

# Basis set dependence of magnetic shielding constant calculated by the Hartree–Fock/finite perturbation method

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## Abstract

We investigate the basis set dependence and the gauge origin dependence in the calculations of Se and Cd nuclear magnetic shielding constants of several selenium and cadmium compounds. We improve the basis set systematically by adding the first-order higher angular momentum basis functions (FOBFs) to the conventional basis sets, as proposed previously, in the *ab initio* Hartree–Fock/finite perturbation method. The calculated results become almost independent on the employed basis sets when this improvement is done. Furthermore, it is shown that the mechanisms of the chemical shifts are basis-set independent. The dominances of the p-hole mechanism in the Se chemical shift and the p-electron mechanism in the Cd chemical shift are valid for all the basis set examined in this paper.

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## 1. Introduction

In recent years, a lot of theoretical investigations on magnetic properties, such as nuclear magnetic shielding constant and magnetic susceptibility, have been performed. In calculating magnetic properties, however, there is a problem that the computed results depend on the gauge origin and the employed basis sets. It is essentially due to the incompleteness of the basis set used in practical computations. It has been believed that very large basis sets are required in the Hartree–Fock/finite perturbation (HF/FP) method [1] to get invariant results [2–5].

Several methods have been proposed in order to solve the gauge origin problem. The gauge invariant atomic orbital (GIAO) method [6–8], the individual gauge factors for localized orbitals (IGLO) method [9,10], and the localized orbital/local origin (LORG)

method [11] have been developed. A method in which the best gauge origin is selected in the finite basis set calculations is also reported [12,13].

Ellis et al. pointed out that the calculated magnetic shielding constants of the Cd and Se molecules are strongly basis set dependent even with the GIAO and the LORG methods as well as the conventional methods [14,15]. This fact probably means that the employed basis sets are not yet saturated. Ellis et al. pointed out that a practical rationalization of the basis set dependence is the potential lack of balance in the basis set. Several investigations on the basis set dependence of magnetic properties have been published for simple molecules including first and second row elements [1–5,16–18]. The improvement of the basis set is mostly done by the addition of polarization functions to the primary basis sets, but the methodology was essentially empirical and there

was no firm theoretical background. Further, the molecules studied did not include atoms heavier than the third row ones. It is necessary to establish a systematic method of solving this problem. The purpose of our study is to find out and establish such a method. We believe this problem is parallel with the gauge origin problem. We want to establish a method of calculating magnetic properties which are independent on the choice of the basis set and of the gauge origin. We believe such a method must give, at the same time, high quality results which agree better with experiments.

In the previous paper, we proposed a new method to improve the gauge origin dependence in the HF/FP method [19]. We add first-order higher angular momentum basis functions (FOBFs) to the original basis set. Test calculations were reported for the first and second row hydrides and for some heavier hydrides. We showed that the calculated values are nearly gauge origin independent. Our results were close to the GIAO results for the first row hydrides but much different for the second row hydrides and closer to the experimental values. This is because our method improves the quality of the basis sets as well as the invariance property. We have also shown the effectiveness of our method for a series of As and Sb chemical shifts [20], and for Ga and In chemical shifts [21].

We have given a perspective concept on the electronic mechanism of the metal chemical shifts for a variety of metal complexes [22,23]. This concept is important for understanding the trend in the observed chemical shifts. A purpose of this paper is to show that such concept is just basis-set independent.

In this paper, we apply our new method to the calculation of the magnetic shielding constants of the Se and Cd compounds for which Ellis et al. pointed out the basis set dependence. Starting from the basis sets which give different magnetic shielding constants, as Ellis et al. pointed out, we apply our method and will get close (basis set independent) and gauge origin independent results, and they will agree better with the experimental values. In particular, we will also show that the p-mechanism is always the dominant mechanism of the Se and Cd chemical shifts; this mechanism is basis set independent.

## 2. Theoretical background and method of calculations

In the GIAO method, the field dependent basis functions are written as

$$\phi_\nu = \exp(-i \mathbf{A}_\nu \cdot \mathbf{r}) \chi_\nu, \quad (1)$$

where  $\chi_\nu$  is a conventional field-independent real basis function, and

$$\mathbf{A}_\nu = \mathbf{B} \times (\mathbf{R}_\nu - \mathbf{R}_0)/2, \quad (2)$$

where  $\mathbf{R}_\nu$  and  $\mathbf{R}_0$  are the position vectors for  $\chi_\nu$  and the gauge origin measured from the coordinate origin, respectively.  $\mathbf{B}$  is the external magnetic field. The GIAO method formally satisfies the gauge invariance, since the basic AO is transformed in a necessary condition shown by Epstein [24].

Expanding Eq. (1) to the first order, we obtain

$$\phi_\nu = \chi_\nu - i \mathbf{A}_\nu \cdot \mathbf{r} \chi_\nu. \quad (3)$$

This relation implies that if we use the basis set  $\{\chi_\nu\}$  augmented with  $\{r\chi_\nu\}$  in the HF/FP method, the calculated results should be approximately gauge origin independent [19]. We call  $\{r\chi_\nu\}$  first-order higher angular momentum basis functions (FOBFs). The coefficients applied to  $\{r\chi_\nu\}$  are determined independently in the variational procedure, though they are given in Eq. (3). The first-order basis is considered to be enough since nuclear magnetic shielding constant is the first-order property with respect to the external magnetic field. Therefore we usually adopt  $\{\chi, r\chi\}$  as a basis set for the calculations of magnetic shielding constants, and we call this the  $\{\chi, r\chi\}$  method. Test calculations for some hydrides have shown the effectiveness of this method. This method has some similarity to the previous one for improving the Hellmann–Feynman force [25].

We apply the above  $\{\chi, r\chi\}$  method starting from the several conventional basis sets  $\{\chi\}$  which give (largely) different Se and Cd magnetic shielding constants. The shielding constant  $\sigma$  and the chemical shift  $\delta$  are calculated by the FP method. The details of the method were described in Ref. [22]. The unperturbed Hartree–Fock wave functions were calculated with the HONDO7 [26] or HONDO8 [27] program. In our calculations the gauge origin is placed at the Cd and Se nuclei. Only when we study

gauge origin dependence, it is put on a neighboring atom.

The basis set used in the present calculations are given in Table 1, Fig. 1, and Fig. 2. Table 1 gives the definition of the basis set type, A, B, etc., and Figs. 1 and 2 the definition of the basis set number  $n$ . For example, basis set B2 indicates that the basis set type is B and basis set number is 2. They are grouped into two different types. One is the basis sets due to Huzinaga et al. [28–31] and Pople et al. [32]. The basis set (A1) for the Se compounds, (C1) for CdMe<sub>2</sub>, and (B1) for CdEt<sub>2</sub> are the same as those used in the previous papers [33,34]. The other is taken from the papers of Ellis et al. [14,15]; the basis set (B1) for the Se compounds, and (D1) and (E1) for the Cd compounds. The FOBFs are added

only to the valence basis functions, since the effects of the FOBFs for the core AOs were small [19].

The geometries of the Cd and Se compounds calculated in this paper are the same as those of the previous papers [33,34]. We also used the geometries optimized by Ellis et al. in order to compare with their results [14,15].

The chemical shift  $\delta$  is defined as the difference between the two magnetic shielding constants, that is,

$$\delta = \sigma(\text{ref}) - \sigma, \quad (4)$$

where  $\sigma(\text{ref})$  denotes the magnetic shielding constant of the reference compound, which is CdMe<sub>2</sub> and SeMe<sub>2</sub> in this study. The magnetic shielding

Table 1  
Definition of the basis set type used for the calculation of the magnetic shielding constants of Se and Cd

Type <sup>a</sup>	Se compounds				
	Se <sup>b,c</sup>	C <sup>d,e</sup>	H <sup>f</sup>		
A $n$	Huzinaga(A)	Huzinaga	4-31G		
B $n$	Huzinaga(B)	Dunning	Dunning		
Type <sup>g</sup>	Cd compounds				
	Cd <sup>h-k</sup>	C1 <sup>l,m</sup>	C2 <sup>l,m</sup>	H1 <sup>n,o</sup>	H2 <sup>n,o</sup>
A $n$	MIDI-1p2	MIDI-1	MIDI-1	MINI-1	MINI-1
B $n$	MIDI-1p2	MIDI-1	MINI-1	MIDI-1	MINI-1
C $n$	MIDI-1p2	MIDI-1	MIDI-1	MIDI-1	MIDI-1
D $n$	MIDI-4p2	Dunning	Dunning	Dunning	Dunning
E $n$	MIDI-4p2d2	Dunning	Dunning	Dunning	Dunning
F $n$	MIDI-4p2d2f2	Dunning	Dunning	Dunning	Dunning

<sup>a</sup> The meaning of  $n$  in A  $n$  and B  $n$  ( $n = 1, 2, \dots, 5$ ) is shown in Fig. 1.

<sup>b</sup> Huzinaga(A) denotes (13s10p4d)/[6s5p1d] plus two polarization d functions ( $\zeta = 0.144, 0.489$ ) taken from the book of Huzinaga et al. [28].

<sup>c</sup> Huzinaga(B) denotes (13s10p4d)/[5s3p1d] taken from the book of Huzinaga et al. [28], plus two polarization p functions ( $\zeta = 1.4026, 0.0751$ ) and two polarization d functions ( $\zeta = 19.618, 0.3307$ ).

<sup>d</sup> Huzinaga denotes (7s4p)/[3s2p] taken from the book of Huzinaga et al. [28].

<sup>e</sup> Dunning denotes Huzinaga–Dunning (9s5p)/[4s2p] (Ref. [29]).

<sup>f</sup> Dunning and 4-31G denote Huzinaga–Dunning (4s)/[2s] (Ref. [29]) and 4-31G (Ref. [32]), respectively.

<sup>g</sup> The meaning of  $n$  in A  $n$ –F  $n$  ( $n = 1, 2, \dots, 6$ ) is shown in Fig. 2.

<sup>h</sup> MIDI-1p2 denotes MIDI-1 (Ref. [30]) plus two polarization p-functions ( $\zeta = 0.16000, 0.04094$ ).

<sup>i</sup> MIDI-4p2 denotes MIDI-4 (Ref. [31]) plus two polarization p functions ( $\zeta = 0.9405, 0.0755$ ).

<sup>j</sup> MIDI-4p2d2 denotes MIDI-4 (Ref. [31]) plus two polarization p functions ( $\zeta = 0.9446, 0.0779$ ) and two polarization d functions ( $\zeta = 0.4113, 0.0990$ ).

<sup>k</sup> MIDI-4p2d2f2 denotes MIDI-4 (Ref. [29]) plus two polarization p functions ( $\zeta = 0.9446, 0.0779$ ), two polarization d functions ( $\zeta = 0.4113, 0.0990$ ) and two polarization f functions ( $\zeta = 0.9731, 0.1193$ ).

<sup>l</sup> C1, C2 denote the C atoms attached to the Cd and C1 atoms, respectively.

<sup>m</sup> Dunning denotes Huzinaga–Dunning (9s5p)/[4s2p] (Ref. [29]).

<sup>n</sup> H1, H2 denote the H atoms attached to C1 and C2, respectively.

<sup>o</sup> Dunning denotes Huzinaga–Dunning (4s)/[2s] (Ref. [29]).

constant is the sum of the diamagnetic term  $\sigma^{\text{dia}}$  and the paramagnetic term  $\sigma^{\text{para}}$ ,

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

where  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  are the first-order and second-order terms, respectively, in the perturbation theory. The MO and AO analyses of  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  are performed by the method described in Ref. [22].

Table 2

Se shielding constant  $\sigma$ , Se chemical shift  $\delta$ , and the diamagnetic and paramagnetic contributions to  $\sigma$  for  $\text{SeH}_2$ ,  $\text{SeHMe}$ , and  $\text{SeMe}_2$  calculated by different basis sets

	$\sigma^{\text{dia}}$	Shift	$\sigma^{\text{para}}$	Shift	$\sigma^{\text{total}}$	Shift $\delta^{\text{a}}$
<b>SeH<sub>2</sub></b>						
(A1)	3003.2	67.9	-884.5	-312.8	2118.7	-244.9
(B1)	3002.4	68.0	-1019.7	-386.3	1982.7	-318.3
(A2)	3003.8	68.0	-948.8	-370.1	2055.0	-302.1
(B2)	3002.4	68.0	-943.9	-432.6	2058.5	-364.6
(A3)	3003.3	67.9	-811.7	-284.6	2191.6	-216.7
(B3)	3002.4	68.0	-819.9	-320.7	2182.5	-252.7
(A5)	3003.9	67.9	-847.2	-319.2	2156.7	-251.3
(B5)	3002.5	68.1	-831.5	-312.8	2171.0	-244.7
(B1)	GIAO	-12.0	-836.1	-197.2	2150.9	-209.1
	Exptl.				2280 <sup>b</sup>	
					2401 <sup>c</sup>	
						-344.8 <sup>d</sup>
<b>SeHMe</b>						
(A1)	3036.9	34.2	-1071.9	-125.4	1965.0	-91.1
(B1)	3036.1	34.3	-1230.3	-175.7	1805.8	-141.4
(A2)	3037.5	34.3	-1166.1	-152.8	1871.4	-118.5
(B2)	3036.1	34.3	-1191.2	-185.3	1844.9	-151.0
(A3)	3036.9	34.3	-986.5	-109.8	2050.4	-75.5
(B3)	3036.1	34.3	-1009.3	-131.3	2026.8	-97.0
(A4)	3037.0	34.3	-988.2	-111.5	2048.8	-77.2
(B4)	3036.1	34.4	-1007.2	-131.0	2028.9	-96.6
(A5)	3037.5	34.3	-1039.5	-126.9	1988.0	-82.6
(B5)	3036.2	34.4	-1020.5	-123.8	2015.7	-89.4
(B1)	GIAO	-6.6	-975.5	-57.8	2006.2	-64.4
	Exptl.					-116 <sup>e</sup>
						-154.7 <sup>d</sup>
<b>SeMe<sub>2</sub></b>						
(A1)	3071.1	0	-1197.3	0	1873.8	0
(B1)	3070.4	0	-1406.0	0	1664.4	0
(A2)	3071.8	0	-1318.9	0	1752.9	0
(B2)	3070.4	0	-1376.5	0	1693.9	0
(A3)	3071.2	0	-1096.3	0	1974.9	0
(B3)	3070.4	0	-1140.6	0	1929.8	0
(A4)	3071.3	0	-1099.7	0	1971.6	0
(B4)	3070.5	0	-1138.2	0	1932.3	0
(A5)	3071.8	0	-1166.4	0	1905.4	0
(B5)	3070.6	0	-1144.3	0	1926.3	0
(B1)	GIAO	0	-1033.3	0	1941.8	0
	Exptl.				2069 <sup>b</sup>	0

<sup>a</sup> The reference compound of the chemical shift is  $\text{SeMe}_2$ .

<sup>b</sup> Liquid phase value [43].

<sup>c</sup> Gas phase value [43].

<sup>d</sup> Gas phase value [15].

<sup>e</sup> Liquid phase value [44].

### 3. Basis set dependence of the Se chemical shift

We first study the basis set dependence of the Se nuclear magnetic shielding constant and the Se chemical shift for the molecules  $\text{SeH}_2$ ,  $\text{MeSeH}$ , and  $\text{SeMe}_2$ . The basis sets employed in the calculations of the Se nuclear magnetic shielding constant  $\sigma$  and the chemical shift  $\delta$  are summarized in Table 1. For the Se atom, the augmented functions (FOBFs) are the p and d functions derived from the 4s and 4p basis functions. For C atom, the FOBFs are the p and d functions derived from the 2s and 2p functions, and for the H atom, they are the p functions derived from the 1s functions. We employ two different starting basis sets, (A1) and (B1), which are the same as those used in the previous paper [34] and in Ellis' paper [14,15], respectively. We add FOBFs successively in order to see their effects. In Fig. 1, we define the basis set number: the atom for which the basis set is augmented by the FOBFs is circled.

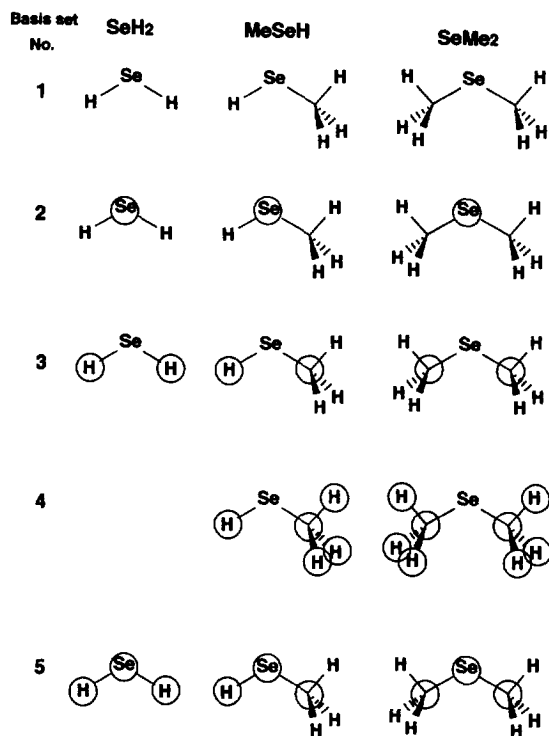


Fig. 1. Definition of the basis set number ( $n$ ) for the Se compounds. The circled atoms indicate that the FOBFs are augmented for the basis set centered on that atoms.

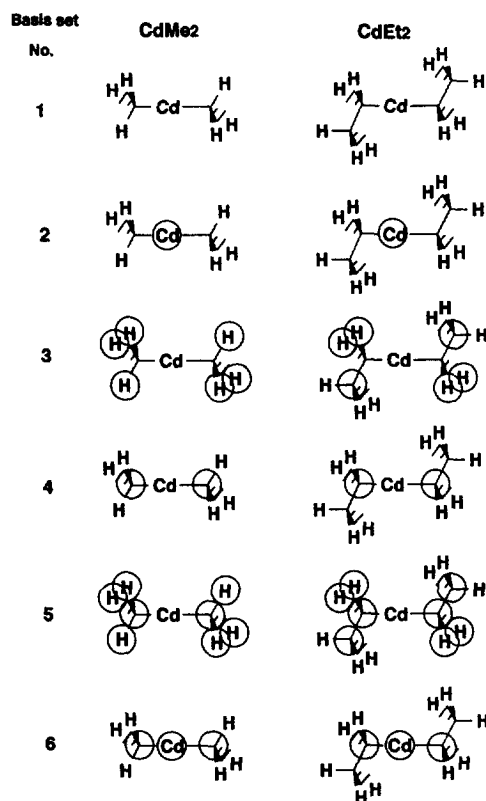


Fig. 2. Definition of the basis set number ( $n$ ) for the Cd compounds. The circled atoms indicate that the FOBFs are augmented for the basis set centered on that atoms.

The employed basis sets are defined completely by Table 1 and Fig. 1. The gauge origin is placed at the position of the Se atom.

Table 2 shows the calculated results for the Se shielding constant and Se chemical shift. It also shows the analysis into the diamagnetic and paramagnetic terms. We confirm that the diamagnetic term is basis set independent and the dependence originates from the paramagnetic term. Since the diamagnetic term is determined solely by the molecular structure around the resonance atom, as shown previously [33,35], this is reasonable. Figs. 3 and 4 show the basis set dependence of the Se magnetic shielding constant and the Se chemical shifts, respectively, for  $\text{SeH}_2$ ,  $\text{MeSeH}$ , and  $\text{SeMe}_2$ .

With the starting basis sets (A1) and (B1), the basis set dependence is large. In the shielding constant, the difference between (A1) and (B1) is 136

ppm for  $\text{SeH}_2$ , 159 ppm for  $\text{MeSeH}$ , and 209 ppm for  $\text{SeMe}_2$  as shown in Fig. 3. In the chemical shift, it is 73 ppm for  $\text{SeH}_2$  and 50 ppm for  $\text{MeSeH}$  as shown in Fig. 4. When we use the basis set (A2) and (B2), i.e., add the FOBFs only for the central atom, the basis set dependence is improved. It is only 4, 27, and 59 ppm, respectively, in the Se shielding constants of  $\text{SeH}_2$ ,  $\text{MeSeH}$ ,  $\text{SeMe}_2$ . However, the improvement for the chemical shift is small: the dependence is still 63 and 33 ppm for  $\text{SeH}_2$  and  $\text{MeSeH}$ , respectively. Further, the improvement in the shielding constant is not appropriate in comparison with the experimental values for  $\text{SeH}_2$  and

$\text{MeSeH}$ . Thus, the effect of the FOBFs for the central atom alone is small.

On the other hand, when we use the basis set (A3) and (B3), namely when the FOBFs are added to the atoms directly connected to Se, the basis set dependence is again improved. It is 9, 24, and 45 ppm for the Se shielding constants of  $\text{SeH}_2$ ,  $\text{MeSeH}$ , and  $\text{SeMe}_2$ , respectively, and 36 and 22 ppm for the Se chemical shifts of  $\text{SeH}_2$  and  $\text{MeSeH}$ . The results for the chemical shift are better than that obtained with the basis set (A2) and (B2). Moreover, the calculated shielding constants become closer to the experimental values observed for  $\text{SeH}_2$  and  $\text{SeMe}_2$ . When we

Table 3  
Breakdown into core and valence MO contributions to the paramagnetic shielding constants

	Core	(Shift)	Valence	(Shift)	$\sigma^{\text{para}}$ (total)
<b><math>\text{SeH}_2</math></b>					
(A1)	-21.7	-14.0	-862.7	-298.8	-884.5
(B1)	-63.9	-26.3	-955.8	-360.0	-1019.7
(A2)	-64.6	-28.2	-884.2	-341.9	-948.8
(B2)	-57.6	-27.8	-886.3	-404.8	-943.9
(A3)	-19.9	-19.5	-791.8	-265.1	-811.7
(B3)	-50.8	-31.8	-769.1	-288.9	-819.9
(A5)	-57.8	-30.6	-789.4	-288.6	-847.2
(B5)	-51.3	-28.9	-780.2	-283.9	-831.5
<b><math>\text{MeSeH}</math></b>					
(A1)	-29.3	-6.4	-1042.6	-125.0	-1071.9
(B1)	-78.0	-12.2	-1152.3	-163.5	-1230.3
(A2)	-80.8	-12.0	-1085.3	-140.8	-1166.1
(B2)	-73.3	-12.1	-1117.9	-173.2	-1191.2
(A3)	-30.3	-9.1	-956.2	-100.7	-986.5
(B3)	-68.3	-14.3	-941.0	-117.0	-1009.3
(A4)	-31.0	-9.8	-957.2	-101.7	-988.2
(B4)	-68.1	-14.2	-939.1	-116.8	-1007.2
(A5)	-75.1	-13.3	-964.4	-113.6	-1039.5
(B5)	-68.1	-12.1	-952.4	-111.7	-1020.5
<b><math>\text{SeMe}_2</math></b>					
(A1)	-35.7	0	-1161.6	0	-1197.3
(B1)	-90.2	0	-1315.8	0	-1406.0
(A2)	-92.8	0	-1226.1	0	-1318.9
(B2)	-85.4	0	-1291.1	0	-1376.5
(A3)	-39.4	0	-1056.9	0	-1096.3
(B3)	-82.6	0	-1058.0	0	-1140.6
(A4)	-40.8	0	-1058.9	0	-1099.7
(B4)	-82.3	0	-1055.9	0	-1138.2
(A5)	-88.4	0	-1078.0	0	-1166.4
(B5)	-80.2	0	-1064.1	0	-1144.3

add further the FOBFs to the atom second neighbor to Se (basis set (A4) and (B4)), the basis set dependence is improved further a little bit. However, the quality of the calculated results of the basis sets (A4) and (B4) is essentially the same as that of (A3) and (B3), showing that the ‘neighboring’ effects are almost saturated by adding the FOBFs only to the atoms directly connected to the Se atom. This observation is important for saving the number of the basis functions to be augmented.

When the FOBFs are augmented for both central atom and its neighboring atoms, the differences between the two basis set results are small, as shown in

the basis set (A5) and (B5). This is especially valid for the chemical shift, showing the stability of the effects for all the compounds studied here: the difference is only 7 ppm for both  $\text{SeH}_2$  and  $\text{MeSeH}$ . Namely, the calculated results are almost converged. In Figs. 3 and 4, and in Tables 2 and 3, we compare our results with the GIAO ones: our converged results are close to the GIAO ones. In particular, the converged values of the chemical shift are closer to the experimental values than the GIAO ones. However, our final results of the chemical shift are still smaller than the experimental values. This difference may be due to the electron correlation effect, since

Table 4  
AO contributions to the Se paramagnetic shielding constants

	Se						Ligand		$\sigma^{\text{para}}$ total
	p	(shift)	d	(shift)	total	p% <sup>a</sup>	H	Me	
<b>SeH<sub>2</sub></b>									
(A1)	-873.4	-272.5	-16.6	-9.7	-890.0	98.1	2.8		-884.5
(B1)	-1003.9	-349.8	-21.0	-8.1	-1025.0	98.0	2.6		-1019.7
(A2)	-935.8	-329.5	-19.6	-9.5	-955.4	97.9	3.3		-948.8
(B2)	-926.3	-396.7	-22.8	-7.8	-949.2	98.0	2.6		-943.9
(A3)	-790.7	-217.9	-18.5	-10.5	-809.2	97.7	-1.2		-811.7
(B3)	-796.6	-249.6	-19.4	-9.2	-816.0	97.6	-1.9		-819.9
(A5)	-823.7	-251.2	-23.4	-11.3	-847.0	97.2	-0.1		-847.2
(B5)	-807.4	-238.8	-20.0	-9.7	-827.2	97.6	-2.2		-831.5
<b>MeSeH</b>									
(A1)	-1041.6	-104.3	-20.6	-5.7	-1062.1	98.1	2.4	-12.2	-1071.9
(B1)	-1197.4	-156.3	-24.1	-5.0	-1221.5	98.0	2.6	-11.4	-1230.3
(A2)	-1132.6	-132.7	-23.5	-5.6	-1156.1	98.0	2.2	-12.2	-1166.1
(B2)	-1156.5	-166.5	-25.7	-4.9	-1182.2	97.8	2.6	-11.6	-1191.2
(A3)	-932.8	-75.8	-23.0	-6.0	-955.8	97.6	-1.6	-29.2	-986.5
(B3)	-950.8	-95.4	-23.2	-5.4	-974.1	97.6	-2.4	-32.8	-1009.3
(A4)	-931.9	-75.1	-23.0	-6.1	-954.9	97.6	-1.4	-31.9	-988.2
(B4)	-946.7	-92.8	-23.5	-5.7	-970.2	97.6	-2.1	-34.9	-1007.2
(A5)	-982.9	-92.0	-28.1	-6.6	-1011.0	97.2	0.2	-28.7	-1039.5
(B5)	-960.7	-85.5	-24.2	-5.5	-984.9	97.5	-2.4	-33.2	-1020.5
<b>SeMe<sub>2</sub></b>									
(A1)	-1145.9	0	-26.3	0	-1172.2	97.8		-12.6	-1197.3
(B1)	-1353.7	0	-29.1	0	-1382.8	97.9		-11.6	-1406.0
(A2)	-1265.3	0	-29.1	0	-1294.4	97.8		-12.2	-1318.9
(B2)	-1323.0	0	-30.6	0	-1353.6	97.7		-11.4	-1376.5
(A3)	-1008.6	0	-29.0	0	-1037.6	97.2		-29.3	-1096.3
(B3)	-1046.2	0	-28.6	0	-1074.8	97.3		-32.9	-1140.6
(A4)	-1007.0	0	-29.1	0	-1036.1	97.2		-31.8	-1099.7
(B4)	-1039.5	0	-29.2	0	-1068.7	97.3		-34.8	-1138.2
(A5)	-1074.9	0	-34.7	0	-1109.7	96.9		-28.3	-1166.4
(B5)	-1046.2	0	-29.7	0	-1076.0	97.2		-34.2	-1144.3

<sup>a</sup> The percentage fraction of the p contribution in the total Se contribution.

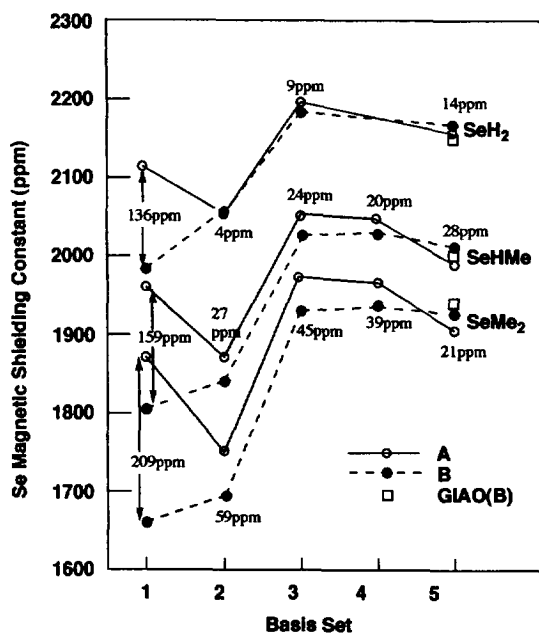


Fig. 3. Basis set dependence of the Se magnetic shielding constants for  $\text{SeH}_2$ ,  $\text{MeSeH}$ , and  $\text{SeMe}_2$ .

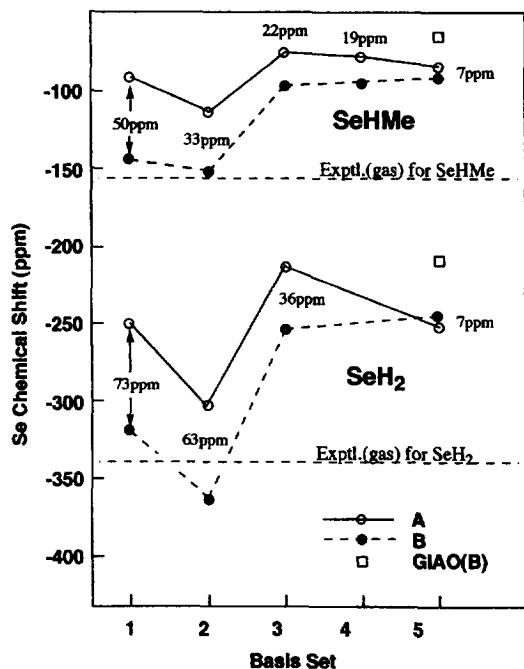


Fig. 4. Basis set dependence of the Se chemical shifts of  $\text{SeH}_2$ ,  $\text{MeSeH}$ , and  $\text{SeMe}_2$ .

Magyarfalvi and Pulay [36] have reported that the Se chemical shifts of  $\text{SeH}_2$  and  $\text{SeHMe}$  calculated by the MP2 method agree well with the experiments.

#### 4. Electronic mechanism of the Se chemical shift

In the previous study [34], we have shown that the Se chemical shift is due to the p-hole mechanism: the Se chemical shift is mainly attributed to the induced angular momentum due to the holes in the Se valence 4p atomic orbitals (AOs). Namely, lower field shifts occur when the p-hole density at the Se atom increases through the electron-donation to the neighbouring atoms. A more comprehensive review on the electronic mechanism of the metal chemical shifts studied in this laboratory is given in Ref. [23]. In Table 3 and Table 4, we show the molecular orbital (MO) contributions and the AO contributions to the paramagnetic term, respectively, calculated by the present various basis sets. We observe that the dominant origin of the Se chemical shift comes from the valence MO contribution and the p AO contribution in all the basis sets. Actually, as shown in Table 4, the percentage fraction of the p-contribution in the total Se contribution is constantly 97–98, and the Se chemical shifts decrease when the methyl group is replaced with H. Therefore the fact that the Se chemical shift is due to the p-hole mechanism is entirely basis set independent. We note that the contribution of the FOBFs to the electronic mechanism is small: they only work to improve the larger p, d, and ligand contributions. Thus, our analyses on the mechanism of the metal chemical shifts [22,23,34] are completely reliable.

#### 5. Basis set dependence of the Cd chemical shift

Next, we study the basis set dependence of the Cd nuclear magnetic shielding constant and the Cd chemical shift for the compounds  $\text{CdMe}_2$  and  $\text{CdEt}_2$ . The basis sets employed for  $\text{CdMe}_2$  and  $\text{CdEt}_2$  are summarized in Table 1 and Fig. 2. For the Cd atom, the augmented functions (FOBFs) are the p, d, and f functions derived from the 5s, 5p, and 4d functions, respectively. For the C atom, the FOBFs are the p and d functions derived from the 2s and 2p func-



tions, and for H atom, they are the p functions derived from the 1s functions. We use five different starting basis sets, (A1), (C1), (D1), (E1), and (F1) for CdMe<sub>2</sub>, and six ones, (A1), (B1), (C1), (D1), (E1), and (F1) for CdEt<sub>2</sub>. The basis set (C1) for CdMe<sub>2</sub> and (B1) for CdEt<sub>2</sub> are the same as those used in the previous paper [33]. The basis sets (D1), (E1), and (F1) are the same as those used by Ellis et al. [14,15]. Among the basis (A)–(C), the Cd basis is common, while, among the basis (D)–(F), the ligand basis is common. Ellis et al. also employed the basis in which the valence p functions (p-polarization functions) were not added to the Cd atom. This basis is, however, physically almost nonsense because it is something like to calculate the chemical bond involving Li atom without including its 2p orbital and furthermore because the Cd chemical shift is due to the p-mechanism. Similarly, it is out of date to use the minimal basis sets for the ligand atoms. Thus, we exclude such basis sets. In Fig. 2 the basis set number is defined and the atom for which the basis set is augmented by the FOBFs is circled. The gauge origin is placed at the position of the Cd atom.

In Tables 5 and 6, we show the calculated Cd nuclear magnetic shielding constants of CdMe<sub>2</sub> and CdEt<sub>2</sub>, respectively, and the analysis into the diamagnetic and paramagnetic terms. The diamagnetic term  $\sigma^{\text{dia}}$  is basis set independent and the paramagnetic term  $\sigma^{\text{para}}$  causes the dependence. Since  $\sigma^{\text{dia}}$  depends only on the structural factors of molecules, as shown previously [22], the independence is natural.

At the stage of the initial starting basis set (1), the results are largely basis set dependent as Ellis et al. pointed out. We define the basis set dependence by the range of the calculated magnetic shielding constant and the chemical shift for the different basis set, and this range is shown in Tables 5 and 6. It is 361 ppm for CdMe<sub>2</sub>, 345 ppm for CdEt<sub>2</sub>, and that for chemical shift is 32 ppm in the initial basis set (1). We now apply our method successively to show the individual effect.

The basis set (A1) for CdMe<sub>2</sub>, and (A1) and (B1) for CdEt<sub>2</sub> are the so-called ‘locally dense’ basis sets named by Chesnut and Moore [37]. The ‘locally dense’ basis set involves a large number of basis functions for the resonant atom of interest in the molecule, that is Cd atom in this case, while other

Table 5  
Cd shielding constant  $\sigma$  and the diamagnetic and paramagnetic contribution to  $\sigma$  for CdMe<sub>2</sub> calculated by different basis sets

	$\sigma^{\text{dia}}$	$\sigma^{\text{para}}$	$\sigma^{\text{total}}$
(A1)	4850.7	-1077.3	3773.4
(C1)	4850.8	-1089.9	3760.9
(D1)	4869.1	-848.3	4020.8
(E1)	4868.9	-904.7	3964.2
(F1)	4869.4	-1210.0	3659.4
width			361.4
(A2)	4846.2	-1089.6	3756.6
(C2)	4846.3	-1125.1	3721.2
(D2)	4869.4	-1207.2	3662.2
(E2)	4869.3	-1221.5	3647.8
(F2)	4869.4	-1233.0	3636.4
width			120.2
(A3)	4850.8	-1148.9	3701.9
(C3)	4850.7	-1136.8	3713.9
(D3)	4869.2	-960.6	3908.6
(E3)	4869.1	-981.7	3887.4
(F3)	4869.4	-1250.3	3619.1
width			289.5
(A4)	4850.6	-1140.7	3709.9
(C4)	4850.6	-1143.1	3707.5
(D4)	4869.2	-1080.8	3788.4
(E4)	4869.1	-1090.3	3778.8
(F4)	4869.4	-1304.3	3565.1
width			223.3
(A5)	4850.6	-1150.9	3699.7
(C5)	4850.5	-1147.9	3702.6
(D5)	4869.2	-1120.0	3749.2
(E5)	4869.1	-1126.6	3742.5
(A6)	4846.2	-1237.0	3609.2
(C6)	4846.2	-1244.3	3601.9
(D6)	4869.4	-1351.2	3518.2
(E6)	4869.3	-1364.8	3504.5
(F6)	4869.4	-1339.2	3530.2
width			104.7
(E1)	GIAO 4801.9	-1144.1	3657.7
(E1)	LORG 4771.9	-931.9	3840.0

atoms are represented by smaller basis sets. Since the chemical shift is sensitive to the electron distribution near the resonant nucleus, they expected that the

Table 6

Cd shielding constant  $\sigma$ , Cd chemical shift  $\delta$ , and the diamagnetic and paramagnetic contribution to  $\sigma$  for CdEt<sub>2</sub> calculated by different basis sets

		$\sigma^{\text{dia}}$	Shift	$\sigma^{\text{para}}$	Shift	$\sigma^{\text{total}}$	Shift $\delta^{\text{a}}$
(A1)		4896.3	-45.6	-1056.0	-21.3	3840.3	-66.9
(B1)		4896.3	-45.5	-1038.4	-51.5	3857.9	-97.0
(C1)		4896.4	-45.6	-1065.4	-24.5	3831.0	-70.1
(D1)		4914.8	-45.7	-814.8	-33.5	4100.0	-79.2
(E1)		4914.6	-45.7	-851.4	-53.5	4063.2	-99.0
(F1)		4915.1	-45.7	-1160.4	-47.1	3754.7	-95.3
width						345.3	32.1
(A2)		4891.8	-45.6	-1064.8	-24.8	3827.0	-70.4
(B2)		4891.8	-45.6	-1062.6	-27.0	3829.2	-72.6
(C2)		4891.9	-45.6	-1093.6	-31.5	3798.3	-77.1
(D2)		4915.1	-45.7	-1173.6	-33.6	3741.6	-79.4
(E2)		4915.0	-45.7	-1184.5	-37.0	3730.5	-82.7
(F2)		4915.1	-45.7	-1193.1	-39.9	3722.0	-85.6
width						107.2	15.2
(A3)		4896.4	-45.6	-1120.2	-28.7	3776.2	-74.3
(B3)		4896.2	-45.5	-1099.5	-37.3	3796.7	-82.8
(C3)		4896.3	-45.6	-1109.4	-27.4	3786.9	-73.0
(D3)		4914.9	-45.7	-980.0	19.4	3934.9	-26.3
(E3)		4914.8	-45.7	-991.7	10.0	3923.1	-35.7
(F3)		4915.1	-45.7	-1222.0	-28.3	3693.1	-74.0
width						241.8	56.5
(A4)		4896.2	-45.6	-1115.4	-25.3	3780.8	-70.9
(B4)		4896.1	-45.5	-1111.7	-31.4	3784.4	-76.9
(C4)		4896.2	-45.6	-1115.9	-27.2	3780.3	-72.8
(D4)		4914.9	-45.7	-1069.1	-11.7	3845.8	-57.4
(E4)		4914.8	-45.7	-1073.5	-16.8	3841.3	-62.5
(F4)		4915.1	-45.7	-1257.2	-47.1	3657.9	-92.8
width						187.9	35.4
(A5)		4896.2	-45.6	-1136.0	-14.9	3760.2	-60.5
(B5)		4896.1	-45.6	-1122.7	-25.2	3773.4	-70.8
(C5)		4896.1	-45.6	-1131.5	-16.4	3764.6	-62.0
(A6)		4891.9	-45.6	-1200.9	-36.1	3691.0	-81.8
(B6)		4891.8	-45.6	-1189.2	-47.8	3702.6	-93.4
(C6)		4891.9	-45.7	-1209.5	-34.8	3682.4	-81.2
(D6)		4915.1	-45.7	-1307.6	-43.6	3607.5	-89.3
(E6)		4915.0	-45.7	-1320.2	-44.6	3594.8	-90.3
(F6)		4915.1	-45.7	-1298.4	-40.8	3616.7	-86.5
width						107.8	12.2
(E1)	GIAO	4802.3	-0.4	-1075.7	-68.5	3726.6	-68.9
(E1)	LORG	4780.5	-8.6	-868.5	-63.4	3912.0	-72.0
	Exptl.						-99.7 <sup>b</sup>
							-142.6 <sup>c</sup>

<sup>a</sup> The reference compound of the chemical shift is CdMe<sub>2</sub>.<sup>b</sup> Neat phase value.<sup>c</sup> Gas phase value.

satisfactory values would be obtained from these ‘locally dense’ basis sets. However, the calculated results of the chemical shift do not agree with the experimental values.

When we use the basis set (2), which is augmented by the FOBFs only for the central atom, the basis set dependence is certainly improved: the dependence is 120 and 107 ppm for the shielding constants of  $\text{CdMe}_2$  and  $\text{CdEt}_2$  and it is 15 ppm for the chemical shift of  $\text{CdEt}_2$ . The chemical shift is close to the final result as shown below, but the shielding constants are still about 100 ppm larger than the final values. We note that the basis set (2) is certainly a ‘locally dense’ basis set. If it is defined by the present theoretical method, it gives fairly good results.

The basis set (3) is chosen for testing the effect of the FOBFs distant from the resonant atom: the FOBFs are added only to the second neighbor atoms from Cd. As expected, the improvement of the basis set dependence is small. The shielding constant is somewhat improved, but the chemical shift is not. Thus, as in the Se case, we may neglect the FOBFs for the atoms second neighbor from the central atom.

With the basis set (4), we examine the effect of the FOBFs on the atoms directly connected to the Cd atom. The basis set dependence are certainly improved, especially when we exclude the basis set (F4) which include the f-basis functions from the beginning. When the FOBFs are added to both first and second neighbor atoms, in the basis set (5), the results are essentially equivalent to the ones of basis

Table 7  
Breakdown into core and valence MO contributions to the paramagnetic shielding constants

	$\text{CdMe}_2$			$\text{CdEt}_2$				
	core	valence	total	core	(shift)	valence	(shift)	total
(A1)	-41.7	-1035.6	-1077.3	-44.5	2.8	-1011.5	-24.1	-1056.0
(B1)				-43.2	1.5	-995.2	-40.4	-1038.4
(C1)	-43.4	-1046.5	-1089.9	-45.9	2.5	-1019.5	-27.0	-1065.4
(D1)	-74.0	-774.3	-848.3	-71.8	-2.2	-743.0	-31.3	-814.8
(E1)	-80.7	-824.0	-904.7	-76.5	-4.2	-774.9	-49.1	-851.4
(F1)	-115.6	-1094.4	-1210.0	-111.1	-4.5	-1049.3	-45.1	-1160.4
(A2)	-107.7	-981.9	-1089.6	-106.9	-0.8	-957.9	-24.0	-1064.8
(B2)				-105.7	-2.0	-956.9	-25.0	-1062.6
(C2)	-110.6	-1014.5	-1125.1	-109.0	-1.6	-984.6	-29.9	-1093.6
(D2)	-120.0	-1087.2	-1207.2	-116.7	-3.3	-1056.9	-30.3	-1173.6
(E2)	-122.2	-1099.3	-1221.5	-118.7	-3.5	-1065.8	-33.5	-1184.5
(F2)	-127.6	-1105.4	-1233.0	-123.3	-4.3	-1069.8	-35.6	-1193.1
(A4)	-54.6	-1086.1	-1140.7	-56.4	1.8	-1059.0	-27.1	-1115.4
(B4)				-55.2	0.6	-1056.5	-29.6	-1111.7
(C4)	-55.0	-1088.1	-1143.1	-56.9	1.9	-1059.0	-29.1	-1115.9
(D4)	-106.0	-974.8	-1080.8	-105.1	-0.9	-964.0	-10.8	-1069.1
(E4)	-107.6	-982.7	-1090.3	-106.2	-1.4	-967.3	-15.4	-1073.5
(F4)	-134.4	-1169.9	-1304.3	-130.1	-4.3	-1127.1	-42.8	-1257.2
(A6)	-124.0	-1113.0	-1237.0	-121.8	-2.2	-1079.1	-33.9	-1200.9
(B6)				-120.5	-3.5	-1068.7	-44.3	-1189.2
(C6)	-124.9	-1119.4	-1244.3	-122.5	-2.4	-1087.0	-32.4	-1209.5
(D6)	-142.4	-1208.8	-1351.2	-138.0	-4.4	-1169.6	-39.2	-1307.6
(E6)	-142.6	-1222.2	-1364.8	-138.2	-4.4	-1182.0	-40.2	-1320.2
(F6)	-144.0	-1195.2	-1339.2	-139.2	-4.5	-1158.9	-36.3	-1298.4

set (4), showing that the ‘neighboring’ effects are almost saturated only by adding the FOBFs on the atoms directly connected to the central atom. Similar

result was also obtained for the Se case for MeSeH and SeMe<sub>2</sub>. This observation is important for saving the number of the basis functions employed. Namely,

Table 8  
AO contributions to the Cd paramagnetic shielding constants

	Cd						Ligand		$\sigma^{\text{para}}$	
	p	(shift) <sup>a</sup>	d	(shift) <sup>a</sup>	f	total	p% <sup>b</sup>	Me	Et	total
<b>CdMe<sub>2</sub></b>										
(A1)	-991.8	0	-60.9	0		-1052.7	94.2	-12.3		-1077.3
(C1)	-992.0	0	-68.1	0		-1060.1	93.6	-14.9		-1089.9
(D1)	-734.6	0	-87.8	0		-822.4	89.3	-12.9		-848.3
(E1)	-785.9	0	-90.4	0		-876.3	89.7	-14.2		-904.7
(F1)	-1102.2	0	-77.3	0	1.7	-1177.8	93.6	-16.1		-1210.0
(A2)	-991.1	0	-73.9	0	1.3	-1063.7	93.2	-13.0		-1089.6
(C2)	-1018.7	0	-76.6	0	1.4	-1093.9	93.1	-15.6		-1125.1
(D2)	-1080.9	0	-95.4	0	-1.2	-1177.6	91.8	-14.8		-1207.2
(E2)	-1102.8	0	-89.7	0	0.8	-1191.7	92.5	-14.9		-1221.5
(F2)	-1115.9	0	-86.5	0	1.6	-1200.8	92.9	-16.1		-1233.0
(A4)	-1019.0	0	-63.3	0		-1082.3	94.2	-29.2		-1140.7
(C4)	-1022.0	0	-62.5	0		-1084.5	94.2	-29.3		-1143.1
(D4)	-933.1	0	-84.8	0		-1017.9	91.7	-31.5		-1080.8
(E4)	-951.3	0	-76.1	0		-1027.4	92.6	-31.4		-1090.3
(F4)	-1178.1	0	-66.0	0	3.0	-1241.1	94.9	-31.6		-1304.3
(A6)	-1118.9	0	-61.9	0	1.7	-1179.1	94.9	-29.0		-1237.0
(C6)	-1125.9	0	-61.8	0	1.6	-1186.1	94.9	-29.1		-1244.3
(D6)	-1200.2	0	-86.8	0	-1.5	-1288.6	93.1	-31.3		-1351.2
(E6)	-1227.7	0	-76.2	0	2.1	-1301.7	94.3	-31.6		-1364.8
(F6)	-1204.1	0	-76.0	0	2.0	-1278.0	94.2	-30.6		-1339.2
<b>CdEt<sub>2</sub></b>										
(A1)	-940.8	-51.0	-69.3	8.4		-1010.0	93.1		-23.0	-1056.0
(B1)	-922.9	-68.9	-74.5	13.6		-997.4	92.5		-20.5	-1038.4
(C1)	-939.0	-53.0	-72.6	4.5		-1011.6	92.8		-26.9	-1065.4
(D1)	-671.5	-63.1	-95.0	7.2		-766.5	87.6		-24.1	-814.8
(E1)	-711.4	-74.5	-89.3	-1.1		-800.7	88.8		-25.3	-851.4
(F1)	-1032.3	-69.9	-75.4	-1.9	0.9	-1106.7	93.3		-26.9	-1160.4
(A2)	-942.2	-48.9	-74.9	1.0	1.1	-1016.0	92.7		-24.4	-1064.8
(B2)	-941.6	-49.5	-77.9	4.0	1.0	-1018.5	92.4		-22.1	-1062.6
(C2)	-963.4	-55.3	-75.5	-1.1	1.2	-1037.7	92.8		-28.0	-1093.6
(D2)	-1027.6	-53.3	-92.8	-2.6	-0.9	-1121.4	91.6		-26.1	-1173.6
(E2)	-1044.2	-58.6	-88.0	-1.7	0.4	-1131.7	92.3		-26.4	-1184.5
(F2)	-1054.5	-61.4	-85.2	-1.3	1.0	-1138.7	92.6		-27.2	-1193.1
(A4)	-970.0	-49.0	-66.1	2.8		-1036.1	93.6		-39.6	-1115.4
(B4)	-972.1	-46.9	-65.7	2.4		-1037.8	93.7		-37.0	-1111.7
(C4)	-966.6	-55.4	-65.6	3.1		-1032.2	93.6		-41.9	-1115.9
(D4)	-899.7	-33.4	-83.5	-1.3		-983.2	91.5		-42.9	-1069.1
(E4)	-913.7	-37.6	-73.7	-2.4		-987.4	92.5		-43.1	-1073.5
(F4)	-1107.7	-70.4	-64.9	-1.1	3.6	-1169.0	94.8		-44.1	-1257.2

Table 8 (continued)

	Cd							Ligand		$\sigma^{\text{para}}$
	p	(shift) <sup>a</sup>	d	(shift) <sup>a</sup>	f	total	p% <sup>b</sup>	Me	Et	total
(A6)	-1059.1	-59.8	-63.6	1.7	1.7	-1121.0	94.5		-40.0	-1200.9
(B6)	-1051.7	-67.2	-64.1	2.2	1.3	-1114.6	94.4		-37.3	-1189.2
(C6)	-1063.9	-62.0	-63.2	1.4	1.5	-1125.5	94.5		-42.0	-1209.5
(D6)	-1135.3	-64.9	-84.5	-2.3	-1.5	-1221.3	93.0		-43.2	-1307.6
(E6)	-1161.2	-66.5	-74.6	-1.6	2.0	-1233.8	94.1		-43.2	-1320.2
(F6)	-1140.2	-63.9	-74.5	-1.5	2.5	-1212.3	94.1		-43.1	-1298.4

<sup>a</sup> CdMe<sub>2</sub> is a reference molecule for (shift).

<sup>b</sup> The percentage fraction of the p contribution in the total Cd contribution.

for the neighboring atoms, the FOBFs should be added only to the atoms directly connected to the resonant atom.

The basis set (6) involves the FOBFs on the Cd atom as well as on the atoms directly connected to the Cd atom. The basis set dependence is smallest within the present examinations. It is 104 and 108 ppm for the shielding constants of CdMe<sub>2</sub> and CdEt<sub>2</sub> and is only 12 ppm for the chemical shift of CdEt<sub>2</sub>. We give, in Tables 5 and 6, the GIAO and LORG results calculated with the basis (E1). For the magnetic shielding constant, the GIAO result is closer to

our final result than the LORG one. For the chemical shift for which the experimental value exists, our final result (with basis set E) is closer to the experimental value than the GIAO and LORG results. This fact is understood as reflecting that our method improves not only the basis-set and origin dependences but also the quality of the wave function itself.

The chemical shift calculated with the basis set (6) is still smaller than the experimental (gas phase) value. This difference between the calculated and experimental values is probably due to the electron

Table 9  
Comparison with other results for CdMe<sub>2</sub> and CdEt<sub>2</sub>

	Other results				FP (our results)					
	LORG <sup>a</sup>		CHF <sup>a</sup>		level (1) <sup>b</sup>		level (4) <sup>c</sup>		level (6) <sup>d</sup>	
	$\sigma$	$\delta$	$\sigma$	$\delta$	$\sigma$	$\delta$	$\sigma$	$\delta$	$\sigma$	$\delta$
CdMe <sub>2</sub>										
MIDI-4p2	3870.9		3927.4		3955.5		3666.1		3380.4	
MIDI-4p2d2	3811.4		3867.5		3895.2		3657.4		3367.1	
MIDI-4p2d2f2	3513.3		3536.7		3533.4		3435.3		3397.5	
basis-set dependence <sup>e</sup>	357.6		390.7		422.1		230.8		30.4	
CdEt <sub>2</sub>										
MIDI-4p2	3919.3	-48.4	3993.8	-66.4	4049.8	-94.3	3789.8	-123.7	3496.6	-116.2
MIDI-4p2d2	3875.7	-64.3	3949.5	-82.0	4002.0	-106.9	3781.7	-124.3	3489.0	-121.9
MIDI-4p2d2f2	3594.9	-81.6	3638.4	-101.7	3638.3	-94.9	3549.4	-114.1	3510.6	-113.1
basis-set dependence <sup>e</sup>	324.4	33.2	355.4	35.3	411.5	12.6	240.4	10.2	21.6	8.8

<sup>a</sup> Refs. [14] and [15].

<sup>b</sup> The original basis set.

<sup>c</sup> The p and d functions derived from the 2s and 2p basis functions of C atom are augmented to the original function at the atom next to Cd atom.

<sup>d</sup> The p and d functions derived from the 2s and 2p basis functions of C atom are augmented to the original function at C atom next to Cd atom, and the p, d, and f functions derived from the 5s, 5p, and 4d basis functions of Cd atom are augmented at Cd atom.

<sup>e</sup> The difference between the maximum and the minimum.

correlation and relativistic effects. The latter effect should be important particularly for heavier atoms like W, Pt, Hg atoms [22].

## 6. Electronic mechanism of the Cd chemical shift

In the previous study [22,33], we have evidenced that the Cd chemical shift is due to the valence p-electron mechanism: the Cd chemical shift reflects the angular momentum of the Cd valence p electrons donated from the ligand. In Tables 7 and 8, we show respectively the MO and AO contributions to the paramagnetic term. As shown from the columns headed by '(shift)' in Tables 7 and 8, the Cd chemical shift is determined by the valence MO contributions and the p AO contributions, and this electronic mechanism is independent of the basis set used for the calculations. The percentage fraction of the p-contribution in the total Cd contribution lies within 88–95 for all the calculations as shown in Table 8. The AO contributions of the added FOBFs themselves are negligibly small, as shown in the d and f AO contributions in Table 8, though the addition of the FOBFs surely makes large effects. Thus, as in the Se chemical shift studied in the previous section, the fact that the valence p-electron mechanism is the major mechanism of the Cd chemical shift is basis set independent.

## 7. Comparison with other results

Ellis et al. calculated the Cd shielding constant and the chemical shift of CdMe<sub>2</sub> and CdEt<sub>2</sub> with the CHF and the LORG methods [14,15]. In Table 9, we show the comparison of our results with the results calculated by Ellis et al. The geometries used for this calculation are the same as the ones optimized by Ellis et al. and are different from those used in the above systematic calculations. The results calculated by Ellis et al. are strongly basis set dependent for both the LORG and the CHF methods, as Ellis et al. pointed out. When the FOBFs are not added, our FPT method using the basis set of level (1) gives the results similar to the CHF results [1]. If we augment the FOBFs for the Cd atom and its neighboring atoms with the basis set of level (6), the results are almost basis set independent: the dependence is only 30.4 and 21.6 ppm for the shielding constants of CdMe<sub>2</sub> and CdEt<sub>2</sub> and only 8.8 ppm for the chemical shift of CdEt<sub>2</sub>. Thus, it is proved that our method is effective for magnetic property calculations.

## 8. Gauge origin dependence of the magnetic shielding constants

We next investigate the gauge origin dependence of the Se and Cd magnetic shielding constants. As an

Table 10  
Gauge origin dependence of the Se shielding constant of SeH<sub>2</sub>

Gauge origin	$\sigma^{\text{dia}}$		$\sigma^{\text{para}}$		$\sigma^{\text{total}}$		$\sigma(\text{H}) - \sigma(\text{Se})^{\text{a}}$
	Se	H	Se	H	Se	H	
(A1)	3003.2	2998.3	-884.5	-941.9	2118.7	2056.4	-62.3
(A2)	3003.8	2998.9	-948.8	-917.4	2055.0	2081.5	(26.5)
(A3)	3003.3	2998.3	-811.7	-898.8	2191.6	2099.5	(-92.1)
(A5)	3003.9	2998.8	-847.2	-857.2	2156.7	2141.6	-15.7
(B1)	3002.4	2997.5	-1019.7	-950.9	1982.7	2046.6	63.9
(B2)	3002.4	2997.5	-943.9	-929.0	2058.5	2068.5	(10.0)
(B3)	3002.4	2997.7	-819.9	-824.1	2182.5	2173.6	(-8.9)
(B5)	3002.5	2997.6	-831.5	-849.1	2171.0	2148.6	-22.4
(B1)	GIAO	2987.1	-836.1		2150.9		
	Exptl.				2280		

<sup>a</sup>  $\sigma(\text{H})$  denotes the total magnetic shielding constant when the gauge origin is placed on H atom,  $\sigma(\text{Se})$  denotes the one when the gauge origin is on Se atom.

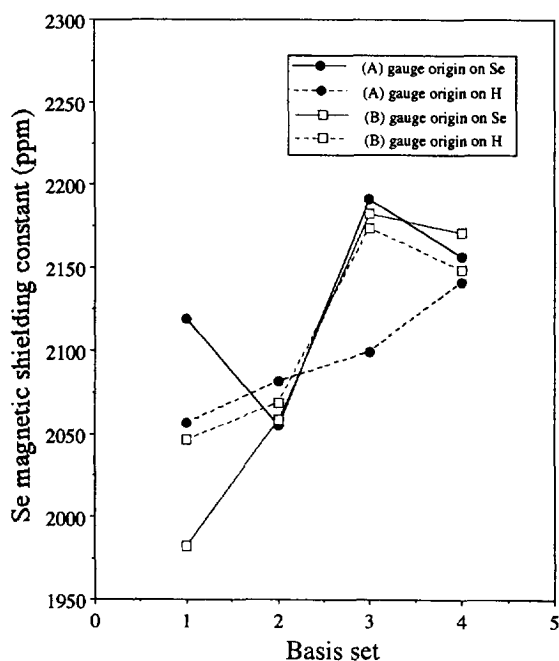


Fig. 5. Gauge origin dependence of the Se magnetic shielding constant of  $\text{SeH}_2$ .

example, we show the gauge origin dependence of the calculated magnetic shielding constant of  $\text{SeH}_2$ . Table 10 and Fig. 5 shows the results obtained by putting the gauge origin either at Se or at H atom for various basis sets. As shown in Table 10, the diamagnetic term is almost gauge origin independent, and it arises from the paramagnetic term. For the basis set (A1) and (B1) the gauge origin dependence is both about 60 ppm. When the basis sets (2) and (3) are used, the atom which basis set is augmented by the FOBFs is either identical with, or different from the gauge origin. Therefore, the origin dependence is not improved especially in the basis set (A). The basis sets (B2) and (B3) remarkably improve the origin dependence. This is probably due to the larger flexibility of these basis, and probably to the existence of the diffuse p functions on selenium at the stage of the (B1) basis. When we use the basis set (5) in which both the Se and H basis sets are augmented by the FOBFs, the origin dependence becomes small, 15.7 ppm for the basis (A5) and 22.4 ppm for the basis (B5). Previously, we have confirmed such gauge origin independence for the results of several hydride molecules calculated by the

present method [19]. This is natural since our method is proposed based on the consideration on the gauge invariance property of the wave function.

We next consider the gauge origin dependence for the Cd complexes  $\text{CdMe}_2$  and  $\text{CdEt}_2$ . Fortunately or unfortunately, the shielding constants of these molecules are gauge origin independent because of the molecular symmetry. The geometries of  $\text{CdMe}_2$  and  $\text{CdEt}_2$  are  $D_{3d}$  and  $C_{2h}$ , respectively, and in these geometries the translations and rotations belong to different irreducible representations: Cd which is the observed nucleus is at the position of the inversion center. Therefore, the gauge transformation and the angular momentum operation do not mix in the first and second-order perturbation equation of the magnetic shielding constant. Note however that if the observed nucleus is not at the inversion center (e.g. the carbon shielding in the above example and the N shielding of  $\text{N}_2$  [38]), the calculated shielding constants are gauge dependent. Note further that such symmetry invariance does not mean that the FOBFs are unnecessary. Actually, for calculating reliable shielding constants for  $\text{CH}_4$  and  $\text{SiH}_4$ , for example, the FOBFs are very important as reported previously [19].

## 9. Concluding remarks

In this paper, we have applied our method for improving the basis set dependence and the gauge origin dependence of the nuclear magnetic shielding constants and the chemical shifts of the Se and Cd compounds,  $\text{SeH}_2$ ,  $\text{MeSeH}$ ,  $\text{SeMe}_2$ ,  $\text{CdMe}_2$ , and  $\text{CdEt}_2$ , within the framework of the ab initio Hartree–Fock/finite perturbation method. The results are as follows:

(1) When the original basis set is augmented by the first-order higher angular momentum basis functions (FOBFs), the basis set dependence and the gauge origin dependence are much improved, as far as the original basis is not too crude. The FOBFs are necessary only for the valence AOs of the resonant atom and the atoms directly bonded to it. The basis set dependence and the gauge origin dependence vanish when the basis set is complete, and present method seems to be an effective method of improv-

ing the basis set for magnetic property calculations along this line.

(2) Probably, a defect of the present method is an increase of the number of the basis functions. However, the added FOBFs work to improve the quality of the wave function particularly on the magnetic properties so that the quality of the calculated shielding constants should be improved. Furthermore, the original basis and the FOBFs form a shell structure so that there are several methods for accelerating the integral evaluations in such cases (Rys polynomial method [39], Pople's algorithm [40], Obara's algorithm [41], and Davidson's method [42], etc.)

(3) Since the FOBFs are included in the variational space, the calculated wave functions are more improved than those of the GIAO method. Therefore, the quality of the calculated results is better, particularly for atoms heavier than the first row ones.

(4) A very important result of this study is that the mechanisms of the nuclear magnetic shielding constants and the chemical shifts are basis set independent. The fact that the p-mechanism is the major mechanism for the Se and Cd chemical shifts (the p-hole mechanism for the former and the p-electron mechanism for the latter which therefore give lower field shift as the p-hole (or p-electron) density increases) is an approximation-invariant result which is independent on the quality of the basis set used. The contributions of the FOBFs themselves are small and the FOBFs work to modify the major terms. This should also be valid for all the mechanisms of the metal chemical shifts studied in our laboratory: a close parallelism with experiments is a basis of this belief. A progress report up to 1993 on the study of the electronic mechanism of the metal chemical shifts carried out in this laboratory was given in Ref. [23].

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