

CLUSTER EXPANSION OF THE WAVEFUNCTION. EXCITED STATES

H. NAKATSUJI

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

Received 16 August 1978

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]

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

where S_I^+ is a symmetry-adapted excitation operator, \mathcal{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

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

where $\Psi_g' = \exp(\sum_I C_I S_I^+) \Phi_0$ and E_g the energy of the ground state. As we include single, double, ..., N -ple 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 $\mathcal{O} S_K^+ \Psi_g'$, included in eq. (2), to the ground state Ψ_g , i.e.,

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

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

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

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

$$\langle \Phi_K | \Psi_g \rangle = 0. \quad (4)$$

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

$$\langle \Phi_K | H | \Psi_g \rangle = 0. \quad (5)$$

