

Spin-orbit effect on the magnetic shielding constant using the ab initio UHF method

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Abstract

A calculational method is proposed for the spin-orbit effect on the magnetic shielding constant using ab initio UHF wavefunctions and the finite perturbation method. The method is applied to the ¹H and ¹³C magnetic shielding constants of hydrogen halides and methyl halides, respectively. When the spin-orbit effect is included, the results are in good agreement with experiment, showing the importance of the spin-orbit effect on the chemical shifts of the molecules containing heavier halogen atoms. The dominant contribution is due to the Fermi contact interaction.

1. Introduction

Ab initio calculations of NMR chemical shifts have become quite popular and reproduce well the experimental values, making possible theoretical assignments [1] and clarification of the electronic mechanisms of the metal chemical shifts [2]. However, the relativistic effect, especially the spin-orbit effect, on the magnetic shielding constant has not been fully investigated despite of its expected great importance.

The relativistic theory of the chemical shift has been formulated by Pyper [3], Pyykkö [4], Zhang and Webb [5], but no relativistic ab initio calculations have been carried out except for the one-electron molecule, H₂⁺ [6], though some calculations were reported by the relativistically parameterized extended Hückel method and the second-order perturbation theory [7]. Other calculations of the magnetic shielding constants containing the spin-orbit interaction are the proton

shielding constants in hydrogen halides [8,9] and the carbon shielding constants in methyl halides [10], both of which have been calculated by the nonrelativistic semiempirical method combined with the third-order perturbation theory. Malin et al. have calculated the proton shielding constants of hydrogen halides by the sum-over-states density functional perturbation (SOS-DFT) method [11].

In this Letter, we propose a calculational method of the spin-orbit effect on the magnetic shielding constant using an ab initio UHF wavefunction and the finite perturbation method [12]. The calculations are performed for the proton and carbon magnetic shielding constants in hydrogen halides and methyl halides, respectively.

2. Theory

The total Hamiltonian for a molecule in an external magnetic field including the spin-orbit interaction [8,10,13] is written as

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$$H = \frac{1}{2} \sum_j \left(\mathbf{P}_j + \frac{1}{c} \mathbf{A}(\mathbf{r}_j) \right)^2 + \sum_{j>k} \frac{1}{r_{jk}} - \sum_N \sum_j \frac{Z_N}{r_{Nj}} + H_{\text{so}} + \frac{1}{c} \sum_j \mathbf{S}_j \cdot [\nabla_j \times \mathbf{A}(\mathbf{r}_j)], \quad (1)$$

where the vector potential $\mathbf{A}(\mathbf{r}_j)$ for an electron j and the spin-orbit interaction operator H_{so} , which consists of the one- and two-electron terms, are given by

$$\mathbf{A}(\mathbf{r}_j) = \frac{1}{2} \mathbf{H} \times (\mathbf{r}_j - \mathbf{d}) + \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_{Nj}}{r_{Nj}^3}, \quad (2a)$$

$$H_{\text{so}} = \frac{1}{2c^2} \sum_N \sum_j Z_N \frac{\mathbf{L}_{Nj} \cdot \mathbf{S}_j}{r_{Nj}^3} - \frac{1}{2c^2} \sum_j \sum_{i \neq j} \frac{\mathbf{L}_{ij} \cdot \mathbf{S}_j + 2\mathbf{L}_{ji} \cdot \mathbf{S}_j}{r_{ij}^3}. \quad (2b)$$

Here, \mathbf{H} denotes the external magnetic field, \mathbf{d} the gauge origin, $\boldsymbol{\mu}_N$ the nuclear magnetic moment, and \mathbf{L} and \mathbf{S} the orbital and spin angular momentum operators, respectively. Expanding the total Hamiltonian in powers of \mathbf{H} and $\boldsymbol{\mu}_N$, we get

$$H = H^{(0,0)} + \sum_t H_t H_t^{(1,0)} + \sum_N \sum_t \boldsymbol{\mu}_{Nt} H_{Nt}^{(0,1)} + \sum_N \sum_t \sum_u \boldsymbol{\mu}_{Nt} H_{Ntu}^{(1,1)} H_u \dots, \quad (3)$$

where t and u denote x , y and z axes, and

$$H^{(0,0)} = \frac{1}{2} \sum_j \mathbf{P}_j^2 + \sum_{j>k} \frac{1}{r_{jk}} - \sum_N \sum_j \frac{Z_N}{r_{Nj}} + H_{\text{so}}, \quad (4a)$$

$$H_t^{(1,0)} = \frac{1}{2c} \sum_j (\mathbf{r}_j \times \mathbf{P}_j)_t + \frac{1}{c} \sum_j S_{jt}, \quad (4b)$$

$$H_{Nt}^{(0,1)} = \frac{1}{c} \sum_j \frac{(\mathbf{r}_{Nj} \times \mathbf{P}_j)_t}{r_{Nj}^3} + \frac{1}{c} \sum_j \left(\frac{3r_{Njt}(\mathbf{S}_j \cdot \mathbf{r}_{Nj}) - S_{jt} r_{Nj}^2}{r_{Nj}^5} + \frac{8}{3} \pi \delta(\mathbf{r}_{Nj}) S_{jt} \right) = H_{Nt}^{(0,1)}(\text{para}) + H_{Nt}^{(0,1)}(\text{SD}) + H_{Nt}^{(0,1)}(\text{FC}), \quad (4c)$$

$$H_{Ntu}^{(1,1)} = \frac{1}{2c^2} \sum_j \frac{\mathbf{r}_j \cdot \mathbf{r}_{Nj} \delta_{tu} - r_{jt} r_{Nju}}{r_{Nj}^3}. \quad (4d)$$

In the presence of the spin-orbit interaction, we describe the magnetic shielding constant as the sum of the diamagnetic term, paramagnetic term, spin-dipolar term and Fermi contact term,

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}} + \sigma^{\text{LS}}(\text{SD}) + \sigma^{\text{LS}}(\text{FC}), \quad (5)$$

and each term is given by

$$\sigma_{Ntu}^{\text{dia}} = \langle \Psi(0) | H_{Ntu}^{(1,1)} | \Psi(0) \rangle, \quad (6a)$$

$$\sigma_{Ntu}^{\text{para}} = \frac{\partial}{\partial H_u} [\langle \Psi(H_u) | H_{Nt}^{(0,1)}(\text{para}) | \Psi(H_u) \rangle]_{H=0}, \quad (6b)$$

$$\sigma_{Ntu}^{\text{LS}}(\text{SD}) = \frac{\partial}{\partial H_u} [\langle \Psi(H_u) | H_{Nt}^{(0,1)}(\text{SD}) | \Psi(H_u) \rangle]_{H=0}, \quad (6c)$$

$$\sigma_{Ntu}^{\text{LS}}(\text{FC}) = \frac{\partial}{\partial H_u} [\langle \Psi(H_u) | H_{Nt}^{(0,1)}(\text{FC}) | \Psi(H_u) \rangle]_{H=0}, \quad (6d)$$

where the wavefunctions $\Psi(0)$ and $\Psi(H_t)$ are defined by

$$H^{(0,0)} | \Psi(0) \rangle = E | \Psi(0) \rangle, \quad (7a)$$

$$(H^{(0,0)} + H_t H_t^{(1,0)}) | \Psi(H_t) \rangle = E(H_t) | \Psi(H_t) \rangle. \quad (7b)$$

Note that the diamagnetic and paramagnetic terms considered here are not exactly the same as those defined without the spin-orbit interaction [2]; see $H^{(0,0)}$ and $H^{(1,0)}$ given by Eqs. (4a) and (4b). The spin-dipolar term and the Fermi contact term are the new terms.

We study the effect of the spin-orbit interaction on the magnetic shielding constant *to first-order* in the perturbation. The wavefunctions $\Psi(0)$ and $\Psi(H_t)$ in Eqs. (7a) and (7b) may be expressed by the sum of the singlet and triplet functions because the Hamiltonians $H^{(0,0)}$ and $H^{(1,0)}$ include spin-dependent operators as expressed by Eqs. (4a) and (4b):

$$\Psi(0) = \sum C(0)^{\text{S}} \Psi(0)^{\text{S}} + \sum C(0)_x^{\text{T}} \Psi(0)_x^{\text{T}} + \sum C(0)_y^{\text{T}} \Psi(0)_y^{\text{T}} + \sum C(0)_z^{\text{T}} \Psi(0)_z^{\text{T}}, \quad (8a)$$

$$\Psi(H_t) = \sum C(H_t)^{\text{S}} \Psi(H_t)^{\text{S}} + \sum C(H_t)_x^{\text{T}} \Psi(H_t)_x^{\text{T}} + \sum C(H_t)_y^{\text{T}} \Psi(H_t)_y^{\text{T}} + \sum C(H_t)_z^{\text{T}} \Psi(H_t)_z^{\text{T}}. \quad (8b)$$

Here Ψ^{S} denote singlet functions, Ψ_x^{T} , Ψ_y^{T} and Ψ_z^{T} triplet functions in x , y and z components, C their coefficients, and the sum runs all over the states. The x , y and z components of the triplet functions are used instead of the $+1$, -1 and 0 components. In Table 1

Table 1
Matrix elements of the spin-linear operator between singlet and triplet wavefunctions

Operator	$\langle \Psi^S \text{Op} \Psi_x^T \rangle$	$\langle \Psi^S \text{Op} \Psi_y^T \rangle$	$\langle \Psi^S \text{Op} \Psi_z^T \rangle$
$\sum_j f_{jx} S_{jx}$	$\langle \Psi^S \sum_j f_{jx} S_{jx} \Psi_x^T \rangle$	0	0
$\sum_j f_{jy} S_{jy}$	0	$\langle \Psi^S \sum_j f_{jy} S_{jy} \Psi_y^T \rangle$	0
$\sum_j f_{jz} S_{jz}$	0	0	$\langle \Psi^S \sum_j f_{jz} S_{jz} \Psi_z^T \rangle$

$\text{Op} = \sum_j f_j \cdot S_j = \sum_j (f_{jx} S_{jx} + f_{jy} S_{jy} + f_{jz} S_{jz})$. Ψ_x^T , Ψ_y^T and Ψ_z^T are obtained by unitary transformation of the triplet $m_s = 1, 0$ and -1 states.

we show the matrix elements of the spin-linear operators between singlet and triplet functions. It is diagonal in the x , y and z representation.

We use the finite-field perturbation method to calculate the wavefunction under the influence of the external magnetic field. We propose to use the UHF method, just as in calculations of the nuclear spin-spin coupling constant [14], because of the easiness of the calculations. It is complex and spin-polarized because of the angular momentum operators and the spin-dependent operators included in the magnetic and spin-orbit terms. We include here only the one-electron term of the spin-orbit interaction. The UHF wavefunction for closed-shell molecules can be expressed in the form of the limited configuration interaction [15] and to first order it is written as

$$\Psi^{\text{UHF}} = C^{\text{RHF}} \Psi^{\text{RHF}} + \sum C_z^T \Psi_z^T, \quad (9)$$

where Ψ^{RHF} denotes the RHF configuration. The UHF wavefunction is an eigenfunction of S_z and satisfies the relation $S_z | \Psi^{\text{UHF}} \rangle = 0$ for closed-shell molecules: it includes only the triplet $m_s = 0$ component, Ψ_z^T , and the other x and y components of Eqs. (8a) and (8b) are not included.

For calculating the diagonal and off-diagonal elements of the magnetic shielding tensors, we need all the terms in Eq. (8). The term $\sum C(0)_t^T \Psi(0)_t^T$ ($t = x, y$ or z) for zero magnetic field is obtained by calculating the UHF wavefunction in the t direction by considering only the t component of the spin-orbit interaction operator. It is the eigenfunction of the S_t operator and is written as

$$\Psi(0)_x^{\text{UHF}} = C(0)_x^{\text{RHF}} \Psi(0)^{\text{RHF}} + \sum C(0)_x^T \Psi(0)_x^T, \quad (10a)$$

$$\Psi(0)_y^{\text{UHF}} = C(0)_y^{\text{RHF}} \Psi(0)^{\text{RHF}} + \sum C(0)_y^T \Psi(0)_y^T, \quad (10b)$$

$$\Psi(0)_z^{\text{UHF}} = C(0)_z^{\text{RHF}} \Psi(0)^{\text{RHF}} + \sum C(0)_z^T \Psi(0)_z^T. \quad (10c)$$

Since the spin-orbit matrix elements are diagonal in the sense of Table 1, the terms $\sum C(0)_t^T \Psi(0)_t^T$ etc. in Eqs. (10a)–(10c) are exactly the same as the corresponding terms of Eq. (8a) to first order in the spin-orbit perturbation.

In the magnetic field, we first apply the magnetic field in the same direction as the spin-orbit component and calculate the UHF wavefunction for *each* direction:

$$\begin{aligned} \Psi(H_x)_x^{\text{UHF}} \\ = C(H_x)^{\text{RHF}} \Psi(H_x)^{\text{RHF}} + \sum C(H_x)_x^T \Psi(H_x)_x^T, \end{aligned} \quad (11a)$$

$$\begin{aligned} \Psi(H_y)_y^{\text{UHF}} \\ = C(H_y)^{\text{RHF}} \Psi(H_y)^{\text{RHF}} + \sum C(H_y)_y^T \Psi(H_y)_y^T, \end{aligned} \quad (11b)$$

$$\begin{aligned} \Psi(H_z)_z^{\text{UHF}} \\ = C(H_z)^{\text{RHF}} \Psi(H_z)^{\text{RHF}} + \sum C(H_z)_z^T \Psi(H_z)_z^T. \end{aligned} \quad (11c)$$

The term $\sum C(H_t)_t^T \Psi(H_t)_t^T$ is actually the same as the term $\sum C(0)_t^T \Psi(0)_t^T$ in Eq. (10) if we neglect the effect of the magnetic field on the spin-orbit interaction, because the spin-dependent operator in Eq. (4b) (spin-Zeeman term) gives the eigenvalue zero for closed-shell molecules. From the six UHF wavefunctions corresponding to Eqs. (10) and (11), we calculate the diagonal elements of the diamagnetic, paramagnetic, and Fermi contact terms (see Eq. (15a) below). Note that the UHF wavefunctions themselves are used without expanding them in the form of Eqs. (10) and (11).

When we calculate the off-diagonal terms of the magnetic shielding tensors, we further need the other six terms $\sum C(H_t)_u^T \Psi(H_t)_u^T$ ($t \neq u$) in Eq. (8b). This

is true even for the diagonal element of the spin–dipolar term σ_{Nu}^{LS} (SD), since the spin–dipolar Hamiltonian includes the operator $S \cdot r$. Similarly to Eq. (11), we may perform the UHF calculation for the u component of the spin–orbit interaction and for the t component of the magnetic field,

$$\begin{aligned} \Psi(H_t)_u^{\text{UHF}} &= C(H_t)^{\text{RHF}} \Psi(H_t)^{\text{RHF}} + \sum C(H_t)_u^{\text{T}} \Psi(H_t)_u^{\text{T}}. \end{aligned} \quad (12)$$

However, when we neglect the coupling between the magnetic field and the spin–orbit interaction, we have

$$\sum C(H_t)_u^{\text{T}} \Psi(H_t)_u^{\text{T}} = \sum C(0)_u^{\text{T}} \Psi(0)_u^{\text{T}}, \quad (13)$$

so that no new UHF calculation is necessary for obtaining the off-diagonal terms. Thus, we can calculate all the diagonal and off-diagonal terms of the magnetic shielding tensors to first order for the influence of the spin–orbit interaction. Again, it is unnecessary to expand the UHF wavefunctions in the limited CI forms. This is because, for the spin-linear operator,

$$F_t = \sum_j f_t(j) S_t(j) \quad (t=x, y \text{ or } z), \quad (14)$$

the matrix elements in Eqs. (6c) and (6d) are calculated as

$$\langle \Psi(H_u) | F_t | \Psi(H_u) \rangle = \langle \Psi(H_u)_u^{\text{UHF}} | F_u | \Psi(H_u)_u^{\text{UHF}} \rangle \quad (t=u) \quad (15a)$$

$$= 2 \langle \Psi(H_u)_u^{\text{UHF}} | F_t | \Psi(H_t)_t^{\text{UHF}} \rangle \quad (t \neq u) \quad (15b)$$

from the present UHF wavefunction to first order in the perturbation because of the diagonal property of the spin-linear operator as given by Table 1. Note in the calculation of the matrix element given by Eq. (15b) we have to handle two different UHF wavefunctions and so the problem of non-orthogonal orbitals arises, but this can be circumvented by calculating the corresponding orbitals [16] of the two UHF wavefunctions.

In the present formulation of the spin–orbit effect on the magnetic shielding constant, we have used only the spin-linear property, like Eq. (14), of the spin–orbit interaction operator. Therefore, the present usage of the UHF method is valid in general for such perturbation operators. Further, the present method is applicable not only for the one-electron terms of the spin–orbit interaction, but also for the two-electron terms, though the

effect of the latter is described only as an average in the sense of the orbital model.

3. Applications

We calculate here the magnetic shielding constant under the influence of the spin–orbit interaction by using the UHF method as described above. We have

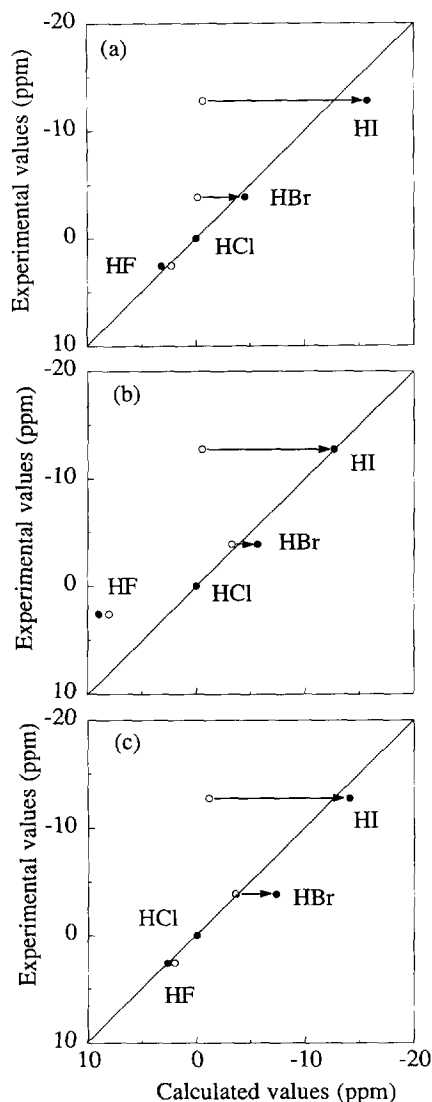


Fig. 1. ^1H chemical shifts in hydrogen halides compared between the experimental values and the calculated ones with and without the spin–orbit (LS) interaction, for (a) the present work, (b) Ref. [8], and (c) Ref. [9]. (○) Without LS; (●) with LS.

considered only the one-electron term of the spin-orbit interaction. Only the diagonal elements of the tensors in the sense of Eq. (15a) are calculated. This is enough for calculating the isotropic terms for the diamagnetic, paramagnetic, and Fermi contact terms. However, the spin-dipolar term calculated here is not perfect, but it should not cause any serious problem since, as shown later, the spin-dipolar term is small and much less important than the Fermi contact term.

3.1. Hydrogen halides

As a first application of our method, we choose the ^1H chemical shifts of the HX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I) compounds because some calculations on the spin-orbit effect have been reported for these molecules [8,9]. The principal axis of the molecule is taken to be the z -axis. The gauge origin is located on the halogen atom. We have shown that the basis set dependence and the gauge-origin dependence of the magnetic shielding constant can be reduced by using the first-order higher angular momentum basis functions (FOBFs) [17,18], and therefore our basis sets are as follows: the Huzinaga double-zeta set [19] plus p-FOBFs with the scale factor 1.2 for hydrogen, and the Huzinaga double-zeta set plus the d-FOBFs for the halogen atom. The bond distances are the same as those in Ref. [8].

We compare in Fig. 1 the proton chemical shifts calculated with and without the spin-orbit effects (LS) to the experimental values [20]: (a) the results of the present work, (b) the results of Morishima, Endo and Yonezawa [8], and (c) the results of Volodicheva and Rebane [9]. The latter two are semiempirical calculations. Chemical shift values are given relative to the HCl molecule.

In Fig. 1, our calculated chemical shifts including LS agree well with the experimental values: the spin-orbit effects are significant for HBr and HI . On the other hand, HF is not good in Fig. 1b and HBr is not good in Fig. 1c due to the semiempirical character of the calculations. Our results with and without LS are both quite similar to those of Malkin and co-workers obtained by the SOS-DFT [11].

Our more detailed results are summarized in Table 2, which lists the proton magnetic shielding constants with and without LS together with the experimental chemical shifts. In any molecules, almost all contributions of the spin-orbit effect come from the Fermi contact interaction. In particular, $\sigma^{LS}(\text{FC})$ in HI is about one-third of the total magnetic shielding constant. It is also seen that the spin-orbit effect hardly affects the diamagnetic and paramagnetic contributions, when it is defined separately as in Eq. (6).

Without the spin-orbit interaction, the halogen p_x and p_y orbitals do not mix with the halogen and proton s orbitals because of the symmetry of the molecule. However, when we include the spin-orbit interactions in the x and y directions, these s orbitals slightly mix with the halogen p_x and p_y orbitals in the $\text{UHF}(x)$ and $\text{UHF}(y)$ calculations (see Eq. (10)). In the HI molecule, the mixing ratio is of the order of 10^{-2} . This induces the Fermi contact interaction.

3.2. Methyl halides

We have applied the present method to the ^{13}C chemical shift in CH_3X ($\text{X} = \text{H}, \text{Cl}, \text{Br}$ and I). The Huzinaga triple-zeta set [19] plus the d-FOBFs [17] are used for carbon. The geometries are taken from Ref. [21]. The shielding constant of CH_4 is gauge-independent because of its T_d symmetry [17,18]. In other mole-

Table 2
Calculated ^1H magnetic shielding constants and the spin-orbit effects in hydrogen halides (ppm)

Compound	Without LS				With LS						δ^{exp}	
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{LS}			σ^{tot}		$\delta^{\text{cal}}(LS)$
							SD	FC	total			
HF	15.89	11.44	27.33	2.43	15.89	11.44	0.02	0.17	0.18	27.52	3.17	2.58
HCl	16.85	12.91	29.76	0	16.85	12.91	0.04	0.88	0.92	30.69	0	0
HBr	16.90	13.00	29.90	-0.14	16.91	13.00	0.18	5.15	5.33	35.24	-4.55	-3.85
HI	17.33	13.07	30.40	-0.64	17.38	13.06	0.40	15.61	16.01	46.45	-15.76	-12.76

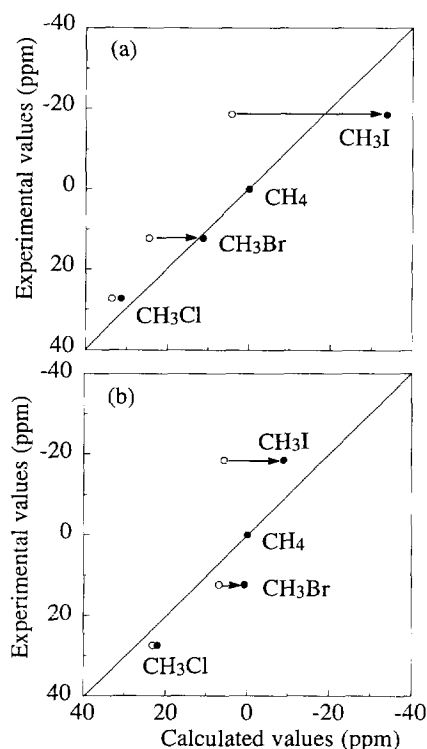


Fig. 2. ^{13}C chemical shifts in methyl halides compared between the experimental values and the calculated ones with and without the spin-orbit (*LS*) interaction, for (a) the present work and (b) Ref. [10]. (○) Without *LS*; (●) with *LS*.

cules, the gauge origin is located on the halogen atom.

We show in Fig. 2 comparisons between the experimental values [22] and the values calculated with and without the spin-orbit effects for (a) the present work and (b) Cheresmin and Schastnev's semiempirical results [10]. Our calculated values show better agreement with experiment than those of Cheresmin and Schastnev. Table 3 shows more detailed results. For

CH_3I , the experimental chemical shift is -18.5 ppm, while our values without and with *LS* are 4.18 and -33.8 ppm, respectively, showing that the spin-orbit effect might be overestimated as in the case of HI . We further see in Table 3 that the Fermi contact interaction is the dominant term, though the spin-dipolar term is larger here than that for hydrogen halides: carbon has *p* orbitals though hydrogen does not. The diamagnetic and paramagnetic terms defined by Eqs. (6a) and (6b) are quite insensitive to the inclusion of the spin-orbit interaction, the largest change being 0.24 ppm for CH_3I .

Our calculated chemical shifts still deviate from the experimental ones. In CH_3I , the theoretical value is 15.30 ppm higher than the experimental one. The reasons are considered to be incompleteness of the basis set, the lack of electron correlation and the two-electron spin-orbit interaction, and so on.

4. Conclusions

We have formulated the spin-orbit effect on the magnetic shielding constant by using the ab initio UHF method and applied to the ^1H chemical shift in the hydrogen halides and the ^{13}C chemical shift in the methyl halides. Our results are in good agreement with experiment and at the same time demonstrate the importance of the spin-orbit effect in the chemical shift of molecules containing heavier halogen atoms. The Fermi contact interaction is the dominant term in the spin-orbit effect.

We have reported Ga and In chemical shifts in the tetrahalide complexes [23], and pointed out the possible importance of the spin-orbit effect.

Table 3

Calculated ^{13}C magnetic shielding constants and the spin-orbit effects in methyl halides (ppm)

Compound	Without <i>LS</i>				With <i>LS</i>						δ^{exp}	
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{LS}			σ^{tot}		$\delta^{\text{cal}}(\text{LS})$
							SD	FC	total			
CH_4	296.46	-99.85	196.61	0	296.46	-99.85	-0.01	-0.03	-0.04	196.57	0	0
CH_3Cl	300.69	-137.68	163.01	33.60	300.69	-137.68	-0.13	2.64	2.51	165.53	31.31	27.4
CH_3Br	301.51	-129.44	172.07	24.53	301.51	-129.39	-0.98	14.08	13.10	185.22	11.35	12.3
CH_3I	302.80	-110.37	192.43	4.18	302.81	-110.13	-3.71	41.40	37.69	230.37	-33.80	-18.5

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