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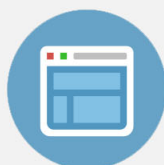
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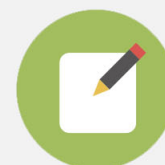


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# Cluster expansion of the wavefunction. Symmetry-adapted-cluster expansion, its variational determination, and extension of open-shell orbital theory

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The symmetry-adapted-cluster (SAC) expansion of an exact wavefunction is given. It is constructed from the generators of the symmetry-adapted excited configurations having the symmetry under consideration, and includes their higher-order effect and self-consistency effect. It is different from the conventional cluster expansions in several important points, and is suitable for applications to open-shell systems as well as closed-shell systems. The variational equation for the SAC wavefunction has a form similar to the generalized Brillouin theorem in accordance with the inclusion of the higher-order effect and the self-consistency effect. We have expressed some existing open-shell orbital theories equivalently in the conventional cluster expansion formulas, and on this basis, we have given the pseudo-orbital theory which is an extension of open-shell orbital theory in the SAC expansion formula.

## I. INTRODUCTION

There are several ways of constructing an exact wavefunction from an approximate one.<sup>1</sup> One way which is most popularly used for the calculations of accurate wavefunctions is the configuration interaction (CI) theory, which may be expressed as

$$\Psi = (1 + \hat{C})\Phi_0, \quad (1a)$$

where  $\Phi_0$  is an appropriate reference wavefunction [e.g., Hartree-Fock (HF) single determinant] and  $\hat{C}$  is a sum of the generators of the one-, two-, ...,  $N$ -electron excited configurations, i.e.,

$$\begin{aligned} \hat{C} &= \hat{C}_1 + \hat{C}_2 + \dots + \hat{C}_N \\ &= \sum_i c_i^* a_i + \sum_{i < j} c_{ij}^* a_i a_j + \dots + c_{12\dots N}^* a_1 a_2 \dots a_N. \end{aligned} \quad (1b)$$

Here,  $a_i$  ( $a_i^*$ ) are the fermion annihilation (creation) operators associated with a complete set of spin orbitals (e.g., HF occupied and unoccupied orbitals) and  $c_i^*$ ,  $c_{ij}^*$ , etc., are the creation operators of the correlated functions [which are reducible,<sup>2</sup> as seen from Eq. (3)]. The merit of this approach lies in its simplicity in computational algorithm, but a defect is that the expansion usually converges very slowly except for some cases (e.g., near degeneracy). Because of this defect, it is usually difficult to assign a particular physical meaning to a particular type of configurations.

Another way of more possibility may be obtained by the cluster expansion of the wavefunction. It gives a compact and precise way of constructing an exact wavefunction from an approximate one. In the notations due to Primas,<sup>2</sup> it is written as

$$\Psi = \exp(\hat{T})\Phi_0, \quad (2a)$$

where  $\hat{T}$  is a sum of the one-, two-, ...,  $N$ -electron linked cluster generators

$$\begin{aligned} \hat{T} &= \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_N \\ &= \sum_i b_i^* a_i + \sum_{i < j} b_{ij}^* a_i a_j + \dots + b_{12\dots N}^* a_1 a_2 \dots a_N, \end{aligned} \quad (2b)$$

and  $b_i^*$ ,  $b_{ij}^*$ , etc., are the (unknown) creation operators of the irreducible cluster functions.<sup>2</sup>

This expansion was originally introduced and developed in the fields of statistical mechanics<sup>3</sup> and nuclear physics.<sup>4</sup> For the study of atoms and molecules this expansion was first recognized to be important by Sinanoğlu<sup>5</sup> and then developed by Sinanoğlu and co-workers,<sup>5,6</sup> Primas,<sup>2</sup> Čížek and Paldus,<sup>7</sup> and others.<sup>8,9</sup> Comparing this expansion with the CI expansion (1), we find that the generators  $\hat{C}_i$  of the CI expansion are related with the generators  $\hat{T}_i$  of the cluster expansion as<sup>10</sup>

$$\hat{C}_1 = \hat{T}_1, \quad (3a)$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}(\hat{T}_1)^2, \quad (3b)$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!}(\hat{T}_1)^3, \quad (3c)$$

$$\hat{C}_4 = \hat{T}_4 + \frac{1}{2}(\hat{T}_2)^2 + \hat{T}_1 \hat{T}_3 + \frac{1}{2}(\hat{T}_1)^2 \hat{T}_2 + \frac{1}{4!}(\hat{T}_1)^4, \text{ etc.}, \quad (3d)$$

for the exact (or nonvariational) wavefunctions.

For closed-shell systems, Sinanoğlu<sup>5</sup> has shown that the contribution of the one-electron cluster  $\hat{T}_1$  is small when we choose the HF wavefunction as the  $\Phi_0$  (when we choose the Brueckner orbitals as our basis, the operator  $\hat{T}_1$  vanishes identically), and that the pair cluster  $\hat{T}_2$  is of predominant importance for correlation energy due to the short-range character of the "fluctuation" potential. He has further observed from the analysis of the CI wavefunctions of Be and LiH that the generator  $\hat{C}_4$  is well approximated by the product of  $\hat{T}_2$ , i.e.,

$$\hat{C}_4 \approx \frac{1}{2}(\hat{T}_2)^2, \quad (4)$$

and stressed the importance of taking into account the higher-order terms of  $\hat{T}_2$  (unlinked terms composed of  $\hat{T}_2$  alone) through the cluster expansion formula as given by

$$\Psi \approx \exp(\hat{T}_2)\Phi_0. \quad (5)$$

The relation (4) has also been confirmed for delocalized

$\pi$ -electron systems by Čížek, Paldus, and Šroubová.<sup>10</sup> [The relation for the triple excitation given by Eq. (3c) has been examined by Paldus, Čížek, and Shavitt.<sup>11</sup>] Many studies on the electron correlations in closed-shell systems have then been developed starting from or extending the approximate wavefunction (5). These studies show a typical procedure in the cluster expansion theory: that is, first select the physically most important *linked* term (e.g.,  $\hat{T}_2$  for correlation energy), and then include their higher-order effects *through* the cluster expansion formalism [e.g., Eq. (5)]. Then, we can expect a *rapid* convergence with a fewer number of variables, in contrast to the CI expansion.

When the reference wavefunction  $\Phi_0$  is not a HF wavefunction but an arbitrary single determinant, or when an external perturbation is applied to the system represented by  $\Phi_0$ , the correction term including the one-electron cluster,  $\hat{T}_1$ , would become significant. Thouless<sup>12</sup> has shown that the cluster expansion given by

$$\Phi = \mathfrak{N} \exp(\hat{T}_1) \Phi_0 \quad (6)$$

is equivalent to a transformation of a single determinant

$$\Phi_0 = \prod_i^N a_i^* | \rangle \quad (7)$$

to another single determinant

$$\Phi = \prod_i^N h_i^* | \rangle, \quad (8)$$

where  $| \rangle$  denotes a vacuum state. For the operator  $h_i^*$ , we may give a different definition from Thouless<sup>12</sup> (by the reason given in the Ref. 13) as

$$h_i^* = n_i \exp(\hat{T}_1) a_i^* \exp(-\hat{T}_1), \quad (9a)$$

which can be simplified further as

$$\bar{h}_i^* = n_i \exp(b_i^* a_i) a_i^* \exp(-b_i^* a_i). \quad (9b)$$

The operators  $h_i^*$  and their Hermitian conjugates  $h_i$  satisfy the quasifermion relation

$$[h_i^*, h_j^*]_* = 0, \quad [h_i, h_j]_* = 0, \quad (10a)$$

$$[h_i, h_j^*]_* | \rangle = \delta_{ij} | \rangle, \quad (10b)$$

where the relation (10b) is valid not only for the vacuum  $| \rangle$  but also for  $| \Phi_0 \rangle$  and  $| \Phi \rangle$  under the condition

$$[b_i, b_j^*]_* = \delta_{ij} (n_i^2 - 1). \quad (11)$$

This condition guarantees the orthonormality of the transformed orbitals so that actually this is not a restriction. So long as the operator  $h_i^*$  applies only to the vacuum as in the present case, the definition given by Eq. (9) is identical with the definition  $h_i^* = n_i (a_i^* + b_i^*)$  given by Thouless.<sup>12,14</sup> Since the anticommutation relations (10) are essentially the same as those of the primitive operators  $a_i^*$  and  $a_i$ , we see that the cluster expansion operator  $\mathfrak{N} \exp(\hat{T}_1)$  in Eq. (6) is essentially unitary.<sup>15</sup> More explicitly, we have shown<sup>16</sup> that the cluster expansion (6) is equivalent to the expansion

$$\Phi = \exp(\hat{T}_1 - \hat{T}_1^*) \Phi_0, \quad (12)$$

where the operator  $\exp(\hat{T}_1 - \hat{T}_1^*)$  is *strictly* unitary.

Thus, when we apply the variational principle to the

cluster wavefunction (6) starting from an *arbitrary* single determinant  $\Phi_0$ , the resultant  $\Phi$  should be equivalent to the HF wavefunction. Therefore, the cluster expansion (6) *completely includes* the self-consistency of orbitals when it is combined with the variational principle. The higher-order unlinked terms  $\frac{1}{2}(\hat{T}_1)^2$ ,  $(1/3!)(\hat{T}_1)^3$ , etc., in Eq. (3) represent in this case the self-consistency effect.

Previously, we have used this formulation for deriving an equivalent expression to the coupled-perturbed HF theory<sup>17</sup> and for obtaining pseudo-orbital theory for open-shell systems.<sup>18</sup> In a separate paper,<sup>16</sup> we will analyze and interconnect various orbital theories for closed-shell systems (some are known, but some are new) starting from the formula

$$\Phi = \mathcal{O} \exp(\hat{T}_1) \Phi_0, \quad (13)$$

where  $\mathcal{O}$  is a various kind of projection operator depending on the orbital theory under consideration.

For open-shell systems, Sinanoğlu, Silverstone, and Öksüz<sup>6</sup> have classified the correlation effects and investigated their natures for several atomic systems. Mukherjee *et al.*<sup>8</sup> have given a cluster expansion starting from a multideterminant reference wavefunction. For open-shell systems we think it important and convenient to take all of the excited configurations included in the expansion to be symmetry adapted. In a preliminary paper,<sup>18</sup> we have reported pseudo-orbital theory which is an extension of open-shell orbital theory based on a symmetry-adapted-cluster expansion formalism and applied it to the calculations of the spin densities of several open-shell atoms. Very recently, Paldus<sup>7d</sup> also studied the merit of a spin-adapted cluster-expansion formalism and gave such a theory for the correlation problems in closed-shell systems.

In the present study, we consider a cluster expansion of an exact wavefunction, which is different from the expansion (2) and which is suitable for applications to open-shell systems as well as closed-shell systems. The expansion is composed of the symmetry-adapted-cluster (SAC) generators, starting from a restricted<sup>19</sup> Slater determinant. Our formalism is primitive and has a similarity to the symmetry-adapted CI formalism. We use the variational principle for the determination of the wavefunction. In Sec. II, we first outline some problems in open-shell electronic systems which do not arise in closed-shell systems, and then introduce the SAC expansion of the wavefunction. In Sec. III, we discuss the merits of the SAC expansion in comparison with the conventional ones. In Sec. IV, we give the variational equation for the SAC wavefunction. It has a form similar to the generalized Brillouin theorem in correspondence with the inclusion of the higher-order or self-consistency effects. We also consider an approximate solution of the variational equation. In Sec. V, we first express some open-shell orbital theories equivalently in the conventional cluster expansion formulas, and then give some extensions of open-shell orbital theories in the SAC expansion formulas (pseudo-orbital theory). They will be applied in the subsequent paper<sup>20</sup> to the calculations of spin density in open-shell systems.

In Sec. VI, the summary of the present study is given.

**II. SYMMETRY-ADAPTED-CLUSTER EXPANSION**

We consider here a cluster expansion of an exact wavefunction which is different from the expansion (2) and which is suitable for the study of open-shell systems as well as closed-shell systems. In open-shell systems we encounter some problems which do not arise for closed-shell systems. For example, the single particle term  $\hat{T}_1$  would not necessarily be small even if we start from the HF (e.g., RHF)<sup>19</sup> reference wavefunction. In the expansion (2), the linked operators are classified according to the number of excitations. However, in open-shell systems, such classification does not accord, in general, with the symmetry requirement for the excitations. Then, when we pick up from Eq. (2) only some terms (e.g., only  $\hat{T}_2$ ), the resultant wavefunction becomes a mixed symmetry state. It is then hoped that the expansion is composed of only the configurations having desired symmetry.

Thus, we consider a cluster expansion of an exact wavefunction on the basis of the generators of the symmetry-adapted excited configurations having the symmetry under consideration. We write it as

$$\Psi = \mathcal{O} \exp(\hat{S}) \Phi_0 = \left[ 1 + \hat{S} + \mathcal{O} \left( \frac{1}{2} \hat{S}^2 + \frac{1}{3!} \hat{S}^3 + \dots \right) \right] \Phi_0, \tag{14}$$

where the operator  $\hat{S}$  is given by

$$\begin{aligned} \hat{S} &= \hat{S}_{(1)} + \hat{S}_{(2)} + \dots + \hat{S}_{(N)} \\ &= \sum_{\sigma_1}^{f_1} \sum_I C_{\sigma_1, I} S_{\sigma_1, I}^* + \sum_{\sigma_2}^{f_2} \sum_{I, J} C_{\sigma_2, I, J} S_{\sigma_2, I, J}^* + \dots \\ &\quad + \sum_{\sigma_N}^{f_N} \sum_{i < j < \dots < n} C_{\sigma_N, i, j, \dots, n} S_{\sigma_N, i, j, \dots, n}^* \\ &= \sum_I C_I S_I^*. \end{aligned} \tag{15}$$

As a reference wavefunction  $\Phi_0$ , we choose a restricted HF (RHF)<sup>19</sup> or restricted-type single determinant given by

$$\begin{aligned} \Phi_0 &= || \varphi_1 \alpha \varphi_1 \beta \dots \varphi_r \alpha \varphi_r \beta \dots \varphi_q \alpha \varphi_q \beta \varphi_{q+1} \alpha \dots \varphi_m \alpha \dots \varphi_p \alpha || \\ &= \prod_{k=1}^q a_{k\alpha}^* a_{k\beta}^* \prod_{m=q+1}^p a_{m\alpha}^* | \rangle. \end{aligned} \tag{16}$$

For simplicity, we have restricted ourselves in this paper to the systems for which the determinant (16) has a correct symmetry. An important exception is a singlet excited state. For such state, it would be preferable to start from a multideterminant reference wavefunction.<sup>8</sup> We define the number of unpaired spins in the system by  $s$ , i.e.,

$$s = p - q. \tag{17}$$

In Eq. (15) the operators  $S_{\sigma_L, i, j, \dots, l}^*$  represent the excitation operators which create symmetry-adapted excited configurations on applying the reference wavefunction  $\Phi_0$ . They are the units of which the present theory is composed. The index  $\sigma_L$  runs over the (degenerate) symmetry functions belonging to the symmetry of interest,

and the number of them, denoted by  $f_L$ , depends on the symmetry of the system and the nature of the excitations specified by the indices  $ij \dots l$ , where  $i$  denotes a pair of orbitals concerning the (real) excitation. For example of  $S_{\sigma_1, i}^*$ , the spin-adapted spin-polarization excitation operator is written as<sup>21</sup>

$$\begin{aligned} S_{P, tk}^* &= (s+2)^{-1/2} \left[ \left( \frac{s}{2} \right)^{1/2} (a_{t\alpha}^* a_{k\alpha} - a_{t\beta}^* a_{k\beta}) \right. \\ &\quad \left. + \left( \frac{2}{s} \right)^{1/2} a_{t\alpha}^* a_{k\beta} \sum_{m=q+1}^p a_{m\beta}^* a_{m\alpha} \right], \end{aligned} \tag{18}$$

where the indices  $k, m$ , and  $t$  represent doubly occupied, singly occupied, and unoccupied orbitals, respectively. This operator is "essentially" a single-excitation operator, though it involves in the last term the two simultaneous elementary excitations (real excitation and spin flip) due to the spin-symmetry requirement. The operators  $\hat{S}_{(1)}, \hat{S}_{(2)}, \dots, \hat{S}_{(N)}$  in Eq. (15) are, respectively, the sums of the essentially single-, double-, ...,  $N$ ple-excitation terms in the above sense:

$$\hat{S}_{(L)} = \sum_{\sigma_L}^{f_L} \sum_{i < j < \dots < l} C_{\sigma_L, i, j, \dots, l} S_{\sigma_L, i, j, \dots, l}^*.$$

The index  $I$  for  $S_I^*$  denotes a set of indices  $\sigma_L, ij \dots l$  and the coefficients  $C_I$  or  $C_{\sigma_L, i, j, \dots, l}$  are determined through the variational or nonvariational methods.

In Eq. (14), the operator  $\mathcal{O}$  denotes a symmetry projection operator. An example of the projector  $\mathcal{O}$  is the spin-projection operator  $\mathcal{O}_s$  given by

$$\mathcal{O}_s = \prod_{s' (\neq s)} \left[ \mathbf{S}^2 - \frac{s'}{2} \left( \frac{s'}{2} + 1 \right) \right], \tag{19}$$

where  $\mathbf{S}^2$  is the spin-squared operator. This operator projects out the undesired spin symmetries. Owing to the above definitions of the symmetry-adapted excitation operators, the symmetry projection operator  $\mathcal{O}$  in Eq. (14) does not affect the linked terms, but affects only the unlinked terms since the unlinked terms like  $S_I^* S_J^* | \Phi_0 \rangle$  do not necessarily belong to the desired pure symmetry even though the terms  $S_I^* | \Phi_0 \rangle$  do. It projects from the unlinked terms (e.g.,  $S_{\sigma_1, i}^*, S_{\sigma_1, i, j}^*$ ) the symmetry-adapted excitation operator (e.g.,  $S_{\sigma_2, i, j}^*$ ) belonging to higher multiple excitations. [Since all of the linked and unlinked excitation operators in Eq. (14) operate on the common  $\Phi_0$ , we can speak as if the projection operator  $\mathcal{O}$  applies only to the operator part of Eq. (14).] Since the linked excitation operator  $\hat{S}$  given by Eq. (15) includes all possible symmetry-adapted excitation operators belonging to the symmetry under consideration, the expansion (14) is closed *within* such group of the excitation operators. Thus, the expansion (14) is *complete*: i.e., the wavefunction  $\Psi$  is defined within the space spanned by the symmetry-adapted configurations having the symmetry under consideration. This property is similar to that of the symmetry-adapted CI expansion. We refer to the cluster expansion given by Eqs. (14) and (15) as *symmetry-adapted-cluster (SAC) expansion* of the exact wavefunction.

In the SAC expansion, we can assume without loss of generality the following commutation relations:

$$[S_I^*, S_J^*] = 0, \quad (20a)$$

$$[S_I, S_J] = 0, \quad (20b)$$

$$[S_I, S_J^*]|\Phi_0\rangle = \delta_{IJ}|\Phi_0\rangle. \quad (20c)$$

Then, these excitation operators behave like boson operators for the reference wavefunction  $\Phi_0$  (quasi-boson operators). The relation (20c) does not hold without  $\Phi_0$  on either side of the commutator. It means that the symmetry-adapted excited configurations  $S_I^*|\Phi_0\rangle$  are chosen to be mutually orthonormal, i. e.,

$$\langle\Phi_0|S_I S_J^*|\Phi_0\rangle = \delta_{IJ}, \quad (21a)$$

since  $S_I|\Phi_0\rangle = 0$ . They are also orthogonal to the reference wavefunction  $\Phi_0$ ,

$$\langle\Phi_0|S_I^*|\Phi_0\rangle = \langle\Phi_0|S_I|\Phi_0\rangle = 0. \quad (21b)$$

A comparison of the SAC expansion with the CI expansion is straightforward. The conventional symmetry-adapted CI expansion can be written as

$$\Psi_{CI} = (1 + \hat{C})\Phi_0, \quad (22a)$$

$$\begin{aligned} \hat{C} &= \hat{C}_{(1)} + \hat{C}_{(2)} + \dots + \hat{C}_{(N)} \\ &= \sum_{\sigma_1} \sum_i C'_{\sigma_1, i} S_{\sigma_1, i}^* + \sum_{\sigma_2} \sum_{i, j} C'_{\sigma_2, i, j} S_{\sigma_2, i, j}^* + \dots \\ &\quad + \sum_{\sigma_N} \sum_{i, j, k, \dots, n} C'_{\sigma_N, i, j, \dots, n} S_{\sigma_N, i, j, \dots, n}^* \\ &= \sum_I C'_I S_I^*. \end{aligned} \quad (22b)$$

Since the CI expansion is linear for the excitation operators, all of the configurations involved have desired symmetry without the projector. Since the unlinked terms of the SAC expansion (e. g.,  $\hat{O}\hat{S}_{(L)}\hat{S}_{(L')}$ ) belong to the space spanned by the higher-order operators (e. g.,  $\hat{S}_{(L+L')}$ ), we see that the SAC expansion is related with the CI expansion by

$$\hat{C}_{(1)} = \hat{S}_{(1)},$$

$$\hat{C}_{(2)} = \hat{S}_{(2)} + \frac{1}{2}\hat{O}\hat{S}_{(1)}^2,$$

$$\hat{C}_{(3)} = \hat{S}_{(3)} + \hat{O}\left(\frac{1}{2}\hat{S}_{(1)}\hat{S}_{(2)} + \frac{1}{3!}\hat{S}_{(1)}^3\right),$$

$$\hat{C}_{(4)} = \hat{S}_{(4)} + \hat{O}\left(\frac{1}{2}\hat{S}_{(2)}^2 + \hat{S}_{(1)}\hat{S}_{(3)} + \frac{1}{2!}\hat{S}_{(1)}^2\hat{S}_{(2)} + \frac{1}{4!}\hat{S}_{(1)}^4\right), \quad (23)$$

etc. This relation is similar to the relation (3) except for the projection operator in front of the unlinked terms. Thus, in contrast to the CI expansion, the SAC expansion includes the higher-order effect and the self-consistency effect of the symmetry-adapted excitation operators. The number of the independent variables are the same for both expansions. In the SAC expansion, they are included only in the linked term  $\hat{S}_{(i)}$ .

Despite of the above difference, the construction of the SAC expansion has a close similarity to that of the ordinary symmetry-adapted CI expansion [compare Eqs. (14) and (15) with Eq. (22)]. This enables us to combine the intuitions obtained from the CI theory with the merit

of the cluster expansion theory, i. e., the rapid convergence owing to the inclusion of the higher-order and self-consistency effects. This is favorable especially when we construct an approximate wavefunction. For instance, physical considerations and/or the experiences based on the CI theory show that for some physical properties only some kinds of excitations are of predominant importance (e. g.,  $\hat{S}_{(2)}$  for correlation energy and the spin-polarization excitations for spin density<sup>20</sup>). In such cases, we may choose only such excitation operators in the SAC expansion and may expect more rapid convergence than the CI expansion with a fewer number of variables. In the SAC expansion any choice does not contradict with the symmetry requirement.

### III. SAC EXPANSION COMPARED WITH THE CONVENTIONAL CLUSTER EXPANSIONS

Next we discuss the difference between the SAC expansion and the conventional cluster expansions. In Table I, we have summarized schematically the differences. We first compare the SAC expansion with the original cluster expansion given by Eq. (2), i. e.,

$$\Psi = \exp(\hat{T})\Phi_0. \quad (2a)$$

In this expansion the cluster generator  $\hat{T}$  includes various symmetries at the same time, so that the number of the independent variables included is larger than that included in the SAC expansion. However, this does not necessarily mean that the expansion (2) is able to give the solutions of different symmetries at the same time<sup>22</sup> (as it is in the ordinary CI expansion). In the unlinked terms of the expansion (2), e. g.,  $\hat{T}_i\hat{T}_j\Phi_0$ , the different symmetries included in each  $\hat{T}_i$  produce another set of different symmetries (for example, doublet  $\times$  doublet can give singlet, doublet, triplet, etc.),

TABLE I. Schematic summaries for the differences of the SAC expansion from the conventional cluster expansions.<sup>a</sup>

Expansion	Linked term	Unlinked term <sup>b</sup>	Number of independent variables <sup>c</sup>	Symmetry <sup>d</sup>	With $\hat{T}_1$ or $\hat{S}_{(1)}$ alone <sup>e</sup>
$\exp(\hat{T})\Phi_0$	$\hat{T}\Phi_0$	$\hat{T}_i\hat{T}_j\Phi_0$	Larger	Mixed	UHF
$\hat{O}\exp(\hat{T})\Phi_0$	$\hat{O}\hat{T}\Phi_0 \rightarrow \hat{S}\Phi_0$	$\hat{O}\hat{T}_i\hat{T}_j\Phi_0$	Larger !	Pure	SEHF
$\hat{O}\exp(\hat{S})\Phi_0$	$\hat{S}\Phi_0$	$\hat{O}\hat{S}_{(i)}\hat{S}_{(j)}\Phi_0$	Just as required	Pure	Pseudo-orbital

<sup>a</sup>The operators  $\hat{T}_i$  are not symmetry-adapted in general, but the operators  $\hat{S}_{(i)}$  are always symmetry-adapted.

<sup>b</sup>We have given only the second-order unlinked terms. These unlinked terms represent the higher-order and self-consistency effects of the linked operators, so long as the corresponding linked terms are not projected out in the expansion  $\hat{O}\exp(\hat{T})\Phi_0$  (see text).

<sup>c</sup>The numbers of the independent variables included in the expansions are compared with that required for the description of the system under consideration.

<sup>d</sup>This column concerns with the symmetry of the wavefunction when some  $\hat{T}_i$ 's or  $\hat{S}_{(i)}$ 's are picked up from the generator  $\hat{T}$  or  $\hat{S}$ .

<sup>e</sup>This column gives the orbital theories which are equivalent to the respective cluster expansions including  $\hat{T}_1$  or  $\hat{S}_{(1)}$  alone. We have assumed that these cluster expansions are solved with the variational principle (Sec. IV). For more details, see Sec. V.

so that *different* symmetry subspaces can interfere each other in the expansion (2). (This can never occur in the ordinary CI expansion so long as the Hamiltonian is totally symmetric.) Thus, in the expansion (2), the unnecessarily larger number of the independent variables can cause a difficulty in the solution.<sup>22</sup> In the SAC expansion, however, the SAC generator  $\hat{S}$  includes only the pure symmetry under consideration so that the number of the independent variables included is *just the same* as that required for the system. Obviously, the above difficulty can not occur in the SAC expansion.

In the original expansion (2), the cluster generator  $\hat{T}$  is classified according to the number of the excitations. For closed-shell systems, such classification may be compatible with the symmetry requirement for the excitations. However, in open-shell systems this is not generally true; i. e., each  $\hat{T}_i$  itself represents a mixed-symmetry excitation. [For example, the spin-polarization operator given by Eq. (18) is obtained by a special combination of  $\hat{T}_1$  and  $\hat{T}_2$ .] The unlinked terms of the expansion (2), which are the higher-order terms of the mixed-symmetry (then unphysical) operator  $\hat{T}_i$ , also represent mixed symmetries. Therefore, if we choose only some  $\hat{T}_i$ 's from the original expansion (2) as done in Eq. (5), the resultant wavefunction can not represent a pure symmetry but represents a *mixed* symmetry. An example is the UHF wavefunction which is written equivalently as  $\Phi_{\text{UHF}} = \pi \exp(\hat{T}_1) \Phi_0$  [see Eq. (49)]. On the other hand, in the SAC expansion, any choice does not contradict with the symmetry requirement. This is important especially for open-shell systems.

The SAC expansion is *also different* from the expansion

$$\Psi = \mathcal{O} \exp(\hat{T}) \Phi_0 \quad (24)$$

though both expansions belong to the pure symmetry under consideration. Although the cluster generator  $\hat{T}$  includes a larger number of variables than that required for the system (since the operator  $\hat{T}$  includes various symmetries at the same time), the unnecessary variables are projected out in the *linked* term,  $\mathcal{O} \hat{T} \Phi_0$  by the symmetry projector  $\mathcal{O}$ . However, this is *not* generally true in the *unlinked* terms,  $\mathcal{O} T^2 \Phi_0$ , etc. For example, when the operator  $\hat{T}_i$  includes the term which does *not* belong to the symmetry under consideration, the projector projects out such term from the linked term. However, in the unlinked terms (e. g.,  $\mathcal{O} \hat{T}_i^2 \Phi_0$ ), such operator generally remains since the product of such operators may include the symmetry under consideration even though the operator itself does not. Thus, the expansion (24) includes the independent variables *not only* in the linked term *but also* in the unlinked terms. The variables included in the latter arise from the different symmetries included in the operator  $\hat{T}$  and are generally unfavorable since they *can* interfere with the *pure* symmetry state under consideration through the unlinked terms. (See, however, a remark given later.) In other words, the different symmetry subspaces can interfere with each other in the expansion (24) [as in the expansion (2)] *despite of* the existence of the projection operator. Thus, the expansion (24) again includes the unnecessary

ly larger number of independent variables than that required for the system, and this can cause a difficulty in the solution.<sup>22</sup> In the SAC expansion, the independent variables are included only in the linked term  $\hat{S} \Phi_0$ , and among the cluster expansions compared in Table I, only the SAC expansion is free from such difficulty.

The expansion (24) belongs to the pure symmetry under consideration because of the symmetry projection. However, in the linked term we will in general have the same symmetry-adapted excitation operators arising from different  $\hat{T}_i$ 's. [For example, the operator given by Eq. (18) arises from both  $\mathcal{O} \hat{T}_1$  and  $\mathcal{O} \hat{T}_2$ .] Even if we rearrange them into the symmetry-adapted form  $\hat{S}$ , the unlinked terms are still different from those of the SAC expansion. In the SAC expansion, they are the higher-order terms of the symmetry-adapted excitation operators. However, in the expansion (24), they are the higher-order terms of the symmetry-non-adapted (then unphysical) operators  $\hat{T}_i$ 's, so that they do not correspond *directly* to the symmetry-adapted operators involved in the projected linked term. In other words, the unlinked terms of the expansion (24) do not correctly represent the higher-order and self-consistency effects of the operators included in the linked terms.

In the orbital theoretic approach, such difference in the unlinked terms causes an important difference in the self-consistency terms. For example, the spin-extended (SE) HF theory,<sup>23,24</sup> which belongs to the expansion (24) since it can be written equivalently as  $\Phi_{\text{SEHF}} = \pi \mathcal{O}_s \exp(\hat{T}_1) \Phi_0$  [see Eq. (58b)], is known to be poor for the description of both the spin density and correlation energy<sup>25,26</sup> of open-shell systems. As analyzed previously,<sup>27</sup> this defect of the SEHF theory is attributed to the unphysical nature of its self-consistency term, which is common in general to the expansion (24). The same is also true for the UHF theory<sup>27</sup> belonging to the expansion (2), which has another defect of the mixed symmetry. As shown in the succeeding paper,<sup>20</sup> such unreasonable SEHF and UHF descriptions of open-shell systems can be made more reasonable with the pseudo-orbital theory based on the SAC expansion.

Here we remark about the case in which the operator  $\hat{T}_i$  in the expansion  $\mathcal{O} \exp(\hat{T}_i) \Phi_0$ , which belongs to the class of the expansion (24), includes the operators having the *different* symmetry from that of the system. Though such operators are projected out in the linked term,  $\mathcal{O} \hat{T}_i \Phi_0$ , they are generally involved in the unlinked terms,  $\mathcal{O} \hat{T}_i^2 \Phi_0$ , etc., and offer the additional variables which are *independent* from those included in the linked term. In this special case, it is possible to utilize such variables *as if* they represent the physics of the higher-order *linked* term (e. g., the physics of  $\mathcal{O} \hat{T}_{2i}$ ) in a *limited* way (the number of the independent variables included in the operator  $\hat{T}_i^2$  is much smaller than that included in  $\hat{T}_{2i}$ ). As shown in the separate paper,<sup>16</sup> the inclusion of the correlation effects (represented by  $\hat{T}_2$ ) in the framework of the orbital theory (including  $\hat{T}_1$  alone)<sup>12</sup> is mostly done in this way. A typical example is the alternant correlation effect<sup>23b</sup> in the closed-shell orbital theories. It is incorporated through the unlinked terms of the triplet-type excitation opera-

tors given by Eq. (55b).<sup>16</sup> This is why the SEHF theory gives a fair correlation energy for closed shell systems in contrast to those obtained for open-shell systems.<sup>26</sup> [In open-shell systems, the triplet-type excitation operators included in  $\hat{T}_1$  remain in the *linked* term after transformed into the spin-polarization operator given by Eq. (18), so that this special case does not hold.] However, since such inclusion of the correlation effect is quite limited in nature, it is recommended to include it more directly by considering the double-excitation operator  $\hat{S}_{(2)}$  in the SAC expansion formula.

$$E = E_0 + 2 \sum_I C_I \langle 0 | HS_I^+ | 0 \rangle + \sum_{I,J} C_I C_J \langle 0 | S_I HS_J^+ | 0 \rangle + \langle 0 | HS_I^+ S_J^+ | 0 \rangle - \delta_{IJ} E_0 \\ + \sum_{IJK} C_I C_J C_K \langle 0 | S_I (H - E_0) S_J^+ S_K^+ | 0 \rangle - 2 \sum_I C_I^2 \sum_J C_J \langle 0 | HS_J^+ | 0 \rangle + O(C^4), \quad (25)$$

but in the expansion (24) it begins from the second order. In Eq. (25),  $|0\rangle$  denotes  $|\Phi_0\rangle$ ,  $E_0 = \langle 0 | H | 0 \rangle$ , and  $C_I$ 's are assumed to be real. Equation (25) is valid for all the expectation values of the operators which commute with the projection operator. For one electron properties, the effect begins from the third order in the SAC expansion, i. e.,

$$\langle \hat{A} \rangle = \langle 0 | \hat{A} | 0 \rangle + 2 \sum_I C_I \langle 0 | \hat{A} S_I^+ | 0 \rangle + \sum_{I,J} C_I C_J \langle 0 | S_I \hat{A} S_J^+ | 0 \rangle - \delta_{IJ} \langle 0 | \hat{A} | 0 \rangle + O(C^3), \quad (26)$$

where we have assumed that the one-electron operator  $\hat{A}$  be Hermitian and the prime on  $\sum$  means the sum over the single-excitation operators. For the expansion (24), however, the projector appears from the first order terms. When the reference wavefunction  $\Phi_0$  is already a reasonably good wavefunction, the coefficients  $C_I$  would be small. Then, in the SAC expansion, we may adopt an approximation to neglect the projection operator from the formalism. The accuracy of such approximation is seen from Eqs. (25) and (26).

Lastly, we note that the cluster expansion method is more suitable than the CI theory for the analyses of various variational theories based on model wavefunctions (e. g., orbital theories, self-consistent geminal theories, etc.). This is because these variational theories necessarily include self-consistency effects when we look upon them from different reference wavefunction. For closed-shell systems, we have given extensive analyses of various orbital theories starting from the expansions (2) and (13).<sup>16</sup> For open-shell systems, we will later give some cluster expansion formulas which are equivalent to some conventional orbital theories. Such expression gives a basis for extending orbital theory in the SAC expansion formula by eliminating unfavorable terms and/or by adding important terms. The resultant theory does not include the unphysical self-consistency terms as shown above.

#### IV. VARIATIONAL EQUATION FOR THE SAC WAVEFUNCTION

The SAC wavefunction may be determined by both variational and nonvariational procedures. For the nonvariational determination the diagrammatic method developed by Čížek and Paldus<sup>7,28</sup> may be applicable.<sup>7d</sup> However, in this section, we consider a variational determination of the SAC wavefunction, since it is primi-

In Table I, we have summarized schematically the above discussions.

In the SAC expansion, the effect of the projection operator is small in contrast to the expansion (24). In the expansion (24) the linked term  $\mathcal{O}\hat{T}\Phi_0$  already includes the projection operator. This is unfavorable for physical visuality. In the SAC expansion the projector appears only in the unlinked terms. For the energy, the effect of the projector begins from the fourth order in the coefficients in the SAC expansion, i. e.,

and since such procedure enables us to extend various variational theories in the SAC expansion formulas.

As given by Eqs. (14) and (15), the SAC wavefunction is written as

$$\Psi = \mathcal{O} \exp \left( \sum_I C_I S_I^+ \right) \Phi_0, \quad (27)$$

where the variables are the coefficients  $C_I$ . We introduce  $\Psi'$  by

$$\Psi' = \exp \left( \sum_I C_I S_I^+ \right) \Phi_0, \quad (28)$$

which does not include the symmetry projector  $\mathcal{O}$  in front of the unlinked terms [see Eq. (14)]. The variational equation for the unnormalized wavefunction  $\Psi$  is given by

$$\langle \Psi | H - E | \delta \Psi \rangle = 0, \quad (29)$$

where

$$\delta \Psi = \sum_I \frac{\partial \Psi}{\partial C_I} \delta C_I. \quad (30)$$

From Eq. (27) we can calculate  $\partial \Psi / \partial C_I$  as

$$\partial \Psi / \partial C_I = \mathcal{O} S_I^+ \Psi'. \quad (31)$$

Since  $\delta C_I$  in Eq. (30) are arbitrary we obtain from Eqs. (29)–(31) the equation

$$\langle \Psi | (H - E) \mathcal{O} S_I^+ | \Psi' \rangle = 0 \quad (32)$$

for all  $I$ . Here the  $\Psi$  has a desired symmetry and  $H - E$  is totally symmetric, so that the projector  $\mathcal{O}$  is unnecessary and we obtain

$$\langle \Psi | (H - E) S_I^+ | \Psi' \rangle = 0, \quad (33)$$

for all  $I$  included in Eq. (27). This is the variational

equation for the SAC wavefunction. In general,  $\Psi$  and  $S_I^* \Psi'$  are not orthogonal.

From the commutation relation for  $S_I^*$  [Eq. (20a)], the SAC wavefunction (27) is written as

$$\begin{aligned} \Psi &= \mathcal{O} \left( \prod_I \exp(C_I S_I^*) \right) \Phi_0 \\ &= \mathcal{O} \left( \prod_I (1 + C_I S_I^* + \frac{1}{2} C_I^2 S_I^{*2} + \dots) \right) \Phi_0. \end{aligned} \quad (34)$$

In general, the expansion in this equation terminates at lower order (first or second order)<sup>29</sup> because of the fermion property,  $a_i^2 = 0$  or  $a_i a_i = 0$ . When  $(S_I^*)^m = 0$  for  $m \geq n+1$ , the SAC equation (33) is a 2 $n$ th order simultaneous equation for the coefficient  $C_I$ .

In comparison with the variational equation for the CI wavefunction (22), i. e.,

$$\langle \Psi_{\text{CI}} | (H - E) S_I^* | \Phi_0 \rangle = 0, \quad (35)$$

the equation (33) for the SAC wavefunction is similar to the generalized Brillouin theorem. When the unlinked terms in Eq. (14) have a desired pure symmetry without the projector  $\mathcal{O}$  {the unlinked terms of the singlet-type excitation operator given by Eq. (62a) have such a property in closed-shell systems [see Eq. (69)]}, or when we can neglect the effect of the projection operator, the variational equation (33) becomes

$$\langle \Psi' | (H - E) S_I^* | \Psi' \rangle = 0, \quad (36)$$

which has just the same form as the generalized Brillouin theorem. In contrast to the CI equation (35), this similarity may be attributed to the inclusion of the higher-order and self-consistency effects in the SAC wavefunction. The analysis similar to Eq. (25) shows that the effect of the projection operator in the SAC equation (33) begins from the third order in the coefficients: i. e., up to the second order, Eq. (33) is identical with Eq. (36).

### A. Linearization of the SAC equation

Although the CI equation is linear in the coefficients, the SAC equation includes higher-order terms. However, when the reference wavefunction  $\Phi_0$  is already a reasonably good wavefunction, the coefficients  $C_I$  would be small so that we may neglect the second- and higher-order terms in Eq. (33). This approximation corresponds to applying the variational principle to an energy expression which is correct to the second order in the coefficients. In this approximation the effect of the projector does not appear and Eqs. (33) and (36) are the same. Thus, we obtain from Eq. (33) the linear equation

$$\begin{aligned} \langle 0 | HS_I^* | 0 \rangle + \sum_J C_J \langle 0 | S_J HS_I^* | 0 \rangle \\ + \langle 0 | HS_I^* S_J^* | 0 \rangle - E \delta_{IJ} = 0, \end{aligned} \quad (37)$$

for all  $I$  included in the SAC wavefunction (27). Here, we have assumed the coefficients to be real. This equation is similar to the CI equation (35) except that it includes an additional term  $\langle 0 | HS_I^* S_J^* | 0 \rangle$  which has arisen from the inclusion of the self-consistency effect. Since

our Hamiltonian is real, we can assume all the integrals to be real without loss of generality so that both of the integrals,  $\langle 0 | S_J HS_I^* | 0 \rangle$  and  $\langle 0 | HS_I^* S_J^* | 0 \rangle$ , are symmetric for the interchange between  $I$  and  $J$ . Then, Eq. (37) can be solved by a single diagonalization as the CI equation. In going from Eq. (33) to Eq. (37), we did not modify the energy  $E$ . However, in order to make Eq. (37) completely linear for the coefficients, we may replace it with  $E_0$ . In such approximation, we obtain

$$\begin{aligned} \langle 0 | HS_I^* | 0 \rangle + \sum_J C_J \langle 0 | S_J HS_I^* | 0 \rangle \\ + \langle 0 | HS_I^* S_J^* | 0 \rangle - E_0 \delta_{IJ} = 0. \end{aligned} \quad (38)$$

It is possible to write the solutions of Eqs. (37) and (38) in a sum-over-state form familiar in the perturbation theory. We introduce the following matrices of integrals:

$$\mathbf{A} = \langle 0 | \mathbf{S} \mathbf{H} \mathbf{S}^* | 0 \rangle, \quad (39a)$$

$$\mathbf{B} = \langle 0 | \mathbf{H} (\mathbf{S}^*)^T \mathbf{S}^* | 0 \rangle, \quad (39b)$$

where  $\mathbf{S}^* = (S_1^*, \dots, S_I^*, \dots)$ . Since these matrices are symmetric, we can introduce an orthogonal transformation  $\mathbf{U}$  by

$$\mathbf{U}^T (\mathbf{A} + \mathbf{B}) \mathbf{U} = \mathbf{D}, \quad (40)$$

where  $\mathbf{D}$  is a diagonal matrix with diagonal elements  $D_I$ . Using this transformation, we define a new set of excitation operators  $\mathbf{R}^*$  and a new set of coefficients  $\mathbf{C}'$  by

$$\mathbf{R}^* = \mathbf{S}^* \mathbf{U}, \quad (41)$$

$$\mathbf{C}' = \mathbf{U}^T \mathbf{C}, \quad (42)$$

where  $\mathbf{C}$  is a column vector composed of  $C_I$ . With the use of these transformations, Eq. (38) is solved at once as

$$C'_I = \langle 0 | HR_I^* | 0 \rangle / (E_0 - D_I). \quad (43)$$

For Eq. (37),  $E_0$  in the denominator of Eq. (43) is replaced with  $E$ . For Eq. (38), the energy of the system is calculated from Eq. (25) as

$$E = E_0 + \sum_I \langle 0 | HR_I^* | 0 \rangle \langle 0 | R_I H | 0 \rangle / (E_0 - D_I), \quad (44)$$

which is correct to the second order in the coefficients. The wavefunction at this level of approximation may be written as

$$\begin{aligned} \Psi &= \left( 1 + \sum_I C_I S_I^* + \frac{1}{2} \sum_{I,J} C_I C_J \mathcal{O} S_I^* S_J^* \right) \Phi_0 \\ &= \left( 1 + \sum_I C'_I R_I^* + \frac{1}{2} \sum_{I,J} C'_I C'_J \mathcal{O} R_I^* R_J^* \right) \Phi_0 \end{aligned} \quad (45)$$

and the normalization factor  $\mathfrak{N}$  is given by

$$\mathfrak{N} = 1 - \sum_I C_I^2 = 1 - \sum_I C_I'^2. \quad (46)$$

The above set of equations is essentially the same as that given previously for rewriting the coupled-perturbed HF theory in a sum-over-state form.<sup>17</sup>



In this linear approximation, the solution requires only a *single* diagonalization as in the CI procedure [for Eq. (38), it is given by Eq. (40)] and at the same time it includes the self-consistency effect through the **B** matrix, which is a merit of the cluster expansion theory. However, when we neglect the single-excitation operator  $\hat{S}_{(1)}$  in Eq. (15), the **B** matrix vanishes identically since it becomes an integral between  $\Phi_0$  and more-than-four electron excited configurations. In such case, the solution of Eq. (37) [not Eq. (38)] becomes identical with that of the CI procedure. Therefore, the above linear approximation is meaningful in the cluster expansion theory only when we include  $\hat{S}_{(1)}$  in the linked term.

$$\begin{aligned} \langle 0 | HS_I^+ | 0 \rangle + \sum_J C_J \langle 0 | S_J (H - E) S_I^+ | 0 \rangle + \langle 0 | HS_I^+ S_I^+ | 0 \rangle + \sum_{J,K} C_J C_K \langle 0 | S_J (H - E) S_I^+ S_K^+ | 0 \rangle \\ + \frac{1}{2} \langle 0 | S_J S_K (H - E) S_I^+ | 0 \rangle + \frac{1}{2} \sum_{J,K,L} C_J C_K C_L \langle 0 | S_J (H - E) S_I^+ S_K^+ S_L^+ | 0 \rangle + \langle 0 | S_J S_K \mathcal{O} (H - E) S_I^+ S_L^+ | 0 \rangle = 0, \end{aligned} \quad (47)$$

where in the third-order term we need the projection operator. When we limit ourselves only to the two-particle excitation operators, Eq. (47) becomes a bit simpler as

$$\begin{aligned} \langle 0 | HS_I^+ | 0 \rangle + \sum_J C_J \langle 0 | S_J (H - E) S_I^+ | 0 \rangle \\ + \sum_{J,K} C_J C_K \langle 0 | S_J HS_I^+ S_K^+ | 0 \rangle + \frac{1}{2} \langle 0 | S_J S_K HS_I^+ | 0 \rangle \\ + \frac{1}{2} \sum_{J,K,L} C_J C_K C_L \langle 0 | S_J S_K \mathcal{O} (H - E) S_I^+ S_L^+ | 0 \rangle = 0. \end{aligned} \quad (48)$$

The second- and third-order terms represent the higher-order effects of the excitation operators. These equations are the third-order simultaneous equations and may be solved through iterative procedure. In a similar way, it is easy to derive the higher-order equations from Eq. (33). So long as we start from a reasonably good wavefunction, the coefficients  $C_J$  would be small, so that such a procedure would terminate at some order within the desired accuracy.

## V. ANALYSIS AND EXTENSION OF OPEN-SHELL ORBITAL THEORIES

As remarked in the previous section, the cluster expansion formalism is very suitable to the analysis of orbital theories. This is because the cluster expansion includes completely the self-consistency effect of orbitals as the Thouless theorem<sup>12</sup> implies. In this section, we first analyze some open-shell orbital theories, the UHF, SEHF, and RHF theories, expressing them equivalently in the *conventional* cluster expansion formulas. We will show that the types of the excitation operators included in these formulas are well related with the Brillouin theorems satisfied by these theories. Based on these analyses, we then give some extensions of open-shell orbital theory in the SAC expansion formulas. The resultant extended theory, called

Lastly, we note that the matrices **A** and **B** defined by Eq. (39) are similar to those which appear in the theories for the random-phase approximation<sup>12,30</sup> and for the instability of the HF solution.<sup>11,31</sup> Some connections between the present and these theories will be discussed in a separate paper.<sup>16</sup>

## B. Higher-order variational equations

When we consider the higher-order effects of more-than-double excitation operators ( $\hat{S}_{(i)}$ ,  $i \geq 2$ ), we have to solve the higher-order variational equation. Up to the third order in the coefficients, we obtain from Eq. (33) the equation

pseduo-orbital theory, will be applied in the subsequent paper<sup>20</sup> to the calculations of spin density of open-shell systems.

## A. Analysis of open-shell orbital theories

### 1. UHF theory

The UHF theory is most naturally expressed by the original cluster expansion given by Eq. (2). As remarked in the Introduction, the cluster expansion including  $\hat{T}_1$  alone, i. e.,

$$\Phi = \mathcal{N} \exp \left( \sum_{i,j} C_{jt} a_j^+ a_i \right) \Phi_0, \quad (49)$$

is just a transformation of a single determinant  $\Phi_0$ ,

$$\Phi_0 = \|\varphi_1 \cdots \varphi_i \cdots \varphi_N\|, \quad (50)$$

into another single determinant  $\Phi$ ,

$$\Phi = \|\psi_1 \cdots \psi_i \cdots \psi_N\|. \quad (51)$$

In Eq. (49) the indices  $i$  and  $j$  represent the occupied and unoccupied spin orbitals  $\varphi_i$  and  $\varphi_j$ , respectively, and the operator  $b_i^+$  in Eq. (2b) is expanded as

$$b_i^+ = \sum_j C_{jt} a_j^+. \quad (52)$$

The proof for the above statement is given by Thouless<sup>12</sup> and is straightforward, as follows. We can rewrite Eq. (49) as

$$\begin{aligned} \Phi &= \mathcal{N} \prod_i \left( 1 + \sum_j C_{jt} a_j^+ a_i \right) \prod_i a_i^+ | \rangle \\ &= \mathcal{N} \prod_i \left( a_i^+ + \sum_j C_{jt} a_j^+ \right) | \rangle, \end{aligned} \quad (53)$$

where we have used the fermion anticommutation relation and especially  $a_i a_i = 0$ . Introducing a new set of spin orbitals

$$\psi_i = \left( \varphi_i + \sum_j C_{jt} \varphi_j \right) \left( 1 + \sum_j |C_{jt}|^2 \right)^{-1/2}, \quad (54)$$

we see that Eq. (53) is just identical with the single determinant given by Eq. (51). This proof can also be done by introducing the operator  $h_i^*$  as given by Eq. (9) and using the procedure given in Footnote 13. The operator  $h_i^*$  generates a new set of spin orbitals given by Eq. (54). The condition given by Eq. (11) corresponds to the orthonormality condition for  $\psi_i$ . Thus, when the coefficients  $C_{ji}$  in Eq. (49) are determined variationally the cluster wavefunction (49) becomes identical with the UHF wavefunction.

In order to rewrite Eq. (49) in a form similar to the SAC expansion, we choose as a reference wavefunction the single determinant given by Eq. (16) and introduce the following excitation operators

$$S_{0,tk}^* = (a_{t\alpha}^* a_{k\alpha} + a_{t\beta}^* a_{k\beta})/\sqrt{2}, \quad (55a)$$

$$S_{T,tk}^* = (a_{t\alpha}^* a_{k\alpha} - a_{t\beta}^* a_{k\beta})/\sqrt{2}, \quad (55b)$$

$$S_{0,tm}^* = a_{t\alpha}^* a_{m\alpha}, \quad (55c)$$

$$S_{0,mk}^* = a_{m\beta}^* a_{k\beta}, \quad (55d)$$

where we have replaced the index for the spin orbital with the set of indices for the space orbital and spin. The index  $t$  indicates the unoccupied space orbital. According to the transformation given by Eq. (55), we transform the coefficients as

$$\begin{aligned} C_{0,tk} &= \sqrt{2}(C_{t\alpha k\alpha} + C_{t\beta k\beta}), \\ C_{T,tk} &= \sqrt{2}(C_{t\alpha k\alpha} - C_{t\beta k\beta}), \\ C_{0,tm} &= C_{t\alpha m\alpha}, \\ C_{0,mk} &= C_{m\beta k\beta}. \end{aligned} \quad (56)$$

Then, the UHF wavefunction given by Eq. (49) is rewritten as

$$\begin{aligned} \Phi_{\text{UHF}} &= \mathcal{N} \exp\left(\sum_{tk} C_{0,tk} S_{0,tk}^* + \sum_{tk} C_{T,tk} S_{T,tk}^* \right. \\ &\quad \left. + \sum_{tm} C_{0,tm} S_{0,tm}^* + \sum_{mk} C_{0,mk} S_{0,mk}^*\right) \Phi_0. \end{aligned} \quad (57)$$

Although this expression resembles the SAC expansion, it is different from the SAC expansion. It belongs to the class of the wavefunctions represented by Eq. (2). Although the operators  $S_{0,tk}^*$ ,  $S_{0,tm}^*$ , and  $S_{0,mk}^*$  are spin adapted and produce the singlet excitations on applying  $\Phi_0$ , the operator  $S_{T,tk}^*$  is not spin adapted (the suffix  $T$  abbreviates triplet-type). It produces a mixed spin state on applying  $\Phi_0$ . The existence of this operator is a main origin of the spin contamination included in the UHF wavefunction.<sup>32</sup> Since Eq. (57) expresses the UHF wavefunction in a compact *closed* form, the present formalism based on the cluster expansion is more convenient than the previous one<sup>27,32a</sup> based on the CI expansion. Lastly we note that the types of the excitation operators included in Eq. (57) are related with the fact that the UHF wavefunction satisfies the Brillouin theorem for these four types of excitations.

## 2. Open-shell SEHF theory (GF theory)

The spin-extended HF (SEHF) wavefunction<sup>23</sup> is obtained by spin projecting the spin-polarized single de-

terminant, which has the same form as the UHF wavefunction, and subsequently applying the variational principle (Goddard<sup>24</sup> has referred to it as the GF wavefunction). Then, from Eq. (57), the SEHF wavefunction is written equivalently in the cluster expansion form as

$$\begin{aligned} \Phi_{\text{SEHF}} &= \mathcal{N} \mathcal{O}_s \exp\left(\sum_{tk} C'_{0,tk} S_{0,tk}^* + \sum_{tk} C'_{T,tk} S_{T,tk}^* \right. \\ &\quad \left. + \sum_{tm} C'_{0,tm} S_{0,tm}^* + \sum_{mk} C'_{0,mk} S_{0,mk}^*\right) \Phi_0, \end{aligned} \quad (58a)$$

where  $\mathcal{O}_s$  is the spin-projection operator given by Eq. (19). From Eq. (49), this wavefunction is also written as

$$\Phi_{\text{SEHF}} = \mathcal{N} \mathcal{O}_s \exp(\hat{T}_1) \Phi_0. \quad (58b)$$

Although this wavefunction has a desired symmetry because of the existence of  $\mathcal{O}_s$ , it is different from the SAC expansion since  $S_{T,tk}^*$  is not spin adapted. The SEHF wavefunction belongs to the class of the wavefunctions represented by Eq. (24). Then, the self-consistency term included in the SEHF wavefunction is unphysical (for open-shell systems) since it is a higher-order term of the unphysical operator  $S_{T,tk}^*$ . This is an origin<sup>20,27</sup> of the results that the SEHF theory was poor for both spin density<sup>25</sup> and correlation energy<sup>26</sup> of open-shell systems. We will later consider an extension of the UHF and SEHF theories in the SAC expansion formula by replacing  $S_{T,tk}^*$  in Eq. (58a) with the spin-polarization excitation operator  $S_{P,tk}^*$  given by Eq. (18).

## 3. Open-shell RHF theory

Although the RHF wavefunction is used in the present formalism as a reference wavefunction  $\Phi_0$ , we investigate here its cluster expansion form since it gives a prototype for studying the nature of the "restricted" condition in the cluster expansion formalism. A basic assumption of the restricted condition is that the orbitals can be classified into blocks (e.g., closed block and open block) and within each block a unitary transformation among orbitals keeps the total wavefunction invariant.<sup>19,33,34</sup> Because of this restriction the cluster expansion form for the RHF wavefunction becomes

$$\Phi_{\text{RHF}} = \mathcal{N} \mathcal{A}_{KM} \exp\left(\sum_K C_K S_K^*\right) \Phi_{0,K} \exp\left(\sum_M C_M S_M^*\right) \Phi_{0,M}, \quad (59)$$

where  $\Phi_{0,K}$  and  $\Phi_{0,M}$  are arbitrary single determinants for the closed and open blocks, respectively,

$$\Phi_{0,K} = \|\varphi_1 \alpha \varphi_1 \beta \cdots \varphi_n \alpha \varphi_n \beta \cdots \varphi_q \alpha \varphi_q \beta\|, \quad (60)$$

$$\Phi_{0,M} = \|\varphi_{q+1} \alpha \cdots \varphi_m \alpha \cdots \varphi_p \beta\|. \quad (61)$$

Here,  $\Phi_{0,K}$  accommodates the first  $2q$  electrons and  $\Phi_{0,M}$  the last  $p-q$  electrons. The operators  $S_K^*$  represent the singlet-type excitation operators for the excitations from the closed block to all other blocks

$$S_{0,tk}^* = (a_{t\alpha}^* a_{k\alpha} + a_{t\beta}^* a_{k\beta})/\sqrt{2}, \quad (62a)$$

$$S_{0,mk}^* = (a_{m\alpha}^* a_{k\alpha} + a_{m\beta}^* a_{k\beta})/\sqrt{2}, \quad (62b)$$

and  $S_M^*$  represent the singlet-type excitation operators

for the excitations from the open block to all other blocks

$$S_{0,tm}^+ = a_{t\alpha}^+ a_{m\alpha}, \quad (63a)$$

$$S_{0,km}^+ = a_{k\alpha}^+ a_{m\alpha}. \quad (63b)$$

$\mathcal{Q}_{KM}$  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 different blocks do not necessarily commute with each other. [If they commute, Eq. (59) can be rewritten in a single exponential form.] In the present case, the commutation relations are given by

$$[S_{0,tk}^+, S_{0,t'm'}^+] = 0,$$

$$[S_{0,tk}^+, S_{0,k'm'}^+] = \delta_{kk'} a_{k\alpha}^+ a_{m\alpha} / \sqrt{2},$$

$$[S_{0,mk}^+, S_{0,t'm'}^+] = -\delta_{mm'} a_{t\alpha}^+ a_{k\alpha} / \sqrt{2}, \quad (64)$$

$$[S_{0,mk}^+, S_{0,k'm'}^+] = (\delta_{kk'} \delta_{mm'} - \delta_{mm'} a_{k'\alpha}^+ a_{k\alpha} + \delta_{kk'} a_{m\alpha}^+ a_{m'\alpha}) / \sqrt{2}.$$

The appearance of these noncommuting excitation operators originates from the restricted condition. Of course, these excitation operators commute each other within each block. From Eqs. (62) and (63), the RHF wavefunction is written more explicitly as

$$\Phi_{\text{RHF}} = \mathcal{N} \mathcal{Q}_{KM} \exp \left( \sum_{tk} C_{0,tk} S_{0,tk}^+ + \sum_{mk} C_{0,mk} S_{0,mk}^+ \right) \Phi_{0,K} \exp \left( \sum_{tm} C_{0,tm} S_{0,tm}^+ + \sum_{km} C_{0,km} S_{0,km}^+ \right) \Phi_{0,M}. \quad (65)$$

The proof for the equivalence between the cluster wavefunction (65) and the RHF wavefunction proceeds straightforwardly. Using relations like

$$\exp \left( \sum_{tk} C_{0,tk} S_{0,tk}^+ \right) = \prod_k \left( 1 + \frac{1}{\sqrt{2}} \sum_t C_{0,tk} a_{t\alpha}^+ a_{k\alpha} \right) \left( 1 + \frac{1}{\sqrt{2}} \sum_t C_{0,tk} a_{t\beta}^+ a_{k\beta} \right), \quad (66)$$

we can rewrite Eq. (65) as

$$\begin{aligned} \Phi_{\text{RHF}} &= \mathcal{N} \mathcal{Q}_{KM} \prod_k^q \left[ \left( a_{k\alpha}^+ + \sum_t C'_{0,tk} a_{t\alpha}^+ + \sum_m C'_{0,mk} a_{m\alpha}^+ \right) \right. \\ &\quad \left. \times \left( a_{k\beta}^+ + \sum_t C'_{0,tk} a_{t\beta}^+ + \sum_m C'_{0,mk} a_{m\beta}^+ \right) \right] |\rangle_K \prod_{m=q+1}^p \left( a_{m\alpha}^+ + \sum_t C_{0,tm} a_{t\alpha}^+ + \sum_k C_{0,km} a_{k\alpha}^+ \right) |\rangle_M \\ &= \| \psi_1 \alpha \psi_1 \beta \cdots \psi_k \alpha \psi_k \beta \cdots \psi_q \alpha \psi_q \beta \psi_{q+1} \alpha \cdots \psi_m \alpha \cdots \psi_p \alpha \|, \end{aligned} \quad (67)$$

where  $C'_{0,tk} = C_{0,tk} / \sqrt{2}$ , etc., and  $|\rangle_K$  and  $|\rangle_M$  denote the vacuum states for closed and open blocks, respectively, and a new set of orbitals  $\psi_k$  and  $\psi_m$  is defined by

$$\begin{aligned} \psi_k &= \left( \varphi_k + \sum_t C'_{0,tk} \varphi_t + \sum_m C'_{0,mk} \varphi_m \right) \left( 1 + \sum_t |C'_{0,tk}|^2 + \sum_m |C'_{0,mk}|^2 \right)^{-1/2}, \\ \psi_m &= \left( \varphi_m + \sum_t C_{0,tm} \varphi_t + \sum_k C_{0,km} \varphi_k \right) \left( 1 + \sum_t |C_{0,tm}|^2 + \sum_k |C_{0,km}|^2 \right)^{-1/2}. \end{aligned} \quad (68)$$

Since each orbital given by Eq. (68) is defined completely freely (the mixing within each block is attained through the unitary ambiguity within each block), the variational determination of the coefficients in Eq. (65) leads to the RHF wavefunction. We note that the RHF wavefunction satisfies the Brillouin theorem for the excitations given by Eqs. (62) and (63).

For closed-shell systems, we have only the closed block and the excitation operators  $S_{0,mk}^+$ ,  $S_{0,tm}^+$ , and  $S_{0,mk}^+$  do not appear. Therefore, the RHF wavefunction for closed-shell systems is written simply as

$$\Phi_{\text{RHF}} = \mathcal{N} \exp \left( \sum_{tk} C_{0,tk} S_{0,tk}^+ \right) \Phi_0, \quad (69)$$

where  $\Phi_0$  is identical with  $\Phi_{0,K}$  given by Eq. (60). This wavefunction is the simplest example of the SAC wavefunction. (In other words, in the closed-shell limit the pseudo-orbital theory given below reduces to the conventional Hartree-Fock theory.) Here, the projection operator  $\mathcal{O}$  is unnecessary since the higher-order un-

linked terms of Eq. (69) automatically belong to the desired singlet state.

## B. Pseudo-orbital theory

The preceding analysis of the conventional orbital theories has clarified the types of the excitation operators included in the equivalent cluster expansion formulas. They are shown to be limited to only those types which are related to the types of the Brillouin theorems satisfied by the respective orbital theories. Many other excitation operators remain excluded especially for open-shell systems. The UHF and SEHF theories belong to the *conventional* cluster expansions given by Eqs. (2) and (24), respectively, so that their self-consistency terms are unphysical. Since in the open-shell systems,  $\hat{S}_{(1)}$  is not necessarily small even if we start from the RHF wavefunction, it is suggested that the open-shell orbital theory can be extended in several ways in the SAC expansion formulas. Here we consider such extensions of the open-shell orbital the-

ory, restricting ourselves to only the single excitation operator  $\hat{S}_{(1)}$ . The resultant theory is called pseudo-orbital theory.<sup>18</sup>

The wavefunction considered in this section (the pseudo-orbital wavefunction) is written as

$$\Phi_{PO} = \theta \exp(\hat{S}_{(1)}) \Phi_0 = \left[ 1 + \hat{S}_{(1)} + \theta \left( \frac{1}{2} \hat{S}_{(1)}^2 + \frac{1}{3!} \hat{S}_{(1)}^3 + \dots \right) \right] \Phi_0, \quad (70)$$

where  $\hat{S}_{(1)}$  represents the sum of the symmetry-adapted single excitation operators

$$\hat{S}_{(1)} = \sum_{\sigma_1}^{f_1} \sum_I C_{\sigma_1, I} S_{\sigma_1, I}^+ = \sum_I C_I S_I^+. \quad (71)$$

The reference wavefunction  $\Phi_0$  is given by Eq. (16). The system has  $s$  unpaired spins [see Eq. (17)].

For such systems we have in general the following spin-adapted single-excitation operators. For excitations from the doubly occupied orbital  $k$  to unoccupied orbital  $t$ , we have  $s + 1$  excitation operators.<sup>21</sup> The first two are given by

$$\begin{aligned} S_{0, tk}^+ &= (a_{t\alpha}^+ a_{k\alpha} + a_{t\beta}^+ a_{k\beta}) / \sqrt{2}, \quad (72) \\ S_{1, tk}^+ &= S_{P, tk}^+ \\ &= (s+2)^{-1/2} \left[ \left( \frac{s}{2} \right)^{1/2} (a_{t\alpha}^+ a_{k\alpha} - a_{t\beta}^+ a_{k\beta}) \right. \\ &\quad \left. + \left( \frac{2}{s} \right)^{1/2} a_{t\alpha}^+ a_{k\beta} \sum_{m=q+1}^p a_{m\beta}^+ a_{m\alpha} \right], \quad (73) \end{aligned}$$

which have been referred to in the text as the singlet-type and spin-polarization excitation operators, respectively. The last  $s - 1$  operators are given by

$$\begin{aligned} S_{r, tk}^+ &= [r(r-1)]^{1/2} a_{t\alpha}^+ a_{k\beta} \\ &\quad \times \left[ \sum_{m=p-r+2}^p a_{m\beta}^+ a_{m\alpha} - (r-1) a_{(p-r+1)\beta}^+ a_{(p-r+1)\alpha} \right] \quad 2 \leq r \leq s \end{aligned} \quad (74)$$

which represent the spin-flip excitation from  $k$  to  $t$  accompanied by the spin flips on the same open orbitals  $m$ . For all the excitations given by Eqs. (72)–(74), the energies required are of the order of the single excitation energy, i. e.,  $\sim (\epsilon_t - \epsilon_k - J_{tk})$ , since for all of them the “real” excitation is only from  $k$  to  $t$ . The spin flips among open orbitals modify the energy by the order of the exchange integral. Then, these excitation operators are included here in  $\hat{S}_{(1)}$ . On the other hand, in the original expansion given by Eq. (2), the operator  $S_{0, tk}^+$  belongs to  $\hat{T}_1$ , the operator  $S_{P, tk}^+$  belongs to a special combination of  $\hat{T}_1$  and  $\hat{T}_2$ , and the operator  $S_{r, tk}^+$  belongs to  $\hat{T}_2$ . For the excitation from the singly occupied orbital  $m$  to the unoccupied orbital  $t$ , we have

$$S_{0, tm}^+ = a_{t\alpha}^+ a_{m\alpha}, \quad (75)$$

and for the excitation from  $k$  to  $m$ , we have

$$S_{0, mk}^+ = a_{m\beta}^+ a_{k\beta}. \quad (76)$$

These operators have also been referred to as the singlet-type excitation operators. All of the operators given by Eqs. (72)–(76) satisfy the commutation relation given by Eq. (20). When the orbitals concerning an excitation

are degenerate, we have sometimes to take into account further the space symmetry. Such spin- and space-symmetry-adapted excitation operators are constructed by modifying the above spin-adapted operators as required from space symmetry.

When all of the excitation operators given above are included in the pseudo-orbital wavefunction (70), we obtain the most general extension of orbital theory within the extent of this section, i. e.,

$$\begin{aligned} \Phi_{PO1} &= \theta \exp \left( \sum_{\sigma=0}^s \sum_{tk} C_{\sigma, tk} S_{\sigma, tk}^+ \right. \\ &\quad \left. + \sum_{tm} C_{0, tm} S_{0, tm}^+ + \sum_{mk} C_{0, mk} S_{0, mk}^+ \right) \Phi_0. \quad (77) \end{aligned}$$

However, since the excitation operators  $S_{r, tk}^+$  ( $2 \leq r \leq s$ ) given by Eq. (74) are composed of the two simultaneous elementary excitations (real excitation and spin flip) and do not contribute to the first-order corrections to the orbitals, we may omit them from the above wavefunction and obtain

$$\begin{aligned} \Phi_{PO2} &= \theta \exp \left( \sum_{tk} C_{0, tk} S_{0, tk}^+ + \sum_{tk} C_{P, tk} S_{P, tk}^+ \right. \\ &\quad \left. + \sum_{tm} C_{0, tm} S_{0, tm}^+ + \sum_{mk} C_{0, mk} S_{0, mk}^+ \right) \Phi_0. \quad (78) \end{aligned}$$

This wavefunction constitutes an extension of the UHF and SEHF wavefunctions given by Eqs. (57) and (58). The excitation operator  $S_{T, tk}^+$  which are not spin adapted are replaced with the spin-adapted spin-polarization operator  $S_{P, tk}^+$ . Further, when the reference wavefunction  $\Phi_0$  in Eq. (78) is restricted to the RHF wavefunction, the effects of the singlet-type operators  $S_{0, tk}^+$ ,  $S_{0, tm}^+$ , and  $S_{0, mk}^+$  would be small<sup>20</sup> since the RHF wavefunction satisfies the Brillouin theorem for these excitations. Then, we obtain another simpler extension of the orbital theory, i. e.,

$$\Phi_{PO3} = \theta \exp \left( \sum_{tk} C_{P, tk} S_{P, tk}^+ \right) \Phi_{RHF}. \quad (79)$$

In contrast to the wavefunction given by Eq. (78), this wavefunction does not include the coupling effect between the spin-polarization and singlet-type excitation operators. The variables  $C_{P, tk}$ , etc., in the pseudo-orbital wavefunctions (77)–(79) are determined by the variational equation (33) or by its approximate variants given in Sec. IV. All of the wavefunctions (77)–(79) belong to the pure symmetry under consideration.

The main difference between the pseudo-orbital wavefunctions given by Eqs. (78) and (79) and the SEHF wavefunction given by Eq. (58) lies in the self-consistency terms.<sup>20</sup> This difference originates from the difference found in general between the SAC expansion and the expansion given by Eq. (24). Although the self-consistency terms of the SEHF theory includes unphysical contributions arising from the spin-non-adapted operator  $S_{T, tk}^+$ , they are improved in the present theory by replacing it with the spin-adapted operator  $S_{P, tk}^+$ . We will show in the subsequent paper<sup>20</sup> that because of this improvement the pseudo-orbital wavefunctions given by Eqs. (77)–(79) are free from the defect found pre-

viously<sup>27</sup> for the SEHF and UHF wavefunctions. Since the present wavefunctions correctly include the spin-polarization effect and its self-consistency effect, it is interesting to apply the present theory for investigating the spin-dependent properties of open-shell systems. In the following paper,<sup>20</sup> we will apply the present theory to the calculations of spin density.

Lastly, we note that the angular correlation effect is easily accommodated in the pseudo-orbital theory. For example, for the first-row atoms, the effect of *d* orbitals is included in the pseudo-orbital theory by considering the spin- and space-symmetry-adapted excitation operators. In the conventional orbital theory, however, it can be done only after the removal of the symmetry constraint to the orbitals and the subsequent symmetry projection in each iteration process.<sup>35</sup> In the subsequent paper, we will show that the angular correlation is very important for both spin density and energy.<sup>20</sup>

## VI. SUMMARY

In this paper, we have considered the symmetry-adapted-cluster (SAC) expansion of an exact wavefunction. It is composed of the symmetry-adapted excitation operators belonging to the symmetry under consideration and includes their higher-order effect and self-consistency effect. It is different from the conventional cluster expansions given by Eqs. (2) and (24) in several important points (see Table I). These merits of the SAC expansion make it suitable for the study of open-shell systems as well as closed-shell systems. We have considered the variational determination of the SAC wavefunction. Based on the cluster expansion analyses of some conventional open-shell orbital theories, we have given some extensions of open-shell orbital theories in the SAC expansion formula (pseudo-orbital theory). The results of the present study may be summarized as follows.

(1) The SAC expansion is *complete* so that it can describe an exact wavefunction. It belongs to the pure symmetry under consideration.

(2) The number of the independent variables included in the SAC expansion is *just the same* as that required for the system under consideration. The conventional cluster expansions given by Eqs. (2) and (24) includes unnecessarily larger number of variables arising from the various symmetries, and this can cause a difficulty in the solution. In the SAC expansion, such difficulty can never occur.

(3) In contrast to the expansion (2), any choice in the SAC generator  $\hat{S}$  (e.g.,  $\hat{S}_{(1)}$  for orbital theoretic approach,  $\hat{S}_{(2)}$  for the calculation of correlation energy, etc.) do not contradict with the symmetry requirement for the wavefunction. This is important especially for open-shell systems. [For example, the UHF theory which is equivalent to the expansion (2) with  $\hat{T}_1$  alone breaks the symmetry requirement.]

(4) In contrast to the expansion (2) and (24), the higher order and self-consistency terms of the SAC expansion

are physically correct. The unphysical natures of the self-consistency terms of the expansions (2) and (24) are seen, for example, in the failures of the UHF and SEHF theories in the descriptions of open-shell systems.

(5) The effect of the symmetry projection operator is small in the SAC expansion in contrast to the expansion (24). This is favorable for the physical visuality of the theory.

(6) The construction of the SAC expansion is analogous to that of the ordinary symmetry-adapted CI expansion, and yet it includes the higher-order and self-consistency effects of the excitation operators, which are important for the *rapid* convergence of the expansion with a smaller number of variables. The SAC expansion then enables us to combine the intuitions based on the CI theory with the merit of the cluster expansion theory (i.e., the rapid convergence).

(7) The variational equation for the SAC wavefunction resembles the generalized Brillouin theorem in accordance with the inclusion of the higher-order and self-consistency effects. In the linear approximation, the equation is solved only by a single diagonalization, though such approximation is useful only when the operator  $\hat{S}$  includes  $\hat{S}_{(1)}$ .

(8) When combined with the variational principle, the cluster expansion method is suitable for analyzing various variational theories based on the model wavefunctions. As an example, the UHF, SEHF, and RHF theories are expressed equivalently in the conventional cluster expansion formulas.

(9) The pseudo-orbital theory, which is an extension of open-shell orbital theory in the SAC expansion formula, do not have the defects found previously for the UHF and SEHF theories (see Ref. 20). It would be suitable especially for the calculations of the spin-dependent properties. In the subsequent paper, it will be applied to the calculations of the spin density.

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<sup>1</sup>Adv. Chem. Phys. **14**, (1969).

<sup>2</sup>H. Primas, in *Modern Quantum Chemistry, Istanbul Lectures*, edited by O. Sinanoğlu (Academic, New York, 1965), Part 2, p. 45.

<sup>3</sup>For example, see J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940), Chap. 13.

<sup>4</sup>For example, see (a) F. Coster, Nucl. Phys. **7**, 421 (1958); F. Coster and H. Kümmel, Nucl. Phys. **17**, 477 (1960); (b) J. da Providência, Nucl. Phys. **46**, 401 (1963); **61**, 87 (1965).

<sup>5</sup>(a) O. Sinanoğlu, J. Chem. Phys. **36**, 706, 3198 (1962); Adv. Chem. Phys. **6**, 315 (1964); (b) D. F. Tuan and O. Sinanoğlu, J. Chem. Phys. **38**, 1740 (1963).

<sup>6</sup>(a) H. J. Silverstone and O. Sinanoğlu, J. Chem. Phys. **44**, 1899, 3608 (1966); (b) O. Sinanoğlu, in *Atomic Physics*, edited

by B. Bedersen, V. W. Cohen, and F. M. J. Pichanick (Plenum, New York, 1969), p. 131; (c) İ. Öksüz and O. Sinanoğlu, *Phys. Rev.* **181**, 42, 54 (1969); P. Westhaus and O. Sinanoğlu, *Phys. Rev.* **183**, 56 (1969).

<sup>7</sup>(a) J. Čížek, *J. Chem. Phys.* **45**, 4256 (1966); (b) J. Čížek, *Adv. Chem. Phys.* **14**, 35 (1969); (c) J. Čížek, and J. Paldus, *Int. J. Quantum Chem.* **5**, 359 (1971); (d) J. Paldus, preprint, "Correlation Problems in Atomic and Molecular Systems, V. Spin-Adapted Coupled Cluster Many-Electron Theory." The authors would like to thank Professor Paldus for sending the preprint prior to publication.

<sup>8</sup>D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, *Mol. Phys.* **30**, 1861 (1975).

<sup>9</sup>D. J. Klein, *J. Chem. Phys.* **64**, 4868 (1976); *Mol. Phys.* **31**, 783 811 (1976); D. J. Klein and M. A. Garcia-Bash, *J. Chem. Phys.* **64**, 4873 (1976); *Mol. Phys.* **31**, 797 (1976).

<sup>10</sup>J. Čížek, J. Paldus, and L. Šroubková, *Int. J. Quantum Chem.* **3**, 149 (1969).

<sup>11</sup>J. Paldus, J. Čížek, and I. Shavitt, *Phys. Rev. A* **5**, 50 (1972).

<sup>12</sup>D. J. Thouless, *Nucl. Phys.* **21**, 225 (1960); **22**, 78 (1961).

<sup>13</sup>To express the cluster expansion as a transformation from a determinant [Eq. (7)] to another determinant is *formally* always possible, even for the exact wavefunction, since

$$\Phi = e^{\hat{T}} \Phi_0 = \prod_i (e^{\hat{T}} a_i^* e^{-\hat{T}}) e^{\hat{T}} | \rangle = \prod_i (e^{\hat{T}} a_i^* e^{-\hat{T}}) | \rangle = \prod_i g_i^* | \rangle,$$

where  $g_i^*$  is not "normalized." When the operator  $\hat{T}$  includes only  $\hat{T}_1$ , the operator  $g_i^*$  reduces to  $h_i^*$  given by Eq. (9). However, in general, this expression would be useful only when we have an exact or correlated wavefunction  $\Phi$ , since then this transformation gives a way of analyzing it in relation to the orbital theory.

<sup>14</sup>When the operator  $b_i^*$  is expanded with the creation operators  $a_i^*$ , it is written as  $b_i^* = \sum_m C_{mi} a_m^*$ , where  $m$  runs over the unoccupied spin orbitals for the  $\Phi_0$ , so that  $h_i^*$  is written as  $h_i^* = n_i(a_i^* + \sum_m C_{mi} a_m^*)$ , which is the equation given by Thouless.<sup>12</sup>

<sup>15</sup>When we adopt the Thouless definition for  $h_i^*$ , it is easy to show that the operator  $\pi \exp(\hat{T}_1)$  is unitary under the condition (11) [i.e., in this case, we can delete the vacuum  $| \rangle$  from Eq. (10b)].

<sup>16</sup>K. Hirao and H. Nakatsuji, to be published.

<sup>17</sup>H. Nakatsuji, *J. Chem. Phys.* **61**, 3728 (1974).

<sup>18</sup>H. Nakatsuji and K. Hirao, *Chem. Phys. Lett.* **47**, 569 (1977), which gives a preliminary result of the present study.

<sup>19</sup>C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).

<sup>20</sup>H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, xxxx (1978), following paper.

<sup>21</sup>See, for example, the Appendix in H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Chem. Phys.* **51**, 3175 (1969).

<sup>22</sup>Even though the operator  $\hat{T}$  includes various symmetries at the same time, it does *not* mean that the cluster expansion (2) [and (24)] is able to give the solutions of different sym-

metries at the same time. In the cluster expansion method we usually assume implicitly that the coefficient for the reference wavefunction  $\Phi_0$  is much larger than those of the other configurations (without the renormalization, the coefficient of the  $\Phi_0$  is unity in the expansion of the exponential operator). We use this assumption in truncating the working equation in a tractable order. However, when the coefficient of the excited configuration other than the  $\Phi_0$  is much larger than that of the  $\Phi_0$ , such truncation would become difficult. Furthermore, when the operator  $\hat{T}$  includes the different symmetries, they can interfere with the pure symmetry state under consideration *through* the unlinked terms (see the text), and this can cause another difficulty in the solution. The number of the independent variables required for the system is definitely the same as that required by the ordinary symmetry-adapted CI expansion (the SAC expansion includes the same number of the independent variables) and the unnecessarily larger number of variables can cause difficulty in the cluster expansion formalism (in contrast to the CI formalism).

<sup>23</sup>(a) P.-O. Löwdin, *Phys. Rev.* **97**, 1490, 1509 (1955); (b) R. Pauncz, *Alternant Molecular Orbital Method* (Saunders, Philadelphia, PA, 1967); (c) K. M. Sando and J. E. Harriman, *J. Chem. Phys.* **47**, 180 (1967).

<sup>24</sup>W. A. Goddard, *Phys. Rev.* **157**, 73, 81 (1967); *J. Chem. Phys.* **48**, 450, 5337 (1968).

<sup>25</sup>W. A. Goddard, *Phys. Rev.* **182**, 48 (1969).

<sup>26</sup>W. A. Goddard, *J. Chem. Phys.* **48**, 1008 (1968).

<sup>27</sup>H. Nakatsuji, *J. Chem. Phys.* **59**, 2586 (1973).

<sup>28</sup>J. Paldus and J. Čížek, *Adv. Quantum Chem.* **9**, 108 (1975).

<sup>29</sup>See, for example, Eq. (14) of Ref. 20.

<sup>30</sup>For example, D. J. Rowe, *Rev. Mod. Phys.* **40**, 153 (1968);

T. Shibuya and V. McKoy, *Phys. Rev. A* **2**, 2208 (1970);

*J. Chem. Phys.* **58**, 500 (1973); J. C. Ho, G. A. Segal, and

H. S. Taylor, *J. Chem. Phys.* **56**, 1520 (1972); D. L. Yeager

and V. McKoy, *J. Chem. Phys.* **63**, 4861 (1975).

<sup>31</sup>For example, J. Čížek, and J. Paldus, *J. Chem. Phys.* **47**, 3976 (1967), and the succeeding papers; H. Fukutome, *Prog. Theor. Phys.* **40**, 998, 1227 (1968); **45**, 1382 (1971), and the succeeding papers.

<sup>32</sup>(a) F. Sasaki and K. Ohno, *J. Math. Phys.* **4**, 1140 (1963);

(b) J. E. Harriman, *J. Chem. Phys.* **40**, 2827 (1964); (c)

T. Amos and L. C. Snyder, *J. Chem. Phys.* **41**, 1773 (1964);

(d) H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Chem. Phys.* **51**, 3175 (1969); (e) D. H. Phillips and J. C. Schug, *J. Chem.*

*Phys.* **61**, 1031 (1974).

<sup>33</sup>K. Hirao and H. Nakatsuji, *J. Chem. Phys.* **59**, 1457 (1973);

K. Hirao, *J. Chem. Phys.* **60**, 3215 (1974).

<sup>34</sup>E. R. Davidson, *Chem. Phys. Lett.* **21**, 565 (1973).

<sup>35</sup>Hay and Goddard reported the UHF calculations for the first-row atoms (B through F) with including  $d$  orbitals [D. J. Hay and W. A. Goddard, *Chem. Phys. Lett.* **9**, 356 (1971)]. Their wavefunctions are the mixed states for both spin and space symmetries.