CLUSTER EXPANSION OF THE WAVEFUNCTION. EXCITED STATES

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A method for excited states is given on the basis of the symmetry-adapted-cluster (SAC) expansion method. It is based on the fact that the SAC expansion method gives incidentally a set of excited functions which satisfies the Brillouin theorem with the ground state.

Cluster expansion gives a precise and effective way of reaching an exact wavefunction from an approximate one [1]. It is more rapidly convergent than the CI expansion owing to the inclusion of the self-consistency effect [2]. Previously, we have extended this approach to open-shell systems, introducing the symmetry-adapted-cluster (SAC) expansion method [3,4]. It was shown that the symmetry adaptation of the excitation operator is essential for open-shell systems because of the non-linear character of the expansion. Recently, several authors have considered cluster expansion approaches to excited states [5,6]. In this communication, we show that the SAC expansion method gives a good basis for the description of excited states.

In the SAC expansion, the ground state Ψ_g of a given spin-space symmetry is written as [3]

$$\Psi_g = \mathcal{N}_g O \exp\left[\sum_I C_I S_I^+\right] \Phi_0, \tag{1}$$

where S_I^+ is a symmetry-adapted excitation operator, O the symmetry projector, $\mathcal{N}_g$ the normalization factor, and Φ_0 the reference wavefunction which we choose the restricted Hartree—Fock (RHF) wavefunction [7]. The coefficients $\{C_I\}$ in eq. (1) are determined by the variational equations

$$\langle \Psi_g | (H - E_g) S_K^+ | \Psi_g' \rangle = 0, \tag{2}$$

where $\Psi_g' = \exp(\Sigma_I C_I S_I^+)\Phi_0$ and E_g the energy of the ground state. As we include single, double, ..., Nple excitations in the operators $\{S_I^+\}$, the wavefunction Ψ_g approaches the exact one [3]. For most

purposes, however, single and double excitations would be sufficient by virtue of the cluster expansion formalism (cf., CI expansion). So far, we have applied the SAC expansion to the calculations of spin density by adopting the spin-polarization excitation operator as S_I^+ [4].

Eq. (2) is similar to the generalized Brillouin theorem. This reflects the fact that the ground state wavefunction Ψ_g completely includes the self-consistency of the excitation operator S_I^+. Further, this fact renders a new efficient way of describing an excited state as shown below.

Let us consider a function Φ_K which is obtained by Schmidt orthogonalizing the function $O S_K^+ \Psi_g'$, included in eq. (2), to the ground state Ψ_g, i.e.,

$$\Phi_K = \mathcal{N}_K \mathcal{P} O S_K^+ \Psi_g', \tag{3}$$

where $\mathcal{P} = 1 - |\Psi_g\rangle\langle\Psi_g|$. The function Φ_K is also written as

$$\Phi_K = \mathcal{N}_K \mathcal{P} O \exp\left[\sum_I C_I S_I^+\right] S_K^+ \Phi_0. \tag{3'}$$

Then, it is shown that the functions $\{\Phi_K\}$ have the following important properties. (A) They are orthogonal to the Ψ_g (by definition);

$$\langle \Phi_K | \Psi_g \rangle = 0. \tag{4}$$

(B) They are hamiltonian-orthogonal to the Ψ_g (Brillouin theorem);

$$\langle \Phi_K | H | \Psi_g \rangle = 0. \tag{5}$$

These properties show that the set of the functions $\{\Phi_K\}$ forms a basis for the *excited* states. Then, we may write the excited state in a CI form as

$$\Psi_e = \sum_K d_K \Phi_K, \tag{6}$$

where the coefficients d_K are determined by the secular equation

$$\sum_L \langle \Phi_K | H - E_e | \Phi_L \rangle d_L = 0. \tag{7}$$

Thus, any excited states belonging to the same symmetry as the Ψ_g can be calculated. They satisfy

$$\langle \Psi_e | \Psi_g \rangle = 0, \quad \langle \Psi_e | H | \Psi_g \rangle = 0, \tag{8}$$

and the nth solution of eq. (7) gives an upper bound of the energy of the nth excited state [8]. By this way, we can reach an *exact* excited state, as well as the ground state, by increasing the number of excitation operators S_I^+ included simultaneously in eqs. (1) and (6).

This method can also be applied to the excited states having the symmetries different from the ground state. In this case, the excited functions, which may be defined similarly to eq. (3) by

$$\Phi_K^{(T)} = \mathcal{N}_K^{(T)} O^{(T)} S_K^{(T)+} \Psi_g', \tag{9}$$

automatically satisfy the relations (A) and (B) by symmetry. In eq. (9), $S_K^{(T)+}$ and $O^{(T)}$ denote respectively the symmetry-adapted excitation operator and the symmetry projector for the different symmetry T. This method is useful when we study, for instance, both singlet and triplet excited states of a closed-shell molecule with a same level of approximation. (Note that the triplet excited state can be studied more directly by the SAC expansion method, if it is lowest.) Similar procedure may also be applied to the states produced by ionization and electron attachment [6]. Further, we note that if we are dealing with the molecules having closed-shell ground state, we can omit the symmetry projectors from eqs. (1), (3), and (9).

It is interesting to compare the present theory based on the SAC expansion with the single excitation (SE) CI (or Tamm—Dancoff) method based on the HF wavefunction (the HF SECI method). In

both cases, the relations (A) and (B) hold for the excited functions by virtue of their Brillouin theorems. In the SAC expansion, these useful relations continue to hold *up to an exact limit*. They apply not only to single excitations but also to multiple excitations. From this analogy, the present method may be called the SAC CI method for excited states.

In the present theory, the electron correlations in the excited states are studied on the basis of the electron correlations in the ground state. For example, analogously to the frozen-orbital approximation in the HF level, we may approximate an excited state by a small number of Φ_K's given by eqs. (3) or (9). Since the cluster operator, $\exp(\Sigma_I C_I S_I^+)$, represents the correlation effect in the ground state, this extreme approximation may be called frozen-correlation approximation. Such approximation would be meaningful when the electron correlation in the excited state is similar to that in the ground state [9].

In conclusion, we have proposed the following way of studying electron correlations in the ground and excited states. (1) The ground state of a given symmetry is studied by the SAC expansion [3]. It is applied to both closed- and open-shell systems. (2) The excited states having the same symmetry as the ground state are studied by the SAC CI method proposed here. It can be applied also to the excited states having symmetries different from the ground state. We are currently investigating further applications [4] of this approach.

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