

CLUSTER EXPANSION OF THE WAVEFUNCTION. CALCULATION OF ELECTRON CORRELATIONS IN GROUND AND EXCITED STATES BY SAC AND SAC CI THEORIES

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The SAC and SAC CI theories are formulated for actual calculations of singlet ground states and their excited states of arbitrary spin multiplicity. Approximations are considered for the variational methods since time-consuming terms are involved. The results of test calculations for singlet states have shown, with much smaller numbers of variables (sizes of the matrices involved), excellent agreement with the full CI and close-to-full CI results. This shows the utility of the SAC theory for ground states and especially of the SAC CI theory for excited states, since the slow convergence of the CI theory is much more critical for excited states than for ground states.

1. Introduction

Cluster expansion theory is one of the most promising approaches for calculations of accurate wavefunctions*. Though applications are still very limited, the results show a promising utility of the theory*. In the preceding paper [1], we have summarized variational and non-variational solutions of the SAC (symmetry-adapted-cluster) expansion of the closed- or open-shell ground state, and of the SAC CI wavefunction of the excited states. The SAC expansion has been considered previously to extend the cluster expansion formalism to open-shell systems [2]. It has been applied to the study of spin correlations in open-shell atoms and molecules [3]. The SAC CI theory has been considered as a rapidly convergent method for excited states [4].

In this paper, we consider applications of these theories to the study of electron correlations in singlet ground and excited states. The results of test calculations for relatively small atoms and molecules will be given and compared with the full CI or close-to-full CI results. In the next section, we explain necessary definitions and truncations of the SAC and SAC CI wavefunctions. In sections 3 and 4, we summarize formulas necessary for actual calculations. Approxima-

tions are considered for the variational methods since they include time-consuming terms. The results of calculations for Be, BH₃, H₂O, and Rydberg excited states of H₂O will be given. The conclusions will be given in the last section.

2. Specifications

For a totally symmetric singlet ground state, the SAC wavefunction is written as

$$\Psi_g = \exp \left[\sum_I C_I S_I^+ \right] \Phi_0, \quad (1)$$

where we need not include the symmetry projector [1]. Then, Ψ'_g in the preceding paper [1] is equal to Ψ_g . In the present calculation we truncate the expansion in eq. (1) at second order

$$\Psi_g = \left[1 + \sum_I C_I S_I^+ + \frac{1}{2} \sum_{IJ} C_I C_J S_I^+ S_J^+ \right] |0\rangle. \quad (2)$$

The reference wavefunction $|0\rangle$ is calculated by the Hartree-Fock theory:

$$|0\rangle = \|1\bar{1} \dots i\bar{i} \dots n\bar{n}\|, \quad (3)$$

$$E_0 = \langle 0|H|0\rangle. \quad (4)$$

* See references cited in the preceding paper [1].

For the symmetry-adapted excitation operator S_I^+ , we have included single and double excitations. The unlinked terms $S_I^+ S_J^+$ then include double, triple, and quadruple excitations. A single excitation from occupied orbital i to virtual orbital a is given by

$$S_i^a = 2^{-1/2} (a_{a\alpha}^+ a_{i\alpha} + a_{a\beta}^+ a_{i\beta}) . \quad (5)$$

Double, triple, and quadruple excitations are written as products of single excitation operators as $S_i^a S_j^b$, $S_i^a S_j^b S_k^c$, and $S_i^a S_j^b S_k^c S_l^d$, respectively. The integrals were restricted to the types $\langle \text{linked} | H | \text{linked} \rangle$ and $\langle \text{linked} | H | \text{unlinked} \rangle$, so that the integrals $\langle \text{single} \times \text{triple} \rangle$, $\langle \text{double} \times \text{triple} \rangle$, and $\langle \text{double} \times \text{quadruple} \rangle$ became necessary additionally to those used in the single and double excitation CI, (1+2)CI. Though the variational methods include the terms composed of the integrals between unlinked terms, we have considered approximations to calculate them from the lower order terms, rather than to calculate them explicitly. A strong reason for this is that the explicit calculations of such terms are too time-consuming to plan calculations of general utility.

The SAC CI wavefunction for the excited state is given by

$$\Psi_e = \sum_K d_K \Phi_K , \quad (6)$$

where a set of excited functions $\{\Phi_K\}$ is defined by

$$\Phi_K = \mathcal{N}_K (R_K^+ - \mathcal{O}_{K_g}) \Psi_g . \quad (7)$$

Again the projector $\mathcal{O}^{(R)}$ is unnecessary [1]. In eq. (7), \mathcal{O}_{K_g} is defined by

$$\mathcal{O}_{K_g} = \langle \Psi_g | R_K^+ \Psi_g \rangle . \quad (8)$$

It vanishes identically when the (spin-space) symmetry of the excited state is different from that of the ground state. Otherwise, it is of the order of C_K . For the Ψ_g included in eq. (7) we have used the SAC wavefunction obtained from the ground-state calculations. The SAC CI wavefunction Ψ_e was truncated at the second order for both the coefficients d_K and C_I , so that it is written as

$$\Psi_e = \sum_K d'_K \left[R_K^+ + \sum_I C_I S_I^+ R_K^+ \right] |0\rangle - \sum_K d'_K \mathcal{O}_{K_g} \Psi_g , \quad (9)$$

where $d'_K = d_K \mathcal{N}_K$. The last term of eq. (9) was not modified for later convenience. For the excitation operators R_K^+ , we have included single and double exci-

tations. The unlinked terms $R_K^+ S_I^+$ then include double, triple, and quadruple excitations. The types of integrals are limited to the same ones as in the ground state calculations. An effective approximation is then introduced in the SAC CI variational calculations. Thus, the integrals required for the SAC CI calculations are of the same types as those used in the SAC calculations. Actually, we have used the same sequence of integrals for both SAC and SAC CI calculations of the ground and excited states of the same symmetry.

3. SAC calculation for ground state

3.1. Non-variational calculation (SAC MET)

We first consider the non-variational procedure since it is simpler than the following variational one. Inserting eq. (2) into eq. (I.10)[†], we obtain

$$\begin{aligned} \langle 0 | HS_I^+ | 0 \rangle + \sum_J C_J \langle 0 | S_J (H - E_g) S_I^+ | 0 \rangle \\ + \frac{1}{2} \sum_{JK} C_J C_K \langle 0 | S_J S_K (H - E_g) S_I^+ | 0 \rangle = 0 , \end{aligned} \quad (10)$$

which may be rewritten as

$$H_{0I} + \sum_J C_J (G_{JI} - E_g T_{JI}) = 0 , \quad (11)$$

where

$$H_{0I} = \langle 0 | HS_I^+ | 0 \rangle , \quad (12)$$

$$\begin{aligned} G_{JI} - E_g T_{JI} = \langle 0 | S_J (H - E_g) S_I^+ | 0 \rangle \\ + \frac{1}{2} \sum_K C_K \langle 0 | S_J S_K (H - E_g) S_I^+ | 0 \rangle . \end{aligned} \quad (13)$$

Note that the matrices G_{JI} and T_{JI} are non-symmetric. The energy is calculated from eq. (I.9) as

$$\begin{aligned} E_g = E_0 + \sum_I C_I \langle 0 | HS_I^+ | 0 \rangle \\ + \frac{1}{2} \sum_{IJ} C_I C_J \langle 0 | HS_I^+ S_J^+ | 0 \rangle . \end{aligned} \quad (14)$$

We have solved these equations iteratively as follows.

[†] We denote by eq. (I.10) the eq. (10) of the preceding paper [1]. Similar abbreviations will be used hereafter.

- (i) Assume initial values for $C^{(0)}$ and $E_g^{(0)}$.
(ii) Construct $G^{(0)}$ and $T^{(0)}$ matrices and solve the simultaneous linear equation (11) to obtain $C^{(1)}$.
(iii) Calculate $E_g^{(1)}$ from eq. (14).
(iv) Repeat the steps (ii)–(iii) using the new quantities $C^{(1)}$ and $E_g^{(1)}$.
(v) The above procedure is iterated until $|E_g^{(n)} - E_g^{(n-1)}| < \Delta\epsilon$.
We have used CI solutions as the initial quantities $C^{(0)}$ and $E_g^{(0)}$, though cruder initial guess seems also to be all right. The iteration converged very smoothly within 3–7 times with $\Delta\epsilon = 0.1 \times 10^{-6}$ au.

3.2. Variational calculation (SAC V)

For the wavefunction given by eq. (2), the variational equation given by (1.5) becomes

$$\begin{aligned} &\langle 0|HS_I^+|0\rangle + \sum_J C_J [\langle 0|S_J(H-E_g)S_I^+|0\rangle + \langle 0|HS_I^+S_J^+|0\rangle] \\ &+ \sum_{JK} C_J C_K [\langle 0|S_J(H-E_g)S_I^+S_K^+|0\rangle \\ &+ \frac{1}{2}\langle 0|S_J S_K(H-E_g)S_I^+|0\rangle] \\ &+ \frac{1}{2} \sum_{JKL} C_J C_K C_L [\langle 0|S_J S_K(H-E_g)S_I^+S_L^+|0\rangle \\ &+ \langle 0|S_J(H-E_g)S_I^+S_K^+S_L^+|0\rangle] \\ &+ \frac{1}{4} \sum_{JKLM} C_J C_K C_L C_M \langle 0|S_J S_K(H-E_g)S_I^+S_L^+S_M^+|0\rangle = 0. \end{aligned} \quad (15)$$

It is almost impossible to solve this equation completely. In the present calculations, we have retained terms up to second order in the coefficients. Then, we obtain

$$H_{0I} + \sum_J C_J (G_{JI} - E_g T_{JI}) = 0, \quad (16)$$

where

$$H_{0I} = \langle 0|HS_I^+|0\rangle, \quad (17)$$

$$\begin{aligned} G_{JI} - E_g T_{JI} &= \langle 0|S_J(H-E_g)S_I^+|0\rangle + \langle 0|HS_I^+S_J^+|0\rangle \\ &+ \sum_K C_K [\langle 0|S_J(H-E_g)S_I^+S_K^+|0\rangle \\ &+ \frac{1}{2}\langle 0|S_J S_K(H-E_g)S_I^+|0\rangle]. \end{aligned} \quad (18)$$

Though the matrices G_{JI} and T_{JI} involved in eq. (18) are not symmetric, they can also be made symmetric as

$$\begin{aligned} G_{JI} - E_g T_{JI} &= \langle 0|S_J(H-E_g)S_I^+|0\rangle + \langle 0|HS_I^+S_J^+|0\rangle \\ &+ \frac{1}{2} \sum_K C_K [\langle 0|S_J(H-E_g)S_I^+S_K^+|0\rangle \\ &+ \langle 0|S_J(H-E_g)S_I^+S_K^+|0\rangle + \langle 0|S_K(H-E_g)S_I^+S_K^+|0\rangle]. \end{aligned} \quad (19)$$

The energy of the SAC wavefunction (2) is calculated from eq. (1.8) as

$$\begin{aligned} E_g &= E_0 + \sum_I C_I \langle 0|HS_I^+|0\rangle \\ &- \frac{1}{2} \sum_{IJK} C_I C_J C_K \langle 0|S_I(H-E_g)S_J^+S_K^+|0\rangle \\ &+ \frac{1}{4} \sum_{IJKL} C_I C_J C_K C_L \langle 0|S_I S_J(H-E_g)S_K^+S_L^+|0\rangle, \end{aligned} \quad (20)$$

where we have assumed that eq. (16) is satisfied. In eq. (20) the last term includes the integrals between unlinked terms. Since the calculation of this term is time-consuming even for molecules of moderate size, we have considered the following approximation. We assume that the variational and non-variational solutions for the SAC wavefunction are close. Then, using the same values for $\{C_I\}$ and E_g in eqs. (10) and (15), we obtain

$$\begin{aligned} &\sum_J C_J \langle 0|HS_I^+S_J^+|0\rangle \\ &+ \sum_{JK} C_J C_K \langle 0|S_J(H-E_g)S_I^+S_K^+|0\rangle \\ &+ \frac{1}{2} \sum_{JKL} C_J C_K C_L \langle 0|S_J S_K(H-E_g)S_I^+S_L^+|0\rangle \approx 0, \end{aligned} \quad (21)$$

where we have neglected the last two terms of eq. (15), the former being neglected because at least one of the excitations S_K^+ and S_L^+ should be a single excitation and the latter is neglected because it is higher by one order. From eqs. (20) and (21) we obtain

$$\begin{aligned} E_g &\approx E_0 + \sum_I C_I \langle 0|HS_I^+|0\rangle \\ &- \frac{1}{2} \sum_{IJ} C_I C_J \langle 0|HS_I^+S_J^+|0\rangle \\ &- \sum_{IJK} C_I C_J C_K \langle 0|S_I(H-E_g)S_J^+S_K^+|0\rangle. \end{aligned} \quad (22)$$

The set of equations (16)–(19) and (22) was solved iteratively by the same procedure as in the non-variational case.

4. SAC CI calculation for excited states

4.1. Non-variational calculation (SAC CI NV)

The formula for the SAC CI non-variational calculation is obtained by inserting eq. (9) into eq. (I.22), namely,

$$\sum_L d'_L \left[\langle 0 | R_K (H - E_e) R_L^\dagger | 0 \rangle + \sum_I C_I \langle 0 | R_K (H - E_e) S_I^\dagger R_L^\dagger | 0 \rangle - \delta_{Lg} \langle 0 | R_K (H - E_e) | \Psi_g \rangle \right] = 0. \quad (23)$$

The last term is non-zero only when both ground and excited states have the same symmetry. It is rewritten from eq. (I.10) as

$$\sum_L d'_L \delta_{Lg} \langle 0 | R_K (H - E_e) | \Psi_g \rangle \approx \sum_L d'_L \delta_{Lg} (E_g - E_e) \langle 0 R_K | \Psi_g \rangle. \quad (24)$$

This term is small since both of the integrals δ_{Lg} and $\langle 0 R_K | \Psi_g \rangle$ are of the order of C_L and C_K , respectively. In the present rule of truncation (section 2) this term may be neglected since the non-variational formula includes the unlinked term only in "bra" or "ket". Then we obtain the working formula

$$\sum_L (H_{KL} - E_e T_{KL}) d_L = 0, \quad (25)$$

where

$$H_{KL} - E_e T_{KL} = \mathcal{N}_L \left[\langle 0 | R_K (H - E_e) R_L^\dagger | 0 \rangle + \sum_I C_I \langle 0 | R_K (H - E_e) S_I^\dagger R_L^\dagger | 0 \rangle \right]. \quad (26)$$

This equation constitutes an eigenvalue problem of a non-symmetric matrix.

4.2. Variational calculation (SAC CI V)

The secular equation for the variational calculation is given by eq. (I.20), i.e.,

$$\sum_L \langle \Phi_K | H - E_e | \Phi_L \rangle d_L = 0. \quad (27)$$

The matrix element is calculated from eq. (7) as

$$\begin{aligned} \langle \Phi_K | H - E_e | \Phi_L \rangle = & \mathcal{N}_K \mathcal{N}_L [\langle \Psi_g | R_K (H - E_e) R_L^\dagger | \Psi_g \rangle \\ & - \delta_{Lg} \langle \Psi_g | R_K (H - E_e) | \Psi_g \rangle \\ & - \delta_{Kg} \langle \Psi_g | (H - E_e) R_L^\dagger | \Psi_g \rangle \\ & + \delta_{Kg} \delta_{Lg} \langle \Psi_g | H - E_e | \Psi_g \rangle]. \end{aligned} \quad (28)$$

The first term of eq. (28) is transformed as

$$\begin{aligned} \langle \Psi_g | R_K (H - E_e) R_L^\dagger | \Psi_g \rangle = & \langle 0 | R_K (H - E_e) R_L^\dagger | 0 \rangle \\ & + \sum_I C_I [\langle 0 | R_K S_I (H - E_e) R_L^\dagger | 0 \rangle \\ & + \langle 0 | R_K (H - E_e) S_I^\dagger R_L^\dagger | 0 \rangle] \\ & + \sum_{IJ} C_I C_J \langle 0 | R_K S_I (H - E_e) S_J^\dagger R_L^\dagger | 0 \rangle, \end{aligned} \quad (29)$$

within the present truncation rules (section 2). With the use of eqs. (I.5)–(I.8), the last three terms of eq. (28) can be summarised into

$$-(E_g - E_e) \delta_{Kg} \delta_{Lg}.$$

It is non-zero only when the symmetries of the ground and excited states are the same. Thus, the matrix element given by eq. (28) becomes

$$\begin{aligned} \langle \Phi_K | H - E_e | \Phi_L \rangle = & \mathcal{N}_K \mathcal{N}_L \left[\langle 0 | R_K (H - E_e) R_L^\dagger | 0 \rangle \right. \\ & + \sum_I C_I [\langle 0 | R_K S_I (H - E_e) R_L^\dagger | 0 \rangle \\ & + \langle 0 | R_K (H - E_e) S_I^\dagger R_L^\dagger | 0 \rangle] \\ & + \sum_{IJ} C_I C_J \langle 0 | R_K S_I (H - E_e) S_J^\dagger R_L^\dagger | 0 \rangle, \\ & \left. - (E_g - E_e) \delta_{Kg} \delta_{Lg} \right], \end{aligned} \quad (30)$$

In this equation the term

$$\sum_{IJ} C_I C_J \langle 0 | R_K S_I (H - E_e) S_J^\dagger R_L^\dagger | 0 \rangle, \quad (31)$$

is characteristic of the variational procedure so that an explicit evaluation may be of interest. However, this term is very time-consuming even for molecules of moderate size and therefore, an appropriate approximation may be hoped. In the present calculation we have adopted the following approximation. In the CI method, the equation

$$\langle 0 | (H - E_g) S_J^+ + \sum_I C_I S_I (H - E_g) S_J^+ | 0 \rangle = 0 \quad (32)$$

holds exactly. We may use this equation to estimate the order of magnitude of the term (32). We assume that eq. (32) holds not only for $|0\rangle$ but also for $R_K^+ |0\rangle$, namely,

$$\langle 0 | R_K \left[(H - E_g) S_J^+ + \sum_I C_I S_I (H - E_g) S_J^+ \right] R_K^+ | 0 \rangle \approx 0. \quad (33)$$

This approximation may be valid when the excitations S_J^+ and R_K^+ concern different pairs of (occupied and virtual) orbitals, so that the present approximation would be better for larger molecules. Multiplying C_I and summing up with respect to the index I , from eq. (33) we obtain

$$\begin{aligned} & \sum_{IJ} C_I C_J \langle 0 | R_K S_I (H - E_e) S_J^+ R_K^+ | 0 \rangle \\ & \approx - \sum_J C_J \langle 0 | R_K (H - E_e) S_J^+ R_K^+ | 0 \rangle \\ & + (E_g - E_e) \sum_{IJ} C_I C_J \langle 0 | R_K S_I S_J^+ R_K^+ | 0 \rangle. \end{aligned} \quad (34)$$

We have also assumed the same relation for the off-diagonal terms of eq. (31). Thus, the secular equation for the SAC CI V method is written as

$$\sum_L (H_{KL} - E_e T_{KL}) d_L = 0, \quad (35)$$

where

$$\begin{aligned} H_{KL} - E_e T_{KL} = & \mathcal{N}_K \mathcal{N}_L \left[\langle 0 | R_K (H - E_e) R_L^+ | 0 \rangle \right. \\ & + \frac{1}{2} \sum_I C_I \langle 0 | R_K S_I (H - E_e) R_L^+ | 0 \rangle \\ & + \langle 0 | R_K (H - E_e) S_I^+ R_L^+ | 0 \rangle + (E_g - E_e) \\ & \left. \times \left(\sum_{IJ} C_I C_J \langle 0 | R_K S_I S_J^+ R_L^+ | 0 \rangle - \delta_{K_g} \delta_{L_g} \right) \right]. \end{aligned} \quad (36)$$

Eq. (35) is symmetric so that several algorithms are available when the matrices are of large dimension [5]. In the present calculations, we have considered only single excitations for the R_K 's in the term $\sum C_I C_J \times \langle 0 | R_K S_I S_J^+ R_L^+ | 0 \rangle$, since it is still time-consuming and since most excited states studied here are essentially of single excitation nature.

5. Results of test calculations

The SAC and SAC CI methods have been applied to the following systems for which the full CI or highly accurate CI results are available for comparison. (i) 1^1S states of the Be atom with a 5S basis [6]. The full CI results were reported by Grein and Banerjee [7] for the first 5 states. (ii) The BH_3 molecule with minimal STO-NG basis ($N = 10$ for 1s and 2s AO's and 8 for 2p AO's) [8]. The geometry and the scale factors of the STO's are the same as those in the full CI calculation for the ground state by Pipano and Shavitt [9]. (iii) The ground state of H_2O with Huzinaga-Dunning's [4s2p/2s] contracted gaussian basis of double-zeta accuracy [10]. The geometry is $R_{OH} = 1.8111$ bohr, $\angle HOH = 104.45^\circ$ taken from Hosteny et al. [11] who gave very accurate CI results. The inner shell orbital was treated as frozen. (iv) The ground and Rydberg excited states of H_2O with a STO-4G basis [12] plus 1G s- and p-type Rydberg orbitals with $\alpha = 0.028$. The geometry and the scale factors are the same as those reported by Hausman et al. [13] who have reported very accurate CI results by their vector method. The excitations from the lowest two orbitals $1a_1$ and $2a_1$ were not included.

In table 1, the present results for the Be atom are compared with the results of different theories. The MC SCF results were obtained by the optimization for each state [7]. Two of the excited states (E_2 and E_4) are essentially of the nature of two-electron excitation. Values in parentheses are relative to the full CI results. For both ground and excited states, the SAC and SAC CI results are very close to the full CI results. They are closer than the other theories by one or two orders of magnitude. For ground state, the non-variational solution (SAC MET) was -0.017488 au which is the same as the SAC V result. For excited states, both SAC CI V and SAC CI NV results are also similar. Note that the cluster effects (differences from the (1+2 CI) are larger for the excited states than for the ground state.

Table 1
Ground and excited 1S states of Be compared with full CI result a,b)

State	HF SECI c)	MC SCF d)	(1+2) CI e)	SAC V SAC CI V	SAC V SAC CI NV	Full CI d)
ground E_0	0.00000 (0.01750)	-0.013947 (0.00355)	-0.017445 (0.000006)	-0.017488 (0.000001)	-0.017488 (0.000001)	-0.017500
excited $E_1(2 \rightarrow 3)$	0.441249 (0.01630)	0.428570 (0.00363)	0.437361 (0.01242)	0.424644 (-0.00030)	0.424785 (-0.00016)	0.424945
$E_2(2 \rightarrow 3)$	-	0.801399 (0.01325)	0.801752 (0.01360)	0.790760 (0.00261)	0.787615 (-0.00053)	0.788148
$E_3(2 \rightarrow 4)$	3.141957 (0.04701)	3.109372 (0.01442)	3.101967 (0.00702)	3.094659 (-0.00029)	3.096674 (0.00172)	3.094951
$E_4(2 \rightarrow 4)$	-	3.566049 (0.01251)	3.567507 (0.01396)	3.560788 (0.00724)	3.558963 (0.00542)	3.553543

a) All energies are relative to the Hartree-Fock energy, -14.572924 au. Values in parentheses are relative to the full CI result.

b) SAC MET result for the ground state is -0.017488 au.

c) HF SECI is an abbreviation for Hartree-Fock single excitation CI.

d) Ref. [7].

e) (1+2)CI denotes the CI with all single and double excitations.

In table 2, we have examined the effects of unlinked terms for the Be atom. The SAC V and SAC CI V methods were used. For the ground state almost all of the cluster effects are due to the unlinked terms of four-electron excitations as products of two-electron excitations [14]. For excited states, the unlinked terms of three-electron excitations as mainly the product $\hat{R}_{(1)}\hat{S}_{(2)}$ are important for the singly excited states E_1 and E_3 , but for the doubly excited states E_2 and E_4 , the unlinked terms of four-electron excitations as the product $\hat{R}_{(2)}\hat{S}_{(2)}$ are important. This result is in accordance with the idea that for inclusion of electron correlation, double excitations from the (multi-) reference wavefunction for *that* state are important.

Table 3 shows the results for BH_3 . For the ground state, calculations due to the coupled-cluster many-electron theory (CC MET) were reported by Paldus et al. [14]. Taylor et al. [15,16] also reported calculations due to the coupled pair approximation and many variants of it. The present result obtained by the SAC V method is similar to the result obtained by Paldus et al., the latter being identical with the SAC MET result. The cluster effects for the ground state are almost entirely due to the quadruple excitations as the product $\hat{S}_{(2)}\hat{S}_{(2)}$. In table 3 we have also given the results for the (calculated) lowest excited state, which is a degenerate state corresponding to the transition from the B-H bonding MO (e-symmetry) to the vacant π MO. The unlinked cluster effect is very large and important for the excited state.

Table 4 gives the result of the SAC calculations for the ground state of H_2O with a CGTO basis of double-zeta accuracy. Here, we have included only the B -matrix [$\langle 0|HS_I^+S_J^+|0\rangle$ in eq. (18)] and the unlinked terms of four-electron excitations, since from tables 1 and 3 this approximation seems to be very good. Further, the unlinked effects are limited only to those excitations which have coefficients larger than 0.005 in the (1+2) CI wavefunction; 130 excitations were included within 223 possible ones. Both the SAC V and SAC MET results are comparable to the more accurate CI results reported by Hosteny et al. [11], though the number of independent variables (size of the matrices involved) is much smaller than that in the CI calculation. This shows a rapid convergence of the cluster expansion in contrast to the CI expansion.

Tables 5 and 6 give the results for the ground and Rydberg excited states of H_2O . The "wavefunction 2"

Table 2
Effects of unlinked terms for the ground and excited states of Be^{a)}

State	Full CI	SAC V (with all) SAC CI V (with all)	SAC V (with $B+4U$) ^{b)} SAC CI V (with all)	SAV V (with all) SAC CI V (without $3U, 2U$)	SAC V (with all) SAC CI V (without $4U$)
ground E_0	-0.017500	-0.017488 (0.00001)	-0.017487 (0.00001)	-0.017488 (0.00001)	-0.017488 (0.00001)
excited $E_1(2 \rightarrow 3)$	0.424945	0.424644 (-0.00030)	0.424644 (-0.00030)	0.437290 (0.01234)	0.424694 (-0.00025)
$E_2(2 \rightarrow 3)$	0.788148	0.790760 (0.00261)	0.790761 (0.00261)	0.787524 (-0.00062)	0.801876 (0.01373)
$E_3(2 \rightarrow 4)$	3.094951	3.094659 (-0.00029)	3.094663 (-0.00029)	3.101553 (0.00660)	3.095048 (0.00010)
$E_4(2 \rightarrow 4)$	3.553543	3.560788 (0.00724)	3.560791 (0.00725)	3.561028 (0.00748)	3.567135 (0.01359)

a) See footnotes to table 1.

b) B denotes the B -matrix $\langle 0 | HS_j^\dagger S_j | 0 \rangle$ in eq. (19) and $4U$ denotes unlinked terms of four-electron excitations as products of two-electron excitations.

(wf 2) and "wavefunction 4" (wf 4) of Hausman et al. [13] are the CI wavefunctions defined by

$$\begin{aligned} \text{wf } 2 &= \varphi_0 + \text{excitations through doubles,} \\ \text{wf } 4 &= \varphi_0 + \text{excitations through sextuples,} \end{aligned} \quad (37)$$

where φ_0 denotes the multi-reference configurations, the number of which is four for 1A_1 , one for 1A_2 , three for 1B_1 , and one for 1B_2 . A detailed comparison

Table 3
Ground and excited states of BH₃

State	Method	Correlation energy (au)
ground (1A_1)	CI(1+2) ^{a)}	-0.047180
	CI(2+4) ^{a)}	-0.048050
	CI(1+2+3+4) ^{a)}	-0.048481
	full CI ^{a)}	-0.048491
	CC MET(1+2+3U+4U) ^{a)}	-0.048079
	SAC V(1+2+2U+3U+4U) ^{b)}	-0.048031
excited (1E) ^{b)}	HF SECI	0.254200
	(1+2) CI	0.210096
	SAC CI V	0.176684

a) These results are from Paldus et al. [14]. Their calculations are based on the STO AO with the Hartree-Fock energy, -26.338999 au.

b) Present results are relative to the Hartree-Fock energy based on STO- AVG basis (-26.338598 au). See also footnote b) to table 2.

between Hausman's and the present results suggested a small difference in the basis set used in the Hartree-Fock calculations. Because of the lack of the Hartree-Fock value in the literature, we have calculated the values for wf 2 and wf 4 of table 5 by equating the ground state energy of wf 2 with that of the (1+2) CI, neglecting the contribution of the limited number of triple excitations included in wf 2.

As for the ground state energy, the SAC V method gives a lower value than the SAC MET method. For the excited states, the SAC CI method gives remarkable improvements over (1+2) CI. Especially, the SAC CI V method gives excellent agreement with the accurate CI results. The results of the SAC CI NV method are

Table 4
Ground state of H₂O with CGTO basis

Method	Number of variables	Correlation energy (au)
CI(1+2)	224	-0.126150
CI(1+2+3) ^{b)}	1558	-0.127225
CI(1+2+3+4) ^{b)}	6779	-0.132991
SAC V($B+4U$) ^{c)}	224	-0.130494
SAC MET($B+4U$) ^{c)}	224	-0.131648

a) All energies are relative to the Hartree-Fock energy, -76.009265 au.

b) Ref. [11].

c) See footnote b) to table 2.

Table 5
Ground and Rydberg excited states of H₂O compared with accurate wavefunctions^{a,b}

State	HF SECI	(1+2) CI	SAC V SAC CI NV	SAC V SAC CI V	Hausman et al. ^{c)}	
					wf 2	wf 4
¹ A ₁	(6) ^{d)}	(59) ^{d)}	(59 for G, 58 for E) ^{d)}		(1051) ^{d)}	(11149) ^{d)}
1 (G)	0.0	-0.04225	-0.04257	-0.04257	-0.04225	-0.04461
2 (E)	0.32171	0.24296	0.22509	0.22096	0.22090	0.21978
3	0.35063	0.26323	0.24403	0.23908	0.23918	0.23816
4	0.42588	0.34275	0.32657	0.32065	0.32090	0.31958
¹ A ₂	(3)	(41)	(41)		(516)	(10952)
1	0.32060	0.22874	0.20932	0.20405	0.20266	0.20162
¹ B ₁	(4)	(43)	(43)		(1088)	(11001)
1	0.24959	0.15946	0.13920	0.13534	0.13505	0.13396
2	0.33066	0.24661	0.22505	0.21981	0.21844	0.21754
3	0.39446	0.32494	0.30792	0.30424	0.30369	0.30306
¹ B ₂	(5)	(47)	(47)		(468)	(11101)
1	0.39093	0.31496	0.30005	0.29452	0.29419	0.29342

a) The present results are relative to the Hartree-Fock energy, -75.52590 au.

b) SAC MET energy for the ground state is -0.04236 au.

c) The values for the wf 2 and wf 4 were calculated from the results of Hausman et al. [13]. For details, see eq. (37) and the succeeding sentences.

d) The integers in parentheses show the numbers of independent variables (sizes of the matrices) involved in the present calculation and the numbers of Slater determinants involved in wf 2 and wf 4.

Table 6
Rydberg excitation energy of H₂O compared with accurate calculations

State	HF SECI	(1+2) CI	SAC V SAC CI NV	SAC V SAC CI V	Hausman et al. [13]	
					wf 2	wf 4
¹ A ₁ 1(G)	0.0	0.0	0.0	0.0	0.0	0.0
2	0.32171	0.28521	0.26766	0.26353	0.26315	0.26439
3	0.35063	0.30548	0.28660	0.28166	0.28143	0.28277
4	0.42588	0.38500	0.36915	0.36323	0.36315	0.36420
¹ A ₂ 1	0.32060	0.27099	0.25189	0.24662	0.24491	0.24623
¹ B ₁ 1	0.24959	0.20171	0.18177	0.17791	0.17730	0.17857
2	0.33066	0.28885	0.26762	0.26239	0.26069	0.26215
3	0.39446	0.36719	0.35049	0.34681	0.34594	0.34767
¹ B ₂ 1	0.39093	0.35720	0.34262	0.33709	0.33644	0.33803

also very good, though they are consistently higher than the accurate values by about 0.004–0.006 au. It is impressive that the present results with about 50 variables for each symmetry are quite comparable with the CI results of much larger dimensions.

In table 6, the Rydberg excitation energies were calculated from the energies given in table 5. The values for wf 2 and wf 4 are independent of the Hartree-

Fock energy. Again, the results of the SAC CI V method agree quite well with the accurate CI results. The SAC CI NV results are consistently higher by about 0.005 au than the results of wf 2 and wf 4. Thus, we see that the SAC and SAC CI methods take into account the correlations in the ground and excited states in a well balanced way.

6. Conclusion

In this paper, we have formulated the SAC and SAC CI theories for actual calculations of electron correlations in ground and excited states. The results of the calculations show excellent agreement with the full CI and close-to-full CI results, though the number of independent variables (size of the matrices involved) is much smaller in the present calculations. It was seen that the cluster effects are larger for the excited states than for the ground state. These results show the utility of the SAC method for ground states and especially of the SAC CI method for excited states, since the slow convergence of the CI method is much more critical for excited states than for ground states. Thus, we may conclude that the present results are quite encouraging for the SAC and SAC CI approaches to the study of electron correlations in ground and excited states.

Very recently, Saute et al. [17] reported a similar calculation for π -electron model systems with the PPP method. Their approach uses a variational method for excited states on the basis of the non-variational (CP MET) calculations for ground states. The formulation is due to a diagrammatic method [18]. For excited states, however, the agreement with the full CI results seems to be worse in their calculations than in the present calculations. A reason for this might be that they did not include four-electron excitations as products of two-electron excitations. On the other hand, for ionized and electron attached states, their results were encouraging, giving also a light on the utility of the cluster expansion approach.

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References

- [1] H. Nakatsuji, *Chem. Phys. Letters* 67 (1979) 000.
- [2] H. Nakatsuji and K. Hirao, *J. Chem. Phys.* 68 (1978) 2053.
- [3] H. Nakatsuji and K. Hirao, *Chem. Phys. Letters* 47 (1977) 569; *J. Chem. Phys.* 68 (1978) 4279; K. Ohta, H. Nakatsuji, K. Hirao and T. Yonezawa, to be published.
- [4] H. Nakatsuji, *Chem. Phys. Letters* 59 (1978) 362.
- [5] E.R. Davidson, *J. Comput. Phys.* 17 (1975) 87; I. Shavitt, C.F. Bender, A. Pipano and R.P. Hosteny, *J. Comput. Phys.* 11 (1973) 90.
- [6] U. Kaldor and F.E. Harris, *Phys. Rev.* 183 (1969) 1.
- [7] F. Grein and A. Banerjee, *Intern. J. Quantum Chem.* S9 (1975) 147.
- [8] K. Oohata, H. Taketa and S. Huzinaga, *J. Phys. Soc. Japan* 21 (1966) 2306.
- [9] A. Pipano and I. Shavitt, *Intern. J. Quantum Chem.* 2 (1968) 741.
- [10] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293; T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [11] R.P. Hosteny, R.R. Gilman, T.H. Dunning Jr., A. Pipano and I. Shavitt, *Chem. Phys. Letters* 7 (1970) 325.
- [12] W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.* 51 (1969) 2657.
- [13] R.F. Hausman Jr., S.D. Bloom and C.F. Bender, *Chem. Phys. Letters* 32 (1975) 483.
- [14] J. Paldus, J. Čížek and I. Shavitt, *Phys. Rev. A* 5 (1972) 50.
- [15] P.R. Taylor, G.B. Bacskay, N.S. Hush and A.C. Hurley, *Chem. Phys. Letters* 41 (1976) 444.
- [16] A.C. Hurley, *Electron correlation in small molecules* (Academic Press, New York, 1976).
- [17] M. Saute, J. Paldus and J. Čížek, *Intern. J. Quantum Chem.* 15 (1979) 463.
- [18] J. Paldus, J. Čížek, M. Saute and A. Laforgue, *Phys. Rev.* 17 (1978) 805.