SAC-CI and full-CI calculations for the singlet and triplet excited states of H_2O

Hiroshi Nakatsuji

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Kimihiko Hirao

Department of Chemistry, College of General Education, Nagoya University, Nagoya, Japan
and Institute for Molecular Science, Okazaki, Japan

and

Yoshihiro Mizukami

Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

The accuracy of the SAC-CI (symmetry-adapted-cluster configuration-interaction) method is examined for the singlet and triplet excited states of H_2O by comparison with the full-CI results for the [4s2p] basis set. The SAC-CI results for the excitation energy agree with the full-CI results to within 1.4%.

The SAC (symmetry-adapted-cluster) [1] and SAC-CI [2] methods were proposed for calculations of the ground and excited states, ionized states and electron-attached states of a molecule. Through many applications, the SAC/SAC-CI method has been proved to be very useful for reliable and effective calculations of the ground, excited, and ionized states of molecules [3].

Some years ago, the accuracy of the SAC/SAC-CI method has been examined for the ground state [4] and the triplet excited, ionized and electron-attached states [5] of H_2O by comparison with the full-CI results. The basis set was the [4s2p] set of Huzinaga [6] and Dunning [7]. The purpose of this paper is to examine the accuracy of the *singlet* excited states of H_2O calculated by the SAC-CI method, since this examination was missing in the previous paper [5]. We carry out comparative full-CI calculations and compare their total energies and excitation energies with the SAC-CI results. Some additional results are also reported for the triplet excited states.

The ground state of H_2O is calculated by the SAC method. The Hartree–Fock (HF) orbitals are calculated by the program GAMESS [8] and used as the reference orbitals in the SAC/SAC-CI calculations. Linked terms in SAC include all single- (S_1) and double- (S_2) excitation operators, and the unlinked terms include quadruple-excitation operators as products of double-excitation operators ($S_2 S_2$).

The excited states are calculated by the SAC-CI theory. Linked terms in SAC-CI include all single- (R_1) and double- (R_2) excitation operators. For unlinked terms, we use two different approximations. The first one, called SAC-CI (A), includes only $R_1 S_2$ operators, and the second one, called SAC-CI (B), includes both $R_1 S_2$ and $R_2 S_2$ operators. No configuration selection is performed in both SAC and SAC-CI calculations. We used the program package SAC85 [9].

The full-CI calculations for the singlet and triplet excited states of H_2O are carried out with the use of the modified version of the determinant integer full-

CI program of Handy [10].

The total energy of the ground state is -76.156254 hartree by SAC and -76.157866 hartree by full-CI. These are the same as those reported previously [5]. The energy difference is only 1.6×10^{-3} hartree (1.0 kcal/mol), so that the SAC method is proved to be very reliable.

The results for the singlet ground and excited states of H_2O are summarized in table 1. The dimensions of the matrices involved in SAC/SAC-CI are the same as those of SDCI and are three-orders-of-magnitude smaller than those of full-CI. The excitation energies of both SAC-CI(A) and SAC-CI(B) are in good agreement with those of full CI. The differences are to within 1.2%. There is a trend that SAC-CI(A) gives larger excitation energies and, in con-

trast, SAC-CI(B) gives smaller ones in comparison with full-CI. Refined unlinked terms in SAC-CI (B) lower the energies of the excited states and give smaller excitation energies. Total energies of SAC-CI are also in very good agreement with those of full-CI. However, we note that the SAC-CI(B) results sometimes overshoot the exact full-CI energies, though the differences are less than 2.1×10^{-3} hartree. This arises from the non-variational nature in the solution of SAC-CI. Variational solution always gives an upper bound for full-CI, but it is very difficult to obtain it for the SAC/SAC-CI expansion [2]. For the $^1A_1$ and $^1B_2$ symmetries, we also give the results for the second excited states. Both total energies and excitation energies of SAC-CI (especially, SAC-CI(B)) compare very well with those of full-CI. We list the

Table 1
Total energies and the excitation energies for the singlet ground and excited states of H_2O calculated by the full-CI and SAC/SAC-CI method

State	Orbital picture		Dimension	Total energy (au)	Excitation energy (eV)	Error from full-CI (%)	CPU time [a] (min)
$^1A_1$	ground state	SAC	361	-76.156254	0.0	0.002	1.8
		full-CI	256474	-76.157866	0.0		55
	$3a_1(n) \rightarrow 4a_1$	SAC-CI(A)	360	-75.754848	10.9229	0.8	0.6 [b]
		SAC-CI(B)	360	-75.761163	10.7511	-0.8	2.0 [b]
		full-CI	256474	-75.759512	10.8399		190 [b]
	$1b_2(\sigma) \rightarrow 2b_2$	SAC-CI(A)	360	-75.450371	19.2082	0.8	
		SAC-CI(B)	360	-75.454417	19.0981	0.2	
		full-CI	256474	-75.457584	19.0558		
$^1A_2$	$1b_1(\pi) \rightarrow 2b_2$	SAC-CI(A)	192	-75.756082	10.8893	0.8	0.1
		SAC-CI(B)	192	-75.761966	10.7292	-0.6	0.6
		full-CI	245000	-75.761050	10.7980		82
$^1B_1$	$1b_1(\pi) \rightarrow 4a_1$	SAC-CI(A)	216	-75.833910	8.7715	0.9	0.2
		SAC-CI(B)	216	-75.840435	8.5940	-1.2	0.8
		full-CI	245776	-75.838288	8.6962		82
$^1B_2$	$3a_1(n) \rightarrow 2b_2$	SAC-CI(A)	312	-75.664680	13.3765	0.8	0.4
		SAC-CI(B)	312	-75.670341	13.2225	-0.4	1.5 [b]
		full-CI	254752	-75.670141	13.2718		193 [b]
	$1b_2(\sigma) \rightarrow 4a_1$	SAC-CI(A)	312	-75.564611	16.0996	0.9	
		SAC-CI(B)	312	-75.568589	15.9913	0.2	
		full-CI	254752	-75.571512	15.9556		

[a] Due to FACOM M780 computer.
[b] This timing data is for the two excited-state solutions belonging to the same symmetry.

timing data in table 1. The CPU time for SAC-CI is much shorter than that for full-CI.

The results of the triplet excited states of H_2O are shown in table 2. Here, we also show the previous result of SAC-CI by Hirao and Hatano [5]. We call it SAC-CI(H). The dimensions of SAC-CI(H) are smaller than those of SAC-CI(A) and SAC-CI(B), because SAC-CI(H) does not include spin-polarization-type double-excitation operators for triplet excited states. We also show the results of the second excited states for the $^3A_1$ and $^3B_2$ states. Total energies and excitation energies of SAC-CI(A) and SAC-CI(B) are in very good agreement with those of full-CI. The SAC-CI excitation energies differ from the full-CI ones only to within 1.4%, though the dimensions of SAC-CI are much less than those of full-CI.

Results of SAC-CI(H) are also comparable and agree well with those of full-CI.

In conclusion, the SAC-CI method is confirmed to be quite accurate for the singlet and triplet excited states of H_2O. The excitation energies calculated by the SAC-CI method agree to within 1.4% with those of full-CI, though the dimensions of SAC-CI are three-orders-of-magnitude smaller than those of full-CI. The CPU time for SAC-CI is also much shorter than that for full-CI. The total energies of SAC-CI(B) sometimes overshoot the full-CI energies because of the non-variational nature of the solution, though the energy differences between SAC-CI(B) and full-CI are very small. We conclude that the SAC/SAC-CI method is quite reliable and effective for the study of ground, excited and ionized states of molecules.

Table 2
Total energies and excitation energies for the triplet excited states of H_2O calculated by the full-CI and SAC-CI methods

State	Orbital picture		Dimension	Total energy (au)	Excitation energy (eV)	Error from full-CI (%)	CPU time [a] (min)
$^3A_1$	$3a_1(n) \rightarrow 4a_1$	SAC-CI(A)	417	−75.794396	9.8467	0.3	1.1 [b]
		SAC-CI(B)	417	−75.799083	9.7192	−1.0	4.0 [b]
		SAC-CI(H)	315	−75.791190	9.934	1.2	
		full-CI	440475	−75.797174	9.8150		246 [b]
	$1b_2(\sigma) \rightarrow 2b_2$	SAC-CI(A)	417	−75.566185	16.0567	0.3	
		SAC-CI(B)	417	−75.568723	15.9877	−0.1	
		full-CI	440475	−75.569523	16.0098		
$^3A_2$	$1b_1(\pi) \rightarrow 2b_2$	SAC-CI(A)	274	−75.775095	10.3720	0.9	0.3
		SAC-CI(B)	274	−75.780262	10.2314	−0.5	1.8
		SAC-CI(H)	192	−75.776939	10.322	0.4	
		full-CI	437640	−75.779926	10.2844		114
$^3B_1$	$1b_1(\pi) \rightarrow 4a_1$	SAC-CI(A)	294	−75.864292	7.9448	0.6	0.4
		SAC-CI(B)	294	−75.869963	7.7904	−1.4	2.1
		SAC-CI(H)	216	−75.868314	7.835	−0.8	
		full-CI	437520	−75.867507	7.9011		113
$^3B_2$	$3a_1(n) \rightarrow 2b_2$	SAC-CI(A)	410	−75.718219	11.9196	0.4	0.9 [b]
		SAC-CI(B)	410	−75.722134	11.8131	−0.5	3.7 [b]
		SAC-CI(H)	312	−75.711568	12.101	1.9	
		full-CI	441120	−75.721626	11.8708		269 [b]
	$1b_2(\sigma) \rightarrow 4a_1$	SAC-CI(A)	410	−75.631970	14.2666	0.4	
		SAC-CI(B)	410	−75.634992	14.1844	−0.2	
		full-CI	441120	−75.635841	14.2151		

[a] Due to FACOM M780 computer.
[b] This timing data is for the two solutions belonging to the same symmetry.

References

[1] H. Nakatsuji and K. Hirao, J. Chem. Phys. 68 (1978) 2053.

[2] H. Nakatsuji, Chem. Phys. Letters 59 (1978) 362; 67 (1979) 329, 334.

[3] H. Nakatsuji, Theoret. Chim. Acta 71 (1987) 201;
H. Nakatsuji, M. Komori and O. Kitao, Lecture notes in chemistry, Vol. 50, ed. D. Mukherjee (Springer, Berlin, 1989) pp. 101–122;
H. Nakatsuji, Reports in Molecular Theory (CRC Press, Boca Raton), in press.

[4] K. Hirao and Y. Hatano, Chem. Phys. Letters 100 (1983) 519.

[5] K. Hirao and Y. Hatano, Chem. Phys. Letters 111 (1984) 533.

[6] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.

[7] T.H. Dunning Jr., J. Chem. Phys. 53 (1970) 2823.

[8] B.R. Brooks, P. Saxe, W.D. Laidig and N. Dupuis, Program Library Gamess (No. 481), Computer Center of the Institute for Molecular Science, Okazaki, Japan.

[9] H. Nakatsuji, Program system for SAC and SAC-CI calculations, Program Library No. 146(Y4/SAC), Data Processing Center of Kyoto University (1985); Program Library SAC85 (No. 1396), Computer Center of the Institute for Molecular Science, Okazaki, Japan (1986).

[10] N.C. Handy, Chem. Phys. Letters 74 (1980) 280.