Ab initio calculation of hyperfine splitting constants of molecules

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Hyperfine splitting (hfs) constants of molecules, methyl, ethyl, vinyl, allyl, cyclopropyl, formyl, O_3^-, NH_2, NO_2, and NF_2 radicals have been calculated by the pseudo-orbital (PO) theory, the unrestricted HF (UHF), projected UHF (PUHF) and single excitation (SE) CI theories. The pseudo-orbital (PO) theory is based on the symmetry-adapted-cluster (SAC) expansion proposed previously. Several contractions of the Gaussian basis sets of double-zeta accuracy have been examined. The UHF results were consistently too large to compare with experiments and the PUHF results were too small. For molecules studied here, the PO theory and SECI theory gave relatively close results. They were in fair agreement with experiments. The first-order spin-polarization self-consistency effect, which was shown to be important for atoms, is relatively small for the molecules studied here. The present result also shows an importance of eliminating orbital-transformation dependence from conventional first-order perturbation calculations. The present calculations have explained well several important variations in the experimental hfs constants.

I. INTRODUCTION

The isotropic hyperfine splitting (hfs) constants of free radicals have been the subject of a number of *ab initio* studies.[1-7] The calculations have been carried out with the conventional open-shell orbital theories, the first-order perturbation theory, and the single excitation (SE) CI theory. The conventional open-shell orbital theories such as the unrestricted HF (UHF) theory[8] or the spin-extended (SE) HF theory[9] have theoretical defects as analyzed previously.[10,11] The UHF wave function does not represent a pure spin symmetry. It usually gives spin densities larger than the experimental values. In the SEHF theory, the spin-correlation effect and the electron-correlation effect interfere with each other through the variational process, so that only poor results are obtained for both spin densities and correlation energies.[1,12,13] On the other hand, the spin-polarization single excitation (SE) CI theory does not include the self-consistency of the spin-polarization effect. The first-order perturbation theory is dependent on the unitary transformations among orbitals (e.g., canonical orbitals and localized orbitals). Such dependence can be eliminated if the single excitation CI matrix is diagonalized completely.[14]

In the previous works,[15,16] we have proposed a new open-shell orbital theory based on the symmetry-adapted-cluster (SAC) expansion of an exact wave function. This theory has been called pseudo-orbital (PO) theory. It does not share the theoretical defects with the conventional open-shell orbital theories. For the first-row atoms, the pseudo-orbital (PO) theory has given spin densities which are fairly better than those of the UHF, SEHF, and SECI theories.[16]

In this work, we extend the calculation to a variety of σ and π radicals of organic and inorganic molecules. For comparison, we have also calculated hfs constants by the UHF, projected UHF (PUHF), and SECI theories. In Sec. II, we outline the pseudo-orbital (PO) theory applied in this work. In Sec. III, we first discuss the selection of the Gaussian basis set which is suitable for the calculation of the hfs constants, and then compare the present results with those of previous *ab initio* studies. In Sec. IV, we give the results of the hfs constants of organic and inorganic σ and π radicals. The conclusions of the present study are given in Sec. V.

II. THEORETICAL BACKGROUND

A. Pseudo-orbital theory

The basis of the pseudo-orbital (PO) theory has been discussed in detail in Refs. 15 and 16. Thouless[17] has shown that, if only the one-particle excitation operator $\hat{T}_1$ is considered in the conventional cluster expansion, i.e.,

$$\Psi = N \exp(\hat{T}_1)\Phi_0 , \tag{1}$$

it is equivalent to a transformation of a single determinant Φ_0 to another single determinant Ψ. Thus, when we apply the variational principle to the cluster expansion (1), the resultant Ψ should be equivalent to the HF wave function. In open-shell systems, the resultant HF wave function is the UHF wave function. The SAC expansion is an extension of the cluster expansion to open-shell systems.[15] It is different from the conventional cluster expansions. The symmetry adaptation is essential because of the nonlinear character of the expansion. The PO theory has been derived, analogously based on Eq. (1), by considering only the single excitation operators in the SAC expansion formalism (see Fig. 1),

CLUSTER EXPANSION
$$\Psi = N \exp(\hat{T}_1)\Phi_0$$
$\hat{T}_1$; ONE-PARTICLE EXCITATION OPERATOR

VARIATIONAL PROCEDURE

THOULESS THEOREM
$$\Psi_{SD} = N \exp(\hat{T}_1)\Phi_{SD}$$
(SD; SINGLE DETERMINANT)

CONVENTIONAL ORBITAL THEORY
UHF, SEHF THEORY

SAC EXPANSION
$$\Psi_{PO} = \mathcal{O} \exp(\hat{S}_{(1)})\Phi_0$$
$\hat{S}_{(1)}$; SYMMETRY-ADAPTED SINGLE EXCITATION OPERATOR

VARIATIONAL PROCEDURE

NEW ORBITAL THEORY IN OPEN-SHELL SYSTEMS
PSEUDO-ORBITAL THEORY
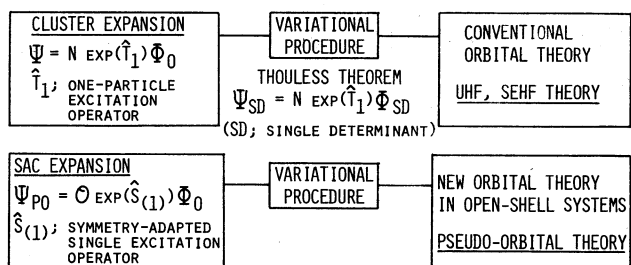
FIG. 1. The concept of the pseudo-orbital theory.

namely,

$$\Phi_{PO} = \mathcal{O} \exp(\hat{S}_{(1)})\Phi_0 \quad . \tag{2}$$

The operator $\hat{S}_{(1)}$ is expanded by the symmetry-adapted single excitation operator $S^+_{\sigma_1,i}$ as

$$\hat{S}_{(1)} = \sum_{\sigma_1}^{f_1} \sum_i C_{\sigma_1,i} S^+_{\sigma_1,i} \quad , \tag{3}$$

where σ_1 denotes an element of the f_1 independent (degenerate) symmetry functions of the single excitations i. In the present calculations, we have adopted only the spin-polarization excitation operator $S^+_{P,tk}$ for the $S^+_{\sigma_1,i}$, namely ,

$$\Psi_{PO3} = \mathcal{O} \exp\left(\sum_t \sum_k C_{P,tk} S^+_{P,tk} \right)\Phi_0$$

$$= \mathcal{O} \exp\left(\sum_I C_I S^+_I \right)\Phi_0 \quad , \tag{4}$$

$$S^+_{P,tk} = (s+2)^{-1/2} \left[(s/2)^{1/2}(a^+_{t\alpha}a_{k\alpha} - a^+_{t\beta}a_{k\beta}) \right.$$

$$\left. + (2/s)^{1/2} a^+_{t\alpha}a_{k\beta} \sum_{m=q+1}^p a^+_{m\beta}a_{m\alpha} \right] \quad , \tag{5}$$

where the excitation operator $S^+_{P,tk}$ generates the spin-adapted spin-polarization excitation from doubly occupied orbital k to vacant orbital t. s denotes the number of unpaired electrons in the system (i.e., $s=1$ for doublet and $s=2$ for triplet). The other types of single excitations were neglected since they satisfy the Brillouin theorem for the restricted HF wave function[16,18] chosen here for the reference wavefunction Φ_0:

$$\Phi_0 = |0\rangle = \| \phi_1\alpha\phi_1\beta \cdots \phi_k\alpha\phi_k\beta \cdots \phi_q\alpha\phi_q\beta\phi_{q+1}\alpha \cdots \phi_p\alpha\| . \tag{6}$$

When the system has degenerate spatial symmetry, a linear combination of the $S^+_{P,tk}$ given by Eq. (5) is necessary for the symmetry adaptation. For example, the methyl radical has D_{3h} symmetry and the symmetry-adapted (a'_1) excitation operator from the degenerate doubly occupied MO pair (k_x, k_y) to the degenerate vacant MO pair (t_x, t_y) is written as

$$S^+_{P,(t_x,t_y)(k_x,k_y)} = 2^{-1/2}(S^+_{P,t_xk_x} + S^+_{P,t_yk_y}) \quad . \tag{7}$$

However, when we adopt a linear approximation in the variational equation [see Eq. (10)], the space symmetry is automatically satisfied and Eq. (7) is not necessarily required. In the variational equation which considers more than second order in the coefficients, the symmetry adaptation as Eq. (7) is inevitably necessary.

We apply the variational principle to solve the PO

wave function Ψ_{PO3} and obtain[15]

$$\langle \Psi_{PO3} | (H-E)S^+_I | \Psi'_{PO3} \rangle = 0 \quad , \tag{8}$$

for all I included in Eq. (4). Here Ψ'_{PO3} is given by

$$\Psi'_{PO3} = \exp\left(\sum_I C_I S^+_I \right)\Phi_0 \quad , \tag{9}$$

which does not have the projection operator $\mathcal{O}$ in front of the unlinked terms. When the reference wave function Φ_0 is already a reasonably good wave function, the coefficient C_I would be small so that we may neglect the second- and higher-order terms in Eq. (8). Thus, retaining terms up to first order in the coefficients, we obtain from Eq. (8) the linear equation

$$\langle 0 | HS^+_I | 0 \rangle + \sum_J C_J (\langle 0 | S_J HS^+_I | 0 \rangle$$

$$+ \langle 0 | HS^+_I S^+_J | 0 \rangle - E\delta_{IJ}) = 0 \quad , \tag{10}$$

for all I included in Eq. (4). Further, we define the H matrix and the normalized eigenvector D as

$$H_{0I} = \langle 0 | HS^+_I | 0 \rangle \quad ,$$

$$H_{IJ} = \langle 0 | S_J HS^+_I | 0 \rangle + \langle 0 | HS^+_I S^+_J | 0 \rangle \quad ,$$

$$D = d_0(1, C_1, C_2, \cdots, C_N) \quad . \tag{11}$$

Then, Eq. (10) is reduced to the secular equation

$$(H-E)D = 0 \quad . \tag{12}$$

A diagonalization of Eq. (12) leads to the energy E and the coefficients $C_{P,tk}$. This solution is simpler than the previous one in a sum-over-state form.[15]

On the other hand, the SECI wave function does not include the self-consistency effect of the symmetry-adapted excitation operator S^+_I. As analyzed previously,[16] it usually gives spin densities smaller than those of the PO theory. The secular equation for the SECI theory is

$$\langle 0 | HS^+_I | 0 \rangle + \sum_J C_J(\langle 0 | S_J HS^+_I | 0 \rangle - E\delta_{IJ}) = 0 \quad . \tag{13}$$

Thus, by dropping off the first-order self-consistency term, i.e., $\langle 0 | HS^+_I S^+_J | 0 \rangle$, from Eq. (10), we obtain the results for the SECI theory.

In order that the calculated results are independent of the unitary transformations among orbitals, the secular equation (12) should be diagonalized completely without neglecting the off-diagonal terms.[14] The present results are thus independent of such transformations. The first-order perturbation theory used by Ellinger et al.[6] are dependent on the unitary transformations among orbitals (e.g., canonical and quasilocalized representations). The dependence is very large. Such dependence is not preferable and should be deleted.

B. Spin density

We have calculated spin densities correct to second order in the coefficients. From Eq. (4), we obtain the spin density as

$$\rho(r) = \rho_{SD}(r) + \rho_{SP}(r) \quad ,$$

$$\rho_{SD}(r) = d_0^2 \langle 0 | \hat{\rho}(r) | 0 \rangle = (d_0^2/s)\sum_m \phi_m^2(r) \quad ,$$

$$\rho_{SP}(r) = d_0^2 \left[2\sum_I C_I \langle 0|S_I \hat{\rho}(r)|0\rangle + \sum_I \sum_J C_I C_J \langle 0|S_I \hat{\rho}(r)S_J^+|0\rangle \right] = (d_0^2/s) \Bigg(2(2s/(s+2))^{1/2} \sum_I C_I \phi_k(r)\phi_t(r)$$

$$+ \sum_I \sum_J C_I C_J \Big\{ \delta_{tu}\delta_{kl}[(s^2 + 2s - 4)/(s^2 + 2s)] \sum_m \phi_m^2(r) + [2/(s+2)][\delta_{tu}\phi_l(r)\phi_k(r) + \delta_{kl}\phi_t(r)\phi_u(r)] \Big\} \Bigg) \quad , \tag{14}$$

where $I = (P, tk)$, $J = (P, ul)$, and $\hat{\rho}$ denotes the normalized spin density operator

$$\hat{\rho}(r) = (2/s) \sum_\nu S_Z(\nu)\delta(r - r_\nu). \tag{15}$$

The subscripts SD and SP mean the spin-delocalization and the spin-polarization contributions, respectively.[10,19] The spin-delocalization term ρ_{SD} arises from the delocalization of the unpaired-spin orbitals over the molecules and is always positive or zero. The spin-polarization term ρ_{SP} arises from the spin-correlation correction to the restricted HF (RHF) wave function. It is either positive or negative. In the case of π radicals, the ρ_{SD} contribution is zero (for the nuclei on the plane), and the spin density is determined only by the spin-polarization term ρ_{SP}.

The hfs constants and the spin densities are connected by the following equation:

$$a^N = (8\pi/3)(g_e/g_0)g_N\beta_N\rho(r_N) \quad , \tag{16}$$

where (g_e/g_0) is the ratio of the g values of the free electron and the radical under consideration and will be taken as unity hereafter; g_N and β_N are the nuclear magnetogyric ratio and nuclear magneton, respectively. Specif-

ically, $a^H = 1592.2\rho(H)$, $a^C = 400.4\rho(^{13}C)$, $a^N = 115.0$ $\rho(^{14}N)$, $a^O = -215.9\rho(^{17}O)$, and $a^F = 1497.9\rho(^{19}F)$, where a is in G and ρ in a.u.

III. CALCULATIONS AND RESULTS FOR CH$_3$ RADICAL

For the ab initio calculation of hfs constants of molecules, the selection of the basis set is as important as the selection of the good theory. This is seen in Table I which summarizes the previous ab initio calculations of the hfs constant of methyl radical together with the present one.

We have determined the basis set based on the calculation of the hfs constant of the methyl radical in its planar geometry.[20] The Gaussian basis set, consisting of Huzinaga's $(9s5p/4s)$ set,[21] was contracted in several ways to $[4s2p]$ on carbon and to $[2s]$ on hydrogen. In Table II, the effects of contraction on the calculated hfs constants of the methyl radical are given. The best basis set for carbon is the $[9s5p]$ uncontracted basis set [(D) in Table II]. The calculated hfs constant is 37.9 G. The best basis set for hydrogen is $[4s]$ uncontracted basis set [(E) in Table II]. The calculated value is

TABLE I. Ab initio calculation of hfs constants (in G) of planar CH$_3$.

Reference	Basis set	Method	a(H)	a(C)
Chang, Davidson, and Vincow[4]	minimal STO (Slater rule)	SECI	−29.2	133.6
	minimal STO (optimized)	SECI	−38.9	132.3
	double ζ STO	SECI	−36.1	23.0
Konishi and Morokuma[5]	minimal STO+S	SECI	−29.6	62.3
	double ζ STO+$2S$	SECI	−27.6	35.6
Millie, Levy, and Berthier[6(a)]	$[6s4p2d/3s1p]$ (CGTO)	FOP[a] canonical	−20.6	10.2
		quasilocalized	−13.0	−5.0
Ellinger, Rassat, Subra and Berthier[6(b)]	$[4s2p/2s]$ (CGTO)	FOP canonical	−24.6	9.7
	$\zeta_H = 1.0$	quasilocalized	−31.0	31.0
This work	$[4s2p/2s]$ $\zeta_H = 1.2$	pseudo-orbital	−26.5	39.4
		UHF	−40.6	71.3
		PUHF	−13.2	24.8
		SECI	−24.3	33.3
Fessenden[25(a)]		Exptl.	−23.0	38.3

[a]First-order perturbation.

TABLE II. Hyperfine splitting constant (in G) and energy (a.u.) calculated by the pseudo-orbital theory with various contraction of the primitive Gaussian set ($\zeta_H = 1.0$).

Contraction type	a(H)	a(C)	Energy
(A)	−25.7	38.4	−39.5211
(B)	−26.8	41.7	−39.5412
(C)	−31.5	36.4	−39.5500
(D)	−27.2	37.9	−39.5451
(E)	−25.7	36.7	−39.5538

(A) C, (9s5p)−[5211/32]; H, (4s)−[22].

(B) C, (9s5p)−[6111/41]; H, (4s)−[22].

(C) C, (9s5p)−[5211/32]; H, (4s)−[31].

(D) C, [9s5p] uncontracted; H, (4s)−[22] (best for C).

(E) C, (9s5p)−[5211/32]; H, [4s] uncontracted (best for H).

−25.7 G for hydrogen. Among the [4s2p/2s] contracted basis sets (A), (B), and (C), the contraction (A) gives the best hfs result in comparison with the uncontracted

TABLE III. Contracted Gaussian basis set used in the present calculation [type (A) in Table II].

Exponents	Coefficients	Exponents	Coefficients
Carbon s set		Nitrogen s set	
4232.6100	0.002336	5909.4400	0.002313
634.8820	0.017884	887.4510	0.017670
146.0970	0.086818	204.7490	0.085745
42.4974	0.298521	59.8376	0.292420
14.1892	0.686791	19.9981	0.693154
5.1477	0.772924	7.1927	0.777532
1.9666	0.257253	2.6859	0.253646
0.4962	1.000000	0.7000	1.000000
0.1533	1.000000	0.2132	1.000000
Carbon p set		Nitrogen p set	
18.1557	0.039196	26.7860	0.038244
3.9864	0.244143	5.9564	0.243846
1.1429	0.816773	1.7074	0.817192
0.3594	0.668140	0.5314	0.669566
0.1146	0.417933	0.1654	0.419782
Oxygen s set		Fluorine s set	
7816.5400	0.002328	9994.7900	0.002315
1175.8200	0.017696	1506.0300	0.017550
273.1880	0.084571	350.2690	0.083893
81.1696	0.283858	104.0530	0.282762
27.1836	0.701408	34.8432	0.702937
9.5322	0.791812	12.2164	0.791631
3.4136	0.240562	4.3689	0.240848
0.9398	1.000000	1.2078	1.000000
0.2846	1.000000	0.3634	1.000000
Oxygen p set		Fluorine p set	
35.1832	0.040023	44.3555	0.042011
7.9040	0.253849	10.0820	0.261899
0.2305	0.806841	2.9959	0.797663
0.7171	0.652812	0.9383	0.644783
0.2137	0.444286	0.2733	0.456370
Hydrogen s set			
13.3615	0.130844		
2.0133	0.921539		
0.4538	0.516820		
0.1233	0.554485		

TABLE IV. ζ_H dependence of hfs constants (in G) of CH_3 and CH_3CH_2. [a]

	ζ_H			
	1.0	1.2	1.4	Exptl.
CH_3				
a(C)	38.4	39.4	38.7	38.3
a(H)	−25.7	−26.5	−27.8	−23.0
Energy (a.u.)	−39.5211	−39.5451	−39.5543	
CH_3CH_2				
$a_{SD}(H_\beta)$	10.6	10.9	11.7	
$a_{SP}(H_\beta)$	9.1	9.2	9.5	
$a(H_\beta)$	19.7	20.1	21.2	26.9
Energy (a.u.)	−78.5232	−78.5585	−78.5709	

[a]Results of the pseudo-orbital theory.

result, though it gives the worst energy. The contraction type [5211/32] on carbon, which was first used by Ellinger et al.,[6(b)] and [22] on hydrogen, i.e., the contraction (A), seems to give more variational flexibility in the vicinity of the nucleus than the contraction type [6111/41] on carbon and [31] on hydrogen originally due to Dunning.[22] The type (A) contraction for the atoms H, C, N, O, and F are listed in Table III.

The hfs constant of hydrogen depends surprisingly little on the change in the scale factor ζ_H.[6(b)] This is shown in Table IV for methyl and ethyl radicals. Both the SD and SP contributions are insensitive to ζ_H. Thus, we have used the value $\zeta_H = 1.2$ from the energetic point of view.

The effect of polarization functions was also examined. The effect of the p function on hydrogen was very small and the effect of the d function on carbon was also not large (Table V). Then, for practical use, we have not included any polarization functions in the following calculations of hfs constants.

In the results of Ellinger et al., shown in Table I, the uses of the canonical orbitals and quasilocalized orbitals give largely different values. This is due to the fact that the first-order perturbation theory depends largely on the unitary transformations among the reference molecular orbitals. This fact is not preferable from the theoretical point of view, and can be corrected by completely diagonalizing the secular equation, i.e., by including the (off-diagonal) coupling terms.[14]

In Table I, we have summarized the present results obtained by the pseudo-orbital (PO) theory, and the UHF,

TABLE V. Effect of polarization functions in CH_3. [a]

Basis set	a(C) (G)	a(H) (G)	Energy (a.u.)
[4s2p/2s]	39.4	−26.5	−39.5451
[4s2p/2s1p][b]	38.9	−26.2	−39.5512
[4s2p1d/2s] α_d(C) = 0.3852	35.8	−24.6	−39.5592

[a]Results of the pseudo-orbital theory.
[b]The p function on hydrogen is 2-GTO ($\alpha_1 = 13.3615$, $\alpha_2 = 2.0133$; $c_1 = 0.13378$, $c_2 = 0.94225$).

TABLE VI. Molecular geometry used for the present calculation.

Molecule	Structure	Reference
CH_3	CH = 1.079 Å	20
CH_3CH_2	CC = 1.498 Å, CH_α = 1.076 Å CH_β = 1.090 Å, CH_β' = 1.086 Å CCH_β = 112.01°, CCH_β' = 111.42° $H_\alpha C_\alpha H_\alpha$ = 118.38°, CCH_α = 120.6°	26
CH_2CHCH_2	CC = 1.40 Å, CH = 1.08 Å, CCC = CCH = HCH = 120°	
NH_2	NH = 1.024 Å, HNH = 103.4°	20
NF_2	NF = 1.37 Å, FNF = 104.2°	20
O_3^-	OO = 1.19 Å, OOO = 100°	27
CH_2CH	CC = 1.34 Å, CH = 1.08 Å HCH = 120°, CCH = 138°	6
cyclo-C_3H_5	CC = 1.524 Å, CH = 1.07 Å HCH = 120°, CCC = 60°, CCH_α = 41°	6
HCO	CO = 1.19 Å, CH = 1.08 Å, HCO = 119.5°	20
NO_2	NO = 1.1934 Å, ONO = 134.1°	20

PUHF, and the SECI theories with the same $[4s2p/2s]$ basis set. The PO theory has given 39.4 G for carbon and − 26.5 G for hydrogen, in good agreement with experiment. The UHF value is too large to compare with the experimental value, while the PUHF value, which is one third of the UHF value as proved theoretically,[10] is too small. The differences between the PO and SECI values show the spin-polarization self-consistency effect included to first order in the present calculation. It is about 2 G for hydrogen and about 6 G for carbon, which is relatively small in comparison with the previous results for atoms.[16] We also see the following inequality as proved previously[11,16]:

$$|\rho_{SP}^{SECI}| < |\rho_{SP}^{PO}| < |\rho_{SP}^{UHF}| \qquad (17)$$

IV. GENERAL RESULTS AND DISCUSSIONS

The hfs constants of π radicals (methyl, ethyl, allyl, NH_2, O_3^- and NF_2) are calculated by the UHF, PUHF, SECI, and PO theories. (The geometries are listed in Table VI.) The results are shown in Table VII. In π radicals, the unpaired spin orbital has a node on the molecular plane so that the a_{SD} term does not contribute to the hfs constants of the nuclei lying on the molecular plane. Thus, for π radicals, it is particularly important to correctly take into account the spin-correlation effect.

The hfs constants calculated by the UHF theory are always much larger than the experimental values for nuclei on the molecular plane. The PUHF results satisfy the relation derived previously[10,11] to a good extent:

$$(\rho_{SP})_{UHF} \cong \frac{s+2}{s} (\rho_{SP})_{PUHF} , \qquad (18)$$

where $s = 1, 2, \ldots$ for doublet, triplet, etc. They are, however, too small to compare with the experimental values. The PO and SECI theories give better agreement with experiments. The spin-polarization self-consistency effect included to first order in the present PO calculation is relatively large for first-row atoms at the radical center. The relation (17) holds for calculated values without exceptions. In comparison with the results of Ellinger et al., the independence of the unitary transformations among occupied or virtual orbitals seems to be important to obtain consistent agreement with experiment.

Next we compare in more detail the PO and SECI results with experiment. The hfs constant for methyl and allyl radicals are in satisfactory agreement with the experimental results. In the case of allyl radical, the calculated hfs constant of proton H_3 is a little larger than that of proton H_4. This result is consistent with the experimental result. For ethyl radical, the hfs constants are in good agreement with the experimental val-

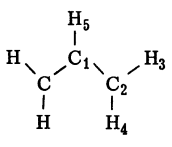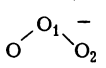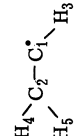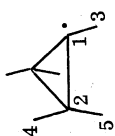TABLE VII. Hyperfine splitting constants of π radicals (G).

Molecule	Nucleus	UHF	PUHF	Pseudo-orbital	SECI	Exptl.	(Ref.)
CH_3	C	71.3	24.8	39.4	33.3	38.3	[25(a)]
	H	− 40.6	− 13.2	− 26.5	− 24.3	− 23.0	
$CH_3\dot{C}H_2$	$\dot{C}$	76.4	28.1	45.1	38.7	39.1	[25 (a), (b)]
	C	− 28.4	− 9.3	− 18.3	− 16.1	− 13.6	
	H_α	− 39.6	− 12.8	− 26.0	− 23.8	− 22.4	
	H_β	24.6	15.7	20.1	19.6	26.9	
allyl	C_1	− 68.2	− 22.1	− 25.2	− 21.8	⋯	[28]
	C_2	65.7	22.8	26.4	22.0	⋯	
	H_3	− 32.7	− 10.7	− 15.8	− 14.0	− 14.8	
	H_4	− 32.2	− 10.6	− 15.4	− 13.7	− 13.9	
	H_5	21.9	7.4	3.8	2.0	4.1	
NH_2	N	15.0	5.2	7.4	6.4	10.3	[29(b)]
	H	− 36.3	− 11.9	− 24.2	− 21.9	− 23.9	
NF_2	N	20.2	7.1	12.7	11.8	17	[30]
	F	118.1	40.4	77.2	69.7	60	
O_1^-	O_1	− 40.6	− 13.8	− 26.2	− 23.9	− 22.2	[31]
	O_2	− 19.3	− 6.5	− 12.4	− 11.3	− 10.5	

TABLE VIII. Hyperfine splitting constants of σ radicals (G).

Molecule	Nucleus	UHF			PUHF			Pseudo-orbital			SECI			Exptl.	(Ref.)
		a_{SD}	a_{SP}	a	a_{SD}	a_{SP}	a	a_{SD}	a_{SP}	a	a_{SD}	a_{SP}	a		
H4\C2=C1\H5 (vinyl)	C1	117.7	88.6	206.3	117.7	29.5	147.2	119.4	23.0	142.4	121.3	19.0	140.4	107.6	[25(a), (b)]
	C2	8.9	−74.5	−65.7	8.9	−24.2	−15.3	9.5	−23.2	−13.7	9.7	−19.1	−9.4	−8.6	
	H3	19.3	−36.5	−17.2	19.3	−12.2	7.1	23.5	−12.4	11.1	23.9	−10.4	13.5	13.3	
	H4	13.0	36.6	49.6	13.0	12.2	25.2	12.9	11.5	24.4	13.1	9.4	22.6	34.2	
	H5	21.5	44.9	66.4	21.5	15.0	36.5	21.8	17.5	39.3	22.2	15.2	37.4	68.5	
(cyclopropyl)	C1	121.8	56.5	178.3	121.8	18.8	140.6	122.2	31.0	153.2	122.2	26.6	148.8	...	(24), [25(b)], (33)
	C2	2.3	−18.1	−15.8	2.3	−6.0	−3.7	2.2	−10.5	−8.3	2.2	−9.1	−6.9	...	
	H3	14.1	−26.5	−12.4	14.1	−8.8	5.3	15.0	−16.2	−1.3	15.0	−14.7	0.3	−6.5	
	H4	8.9	9.4	18.3	8.9	3.1	12.0	8.6	6.6	15.1	8.6	5.9	14.5	larger (23.4)	
	H5	6.8	6.9	13.7	6.8	2.3	9.1	6.7	4.4	11.1	6.7	3.8	10.5	smaller	
O=C\H (formyl)	C	157.8	18.8	167.6	157.8	6.3	164.1	154.8	4.4	159.1	154.8	4.6	159.4	134.5	[29(a)]
	H	86.4	28.4	114.8	86.4	9.5	95.9	84.7	24.5	109.2	84.7	23.9	108.6	136.5	
	O	−4.5	−10.3	−14.8	−4.5	−3.4	−7.9	−3.9	−10.2	−14.1	−3.9	−9.7	−13.6	...	
NO2	N	44.2	−0.7	43.5	44.2	−0.2	44.0	43.3	−0.8	42.5	43.3	−1.1	42.2	52.3	(32)
	O	−7.3	−2.8	−10.1	−7.3	−0.9	−8.2	−5.8	−3.3	−9.1	−5.8	−2.6	−8.4	...	

ues except for the β proton, for which the calculated value 20.1 G, which is obtained assuming free rotation, is rather small compared to the experimental value of 26.9 G. For the hfs value of this β proton, the geometry dependence was found to be large. In our calculation, the hfs value increased about 6 G when the C–C length was shortened by 0.1 Å. Note that the SP contribution is comparable to the SD contribution for the β-proton hfs constant as seen in Table IV. The $\cos^2\theta$ dependence of the SP contribution has been shown previously.[23] For the hfs constants of the nuclei N, O, and F of NH_2, O_3^-, and NF_2 radicals, respectively, we have also obtained satisfactory results in comparison with experimental values.

Table VIII shows the results for σ radicals. The hfs constants are the sums of the SD and SP contributions. The SD and SP contributions in the UHF and PUHF theories are calculated using the previous formulas[10,11]:

$$(\rho_{UHF})_{SP} = \tfrac{1}{2} s[1 + (2/s)](\rho_{UHF} - \rho_{PUHF}) ,$$

$$(\rho_{PUHF})_{SP} = \tfrac{1}{2} s(\rho_{UHF} - \rho_{PUHF}) ,$$

$$(\rho)_{SD} = \rho - (\rho)_{SP} . \tag{19}$$

Also, for σ radicals, the UHF values seem to be consistently larger than the experimental values. This is due to the failure in the SP contribution. Therefore, the UHF theory does not explain the positive hfs constant of H_3 nucleus of vinyl radical. Though the PUHF theory does give a positive value for this hfs constant, it does not explain the negative hfs constant of the H_3 nucleus of cyclopropyl radical. The results of the PO and SECI theory are close. However, among these theories, only the PO theory is successful in explaining the different signs of the α-proton (H_3) hfs constants of vinyl and cyclopropyl radicals.

Next, we compare in more detail the PO and SECI results with the experimental values. For vinyl radical, the hfs constant of β proton H_5, trans to the radical lobe, is calculated to be larger than that of the cis β proton H_4. For cyclopropyl radical, however, the calculated hfs constants of β protons show the opposite relation to vinyl radical. This fact has been confirmed experimentally.[24] For vinyl and cyclopropyl radicals, the SP contributions to α-proton hfs constants are negative, but different relative contributions between a_{SD} and a_{SP} terms result in positive and negative hfs constants for vinyl and cyclopropyl radicals, respectively. Only the PO theory gives correct signs for both radicals. On the other hand, the a_{SP} term of the α proton of formyl radical is a large positive value of 24.5 G and adds up to a large a_{SD} term of 84.7 G. This is one of the reasons that the large hfs constant has been observed for the α proton of formyl radical.

V. CONCLUSIONS

In this paper, the hfs constants of various σ and π radicals which contain H, C, N, O, and F nuclei are calculated with the UHF, PUHF, SECI, and pseudo-orbital (PO) theories. The basis sets are examined to give good hfs constants. The [5211/32] contraction of Huzinaga's $(9s5p)$ basis of first-row atoms and [22] con-

traction of hydrogen $(4s)$ basis are adopted. Within the range examined here (changes in contraction, addition of p- or d-polarization functions, and variations in the scale factor ζ_H), the basis set dependence was small. On the other hand, the calculated hfs constants depend strongly on the theory used. The UHF theory gives consistently too large values to compare with experiments, while the PUHF values were too small. The reason for this failure is already clear.[11,16] The PO and SECI theories have given fairly good agreements with experiment. For molecules studied here, the spin-polarization self-consistency effect, which is included to first order in the present PO calculation but is absent in the SECI theory, was relatively small in contrast to the previous results for atoms.[16] It was about 6 G for a_C and 2 G for a_H of methyl radical. A comparison with the results of the first-order perturbation theory due to Ellinger *et al.*[6] implies an importance of eliminating the orbital unitary transformation dependence to obtain consistent agreement with experiment. The present results with the PO and SECI theories have well explained several important variations in the experimental hfs constants of organic and inorganic σ and π radicals.

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