Hyperfine splitting constants studied by the symmetry adapted cluster-configuration interaction method

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The accuracy of the symmetry adapted cluster-configuration interaction (SAC-CI) method for calculating hyperfine splitting constants (hfscs) is examined. Two kinds of SAC-CI expansion are performed: one is the SAC-CI(SD-R, DT-R) method in which single and double (double and triple for high-spin multiplicity) excitation operators are included in the linked operators and the other is the SAC-CI (general-R) method in which higher excitation operators are further included. The hfscs for the doublet, triplet, and quartet states of small radicals, OH, CH_2, BH_2, CH_3, and H_2O^+, calculated by the SAC-CI method compare very well with the full CI results. A convenient configuration selection method, in which both energy and hfsc are used as criteria, is shown to be useful. This method, which is also applicable to the ordinary CI method, is effective for accurate calculations of the hfscs especially for large systems and high-spin systems, where a large number of configurations are required. Finally, the basis-set dependence of the hfscs is examined using the configuration selection method developed here. Within the Gaussian set, the improvement in energy does not necessarily result in the improvement of the hfscs. We have to use the basis set which satisfies the cusp condition, as shown previously.

I. INTRODUCTION

The hyperfine splitting constant (hfsc) is an important quantity which gives the information of the unpaired electron-spin distribution at the positions of the nuclei in a molecule. It is experimentally observed by electron-spin resonance (ESR) and electron-nuclear double resonance (ENDOR) techniques. For reliable calculations of this quantity by an *ab initio* method, the spin polarization and electron correlation effects and the cusp condition are necessarily included in the calculation.[1–9] This indicates that the theoretical description of the hfscs requires a highly accurate and yet useful method of calculating correlated wave functions.

Several studies[10–12] report that a cancellation between the incompleteness of the basis sets and the neglect of the higher-order correlation terms gives an accidental agreement of the calculated hfscs with the experimental values. However, for the theory to be truly reliable, it is important to establish the method which describes both spin polarization and electron correlation effects in high accuracy and based on such theory, we have to examine a method of systematic improvement of the basis set for hfsc calculations.

The symmetry adapted cluster-configuration interaction (SAC-CI) method[13] has been successfully applied to the spectroscopies of the excited and ionized states of various molecules and also to the calculations of the hfscs of various doublet radicals.[3–9] The SAC-CI method, which properly includes both of the spin polarization and electron correlation corrections, gives a reliable estimate of the hfscs. The method, in which the higher-order correlation terms are described by the unlinked terms, is computationally useful especially for large systems. The SAC-CI method is applicable

to arbitrary spin multiplicity[13] and its implementation to the high-spin multiplicities of quartet to septet states has been performed recently.[14] We expect that the method would be effective for evaluating the hfscs of high-spin multiplet systems, as well as lower-spin multiplet systems. The first purpose of this paper is to examine the accuracy of the SAC-CI method for calculating the hfscs by comparing with the full CI results. The hfscs for the doublet, triplet, and quartet states of small radicals, OH, CH_2, BH_2, CH_3, and H_2O^+, are examined by the two types of SAC-CI method reported previously, i.e., SAC-CI(SD-R, DT-R),[13–15] and SAC-CI(general-R) method.[16] The former method includes only single and double (double and triple for the quartet states) excitation operators in the linked operators, while the latter includes higher-order operators as well.

Accurate calculations of the hfscs including electron correlations often result in large calculational dimensions for the following reasons. (1) Since the inner core polarization is extremely important for the hfscs, the calculation should be performed with the active space including both core and valence MOs. (2) Extended basis set including flexible AOs even near the nucleus is necessary for highly reliable results. (3) The excitation configurations which are important for describing the hfscs do not necessarily give a large energy contribution and therefore, the configuration selection using only energy threshold is dangerous for the calculation of the hfscs. Another purpose of this paper is to propose a convenient configuration selection method which avoids discarding such important configurations and guarantees the quality of the calculated hfscs. Finally, we examine the basis-set dependence of the calculated hfscs within the Gaussian-type basis set.

II. METHOD

The SAC-CI wave function is constructed by applying the reaction operator to the SAC wave function as[13]

$$\Psi_e^{\text{SAC-CI}} = \mathfrak{R}\Psi_g^{\text{SAC}}, \tag{1}$$

where the excitator $\mathfrak{R}$ generates excited, ionized, or electron attached states from the ground state. The excitator is expanded as

$$\mathfrak{R} = \sum_K d_K \, PR_K^\dagger, \tag{2}$$

where P is the projector which projects out the Ψ_g^{SAC} component, and $R_K^\dagger$ is the (linked) excitation, ionization, or electron attachment operator of the corresponding spin multiplicity. The Ψ_g^{SAC} usually represents a totally symmetric singlet closed-shell system and therefore, the projector P is unnecessary for the $\Psi_e^{\text{SAC-CI}}$ of different spin multiplicity.

There exist two ways of choosing the $R_K^\dagger$ operators in the SAC-CI calculations. One choice is to limit $R_K^\dagger$ operators to the lower two levels of excitation operators, single- and double-excitation operators for singlet to triplet multiplicities,[13(b)] and double- and triple-excitation operators for quartet and quintet multiplicities.[14] The other is to further include the higher-order excitation operators for the $R_K^\dagger$ operators.[16] The former method is designated as SAC-CI(SD-R or DT-R) and the latter as the SAC-CI (general-R) method. The latter method is found to be effective for quantitative descriptions of the states characterized by the multiple excitations[16] from the SAC state. Explicit forms[13-15] of the excitation operators and the method of generating higher-order excitation operators[16] are given elsewhere.

We examine two different configuration selection methods in the present calculations. The first is the usual selection method[15] based on the energy selection alone and the second is the method proposed here for the calculation of hfscs. In the SAC-CI(SD-R, DT-R) calculations, double- (triple-) excitation operators are selected according to their contributions to the second-order perturbation energy in the following way.[15] Let $\Psi^{(p)}$ represent the state to be calculated and expanded as

$$\Psi^{(p)} = \sum_i \alpha_i^{(p)} \phi_i^{(p)} \quad (p=1,\dots,N), \tag{3}$$

where $\phi_i^{(p)}$ is a component configuration and N is the number of states to be considered. The excited configuration to be selected is denoted as ϕ_s and $\Delta E_{si}^{(p)}$ is defined as

$$\Delta E_{si}^{(p)} = \frac{|H_{si}^{(p)}|^2}{H_{ii}^{(p)} - H_{ss}}, \tag{4}$$

where $H_{si}^{(p)} = \langle \phi_s | H | \phi_i^{(p)} \rangle$, $H_{ii}^{(p)} = \langle \phi_i^{(p)} | H | \phi_i^{(p)} \rangle$, and $H_{ss} = \langle \phi_s | H | \phi_s \rangle$. The excitation configuration ϕ_s is included as a linked configuration when it satisfies

$$\Delta E_{si}^{(p)} \geq \lambda_e \tag{5}$$

with at least one of the configurations $\phi_i^{(p)}$, where λ_e is a given energy threshold.

The configurations which involve the excitations from the innermost core MOs are very important for the description of hfscs, though they usually give only a marginal energy contribution. In order not to discard such important configurations in the configuration selection step, the selection should be done on the basis of the contributions not only to the energy but also to the hfsc. Such configuration selection is performed in the following manner. Adopting the first-order perturbation method, the coefficient c_{si} of the configuration ϕ_s contributing to the reference function $\phi_i^{(p)}$ is written as

$$c_{si} = \frac{H_{si}^{(p)}}{H_{ii}^{(p)} - H_{ss}}. \tag{6}$$

On the other hand, the integral necessary for the hfsc is written as

$$\langle \chi_k | \delta(r - R_A) | \chi_l \rangle, \tag{7}$$

where X_k is the basis function used and this integral is stored beforehand in the MO basis. Then, the contribution of ϕ_s to the hfsc of the nucleus A is approximated as

$$\Delta V_{\text{hfsc,A}} = \frac{8\pi}{3} \frac{g_e}{g_0} \, g_N \beta_N \sum_{k,l} D_{kl} \langle \chi_k | \delta(r - R_A) | \chi_l \rangle$$

$$(\text{in Gauss}), \tag{8}$$

with D_{kl} given by

$$D_{kl} = \alpha_i^{(p)} c_{si} \langle \phi_s | S_z | \phi_i^{(p)} \rangle / 2M_s. \tag{9}$$

The configuration ϕ_s is included in the linked configuration if it satisfies

$$\Delta V_{\text{hfsc,A}} \geq \lambda_{\text{hfsc,A}} \tag{10}$$

with at least one of the configurations $\phi_i^{(p)}$ and for the one of nuclei A in molecules, where $\lambda_{\text{hfsc,A}}$ is the threshold for the hfsc of the nucleus A in gauss. The resultant selected configurations are the sum of those which satisfy Eqs. (5) and/or (10).

III. CALCULATION

The SAC-CI method and the full CI method are applied to the calculation of the hfscs of the doublet, triplet, and quartet states of small radicals, OH, CH_2, BH_2, CH_3, and H_2O^+. The ground states of these radicals and the low-lying excited states of the OH radical are examined. The geometries of these radicals are due to the experimental values; namely, $R_{OH} = 0.969\,66$ Å[17] for all the states of OH, $R_{CH} = 1.08$ Å and $\theta_{HCH} = 134°$ for the $^3B_1$ state of CH_2, $R_{BH} = 1.18$ Å and $\theta_{HBH} = 131°$ for the $^2A_1$ state of BH_2,[18] $R_{CH} = 1.079$ Å for the $^2A_2''$ state of CH_3,[19] $R_{OH} = 0.999$ Å and $\theta_{HOH} = 110.5°$ for the $^2B_1$ state of H_2O^+.[20] In the examination of the present method, the basis sets are limited to double-zeta quality, a $[4s2p]$ set for B, C, and O atoms and a $[2s]$ set for the H atom of Huzinaga and Dunning,[21] in order to keep the size of the full CI practical. For examining the basis-set dependence, various contractions based on the primitive set of Huzinaga $(9s5p/4s)$[21] and the d functions with $\zeta_d = 0.85(O)$, $0.80(C)$, and $0.70(B)$ are examined. The

TABLE I. Dimension of the CI, SAC-CI, and full CI calculations.

Molecule	State	CI, SAC-CI[a]			Full CI
		$N=1,2$	$N=1-3$	$N=1-4$	
OH	$X\ ^2\Pi$	44	292	814	97 616
	$A\ ^2\Sigma^+$	70[b]	295	676	98 044
	$1\ ^4\Sigma^-$	328	893	1452	66 351
	$1\ ^4\Pi$	356	658	896	50 904
CH_2	$^3B_1$	190	576	981	181 760
BH_2	$^2A_1$	71	288	484	94 128
CH_3	$^2A_2''$	60	496	1466	1 955 576
H_2O^+	$^2B_1$	48	388	1133	500 638

[a]N is the excitation level of the linked operators.
[b]Previously (Ref. 14) this dimension was erroneously written as 77.

closed-shell RHF MOs of the ground states are calculated by the program HONDO7[22] and are used as the reference orbitals. All MOs are included in the active space without frozen MOs. The SAC/SAC-CI calculations are performed by the modified version of the SAC85 program[23] and the MEG4/EX-MEG4 program.[24] The full CI calculations are carried out by using the Slater determinant-based algorithm of Knowles et al.[25] coded by Momose.[26]

In the SAC-CI calculation, all single- and double- (or double- and triple-) excitation operators are included without configuration selection both in the SD-R (or DT-R) and general-R method. In the general-R method, higher-order excitation operators are included using the configuration selection method. The reference functions $\phi_i^{(p)}$ are those whose SD-CI coefficients are larger than 0.1 in the reference states. This method is different from the original scheme.[16] The perturbation energy threshold in the configuration selection is $\lambda_e = 1.0 \times 10^{-5}$ a.u. Since the higher-order excitation operators are included in the linked operators, some unlinked terms may have the same excitation operators, and in the present calculation, such unlinked terms are neglected.

In the examination of the configuration selection methods, the threshold $\lambda_{hfsc,A}$ is set to 3 G for all the nuclei. This threshold is improved as $\lambda_{hfsc,A} = 1$ G for the basis-set examination.

IV. COMPARISON WITH THE FULL CI RESULTS

The doublet, triplet, and quartet states of the OH, CH_2, BH_2, CH_3, and H_2O^+ radicals are investigated by the SAC-CI(SD-R, DT-R), SAC-CI(general-R), and full CI methods in order to examine the accuracy of the SAC-CI method. The CI calculation using the same linked operators as the SAC-CI calculation is also performed for comparison. The SAC-CI method is performed with systematic inclusion of the $R^\dagger$ operators; namely, the SAC-CI(SDT-R) method includes up to triple-excitation operators (denoted as $N=1-3$) and the SAC-CI(SDTQ-R) method includes up to quadruple ones (denoted as $N=1-4$). The calculational dimensions are given in Table I. Table II shows the summary of the total energies calculated by these methods, and Table III summarizes the results for the hfscs.

A. The OH radical

We first investigate the two doublet ($X\ ^2\Pi$ and $A\ ^2\Sigma^+$) and two quartet ($1\ ^4\Sigma^-$ and $1\ ^4\Pi$) states of the OH radical. The results of the total energies calculated by the SAC-CI(SD-R, DT-R) method are given in Table II, and some discussions were given in the previous paper.[14] We summarize here only the relevant result. The $1\ ^4\Sigma^-$ state has some triple-excitation nature and therefore, the unlinked terms of the form $\{S_i^a S_j^b \times R_{klm}^{cd}\}$ are important for an appropriate description in the SAC-CI(DT-R) method. On the other hand, the energy calculated by the SAC-CI(SDT-R, DTQ-R) method first given in this paper is very accurate for all the states, though the calculated values slightly overshoot the full CI ones: The average discrepancy is only 0.51 mhartree. The effects of the unlinked terms are estimated to be 11–16 mhartree in the SAC-CI(SDT-R, DTQ-R) method.

We examine the hfscs of the ground and excited states of the OH radical. The full CI method gives the hfscs of the $X\ ^2\Pi$ state as -18.70 and -31.87 G for the O and H atoms, respectively. The experimental values are -18.1 (O)[27] and -26.1 G(H).[28] The SD-CI calculation underestimates the hfscs of this state as -5.28 (O) and -23.48 G (H), while the SAC-CI(SD-R) method improves the values to -12.23 (O) and -25.61 G (H), but the difference from the full CI values are still 6.47 and 6.26 G, respectively. This improvement of

TABLE II. Total energy of small radicals calculated by the SAC-CI(SD-R, DT-R), SAC-CI(general-R), and full CI methods (in hartree).[a]

Molecule	State	$N=1,2$		$N=1-3$		$N=1-4$		Full CI
		CI	SAC-CI(R-SD[b])	CI	SAC-CI(R-SDT[b])	CI	SAC-CI(R-SDTQ[b])	
OH	$X\ ^2\Pi$	$-75.412\ 47$ (82.16)	$-75.492\ 96$ (1.67)	$-75.478\ 61$ (16.02)	$-75.494\ 95$ (-0.32)	$-75.490\ 49$ (4.14)	$-75.495\ 07$ (-0.44)	$-75.494\ 63$
	$A\ ^2\Sigma^+$	$-75.258\ 40$ (81.13)	$-75.337\ 80$ (1.73)	$-75.325\ 79$ (13.74)	$-75.339\ 62$ (-0.09)	$-75.335\ 56$ (3.97)	$-75.340\ 13$ (-0.60)	$-75.339\ 53$
	$1\ ^4\Sigma^-$	$-75.150\ 44$ (41.62)	$-75.187\ 34$ (4.72)	$-75.180\ 85$ (11.21)	$-75.192\ 03$ (0.03)	$-75.190\ 41$ (1.65)	$-75.190\ 91$ (1.15)	$-75.192\ 06$
	$1\ ^4\Pi$	$-75.038\ 85$ (37.72)	$-75.077\ 38$ (-0.81)	$-75.065\ 22$ (11.35)	$-75.074\ 98$ (1.59)	$-75.071\ 98$ (4.59)	$-75.073\ 14$ (3.43)	$-75.076\ 57$
CH_2	$^3B_1$	$-38.936\ 27$ (61.72)	$-38.995\ 09$ (2.90)	$-38.992\ 79$ (5.20)	$-38.995\ 73$ (2.26)	$-38.994\ 56$ (3.43)	$-38.997\ 02$ (0.97)	$-38.997\ 99$
BH_2	$^2A_1$	$-25.747\ 20$ (57.74)	$-25.800\ 46$ (4.48)	$-25.797\ 99$ (6.95)	$-25.803\ 61$ (1.33)	$-25.799\ 47$ (5.47)	$-25.803\ 63$ (1.31)	$-25.804\ 94$
CH_3	$^2A_2''$	$-39.567\ 05$ (90.69)	$-39.652\ 94$ (4.80)	$-39.646\ 58$ (11.16)	$-39.658\ 47$ (-0.73)	$-39.652\ 35$ (5.39)	$-39.658\ 63$ (-0.89)	$-39.657\ 74$
H_2O^+	$^2B_1$	$-75.637\ 16$ (85.70)	$-75.721\ 29$ (1.57)	$-75.705\ 86$ (17.0)	$-75.723\ 22$ (-0.36)	$-75.717\ 28$ (5.58)	$-75.722\ 71$ (0.15)	$-75.722\ 86$
Average discrepancy		(67.31)	(2.84)	(11.58)	(0.84)	(4.28)	(1.12)	

[a]Deviations from the full CI values are given in the parentheses in mhartree.
[b]For quartet states, SD-R, SDT-R, and SDTQ-R methods correspond to DT-R, DTQ-R, and DTQQ-R methods, respectively.

TABLE III. Hyperfine splitting constants of small radicals calculated by the SAC-CI(SD-R, DT-R), SAC-CI(general-R), and full CI methods (in G).[a]

Molecule atom	RHF	N=1,2		N=1-3		N=1-4		Full CI	Expt.
		CI	SAC-CI(R-SD[b])	CI	SAC-CI(R-SDT[b])	CI	SAC-CI(R-SDTQ[b])		
OH									
$X\,^2\Pi$									
O	···	−5.28(13.42)	−12.23(6.47)	−15.41(3.29)	−20.28(−1.58)	−17.56(1.14)	−20.88(−2.18)	−18.70	−18.1[c]
H	···	−23.48(8.39)	−25.61(6.26)	−29.74(2.13)	−31.72(0.15)	−30.58(1.29)	−31.50(0.37)	−31.87	−26.1[d]
$A\,^2\Sigma^+$									
O	−161.47	−221.69(−8.45)	−214.78(−1.54)	−207.82(5.42)	−215.81(−2.57)	−212.53(0.71)	−215.87(−2.63)	−213.24	···
H	247.48	276.00(−8.82)	273.24(−11.58)	290.89(6.07)	285.96(1.14)	287.18(2.36)	285.79(0.97)	284.82	···
$1\,^4\Sigma^-$									
O	−35.55	−64.05(14.12)	−73.40(4.77)	−80.40(−2.23)	−81.67(−3.50)	−81.87(−3.70)	−82.40(−4.23)	−78.17	···
H	0.63	29.92(0.94)	29.67(0.69)	29.16(0.18)	29.02(0.04)	28.63(−0.35)	29.04(0.06)	28.98	···
$1\,^4\Pi$									
O	−89.38	−101.85(6.61)	−105.56(−2.90)	−110.72(−2.26)	−112.49(−4.03)	−111.73(−3.27)	−112.14(−3.68)	−108.46	···
H	83.13	112.37(−2.51)	115.06(0.18)	115.64(0.76)	113.77(−1.11)	114.35(−0.53)	114.42(−0.46)	114.88	···
$CH_2\,^3B_1$									
C	53.43	92.57(−10.33)	96.45(−6.45)	96.91(−5.99)	104.54(1.64)	98.69(−4.21)	102.88(−0.02)	102.90	(85.2)[e]
H	9.58	−13.36(−4.45)	−15.75(−2.06)	−16.11(−1.70)	−17.40(−0.41)	−16.66(−1.15)	−17.48(−0.33)	−17.81	−7.2[f]
$BH_2\,^2A_1$									
B	72.57	130.30(−1.05)	123.80(−7.55)	123.55(−7.80)	131.34(−0.01)	125.83(−5.52)	130.86(−0.49)	131.35	128[g]
H	11.70	1.64(0.06)	0.93(−0.65)	1.41(−0.17)	1.64(0.06)	1.42(−0.16)	1.73(0.15)	1.58	±13.6[g]
$CH_3\,^2A_2''$									
C	···	25.77(−15.80)	28.69(−12.88)	31.46(−10.11)	42.06(0.49)	35.12(−6.45)	42.45(0.88)	41.57	28.7[h]
H	···	−26.80(8.51)	−28.67(6.64)	−31.68(3.63)	−35.18(0.13)	−32.85(2.46)	−34.90(0.41)	−35.31	−24.7[h]
$H_2O^+\,^2B_1$									
O	···	−15.20(18.43)	−20.09(13.54)	−28.94(4.69)	−34.09(−0.46)	−34.55(−0.92)	−34.64(−1.01)	−33.63	±29.7[i]
H	···	−23.81(11.00)	−28.23(6.58)	−32.17(2.64)	−34.68(0.13)	−34.31(0.50)	−34.49(0.32)	−34.81	±26.1[i]
Average discrepancy in absolute value[j]									
A		11.03	7.01	5.22	1.79	3.24	1.89		
H		5.59	4.33	2.16	0.40	1.10	0.38		

[a]Deviations from the full CI values are given in the parentheses (in G).
[b]For quartet states, SD-R, SDT-R, and SDTQ-R methods correspond to DT-R, DTQ-R, and DTQQ-R methods, respectively.
[c]Reference 27.
[d]Reference 28.
[e]MRD-CI value calculated with the extended basis sets; Ref. 30.
[f]Reference 29.
[g]Reference 30.
[h]Reference 31.
[i]Reference 32.
[j]A is the first row atom.

the SAC-CI is attributed to (1) the reorganization of the linked terms due to the inclusion of the unlinked terms and (2) the contribution of the unlinked terms itself. Similar improvements are also obtained for the hfscs of the excited states: The improvement is more remarkable for the hfscs of the O atom than for those of the H atom. The SAC-CI(SDT-R) method, in which the excitation operators up to triple ones are included in the $R^\dagger$ operators, gives more accurate values as −20.28 (O) and −31.72 G (H) for the $X\,^2\Pi$ state: The errors are only −1.58 and 0.15 G, respectively. Comparing the results of the CI method with those of the SAC-CI method, the effect of the higher-order terms is recognized as to increase the spin density at the nucleus especially of the radical center.

The two quartet states, $1\,^4\Sigma^-$ and $1\,^4\Pi$, have the electronic configurations of $(p\sigma)^2(p\pi)^2(\sigma^*)^1$ and $(p\sigma)^1(p\pi)^3(\sigma^*)^1$, respectively. First, the analysis of the spin appearing mechanism for these states is performed: i.e., the decomposition into the spin delocalization, spin polarization, and electron correlation effects. The RHF contributions which correspond to the spin-delocalization ones are calculated to be −35.55 (O) and 0.63 G (H) for the $1\,^4\Sigma^-$ state and −89.38 (O) and 83.13 G (H) for the $1\,^4\Pi$ state. Reflecting the two and one unpaired spins in the π orbitals of the

$1\,^4\Sigma^-$ and $1\,^4\Pi$ states, respectively, total correlation contributions are large for these states; −42.6 (O) and 28.4 G (H) for the $1\,^4\Sigma^-$ state and −19.1 (O) and 31.8 G (H) for the $1\,^4\Pi$ state. The accuracy of the SAC-CI(DT-R) method is excellent for the quartet states. The deviations from the full CI results are only 4.77 (O) and 0.69 G (H) for the $1\,^4\Sigma^-$ state, which correspond to 6.1% and 2.4% of the exact values. Those for the $1\,^4\Pi$ state are −2.90 (O) and 0.18 G (H), which are 2.7% and 0.2% of the exact values. The hfscs of the quartet states calculated by the SAC-CI(general-R) method are almost in the same accuracy as those calculated by the SAC-CI(DT-R) method. The SAC-CI(DT-R) method is very accurate because (1) these quartet states have some RHF contributions and (2) $\{R^\dagger|0\rangle\}$ space for the quartet multiplicity covers wider variational space than that for the doublet one.

The present examination shows that the SAC-CI method gives quantitatively reliable values not only for the energies but also for the hfscs in spite of the smallness of the calculational dimensions: 44 (SD-R) and 292 (SDT-R) compared with the full CI dimension 97 616 for the $X\,^2\Pi$ state. In particular, the SAC-CI(SD-R) method largely improves the result of the SD-CI method. Quantitative agreement of the hfscs guarantees the accuracy of the fine details of the

SAC-CI wave function with respect to the spin correlations and electron correlations.

B. The CH₂ and BH₂ radicals

We next examine the ground states of the CH_2 and BH_2 radicals, $^3B_1$ and $^2A_1$. The full CI total energies are calculated to be $-38.997\,99$ a.u. for CH_2 and $-25.804\,94$ a.u. for BH_2, respectively, and for all the excitation levels of the $R^\dagger$ operators, the SAC-CI method reproduces well the full CI values, as shown in Table II. The errors reduce as the higher-order operators are included in the $R^\dagger$ operators. The errors of the SAC-CI(SDTQ-R) is only 0.97 a.u. and 1.31 a.u. for CH_2 and BH_2 respectively.

The hfscs of the $^3B_1$ state of CH_2 are calculated to be 102.90 (C) and -17.81 G (H) using the $[4s2p/2s]$ basis set by the full CI method. The experimental value of -7.2 G is available for the H atom.[29] The MRD-CI calculation with the extended basis set gives the hfsc of 85.2 G for the C atom.[30] The RHF contributions are estimated to be 53.43 (C) and 9.58 G (H), where the value for the H atom is positive. The effects of the spin and electron correlations are as large as 49.5 (O) and -27.4 G (H). The results of the SAC-CI method are excellent; the SAC-CI method improves the hfsc values of C and H estimated by the CI method in all cases of the excitation levels. The effects of including unlinked terms are approximately 4 G for the C atom and -1 to -2 G for the H atom, respectively. The deviations from the full CI results are only 1.64 (C) and -0.41 G (H) in the SAC-CI(SDT-R) method.

The hfsc of the B atom for the $^2A_1$ state of BH_2 is calculated to be 131.35 G by the full CI method in good agreement with the experimental value of 128 G.[30] The RHF contributions are large and estimated as 72.57 (B) and 11.70 G (H). The SD-CI method gives, perhaps accidentally, a very good value of 130.30 G for B. However, the inclusion of the higher-order terms reduces the spin density at B and the results become seemingly worse. On the other hand, the SAC-CI results behave more naturally and again the SAC-CI(SDT-R) method gives excellent results with the errors of only -0.01 (B) and 0.06 G (H).

C. The CH₃ and H₂O⁺ radicals

The CH_3 and H_2O^+ radicals are doublet π radicals and therefore, their spin distributions are determined solely by the spin polarization and electron correlation effects. The total energy of the $^2A_2''$ state of the CH_3 radical is calculated to be $-39.657\,74$ a.u. and the dimension of the full CI calculation is as large as 1 955 576. The SAC-CI method gives $-39.652\,94$ and $-39.658\,47$ a.u. with the dimensions of only 60 and 496 by the SD-R and SDT-R methods, respectively. The hfscs of CH_3 are calculated to be 41.57 (C) and -35.31 G (H) by the full CI method, which are larger than the experimental values of 28.7 (C) and -24.7 G (H).[31] The CI calculation of the $N=1-3$ level gives the values of 31.46 (C) and -31.68 G (H): The errors are as large as -10.11 (C) and 3.63 G (H). The SAC-CI(SDT-R) method improves the

values as 42.06 (C) and -35.18 G (H), whose deviations from the full CI are only 0.49 and 0.13 G for C and H, respectively.

The results for the $^2B_1$ state of H_2O^+ are very similar to those of the $X\ ^2\Pi$ state of OH. The total energy of the $^2B_1$ state of H_2O^+ is calculated to be $-75.722\,86$ a.u. by the full CI method. Even the CI calculation of the $N=1-3$ level gives the error of 17 mhartree. The SAC-CI method shows good agreement in all cases of the excitation levels; the errors are within 2 mhartree. The hfscs of H_2O^+ are calculated to be -33.63 (O) and -34.81 G (H) by the full CI method. Experimental values are reported to be ±29.7 (O) and ±26.1 G (H),[32] whose signs are not determined. As for the hfsc of the O atom, it is difficult to reproduce the full CI value and the inclusion of the higher-order terms is necessary for an accurate description. The CI calculations of $N=1,2$ and $N=1-3$ levels give -15.20 and -28.94 G for the hfsc of the O atom, whose errors are as large as 18.43 and 4.69 G, respectively. The SAC-CI method improves these values to -20.09 and -34.09 G, respectively, and the errors are 13.54 and -0.46 G, respectively. The effects of including unlinked terms are estimated to be -4.9 and -5.2 G, respectively. The result of the SAC-CI(SDT-R) method is satisfactory and the errors are as small as -0.46 (O) and 0.13 G (H).

V. CONFIGURATION SELECTION METHOD FOR THE HFSCs

We next consider the effect of the configuration selection on the calculation of the hfscs. Two configuration selection methods described in Sec. II are examined for the SAC-CI(SD-R, DT-R), and SAC-CI(general-R) calculations. The calculational dimensions and the results are summarized in Table IV. The first one, named "method I," corresponds to the usual selection method in which only energy is used for the criterion according to Eq. (5). In the second method (method II), the contribution to the hfsc of each atom is also taken into account: Selected configurations are the sum of those which satisfy Eqs. (5) and (10). The results of these two methods are compared with those obtained without doing configuration selection, which are shown in the column under "full."

The effectiveness of method II is discussed in terms of the results of the SAC-CI(SD-R, DT-R) method. The difference of the two methods is remarkable for the hfscs of the radical center atoms. For the $X\ ^2\Pi$ state of the OH radical, e.g., the hfsc of the O atom is calculated as -12.23 G without configuration selection. Method I whose energy criterion is $\lambda e = 5\times10^{-5}$ a.u. gives -56.12 G, but method II gives the reliable value of -11.24 G. This difficulty of method I is caused by the fact that it discards the important (only three) excitation configurations which describe the inner-core polarization. Method II is also reliable for the hfscs of the quartet states. The hfscs of the O atom calculated by method II deviate only -0.65 and 1.36 G for the $1\ ^4\Sigma^-$ and $1\ ^4\Pi$ states, respectively, from those obtained without the selection, while those by method I deviate by as much as -23.38 and -17.60 G, respectively. The excitation configurations, which are important for describing the hfscs of the H atom, also give large perturbation energy contributions to the reference functions.

TABLE IV. Two types of the configuration selection methods applied to the calculations of the energy (a.u.) and hyperfine splitting constants (hfscs) (G) of small radicals by the SAC-CI method.

		SAC-CI (SD-R, DT-R)			SAC-CI (SDTQ-R, DTQQ-R)		
		Method I[a]	Method II[b]	Full[c]	Method I[a]	Method II[b]	Full[c]
OH							
$X\,^2\Pi$	Dimension	26	29	44	525	528	814
	Energy (a.u.)	−75.492 85	−75.492 88	−75.492 96	−75.494 27	−75.494 30	−75.495 07
	Hfsc (G) O	−56.12	−11.24	−12.23	−68.98	−25.62	−20.88
	H	−25.60	−25.61	−25.61	−30.85	−30.86	−31.50
$A\,^2\Sigma^+$	Dimension	36	39	70	422	425	676
	Energy (a.u.)	−75.336 77	−75.337 63	−75.337 80	−75.338 81	−75.338 82	−75.340 13
	Hfsc (G) O	−221.76	−202.72	−214.78	−224.11	−206.04	−215.87
	H	273.71	273.70	273.24	286.92	286.91	285.79
$1\,^4\Sigma^-$	Dimension	132	164	328	833	865	1452
	Energy (a.u.)	−75.177 87	−75.177 95	−75.178 13	−75.189 71	−75.189 78	−75.190 91
	Hfsc (G) O	−97.17	−74.44	−73.79	−107.36	−85.78	−82.40
	H	30.37	30.37	30.35	28.96	28.96	29.04
$1\,^4\Pi$	Dimension	108	124	356	447	463	896
	Energy (a.u.)	−75.070 35	−75.070 39	−75.070 75	−75.071 71	−75.071 75	−75.073 14
	Hfsc (G) O	−122.41	−106.17	−104.81	−130.81	−114.93	−112.14
	H	116.05	116.05	116.00	114.51	114.52	114.42
CH₂							
$^3B_1$	Dimension	77	89	190	562	575	981
	Energy (a.u.)	−38.994 24	−38.994 31	−38.995 09	−38.994 06	−38.994 13	−38.997 02
	Hfsc (G) C	124.61	98.95	96.45	132.99	107.98	102.88
	H	−16.43	−16.43	−15.75	−17.31	−17.31	−17.48
BH₂							
$^2A_1$	Dimension	32	36	71	334	338	481
	Energy (a.u.)	−25.799 86	−25.799 88	−25.800 46	−25.801 65	−25.801 66	−25.803 63
	Hfsc (G) B	128.26	125.11	123.80	137.81	134.70	130.86
	H	2.50	2.50	0.93	3.09	3.09	1.73
CH₃							
$^2A_2''$	Dimension	34	38	60	840	844	1466
	Energy (a.u.)	−39.652 86	−39.652 89	−39.652 94	−39.657 71	−39.657 74	−39.658 63
	Hfsc (G) C	63.32	30.99	28.69	83.00	51.29	42.45
	H	−28.67	−28.68	−28.67	−34.43	−34.44	−34.90
H₂O⁺							
$^2B_1$	Dimension	29	34	48	272	277	1133
	Energy (a.u.)	−75.721 14	−75.721 19	−75.721 29	−75.722 28	−75.722 33	−75.722 71
	Hfsc (G) O	−71.13	−18.93	−20.09	−87.75	−37.26	−34.64
	H	−28.17	−28.18	−28.23	−34.46	−34.49	−34.49

[a]Configuration selection is performed with only the energy criterion [Eq. (5)].
[b]Configuration selection is performed with the criterions of both energy and hfsc [Eqs. (5) and (10)].
[c]Without configuration selection.

Therefore, method I also gives good description for the proton hfscs. These trends hold good for other radicals except for the $^2A_1$ state of BH₂ in which core MOs of the B atom are not so much deeply bounded. The deviations of method I for the hfscs of the radical centers are calculated to be 28.16, 34.63, and −51.04 G for CH₂, CH₃, and H₂O⁺, respectively, while those of method II are only 2.50, 2.30, and 1.16 G. The effectiveness of method II is also observed in the SAC-CI (general-R) method as shown in Table IV.

The increases of the dimensions from method I to method II from 3 to 32 configurations are required for the accurate description of the hfscs. They are very small but the effects on the hfscs are very important, though the effects on the energies are marginal. They represent the inner-core polarization effect. The efficiency of the present method would increase as the system becomes large, as the system includes heavy atoms, and as the spin multiplicity of the molecule increases.

VI. BASIS-SET EXAMINATIONS

We have now shown the accuracy of the SAC-CI method and the usefulness of the proposed configuration selection method for calculating the hfscs. The SAC-CI (SDT-R) method combined with the present configuration selection procedure is considered to give a very accurate result for the hfscs. Therefore, we finally examine here the basis-set dependence by changing the contractions of the Gaussian basis functions and by adding the polarization functions.

Table V gives the total energies and the hfscs for the ground state of five radicals, OH($X\,^2\Pi$), CH₂($^3B_1$), BH₂($^2A_1$), CH₃($^2A_2''$), and H₂O⁺($^2B_1$), calculated by using some different Gaussian basis sets. Entries 1 and 2 are the results of the $[4s2p/2s]$ and $[4s2p1d/2s1p]$ set,[21] respectively, and therefore we can see the effect of the polarization functions. In particular, the hfscs of CH₂ are much improved: from 96.91 (C) and −16.11 G(H) with the $[4s2p/2s]$ set to

TABLE V. Energies (a.u.) and hyperfine splitting constants hfscs (G) of small radicals calculated by the SAC-CI (SDT-R) method using the energy and hfsc configuration selection method [Eqs. (5) and (10)].

	OH $X\,^2\Pi$	CH$_2$ $^3B_1$		BH$_2$ $^2A_1$	CH$_3$ $^2A_2''$		H$_2$O$^+$ $^2B_1$
1. $[4s2p/2s]^a$							
Energy	−75.494 95	−38.995 73		−25.803 61	−39.658 47		−75.723 22
Hfsc	O−15.41	C 96.91	B	123.55	C 31.46	O	−28.94
	H−29.74	H−16.11	H	1.41	H−31.68	H	−32.17
2. $[4s2p1d/2s1p]^a$							
Energy	−75.580 46	−39.051 15		−25.845 38	−39.733 02		−75.821 47
Hfsc	O−16.88	C 83.02	B	128.45	C 26.41	O	−33.47
	H−26.15	H −8.79	H	7.23	H−26.54	H	−28.52
3. $[5s2p1d/2s1p]^a$							
Energy	−75.582 45	−39.052 03		−25.846 26	−39.734 02		−75.822 89
Hfsc	O−21.99	C 78.63	B	114.39	C 30.80	O	−42.14
	H−26.13	H −8.77	H	7.28	H−26.52	H	−28.65
4. $[5s2p1d/3s^\dagger1p]^b$							
Energy	−75.582 90	−39.052 66		−25.846 56	−39.735 08		−75.824 33
Hfsc	O−22.46	C 79.66	B	114.34	C 30.79	O	−39.35
	H−26.04	H −7.62	H	7.74	H−25.12	H	−26.74
5. $(9s5p1d/4s1p)^a$							
Energy	−75.620 45	−39.075 96		−25.873 91	−39.761 94		−75.862 34
Hfsc	O−22.97	C 80.66	B	111.24	C 35.08	O	−38.32
	H−22.00	H −6.92	H	9.06	H−22.19	H	−24.46
Expt.							
Hfsc	O−15.2^c	C (85.2)^e	B	128^g	C 28.7^h	O	±29.7^i
	H−26.1^d	H −7.2^f	H	±13.6^g	H−24.7^h	H	±26.1^i

^{a}Reference 21.
^{b}Reference 33.
^{c}Reference 27.
^{d}Reference 28.
^{e}MRD-CI calculation with extended basis sets; Ref. 30.

^{f}Reference 29.
^{g}Reference 30.
^{h}Reference 31.
^{i}Reference 32.

83.02 (C) and −8.79 G(H) with the $[4s2p1d/2s1p]$ set. For carbon the MRD-CI calculation[30] with extended basis set gave 85.2 G and for proton the experimental value is −7.2 G.[29] Such improvements are also obtained for the hfscs of BH$_2$ and CH$_3$ and also for the H atoms of OH and H$_2$O$^+$. In entries 3 and 4, the flexibility of the s shell is enlarged for the radical center atoms and for the H atom, respectively. Chipman's contraction scheme[33] is adopted in entry 4. In entry 5, the primitive set of Huzinaga[21] with the polarization function $(9s5p1d/4s1p)$ is examined. The total energies are improved as the basis sets are qualified, however, the values of the hfscs are not necessarily improved. This difficulty of calculating the hfscs is also pointed out in the studies using the Gaussian basis sets.[5,10,11] As we have pointed out previously, further improvement will be obtained only by the wave function which satisfies the cusp condition.[5] Slater-type orbitals are necessary at least for the s-type orbitals. The Huzinaga–Dunning $[4s2p1d/2s1p]$ contraction seems to give good compromise values among these basis sets.[3–5]

for the first time and is found to give an accurate description of the hfscs. In particular, the SAC-CI(SDT-R) method gives highly accurate hfsc results.

A convenient configuration selection method which keeps the quality of both the calculated energy and hfsc is proposed. This method, in which both energy and hfsc are used as the criteria in the configuration selection procedure, is also applicable to an ordinary CI method and is effective for accurate calculations of hfscs especially for large systems and for high-spin molecules, where a large number of configurations are required. Furthermore, it is easy to modify this method to the properties other than the hfsc.

The basis-set dependence of the calculated hfscs is examined. Within the Gaussian set, the improvement in energy does not necessarily result in the improvement of the hfsc. We have to use the basis set which satisfies the cusp condition, like STO. Within the GTOs, the Huzinaga–Dunning $[4s2p1d/2s1p]$ contraction is a good compromise for the hfscs.

VII. CONCLUDING REMARKS

The accuracy and the usefulness of the SAC-CI method for calculating hyperfine splitting constants (hfscs) are examined and confirmed for the doublet, triplet, and quartet states of several small radicals. The results of the SAC-CI method show good agreement with those of the full CI ones. The SAC-CI (general-R) method is applied to the high-spin states

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