sigma(SD) = 2116.7$ ppm by the DF method and 1898.8 ppm by the QR method. On the other hand, when we define the spin-independent term as $\sigma(dia) + \sigma(para)$, the differences between the DF and QR methods are significantly large, and they directly contribute to the differences of the total $\sigma(X)$. It is remarkable that the differences between the calculated values by the DF and QR methods appear mainly in the spin-independent term, and not in the spin-dependent term, in $\sigma(Te)$.

3.3. Large- and small-component contributions

As describe in the Section 2, the Gordon-decomposed magnetic shielding constants are divided into

Table 3

Large- and small-component contributions[a] to the ^{1}H and X magnetic shielding constants in XH_2 (X = O and Te) (ppm)[b]

Molecule component	Gordon decomposition				σ^{GD}	Exptl.
	σ(dia)	σ(para)	σ(FC)	σ(SD)		
Proton magnetic shielding constant						
OH$_2$						
Large	21.24	8.28	0.07	0.01	29.67	
Small	0.00	0.00	0.00	0.00	0.00	
Total	21.24	8.28	0.07	0.01	29.67	30.05
TeH$_2$						
Large	20.42	8.39	5.61	0.22	34.64	
Small	0.00	0.00	0.00	0.00	0.00	
Total	20.42	8.39	5.61	0.22	34.64	–
O and Te magnetic shielding constant						
OH$_2$						
Large	416.3	−89.3	4.2	0.0	331.2	
Small	−0.2	−0.9	0.1	−0.5	−1.5	
Total	416.1	−90.2	4.3	−0.53	29.7	324
TeH$_2$						
Large	5533.6	−1853.7	2799.5	6.6	6486.0	
Small	−112.7	−946.3	70.9	−760.3	−1748.4	
Total	5420.9	−2800.0	2870.4	−753.7	4737.6	4954

[a] Large- and small-component contributions are explained in Section 2.
[b] σ^{GD} is defined by Eq. (2), and $\sigma^{GD} = \sigma$(dia) + σ(para) + σ(FC) + σ(SD).

the large-component contribution and the small-component one, and these contributions are listed in Table 3. Roughly speaking, the small component is 'smaller' than the large-component by a factor of $(\hat{p} - (e/c)A)/2mc \approx v/2c$, where v is speed of electron, and therefore the small-component contribution to the magnetic shielding is smaller by a factor of roughly $(v/2c)^{-2}$ than the large-component one, in light elements.

For the proton magnetic shielding constants, the small-component contribution is quite small in both OH$_2$ and TeH$_2$, and only the large-component contributions determine the total values. On the other hand, in the X magnetic shielding constants σ(X) in XH$_2$, the situation is different. Although the small-component contributions are negligibly small in OH$_2$ as expected from the above order estimation, they are significantly large in TeH$_2$. In particular, the small-component contributions are quite large in the paramagnetic term and the SD term. This suggests that the higher-order relativistic terms in the QR theories are not so small, and the decoupling of a four-component Hamiltonian into a two-component one is not completely well done by the second-order

DK method, when it is applied to extremely heavy elements like Te. All the small-component terms except for the FC term have negative contribution to the total magnetic shielding constant of TeH$_2$. This is a reason why σ(Te) by the DF method is smaller than that by the QR method.

4. Concluding remarks

The magnetic shielding constants σ(X) and σ(H) in XH$_2$ (X = O, S, Se, and Te) are calculated by the DF method based on the no-pair DC Hamiltonian incorporated into the finite perturbation method. These results are compared with those calculated by the QR method. The present results may be summarized as follows.

1. The present method is valid for calculations of the magnetic shielding constants of heavy elements up to Te. The calculated results reproduce fairly well the experimental values.
2. The origin of the proton chemical shifts in XH$_2$ (X = O, S, Se, and Te) is essentially the FC term.

3. The X magnetic shielding constants, $\sigma(X)$, calculated by the DF method and the QR method are quite similar in OH_2 and SH_2, while the ones calculated by the QR method significantly overestimates in TeH_2.

4. The diamagnetic and paramagnetic terms of the DF method are significantly different from those of the QR method especially in TeH_2, while the spin-dependent contribution (sum of FC and SD terms) is similar.

5. The small-component contributions to $\sigma(Te)$ are quite large especially in the paramagnetic term, and this fact may be an evidence of break-down of the QR method when it is applied to really heavy elements.

Acknowledgements

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