Gauge-invariant basis sets for magnetic property calculations

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The use of augmented basis sets of the form, $\{\chi, \ r_t\chi, \ r_t r_u\chi, \ ...\}$ $(r_t, \ r_u = x, y, z)$, is proposed for calculating magnetic properties which are almost gauge-origin independent. It is derived from Epstein's theorem which states the sufficient condition for unitary invariance. Test calculations using the coupled-Hartree–Fock/finite perturbation method show that the augmented sets correctly reduce the origin dependence of magnetic shielding constants, and that the results agree well with the experiment. Through systematic modifications of the basis set, a practical procedure in choosing basis functions to be added is suggested. © *1995 American Institute of Physics.*

I. INTRODUCTION

In this paper, we investigate how basis sets should be improved in order for the conventional coupled Hartree–Fock (CHF) (Ref. 1) or finite perturbation (FP) (Ref. 2) method to give accurate and gauge-independent results in calculating magnetic properties of molecules.

Nowadays, various methods[1–5] are available for calculating magnetic properties of molecules such as magnetic susceptibility and nuclear magnetic shielding constant. As is well known, there is one obstacle known as the gauge invariance problem in these calculations.[6–9] Since, in the CHF/FP theory, the invariance can be achieved only when one uses a complete basis set,[1] it is difficult to exactly insure it in practical calculations.

In order to cope with the problem, there are two strategies at present. One is the use of the elaborate basis sets[10,11] in the CHF/FP method.[12] In these calculations, basis sets are carefully chosen following the conventional procedure for modifying basis sets. The choice seems to be based on an experience rather than on some definite theoretical reasons. Sadlej[13] and Yaris[14] proposed the use of the best origin in a predetermined basis set space. The other is the use of the basis functions or orbitals by which the calculated results are formally or approximately independent of the position of the gauge origin. In the gauge invariant (or including) atomic orbital (GIAO) method,[3,15] the field dependent orbitals, originally proposed by London,[16] are used,

$$\phi_\nu = \exp(-i\lambda_\nu)\chi_\nu, \tag{1}$$

where

$$\lambda_\nu = \tfrac{1}{2}\,\mathbf{B}\times(\mathbf{R}_\nu - \mathbf{d})\cdot\mathbf{r}, \tag{2}$$

and χ_ν, $\mathbf{B}$, $\mathbf{R}_\nu$, and $\mathbf{d}$ are the conventional basis function (BF), external magnetic field, the center of the BF, and the gauge origin, respectively. Pulay *et al.*[17] recently gave an efficient scheme for its implementation. Kutzelnigg,[4,9] and Hansen and Bouman[5] proposed the individual gauge for localized orbital (IGLO) and local origin/local orbital (LORG)

methods, respectively, in which different gauge origins are used for different localized orbitals. It is believed that these methods give better results even with the basis sets of moderate size, compared with the CHF/FP method. However, the IGLO and LORG methods have a problem of indistinguishability of electrons as originally noted by Kutzelnigg.[4] In the GIAO method, the gauge invariance is, in some sense, artificial as criticized by Epstein.[7,8,18,19]

Recently, there are some developments in investigating electron correlation effects on magnetic properties. Gauss[20] and Fukui *et al.*[21] independently developed the GIAO version of the Møller–Plesset perturbation theory. Bouman and Hansen[22] suggested the localized orbital version of the second order polarization propagator approximation (SOPPA). As approaches related to the CHF/FP methods, the studies due to Daborn and Handy,[23] and Iwai and Saika[24] in early 1980's are remarkable. However, they also seem to have the gauge-dependence problem due to the insufficient quality of the basis sets. The lack of the underlying principle for a correct choice of the basis set is a source of the problem in the CHF/FP and related methods.

The gauge origin problem in the CHF/FP calculations is a critical test for the quality of the basis set. Thus, it is interesting to know what is a desired quality which a set should have for reducing the gauge origin dependence. In this paper, we propose a new method for systematically improving basis sets such that the magnetic properties calculated by the CHF/FP method are nearly gauge independent, and further that the calculated values are improved in comparison with the experimental values. This method is similar to that proposed by Nakatsuji *et al.* for calculating the Hellmann–Feynman force.[25]

The organization of this paper is as follows. In Sec. II, our new method is explained in some detail. Following the computational details given in Sec. III, the numerical results are shown in Sec. IV for various hydrides. Section V gives the summary of this paper.

II. THEORY FOR THE DESIRED BASIS IN MAGNETIC PROPERTY CALCULATIONS

The electronic Hamiltonian in external magnetic field is given by[6]

$$H(\mathbf{A}) = \frac{1}{2} \sum_j \left[\mathbf{p}_j + \frac{1}{c} \mathbf{A}(\mathbf{r}_j) \right]^2 + \sum_{j>k} \frac{1}{r_{jk}} - \sum_j \sum_N \frac{Z_N}{r_{jN}},$$

$$(3)$$

where $\mathbf{A}$ is the vector potential defined by

$$\mathbf{A} = \tfrac{1}{2} \mathbf{B} \times \mathbf{r}. \tag{4}$$

Since $\mathbf{B} = \text{rot } \mathbf{A}$, it is easily found that $\mathbf{A}$ is arbitrary with respect to the addition of div $\lambda(\mathbf{r})$, where $\lambda(\mathbf{r})$ is an arbitrary function of electron coordinate. Explicitly, the vector potential of the form,

$$\mathbf{A}' = \tfrac{1}{2} \mathbf{B} \times \mathbf{r} + \text{div } \lambda(\mathbf{r}), \tag{5}$$

gives the same $\mathbf{B}$. The transformation[7,26] of H $(\mathbf{A})$ into H $(\mathbf{A}')$ is called gauge transformation and is written as

$$H(\mathbf{A}') = U^\dagger H(\mathbf{A})U, \tag{6}$$

where U is the unitary transformation operator given by

$$U = \exp\left[i \sum_j \lambda(\mathbf{r}_j) \right]. \tag{7}$$

Now, we restrict ourselves in this paper to choose $\lambda(\mathbf{r}_j)$ as

$$\lambda(\mathbf{r}_j) = - \tfrac{1}{2} (\mathbf{B} \times \mathbf{d}) \cdot \mathbf{r}_j, \tag{8}$$

which leads to

$$\mathbf{A}'(\mathbf{r}_j) = \tfrac{1}{2} \mathbf{B} \times (\mathbf{r}_j - \mathbf{d}), \tag{9}$$

where $\mathbf{d}$ is called gauge origin. In comparison with Eq. (4) we see that U represents a translation of the origin of the electron coordinate, and the $\mathbf{d}$ dependence of the calculated value is the so-called gauge-dependence, which we study in this paper.

According to Epstein, a sufficient condition for a given basis set $\{\chi\}$ to give origin independent results[7,8,18,19] is that the transformed basis set $\{U_\chi\}$ spans the same space as the original one $\{\chi\}$ does. Applying this theorem to the present case, we see that the basis set satisfying,

$$\{\chi\} = \left\{ \exp\left[-\frac{i}{2} (\mathbf{B} \times \mathbf{d}) \cdot \mathbf{r} \right] \chi \right\}, \tag{10}$$

should give gauge-invariant results. Expanding the exponential factor, we obtain

$$\exp\left[-\frac{i}{2} (\mathbf{B} \times \mathbf{d}) \cdot \mathbf{r} \right] \chi$$

$$= \left[1 - \frac{i}{2} \sum_t (\mathbf{B} \times \mathbf{d})_t r_t - \frac{1}{8} \sum_t \sum_u (\mathbf{B} \times \mathbf{d})_t \right.$$

$$\left. \times (\mathbf{B} \times \mathbf{d})_u r_t r_u \cdots \right] \chi, \tag{11}$$

where r_t and r_u denote x, y, or z.

We propose here the use of the basis set $\{\chi, r_t\chi, r_t r_u\chi...\}$ for magnetic property calculations. Namely, we augment the basis $r_t\chi$, $r_t r_u\chi$, etc. to the parent basis $\{\chi\}$ in the CHF/FP procedure. When the original basis

$\{\chi\}$ is sufficiently good, the proposed basis set would satisfy the Epstein's requirement. Hereafter, we call $r_t\chi$ and $r_t r_u\chi$ first and second order basis functions (FOBFs and SOBFs), respectively. This procedure gives a necessary condition for the complete basis set to satisfy.

Although the above set of the augmented basis includes infinite order terms, it is unnecessary to include all of them. Since the nuclear magnetic shielding constant is a first-order property with respect to the applied external magnetic field, we need only the basis up to the first order in $\mathbf{B}$. Therefore, we use the augmented basis set, $\{\chi, r_t\chi\}$. Strictly speaking, the contribution of the SOBFs is not zero, since in our procedure, the augmented set is used for improving not only the gauge invariance property but also the energy of the system in an ordinary variational sense.

In our procedure, the BFs to be augmented have the same exponent and contraction coefficients as the original BFs. Namely, they constitute the shell structure. Therefore, the N-31G type basis sets by Pople and his co-workers[27] are preferable since the valence s and p basis already form a shell structure. We note that the Obara's algorithm for AO integral evaluations[28] is useful for such cases, because the integrals for the original BFs can be used as an intermediate data of those for the augmented functions.

A related method to the present one is the inclusion of the derivative BFs proposed by Nakatsuji et al.[25] It was derived from the sufficient condition for the variational wave function to satisfy the Hellmann–Feynman theorem for geometric gradient. If we use uncontracted gaussian basis functions, two methods give completely identical basis functions.

Karplus and Kolker[29] suggested a variation-perturbation theory,[30] in which the first order correction for the ith MO, ϕ_i, due to the external perturbation is expressed in a product form, $f\phi_i$, where f is an arbitrary function containing variational parameters. In their approach, the second order energy is minimized by optimizing f. Sadlej and Jaszunski[31] proposed to use a geometric expansion of f, i.e., a linear combination of $\{x,y,z,x^2,y^2,z^2,xy,xz,yz,...\}$. Note that we improve both unperturbed and perturbed wave functions by augmenting $r\chi$ where χ is an AO, while in the Karplus–Kolker method $r\phi$ where ϕ is a MO is used for calculating second order properties.

The method proposed above has some connection with the GIAO method in which the BFs defined by Eqs. (1) and (2) are used.[3,15,17,20,21,32–34] With this $\{\phi_\nu\}$, the origin dependent terms are eliminated from the AO integrals so that origin independent results are obtained; this method is somewhat artificial and not the result of the variational principle, as commented upon by Epstein.[18,19] Actually, the GIAO results are dependent on the choice of $\mathbf{d}$ because, if $\mathbf{d} = \mathbf{R}_\nu$, ϕ_ν becomes the conventional BF χ_ν. For the second order properties such as magnetic shielding constant, the expansion is terminated at the first order also in the GIAO method,[3] like in the present method.

There are two difference between the GIAO method and the present method; the exponential factor in Eq. (10) is different from that in Eq. (2), and the expansion coefficients of the FOBFs are fixed in the GIAO method, but are variationally determined in our method. A defect of the present

TABLE I. Geometric parameters.

Molecule	Symmetry	r(X–H)/Å	θ(H–X–H)/deg
CH_4^a	T_d	1.087	109.471
NH_3^a	C_{3v}	1.0138	107.23
H_2O^b	C_{2v}	0.9572	104.52
HF^b	$C_{\infty v}$	0.9170	
SiH_4^a	T_d	1.4812	109.471
PH_3^a	C_{3v}	1.4116	93.328
H_2S^a	C_{2v}	1.3356	92.11
HCl^c	$C_{\infty v}$	1.2746	
HBr^c	$C_{\infty v}$	1.4145	
HI^c	$C_{\infty v}$	1.6092	
SeH_2^a	C_{2v}	1.460	90.9
TeH_2^a	C_{2v}	1.658	90.25

[a]Reference 39.
[b]Reference 21.
[c]Reference 40.

TABLE II. Definition of the basis functions augmented to the 6-31G basis set.

Basis function	Atom	χ	$r\chi$	$r^2\chi$
(a)	hydrogen	$1s$	p	$\cdots$
(b)	hydrogen	$1s$	$\cdots$	d
(c)	nonhydrogen	core s/p ($1s$ or $2s/2p$)	p/d	$\cdots$
(d)	nonhydrogen	valence s ($2s$ or $3s$)	p	$\cdots$
(e)	nonhydrogen	valence p ($2p$ or $3p$)	d	$\cdots$

method is that it requires a larger basis set than the GIAO one. However, our added basis improves not only the gauge-dependence but also the quality of the calculated result through the variational principle. We will see later that this certainly gives large difference in the calculated magnetic properties of the second row hydrides in favor of our method.

III. COMPUTATIONAL DETAILS

In this study, we calculate magnetic shielding tensor. For this purpose, we use the FP method in the Hartree–Fock level whose details are described in Ref. 35. The unperturbed wave functions are calculated with the HONDO7 program by Dupuis et al.[36]

The molecules calculated are first row hydrides (CH_4, NH_3, H_2O, HF) and second row hydrides (SiH_4, PH_3, H_2S, HCl) for which the 6-31G set are used.[27] In order to investigate the row dependence, we also study the hydrides of the group VI and VII elements (HX; X=F, Cl, Br, I: H_2X; X=O, S, Se, Te). For these calculations, we use the basis sets by Huzinaga et al.[37] for X, and $(4s)/[2s]$ set for H.[38] The basis sets for X are, in general, expressed as (433...33/43...33/43...3), and are contracted into the split valence set of the type, [433...321/433...321/43...3]. The d functions are singly contracted for all atoms, since they belong to the inner shell. We use experimental geometries,[21,39,40] which are tabulated in Table I. The definition of the functions, $r_t\chi$ or $r_t r_u\chi$, to be augmented to the parent basis set $\{\chi\}$ is summarized in Table II.

IV. RESULTS AND DISCUSSION

In this section, we discuss nuclear magnetic shielding tensor σ of several hydrides calculated by augmenting the basis sets by the method described in Sec. II. We are interested in whether the gauge dependence is largely reduced, and whether it works at the same time to reproduce well the experimental values. Furthermore, it is also important to examine how the augmented basis functions improve the cal-

culated results. For that purpose, we systematically expand the basis set space, and perform the analysis used in our previous studies.[35,41]

Hereafter, we use the notation $\sigma(A/B)$, which stands for the magnetic shielding tensor of an atom A with the gauge origin on an atom B.

A. Test applications to HF and H_2O

Tables III and IV show the $\sigma(^{19}F)$ and $\sigma(^1H)$ in HF, and $\sigma(^{17}O)$ and $\sigma(^1H)$ in H_2O, respectively. σ_{iso} and σ_{aniso} denote the isotropic and anisotropic terms. In these tables, the basis sets, $(A$-6) and $(B$-7) consist of the parent set $\{\chi\}$ and full FOBFs $\{r\chi\}$.

For the parent 6-31G set alone (A-1 and B-1), the gauge dependence is very large; e.g., the difference between $\sigma_{iso}(^{19}F/F)$ and $\sigma_{iso}(^{19}F/H)$ amounts to 75.9 ppm. For $\sigma_{aniso}(^{19}F)$, it is 113.7 ppm. By augmenting the FOBFs for all atoms involved (A-6 and B-7), the errors are drastically reduced; in the above case, only 3.7 ppm and 5.6 ppm for σ_{iso} and σ_{aniso}, respectively. Our basis set also gives nearly gauge-invariant result for $\sigma(^1H)$ within the error of 5 ppm. In the previous CHF calculations with more extensive basis sets,[24] the dependence for $\sigma(^1H)$ is slightly larger than ours. Thus, we see that the present method effectively reduces the unfavorable origin dependence. Moreover, our calculated results are also very close to the experimental values,[33] the previous CHF results,[24] and the GIAO (Ref. 21) ones. Our best value deviates in less than 4% from the experimental values. This simultaneous improvement in the gauge dependence and the accuracy clearly proves the effectiveness of our method.

In Tables III and IV, we have also examined various intermediate approximations to the full $\{\chi,r\chi\}$ method proposed here. The comparison between the results for bases (A-2) and (A-3) shows that the second order (SO) BFs are unimportant; only 0.5 and 3.9 ppm for $\sigma_{iso}(^{19}F)$ and $\sigma_{iso}(^{17}O)$, respectively. Thus, the inclusion of only FOBFs seems to be enough to get satisfactory results.

From Eqs. (1) and (2), if we put the gauge origin d at the origin of the coordinate at which the nucleus we are interested in is also placed, the FOBFs for that atom disappear and those for the rest of the atoms are required. The bases (A-2) and (B-5) correspond to such basis and the results show that such augmentation gives almost good values. For $\sigma_{iso}(^{19}F/F)$ and $\sigma_{iso}(^{17}O/O)$, the calculated values are rapidly convergent after the addition of the FOBFs on the H atom. This is practically very effective. However, large deviation is

TABLE III. Basis set dependence of ^{19}F and ^{1}H magnetic shielding constant of the HF molecule (in ppm).[a]

	^{19}F		^{1}H	
Basis set[b]	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}
(A) Gauge origin on F atom				
(1) 6-31G	345.5	206.2	25.21	27.31
(2) (1)+(a)	417.4	96.5	26.56	26.45
(3) (1)+(a)+(b)	416.9	96.8	27.85	24.48
(4) (1)+(d)+(e)	371.6	166.1	26.41	26.15
(5) (1)+(a)+(d)+(c)	419.6	92.8	27.62	24.89
(6) (1)+(a)+(c)+(d)+(e)	416.8	97.3	27.61	24.84
CHF[c] (I)	412.7	103.7	27.26	25.24
(II)	413.5	102.5	27.50	24.83
(B) Gauge origin on H atom				
(1) 6-31G	421.4	92.5	98.09	−82.01
(2) (1)+(d)	430.6	78.6	85.58	−63.29
(3) (1)+(e)	401.8	120.7	50.84	−10.44
(4) (1)+(d)+(e)	415.6	100.1	38.30	8.32
(5) (1)+(c)+(d)+(e)	417.4	97.7	32.18	17.43
(6) (1)+(a)+(d)+(c)	411.8	104.4	36.53	11.53
(7) (1)+(a)+(c)+(d)+(e)	413.1	102.9	30.49	20.53
CHF[c] (I)	413.4	102.8	35.76	12.49
(II)	410.9	106.4	32.58	17.15
GIAO[d] 6-31G	411.2	107.8	30.60	19.23
6-31G*	417.8	96.9	29.36	21.73
6-311G*	415.2	101.5	29.68	20.58
GIAO[e]	411.8		29.49	
Experiment[f]	410±6		28.72	

[a] $\sigma_{iso} = 1/3(\sigma_{\|}+2\sigma_{\perp})$; $\sigma_{aniso} = \sigma_{\|} - \sigma_{\perp}$.
[b] The definition of the augmented basis functions is given in Table II.
[c] Reference 24. (I) Lie–Clementi's $(13s8p2d)/[7s4p2d]$ for F, $(8s2p)/[5s2p]$ for H: (II) the basis (I) with the polarization functions, $(1s2p1d)$ and $(1p1d)$ for F and H, respectively.
[d] Reference 21.
[e] References 15(d) and 15(e).
[f] Reference 34.

found for $\sigma(^{17}$O/H). Thus, this augmentation is not necessarily good in general.

Our previous studies for the metal NMR chemical shifts,[35,41] have shown that the change in the magnetic shielding constant is determined by the valence AO contribution. Then, we examine whether the modification only for the valence AOs is effective or not. Comparing (A-5) and (A-6), (B-4) and (B-5), and (B-6) and (B-7), we see that the FOBFs for the core AOs are not effective and can be omitted. This fact is advantageous in practical applications of the present method. The augmentation of either s or p valence AOs of the F or O atom seems to be inappropriate [compare (B-2), (B-3), and (B-4) results]; we must add all FOBFs of the valence AOs.

Now, how do the BFs augmented improve the calculated values? We next break down the diamagnetic (σ^{dia}) and paramagnetic (σ^{para}) terms into AO contributions by the method similar to the Mulliken population analysis.[35,41] The results are tabulated in Tables V and VI for $\sigma(^{19}$F/F) and $\sigma(^{17}$O/O), respectively. From the analysis of σ^{dia}, we see that all the components are nearly constant and σ^{dia} is insensitive to the basis set improvement.[41] On the other hand, σ^{para} changes drastically. Interestingly, the augmentation of the basis set for

adjacent H atoms largely affects the contribution of the AOs belonging to the nucleus on the gauge origin. In particular, the largest change is seen in the contribution from the $2p$ function of F and O, which is an inner p function of the double zeta 6-31G basis set. This is reasonable since σ^{para} is mainly described by the inner part of the valence AOs of the resonant nucleus.[35] The contributions from the s orbitals of F and O are exactly zero since they have no angular momentum. Furthermore, note that the augmented BFs themselves give negligibly small contributions to σ^{para}. The p AO contributions are always dominant to σ^{para}, independent of the basis set used.

Another noticeable point is that the FOBFs reduce the paramagnetic contribution of the hydrogen atom. It seems to imply that the appropriate extension of the basis set correctly cancels the spurious paramagnetic current on the adjacent atom, produced by the incompleteness of the crude set. Since magnetic shielding is a local property, correct basis set seems to make the expectation value more local. This might be one of the reasons why "locally dense" basis set,[42] which enriches the quality of the basis set on a resonant nucleus, has been successful in calculating the metal chemical shifts in our previous studies.[35,41] Chesnut et al.[33,34] showed the im-

TABLE IV. Basis set dependence of ^{17}O and ^1H magnetic shielding constant of H_2O (in ppm).[a]

		^{17}O			^1H		
Basis set[b]		σ_{iso}	σ_{a1}	σ_{a2}	σ_{iso}	σ_{a1}	σ_{a2}
(A) Gauge origin on O atom							
(1)	6-31G	268.5	61.3	15.6	26.47	23.93	2.32
(2)	(1)+(a)	332.8	48.7	4.7	29.56	22.84	0.87
(3)	(1)+(a)+(b)	336.7	52.0	3.6	30.21	21.66	1.34
(4)	(1)+(d)+(e)	296.5	53.6	15.5	27.54	24.00	1.44
(5)	(1)+(a)+(d)+(e)	334.3	53.4	7.3	30.16	21.65	1.10
(6)	(1)+(a)+(c)+(d)+(e)	330.0	56.2	7.2	30.14	21.61	1.10
(B) Gauge origin on H atom							
(1)	6-31G	282.9	129.9	1.2	87.60	40.95	62.97
(2)	(1)+(d)	281.1	150.4	4.2	76.06	31.98	45.82
(3)	(1)+(e)	302.3	70.1	3.2	52.12	9.48	11.81
(4)	(1)+(d)+(e)	307.1	80.6	18.7	40.60	5.81	1.78
(5)	(1)+(c)+(d)+(e)	306.2	85.3	25.1	34.41	13.89	2.44
(6)	(1)+(a)+(d)+(e)	329.6	46.6	12.2	38.28	9.65	2.67
(7)	(1)+(a)+(c)+(d)+(e)	328.2	50.9	7.2	32.26	18.42	2.56
GIAO[c] 6-31G		327.2	42.2	10.8	32.74	17.80	1.72
6-31G*		329.2	44.2	14.4	31.85	19.31	1.42
6-311G*		348.1	22.6	42.2	31.88	18.97	1.60
Experiment[d]		334			30.09		

[a] $\sigma_{iso} = 1/3(\sigma_{11}+\sigma_{22}+\sigma_{33})$, $\sigma_{a1}=\sigma_{11}-\frac{1}{2}(\sigma_{22}+\sigma_{33})$, and $\sigma_{a2}=\sigma_{22}-\sigma_{33}$, where σ_{ii} is the principal component of the tensor σ, and $\sigma_{11} \geqslant \sigma_{22} \geqslant \sigma_{33}$.
[b] The definition of the augmented basis functions is given in Table II.
[c] Reference 21.
[d] Reference 34.

portance of the diffuse functions in the GIAO calculations. Since the effect of such diffuse functions on a "very local" property seems curious, we speculate that they are used to cancel the artificial currents produced on the surrounding atoms.

B. First row hydrides

We have shown that the simple method proposed in Sec. II gives very accurate results for H_2O and HF. In this section, we further investigate NH_3 and CH_4.

TABLE V. AO analysis of the ^{19}F magnetic shielding constant of the HF molecule.[a]

AO[b]		σ^{dia}				σ^{para}			
		A-1	A-2	A-5	A-6	A-1	A-2	A-5	A-6
F	$1s$	316.4	316.4	316.0	315.9	0.0	0.0	0.0	0.0
	$2s$	22.3	22.4	21.6	21.6	0.0	0.0	0.0	0.0
	$2s'$	17.7	16.5	16.1	16.1	0.0	0.0	0.0	0.0
	$2p$	88.6	88.5	88.3	84.2	−129.0	−62.3	−58.3	−56.3
	$2p'$	31.6	28.9	29.3	28.8	−17.0	−4.0	−3.4	−3.4
	$p(1s)$				1.4				−4.1
	$p(2s)$			0.3	3.6			−0.9	−1.8
	$d(2p)$			0.8	0.8			−0.2	−0.2
	$d(2p')$			−0.7	−0.7			−0.1	−0.1
	Total	476.6	472.6	471.7	471.8	−146.0	−66.4	−63.0	−66.1
H	$1s$[c]	5.8	6.4	7.1	7.1	9.1	5.5	4.8	4.9
	$p(1s)$		3.0	3.0	3.0		−3.8	−4.0	−4.0
	Total	5.8	9.4	10.1	10.1	9.1	1.7	0.8	0.9
Total		482.4	482.0	481.7	481.9	−136.9	−64.7	−62.2	−65.2

[a] For example, A-1 indicates the basis 1 in Table II with the gauge origin on F atom.
[b] The prime indicates the outer function involved in the split valence basis set. The $p(1s)$ is an augmented p function derived from $1s$ basis function. The $p(2s')$ function for F is omitted since it is identical with the $2p'$ function in the 6-31G basis set.
[c] The contribution from the $1s$ and $1s'$ functions.

TABLE VI. AO analysis of the ^{17}O magnetic shielding constant of H_2O molecule.[a]

AO[b]		σ^{dia}				σ^{para}			
		A-1	A-2	A-5	A-6	A-1	A-2	A-5	A-6
O	1s	279.3	279.2	279.0	278.9	0.0	0.0	0.0	0.0
	2s	18.8	18.6	18.1	18.1	0.0	0.0	0.0	0.0
	2s'	14.7	12.8	12.1	12.1	0.0	0.0	0.0	0.0
	2p	66.1	65.6	66.0	62.4	−136.3	−77.2	−73.4	−70.6
	2p'	24.4	20.3	22.5	21.9	−26.6	−6.7	−3.7	−3.8
	p(1s)				1.2				−6.0
	p(2s)			−0.3	2.7			−1.1	−2.5
	d(2p)			0.1	0.1			−0.7	−0.7
	d(2p')			−0.8	−0.8			−0.3	−0.3
	Total	403.1	396.6	396.6	396.6	−162.9	−83.9	−79.2	−83.8
H	1s[c]	6.4	7.4	7.2	7.3	7.7	5.7	3.8	3.9
	p(1s)		2.1	2.3	2.3		−5.1	−4.8	−4.9
	Total	6.4	9.5	9.5	9.6	7.7	0.6	−1.0	−1.0
Total		416.0	415.6	415.6	415.7	−147.5	−82.8	−81.3	−85.8

[a]For example, A-1 indicates the basis 1 in Table III with the gauge origin on O atom.
[b]The prime indicates the outer function involved in the split valence basis set. The $p(1s)$ is an augmented p function derived from $1s$ basis function. The $p(2s')$ function for O is omitted since it is identical with the $2p'$ function in the 6-31G basis set.
[c]The contribution from the $1s$ and $1s'$ functions.

We show in Table VII the results of the isotropic magnetic shielding constant for the first row hydrides; we tabulate again the results for H_2O and HF for easy comparison. We clearly see an interesting trend both in the origin dependence and in the errors from the experimental values. As the symmetry of the molecule becomes higher, the gauge dependence is reduced, as expected, and the error becomes smaller. However, the error from the experimental values are notice-

able even in CH_4 for which there is no origin dependence. Basis 6 includes the full FOBFs and certainly improves the results as expected. This supports the validity of our method.

Figure 1 depicts the basis set dependence of the relative errors in $\sigma_{iso}(X/X)$ (X=C, N, O, F) for our best results (basis 6). The augmentation of the FOBFs only for hydrogen is fairly good. Basis 4, which is the 6-31G set with FOBFs for nonhydrogen atoms, improves the results, but the amount is

TABLE VII. Isotropic magnetic shielding constant of the nucleus X in first row hydrides, $H_{4-n}X$ (X=C, N, O, F; n=0-3) (in ppm).

Basis set		$\sigma_{iso}(C)$		$\sigma_{iso}(N)$		$\sigma_{iso}(O)$		$\sigma_{iso}(F)$	
		C	H	N	H	O	H	F	H
This work[a]									
(1)	6-31G	221.3	221.3	245.1	237.7	268.5	282.9	345.5	421.4
(2)	(1)+(a)	205.7	205.7	268.6	259.7	332.8	312.3	417.4	386.8
(4)	(1)+(d)+(e)	200.5	200.5	250.7	251.3	296.5	307.1	371.6	415.6
(5)	(1)+(a)+(d)+(e)	200.5	200.5	265.9	264.6	334.3	329.6	419.6	411.8
(6)	(1)+(a)+(c)+(d)+(e)	196.2	196.2	261.7	261.5	330.0	328.2	416.8	413.1
Expt.[b]		197.4/195.1[c]		264.5		334		410±6	
GIAO[c]	6-31G	206.0		266.9		327.2		411.2	
	6-311G*	194.9		271.0		348.1		415.2	
CHF[d]	Höller–Lischka	195.8	195.8	266.1		328.1		415.0	414.3
IGLO[e]		193.8		255.6		305.7		413.5	

[a]Our largest basis set (basis 5) is $(10s13p4d)/[3s4p2d]$ for the first row atoms and $(4s4p)/[2s2p]$ for hydrogen.
[b]Reference 34.
[c]Reference 21.
[d]Reference 11. $(12s8p3d)/[9s7p(3d$ or $4d)1f]$ for F or O, respectively. $(11s7p3d)/[8s6p3d]$ or $(6s3p)/[5s3p]$ for nonhydrogen or hydrogen atoms, respectively.
[e]References 4 and 9. The IGLO(III) results in their notation are cited except for H_2O for which IGLO(II) results are shown. IGLO(II): $(9s5p1d)/[5s4p1d]$ for nonhydrogen and $(5s2p)/[3s2p]$ for hydrogen, IGLO(III): $(11s7p2d)/[7s6p2d]$ and $(6s2p)[4s2p]$.
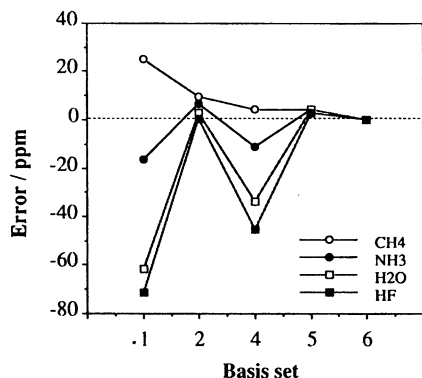
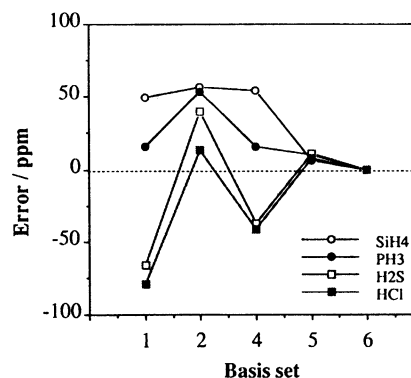FIG. 1. Basis set dependence of the relative errors for the first row hydrides.

FIG. 2. Basis set dependence of the relative errors for the second row hydrides.

less satisfactory. As discussed above, a satisfactory result is obtained by the addition of the FOBFs on a valence shell (basis 5).

It is interesting to note that, in CH_4, the result of basis 4 is closer to the most accurate value than that of basis 2. Bases 2 and 4 give almost the same deviation (in a different direction) in NH_3. Thus, the effect of basis set modification is not monotonous, and a partial enrichment does not necessarily insure an increase in accuracy. In addition, it should be pointed out that the GIAO/6-31G results are very close to our basis 2 result for CH_4. Although the coordinate of the molecule is not given in the literature, we think that the gauge origin was taken at the position of the carbon atom, i.e., $\lambda_\nu = 0$ for carbon, in the GIAO calculation.

C. Second row hydrides

Next we examine $\sigma_{iso}(X)$ for second row hydrides, SiH_4, PH_3, H_2S, and HCl. The results are summarized in Table VIII. The 6-31G results are gauge dependent except for SiH_4. Figure 2 shows the basis set dependence of relative errors for the second row hydrides. The overall trend observed here is similar to that for the first row hydrides. However, it should be noted that the error in the smaller basis set is much larger than that in the first row hydrides.

For PH_3 and HCl, the experimental values are available, and we can examine the accuracy of the calculated result. We see that our full $\{\chi, r\chi\}$ set gives very good agreement with the experiment as well as their invariance property. Noticeable point is that our result is much better than the corre-

TABLE VIII. Isotropic magnetic shielding constant of the nucleus X in second row hydrides, $H_{4-n}X$ (X=Si, P, S, Cl; n=0–3) (in ppm).

	Basis set	$\sigma_{iso}(Si)$		$\sigma_{iso}(P)$		$\sigma_{iso}(S)$		$\sigma_{iso}(Cl)$	
		Si	H	P	H	S	H	Cl	H
This work[a]									
(1)	6-31G	538.0	538.0	615.9	558.7	656.0	639.3	868.1	915.3
(2)	(1)+(a)	545.0	545.0	653.7	623.2	762.1	703.9	960.1	904.0
(4)	(1)+(d)+(e)	542.8	542.8	616.5	604.2	684.8	690.6	905.9	937.5
(5)	(1)+(a)+(d)+(e)	494.4	494.4	610.4	618.1	733.4	741.0	954.3	953.2
(6)	(1)+(a)+(c)+(d)+(e)	488.4	488.4	600.6	592.8	722.5	716.7	946.9	952.7
Expt.[b]				594				950	
GIAO	6-31G	565.5[c]		667.0[b]				767.9(6-311G)[d]	
CHF[c]	Höller–Lischka	481.8		584.9		716.5		947.6	
IGLO[f]		478.4		575.5		672.2		912.4	

[a]Our largest basis set (basis 5) is $(16s25p10d)/[4s6p3d]$ for the second row atoms and $(4s4p)/[2s2p]$ for hydrogen.
[b]Reference 33.
[c]Reference 32.
[d]Reference 17.
[e]Reference 11. $(13s9p3d)/[10s8p3d]$, $(12s8p3d)/[9s7p3d]$, $(13s9p4d)/[10s8p4d]$, $(13s8p5d1f)/[10s7p5d1f]$, and $(5s2p)/[4s2p]$ for Si, P, S, Cl, and H, respectively.
[f]References 4 and 9. IGLO(II) results: $(11s7p2d)/[7s6p2d]$ for nonhydrogen and $(5s2p)/[3s2p]$ for hydrogen.

TABLE IX. Isotropic magnetic shielding constant of the nucleus X in HX (X=F, Cl, Br, I), and H_2X (X=O, S, Se, Te) molecules (in ppm).[a]

Molecule	Basis 1 (1)	Basis 2 (1)+(a)	Basis 5 (1)+(a)+(d)+(e)
HF	347.2(−16.0)	413.1(−0.5)	415.0
HCl	757.8(−20.6)	1001.5(5.0)	954.1
HBr	2364.4(−9.8)	2648.1(1.1)	2620.0
HI	4201.6(−8.4)	4638.5(1.1)	4587.6
H_2O	262.0(−20.8)	328.4(−0.7)	330.6
H_2S	532.7(−26.4)	801.1(10.7)	723.8
H_2Se	1897.1(−12.3)	2241.4(3.6)	2163.7
H_2Te	3431.1(−9.7)	3924.3(3.2)	3800.8

[a]The value in parentheses shows the error in % from the result for the basis set (1)+(a)+(d)+(e). The parent bias set is due to Huzinaga et al. (Ref. 37).

sponding GIAO/6-31G result. This shows that our method improves not only the invariance property, but also the quality of the wave function through variational calculations of the coefficients of the FOBFs.

Another noticeable feature in comparison with the first row hydrides is that the accuracy obtained by using basis 2 is unsatisfactory here. For SiH_4 and PH_3, they become even worse than the 6-31G results. Basis 5 which includes FOBFs only for valence AOs gives already accurate values in comparison with basis 6. From these results, it is safe to conclude that the augmentation scheme 2 is not necessarily good and, for general purposes, we recommend to use, at least, basis 5. For basis 6, the gauge dependence is very small and the error from the experimental values is as small as about 1%.

Similar to $\sigma(C/C)$ in CH_4, the GIAO/6-31G result for SiH_4 is close to our result obtained with basis 2. This seems to show the coordinate dependence of the GIAO result. A slight difference is due to the optimization of the MO coefficients for the augmented basis functions.

D. Row dependence of the relative errors

It has been found that the error of the 6-31G set, including that of the GIAO/6-31G result, is larger for the second low hydrides than for the first row hydrides. Here we examine the dependence of the relative errors on the row of the Periodic Table; we calculate $\sigma_{iso}(X/X)$ for two series of mol-

ecules, HX (X=F, Cl, Br, I) and H_2X(X=O, S, Se, Te). In these calculations, the basis sets by Huzinaga et al.[37] for X and by Dunning for H (Ref. 38) are used.

The results are tabulated in Table IX. Interestingly, the error is largest for the second row hydrides when the unmodified set is used. This is also true for the augmented set. For the first, third and fourth row molecules, even basis 2 gives reasonably good values: an error is less than 4% relative to basis 5. Thus, we conclude that, for calculating molecules containing second row elements, the basis set should be carefully chosen.

Comparing with Tables VII and VIII, we see that $\sigma(X/X)$ strongly depends on the choice of the parent basis set; e.g., for HCl, the 6-31G and Huzinaga's sets give 868.1 and 757.8 ppm, respectively, while for H_2S they are 656.0 and 532.7 ppm, respectively. The 6-31G results are closer to the experimental or more accurate values. This might show that the electronic distribution in the core region in a molecule is better described with this set. After augmenting FOBFs, the difference is significantly reduced; it becomes only 0.2 ppm for HCl. This means that an arbitrary parent set can be successfully used for calculating σ if FOBFs are augmented. This is one of the desired characteristics for basis sets used in practical electronic structure calculations.

E. ¹H chemical shift

In this section, we discuss the isotropic magnetic shielding constant $\sigma_{iso}(^1H)$ and the ^1H chemical shift defined by

$$\delta = \sigma_{iso}(CH_4) - \sigma_{iso}. \tag{12}$$

For comparison, we refer to the experimental values[9] measured in a gas phase and the IGLO results obtained by Kutzelnigg et al.[9] The basis set used is the 6-31G set augmented by the FOBFs for all atoms (basis 6 in the definition of Tables VIII and IX).

Table X shows the calculated results of $\sigma_{iso}(^1H)$ for which the nonhydrogen atom is taken as a gauge origin. Since the experimental chemical shifts are very small quantity, a comparison with the experiment gives a very severe test. In our calculations, the ordering of the chemical shifts is correctly reproduced except for HCl, though the results tend

TABLE X. ^1H magnetic shielding constant and chemical shift in the first and second row hydrides.[a]

	This work[b]		IGLO[c]		Expt.
	$\sigma(H/X)$	δ	$\sigma(H)$	δ	δ
CH_4	31.44	0.0	31.07	0.0	0.0
NH_3	31.25	0.19	30.92	0.15	−0.08/−0.03
H_2O	30.14	1.30	30.54	0.53	0.6
HF	27.61	3.83	28.15	2.92	2.47
SiH_4	28.17	3.27	28.24	2.83	3.00
PH_3	29.61	1.83	29.66	1.41	1.48
H_2S	30.34	1.10	30.76	0.31	0.08
HCl	30.03	1.41	31.25	−0.18	−0.45

[a]$\delta = \sigma(CH_4) - \sigma$.
[b]6-31G+FOBFs (for all atoms).
[c]Reference 9. IGLO(II) results.

to overestimate the experimental values. The IGLO method gives better results than ours; even for HCl, it gives a correct sign.

V. CONCLUDING REMARKS

In this paper, we have proposed to augment the basis functions $\{r_t\chi, \; r_t r_u\chi, \; ...\}$ to the conventionally used Gaussian basis set $\{\chi\}$, and have shown its usefulness in computing magnetic properties. This method is derived from the sufficient condition for the gauge invariance given by Epstein.[7,8,18,19] With this basis set, the conventional CHF/FP method gives reliable magnetic shielding constants; the origin dependence is drastically reduced, and the calculated values are improved in agreement with the experiments. This method is similar to the previous method for improving the Hellmann–Feynman force.[25]

Some features of the proposed method are as follows: (i) the calculated magnetic properties are almost gauge origin independent; (ii) the calculated results agree well with the experiment; (iii) the augmented functions are uniquely determined; (iv) after the augmentation, the results become independent of the parent basis set. We think that these are the desired characteristics which basis sets should have in general. A largest disadvantage in our method is an increase in the size of the basis sets. Thus, an idea such as the one in "polarized basis set" by Sadlej[45] is definitely encouraged. Exact implementation using a set $\{\chi, \; r_t\chi, \; r_t r_u\chi, \; ...\}$ is impossible, but complementing only FOBFs leads to enough accurate results. As a compromise, the FOBFs of the valence basis of the constituent atoms would be a practical choice.

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