CLUSTER EXPANSION OF THE WAVEFUNCTION. ELECTRON CORRELATIONS IN GROUND AND EXCITED STATES BY SAC (SYMMETRY-ADAPTED-CLUSTER) AND SAC CI THEORIES

Hiroshi NAKATSUJI
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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We have summarized the solutions of the SAC (symmetry-adapted-cluster) and SAC CI theories for the study of electron correlations in ground and excited states, respectively. Variational and non-variational solutions are considered for both theories and their features are discussed.

1. Introduction

For studies of accurate wavefunctions (electron correlations) of ground and excited states, only the CI expansion has been a practical method which is interconsistent for both states. Because of its linear variational nature, the solutions constitute upper bounds for both states [1]. The wavefunctions of the ground and excited states are mutually orthogonal and hamiltonian-orthogonal [see, e.g., eqs. (17) and (18)]. However, another feature of the CI expansion lies in its slow convergence. This becomes severe especially when we aim at accurate wavefunctions of excited states. A choice of a single reference wavefunction seems to be insufficient, and a large-scale multi-reference CI combined with energy extrapolation procedure has been done by Buenker, Peyerimhoff, and co-workers [2].

The cluster expansion theory gives, on the other hand, a rapidly convergent method with inclusion of the higher-order unlinked terms [3–10]. It also shows the correct dependence on the number of particles involved, in contrast to standard single and double excitation CI [10,11]. Though the applications are still very limited [7,12–14] including those to model systems [15,16], the results seem to show a promising utility of the theory.

Previously, we have considered an extension of this approach to open-shell systems, introducing a symmetry-adapted-cluster (SAC) expansion [17]. Combining the idea of this expansion with the Thouless theorem [18], we have also proposed a pseudo-orbital theory and applied it to the study of spin correlations in open-shell atoms and molecules [19]. Further, a method for excited states, called the SAC CI method, has been reported on the basis of the SAC expansion [20]. It is based on the fact that the SAC expansion combined with the variational principle gives incidentally a set of excited functions which satisfy the Brillouin theorem with the ground state.

The purpose of this paper is to summarize solutions of the SAC and SAC CI theories for ground and excited states, respectively. The variational and non-variational solutions are considered for both theories, and the features of the solutions and the relations to other theories are discussed. Applications of these methods to relatively small atoms and molecules will be given in the succeeding paper [21].

2. SAC expansion for ground state

In the symmetry-adapted-cluster (SAC) expansion, the ground state of a given spin–space symmetry is expressed by

$$\Psi_g = \hat{O}\, e^{\hat{S}} \Phi_0 = [1 + \hat{S} + \hat{O}(\hat{S}^2/2! + \hat{S}^3/3! + ...)]\, \Phi_0 = \hat{O} \exp\Big[\sum_I C_I S_I^+\Big] \Phi_0, \quad (1)$$

$$\hat{S} = \hat{S}_{(1)} + \hat{S}_{(2)} + \hat{S}_{(3)} + ... + \hat{S}_{(N)} = \sum_I C_I S_I^+, \quad (2)$$

where $\hat{S}$ is a sum of the essentially i-ple excitation operator $\hat{S}_{(i)}$ [17]. S_I^+ denotes a symmetry-adapted excitation operator which produces a symmetry-adapted configuration on applying the reference wavefunction Φ_0, which is chosen as restricted HF wavefunction,

$$\Phi_0 = |0\rangle = \|\varphi_1 \bar{\varphi}_1 \ ... \ \varphi_k \bar{\varphi}_k \ ... \ \varphi_q \bar{\varphi}_q \varphi_{q+1} \ ... \ \varphi_p\|. \quad (3)$$

In eq. (1) the symmetry projector $\hat{O}$ applies only to the unlinked terms since the linked term $\hat{S}\Phi_0$ is symmetry adapted. The symmetry adaptation of the excitation operator is necessary because of the non-linear nature of the cluster expansion. Otherwise, a mixing of different symmetry spaces may occur as discussed in detail previously [17].

We note that for singlet states the spin projector $\hat{O}_s$ is unnecessary, since the products of singlet excitation operators are singlet so that all the unlinked terms are purely singlet without the projector $\hat{O}_s$. Similarly the space symmetry projector is unnecessary for a totally symmetric ground state. Then, in this case, the SAC wavefunction is written as

$$\Psi_g = \exp\Big[\sum_I C_I S_I^+\Big] \Phi_0. \quad (4)$$

2.1. Variational solution

Application of the variational principle to the SAC wavefunction given by eq. (1) leads to the equation

$$\langle \Psi_g | (H - E_g) S_K^+ | \Psi_{g'} \rangle = 0, \quad (5)$$

where

$$\Psi_{g'} = \exp\Big[\sum_I C_I S_I^+\Big] \Phi_0. \quad (6)$$

For totally symmetric singlet states we note

$$\Psi_{g'} = \Psi_g, \quad (7)$$

as seen from eq. (4). The energy of the system may be calculated from

$$\langle \Psi_g | H - E_g | \Psi_g \rangle = 0. \quad (8)$$

Eqs. (5) and (8) suffice to determine all the unknowns $\{C_I\}$ and E_g. The features of the variational solution are as follows. It gives an upper bound to the exact energy. It gives a basis for an analysis and extension of various variational model theories (e.g., orbital theories [22]), since formally it includes completely the self-consistency in an expansion form. Based on what the Thouless theorem [18] implies, we have proposed a pseudo-orbital theory in the SAC expansion form [19], and a modified spin-extended HF theory in a conventional cluster expansion form [22]. On the other hand, a computational problem of this procedure is that it includes matrix elements between unlinked terms. This makes a complete solution of eqs. (5) and (8) almost prohibitive. In applications we shall introduce some approximations which express high-order terms in terms of the lower-order ones.

2.2. Non-variational solution

If the SAC wavefunction were the exact wavefunction, the function $(H - E_g)|\Psi_g\rangle$ would be identically zero. We require this condition in the space of the linked configurations $|0\rangle$ and $S_K^+|0\rangle$, that is

$$\langle 0 | H - E_g | \Psi_g \rangle = 0, \quad (9)$$

$$\langle 0 | S_K (H - E_g) | \Psi_g \rangle = 0. \quad (10)$$

These equations are sufficient to determine the unknowns $\{C_I\}$ and E_g. We may also deem eqs. (9) and (10) as obtained from the CI secular equation by replacing the CI wavefunction Ψ_g^{CI} with the cluster wavefunction Ψ_g. For a closed-shell ground state, the solution of eqs. (9) and (10) is equivalent to that of the coupled-cluster many-electron theory (CC MET) by Čížek and Paldus [6,9,23], though the latter was derived in diagrammatic form. We may therefore call the present solution SAC MET. It applies also to open-shell systems. The features of the SAC MET are as follows. Its energy does not have an upper bound nature. The concept of self-consistency seems not to apply to the non-variational solution. However, a remarkable merit of this solution over the variational one is that the former does not include matrix elements between unlinked terms but includes at most elements between linked and unlinked terms. This is favorable in actual calcula-

tions. We note that the matrices involved in eqs. (9) and (10) are non-symmetric.

3. SAC CI theory for excited states

We define a set of functions $\{\Phi_K\}$ on the basis of the SAC ground state $\Psi_{g'}$ as

$$\Phi_K = \mathcal{N}_K \mathcal{P} O^{(R)} R_K^+ \Psi_{g'}, \tag{11}$$

where $\mathcal{P}$ is a projector

$$\mathcal{P} = 1 - |\Psi_g\rangle\langle\Psi_g|, \tag{12}$$

and R_K^+ is a symmetry-adapted excitation operator for the symmetry of the excited state under consideration. $O^{(R)}$ is the projector for this symmetry. We may also deal with ionized and electron attached states by taking as R_K^+ the symmetry-adapted ionization (annihilation) and electron attachment (creation) operators, respectively.

We note that when the ground state is singlet (spin) and totally symmetric (space), the symmetry projector $O^{(R)}$ is unnecessary in eq. (11), that is

$$\Phi_K = \mathcal{N}_K \mathcal{P} R_K^+ \Psi_g, \tag{13}$$

where we have used eq. (7). This is because the products of operators like $R_K^+ S_I^+ S_J^+$, etc. always belong to the symmetry $\mathcal{R}$ of the excited state under consideration.

We first consider excited states having the same symmetry as the ground state. Then, the operators R_K^+ and $O^{(R)}$ are actually S_K^+ and O, respectively, defined previously. When the SAC wavefunction Ψ_g for the ground state satisfies the *variational* equation [eq. (5)], the functions $\{\Phi_K\}$ satisfy the relations,

$$\langle\Phi_K|\Psi_g\rangle = 0, \tag{14}$$

$$\langle\Phi_K|H|\Psi_g\rangle = 0, \tag{15}$$

which is the Brillouin theorem in a generalized sense. This relation means that the functions $\{\Phi_K\}$ form a basis *for excited states*. Then, we may express the excited states in a CI form as

$$\Psi_e = \sum_K d_K \Phi_K. \tag{16}$$

This is the SAC CI wavefunction for the excited states. Under eqs. (14) and (15), the excited states Ψ_e given by eq. (16) automatically satisfy the correct relation with the ground state,

$$\langle\Psi_e|\Psi_g\rangle = 0, \tag{17}$$

$$\langle\Psi_e|H|\Psi_g\rangle = 0. \tag{18}$$

On the other hand, when the SAC ground state Ψ_g is solved by the non-variational procedure [e.g., eqs. (9) and (10)], the excited functions $\{\Phi_K\}$ and Ψ_e no longer satisfy relations (15) and (18). One way to resolve this problem is to add to eq. (16) the ground state function as

$$\Psi_{e'} = d_0 \Psi_g + \sum_K d_{K'} \Phi_K \tag{19}$$

and solve for $\Psi_{e'}$ by the variational procedure. In this case, the ground state is no longer given by the Ψ_g but takes the form of eq. (19). However, so long as the cluster expansion method is accurate enough for the ground state, we may expect that the difference between the variational and non-variational solutions of the SAC wavefunction Ψ_g should be small. Then, for simplicity, we may use the above SAC CI formalism even if the Ψ_g does not strictly satisfy the variational equation (5).

When the symmetry of the excited state is different from that of the ground state, the relations given by eqs. (14) and (15) hold automatically. Further, in such a case, the projector $\mathcal{P}$ is actually unnecessary in eqs. (11) and (13). The ionized and electron-attached states are dealt with similarly.

The SAC CI wavefunction for the excited state seems to converge more rapidly to the exact solution than the conventional CI wavefunction. The reasons are as follows. (a) Theoretically the basis functions $\{\Phi_K\}$ already satisfy the necessary conditions (14) and (15) for the excited state. (b) Since the basis functions Φ_K include the electron correlations in the ground state through $\Psi_{g'}$, the SAC CI method has only to express the reorganizations in the electron correlations in the excited state. The greater the similarity of two correlations is, the faster the convergence.

3.1. Variational solution

Since the SAC CI wavefunction includes the unknown coefficients d_K linearly, the variational equation becomes a secular equation

$$\sum_L \langle \Phi_K | H - E_e | \Phi_L \rangle d_L = 0, \quad (20)$$

which is also written as

$$\langle \Phi_K | H - E_e | \Psi_e \rangle = 0. \quad (21)$$

This is solved by the method of diagonalization of symmetric matrices. For large dimensions, Davidson's algorithm [24] seems to be useful. When eqs. (14) and (15) are satisfied by the basis functions $\{\Phi_K\}$, the nth solution of eq. (20) gives an upper bound to the energy of the nth excited state [1]. A problem of the variational solution is, as in the ground state case, that it includes matrix elements between unlinked terms. This is not the case, however, in the following non-variational solution.

Recently, Paldus, Čížek, and co-workers [8,16] have considered in a diagrammatic form a similar variational theory for open-shell systems using the non-variational CP MET solution for a closed-shell ground state. In their formulation the relation given by eqs. (14) and (15) which is a key in the SAC CI formalism does not arise.

3.2. Non-variational solution

If the SAC CI wavefunction were the exact wavefunction, it would satisfy the Schrödinger equation $(H - E_e)|\Psi_e\rangle = 0$. In the SAC CI wavefunction, the independent variables are associated only to the linked operators $\{R_K^+\}$. Therefore, the SAC CI wavefunction may be determined by requiring the above identity in the space of the linked configurations $R_K^+|0\rangle$, that is,

$$\langle 0 | R_K (H - E_e) | \Psi_e \rangle = 0, \quad (22)$$

which is rewritten as

$$\sum_L \langle 0 | R_K (H - E_e) | \Phi_L \rangle d_L = 0. \quad (23)$$

This equation suffices to determine all the unknowns involved in the SAC CI wavefunction. Eq. (22) may also be regarded as obtained from the CI equation by replacing the CI wavefunction Ψ^{CI} with the SAC CI wavefunction Ψ_e.

The non-variational equation (23) constitutes an eigenvalue problem of a non-symmetric matrix. The energies do not have an upper bound nature. Further, the non-symmetric nature may result in non-orthogonality of the solutions corresponding to different energies, though the extent should be very small. However, a computational advantage is that the method does not include matrix elements between unlinked terms, but includes at most elements between linked and unlinked terms.

4. Summary and discussion

In table 1, we summarize the features of the variational and non-variational solutions of the SAC expansion for ground states and of the SAC CI wavefunctions for excited states. Theoretically, the variational solutions for both states are consistent and superior to the non-variational ones in that they give upper bounds to the exact energies of both states. Especially, relation (15) has a key importance as a theoretical basis of the SAC CI method. Computationally, the non-variational procedures are simpler than the variational ones since the former include at most matrix elements between linked and unlinked terms.

In table 1 we have also considered a SAC CI like procedure in which the CI wavefunction for the ground state Ψ_g^{CI} is used in the definition of the excited functions $\{\Phi_K\}$ in place of the SAC wavefunction $\Psi_{g'}$ in eq. (11). Both variational and non-variational methods may be applied as discussed above. However, in such a method it would be difficult to assume the relation (15) between the excited functions Φ_K^{CI} and the CI

Table 1
Summary of results

Ground state / Excited state	SAC variational	SAC non-variational	CI
	a), b), e)	d)	a)
SAC CI variational	a), b), c), e)	c), e)	c), e)
SAC CI non-variational	b), d)	d)	d)

a) Upper bound nature.
b) $\langle \Psi_g | \Psi_e \rangle = 0$, $\langle \Psi_g | H | \Psi_e \rangle = 0$.
c) $\langle \Psi_e | \Psi_{e'} \rangle = 0$, $\langle \Psi_e | H | \Psi_{e'} \rangle = 0$.
d) Highest-order term, $\langle$linked$|H|$ unlinked$\rangle$.
e) Highest-order term, $\langle$unlinked$|H|$ unlinked$\rangle$.

ground state Ψ_g^{CI}. Explicitly, the matrix element is written as

$$\langle \Phi_K^{CI}|H|\Psi_g^{CI}\rangle = \mathcal{N}_K\Big[\langle 0|R_K H|0\rangle + \sum_I C_I[\langle 0|R_K(H-E_g^{CI})S_I^+|0\rangle + \langle 0|R_K S_I H|0\rangle] + \sum_{IJ} C_I C_J\langle 0|R_K S_I(H-E_g^{CI})S_J^+|0\rangle\Big]$$

$$= \mathcal{N}_K\Big[\sum_I C_I\langle 0|R_K S_I H|0\rangle + \sum_{IJ} C_I C_J\langle 0|R_K S_I(H-E_g^{CI})S_J^+|0\rangle\Big], \qquad (24)$$

where we have used the CI secular equation. The matrix element given by eq. (24) is not small generally, though the first term $\Sigma C_I\langle 0|R_K S_I H|0\rangle$ may be neglected since the integral is non-zero only when both R_K^+ and S_I^+ are single excitations where C_I is very small. For this problem, it would be better to include the Ψ_g^{CI} as an independent basis for the description of the excited states as in eq. (19), though then the ground state is also changed from the Ψ_g^{CI}. This method is essentially equivalent to the renormalized CI method given by Ohmine et al. [25] who have considered it for the interpretation of the polyene spectra with the PPP (Pariser–Parr–Pople) method.

In the succeeding paper [21], the results of calculations by the SAC and SAC CI methods will be given for the ground and excited states of relatively small atoms and molecules. They will be compared with the full CI and close-to-full CI results, and the prospects of the present approach will be given.

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