# Multireference cluster expansion theory: MR–SAC theory

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Multireference cluster expansion theory, called MR–SAC (multireference symmetry-adapted-cluster) theory, is presented. This theory is exact and unique, and yet does not include noncommutative algebra operator without imposing the completeness of the multireference space. The ansatz is simple enough for a general use in the study of potential energy surfaces of the ground and excited states of molecules. We have explained a recommended choice of the multireference operators on the basis of the analysis of an origin of the breakdown of the single reference theory. The method of solution of the MR–SAC theory is shown. The theory is given for the ground and excited states of closed-shell molecules, doublet and triplet states, and molecules with other symmetries. Test calculations are given for the ground and excited states of the CO molecule at the equilibrium and elongated distances.

## I. INTRODUCTION

Accurate descriptions of the wave functions and potential energy surfaces of the ground and excited states of molecules are current topics in theoretical quantum chemistry. These informations are important for the design, analysis, and understanding of recent experiments in molecular spectroscopy and molecular dynamics. Theoretically, it is generally recognized that electron correlation plays a crucial role in the studies of accurate wave functions and potential energy surfaces of molecules in ground and excited states. Now, there seems to be only two methods which are of general applicability for the study of electron correlations in both ground and excited states, namely, the CI method and the cluster expansion method.

Currently, the CI method is probably the most used method for calculations of accurate wave functions and potential energy surfaces. The reason is simply that there are, at present, no other theories of comparable utility. The SDCI method which includes single and double excitations from the Hartree–Fock determinant is generally used for the studies of ground electronic structure. The MR–SDCI method[1,2] which includes single and double excitations from several main reference configurations is used for the studies of quasidegenerate states, excited states, etc. Especially, the MR–CI method is of general utility and gives reliable descriptions of various states in wide range of nuclear configurations,[3] as long as a sufficient number of main reference configurations are considered. However, the problem is slow convergence. Even for a moderate scale calculation, the dimension of the matrices involved soon reaches to $10^4$–$10^5$ especially for quasidegenerate states and excited states. Other problems are that the theory is not size consistent[4,5] and rather dependent on the choice of the reference orbital set. Further, it is usually difficult to solve dense excited states, e.g., several hundreds of states in a relatively narrow energy region.

The cluster expansion method is based on the theory currently growing.[5–24] It is originally based on the ansatz

$$\Psi = e^T |0\rangle, \tag{1}$$

where $|0\rangle$ is the Hartree–Fock single determinant and $T$ is a sum of one-to-$N$ particle excitation operators

$$T = T^{(1)} + T^{(2)} + \cdots + T^{(N)}. \tag{2}$$

The coupled cluster singles and doubles (CCSD) method[20] simulates well an exact wave function when applied to the closed-shell ground state.[12,21,25–27] The SAC (symmetry-adapted-cluster) theory[16,21] is a generalization of the expansion (1) to open shells. It is based on the ansatz

$$\Psi = Q \, e^S |0\rangle, \tag{3}$$

where $S$ is a sum of symmetry adapted single-to-$N$ple excitation operators

$$\begin{aligned} S &= S^{(1)} + S^{(2)} + \cdots + S^{(N)} \\ &= \sum_I C_I S_I^{\dagger} \end{aligned} \tag{4}$$

and $Q$ is a symmetry projector which applies only to the unlinked part of the expansion. For singlet closed shells, $Q$ is unnecessary. This expansion is based on the fact that the symmetry adaptation is essentially necessary for a nonlinear expansion-like cluster expansion. When only $T^{(1)}$ is adopted, the ansatz (1) is identical with the UHF wave function,[28] while the ansatz (3) gives pseudo-orbital theory,[16] when only $S^{(1)}$ is included. Though these theories are essentially a single reference theory, it has several merits over the CI method. The theory is more rapidly convergent than CI because it includes multiple effects of correlations,[8] it is size consistent and depends correctly on the number of particles involved, and it is independent of the choice of the reference orbitals and includes completely the self-consistency effect of the orbitals (Thouless theorem).[28,29]

The single reference cluster expansion theory, however, sometimes breaks down when applied to the states for which the RHF determinant is not at all a good starting wave function.[5,30] Such cases occur as quasidegenerate states when we study potential energy surfaces of molecules in a wide range of nuclear configurations. They also occur, when we study open shells and excited states, as internal correlation and

semi-internal correlation which are specific to open shells. There is also a case in which several determinants are degenerate due to spin-space symmetry restriction. (This case is easily treated by a simple extension of the SAC theory.[31]) For the study of such systems, a multireference version of the theory is necessary.

For studies of excited and ionized states of molecules,[32] we have currently used SAC–CI theory.[18,21] It is based on the fact that the SAC theory determines not only the ground state but also the excited functions which are orthogonal and Hamiltonian orthogonal to the SAC ground state. Namely, these excited functions span the space for excited states. We, therefore, describe the excited states by a linear combination of these excited functions, which we call SAC–CI theory. Physically, this theory starts from the electron correlation of the ground state so that only a modification in electron correlation on going from the ground to excited states needs to be described. The SAC–CI theory is appropriate for describing the correlations in open shells and quasidegenerate systems, as we have shown through many applications.[32] It was shown that the theory simulates well the full CI and nearly full CI results.[21,33] However, the problem of the SAC–CI theory is that it depends critically on the SAC solution. When the SAC solution could not be obtained, the SAC–CI method could not be defined. Thus again, we need the multireference version of the SAC theory.

We note that the CCSD method usually fails for the chemical process including a fission of a more-than-double bond or more-than-two bonds.[5] It works when the process involves a fission of only a single bond. For example, the SAC and SAC–CI methods including single and double excitations as linked operators were successfully applied to the study of the potential energy curves of the ground and excited states of the $Li_2$ molecule.[34]

A general formalism of the multireference cluster expansion theory was given by Mukherjee et al.[13] and by Jeziorski and Monkhorst.[22] The theory due to Mukherjee et al. is based on the ansatz

$$\Psi = e^{T}\Phi_M,$$ (5)

where $\Phi_M$ spans a model multireference space

$$\Phi_M = \sum_i C_i \psi_i$$ (6)

and $\psi_i$'s are $N$-electron determinants. $T$ is an excitation operator given by

$$T = t_i^a a^a a_i + \left(\frac{1}{2!}\right)^2 t_{ij}^{ab} a^a a^b a_j a_i + \cdots.$$ (7)

The ansatz given by Eq. (5) is a straightforward generalization of the single reference theory given by Eq. (1). However, in this form of the theory, it has some serious defects as summarized by Jeziorski and Monkhorst.[22] The theory involves noncommutative algebra for the operators which include the creation and annihilation operators of the "valence" orbitals which are active in the model multireference space. The operator $T$ is not unique unless some additional complex conditions are imposed simultaneously. When the excitations including valence orbitals are neglected, one may circumvent these difficulties.[35] However, such theory can-

not be exact and therefore useless as a theory of general utility.

Jeziorski and Monkhorst[22] proposed a multireference coupled-cluster theory which is free from such difficulties. They started from the ansatz

$$\Psi_\nu = \sum_\mu^M C_{\nu\mu} \exp\left(T^\mu\right)\Phi_\mu,$$ (8)

where $\{\Phi_\mu\}$ spans a complete reference space within the valence orbitals. $T^\mu$ is the sum of one-to-$N$ particle excitation operators as given by Eq. (7) and is different for each reference determinant. This ansatz was first given by Sinanoglu and co-workers[9,11] as a generalization of his many electron theory to open-shell systems. Sinanoglu et al., however, did not formulate up the theory to a complete solution but rather introduced a "semiempirical" way of solution.[11] In the formulation of Jeziorski and Monkhorst, the theory is unique and does not include noncommutative algebra because of the completeness of the reference space. They further stressed that the expansion (8) makes sense only if it applies simultaneously to all $M$ wave functions from the exact manifold.[22]

From a practical point of view, the theory of Jeziorski and Monkhorst seems to be too difficult to be applied, except when some linear appoximation is introduced.[36] The completeness requirement for the reference space means that the dimension $M$ of the $\{\Phi_\mu\}$ functions soon becomes large. The coupled cluster operator $T^\mu$ is associated to each reference determinant. It would indeed be difficult to solve simultaneously all of these coupled-cluster operators for all of the $M$ wave functions. Even if we need only a lowest solution, such procedure is necessary in this formalism. Certainly, more practical and yet exact multireference theory is necessary.

Paldus et al.[25,37] and Dykstra et al.[38] reported that an approximate coupled-cluster theory in which certain diagrams in the unlinked terms are neglected from the single reference coupled-cluster theory behaves better than the original theory in the region of a near quasidegeneracy. However, in order for a theory to have a general a priori applicability to any molecular systems, it would be better to start from a general enough theory.

In this paper, we develop a multireference version of the SAC theory which is free from the problems we have seen so far. We call it MR–SAC (multireference symmetry-adapted-cluster) theory. In the next section, we briefly analyze an origin of the breakdown of the single-reference theory in a perspective model system. We then formulate the MR–SAC theory first for closed-shell systems, then for doublet and triplet systems, and finally for the systems which have different symmetries from these ones. We have preferred this type of presentation for simplicity, rather than to first give the theory in a completely general way, which is of course possible and given in Sec. VI together with the concluding summary. Test calculations are given for the ground and excited states of the CO molecule at some internuclear distances.

## II. BREAKDOWN OF SINGLE-REFERENCE THEORY

We consider a model system in which only three configurations are enough to describe the system. They are $|0\rangle$,

$S_I^\dagger |0\rangle$, and $S_I^{\dagger 2}|0\rangle$, where $|0\rangle$ is the closed-shell HF determinant and $S_I^\dagger$ is an excitation operator (e.g., double excitation operator). We assume that these configurations are normalized to unity. In the exact case, the wave function is written as

$$\Psi^e = |0\rangle + C_I S_I^\dagger |0\rangle + D_I S_I^{\dagger 2}|0\rangle, \tag{9}$$

where the superscript $e$ denotes the exact case. This wave function is determined by the equations

$$\langle 0|H - E|\Psi^e\rangle = 0,$$

$$\langle 0|S_I(H - E)|\Psi^e\rangle = 0, \tag{10}$$

$$\langle 0|S_I^2(H - E)|\Psi^e\rangle = 0,$$

where we require the Schrödinger equation within the space under consideration. The energy $E$ of the system is written as

$$E = E_0 - \cfrac{|\langle 0|S_I H|0\rangle|^2}{\langle 0|S_I H S_I^\dagger|0\rangle - E - \cfrac{|\langle 0|S_I^2 H S_I^\dagger|0\rangle|^2}{\langle 0|S_I^2 H S_I^{\dagger 2}|0\rangle - E}}, \tag{11}$$

where $E_0$ is the HF energy. On the other hand, in the cluster expansion theory, we approximate the wave function in the form

$$\Psi^c = \exp{(C_I S_I^\dagger)}|0\rangle$$
$$= |0\rangle + C_I S_I^\dagger|0\rangle + \tfrac{1}{2}C_I^2 S_I^{\dagger 2}|0\rangle, \tag{12}$$

where the coefficient of the unlinked term is a product of that of the linked term. The superscript $c$ denotes the cluster expansion case. The solution is determined by solving

$$\langle 0|H - E|\Psi^c\rangle = 0,$$
$$\langle 0|S_I(H - E)|\Psi^c\rangle = 0, \tag{13}$$

which require the Schrödinger equation within the space of the linked operators. The energy $E$ of the cluster expansion is given by

$$E = E_0 - \cfrac{|\langle 0|S_I H|0\rangle|^2}{\langle 0|S_I H S_I^\dagger|0\rangle - E - \cfrac{\langle 0|S_I H|0\rangle\langle 0|S_I H S_I^{\dagger 2}|0\rangle}{2\{\langle 0|S_I H S_I^\dagger|0\rangle + \tfrac{1}{2}C_I\langle 0|S_I H S_I^{\dagger 2}|0\rangle - E\}}}. \tag{14}$$

We compare the two energy expression (11) and (14) in order to see the conditions under which the cluster expansion theory simulates well the exact theory. They are as follows.

(1) The excitation energy from $E$ to $S_I^{\dagger 2}|0\rangle$ is approximately twice of the excitation energy from $E$ to $S_I^\dagger|0\rangle$.

(2) $\langle 0|S_I H S_I^{\dagger 2}|0\rangle \simeq \langle 0|H S_I^\dagger|0\rangle$.

(3) When $S_I^{\dagger 2}|0\rangle = 0$, two solutions are trivially equal. When only dynamic correlations are important and when the correlation energy is small relative to the excitation energy (then, $E$ in the condition 1 is approximated by $E_0$), we expect that these conditions would hold approximately. However, when the operator $S_I^\dagger$ describes the internal correlation, the excitations among quasidegenerate configuration, etc., these conditions will easily break down.

As an example, we consider the CO molecule at a large separation. In Fig. 1, we have defined $|0\rangle$, $S_I^\dagger|0\rangle$, and $S_I^{\dagger 2}|0\rangle$ and given a sketch of these electron configurations. Here, $S_I^\dagger$ denotes a double excitation from the occupied $\sigma_C$ and $\pi_0$ MO's to the unoccupied $\sigma_0$ and $\pi_C$ MO's and may be written as

$$\left| \begin{matrix} \sigma_C \to \sigma_0 \\ \pi_0 \to \pi_C \end{matrix} \right|.$$

(We of course need the configurations which are symmetric pairs with respect to the occupations of the $\pi_0$ and $\pi_C$ MO's. We omitted them just for simplicity.) At an infinite separation, the configurations $|0\rangle$, $S_I^\dagger|0\rangle$, and $S_I^{\dagger 2}|0\rangle$ represent the states corresponding to $C(^1D) + O(^1D)$, $C(^3P) + O(^3P)$, and $C(^1D) + O(^1D)$, respectively. Therefore, there the energies of the ground and quadruply excited configurations $|0\rangle$ and $S_I^{\dagger 2}|0\rangle$ are equal and the energy of the doubly excited config-

uration $S_I^\dagger|0\rangle$ is about 3.2 eV _lower_ than the energy of the configuration $|0\rangle$.[39] Thus, in this case, the condition 1 completely breaks down. Actually, the SAC calculation of the ground state of the CO molecule does not converge when the CO distance is larger than about 3.5 a.u.[40] In the region where the CO distance is larger than 5 a.u., we obtain the
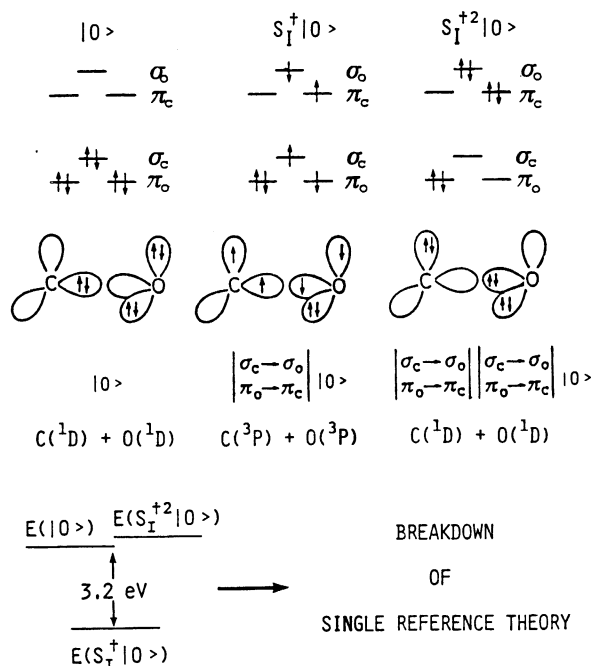


FIG. 1. Sketch of the electronic structure of the CO molecule at large separation which shows the origin of the breakdown of the single reference theory.

SAC solution which represents well the excited $\Sigma^+$ state which dissociates into $C(^1D)$ and $O(^1D)$. There, we can calculate the ground state by the SAC–CI theory by de-exciting two electrons from this excited $\Sigma^+$ state.[40] However, in order to calculate the ground state of the CO molecule in all nuclear separations by a single theory, we have to use the multireference version of the SAC theory, which we present in the next section.

## III. MR–SAC THEORY

We now propose multireference symmetry-adapted-cluster (MR–SAC) expansion theory. In this section, our concern is the singlet closed-shell system and its excited states of the same symmetry.

After considerations, we think it appropriate to start from the following ansatz:

$$\Psi^\mu = \left[\sum_{K=0} b_K^\mu M_K^\dagger\right]\exp\left(\sum_I C_I^\mu S_I^\dagger\right)|0\rangle$$
$$= \exp\left(\sum_I C_I^\mu S_I^\dagger\right)\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]|0\rangle. \tag{15}$$

Here, $\mu$ denotes a state under consideration and $|0\rangle$ is the closed-shell single determinant

$$|0\rangle = \|\varphi_1\alpha\varphi_1\beta \cdots \varphi_i\alpha\varphi_i\beta \cdots \varphi_N\alpha\varphi_N\beta\|. \tag{16}$$

The occupied orbitals are denoted by $\{i\}$ and the unoccupied orbitals by $\{a\}$. These orbitals are not necessarily the HF orbitals of the system under consideration. Rather, sometimes, the MC–SCF orbitals separated into two sets $\{i\}$ and $\{a\}$ could be more appropriate. The operators $\{M_K^\dagger\}$ and $\{S_I^\dagger\}$ are both symmetry-adapted operators in that they give symmetry adapted configurations when applied to $|0\rangle$. We note that $M_0^\dagger = I$ is an identity operator. These operators are defined by the excitations from the occupied set $\{i\}$ to the unoccupied set $\{a\}$.

In this formalism, no noncommutative algebra occurs because all the operators involved are defined by the creation operators associated with the unoccupied orbital set $\{a\}$ and the annihilation operators associated with the occupied orbital set $\{i\}$. Our orbital set does not have a so-called valence space which is the cause of the noncommutative operator algebra. Thus, all the operators involved are commutative. Therefore, the two expressions of the MR–SAC ansatz given by Eq. (15) are equivalent. It may be noticed that the ansatz given by Eq. (15) constitutes a generalization of both the SAC and SAC–CI theories. The first expression of Eq. (15) corresponds to the generalization of the SAC–CI theory and the second one to that of the SAC theory.

This theory is exact because any excitation operators can be included in the ansatz (15). In other words, any configurations necessary to full CI can be defined and incorporated in the wave function (15).

In the MR–SAC ansatz given above, the part $[\sum_{K=0} b_K^\mu M_K^\dagger]|0\rangle$ of the second equation corresponds to the multireference (MR) part and the operator $\exp(\sum_I C_I^\mu S_I^\dagger)$ represents the cluster expansion around this MR part. Our $C_I^\mu$ is state $(\mu)$ dependent but independent of the $M_K^\dagger$ operator. A merit of the present theory is that the MR part needs not be complete, in contrast to the existing theories.[13,22]

since all the operators involved are commutative.

There are two ways of formulation starting from this ansatz. One is to treat both of the coefficients $\{C_I^\mu\}$ and $\{b_K^\mu\}$ as unknown variables and determine them iteratively. The operators $\{S_I^\dagger\}$ and $\{M_K^\dagger\}$ should be chosen to be exclusive in order to uniquely determine the variables $\{C_I^\mu\}$ and $\{b_K^\mu\}$. The other is to treat the MR part to be given in advance from for example different calculations. There, the operators $\{S_I^\dagger\}$ need not be exclusive to the $\{M_K^\dagger\}$ operators. Rather, they should have some important elements in common. In this section we first describe the first formalism and the second one which is described at the end of this section is only a special case of the first one.

Physically, the operators $\{M_K^\dagger\}$ represent state-specific correlations. Quasidegenerate correlations, first-order correlations, internal correlations in open shells, etc. are the examples of such correlations. The operator

$$\exp\left(\sum_I C_I^\mu S_I^\dagger\right)$$

represents a more or less transferable part of the correlations. The dynamic correlation considered by Sinanoglu[8,11] is just described by this part. For closed-shell ground state of molecules at stable geometry, only the dynamic correlations are important, so that we do not need the $M_K^\dagger$ part of the operators except for the $M_0^\dagger (= I)$. Then, the theory reduces to the single reference SAC theory.

This theory is applicable to the excited states of the same symmetry within the same framework of the theory. When two states are solved separately, the orthogonality and the Hamiltonian orthogonality between the two states do not hold exactly, as the MC–SCF wave function of the two states do not satisfy these relations.

Generally speaking, the cluster expansion theory is insensitive to the choice of the reference orbitals. This is exactly so in the case of the single reference theory as Thouless' theorem states.[28] We can expect a similar property even for the multireference version of the theory.

The MR–SAC wave function given by Eq. (15) is expanded as

$$\Psi^\mu = b_0^\mu|0\rangle + \sum_{K=1} b_K^\mu M_K^\dagger|0\rangle + b_0^\mu\sum_I C_I^\mu S_I^\dagger|0\rangle$$
$$+ \sum_{K=1}\sum_I b_K^\mu C_I^\mu M_K^\dagger S_I^\dagger|0\rangle + \frac{1}{2}b_0^\mu\sum_{IJ}C_I^\mu C_J^\mu S_I^\dagger S_J^\dagger|0\rangle$$
$$+ \frac{1}{2}\sum_{K=1}\sum_{I,J}b_K^\mu C_I^\mu C_J^\mu M_K^\dagger S_I^\dagger S_J^\dagger|0\rangle + \cdots. \tag{17}$$

Here the first two terms are the zeroth order reference term, the next two terms are first order to the coefficient $C_I^\mu$ and the next two terms are the second order term. Note that the order classification is somewhat different between the single-reference and multireference theories.

In the multireference theory, the choice of the multireference operators is obviously very important to get accurate results. Since the $M$ part needs not to be complete in the MR–SAC theory, we can choose this part only from physical considerations. We recommend the following choice of the $M$-part operators. Namely, we may start from the ansatz

$$\Psi^\mu = \left[ \sum_{K=0} b^\mu_K M^\dagger_K + \frac{1}{2!} \sum_{K,L=1} b^\mu_{KL} M^\dagger_K M^\dagger_L \right.$$

$$\left. + \frac{1}{3!} \sum_{J,K,L=1} b^\mu_{JKL} M^\dagger_J M^\dagger_K M^\dagger_L + \cdots \right]$$

$$\times \exp\left( \sum_I C^\mu_I S^\dagger_I \right) |0\rangle, \tag{18}$$

where the operators in the second and third sums are taken as the products of the lower operators, but the coefficients $b^\mu_{KL}$, $b^\mu_{JKL}$, etc. are taken to be *independent* of the coefficients $b^\mu_K$ of the lower operators. This choice is suggested from the analysis of the origin of the breakdown of the single reference theory as given in Sec. II. The configurations $M^\dagger_K M^\dagger_L |0\rangle$, which cause the breakdown of the single reference theory and which are important as manifested directly by the breakdown of the theory itself, are treated correctly in the ansatz (18), giving the independent coefficients $b^\mu_{KL}$. We note that a set of the product operators may involve redundant terms. We include only the linearly independent terms in the summations of Eq. (18). We further note that in the braces [ ], it is physically unnecessary to include all the higher order product operators since this is a multireference part. We actually need here only such operators which represent state specific correlations like quasidegeneracy, etc. For convenience in notations, we assume that the ansatz (18) is included in the ansatz (15) as a special choice of the $\{M^\dagger_K\}$ operators.

It is interesting to define an exponential type operator $\mathcal{S}\mathcal{X}\mathcal{P}$ by

$$\mathcal{S}\mathcal{X}\mathcal{P}\left( \sum_K a_K A^\dagger_K \right) = a_0 + \sum_K a_K A^\dagger_K + \frac{1}{2!} \sum_{K,L} a_{KL} A^\dagger_K A^\dagger_L$$

$$+ \frac{1}{3!} \sum_{K,L,M} a_{KLM} A^\dagger_K A^\dagger_L A^\dagger_M + \cdots, \tag{19}$$

where $K, L, M$, etc. run nonzero positive integers. Then, the ansatz given by Eq. (18) is written as

$$\Psi^\mu = \mathcal{S}\mathcal{X}\mathcal{P}\left( \sum_K b^\mu_K M^\dagger_K \right) \exp\left( \sum_I C^\mu_I S^\dagger_I \right) |0\rangle. \tag{20}$$

This expression of the MR-SAC theory may be useful to understand it in relation to the single reference theory as expressed by

$$\Psi = \exp\left( \sum_K b^\mu_K M^\dagger_K + \sum_I C^\mu_I S^\dagger_I \right) |0\rangle$$

$$= \exp\left( \sum_K b^\mu_K M^\dagger_K \right) \exp\left( \sum_I C^\mu_I S^\dagger_I \right) |0\rangle. \tag{21}$$

In the MR-SAC theory, the source of the breakdown of the single reference theory, which is due to the part

$$\exp\left( \sum_K b^\mu_K M^\dagger_K \right)$$

of Eq. (21), is corrected by replacing it with the general operator

$$\mathcal{S}\mathcal{X}\mathcal{P}\left( \sum_K b^\mu_K M^\dagger_K \right).$$

This comparison further convinces us that the MR-SAC theory, based on the ansatz (20) or (18), is rather insensitive to the choice of the multireference operators $\{M^\dagger_K\}$ (or to the

way of the separation of the operators into the $M$ and $S$ parts), so long as the first candidates of the $M^\dagger_K$ operators are already included into the $M$ space. This property is important in contrast to the practical problem often encountered in the application of the MR-CI method.

Size consistency is one of the most important properties of the cluster expansion theory. Then, is the MR-SAC theory size consistent? It is easy to show that the MR-SAC ansatz given by Eq. (20) is size consistent. The $S$ part of Eq. (20) is size consistent because of the property

$$\exp(A + B) = \exp(A)\exp(B),$$

and the $M$ part is also size consistent because the $\mathcal{S}\mathcal{X}\mathcal{P}$ operator is more general than the exp operator and includes exp operator as a special case. When the systems $A$ and $B$ is noninteracting, we can therefore expect the relation

$$\mathcal{S}\mathcal{X}\mathcal{P}(A + B) = \mathcal{S}\mathcal{X}\mathcal{P}(A)\mathcal{S}\mathcal{X}\mathcal{P}(B)$$

from the physical requirement. Thus, the MR-SAC theory written in the form of Eq. (20) is size consistent. However, for the MR-SAC ansatz given by Eq. (15), the size consistency property is satisfied in general only by the $S$ part. For the $M$ part, the size consistency depends on the explict form of the $M$ operator part. When it is in a form of the full CI within some active space, or in a form of the $\mathcal{S}\mathcal{X}\mathcal{P}$ operator, it is size consistent, but otherwise we cannot expect size consistency. Thus, in an actual application we recommend to start from the MR-SAC ansatz given by Eq. (20).

Now is the solution of the MR-SAC expansion given by Eq. (15). We require the Schrödinger equation $(H - E_\mu)\Psi^\mu = 0$ within the space of the linked configurations and obtain

$$\langle 0 | H - E_\mu | \Psi^\mu \rangle = 0, \tag{22a}$$

$$\langle 0 | M_K (H - E_\mu) | \Psi^\mu \rangle = 0, \tag{22b}$$

$$\langle 0 | S_I (H - E_\mu) | \Psi^\mu \rangle = 0. \tag{22c}$$

This is sufficient to determine all the unknown coefficients $\{b^\mu_K\}$ and $\{C^\mu_I\}$. In the solution, it is important to treat the MR part together.

. Equations (22a)–(22c) may be written in the form of an eigenvalue problem

$$\sum_L [A^\mu_{KL} - E_\mu S^\mu_{KL}] d^\mu_L = 0, \tag{23}$$

where the matrices involved are nonsymmetric and the coefficients $\{d^\mu_L\}$ represent $\{b^\mu_K\}$ and $\{C^\mu_I\}$. When the dimensions of the matrices are large, an iterative method for eigenvalue problems of nonsymmetric matrix is available.[42] It is also possible to transform Eqs. (22a)–(22c) in the two sets of equations, Eqs. (23) and (24),

$$\sum_J G^\mu_{IJ} d^\mu_J = B^\mu_I. \tag{24}$$

In both methods, the solution is performed iteratively until self-consistency is attained since the matrices $A^\mu$ and $G^\mu$ depend on the coefficients $\{C^\mu_I\}$. More details of the calculational method will be given in a forthcoming paper.[41]

It is also possible to formulate the MR-SAC theory assuming that the multireference part $[\sum_{K=0} b^\mu_K M^\dagger_K]|0\rangle$ of Eq. (15) is *given* in advance from for example a preliminary

calculation. In such a calculation, the choice of the $M$-part operators as represented by Eq. (18) would be suggestive especially because of the size-consistency property. In this formalism the operators $\{S_I^\dagger\}$ and $\{M_K^\dagger\}$ need not be exclusive. Rather some important elements should be in common. For example, $\{S_I^\dagger\}$ includes all the singles and doubles and $\{M_K^\dagger\}$ includes some selected singles and doubles and their product operators, i.e., the triples and quadruples. In this formalism, only the $\{C_I^\mu\}$ coefficients are unknown variables and are determined by Eqs. (22a) and (22c) only. The iterative procedure coupled with the $M$ part is unnecessary though a few cycles may be meaningful. In Eq. (17), the first two terms are already given and a role of the third term is to modify and relax the second fixed term. The fourth and higher terms represent the unlinked effects and modify and represent higher excitation terms. Almost all the features of the MR–SAC theory described above are satisfied also in this form of the MR–SAC theory.

This formalism of the MR–SAC theory is closely related with the SAC–CI theory.[18,21] In the SAC–CI theory the $S$ part is given by the SAC calculation and the $M$ part is determined by the SAC–CI formalsim. The procedure of the MR–SAC theory given here is reverse of this procedure. This formalism resembles also to the multireference theory of Mukherjee et al.[13] given by Eq. (5), though the present theory does not involve noncommutative operator algebra.

## IV. MR–SAC THEORY FOR DOUBLET AND TRIPLET SYSTEMS

The MR–SAC theory is easily extended to the doublet and triplet systems. Here, we start from the ansatz

$$\Psi^\mu = Q \exp\left(\sum_I C_I^\mu S_I^\dagger\right)\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]|0\rangle$$

$$= Q\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]\exp\left(\sum_I C_I^\mu S_I^\dagger\right)|0\rangle, \qquad (25)$$

where $|0\rangle$ denotes an open-shell restricted determinant

$$|0\rangle = \|\varphi_1\alpha\varphi_1\beta\cdots\varphi_q\alpha\varphi_q\beta\varphi_{q+1}\alpha\cdots\varphi_N\alpha\| \qquad (26)$$

and $Q$ is a symmetry projector. Since the operators $M_K^\dagger$ and $S_I^\dagger$ are symmetry adapted, the projector $Q$ applies only to the unlinked terms of the expansion. Further, as will be shown below, the projector $Q$ has nothing to do with the determination of the wave function itself.

The determinant given by Eq. (26) defines uniquely the occupied and unoccupied spin orbitals $\{i\}$ and $\{a\}$, respectively. The excitation operators $M_K^\dagger$ and $S_I^\dagger$ are defined by the excitations from the occupied spin orbitals to the unoccupied spin orbitals. Then, all the operators involved in Eq. (25) are commutative. The theory is exact since any excitation operators can be included in this way. The physical meaning of the operators $M_K^\dagger$ and $S_I^\dagger$ are the same as those summarized in the preceding section. Especially here, the $M_K^\dagger$ operators are important to describe the internal correlations in open shells. The quasidegeneracy also occurs in the dissociation processes. The $S_I^\dagger$ part of the operators describes the dynamic correlation which is more or less transferable among the different states of the molecule. We can apply this form of the wave function to both the ground and

excited states which have the same symmetry as the determinant $|0\rangle$.

The method of solution of the MR–SAC expansion given by Eq. (25) is similar to that given in the preceding section. We assume the Schrödinger equation within the space of the linked operators. Here, however, the symmetry projector $Q$ in the right-hand side of Eq. (25) is unnecessary and we obtain

$$\langle 0|H - E_\mu|\Psi^{\mu'}\rangle = 0, \qquad (27a)$$

$$\langle 0|M_K(H - E_\mu)|\Psi^{\mu'}\rangle = 0, \qquad (27b)$$

$$\langle 0|S_I(H - E_\mu)|\Psi^{\mu'}\rangle = 0, \qquad (27c)$$

where $\Psi^{\mu'}$ is the same as $\Psi^\mu$ given by Eq. (25) except that the projector $Q$ is absent here, i.e.,

$$\Psi^{\mu'} = \exp\left(\sum_I C_I^\mu S_I^\dagger\right)\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]|0\rangle. \qquad (28)$$

Equation (27b) is unnecessary when the $M$ part is given in advance. The projector $Q$ became unnecessary in Eq. (27) because the linked configurations $|0\rangle$, $M_K^\dagger|0\rangle$, and $S_I^\dagger|0\rangle$ are symmetry adapted. This is due to the SAC formalism and is common to the previous cases of the nonvariational solutions of the SAC and SAC–CI theories. Though the projector $Q$ is unnecessary for the determination of the wave function itself, it is necessary when we calculate some properties of molecules.

As a choice of the $M$-part operators, we recommend the following ansatz similarly to Eq. (18):

$$\Psi^\mu = Q\left[\sum_{K=0} b_K^\mu M_K^\dagger + \frac{1}{2!}\sum_{K,L=1} b_{KL}^\mu M_K^\dagger M_L^\dagger\right.$$

$$\left. + \frac{1}{3!}\sum_{J,K,L=1} b_{JKL}^\mu M_J^\dagger M_K^\dagger M_L^\dagger + \cdots\right]$$

$$\times \exp\left(\sum_I C_I^\mu S_I^\dagger\right)|0\rangle$$

$$= Q\mathscr{S}\mathscr{P}\left(\sum_K b_K^\mu M_K^\dagger\right)\exp\left(\sum_I C_I^\mu S_I^\dagger\right)|0\rangle. \qquad (29)$$

In this ansatz, the source of the breakdown of the single reference theory, as analyzed in Sec. II, is corrected. Here we note that in the open-shell case the products of the symmetry-adapted operators, e.g., $M_K^\dagger M_L^\dagger$, in Eq. (29) are not necessarily symmetry adapted, though they are always so in the case of the singlet $A_1$ symmetry studied in the preceding section. Therefore, when we impose Eq. (27b) for the product operators $M_K^\dagger M_L^\dagger$, etc., we have to use $QM_K^\dagger M_L^\dagger$.

## V. MR–SAC THEORY FOR THE STATE WHOSE SYMMETRY IS DIFFERENT FROM THAT OF $|0\rangle$

The MR–SAC theory derived so far is for the states whose spin-space symmetry is the same as that of the reference wave function $|0\rangle$. Here, we consider the MR–SAC theory for the nondegenerate states whose symmetry is different from that of $|0\rangle$. We call such symmetry "singlet $B_1$" for simplicity.

For the singlet $B_1$ state, we propose the following MR–SAC expansion:

$$\Psi^\mu = Q \exp\left(\sum_I C_I^\mu S_I^\dagger\right)\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]\Phi_0, \qquad (30)$$

$$\Phi_0 = R_0^\dagger |0\rangle. \tag{31}$$

Here, $\Phi_0$ is one of the main configurations for the state under consideration. $R_0^\dagger$ is the symmetry-adapted excitation operator which generates such configuration from the determinant $|0\rangle$. For example, the configuration $R_0^\dagger |0\rangle$ may be illustrated as
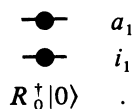


We note that the configuration $R_0^\dagger |0\rangle$ spans a complete reference space, by a single configuration, within the space of the valence orbitals $i_1$ and $a_1$ shown above. This is because within the two active orbital space, three configurations constitute the complete space,
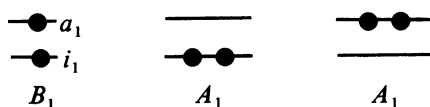


of which only the first configuration is singlet $B_1$. Thus, since the reference configuration spans a complete space, no noncommutative algebra occurs and the theory is unique. The operators $M_K^\dagger$ and $S_I^\dagger$ are defined by the excitations from the ground occupancy defined by the $\Phi_0$.

As the configuration $\Phi_0$, we need not necessarily choose the dominant configuration of the state under consideration, though such choice may be convenient. It is all right if it is included within the space of the multireference configurations. The MR–SAC expansion given here is applicable to both ground and excited states of the singlet $B_1$ symmetry.

The solution of the MR–SAC expansion given here is very similar to the previous cases. We assume the Schrödinger equation within the space $|\Phi_0\rangle$, $M_K^\dagger|\Phi_0\rangle$, and $S_I^\dagger|\Phi_0\rangle$; namely,

$$\langle \Phi_0 | H - E_\mu | \Psi^{\mu'} \rangle = 0,$$
$$\langle \Phi_0 | M_K (H - E_\mu) | \Psi^{\mu'} \rangle = 0, \tag{32}$$
$$\langle \Phi_0 | S_I (H - E_\mu) | \Psi^{\mu'} \rangle = 0.$$

Again here the symmetry projector $Q$ is unnecessary because of the SAC formalism. The $\Psi^{\mu'}$ in Eq. (32) is different from $\Psi^\mu$ in Eq. (30) in that the symmetry projector is absent in the $\Psi^{\mu'}$:

$$\Psi^{\mu'} = \exp\left(\sum_I C_I^\mu S_I^\dagger\right)\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]\Phi_0. \tag{33}$$

It is also appropriate to choose the $M$-part operators as given by

$$\Psi^\mu = Q\,\mathscr{S}\mathscr{P}\mathscr{P}\left(\sum_K b_K^\mu M_K^\dagger\right)\exp\left(\sum_I C_I^\mu S_I^\dagger\right)\Phi_0. \tag{34}$$

The reasoning of this choice is entirely the same as in the previous section.

## VI. GENERAL THEORY AND CONCLUDING REMARKS

So far, we have developed the MR–SAC theory for different symmetry types. Now, it is easy to write down in a common general form. The ansatz of the MR–SAC theory is written as

$$\Psi^\mu = Q\exp\left(\sum_I C_I^\mu S_I^\dagger\right)\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]\Phi_0, \tag{35}$$

where the part $\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]\Phi_0$ corresponds to the multireference part and the operator $\exp(\sum_I C_I^\mu S_I^\dagger)$ represents the cluster expansion around it. In Eq. (35), $\Phi_0$ is the closed-shell or open-shell restricted-type single determinant $|0\rangle$ given by Eqs. (16) or (26), respectively, or the configuration $R_0^\dagger|0\rangle$ for the singlet $B_1$ state. $R_0^\dagger$ is a symmetry-adapted exciton operator which generates a (main) configuration of the singlet $B_1$ state. The operators $\{S_I^\dagger\}$ and $\{M_K^\dagger\}$ are symmetry adapted and are uniquely defined using the creation and annihilation operators associated with the unoccupied and occupied orbitals of $\Phi_0$. All the operators involved are commutative. The set $\{M_K^\dagger\}$ involves the identity operator $I = M_0^\dagger$. $Q$ is a symmetry projector and applies only to the unlinked terms of the expansion. It is unnecessary for the singlet $A_1$ state because there the products of the operators belong again to the singlet $A_1$ space. Further, the projector $Q$ has nothing to do with the determination of the wave function. Namely, the nonvariational solution is obtained from a set of the equations

$$\langle \Phi_0 | H - E_\mu | \Psi^{\mu'} \rangle = 0,$$
$$\langle \Phi_0 | M_K (H - E_\mu) | \Psi^{\mu'} \rangle = 0, \tag{36}$$
$$\langle \Phi_0 | S_I (H - E_\mu) | \Psi^{\mu'} \rangle = 0,$$

where $\Psi^{\mu'}$ does not include the projector $Q$:

$$\Psi^{\mu'} = \exp\left(\sum_I C_I^\mu S_I^\dagger\right)\left[\sum_{K=0} b_K^\mu M_K^\dagger\right]\Phi_0. \tag{37}$$

In the multireference theory, the choice of the multireference operators is obviously very important to get accurate results. Since the $M$ part needs not to be complete in the MR–SAC theory, we can choose this part only from physical considerations. From a consideration of the cases in which the single reference theory breaks down, we recommend the following choice of the $\{M_K^\dagger\}$ operators:

$$\Psi^\mu = Q\left[\sum_{K=0} b_K^\mu M_K^\dagger + \frac{1}{2!}\sum_{K,L=1} b_{KL}^\mu M_K^\dagger M_L^\dagger\right.$$
$$\left. + \frac{1}{3!}\sum_{J,K,L=1} b_{JKL}^\mu M_J^\dagger M_K^\dagger M_L^\dagger + \cdots\right]$$
$$\times \exp\left(\sum_I C_I^\mu S_I^\dagger\right)|0\rangle. \tag{38}$$

This wave function may be rewritten, introducing the operator $\mathscr{S}\mathscr{P}\mathscr{P}$ defined by Eq. (19), as

$$\Psi^\mu = Q\,\mathscr{S}\mathscr{P}\mathscr{P}\left(\sum_K b_K^\mu M_K^\dagger\right)\exp\left(\sum_I C_I^\mu S_I^\dagger\right)\Phi_0. \tag{39}$$

This form of the wave function is appropriate to imagine its physical meaning, especially in connection with the single reference SAC theory written as

$$\Psi = Q\exp\left(\sum_K b_K^\mu M_K^\dagger + \sum_I C_I^\mu S_I^\dagger\right)\Phi_0$$
$$= Q\exp\left(\sum_K b_K^\mu M_K^\dagger\right)\exp\left(\sum_I C_I^\mu S_I^\dagger\right)\Phi_0. \tag{40}$$

We note that except for the singlet $A_1$ state, the product operators $M_K^\dagger M_L^\dagger$, etc. are not generally symmetry adapted.

The MR–SAC theory presented here has the following properties.

(1) The theory does not include noncommutative alge-

bra. All the operators involved are commutative.

(2) The theory is exact. Any excitation operators can be included in the theoretical framework.

(3) The theory is unique. All of the unknown variables are determined uniquely by Eq. (36). When both of the coefficients $\{b_K^\mu\}$ and $\{C_I^\mu\}$ are treated as unknown variables, the operators $\{M_K^\dagger\}$ and $\{S_I^\dagger\}$ should be exclusive to each other, but when the $M$ part is assumed to be given, the $\{S_I^\dagger\}$ operators are chosen freely. Physically, the $M_K^\dagger$ operators represent the state-specific correlations like quasidegeneracy, first-order correlation, internal correlation in open shells, etc. The part

$$\exp\left(\sum_I C_I^\mu S_I^\dagger\right)$$

represents a more-or-less transferable part of the correlations which was called dynamic correlation by Sinanoglu.[8,11] For closed-shell ground states at stable geometry, only dynamic part is important so that the single reference theory works well.

(4) The $\{M_K^\dagger\}$ operator space need not be complete in the MR–SAC theory, in contrast to the existing multireference cluster expansion theory.[13,22] We can choose the $\{M_K^\dagger\}$ operators only from the physical considerations without introducing a noncommutative operator algebra.

(5) Excited states are solved simultaneously within the same framework.

(6) The cluster expansion formalism is rather insensitive to the choice of the reference orbitals as it is exactly so in the single reference theory (Thouless' theorem[28]).

(7) The theory corrects the source of the breakdown of the single reference theory as analyzed in Sec. II. This is done by introducing a general operator $\mathscr{E}\mathscr{X}\mathscr{P}$ as Eq. (19) and replacing the defective part of the single reference theory with it. This is apparent from a comparison of Eq. (39) with Eq. (40).

(8) The theory is expected to be less dependent on the choice of the multireference $M$ space than the multireference CI theory.

(9) The MR–SAC theory based on the ansatz given by Eq. (20) is size consistent. For the MR–SAC ansatz given by Eq. (15), the $S$ part is size consistent so that the size consistency is satisfied if the $M$ part is chosen to be so. The $\mathscr{E}\mathscr{X}\mathscr{P}$ operator or the full CI within some active space is, e.g., such a choice.

The MR–SAC theory is of general utility, especially for the studies of the potential energy surfaces of the ground and excited states. The properties summarized above are very important for general utility of the theory. Especially, the properties (1)–(4) and the simplicity of the present ansatz itself are the important merits of the present theory over the existing multireference versions of the coupled cluster theory.[13,22] We note that the symmetry-adapted formulation was useful for extending the theory to the general cases, in addition to the fact that it is essential for the nonlinear expansion.[16]

We have verified from many applications[32] that the SAC[16,21] and SAC–CI[18,21] theories are very useful for the studies of molecular spectroscopies which involve ground,

excited, ionized, and anion states of molecules and their dynamics. The MR–SAC theory is a multireference version of the SAC theory and is also considered as a generalization of the SAC–CI theory. Therefore, the MR–SAC theory will become useful for the problems for which the SAC and SAC–CI theories are difficult to be applied. The results of the test calculations given below for the CO molecule at several internuclear distances may be considered to support this expectation.

## VII. TEST CALCULATIONS OF THE GROUND AND EXCITED STATES OF CO

The MR–SAC theory developed in this paper has been applied to the lower four $^1\Sigma^+$ states of the CO molecule at the equilibrium and two elongated distances $R = 2.132$, 3.75, and 5.5 a.u., respectively. The reason we have chosen the CO molecule is as follows. Near the equilibrium distance the HF configuration is a dominant configuration of the ground state but when it is elongated, the weight of the HF configuration decreases monotonously and approaches zero in the dissociation limit $C(^3P) + O(^3P)$. The HF configuration itself approaches the dissociation limit $C(^1D) + O(^1D)$. At $R = R_{eq}$, the single reference SAC theory is valid for the ground state but at $R = 3.75$ a.u., the theory does not even converge and at $R = 5.5$ a.u., it converges to the third $^1\Sigma^+$ state. For a uniform description of these states, the multireference theory is essential.

The basis set of the calculation is $[4s2p]$ set of Huzinaga–Dunning.[43] We did not add $d$-polarization functions because this is a test calculation in nature. We have used the Hartree–Fock MO's as reference orbitals. The active MO's are limited to only eight MO's, four upper occupied MO's and four lower unoccupied MO's. The details of the MR–SAC calculations are described separately.[41] Since we neglected the last term of Eq. (17), we approximated the fifth term to be a product of the third term. As the $M$ operators, we chose all the single excitation operators and the double excitation operators whose coefficients in the SDCI is larger than 0.06. In addition, we have included double excitations from $\pi$ to $\pi^*$ and from $\sigma$ to $\sigma^*$. The triple and quadruple excitation operators were generated according to Eq. (18), but higher excitations were neglected. The $S$ operators are the rest of the double excitation operators. The MR–SAC calculations converged nicely at all the distances for both the ground and excited states. For a comparison, we have also performed the SAC and SAC–CI calculations and full CI and lower-order CI's.[44] For example, SDTQ–CI denotes a CI which includes all single, double, triple, and quadruple excitations from the HF configuration.

Table I shows the results of the calculations. The results of the MR–SAC theory show excellent agreement with the results of the full-CI and SDTQ–CI methods. This is so not only for the ground state but also for the excited states, and so not only for the equilibrium distance but also for the well separated and moderately separated distances. The MR–SAC theory is accurate not only for an ordinary ground state but also for excited states and quasidegenerate states. The number of the variables of the present MR–SAC calculations were about one-fourth to one-half of that of the full CI. Therefore, we conclude that the MR–SAC theory is a good

TABLE I. Energies of the lower four $^1\Sigma^+$ states of the CO molecule calculated by the CI, SAC, SAC–CI, and MR–SAC theories (a.u.).[a]

| $R$ (a.u.) | No. of $\Sigma$ state | Main configuration[b] | SD–CI | SDT–CI | SDTQ–CI | Full-CI | MR–SAC | SAC SAC–CI |
|---|---|---|---|---|---|---|---|---|
| 2.132 | 1 | $|0\rangle$ | − 112.739 91 | − 112.742 77 | − 112.743 70 | − 112.743 74 | − 112.743 71 | − 112.741 16[c] |
| | 2 | $|1\rangle$ | − 112.159 84 | − 112.197 61 | − 112.200 68 | − 112.201 40 | − 112.199 23 | − 112.198 53 |
| | 3 | $|1\rangle$ | − 112.088 67 | − 112.106 30 | − 112.114 77 | − 112.114 98 | − 112.113 90 | − 112.118 77 |
| | 4 | $|2\rangle$ | − 112.006 17 | − 112.042 26 | − 112.055 27 | − 112.055 41 | − 112.048 50 | − 112.048 97 |
| 3.75 | 1 | $|0\rangle,|1\rangle$ | − 112.489 76 | − 112.500 24 | − 112.512 79 | − 112.514 73 | − 112.513 03 | ⋯ |
| | 2 | $|0\rangle,|3\rangle$ | − 112.348 44 | − 112.357 12 | − 112.380 23 | − 112.387 11 | − 112.379 48 | ⋯ |
| | 3 | $|0\rangle,|3\rangle$ | − 112.240 78 | − 112.260 04 | − 112.334 35 | − 112.338 18 | − 112.333 11 | ⋯ |
| | 4 | $|2\rangle$ | − 112.194 21 | − 112.214 03 | − 112.272 92 | − 112.274 47 | − 112.271 64 | ⋯ |
| 5.5 | 1 | $|2\rangle$ | − 112.406 74 | − 112.414 51 | − 112.424 49 | − 112.424 90 | − 112.423 38 | − 112.415 89 |
| | 2 | $|4\rangle$ | (absent)[c] | (absent)[c] | − 112.354 09 | − 112.357 62 | − 112.353 65 | (absent)[d] |
| | 3 | $|0\rangle$ | − 112.331 35 | − 112.331 54 | − 112.335 57 | − 112.335 71 | − 112.335 59 | − 112.335 22[c] |
| | 4 | $|2\rangle$ | − 112.287 87 | − 112.292 27 | − 112.302 69 | − 112.302 94 | − 112.301 53 | − 112.296 64 |

[a] The Hartree–Fock energies are − 112.685 05, − 112.348 90, and − 112.286 63 a.u. for $R$ = 2.132, 3.75, and 5.5 a.u., respectively.
[b] $|i\rangle$ means $i$-electron excited configuration from the Hartree-Fock configuration $|0\rangle$.
[c] SAC solution.
[d] This state is absent because it is essentially a quadruply excited state from the HF configuration.

approximation of the exact theory.

The single reference SAC theory gives good results for the ground state at the equilibrium distance and for the third excited state at $R$ = 5.5 a.u. The SAC–CI theory was used to calculate the other states. The results are also reasonable. For the third state at $R$ = 2.132 a.u., the SAC–CI energy overshoots the full-CI energy. This is due to the nonvariational nature of the solution. At $R$ = 3.75 a.u., however, the single reference SAC theory did not converge so that we could not define the SAC–CI theory at this distance. This situation also shows a necessity of the MR–SAC theory. Though the number of the test calculations are very limited at present, the results of Table I may be considered to show a practical utility and an accuracy of the MR–SAC theory for the studies of the potential energy surfaces of both the ground and excited states of molecules in wide range of nuclear configurations.

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