

# Cluster expansion of the wavefunction. The open-shell orbital theory including electron correlation

K. Hirao and H. Nakatsuji

*Department of Chemistry, Shiga University of Medical Science, Seta, Otsu, Japan*

*and Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan*  
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A previously developed new approach to the orbital theory with the formalism of the cluster expansion of a wavefunction is applied to open-shell electronic systems in order to include the electron correlation effect within the conventional formalism of the orbital theory. The open-shell orbital theory involving the electron correlation is defined as  $|\Phi\rangle = \mathcal{P} \exp[iF_K + iF_M] |0\rangle$ . The  $\mathcal{P}$  is the projection operator to resolve the stability dilemma and the  $F_K$  and  $F_M$  are the excitation operators for closed-shell and open-shell orbitals, respectively. The new orbital theories, which are called Modified SEHF (MSEHF) theory and complex GSO theory, have been proposed with special choices of  $F$  and  $\mathcal{P}$ . They are analyzed in contrast to the conventional orbital theories such as UHF, SEHF, CMO, and GVB theories in the form of the limited CI based on their own natural orbitals. The MSEHF theory includes the correlation effect effectively in open-shell systems and constitutes a natural extension of the closed-shell SEHF theory (the conventional SEHF theory fails in open-shell systems). The complex GSO theory is the most suitable orbital theory to include the electron correlation effect within the orbital theory (to include spin correlation we have to adopt the symmetry-adapted-cluster (SAC) expansion formalism as shown previously).

## I. INTRODUCTION

In the preceding paper<sup>1</sup> (hereafter referred to as I) we developed a new approach to the closed-shell orbital theory with the formalism of the cluster expansion of the wavefunction. The four independent excitation operators are used to represent the general determinantal wavefunctions and also to discuss the stability of the Hartree-Fock (HF) solution. This leads to the new concept called the "stability dilemma," which is the key not only in understanding the structure of the orbital theory but also in constructing the new orbital theory. We emphasized in I how important the removal of the stability dilemma is to the obtaining the orbital theory including the electron correlation. The stability dilemma can be resolved by projecting the determinantal wavefunction onto an appropriate symmetry space. The various closed-shell orbital theories (some are known but some are new) can be obtained by appropriate choices of the excitation and projection operators. We have shown in I that the one-particle cluster expansion method is a useful expression to construct and to analyze the orbital theory. In this paper, we continue the development for an open-shell case.

In contrast to the closed-shell case, the correlation problems in open-shell systems are the electron correlation and the spin correlation.<sup>2</sup> In order to include both correlations at the same time, we find it more convenient to start with the symmetry-adapted-cluster (SAC) expansion of an exact wavefunction.<sup>3</sup> The SAC expansion is constructed from the generators of the excited configurations having the symmetry under consideration. In our separate papers,<sup>3,4</sup> we have presented the pseudo-orbital theory which is an extension of the orbital theory based on the SAC expansion and applied it to the spin correlation problem in open-shell systems. In the present study, we will consider the open-shell orbital theory based on the conventional cluster expansion of a wavefunction.<sup>5</sup> A principal purpose of this paper is to obtain

open-shell orbital theories including the electron correlation. The theory involving both electron and spin correlations will be examined elsewhere.

The one-particle cluster expansion of a wavefunction for open-shell systems will be discussed in the next section. We will define the excitation operators for open-shell systems and discuss their properties deduced. Also we will show how the open-shell determinantal functions can be represented in terms of these excitation operators. In Sec. III, we will go beyond the restricted HF (RHF) approximation and present a theory which includes the electron correlation with the framework of the orbital theory. This can be done only when the stability dilemma is resolved. Thus, we will first derive the stability conditions for the RHF solution in order to examine the stability dilemma. Then, we will define the general open-shell orbital theory including the electron correlation effect by resolving the stability dilemma. Some new orbital theories will be proposed. They are analyzed in Sec. IV in contrast to the conventional orbital theories such as the UHF, SEHF, CMO, and GVB theories in the form of the limited configuration interaction (CI) based on their own natural orbitals. In the final section, the present study will be summarized.

The notation used in this paper depends very heavily on that given in I.

## II. THE EXCITATION OPERATORS FOR OPEN-SHELL SYSTEMS

To obtain a unified approach to the open-shell orbital theory, it is useful to start from the one-particle cluster expansion of a wavefunction. Let us consider a wavefunction of the form

$$|\Phi\rangle = \exp[\hat{T}_1] |\Phi_0\rangle, \quad (1)$$

where

$$|\Phi_0\rangle = \prod_i a_i^\dagger | \rangle, \quad (2)$$

$$\hat{T}_1 = \sum_i f_i b_i^\dagger a_i. \quad (3)$$

The ket  $| \rangle$  denotes a vacuum state,  $a_i^\dagger$  and  $a_i$  are creation and annihilation operators for single-particle states,  $b_i^\dagger$  are the normalized one-particle cluster generators and the coefficients  $f_i$  are complex numbers. Thouless' theorem<sup>6</sup> states that the cluster expansion given above corresponds to a transformation of a single Slater determinant  $|\Phi_0\rangle$  to another single determinantal function  $|\Phi\rangle$ .

Now we consider the one-particle cluster expansion of a wavefunction for open-shell systems. As a reference wavefunction, we choose a restricted open-shell single determinant given by

$$|\Phi_0\rangle = \left[ \sum_{k=1}^q a_{k\alpha}^\dagger a_{k\beta}^\dagger \right] \left[ \sum_{m=q+1}^p a_{m\alpha}^\dagger \right] | \rangle \\ = || \phi_1 \bar{\phi}_1 \cdots \phi_q \bar{\phi}_q \cdots \phi_p \bar{\phi}_p ||, \quad (4)$$

where  $|| \cdots ||$  denotes the normalized Slater determinant. A bar above a spin orbital indicates that it is associated with  $\beta$  spin and no bar indicates  $\alpha$  spin. For simplicity, we have restricted ourselves in this paper to the systems for which the determinant (4) has a correct symmetry. An important exception is a singlet excited state. For such state, it would be more preferable to start from a multideterminant reference wavefunction.<sup>7</sup> We define the number of unpaired spins in the system by  $s$ , i. e.,

$$s = p - q.$$

The  $|\Phi_0\rangle$  or  $|0\rangle$  in shorter version is an eigenfunction of the spin operators  $\mathbf{S}^2$  and  $\mathbf{S}_z$  with eigenvalues  $s/2(s/2+1)$  and  $s/2$ , respectively. We will denote the simultaneous spin eigenfunctions of  $\mathbf{S}^2$  and  $\mathbf{S}_z$  by  $\Theta_{SM}^j$  ( $j=1, 2, \dots, f$ )

$$\mathbf{S}^2 \Theta_{SM}^j = S(S+1) \Theta_{SM}^j, \quad \mathbf{S}_z \Theta_{SM}^j = M \Theta_{SM}^j. \quad (5)$$

The index  $j$  runs over the independent spin eigenfunctions belonging to the same eigenvalues of  $\mathbf{S}^2$  and  $\mathbf{S}_z$ , the number of which is denoted by  $f$ . We will construct the spin eigenfunctions through the genealogical scheme<sup>8</sup> as done in I. Throughout the paper, the indices  $k, l$  refer to the closed-shell orbitals,  $m, n$  to open-shell orbitals and  $i, j$  to general orbitals. For the sake of convenience, we will separate the spin index and employ the two-component operators defined by

$$\mathbf{a}_i = \begin{pmatrix} a_{i\alpha} \\ a_{i\beta} \end{pmatrix}, \quad \mathbf{b}_i = \begin{pmatrix} b_{i\alpha} \\ b_{i\beta} \end{pmatrix}. \quad (6)$$

The one-particle cluster generator  $\hat{T}_1$  is written for open-shell systems as

$$\hat{T}_1 = \hat{T}_{1K} + \hat{T}_{1M}, \quad (7)$$

where the  $\hat{T}_{1K}$  and  $\hat{T}_{1M}$  are the one-particle cluster generators for closed-shell and open-shell manifolds respectively. These are expressed in terms of the excitation operators as

$$\hat{T}_{1K} = \sum_k \left[ f_{0,k} S_{0,k}^\dagger + \sum_\tau f_{\tau,k} S_{\tau,k}^\dagger \right], \quad (\tau = x, y, z)$$

$$\hat{T}_{1M} = \sum_m [f_{0,m} S_{0,m}^\dagger + f_{x,m} S_{x,m}^\dagger]. \quad (8)$$

The closed-shell excitation operators are defined as

$$S_{0,k}^\dagger = (1/\sqrt{2}) \mathbf{b}_k^\dagger \sigma_0 \mathbf{a}_k, \\ S_{\tau,k}^\dagger = (1/\sqrt{2}) \mathbf{b}_k^\dagger \sigma_\tau \mathbf{a}_k, \quad (\tau = x, y, z), \quad (9)$$

and the open-shell excitation operators<sup>9</sup> as

$$S_{0,m}^\dagger = \mathbf{b}_m^\dagger \sigma_0 \mathbf{a}_m, \\ S_{x,m}^\dagger = \mathbf{b}_m^\dagger \sigma_x \mathbf{a}_m. \quad (10)$$

Here  $\sigma_0$  and  $\sigma_\tau$  ( $\tau = x, y, z$ ) are the unit matrix and Pauli matrix respectively. The  $f$  in (8) are the complex quantities and their real part is referred to as  $g$  and imaginary part to as  $h$ , namely  $f = g + ih$ . Let  $S$  be the Hermitian conjugate of  $S^\dagger$ ,  $S \equiv (S^\dagger)^\dagger$ . From the definition of the excitation operators

$$S|0\rangle = 0 \quad \langle 0|S^\dagger = 0 \quad (11)$$

and we see that they satisfy quasiboson commutation relations

$$[S_I, S_J] = [S_I^\dagger, S_J^\dagger] = 0, \quad \langle 0|[S_I, S_J^\dagger]|0\rangle = \delta_{IJ}. \quad (12)$$

Now let us examine the properties of these excitation operators. First, consider the closed-shell excitation operators. The singlet and triplet excitation operators in (9) generate singlet and triplet excited states respectively when operating on the closed-shell determinantal function. However, when the reference function  $|0\rangle$  is an open-shell determinant as in (4), three triplet excitation operators generate the spin contaminating excited states, while the singlet excitation operators preserve the spin symmetry.

The  $S_{x,k}^\dagger$  operator is a sum of spin-adapted excitation operators<sup>4,10</sup>

$$S_{x,k}^\dagger = \left( \frac{s}{s+2} \right)^{1/2} s/2 S_{p,k}^\dagger + \left( \frac{2}{s+2} \right)^{1/2} (s+2)/2 S_{1,k}^\dagger, \quad (13)$$

where

$$s/2 S_{p,k}^\dagger = (s+2)^{-1/2} \left[ \left( \frac{s}{2} \right)^{1/2} (b_{k\alpha}^\dagger a_{k\alpha} - b_{k\beta}^\dagger a_{k\beta}) \right. \\ \left. + \left( \frac{2}{s} \right)^{1/2} b_{k\alpha}^\dagger a_{k\beta} \sum_m a_{m\beta}^\dagger a_{m\alpha} \right] \\ (s+2)/2 S_{1,k}^\dagger = (s+2)^{-1/2} \left[ b_{k\alpha}^\dagger a_{k\alpha} - b_{k\beta}^\dagger a_{k\beta} - b_{k\alpha}^\dagger a_{k\beta} \sum_m a_{m\beta}^\dagger a_{m\alpha} \right]. \quad (14)$$

The  $s/2 S_{p,k}^\dagger$  and  $(s+2)/2 S_{1,k}^\dagger$  generate singly excited states of spin eigenfunctions,

$$s/2 S_{p,k}^\dagger |0\rangle = || v_k \phi_k \phi_{q+1} \cdots \phi_m \cdots \phi_p \Theta_{(s/2)(s/2)}^0 || \\ (s+2)/2 S_{1,k}^\dagger |0\rangle = || v_k \phi_k \phi_{q+1} \cdots \phi_m \cdots \phi_p \Theta_{(s/2+1)(s/2)}^1 ||, \quad (15)$$

where

$$\Theta_{(s/2)(s/2)}^0 = (s+2)^{-1/2} \left[ \left( \frac{s}{2} \right)^{1/2} (\alpha\beta + \beta\alpha) \alpha \cdots \alpha \cdots \alpha \right. \\ \left. - \left( \frac{2}{s} \right)^{1/2} \alpha \alpha \sum_m \alpha \cdots \beta \cdots \alpha \right]$$

$$\Theta_{(s/2+1)(s/2)}^1 = (s+2)^{-1/2} \left[ (\alpha\beta + \beta\alpha)\alpha \dots \alpha \dots + \alpha\alpha \sum_m \alpha \dots \beta \dots \alpha \right] \quad (16)$$

In (15), we used the abbreviations like

$$\begin{aligned} & ||\phi_1 \bar{\phi}_1 \dots v_k \phi_k (\alpha\beta + \beta\alpha) \dots \phi_q \bar{\phi}_q \phi_{q+1} \dots \phi_p || \\ & = ||v_k \phi_k \phi_{q+1} \dots \phi_p (\alpha\beta + \beta\alpha) \alpha \dots \alpha ||, \end{aligned} \quad (17)$$

since the doubly occupied orbitals do not affect the spin symmetry. The  $v_k$  is the spatial orbital generated by  $b_k^*$ . Note here that the  $\Theta^p$  is a linear combination of the spin eigenfunctions constructed by the genealogical scheme

$$\begin{aligned} \Theta_{(s/2)(s/2)}^p & = \left[ \frac{s+2}{2(s+1)} \right]^{1/2} \Theta_{(s/2)(s/2)}^{f-1} + \left[ \frac{s}{2(s+1)} \right]^{1/2} \Theta_{(s/2)(s/2)}^f. \end{aligned} \quad (18)$$

These operators in (14) are essentially single excitation operators, though they involve in the last term the two simultaneous elementary excitations (real excitation and spin-flip) due to the spin-symmetry requirement. Note here that the  $s^{1/2}S_{p,k}^*$  makes an important role in the spin correlation problem and is called as the spin polarization excitation operator.<sup>3,4</sup> In open-shell systems, the singlet excitation operator  $S_{0,k}^*$  and the triplet excitation operator  $S_{x,k}^*$  do interact with respect to the Hamiltonian  $H$ . This is different from the previous closed-shell case in I.

The  $S_{x,k}^*$  and  $S_{y,k}^*$  excitation operators also generate the spin contaminating excited states when operating on  $|0\rangle$ , e.g.,

$$S_{x,k}^* |0\rangle = ||\phi_k v_k \phi_{q+1} \dots \phi_m \dots \phi_p (\alpha\alpha - \beta\beta) \alpha \dots \alpha \dots \alpha / \sqrt{2} || \quad (19)$$

Now consider the operator  $S_x - iS_y$ , which lowers  $M$  without changing the value of  $S$  and define the spin eigenfunctions by

$$\begin{aligned} \Theta_{(s/2)(s/2-1)}^p & = s^{-1/2} (S_x - iS_y) \Theta_{(s/2)(s/2)}^p \\ \Theta_{(s/2+1)(s/2-1)}^1 & = [2(s+2)]^{-1/2} (S_x - iS_y) \Theta_{(s/2+1)(s/2)}^1. \end{aligned} \quad (20)$$

Then we can rewrite the spin function in (19) in terms of spin eigenfunctions<sup>11</sup>

$$\begin{aligned} (\alpha\alpha - \beta\beta) \alpha \dots \alpha \dots \alpha / \sqrt{2} & = \left(\frac{1}{2}\right)^{1/2} \Theta_{(s/2+1)(s/2+1)}^1 \\ & - \left[ \frac{1}{(s+1)(s+2)} \right]^{1/2} \Theta_{(s/2+1)(s/2-1)}^1 - \left( \frac{1}{s+2} \right)^{1/2} \Theta_{(s/2)(s/2-1)}^1 \\ & - \left[ \frac{s-1}{2(s-1)} \right]^{1/2} P \Theta_{(s/2-1)(s/2-1)}^f. \end{aligned} \quad (21)$$

Here the  $P$  is the permutation operator given by

$$P = (1 \ s+1)(2 \ s+2) \quad (22)$$

where  $(ij)$  denotes the transposition which interchanges the  $i$ th and  $j$ th spins and leaves other fixed. Similarly the  $S_{y,k}^*$  operator generates the spin contaminating excited state. The Hamiltonian matrix element between the singly excited state generated by  $S_{x,k}^*$  and that by

$S_{y,k}^*$  is not zero. Thus, the  $S_{x,k}^*$  and  $S_{y,k}^*$  are not independent of each other.

The excitation operator for open-shell orbitals  $S_{x,m}^*$  also generates the spin contaminating excited states while the  $S_{0,m}^*$  does the pure spin eigenstates:

$$S_{x,m}^* |0\rangle = ||\phi_{q+1} \dots v_m \dots \phi_p \alpha \dots \beta \dots \alpha ||. \quad (23)$$

The spin function above can be expressed as

$$\begin{aligned} & \alpha \dots \beta \dots \alpha \\ & = \left( \frac{1}{s} \right)^{1/2} \Theta_{(s/2)(s/2-1)}^1 + \left( \frac{s-1}{s} \right)^{1/2} \Theta_{(s/2-1)(s/2-1)}^f, \end{aligned} \quad (24)$$

where

$$\begin{aligned} \Theta_{(s/2)(s/2-1)}^1 & = (\alpha \dots \beta \dots \alpha \dots \alpha + \sum_{n(\neq m)} \alpha \dots \alpha \dots \beta \dots \alpha) / \sqrt{s}, \\ \Theta_{(s/2-1)(s/2-1)}^f & = \left[ (s-1)^{1/2} \alpha \dots \beta \dots \alpha \dots \alpha - \left( \frac{1}{s-1} \right)^{1/2} \right. \\ & \quad \left. \times \sum_{n(\neq m)} \alpha \dots \alpha \dots \beta \dots \alpha \right] / \sqrt{s}. \end{aligned} \quad (25)$$

Thus, the  $S_{0,m}^*$  and  $S_{x,m}^*$  are independent of each other but they do interact, with respect to the Hamiltonian, with the closed-shell excitation operators.

Now let us see how the class of the open-shell determinantal function can be expressed in terms of these excitation operators. Suppose that  $|\Phi_0\rangle$  is a general product function for open-shell systems as defined in (4). Any other determinantal wavefunction, not actually orthogonal to  $|\Phi_0\rangle$ , can be expressed as

$$|\Phi\rangle = \mathcal{N} \exp \left[ \sum_k f_{\gamma,k} S_{\gamma,k}^* + \sum_m f_{\delta,m} S_{\delta,m}^* \right] |0\rangle. \quad (26)$$

In the following, we use the index  $\gamma$  for closed-shell excitation operators, 0,  $x$ ,  $y$ , and/or  $z$  and the  $\delta$  for open-shell ones, 0 and/or  $x$ . The  $|\Phi\rangle$  given by (26) can be rewritten into a determinantal form,

$$|\Phi\rangle = \left[ \prod_k c_{\gamma,k\alpha}^* c_{\gamma,k\beta}^* \right] \left[ \prod_m c_{\delta,m\alpha}^* \right] |\rangle \quad (27)$$

where

$$\begin{aligned} c_{\gamma,k}^* & = (a_k^* + f'_{\gamma,k} b_k^* \sigma_{\gamma}) / (1 + |f'_{\gamma,k}|^2)^{1/2}, \\ c_{\delta,m}^* & = (a_m^* + f_{\delta,m} b_m^* \sigma_{\delta}) / (1 + |f_{\delta,m}|^2)^{1/2}, \end{aligned} \quad (28)$$

and  $f'$  denotes  $f/\sqrt{2}$ . If we also define

$$\begin{aligned} c_{\gamma,k}^{*+} & = (b_k^* - f'_{\gamma,k} a_k^* \sigma_{\gamma}) / (1 + |f'_{\gamma,k}|^2)^{1/2}, \\ c_{\delta,m}^{*+} & = (b_m^* - f_{\delta,m} a_m^* \sigma_{\delta}) / (1 + |f_{\delta,m}|^2)^{1/2}, \end{aligned} \quad (29)$$

we can check that

$$\begin{aligned} c_{\gamma,k}^{*+} |\Phi\rangle & = c_{\gamma,k}^* |\Phi\rangle = 0, \\ c_{\delta,m}^{*+} |\Phi\rangle & = c_{\delta,m}^* |\Phi\rangle = 0. \end{aligned} \quad (30)$$

The anticommutation relations of  $a_i^*$ ,  $b_j^*$  give with (28) and (29) that

$$\begin{aligned} [c_i, c_j]_{+} & = [c_i^*, c_j^*]_{+} = 0, \\ [c_i, c_j^*]_{+} & = \delta_{ij}. \end{aligned} \quad (31)$$

The equations (28) and (29) represent a canonical transformation.

An alternative prescription may be used to obtain the determinantal wavefunction

$$\begin{aligned} |\Phi\rangle &= \exp[iF_\gamma + iF_\delta] |0\rangle \\ &= \exp[iF_\gamma] \cdot \exp[iF_\delta] |0\rangle, \end{aligned} \quad (32)$$

where

$$\begin{aligned} F_\gamma &= \frac{1}{i} \sum_k (f_{\gamma,k} S_{\gamma,k}^* - f_{\gamma,k}^* S_{\gamma,k}) = F_\gamma^\dagger \\ F_\delta &= \frac{1}{i} \sum_m (f_{\delta,m} S_{\delta,m}^* - f_{\delta,m}^* S_{\delta,m}) = F_\delta^\dagger. \end{aligned} \quad (33)$$

The exponential operator  $e^{iF}$  is strictly unitary due to the Hermitian property of  $F$ . That is, the  $|\Phi\rangle$  can be obtained from  $|0\rangle$  by a unitary transformation. If we define the new fermion operators by

$$\begin{aligned} d_{\gamma,k}^* &= e^{iF_\gamma} a_k^* e^{-iF_\gamma}, \\ d_{\delta,m}^* &= e^{iF_\delta} a_m^* e^{-iF_\delta}, \end{aligned} \quad (34)$$

we can rewrite  $|\Phi\rangle$  as a determinantal form

$$|\Phi\rangle = \left[ \prod_k d_{\gamma,k\alpha}^* d_{\gamma,k\beta}^* \right] \left[ \prod_m d_{\delta,m\alpha}^* \right] | \rangle. \quad (35)$$

We can also define the new creation operators  $d_{\gamma,k}^*$  and  $d_{\delta,m}^*$  by making a canonical transformation

$$\begin{aligned} d_{\gamma,k}^* &= e^{iF_\gamma} b_k^* e^{-iF_\gamma} \\ d_{\delta,m}^* &= e^{iF_\delta} b_m^* e^{-iF_\delta}. \end{aligned} \quad (36)$$

Note here that the operators  $F_\gamma$ ,  $F_\delta$  are invariant to a canonical transformation of the fermion operators. On the basis of (26) and (32) we can construct more general determinantal wavefunction in terms of the excitation operators.

It is not difficult to show that the two representations of an open-shell determinantal function in (26) and (32) are equivalent. Thus, we may use whichever we like as the case may be.

### III. STABILITY DILEMMA IN OPEN-SHELL ORBITAL THEORY AND NEW ORBITAL THEORIES INCLUDING ELECTRON-CORRELATION EFFECT

The RHF wavefunction<sup>12</sup> is the optimized one within the space spanned by the determinantal functions generated by the real spin symmetry preserving excitation operators,  $S_{0,k}^*$  and  $S_{0,m}^*$ :

$$\begin{aligned} |\Phi\rangle &= \mathcal{N} \exp \left[ \sum_k g_{0,k} S_{0,k}^* + \sum_m g_{0,m} S_{0,m}^* \right] |0\rangle \\ &= \left[ \prod_k c_{0,k\alpha}^* c_{0,k\beta}^* \right] \left[ \prod_m c_{0,m\alpha}^* \right] | \rangle \end{aligned} \quad (37)$$

where

$$\begin{aligned} c_{0,k}^* &= (a_k^* + g'_{0,k} b_k^*) / [1 + (g'_{0,k})^2]^{1/2}, \\ c_{0,m}^* &= (a_m^* + g_{0,m} b_m^*) / [1 + (g_{0,m})^2]^{1/2}. \end{aligned} \quad (38)$$

The equivalent expression of the RHF wavefunction is given by

$$|\Phi\rangle = \exp[iG_{K0} + iG_{M0}] |0\rangle, \quad (39)$$

with

$$\begin{aligned} G_{K0} &= \frac{1}{i} \sum_k g_{0,k} (S_{0,k}^* - S_{0,k}), \\ G_{M0} &= \frac{1}{i} \sum_m g_{0,m} (S_{0,m}^* - S_{0,m}). \end{aligned} \quad (40)$$

It is apparent that the  $|\Phi\rangle$  takes a determinantal form,

$$|\Phi\rangle = \left[ \prod_k d_{0,k\alpha}^* d_{0,k\beta}^* \right] \left[ \prod_m d_{0,m\alpha}^* \right] | \rangle, \quad (41)$$

where

$$\begin{aligned} d_{0,k}^* &= \cos(g'_{0,k}) \cdot a_k^* + \sin(g'_{0,k}) \cdot b_k^*, \\ d_{0,m}^* &= \cos(g_{0,m}) \cdot a_m^* + \sin(g_{0,m}) \cdot b_m^*. \end{aligned} \quad (42)$$

The double occupancy of the closed-shell orbitals is preserved. That is, the uniquely determined optimal wavefunction described by (37) or (39) is the RHF wavefunction. In Appendix, we expressed a general restricted Slater determinant for open-shell systems by making use of the primitive cluster expansion of a wavefunction and also derived the variational equations for the RHF wavefunction.

We wish to go beyond the RHF approximation. However, even if we extend the variational space by introducing the remaining excitation operators, we cannot reach beyond the HF approximation in case the RHF solution is stable. This dilemma is called "stability dilemma". The stability dilemma can be resolved by projecting the determinantal function onto the symmetry space. The correlation effect can be taken into account within the framework of the orbital theory only when the stability dilemma is resolved. In this section, we will first derive the stability conditions for the RHF solution in order to examine the stability dilemma in open-shell orbital theory. Then, we will present new orbital theories including correlation effects by removing the stability dilemma.

#### A. Stability condition for the RHF solution

The stability conditions for closed-shell HF solution have been fully examined by several authors,<sup>13,14</sup> but the study for open-shell systems has been restricted. Only the most simple case, the doublet stability condition, has been examined by Paldus and Čížek.<sup>15</sup> In the following, we will derive the stability conditions for the fluctuations of closed-shell and open-shell orbitals by mixing virtual orbitals to them. The fluctuations mixing occupied and virtual open-shell orbitals can be excluded since the present formalism is based on the natural orbitals. The fluctuations of occupied orbitals can be brought about by four closed-shell and two open-shell excitation operators. The closed-shell excitation operators are mutually independent for closed-shell systems and we get the four independent stability conditions for closed-shell HF solution. In open-shell systems, however, these excitation operators do interact with respect to the Hamiltonian since the spin-flip excitation operators generate the spin contaminating excited states when operating on the open-shell reference function.



Thus, we will consider the stability conditions separately for each fluctuation described by each closed-shell and open-shell excitation operator.

### 1. The spin-symmetry preserving (SSP) stability condition for closed-shell orbitals

First, we will consider the stability conditions for the fluctuations brought about by the closed-shell excitation operators. Let us start by considering the small displacement of the RHF wavefunction given by the unitary transformation

$$|\Phi\rangle = \exp[iF_{K0}]|\text{HF}\rangle \quad (43)$$

with

$$F_{K0} = \frac{1}{i} \sum_k (f_{0,k} S_{0,k}^* - f_{0,k}^* S_{0,k}) = F_{K0}^\dagger, \quad (44)$$

where  $|\text{HF}\rangle$  denotes the open-shell restricted HF wavefunction. This fluctuation corresponds to the singlet type excitation of the closed-shell orbitals to virtual orbitals and therefore the spin-symmetry is preserved. The energy expectation is given by

$$E = E_0 + i \langle \text{HF} | [H, F_{K0}] | \text{HF} \rangle + \frac{i^2}{2!} \langle \text{HF} | [[H, F_{K0}], F_{K0}] | \text{HF} \rangle + \dots, \quad (45)$$

where  $E_0$  is the HF energy. The first-order energy shift is zero due to the Brillouin theorem. Thus, we obtain the stability condition for the variation given by (43)

$$\frac{i^2}{2!} \langle \text{HF} | [[H, F_{K0}], F_{K0}] | \text{HF} \rangle \geq 0. \quad (46)$$

Expanding (46), we get the stability condition for all the coefficients  $f$ ,

$$\frac{1}{2} \begin{pmatrix} f_{K0} \\ f_{K0}^* \end{pmatrix}^\dagger \begin{pmatrix} A_{K0} & B_{K0} \\ B_{K0}^* & A_{K0}^* \end{pmatrix} \begin{pmatrix} f_{K0} \\ f_{K0}^* \end{pmatrix} \geq 0, \quad (47)$$

where the  $f_{K0}$  is the column vector formed by  $f_{0,k}$  and the submatrices  $A_{K0}$  and  $B_{K0}$  are defined by

$$\begin{aligned} (A_{K0})_{ki} &= \langle \text{HF} | S_{0,k} H S_{0,i}^* - E_0 | \text{HF} \rangle \\ (B_{K0})_{ki} &= \langle \text{HF} | S_{0,k} S_{0,i} H | \text{HF} \rangle. \end{aligned} \quad (48)$$

This stability condition is called as the spin-symmetry preserving (SSP) stability condition for closed-shell orbitals since the infinitesimal variation described by (43) preserves the spin-symmetry. When  $A_{K0}$  and  $B_{K0}$  matrices are real, as is usually the case, the above stability condition may be factored into two subproblems,

$$\mathbf{g}_{K0}^\dagger (A_{K0} + B_{K0}) \mathbf{g}_{K0} + \mathbf{h}_{K0}^\dagger (A_{K0} - B_{K0}) \mathbf{h}_{K0} \geq 0 \quad (49)$$

where  $\mathbf{g}_{K0}$  and  $\mathbf{h}_{K0}$  are column vectors of real and imaginary parts of the complex column vector  $f_{K0}$ , i.e.,  $f_{K0} = \mathbf{g}_{K0} + i\mathbf{h}_{K0}$ . The  $A_{K0} \pm B_{K0}$  are symmetric under the assumption that both  $A_{K0}$  and  $B_{K0}$  are real. Therefore the unitary matrices  $U \pm$  may be found by which  $(A_{K0} \pm B_{K0})$  are diagonalized,

$$U^\dagger (A_{K0} + B_{K0}) U = D_{K0}^+$$

$$U^{-\dagger} (A_{K0} - B_{K0}) U = D_{K0}^-, \quad (50)$$

where the  $D$  are the diagonal matrices. If we define the unitary transformed excitation operators  $P^*$  and  $Q^*$  by

$$\begin{aligned} P_{0,k}^* &= \sum_i S_{0,k}^* (U^+)_{ik}, \\ Q_{0,k}^* &= \sum_i S_{0,k}^* (U^-)_{ik}, \end{aligned} \quad (51)$$

together with

$$\begin{aligned} \tilde{\mathbf{g}}_{K0} &= (U^+)^\dagger \mathbf{g}_{K0} \\ \tilde{\mathbf{h}}_{K0} &= (U^-)^\dagger \mathbf{h}_{K0}. \end{aligned} \quad (52)$$

Then, we have from (49)

$$\sum_k (\tilde{\mathbf{g}}_{0,k})^2 (D_{K0}^+)_{kk} + \sum_k (\tilde{\mathbf{h}}_{0,k})^2 (D_{K0}^-)_{kk} \geq 0 \quad (53)$$

where

$$\begin{aligned} (D_{K0}^+)_{kk} &= \langle \text{HF} | P_{0,k} H P_{0,k}^* - E_0 + P_{0,k} P_{0,k} H | \text{HF} \rangle \\ (D_{K0}^-)_{kk} &= \langle \text{HF} | Q_{0,k} H Q_{0,k}^* - E_0 - Q_{0,k} Q_{0,k} H | \text{HF} \rangle. \end{aligned} \quad (54)$$

Thus, the SSP stability condition for closed-shell orbitals can be grouped into real and imaginary conditions

- (a)  $(D_{K0}^+)_{kk} \geq 0$ , for all  $k$   
real SSP stability condition for closed-shell orbitals
- (b)  $(D_{K0}^-)_{kk} \geq 0$ , for all  $k$   
imaginary SSP stability condition for closed-shell orbitals

Now we analyze the instability conditions. We employ the uncoupled approximation, namely the unitary transformed excitation operators  $P^*$  and  $Q^*$  are replaced by the primitive excitation operators  $S^*$ . From (55), we get the SSP instability conditions for closed-shell orbitals

- (a)  $s^{1/2} E_{0,k} - E_0 + K_{kk}^* < 0$ , for any  $k$   
real SSP instability condition for closed-shell orbitals
- (b)  $s^{1/2} E_{0,k} - E_0 - K_{kk}^* < 0$ , for any  $k$   
imaginary SSP instability condition for closed-shell orbitals

where  $s^{1/2} E_{0,k}$  is the energy of the singly excited state and the  $K_{kk}^*$  is the usual exchange integral

$$s^{1/2} E_{0,k} = \langle \text{HF} | S_{0,k} H S_{0,k}^* | \text{HF} \rangle \quad K_{kk}^* = \langle \text{HF} | H S_{0,k}^* S_{0,k} | \text{HF} \rangle \quad (57)$$

If these instability conditions are satisfied, the RHF solution does not represent a true minimum but another solution, having lower energy than the RHF solution, must exist. Although such solution preserves the double occupancy of the closed-shell orbitals and also preserves the spin-symmetry, it violates the space symmetry.<sup>15</sup> It must be noted that the real SSP condition in (56) is rewritten as

$$E_0 - s^{1/2} E_{0,k} > K_{kk}^* \geq 0 \quad (58)$$

This means that the singly excited state with  $S = s/2$  has the lower energy than the ground state.

## 2. The spin-symmetry breaking (SSB) stability conditions for closed-shell orbitals

As known well, the unrestricted HF (UHF) wavefunction<sup>16</sup> for open-shell systems always leads to lower energy, unlike the closed-shell systems, than the RHF wavefunction. A standard form of UHF orbitals, the DODS orbitals, can be generated by making use of the  $S_{\tau,k}^*$  excitation operators. Thus, the open-shell RHF solution is always unstable to the variation fluctuated by the  $S_{\tau,k}^*$  operators. The proof is easy. Consider the unitary transformation given by

$$|\Phi\rangle = \exp[iF_{KZ}]|\text{HF}\rangle \quad (59)$$

with

$$F_{KZ} = \frac{1}{i} \sum_k (f_{\tau,k} S_{\tau,k}^* - f_{\tau,k}^* S_{\tau,k}) . \quad (60)$$

The energy for  $|\Phi\rangle$  is

$$E = E_0 + i\langle\text{HF}|[H, F_{KZ}]|\text{HF}\rangle + \dots \quad (61)$$

The first-order energy shift can be reduced to

$$\begin{aligned} i\langle\text{HF}|[H, F_{KZ}]|\text{HF}\rangle \\ = \left(\frac{s}{s+2}\right)^{1/2} \sum_k f_{\tau,k} \langle\text{HF}|H^{s/2} S_{\tau,k}^*|\text{HF}\rangle + \text{C.C.} \end{aligned} \quad (62)$$

by virtue of the relation (13). Thus, the first-order energy shift does not vanish, implying that the RHF solution is not stationary to the variation described by (59).

Next let us consider the infinitesimal unitary transformation of the RHF wavefunction

$$|\Phi\rangle = \exp[iF_{K\tau}]|\text{HF}\rangle, \quad (63)$$

with  $\tau = x, y$  and

$$F_{K\tau} = \frac{1}{i} \sum_k (f_{\tau,k} S_{\tau,k}^* - f_{\tau,k}^* S_{\tau,k}) . \quad (64)$$

The energy for  $|\Phi\rangle$  is given by

$$\begin{aligned} E = E_0 + i\langle\text{HF}|[H, F_{K\tau}]|\text{HF}\rangle \\ + \frac{i^2}{2!} \langle\text{HF}|[H, F_{K\tau}]|\text{HF}\rangle + \dots \end{aligned} \quad (65)$$

The first-order energy shift vanishes due to the spin symmetry, indicating that the energy be stationary. The stability condition for the variation given by (63) is

$$\frac{i^2}{2!} \langle\text{HF}|[H, F_{K\tau}], F_{K\tau}]|\text{HF}\rangle \geq 0 \quad (66)$$

This is called the spin-symmetry breaking (SSB) stability condition for closed-shell orbitals since the fluctuations given by (63) break the spin-symmetry. Expanding (66), we have

$$\frac{1}{2} \begin{pmatrix} f_{K\tau} \\ f_{K\tau}^* \end{pmatrix}^\dagger \begin{pmatrix} A_{K\tau} & B_{K\tau} \\ B_{K\tau}^* & A_{K\tau}^* \end{pmatrix} \begin{pmatrix} f_{K\tau} \\ f_{K\tau}^* \end{pmatrix} \geq 0, \quad (67)$$

with

$$\begin{aligned} (A_{K\tau})_{ik} &= \langle\text{HF}|S_{\tau,k} H S_{\tau,i}^* - E_0|\text{HF}\rangle \\ (B_{K\tau})_{ik} &= \langle\text{HF}|S_{\tau,k} S_{\tau,i} H|\text{HF}\rangle . \end{aligned} \quad (68)$$

When  $A_{K\tau}$  and  $B_{K\tau}$  matrices are real, the stability condition can be factored into real and imaginary parts:

$$(c) (D_{K\tau}^*)_{kk} = \langle\text{HF}|P_{\tau,k} H P_{\tau,k}^* - E_0 + P_{\tau,k} P_{\tau,k} H|\text{HF}\rangle \geq 0$$

for all  $k$

real SSB stability condition for closed-shell orbitals

$$(d) (D_{K\tau})_{kk} = \langle\text{HF}|Q_{\tau,k} H Q_{\tau,k}^* - E_0 - Q_{\tau,k} Q_{\tau,k} H|\text{HF}\rangle \geq 0$$

for all  $k$

imaginary SSB stability condition for closed-shell orbitals.

(69)

Here the unitary transformed excitation operators  $P_{\tau,k}^*$ ,  $Q_{\tau,k}^*$  are defined in the same manner as (51). These stability conditions ensure that the RHF wavefunction represents a true minimum of the energy functional within the space considered. Now employing the uncoupled approximation, we obtain the approximate SSB instability conditions for closed-shell orbitals

$$(c) E_{\tau,k} - E_0 - K_{kk}^* < 0, \text{ for any } k$$

real SSB instability condition for closed-shell orbitals

$$(d) E_{\tau,k} - E_0 + K_{kk}^* < 0, \text{ for any } k$$

imaginary SSB instability condition for closed-shell orbitals

(70)

where the  $E_{\tau,k}$  is the energy of the singly excited state, which is not an eigenfunction of  $S^2$ ,

$$\begin{aligned} E_{\tau,k} &= \langle\text{HF}|S_{\tau,k} H S_{\tau,k}^*|\text{HF}\rangle, \\ K_{kk}^* &= -\langle\text{HF}|H S_{\tau,k}^* S_{\tau,k}|\text{HF}\rangle . \end{aligned} \quad (71)$$

In case the above conditions are satisfied, the new solution having the lower energy than the RHF energy appears. Such solution breaks the double occupancy of the closed-shell orbitals, therefore the spin-symmetry. From (70), we see that if the imaginary SSB instability condition is satisfied, the singly excited state  $S_{\tau,k}^*|\text{HF}\rangle$  has lower energy than the ground state

$$E_0 - E_{\tau,k} > K_{kk}^* \geq 0 . \quad (72)$$

## 3. The SSP and SSB stability conditions for open-shell orbitals

Next let us consider the stability conditions for the fluctuations mixing open-shell orbitals and virtual orbitals. These fluctuations can be described by the following infinitesimal unitary transformation of the RHF wavefunction

$$\begin{aligned} |\Phi\rangle &= \exp[iF_M]|\text{HF}\rangle \\ F_M &= \frac{1}{i} \sum_{\delta} \sum_m (f_{\delta,m} S_{\delta,m}^* - f_{\delta,m}^* S_{\delta,m}) = F_M^\dagger, \quad (\delta = 0, x) . \end{aligned} \quad (73)$$

The energy for  $|\Phi\rangle$  is given by

$$\begin{aligned} E &= E_0 + i\langle\text{HF}|[H, F_M]|\text{HF}\rangle \\ &+ \frac{i^2}{2!} \langle\text{HF}|[[H, F_M], F_M]|\text{HF}\rangle + \dots \end{aligned} \quad (74)$$

The first order energy shift vanishes due to the Brillouin theorem. The stability condition for the variation given by (73) is

$$\frac{i^2}{2!} \langle \text{HF} | [[H, F_M], F_M] | \text{HF} \rangle \geq 0. \quad (75)$$

Expanding the above condition, we have two independent stability conditions called SSP and SSB stability conditions for open-shell orbitals,

$$\frac{1}{2} \begin{pmatrix} \mathbf{f}_{M0} \\ \mathbf{f}_{M0}^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{A}_{M0} & \mathbf{B}_{M0} \\ \mathbf{B}_{M0}^* & \mathbf{A}_{M0}^* \end{pmatrix} \begin{pmatrix} \mathbf{f}_{M0} \\ \mathbf{f}_{M0}^* \end{pmatrix} \geq 0,$$

SSP stability condition for open-shell orbitals;

$$\frac{1}{2} \begin{pmatrix} \mathbf{f}_{Mx} \\ \mathbf{f}_{Mx}^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{A}_{Mx} & \mathbf{B}_{Mx} \\ \mathbf{B}_{Mx}^* & \mathbf{A}_{Mx}^* \end{pmatrix} \begin{pmatrix} \mathbf{f}_{Mx} \\ \mathbf{f}_{Mx}^* \end{pmatrix} \geq 0,$$

SSB stability condition for open-shell orbitals, (76)

where  $\mathbf{f}_{M0}$  and  $\mathbf{f}_{Mx}$  are the column vectors formed by  $f_{0,m}$  and  $f_{x,m}$ , respectively, and  $\mathbf{A}_M$  and  $\mathbf{B}_M$  matrices are defined as

$$\begin{aligned} (\mathbf{A}_{M0})_{mn} &= \langle \text{HF} | S_{0,m} H S_{0,n}^* - E_0 | \text{HF} \rangle, \\ (\mathbf{B}_{M0})_{mn} &= \langle \text{HF} | S_{0,m} S_{0,n} H | \text{HF} \rangle, \quad (\delta=0, x). \end{aligned} \quad (77)$$

Note here that the diagonal elements of  $\mathbf{B}_M$  matrices are zero due to the Pauli principle. Each stability condition can be factored into real and imaginary parts when the  $\mathbf{A}_M$  and  $\mathbf{B}_M$  matrices are real. Using the diagonal transformations, we can define the new sets of the excitation operators  $P^*$ ,  $Q^*$  and coefficients, as done in (51), (52). Then we have

- (e)  $(\mathbf{D}_{M0}^*)_{mm} = \langle \text{HF} | P_{0,m} H P_{0,m}^* - E_0 | \text{HF} \rangle \geq 0$ , for all  $m$   
real SSP stability condition for open-shell orbitals
- (f)  $(\mathbf{D}_{M0}^-)_{mm} = \langle \text{HF} | Q_{0,m} H Q_{0,m}^* - E_0 | \text{HF} \rangle \geq 0$ , for all  $m$   
imaginary SSP stability condition for open-shell orbitals
- (g)  $(\mathbf{D}_{Mx}^*)_{mm} = \langle \text{HF} | P_{x,m} H P_{x,m}^* - E_0 | \text{HF} \rangle \geq 0$ , for all  $m$   
real SSB stability condition for open-shell orbitals
- (h)  $(\mathbf{D}_{Mx}^-)_{mm} = \langle \text{HF} | Q_{x,m} H Q_{x,m}^* - E_0 | \text{HF} \rangle \geq 0$ , for all  $m$   
imaginary SSB stability condition for open-shell orbitals. (78)

Now we analyze the instability conditions, employing the uncoupled approximation. The uncoupled approximation removes the difference between the real and imaginary conditions of the SSP and SSB instability conditions for open-shell orbitals, since the trace of  $\mathbf{B}_M$  matrices is zero. The uncoupled approximation simplifies the instability conditions to the following form

$$^{s/2} E_{0,m} - E_0 < 0, \quad \text{for any } m$$

SSP instability condition for open-shell orbitals

$$E_{x,m} - E_0 < 0, \quad \text{for any } m$$

SSB instability condition for open-shell orbitals (79)

where

$$\begin{aligned} ^{s/2} E_{0,m} &= \langle \text{HF} | S_{0,m} H S_{0,m}^* | \text{HF} \rangle \\ E_{x,m} &= \langle \text{HF} | S_{x,m} H S_{x,m}^* | \text{HF} \rangle \end{aligned} \quad (80)$$

When these instability conditions are satisfied, the corresponding singly excited states have lower energies than the ground state.

The instability problems for the RHF solution indicate that even if we expand the space spanned by the determinantal functions by introducing the remaining excitation operators (except  $S_{\alpha,h}^*$ ), we cannot go beyond the HF approximation in case the RHF solution is stable. This is the stability dilemma of the open-shell orbital theory.

## B. Stability dilemma and new open-shell orbital theories including electron correlation

The RHF wavefunction is the optimized one within the variational space generated by the real spin-symmetry preserving excitation operators,  $S_{0,h}^*$  and  $S_{0,m}^*$ . Even if we extend the variational space by introducing other excitation operators (except  $S_{\alpha,h}^*$ ), we cannot go beyond the HF approximation in case the RHF solution is stable. This dilemma is called the stability dilemma. In case the RHF solution is unstable, another solution, having lower energy than the RHF energy, must exist. Unfortunately, the corresponding wavefunction is no longer symmetry-adapted. This release from the stability dilemma results in the symmetry dilemma proposed by Löwdin.<sup>17</sup> We have shown in I that the stability dilemma and the symmetry dilemma can be removed by projecting the determinantal wavefunction onto an appropriate symmetry space, i.e., by projecting out the singly-excited functions giving rise to  $A$  matrix. It must be noted that the electron correlation effect can be taken into account within the orbital approximation *only* when the stability dilemma is resolved. In the following, we will go beyond the RHF approximation and construct the open-shell orbital theory including electron correlation.

In general, the stability condition for the wavefunction having the stability dilemma has the form

$$A \pm B \geq 0 \quad (81)$$

as shown in A of this section. On the other hand, it has been shown in I that the stability condition for the wavefunction projected onto an appropriate symmetry space is given by

$$\pm B \geq 0 \quad (82)$$

That is, the  $A$  matrix disappears by virtue of the projection and only the  $B$  matrix remains. The above condition (82) is equivalent to requiring that  $\pm B$  matrix be positive definite. When the trace of  $\pm B$  matrix is non-positive, there always exists at least one negative eigenvalue of  $\pm B$  and the above stability condition (82) can be violated. Thus, we can go beyond the HF approximation. First consider the stability dilemma in closed-shell orbitals. Noting the sign of the  $\mathbf{B}_{K0}$  and  $\mathbf{B}_{Kt}$  matrices defined by (48) and (68),

$$\begin{aligned} \text{Tr}(\mathbf{B}_{K0}) &= \sum_k \langle \text{HF} | S_{0,h} S_{0,h} H | \text{HF} \rangle = \sum_k K_{hh*} \geq 0, \\ \text{Tr}(\mathbf{B}_{Kt}) &= \sum_h \langle \text{HF} | S_{\tau,h} S_{\tau,h} H | \text{HF} \rangle \end{aligned}$$

TABLE I. The open-shell orbital theory:  $|\Phi\rangle = \mathcal{O} \exp[iF_K + iF_M] |0\rangle$ .

	Excitation operators, $F$				Projection operators, $\mathcal{O}$
	$G_{K0}(G_{M0})$	$iH_{K0}(iH_{M0})$	$G_{Kx}(G_{Mx})$	$G_{Ky}(G_{My})$	
RHF	○				
PHF1	○		○		$\mathcal{O}_S \mathcal{O}_M$
PHF2	○	○			$\mathcal{O}_R$
PHF3	○	○	○		$\mathcal{O}_R \mathcal{O}_S \mathcal{O}_M$
PHF4	○	○	○	○	$\mathcal{O}_R \mathcal{O}_S \mathcal{O}_M$

$$= - \sum_k K_{kk^*} \leq 0, \quad (\tau = x, y), \quad (83)$$

where Tr denotes the trace, we see that the imaginary SSP and real SSB stability dilemmas in closed-shell orbitals can be removed by appropriate projection operators. Namely, the imaginary singlet ( $S_{0,k}^*$ ) and real triplet ( $S_{x,k}^*, S_{y,k}^*$ ) closed-shell excitation operators generate the variational spaces for the improvement of the open-shell HF theory for the ground state. On the other hand, the real singlet and imaginary triplet excitation operators reserve the variational space for the excited state. This corresponds to the fact that in both cases the RHF solution is unstable, the corresponding excited states have lower energies than the ground state. Second, consider the open-shell stability dilemmas. The trace of  $\mathbf{B}_M$  matrices is zero due to the Pauli principle. Thus, we can always remove the stability dilemma in open-shell orbitals, if we have the appropriate projection operators to project the determinantal function onto the symmetry space. In this respect, the system where there is no closed-shell orbitals would be interesting to see the role of the open-shell orbitals.<sup>18</sup> When we start with an arbitrary open-shell determinant, not with the RHF wavefunction, the real spin-symmetry preserving excitation operators  $S_{0,k}^*, S_{x,m}^*$  are necessary to produce the RHF wavefunction.

The open-shell orbital theory including the electron correlation effect can be defined as

$$|\Phi\rangle = \mathcal{O} \exp[iF_K + iF_M] |0\rangle, \quad (84)$$

where the  $F_K$  and  $F_M$  are the closed-shell and open-shell excitation operators respectively to generate the variational space. The  $\mathcal{O}$  is the projection operator to remove the stability dilemma. The open-shell stability dilemma can always be resolved and therefore the choice of the open-shell excitation operator  $F_M$  follows that of the closed-shell excitation operator  $F_K$ .<sup>18</sup> By making use of the real singlet ( $G_{K0}$ ), imaginary singlet ( $iH_{K0}$ ) excitation operators and two types of real triplet ( $G_{Kx}, G_{Ky}$ ) excitation operators, we can construct five types of the open-shell orbital theories. They are summarized in Table I, where the PHF denotes the projected HF theory. There are two equivalent orbital theories in the PHF1 and PHF3 theories with the use of either the  $G_{Kx}$  or the  $G_{Ky}$  operators. The PHF1, PHF3, and PHF4 theories are the new orbital theories. Below are outlined some of the orbital theories including electron correlation effects. The analysis and the de-

tailed discussion of these orbital theories will be given in the next section.

### 1. The modified spin extended HF (MSEHF) theory

When we consider one of the real triplet excitation operators, we obtain

$$|\Phi\rangle = \mathcal{O} \exp[iG_{K0} + iG_{Kx} + iG_{M0} + iG_{Mx}] |0\rangle \quad (85)$$

where

$$G_{x,h} = \frac{1}{i} \sum_k g_{x,h} (S_{x,h}^* - S_{x,h})$$

$$G_{x,m} = \frac{1}{i} \sum_m g_{x,m} (S_{x,m}^* - S_{x,m}) \quad (86)$$

The projection operator  $\mathcal{O}$  resolving the SSB stability dilemma takes the form

$$\mathcal{O} = \mathcal{O}_S \mathcal{O}_M \quad (87)$$

where the  $\mathcal{O}_S$  and  $\mathcal{O}_M$  select out the spin-symmetry-adapted component characterized by  $S$  and  $M$

$$S^2 \mathcal{O}_S = \frac{S}{2} \left( \frac{S}{2} + 1 \right) \mathcal{O}_S, \quad S_z \mathcal{O}_M = \frac{S}{2} \mathcal{O}_M \quad (88)$$

This is the function we call the modified spin extended HF (MSEHF) wavefunction. This new orbital theory is a natural extension of the closed-shell SEHF (the alternant molecular orbital theory<sup>19,20</sup>) and removes the defect on the electron correlation problem of the open-shell SEHF theory proposed by Kaldor<sup>21</sup> and Goddard<sup>22</sup> (who refers to this method as GF). The  $\Phi$  in (85) can be rewritten into the determinantal form

$$\Phi = \mathcal{O}_S \mathcal{O}_M \left| \left| \dots (\xi_k \lambda_k + \eta_k \bar{\nu}_k) (\xi_k \bar{\lambda}_k - \eta_k \nu_k) \dots \right. \right. \\ \left. \left. (\xi_m \lambda_m + \eta_m \bar{\nu}_m) \dots \right| \right| \quad (89)$$

Both the spatial orbitals  $\lambda_i, \nu_i$  and the ratio of the coefficients  $\eta_i/\xi_i$  are to be determined variationally. This wavefunction involves the choice of the specific spin coupling represented by  $\Theta^f$  associated with the standard tableaux  $S_1$ .

### 2. Complex general spin orbitals (PHF3)

When we consider the complex singlet excitation operator and one of the real triplet excitation operators at a time, we will obtain the PHF3 function given by

$$|\Phi\rangle = \mathcal{O} \exp[iF_{K0} + iG_{Kx} + iF_{M0} + iG_{Mx}] |0\rangle. \quad (90)$$

The projection operator takes the form in this case as

$$\mathcal{O} = \mathcal{O}_R \mathcal{O}_S \mathcal{O}_M \quad (91)$$

where the  $\mathcal{O}_R$  is the projection operator which selects out the real part of the function. The best possible variationally determined function of the form is called complex general spin orbitals (GSO) theory. The above cluster expansion can be rewritten as

$$\Phi = \mathcal{O} \left| \left| \phi_{1a} \phi_{1b} \dots \phi_{ka} \phi_{kb} \dots \phi_{qa} \phi_{qb} \dots \phi_{ma} \dots \phi_{pa} \right| \right| \quad (92)$$

where

$$\phi_a = \xi_0 \xi_x [\lambda + i(\eta_0/\xi_0)\nu + (\eta_x/\xi_x)\bar{\nu} - i(\eta_0/\xi_0)(\eta_x/\xi_x)\bar{\lambda}]$$

$$\phi_b = \xi_0 \xi_x [\bar{\lambda} + i(\eta_0/\xi_0)\bar{\nu} + (\eta_x/\xi_x)\nu - i(\eta_0/\xi_0)(\eta_x/\xi_x)\lambda]. \quad (93)$$

Both the spatial orbitals and the coefficients are allowed to vary freely so as to minimize the energy. This new wavefunction involves both spin couplings specified by  $\Theta^1$  and  $\Theta^f$ . Thus, the complex GSO theory is a generalization of what we call the complex DODS theory in I.

### 3. Other open-shell orbital theories

If we construct the wavefunction using the complex singlet excitation operators and project out the real part of the wavefunction, we will get the PHF2 wavefunction in Table I. This function is the open-shell complex molecular orbital (CMO) theory.<sup>23</sup> The spin coupling scheme in the CMO wavefunction is the  $\Theta^1$  type associated with standard tableaux  $S_f$ .

From the study of the stability problems of the RHF solution, we see that the RHF solution is always unstable to the DODS type variation generated by  $S_{\alpha,k}^+$  operator. The UHF and SEHF wavefunctions are constructed by making use of this type of excitation operator. The UHF wavefunction is not the symmetry-adapted, namely the spin-symmetry is not preserved. If we project out the symmetry-adapted component of the UHF wavefunction before variation, we have the SEHF wavefunction. The projection operator in (84) not only restores the symmetry properties by projecting out the symmetry-adapted component but also resolves the stability dilemma by violating the stability condition. However, the spin projection operator in the SEHF theory only selects out the symmetry-adapted component and does not help to include the electron correlation effect.<sup>3,4</sup>

## IV. ANALYSIS OF THE NEW OPEN-SHELL ORBITAL THEORIES

In this section, we will analyze the new open-shell orbital theories proposed in the previous section in contrast to the conventional orbital theories in the form of the limited CI based on their own natural orbitals. First, we will analyze the UHF and SEHF theories and examine why these methods are poor for both the electron correlation and the spin correlation. The SEHF theory is a good example to understand the importance of resolving the stability dilemma in orbital theory. Second, we will discuss the MSEHF theory, which is free from the faults which the SEHF theory has. The CMO and the generalized valence bond (GVB)<sup>24</sup> theories will also be examined in terms of their own natural orbitals. Finally, the complex GSO theory will be discussed. This would be the most suitable orbital theory to include the electron correlation effect within the framework of the orbital approximation.

### A. The UHF and SEHF wavefunctions

We now start by considering the UHF wavefunction represented by

$$|\Phi\rangle = \mathcal{N} \exp \left[ \sum_k g_{0,k} S_{0,k}^+ + \sum_k g_{\alpha,k} S_{\alpha,k}^+ + \sum_m g_{0,m} S_{0,m}^+ \right] |0\rangle. \quad (94)$$

If we define the new fermion operators by making a canonical transformation

$$\begin{aligned} c_{0,k}^+ &= (a_k^+ + g'_{0,k} b_k^+) / [1 + (g'_{0,k})^2]^{1/2}, \\ c_{0,k}^{+*} &= (b_k^+ - g'_{0,k} a_k^+) / [1 + (g'_{0,k})^2]^{1/2}, \\ c_{0,m}^+ &= (a_m^+ + g_{0,m} b_m^+) / [1 + (g_{0,m})^2]^{1/2}, \\ c_{0,m}^{+*} &= (b_m^+ - g_{0,m} a_m^+) / [1 + (g_{0,m})^2]^{1/2}, \end{aligned} \quad (95)$$

together with the coefficients

$$\begin{aligned} \xi_k &= 1 / [1 + (g'_{0,k})^2]^{1/2}, \\ \eta_k &= g'_{0,k} / [1 + (g'_{0,k})^2]^{1/2}, \\ \xi_m &= 1 / [1 + (g_{0,m})^2]^{1/2}, \\ \eta_m &= g_{0,m} / [1 + (g_{0,m})^2]^{1/2}, \end{aligned} \quad (96)$$

then we can rewrite the above wavefunction as a determinantal form

$$|\Phi\rangle = \left[ \prod_k c_{k\alpha}^+ c_{k\beta}^+ \right] \left[ \prod_m c_{0,m}^+ \right] |\rangle, \quad (97)$$

where

$$c_k^+ = \xi_k c_{0,k}^+ + \eta_k c_{0,k}^{+*} \sigma_z. \quad (98)$$

We will find it useful to introduce the spatial orbitals  $\lambda_k, \nu_k$  for  $c_{k\alpha}^+$  and  $c_{k\beta}^{+*}$  and  $\lambda_m, \nu_m$  for  $c_{0,m}^+$  and  $c_{0,m}^{+*}$ . All the functions are spatially orthonormal and the reduced density matrix for  $\Phi$  becomes

$$\begin{aligned} \rho(1|2) &= \sum_k 2\xi_k^2 \lambda_k(1) \lambda_k(2) \\ &+ \sum_k 2\eta_k^2 \nu_k(1) \nu_k(2) + \sum_m \lambda_m(1) \lambda_m(2). \end{aligned} \quad (99)$$

These functions  $\lambda_k, \nu_k$  and  $\lambda_m$  are therefore the natural orbitals. Due to the relations that  $\xi_k^2 + \eta_k^2 = 1$ , the  $\xi_k^2$  and  $\eta_k^2$  are the fractional occupation probabilities of the corresponding natural orbitals. If these natural orbitals are replaced by

$$\begin{aligned} \phi_{ka} &= \xi_k \lambda_k + \eta_k \nu_k, \\ \phi_{kb} &= \xi_k \lambda_k - \eta_k \nu_k, \\ \phi_{ma} &= \lambda_m, \end{aligned} \quad (100)$$

then we obtain the expression for  $\Phi$  except the phase factor

$$\Phi = || \phi_{1a} \phi_{2a} \cdots \phi_{pa} \bar{\phi}_{1b} \bar{\phi}_{2b} \cdots \bar{\phi}_{qb} ||. \quad (101)$$

The new orbitals  $\phi$  have the property that their spatial overlap integral is diagonal. These orbitals are called corresponding orbitals.<sup>25</sup> That is, the optimized cluster expansion (94) is the UHF wavefunction for open-shell systems.

Since the  $\eta_k$  are small numbers, we can expand  $\Phi$  by means of the natural orbitals,

$$\Phi = C^{rf} \Phi^{rf} + C^{se} \Phi^{se} + C^{de} \Phi^{de} + \cdots \quad (102)$$

in the form of the limited CI. Here the  $\Phi^{rf}$  is the normalized open-shell restricted function

$$\Phi^{rf} = || \lambda_1 \bar{\lambda}_1 \cdots \lambda_q \bar{\lambda}_q \lambda_{q+1} \cdots \lambda_p || \quad (103)$$

with the coefficient

$$C^{rf} = \prod_k (\xi_k)^2 \quad (104)$$

The  $\Phi^{rf}$  should be approximated as the RHF wavefunction

TABLE II. Energies for He, Li, and Be using SEHF and MSEHF wavefunctions. Recovered correlation energies in percent are in parentheses.

	He	Li	Be
HF	-2.861680	-7.432726	-14.57302
SEHF <sup>a</sup>	-2.877996(39.0)	-7.432813(0.22)	-14.58726(15.1)
MSEHF <sup>b</sup>	-2.877996(39.0)	-7.445176(27.5)	-14.58718(15.0)
Expt. <sup>c</sup>	-2.90378	-7.4780	-14.6674

<sup>a</sup>W. A. Goddard, J. Chem. Phys. 48, 1008 (1968).<sup>b</sup>We solved the variational equations which are correct up to third order in the coefficients (see Ref. 3).<sup>c</sup>E. Clementi, J. Chem. Phys. 38, 2248 (1963).

but, of course, they will not be *identical*. The function  $\Phi^{se}$  is the sum of the normalized singly excited configurations

$$C^{se}\Phi^{se} = \sum_k C^{se}(kk^*)\Phi^{se}(kk^*) \quad (105)$$

with

$$C^{se}(kk^*) = \sqrt{2}(\eta_k/\xi_k) \cdot C^{rf} \\ \Phi^{se}(kk^*) = ||\lambda_1 \bar{\lambda}_1 \dots \nu_k \lambda_k (\alpha\beta + \beta\alpha)/\sqrt{2} \dots \lambda_q \bar{\lambda}_q \lambda_{q+1} \dots \lambda_p || \quad (106)$$

Note here that the singly excited configuration  $\Phi^{se}(kk^*)$  is not an spin eigenfunction and can be expressed as

$$\Phi^{se}(kk^*) = \left(\frac{s}{s+2}\right)^{1/2} s^{1/2} \Phi^{se}(kk^*) + \left(\frac{2}{s+2}\right)^{1/2} (s+2)^{1/2} \Phi^{se}(kk^*) \quad (107)$$

where

$$s^{1/2} \Phi^{se}(kk^*) = ||\nu_k \lambda_k \lambda_{q+1} \dots \lambda_m \dots \lambda_p \Phi_{(s/2)(s/2)}^p || \\ (s+2)^{1/2} \Phi^{se}(kk^*) = ||\nu_k \lambda_k \lambda_{q+1} \dots \lambda_m \dots \lambda_p \Phi_{(s/2+1)(s/2)}^1 || \quad (108)$$

This result is a consequence of the relation given by (13). Thus the  $(s+2)^{1/2} \Phi^{se}(kk^*)$  are the main spin-contaminating configurations of the UHF wavefunction. The higher order terms are given in a similar manner as above. The same expansion of the UHF wavefunction has been given by one of the present authors.<sup>10</sup>

It should be noticed that the open-shell UHF wavefunction always exists by virtue of the configurations of  $s^{1/2} \Phi^{se}(kk^*)$ , which is a striking contrast to the closed-shell UHF wavefunction. That is, the closed-shell UHF wavefunction may exist only when the HF solution is real triplet unstable as shown in I.

Now let us consider the SEHF(GF) theory along the same line given above. The SEHF wavefunction is the optimized one of the form

$$|\Phi\rangle = \mathcal{O}_S \mathcal{N} \exp \left[ \sum_k g_{0,k} S_{0,k}^+ + \sum_k g_{\alpha,k} S_{\alpha,k}^+ + \sum_m g_{0,m} S_{0,m}^+ \right] |0\rangle \\ = \mathcal{O}_S \left[ \prod_k c_{k\alpha}^+ c_{k\beta}^+ \right] \left[ \prod_m c_{0,m\alpha}^+ \right] | \rangle \quad (109)$$

where the  $|\Phi\rangle$  is not necessarily normalized to unity. The  $\mathcal{O}_S$  is the spin projection operator defined by (88).

Expanding  $\Phi$  in terms of the natural orbitals, we obtain, instead of (102), that

$$\Phi = C^{rf} \Phi^{rf} + C^{se} \mathcal{O}_S \Phi^{se} + C^{de} \mathcal{O}_S \Phi^{de} + \dots \quad (110)$$

In the closed-shell SEHF wavefunction, the singly excited configurations vanish due to the projection operator. In open-shell case, however, the singly excited configurations remain even if we operate the projection operator. The singly excited configurations in open-shell SEHF theory take the form

$$\Phi^{se}(kk^*) = \left(\frac{2}{s+2}\right)^{1/2} s^{1/2} \Phi^{se}(kk^*) \quad (111)$$

Note here that the improvement from the RHF energy originates mainly from the singly excited configurations, not from the doubly excited configurations. In other words, the open-shell SEHF theory takes the orbital correction into account but it does not involve the electron correlation through the two-body interactions. Thus, the closed-shell and open-shell SEHF theories are constructed on a quite different approximation. The correlation energies for He and Be (closed-shell) and Li (open-shell) calculated by the SEHF method in Table II also confirm the above conclusion.

Now there arises a problem. What is the open-shell orbital theory which is equivalent to the closed-shell SEHF approximation? In the latter, we will answer the question.

In connection with the spin correlation problem, we examine the  $S_{\alpha,k}^+$  operator in more detail. As shown in (13), the  $S_{\alpha,k}^+$  operator is a sum of the spin-adapted excitation operators,  $s^{1/2} S_{p,k}^+$  and  $(s+2)^{1/2} S_{1,k}^+$ . If the  $S_{\alpha,k}^+$  operators are replaced by  $s^{1/2} S_{p,k}^+$  operators in (109), the resultant wavefunction constitutes our previous pseudo-orbital theory,

$$|\Phi\rangle = \mathcal{O}_S \mathcal{N} \exp \left[ \sum_k g_{0,k} S_{0,k}^+ + \sum_k g_{\alpha,k} s^{1/2} S_{p,k}^+ + \sum_m g_{0,m} S_{0,m}^+ \right] |0\rangle \quad (112)$$

The pseudo-orbital theory involves the spin correlation correctly, as discussed in our previous papers.<sup>4</sup> On the other hand, if the  $(s+2)^{1/2} S_{1,k}^+$  operators are considered instead of the  $S_{\alpha,k}^+$ , we have

$$|\Phi\rangle = \mathcal{O}_S \mathcal{N} \exp \left[ \sum_k g_{0,k} S_{0,k}^+ + \sum_k g_{s,k} {}^{(s+2)/2} S_{1,k}^+ + \sum_m g_{0,m} S_{0,m}^+ \right] |0\rangle. \quad (113)$$

The unprojected wavefunction of (113) has the stability dilemma, unlike the SEHF wavefunction, and the projection operator solves the dilemma. Thus, the electron correlation effect can be included in the above wavefunction. These discussions indicate that when the two excitation operators  ${}^{s/2} S_{p,k}^+$  and  ${}^{(s+2)/2} S_{1,k}^+$  are treated independently, both the electron and spin correlations will be included. However, when these two operators are combined to yield the  $S_{x,k}^+$  operator like the SEHF theory, both electron and spin correlation effects interfere with each other as discussed previously and both corrections become poor. The stability dilemma could never occur in the unprojected SEHF (e.g., UHF) wavefunction due to the existence of the  ${}^{s/2} S_{p,k}^+$  operators and the unlinked clusters of the spin polarization excitation operators should be distorted by those of the  ${}^{(s+2)/2} S_{1,k}^+$  operators, which leads to the unphysical nature of the self-consistency terms of the spin correlation effect. That is, there is a serious interference between the spin correlation and the electron correlation effects in the open-shell SEHF theory.<sup>3,4</sup> Thus, the open-shell SEHF theory is poor for both electron and spin correlation problems.

## B. The modified SEHF wavefunction

Next, consider the MSEHF wavefunction represented by

$$|\Phi\rangle = \mathcal{N} \exp \left[ \sum_k g_{0,k} S_{0,k}^+ + \sum_k g_{x,k} S_{x,k}^+ + \sum_m g_{0,m} S_{0,m}^+ + \sum_m g_{x,m} S_{x,m}^+ \right] |0\rangle. \quad (114)$$

The above wavefunction can be rewritten as

$$|\Phi\rangle = \left[ \prod_k c_{k\alpha}^* c_{k\beta}^* \right] \left[ \prod_m c_{m\alpha}^* \right] |\rangle, \quad (115)$$

where

$$\begin{aligned} c_k^* &= (c_{0,k}^* + g'_{x,k} c_{0,k}^* \sigma_x) / [1 + (g'_{x,k})^2]^{1/2}, \\ c_m^* &= (c_{0,m}^* + g_{x,m} c_{0,m}^* \sigma_x) / [1 + (g_{x,m})^2]^{1/2}. \end{aligned} \quad (116)$$

If we define the coefficients in a similar manner as (96)

$$\begin{aligned} \xi_k &= 1/[1 + (g'_{x,k})^2]^{1/2}, \\ \eta_k &= g'_{x,k}/[1 + (g'_{x,k})^2]^{1/2}, \\ \xi_m &= 1/[1 + (g_{x,m})^2]^{1/2}, \\ \eta_m &= g_{x,m}/[1 + (g_{x,m})^2]^{1/2}, \end{aligned} \quad (117)$$

then we have

$$\Phi = \left| \cdots (\xi_k \lambda_k + \eta_k \bar{\nu}_k) (\xi_k \bar{\lambda}_k + \eta_k \nu_k) \cdots (\xi_m \lambda_m + \eta_m \bar{\nu}_m) \cdots \right|. \quad (118)$$

Here the spatial orbitals are defined in a same manner as in (A). These functions  $\lambda_k$ ,  $\nu_k$ ,  $\lambda_m$ ,  $\nu_m$  are again the natural orbitals. The  $\Phi$  has the troubles of the stability

dilemma and the symmetry dilemma. Thus, we must project the  $\Phi$  onto the symmetry space, namely

$$|\Phi'\rangle = \mathcal{O}_S \mathcal{O}_M |\Phi\rangle. \quad (119)$$

We find that the  $\Phi'$  is equivalent to the limited CI based on its own natural orbitals,

$$\Phi' = C^{\text{rf}} \Phi^{\text{rf}} + C^{\text{de}} \mathcal{O}_S \Phi^{\text{de}} + \cdots \quad (120)$$

The leading term  $\Phi^{\text{rf}}$  is a restricted function with the coefficient  $C^{\text{rf}} = [\prod_k \xi_k^2] [\prod_m \xi_m]$ . The singly excited configurations vanish due to the projection operator  $\mathcal{O}_M$ . The doubly excited configurations are given by

$$\begin{aligned} C^{\text{de}} \mathcal{O}_S \Phi^{\text{de}} &= \sum_k C^{\text{de}}(kk^*) \Phi^{\text{de}}(kk^*) \\ &+ \sum_{k < l} \sum C^{\text{de}}(kk^*; ll^*) \mathcal{O}_S \Phi^{\text{de}}(kk^*; ll^*) \\ &+ \sum_k \sum_m C^{\text{de}}(kk^*; mm^*) \mathcal{O}_S \Phi^{\text{de}}(kk^*; mm^*) \end{aligned} \quad (121)$$

with

$$C^{\text{de}}(kk^*) = -(\eta_k/\xi_k)^2 C^{\text{rf}},$$

$$\Phi^{\text{de}}(kk^*) = \left| \lambda_1 \bar{\lambda}_1 \cdots \nu_k \bar{\nu}_k \cdots \lambda_q \bar{\lambda}_q \lambda_{q+1} \cdots \lambda_p \right|,$$

$$C^{\text{de}}(kk^*; ll^*) = -\sqrt{2} (\eta_k/\xi_k) (\eta_l/\xi_l) C^{\text{rf}},$$

$$\Phi^{\text{de}}(kk^*; ll^*)$$

$$= \left| \nu_k \lambda_k \nu_l \lambda_l \lambda_{q+1} \cdots \lambda_p (\alpha \alpha \beta \beta + \beta \beta \alpha \alpha) \alpha \cdots \alpha / \sqrt{2} \right|,$$

$$C^{\text{de}}(kk^*; mm^*) = (\eta_k/\xi_k) (\eta_m/\xi_m) C^{\text{rf}},$$

$$\Phi^{\text{de}}(kk^*; mm^*) = \left| \nu_k \lambda_k \lambda_{q+1} \cdots \nu_m \cdots \lambda_p \alpha \alpha \alpha \cdots \beta \cdots \alpha \right|. \quad (122)$$

The projection operator  $\mathcal{O}_S$  selects out the spin eigenfunctions according to the relations

$$\mathcal{O}_S (\alpha \alpha \beta \beta + \beta \beta \alpha \alpha) \alpha \cdots \alpha / \sqrt{2} = \left[ \frac{s+1}{2(s+3)} \right]^{1/2} \cdot P_1 \Theta_{(s/2)(s/2)}^f,$$

$$\mathcal{O}_S \alpha \alpha \alpha \cdots \beta \cdots \alpha = \left( \frac{s+1}{s+2} \right)^{1/2} P_2 \Theta_{(s/2)(s/2)}^f, \quad (123)$$

where the permutation operators  $P_1$ ,  $P_2$  are defined, in this case, as

$$\begin{aligned} P_1 &= (1 \ s+3)(2 \ s+4) + (3 \ s+3)(4 \ s+4), \\ P_2 &= (m - q + 2 \ s+2). \end{aligned} \quad (124)$$

The higher order terms are given in a similar manner as above. Note again that the singly excited configurations vanish and the doubly excited configurations involve the spin coupling of  $\Theta^f$  associated with the standard tableaux  $S_1$ . Thus, this orbital theory involves two-body interactions through the unlinked clusters of the excitation operators  $S_{x,k}^+$  and is equivalent to the closed-shell SEHF approximation. We call this orbital theory as the modified SEHF theory. Preliminary calculation on Li in Table II indicates that the MSEHF correlation energy of the three-electron open-shell atom is comparable with those of the two- and four-electron closed-shell atoms.

### C. The CMO and GVB wavefunctions

Now consider the CMO wavefunction<sup>23</sup> defined by

$$|\Phi\rangle = \mathcal{O}_R \mathcal{N} \exp \left[ \sum_k f_{0,k} S_{0,k}^+ + \sum_m f_{0,m} S_{0,m}^+ \right] |0\rangle \\ = \mathcal{O}_R \left[ \prod_k c_{k\alpha}^+ c_{k\beta}^+ \right] \left[ \prod_m c_{m\alpha}^+ \right] |\rangle, \quad (125)$$

where

$$c_k^+ = (c_{0,k}^+ + i h'_{0,k} c_{0,k*}^+) / [1 + (h'_{0,k})^2]^{1/2}, \\ c_m^+ = (c_{0,m}^+ + i h_{0,m} c_{0,m*}^+) / [1 + (h_{0,m})^2]^{1/2}, \quad (126)$$

Let us define  $\xi_k$ ,  $\eta_k$ ,  $\xi_m$ , and  $\eta_m$  as in (117)

$$\xi_k = 1/[1 + (h'_{0,k})^2]^{1/2}, \\ \eta_k = h'_{0,k}/[1 + (h'_{0,k})^2]^{1/2}, \\ \xi_m = 1/[1 + (h_{0,m})^2]^{1/2}, \\ \eta_m = h_{0,m}/[1 + (h_{0,m})^2]^{1/2}. \quad (127)$$

Further, let  $\lambda_k$ ,  $\nu_k$  be the spatial orbitals for  $c_{0,k}^+$  and  $c_{0,k*}^+$  and  $\lambda_m$ ,  $\nu_m$  for  $c_{0,m}^+$  and  $c_{0,m*}^+$ . These functions are again the natural orbitals. Then, we can rewrite the CMO wavefunction by means of paired-orbitals as done in I,

$$\Phi = \mathcal{O}_R || \phi_{11} \phi_{22} \cdots \phi_{qq} \phi_{q+1} \cdots \phi_p (\alpha\beta - \beta\alpha) \\ \cdots (\alpha\beta - \beta\alpha) \alpha \cdots \alpha / \sqrt{2q} ||, \quad (128)$$

where

$$\phi_{kk} = (\xi_k \lambda_k + \eta_k \nu_k) (\xi_k \lambda_k - \eta_k \nu_k) / \sqrt{2} + \sqrt{2} i \xi_k \eta_k \lambda_k \nu_k, \\ \phi_m = \xi_m \lambda_m + i \eta_m \nu_m. \quad (129)$$

The CMO wavefunction is expanded in terms of its own natural orbitals,

$$\Phi = C^{rf} \Phi^{rf} + C^{de} \Phi^{de} + \cdots \quad (130)$$

in the limited CI form. The  $\Phi^{rf}$  is again the restricted function with  $C^{rf} = [\Pi_k \xi_k^2] [\Pi_m \xi_m]$ . The singly excited configurations do not appear because of their pure imaginary property. The  $\Phi^{de}$  is a sum of the doubly excited configurations:

$$C^{de} \Phi^{de} = \sum_k C^{de}(kk^*; \Phi^{de}(kk^*)) \\ + \sum_{k < l} C^{de}(kk^*; ll^*) \Phi^{de}(kk^*; ll^*) \\ + \sum_{m < n} C^{de}(mm^*; nn^*) \Phi^{de}(mm^*; nn^*) \\ + \sum_k \sum_m C^{de}(kk^*; mm^*) \Phi^{de}(kk^*; mm^*), \quad (131)$$

where

$$C^{de}(kk^*) = -(\eta_k/\xi_k)^2 C^{rf}, \\ \Phi^{de}(kk^*) = || \lambda_1 \bar{\lambda}_1 \cdots \nu_k \bar{\nu}_k \cdots \lambda_q \bar{\lambda}_q \lambda_{q+1} \cdots \lambda_p ||, \\ C^{de}(kk^*; ll^*) = -2(\eta_k/\xi_k)(\eta_l/\xi_l) C^{rf}, \\ \Phi^{de}(kk^*; ll^*) \\ = || \nu_k \lambda_k \nu_l \lambda_l \lambda_{q+1} \cdots \lambda_p (\alpha\beta - \beta\alpha) (\alpha\beta - \beta\alpha) \alpha \cdots \alpha / 2 ||, \\ C^{de}(mm^*; nn^*) = -(\eta_m/\xi_m)(\eta_n/\xi_n) C^{rf}, \\ \Phi^{de}(mm^*; nn^*) = || \lambda_1 \bar{\lambda}_1 \cdots \lambda_q \bar{\lambda}_q \lambda_{q+1} \cdots \nu_m \cdots \nu_n \cdots \lambda_p ||,$$

$$C^{de}(kk^*; mm^*) = -\sqrt{2}(\eta_k/\xi_k)(\eta_m/\xi_m) C^{rf}, \\ \Phi^{de}(kk^*; mm^*) \\ = || \nu_k \lambda_k \lambda_{q+1} \cdots \nu_m \cdots \lambda_p (\alpha\beta - \beta\alpha) \alpha \cdots \alpha / \sqrt{2} ||. \quad (132)$$

The higher order terms are given in a similar manner as above. Thus, the CMO wavefunction involves the singlet type spin couplings  $\Theta^1$  associated with the standard tableaux  $S_f$ .

The GVB wavefunction<sup>24</sup> is also given by a cluster expansion method

$$|\Phi\rangle = \mathcal{N} \exp \left[ \sum_k g_{0,k} S_{0,k}^+ + \frac{1}{2} \sum_k (i h_{0,k} S_{0,k}^+)^2 \right. \\ \left. + \sum_m g_{0,m} S_{0,m}^+ \right] |0\rangle \\ = \left[ \prod_k c_{kk}^+ \right] \left[ \prod_m c_{0,m\alpha}^+ \right] |\rangle, \quad (133)$$

where the  $c_{kk}^+$  are the two-particle creation operators,

$$c_{kk}^+ = [c_{0,k\alpha}^+ c_{0,k\beta}^+ - (h'_{0,k})^2 c_{0,k*}^+ c_{0,k*}^+] / \\ [1 + (h'_{0,k})^4]^{1/4}. \quad (134)$$

If we define

$$\xi_k = 1/[1 + (h'_{0,k})^4]^{1/4}, \\ \eta_k = h'_{0,k}/[1 + (h'_{0,k})^4]^{1/4}, \quad (135)$$

together with the spatial orbitals  $\lambda_k$ ,  $\nu_k$  for  $c_{0,k}^+$  and  $c_{0,k*}^+$ , then we have

$$\Phi = || \phi_{1a} \phi_{1b} \cdots \phi_{qa} \phi_{qb} \phi_{q+1} \cdots \phi_p (\alpha\beta - \beta\alpha) \\ \cdots (\alpha\beta - \beta\alpha) \alpha \cdots \alpha / \sqrt{2q} ||. \quad (136)$$

Here we set

$$\phi_{ka} = \xi_k \lambda_k + \eta_k \nu_k \\ \phi_{kb} = \xi_k \lambda_k - \eta_k \nu_k \\ \phi_m = \lambda_m. \quad (137)$$

The  $\phi_{ka}$  and  $\phi_{kb}$  satisfy the strong orthogonality condition.<sup>26</sup> Thus, the optimized  $\Phi$  in (133) is the GVB wavefunction for open-shell systems. The GVB wavefunction is also expanded as a limited CI based on its own natural orbitals,

$$\Phi = C^{rf} \Phi^{rf} + C^{de} \Phi^{de} + \cdots \quad (138)$$

This expansion is analogous to those of the MSEHF and CMO wavefunctions. However, the  $\Phi^{de}$  in (138) only contains the paired-type doubly excited configurations  $\Phi^{de}(kk^*)$  and no such terms as  $\Phi^{de}(kk^*; ll^*)$  and  $\Phi^{de}(kk^*; mm^*)$ .

### D. Complex GSO wavefunction

Last, we consider the new orbital theory, PHF3, given by the cluster expansion

$$|\Phi\rangle = \mathcal{O} \mathcal{N} \exp \left[ \sum_k f_{0,k} S_{0,k}^+ + \sum_k g_{x,k} S_{x,k}^+ \right. \\ \left. + \sum_m f_{0,m} S_{0,m}^+ + \sum_m g_{x,m} S_{x,m}^+ \right] |0\rangle \quad (139)$$

The projection operator  $\mathcal{O}$ , which solves the stability



dilemma, takes the form  $\mathcal{O} = \mathcal{O}_R \mathcal{O}_S \mathcal{O}_M$ . The  $|\Phi\rangle$  can be rewritten as a determinantal form

$$|\Phi\rangle = \mathcal{O} \left[ \prod_k c_{k\alpha}^* c_{k\beta}^* \right] \left[ \prod_m c_{m\alpha}^* \right] | \rangle, \quad (140)$$

where

$$\begin{aligned} c_k^* &= [(c_{0,k}^* + g'_{x,k} c_{0,k}^* \sigma_x) + i h'_{0,k} (c_{0,k}^* - g'_{x,k} c_{0,k}^* \sigma_x)] \\ &\quad \times 1/[1 + (h'_{0,k})^2 (1 + (g'_{x,k})^2)^{1/2}] \\ c_m^* &= [(c_{0,m}^* + g_{x,m} c_{0,m}^* \sigma_x) + i h_{0,m} (c_{0,m}^* - g_{x,m} c_{0,m}^* \sigma_x)] \\ &\quad \times 1/[1 + (h_{0,m})^2 (1 + (g_{x,m})^2)^{1/2}]. \end{aligned} \quad (141)$$

If we define

$$\begin{aligned} \xi_{0,k} &= 1/[1 + (h'_{0,k})^2]^{1/2}, \\ \eta_{0,k} &= h'_{0,k}/[1 + (h'_{0,k})^2]^{1/2}, \\ \xi_{x,k} &= 1/[1 + (g'_{x,k})^2]^{1/2}, \\ \eta_{x,k} &= g'_{x,k}/[1 + (g'_{x,k})^2]^{1/2}, \\ \xi_{0,m} &= 1/[1 + (h_{0,m})^2]^{1/2}, \\ \eta_{0,m} &= h_{0,m}/[1 + (h_{0,m})^2]^{1/2}, \\ \xi_{x,m} &= 1/[1 + (g_{x,m})^2]^{1/2}, \\ \eta_{x,m} &= g_{0,m}/[1 + (g_{x,m})^2]^{1/2}, \end{aligned} \quad (142)$$

then we have

$$\begin{aligned} c_k^* &= \xi_{0,k} \xi_{x,k} [c_{0,k}^* + i(\eta_{0,k}/\xi_{0,k}) c_{0,k}^* + (\eta_{x,k}/\xi_{x,k}) c_{0,k}^* \sigma_x \\ &\quad - i(\eta_{0,k}/\xi_{0,k})(\eta_{x,k}/\xi_{x,k}) c_{0,k}^* \sigma_x], \\ c_m^* &= \xi_{0,m} \xi_{x,m} [c_{0,m}^* + i(\eta_{0,m}/\xi_{0,m}) c_{0,m}^* + (\eta_{x,m}/\xi_{x,m}) c_{0,m}^* \sigma_x \\ &\quad - i(\eta_{0,m}/\xi_{0,m})(\eta_{x,m}/\xi_{x,m}) c_{0,m}^* \sigma_x]. \end{aligned} \quad (143)$$

It is convenient to introduce the spatial orbitals  $\lambda_k$ ,  $\nu_k$ ,  $\lambda_m$ , and  $\nu_m$ . In terms of these natural orbitals, we obtain

$$\Phi = C^{\text{rf}} \Phi^{\text{rf}} + C^{\text{de}} \Phi^{\text{de}} + \dots, \quad (144)$$

where the leading term is again the open-shell restricted function

$$\begin{aligned} \Phi^{\text{rf}} &= ||\lambda_1 \bar{\lambda}_1 \cdots \lambda_q \bar{\lambda}_q \lambda_{q+1} \cdots \lambda_p|| \\ C^{\text{rf}} &= \left\{ \prod_k [(\xi_{0,k} \xi_{x,k})^2 + (\eta_{0,k} \eta_{x,k})^2] \right\} \left\{ \prod_m \xi_{0,m} \xi_{x,m} \right\}. \end{aligned} \quad (145)$$

The singly excited configurations vanish due to the projection operators. The  $\Phi^{\text{de}}$  is a sum of the doubly excited configurations:

$$\begin{aligned} C^{\text{de}} \Phi^{\text{de}} &= \sum_k C^{\text{de}}(kk^*; \Phi^{\text{de}}(kk^*)) + \sum_{k < l} \sum C^{\text{de}}(kk^*; ll^*) \Phi_0^{\text{de}}(kk^*; ll^*) \\ &\quad + \sum_{k < l} \sum C_x^{\text{de}}(kk^*; ll^*) \Phi_x^{\text{de}}(kk^*; ll^*) + \sum_{m < n} \sum C^{\text{de}}(mm^*; nn^*) \Phi^{\text{de}}(mm^*; nn^*) \\ &\quad + \sum_k \sum_m C_0^{\text{de}}(kk^*; mm^*) \Phi_0^{\text{de}}(kk^*; mm^*) + \sum_k \sum_m C_x^{\text{de}}(kk^*; mm^*) \Phi_x^{\text{de}}(kk^*; mm^*), \end{aligned} \quad (146)$$

where

$$\begin{aligned} C^{\text{de}}(kk^*) &= -[(\eta_{0,k}/\xi_{0,k})^2 + (\eta_{x,k}/\xi_{x,k})^2] \\ &\quad \times 1/[1 + (\eta_{0,k}/\xi_{0,k})^2 (\eta_{x,k}/\xi_{x,k})^2] C^{\text{rf}}, \\ \Phi^{\text{de}}(kk^*) &= ||\lambda_1 \bar{\lambda}_1 \cdots \nu_k \bar{\nu}_k \cdots \lambda_q \bar{\lambda}_q \lambda_{q+1} \cdots \lambda_p||, \\ C_0^{\text{de}}(kk^*; ll^*) &= -X_k X_l C^{\text{rf}}, \\ \Phi_0^{\text{de}}(kk^*; ll^*) &= ||\nu_k \lambda_k \nu_l \lambda_l \alpha_{q+1} \cdots \lambda_p (\alpha\beta - \beta\alpha) (\alpha\beta - \beta\alpha) \alpha \cdots \alpha/2||, \\ C_x^{\text{de}}(kk^*; ll^*) &= -Y_k Y_l C^{\text{rf}}, \\ \Phi_x^{\text{de}}(kk^*; ll^*) &= ||\nu_k \lambda_k \nu_l \lambda_l \alpha_{q+1} \cdots \lambda_p P_l \Theta_{(s/2)(s/2)}^f||, \\ &= \left[ \frac{s+1}{2(s+3)} \right]^{1/2} \cdot ||\nu_k \lambda_k \nu_l \lambda_l \alpha_{q+1} \cdots \lambda_p P_l \Theta_{(s/2)(s/2)}^f||, \\ C^{\text{de}}(mm^*; nn^*) &= -(\eta_{0,m}/\xi_{0,m})(\eta_{0,n}/\xi_{0,n}) C^{\text{rf}}, \\ \Phi^{\text{de}}(mm^*; nn^*) &= ||\lambda_1 \bar{\lambda}_1 \cdots \lambda_q \bar{\lambda}_q \lambda_{q+1} \cdots \nu_m \cdots \nu_n \cdots \lambda_p||, \\ C_0^{\text{de}}(kk^*; mm^*) &= -X_x (\eta_{0,m}/\xi_{0,m}) C^{\text{rf}}, \\ \Phi_0^{\text{de}}(kk^*; mm^*) &= ||\nu_k \lambda_k \lambda_{q+1} \cdots \nu_m \cdots \lambda_p (\alpha\beta - \beta\alpha) \alpha \cdots \alpha \cdots \alpha/\sqrt{2}||, \\ C_x^{\text{de}}(kk^*; mm^*) &= -Y_x (\eta_{0,m}/\xi_{0,m}) C^{\text{rf}}, \end{aligned}$$

$$\Phi_x^{\text{de}}(kk^*; mm^*)$$

$$= \left( \frac{s+1}{s+2} \right)^{1/2} ||\nu_k \lambda_k \lambda_{q+1} \cdots \nu_m \cdots \lambda_p P_2 \Theta_{(s/2)(s/2)}^f||, \quad (147)$$

where the permutation operators  $P_1$  and  $P_2$  for spins are defined in (124). We set in (147)

$$\begin{aligned} X_x &= \sqrt{2} (\eta_{0,k}/\xi_{0,k}) [1 + (\eta_{x,k}/\xi_{x,k})^2] / \\ &\quad [1 + (\eta_{0,k}/\xi_{0,k})^2 (\eta_{x,k}/\xi_{x,k})^2] \\ Y_k &= \sqrt{2} (\eta_{x,k}/\xi_{x,k}) [1 - (\eta_{0,k}/\xi_{0,k})^2] / \\ &\quad [1 + (\eta_{0,k}/\xi_{0,k})^2 (\eta_{x,k}/\xi_{x,k})^2]. \end{aligned} \quad (148)$$

We see that the doubly excited configurations in PHF3 wavefunction involve two types of the independent spin eigenfunctions, that is, the singlet type  $\Theta^1$  and the spin polarization type  $\Theta^f$ . Thus, this orbital theory, complex GSO theory, leads to lower energy than the other orbital theories discussed above. This orbital theory is a generalization of what we call complex DODS in I.

The limited CI in terms of natural orbitals can be used to examine the internal relationships of various open-shell orbital theories. The leading excited configurations are most important since the higher order

TABLE III. The leading excited configurations in the limited CI based on the natural orbitals of various open-shell wavefunctions for the doublet spin state.

	Singly excited configurations	Doubly excited configurations
UHF	$\ \nu_k \lambda_k \lambda_m (\alpha\beta + \beta\alpha) \alpha / \sqrt{2}\ $	
SEHF	$\ \nu_k \lambda_k \lambda_m (\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta) / \sqrt{6}\ $	
GVB		$\ \nu_k \nu_k \lambda_m \alpha\beta\alpha\ $
MSEHF		$\ \nu_k \nu_k \lambda_m \alpha\beta\alpha\ $
		$\ \nu_k \lambda_k \nu_l \lambda_l \lambda_m \{ (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)\beta - (\alpha\beta\beta + \beta\alpha\beta - 2\beta\beta\alpha)\alpha \} / \sqrt{12}\ $
CMO		$\ \nu_k \lambda_k \nu_m (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) / \sqrt{6}\ $
		$\ \nu_k \nu_k \lambda_m \alpha\beta\alpha\ $
Complex GSO		$\ \nu_k \lambda_k \nu_l \lambda_l \lambda_m (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \alpha / 2\ $
		$\ \nu_k \lambda_k \nu_m (\alpha\beta - \beta\alpha) \alpha / \sqrt{2}\ $
		$\ \nu_k \nu_k \lambda_m \alpha\beta\alpha\ $
		$\ \nu_k \lambda_k \nu_l \lambda_l \lambda_m (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \alpha / 2\ $
		$\ \nu_k \lambda_k \nu_l \lambda_l \lambda_m \{ (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)\beta - (\alpha\beta\beta + \beta\alpha\beta - 2\beta\beta\alpha)\alpha \} / \sqrt{12}\ $
		$\ \nu_k \lambda_k \nu_m (\alpha\beta - \beta\alpha) \alpha / \sqrt{2}\ $
		$\ \nu_k \lambda_k \nu_m (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) / \sqrt{6}\ $

terms arise just from the self-consistency effects. In Table III, we summarized the leading excited configurations in the limited CI expansion for various orbital theories with the doublet spin state. We can expect from this the following relation

$$E^{\text{complex GSO}} \leq E^{\text{CMO}} \leq E^{\text{MSEHF}} \leq E^{\text{GVB}} \ll E^{\text{SEHF}}, E^{\text{UHF}} \quad (149)$$

Note that the above relation stands on the two basic assumptions. The first is that natural orbitals  $\lambda_k$ ,  $\nu_k$ ,  $\lambda_m$ , and  $\nu_m$  defined in each orbital theory are not identical but similar. The second assumption is that the singlet type spin coupling may cause the lower energy than the corresponding spin polarization type spin coupling, since the former might be thought as representing covalent bonds but the latter is not in keeping our intuitive idea such as electron pair bonds.

## V. SUMMARY

The one-particle cluster expansion of a wavefunction is a useful expression to construct and to analyze the orbital theory. In this paper, we applied the previously developed new approach to the orbital theory to open-shell systems and construct the open-shell orbital theory including the electron correlation effects. New orbital theories, the MSEHF theory and complex GSO theory, have been presented. They are analyzed in contrast to the conventional orbital theories such as UHF, SEHF, CMO, and GVB theories in the form of the limited CI based on their own natural orbitals. The MSEHF theory includes effectively the correlation effects in open-shell systems and constitutes a natural extension of the closed-shell SEHF theory (the conventional SEHF theory fails in open-shell systems). The complex GSO theory is a generalization of what we call the complex DODS in I. This orbital theory is the most

suitable orbital theory to include the electron correlation effect within the orbital approximation.

We hope and expect that the present work will suggest new viewpoints and approaches to the open-shell orbital theory.

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## APPENDIX: THE RHF WAVEFUNCTION AND THE VARIATIONAL EQUATIONS

The restricted Slater determinantal function is used in the present formalism as a reference wavefunction. We investigate here its primitive cluster expansion form. In the previous paper,<sup>3</sup> we showed that the RHF wavefunction is expressed as

$$|\Phi\rangle = \pi \alpha_{KM} \exp \left[ \sum_K C_K S_K^+ \right] |\Phi_{0,K}\rangle \exp \left[ \sum_M C_M S_M^+ \right] |\Phi_{0,M}\rangle \quad (A1)$$

by making use of the symmetry-adapted excitation operators. Here  $|\Phi_{0,K}\rangle$ ,  $|\Phi_{0,M}\rangle$  are arbitrary single determinants for the closed and open blocks, respectively and the  $S_K^+$ ,  $S_M^+$  represent the singlet-type excitation operators for the excitation from the corresponding blocks to all other blocks. The  $\alpha_{KM}$  denotes the antisymmetrizer for the interchange of electrons between the closed and open blocks. The reason that we have used different exponential operators for different blocks is that the excitation operators belonging to the dif-

ferent blocks do not necessarily commute with each other.

Here we relax the restriction that the symmetry-adapted excitation operators should be used and represent a general restricted Slater determinant in a single exponential form. Let us consider the cluster expansion of the form

$$|\Phi\rangle = \mathcal{N} \exp \left[ \sum_{tk} C_{tk} (a_{t\alpha}^* a_{k\alpha} + a_{t\beta}^* a_{k\beta}) + \sum_{tm} C_{tm} a_{t\alpha}^* a_{m\alpha} + \sum_{km} C_{km} (a_{m\beta}^* + \sum_t C_{tm} a_{t\beta}^*) a_{k\beta} \right] |0\rangle. \quad (\text{A2})$$

where the coefficients  $C$  are assumed to be real. This can be rewritten as

$$|\Phi\rangle = \left[ \prod_k A_{k\alpha}^* \frac{A_{k\beta}^* + \sum_m \tilde{C}_{mk} A_{m\beta}^*}{(1 + \sum_m \tilde{C}_{mk}^2)^{1/2}} \right] \left[ \prod_m A_{m\alpha}^* \right] |0\rangle \quad (\text{A3})$$

where

$$\begin{aligned} A_k^* &= (a_k^* + \sum_t C_{tk} a_t^*) / \left[ 1 + \sum_t (C_{tk})^2 \right]^{1/2} \\ A_m^* &= (a_m^* + \sum_t C_{tm} a_t^*) / \left[ 1 + \sum_t (C_{tm})^2 \right]^{1/2} \\ \tilde{C}_{mk} &= C_{mk} \left[ \left( 1 + \sum_t (C_{tm})^2 \right) / \left( 1 + \sum_t (C_{tk})^2 \right) \right]^{1/2}. \end{aligned} \quad (\text{A4})$$

A unitary transformation of the  $\alpha$ -spin orbitals leaves  $|\Phi\rangle$  unchanged since it is a determinant. Thus, we have

$$|\Phi\rangle = \left[ \prod_k \tilde{A}_{k\alpha}^* \tilde{A}_{k\beta}^* \right] \left[ \prod_m \tilde{A}_{m\alpha}^* \right] |0\rangle \quad (\text{A5})$$

where

$$\begin{aligned} \tilde{A}_k^* &= (\tilde{A}_k^* + \sum_m \tilde{C}_{mk} A_m^*) / \left[ 1 + \sum_m (\tilde{C}_{mk})^2 \right]^{1/2} \\ \tilde{A}_m^* &= (A_m^* - \sum_k \tilde{C}_{km} \tilde{A}_k^*) / \left[ 1 + \sum_k (\tilde{C}_{km})^2 \right]^{1/2} \end{aligned} \quad (\text{A6})$$

with  $\tilde{C}_{mk} = \tilde{C}_{km}$ . It should be noticed that the double occupancy of the closed-shell orbitals is preserved. Thus, the cluster expansion of the wavefunction (A2) gives the general *restricted* open-shell determinant. The uniquely determined optimal determinant is the RHF wavefunction.

Now we consider the variational determination of the RHF wavefunction. The energy of the system  $E$  is a function of parameters  $C$  which are embedded in  $\Phi$ . The variational equation for  $\Phi$  is given by

$$\langle \Phi | (H - E) | \delta\Phi \rangle = 0 \quad (\text{A7})$$

where

$$\delta\Phi = \sum_i (\delta C_i / \delta C_i) \delta C_i \quad (\text{A8})$$

Since  $\delta C_i$  in (A8) are arbitrary, we obtain from (A2) the equations

$$\langle \Phi | (H - E) (a_{t\alpha}^* a_{k\alpha} + a_{t\beta}^* a_{k\beta}) | \Phi \rangle = 0$$

$$\langle \Phi | (H - E) a_{t\alpha}^* \left( a_{m\alpha} - \sum_k C_{mk} a_{k\alpha} \right) | \Phi \rangle = 0$$

$$\langle \Phi | (H - E) \left( a_{m\beta}^* + \sum_t C_{tm} a_{t\beta}^* \right) a_{k\beta} | \Phi \rangle = 0 \quad (\text{A9})$$

To derive the above equations, we assumed that the normalization factor  $\mathcal{N}$  is free from the variational parameters. The first two in (A9) correspond to the variational equations between the occupied orbitals and the virtual orbitals and the last one in (A9) corresponds to the variational equation among the occupied orbitals.<sup>27</sup>

The complexity of the cluster expression of the RHF wavefunction given by (A1) or (A2) and the variational equations in (A9) originates from the basic assumption of the "restricted condition" that the orbitals can be grouped into separate blocks (e.g., closed-shell manifold and open-shell manifold) and within each block a unitary transformation among orbitals keeps the total wavefunction invariant.

<sup>1</sup>K. Hirao and H. Nakatsuji, J. Chem. Phys. **68**, 4516 (1978), preceding paper.

<sup>2</sup>In contrast to closed-shell systems, open-shell paramagnetic systems include two important correlation effects; electron correlation and spin correlation. The former is defined by

$$\langle H \rangle_{\text{corr}} = \langle H \rangle_{\text{exact}} - \langle H \rangle_{\text{RHF}}$$

as usual and the latter by

$$\langle f \rangle_{\text{corr}} = \langle f \rangle_{\text{exact}} - \langle f \rangle_{\text{RHF}}$$

where  $\langle f \rangle$  is the expectation value of a spin-dependent operator  $f$ .

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<sup>9</sup>Strictly speaking, the  $\hat{T}_{1M}$  should be defined as

$$\hat{T}_{1M} = \sum_m [f_{0,m} (S_{0,m}^* + S_{x,m}^*) / 2 + f_{x,m} (S_{x,m}^* - iS_{y,m}^*) / 2]$$

where  $S_{x,m}^*$  and  $S_{y,m}^*$  are defined in a same manner as in (10). However, since the operator  $\hat{T}_{1M}$  is meaningful only when it acts on  $|0\rangle$ , we may use the expression in (8).

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<sup>11</sup>For example, when  $|0\rangle$  is the triplet state, namely  $s=2$ , we have

$$(\alpha\alpha - \beta\beta)\alpha\alpha / \sqrt{2} = \phi_{22}^1 / \sqrt{2} - \phi_{20}^1 / \sqrt{12} - \phi_{00}^1 / \sqrt{4} - P\phi_{00}^3 / \sqrt{6}$$

where

$$\phi_{22}^1 = \alpha\alpha\alpha\alpha$$

$$\phi_{20}^1 = (\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha + \beta\beta\alpha\alpha) / \sqrt{6}$$

$$\phi_{00}^1 = (\beta\beta\alpha\alpha - \alpha\alpha\beta\beta) / \sqrt{2}$$

$$P\phi_{00}^3 = [(2\beta\beta\alpha\alpha - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha) - (\alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha - 2\alpha\alpha\beta\beta)] / \sqrt{12}.$$

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- <sup>18</sup>In case there is no fluctuations mixing closed-shell and virtual orbitals such as  $^3\Sigma_u^+$  state of  $H_2$ , only the imaginary SSP stability dilemma can be resolved by the projection operator. For other stability dilemmas, there are no appropriate projection operators to remove the singly-excited configurations giving rise to  $A_M$  matrix and to recover the symmetry properties. That is, the symmetry dilemma becomes more significant than the stability dilemma in this case.
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$$\langle \phi_{ka} | \phi_{kb} \rangle = 0$$

$$\langle \phi_k | \phi_l \rangle \neq 0 \text{ otherwise}$$
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