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Cluster Expansion of the Wave Function. Spin and Electron Correlations in Doublet Radicals Studied by the Symmetry Adapted Cluster and Symmetry Adapted Cluster–Configuration Interaction Theories

H. Nakatsuji,* K. Ohta,† and T. Yonezawa

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan *(Received: August 9, 1982; In Final Form: January 21, 1983)*

Spin and electron correlations in the doublet radicals BeH, CH_3, CH_3CH_2 (ethyl), HCO (formyl), and CH_2CH (vinyl) are studied by the SAC (symmetry adapted cluster) and SAC–CI (symmetry adapted cluster–configuration interaction) theories. The spin densities and the hyperfine splitting constants calculated by the SAC and SAC–CI theories compare well with the experimental results. The electron correlation couples largely with the spin correlation so that the present spin densities are improved from the results of the pseudo-orbital (PO) theory which includes only spin correlation. We have examined two methods of calculating doublet wave functions, i.e., the direct doublet SAC method and the SAC–CI method based on the SAC wave function of the cation or anion (singlet). For BeH, the two methods gave similar results. In the SAC–CI theory, the results were rather independent of the choice of the reference wave functions and orbitals (e.g., cation orbitals or anion orbitals).

I. Introduction

In this paper we study correlation effects in open-shell doublet radicals. In doublet radicals, two kinds of correlation effects are important. They are spin correlation and electron correlation. Spin correlation originates from the existence of an excess α-spin electron and represents the difference between interactions of electrons with the same spins and of electrons with different spins. It is important for spin-dependent properties, such as spin densities at nuclei which are observed as hyperfine splitting (hfs) constants. On the other hand, the electron correlation in open-shell molecules is of the same origin as that in closed-shell molecules. Since this correlation originates from the charge of the electrons, we may call it charge correlation in contrast to spin correlation. (Here we use electron correlation in the same sense as charge correlation.) Energetically, it is more important than the spin correlation. Though these two correlation effects are not necessarily clear-cut concepts and interact with each other when we go beyond the first-order perturbed wave function, the extent of the interaction is still an open question. Especially, the effects of electron correlation on spin-dependent one-electron properties such as hfs constants are of interest.

In this series of studies, we are developing cluster expansion approaches, i.e., SAC (symmetry adapted cluster)[1]

†Present address: Institute for Molecular Science, Okazaki, Aichi, Japan.

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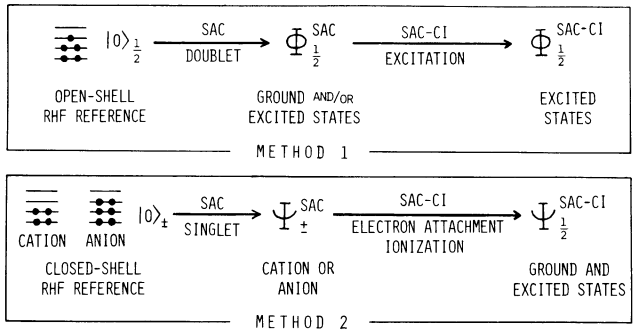

Figure 1. Schematic explanation of method 1 and method 2 which are two ways of constructing doublet wave functions in the SAC and SAC-CI formalism.

and SAC-CI[2] (symmetry adapted cluster-configuration interaction) theories, for the studies of spin correlation and electron correlation in the ground and various excited states of molecules. The excited states so far studied are singlet and triplet excited states, ionized states, and electron-attached states, which are essentially one-electron excited states,[3,4] and the shake-up states involved in the satellite peaks of inner-valence ionization, which are essentially two-electron excited states.[5,6] The results obtained so far are quite satisfactory.

For the study of spin correlation, we have proposed pseudo-orbital (PO) theory[1] which is an orbital theory derived from the SAC expansion formalism, as the UHF (unrestricted Hartree-Fock) theory is derived from the conventional cluster expansion formalism through the Thouless theorem.[7] We have considered only the spin-polarization single-excitation operator within the SAC expansion formalism (PO3).[1b] We have applied the PO theory to various doublet radicals (atoms and molecules) by assuming that the effect of electron correlation would be small.[8]

Here, we report the results for doublet radicals obtained by considering both spin correlation and electron correlation explicitly with the SAC and SAC-CI formalism. The radicals studied here are BeH, CH_3, CH_3CH_2 (ethyl), CHO (formyl), and CH_2CH (vinyl) radicals. Though there are many works which studied spin correlation and electron correlation for atoms at the same time by the Brueckner-Goldstone type many-body perturbation theory,[9a] Bethe-Goldstone type theory,[9b] and CI theory,[9c] only few studies have been performed for molecules.[10] We are most interested in the spin density distributions in these radicals. Coupling effects of the spin and electron correlations are studied by comparing the results of the SAC and SAC-CI theories with those of the PO theory. We will also study excitation energies, ionization potentials, and electron affinities of these radicals. Detailed results on these spectroscopic properties of doublet radicals will be published separately.

In the next section we briefly explain the calculational method, the results are discussed in section III, and the conclusions of this study are summarized in section IV.

II. Calculational Method

In the present approach, there are two methods of constructing doublet wave functions. Figure 1 shows a schematic explanation of the two methods. One is to construct the SAC wave funtion directly for the doublet radical, i.e.[1]

$$\Phi_{1/2}^{SAC} = O_{1/2} \exp(\sum_I C_{I,1/2} S^\dagger_{I,1/2})|0\rangle_{1/2} \quad (1)$$

where $|0\rangle_{1/2}$ is a reference configuration which is an open-shell restricted HF function,[11] $S^\dagger_{I,1/2}$ is a spin-adapted excitation operator in doublet space, and $O_{1/2}$ is a doublet spin projector. For open shells, we have calculated previously the SAC wave functions for various singlet and triplet excited states of H_2O and CH_2.[4] The calculational method is essentially the same as in the previous case.[3a] We have included all single and double excitations for $S^\dagger_{I,1/2}$ and terminated the expansion (1) at second order in the coefficients, $C_{I,1/2}$. The triple and quadruple excitations were included as unlinked terms. The excited states of the doublet radicals are calculated by the SAC-CI theory on the basis of the SAC wave function given by eq 1. This scheme of calculation is referred to as method 1.

Another way of constructing the doublet wave function, which we call method 2, is to use the SAC-CI theory.[2] We first calculate the SAC wave function for the cation or anion, which is a singlet, of the doublet radical, i.e.

$$\Psi_+^{SAC} = \exp(\sum C_{I,+} S^\dagger_{I,+})|0\rangle_+ \quad (2a)$$

$$\Psi_-^{SAC} = \exp(\sum C_{I,-} S^\dagger_{I,-})|0\rangle_- \quad (2b)$$

where Ψ_+^{SAC} and Ψ_-^{SAC} are the SAC wave functions for the cation or anion, $S^\dagger_{I,+}$ and $S^\dagger_{I,-}$ are singlet excitation operators, and $|0\rangle_+$ and $|0\rangle_-$ are reference configurations which are the closed-shell RHF wave function for the cation or anion, respectively. We then calculate the doublet wave function by the SAC-CI theory as

$$\Psi_{1/2}^{SAC\text{-}CI} = \sum d_K A^\dagger_K \Psi_+^{SAC} \quad (3a)$$

$$\Psi_{1/2}^{SAC\text{-}CI'} = \sum d'_K I^\dagger_K \Psi_-^{SAC} \quad (3b)$$

where $A^\dagger_K$ and $I^\dagger_K$ are symmetry-adapted electron-attachment operators and ionization operators, respectively. d_K and d'_K are variational parameters. $\Psi_{1/2}^{SAC\text{-}CI}$ and $\Psi_{1/2}^{SAC\text{-}CI'}$ are the SAC-CI wave functions for the doublet radical under consideration and are different in general. Both the ground and excited states of the doublet radical are calculated simultaneously in the form of eq 3a and 3b. The calculations are essentially the same as the SAC-CI calculations of ionized and electron-attached states of singlet molecules, which have been reported for several

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molecules.[3,5] The methods of calculation are the same as reported previously,[3b,3c] except that we did not adopt configuration selection in the SAC–CI calculation[5] since the spin density depends differently from the correlation energy. Note that the operators $A^{\dagger}_{K}$ and $I^{\dagger}_{K}$ in eq 3a and 3b include both one- and two-electron operators.[3]

Between the above two methods, the second SAC–CI method (method 2) is much more efficient than the first doublet SAC method (method 1) mainly because an advanced program coded by Nakatsuji is already available.[12] The larger number of doublet excitation operators appearing in eq 1 may also be a cause of the inefficiency of the program for method 1. For these reasons, most of the calculations in this reports were performed by method 2. For the BeH radical, we have performed both methods 1 and 2 and give a comparison.

The SAC and SAC–CI methods are solved in two ways, namely, by variational (V) and nonvariational (NV) methods.[2b] The SAC–CI-NV method involves a diagonalization of a nonsymmetric matrix of large dimension. We have extended the Davidson's algorithm[13] for the symmetric matrix to a nonsymmetric case.[14]

The spin density (ρ_A) and the hyperfine splitting (hfs) constant (a_A) of the nucleus A are analyzed as the sum of the RHF contribution and the correlation contribution:

$$\rho_A = \rho_A^{RHF} + \rho_A^{cor} \quad (4)$$

The RHF contribution corresponds to the previous spin-delocalization (SD) contribution[15] which is due to the delocalization of an RHF unpaired electron orbital over the molecule:

$$\rho_A^{RHF} = \rho_A^{SD} \quad (5)$$

ρ_A^{RHF} is therefore always positive. The correlation contribution represents the correction to the RHF contribution due to correlation effects. It includes the effects of both spin correlation and electron correlation. Previously, we have used the term spin polarization (SP) contribution in order to denote the contribution due to the spin correlation.[15]

The geometry of the radical is as follows. For BeH, CH_3, and HCO, we have used experimental geometries.[16] For vinyl (C_2H_3) and ethyl (C_2H_5) radicals, we have used the geometries optimized by the ab initio calculations by Millie et al.[17] and by Pacansky et al.,[18] respectively.

For spin density calculations, the selection of the basis set is very important.[8c,19] Ellinger et al.[19a] examined the contraction scheme of the GTO basis[20] for spin density calculations and reported a scheme different from the ordinary one due to Dunning.[21] In Ellinger's contraction scheme, the freedom of inner shell is larger than that in Dunning's. We reported previously[8c] that Ellinger's contraction is a better approximation of the uncontracted set than Dunning's. Here, we use the GTO basis with Ellinger's contraction. Dunning's is used for comparison. For Be, we have used the [3s2p] CGTO's of Dunning and Hay.[21]

TABLE I: Correlation Energy of BeH ($^2\Sigma^+$)

method	ref config	E_{cor},[a] au
open-shell RHF		0.0
pseudo-orbital	$\|0\rangle_{1/2}$	−0.000 70
(1+2)CI	$\|0\rangle_{1/2}$	−0.024 50
method 1 (doublet SAC)		
SAC-V	$\|0\rangle_{1/2}$	−0.024 56
SAC-NV	$\|0\rangle_{1/2}$	−0.024 77
method 2 (SAC–CI from cation or anion)		
SAC-CI-V	$\|0\rangle_{+}$	−0.024 85
SAC-CI-NV	$\|0\rangle_{+}$	−0.024 74
SAC-CI-V	$\|0\rangle_{-}$	−0.024 93

[a] Relative to the open-shell RHF energy −15.143 61 au.

TABLE II: Excitation, Ionization Energies, and Electron Affinity of the BeH Radical (eV)[a]

Excitation Energy, $^2\Sigma^+ \rightarrow {}^2\Pi$ ($3\sigma^+ \rightarrow 1\pi$)	
method 1	2.76
method 2	2.60
exptl[b]	2.48
Ionization Potential	
method 2	8.19
exptl[b]	8.21
Electron Affinity	
method 2	−0.418

[a] The results of SAC–CI-V are given for both methods 1 and 2. The SAC–CI-NV results are very close to the SAC–CI-V results. [b] Reference 15.

III. Results and Discussions

Here, we give the results for the doublet radicals BeH, CH_3 (methyl), C_2H_5 (ethyl), HCO (formyl), and CH_2CH (vinyl). First, we give the results for BeH, which was calculated by both methods 1 and 2. We compare these two methods. The other radicals were studied only with method 2 for computational efficiency. For the ethyl radical, we have studied basis set dependence.

The radicals studied here are grouped into two types. The radicals BeH, HCO, and CH_2CH are σ-radicals where an unpaired electron lies in an orbital of σ-symmetry. The radicals CH_3 and C_2H_5 are π-radicals where an unpaired electron occupies a π-orbital. In the π-radicals, the hyperfine splitting constants of the nuclei lying on a molecular plane are entirely due to the correlation effects.

A. BeH Radical Calculated by Method 1 and Method 2. BeH radical was calculated by both method 1 and method 2. Table I shows the calculated correlation energies relative to the energy of the open-shell RHF wave function. The pseudo-orbital (PO) theory gives a very small correlation energy since it considers only spin-polarization single excitations within the framework of the SAC theory. Method 1, which may be called the doublet SAC method, gives −0.024 56 and −0.024 77 au by the variational (SAC-V) and nonvariational (SAC-NV) solutions, respectively. This wave function includes both spin correlation and electron correlation. Unlinked effect is as small as −0.000 06 (SAC-V) or −0.000 27 au (SAC-NV) in comparison with the CI results including all single and double excitations, (1+2)CI, since BeH is a small doublet

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TABLE III: Hyperfine Splitting Constants of BeH ($^2\Sigma^+$)

		hfs,[a] G					
		Be			H		
method	ref config	RHF	cor	total	RHF	cor	total
open-shell RHF		−62.8	0.0	−62.8	24.5	0.0	24.5
pseudo-orbital	$\|0\rangle_{1/2}$	−62.8	0.7	−62.1	24.5	22.7	47.2
(1+2)CI	$\|0\rangle_{1/2}$	−62.8	7.6	−55.2	24.5	48.7	73.2
method 1							
SAC-V	$\|0\rangle_{1/2}$	−62.8	7.9	−54.9	24.5	52.6	77.1
method 2							
SAC-CI-V	$\|0\rangle_+$	−62.8	6.6	−56.2	24.5	42.1	66.6
SAC-CI-NV	$\|0\rangle_+$	−62.8	8.1	−54.7	24.5	47.6	72.2
SAC-CI-V	$\|0\rangle_-$	−62.8	7.7	−55.1	24.5	42.7	67.2
exptl[b]				−74.1			69.1

[a] For the partitioning of the hfs constant, see eq 4. [b] Reference 22.

TABLE IV: RHF Energy and Correlation Energy (au) of CH_3, CH_3CH_2, CH_2CH, and HCO Radicals

			SAC-CI	
			corr energy	
radical	open-RHF	ref config	V	NV
CH_3[a]	−39.537 26	$\|0\rangle_+$	−0.106 68	−0.102 50
		$\|0\rangle_-$	−0.106 53	−0.100 61
C_2H_5	−78.549 92	$\|0\rangle_-$	−0.185 37	−0.185 07
	(−78.574 29)[b]		(−0.179 92)[b]	(−0.179 50)[b]
HCO	−113.177 88	$\|0\rangle_-$	−0.238 25	−0.211 56
CH_2CH	−77.343 84	$\|0\rangle_-$	−0.182 17	−0.181 65

[a] The ionization potential of the CH_3 radical was calculated to be 10.3 and 10.2 eV by the SAC-CI-V and SAC-CI-NV methods, respectively, in comparison with the experimental value 9.84 eV.[16] [b] Due to the contraction scheme of GTO's by Dunning.

system which includes only five electrons. The correlation energies calculated by method 2, the SAC–CI method, are close to and even lower than the results of method 1. Further, the results of method 2 are very independent of the choice of the reference configuration, i.e., cation configuration $|0\rangle_+$ or anion configuration $|0\rangle_-$.

In Table II we give the vertical excitation energy, ionization potential, and electron affinity of BeH. For excitation energy, the results of methods 1 and 2 are very close and show good agreement with the experimental value. The ionization potential by method 2 is also satisfactory in comparison with the experimental value. The electron affinity was calculated to be −0.418 eV with the basis set of [3s2p/2s] CGTO, which is a poor basis for a description of an anion. When we add a more diffuse basis, this value should become smaller.

Table III shows the hyperfine splitting constants of BeH obtained by various theories. This quantity is proportional to the spin density at the nucleus. We have partitioned the hfs constants into the RHF contribution and the correlation contribution according to eq 4. BeH is a σ-radical and there are large RHF contributions: −62.8 G for Be and 24.5 G for H. The correlation contributions by the PO theory are 0.7 G for Be and 22.7 G for H and they come from only the spin-correlation effect. The (1+2)CI method, method 1, and method 2 includes both spin-correlation and electron-correlation effects. The total correlation effect is calculated to be 7–8 G for Be and as large as 40–50 G for H. In comparison with the results of the PO theory, the effect of electron correlation coupling with the spin correlation amounts to 6–7 G for Be and as much as 20–30 G for H. The total hfs constant of H is much improved by considering the electron correlation effect in comparison with the experimental value.[22] For beryllium, a more flexible basis set seems to be necessary.

We see that methods 1 and 2 give similar results for the hfs constants, though the unlinked effects are small for BeH. In comparison with the results of the PO theory, there is a large coupling effect between spin and electron correlations even for a small doublet radical as BeH. It is also noticeable that within method 2 the calculated results are independent of the choice of the reference configurations and orbitals, i.e., those for the cation and anion. This result, which was also found for other molecules, indicates that the SAC and SAC–CI theories take into account not only the spin and electron correlation effect but also the orbital reorganization effect. This is expected from the Thouless theorem.[7]

TABLE V: Hyperfine Splitting Constants of the CH_3 Radical

	ref	hfs, G	
method	config	C	H
open-shell RHF		0.0	0.0
Chang, Davidson, Vincow[a]			
SECI	$\|0\rangle_{1/2}$	23.04	−36.14
(1+2)CI	$\|0\rangle_{1/2}$	25.68	−38.21
present			
pseudo-orbital	$\|0\rangle_{1/2}$	39.4	−26.5
SAC-CI-V	$\|0\rangle_+$	22.4	−21.3
SAC-CI-NV	$\|0\rangle_+$	24.8	−22.3
SAC-CI-V	$\|0\rangle_-$	26.8	−21.0
SAC-CI-NV	$\|0\rangle_-$	28.4	−21.9
exptl[b]		28.7	−24.7
		(38.3)	(−23.0)

[a] Reference 10b. [b] From the observed values given in the parentheses (ref 24), the effects of molecular vibration are subtracted. They are 9.6 G for C and 1.7 G for H (ref 8d).

B. Methyl and Ethyl Radicals. We next show the results for the prototype hydrocarbon radicals CH_3 and C_2H_5. The geometry of CH_3 is planar, but that of C_2H_5

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TABLE VI: Hyperfine Splitting Constants (G) of CH_3CH_2

nucleus	contribution[a]	PO[b]	SAC-CI[b] V	SAC-CI[b] NV	exptl[c]
C_α	RHF	2.5 (2.4)	2.5 (2.4)	2.5 (2.4)	
	cor	42.6 (38.5)	21.1 (16.9)	21.4 (17.8)	29.47[d]
	total	45.2 (40.9)	23.6 (19.2)	23.9 (20.2)	(39.07)
H_α	RHF	0.2 (0.2)	0.2 (0.2)	0.2 (0.2)	
	cor	−26.2 (−33.8)	−18.4 (−23.3)	−18.9 (−23.6)	
	total	−26.0 (−33.6)	−18.2 (−23.1)	−18.7 (−23.4)	−22.39
C_β	RHF	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)	
	cor	−18.3 (−18.2)	−13.1 (−12.2)	−13.8 (−12.6)	
	total	−18.2 (−18.1)	−13.0 (−12.1)	−13.6 (−12.4)	−13.57
H_β	RHF	11.2 (11.0)	11.2 (11.0)	11.2 (11.0)	
	cor	9.3 (10.4)	11.2 (12.7)	11.5 (12.5)	
	total	20.6 (21.4)	22.4 (23.7)	22.7 (23.5)	26.87

[a] The partitioning is defined by eq 4. [b] The results of Dunning's CGTO are given in parentheses. [c] Reference 24. [d] For the hfs constant of the α-carbon, the effect of vibration is estimated to be −9.6 G from the result for the CH_3 radical (ref 8d).

is not strictly planar at the radical carbon.[18] For the ethyl radical, we have compared the effect of different contraction schemes of the GTO's. Table IV shows the correlation energy. Again, the variational solution of the SAC–CI is lower slightly than the nonvariational solution. This trend is seen for all the molecules in Table IV. For the methyl radical, the dependence on the choice of the reference configuration, $|0\rangle_+$ or $|0\rangle_-$, is very small. The ionization potential of CH_3 was calculated to be 10.2 eV (SAC–CI-NV) in comparison with the experimental value of 9.84 eV.[16] For the ethyl radical, the contraction scheme due to Ellinger et al.[19a] gave a lower correlation energy than the concentration due to Dunning,[21] though for the Hartree–Fock energy the reverse was true.

Tables V and VI show the hyperfine splitting constants of the methyl and ethyl radicals, respectively. For the methyl radical the RHF value is zero and the hfs constants are entirely due to the correlation effects. In Table V, we have also shown the CI results by Chang, Davidson, and Vincow,[10b] who used double-ζ STO's. SECI is an abbreviation for single-excitation CI and is close to the pseudo-orbital theory except for self-consistency.[1,8c] The effect of electron correlation, which is estimated from the difference between the results of (1+2)CI and SECI or between the results of SAC–CI and PO, is smaller in the results of Chang et al. than in the present results. Further, the effect is reversed in the two calculations for both C and H nuclei. In the present calculations, the effect of electron correlation is as large as 11–17 G for C and 4–5 G for H. The previous studies[8d,10b,19c,23] showed that the effect of molecular vibration (mainly out-of-plane vibration) is very large for the CH_3 radical and as large as 9.6 G for C and 1.7 G for H.[8d] The experimental value shown in Table V includes this correction. (The values in parentheses are the uncorrected observed values.[24]) When the electron correlation is considered by the SAC–CI theory as well as spin correlation, the hfs constant of C comes closer to the corrected experimental value. Further, the dependence on the choice of the reference configuration, e.g., $|0\rangle_+$ or $|0\rangle_-$, is much smaller than the effect of electron correlation.

In the ethyl radical, the local electronic structure near the radical center is similar to that of the CH_3 radical, a π-radical, though the geometry used here is not planar at the radical center.[18] For the α-carbon (radical center), the

TABLE VII: Hyperfine Splitting Constants (G) of HCO

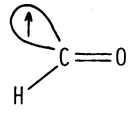
nucleus	contribution[a]	PO	SAC-CI V	SAC-CI NV	exptl[b]
C	RHF	154.8	154.8	154.8	
	cor	4.4	−20.6	−20.5	
	total	159.1	134.2	134.3	131.0
O	RHF	−3.9	−3.9	−3.9	
	cor	−10.2	−4.9	−5.4	
	total	−14.1	−8.8	−9.3	
H	RHF	84.7	84.7	84.7	
	cor	24.5	29.7	30.6	
	total	109.2	114.4	115.3	127.0

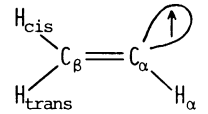
[a] The partitioning is defined by eq 4. [b] Reference 25.

experimental value is shown with the vibrational correction considered (9.6 G from the CH_3 radical).[8d] The values calculated with Dunning's CGTO's are given in parentheses. We first discuss the basis set dependence. We see that only the correlation contributions are basis-set dependent. The RHF contribution is very insensitive. In going from the contractions of Ellinger et al. to Dunning, the proton hfs constants increase and the carbon hfs constants decrease in magnitude. For the SAC–CI results, the difference is 4–5 G for C_α and H_α and ~1 g for C_β and H_β. For the PO results, it is 4.3 G for C_α, 7.6 G for H_α, and less than 1 G for C_β and H_β. In comparison with experiments, the Ellinger scheme is better for carbon but the Dunning scheme is better for the proton.

We next consider the effect of electron correlation in addition to the spin correlation included in the PO theory. It is estimated from the difference between the SAC–CI and PO values. It is as large as −21 G for C_α, 7–10 G for H_α, 5 G for C_β, and 2 G for H_β. They are much larger than the effects of the basis set difference. By considering the effect of electron correlation, the SAC–CI values become closer to the experimental values for all the nuclei than the PO results. Thus, the coupling between spin correlation and electron correlation seems to be very important.

C. Formyl and Vinyl Radicals. Formyl and vinyl radicals are σ-radicals. The unpaired electron is localized on the sp^2 type orbital on carbon





The correlation energies of these radicals are given in Table

(23) D. L. Beveridge and K. Miller, *Mol. Phys.*, **14**, 401 (1968); B. T. Sutcliffe and C. Gaze, *ibid.*, **35**, 525 (1978).
(24) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967); R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

TABLE VIII: Hyperfine Splitting Constants (G) of CH_2CH

nucleus	contribution[a]	PO	SAC-CI V	SAC-CI NV	exptl[b]
C_α	RHF	119.4	119.4	119.4	
	cor	23.0	−4.5	−6.0	
	total	142.4	114.9	113.4	107.6
C_β	RHF	9.5	9.5	9.5	
	cor	−23.2	−16.2	−16.9	
	total	−13.7	−6.7	−7.4	−8.6
H_α	RHF	23.5	23.5	23.5	
	cor	−12.4	−6.1	−6.1	
	total	11.1	17.4	17.4	13.3
H_β^{cis}	RHF	12.9	12.9	12.9	
	cor	11.5	16.2	16.4	
	total	24.4	29.1	29.3	34.2
H_β^{trans}	RHF	21.8	21.8	21.8	
	cor	17.5	25.7	25.7	
	total	39.3 (1.61)	47.5 (1.63)	47.5 (1.62)	68.5 (2.00)

[a] The partitioning is defined by eq 4. [b] Reference 24.

TABLE IX: Hyperfine Splitting Constants (G) of Doublet Radicals

molecule	nucleus	UHF	AUHF	PO	SAC-CI[a]	exptl	Δa_{ec}[c]
CH_3	C	71.3	24.8	39.4	28.4	28.7[b] (38.3)	−11.0
	H	−40.6	−13.2	−26.5	−21.9	24.7[b] (−23.0)	4.6
CH_3CH_2	C_α	76.4	28.1	45.1	23.9	29.5[b] (39.1)	−21.2
	C_β	−28.4	−9.3	−18.3	−13.6	−13.6	4.7
	H_α	−39.6	−12.8	−26.0	−18.7	−22.4	7.3
	H_β	24.6	15.7	20.1	22.7	26.9	2.6
BeH	Be	−64.2	−65.8	−62.1	−55.1	−74.1	7.0
	H	71.7	55.0	47.2	67.2	69.1	20.0
HCO	C	167.6	164.1	159.1	134.3	131.0	−24.8
	H	114.8	95.9	109.2	115.3	127.0	6.1
	O	−14.8	−7.9	−14.1	−9.3		4.8
CH_2CH	C_α	206.3	147.2	142.4	113.4	107.6	−29.0
	C_β	−65.7	−15.3	−13.7	−7.4	−8.6	6.3
	H_α	−17.2	7.1	11.1	17.4	13.3	6.3
	H_{cis}	49.6	25.2	24.4	29.3	34.2	4.9
	H_{trans}	66.4	36.5	39.3	47.5	68.5	8.2

[a] SAC-CI-NV results with the reference configuration $|0\rangle_-$. [b] The effect of molecular vibration is considered (9.6 G for C and 1.7 G for H from ref 8d). [c] Δa_{ec} is define by eq 7 and shows the effect of electron correlation coupling with spin correlation.

IV. Table VII shows the results for the hyperfine splitting constants of the formyl radical. Because an unpaired electron lies in the σ-orbital, the RHF contribution is large. For the radical carbon of HCO, the spin correlation effect included in the PO theory gives 4.4 G, but when both spin correlation and electron correlation are included, the correlation contribution even changes sign and becomes −20.6 G. Because of this negative contribution, the hfs constant changes from the PO value of 159 G to the SAC–CI value of 134 G which is close to the experimental value, 131 G.[25] For oxygen and the proton, the effect of electron correlation is ~5 G and the hfs constant of the proton is again improved.

Table VIII shows the hyperfine splitting constants of the vinyl radical. The radical center is localized to one of the sp^2 σ-lobes at the carbon. The RHF contribution is large and shows the extent of delocalization of this unpaired electron orbital. For the radical carbon C_α, the correlation contribution is 23.0 G when only spin correlation is considered by the PO theory, but when both spin and electron correlations are considered, it becomes negative, −4.5 ~ −6.0 G. The effect of electron correlation is as large as −28 G and it improves considerably the theoretical value in comparison with the experimental value. This is the same trend as for the hfs constant of the carbon of HCO. For the other nuclei, the effects of electron correlation are 5–8 G. The hfs constants are improved by the SAC–CI theory for all the nuclei except for the α-proton.

IV. Summary and Conclusion

In Table IX we have summarized the present results for the hyperfine splitting constants. We have given the SAC–CI-NV results obtained from the reference configuration $|0\rangle_-$. The results of the UHF theory and the results obtained by annihilating the quartet component from the UHF wave function (AUHF) are given for comparison. For the spin-polarization contribution of the UHF and AUHF theories, we have shown the relation[15]

$$(a_{SP})_{AUHF} \simeq \frac{1}{3}(a_{SP})_{UHF} \quad (6)$$

for doublet radicals. As already clarified theoretically,[1,8a,b,15,26] the UHF and AUHF results are unreliable.

(25) R. W. Holmberg, *J. Chem. Phys.*, **51**, 3255 (1969).

(26) W. Meyer, *J. Chem. Phys.*, **51**, 5149 (1969); H. Nakatsuji, *ibid.*, **59**, 2586 (1973).

Most of the UHF values are larger than the experimental values, while most AUHF values are smaller. Within the orbital theories, the pseudo-orbital theory gives better agreement. This is reasonable since the pseudo-orbital theory has been so designed to include the spin correlation in a correct way.[1a,8a] However, the present results of the SAC–CI theory, which includes both spin correlation and electron correlation, show the importance of the electron correlation for the calculation of the hfs constants. The last column of Table IX shows the difference of the results of the SAC–CI and pseudo-orbital theories

$$\Delta a_{ec} = a_{SAC\text{-}CI} - a_{PO} \tag{7}$$

which shows the effect of the electron correlation coupling with the spin correlation. It is large especially for the radical center atom (for carbon, $-11 \sim -30$ G), and works to reduce the spin density. For the other nuclei, the effect of electron correlation Δa_{ec} is always positive and ranges from 3 to 8 G. By inclusion of the electron correlation effect, all of the SAC–CI values come closer to the experiments than the PO values, except for the α-proton hfs constants of CH_3, C_2H_3, and C_2H_5. For the Be hfs constants of BeH, we have to use a better basis set.

We have studied in this paper the spin and electron correlations in various doublet radicals by the SAC and SAC–CI theories. We may summarize the conclusions of the present study as follows. (1) The hyperfine splitting constants calculated by the SAC and SAC–CI theories compare well with the experimental results. (2) The electron correlation couples largely with the spin correlation so that the hfs constants calculated by the SAC–CI theory are improved from the results of the PO theory. Some regularities of the effect of electron correlation were observed. (3) Two methods of constructing the doublet wave function are tested in this study; the direct doublet SAC method, method 1, and the doublet SAC–CI method based on the SAC wave function of the cation or anion (singlet), method 2. For the BeH radical these two methods gave similar results for both the spin and electron correlations. (4) Within method 2, the calculated results are independent of the choice of the reference wave function and molecular orbitals, such as anion or cation orbitals. This is a result that the SAC and SAC–CI theories include not only the spin and electron correlations but also orbital reorganization effects correctly.

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Registry No. BeH radical, 13597-97-2; CH_3 radical, 2229-07-4; ethyl radical, 2025-56-1; formyl radical, 2597-44-6; vinyl radical, 2669-89-8.