

# Calculation of hyperfine splitting constants with Slater-type cusp basis by the symmetry adapted cluster-configuration interaction theory

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A method of calculating hyperfine splitting constants (hfsc) of open-shell radicals is reported. Since the hfsc reflects a very local property of the wave function at the position of the nuclei, we use Slater-type orbitals (STOs) which have cusps at the centers. Spin correlation (spin polarization) and electron correlation are taken into account with the use of the SAC-CI (symmetry adapted cluster-configuration interaction) theory. Configuration selection is not done since energy and spin density are very different properties. The dimensions of the matrices involved in the SAC-CI method are small enough to permit such a procedure. The integrals necessary for the SCF and SAC-CI methods are calculated by the STO-6G method with the use of the available Gaussian program, and the hfsc's and the cusp values are calculated from the original STOs. Several STOs are examined for  $\text{H}_2^+$  and  $\text{H}_2\text{O}^+$ . The resultant standard method is applied to the organic  $\pi$  and  $\sigma$  radicals  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_3\text{NH}$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3\text{OCH}_3^+$ ,  $\text{H}_2\text{CO}^+$ ,  $\text{CH}_2\text{CH}$ , and  $\text{HCO}$ . The present results of hfsc's show generally better agreement with experiment than the previous calculations based on the Gaussian-type orbitals (GTOs). In particular, the present results are free from the theoretical dilemma seen for the GTO calculations that a variationally better wave function does not necessarily give a better hfsc. This is important in developing a reliable theory for calculating hfsc's.

## I. INTRODUCTION

Fermi contact hyperfine splitting constants (hfsc's) observed by electron-spin resonance (ESR) and microwave spectroscopy give information on the spin densities at the nuclei of an open-shell molecule. Since this is a very local property, *ab initio* calculations of the hfsc's are more difficult than the other electronic properties such as dipole moments, polarizabilities, etc. It has been clarified that the following factors are very important for adequate descriptions of the hfsc's: (i) spin-polarization correction<sup>1-4</sup>; (ii) electron correlation correction.<sup>5-10</sup>

Unrestricted Hartree-Fock (UHF) and projected UHF methods only poorly include the spin-polarization correction.<sup>1,3</sup> Pseudo-orbital theory<sup>4</sup> adequately includes the spin-polarization effect, but does not include the electron correlation effect which has been shown to be very important, particularly for the hfsc's of radical center atoms.<sup>7</sup> Symmetry adapted cluster-configuration interaction (SAC-CI) theory<sup>11,12</sup> has been shown to be very effective in including both spin-polarization and electron correlation corrections.<sup>7,10</sup> We have noted that in the calculations of hfsc's, we have to be very careful about configuration selection, since the energy and spin density are very different properties. In the SAC-CI method, we can avoid the configuration selection,<sup>7,10</sup> because the sizes of the matrices to be diagonalized are very small without selection, in contrast to ordinary CI methods.<sup>8</sup> In the previous papers,<sup>7,10</sup> the SAC-CI method has been shown to be able to provide hfsc's of various radicals that are in reasonable agreement with experiments. The Huzinaga-Dunning contracted Gaussian-type orbital (GTO) basis sets<sup>13</sup> were recommended from a practical

point of view. However, we have observed, at the same time, the peculiar result that a variational improvement of the wave function (e.g., uncontraction of the GTO set) does not necessarily lead to an improvement of the calculated hfsc's.<sup>8,10</sup>

In this paper, we examine the necessity of the cusp condition for the calculation of hfsc's. Following Kato,<sup>14</sup> the exact electron density  $\rho$  should satisfy the following equation at the position  $\{R_A\}$  of the nucleus  $\{A\}$ :

$$\lim_{r \rightarrow R_A} \left\{ \frac{d}{dr} \ln \rho(r) \right\} = -2Z_A, \quad (1)$$

where  $Z_A$  is the nuclear charge. The wave function calculated with GTOs does not satisfy this condition. Since the cusps and the hfsc's are both properties dependent upon the electron density at the position of the nucleus, these two properties should be closely related. We expect that the density at the nucleus calculated by the cusplless basis may underestimate the true value. We have observed some examples in which the primitive GTO calculations give poorer hfsc's than the contracted ones, though the energy is better (lower), as expected, for the primitives.<sup>10</sup> Ishida,<sup>15</sup> and Momose and Shida<sup>16</sup> have suggested the use of the Hiller-Sucher-Feinberg (HSF) identity<sup>17,18</sup> in order to replace the very local delta function operator with a more global operator. We here undertake a more straightforward method of using Slater-type orbitals (STOs) as a basis set, since they have cusps at the position of the nuclei, as the functional form of the STOs is determined with reference to the exact wave functions of the hydrogenic atoms. We use here the idea of an STO-GTO expansion,<sup>19</sup> so that a conventional GTO program is enough for the calculations of the integrals necessary

TABLE I. The contributions of STO and GTO to the one-center term of the cusp value.

Orbital	Contribution of the cusp value	
Slater type	$\chi_{1s} = \eta_{1s} \exp(-\xi_{1s} r)$ $\chi_{2s} = \eta_{2s} r \exp(-\xi_{2s} r)$ $\chi_{3s} = \eta_{3s} r^2 \exp(-\xi_{3s} r)$ $\chi_{2pz} = \eta_{2pz} r \cos \theta \exp(-\xi_{2p} r)$	$(1s - 1s')_{r=0} = -\xi_{1s} \eta_{1s}^2$ $(1s - 2s')_{r=0} = -\eta_{1s} \eta_{2s}$ $(2s - 1s')_{r=0} = 0$ other terms $(nl - mk')_{r=0} = 0$
Gaussian type	$\chi_s = \eta_s \exp(-\alpha_s r^2)$ $\chi_{pz} = \eta_{pz} r \cos \theta \exp(-\alpha_p r^2)$	All terms $(nl - mk')_{r=0} = 0$

for the SCF and SAC-CI calculations. The spin densities and the cusp values are calculated from the original STO wave functions, since here the accuracy of the STO-GTO expansion is not good. The importance of the cusp condition for improving the wave function has been discussed by Steiner.<sup>20</sup>

## II. METHOD

The cusp value, defined by the left-hand-side term of Eq. (1), is written in a basis set expansion as

$$\lim_{r \rightarrow R_A} \left\{ \frac{d}{dr} \ln \rho(r) \right\} = \lim_{r \rightarrow R_A} \left( 2 \sum_{p,q} D_{pq} \chi_p \chi'_q / \sum_{p,q} D_{pq} \chi_p \chi_q \right) \quad (2)$$

where  $\{\chi_p\}$  is the basis set used and  $\{D_{pq}\}$  the bond-order density matrix. The prime on  $\chi_q$  indicates a differentiation. The cusp condition shows that the cusp value should be equal to  $-2Z_A$ . The contribution of the basis functions to the cusp value may be divided into a one-center term, which is dominant, and two- and three-center terms, which are small. The one-center term is the contribution of the basis functions centered on the nucleus  $A$ , and the two- and three-center terms represent the contributions of the tails of the basis functions centered on the different nuclei  $B$ . The difference between the STO and GTO is critical for the one-center term. Table I shows the contributions of the STO and GTO to the one-center term of the cusp value. The GTO does not have the cusp at the center, so that the wave function based on (a finite number of) GTOs never satisfies the cusp condition. On the other hand, the  $1s$  STO does have the cusp and the terms  $(1s - 1s')_{r=0}$  and  $(1s - 2s')_{r=0}$  give a predominant contribution to the cusp value. Since the radial function of the STO simulates the exact wave function for hydrogen-like atoms, it would well describe a correct behavior of the wave function near the nucleus. For instance, a single STO  $N \exp(-Z_A r)$  satisfies the cusp condition.

Most self-consistent field (SCF) programs currently available are for the GTO functions. We therefore undertake the following procedure: We first choose some appropriate STO set. We then expand them using the Gaussian expansion method, STO-NG method, due to Oohata *et al.*<sup>19</sup> and calculate all the integrals necessary for the SCF and SAC-CI calculations by the GTO program. We here need integrals related only to the Hamiltonian operator, for which the STO-NG method is accurate if  $N$  is large.<sup>19</sup> We have used the program GAMESS<sup>21</sup> for the SCF calculations and

TABLE II. The dimension of the matrices involved in the SAC/SAC-CI calculations.

Molecule	SAC	SAC-CI
H <sub>2</sub> O <sup>+</sup>	298	62
CH <sub>3</sub>	364	130
CH <sub>3</sub> CH <sub>2</sub>	2322	1291
CH <sub>3</sub> NH	2502	827
CH <sub>3</sub> O	1462	743
CH <sub>3</sub> OCH <sub>3</sub> <sup>+</sup>	4184	1371
H <sub>2</sub> CO <sup>+</sup>	1034	404
CH <sub>2</sub> CH	2059	1049
HCO	1366	749

SAC85<sup>22</sup> for the SAC/SAC-CI calculations. After obtaining the SCF and the SAC-CI wave functions for doublet radicals, we calculate the hfsc's and the cusp values using the original STO set, since for these quantities, the STO-NG method is unreliable. In this procedure, an additional program is used only for calculating the hfsc's and the cusp values based on the STO's, so that this procedure is of general utility. In the present calculations, we have used the STO-6G expansion of Stewart.<sup>23</sup>

The SAC-CI method<sup>12</sup> is used to calculate the correlated wave functions of doublet radicals.<sup>7</sup> It appropriately includes the spin-polarization and electron correlation corrections.<sup>7,10</sup> For H<sub>2</sub>O<sup>+</sup>, for example, we first calculate the SAC wave function<sup>11</sup> for the closed-shell H<sub>2</sub>O, and then construct the doublet wave function of H<sub>2</sub>O<sup>+</sup> using ionization operators in the SAC-CI formalism.<sup>12,22</sup> In the second SAC-CI step, we avoid configuration selection, because spin density is sensitive to this procedure.<sup>7,11</sup> In the first step, we do configuration selection with  $\lambda_g = 10^{-5}$  a.u.<sup>24</sup> The negligible terms in the unlinked terms of the SAC and SAC-CI expansions are dropped off as usual.<sup>22,24</sup>

Table II shows the dimensions of the matrices involved in the SAC/SAC-CI calculations carried out in the present study. They are identical with the numbers of the unknown variables involved. We see that they are extremely small, in comparison with those of the conventional CI method, as seen below, particularly in the SAC-CI calculations, even though we have avoided configuration selection. This makes the SAC/SAC-CI calculations computationally very easy and feasible, and useful because of the reliability of the calculated results as shown below.

## III. RESULTS AND DISCUSSIONS

We have applied the present method to H<sub>2</sub><sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>NH, CH<sub>3</sub>O, CH<sub>3</sub>OCH<sub>3</sub><sup>+</sup>, H<sub>2</sub>CO<sup>+</sup>, CH<sub>2</sub>CH, and HCO. We first examine several STO sets for H<sub>2</sub><sup>+</sup> and H<sub>2</sub>O<sup>+</sup>, and select a standard set from a practical point of view. We then apply this standard procedure to the rest of the doublet radicals, organic  $\pi$  and  $\sigma$  radicals.

### A. H<sub>2</sub><sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, and examination of basis sets

Table III summarizes the hfsc, cusp value, and total energy of H<sub>2</sub><sup>+</sup>. Since H<sub>2</sub><sup>+</sup> is a one-electron system, the SCF

TABLE III. Hyperfine splitting constant (hfsc) (G), cusp value, and energy of  $\text{H}_2^+$ .

Basis set	STO-6G/GTO		STO		Energy (a.u.)
	hfsc	Cusp	hfsc	Cusp	
STO <sup>a</sup>					
1. 1s(1.0)	184.6	-0.12	205.9	-2.00	-0.553 63
2. 1s(1.2)	313.6	-0.21	351.4	-2.40	-0.585 51
3. 1s(0.8, 1.2)	352.3	-0.21	395.1	-2.47	-0.587 67
4. 1s,2p(1.2)	293.0	-0.25	327.1	-2.37	-0.598 11
5. 1s*3,2s*2,2p*2 <sup>b</sup>	289.4	-0.27	327.9	-2.11	-0.601 63
6. 1s(1.0),1s,2s(0.5)	294.4	-0.23	327.4	-2.24	-0.587 95
7. No. 6 + 2p(0.5)	292.6	-0.23	324.6	-2.23	-0.589 77
GTO					
(4s)/[2s]					
(3,1) <sup>c</sup> Dunning <sup>d</sup>	330.1	-0.21			-0.586 38
(2,2)	280.8	-0.23			-0.585 73
(1,3)	236.2	-0.03			-0.585 64
Primitive	294.2	-0.23			-0.589 15
Large GTO basis <sup>e</sup>	323.7				-0.602 56
Primitive	324.1	-0.28			-0.602 56
Exact <sup>f</sup>	333.7	-2.00	333.7	-2.00	-0.602 62

<sup>a</sup> Values in parentheses show orbital exponents.

<sup>b</sup> The exponents are 1s(0.8,1.2,2.0), 2s(1.2,2.4), and 2p(1.2,2.0).

<sup>c</sup> Contraction is shown in parentheses.

<sup>d</sup> Reference 13.

<sup>e</sup> The result of (10s,2p,1d)/[6s,2p,1d] set in Ref. 8.

<sup>f</sup> Reference 25.

solution is the correct solution within a given basis set. The internuclear distance is fixed to 2.0 Bohr. The exact values were published by Stephens and Auffray.<sup>25</sup> We have examined several STOs and GTOs. As STO results, we have given the hfsc's and the cusp values calculated from the STO-6G Gaussian set and from the original STO set. The cusp values calculated from the Gaussian wave functions are too small, as expected. These cusp values arise merely from the contributions of the tails of the GTOs on the neighboring H atom. This is so even for the very large GTO basis set, the (10s2p1d) set, which gives almost the exact energy.<sup>8</sup> The hfsc's due to the STO-6G sets are always smaller, as expected, than those due to the original STOs. This difference shows the error of the STO-NG method at the position of the nucleus. The hfsc calculated by the Huzinaga-Dunning (3,1)/[2s] set compares very nicely with the experimental value, as pointed out previously.<sup>10</sup> However, when its primitive set is used, the hfsc becomes much worse, contrary to the improvement in the energy. We see that Dunning's (3,1) contraction is the best. The other [2s] contractions (2,2) and (1,3) give poorer results for the hfsc, though these contractions give a larger freedom for the inner part of the wave function close to the nucleus.

When we use the original STOs, on the other hand, the cusp values and the hfsc's are much improved. The cusp values are slightly larger than the exact value, except for the trivial case of using the single 1s STO with  $\xi = 1.0$ . Comparing the STOs Nos. 1 and 2, we see that the shrinking of the 1s atomic orbital (AO) is favorable for the hfsc, as for the energy. From the STOs Nos. 2 and 4, we see the importance of

the polarization function. No. 5 is the best STO set, so that it gives the best results for all the properties, as well as the energy. The STOs Nos. 6 and 7 are constructed from the first few members of the complete set of the exact wave functions of the hydrogen atom. Though they are small sets, their results are fairly good for all the properties given in Table III. We therefore recommend the use of the STO set No. 6 or No. 7 in more comprehensive calculations. No. 6 involves only *s*-type AOs and No. 7 involves the additional polarization function.

Table IV gives the results for  $\text{H}_2\text{O}^+$ , which are calculated by the SAC/SAC-CI method with the use of the experimental geometry.<sup>26</sup> In the first four calculations, we have used the (5s4p) STO set of Bagus and Gilbert<sup>27</sup> for oxygen, and various hydrogen STO sets are examined. In the next four calculations, we have used the hydrogen No. 6 STO set of Table III and various oxygen STO sets are examined. BG1 and BG2 denote nominal (4s3p) and accurate (5s4p) STO bases of Bagus and Gilbert.<sup>27</sup> *p*(GTO) means that the (5p)/[2p] CGTO of Huzinaga-Dunning<sup>13</sup> is used for the *p* functions of oxygen. This replacement serves to save computer time without much affecting the cusp values. We have also examined Clementi's oxygen STO set.<sup>28</sup>

Comparing the results of the STO-6G and STO sets, we see that the hfsc's are much improved by imposing the cusp condition. The hfsc's of oxygen and hydrogen increase by about 7 G and 2-3 G, respectively, with an improvement of the cusp values at oxygen and hydrogen from 0 to -16.15 (exptl. -16.00) and from -0.7 to -2.5 (exptl. -2.0), respectively, in average. The cusp value of oxygen agrees better with the experimental value than that of hydrogen. Though the hfsc of oxygen calculated by the BG1 set is wrong, the other STO results compare well with the experimental values for both oxygen and hydrogen. For oxygen, the BG2 set is better than Clementi's. The *p*-STOs of the BG2 set are safely replaced by the *p*-GTOs of Huzinaga-Dunning, though the energy becomes considerably worse. The result of the BG1 set may suggest a large basis set dependence even for the STO case. Experimentally, the oxygen hfsc is larger than the hydrogen hfsc.<sup>29</sup> This trend is reproduced in all the STO results using the BG2 set, but not so in the corresponding STO-6G results. This shows that the failure of the GTO results in reproducing the order of the hfsc's of oxygen and hydrogen is mainly due to the cusplless nature of the GTOs, and shows the superiority of the STO over the GTO for the calculations of the hfsc's. Further, we note a rough trend in Table IV that when the STO sets are used, the wave function having lower energy, which is better variationally, gives better hfsc. This is theoretically natural and very important in contrast to the GTO case shown below.

Table IV also gives the results calculated by the conventional GTO sets. We have used Huzinaga-Dunning [4s2p/2s] set,<sup>13</sup> its primitive and fairly elaborate even-tempered (11s5p1d/9s1p) Gaussian primitive sets.<sup>10,30</sup> The quality of the wave function increases in this order, as the calculated energy indicates. However, what is remarkable is that the calculated hfsc is *not* improved. The Dunning [4s2p/2s] CGTO gives the best agreement, particularly for the proton hfsc.<sup>10</sup> The oxygen hfsc is calculated to be smaller

TABLE IV. Hyperfine splitting constant (hfsc) (G), cusp value, and energy of  $\text{H}_2\text{O}^+$  calculated by the SAC-CI method.

Basis set	STO-6G/GTO				STO				Energy (a.u.)
	hfsc		Cusp		hfsc		Cusp		
	O	H	O	H	O	H	O	H	
<b>STO</b>									
<b>O BG2<sup>a</sup></b>									
H 1s(1.2)	-21.91	-21.35	0.00	-0.70	-28.93	-24.03	-16.16	-2.59	-75.732 07
H 1s2p(1.2)	-21.19	-23.84	0.00	-0.57	-28.17	-26.99	-16.16	-2.58	-75.760 14
H No. 6 <sup>b</sup>	-19.59	-21.73	0.00	-0.70	-26.17	-24.09	-16.15	-2.50	-75.732 69
H No. 6 + p(0.5)	-20.83	-21.78	0.00	-0.66	-27.64	-24.16	-16.15	-2.47	-75.734 37
<b>H No. 6<sup>b</sup></b>									
O BG1 <sup>a</sup>	-1.72	-18.14	0.00	-0.07	-8.13	-24.80	-16.05	-2.51	-75.712 60
O BG2 <sup>a</sup>	-19.59	-21.73	0.00	-0.70	-26.17	-24.09	-16.15	-2.50	-75.732 69
p(GTO) <sup>c</sup>	-23.45	-23.18	0.00	-0.70	-30.83	-25.73	-16.15	-2.52	-75.693 80
O Clementi <sup>d</sup>	-22.49	-21.96	0.00	-0.70	-24.10	-24.36	-16.17	-2.50	-75.736 35
<b>GTO</b>									
Dunning [4s2p/2s]	-23.10	-26.16	0.00	-0.69					-75.721 58
Primitive	-15.73	-20.35	0.00	-0.73					-75.765 59
Even-tempered <sup>e</sup>	-19.45	-20.44							-75.850 14
Exptl. <sup>f</sup>	29.7	26.1	-16.00	-2.00	29.7	26.1	-16.00	-2.00	

<sup>a</sup>BG1 and BG2 mean nominal and accurate basis sets of Bagus and Gilbert (Ref. 27).

<sup>b</sup>No. 6 denotes the No. 6 basis set in Table III.

<sup>c</sup>p (GTO) means that the Huzinaga–Dunning (5p)/[2p] set is used for the p functions.

<sup>d</sup>Reference 28.

<sup>e</sup>(11s5p1d/9s1p) primitive basis set. See Refs. 10 and 30.

<sup>f</sup>Reference 29. The signs of the hfsc's could not be determined.

than the proton's in disagreement with the experiment. This is so for all the GTO calculations. When the wave function is improved by giving a larger freedom by the uncontraction, the energy is certainly lowered, but the hfsc's become worse. Even the very elaborate even-tempered basis gives only poor hfsc's, in spite of its remarkably low energy. This observation is critically different from the STO case given above and so is due to the cuspleness nature of the GTO bases. In other words, as long as the GTO's are used, the labor for improving the wave function may end in getting worse results for the hfsc's. For a theoretical study, this has caused a dilemma, as Feller and Davidson pointed out.<sup>8</sup> However, we may escape from this dilemma by adopting the STO set as in the present study. This is important in developing a reliable theory for calculating hfsc's.

On the basis of the above calculations, we choose as standard STO sets the No. 6 or No. 7 set of Table III for hydrogen and the BG2 set for the first row atoms. The replacement of the p-type STOs with the GTOs (e.g., Dunning's [2p] set) helps to save computer time without much affecting the hfsc's and the cusp values. The same should be true for the d and f functions by the same reason. The calculations of organic  $\pi$  and  $\sigma$  radicals given in the following two sections are due to this standard STO set modified with the p-type GTOs.

## B. Organic $\pi$ radicals, $\text{CH}_3$ , $\text{CH}_3\text{CH}_2$ , $\text{CH}_3\text{NH}$ , $\text{CH}_3\text{O}$ , and $\text{CH}_3\text{OCH}_3^+$

We apply here the present method to the organic  $\pi$  radicals, methyl ( $\text{CH}_3$ ), ethyl ( $\text{CH}_3\text{CH}_2$ ), methylamino, ( $\text{CH}_3\text{NH}$ ), methoxy ( $\text{CH}_3\text{O}$ ), and dimethyl ether cation

( $\text{CH}_3\text{OCH}_3^+$ ) radicals, which have the unpaired electron in the  $\pi$  orbitals. The basis set is the No. 6 STO for hydrogen and the BG2 set for the first row atoms. Except for  $\text{CH}_3$ , we have replaced the p-type STO set by the Huzinaga–Dunning (5s)/[2p] GTO set.<sup>13</sup> This replacement serves to save com-

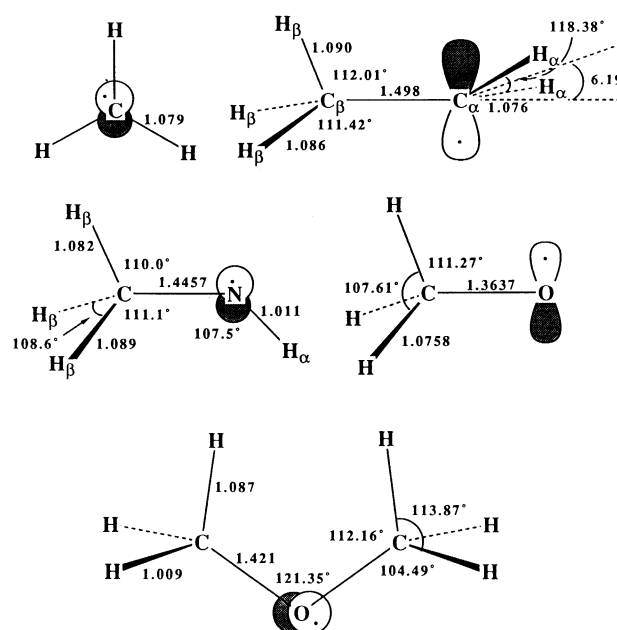


FIG. 1. Geometries of the organic  $\pi$  radicals. The dot in the lobe means an unpaired electron in an orbital.

TABLE V. Hyperfine splitting constant (hfsc) (G) and energy of CH<sub>3</sub>.

Basis set	Method	hfsc		Energy (a.u.)
		C	H	
Feller and Davidson <sup>a</sup> GTO (10s5p1d/8s1p) [8s4p1d/6s1p]	SD-CI(17819)	16.3	-26.3	-39.757 7
Sekino and Bartlett <sup>b</sup> GTO [4s2p1d/2s1p]	CCSD	28	-27	-39.735 88
Nakatsuji, Ohta, and Yonezawa <sup>c</sup> GTO [4s2p/2s]	SAC-CI	28.4	-21.9	-39.639 76
Present <sup>d</sup> STO	SAC-CI	25.6	-29.6	-39.660 88
STO <i>p</i> (GTO)	SAC-CI	30.1	-29.8	-39.629 80
Exptl. <sup>e</sup>		28.7 <sup>f</sup>	-24.7 <sup>f</sup>	

<sup>a</sup> Reference 8.<sup>b</sup> Reference 9.<sup>c</sup> Reference 7.<sup>d</sup> *p*(GTO) means that the Huzinaga–Dunning (5*p*)/[2*p*] set is used for *p* functions.<sup>e</sup> Reference 34.<sup>f</sup> The effect of molecular vibration is estimated to be 9.6 G for C and 1.7 G for H from Ref. 35.

puter time. The geometries used in the present calculations are summarized in Fig. 1. For CH<sub>3</sub> and CH<sub>3</sub>O, we have used the experimental geometries.<sup>31,32</sup> For the other molecules, we have used the geometries optimized by the *ab initio* calculations, for CH<sub>3</sub>CH<sub>2</sub> by Pacansky and Dupuis,<sup>33</sup> and for CH<sub>3</sub>NH and CH<sub>3</sub>OCH<sub>3</sub><sup>+</sup> by Momose, Nakatsuji, and Shida.<sup>10</sup> The methyl group is assumed to rotate freely. We have used the SAC/SAC-CI method as in the previous section. Tables V–IX show the present results and the comparisons with the previous theoretical results obtained by including electron correlation. Analysis of spin appearing mechanisms like spin delocalization, spin polarization, and electron correlation has been given previously for ethyl radical.<sup>7</sup>

Table V gives the results for the methyl radical. We have examined two basis sets for carbon: one is the accurate STO basis (BG2 set) of Bagus and Gilbert,<sup>27</sup> and the other is the *s*-type STO basis of BG2 plus (5*p*)/[2*s*] CGTO of Huzinaga–Dunning<sup>13</sup> for *p* functions. In Table IV, the former set was denoted as BG2 and the latter as BG2-*p*(GTO). By this replacement, the hfsc of carbon increases by 4.5 G, but that of hydrogen does not change. The present result shows a reasonable agreement with experiment. In Table V, the calculations due to Feller and Davidson,<sup>8</sup> Sekino and Bartlett,<sup>9</sup> and Nakatsuji, *et al.*<sup>7</sup> are all based on the GTO bases. The wave function due to Feller and Davidson should be the best one, as seen from the energy, from the variational point of view, but their hfsc's do not necessarily compare best with

TABLE VI. Hyperfine splitting constant (hfsc) (G) and energy of CH<sub>3</sub>CH<sub>2</sub>.

Basis set	Method	hfsc				Energy (a.u.)
		Cβ	Hβ	Cα	Hα	
Feller and Davidson (6-31G** MCSCF geometry) <sup>a</sup> GTO (13s7p2d/10s2p) [8s5p2d/6s2p]	MR-SDCI	-11.6	19.7	18.3	-21.2	
Nakatsuji, Ohta, and Yonezawa <sup>b</sup> GTO [4s2p/2s]	SAC-CI	-13.6	22.7	23.9	-18.7	-78.734 99
Momose, Nakatsuji, and Shida <sup>c</sup> GTO [4s2p/2s]	SAC-CI	-12.2	23.9	22.2	-23.1	-78.757 81
Present STO <i>p</i> (GTO)	SAC-CI	-12.1	24.5	24.0	-25.9	-78.720 78
Exptl. <sup>d</sup>		-13.6	26.9	29.5 <sup>e</sup>	-22.4	

<sup>a</sup> Reference 8.<sup>b</sup> Reference 7.<sup>c</sup> Reference 10.<sup>d</sup> Reference 34.<sup>e</sup> The effect of molecular vibration is estimated to be -9.6 G for Cα (Ref. 35).

TABLE VII. Hyperfine splitting constant (hfsc) (G) and energy of CH<sub>3</sub>NH.

Basis set	Method	hfsc				Energy (a.u.)
		C	H $\beta$	N	H $\alpha$	
Momose, Nakatsuji, and Shida <sup>a</sup>						
GTO [4s2p/2s]	SAC-CI	- 11.93	29.01	6.69	- 21.47	- 94.755 63
Present						
STO <i>p</i> (GTO)	SAC-CI	- 12.3	29.6	7.8	- 21.2	- 94.719 48
Exptl. <sup>b</sup>			34	13	22	

<sup>a</sup> Reference 10.<sup>b</sup> Reference 37. The signs could not be determined.

the experimental values,<sup>34,35</sup> particularly for carbon. This, we believe, is due to the cuspless nature of the Gaussian bases used. Though the other GTO results show better agreement with experiments, this is essentially a fortunate result; the fixed contraction of the inner Gaussian functions has led to a larger amplitude at the carbon nucleus than that of the freely variational wave function as that of Feller and Davidson. Sekino and Bartlett performed finite perturbation calculations based on the coupled cluster singles and doubles (CCSD) method and obtained fairly good results. However, their wave functions are not eigenfunctions of the spin-squared operator  $S^2$ , since their cluster expansion is symmetry nonadapted, though for methyl radical, the spin contamination was very small.<sup>9</sup> In our previous SAC-CI calculations,<sup>7</sup> we have used Ellinger's contraction<sup>36</sup> for Huzinaga's GTO set.<sup>13</sup>

Table VI shows the result for the ethyl radical. Our previous and present calculations are based on the theoretically optimized geometry due to Pacansky and Dupuis,<sup>33</sup> but Feller and Davidson<sup>8</sup> have used the geometry in which the atoms C-CH<sub>2</sub> are co-planar. The hfsc's of Feller and Davidson are all smaller than the present STO results. Our three sets of calculations differ only in the basis set. The first one is

due to Ellinger's contraction of Huzinaga's GTO set, the second one due to Dunning's contraction of the same set, and the present one due to the BG2 *s*-type STOs plus the Huzinaga-Dunning *p*-type CGTO. These three calculations give practically similar results.

The methylamino (CH<sub>3</sub>NH) and methoxy (CH<sub>3</sub>O) radicals are isoelectronic with the ethyl (CH<sub>3</sub>CH<sub>2</sub>) radical. Their results are shown in Tables VII and VIII, respectively. Among these radicals, the change in the proton hfsc's of the methyl groups is interesting. The observed hfsc's are 26.9, 34, and 43.7 G for CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>NH, and CH<sub>3</sub>O, respectively.<sup>32,34,37</sup> Historically, the appearance of the  $\alpha$ -spin density on the methyl group neighboring to the radical center atom has been considered<sup>34</sup> as a proof of "hyperconjugation" proposed by Mulliken.<sup>38</sup> Later, we have shown that the spin delocalization (direct hyperconjugation) explains about 75% of the spin density, the rest (25%) being due to the spin-polarization mechanism.<sup>39</sup> Both mechanisms are functions of the bond distance and the rotational angles around the axis connecting CH<sub>3</sub> and the radical center atom. This bond distance decreases considerably as  $R(\text{C}-\text{C}) = 1.498 \text{ \AA}$ ,  $R(\text{C}-\text{N}) = 1.4457 \text{ \AA}$ , and  $R(\text{C}-\text{O}) = 1.3637 \text{ \AA}$ , so that the  $\beta$ -proton hfsc increases in this order. In the

TABLE VIII. Hyperfine splitting constant (hfsc) (G) and energy of CH<sub>3</sub>O.

Basis set	Method	hfsc			Energy (a.u.)
		C	H	O	
Feller and Davidson <sup>a</sup>					
GTO [8s6p2d/6s2p]	SDTCI		27.7		- 114.537 5
	SDCI		23.3		- 114.763 5
Momose, Nakatsuji, and Shida <sup>b</sup>					
GTO [4s2p/2s]	SAC-CI	- 13.92	37.74	- 9.04	- 114.597 89
Present					
STO <i>p</i> (GTO)	SAC-CI	- 13.7	39.4	- 18.3	- 114.564 87
Exptl. <sup>c</sup>		- 15.56	43.67		

<sup>a</sup> Reference 8.<sup>b</sup> Reference 10. Recalculated using corrected experimental data (Ref. 32).<sup>c</sup> Reference 32.

TABLE IX. Hyperfine splitting constant (hfsc) (G) and energy of  $\text{CH}_3\text{OCH}_3^+$ .

Basis set	Method	hfsc			Energy (a.u.)
		C	H	O	
Momose, Nakatsuji, and Shida <sup>a</sup>					
GTO [4s2p/2s]	SAC-CI	-9.29	39.40	-16.86	-153.978 54
Present					
STO p(GTO)	SAC-CI	-8.5	39.8	-23.9	-153.928 83
Exptl. <sup>b</sup>			43		

<sup>a</sup> Reference 10.<sup>b</sup> Reference 40.

previous paper,<sup>7</sup> we have shown that the effect of electron correlation is small ( $\sim 3$  G) for the  $\beta$ -proton hfsc of ethyl radical. For the  $\beta$ -carbon hfsc, the change among these radicals is relatively small. The experimental values are  $-13.6$  and  $-15.6$  G for  $\text{CH}_3\text{CH}_2$  and  $\text{CH}_3\text{O}$ , respectively, in comparison with the theoretical values  $-12.1$  and  $-13.7$  G, respectively. For  $\text{CH}_3\text{NH}$ , the corresponding experimental value is not reported, but the theoretical value is  $-12.3$  G.

Table IX shows the result for the dimethylether cation radical. This radical has interestingly large  $\beta$ -proton hfsc as 43 G.<sup>40</sup> The present theoretical value is 40 G. Referring to Fig. 1, we see that the CO distance of  $\text{CH}_3\text{OCH}_3^+$  is longer than that of  $\text{CH}_3\text{O}$ , but the  $\beta$ -proton hfsc is larger in  $\text{CH}_3\text{OCH}_3^+$  than in  $\text{CH}_3\text{O}$ . This is due to the positive charge at the radical center atom of  $\text{CH}_3\text{OCH}_3^+$ . Since the orbital level of the unpaired electron is lower in the cation than in the neutral radical, the flowing-in of the  $\beta$  electron from the adjacent methyl group through the hyperconjugation should be larger in the cation radical than in the neutral radical.

The STO and GTO results differ considerably for oxygen. From the experience of  $\text{H}_2\text{O}^+$  shown in Table IV and since  $\text{CH}_3\text{OCH}_3^+$  is a substituent of  $\text{H}_2\text{O}^+$ , we predict that the experimental oxygen hfsc should be close to the present value  $-23.9$  G, which is smaller than  $-27.9$  G for  $\text{H}_2\text{O}^+$  because of the delocalization of the unpaired electron into the methyl groups.

### C. Organic $\sigma$ radicals, $\text{H}_2\text{CO}^+$ , $\text{CH}_2\text{CH}$ , and $\text{HCO}$

We here give the results for the formaldehyde cation ( $\text{H}_2\text{CO}^+$ ), vinyl ( $\text{CH}_2\text{CH}$ ), and formyl ( $\text{HCO}$ ) radicals, which have an unpaired electron on the molecular  $\sigma$  plane. The calculational method is the same as that for the organic  $\pi$  radicals. The geometries are summarized in Fig. 2. For the  $\text{HCO}$  radical, it is the experimental geometry, and for  $\text{H}_2\text{CO}^+$  and  $\text{CH}_2\text{CH}$ , they are optimized by the *ab initio* calculations; for  $\text{H}_2\text{CO}^+$  by Feller and Davidson<sup>8</sup> and for vinyl radical by Millie, Levy, and Berthier.<sup>41</sup>

Table X shows the results for  $\text{H}_2\text{CO}^+$  together with the previous theoretical results. The unpaired electron lies mainly on the  $p_\sigma$  orbital of oxygen which is perpendicular to the CO axis. The proton hfsc is extremely large (90–133 G),<sup>42</sup> but the direct spin-delocalization contribution estimated from the RHF result is only about 40 G, so that the rest (50–

93 G) should be due to the effects of the spin polarization and electron correlation. The pseudo-orbital (PO) theory<sup>4</sup> includes the spin-delocalization and spin-polarization contributions, but not the electron correlation effect. We therefore estimate the individual contributions as 40 G for spin delocalization, 31 G for spin polarization, and 48 G for electron correlation. We see that the spin-polarization and electron correlation contributions are extremely large. The  $d$ -polarization functions on carbon and oxygen have moderate effects on the O and H hfsc's.

Tables XI and XII show the results for vinyl and formyl radicals. The analysis of the spin appearing mechanism has been given previously.<sup>7</sup> For the proton hfsc's of the vinyl radical, the present calculation considerably improves the previous results due to the Gaussian basis set. The hfsc of the proton *trans* to the radical lobe is very large (68.5 G) and the present result explains 75% of the observed value. For the  $\alpha$  carbon, the present result agrees well with the experimental value, but for the  $\beta$  carbon, the present result is small. As shown previously,<sup>7</sup> the  $\beta$  carbon hfsc is the canceling result of large negative spin-polarization contribution, small positive spin-delocalization contribution, and small positive electron correlation contribution.

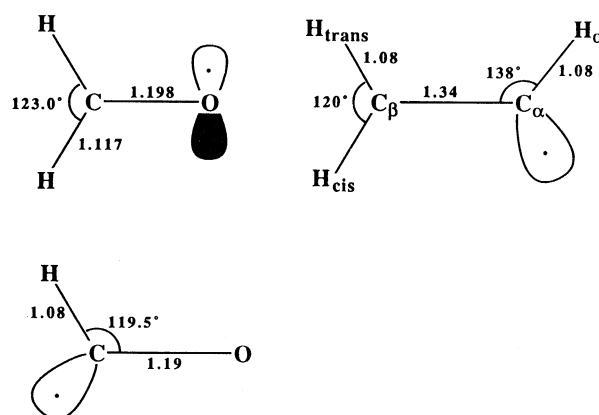


FIG. 2. Geometries of the organic  $\sigma$  radicals. The dot in a lobe means an unpaired electron in an orbital.

TABLE X. Hyperfine splitting constant (hfsc) (G) and energy of  $\text{H}_2\text{CO}^+$ .

Basis set	Method	hfsc			Energy (a.u.)
		C	H	O	
Feller and Davidson <sup>a</sup> GTO (10s5p1d/8s1p) [8s4p1d/6s1p]	MRCI	-24	80	-14	-113.881 3
Sekino and Bartlett <sup>b</sup> GTO [4s2p1d/2s1p]	CCSD	-37	100(93) <sup>g</sup>	-21	-113.869 18
Momose, Nakatsuji, and Shida <sup>c</sup> GTO [4s2p/2s]	SAC-CI	-28.82	117.11	-13.27	-113.678 62
Present					
STO <i>p</i> (GTO)	RHF	0.0	40.3	0.0	-113.446 54
	PO	-30.5	71.7	-64.9	-113.456 07
	SAC-CI	-29.8	119.4	-19.9	-113.652 10
STO <i>p</i> (GTO) + 1d <sup>d</sup>	SAC-CI	-28.0	111.3	-14.0	-113.787 43
Exptl.		-38.8	132.7 <sup>e</sup> 90.3 <sup>f</sup>		

<sup>a</sup> Reference 8.<sup>b</sup> Reference 9.<sup>c</sup> Reference 10.<sup>d</sup> The exponents of the d-polarization functions are 0.600 for carbon 1.154 for oxygen.<sup>e</sup> Reference 42(a).<sup>f</sup> Reference 42(b).<sup>g</sup> The value in parentheses: [5s3p1d/3s1p].TABLE XI. Hyperfine splitting constant (hfsc) (G) and energy of  $\text{C}_2\text{H}_3$ .

Basis set	Method	hfsc					Energy (a.u.)
		$C\beta$	$H_{trans}$	$H_{cis}$	$C\alpha$	$H\alpha$	
Sekino and Bartlett <sup>a</sup> GTO [4s2p1d/2s1p]	CCSD	-8	48	28	121	9	-77.703 26
Nakatsuji, Ohta, and Yonezawa <sup>b</sup> GTO [4s2p/2s]	RHF	9.5	21.8	12.9	119.4	23.5	-77.343 84
	PO	-13.7	39.3	24.4	142.4	11.1	
	SAC-CI	-7.4	47.5	29.3	113.4	17.4	-77.525 49
Present							
STO <i>p</i> (GTO)	SAC-CI	-1.1	51.4	34.1	102.2	12.1	-77.509 75
Exptl. <sup>c</sup>		-8.6	68.5	34.2	107.6	13.3	

<sup>a</sup> Reference 9.<sup>b</sup> Reference 7.<sup>c</sup> Reference 34.

TABLE XII. Hyperfine splitting constant (hfsc) (G) and energy of HCO.

Basis set	Method	hfsc			Energy (a.u.)
		C	H	O	
Feller and Davidson <sup>a</sup> GTO [8s4p2d/6s2p]	MRCI	127	127	-13	-113.548 2
Nakatsuji, Ohta, and Yonezawa <sup>b</sup> GTO [4s2p/2s]	SAC-CI	134.3	115.3	-9.3	-113.389 44
Present					
STO <i>p</i> (GTO)	SAC-CI	119.0	119.0	-16.3	-113.396 46
Exptl. <sup>c</sup>		131.0	127.0		

<sup>a</sup> Reference 8.<sup>b</sup> Reference 7.<sup>c</sup> Reference 43.



For HCO, the result of Feller and Davidson is excellent in comparison with the experimental value.<sup>43</sup> The present result of oxygen is again larger than the previous GTO result and we believe that the present result should be closer to the experimental value.

#### IV. SUMMARY AND CONCLUSIONS

We have summarized the present results of the hfsc's in Table XIII. Figure 3 shows the correlation between the present theoretical results and the experimental values. When the sign of the hfsc is not determined experimentally, we have adopted the sign of the present theoretical result. Generally speaking, the agreement between theory and experiment is fairly good, so that the present method may be used, by experimentalists, for the assignment of the experimental values. From Fig. 3, we see that the present theoretical values tend to be smaller, in absolute value, than the experimental ones for both protons and the first row atoms. The average discrepancies are 3.6, 8.2, 5.2, and 2.3 G for proton, carbon, nitrogen, and oxygen, respectively.

Probably, one of the most attractive features of the present method lies in its theoretically natural behavior. We have seen in Tables III and IV that the theoretically better STO wave function, which gives lower energy, gives generally the better hfsc's. This was not so, on the contrary, for the Gaussian wave function. For example, we have seen that the

primitive Gaussian set gives often worse hfsc's than the contracted basis, though the former gives a lower energy than the latter. We have also observed that the variationally good Gaussian wave functions do not necessarily give good results for the hfsc's. This certainly causes an undesirable dilemma in the effort of developing a reliable theory for calculating hfsc's.<sup>8</sup> In the present approach, however, we can believe that as we improve the wave function by a standard quantum mechanical method, we will improve the hfsc's as well. This feature is very important in developing the theory of the hfsc's, particularly, of the heavier atoms.

We note that for the radicals studied here, the present STO results are similar to the previous GTO results<sup>7,10</sup> based on Huzinaga–Dunning CGTOs. The use of the SAC-CI method is common and has guaranteed the inclusion of the spin and electron correlation effects. We must note, however, that this similarity does not mean a general similarity between the STO and GTO results, but is a special case for Dunning's contraction of Huzinaga's GTOs. In the Dunning contraction, a largest number of GTOs are contracted for the innermost orbital which results in a larger amplitude at the position of the nucleus, though the cusp there is zero because of the functional form of the Gaussians. Actually, when we use the primitive GTO set, the hfsc's become worse though the energy is lowered.

We thus conclude that the present method is promising as a method of calculating hfsc's. We use the STO basis, which has the cusp, and take into account both spin polarization and electron correlation adequately by using the SAC/SAC-CI method. The STO-NG method is useful in evaluating the integrals. The use of the GTOs for the  $p$  and  $d$

TABLE XIII. Hyperfine splitting constants (hfsc's) calculated with STO basis.

Molecule	Nucleus	Theoretical	Experimental <sup>a,b</sup>
H <sub>2</sub>	H	327.4	333.7
H <sub>2</sub> O <sup>+</sup>	O	-26.2	(-)29.7
	H	-24.1	(-)26.1
CH <sub>3</sub>	C	25.6	28.7
	H	-29.6	-24.7
CH <sub>3</sub> CH <sub>2</sub>	Cβ	-12.1	-13.6
	Hβ	24.5	26.9
	Cα	24.0	29.5
	Hα	-25.9	-24.5
CH <sub>3</sub> NH	C	-12.3	
	Hβ	29.6	34
	N	7.8	13
	Hα	-21.2	(-)22
CH <sub>3</sub> O	C	-13.7	-15.6
	H	39.4	43.7
	O	-18.3	
CH <sub>3</sub> OCH <sub>3</sub> <sup>+</sup>	C	-8.5	
	H	39.8	43
	O	-23.9	
H <sub>2</sub> CO <sup>+</sup>	C	-29.8	-38.8
	H	119.4	132.7, 90.3
	O	-19.9	
CH <sub>2</sub> CH	Cβ	-1.1	-8.6
	H <sub>trans</sub>	51.4	68.5
	H <sub>cis</sub>	34.1	34.2
	Cα	102.2	107.6
	Hα	12.1	13.3
HCO	C	119.0	131.0
	H	119.0	127.0
	O	-16.3	

<sup>a</sup> The sign ( - ) is based on the present theoretical result.

<sup>b</sup> The citations of the experimental values are given in the individual tables.

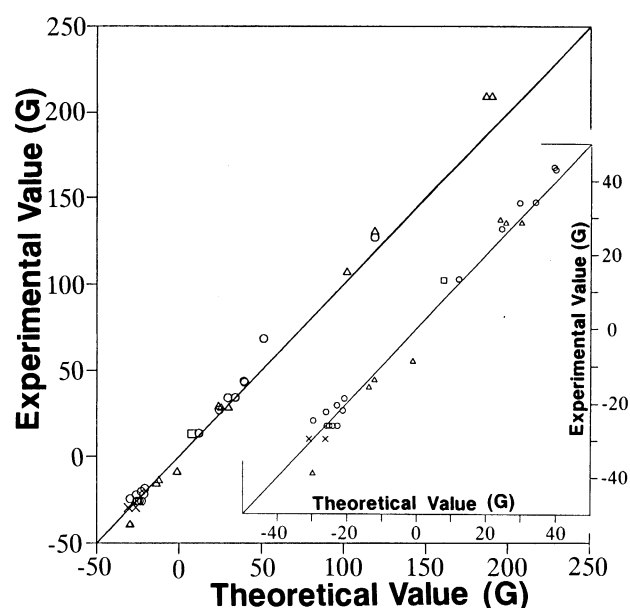


FIG. 3. Comparison between experimental and theoretical values of the hfsc's for hydrogen (O), carbon (Δ), nitrogen (□), and oxygen (×) atoms of the doublet radicals studied in this paper. The region of small hfsc's is enlarged in the figure in order to make the correlation clearer.

functions, which have nodes at the centers, helps to save the computer time.

As a result of the present calculation, we found a relatively large dependence on the quality of the STO basis sets. For example, between the two sets of the STOs given by Bagus and Gilbert,<sup>27</sup> the "accurate" set (the BG1 set in Table IV) has given much superior results. Probably, a systematic study of such dependence is necessary for achieving the above goal.

In the present calculations, we have given the results of only the ground state of doublet radicals. However, in the present SAC/SAC-CI method, it is very easy to calculate the excited states of the doublet radicals. Actually, we have such results additionally in the present calculations, though we did not summarize such results here. We encourage experimentalists to observe the hfsc's of the excited states, though a few results have already been reported,<sup>44</sup> since it is expected that they will open a new field for investigating the electronic structures of excited states.

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