Quasi-Relativistic Study of ^{199}Hg Nuclear Magnetic Shielding Constants of Dimethylmercury, Disilylmercury and Digermylmercury

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Quasi-relativistic ab initio calculations were performed for ^{199}Hg nuclear magnetic shielding constants and chemical shifts in a series of $Hg(XH_3)_2$ (X = C, Si, and Ge) compounds. The relativistic terms included were the spin-free relativistic (SFR) term, the one- and two-electron spin−orbit (SO) terms, and the relativistic magnetic interaction (RMI) term. The second-order Douglas−Kroll (D-K) form was adopted for the one-electron SO, SFR, and RMI terms, and the Breit−Pauli form for the two-electron SO term. The calculated results show that the SFR, SO, and RMI terms are all important for calculating the ^{199}Hg shielding constants and chemical shifts of the compounds in question. The SFR and SO terms strongly couple with each other, and the RMI term also strongly affects the paramagnetic and Fermi-contact (FC) terms. The calculated ^{199}Hg chemical shifts are in reasonable agreement with experimental data only if the SFR, SO, and RMI terms are included and tight s basis functions of mercury are used. We found that the total trend of the chemical shifts in $Hg(XH_3)_2$ (X = C, Si, and Ge) originates from the sum of the FC and paramagnetic terms, which are the effects of the relativity and the electronegativity of the ligand, respectively.

I. Introduction

With the development of the multinuclear NMR technique, many experimental observations of metal chemical shifts have been reported,[1,2] including those of heavy elements of the fifth row, such as mercury, tungsten, and platinum. However, few theoretical attempts have been made to calculate NMR parameters of these heavy elements, due to the extra difficulty of the relativistic effect, in addition to the effects of the basis set and electron correlation and the gauge origin dependence. Relativistic effective core potential methods are not adequate for calculating heavy-element NMR parameters.

Pyykkö[3] has given a fully relativistic formulation of the NMR shielding tensor originating from the complete four-component wave function. Furthermore, Pyykkö et al.[4] have calculated the shielding tensor using a semiempirical relativistic scheme. However, the scalar relativistic effects are difficult to extract from semiempirical calculations. Very recently, an ab initio matrix Dirac−Fock method that incorporated the finite perturbation method was applied to the proton chemical shifts in HX (X = F, Cl, Br, I)[5] and O, S, Se, Te in their dihydrides.[6]

We have proposed a method of calculating the spin−orbit (SO) effect using the ab initio unrestricted Hartree−Fock (UHF) method,[7] and shown that the SO effect is very important for the chemical shift of a light nucleus bonded to heavy atoms,[7−11] such as the proton chemical shifts in HX (X = F, Cl, Br, I). We used the SO-UHF method to systematically include the SO effect, and have successfully elucidated the importance of the SO effects in the NMR chemical shifts of several halides, such as HX, CH_3X,[7] GaX_4^-, InX_4^-,[8] SiX_4, $SiXI_3$,[9] AlX_4^-,[10] and SnX_4.[11]

When the resonant nucleus is heavy, the spin-free relativistic (SFR) effect, which includes the mass−velocity (MV) and Darwin (DW) terms in the lowest order (c^{-2}), becomes important. Hence, we have combined the relativistic spin-free no-pair theory proposed by Sucher[12] and Hess[13] and the SO-UHF method to calculate the magnetic shielding constant and chemical shift of heavy elements. This approach is referred to as the quasi-relativistic (QR)-SO-UHF method.[14]

The QR-SO-UHF method has been used to calculate ^{1}H, ^{199}Hg, and ^{183}W magnetic shielding constants of HX (X = F, Cl, Br, and I),[14] HgX_2 (X = Cl, Br, and I),[15] WX_6 (X = F and Cl), and WO_4^{2-} series.[16] These studies have shown that the SFR and SO terms strongly couple with each other, and remarkably affect the magnetic shielding constants and chemical shifts of heavy elements, especially for the case of HgI_2. Without the SO and SFR terms, the experimental trend of chemical shifts in mercury dihalides cannot be reproduced.

Recently, we have generalized this line of our studies by introducing a quasi-relativistic SO-generalized UHF (QR-SO-GUHF) method[17] in which the orbitals are general spin−orbital. Further, we have adopted a more reasonable quasi-relativistic Hamiltonian that includes a relativistic correction to the magnetic interaction term, the one-electron SO term in Douglas−Kroll (D-K) form, and the two-electron SO term of Breit−Pauli (B-P) form. This method has been used to calculate NMR shielding constants and chemical shifts of a series of mercury compounds,[17] $Hg(CH_3)_2$, $Hg(CH_3)X$, HgX_2 (X = Cl, Br, and I), and has given much closer agreement with the experimental values than the previous one.[15]

Another study of importance in NMR calculations is that by Ziegler et al.[18−21] They carried out a density functional theory (DFT) calculation, in which the scalar-relativistic and spin−orbit coupling effects were taken into account, and gauge-including atomic orbitals (GIAO) and a frozen-core approximation was used. The ^{1}H NMR shifts of hydrogen halides and the ^{13}C NMR shifts of methyl halides and 5d transition metal carbonyls were calculated by the scalar-relativistic DFT-GIAO

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method. More recently, they have made use of the zeroth-order regular approximation (ZORA)[22−25] to incorporate the effects of relativity into the calculation of NMR shielding tensors and evaluated the ^{199}Hg, ^{183}W, and ^{207}Pb chemical shifts.[20,21] On the other hand, Kaupp et al.[26,27] have extended DFT-based individual gauge for localized orbitals method (DFT-IGLO) of Malkin et al.[28] to include scalar relativistic effects. Generally speaking, DFT calculations are relatively inexpensive, and numerical evidence indicates that when the SCF and DFT results differ significantly (for example, when the correlation effects are large), the DFT values are usually more reliable.

However, we should keep in mind that "although DFT has a rigorous base, in application it is "semi-emipirical" and that there is "no way to systematically converge to the exact result".[29] This contrasts with conventional ab initio approaches, for which we can estimate a priori the quality of a calculation and so improve the calculation systematically by extending the basis set and by improving the correlation treatment.

In the present paper, we report ab initio QR-SO-GUHF calculations for the ^{199}Hg magnetic shielding constants in $Hg(XH_3)_2$ (X = C, Si, Ge). To our knowledge, Ziegler et al.[21] have also systematically calculated the mercury shifts including $Hg(CH_3)_2$ and $Hg(SiH_3)_2$, but not $Hg(GeH_3)_2$. The chemical shifts of this series of compounds seem to be different from those of HgX_2 and $Hg(CH_3)X$ (X = Cl, Br, I) studied separately.[17] The range of the chemical shifts in these molecules is relatively narrow, a few hundred parts per million, in comparison with those in HgX_2 and $Hg(CH_3)X$ (X = Cl, Br, I). The chemical shifts do not monotonically increase in the order C, Si, and Ge. Therefore, the electronic mechanism of the chemical shifts in $Hg(XH_3)_2$ (X = C, Si, Ge) may be different from those in HgX_2 and $Hg(CH_3)X$. We also examine the basis set dependence and the effects of each relativistic term.

II. Method

The details of the present QR-SO-GUHF method for calculating the magnetic shielding constant and chemical shift are presented in a separate paper.[17] Here, we only briefly summarize this method as it pertains to the present calculations.

To derive the two-component quasi-relativistic formula for the magnetic shielding constant, we start with the one-electron Dirac Hamiltonian with scalar potential V and vector potential $\boldsymbol{A}$:

$$\hat{\boldsymbol{H}}_D = c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \boldsymbol{\beta}c^2 + V + c\boldsymbol{\alpha}\cdot\boldsymbol{A} \tag{1}$$

where $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ represent the usual Dirac 4 × 4 matrix. The last term ($\boldsymbol{\alpha}\cdot\boldsymbol{A}$) is separated from the general momentum term, $\boldsymbol{\pi} = \boldsymbol{\alpha}\cdot(\boldsymbol{p} + \boldsymbol{A})$, since we want to treat it independently. The free-particle Foldy−Wonthuysen transformation is defined as

$$U_0 = K + \boldsymbol{\beta}R\boldsymbol{\alpha}\cdot\boldsymbol{p} \tag{2}$$

where

$$K = \left[\frac{(E_p + c^2)}{2E_p}\right]^{1/2} \tag{3}$$

$$R = [2E_p(E_p + c^2)]^{-1/2} \tag{4}$$

$$E_p = c(\boldsymbol{p}^2 + c^2)^{1/2} \tag{5}$$

The first-order Hamiltonian is obtained as

$$U_0\hat{\boldsymbol{H}}_D U_0 = \boldsymbol{\beta}E_p + \hat{\boldsymbol{H}}^{\mathrm{int}}(V) + \hat{\boldsymbol{H}}^{\mathrm{int}}(\boldsymbol{A}) + \hat{\boldsymbol{O}}(V) + \hat{\boldsymbol{O}}(\boldsymbol{A}) \equiv \hat{\boldsymbol{H}}_1 \tag{6}$$

where

$$\hat{\boldsymbol{H}}^{\mathrm{int}}(V) = KVK + R(c^2\boldsymbol{p}V\cdot\boldsymbol{p})R + R[ic^2\hat{\boldsymbol{a}}\cdot(\boldsymbol{p}V\times\boldsymbol{p})]R \tag{7}$$

$$\hat{\boldsymbol{H}}^{\mathrm{int}}(\boldsymbol{A}) = \boldsymbol{\beta}\left[K\frac{2c(\boldsymbol{A}\cdot\boldsymbol{p})}{E_p + c^2}K - K\frac{ic\boldsymbol{\alpha}(\boldsymbol{p}\times\boldsymbol{A})}{E_p + c^2}K\right] \tag{8}$$

$$\hat{\boldsymbol{O}}(V) = \boldsymbol{\beta}[R(c\boldsymbol{\alpha}\cdot\boldsymbol{p}V)K - K(cV\boldsymbol{\alpha}\cdot\boldsymbol{p})R] \tag{9}$$

$$\hat{\boldsymbol{O}}(\boldsymbol{A}) = K(\boldsymbol{\alpha}\cdot\boldsymbol{A})K + R[c^2\boldsymbol{\alpha}\cdot\boldsymbol{p}(\boldsymbol{\alpha}\cdot\boldsymbol{A})\boldsymbol{\alpha}\cdot\boldsymbol{p}]R. \tag{10}$$

To remove the remaining odd term $\hat{\boldsymbol{O}}(V)$ and $\hat{\boldsymbol{O}}(\boldsymbol{A})$, we used the second-order Douglas−Kroll transformation[30] as

$$U_1 = \{1 + [\hat{W}(V) + \hat{W}(\boldsymbol{A})]^2\}^{1/2} + [\hat{W}(V) + \hat{W}(\boldsymbol{A})] \tag{11}$$

where $\hat{W}$ is the momentum space integral operator, and the kernel is

$$\hat{W}(V_{pp'}) = \boldsymbol{\beta}\hat{\boldsymbol{O}}(V_{pp'})/(E_p + E_{p'}) \tag{12}$$

$$\hat{W}(\boldsymbol{A}_{pp'}) = \boldsymbol{\beta}\hat{\boldsymbol{O}}(\boldsymbol{A}_{pp'})/(E_p + E_{p'}) \tag{13}$$

The transformed Hamiltonian is written as

$$U_1\hat{\boldsymbol{H}}U_1^{-1} = \boldsymbol{\beta}E_p + \hat{\boldsymbol{H}}^{\mathrm{int}}(V) + \hat{\boldsymbol{H}}^{\mathrm{int}}(\boldsymbol{A}) + \frac{1}{2}[\hat{W}(V),\hat{\boldsymbol{O}}(V)] + \frac{1}{2}[\hat{W}(\boldsymbol{A}),\hat{\boldsymbol{O}}(\boldsymbol{A})] + \frac{1}{2}[\hat{W}(V),\hat{\boldsymbol{O}}(\boldsymbol{A})] + \frac{1}{2}[\hat{W}(\boldsymbol{A}),\hat{\boldsymbol{O}}(V)] + \ldots \tag{14}$$

By taking only the upper two components in eq 14, we can get a two-component positive energy Hamiltonian in which both the scalar potential V and the vector potential $\boldsymbol{A}$ are treated equally up to the second-order expansion. In our formulism, the Hamiltonian can be easily expanded with regard to the powers of the magnetic field and the nuclear magnetic moment, and therefore it can be applied to the NMR theory.

The two-electron term is added in the Breit−Pauli form to the two-component Hamiltonian obtained by the above formulation. The lowest-order (c^{-2}) relativistic correction terms without the magnetic field appear in the $\hat{\boldsymbol{H}}^{\mathrm{int}}(V)$ term of eq 7. The first and second terms are the spin-free relativistic (SFR) terms, and the third term is the spin−orbit term. $[\hat{W}(V),\hat{\boldsymbol{O}}(V)]$ in eq 14 gives a higher-order relativistic correction of the SFR and SO terms. The $\hat{\boldsymbol{H}}^{\mathrm{int}}(\boldsymbol{A})$ term includes the electron−magnetic interaction and its relativistic correction. The terms $\hat{\boldsymbol{H}}^{\mathrm{int}}(\boldsymbol{A})$, $[\hat{W}(V),\hat{\boldsymbol{O}}(\boldsymbol{A})]$, and $[\hat{W}(\boldsymbol{A}),\hat{\boldsymbol{O}}(V)]$ give the paramagnetic, Fermi-contact, and spin-dipolar contributions in the magnetic shielding constant, while $[\hat{W}(\boldsymbol{A}),\hat{\boldsymbol{O}}(\boldsymbol{A})]$ gives a diamagnetic contribution. We can treat these terms independently and analyze the effect of each term.

Due to the presence of the spin-dependent operators, the relativistic wave function at the Hartree−Fock level is best described by the GUHF method:[31]

$$\Psi^{GUHF} = |\varphi_1\varphi_2 \ldots \varphi_i \ldots \varphi_n| \tag{15}$$

TABLE 1: Optimized Geometric Parameters of $Hg(XH_3)_2$ (X = C, Si, and Ge)

$Hg(XH_3)_2$	bond length (angstrom)		bond angle (degree)	
X	Hg−X	X−H	X−Hg−X	H−X−Hg
C	2.1274 (2.0835, 2.0945)[a]	1.0990	180.0	110.7616
Si	2.5177	1.4763	180.0	111.2158
Ge	2.5882	1.5483	180.0	111.3824

[a] Bond lengths in parentheses were obtained by different experimental methods in ref 36.

in which the one-electron function φ_i is a general spin−orbital given by

$$\varphi_i = \phi_i^{\alpha}\alpha + \phi_i^{\beta}\beta \tag{16}$$

where ϕ_i denotes the ith spatial function.

In the presence of SO interaction, the magnetic shielding constant of the QR-SO-GUHF method is expressed as the sum of the diamagnetic term σ^{dia}, the paramagnetic term σ^{para}, the spin-dipolar term σ^{SO} (SD), and the Fermi contact term σ^{SO}(FC):[17]

$$\sigma^{tot} = \sigma^{dia} + \sigma^{para} + \sigma^{SO}\,(SD) + \sigma^{SO}\,(FC) \tag{17}$$

This partitioning is the same as that in the previous study on SO and SFR effects.[7,14]

To avoid a strong singularity around heavy elements in the relativistic Hamiltonian, the finite nucleus model was taken into account by adopting a Gaussian distribution for both nuclear charge[32] and nuclear magnetic moment.

III. Basis Sets and Geometry

The geometries of HgR_2 molecules are assumed to be linear, since the vast majority of diorganomercury compounds exhibit linear geometries in both the solid and gas phases, and were optimized at the MP2 level assuming C_{3V} symmetry and using the following basis sets: LanL2DZ[33] augmented with the two-membered *p*-polarization functions of Huzinaga[34] for Hg atom; LanL2DZ augmented with the two-membered *d*-polarization functions of Huzinaga for Si and Ge atoms; D95[35] augmented with the two-membered *d*-polarization functions of Huzinaga for C atom; and D95 for H atom. LanL2DZ includes a double-ζ basis set and the relativistic effective core potential (RECP) determined from a relativistic calculation of an atom. The optimized geometrical parameters of the $Hg(XH_3)_2$ series of interest are listed in Table 1. Note that in the case of $Hg(CH_3)_2$, the difference between the optimized and experimental[36] Hg−C bond length is 0.0329 Å, suggesting that the calculated Hg−C bond length is well corrected relativistically using LanL2DZ.

For the quasi-relativistic calculations of NMR shielding constants and chemical shifts, the Gleichmann and Hess[37] (21*s*17*p*10*d*7*f*) set, augmented with relativistically optimized 1*s*1*p*,[17] contracted to [22*s*18*p*6*d*3*f*] all-electron sets is used for Hg atom. We use the Huzinaga (10*s*7*p*)/[10*s*3*p*] plus 3*d* first-order higher angular momentum functions[38,39] (3*d*-FOBFs) for C atom, the Huzinaga (11*s*8*p*)/[11*s*8*p*] plus 3*d*-FOBFs for Si atom, (13*s*10*p*5*d*)/[13*s*10*p*3*d*] plus 3*d*-FOBFs and 3*f*-FOBFs for Ge atom, and (4*s*)/[2*s*] plus 2*p*-FOBFs for H atom. The gauge origin is located at the Hg atom. FOBFs have been shown to be effective in decreasing the gauge origin dependence and in improving the quality of the calculated results.[38,39]

In our previous studies,[17] a suitably flexible basis set, such as those used in the present calculations, was shown to be important for studying the relativistic effects on the NMR chemical shifts, since the relativity (SFR and SO) affects not only the inner-core orbitals but also the valence orbitals because they have to be orthogonal to the core MOs.

TABLE 2: Levels of Approximation in the Relativistic Methods[a,b,c]

level	$(T+V)$[d]	one-electron SO	two-electron SO	magnetic interaction
1	non-R			non-R
2	non-R	B−P	B−P	non-R
3	D−K−H			D−K−H
4	D−K−H	D−K−H	B−P	non-R
5	D−K−H	D−K−H	B−P	D−K−H

[a] D-K−H: relativistic Douglas−Kroll−Hess method. [b] B−P: Breit−Pauli relativistic correction. [c] non-R: nonrelativistic method. [d] $(T+V)$: kinetic energy and nuclear attraction energy.

IV. Results and Discussion

In our previous studies,[14−16] we showed that the SFR and SO terms play an important role in calculating the NMR shielding constants of heavy elements. Since the two terms strongly couple with each other, they cannot be separated in calculations of the relativistic effects on the magnetic shielding constants of heavy elements. To show this in detail, we performed calculations at five different levels of approximation, as shown in Table 2.

The differences between these calculations at different levels can help us to understand the particular contribution of the term of interest:

Level 2−Level 1 (2−1): effect of the SO term;

Level 3−Level 1 (3−1): effect of the SFR term, including relativistic magnetic interaction;

Level 5−Level 4 (5−4): effect of quasi-relativistic magnetic interaction;

Level 5−Level 1 (5−1): full quasi-relativistic effect. In comparison with the previous analysis,[15,16] Level 4 is newly added to show the effect of the relativistic correction to the magnetic interaction term.

The calculated ^{199}Hg magnetic shielding constants and chemical shifts of $Hg(XH_3)_2$ (X = C, Si, and Ge) molecules at these five levels of approximation are listed in Table 3, which also shows the corresponding calculated values of particular contributions, σ^{dia}, σ^{para}, σ^{SO} (SD), and σ^{SO} (FC). The experimental chemical shifts of this series of compounds are taken from the literature.[40] An analysis of the calculated results using the differences between the different-level calculations is shown in Table 4, from which we can derive the contributions of the various relativistic effects to the shielding constants.

The correlations between the theoretical and experimental results for the ^{199}Hg chemical shifts at Levels 1, 2, 3, and 5 are shown in Figure 1. Both theoretically and experimentally, $Hg(CH_3)_2$ is taken as the reference compound.

As shown in Table 3, at various levels, the contributions of the diamagnetic terms to the chemical shifts are almost constant (−47 ppm for $Hg(SiH_3)_2$ and −173/−174 ppm for $Hg(GeH_3)_2$), though the absolute values of the diamagnetic contributions are different. Taking into account the SO term (Level 2) and the SFR term (Level 3) separately, the calculated chemical shifts are even worse in comparison with the experimental data than the pure nonrelativistic data (Level 1). The best results are obtained when both the SFR and SO terms are taken into account in the presence of relativistic magnetic interaction, i.e., Level 5, in which the SFR and SO terms strongly couple with each other. In particular, the SO term is strongly enhanced under the presence of the SFR term, so that the contribution of the

TABLE 3: ^{199}Hg Magnetic Shielding Constants and Chemical Shifts (ppm) Calculated at Different Levels of Relativistic Calculations

	without SO				with SO							
							σ^{SO}					
compound	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	SD	FC	total	σ^{tot}	δ^{cal}	δ^{expt}
	level 1							level 2				
$Hg(CH_3)_2$	9817	−2943	6874	0	9845	−3309	−243	317	74	6610	0	0
	(0)	(0)			(0)	(0)	(0)	(0)	(0)			
$Hg(SiH_3)_2$	9864	−3239	6625	+249	9892	−3685	−325	411	86	6294	+317	+196
	(−47)	(+296)			(−47)	(+376)	(+82)	(−94)	(−12)			
$Hg(GeH_3)_2$	9991	−3182	6809	+65	10019	−3611	−309	441	132	6540	+70	−147
	(−174)	(+239)			(−174)	(+302)	(+66)	(−124)	(−58)			
	level 3							level 4				
$Hg(CH_3)_2$	9034	−3242	5791	0	11549	−5661	−566	10166	9600	15487	0	0
	(0)	(0)			(0)	(0)	(0)	(0)	(0)			
$Hg(SiH_3)_2$	9081	−3755	5326	+466	11596	−6590	−742	13352	12610	17615	−2128	+196
	(−47)	(+513)			(−47)	(+929)	(+176)	(−3186)	(−3010)			
$Hg(GeH_3)_2$	9207	−3548	5659	+133	11723	−6236	−692	14197	13505	18992	−3504	−147
	(−173)	(+306)			(−174)	(+575)	(+126)	(−4031)	(−3905)			
								level 5				
$Hg(CH_3)_2$					9048	−3620	−269	9969	9700	15128	0	0
					(0)	(0)	(0)	(0)	(0)			
$Hg(SiH_3)_2$					9095	−4188	−379	10368	9989	14896	+232	+196
					(−47)	(+568)	(+110)	(−399)	(−289)			
$Hg(GeH_3)_2$					9221	−3978	−353	10527	10174	15417	−289	−147
					(−173)	(+358)	(+84)	(−558)	(−474)			

TABLE 4: Differences between Different Levels of Approximation in the Relativistic Calculations of the ^{199}Hg Shielding Constants and Chemical Shifts (in ppm) of $Hg(XH_3)_2$ (X = C, Si, and Ge) Molecules

difference	σ^{tot} ($Hg(CH_3)_2$)	σ^{tot} ($Hg(SiH_3)_2$)	σ^{tot} ($Hg(GeH_3)_2$)	δ^{cal} ($Hg(SiH_3)_2$)	δ^{cal} ($Hg(GeH_3)_2$)
2−1	−264	−331	−268	+68	+5
3−1	−1083	−1299	−1150	+217	+68
5−4	−359	−2719	−3575	2360	3215
5−1	8254	8271	8608	−17	−354

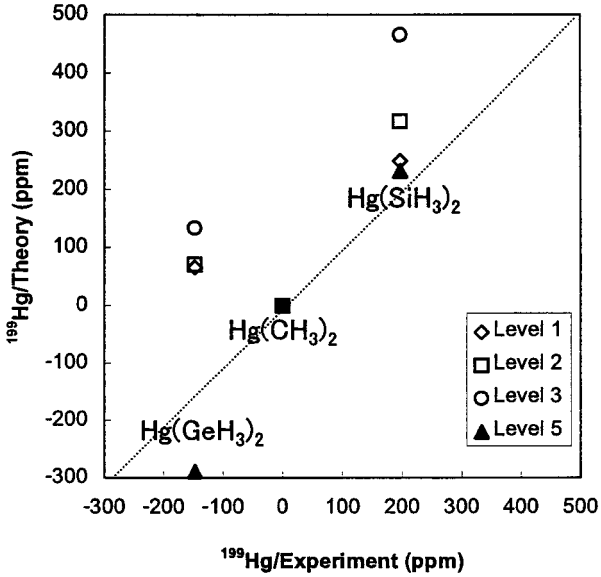

Figure 1. Correlation between experimental and theoretical chemical shifts of $Hg(XH_3)_2$ (X = C, Si, and Ge).

FC term to the shielding constant increased from on the order of 10^2 at Level 2 to on the order of 10^5 at Level 5.

Comparing the results at Level 5 with those at Level 4, we can see that the contribution of the FC term to the chemical shift is too large at Level 4, which makes the chemical shifts of $Hg(SiH_3)_2$ and $Hg(GeH_3)_2$ too large in comparison with the experimental value. This shows the importance of the relativistic correction to the magnetic interaction term, as discussed in detail in our previous study.[17] In brief, this is due to the divergent behavior of the contributions of the very tight s functions to the FC term when the magnetic interaction is nonrelativistic. In other words, when the magnetic interaction is considered in a relativistic manner (Level 5), the contributions of very tight s functions to the FC term become convergent. Table 5 shows these nonconvergent and convergent behaviors, respectively, for Level 4 and Level 5 calculations.

Table 4 shows an analysis based on the difference between the two different levels of calculations. This clearly shows the importance and strong coupling of the various relativistic effects of the SO, SFR, and RMI terms. The independent SO effects on ^{199}Hg shielding constants are −264, −331, and −268 ppm for $Hg(CH_3)_2$, $Hg(SiH_3)_2$, and $Hg(GeH_3)_2$, respectively. The independent SFR effects in the presence of RMI are −1083, −1299, and −1150 ppm, respectively. However, when the SO and SFR effects join together in the presence of RMI, the effects are enhanced up to 8254, 8271, and 8608 ppm, respectively, showing that there is strong coupling between the SFR and SO terms in the presence of RMI. Furthermore, the difference between Levels 5 and 4, which shows the independent effect of the RMI term, is interesting. The FC term in the nonrelativistic magnetic interaction causes a divergent behavior of the shielding constant, −359, −2719, and −3575 ppm for $Hg(CH_3)_2$, $Hg(SiH_3)_2$, and $Hg(GeH_3)_2$, respectively, while the final results at Level 5 due to the RMI give a smooth change in reasonable agreement with the experimental results.

The influence of the relativistic effects on the chemical shift, which is a relative quantity, is somewhat more difficult to evaluate. To better understand the origin of the ^{199}Hg chemical shifts of the $Hg(XH_3)_2$ series, Figure 2 shows the analysis for the contribution of the diamagnetic term σ^{dia}, paramagnetic term σ^{para}, spin−dipolar term σ^{SO} (SD), and Fermi-contact term σ^{SO} (FC) to the chemical shifts calculated at Level 5. The contribu-

TABLE 5: Exponents of the *s* Functions and Their Contributions to the Fermi Contact Term of the Shielding Constant of $Hg(XH_3)_2$ (X = C, Si, and Ge) Molecules

		$Hg(CH_3)_2$		$Hg(SiH_3)_2$		$Hg(GeH_3)_2$	
order of *s*	exponent	Level 5	Level 4	Level 5	Level 4	Level 5	Level 4
1	26780000.0	635.86	3431.86	670.68	4517.41	685.09	4816.93
2	3260982.0	1248.40	3233.45	1316.23	4257.24	1344.37	4540.52
3	469370.5	1543.51	2368.72	1626.42	3116.91	1660.61	3322.48
4	105124.2	1671.72	1756.43	1760.06	2314.07	1796.70	2468.34
5	29609.54	1940.33	1554.15	2042.48	2042.22	2084.34	2175.31
6	9741.310	2083.42	1391.15	2197.57	1837.55	2245.70	1963.48
7	3603.125	1785.81	1295.01	1903.08	1694.79	1949.74	1800.04
8	1467.629	852.21	954.63	950.34	1265.17	997.63	1369.17
9	639.1015	−380.55	141.13	−373.25	163.23	−368.28	174.11
10	251.7650	−765.42	−892.06	−852.34	−1149.45	−884.81	−1208.22
11	126.8379	−397.61	−1009.92	−528.63	−1389.67	−575.44	−1480.42
12	67.05787	201.61	131.32	233.69	222.76	237.10	225.58
13	28.32247	530.19	1276.15	671.58	1685.64	713.96	1756.18
14	14.52412	−226.23	−421.16	−266.60	−538.17	−283.86	−571.15
15	5.496432	−266.64	−682.12	−348.68	−918.36	−372.74	−959.11
16	2.200000	162.78	406.63	209.94	541.96	229.68	581.21
17	0.880000	26.91	69.58	38.19	102.25	37.92	98.63
18	0.350000	−19.91	−50.95	−29.35	−77.86	−28.52	−73.58
19	0.140000	−3.31	−9.33	0.38	0.56	−0.18	−0.94
20	0.056000	−6.47	−16.36	−3.29	−8.96	−4.83	−13.00
21	0.022000	−0.71	−1.91	−0.67	−1.78	−0.52	−1.38
22	0.010000	0.06	0.16	0.08	0.22	0.13	0.36

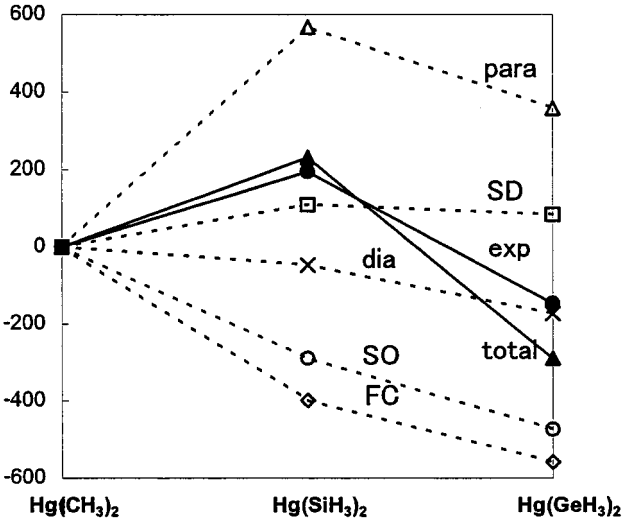

Figure 2. Dependence of ^{199}Hg chemical shifts and the contributions of the diamagnetic term, paramagnetic term, and spin−orbit term (SD + FC) in the series $Hg(XH_3)_2$ (X = C, Si, and Ge) calculated at the Level 5 approximation.

tions of all of the terms are considerable compared with the absolute values of the ^{199}Hg chemical shifts, and it is difficult to say which term is dominant. Relatively, the contributions of the relativistic FC term to the chemical shifts are negative and increase with the nuclear charge in the order C, Si, and Ge, whereas the contributions of the paramagnetic term (electronegativity) are positive and largest (+568 ppm) for $Hg(SiH_3)_2$. The sum of the contributions of the FC and paramagnetic terms controls the total trend of the chemical shifts in the HgR_2 series: the sign of the ^{199}Hg chemical shift of $Hg(SiH_3)_2$ is positive, while that of $Hg(GeH_3)_2$ is negative.

In light of the above observations, we conclude that it is absolutely crucial to include all of the relativistic effects to calculate the heavy-element NMR chemical shifts.

Electron correlation is not taken into account in the present method, but will be addressed in future studies. For the calculated ^1H shielding constants in HI, the electronic correlation effect on the Fermi-contact term and the total shielding constant is about 3 ppm,[41,42] while the relativistic effect is about 15 ppm at the Hartree−Fock level.[14] In the case of heavy elements, the relativistic effect is easily beyond 1000 ppm. The basis set effect and solvation effect are also very large and easily beyond 10 ppm. The electronic correlation effect might also be important for the absolute value, i.e., nuclear magnetic shielding constant. However, in the NMR chemical shift of heavy elements, which is a relative quantity, most of the electronic correlation effect may be canceled. At present, our calculated results are meaningful since they qualitatively agree with experimentally observed trends in the ^{199}Hg NMR chemical shift using well-considered relativistic basis sets in the framework of the present quasi-relativistic approach. To obtain more accurate numerical results, however, we plan to extend our method by also incorporating electronic correlations.

V. Conclusions

We have reported here quasi-relativistic calculations of the ^{199}Hg magnetic shielding constants and chemical shifts for $Hg(XH_3)_2$ (X = C, Si, and Ge) molecules. The present results can be summarized as follows:

(1) The relativistic effects are very important for the ^{199}Hg magnetic shielding constant and chemical shift: both the SFR and SO terms play an important role and strongly couple with each other. Furthermore, the calculated results agree reasonably with the experimental values only after considering the relativistic magnetic interaction term.

(2) The experimental ^{199}Hg chemical shifts of $Hg(XH_3)_2$ are reproduced only when all of the relativistic terms are considered. The electronic mechanism of the ^{199}Hg chemical shifts of the $Hg(XH_3)_2$ (X = C, Si, and Ge) series is quite different from that of the HgX_2 (X=Cl, Br, I) series.

(3) It is important to increase the flexibility of the innermost as well as the outermost orbitals of the basis set. Only a sufficiently flexible basis set can adequately describe the relativistic effects on the inner-core MOs as well as the valence MOs. Inclusion of the relativistic effect on the magnetic field is important, since otherwise the contributions of the very tight *s* functions to the FC term do not converge.

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