Cluster expansion of the wavefunction. Structure of the closed-shell orbital theory

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A new approach to the closed-shell orbital theory is presented with the formalism of the cluster expansion of the wavefunction. The four independent excitation operators are used to represent the general determinantal wavefunction and also to discuss the stability of the Hartree–Fock solution. This leads to a new concept called the "stability dilemma," which is the key not only in understanding the structure of the orbital theory but also for the extension of the orbital model. Only when the stability dilemma is removed, the correlation effect is taken into account within the framework of the orbital approximation. The closed-shell orbital theory including the electron correlation is defined as $|\Phi\rangle = \mathcal{P}\exp[iF]|0\rangle$, where the F is the excitation operator to generate the variational space and the $\mathcal{P}$ is the projection operator to remove the stability dilemma. The various orbital theories (some are known but some are new) can be obtained by appropriate choices of the F and $\mathcal{P}$. It is shown that the above cluster expression makes it possible to analyze and interconnect the various orbital theories in the form of the limited CI based on their own natural orbitals. The complex DODS theory is proposed. This new orbital theory is the most suitable one to include the correlation effect within the orbital model in the closed-shell system.

I. INTRODUCTION

An exact many-electron wavefunction can be obtained in an infinite series of all ordered Slater determinants that can be formed from a complete orthonormal basic set of one-particle functions. This expansion is connected with the so-called configuration interaction (CI) method. The CI method is in principle simple although analytical or numerical work is necessary for evaluating the matrix elements and for solving the secular equation. However, the CI expansion is suitable for the removal of actual or near degeneracies but it is slow convergent. This defect may be characterized by the fact that the CI expansion includes the physically important and unimportant terms in disorder. There is nothing wrong in this from the purely mathematical point of view. But another expansion of an exact wavefunction, based a bit more on physics, is desired. One of the possibilities for such an expansion is the cluster expansion of a wavefunction.[1,2]

The cluster expansion gives a compact and precise way of constructing an exact wavefunction $|\Psi\rangle$ from an approximate one $|\Phi\rangle$

$$|\Psi\rangle = \exp[\hat{T}]|\Phi\rangle \ , \tag{1}$$

where the total cluster generating operator $\hat{T}$ may be expressed as a sum of i-particle terms

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N \ . \tag{2}$$

Each T_i represents all possible i-particle linked clusters. The basic principles of a cluster expansion method are well known in nuclear physics and have been discussed by several authors.[3] It has been shown that the cluster expansion of the form

$$|\Phi'\rangle = \exp[\hat{T}_1]|\Phi\rangle \tag{3}$$

corresponds to a transformation of a single Slater determinant $|\Phi\rangle$ to another single determinantal function $|\Phi'\rangle$. This is known as the Thouless' theorem.[4] If we choose the reference function $|\Phi\rangle$ correctly to eliminate one-particle clusters and neglect linked clusters more than two particles, the corresponding cluster development is

$$|\Phi'\rangle = \exp[\hat{T}_2]|\Phi\rangle \ , \tag{4}$$

and we have the starting wavefunction of the so-called electron-pair approximation or the many-electron theory developed by Sinanoğlu and co-workers,[5] Szass,[6] Nesbet,[7] and Čížek and Paldus.[8] These various approaches based on (4) turn out to be useful to investigate the electron correlation problems in atomic and molecular systems. Some important contributions to the cluster expansion method have been made by others.[9–11] It must be noticed that in comparison with the very extensive works concerned with the two-particle cluster $\hat{T}_2$, little attention has been paid to the one-particle cluster $\hat{T}_1$. The reason, of course, is that for closed-shell systems the one-particle cluster functions can be eliminated in fairly good approximation when we start with the Hartree–Fock (HF) orbitals. For closed-shell systems, the cluster expansion (1) or the truncated form of it gives a way of constructing a wavefunction to success. For open-shell systems, however, we find it more convenient to take the symmetry-adapted-cluster (SAC) expansion of a wavefunction as a basis.[12] The SAC expansion is different from (1). It is constructed from the generators of the excited configurations having symmetry under consideration. In our separate papers,[13] we have presented the pseudo-orbital theory which is an extension of the orbital theoretic idea based on an SAC expansion and applied it to the spin correlation problem for open-shell systems.

On the other hand, in any discussion of the electronic structure of atoms and molecules it is important to recognize the central role of the HF approximation.[14]

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Due to its connection with an independent-particle model, the HF scheme has a physical simplicity and visuality. It has been successfully applied to the electronic structure of atoms and molecules in forms of the so-called self-consistent-field (SCF) schemes. The success of the HF approximation has important implications about the qualitative validity of the orbital model and the utility of the various orbital theories proposed for improving upon it. In this connection, it is useful to relate any orbital theory to an exact theory based on a cluster expansion of a wavefunction. This is of importance not only in understanding and constructing the orbital theory but also in developing a beyond orbital theory. The purpose of the present paper is to develop a new approach to the closed-shell orbital theory with the formalism of the one-particle cluster expansion method. It is hoped that the discussion gives some new ideas on the theoretical and conceptual structure of the orbital theories and their relationships.

To obtain a unified approach to the closed-shell orbital theory, it is useful to start from the cluster development given by (3). In the next section, we will show that the one-particle cluster generator $\hat{T}_1$ is partitioned into four independent excitation operators and discuss their properties deduced. Also we will discuss how the general determinantal functions can be expressed in terms of these excitation operators. The instability of the HF solution indicates inadequancy of the orbital picture. If we go beyond the HF approximation within the framework of the orbital model, we always encounter stability problems of the HF state. The stability of the HF state leads to a new concept called the "stability dilemma," which is the key not only in understanding the structure of the orbital theory but also for extension of the orbital model. In Sec. III, we will go beyond the HF approximation and present the orbital theory which includes the electron correlation. This can be done only when the stability dilemma can be removed. Thus, we will first rederive the stability conditions for the HF solution in order to examine the stability dilemma. Then, we will define the general closed-shell orbital theories by resolving the stability dilemma. Section IV is devoted to the analysis of these orbital theories in the form of the limited CI based on their own natural orbitals. In the final section, the present study is summarized.

II. REPRESENTATION OF A SLATER DETERMINANT

We wish to represent a general Slater determinant by use of the cluster expansion of a wavefunction. Let a_i^+, a_i be the creation and annihilation operators generated by an arbitrary but complete orthonormal set of one-particle functions $\{\phi_i\}$. The one-particle cluster expansion is

$$|\Phi'\rangle = \exp[\hat{T}_1]|\Phi\rangle \ . \tag{3}$$

The reference function $|\Phi\rangle$ is a determinantal wavefunction built from occupied orbitals

$$|\Phi\rangle = a_1^+ a_2^+ \cdots a_N^+ |\rangle \ , \tag{5}$$

where the ket $|\rangle$ denotes the physical vacuum, in which no particles are present. Written in this form, the $|\Phi\rangle$ is normalized to unity. The one-particle cluster generator is defined by

$$\hat{T}_1 = \sum_{i=1}^{N} f_i b_i^+ a_i \ , \tag{6}$$

Here the b_i^+ is the one-particle cluster creation operator and generates the one-particle cluster function v_i when operating on $|\rangle$. We assume that each v_i is real and normalized to unity and hence the f_i is the complex value. Because the cluster functions v_i are orbital orthogonal to the occupied orbitals, the orbital operators anticommute with the cluster creation operator b_j^+

$$[a_i, b_j^+]_+ = 0 \ , \quad 1 \le i, j \le N \ . \tag{7}$$

Thus, the $|\Phi'\rangle$ takes the determinantal form

$$|\Phi'\rangle = \prod_i (a_i^+ + f_i b_i^+)|\rangle \ . \tag{8}$$

We can assume without loss of generality that occupied orbital operators a_i^+ and cluster operators b_j^+ satisfy the fermion anticommutation relations. That is, the occupied orbitals in $|\Phi\rangle$ and the cluster functions form an orthonormal set. Therefore, we see that they constitute *natural orbitals* of the wavefunction $|\Phi'\rangle$.

Now we limit ourselves to the closed-shell $2n$-electron system. For convenience, we will separate the spin index and employ the two-component operators defined by

$$\mathbf{a}_k = \begin{pmatrix} a_{k\alpha} \\ a_{k\beta} \end{pmatrix} ,$$

$$\mathbf{b}_k = \begin{pmatrix} b_{k\alpha} \\ b_{k\beta} \end{pmatrix} . \tag{9}$$

We denote $|\Phi_0\rangle$ or $|0\rangle$ in shorter version by a determinantal wavefunction for closed-shell systems,

$$|\Phi_0\rangle = \prod_k a_{k\alpha}^+ a_{k\beta}^+ |\rangle = ||\phi_1\bar{\phi}_1 \cdots \phi_k\bar{\phi}_k \cdots \phi_n\bar{\phi}_n|| \ , \tag{10}$$

where $|| \cdots ||$ denotes the normalized Slater determinant. A bar above a spin orbital indicates that it is associated with β spin and no bar indicates α spin. Identifying spin variables, we have the expression for $\hat{T}_1$ in terms of the excitation operators S^+,

$$\hat{T}_1 = \sum_k \left(f_{0,k} S_{0,k}^+ + \sum_\tau f_{\tau,k} S_{\tau,k}^+ \right) \ , \tag{11}$$

with

$$S_{0,k}^+ = (1/\sqrt{2})\, \mathbf{b}_k^+ \sigma_0 \mathbf{a}_k \ ,$$

$$S_{\tau,k}^+ = (1/\sqrt{2})\, \mathbf{b}_k^+ \sigma_\tau \mathbf{a}_k \ . \tag{12}$$

Here the σ_0 and $\sigma_\tau (\tau = x, y, z)$ are a unit matrix and Pauli matrices, respectively. Throughout the paper we reserve the index τ for x, y, and/or z and the index γ for 0, x, y, and/or z. The f in (11) are the complex quantities and their real part is referred to as g and imaginary part to as h, namely $f = g + ih$. The operator $S_{0,k}^+$ is called the singlet excitation operator since it generates a singlet excited configuration when operating on $|\Phi_0\rangle$,

$$S^{+}_{0,k}|0\rangle = ||\phi_1\bar{\phi}_1\cdots v_k\phi_k(\alpha\beta-\beta\alpha)/\sqrt{2}\ldots\phi_n\bar{\phi}_n|| \ . \quad (13)$$

Similarly $S^{+}_{\tau,k}$ is named as the triplet excitation operator since it gives a triplet excited configuration which is an eigenfunction of the operator corresponding to τ component of the total spin angular momentum, e.g.,

$$S^{+}_{z,k}|0\rangle = ||\phi_1\bar{\phi}_1\cdots v_k\phi_k(\alpha\beta+\beta\alpha)/\sqrt{2}\cdots\phi_n\bar{\phi}_n|| \ . \quad (14)$$

The unlinked clusters $S^{+}S^{+}$, $S^{+}S^{+}S^{+}, \ldots$, generate doubly, triply, ..., excited configurations, respectively. It should be noticed that the $(S^{+}_{0,k})^2$ and $(S^{+}_{\tau,k})^2$ give the same doubly excited configuration with a difference of a sign

$$(S^{+}_{0,k})^2|0\rangle = -(S^{+}_{\tau,k})^2|0\rangle = ||\phi_1\bar{\phi}_1\cdots v_k\bar{v}_k\cdots\phi_n\bar{\phi}_n|| \ . \quad (15)$$

Let S be the Hermitian conjugate of S^{+}, $S\equiv(S^{+})^{\dagger}$. From the definition of the excitation operators,

$$S|0\rangle = 0 \ ,$$
$$\langle 0|S^{+} = 0 \ , \quad (16)$$

and we see that they satisfy the so-called quasiboson commutation relations

$$[S_I, S_J] = [S^{+}_I, S^{+}_J] = 0 \ ,$$
$$\langle 0|[S_I, S^{+}_J]|0\rangle = \delta_{IJ} \ . \quad (17)$$

Thus, the four types of the excitation operators are essentially independent of each other.

Let us now examine how the determinantal wavefunction can be expressed in terms of these excitation operators. Any other Slater determinant, not actually orthogonal to $|\Phi_0\rangle$, can be expressed

$$|\Phi\rangle = \exp[iF_\gamma]|0\rangle \ , \quad (18)$$

with

$$F_\gamma = \frac{1}{i}\sum_k (f_{\gamma,k}S^{+}_{\gamma,k} - f^{*}_{\gamma,k}S_{\gamma,k}) = F^{\dagger}_\gamma \ . \quad (19)$$

The exponential operator e^{iF} is unitary due to the Hermitian property of F. Thus, the wavefunction $|\Phi\rangle$ can be obtained from the wavefunction $|\Phi_0\rangle$ by a unitary transformation. If we define the new fermion operators by

$$\mathbf{d}^{+}_{\gamma,\mathbf{k}} = e^{iF_\gamma}\mathbf{a}^{+}_{\mathbf{k}}e^{-iF_\gamma}$$
$$= \cos|f'_{\gamma,k}|\cdot\mathbf{a}^{+}_{\mathbf{k}} + (f'_{\gamma,k}/|f'_{\gamma,k}|)\sin|f'_{\gamma,k}|\cdot\mathbf{b}^{+}_{\mathbf{k}}\sigma_\gamma \ , \quad (20)$$

where we denote f' by $f/\sqrt{2}$, then we can rewrite the $|\Phi\rangle$ as a determinantal form

$$|\Phi\rangle = \prod_k d^{+}_{\gamma,k\alpha}d^{+}_{\gamma,k\beta}|\rangle \ . \quad (21)$$

If we also define

$$\mathbf{d}^{+}_{\gamma,\mathbf{k}*} = e^{iF_\gamma}\mathbf{b}^{+}_{\mathbf{k}}e^{-iF_\gamma}$$
$$= \cos|f'_{\gamma,k}|\cdot\mathbf{b}^{+}_{\mathbf{k}} - (f'_{\gamma,k}/|f'_{\gamma,k}|)\sin|f'_{\gamma,k}|\cdot\mathbf{a}^{+}_{\mathbf{k}}\sigma_\gamma \ , \quad (22)$$

we can check that

$$d_{\gamma,k*}|\Phi\rangle = d^{+}_{\gamma,k}|\Phi\rangle = 0 \ , \quad (23)$$

and that these new fermion operators satisfy the fermion anticommutation relations. Thus, (20) and (22) represent a canonical transformation. Note here that the F_γ is invariant to a canonical transformation of the fermion operators, i.e.,

$$F_\gamma = \frac{1}{i}\sum_k (f_{\gamma,k}S^{+}_{\gamma,k} - f^{*}_{\gamma,k}S_{\gamma,k})$$
$$= \frac{1}{i}\sum_k (f_{\gamma,k}R^{+}_{\gamma,k} - f^{*}_{\gamma,k}R_{\gamma,k}) \ , \quad (24)$$

where the excitation operator R^{+} is defined by means of the unitary transformed fermion operators such as

$$R^{+}_{\gamma,k} = (1/\sqrt{2})\,\mathbf{d}^{+}_{\gamma,\mathbf{k}*}\,\sigma_\gamma\,\mathbf{d}_{\gamma,\mathbf{k}} \ . \quad (25)$$

With the help of this property, we can express more general determinantal wavefunctions in terms of excitation operators.

An alternative prescription may be used to obtain the determinantal wavefunction. Thouless' theorem can be written in terms of the excitation operators as

$$|\Phi\rangle = \mathfrak{N}\exp\left[\sum_k f_{\gamma,k}S^{+}_{\gamma,k}\right]|0\rangle \ . \quad (26)$$

The factor $\mathfrak{N}$ assures the normalization.[15] It is apparent that the $|\Phi\rangle$ takes a determinantal form

$$|\Phi\rangle = \prod_k c^{+}_{\gamma,k\alpha}c^{+}_{\gamma,k\beta}|\rangle \ , \quad (27)$$

where

$$\mathbf{c}^{+}_{\gamma,\mathbf{k}} = (\mathbf{a}^{+}_{\mathbf{k}} + f'_{\gamma,k}\mathbf{b}^{+}_{\mathbf{k}}\sigma_\gamma)/(1+|f'_{\gamma,k}|^2)^{1/2} \ . \quad (28)$$

We have also $\mathbf{c}^{+}_{\gamma,\mathbf{k}*}$ by making a canonical transformation

$$\mathbf{c}^{+}_{\gamma,\mathbf{k}*} = (\mathbf{b}^{+}_{\mathbf{k}} - f'_{\gamma,k}\mathbf{a}^{+}_{\mathbf{k}}\sigma_\gamma)/(1+|f'_{\gamma,k}|^2)^{1/2} \ . \quad (29)$$

It is easy to prove that the two representations of a Slater determinant given by (18) and (26) are equivalent.[16] So we may use whichever we like as the case may be. The former expression (18) makes it possible to evaluate the exponential operator as an operator equation with the aid of Lie algebra. On the other hand, we can evaluate the exponential operator in the latter expression (26) as a finite expansion due to the Pauli principle.

III. THE STABILITY DILEMMA AND THE CLOSED-SHELL ORBITAL THEORIES INCLUDING ELECTRON CORRELATION

The most successful orbital theory is the HF theory in primitive sense, the basic idea of which is simply that each electron moves in the average field of all the other electrons. We shall take HF orbitals, or approximation to them, as the starting point because of their theoretical significance and the resulting formal simplicity. the HF wavefunction is the optimized one within the space spanned by the determinantal functions generated by the real singlet excitation operators, the simplest variational cluster wavefunction, i.e.,

$$|\Phi\rangle = \mathfrak{N}\exp\left[\sum_k g_{0,k}S^{+}_{0,k}\right]|0\rangle = \prod_k c^{+}_{0,k\alpha}c^{+}_{0,k\beta}|\rangle \ , \quad (30)$$

where

$$\mathbf{c}^{+}_{0,\mathbf{k}} = (\mathbf{a}^{+}_{\mathbf{k}} + g'_{0,k}\mathbf{b}^{+}_{\mathbf{k}})/[1+(g'_{0,k})^2]^{1/2} \ . \quad (31)$$

It should be noted that the double occupancy of the orbitals is preserved. Thus, the variational cluster expansion of the wavefunction described by (30) or that of the form

$$|\Phi\rangle = \exp[iG_0]|0\rangle \ ;$$

$$G_0 = \frac{1}{i}\sum_k g_{0,k}(S^\dagger_{0,k} - S_{0,k}) \ , \tag{32}$$

is the HF wavefunction for the closed-shell systems.

We wish to go beyond the HF approximation within the framework of the orbital model, that is, within the space spanned by the determinantal functions. However, even if we extend the variational space by introducing the remaining excitation operators, we cannot reach beyond the HF approximation in case the HF solution is stable. This dilemma is called the "stability dilemma." It is clearly concerned with the problems of the symmetry dilemma proposed by Löwdin.[17] The stability dilemma can be resolved by projecting the determinantal function onto the symmetry space. We can go beyond the HF approximation only when the stability dilemma is resolved. In this section, we will first rederive the stability conditions for the HF solution in order to elucidate the stability dilemma. Then, we will consider the closed-shell orbital theories including the correlation effect by removing the stability dilemma.

A. Stability conditions for the HF solution

A general condition for stability problems of the HF state was first formulated by Thouless.[4] Čížek and Paldus[18] and Fukutome[19] have shown that the stability of a closed-shell HF solution involves four different types of stability. We will rederive the stability conditions for the HF solution in terms of the four independent excitation operators.

Consider a small displacement of the HF wavefunction, given by the unitary transformation,

$$|\Phi\rangle = \exp[iF]|\mathrm{HF}\rangle \ ;$$

$$F = \frac{1}{i}\sum_\gamma\sum_k (f_{\gamma,k}S^\dagger_{\gamma,k} - f^*_{\gamma,k}S_{\gamma,k}) = F^\dagger \ , \tag{33}$$

where $|\mathrm{HF}\rangle$ denotes the HF wavefunction. In this case, the excitation operators are defined by the HF orbitals as a basis. The energy expectation is given by

$$E = E_0 + i\langle \mathrm{HF}|[H, F]|\mathrm{HF}\rangle + \frac{i^2}{2!}\langle \mathrm{HF}|[[H, F], F]|\mathrm{HF}\rangle + \cdots \ , \tag{34}$$

where E_0 is the HF energy, $E_0 = \langle \mathrm{HF}|H|\mathrm{HF}\rangle$. Due to the Brillouin theorem, we have

$$\langle \mathrm{HF}|[H, F]|\mathrm{HF}\rangle = 0 \ . \tag{35}$$

This leads to a simple criterion that the energy corresponding to $|\Phi_{\mathrm{HF}}\rangle$ should be stationary with respect to the type of variation given by (33). The energy is stable with respect to the variation described by (33) if

$$\frac{i^2}{2!}\langle \mathrm{HF}|[[H, F], F]|\mathrm{HF}\rangle \geq 0 \ . \tag{36}$$

This inequality is known as the stability condition for the HF state.[4] Expanding (36) we obtain the stability condition

$$\frac{1}{2}\begin{pmatrix} \mathbf{f}_0 \\ \mathbf{f}_0^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{A}_0 & \mathbf{B}_0 \\ \mathbf{B}_0^* & \mathbf{A}_0^* \end{pmatrix}\begin{pmatrix} \mathbf{f}_0 \\ \mathbf{f}_0^* \end{pmatrix} + \frac{1}{2}\sum_\tau \begin{pmatrix} \mathbf{f}_\tau \\ \mathbf{f}_\tau^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{A}_t & \mathbf{B}_t \\ \mathbf{B}_t^* & \mathbf{A}_t^* \end{pmatrix}\begin{pmatrix} \mathbf{f}_\tau \\ \mathbf{f}_\tau^* \end{pmatrix} \geq 0 \tag{37}$$

for all the coefficients f. Here the $\mathbf{f}_0$ and $\mathbf{f}_\tau$ are the column vectors formed by $f_{0,k}$ and $f_{\tau,k}$, respectively. The submatrices $\mathbf{A}$ and $\mathbf{B}$ are defined

$$(\mathbf{A}_0)_{kl} = \langle \mathrm{HF}|S_{0,k}HS^\dagger_{0,l} - E_0|\mathrm{HF}\rangle \ ,$$
$$(\mathbf{B}_0)_{kl} = \langle \mathrm{HF}|S_{0,k}S_{0,l}H|\mathrm{HF}\rangle \ ,$$
$$(\mathbf{A}_t)_{kl} = \langle \mathrm{HF}|S_{\tau,k}HS^\dagger_{\tau,l} - E_0|\mathrm{HF}\rangle \ ,$$
$$(\mathbf{B}_t)_{kl} = \langle \mathrm{HF}|S_{\tau,k}S_{\tau,l}H|\mathrm{HF}\rangle \ . \tag{38}$$

From the definition we see that $\mathbf{A}$ are Hermitian matrices while $\mathbf{B}$ are not, since $\mathbf{B}^\dagger = \mathbf{B}^*$. However, the supermatrices in (37) are again Hermitian. The three identical supermatrices correspond to the triplet-type excitations and the remaining supermatrix is associated with the singlet-type excitations. Thus, the two types of independent stability conditions obtained are called as singlet and triplet (nonsinglet) stability conditions.[18,19] This implies that we can separate the general variational space spanned by the determinantal functions into four independent subspaces since they are orthogonal and noninteracting with respect to H and hence, obtain an independent stability condition for each subspace.

When the matrices $\mathbf{A}$ and $\mathbf{B}$ are real matrices, as is usually the case, the stability conditions may be further simplified. First consider the singlet stability condition. The singlet stability condition may be factored into two subproblems,

$$\mathbf{g}_0^\dagger(\mathbf{A}_0 + \mathbf{B}_0)\mathbf{g}_0 + \mathbf{h}_0^\dagger(\mathbf{A}_0 - \mathbf{B}_0)\mathbf{h}_0 \geq 0 \ , \tag{39}$$

where the $\mathbf{g}_0$ and $\mathbf{h}_0$ are column vectors of real and imaginary parts of the complex column vector $\mathbf{f}_0$, i.e., $\mathbf{f}_0 = \mathbf{g}_0 + i\mathbf{h}_0$. The matrices $(\mathbf{A}_0 \pm \mathbf{B}_0)$ are symmetric under the assumption that $\mathbf{A}_0$ and $\mathbf{B}_0$ are real. Therefore the unitary matrices $\mathbf{U}\pm$ may be found by which the matrices $(\mathbf{A}_0 \pm \mathbf{B}_0)$ are diagonalized,

$$\mathbf{U}+^\dagger(\mathbf{A}_0 + \mathbf{B}_0)\mathbf{U}+ = \mathbf{D}_0^+ \ ,$$
$$\mathbf{U}-^\dagger(\mathbf{A}_0 - \mathbf{B}_0)\mathbf{U}- = \mathbf{D}_0^- \ , \tag{40}$$

where $\mathbf{D}_0^\pm$ are the diagonal matrices. If we further define the unitary transformed excitation operators

$$P^\dagger_{0,k} = \sum_l S^\dagger_{0,l}(\mathbf{U}+)_{lk} \ ,$$
$$Q^\dagger_{0,k} = \sum_l S^\dagger_{0,l}(\mathbf{U}-)_{lk} \ , \tag{41}$$

together with

$$\tilde{\mathbf{g}}_0 = (\mathbf{U}+)^\dagger\mathbf{g}_0 \ ,$$
$$\tilde{\mathbf{h}}_0 = (\mathbf{U}-)^\dagger\mathbf{h}_0 \ . \tag{42}$$

Then, we have from (39) that

$$\sum_k (\tilde{g}_{0,k})^2(\mathbf{D}_0^+)_{kk} + \sum_k (\tilde{h}_{0,k})^2(\mathbf{D}_0^-)_{kk} \geq 0 \ , \tag{43}$$

where

$$(\mathbf{D}_0^+)_{kk} = \langle \mathrm{HF}|P_{0,k}HP^\dagger_{0,k} - E_0 + P_{0,k}P_{0,k}H|\mathrm{HF}\rangle \ ,$$
$$(\mathbf{D}_0^-)_{kk} = \langle \mathrm{HF}|Q_{0,k}HQ^\dagger_{0,k} - E_0 - Q_{0,k}Q_{0,k}H|\mathrm{HF}\rangle \ . \tag{44}$$

Thus, the singlet stability condition can be classified into real and imaginary conditions

(a) $(\mathbf{D}_0^+)_{kk} \geq 0$, for all k,

real singlet stability condition,

(b) $(\mathbf{D}_0^-)_{kk} \geq 0$, for all k, (45)

imaginary singlet stability condition.

In the same manner, each triplet stability condition is factored into real and imaginary conditions when $\mathbf{A}_t$ and $\mathbf{B}_t$ matrices are real. Using the diagonal transformations, we can define the new sets of the triplet excitation operators P_τ^+, Q_τ^+ and coefficients $\tilde{g}_\tau$, $\tilde{h}_\tau$, as done in (41) and (42). Then we have

(c) $(\mathbf{D}_t^+)_{kk} = \langle \mathrm{HF} | P_{\tau,k} H P_{\tau,k}^+ - E_0 + P_{\tau,k} P_{\tau,k} H | \mathrm{HF} \rangle \geq 0$,

for all k, real triplet (nonsinglet)

stability condition,

(d) $(\mathbf{D}_t^-)_{kk} = \langle \mathrm{HF} | Q_{\tau,k} H Q_{\tau,k}^+ - E_0 - Q_{\tau,k} Q_{\tau,k} H | \mathrm{HF} \rangle \geq 0$,

for all k, imaginary triplet (nonsinglet)

stability condition. (46)

These stability conditions ensure that the HF single determinantal wavefunction represents a true local minimum of the energy functional within the space spanned by all determinantal functions. As derived above the general variational space is separated into independent subspaces generated by the excitation operators and hence, we obtain an independent stability condition for each subspace. This factorization leads to a useful classifiaction of the orbital theories which will be discussed in the latter section.

We shall now discuss the instability of the HF solution, suggested by the form of the above stability conditions. For sake of the resulting formal simplicity, we employ the uncoupled approximation, namely the unitary transformed excitation operators P^+, Q^+ are replaced by the primitive excitation operators S^+. The uncoupled approximation simplifies the instability conditions to the following forms

(a) $E_{0,k} - E_0 + K_{kk^*} < 0$, for any k,

real singlet instability condition,

(b) $E_{0,k} - E_0 - K_{kk^*} < 0$, for any k,

imaginary singlet instability condition,

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

real triplet instability condition,

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

imaginary triplet instability condition, (47)

where $E_{0,k}$ and $E_{t,k}$ are energies of the singlet and triplet excited states respectively and K_{kk^*} is the usual exchange integral

$$E_{0,k} = \langle \mathrm{HF} | S_{0,k} H S_{0,k}^+ | \mathrm{HF} \rangle ,$$

$$E_{t,k} = \langle \mathrm{HF} | S_{\tau,k} H S_{\tau,k}^+ | \mathrm{HF} \rangle ,$$

$$K_{kk^*} = \langle \mathrm{HF} | S_{0,k} S_{0,k} H | \mathrm{HF} \rangle = - \langle \mathrm{HF} | S_{\tau,k} S_{\tau,k} H | \mathrm{HF} \rangle . \quad (48)$$

If these instability conditions are satisfied in the HF solution, this means that it does not represent a true minimum with respect to the corresponding fluctuation and that another solution, having the lower energy than the HF solution, must exist. In case of the singlet instability problems, the new solutions preserve the double occupancy of the orbitals and therefore preserve the spin symmetry but they violate the space symmetry.[18,19] It must be noted that the real instability condition is rewritten as

$$E_0 - E_{0,k} > K_{kk^*} \geq 0 \quad (49)$$

This implies that the singlet excited state has lower energy than the ground state. This is valid, of course, under the uncoupled approximation. Strictly speaking, it depends on a sign of the generalized exchange integral $K'_{kk^*} = \langle \mathrm{HF} | P_{0,k} P_{0,k} H | \mathrm{HF} \rangle$. The generalized exchange integral is not necessarily positive while the usual exchange integral K_{kk^*} is positive. However taking account of the relation

$$\sum_k K'_{kk^*} = \sum_k K_{kk^*} \geq 0 , \quad (50)$$

we can conclude that at least one of the singlet excited states, $P_{0,k}^+ | \mathrm{HF} \rangle$ has lower energy than the ground state when the HF solution is real singlet unstable. Comparing with the real and imaginary singlet instability conditions, we observe that the imaginary singlet instability condition may precede the real singlet instability. In case of the triplet instability problems, the double occupancy, and therefore the singlet character of the HF wavefunction, is not preserved and the unrestricted HF (UHF) solutions, in the wider sense of the words, appear. From the imaginary triplet instability condition we see that the triplet excited state has lower energy than the ground state

$$E_0 - E_{t,k} > K_{kk^*} \geq 0 , \quad (51)$$

when the HF solution is imaginary triplet unstable. We also observe that the real triplet instability precedes the imaginary triplet instability.

Before concluding this section, it must be stressed that the stability of the HF solution indicates that even if we expand the variational space spanned by the determinantal functions by introducing the remaining excitation operators, we cannot go beyond the HF approximation in case the HF solution is stable.

B. Stability dilemma and closed-shell orbital theories including electron correlation

The study of the stability conditions of the HF solution tells us that the general variational space spanned by the determinantal functions can be put into independent subspaces. They are specified by real and imaginary singlet excitation operators and three types of real and imaginary triplet excitation operators. The HF wavefunction is the optimized one within the variational space spanned by the determinantal functions generated by real singlet excitation operators. We wish to go beyond the HF approximation from the energetic point of view by adding the remaining excitation operators.

We start from the reference determinant $|\mathrm{HF}\rangle$ built from the HF orbitals. By adding the variational subspace generated by one of the real triplet excitation operators, we have the function

$$|\Phi\rangle = \exp[iG_z]|\mathrm{HF}\rangle \;;$$

$$G_z = \frac{1}{i}\sum_k g_{z,k}(S^+_{z,k} - S_{z,k}) \;, \tag{52}$$

where g_z are real quantities. The energy for $|\Phi\rangle$ is

$$E = E_0 + i\langle \mathrm{HF}|[H, G_z]|\mathrm{HF}\rangle + (i^2/2!)\langle \mathrm{HF}|[[H, G_z], G_z]|\mathrm{HF}\rangle + \cdots \;. \tag{53}$$

Now the first order energy shift vanishes due to the spin symmetry indicating that the energy be stationary. Thus, the subspace added *does* work as the variational space *only* if the HF solution is real triplet unstable, namely *only* if

$$(i^2/2!)\langle \mathrm{HF}|[[H, G_z], G_z]|\mathrm{HF}\rangle = \mathbf{g}_z^\dagger(\mathbf{A}_t + \mathbf{B}_t)\mathbf{g}_z < 0 \;, \tag{54}$$

Thus, even if we extend the variational space by introducing the excitation operators, we cannot reach beyond the HF approximation in case the HF solution is *stable*. This dilemma is what we call the "stability dilemma." In this case, it is called the real triplet stability dilemma. When the HF solution is unstable, another solution, having lower energy than the HF energy, must exist. Unfortunately, the corresponding wavefunction is no longer symmetry adapted. In the present case, the spin symmetry is not preserved. This release from the stability dilemma results in the symmetry dilemma.[17]

Now consider the wavefunction by projecting out the symmetry-adapted component,

$$|\Phi'\rangle = \mathcal{O}_S|\Phi\rangle = \mathcal{O}_S \exp[iG_z]|\mathrm{HF}\rangle \;, \tag{55}$$

where $\mathcal{O}_S$ is the spin projection operator which selects the singlet spin eigenfunctions. The $|\Phi'\rangle$ is not necessarily normalized to unity. We see that the first order energy shift for $|\Phi'\rangle$ vanishes and the stability condition is reduced to

$$\mathbf{g}_z^\dagger \mathbf{B}_t \mathbf{g}_z \geq 0 \tag{56}$$

due to the projection operator. In comparison with the stability condition for $|\Phi\rangle$ given by (54), the $\mathbf{A}_t$ matrix disappears and only the $\mathbf{B}_t$ matrix remains, which is formed by the generalized exchange integrals. The stability condition (56) is equivalent to requiring that the $\mathbf{B}_t$ matrix be positive definite. Since the trace of $\mathbf{B}_t$ matrix is nonpositive,

$$\mathrm{Tr}(\mathbf{B}_t) = \sum_k \langle \mathrm{HF}|S_{z,k}S_{z,k}H|\mathrm{HF}\rangle = -\sum_k K_{kk*} \leq 0 \;, \tag{57}$$

where Tr denotes the trace, there always exists at least one negative eigenvalue of the $\mathbf{B}_t$. If the $\mathbf{B}_t$ has any negative eigenvalue, it is possible to construct an anti-Hermitian operator iG_z which violates the stability condition (56). Thus, we can go beyond the HF approximation. The spin symmetry is also restored. That is, the projection operator introduced not only preserves the symmetry property by projecting the symmetry-adapted component but also solves the stability dilemma by violating the stability condition.

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

$$\mathbf{A} \pm \mathbf{B} \geq 0 \;, \tag{58}$$

as shown in the previous study of the stability problems for the HF state. On the other hand, the stability condition for the wavefunction projected onto an appropriate symmetry space is given by

$$\pm\mathbf{B} \geq 0 \;. \tag{59}$$

That is, the $\mathbf{A}$ matrix disappears by virtue of the projection and only the $\mathbf{B}$ matrix remains. Noting the sign of the trace of the $\mathbf{B}_0$ and $\mathbf{B}_t$ matrices defined by (38),

$$\mathrm{Tr}(\mathbf{B}_0) = \sum_k \langle \mathrm{HF}|S_{0,k}S_{0,k}H|\mathrm{HF}\rangle = \sum_k K_{kk*} \geq 0 \;,$$

$$\mathrm{Tr}(\mathbf{B}_t) = \sum_k \langle \mathrm{HF}|S_{\tau,k}S_{\tau,k}H|\mathrm{HF}\rangle = -\sum_k K_{kk*} \leq 0 \;, \tag{60}$$

we see that the imaginary singlet and real triplet stability dilemmas can be removed by the appropriate projection operators. Namely, the imaginary singlet and three types of real triplet excitation operators generate the variational space for the improvement of the HF theory. On the other hand, the real singlet and imaginary triplet stability conditions cannot be violated by the corresponding projection operators. That is, the real singlet and imaginary triplet excitation operators cannot be utilized to improve the HF theory for the ground state. This corresponds to the fact that in both cases the HF solution is unstable, the corresponding excited states have lower energies than the ground state. These excitation operators reserve the variational spaces for the excited states. When we start from the arbitrary determinant, not from the HF wavefunction, the real singlet excitation operators are indispensable to generate the HF determinant. It must be stressed again that *only* when the stability dilemma can be resolved, the correlation effect can be taken into account through the unlinked clusters of the excitation operators within the orbital approximation.[20,21]

Thus, the closed-shell orbital theories including the electron correlation effect can be defined as

$$|\Phi\rangle = \mathcal{P}\exp[iF]|0\rangle \;, \tag{61}$$

where the F is the excitation operator to generate the variational space and the $\mathcal{P}$ is the projection operator to remove the stability dilemma. By appropriate choices of the excitation operator and the projection operator, we can obtain the various orbital theories proposed for improving upon the HF approximation. In addition, some new orbital theories can be obtained by starting with the above definition. By making use of the real singlet (G_0) and imaginary singlet (iH_0) excitation operators and three types of real triplet (G_τ) excitation operators, we can construct eight types of the orbital theories. They are summarized in Table I, where the PHF denotes the projected HF theory. The projection operator $\mathcal{O}_R$ selects out the real part of the wavefunction, $\mathcal{O}_R|\Phi\rangle = \mathrm{Re}\{|\Phi\rangle\}$. This projection operator recovers the space symmetry violated by the imaginary singlet excitation operators. The $\mathcal{O}_M$ is the operator projecting out the eigenfunctions of the $\mathbf{S}_z$. There are

TABLE I. The closed-shell orbital theory: $|\Phi\rangle = \mathcal{P}\exp[iF]|0\rangle$.

	Excitation operators, F					Projection operators, $\mathcal{P}$
	G_0	iH_0	G_z	G_x	G_y	
HF	o					
PHF 1	o		o			$\mathcal{O}_S$
PHF 2	o	o				$\mathcal{O}_R$
PHF 3	o		o	o		$\mathcal{O}_S\mathcal{O}_M$
PHF 4	o	o	o			$\mathcal{O}_R\mathcal{O}_S$
PHF 5	o		o	o	o	$\mathcal{O}_S\mathcal{O}_M$
PHF 6	o	o	o	o		$\mathcal{O}_R\mathcal{O}_S\mathcal{O}_M$
PHF 7	o	o	o	o	o	$\mathcal{O}_R\mathcal{O}_S\mathcal{O}_M$

three equivalent orbital theories in PHF1, PHF3, and PHF6, respectively, whether we employ the G_x, G_y, and/or G_z operators. The above cluster expression of the orbital theory makes it possible to analyze the various orbital theories in terms of their own natural orbitals and the internal relationships of these orbital theories become clear. The analysis of the structure of the orbital theories will be given in the next section.

IV. ANALYSIS OF CLOSED-SHELL ORBITAL THEORIES

In this section, we will analyze the closed-shell orbital theories including the correlation effect which are constructed according to the idea outlined in the previous section. First, we will analyze the alternant molecular orbital (AMO) theory proposed by Löwdin[22,23] and examine why one can remove a large part of the correlation error simply by permitting so-called different orbitals for different spins (DODS). The complex molecular orbital method[24] and the generalized valence bond (GVB) method[25] will also be discussed in terms of their own natural orbitals. Finally, the complex DODS method will be discussed. This new orbital theory may be the most suitable orbital theory to include the electron correlation effect.

A. The UHF and AMO wavefunctions

We start by considering the unprojected form of the PHF1 wavefunction in Table I represented by

$$|\Phi\rangle = \mathfrak{N}\exp\left[\sum_k g_{0,k} S^+_{0,k} + \sum_k g_{z,k} S^+_{z,k}\right]|0\rangle \ . \tag{62}$$

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

$$\mathbf{c}^+_{0,\mathbf{k}} = (\mathbf{a}^+_{\mathbf{k}} + g'_{0,k}\mathbf{b}^+_{\mathbf{k}})/[1+(g'_{0,k})^2]^{1/2} \ ,$$

$$\mathbf{c}^+_{0,\mathbf{k}*} = (\mathbf{b}^+_{\mathbf{k}} - g'_{0,k}\mathbf{a}^+_{\mathbf{k}})/[1+(g'_{0,k})^2]^{1/2} \ ,$$

together with

$$\xi_k = 1/[1+(g'_{z,k})^2]^{1/2} \ , \quad \eta_k = g'_{z,k}/[1+(g'_{z,k})^2]^{1/2} \ ,$$

then the above wavefunction can be rewritten as

$$|\Phi\rangle = \prod_k c^+_{k\alpha} c^+_{k\beta}|\rangle \ ,$$

where

$$\mathbf{c}^+_{\mathbf{k}} = \xi_k \mathbf{c}^+_{0,\mathbf{k}} + \eta_k \mathbf{c}^+_{0,\mathbf{k}*}\sigma_z \ . \tag{64}$$

We will find it useful to introduce the spatial orbitals for $\mathbf{c}^+_{0,\mathbf{k}}$ and $\mathbf{c}^+_{0,\mathbf{k}*}$ λ_k and ν_k, respectively

$$\mathbf{c}^+_{0,\mathbf{k}}|\rangle = (\lambda_k\alpha, \lambda_k\beta) \ ,$$

$$\mathbf{c}^+_{0,\mathbf{k}*}|\rangle = (\nu_k\alpha, \nu_k\beta) \ . \tag{65}$$

The λ_k are spatially orthogonal to each other and to the ν_k and the reduced density matrix for Φ becomes diagonal

$$\rho(1|2) = \sum_k 2\xi_k^2\lambda_k(1)\lambda_k(2) + \sum_k 2\eta_k^2\nu_k(1)\nu_k(2) \ . \tag{66}$$

These functions λ_k, ν_k are therefore the natural orbitals.[26] Due to the relation that $\xi_k^2+\eta_k^2=1$, the ξ_k^2 is the fractional occupation probability for the natural orbital λ_k and η_k^2 is that for the ν_k. In terms of these natural orbitals, we have, except the phase factor,

$$\Phi = ||\phi_{1a}\phi_{2a}\cdots\phi_{na}\bar{\phi}_{1b}\bar{\phi}_{2b}\cdots\bar{\phi}_{nb}|| \ , \tag{67}$$

where

$$\phi_{ka} = \xi_k\lambda_k + \eta_k\nu_k \ ,$$

$$\phi_{kb} = \xi_k\lambda_k - \eta_k\nu_k \ . \tag{68}$$

The new orbitals ϕ have the property that their spatial overlap integral is diagonal and are called the corresponding orbitals.[26] This expression suggests that the optimized cluster expansion of the wavefunction of the form given by (62) is the UHF wavefunction[27] for closed-shell systems. Since the η_k are small numbers, we can expand Φ in terms of the natural orbitals

$$\Phi = C^{\mathrm{rf}}\Phi^{\mathrm{rf}} + C^{\mathrm{se}}\Phi^{\mathrm{se}} + C^{\mathrm{de}}\Phi^{\mathrm{de}} + \cdots \ . \tag{69}$$

in the form of the limited CI. Here, the Φ^{rf} is the normalized restricted function with doubly occupied orbitals

$$\Phi^{\mathrm{rf}} = ||\lambda_1\bar{\lambda}_1\cdots\lambda_k\bar{\lambda}_k\cdots\lambda_n\bar{\lambda}_n|| \ , \tag{70}$$

with the coefficient given by

$$C^{\mathrm{rf}} = \prod_k (\xi_k)^2 \ . \tag{71}$$

The reference function Φ^{rf} should be approximated as the HF wavefunction but, of course, they will not be identical. The functions Φ^{se} and Φ^{de} are, respectively, the sum of the normalized singly and doubly excited configurations

$$C^{\mathrm{se}}\Phi^{\mathrm{se}} = \sum_k C^{\mathrm{se}}(kk^*)\Phi^{\mathrm{se}}(kk^*) \ ,$$

with

$$C^{\mathrm{se}}(kk^*) = \sqrt{2}(\eta_k/\xi_k)C^{\mathrm{rf}} \ ,$$

$$\Phi^{\mathrm{se}}(kk^*) = ||\lambda_1\bar{\lambda}_1\cdots\nu_k\lambda_k(\alpha\beta+\beta\alpha)/\sqrt{2}\cdots\lambda_n\bar{\lambda}_n|| \ , \tag{72}$$

and

$$C^{\mathrm{de}}\Phi^{\mathrm{de}} = \sum_k C^{\mathrm{de}}(kk^*)\Phi^{\mathrm{de}}(kk^*) + \sum_{k<l}\sum C^{\mathrm{de}}(kk^*;ll^*)\Phi^{\mathrm{de}}(kk^*;ll^*) \ ,$$

with

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

$$\Phi^{\mathrm{de}}(kk^*) = ||\lambda_1\bar{\lambda}_1\cdots\nu_k\bar{\nu}_k\cdots\lambda_n\bar{\lambda}_n|| \ ,$$

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

$$\Phi^{de}(kk^*;\, ll^*) = ||\lambda_1\bar{\lambda}_1 \cdots \nu_k\lambda_k\nu_l\lambda_l(\alpha\beta+\beta\alpha)(\alpha\beta+\beta\alpha)/2 \cdots \lambda_n\bar{\lambda}_n||\ . \tag{73}$$

The higher order terms are written in the same manner as above. Note here that the singly and doubly excited configurations given above are not the singlet spin states except $\Phi^{de}(kk^*)$. The same expansion of the UHF wavefunction has been given by one of the present authors.[28] It should be noted that the closed-shell UHF wavefunction may exist *only* when the HF solution is real triplet unstable, which is a striking contrast to the open-shell UHF wavefunction. Namely, in case the HF state is stable, the coefficients η_k are all zero due to the stability dilemma.

Now consider the wavefunction by selecting out the components of the singlet spin eigenfunction

$$|\Phi'\rangle = \mathcal{O}_S|\Phi\rangle\ . \tag{74}$$

The variational cluster expansion of (74) is the AMO wavefunction.[22,23] It is called the spin extended HF (SEHF) wavefunction by Kaldor[29] and GF wavefunction by Goddard.[30] As the projection operator $\mathcal{O}_S$ acts only on the spin part of the wavefunction, we can rewrite $|\Phi'\rangle$, except the phase factor,

$$|\Phi'\rangle = ||\phi_{1a}\phi_{2a}\cdots\phi_{na}\phi_{1b}\cdots\phi_{nb}\Theta^f_{00}||\ , \tag{75}$$

where the spin part is replaced by an eigenfunction of $\mathbf{S}_z$ and $\mathbf{S}^2$. We will denote by Θ^j_{SM} $(j=1, 2, \ldots, f)$ the simultaneous spin eigenfunctions of $\mathbf{S}_z$ and $\mathbf{S}^2$, i.e.,

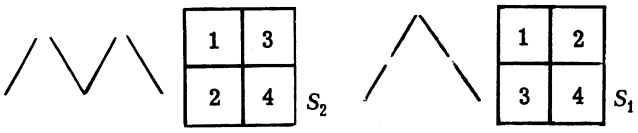
$$\mathbf{S}^2\Theta^j_{SM} = S(S+1)\Theta^j_{SM}\ ,$$

$$\mathbf{S}_z\Theta^j_{SM} = M\Theta^j_{SM}\ . \tag{76}$$

The index j distinguishes spin eigenfunctions corresponding to the same eigenvalues of $\mathbf{S}^2$ and $\mathbf{S}_z$ but which arise through different spin couplings. There are many ways of constructing spin eigenfunctions. One of the most illuminating constructions is the so-called genealogical scheme.[31] For four electrons the spin coupling schemes leading to $S=0$, for instance, are

$$\Theta^1_{00} = (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)/2\ ,$$

$$\Theta^2_{00} = \{(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)\beta-(\alpha\beta\beta+\beta\alpha\beta-2\beta\beta\alpha)\alpha\}/\sqrt{12}\ ,$$



These functions are identical with those that carry the standard irreducible representations of the spin permutation group, associated with standard tableaux,[32] respectively. We assign a number to the standard tableaux according to what is known as the last letter sequence. The spin coupling appeared in the AMO wavefunction is Θ^f_{00}, associated with the standard tableaux S_1.

Expanding Φ' in terms of the natural orbitals, we have

$$\Phi' = C^{rf}\Phi^{rf} + C^{de}\,\mathcal{O}_S\Phi^{de} + \cdots\ . \tag{77}$$

The singly excited configurations vanish due to the projection operator. The leading excited configurations are the doubly excited ones. This is the reason why we can remove a very large part of the correlation error simply by permitting so-called DODS in closed-shell case. Note here that the situation is quite different in open-shell systems, where singly excited configurations remain even if we operate the projection operator.[33] For closed-shell case, the projection operator in (74) not only restores the symmetry properties but also resolves the stability dilemma. However, the spin projection operator in the open-shell SEHF theory only selects out the symmetry-adapted component and does not help to include the electron correlation.[34] Thus, the open-shell SEHF theory is poor for both electron and spin correlation problems.[12,33,34] The doubly excited configurations $\Phi^{de}(kk^*;\, ll^*)$ take the form due to the projection operator,

$$\mathcal{O}_S\Phi^{de}(kk^*;\, ll^*) = -(1/\sqrt{3})||\lambda_1\bar{\lambda}_1\cdots\nu_k\lambda_k\nu_l\lambda_l\,\Theta^2_{00}\cdots\lambda_n\bar{\lambda}_n||\ , \tag{78}$$

where the four-electron spin eigenfunction is defined above. The $\Phi^{de}(kk^*)$ are unaffected through the projection and take the same form as in (73) but, of course, the functions λ_k, ν_k are different in both cases. The spin couplings in the higher terms of the expansion of the AMO wavefunction are the Θ^f. This type of the spin coupling is not keeping our intuitive idea such as electron-pair bond.

B. CMO and GVB wavefunctions

Next we start by considering the PHF2 wavefunction described by

$$|\Phi\rangle = \mathcal{O}_R\mathfrak{N}\exp\left[\sum_k f_{0,k}S^+_{0,k}\right]|0\rangle\ . \tag{79}$$

The $f_{0,k}$ are the complex quantities and hence the unprojected form of (79) leads to the complex HF theory.[35] The complex HF theory has the trouble of stability and symmetry dilemmas. These dilemmas can be removed, as discussed in the previous section, by the projection operator $\mathcal{O}_R$. Thus, the PHF2 is the complex molecular orbital (CMO) theory proposed by Hendekovic.[24] It is apparent that

$$|\Phi\rangle = \mathcal{O}_R\prod_k c^+_{k\alpha}c^+_{k\beta}|\rangle\ , \tag{80}$$

where

$$\mathbf{c}^+_k = (\mathbf{c}^+_{0,k} + ih'_{0,k}\mathbf{c}^+_{0,k^*})/[1+(h'_{0,k})^2]^{1/2}\ . \tag{81}$$

The $\mathbf{c}^+_{0,k}$ and $\mathbf{c}^+_{0,k^*}$ have the same forms as defined by (62) and (63). In a similar manner, let us define the coefficients

$$\xi_k = 1/[1+(h'_{0,k})^2]^{1/2}\ ,$$

$$\eta_k = h'_{0,k}/[1+(h'_{0,k})^2]^{1/2}\ , \tag{82}$$

and the spatial orbitals λ_k and ν_k for $\mathbf{c}^+_{0,k}$ and $\mathbf{c}^+_{0,k^*}$, respectively. Then, λ_k and ν_k are again the natural orbitals of the unprojected wavefunction of $|\Phi\rangle$. We find that the CMO wavefunction is equivalent to the limited CI based on its natural orbitals

$$\Phi = \mathcal{O}_R||\cdots(\xi_k\lambda_k + i\eta_k\nu_k)(\xi_k\bar{\lambda}_k + i\eta_k\bar{\nu}_k)\cdots||\ ,$$

$$= C^{\mathrm{rf}}\Phi^{\mathrm{rf}} + C^{\mathrm{de}}\Phi^{\mathrm{de}} + \cdots \ . \tag{83}$$

The leading term Φ^{rf} is a restricted wavefunction with doubly occupied orbitals which has the same form as (70). Due to the projection operator $\mathcal{O}_R$, the singly excited configurations are excluded because of their pure imaginary property. The function Φ^{de} is, in this case, the doubly excited configurations with singlet spin states,

$$C^{\mathrm{de}}\Phi^{\mathrm{de}} = \sum_k C^{\mathrm{de}}(kk^*)\Phi^{\mathrm{de}}(kk^*) + \sum_{k<l}\sum C^{\mathrm{de}}(kk^*;\, ll^*)\Phi^{\mathrm{de}}(kk^*;\, ll^*) \ . \tag{84}$$

While the $\Phi^{\mathrm{de}}(kk^*)$ take the same form as in (73), the $\Phi^{\mathrm{de}}(kk^*;\, ll^*)$ are different, i.e.,

$$\Phi^{\mathrm{de}}(kk^*;\, ll^*) = ||\lambda_1\bar{\lambda}_1 \cdots \nu_k\lambda_k\nu_l\lambda_l\Theta^1_{00}\cdots\lambda_n\bar{\lambda}_n|| \ . \tag{85}$$

Thus, the CMO wavefunction involves the choice of spin coupling represented by Θ^1, specified by S_f. The higher order terms are written in the same manner. If we notice the relation that

$$(\xi\lambda + i\eta\nu)\alpha(\xi\lambda + i\eta\nu)\beta = [(\xi\lambda + \eta\nu)(\xi\lambda - \eta\nu)/\sqrt{2} + \sqrt{2}i\xi\eta\lambda\nu](\alpha\beta - \beta\alpha)/\sqrt{2} \ , \tag{86}$$

we can rewrite the wavefunction by means of paired-electron orbitals

$$\Phi = \mathcal{O}_R||\phi_{11}\phi_{22}\cdots\phi_{nn}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\cdots(\alpha\beta - \beta\alpha)/\sqrt{2n}|| \ , \tag{87}$$

where

$$\phi_{kk} = (\xi_k\lambda_k + \eta_k\nu_k)(\xi_k\lambda_k - \eta_k\nu_k)/\sqrt{2} + \sqrt{2}i\xi_k\eta_k\lambda_k\nu_k \ . \tag{88}$$

The CMO wavefunction involves the singlet type spin coupling as in the G1[36] and GVB[25] wavefunctions. This spin coupling might be thought as representing covalent bonds.

The above CMO wavefunction in (87) suggests that the GVB wavefunction is also given by a cluster expansion of the wavefunction[37]

$$|\Phi\rangle = \mathfrak{N}\exp\left[\sum_k g_{0,k}S^+_{0,k} + \frac{1}{2}\sum_k (ih_{0,k}S^+_{0,k})^2\right]|0\rangle \ . \tag{89}$$

Introducing the two-particle creation operators c^+_{kk}, we can rewrite the above wavefunction as

$$|\Phi\rangle = \prod_k c^+_{kk}|\rangle \ , \tag{90}$$

where

$$c^+_{kk} = [c^+_{0,k\alpha}c^+_{0,k\beta} - (h'_{0,k})^2 c^+_{0,k^*\alpha}c^+_{0,k^*\beta}]/[1 + (h'_{0,k})^4]^{1/4} \ . \tag{91}$$

Note here that the operator $(ih_{0,k}S^+_{0,k})^2$ generates a kind of two-particle cluster function. That is, the cluster expansion with n two-particle clusters among possible $n(n+1)/2$ ones gives the basis for the wavefunction constructed by geminals.[38] If we further define ξ_k, η_k

$$\xi_k = 1/[1 + (h'_{0,k})^4]^{1/4} \ ,$$
$$\eta_k = h'_{0,k}/[1 + (h'_{0,k})^4]^{1/4} \ , \tag{92}$$

and the spatial orbitals λ_k, ν_k for $c^+_{0,k}$ and c^+_{0,k^*} as in (65), then we have

$$\Phi = ||\Phi_{1a}\phi_{1b}\phi_{2a}\phi_{2b}\cdots\phi_{na}\phi_{nb}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\cdots(\alpha\beta - \beta\alpha)/\sqrt{2n}|| \ , \tag{93}$$

where

$$\phi_{ka} = \xi_k\lambda_k + \eta_k\nu_k \ ,$$
$$\phi_{kb} = \xi_k\lambda_k - \eta_k\nu_k \ . \tag{94}$$

The ϕ_{ka}, ϕ_{kb} satisfy the strong orthogonality condition that the orbitals are orthogonal to each other unless they are singlet paired, i.e.,

$$\langle\phi_{ka}|\phi_{kb}\rangle \neq 0 \ ,$$
$$\langle\phi_k|\phi_l\rangle = 0 \text{ otherwise} \ . \tag{95}$$

Therefore, the optimized Φ in (89) is the GVB wavefunction proposed by Goddard.[25] This type of wavefunction was first suggested by Hurley *et al.* under the name of the paired-electron approximation.[39]

It is appropriate to mention in this place that the stability dilemma is a problem which occurs under the approximation of the one-particle cluster expansion of a wavefunction. That is, the stability dilemma would never occur, if we consider more than one-particle clusters at a time. Thus, there is no stability dilemma in the GVB wavefunction. The GVB wavefunction is constructed from the generator of singly and doubly excited configurations having desired pure symmetry of the system. That is, the GVB wavefunction is based on the SAC expansion of the wavefunction.[12] However, by making use of the projection operator, the GVB wavefunction is redefined, in terms of one-particle clusters, as

$$|\Phi_{\mathrm{GVB}}\rangle = \left[\prod_k (\mathcal{O}_R\exp[ih_{0,k}S^+_{0,k}])\right] \times\exp\left[\sum_k g_{0,k}S^+_{0,k}\right]|0\rangle \ . \tag{96}$$

It is interesting to compare with the form given by the CMO wavefunction

$$|\Phi_{\mathrm{CMO}}\rangle = \mathcal{O}_R\left[\prod_k \exp[ih_{0,k}S^+_{0,k}]\right] \times\exp\left[\sum_k g_{0,k}S^+_{0,k}\right]|0\rangle \ . \tag{97}$$

The GVB wavefunction is also expanded in the limited CI based on its own natural orbitals λ_k, ν_k

$$\Phi = C^{\mathrm{rf}}\Phi^{\mathrm{rf}} + C^{\mathrm{de}}\Phi^{\mathrm{de}} + \cdots \ . \tag{98}$$

This expression is analogous to that of the CMO wavefunction given by (83) except that Φ^{de} contains no such doubly excited configurations as $\Phi^{\mathrm{de}}(kk^*;\, ll^*)$.

C. Complex DODS wavefunction

Next, consider the PHF4 wavefunction defined by

$$|\Phi\rangle = \mathcal{O}_R\mathcal{O}_S\mathfrak{N}\exp\left[\sum_k f_{0,k}S^+_{0,k} + \sum_k g_{z,k}S^+_{z,k}\right]|0\rangle \ . \tag{99}$$

The $|\Phi\rangle$ can be rewritten in the following determinantal form

TABLE II. The doubly excited configurations in the limited CI based on the natural orbitals of GVB, AMO, CMO, and complex DODS wavefunctions.

GVB	$\lVert \nu_k \nu_k \alpha\beta \rVert$
AMO	$\lVert \nu_k \nu_k \alpha\beta \rVert$
	$\lVert \nu_k \lambda_k \nu_l \lambda_l \{(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)\beta - (\alpha\beta\beta + \beta\alpha\beta - 2\beta\beta\alpha)\alpha\}/\sqrt{12} \rVert$
CMO	$\lVert \nu_k \nu_k \alpha\beta \rVert$
	$\lVert \nu_k \lambda_k \nu_l \lambda_l (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)/2 \rVert$
complex DODS	$\lVert \nu_k \nu_k \alpha\beta \rVert$
	$\lVert \nu_k \lambda_k \nu_l \lambda_l (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)/2 \rVert$
	$\lVert \nu_k \lambda_k \nu_l \lambda_l \{(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)\beta - (\alpha\beta\beta + \beta\alpha\beta - 2\beta\beta\alpha)\alpha\}/\sqrt{12} \rVert$

$$|\Phi\rangle = \mathcal{O}_R \mathcal{O}_S \prod_k c^+_{k\alpha} c^+_{k\beta} |\rangle \,, \tag{100}$$

where

$$\mathbf{c}^+_{\mathbf{k}} = [(\mathbf{c}^+_{0,\mathbf{k}} + g'_{z,k}\mathbf{c}^+_{0,\mathbf{k}^*}\sigma_z) + ih'_{0,k}(\mathbf{c}^+_{0,\mathbf{k}^*} - g'_{z,k}\mathbf{c}^+_{0,\mathbf{k}}\sigma_z) \times 1/\{[1+(g'_{z,k})^2][(1+(h'_{0,k})^2]\}^{1/2} \,. \tag{101}$$

If we further define

$$\begin{aligned} \xi_{0,k} &= 1/[1+(h'_{0,k})^2]^{1/2} \,, \\ \eta_{0,k} &= h'_{0,k}/[1+(h'_{0,k})^2]^{1/2} \,, \\ \xi_{z,k} &= 1/[1+(g'_{z,k})^2]^{1/2} \,, \\ \eta_{z,k} &= g'_{z,k}/[1+(g'_{z,k})^2]^{1/2} \,, \end{aligned} \tag{102}$$

then we have

$$\mathbf{c}^+_{\mathbf{k}} = \xi_{0,k}\,\xi_{z,k}[\mathbf{c}^+_{0,\mathbf{k}} + (\eta_{z,k}/\xi_{z,k})\mathbf{c}^+_{0,\mathbf{k}^*}\sigma_z + i(\eta_{0,k}/\xi_{0,k})\mathbf{c}^+_{0,\mathbf{k}^*} - i(\eta_{0,k}/\xi_{0,k})(\eta_{z,k}/\xi_{z,k})\mathbf{c}^+_{0,\mathbf{k}}\sigma_z] \tag{103}$$

It is convenient to introduce the spatial orbitals λ_k, ν_k for $\mathbf{c}^+_{0,\mathbf{k}}$ and $\mathbf{c}^+_{0,\mathbf{k}^*}$, respectively. In terms of these functions, we can expand Φ as

$$\Phi = C^{\mathrm{rf}}\Phi^{\mathrm{rf}} + C^{\mathrm{de}}\Phi^{\mathrm{de}} + \cdots \,. \tag{104}$$

The reference function is again the restricted wavefunction which doubly occupied orbitals

$$\begin{aligned} \Phi^{\mathrm{rf}} &= \lVert \lambda_1\bar{\lambda}_1 \cdots \lambda_k\bar{\lambda}_k \cdots \lambda_n\bar{\lambda}_n \rVert \,, \\ C^{\mathrm{rf}} &= \prod_k [(\xi_{0,k}\,\xi_{z,k})^2 + (\eta_{0,k}\,\eta_{z,k})^2] \,. \end{aligned} \tag{105}$$

The singly excited configurations vanish due to the projection operators. The Φ^{de} is the sum of the doubly excited configurations, i.e.,

$$\begin{aligned} \Phi^{\mathrm{de}} = &\sum_k C^{\mathrm{de}}(kk^*)\Phi^{\mathrm{de}}(kk^*) \\ &+ \sum_{k<l}\sum C^{\mathrm{de}}_0(kk^*;\, ll^*)\Phi^{\mathrm{de}}_0(kk^*;\, ll^*) \\ &+ \sum_{k<l}\sum C^{\mathrm{de}}_z(kk^*;\, ll^*)\Phi^{\mathrm{de}}_z(kk^*;\, ll^*) \,, \end{aligned} \tag{106}$$

where

$$\begin{aligned} C^{\mathrm{de}}(kk^*) &= -[(\eta_{0,k}/\xi_{0,k})^2 + (\eta_{z,k}/\xi_{z,k})^2] \times 1/[1+(\eta_{0,k}/\xi_{0,k})^2(\eta_{z,k}/\xi_{z,k})^2]\, C^{\mathrm{rf}} \,, \\ \Phi^{\mathrm{de}}(kk^*) &= \lVert \lambda_1\bar{\lambda}_1 \cdots \nu_k\bar{\nu}_k \cdots \lambda_n\bar{\lambda}_n \rVert \,, \\ C^{\mathrm{de}}_0(kk^*;\, ll^*) &= -X_k X_l C^{\mathrm{rf}} \,, \\ \Phi^{\mathrm{de}}_0(kk^*;\, ll^*) &= \lVert \lambda_1\bar{\lambda}_1 \cdots \nu_k\lambda_k\nu_1\lambda_1\Theta^1_{00} \cdots \lambda_n\bar{\lambda}_n \rVert \,, \\ C^{\mathrm{de}}_z(kk^*;\, ll^*) &= -Y_k Y_1 C^{\mathrm{rf}} \,, \\ \Phi^{\mathrm{de}}_z(kk^*;\, ll^*) &= (1/\sqrt{3})\lVert \lambda_1\bar{\lambda}_1 \cdots \nu_k\lambda_k\nu_1\lambda_1 \times \Theta^2_{00} \cdots \lambda_n\bar{\lambda}_n \rVert \,. \end{aligned} \tag{107}$$

Here we set X_k and Y_k as follows

$$\begin{aligned} X_k &= \sqrt{2}(\eta_{0,k}/\xi_{0,k})[1+(\eta_{z,k}/\xi_{z,k})^2]/[1+(\eta_{0,k}/\xi_{0,k})^2(\eta_{z,k}/\xi_{z,k})^2] \,, \\ Y_k &= \sqrt{2}(\eta_{z,k}/\xi_{z,k})[1-(\eta_{0,k}/\xi_{0,k})^2]/[1+(\eta_{0,k}/\xi_{0,k})^2(\eta_{z,k}/\xi_{z,k})^2] \,. \end{aligned} \tag{108}$$

We observe that the doubly excited configurations contain possible two independent spin eigenfunctions Θ^1_{00} and Θ^2_{00}. Similarly, the higher order terms involve the choice of spin functions represented by Θ^1, Θ^f, and some other partly-paired spin eigenfunctions. This orbital theory, the complex DODS theory, is clearly a new one which has not been proposed so far.

It is interesting to note that the limited CI in terms of natural orbitals can also be used to examine the internal relationships of various closed-shell orbital theories. Equations (77), (83), (98), and (104) relate the AMO, CMO, GVB, and complex DODS wavefunctions. The leading excited configurations are most important since the higher order terms arise just from the self-consistency effects. The doubly excited configurations in the limited CI of these wavefunctions are summarized in Table II. The spin polarization type of the spin coupling, Θ^f, is not in keeping our intuitive idea such as electron-pair bonds, while the singlet type of the spin coupling, Θ^1, might be thought as representing the covalent bond. This lack of intuitive basis for the spin coupling may be reflected in poorer energy values. Thus, if we assume that the natural orbitals λ_k, ν_k defined in each orbital theory are not identical but similar, then the corresponding energies calculated might be ordered as

$$E^{\text{complex DODS}} \le E^{\text{CMO}} \le E^{\text{AMO}} \le E^{\text{GVB}} \,, \tag{109}$$

on the basis of the spin couplings involved.

Lunell[40] has proposed to use the general spin orbitals in the projected HF scheme. Lunell's wavefunction can easily be constructed by making use of the following excitation operators

$$|\Phi\rangle = \mathcal{O}_S \mathcal{O}_M \mathfrak{N} \exp\left[\sum_k (g_{0,k} S^+_{0,k} + g_{z,k} S^+_{z,k} + g_{x,k} S^+_{x,k})\right] |0\rangle \ . \tag{110}$$

The above wavefunction can be reduced to the form

$$|\Phi\rangle = \mathcal{O}_S \mathcal{O}_M \prod_k c^+_{k\alpha} c^+_{k\beta} |\rangle \ , \tag{111}$$

where

$$\mathbf{c}^+_{\mathbf{k}} = [(\mathbf{c}^+_{0,\mathbf{k}} + g'_{z,k} \mathbf{c}^+_{0,\mathbf{k}^*} \sigma_z) + g'_{x,k}(\mathbf{c}^+_{0,\mathbf{k}^*} - g'_{z,k} \mathbf{c}^+_{0,\mathbf{k}} \sigma_z)\sigma_x] \times 1/[(1+(g'_{z,k})^2)(1+(g'_{x,k})^2]^{1/2}. \tag{112}$$

Let us define

$$\begin{aligned} \xi_{z,k} &= 1/[1+(g'_{z,k})^2]^{1/2} \ , \\ \eta_{z,k} &= g'_{z,k}/[1+(g'_{z,k})^2]^{1/2} \ , \\ \xi_{x,k} &= 1/[1+(g'_{x,k})^2]^{1/2} \ , \\ \eta_{x,k} &= g'_{x,k}/[1+(g'_{x,k})^2]^{1/2} \ . \end{aligned} \tag{113}$$

Now we shall introduce the spatial orbitals λ_k, ν_k for $\mathbf{c}^+_{0,\mathbf{k}}$ and $\mathbf{c}^+_{0,\mathbf{k}^*}$. The general spin orbitals are given by

$$\begin{aligned} c^+_{k\alpha}|\rangle &= \xi_{x,k}(\xi_{z,k}\lambda_k + \eta_{z,k}\nu_k)\alpha + \eta_{x,k}(\xi_{z,k}\lambda_k + \eta_{z,k}\nu_k)\beta \ , \\ c^+_{k\beta}|\rangle &= \xi_{x,k}(\xi_{z,k}\lambda_k - \eta_{z,k}\nu_k)\beta + \eta_{x,k}(\xi_{z,k}\lambda_k - \eta_{z,k}\nu_k)\alpha \ . \end{aligned} \tag{114}$$

In terms of these natural orbitals, we can expand the wavefunction as

$$\Phi = C^{\mathrm{rf}}\Phi^{\mathrm{rf}} + C^{\mathrm{de}}\Phi^{\mathrm{de}} + \cdots \ . \tag{115}$$

The Φ^{rf} is the restricted wavefunction

$$\begin{aligned} \Phi^{\mathrm{rf}} &= ||\lambda_1\bar{\lambda}_1 \cdots \lambda_k\bar{\lambda}_k \cdots \lambda_n\bar{\lambda}_n|| \ , \\ C^{\mathrm{rf}} &= \prod_k [(\xi_{z,k}\xi_{x,k})^2 + (\eta_{z,k}\eta_{x,k})^2]^{1/2} \ . \end{aligned} \tag{116}$$

The Φ^{de} is the sum of the doubly excited configurations

$$C^{\mathrm{de}}\Phi^{\mathrm{de}} = \sum_k C^{\mathrm{de}}(kk^*)\Phi^{\mathrm{de}}(kk^*) + \sum_{k<l}\sum C^{\mathrm{de}}(kk^*;\, ll^*)\Phi^{\mathrm{de}}(kk^*;\, ll^*) \ ,$$

with

$$\begin{aligned} C^{\mathrm{de}}(kk^*) &= -[(\eta_{x,k}/\xi_{x,k})^2 + (\eta_{z,k}/\xi_{z,k})^2] \times 1/[1+(\eta_{x,k}/\xi_{x,k})^2(\eta_{z,k}/\xi_{z,k})^2]C^{\mathrm{rf}} \ , \\ \Phi^{\mathrm{de}}(kk^*) &= ||\lambda_1\bar{\lambda}_1 \cdots \nu_k\bar{\nu}_k \cdots \lambda_n\bar{\lambda}_n|| \ , \\ C^{\mathrm{de}}(kk^*;\, ll^*) &= -(X_kX_l + Y_kY_l)C^{\mathrm{rf}} \ , \\ \Phi^{\mathrm{de}}(kk^*;\, ll^*) &= (1/\sqrt{3})\, ||\lambda_l\bar{\lambda}_l \cdots \nu_k\lambda_k\nu_l\lambda_l\Theta^2_{00} \cdots \lambda_n\bar{\lambda}_n|| \ . \end{aligned} \tag{117}$$

Here we defined X_k and Y_k in a similar manner as in (113)

$$\begin{aligned} X_k &= \sqrt{2}(\eta_{z,k}/\xi_{z,k})[1-(\eta_{x,k}/\xi_{x,k})^2]/[1+(\eta_{z,k}/\xi_{z,k})^2(\eta_{x,k}/\xi_{x,k})^2] \ , \\ Y_k &= \sqrt{2}(\eta_{x,k}/\xi_{x,k})[1-(\eta_{z,k}/\xi_{z,k})^2]/[1+(\eta_{z,k}/\xi_{z,k})^2(\eta_{x,k}/\xi_{x,k})^2] \ . \end{aligned} \tag{118}$$

The higher order terms are given in the same manner. It should be noticed that the spin eigenfunction appeared in the $\Phi^{\mathrm{de}}(kk^*;\, ll^*)$ is Θ^2_{00}. Thus, this wavefunction is essentially equivalent to the AMO wavefunction up to doubly excited configurations although the higher order terms are different from those of the AMO wavefunction. Namely, consideration of more than one triplet excitation operator at a time affects the spin structure of only the higher-than second terms of the CI expansion.

In principle, we can construct the more general orbital theories according to the idea outlined in the previous section. From a practical point of view, however, the complicated structure of these wavefunction might cause difficulties in actual calculation and also inconvience in the interpretation of the wavefunction. The determination of these wavefunction would rapidly become very cumbersome and the amount of labor probably too large when measured against the extra information gained. So we will not discuss these orbital theories any more. However, it should be mentioned that the PHF7 in Table I is defined as the best Slater determinant built on one-electron spin orbitals having a complete flexibility and projected onto an appropriate symmetry space. That is, the PHF7 involves all possible choices of spin eigenfunctions as in the spin optimized HF theory.[41]

In contrast to the open-shell case, the correlation problem in the closed-shell case is only the electron correlation. From this energetic point of view, the first step to take the correlation effect into account is to consider the imaginary singlet excitation operator since it generates the spin eigenfuncations specified by Θ^1. This leads to the GVB and CMO approximation as shown above. If we wish to cover further correlation energy, we recommend to consider the imaginary singlet and one of the real triplet excitation operators at a time, which leads to the complex DODS theory. We believe that one can remove a very large part of the correlation error simply by permitting complex DODS.

V. SUMMARY

In this paper, we have developed a new approach to the closed-shell orbital theory with the formalism of the one-particle cluster expansion of the wavefunction. The stability of the HF solution 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 theories. Only when the stability dilemma is removed, the correlation effect can be taken into account through the unlinked clusters of the excitation operators within the framework of the orbital approximation. We have shown that the stability and symmetry dilemmas can be resolved by projecting the determinantal wavefunction onto an appropriate symmetry space. The various orbital theories (some are known but some are new) can be obtained by appropriate choices of the excitation and projection operators. The new orbital theory, the complex DODS theory, is presented by special choices of excitation and projection operators. It is also shown that the one-particle cluster expansion method is a useful expression to construct and to analyze the orbital theory. The complex DODS theory is analyzed in contrast to the conventional orbital theories such as AMO, CMO, and GVB

theories. The complex DODS theory is the most suitable one to include the correlation effect within the orbital approximation.

The approach to the closed-shell orbital theory developed here can easily be applied to the open-shell systems. In the following paper,[34] we have proposed some useful open-shell orbital theories including the electron correlation by solving the open-shell stability dilemma.

We hope and expect that the present work will suggest new viewpoints and approaches to the orbital theory for many-electron systems.

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[15]The $\mathfrak{A}$ is just the overlap integral of the wavefunction $|\Phi\rangle$ with $|\Phi_0\rangle$. If we define the quantity, $\epsilon = 1 - |\langle\Phi|\Phi_0\rangle|^2$, ϵ is a good measure of the amplitude of the component of $|\Phi\rangle$ orthogonal to $|\Phi_0\rangle$.

[16]The equivalence of two representations of determinantal functions implies that the operator $\mathfrak{A}\exp[\sum_k f_{\gamma,k} S^+_{\gamma,k}]$ is unitary, while the $\exp[\sum_k f_{\gamma,k} S^+_{\gamma,k}]$ is nonunitary. See also Ref. 9.

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[21]It is interesting to compare the orbital theory including the correlation effect with the electron-pair approximation (EPA). These theories start with the following wavefunctions

$$|\Phi_{\mathrm{EPA}}\rangle = \mathcal{P}\exp[\hat{T}_1]|0\rangle, \quad |\Phi_{\mathrm{EPA}}\rangle = \exp[\hat{T}_2]|0\rangle ,$$

where PHF denotes the projected Hf theory. By introducing the one-particle and two-particle linked cluster generators $\hat{t}_i, \hat{t}_{ij}$ and the corresponding coefficients c_i, c_{ij}, we may express $\hat{T}_1$ and $\hat{T}_2$ as

$$\hat{T}_1 = \sum_i c_i \hat{t}_i, \quad \hat{T}_2 = \sum_{i<j}\sum c_{ij}\hat{t}_{ij} ,$$

where i and j run over all occupied orbitals. Putting these into the above wavefunctions, we find

$$|\Phi_{\mathrm{PHF}}\rangle = \left(1 + \frac{1}{2}\sum_i\sum_j c_i c_j \hat{t}_i \hat{t}_j + \cdots\right)|0\rangle ,$$

$$|\Phi_{\mathrm{EPA}}\rangle = \left(1 + \sum_{i<j}\sum c_{ij}\hat{t}_{ij} + \cdots\right)|0\rangle ,$$

by expanding the exponential operators. Thus, we see that the orbital theory takes account of the two-particle interactions through the unlinked clusters due to the restriction of the orbital model while the EPA does in linked clusters directly. We find that the number of the variational parameters are also different in both theories. The PHF wavefunction has n variational parameters for $2n$-electron system while the EPA wavefunction has $n(n+1)/2$.

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$$|\Phi\rangle = \mathfrak{N} \exp\left[\sum_k g_{0,k} S^+_{0,k} + \frac{1}{2}\sum_k (g_{\tau,k} S^+_{\tau,k})^2\right] |0\rangle .$$

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