Exponentially generated wave functions

Hiroshi Nakatsuji
Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

(Received 22 April 1985; accepted 12 August 1985)

We consider several generalizations of the exponential ansatz in a rather formal way, giving several new wave functions which we call exponentially generated (EG) wave functions. There are three distinct ways of the exponential-type generations of the wave functions, two of which are new. They are named ESAC (extended symmetry-adapted-cluster) wave function and exponentially generated CI (EGCI) wave function. The ESAC wave function is a simple extension of the SAC wave function and is applicable even when the Hartree–Fock reference configuration is not dominant. The EGCI wave function is a CI wave function constructed in the spirit of the cluster expansion theory. Formally, it has the merits of both the CI theory and the cluster expansion theory; for example, the upper bound nature, size consistency, and the applicability to quasidegenerate states and excited states. We then introduce several new wave functions by a multiple and mixed use of the exponential-type operators. We call such a class of wave functions multiexponentially generated (MEG) wave functions. There are many possibilities for the MEG wave functions, and the MR-SAC wave function proposed previously is one of them. When the system involves several classes of electron correlations, the MEG wave function permits an optimal (physically and practically) use of the exponential-type operators for the distinct classes of electron correlations. We described the method of solution of the EG and MEG wave functions and examined size consistency and some other properties.

I. INTRODUCTION

One of the important topics of modern quantum chemistry is to develop accurate and useful theories of molecular excited states, especially for the studies of the dynamic processes of molecular excited states. This is largely based on a recent development in molecular spectroscopy experiments. Reliable theoretical information on the potential surfaces and electronic structures of excited and ground states is useful for the design, analysis, and understanding of dynamic processes in molecular spectroscopy. Theoretically, this requires detailed and balanced inclusion of different kinds of electron correlations, since they reorganize and transform themselves along the reaction paths, specifically to each of the excited states. Therefore, the theory should be accurate and general, and yet should be efficient enough for a practical utility.

The structures an exact wave function should have are an interesting theoretical subject. Requiring such structures even to an approximate wave function, we will be able to obtain an accurate and yet practical theory. The cluster expansion of the wave function based on the exponential ansatz[1–6]

$$\Psi = \exp(T)|0\rangle$$

describes the electron correlation of a molecule quite well, if the Hartree–Fock configuration $|0\rangle$ is a good zeroth order wave function of the system. This property is essentially due to an approximate "separability" in the electron correlation of such a system. Sinanoglu described the physics of this separability concept in detail in the field of molecular quantum chemistry.[3] This wave function behaves well when a system dissociates into some fragments, as in chemical reactions. In such a process, the wave function of a system should approach a product of the wave functions of the fragments. The exponential ansatz satisfies this condition because $\exp(A+B) = \exp(A)\exp(B)$, as long as the operators A and B are commutative. Primas studied this separability property of the wave function in some detail.[4] Pople *et al.*[7] called this property size consistency and Bartlett *et al.*[8] size extensivity. We note however that the exponential ansatz can be too restrictive when A and B are not separable but strongly interacting.

The desirable properties accurate wave functions should have may be summarized as follows:[9–11] (1) upper-bound nature; (2) orthogonality and Hamiltonian orthogonality between different states; (3) exactness; (4) uniqueness; (5) effectiveness...rapid convergence; (6) applicability to quasidegenerate states; (7) applicability to open shells and excited states; (8) size consistency; (9) self-consistency; (10) independence from a practical choice in computations such as reference orbitals and reference configurations. Property (2) is important when we study excited states and especially the dynamic processes involving several states.[11,12] Property (5) is important for a practical utility of the theory. Properties (6) and (7) are important when we study potential energy surfaces of molecules in ground and excited states. For example in the potential curves of the several lower states of the CO molecule, there are no dominant configurations and the weights of the important configurations change from state to state and from distance to distance.[13] Self-consistency is a property most appropriately expressed by the Thouless theorem.[14] When the theory has this property, it satisfies a part of property (10), namely, independence of the orbital choice. Though property (10) is very important in actual applications, it is not a well-defined property. It is closely related, for example, to properties (5), (8), and (9).

Two general approaches are now available for calcula-

 0021-9606/85/235743-06$02.10

tions of accurate wave functions of molecular ground and excited states. One is the CI approach and the other is the cluster expansion approach. The former is a linear expansion theory and the latter is a nonlinear expansion theory. The CI theory is simple[15] and has an upper-bound nature but converges slowly and is not size consistent. The MR (multireference) CI theory[16,17] is important especially due to properties (1), (6), and (7). The cluster expansion theory, like the CC-MET (coupled-cluster many electron theory)[5] and the SAC (symmetry adapted cluster) theory,[11,18] is more rapidly convergent, size consistent, and includes self-consistency, but usually does not have an upper-bound nature. The single reference theory sometimes fails for quasidegenerate states and excited states.[19,20] The SAC-CI theory[11,21] for excited states, which is a linear expansion theory within a subspace of the SAC wave function, is important especially due to properties 2, 5, 6, and 7 but depends critically on the existence of the SAC solution for the ground state (or for the reference state).[22] Recently, we have proposed a multireference version of the SAC theory, called MR-SAC theory.[20] The theory has the merit of the cluster expansion theory and yet is applicable to quasidegenerate states and excited states, but the solution does not have an upper-bound nature because the nonvariational solution is easier than the variational solution for a nonlinear expansion theory.[11]

In this paper, we consider several generalizations of the exponential ansatz in a rather formal way. We call such classes of wave functions exponentially generated (EG) wave functions. In the next section, we consider four exponential-type expansion operators, three of which are new. We construct new wave functions called ESAC (extended SAC) and EG (exponentially generated) CI wave functions. We consider the method of solution, size consistency, and some other properties of the wave functions. In Sec. III, we consider the wave functions constructed by a multiple use of the exponential-type operators. We call such wave functions multiexponentially generated (MEG) wave functions. Many new wave functions can be generated in this way and the MR-SAC wave function[20] is one of them. This type of the wave function is useful when the system involves several distinct classes of electron correlations. It permits an optimal use of each exponential-type operator for each distinct class of the electron correlations. Summary and discussions are given in the last section.

II. EXPONENTIALLY GENERATED WAVE FUNCTIONS

We consider here the following four expansion operators:

$$\text{(I) } \exp\Big(\sum_K a_K A_K^\dagger\Big) \equiv 1 + \sum_K a_K A_K^\dagger + \frac{1}{2!}\sum_{K,L} a_K a_L A_K^\dagger A_L^\dagger + \frac{1}{3!}\sum_{K,L,M} a_K a_L a_M A_K^\dagger A_L^\dagger A_M^\dagger + \cdots, \tag{1}$$

$$\text{(II) } \mathrm{EXP}\Big(\sum_K a_K A_K^\dagger\Big) \equiv a_0 + \sum_K a_K A_K^\dagger + \frac{1}{2!}\sum_{K,L} a_K a_L A_K^\dagger A_L^\dagger + \frac{1}{3!}\sum_{K,L,M} a_K a_L a_M A_K^\dagger A_L^\dagger A_M^\dagger + \cdots, \tag{2}$$

$$\text{(III) } \mathit{exp}\Big(\sum_K a_K A_K^\dagger\Big) \equiv 1 + \sum_K a_K A_K^\dagger + \frac{1}{2!}\sum_{K,L} a_{KL} A_K^\dagger A_L^\dagger + \frac{1}{3!}\sum_{K,L,M} a_{KLM} A_K^\dagger A_L^\dagger A_M^\dagger + \cdots, \tag{3}$$

$$\text{(IV) } \mathscr{E}\mathscr{X}\mathscr{P}\Big(\sum_K a_K A_K^\dagger\Big) \equiv a_0 + \sum_K a_K A_K^\dagger + \frac{1}{2!}\sum_{K,L} a_{KL} A_K^\dagger A_L^\dagger + \frac{1}{3!}\sum_{K,L,M} a_{KLM} A_K^\dagger A_L^\dagger A_M^\dagger + \cdots. \tag{4}$$

The first one is an ordinary exponential operator and the others are extensions of this operator. All of the expansion operators are defined with the use of the "linked" operators $\Sigma_K a_K A_K^\dagger$ with $A_K^\dagger$ being an excitation operator as defined below. The operator EXP in Eq. (2) may be defined alternatively using an operator $\mathscr{A}_0$,

$$\mathrm{EXP}\Big(\sum_K a_K A_K^\dagger\Big) \equiv \mathscr{A}_0 \exp\Big(\sum_K a_K A_K^\dagger\Big), \tag{5}$$

where $\mathscr{A}_0$ is the operator which makes the coefficient of the identity operator to be a_0. The operator $\mathscr{E}\mathscr{X}\mathscr{P}$ was introduced for the first time in a previous paper[20] in developing the MR-SAC theory. We note that for a unique definition of the EXP and $\mathscr{E}\mathscr{X}\mathscr{P}$ operators, we need an additional condition like a normalization condition. The normalization to all orders or for the EXP operator the normalization to within the linked operators will be a recommended choice. In the followings, we explain these four types of operators in detail.

The operator exp is an ordinary exponential expansion operator. The SAC wave function[18] is written as

$$\Psi^{\mathrm{SAC}} = \exp\Big(\sum_K a_K A_K^\dagger\Big)|0\rangle, \tag{6}$$

where $A_K^\dagger$ is a symmetry-adapted excitation operator. When $A_K^\dagger$ is a particle excitation operator, which is not generally symmetry adapted, it is a coupled-cluster (CC) wave function.[5,6] We note that the operators in the nonlinear expansion theory should be symmetry adapted, because otherwise some difficulties arise as we already showed before.[18] For simplicity in this paper, we consider only the ground and excited states of the totally symmetric singlet state. The reference function $|0\rangle$ in Eq. (6) is a single determinant for closed shells given by

$$|0\rangle = \|\varphi_1\alpha\varphi_1\beta\cdots\varphi_i\alpha\varphi_i\beta\cdots\varphi_N\alpha\varphi_N\beta\|. \tag{7}$$

The operators $\{A_K^\dagger\}$ are defined by the excitations from the occupied orbitals $\{i\}$ to the unoccupied orbitals $\{a\}$. All of the excitation operators involved are commutative. Therefore, an important property of the exp operator follows, i.e.,

$$\exp\left(\sum_K a_K A_K^\dagger\right)\exp\left(\sum_L b_L B_L^\dagger\right) = \exp\left(\sum_K a_K A_K^\dagger + \sum_L b_L B_L^\dagger\right) \tag{8}$$

which assures the size consistency. However, a shortcoming of this expansion is that it is meaningful only when the weight of the identity operator is large. This is shown later in comparison with the EXP operator. This shortcoming of the exp operator is one of the reasons of the breakdown of a single reference cluster expansion theory for quasidegenerate systems.[20]

Unknown in the SAC wave function, all the unknown variables are associated with the linked operators. Therefore, requiring the Schrödinger equation $(H-E)\Psi^{\mathrm{SAC}}=0$ in the space of the linked configurations, these variables are uniquely determined, namely by

$$\langle 0|H-E|\Psi^{\mathrm{SAC}}\rangle = 0,$$
$$\langle 0|A_K(H-E)|\Psi^{\mathrm{SAC}}\rangle = 0. \tag{9}$$

This equation is a nonvariational equation so that the solution does not necessarily satisfy the upper bound condition. The variational equation is also easily derived by applying the variational principle,[18] but the solution is generally more difficult than the nonvariational case since there we need the integrals between unlinked terms not included in Eq. (9).[11]

The operator EXP is different from the exp operator only in the coefficient of the identity operator. For the EXP operator, we assume the normalization within the linked terms. The operators exp and EXP behave differently when a weight of the identity operator becomes small. For a direct comparison, we renormalize the exp operator as

$$a_0\exp\left(\sum_K a_K A_K^\dagger\right) = a_0 + \sum_K a'_K A_K^\dagger + \frac{1}{2!}\frac{1}{a_0}\sum_{K,L} a'_K a'_L A_K^\dagger A_L^\dagger + \cdots, \tag{10}$$

where $a'_K = a_0 a_K$. When the weight of the identity operator, a_0 becomes close to zero, the unlinked term of Eq. (10) tends to diverge. However, in the EXP operator such divergence does not occur. In other words, the operator exp behaves well only when the weight of the identity operator is not small. When it is small, the EXP operator may behave better because such divergence does not occur. When the weight of the identity operator is large or dominant, the difference between the expansions exp and EXP is small. Note that the EXP operator is not a multiplicative operator in the sense

$$\mathrm{EXP}\left(\sum_K a_K A_K^\dagger\right)\mathrm{EXP}\left(\sum_L b_L B_L^\dagger\right) \neq \mathrm{EXP}\left(\sum_K a_K A_K^\dagger + \sum_L b_L B_L^\dagger\right). \tag{11}$$

We define a new wave function by

$$\Psi^{\mathrm{ESAC}} \equiv \mathrm{EXP}\left(\sum_K a_K A_K^\dagger\right)|0\rangle, \tag{12}$$

where ESAC stands for "extended" SAC. A merit of this expansion over the SAC wave function is evident. It will behave better than the ordinary SAC wave function in the region of the nuclear configuration where the weight of the configuration $|0\rangle$ becomes small. However, this does not necessarily mean that an ordinary singles and doubles theory is improved only by adopting the EXP operator instead of the exp operator, because in such a region some of the triple and quadruple excited configurations are sometimes important as members of the main configurations which cannot be expressed by the unlinked terms.[20] In such a case, we expect a better result by including such triple and quadruple excitation operators in the linked $\{A_K^\dagger\}$ operators of the ESAC wave function. Probably, a more systematic solution is to adopt the MR-SAC formalism.[20] Further, the ESAC wave function is not size consistent because the EXP operator is not a multiplicative operator as shown by Eq. (11).

The solution of the ESAC wave function is very similar to that of the SAC method. The nonvariational solution is obtained from the equations

$$\langle 0|H-E|\Psi^{\mathrm{ESAC}}\rangle = 0,$$
$$\langle 0|A_K(H-E)|\Psi^{\mathrm{ESAC}}\rangle = 0, \tag{13}$$

which are solved similarly to the SAC method.

The operators exp and $\mathscr{E}\mathscr{L}\mathscr{P}$ are the generalizations of the operators exp and EXP, respectively. Though the exp and exp operators are the same in the linear term, they are different in the product operator terms. Though the product operators in the exp expansion have the coefficients which are the products of the linear terms, those in the exp expansion have the coefficients which are free from the lower order terms. Though the terms in the exp and $\mathscr{E}\mathscr{L}\mathscr{P}$ expansions may involve some redundant terms, we include only the linearly independent terms in the expansions of Eqs. (3) and (4). The $\mathscr{E}\mathscr{L}\mathscr{P}$ operator is different from the exp operator only in the coefficient of the identity operator. However, since all the coefficients in these expansions are independent (except for a normalization condition), these two operators are essentially the same. The operator $\mathscr{E}\mathscr{L}\mathscr{P}$ was introduced previously on the basis of an analysis of the origin of the breakdown of the single reference cluster expansion theory in the case of the quasidegeneracy.[20]

We define a new wave function using the $\mathscr{E}\mathscr{L}\mathscr{P}$ operator as

$$\Psi^{\mathrm{EGCI}} \equiv \mathscr{E}\mathscr{L}\mathscr{P}\left(\sum_K a_K A_K^\dagger\right)|0\rangle, \tag{14}$$

where EGCI means "exponentially generated" CI. In this expansion, the operator parts are the same as the cluster expansion, but all the terms have independent variables. Therefore, this expansion is a linear CI expansion. The construction of the configurations involved is done in the spirit of the cluster expansion theory. Since this expansion is a generalization of the cluster expansion theory, it has the merits of the cluster expansion theory. For example, it is size consistent. Since this expansion is more general than the

cluster expansion, it has the freedom to become a product of the wave functions of the two subsystems when it deals with two noninteracting (closed-shell) subsystems. Therefore, the physical solution of the EGCI wave function should be size consistent. This situation is similar to the situation that the full CI wave function is size consistent. Also, this wave function has the self-consistency property as shown below. The EGCI wave function does not presume a dominance of the Hartree–Fock reference configuration. Since the "unlinked" term in this expansion has an independent variable, it can represent a strong and synthetic coupling[20] of the lower operators. Thus, this wave function is applicable to quasidegenerate states and excited states as well as ordinary ground states. Moreover, since this expansion is a linear expansion, we can easily apply the variational principle, and obtain the equations,

$$\langle 0|H-E|\Psi^{\mathrm{EGCI}}\rangle = 0,$$

$$\langle 0|A_K(H-E)|\Psi^{\mathrm{EGCI}}\rangle = 0,$$

$$\langle 0|A_K A_L(H-E)|\Psi^{\mathrm{EGCI}}\rangle = 0, \tag{15}$$

etc. The solution of Eq. (15) satisfies an upper-bound property for both ground and excited states. Different solutions for different states satisfy orthogonality and Hamiltonian orthogonality to each other. Because of the linear nature of the expansion, the variational and nonvariational formulations give the same results. Further, we note that in the EGCI expansion, the operators $A_K^\dagger$, $A_K^\dagger A_L^\dagger$, etc., need not be symmetry adapted, in contrast to the SAC and ESAC theories. Since the EGCI expansion is a linear expansion, the solutions of Eq. (15) automatically satisfy a symmetry requirement, as long as enough space necessary to span the symmetry space is given. Thus, actually, the EGCI theory satisfies almost all the desirable properties summarized in the introduction. Though this is only when we include all the possible terms in the expansion (3) or (4),it is important to have such a theory in a more physically imaginative form than the full CI theory.

The EGCI wave function is related to a different CI wave function depending on a different choice of the operators $\{A_K^\dagger\}$. It is written explicitly as

$$\Psi^{\mathrm{EGCI}} = a_0|0\rangle + \sum_K a_K A_K^\dagger|0\rangle + \frac{1}{2!}\sum_{K,L} a_{KL}A_K^\dagger A_L^\dagger|0\rangle + \frac{1}{3!}\sum_{K,L,M} a_{KLM}A_K^\dagger A_L^\dagger A_M^\dagger|0\rangle + \cdots. \tag{14'}$$

When we choose as $\{A_K^\dagger\}$ *all* single excitation operators within a given orbital space, Ψ^{EGCI} becomes equivalent to the full CI. The terms in Eq. (14') correspond to Hartree–Fock, all singles, doubles, triples, etc. In this sense, the EGCI wave function satisfies self-consistency. However, when we choose only *some* single excitation operators, Ψ^{EGCI} is not a full CI but corresponds to a selective limited CI. When $\{A_K^\dagger\}$ is a set of double excitations, Ψ^{EGCI} includes only $2n$-ple ($n = 0, 1, \ldots$) excitations. When $\{A_K^\dagger\}$ includes single and double excitations, Ψ^{EGCI} is a sum of Hartree–Fock, single, double, triple, etc. excitations. We have to delete redundant terms. Thus, with a different choice of the operators $\{A_K^\dagger\}$, we can form a different level of approximate wave function.

Practically speaking, a problem of the EGCI theory would be how to establish a general rule of the selection of the $\{A_K^\dagger\}$ operators and the truncation of the expansion in order to include only the important terms, since it is impossible to include all of the higher-order terms. Though the dimensions of the matrices involved in the calculations would become much larger than that of the cluster expansion theory, this demerit may be compensated by the merits mentioned above. Further, we can take advantage of the advanced algorithms developed for handling a linear expansion theory.

Another method of solution of this situation is to use the $\mathscr{E}\mathscr{X}\mathscr{P}$ operator only for such a part of the electron correlations which really needs the $\mathscr{E}\mathscr{X}\mathscr{P}$ operator. For the other parts, we may use exp and/or EXP operators. This is the idea of the MEG wave function described in the next section.

III. MULTIEXPONENTIALLY GENERATED WAVE FUNCTIONS

In the preceding section, we constructed the wave function using only one exponential-type expansion operator. Here, we consider the wave functions constructed by using two or more exponential-type operators given by Eqs. (1)–(4). A merit immediately expected is that this would permit an *optimal* use of each exponential-type operator for each distinct class of the electron correlations involved in the system under consideration.

Use of the two exponential-type operators gives the following five different wave functions:

$$\Psi^{\mathrm{MEG1}} \equiv \mathrm{EXP}\left(\sum_K a_K A_K^\dagger\right)\mathrm{EXP}\left(\sum_L b_L B_L^\dagger\right)|0\rangle; \tag{16}$$

$$\Psi^{\mathrm{MEG2}} \equiv \mathscr{E}\mathscr{X}\mathscr{P}\left(\sum_K a_K A_K^\dagger\right)\mathscr{E}\mathscr{X}\mathscr{P}\left(\sum_L b_L B_L^\dagger\right)|0\rangle; \tag{17}$$

$$\Psi^{\mathrm{MEG3}} \equiv \exp\left(\sum_K a_K A_K^\dagger\right)\mathrm{EXP}\left(\sum_L b_L B_L^\dagger\right)|0\rangle; \tag{18}$$

$$\Psi^{\mathrm{MEG4}} \equiv \exp\left(\sum_K a_K A_K^\dagger\right)\mathscr{E}\mathscr{X}\mathscr{P}\left(\sum_L b_L B_L^\dagger\right)|0\rangle; \tag{19}$$

$$\Psi^{\mathrm{MEG5}} \equiv \mathrm{EXP}\left(\sum_K a_K A_K^\dagger\right)\mathscr{E}\mathscr{X}\mathscr{P}\left(\sum_L b_L B_L^\dagger\right)|0\rangle. \tag{20}$$

Here, the superscript MEG stands for multiexponentially generated. These MEG wave functions are appropriate when the system involves two kinds of electron correlations, say, correlation A and correlation B. These two kinds of correlations are represented by the sets of the excitation operators $\{A_K^\dagger\}$ and $\{B_L^\dagger\}$. The order of a multiplication of different exponential-type operators is arbitrary because all of the excitation operators involved are commutative. Among these MEG wave functions, the MEG4 wave function is equivalent to the MR-SAC wave function.[20] The other four MEG wave functions, Ψ^{MEG1}, Ψ^{MEG2}, Ψ^{MEG3}, and Ψ^{MEG5} are defined for the first time in the present study.

The wave function constructed from the two exp operators is identical to the one constructed from a single exp operator in the sense,

$$\Psi^{\mathrm{SAC}} = \exp\Big(\sum_K a_K A_K^\dagger\Big)\exp\Big(\sum_L b_L B_L^\dagger\Big)|0\rangle$$
$$= \exp\Big(\sum_K a_K A_K^\dagger + \sum_L b_L B_L^\dagger\Big)|0\rangle. \quad (21)$$

This wave function is just a SAC wave function. The MEG1 and MEG2 wave functions are also constructed from the two EXP and $\mathscr{C}\mathscr{X}\mathscr{P}$ operators, respectively. These wave functions are, however, different from the ESAC and EGCI wave functions defined by the single EXP and $\mathscr{C}\mathscr{X}\mathscr{P}$ operators, respectively, as

$$\Psi^{\mathrm{ESAC}} = \mathrm{EXP}\Big(\sum_K a_K A_K^\dagger + \sum_L b_L B_L^\dagger\Big)|0\rangle \quad (22)$$

and

$$\Psi^{\mathrm{EGCI}} = \mathscr{C}\mathscr{X}\mathscr{P}\Big(\sum_K a_K A_K^\dagger + \sum_L b_L B_L^\dagger\Big)|0\rangle, \quad (23)$$

because the operators EXP and $\mathscr{C}\mathscr{X}\mathscr{P}$ do not satisfy a multiplicative property as expressed by Eq. (21). The MEG1 and MEG2 wave functions are appropriate when the correlations A and B are "separable" and they are expressed by the EXP operators or by the $\mathscr{C}\mathscr{X}\mathscr{P}$ operators.

The MEG3–MEG5 wave functions use two different operators for the two different classes of electron correlations. For example, the MEG4 wave function will be useful when the exp operator is most suitable for the correlation A and the $\mathscr{C}\mathscr{X}\mathscr{P}$ operator is most suitable for the correlation B and these two correlations are separable. An example of the MEG4 wave function is the MR-SAC wave function introduced previously[20]

$$\Psi^{\mathrm{MR\text{-}SAC}} = \exp\Big(\sum_I C_I S_I^\dagger\Big)\mathscr{C}\mathscr{X}\mathscr{P}\Big(\sum_K b_K M_K^\dagger\Big)|0\rangle. \quad (24)$$

In the systems for which the MR-SAC theory is considered, there exist at least two kinds of electron correlations. One is the quasidegenerate (or internal[23]) correlation and the other is the dynamic correlation.[3] For the quasidegenerate correlation, the $\mathscr{C}\mathscr{X}\mathscr{P}$ operator is suitable because it does not assume the Hartree–Fock configuration to be dominant and includes the strong and synthetic coupling of the two excitation operators.[20] For the dynamic correlation, the exp operator is most suitable because of the approximate separability of the correlated pair of electrons.[3] In the MR-SAC wave function given by Eq. (24), the $\mathscr{C}\mathscr{X}\mathscr{P}$ part represents the multireference part and the exp part represents a cluster expansion around this multireference part.

The wave function MEG3 has a similar meaning to the MEG4 (MR-SAC) wave function. The exp part represents the dynamic correlation and the EXP part represents the quasidegenerate correlation. In contrast to the $\mathscr{C}\mathscr{X}\mathscr{P}$ operator, the EXP operator cannot represent the strong and synthetic coupling effects. Therefore, such effects should be included beforehand in the set of the linked operators $\{B_L^\dagger\}$.

Let us consider some other examples of the systems which are described adequately by the MEG wave functions. For example, the MEG2 wave function would be adequate for the system which consists of two interacting quasidegenerate subsystems. The operators $\{A_K^\dagger\}$ and $\{B_L^\dagger\}$ are assigned to different subsystems, and the interaction between the two subsystems is not so strong as to produce the strong and synthetic couplings, i.e., separable. Further, when the subsystems are large, the electron correlations in the subsystems would be classified into quasidegenerate part and dynamic correlation part. Accordingly, the operators may be classified as

$$\{A_K^\dagger\} = \{{}^qA_K^\dagger\} + \{{}^dA_K^\dagger\},$$
$$\{B_L^\dagger\} = \{{}^qB_L^\dagger\} + \{{}^dB_L^\dagger\}, \quad (25)$$

and we may construct the following MEG wave function:

$$\Psi^{\mathrm{MEG6}} \equiv \exp\Big(\sum_K {}^da_K {}^dA_K^\dagger\Big)\mathscr{C}\mathscr{X}\mathscr{P}\Big(\sum_K {}^qa_K {}^qA_K^\dagger\Big)$$
$$\times\exp\Big(\sum_L {}^db_L {}^dB_L^\dagger\Big)\mathscr{C}\mathscr{X}\mathscr{P}\Big(\sum_L {}^qb_L {}^qB_L^\dagger\Big)|0\rangle$$
$$= \exp\Big(\sum_K {}^da_K {}^dA_K^\dagger + \sum_L {}^db_L {}^dB_L^\dagger\Big)$$
$$\times\mathscr{C}\mathscr{X}\mathscr{P}\Big(\sum_K {}^qa_K {}^qA_K^\dagger\Big)\mathscr{C}\mathscr{X}\mathscr{P}\Big(\sum_L {}^qb_L {}^qB_L^\dagger\Big)|0\rangle. \quad (26)$$

This wave function is actually a product of the two MR-SAC (MEG4) wave functions. It includes two $\mathscr{C}\mathscr{X}\mathscr{P}$ operators and one exp operator. The dynamic correlation parts of the two subsystems are summarized into one because of the multiplicative property.

Size consistency is one of the important properties of the cluster expansion theory. How is this property kept for the MEG wave functions? When the wave function consists of the products of the size consistent components alone, it is size consistent. If one of the components is not size consistent, the wave function is not size consistent. We already know from the previous discussions that the exp and $\mathscr{C}\mathscr{X}\mathscr{P}$ operators are size consistent, but the EXP operator is not. Therefore, among the MEG wave functions given above, the MEG2, MEG4, and MEG6 wave functions are size consistent. The same is true for the self-consistency.

The solution of the MEG wave functions is done similarly to the previous section. We require the Schrödinger equation $(H - E)\Psi^{\mathrm{MEG}} = 0$ within the space spanned by the configurations which have independent variables, e.g., $A_K^\dagger|0\rangle, B_L^\dagger|0\rangle$, etc. It gives a nonvariational solution, so that it does not satisfy the upper-bound nature. However, as long as the wave function is already accurate, the difference between the variational and nonvariational solutions should be small.

It is easy to construct the MEG wave functions involving more than three exponential-type operators. By doing so, we can construct an optimal wave function of the system which requires different descriptions for different classes of electron correlations. Note that in the MEG wave functions, the interactions between different classes of electron correlations are assumed to be expressed multiplicatively. When more strong interactions exist, it is better to include them within a single $\mathscr{C}\mathscr{X}\mathscr{P}$ operator. (The exp operator is a multiplicative operator and the EXP operator is not appropriate

for a strong interaction.) The MEG6 wave function given by Eq. (26) is an example of the MEG wave functions involving more than three exponential-type operators.

IV. SUMMARY AND DISCUSSION

In this paper, we considered the exponential-type expansion operators defined by Eqs. (1)–(4). The exp operator is an ordinary exponential operator and the EXP, *exp*, and $\mathscr{E}\mathscr{X}\mathscr{P}$ operators are the variations and extensions of this operator. Using these operators, we could define a class of the wave functions which we call exponentially generated (EG) wave functions. Several of them are new.

From a single use of the exponential-type operators, we obtained the new wave functions called the ESAC (extended SAC) wave function,

$$\Psi^{\mathrm{ESAC}} = \mathrm{EXP}\left(\sum_K a_K A_K^\dagger\right)|0\rangle$$

and the EG (exponentially generated) CI wave function,

$$\Psi^{\mathrm{EGCI}} = \mathscr{E}\mathscr{X}\mathscr{P}\left(\sum_K a_K A_K^\dagger\right)|0\rangle.$$

The ESAC wave function is an extension of the ordinary cluster expansion and is applicable even when the Hartree–Fock configuration is not a main configuration of the system. Since the EXP operator can not represent the strong and synthetic coupling of two operators,[20] such effect should be included beforehand in the linked operators $\{A_K^\dagger\}$. A defect of the EXP operator is that it is not size consistent. The EGCI wave function is a synthesis of the spirits of the cluster expansion theory and the CI theory. It has an upper bound nature since it is a linear expansion and satisfies formally the size consistency and self-consistency because it is a generalization of the cluster expansion. It is applicable to quasidegenerate states and excited states. However, since the dimension of the calculation becomes larger for the EGCI wave function than for the SAC and ESAC wave functions, we must take advantage of the advanced algorithms developed in the field of the CI theory.

The multiple and mixed use of the exponential-type operators gives also several new wave functions. We call such wave functions multiexponentially generated (MEG) wave functions. The MR-SAC wave function proposed previously[20] is one of the MEG wave functions (MEG4). When the system involves several kinds of electron correlations, the MEG formalism permits an optimal (physically and practically) use of the exponential-type operators for distinct classes of electron correlations. For example, in the systems for which we considered the MR-SAC theory, there are at least two kinds of electron correlations, namely, the quasidegenerate (first order) correlation and the dynamic correlation. We used the $\mathscr{E}\mathscr{X}\mathscr{P}$ operator for the former and the exp operator for the latter. We have given some other examples of the usage of the MEG wave functions, like the MEG6 wave function given by Eq. (26), which includes three exponential-type operators. We also examined the size consistency. The exp and $\mathscr{E}\mathscr{X}\mathscr{P}$ operators are size consistent, so that if a MEG wave function involves only these operators it is size consistent but if it includes the EXP operator, it is not size consistent. The same is true for the self-consistency.

Formally, all the wave functions studied here are exact. They become different and represent different levels of electron correlations when the operators involved are limited to some level, for example, to single and double excitations or to only some of them. Some wave function may become similar to another wave function, when they are compared in different levels of approximations. For example, the ESAC wave function would be applicable even to the quasidegenerate state when we include the strong and synthetic coupling effect beforehand in the linked operators. The MR-SAC function, which is the MEG4 wave function, is also suitable for such quasidegenerate case. It includes automatically the strong and synthetic coupling effect. Though these two theories are of course different in detail, the choice would depend on the systems to be studied and the principal algorithms of the program. The MR-SAC (MEG4) wave function is more systematic and probably would be more efficient for such systems. The MR-SAC wave function is size consistent and self-consistent but the ESAC wave function is not.

ACKNOWLEDGMENT

This study was supported partially by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

[1] F. Coester, Nucl. Phys. **7**, 421 (1958).
[2] F. Coester and H. Kümmel, Nucl. Phys. **17**, 477 (1960).
[3] O. Sinanoglu, J. Chem. Phys. **36**, 706, 3198 (1962); Adv. Chem. Phys. **6**, 315 (1964).
[4] H. Primas, in *Modern Quantum Chemistry, Istanbul Lectures*, edited by O. Sinanoglu (Academic, New York, 1965), Part 2, p. 45.
[5] J. Cizek, J. Chem. Phys. **45**, 4256 (1966).
[6] J. Paldus, in *New Horizons of Quantum Chemistry*, edited by P.-O. Löwdin and B. Pullman (Reidel, Dordrecht, 1983), p. 81.
[7] J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quantum Chem. Symp. **10**, 1 (1976); J. A. Pople, R. Seeger, and R. Krishnan, Int. J. Quantum Chem. Symp. **11**, 149 (1977).
[8] R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. **14**, 561 (1978).
[9] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. **14**, 545 (1978).
[10] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).
[11] H. Nakatsuji, Chem. Phys. Lett. **67**, 329 (1979).
[12] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1962).
[13] H. Nakatsuji and M. Hada, *Proceeding of the Nobel Laureate Symposium on Applied Quantum Chemistry*, edited by V. H. Smith, Jr. (Reidel, Dordrecht, 1985).
[14] D. J. Thouless, Nucl. Phys. **21**, 225 (1960).
[15] P.-O. Löwdin, Adv. Chem. Phys. **2**, 209 (1959).
[16] R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, Mol. Phys. **35**, 771 (1978).
[17] R. J. Buenker and S. D. Peyerimhoff, in *New Horizons of Quantum Chemistry*, edited by P.-O. Löwdin and B. Pullman (Reidel, Dordrecht, 1983). p. 31.
[18] H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978).
[19] R. J. Bartlett and G. D. Purvis III, Phys. Scr. **21**, 255 (1980).
[20] H. Nakatsuji, J. Chem. Phys. **83**, 713 (1985).
[21] H. Nakatsuji, Chem. Phys. Lett. **59**, 362 (1978).
[22] O. Kitao and H. Nakatsuji, J. Indian Chem. Soc. (in press).
[23] O. Sinanoglu and I. Öksüz, Phys. Rev. Lett. **21**, 507 (1968); Phys. Rev. **181**, 42 (1969).