CLUSTER EXPANSION OF THE WAVEFUNCTION. SYMMETRY-ADAPTED-CLUSTER (SAC) THEORY FOR EXCITED STATES

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SAC (symmetry-adapted-cluster) theory has been extended to excited states. Calculations are reported for excited states of Be, H_2O and CH_2. SAC theory reproduces full CI results to high accuracy for singlet excited states of Be. Calculated Rydberg excitation energies for H_2O show good agreement with experiment. The singlet–triplet separation in CH_2 is estimated to be 11.8 kcal/mol.

1. Introduction

One of the more successful ways of studying electron correlation in atoms and molecules has been that based on the so-called cluster expansion of the wavefunction [1–3]. In the symmetry-adapted-cluster (SAC) expansion [4], the ground state of a given symmetry is expressed as

$$\Psi_g = \bar{O}\exp(\hat{S})\Phi_0 = [1 + \hat{S} + \bar{O}(\hat{S}^2/2! + \hat{S}^3/3! + \dots)]\Phi_0 , \quad (1)$$

where the $\hat{S}$ is the linked cluster generator and a sum of essentially i-fold excitation operators

$$\hat{S} = \hat{S}_1 + \hat{S}_2 + \dots + \hat{S}_N = \sum_I C_I S_I^\dagger \quad (2)$$

and $S_I^\dagger$ is a symmetry-adapted excitation operator which generates a symmetry-adapted configuration when operating on the reference function. The C_I is the expansion coefficient. The Φ_0 is the reference function and chosen usually as a restricted Hartree–Fock (HF) wavefunction

$$\Phi_0 = \| \psi_1\alpha\psi_1\beta \dots \psi_q\alpha\psi_q\beta\psi_{q+1}\alpha \dots \psi_p\alpha \| . \quad (3)$$

$\bar{O}$ is the symmetry projection operator which applies in the ground-state theory only to the unlinked clusters.

The main advantages of the cluster expansion theory are as follows. First, the expansion is based more on physics. That is, one can choose the physically most important terms as linked clusters for the investigation of a particular physical problem, such as pair excitation operators for the closed-shell electron correlation problem, the spin polarization excitation operators for the open-shell spin correlation problem, etc. Then, these higher-order effects can be automatically accounted for through the unlinked clusters and one can get rapid convergence compared to the configuration interaction (CI) expansion. Second, the variational cluster expansion includes self-consistency effects for orbitals in an expansion form. The function space spanned by the one-electron cluster expansion wavefunction is invariant with respect to the choice of the reference function. The variational cluster expansion $\Psi = \exp(\hat{S}_1)\Phi_0$ is reduced to the conventional HF wavefunction, which is known as Thouless' theorem [5]. Thus, the general cluster expansion theory is a natural extension of SCF theory, which has been successfully applied to the electronic struc-

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tures of atoms and molecules. We have already proposed new orbital theories [6], a pseudo-orbital theory [7] and SAC theory [4] by taking advantages of the cluster expansion of the wavefunction.

There are several possible ways to extend the cluster expansion theory, which is suitable for the ground state, to excited states [8–10]. An interesting approach, termed SAC CI was formulated by one of us and applied to various excited states, ionized states and electron attached states of molecules having a closed-shell ground state [11]. The most essential feature of the SAC CI is that it starts from the correlated ground state (SAC ground state) and calculates the change with respect to the SAC ground state, rather than to introduce again all the correlations into the uncorrelated reference function. Clearly, it is based on the assumption that since the excitation or ionization only involves one or two valence electrons, the majority of the correlation effects will not be drastically changed.

On the other hand, the cluster expansion of the exact wavefunction for each excited state is also possible as well as for the ground state. The SAC theory based on this expansion might be equally justified. The alternative, closely paralleling the ground-state formalism, is called the SAC theory for excited states. This formalism may be advantageous for more general excited states and expected to give a higher accuracy than the SAC CI theory. The purpose of the present paper is to develop the SAC theory for excited states and to examine utility and accuracy of the theory.

2. SAC theory for excited states

In the following, we treat the singlet excited state as an example but the formalism is general enough and can easily be extended to other states with different spin multiplicity.

For dealing with excited states, the SAC theory has some difficulties. One of them is how to choose the reference function. Consider the singlet excitation in the orbital approximation from ψ_m to ψ_n, then the wavefunction for this state is expressed as

$$\Phi_0' = \| 2^{-1/2}\, \psi_1\alpha\psi_1\beta \ldots \psi_m\psi_n(\alpha\beta - \beta\alpha)\| \,. \tag{4}$$

This is not a single-determinant function. To select the reference function for excited states, we considered three guiding principles. First, the formal simplicity of the cluster expansion lies in the fact that it starts from a single Slater determinant. It is desired to choose a single determinant as a reference function. A formulation based on the multi-reference function is, of course, possible but in such a theory, the simplicity and beauty of the cluster expansion may no longer be preserved. Second the excitation operators should be mutually commutable. This arises from a purely mathematical requirement. The third point is that it is expected that the derived theory can be related to some other SCF theories for excited states.

Another difficulty is the variational theorem for excited states. On this point we call attention to the following theorem. Let Ψ_i and E_i be exact eigenfunctions and eigenvalues

$$H\Psi_i = E_i\Psi_i \,, \quad E_0 \leqslant E_1 \leqslant E_2 \leqslant \ldots . \tag{5}$$

Assume that we have the corresponding approximate wavefunctions Φ_i and their energies J_i. Suppose that we are interested in the kth excited state. If the approximate wavefunctions Φ_i fulfil the relations

$$\langle\Phi_i|H|\Phi_j\rangle = J_i\delta_{ij} \,, \quad \langle\Phi_i|\Phi_j\rangle = \delta_{ij} \,,$$
$$0 \leqslant i, j \leqslant k \,, \tag{6}$$

that is, they are orthogonal and orthogonal with respect to the hamiltonian, then the approximate energy J_k for the kth excited state is an upper bound for the kth exact eigenvalue E_k

$$E_k \leqslant J_k \tag{7}$$

and the mean-square deviation of the kth excited wavefunction Φ_k from the true eigenfunction Ψ_k is expressed as

$$\int |\Psi_k - \Phi_k|^2 \, \mathrm{d}\tau \leqslant \frac{J_k - E_k}{E_{k+1} - E_k}\left[1 + \sum_{j=0}^{k-1} \frac{E_k - J_j}{E_k - J_{k-1}}\right]. \tag{8}$$

This is the application of the Eckart theorem for the ground state to the excited states [12]. The error expression is in the limit proportional to $J_k - E_k$. Therefore, one can make the error as small as one likes by making J_k sufficiently close to E_k without knowledge of the exact lower state wavefunctions.

Keeping these two problems in mind, we formulated the SAC theory for excited states. We choose the following Φ_0 as a reference function:

$$\Phi_0 = \| \psi_1 \alpha \psi_1 \beta \ldots \psi_m \alpha \psi_n \beta \| . \quad (9)$$

Φ_0 is a single determinant but symmetry-broken. The SAC expansion of the wavefunction for the excited state is given by

$$\Psi_e = \hat{O} \exp(\hat{S}) \Phi_0 = \hat{O} (1 + \hat{S} + \hat{S}^2/2! + \ldots) \Phi_0 . \quad (10)$$

$\hat{O}$ is the symmetry projection operator. Note here that unlike the ground-state theory in (1), $\hat{O}$ applies even to the reference function to recover the spin symmetry:

$$\hat{O} \Phi_0 = \Phi_0' = \| 2^{-1/2} \psi_1 \alpha \psi_1 \beta \ldots \psi_m \psi_n (\alpha\beta - \beta\alpha) \| . \quad (11)$$

This selection of the reference function follows the three guiding principles mentioned above. If one chooses one-electron singlet type excitation operators for $\hat{S}$, then one can obtain the so-called non-orthogonal HF wavefunction in an expansion form.

Let us examine the variational theorem. Applying the variational principle, one can obtain the SAC variational equation [4]

$$\langle \Psi_e | (H - E_e) S_I^\dagger | \Psi_e' \rangle = 0 , \quad \Psi_e' = \exp(\hat{S}) \Phi_0 . \quad (12)$$

This variational equation has the same form as the generalized Brillouin theorem, which implies the inclusion of the SCF effects in the SAC wavefunction. Now define a set of functions $\{\chi_K\}$ on the basis of the SAC excited state Ψ_e,

$$\chi_K = \mathcal{P} \hat{O} S_K^\dagger \Psi_e' , \quad \mathcal{P} = 1 - |\Psi_e\rangle\langle\Psi_e| / \langle\Psi_e|\Psi_e\rangle . \quad (13)$$

$\mathcal{P}$ is the projector and $S_K^\dagger$ is a symmetry-adapted excitation operator. Then, we see that the functions χ_K satisfy the relations

$$\langle \Psi_e | \chi_K \rangle = 0 , \quad \langle \Psi_e | H | \chi_K \rangle = 0 . \quad (14)$$

It means that a set of functions χ_K form a basis for the excited states including lower states relative to the excited state Ψ_e under consideration. Thus, it is guaranteed that the energy E_e for the excited state Ψ_e gives an upper bound to the exact energy with an appropriate choice of $S_K^\dagger$. Thus, the expansion in (10) is our SAC expansion for the singlet excited state.

The variational and non-variational solutions are considered as the ground-state theory [11]. Application of the variational principle leads to (12) as shown above. The energy of the system can be calculated by

$$\langle \Psi_e | H - E_e | \Psi_e' \rangle = 0 . \quad (15)$$

The features of the SAC variational (SAC V) solution are as follows. It gives an upper bound to the exact energy. It includes SCF effects in an expansion form. However, a computational difficulty of this procedure is that it includes matrix elements between unlinked clusters. This leads to a very complicated system of non-linear equations for $\hat{S}$.

The SAC non-variational (SAC NV) treatment can be derived by projection of the Schrödinger equation onto the subspace spanned by the reference function and linked clusters:

$$\langle \Phi_0 | H - E_e | \Psi_e \rangle = 0 , \quad (16)$$

$$\langle \Phi_0 | S_I (H - E_e) | \Psi_e \rangle = 0 . \quad (17)$$

The energy does not have the upper bound nature and there is no SCF concept. However, a remarkable merit of the procedure is that is does not involve matrix elements between unlinked clusters. It is very useful from a practical point of view.

So long as the SAC expansion is accurate enough, we may expect that the difference between SAC V and SAC NV solutions should be small.

Now we derive formulas necessary for actual calculations. We limit ourselves to one- and two-electron excitations in the linked cluster expansion. The unlinked clusters which appeared in the linked cluster expansion are neglected. In the variational treatment, we truncate the expansion of the wavefunction at second order, assuming that $\hat{S}$ is small, that is, the absolute value of the coefficient C_I is small compared to unity. The energy expression and the SAC V equation are given by

$$E_e = E_0 + \sum_I C_I \langle 0 | \hat{O} S_I^\dagger | 0 \rangle - \sum_{IJK} C_I C_J C_K \langle 0 | S_J S_K H \hat{O} S_I^\dagger | 0 \rangle , \quad (18)$$

$$\langle 0 | H \hat{O} S_I^\dagger | 0 \rangle + \sum_J C_J \langle 0 | S_J (H - E_e) \hat{O} S_I^\dagger | 0 \rangle + \frac{1}{2} \sum_{JK} C_J C_K (\langle 0 | S_J S_K H \hat{O} S_I^\dagger | 0 \rangle + \langle 0 | S_K S_I H \hat{O} S_J^\dagger | 0 \rangle + \langle 0 | S_I S_J H \hat{O} S_K^\dagger | 0 \rangle) = 0 . \quad (19)$$

These equations are the same as those for the ground-state theory except for the projection operator. The energy expression and the SAC NV equation are also derived in the present approximation as

$$E_e = E_0 + \sum_I C_I \langle 0|H\bar{O}S_I^\dagger|0\rangle , \quad (20)$$

$$\langle 0|H\bar{O}S_I^\dagger|0\rangle + \sum_J C_J \langle 0|S_J(H - E_e)\bar{O}S_I^\dagger|0\rangle + \frac{1}{2}\sum_{JK} C_J C_K \langle 0|S_J S_K H\bar{O}S_I^\dagger|0\rangle = 0 . \quad (21)$$

We denoted $|0\rangle$ by a reference function $|\Phi_0\rangle$ and E_0 by $\langle 0|H\bar{O}|0\rangle$. Note here that in the non-variational procedure one must solve the non-symmetric equation for determining the unknown coefficients. We have developed a new procedure for calculation of the real eigenvalues and eigenvectors of large, non-symmetric matrices by extending Davidson's algorithm [3] for the iterative calculation of eigenvalues of real symmetric matrices. Details of this procedure will be published elsewhere. On the other hand, one can obtain solutions for SAC V method by solving the symmetric equation. These two equations, (19) and (21), are solved iteratively.

3. Some numerical results

To illustrate some of the points mentioned here and to test the accuracy of the theory, we treated the Be atom, and the H_2O and CH_2 molecules with the SAC theory for excited states.

In the linked cluster expansion, all single and double excitations are generated relative to the reference function, having non-zero hamiltonian matrix elements with the reference function. The linked clusters which do not interact directly with the reference function are not included in the present treatment. Note here that one-electron excitation among open-shell orbitals for excited singlet states includes de-excitation from the excited state Ψ_e to the ground state. When we construct the unlinked clusters, $C_I C_J S_I^\dagger S_J^\dagger|0\rangle$, we discard them if the absolute values of C_I and/or C_J in the CI expansion are less than 10^{-3}.

The SAC expansion uses ground-state orbitals for all states for Be. While, for H_2O and CH_2, the SAC expansion for each state uses orbitals from an SCF calculation on that state or at least from a closely related state, rather than using ground-state orbitals for all states.

First, the SAC theory is applied to singlet excited states of Be with a 5s STO basis. Table 1 summarizes

Table 1
Ground and excited ^1S states of Be compared with full CI results [a]

State		MC SCF [14]	(1 + 2) CI [b]	SAC V SAC CI V [11]	SAC V SAC CI NV [11]	SAC V	SAC NV	Full CI [14]
ground	E_0	−0.013947 (0.00355)	−0.017445 (0.00006)	−0.017488 (0.00001)	−0.017488 (0.00001)	−0.017488 (0.00001)	−0.017488 (0.00001)	−0.017500
excited	$E_1(2 \to 3)$	0.428570 (0.00363)	0.437361 (0.01242)	0.424644 (−0.00030)	0.424785 (−0.00016)	0.424947 (0.00000)	0.424945 (0.00000)	0.424945
	$E_2(2 \to 3, 2 \to 3)$	0.801399 (0.01325)	0.801752 (0.01360)	0.790760 (0.00261)	0.787615 (−0.00053)	0.788155 (0.00001)	0.788157 (0.00001)	0.788148
	$E_3(2 \to 4)$	3.109372 (0.01442)	3.101967 (0.00702)	3.094659 (−0.00029)	3.096674 (0.00172)	3.095003 (0.00005)	3.094992 (0.00004)	3.094951
	$E_4(2 \to 3, 2 \to 4)$	3.566049 (0.01251)	3.567507 (0.01396)	3.560788 (0.00724)	3.558963 (0.00542)	3.553533 (−0.00001)	3.553544 (0.00001)	3.553543

a) All energies are relative to the Hartree–Fock energy, −14.572924 au. Values in parentheses are relative to the full CI results.
b) (1 + 2) CI denotes the CI with all single and double excitations.

the results. The SAC solutions obtained are optimized for each state. The present results are compared with results of different theories and full CI results [14]. Values in parentheses are relative to the full CI results. For both ground and excited states, the SAC theory reproduces the full CI results to very high accuracy. SAC results are closer than those of other methods by two or three orders of magnitude. We can see that the SAC theory for excited states is more accurate than the SAC CI method. Another interesting point is that there is little difference between SAC V and SAC NV solutions. This is true for triplet excited states summarized in table 2.

Table 2
Excited ^3S states of Be [a]

State	(1 + 2) CI [b]	SAC V	SAC NV
$E_1(2 \rightarrow 3)$	0.337467	0.325053	0.325053
$E_2(2 \rightarrow 3, 2 \rightarrow 3)$	3.062086	3.055410	3.055409
$E_3(2 \rightarrow 3, 2 \rightarrow 4)$	3.457463	3.440685	3.440686

a) All energies are relative to the Hartree–Fock energy, −14.0572924 au.
b) (1 + 2) CI denots the CI with all single and double excitations.

The second system to which the SAC theory was applied is H_2O. We used the standard Huzinaga–Dunning [3s2p/2s] basis [15,16] augmented by Rydberg 3s (ζ = 0.032) and 3p (ζ = 0.028) gaussians on oxygen. The 1s oxygen core orbital remains doubly occupied. The calculation was performed on the equilibrium geometry (OH = 1.8111 au, ∠HOH = 104.45°). The CI with single and double excitations gives −0.11536 au for the ground state relative to the HF energy and the SAC NV gives −0.12139 au. Thus, the energy lowering due to the inclusion of unlinked clusters is 0.006 au. Table 3 shows the vertical excitation energies of H_2O for various Rydberg excitations. The SAC NV results are compared with the CI results with larger basis sets [17,18] and with results obtained by the equation-of-motion method [19]. The SAC NV results give good agreement with experiment. This excellent agreement is rather fortuitous. However, this may be attributed partly to the fact that the SAC theory takes into account correlation effects in the ground and excited states in a well-balanced way. Our

Table 3
Vertical excitation energies (eV) of water [a]

State	Orbital picture	CI [17]	CI [18]	EOM [19]	SAC NV	Exp. [17]
$1\,^3B_1$	$1b_1 \rightarrow 3s\,a_1$	7.26	6.90	6.89	7.02	7.0, 7.2
$1\,^1B_1$		7.61	7.30	7.22	7.46	7.4, 7.49 $\tilde{A}$
$1\,^3A_2$	$1b_1 \rightarrow 3p_y b_2$	9.34	9.04	8.97	8.96	8.9, 9.1, 9.2
$1\,^1A_2$		9.46	9.20	8.89	9.12	9.1
$2\,^3B_1$	$1b_1 \rightarrow 3p_z a_1$	9.99	9.84	9.47	9.77	9.98
$2\,^1B_1$		10.06	9.90	9.48	9.83	10.01, 9.996 $\tilde{C}$
$3\,^3A_1$	$1b_1 \rightarrow 3p_x b_1$	9.74	9.65	9.39	9.45	9.81, 9.80
$3\,^1A_1$		10.16	10.32	9.61	9.76	10.17, 10.14 $\tilde{D}$
$2\,^3A_1$	$3a_1 \rightarrow 3s\,a_1$	9.44	9.01	9.34	9.22	9.3
$2\,^1A_1$		9.82	9.80	9.54	9.60	9.67, 9,73 $\tilde{B}$
$1\,^3B_2$	$3a_1 \rightarrow 3p_y b_2$	11.11	10.99	–	10.88	
$1\,^1B_2$		11.47	11.21	–	11.19	
$3\,^3B_1$	$3a_1 \rightarrow 3p_x b_1$	11.87	11.68	–	11.55	
$3\,^1B_1$		11.92	11.72	–	11.64	11.91
$4\,^3A_1$	$3a_1 \rightarrow 3p_z a_1$	11.77	11.53	11.69	11.47	
$4\,^1A_1$		12.08	–	11.82	11.76	

a) The molecule is in the yz plane and the z axis is the C_2 axis. HF energy for the ground state is −76.010267 au and SAC NV energy is −76.131658 au.

results are comparable to the more accurate CI calculations although the number of independent variables is much smaller than in the other methods. This suggests a rapid convergence of the cluster expansion in contrast to the CI expansion.

Finally, we applied the SAC NV theory to CH_2. In recent years, there have been many experiments [20] and calculations [21] to determine the singlet–triplet energy separation. So this is a good example to test the accuracy of the theory. We calculated first the three lowest $^3B_1$, $^1A_1$ and $^1B_1$ states.The basis set used is the Huzinaga–Dunning [4s2p/2s] basis [15,16] augmented with carbon d and hydrogen p polarization functions. The d exponents for CH_2 are employed as 0.74 for triplet and 0.51 for two singlet states. The p function on hydrogen has exponent 1.0. The equilibrium geometries of the $^3B_1$ (CH = 1.08 Å, ∠HCH = 134°), $^1A_1$ (CH = 1.11 Å, ∠HCH = 102.4°) and $^1B_1$ (CH = 1.05 Å, ∠HCH = 140°) states of methylene are well known and assumed here. The 1s core orbital for carbon is treated as frozen. In table 4, we give SCF, CI and SAC NV energies for these three states. We also list the number of variables (number of linked clusters) and contributions from the unlinked clusters in parentheses. The energy separation between $^1A_1$ and $^3B_1$ is calculated to be 25.9 kcal/mol on the SCF level. In the CI calculation, the splitting is estimated to be 13.7 kcal/mol. The inclusion of unlinked clusters decreases the separation from 13.7 to 11.8 kcal/mol. The SAC theory also confirms the importance of the quadruple excitations to get an accurate singlet–triplet separation. The actual splitting is established to be ≈9 kcal/mol. So there is still a few kcal error but we think the accuracy of the present theory is satisfactory, taking the double-zeta quality of the basis set into consideration. As to the energy separation between $^1B_1$ and $^1A_1$, SAC theory predicts the splitting to be 27.9 kcal/mol.

Table 4
Total energies (au) for the three lowest states of CH_2

$^3B_1$	
RHF energy	−38.927783 au
CI energy (909) [a]	−39.030023 au
SAC NV energy (909)	−39.031821 au (1.13 kcal/mol) [b]
$^1A_1$	
RHF energy	−38.886484 au
CI energy (729)	−39.008204 au
SAC NV energy (729)	−39.012950 au (2.98 kcal/mol)
$^1B_1$	
RHF energy	−38.862088 au
CI energy (893)	−38.966580 au
SAC NV energy (893)	−38.968433 au (1.16 kcal/mol)
energy separation ($^1A_1 - {}^3B_1$)	
RHF	25.9 kcal/mol
CI	13.7 kcal/mol
SAC NV	11.8 kcal/mol
exp. [20]	8.3, 9.0, 19.5, 8.1
energy separation ($^1B_1 - {}^1A_1$)	
RHF	15.3 kcal/mol
CI	26.1 kcal/mol
SAC NV	27.9 kcal/mol
exp. [20]	20–31 kcal/mol

a) Number of independent variables.
b) Contribution from unlinked clusters.

The results obtained for a few model systems are encouraging. We conclude that the SAC theory yields a very good approximation for the calculation of correlation energies for both ground and excited states.

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