Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 408 (2005) 150–156
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Relativistic configuration interaction and coupled cluster methods using four-component spinors: Magnetic shielding constants of HX and CH_3X (X = F, Cl, Br, I)

Mitsunori Kato [a], Masahiko Hada [a,1], Ryoichi Fukuda [a], Hiroshi Nakatsuji [a,b,*]

[a] *Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-Daigaku-Katsura, Nishikyou-ku, Kyoto 615-8510, Japan*

[b] *Fukui Institute for fundamental Chemistry, Kyoto University, 34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan*

Received 7 January 2005; in final form 3 March 2005
Available online 28 April 2005

Abstract

A correlation method in the relativistic theory using four-component spinors is proposed for the calculations of magnetic shielding constants. The relativistic effects are included by solving Dirac–Fock equation, and the electron-correlation effects are included by the SDCI method and the CCSD method. Some improvement on the integral transformation algorithm and the use of the direct CI method were essential for a performance of this method. It is applied to the calculations of the magnetic shielding constants of hydrogen halides and methyl halides. For hydrogen halides the calculated values excellently reproduce the experimental values to within 0.8 ppm.

1. Introduction

Nuclear magnetic resonance (NMR) is one of the most popular spectroscopic procedures in chemistry and numerous data have been accumulated. It is very sensitive to a change of the chemical environment around the resonant nucleus and reflects an interesting electronic mechanisms of the valence electrons of molecules [1,2]. Since the magnetic shielding constant strongly reflects the valence electron state in the region close to the nucleus, where the electron has high velocity, the relativistic effect is sometimes very important and even dominant in some cases [3]. Therefore, the relativistic theory is essential for the quantitative calculation of the magnetic shielding constant.

Nakatsuji et al. [4] reported in 1995 the first ab initio relativistic calculations of magnetic shielding constants. They adopted the finite-perturbation UHF method and demonstrated that the spin–orbit (SO) interaction, originating from the relativistic theory, is an essential origin of the chemical shifts in the HX and CH_3X (X = F, Cl, Br, I) series. They further carried out a series of calculations for many different molecules and confirmed that the SO interaction is an essential origin of the chemical shifts in many series of molecules [5–7]. They then proposed a method that could take into account the SO term and the spin-free-relativistic (SFR) term simultaneously [8] and showed that both terms were important and strongly coupled in the heavy nuclear systems like mercury compounds [9] and tungsten compounds [10].

Recently, the method has been improved along the line of the Douglas–Kroll–Hess (DKH) theory [11–14] by including the relativistic magnetic interaction operator incorporated into the generalized UHF scheme

* Corresponding author. Fax: +81 75 753 5910/383 2741.
E-mail address: hiroshi@sbchem.kyoto-u.ac.jp (H. Nakatsuji).
[1] Present address: Department of Chemistry, Tokyo Metropolitan University, Minami-osawa 1-1, Hachioji, Tokyo 192-0397, Japan.

0009-2614/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2005.03.147

[15,16]. We have figured out that the effect of the so-called 'picture change' is so important for the Hg chemical shifts in mercury dihalides that it is not able to reproduce the experimental results without this correction [16]. In the framework of the density functional theory, Wolff et al. [17] made use of the zeroth-order regular approximation to incorporate the relativistic effects into the calculations of the NMR shielding of Hg, W, and Pb.

The theory using four-component spinors is necessary to consider the exact relativistic effects. Nakatsuji and coworkers [18,19] calculated the NMR chemical shifts using the Dirac–Fock (DF) theory. The DF calculations showed that the second-order DKH theory slightly breaks down even in moderately heavy elements, such as Te [19]. Quiney et al. [20] used the sum-over-state method in the four-component formalism to calculate the magnetic shielding constants in water. Visscher et al. [21] studied magnetic shielding and spin–spin coupling constants of HX (X = F, Cl, Br, and I) using the relativistic random phase approximation.

In addition to the relativistic effect, the correlation effect is important for precise calculations of magnetic shielding constants. Nakatsuji and coworkers [22] suggested the relativistic coupled cluster (CCSD) theory in the DKH level, and applied to the proton and carbon shielding constants of HX (X = F, Cl, Br, and I), H_2X (X = O, S, Se, and Te), and CH_3X (X = F, Cl, Br, and I). They concluded that the coupling of the relativistic effect and the electron correlation is significant for the compounds including heavy elements. Visscher et al. [23] applied the relativistic CCSD and CCSD(T) theories to some properties of hydrogen halides and examined the relativistic effect by the four-component correlation methods [24].

In this Letter, we describe the relativistic singles and doubles configuration interaction (SDCI) method and the relativistic CCSD method using four-component spinors. The reference function is written with the single determinant that is constructed from the spinors belonging to the so-called 'electron state', because our interest is focused only on electron behaviors. This theory is applied to the calculations of the magnetic shielding constants of hydrogen halides and methyl halides.

2. Theory

Our starting point is the no-pair Dirac–Coulomb–Breit (DCB) Hamiltonian described by Sucher [12] and Mittleman [25]. In the presence of the magnetic vector potential, the effective many-body Hamiltonian is given by

$$H_+^{\mathrm{DCB}}(\mathbf{B}_0) = \sum_i \left[c\alpha \cdot (\mathbf{P}_i + \mathbf{A}_i) + \beta' c^2 + \sum_n V_{\mathrm{n}}(i) \right] + L_+ \left(\frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right) L_+, \tag{1}$$

where c is the speed of light and α and β' are the Dirac matrices. V_{n} is the nuclear attraction term due to the nucleus n. L_+ is the product multiplied n times by $\Lambda_+(i)$, $i = 1, \ldots, n$, which is the projection operator onto the space spanned by the positive-energy eigenfunctions of the matrix DF equation. Throughout this study, atomic units are used. The Breit interaction was not considered here.

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

$$\mathbf{A}_i = \frac{1}{2} \mathbf{B}_0 \times (\mathbf{r}_i - \mathbf{d}) - \frac{1}{c^2} \sum_n \mu_{\mathrm{n}} \times \nabla G_{\mathrm{n}}, \tag{2}$$

where

$$G_{\mathrm{n}} = \int \frac{w_{\mathrm{n}}(R_{\mathrm{n}})}{|\mathbf{r} - \mathbf{R}|} \mathrm{d}\mathbf{R}. \tag{3}$$

Here, the position of the nth nucleus is $\mathbf{N}$ and $R_{\mathrm{n}} = |\mathbf{R} - \mathbf{N}|$. The weight function $w_{\mathrm{n}}(R_{\mathrm{n}})$ of the Gaussian nucleus model is given by

$$w_{\mathrm{n}}(R_{\mathrm{n}}) = \left(\frac{\eta_{\mathrm{n}}}{\pi} \right)^{3/2} \exp\left(-\eta_{\mathrm{n}} R_{\mathrm{n}}^2 \right). \tag{4}$$

The nuclear exponent η_{n} was taken from [26].

Molecular DF spinors are obtained from the Dirac–Fock equation

$$\left[c\alpha \cdot \mathbf{P} + \beta' c^2 + \sum_n V_{\mathrm{n}} + \frac{1}{2} c B_{0t} \{ (\mathbf{r} - \mathbf{d}) \times \alpha \}_t - \frac{1}{c} \sum_n \mu_{\mathrm{n}t} \{ \nabla G_{\mathrm{n}} \times \alpha \}_t + \mathbf{J} - \mathbf{K} \right] \phi_i^{\mathrm{DF}} = \varepsilon_i \phi_i^{\mathrm{DF}}, \tag{5}$$

where $\mathbf{J}$ and $\mathbf{K}$ are Coulomb and exchange operators, respectively. In Eq. (5), the nuclear magnetic moment term is included explicitly. In the SCF level of calculations, the Hellmann–Feynman theorem is satisfied and utilized, but in this study the calculations are done in the post-SCF levels of SDCI and CCSD, where the Hellmann–Feynman theorem is not satisfied. This is why the perturbation of the nuclear magnetic moment must be considered.

We are interested only in the positive energy solutions of Eq. (5), which is the so-called 'electronic state'. The zero-order wave function in the electron-correlation calculations is approximated by a single Slater determinant of the molecular DF spinors belonging to the 'electronic state'.

For the electron-correlation calculations of relativistic treatment, we used SDCI method and CCSD

method. Since the relativistic effects are already taken into account at the SCF level, the post-SCF method can be similar to the non-relativistic one. But in the case of the relativistic calculation, especially with four-component spinors, the computational cost is so big that its application is limited to a small system. Therefore, we implement direct SDCI algorithm [27] and an efficient integral transformation algorithm, which are written in the following section in some detail.

The magnetic shielding constant $\sigma_{\mathrm{n},tu}$ ($t, u = x, y, z$) is given by Ramsey [28] as

$$\sigma_{\mathrm{n},tu} = \left.\frac{\partial^2 E}{\partial B_{0t}\partial \mu_{\mathrm{n},u}}\right|_{B_{0t}=\mu_{\mathrm{n},u}=0}, \tag{6}$$

where E is the total energy. In this Letter, we calculate the isotropic term given by

$$\sigma_{\mathrm{n}} = \frac{\sigma_{\mathrm{n},xx} + \sigma_{\mathrm{n},yy} + \sigma_{\mathrm{n},zz}}{3}. \tag{7}$$

3. Computational details

The step to transform one-electron and two-electron atomic integrals to molecular ones is costly even in the non-relativistic theory. In the relativistic theory, four-component spinors are used and the cost is bigger than that in the non-relativistic theory. We propose a new efficient scheme of the integral transformation. The number of one-electron integrals is small and its treatment is easy. Therefore, we concentrate on the two-electron integrals. The molecular spinors are designed for the symmetry adapted Kramers' restricted calculation. However, we have to employ the unrestricted DF calculation because magnetic field breaks the Kramers' degeneracy. Thus, we design an efficient scheme of integral transformation for unrestricted four-component spinors.

A scalar basis set consists of linear combinations of primitive cartesian Gaussian basis functions, $g_u^{\mathrm{L}}, g_v^{\mathrm{S}}$, where the superscripts 'L' and 'S' represent large and small components, respectively,

$$g_p^{\mathrm{L}} = \sum_u c_{up}^{\mathrm{L}} g_u^{\mathrm{L}}, \quad g_q^{\mathrm{S}} = \sum_v c_{vq}^{\mathrm{S}} g_v^{\mathrm{S}}. \tag{8}$$

The four-component spinor is constructed with this scalar basis set in the following way:

$$\chi_l^{\mathrm{L}} = \begin{pmatrix} \chi_l^{\mathrm{L}\alpha} \\ \chi_l^{\mathrm{L}\beta} \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \sum_p d_{pl}^{\mathrm{L}\alpha} g_p^{\mathrm{L}} \\ \sum_p d_{pl}^{\mathrm{L}\beta} g_p^{\mathrm{L}} \\ 0 \\ 0 \end{pmatrix}, \quad \chi_s^{\mathrm{S}} = \begin{pmatrix} 0 \\ 0 \\ \chi_s^{\mathrm{S}\alpha} \\ \chi_s^{\mathrm{S}\alpha} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \sum_q d_{ql}^{\mathrm{S}\alpha} g_q^{\mathrm{S}} \\ \sum_q d_{ql}^{\mathrm{S}\beta} g_q^{\mathrm{S}} \end{pmatrix}. \tag{9}$$

The transformation coefficients, $d_{pl}^{\mathrm{L}\alpha}$ and $d_{ql}^{\mathrm{S}\alpha}$, is defined as complex numbers. One-electron and two-electron integrals are calculated and stored using the basis of the form in Eq. (8)

$$\begin{aligned}\left[r^X s^X \| t^Y u^Y\right] &= \int g_r^{X^*}(1) g_s^X(1) r_{12}^{-1} g_t^{Y^*}(2) g_u^Y(2)\,\mathrm{d}\tau \\ &\quad - \int g_r^{X^*}(1) g_u^X(1) r_{12}^{-1} g_t^{Y^*}(2) g_s^Y(2)\,\mathrm{d}\tau, \\ X, Y &= \mathrm{L} \text{ or } \mathrm{S}.\end{aligned} \tag{10}$$

But the molecular spinors are expanded with the basis of the form in Eq. (9)

$$\begin{aligned}|i\rangle &= \sum l C_{li}^{\mathrm{L}} \begin{pmatrix} \chi_l^{\mathrm{L}\alpha} \\ \chi_l^{\mathrm{L}\beta} \\ 0 \\ 0 \end{pmatrix} + \sum_s C_{si}^{\mathrm{S}} \begin{pmatrix} 0 \\ 0 \\ \chi_s^{\mathrm{S}\alpha} \\ \chi_s^{\mathrm{S}\beta} \end{pmatrix} \\ &= \sum_l C_{li}^{\mathrm{L}} \begin{pmatrix} \sum_p d_{pl}^{\mathrm{L}\alpha} g_p^{\mathrm{L}} \\ \sum_p d_{pl}^{\mathrm{L}\beta} g_p^{\mathrm{L}} \\ 0 \\ 0 \end{pmatrix} + \sum_s C_{si}^{\mathrm{S}} \begin{pmatrix} 0 \\ 0 \\ \sum_q d_{ql}^{\mathrm{S}\alpha} g_q^{\mathrm{S}} \\ \sum_q d_{ql}^{\mathrm{S}\beta} g_q^{\mathrm{S}} \end{pmatrix}.\end{aligned} \tag{11}$$

Therefore, a transformation from the form in Eq. (8) to the form in Eq. (9) is needed. The four-component spinors in Eq. (9) are adapted for the point group symmetry. There is no restriction for the coefficients, C in the unrestricted DF calculation. Therefore, the computation scheme is rather straightforward. A simple idea is that four atomic bases are transformed into four spinors at once

$$\begin{aligned}&\left[r^{\mathrm{L}} s^{\mathrm{L}} \| t^{\mathrm{L}} u^{\mathrm{L}}\right] \to \left[R^{\mathrm{L}} S^{\mathrm{L}} \| T^{\mathrm{L}} U^{\mathrm{L}}\right] \\ &= \left[\begin{pmatrix} \chi_r^{\mathrm{L}\alpha^*} \\ \chi_r^{\mathrm{L}\beta^*} \\ 0 \\ 0 \end{pmatrix} \cdot \begin{pmatrix} \chi_s^{\mathrm{L}\alpha} \\ \chi_s^{\mathrm{L}\beta} \\ 0 \\ 0 \end{pmatrix} \middle\| \begin{pmatrix} \chi_t^{\mathrm{L}\alpha^*} \\ \chi_t^{\mathrm{L}\beta^*} \\ 0 \\ 0 \end{pmatrix} \cdot \begin{pmatrix} \chi_u^{\mathrm{L}\alpha} \\ \chi_u^{\mathrm{L}\beta} \\ 0 \\ 0 \end{pmatrix}\right], \ldots,\end{aligned} \tag{12}$$

Generally, the integral transformation can be divided into four stages

$$\begin{aligned}[iS\|TU] &= \sum_r C_{ri}^* [RS\|TU], \\ [ij\|TU] &= \sum_s C_{sj} [iS\|TU], \\ [ij\|kU] &= \sum_t C_{tk}^* [ij\|TU], \\ [ij\|kl] &= \sum_u C_{ul} [ij\|kU].\end{aligned} \tag{13}$$

where i, j, k, l are molecular four-component spinors expressed by Eq. (9). The first step is most costly because the number of $[RS\|TU]$ is the biggest of other integrals

and in addition, four-component spinors are used. Here, we note that the two latter spinors, t and u, are not changed during the first two steps and we implemented so that these spinors are not transformed during the first two steps

$$\begin{aligned}
&\left[r^{\mathrm{L}}s^{\mathrm{L}}\|t^{\mathrm{L}}u^{\mathrm{L}}\right] \rightarrow \left[R^{\mathrm{L}}S^{\mathrm{L}}\|t^{\mathrm{L}}u^{\mathrm{L}}\right], \ldots, \\
&[iS\|tu] = \sum_r C^*_{ri}[RS\|tu], \\
&[ij\|tu] = \sum_s C_{sj}[iS\|tu],
\end{aligned} \tag{14}$$

$$\begin{aligned}
&\left[ij\|t^{\mathrm{L}}u^{\mathrm{L}}\right] \rightarrow \left[ij\|T^{\mathrm{L}}U^{\mathrm{L}}\right], \ldots, \\
&[ij\|kU] = \sum_t C^*_{tk}[ij\|TU], \\
&[ij\|kl] = \sum_u C_{ul}[ij\|kU].
\end{aligned} \tag{15}$$

The number of operations in the first-half transformation is reduced to 1/4 with using Eq. (14) because $|TU]$ includes four elements. The core memory required for the step is also reduced to 1/4. The efficient use of memory further accelerated computations. The CPU time for the integral transformation step was shown in Table 4. The computations with Eq. (14) were approximately six times faster than those with Eq. (13). In the four-component method, the first-half transformation is much more costly than the second-half transformation; therefore, the present scheme has worked very efficiently.

The direct CI method for the relativistic theory was implemented. The direct method diminished the disk I/O of matrix elements which was a bottleneck of CI calculations.

4. Calculation

We calculated the magnetic shielding constants of ^{1}H in HX (X = F, Cl, Br, I) and ^{13}C in CH_3X (X = F, Cl, Br, I). In the calculation of hydrogen halides, uncontracted Csizmadia and coworkers [29] (6s3p), (9s6p), (14s11p5d), and (15s11p6d) sets were used for the large-components of F, Cl, Br, and I, respectively. For the large-component of hydrogen, the uncontracted Huzinaga–Dunning's (4s) plus their first-order basis function (FOBFs) [30] (4p) was used: improving basis functions by adding the FOBFs is a systematic method for reducing the gauge origin dependence. The small-component basis sets were the first derivatives of the large-component basis functions so as to satisfy the condition of 'kinetic balance'. In the calculation of methyl halides, we used the same basis functions for hydrogen. For the large-component of C, F, and Cl, Dunning's cc-pVDZ [31] sets were used, and for the small-component the first derivatives of the large-component basis functions were included. For Br and I, Dyall's [32] sets were used. The molecular geometries used are collected in Table 1, which are taken from [33]. The gauge center was located on the halogen atom.

Table 1
Molecular geometries used in the calculations[a]

X	HX	CH_3X		
	r_{HX}	r_{CX}	r_{CH}	θ_{HCX}
F	0.9175	1.3907	1.0979	108.81
Cl	1.2747	1.7859	1.0944	108.43
Br	1.4141	1.9434	1.0930	107.69
I	1.6046	2.1417	1.0939	107.66

[a] Bond lengths in Å and angles in degrees.

In the calculations of ^{1}H magnetic shielding constants eight occupied electrons were correlated. In the calculations of CH_3F and CH_3Cl, all 18 and 26 electrons, respectively, and in the calculations of CH_3Br and CH_3I, 18 and 24 electrons, respectively, were correlated. The virtual orbitals with energies below 2 hartree were included, except for CH_3F and CH_3Cl for which all virtual orbitals were correlated. The number of active orbitals were then 32 for HF, 32 for HCl, 42 for HBr, 48 for HI, 76 for CH_3F, 76 for CH_3Cl, 44 for CH_3Br, and 44 for CH_3I.

We chose the field strength of μ_n so that the perturbation energies due to the applied B_0 and μ_n come to the same magnitude: we used the field strengths that change the energy around 10^{-6} hartree. The accuracy of the numerical differentiations was confirmed with these field strengths. The field strengths used in this study were then $B_0 = 0.005$, $\mu_n = 50.0$ for HF and HCl, $B_0 = 0.001$, $\mu_n = 10.0$ for HBr, and $B_0 = 0.0005$, $\mu_n = 10.0$ for HI, all in a.u.

5. Results and discussion

5.1. ^{1}H Magnetic shielding constants of HX (X = F, Cl, Br, I)

The calculations of ^{1}H magnetic shielding constants were carried out for HX (X = F, Cl, Br, I) using SDCI and CCSD methods. Table 2 shows the calculated ^{1}H magnetic shielding constants. The calculated values in the quasi-relativistic theory and non-relativistic theory were taken from [22], and the experimental values were taken from [33]. All experimental values are the results of gas-phase NMR measurements with respect to CH_4. The absolute value of CH_4 was estimated by a measurement of the rotational constant of CH_4, and then the NMR chemical shifts of CH_3X were converted into the absolute values with this value.

Fig. 1 shows the relativistic effects on the ^{1}H magnetic shielding constants: the vertical axis is the difference

Table 2
^{1}H magnetic shielding constants of HX (in ppm)

	Non-relativistic[a]		Quasi-relativistic[a]		Relativistic			Experimental[b]
	SCF	MP2	SCF	CCSD	SCF	SDCI	CCSD	
HF	28.83	29.39	29.06	29.87	27.17	28.47	28.53	28.50 ± 0.2[c]
HCl	30.76	30.96	31.88	32.90	30.07	31.12	31.14	31.06
HBr	31.09	31.20	36.87	36.39	34.09	34.19	34.20	34.96
HI	31.77	31.81	48.01	44.29	45.10	44.03	43.92	43.86

[a] Ref. [22].
[b] Ref. [33].
[c] The rovibrational contribution at $T = 300$ K was estimated at -0.52 ppm.

between the experimental and calculated values, and ●, ■, and ▲ represent the results of the non-relativistic, quasi-relativistic, and relativistic methods, respectively. The results of the relativistic method agree somewhat badly with the experimental values in HF and HCl, but agree fairly well in HBr and HI. This behavior is opposite to the behaviors of the non-relativistic and the quasi-relativistic method, which agree better with the experimental values in HF and HCl than in HBr and HI. It is expected that as the atom becomes heavier, the relativistic effect becomes larger, so the result of the relativistic method is most reasonable.

Fig. 2 shows the electron-correlation effects on the ^{1}H magnetic shielding constants: the vertical axis is the difference between the experimental and calculated values, and ▲, ◆, ●, and ■ represent the result of the quasi-relativistic SCF, the quasi-relativistic CCSD, the relativistic SCF, and the relativistic CCSD method, respectively. The relativistic CCSD values obtained in this study reproduce well the experimental values, and the biggest error is only 0.76 ppm in HBr. It is seen from Table 2 that the SDCI method already includes the electron-correlation effects appropriately. The results of the relativistic SCF theory for HF and HCl, which agree somewhat badly, are corrected excellently at the CCSD level in close agreement with the experimental values. This behavior is opposite to the behavior of the quasi-relativistic CCSD method, which disagrees for HF and HCl. It is expected that the electron-correlation effects would also increase as the atom becomes heavier, and so the present study expresses appropriately the coupling between the electron-correlation effects and the relativistic effects.

The relativistic SCF result of the same series using larger basis sets was reported by Visscher et al. [21]. Their results of HBr and HI are around 2 ppm larger than ours. The basis set convergence is not good in the single gauge-origin calculation and the basis set should be systematically improved. We use the FOBF method for improving basis set. The SCF calculation

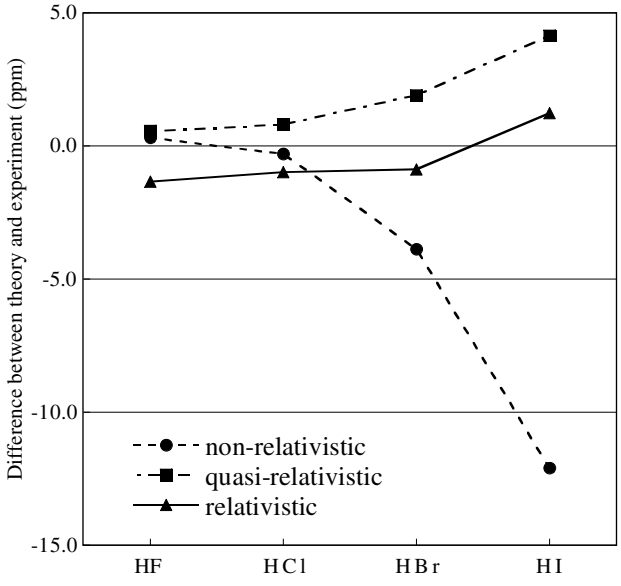

Fig. 1. The difference between theory and experiment for the ^{1}H magnetic shielding constants of HX at the SCF level.

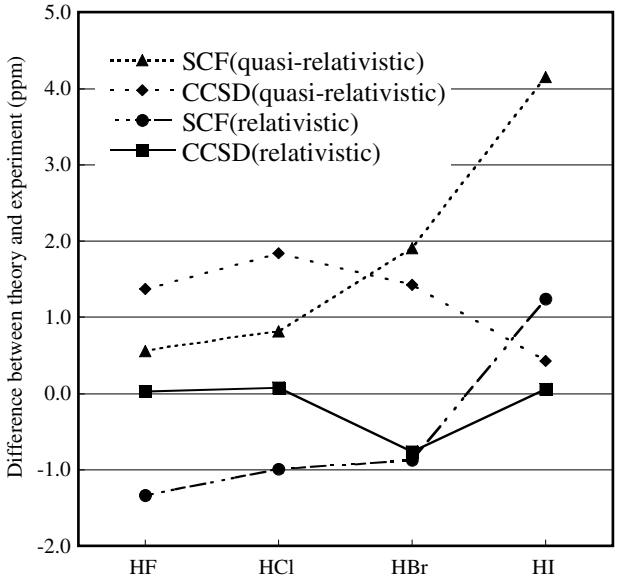

Fig. 2. The differences between theory and experiment for the ^{1}H magnetic shielding constants of HX at the CCSD level.

overestimates the relativistic effect. The coupling between the electron-correlation effect and relativistic effect, which reduces the ^{1}H shielding constants in heavy halides, supports our results and does not contradict with the findings of Visscher et al. [21].

5.2. ^{13}C Magnetic shielding constants of CH_3X ($X = F, Cl, Br, I$)

The calculations of ^{13}C NMR chemical shifts were carried out for CH_3X (X = F, Cl, Br, I) using the SDCI method and the results are summarized in Table 3 together with the experimental value. The reference molecule is CH_3F. All the experimental values except for CH_3F are due to the NMR measurements in neat liquid and that of CH_3F is due to the gas-phase NMR measurement.

The SCF results reproduce the experimental values qualitatively, but the agreement is not satisfactory. Unfortunately, the electron-correlation effect did not improve these results, in particular for CH_3I. We think that the reason of the deviation at the SCF level is the lack of the basis functions, especially tight s-type functions, because in the quasi-relativistic study of the NMR chemical shifts, the Fermi-Contact term was the most important origin [4–10] and the tight s-type functions are necessary to describe the Fermi-Contact term appropriately. The deviation at the SDCI level would also be due to the lack of the basis functions, especially tight p-type functions, because these are necessary to describe the reorganization of the orbitals in the correlation of core electrons. For the CH_3X series, it was severe to include these basis functions up to the SDCI level because of the heavy demands on computers.

Table 3
^{13}C NMR chemical shifts of CH_3X (in ppm)

	Relativistic		Experimental[a]
	SCF	SDCI	
CH_3F	0	0	0
CH_3Cl	−39.34	−43.25	−51.30
CH_3Br	−51.48	−45.41	−66.80
CH_3I	−77.68	−82.62	−98.50

[a] Ref. [33].

Table 4
Computational time for the integral transformation step

	Basis[a]	Active space	CPU time[b] (h)	
			Eq. (13)	Eq. (14)
CH_3F	336	18 × 76	26	4
CH_3Cl	364	26 × 76	67	13
CH_3Br	488	18 × 44	200	32

[a] The number of spinor basis.
[b] COMPAQ XP1000 workstation (2 GB memory).

6. Conclusion

We have performed the relativistic electron-correlation calculations of the magnetic shielding constants and chemical shifts. The relativistic effect is considered at the Dirac–Fock level, and the electron correlation effect is considered at the SDCI and the CCSD levels. An improvement in the integral transformation step and the direct CI algorithm were necessary to perform this calculation. We have applied the method to the calculations of the ^{1}H magnetic shielding constants of HX (X = F, Cl, Br, I) and ^{13}C chemical shifts of CH_3X (X = F, Cl, Br, I). For the HX series, the calculated values reproduced excellently the experimental values: the differences were within 0.8 ppm. For the CH_3X series, the results were not so satisfactory mainly because we could not use large enough basis set for severe demand of the relativistic correlation method on computational facilities.

Acknowledgment

This work has been supported by the Grant for Creative Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] H. Nakatsuji, in: J.A. Tossell (Ed.), Nuclear Magnetic Shieldings and Molecular Structure, NATO ASI Series C-386, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993, p. 263.
[2] H. Nakatsuji, K. Kanda, K. Endo, T. Yonezawa, J. Am. Chem. Soc. 106 (1984) 4653.
[3] P. Pyykkö, Adv. Quantum Chem. 11 (1978) 353.
[4] H. Nakatsuji, H. Takashima, M. Hada, Chem. Phys. Lett. 233 (1995) 95.
[5] H. Takashima, M. Hada, H. Nakatsuji, Chem. Phys. Lett. 235 (1995) 13.
[6] H. Nakatsuji, T. Nakajima, M. Hada, H. Takashima, S. Tanaka, Chem. Phys. Lett. 247 (1995) 418.
[7] H. Nakatsuji, M. Hada, T. Tejima, T. Nakajima, M. Sugimoto, Chem. Phys. Lett. 249 (1996) 284.
[8] C.C. Ballard, M. Hada, H. Kaneko, H. Nakatsuji, Chem. Phys. Lett. 254 (1996) 170.
[9] H. Nakatsuji, M. Hada, H. Kaneko, C.C. Ballard, Chem. Phys. Lett. 255 (1996) 195.
[10] M. Hada, H. Kaneko, H. Nakatsuji, Chem. Phys. Lett. 261 (1996) 7.
[11] M. Douglas, N.M. Kroll, Ann. Phys. (N. Y.) 82 (1974) 89.
[12] J. Sucher, Phys. Rev. A 22 (1980) 348.
[13] B.A. Hess, Phys. Rev. A 32 (1985) 756.
[14] B.A. Hess, Phys. Rev. A 33 (1986) 3742.
[15] R. Fukuda, M. Hada, H. Nakatsuji, J. Chem. Phys. 118 (2003) 1015.

[16] R. Fukuda, M. Hada, H. Nakatsuji, J. Chem. Phys. 118 (2003) 1027.
[17] S.K. Wolff, T. Ziegler, E. van Lenthe, E. Baerends, J. Chem. Phys. 110 (1999) 7698.
[18] M. Hada, Y. Ishikawa, J. Nakatani, H. Nakatsuji, Chem. Phys. Lett. 310 (1999) 342.
[19] M. Hada, R. Fukuda, H. Nakatsuji, Chem. Phys. Lett. 321 (2000) 452.
[20] H.M. Quiney, H. Skaane, I.P. Grant, Chem. Phys. Lett. 290 (1998) 473.
[21] L. Visscher, T. Enevoldsen, T. Saue, H.J.A. Jensen, J. Oddershede, J. Comput. Chem. 20 (1999) 1263.
[22] K. Ishimura, R. Fukuda, M. Hada, H. Nakatsuji (submitted).
[23] L. Visscher, K.G. Dyall, T.J. Lee, Int. J. Quantum Chem. Symp. 29 (1995) 411.
[24] L. Visscher, J. Styszynski, W.C. Nieuwpoort, J. Chem. Phys. 105 (1996) 1987.
[25] M.H. Mettleman, Phys. Rev. A 24 (1981) 1167.
[26] O. Visser, P.J.C. Aerts, D. Hegarty, W.C. Nieuwpoort, Chem. Phys. Lett. 134 (1987) 34.
[27] B. Roos, Chem. Phys. Lett. 15 (1972) 153.
[28] N.F. Ramsey, Phys. Rev. 78 (1950) 699.
[29] R. Poirier, R. Kari, I.G. Csizmadia, Handbook of Gaussian Basis Sets, Elsevier, Amsterdam, 1985.
[30] M. Sugimoto, H. Nakatsuji, J. Chem. Phys. 102 (1995) 285.
[31] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
[32] K.G. Dyall, Theor. Chem. Acc. 99 (1998) 366.
[33] J. Vaara, K. Ruud, O. Vahtras, H. Ågren, J. Jokisaari, J. Chem. Phys. 109 (1998) 1212.