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Molecular Applications of a State-Specific Multireference Coupled Electron-Pair Approximation (SS-MRCEPA)-like Method

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In this paper, we present a coupled electron-pair (CEPA) type variant of the state-specific multireference coupled cluster (SS-MRCC) method [Mahapatra, U. S., et al. *J. Chem. Phys.* **1999**, *110*, 6171]. The method termed as SS-MRCEPA based on complete active space (CAS) can handle quasi-degeneracy of varying degrees over a wide range of potential energy curves (PECs), including regions of real or avoided curve-crossing. The method is size-extensive and avoids the intruder problem in a natural manner. Exploiting a two-dimensional CAS-based SS-MRCEPA method, we consider, in this paper, several demanding molecular systems that benefit from multireference description. The reliability of computational results of the method for PECs of the ground state of P4, H4, H_8, perpendicular insertion of Be into H_2, Li_2, and ground-state energy at the equilibrium point of CH_2 will be discussed with respect to the parent SS-MRCC and full CI/large scale CI results. We have also reported the excitation energies corresponding to the ground states of H_8 and CH_2 systems. The method has also been applied to study the bond breaking in the F_2 molecule which is a challenging task for any ab initio method. In all cases, the comparison is also made with the results obtained from other CC- and CEPA-type methods wherever available.

I. Introduction

Although nonvariational methods such as single reference (SR) based coupled cluster (CC)[1,2] and perturbation (MBPT) theories[3] are widely used, the most straightforward and conceptually simple method to treat the correlation is the variational SR-based configuration interaction method (CI).[4] In contrast to the CC method and MBPT, the main objection for the truncated SRCI method is the lack of size-extensivity of the computed energies. Many methods have been reported in the literature regarding removal of the size-extensivity error of the energy obtained from the truncated SRCI method via physically appealing and heuristically motivated empirical correction factors such as Davidson's correction.[5] Davidson's correction is very simple and can be justified by perturbation theory. Other modifications are very close to Davidson's proposal. Unfortunately, none of these corrections to CI are accurate for large systems. Hence, the most natural way out is the casting of the truncated CI equation in a size-extensive manner which leads to the coupled electron-pair approximation (CEPA) method.[6−11] Meyer[6] and Kelly[7] developed the CEPA methods before the popularization of the CC method.[1,2] The CEPA method is size-extensive as well as structurally and hence computationally much simpler than the singles and doubles (SD) SRCC method. Normally the working equation of the CEPA method comprises simultaneous algebraic equations similar to that of the SRCC method rather than the eigenvalue equation of the CI method. Hence one can consider the CEPA method as a specific approximation of the SD-based SRCC equation in a size-extensive manner or a version of size-extensive corrections to the truncated CI (CISD) method. In this context, we refer to some reviews for an extensive survey of SRCEPA theories.[11−13] The relation between CEPA approaches and the Davidson correction has also been studied extensively.[14]

An alternative way of restoring the extensivity of the CISD method yet continuing to have its eigenvalue equation form is to dress the CISD matrix suitably by some or all of the exclusion principle violating (EPV) terms. An advantage of the method is that one can partly utilize the extensively developed CI computational procedure. This was pioneered by Malrieu and co-workers[9,10] who showed that all the EPV terms can in principle be included exactly in a dressed CI formulation. In this method,[9,10] termed as self-consistent−size-consistent (SC)^{2}CI, they included all the EPV terms although the calculation of EPV terms is not trivial. The CEPA-like approximation which we have presented in this paper, developed for multireference situations, is conceptually related to the method of Malrieu and co-workers[9,10] in the sense that all the EPV terms can also be included naturally in our formulation as well.

The efficacy of the SR methods goes down in the presence of quasi-degeneracy of the certain virtual functions with the reference functions. This warrants the development of multireference (MR) methods.[15−19] The MR generalization of CC and PT is not a trivial aspect due to the various theoretical and computational complications. There are three main classes of MRCC methods: (i) valence-universal (VU),[18] a Fock space approach, which is very useful for the computation of spectroscopic energies; (ii) state-universal (SU),[19] a Hilbert space approach, which is widely used for the study of the potential energy curve (PEC); and (iii) the state-specific (SS) method.[20−25]

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The main difficulty associated with the effective Hamiltonian-based MR theories using complete active space (CAS) is the problem of the intruder state.[26] This is due to the fact that the method generates several states simultaneously. It is thus useful to search for a method which would not generate several states but instead would focus on a specific target state so that the intruders are not encountered. The state-specific MR method addresses the solution of a specific state of interest at a time and is thus free from the intruder state problem. Although the SS method using a SR starting point with selective higher rank operators is also studied,[27] a MR-based SS approach is more natural and more flexible to tackle the intruders. Among the various state-specific MR methods given by Malrieu and co-workers,[21] Mukherjee and co-workers,[22,23] and Hubač and co-workers,[24] Mukherjee and co-workers[22,23] and Hubač and co-workers[24] use the Jeziorski−Monkhorst ansatz (JM)[19] while Malrieu and co-workers[21] use the low order quasi-linearized truncation schemes. The method of Hubač and co-workers is structurally much simpler than that of Mukherjee and co-workers, but the method is not rigorously size-extensive. In a latter development, Hubač and co-workers[28] have proposed a way to eliminate the size-inextensive terms from the cluster finding equations via an additional iteration, where they modify the BW resolvent and drop the terms that are not size-extensive. The idea is to make MRBWCC a posterior close to its Rayleigh−Schrödinger version. An analysis indicating how a continuous transition from the state-universal theory of Jeziorski and Monkhorst[19] to the state-specific theories of Hubač and co-workers[24] and of Mukherjee and co-workers[22,23] can be accomplished has recently been done by Pittner.[29]

The state-specific MRCC method based on CAS proposed by Mukherjee and co-workers[22,23] [termed as SS-MRCC] is manifestly size-extensive and size-consistent. In all these SSMR many-body methods,[21−24] the diagonalization of the effective Hamiltonian operators constructed within the model space generates the energies and hence the method uses *relaxed* coefficients for the model space functions. There is a corresponding formulation of the *unrelaxed* variety.[20,22] Since the dimension of a CAS rapidly increases with the number of active orbitals considered, it is of utmost practical importance to be able to employ an arbitrary general model space (incomplete model space, IMS), rather than to be restricted to a CAS, while at the same time preserving the size-extensivity of the resulting method.[30,31] Although the intruder state problem of the traditional effective Hamiltonian can be avoided at a given geometry using judicial choice of the IMS,[30] it is not useful over the whole range of the PEC. There are usually different intruders in the different regions of the PEC; thus it is impossible to find a unique IMS that is suitable in the entire range of geometry. Of course, one can always apply different IMSs for different geometries, but this does not generate a smooth PEC. The SSMR method is free from such an objection and the intruder problem. Recently Krylov and co-workers[32] have proposed a promising approach to tackle the MR situation but in a SR fashion, the spin-flip method. Significant research on the MRCC methods is still in progress. However, MRCC methods are challenged even now when it comes to mapping out the PECs. The computation of PECs is, of course, much more demanding.

Another class of methods try to generate states of interest via the action of an excitation operator on a simple base function, usually of the ground state. The linear response based theories based on CC reference functions have been proposed sometime back to achieve this goal, starting from the HF or ROHF ground reference state.[33−37]

The MR generalization of CI (MRCI)[15] is quite straightforward from both the theoretical and computational point of view. Several groups have developed various versions of the MRCI method.[16] While the MRCI is known to be the most common form of CI that is practical to use, as that of the SR case, the truncated MRCI (say MRCISD) method is also not size-extensive in nature. The Davidson type corrections to the truncated MRCI case have also been reported.[38,39] When these corrections are applied to the MR case, the error in size-extensive corrected MRCISD not only increases linearly or even faster with the number of subsystems but also with the size of the model space. As we have already discussed, a more logical way of handling the problem of the size-inextensivity of the MRCI method is to correct the working equation rather than the computed energy. Much effort has been invested into this type of research recently. The multireference CEPA (MRCEPA) methods fall in this class.[8,11,21,40−46] There are broadly two types of MRCEPA approaches. One is state-universal MRCEPA,[45,46] and the other is state-specific MRCEPA.[8,11,21,40−43] All these MRCEPA methods avoid the redundancy problem using non-redundant cluster operators to compute the dynamical correlation on the zeroth-order MR wave function. To get a detailed discussion in this context, we refer to the recent review of Szalay.[11] As pointed out earlier, the perennial problem associated with the SU-based MRCEPA method is the intruder states, where as the SS-based MRCEPA method is free from such objection and hence is very suitable to compute the energy over the wide range of geometries.

The MR version of the $(SC)^2$CI method, termed as MR-$(SC)^2$CI,[21] can be viewed as the size-extensive dressing of the MRCISD method just as the $(SC)^2$CI is considered to be the size-extensive dressing of the SRCID method. Similar to the SR case, all EPV terms are included in an exact manner. The direct discussion of the redundancy terms of this method with respect to the above-mentioned state-specific MRCEPA methods is not possible. The source of the generating redundancy terms in these two situations is completely different. We will discuss this issue later.

In this paper, we will go on to present a SS version of the MRCEPA method starting from the full-blown SS-MRCC method[22,23] using the same spirit of Malrieu and co-workers as done in the SR.[9] The method is termed by us as SS-MRCEPA-(D) [D stands for "diagonal dressing"]. The SS-MRCEPA(D) has close resemblance to the MR-$(SC)^2$CI method of Malrieu and co-workers.[21] The method is structurally very simple compared to the parent SS-MRCC method, but it captures most of the essential physics of the parent method despite neglecting a host of nonlinear terms. Although a brief report has already been published,[47] this article is a detailed theoretical and numerical account of the SS-MRCEPA(D) method.

In this paper, our main focus is on testing the performance of the SS-MRCEPA(D) method. We present the results of its application to various archetypical model systems for which we can generate the exact full CI (FCI) results and thus illustrate the potential and flexibility of this method.

The paper is organized as follows: In section II, we shall first recall the principle of the SRCEPA method. After that, we discuss the basic issues of the SS-MRCC theory. In the same section, we then present the development of the SS-MRCEPA-(D) method. In secction III, we will discuss the aspect of size-extensivity and consistency of the method. We will cover the comparison of the SS-MRCEPA(D) with the other allied methods in section IV from the theoretical point of view.

Computational details and results are provided in section V. Finally, we summarize the pros and cons of the SS-MRCEPA-(D) method.

II. Theory

In this section, we will discuss and develop the SS-MRCEPA-(D) method. In the first subsection, we will briefly outline the principal ideas behind the SRCEPA-like methods before embarking on a discussion of the parent SS-MRCC method and the CEPA-like approximants thereof. This will motivate us toward the types of approximations needed in generating the MRCEPA equations starting from the SS-MRCC equations.

A. An Overview of the SRCEPA Method. In this section, we examine the SR case in order to understand the basic concept of the SR-based CEPA scheme from the SRCC equations. Let us start with a Hartree−Fock (HF) reference function, ϕ_0, and a correlated wave function: $\psi = \exp(T_2)|\phi_0\rangle$, where $T_2 = \sum_a T_a t_a$ (the index a denotes the electron pairs). For the sake of easier understanding of basic relations, we neglect single excitation, i.e., we consider the CCD model. After simple manipulation, we obtain the following equations:

$$E = \langle\phi_0|H|\phi_0\rangle + \sum_b \langle\phi_0|HT_b|\phi_0\rangle t_b \tag{2.1}$$

$$Et_a = \langle\chi_a|H|\phi_0\rangle + \sum_b \langle\chi_a|HT_b|\phi_0\rangle t_b + \frac{1}{2}\sum_{b,b'}^{b\neq b'} \langle\chi_a|HT_bT_{b'}|\phi_0\rangle t_b t_{b'} \tag{2.2}$$

Combining the above two equations leads to the following expression:

$$\langle\chi_a|H|\phi_0\rangle = \sum_b [\langle\phi_0|H|\phi_0\rangle\delta_{ab} - \langle\chi_a|HT_b|\phi_0\rangle]t_b + \sum_b \langle\phi_0|HT_b|\phi_0\rangle t_b t_a + \frac{1}{2}\sum_{b,b'}^{b\neq b'} \langle\chi_a|HT_bT_{b'}|\phi_0\rangle t_b t_{b'} \tag{2.3}$$

After the cancellation of the disconnected terms in the last two terms of the above equation, an important part, the so-called EPV terms, remains. Though EPV terms are disconnected in the form given above, they do not cause the error of extensivity, since they can equally be written in the connected form. The above equation can be written as follows:

$$\langle\chi_a|H|\phi_0\rangle = \sum_b [(\langle\phi_0|H|\phi_0\rangle + \Delta_b)\delta_{ab} - \langle\chi_a|HT_b|\phi_0\rangle]t_b \tag{2.4}$$

Several methods have been developed to include EPV terms, Δ. These methods are often referred to as CEPA methods.[13] The CEPA(0) corresponds to ignoring entirely the term Δ in eq 2.4; the CEPA(0) approximation is equivalent to the linearized CCD. The CEPA(0) method is not exact for the two-electron problem. The diagonal dressing[9,10] of Malrieu and co-workers (to be called CEPA(D) from now on) involves the most complete inclusion of the EPV terms, by retaining all the terms in Δ in the projection onto $\chi_{\alpha\beta}^{pq}$ [it is important to note that in χ_a, a denotes electron pairs, but here we are explicitly showing the labels for electron pairs] which have at least one orbital in common with α, β, p and q. In the SRCCD context, this amounts to keeping in the quadratic terms one T_2 amplitude with the labels α, β, p, and q and the other having at least one of the labels of the first T_2. This amounts to approximating $1/2\langle\chi_{\alpha\beta}^{pq}|[H, T_2], T_2]|\phi_0\rangle$ as$[-\Delta\, t_{\alpha\beta}^{pq}]$, where Δ has the value as given in refs 9 and 10. When the singles are included, the CEPA-like approximations are modified by including all the linear and quadratic powers of T_1. The MRCEPA formulation using the same concept within the SS framework would be presented in the next section.

B. An Overview of the SS-MRCC Method. The full account of the SS-MRCC method and its illustrative applications can be found in refs 22 and 23; we only briefly describe essential features below.

In the SS-MRCC approach, the exact wave function is expressed as

$$\psi = \sum_\mu \exp(T^\mu)\phi_\mu c_\mu \tag{2.5}$$

where

$$T^\mu = T_1^\mu + T_2^\mu + \cdots + T_n^\mu \tag{2.6}$$

$$T_n^\mu = \left(\frac{1}{n!}\right)^2 \sum_{\alpha_1\cdots\alpha_n, r_1\cdots r_n} t_{r_1\cdots r_n}^{\alpha_1\cdots\alpha_n}(\mu)a^{r_1}\cdots a^{r_n}a_{\alpha_n}\cdots a_{\alpha_1} \tag{2.7}$$

The t coefficients are antisymmetric, and $\alpha_1\cdots\alpha_n$ and $r_1\cdots r_n$ are labels of occupied and unoccupied orbitals in each ϕ_μ, respectively. Moreover, $\alpha_1\cdots\alpha_n$ and $r_1\cdots r_n$ cannot be exclusively valence labels which means that T_n^μ generates only external excitations, i.e., excitations outside the model space when acting on ϕ_μ. Such a definition of T^μ follows from the intermediate normalization condition for the wave operator.

Each model space function, $\{\phi_\mu\}$, spans a CAS and plays the role of a vacuum. As a consequence, this method provides an unambiguous definition of the MR problem within the Hilbert space framework. This has computational advantages. Due to the action of the cluster operators T^μ on the reference space functions, some virtual functions are generated *more than once*, which leads to the problem of redundancy. Thus the problem of redundancy in SS-MRCC and hence the SS-MRCEPA method is completely different from the other aforesaid state-specific MRCEPA[8,11,40,41] methods. This problem in the SS-MRCC method is removed using suitable physically motivated sufficiency conditions, which leads to the following coupled equations.

The cluster amplitudes defining the T^μ operators are determined by solving the following equation:

$$\langle\chi_l|\bar{H}_\mu|\phi_\mu\rangle c_\mu + \sum_\nu \langle\chi_l|\exp(-T^\mu)\exp(T^\nu)|\phi_\mu\rangle \tilde{H}_{\mu\nu}c_\nu = 0\ \forall l,\mu \tag{2.8}$$

where $\bar{H}_\mu = \overline{H\exp(T^\mu)}$ and $\tilde{H}_{\mu\nu} = \langle\phi_\mu|\bar{H}_\nu|\phi_\nu\rangle$.

The equation determining the model space coefficients $\{c_\mu\}$ and the target state energy is given by

$$\sum_\nu \tilde{H}_{\mu\nu}c_\nu = Ec_\mu \tag{2.9}$$

For practical purposes, the T^μ operators are truncated at the SD level, leading to the SS-MRCCSD method. The method based on CAS is rigorously size-extensive and size-consistent with respect to the dissociation process at hand. The proof of connectedness of the SS-MRCC theory bears close resemblance to the SU-MRCC theory of Jeziorski and Monkhorst.[19] We now discuss some important issues regarding the SS-MRCC theory which are pertinent for further development of the CEPA-like theory from it. If the cluster operator T^μ is connected, one can easily show that the dressed Hamiltonian $\bar{H}_\mu$ and the matrix elements $\tilde{H}_{\mu\nu}$ are also connected via multicommutator expansion. Hence, the proof of the connectedness of the first term of eq 2.8 is quite straightforward, but this is a nontrivial issue for the second term. The term $\langle\chi_l|\exp(-T^\mu)\exp(T^\nu)|\phi_\mu\rangle$ can be written as $\langle\chi_l|\exp\{(T^\nu - T^\mu) + (1/2)[T^\nu, T^\mu] + \cdots\}|\phi_\mu\rangle$. Except the term $(T^\nu - T^\mu)$, all other terms involving multicommutator of the cluster operators T^μ's must have common orbital labels with $\tilde{H}_{\mu\nu}$. Since in the SS-MRCC theory all the model space functions are treated on the same footing, the cluster operators T^ν and T^μ have the same functional form and consequently the difference $(T^\nu - T^\mu)$ also has common labels with the matrix $\tilde{H}_{\mu\nu}$. As a result of this, the second term of eq 2.8 is connected as a whole. This aspect is *very important* while formulating any approximate method, e.g., SS-MRCEPA, from the parent SS-MRCC theory in a size-extensive manner. We are now in a position to present the development of the CEPA-like method of the SS-MRCC theory.

C. The SS-MRCEPA(D) Method. One can consider several schemes for the development of the CEPA-like approximation from the parent SS-MRCC theory. One may, e.g., emphasize that only the single and double excitations $\{\chi_l^\mu\}$ reached by the action of T^μ on ϕ^μ should be included in eq 2.8 for every χ_l^μ used in the projection. Another possibility could be to include all the virtual functions which are obtained from single and double excitations from the model space. There are structural differences in the CEPA-like schemes obtained with the above two choices. In the former, up to quadratic powers of one-body operators T_1^μ can be included, and the quadratic powers of T_2^μ must include only the EPV terms. In the latter scheme, up to quartic powers of T^μ leading to the entire singles−doubles excitation space with respect to the model space can appear. In our formulation described below, we present the CEPA-like equations for the latter scheme as the most general theoretical development. We, however, approximate our equations used in our numerical implementation by neglecting more than quadratic powers of every T^μ and retaining only the EPV terms coming from the powers of T_2^μ. In this case, the two CEPA schemes become equivalent in our applications.

The most general CEPA-like equations for both the schemes can generically be written as

$$\langle\chi_l^\mu|\overline{H(P + Q_\mu)\exp(T^\mu)}|\phi_\mu\rangle c_\mu + \sum_\nu \langle\chi_l^\mu|\exp(-T^\mu)\exp(T^\mu)|\phi_\mu\rangle\langle\phi_\mu|\overline{H(P + Q_\mu)\exp(T^\nu)}\,|\phi_\nu\rangle c_\nu = 0 \ \forall l,\mu \quad (2.10)$$

The projector Q_μ in this scheme refers to the virtual space reached by the single and double excitations from ϕ_μ. The more general scheme not further discussed would have involved the projector of the entire CISD space.

To develop the CEPA-like methods, the quasi-linearized form of the SS-MRCC equations can be written as follows:

$$[\underset{\text{I}}{\langle\chi_l|H|\phi_\mu\rangle} + \underset{\text{II}}{\langle\chi_l|[H, T^\mu]|\phi_\mu\rangle} + \underset{\text{III}}{\frac{1}{2}\langle\chi_l|[[H, T^\mu], T^\mu]|\phi_\mu\rangle}]c_\mu + \underset{\text{IV}}{\sum_\nu \langle\chi_l|(T^\nu - T^\mu)|\phi_\mu\rangle\,\tilde{H}_{\mu\nu}c_\nu} + \text{other terms} = 0 \quad (2.11)$$

If we suppress the fourth term (the so-called coupling term) on the left-hand side of the above equation, then from the point of view of the particular reference function ϕ_μ we obtain the equation of the corresponding SR case. The only difference is that certain amplitudes responsible for excitations within the model space are excluded from the equation of the cluster operators. The first three terms are connected in nature provided the cluster operator T^μ is connected. Since we adopt the same philosophy as that of SRCEPA, the χ_l's in eq 2.11 must be doubly excited for each ϕ_μ. Thus the III term should contain the product of singles and exclude the product terms of more than doubly excited with respect to the model space functions. The EPV terms coming from term III must include the product of the cluster operators in such a way that the excitation involved in one T_l^μ has at least one orbital in common with those involved in the other T_l^μ. As we have already mentioned, the two parts in the coupling term (term IV) should be treated on the same footing to maintain the size-extensivity of the full-blown SS-MRCC theory and any approximate theory starting from it.

Considering the above discussion, we present the leading terms of eq 2.11 explicitly in the following form:

$$[\underset{\text{I}}{\langle\chi_l|H|\phi_\mu\rangle} + \underset{\text{II}}{\sum_m (H_{lm} - H_{\mu\mu}\delta_{lm})t_m^\mu} - \underset{\text{IIIa}}{\Delta_\mu t_l^\mu} + \underset{\text{IIIb}}{\frac{1}{2}{\sum_{m,n}}' g_{m,n}^l\, t_m^\mu\, t_n^\mu}]c_\mu + \underset{\text{IVa}}{\sum_\nu \langle\chi_l|T^\nu|\phi_\mu\rangle\,\tilde{H}_{\mu\nu}c_\nu} + \text{other terms} = \underset{\text{IVb}}{\mathcal{E}t_l^\mu c_\mu} \quad (2.12)$$

The negative sign of the term Δ_μ is the EPV correction in IIIa in eq 2.12 to keep conformity with the analogous SR term. The term IIIb confined to the product of two singles (which is indicated by the prime in the sum) leads to the doubles. The two pieces IVa and IVb serve two specific and distinct purposes. A portion of the term in IVa for $\nu = \mu$,

$$\tilde{H}_{\mu\mu} = H_{\mu\mu} + \Delta_\mu^l + D_{\mu\text{NEPV}}^l \quad (2.13)$$

cancels both $H_{\mu\mu}\delta_{lm}$ and $\Delta_\mu t_l^\mu$ terms of II and IIIa, while the rest of the expression for $\nu \neq \mu$ of IVa corrects for the lack of extensivity coming from the terms appearing in $\mathcal{E}t_l^\mu c_\mu$. As Malrieu and co-workers[9,10] have done in the (SC)^{2}CI method, we approximate Δ_μ by the terms containing all T^μ's with at least one orbital in common with those appearing in t_l^μ. Δ_μ in each equation for t_l^μ is thus l-dependent, and we indicate this by Δ_μ^l. Denoting the energy $\mathcal{E}$ as $\mathcal{E}_{\text{CEPA(D)}}$, eq 2.12 for this scheme, referred to as SS-MRCEPA(D), takes the form

$$\left[\langle\chi_l|H|\phi_\mu\rangle + \sum_m [H_{lm} - (\mathcal{E}_{\text{CEPA(D)}} + D_{\mu\text{NEPV}}^l)\delta_{lm}]t_m^\mu + \frac{1}{2}{\sum_{m,n}}' g_{m,n}^l\, t_m^\mu\, t_n^\mu\right]c_\mu + \sum_{\nu\neq\mu}\langle\chi_l|T^\nu|\phi_\mu\rangle\tilde{H}_{\mu\nu}c_\nu = 0 \quad (2.14)$$

where $\mathcal{E}$ satisfies the equation

$$\sum_\nu \tilde{H}_{\mu\nu}c_\nu = \mathcal{E}c_\mu$$

Ignoring $D_{\mu\text{NEPV}}^l$ entirely in eq 2.14 and replacing $\mathcal{E}_{\text{CEPA(D)}}$ by the CAS energy E_0 leads to the SS-MRCEPA(0) scheme:

$$\left[\langle\chi_l|H|\phi_\mu\rangle + \sum_m (H_{lm} - E_0\delta_{lm})t_m^\mu + \frac{1}{2}\sideset{}{'}\sum_{m,n} g_{m,n}^l\, t_m^\mu\, t_n^\mu\right]c_\mu + \sum_{\nu\neq\mu}\langle\chi_l|T^\nu|\phi_\mu\rangle H_{\mu\nu}c_\nu = 0 \quad (2.15)$$

with E_0 satisfying the equation

$$\sum_\nu H_{\mu\nu}c_\nu = E_0 c_\mu$$

The intruder-free nature of the SS-MRCEPA equations is evident from the following form:

$$t_l^\mu = \frac{\langle\chi_l|H|\phi_\mu\rangle + \frac{1}{2}\sideset{}{'}\sum_{m,n} g_{m,n}^l\, t_m^\mu\, t_n^\mu + \sum_{\nu\neq\mu}\langle\chi_l|T^\nu|\phi_\mu\rangle\tilde{H}_{\mu\nu}(c_\nu/c_\mu)}{(\mathcal{E} - H_{ll} - D_\mu^l)} \quad (2.16)$$

$\tilde{H}_{\mu\nu} = H_{\mu\nu}$ and $D_\mu^l = 0$ for SS-MRCEPA(0). The SS-MRCEPA is free from divergence due to the intruder effect if $\mathcal{E}$ is well-removed from any H_{ll}, even when $H_{\mu\mu}$ is close to this H_{ll}. Thus the SS-MRCEPA theory is intruder free in nature which will be evident from the computation of the PEC of various systems, discussed in section V.B.

We summarize here the most important key facts of the SS-MRCEPA formulation:

(i) The method based on CAS is size-extensive in nature.

(ii) The method avoids the problem of intruders (as long as the target state is well separated from the virtual one) in a natural manner.

(iii) The formalism employs the relaxed coefficients description of the multideterminantal reference function which can also be cast in the unrelaxed coefficients description.

The real merit of the SS-MRCEPA(D) method in comparison to the mother SS-MRCC theory is that we save a lot of computer time since in CEPA, we neglect a host of complicated nonlinear terms. The discussion in section V.B will clearly demonstrate the accuracy of the SS-MRCEPA schemes. We will also show that the SS-MRCEPA(D) performs very well over a wide range of potential energy curves of the states of diverse complexity and arbitrary generality. The SS-MRCEPA(D) method does not have a manifest orbital invariance property as that of the SS-MRCEPA(0) theory. This is due to the inclusion of only the EPV terms in a cluster expansion which makes the formalism noninvariant with respect to the separate unitary transformations among core, active, and virtual orbitals defined within the framework of CAS. This criticism is persistent for all the CEPA-like approaches for MR (and also SR) situations. But the most simple CISD satisfies this invariance property in an explicit manner. To circumvent this difficulty, attempts were made in the past to include the EPV terms via certain pair-correlation energies averaged over all the pairs, which preserve the invariance. These corrections are, however, rather empirical in nature or, at the most, are based on heuristic considerations. Moreover, the methods have also been shown not to be rigorously size-extensive. Although the error does not grow alarmingly with increase in the number of electrons, this limitation is aesthetically unpleasant and in a way belies the very purpose of involving CEPA-like approximations. Recently Chattopadhyay et al.[48] proposed a specific version of a SS-MRCEPA which displays the orbital invariance with respect to the restricted rotations among doubly occupied, active orbitals and virtual orbitals separately while preserving size-extensivity and size-consistency rigorously. The theory does not bring in empirical correction factors, nor does it require averaging of the pair-correlation terms. The theory instead relies on natural and automatic cancellation of the disconnected terms which are non-EPV in nature by certain counter terms intrinsically present in the parent SS-MRCC equations.

We may remark here that one generic criticism associated with any many-body formalism using the JM ansatz[19] (both in SU-MRCC and SS-MRCC as well as their CEPA counterparts) is the large number of cluster amplitudes. The SS-MRCC formalism developed by Mahapatra[22,23] using CAS (and also incomplete model space[31]) and the CAS-based SS-MRCEPA also share this feature. While attempts have been made from time to time to reduce the number of variables in the cluster amplitudes, a fully satisfactory solution has not yet been found either for the state-universal or the state-specific formalism. Considerable simplification can be made using partially contracted descriptions, such as positing the sensible approximation of equal amplitudes for all the one- or two-body inactive to virtual excitations or both, as done in the internally contracted CI.[49]

III. Extensivity of the Computed Energy of the SS-MRCEPA Method

From the mode of derivations, it is quite clear that the SS-MRCEPA(D) theory is manifestly size-extensive, since our CEPA-like approximation from the parent size-extensive and size-consistent SS-MRCC theory retains only the connected terms. In the truncated equations, however, the invariance property of the parent theory under localized transformations of the core, valence, and virtual orbitals separately cannot be retained. This, anyway, is generally the situation for the CEPA-like approaches, except the CEPA(0) approach. The CAS energy is invariant under localizing transformations separately among the core and the active orbitals. It would be quite instructive if we can verify the size-consistency (strict separability) of the SS-MRCEPA(D) theory by analyzing the actual expressions in the limit of noninteracting fragments, using orbitals localized on fragments. Let us partition the full CI space into three subspaces: P space composed of reference functions, Q_μ space of all single and double excitations from each reference function ϕ_μ, and R space of all the higher excited functions outside the MRCISD space. Since the demonstration of separability depends essentially on the connected nature of certain terms in the SS-MRCEPA equations, our discussion of separability can be started with the following expression:

$$\begin{aligned}&\langle\chi_l^\mu|\overline{H(P+Q_\mu)\exp(T^\mu)}|\phi_\mu\rangle c_\mu + \sum_\nu\langle\chi_l^\mu|\exp(-T^\mu)\\ &\qquad \exp(T^\mu)|\phi_\mu\rangle\langle\phi_\mu|\overline{H(P+Q_\mu)\exp(T^\nu)}|\phi_\nu\rangle c_\nu = 0 \;\forall l,\mu \quad (3.17)\end{aligned}$$

Let us consider a supermolecule composed of mutually noninteracting molecules A and B. The Hamiltonian for the supermolecule can be expressed as

$$H = H_\mathrm{A} + H_\mathrm{B} \quad (3.18)$$

where H_A and H_B are the Hamiltonians for the subsystems A and B, respectively. To apply the SS-MRCEPA method to system 3.18, we assume that one can find reference functions separating properly into fragments in their well-defined states and therefore the zeroth-order energies can be added. We start with associating a complete set of orthonormal functions (ϕ_μ^A) and (ϕ_μ^B) with the subsystem A and B, respectively. The corresponding identity operators for the subsystems are defined to be

$$I_\alpha = \sum_\mu |\phi_\mu^\alpha\rangle\langle\phi_\mu^\alpha|;\ \alpha = \mathrm{A, B}$$

$$I_\alpha = P_\alpha + Q_\alpha + R_\alpha$$

The relevant composite entities satisfy the appropriate separability conditions:

$$I_{AB} = I_A I_B \qquad T_{AB} = T_A + T_B$$

$$c_{AB} = c_A c_B \qquad \phi_{AB} = \phi_A\phi_B$$

In the expressions above, the indices μ are not explicitly shown.

We decompose composite projectors P_{AB} and Q_{AB} into the following:

$$P_{AB} = P_A P_B$$

$$Q_{AB} = P_A Q_{1B} + Q_{1A}P_B + Q_{1A}Q_{1B} + P_A Q_{2B} + Q_{2A}P_B$$

Since we intend to show the separability property of E, we note that the set of model functions (ϕ_μ) goes over to the product set $\mathcal{A}[\phi_{\mu_A}\phi_{\nu_B}]$ (where $\mathcal{A}$ is the antisymmetrizer), while the set of virtual functions (χ_l^μ) goes over to five different types of product functions: (a) $\mathcal{A}[\chi_{l_1}^{\mu_A}\phi_{\lambda_B}]$, (b) $\mathcal{A}[\chi_{l_2}^{\mu}\phi_{\lambda_B}]$, (c) $\mathcal{A}[\chi_{l_1}^{\lambda_B}\phi_{\mu_A}]$, (d) $\mathcal{A}[\chi_{l_2}^{\lambda_B}\phi_{\mu_A}]$, and (e) $\mathcal{A}[\chi_{l_1}^{\mu_A}\,\chi_{l_1}^{\lambda_B}]$,

We shall now show that our SS-MRCEPA equations do allow additive energies for those cases which correspond to excitation on one fragment only, i.e., for functions of the type a−d.

Projecting onto the composite virtuals where one fragment is singly excited while the other is not, we get

$$\begin{aligned}&\langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\overline{(H_A + H_B)(P + Q)\exp(T^{\mu_A} + T^{\nu_B})}|\phi_{\mu_A}\phi_{\nu_B}\rangle c_{\mu_A}c_{\nu_B} + \\ &\quad\sum_{\alpha_A\sigma_B}\langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\exp(-(T^{\mu_A} + T^{\nu_B}))\exp(T^{\alpha_A} + T^{\sigma_B})|\phi_{\mu_A}\phi_{\nu_B}\rangle \\ &\langle\phi_{\mu_A}\phi_{\nu_B}|\overline{(H_A + H_B)(P + Q)\exp(T^{\alpha_A} + T^{\sigma_B})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B} = 0\end{aligned} \tag{3.19}$$

We now simplify eq 3.19 term-by-term. We consider the first term which upon simplification yields

$$\begin{aligned}&\langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\overline{(H_A + H_B)(P + Q)\exp(T^{\mu_A} + T^{\nu_B})}|\phi_{\mu_A}\phi_{\nu_B}\rangle c_{\mu_A}c_{\nu_B} = \\ &\quad\langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\overline{H_A(P_AP_B + P_AQ_{1B} + Q_{1A}P_B + P_AQ_{2B} + Q_{2A}P_B +} \\ &\quad\overline{Q_{1A}Q_{1B})\exp(T^{\mu_A})}|\phi_{\mu_A}\phi_{\nu_B}\rangle c_{\mu_A}c_{\nu_B} + \langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\overline{H_B(P_AP_B + P_AQ_{1B} +} \\ &\quad\overline{Q_{1A}P_B + Q_{1A}Q_{1B} + P_AQ_{2B} + Q_{2A}P_B)\exp(T^{\nu_B})}|\phi_{\mu_A}\phi_{\nu_B}\rangle c_{\mu_A}c_{\nu_B}\end{aligned}$$

which, upon taking care of the excitation to proper fragments, yields

$$\begin{aligned}&\langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\overline{(H_A + H_B)(P + Q)\exp(T^{\mu_A} + T^{\nu_B})}|\phi_{\mu_A}\phi_{\nu_B}\rangle c_{\mu_A}c_{\nu_B} = \\ &\quad\langle\chi_{l_{1A}}^{\mu_A}|\overline{H_A(P_A + Q_{1A} + Q_{2A})\exp(T^{\mu_A})}|\phi_{\mu_A}\rangle c_{\mu_A}c_{\nu_B}\end{aligned}$$

Likewise, the second term of eq 3.19, the *coupling* term, is

$$\begin{aligned}&\sum_{\alpha_A\sigma_B}\langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\exp(-(T^{\mu_A} + T^{\nu_B}))\exp(T^{\alpha_A} + T^{\sigma_B})|\phi_{\mu_A}\phi_{\nu_B}\rangle \\ &\langle\phi_{\mu_A}\phi_{\nu_B}|\overline{(H_A + H_B)(P + Q)\exp(T^{\alpha_A} + T^{\sigma_B})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B} = \\ &\quad\sum_{\alpha_A\sigma_B}\langle\chi_{l_{1A}}^{\mu_A}|\exp(-T^{\mu_A})\exp(T^{\alpha_A})|\phi_{\mu_A}\rangle \\ &\quad\langle\phi_{\mu_A}\phi_{\nu_B}|\overline{H_A(P_AP_B + P_AQ_{1B} + Q_{1A}P_BQ_{1A}Q_{1B} +} \\ &\quad\overline{P_AQ_{2B} + Q_{2A}P_B)\exp(T^{\alpha_A})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B} + \\ &\quad\sum_{\alpha_A\sigma_B}\langle\chi_{l_{1A}}^{\mu_A}|\exp(-T^{\mu_A})\exp(T^{\alpha_A})|\phi_{\mu_A}\rangle\langle\phi_{\mu_A}\phi_{\nu_B}|\overline{H_B(P_AP_B +} \\ &\overline{P_AQ_{1B} + Q_{1A}P_BQ_{1A}Q_{1B} + P_AQ_{2B} + Q_{2A}P_B)\exp(T^{\sigma_B})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B}\end{aligned}$$

which upon further simplification gives

$$\begin{aligned}&\sum_{\alpha_A\sigma_B}\langle\chi_{l_{1A}}^{\mu_A}\phi_{\lambda_B}|\exp(-(T^{\mu_A} + T^{\nu_B}))\exp(T^{\alpha_A} + T^{\sigma_B})|\phi_{\mu_A}\phi_{\nu_B}\rangle \\ &\langle\phi_{\mu_A}\phi_{\nu_B}|\overline{(H_A + H_B)(P + Q)\exp(T^{\alpha_A} + T^{\sigma_B})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B} = \\ &\quad\sum_{\alpha_A}\langle\chi_{l_{1A}}^{\mu_A}|\exp(-T^{\mu_A})\exp(T^{\alpha_A})|\phi_{\mu_A}\rangle \\ &\quad\langle\phi_{\mu_A}|\overline{H_A(P_A + Q_{1A} + Q_{2A})\exp(T^{\mu_A})}|\phi_{\mu_A}\rangle c_{\alpha_A}c_{\nu_B}\end{aligned}$$

Hence, for the single excitation of fragment A, our SS-MRCEPA equations take the form

$$\begin{aligned}&\langle\chi_{l_{1A}}^{\mu_A}|\overline{H_A(P_A + Q_{1A} + Q_{2A})\exp(T^{\mu_A})}|\phi_{\mu_A}\rangle c_{\mu_A} + \\ &\quad\sum_{\alpha_A}\langle\chi_{l_{1A}}^{\mu_A}|\exp(-T^{\mu_A})\exp(T^{\alpha_A})|\phi_{\mu_A}\rangle \\ &\quad\langle\phi_{\mu_A}|\overline{H_A(P_A + Q_{1A} + Q_{2A})\exp(T^{\alpha_A})}|\phi_{\alpha_A}\rangle c_{\alpha_A} = 0\end{aligned}$$

Similar relations hold true for the projections where fragment A is doubly excited but fragment B is not:

$$\begin{aligned}&\langle\chi_{l_{2A}}^{\mu_A}|\overline{H_A(P_A + Q_{1A} + Q_{2A})\exp(T^{\mu_A})}|\phi_{\mu_A}\rangle c_{\mu_A} + \\ &\quad\sum_{\alpha_A}\langle\chi_{l_{2A}}^{\mu_A}|\exp(-T^{\mu_A})\exp(T^{\alpha_A})|\phi_{\mu_A}\rangle \\ &\quad\langle\phi_{\mu_A}|\overline{H_A(P_A + Q_{1A} + Q_{2A})\exp(T^{\alpha_A})}|\phi_{\alpha_A}\rangle c_{\alpha_A} = 0\end{aligned}$$

These are just the SS-MRCEPA equations for fragment A. There are similar expressions for the single and double excitations for fragment B, with fragment A remaining unexcited.

We can also verify the projections onto the composite virtuals where both the fragments are excited, i.e., for the function of the type $\mathcal{A}[\chi_{l_1}^{\mu_A}\,\chi_{l_1}^{\lambda_B}]$. By similar reasoning, one can show in a straightforward manner that the total contribution is *identically* zero. Thus there are no working equations for such excitations.

We now consider the active space projections.

$$Ec_\mu = \sum_\alpha\langle\phi_\mu|\overline{H(P + Q)\exp(T^\alpha)}|\phi_\alpha\rangle c_\alpha$$

For the composite system,

$$Ec_{\mu_A}c_{\nu_B} = \sum_{\alpha_A\sigma_B}\langle\phi_{\mu_A}\phi_{\nu_B}|\overline{(H_A + H_B)(P + Q)\exp(T^{\alpha_A} + T^{\sigma_B})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B} = \sum_{\alpha_A\sigma_B}\langle\phi_{\mu_A}\phi_{\nu_B}|\overline{H_A(P_AP_B + Q_{1A}P_B + P_AQ_{1B} + Q_{1A}Q_{1B} + P_AQ_{2B} + P_BQ_{2A})\exp(T^{\alpha_A})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B} + \sum_{\alpha_A\sigma_B}\langle\phi_{\mu_A}\phi_{\sigma_B}|\overline{H_B(P_AP_B + Q_{1A}P_B + P_AQ_{1B} + Q_{1A}Q_{1B} + P_AQ_{2B} + P_BQ_{2A})\exp(T^{\sigma_B})}|\phi_{\alpha_A}\phi_{\sigma_B}\rangle c_{\alpha_A}c_{\sigma_B}$$

which on some mathematical manipulation yields

$$Ec_{\mu_A}c_{\nu_B} = E_Ac_{\mu_A}\sum_{\sigma_B}\delta_{\nu\sigma}c_{\sigma_B} + E_Bc_{\nu_B}\sum_{\alpha_A}\delta_{\mu\alpha}c_{\alpha_A} = (E_A + E_B)c_{\mu_A}c_{\nu_B}$$

Therefore,

$$E = E_A + E_B$$

Thus the SS-MRCEPA(D) method is size-consistent in nature only for localized orbitals on each subsystem, since the method is not invariant under orbital rotations.

The various numerical examples which will be discussed in this paper use the symmetry-adapted delocalized orbitals in practice. Then one can easily say that the theory is not really extensive in this case. This issue can be checked as one might rotate the orbitals from delocalized to localized and check the invariance of the results in the limit of large separation. Unfortunately, it is not possible in this paper to test the change of the results due to the orbital rotations.

IV. Comparison with Other Allied Theories

In the following part, we will discuss the relationship of the present method with other state-universal and state-specific MRCEPA methods from the theoretical point of view. In the theoretical analysis of various MRCEPA methods, we mainly focused on two terms: EPV and redundancy. The former is already present in the SR case, while the latter is clearly due to the MR extension. The term "redundancy" has been used in the SS-MRCEPA method and in the MRCEPA methods discussed by Szalay[11] and Tanaka,[45] but in totally different contexts. The redundancy of the MRCEPA methods discussed by Szalay and Tanaka is altogether unrelated to the redundancy discussed by us and appears only when one rewrites the CEPA equations in terms of CI-like coefficients rather than cluster amplitudes. This type of redundancy thus is an artifact due to the transcription of the CEPA equations involving cluster amplitudes to one containing CI-like coefficients for the "direct" terms. The aspect of redundancy discussed by us, on the other hand, arises in an entirely different context. It is a physical requirement where we deliberately use for projections the virtual functions $\langle\chi_l^{\mu}|$, which might appear more than once as excitations from different ϕ_μ's. This is required to preserve the size-extensivity of SS-MRCC and SS-MRCEPA equations.

Tanaka[45,46] has reviewed the various state-universal MRCEPA approaches, and their reliability is assessed by comparing the working equations and the numerical results in detail. In the SU-based MRCEPA, if the reference functions are selected to describe the excited state on top of the ground state appropriately, the SU theory provides correlated wave functions of these states at the same time. But the working equations sometimes suffer from the so-called "intruder state" problem. In such cases, the state-specific-based theories become a natural choice.

As Szalay[11] has already reviewed state-specific methods extensively and focused on the way of approximating EPV terms, Δ, and treatment of reference space by comparing various approaches, we will not go into such a detailed comparison, but we will discuss how the various previously developed state-specific MRCEPA methods are different from the SS-MRCEPA(D) method.

In the MRCEPA methods of Gdanitz and Ahlrichs[8] and Szalay and Bartlett,[40] the EPV terms, Δ, are treated in an averaged way. The use of an average value for Δ means that Δ is independent of electron-pair excitation in the equation to determine the correlation coefficients. These MRCEPA methods are orbital invariant in nature since electron pairs do not appear explicitly in the final equations. The methods are not strictly size-extensive, although it has been observed that the error due to the size-extensivity does not increase much with the simultaneous increase in the number of the electrons.

Ruttink et al.[42] proposed a way of approximating the redundancy terms using the determinantal basis in their MRCEPA method by neglecting the EPV terms completely; thereby the resulting equations remain at the CEPA(0) level. In this method, the treatment of the redundancy terms is not straightforward and uniform but depends on the excitation class. The MRCEPA method by Fink and Staemmler[43] analogous to SRCEPA of Kelly neglects the redundancy terms completely but the EPV terms are considered in detail. Their method is not size-extensive in nature and does not show orbital invariance also. The state-specific MRCEPA methods discussed till now belong to the category of SS-based theories without relaxation of the reference space due to the inclusion of electron correlations.

In contrast to these above schemes, our SS-MRCEPA equations can simultaneously handle both the inclusion of all the Q_μ-space functions and the EPV terms beyond CEPA(0). Of course, our method uses each model function ϕ_μ rather than the entire function ψ_0, and this aspect, coupled with the use of redundancy, distinguishes our approach from the rest of the methods mentioned above. Also, since the combining coefficients $\{c_\mu\}$ are iteratively updated, we use relaxed coefficients in our SS-MRCEPA schemes.

In the multireference size-consistent self-consistent CI method, MR(SC)^{2}CI, Malrieu et al.[21] considered both the EPV and redundancy terms exactly and hence the method is extensive in nature. But calculating these two terms is not trivial. This method is conceptually very close to our SS-MRCEPA method. Since Malrieu et al. generate the functions in the virtual space by acting on the individual functions of the reference space, some of the virtual space functions are generated more than once as that in our SSMR approach. We overcome the problem of redundancy using suitable sufficiency conditions, while Malrieu et al. resolved this problem via the use of a suitable "genealogical weight" factor of the corresponding terms. The method also uses *relaxed* coefficients for the model space functions.

V. Numerical Tests

A. Computational Details. We discuss here both the details of the working equations and the computational strategy leading to the numerical implementation of the SS-MRCEPA(D) method.

In the SS-MRCEPA(D) strategy (eq 2.14), in addition to the terms in the SS-MRCEPA(0), some EPV terms are also taken into account:

$$\Bigg[\langle\chi_l|H|\phi_\mu\rangle + \sum_m [H_{lm} - (\mathscr{E}_{\text{CEPA(D)}} + D^l_{\mu\text{NEPV}})\delta_{lm}]t^\mu_m + \frac{1}{2}\sum_{m,n} g^l_{m,n}\, t^\mu_{1m}\, t^\mu_{1n} + \frac{1}{2}\sum_{m,n} g^l_{m,n}\, t^\mu_{2m}\, t^\mu_{2n}\Bigg]c_\mu + \sum_{\nu\neq\mu}\langle\chi_l|T^\nu|\phi_\mu\rangle\, \tilde{H}_{\mu\nu}c_\nu = 0 \quad (5.20)$$

There is at least one orbital in common between t^μ_{2m} and t^μ_{2n} in the term $\sum_{m,n} g^l_{m,n}\, t^\mu_{2m}\, t^\mu_{2n}$. The diagonal matrix element of $\tilde{H}$ which is used in the energy finding equation is of the following form:

$$\tilde{H}_{\mu\mu} = \left\langle \phi_\mu \middle| H + \overline{HT^\mu_1} + \overline{HT^\mu_2} + \frac{1}{2}\sum_{m,n} g^l_{m,n}\, t^\mu_{1m}\, t^\mu_{1n} \middle| \phi_\mu \right\rangle$$

and the off-diagonal matrix element of $\tilde{H}$ corresponding to this scheme looks like

$$\tilde{H}_{\nu\mu} = \left\langle \phi_\nu \middle| H + \overline{HT^\mu_1} + \overline{HT^\mu_2} + \frac{1}{2}\sum_{m,n} g^l_{m,n}\, t^\mu_{1m}\, t^\mu_{1n} + \frac{1}{2}\sum_{m,n} g^l_{m,n}\, t^\mu_{2m}\, t^\mu_{2n} \middle| \phi_\mu \right\rangle$$

Two sets of variables, the cluster operators, T^μ's, and the combining coefficients, c_μ's, constitute the SS-MRCEPA(D) equations in a coupled form. We trace the following scheme to obtain a stable and a rapidly converging solution.

To achieve converged quantities, such as the energy, the combining coefficients, and the cluster amplitudes, three levels of iterations are needed through a nested loop structure. The outermost loop (macroiteration cycle) provides the converged coefficients and consequently the corresponding energy by solving the eigenvalue problem. In the next level of the iterative process, the coupling between the various cluster amplitudes, t_μ's and t_ν's, is taken care of, while the innermost step of iteration leads to the converged cluster amplitudes. The cluster amplitudes are then used to construct the matrix of $\tilde{H}$. It is important to highlight the fact that the couplings between the various cluster amplitudes that are present in the SS-MRCEPA(D) equations are not too many. Only those components of t_ν's can couple with $\mu \neq \nu$, which can result in excitations to χ_l by their action on ϕ_μ. The converged cluster amplitudes for each updated coefficient are then used to construct $\tilde{H}_{\mu\nu}$. The $\tilde{H}_{\mu\nu}$ matrix obtained therefrom and the set of updated c_μ's are used in the virtual projection in the next macroiteration. Upon convergence at all levels, a diagonalization of the $\tilde{H}_{\mu\nu}$ matrix leads to the required energy. Thus, in SS-MRCEPA(D) we update the combining coefficients, the cluster amplitudes, and the energy through the operation of three levels of iteration. Since the reference determinants are closed-shell singlet in our applications in this paper, the spin-adaptation of the methods is trivial. In our implementation, we use the *same tolerance*, $\eta(\mu)$ (say 10^{-8}), for different cluster amplitudes t^μ_i. When the $\delta(\mu)$ [$=|\mathbf{t}^{\mathbf{i}}_\mu$(new) $- \mathbf{t}^{\mathbf{i}}_\mu$(old)$|$] becomes smaller than the tolerance, convergence is reached. In the iteration loop for obtaining the cluster amplitudes, when the condition $\delta(\mu) \leq \eta(\mu)$ is reached for the cluster amplitude t^i_μ, the t^i_μ amplitude is frozen, while the iteration process is started for the other cluster amplitude t^i_ν, $\mu \neq \nu$ till the condition $\delta(\nu) \leq \eta(\nu)$ is attained. The working equations for SS-MRCEPA are much simpler than the full-blown SS-MRCC theory. A host of complicated nonlinear terms are simply not present. The most time-consuming step in the CCSD method is the computation of the nonlinear terms. The real advantage of the SS-MRCEPA method over the SS-MRCCSD method is that we save a lot of computer time, since in CEPA we neglect a host of complicated nonlinear terms in a size-extensive and intruder-free manner. This holds the key to a faster performance.

B. Results. In this section, we shall apply the SS-MRCEPA-(D) formulation to compute the ground (and also excited) state energies of some interesting prototypical systems which are frequently used to test the performance of various SR- and MR-based methods.

All the model space functions are considered on an equal footing in our SS-MRCEPA methods, and hence these methods are very useful to study the PEC. We have studied the PEC of the ground state of H_4 (P4 and H4), H_8, Li_2, and the perpendicular insertion of Be into H_2 to test the performance of the SS-MRCEPA(D) method. The PEC of the ground state of such systems possesses quasi-degeneracy at some point and there are potential intruders at some other points, and hence these systems are appropriate to test the efficacy of the SS-MRCEPA methods. Since the lowest $^1A_1$ state of CH_2 possesses quasi-degeneracy to a strong degree, this has also been considered. The model space (also called active space) of such systems can be adequately described by two closed-shell reference functions: $\phi_1 = [core]a^2$ and $\phi_2 = [core]b^2$. The active orbitals (a and b) are of two different symmetries, and hence the active space is complete in nature. The most natural example of this type employs the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as active orbitals. In all calculations, we use CASSCF MOs generated by the use of GAMESS. In this paper, we have presented only the results of the *relaxed* description of the SS-MRCEPA(D) method. The results obtained via SS-MRCEPA-(D) have been compared with those of the parent SS-MRCC along with the FCI or high order CI calculations.

1. H_4 Model. The H_4 model is rather well-studied[10,23,24,50,51] since it serves as a benchmark to test the applicability of different SR- and MR-based many-body methods. Among the various types of H_4 systems possible, we will consider here two often employed models: the rectangular (P4) and the trapezoidal (H4) models to assess the performance of our SS-MRCEPA methods.

(a) P4 Model. In the P4 model,[10,50,51] the four H atoms are placed at the four corners of a rectangle, constituting the rectangular geometry of the H_4 system. Starting with the pure square configuration, in which the internuclear separations are fixed at 1.40158 au, two parallel hydrogen molecules, located on the opposite sides of the square geometry (designated by a single geometrical parameter R), are symmetrically pulled apart, giving rise to different rectangular geometries. The system in the square geometry possesses maximum configurational quasi-degeneracy which is systematically lifted by increasing the parameter R. We use a model space consisting of two molecular orbitals (one HOMO and the other LUMO) and two electrons. $\phi_1 = 1a_1^2 1b_2^2$ and $\phi_2 = 1a_1^2 2a_1^2$ are the two corresponding model space functions for the ground state. Although the system possesses D_{4h} symmetry when $R = 1.40158$, in this model

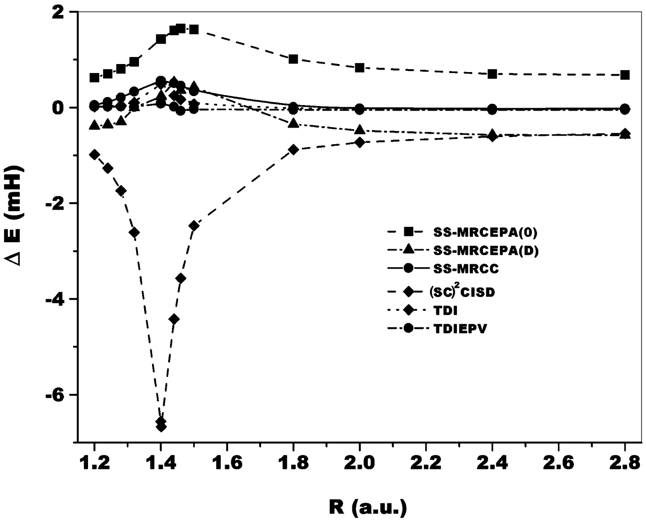

Figure 1. PEC (relative energies with respect to FCI) of the P4 model.

system, all the molecular calculations are carried out using C_{2v} symmetry. The geometry and basis considered here are the same as in ref 10.

We plot in Figure 1 the ground-state energies obtained by the SS-MRCEPA(0) and SS-MRCEPA(D) as a function of *R*, along with the corresponding FCI results using the same basis. To get a better feeling for the relative performance of the various methods, we plot in Figure 1 the deviations of energy values obtained via different methods from the FCI values as well. For comparison, the results of the parent SS-MRCC and (SC)^{2}CI of Malrieu and co-workers[10] have also been presented in the figure. It is clear from the figure that the performance of the SS-MRCEPA methods is promising while describing the ground state of the P4 model system over the entire region of the PEC. The deviations of SS-MRCEPA results from the FCI energies are uniform and quite encouraging. The SR-based (SC)^{2}CI scheme dresses each excited determinant by the unlinked effects of the triples and quadruples from the outer space only. To improve the accuracy of the SRCISD method, Malrieu and co-workers[10] proposed a perturbative and iterative full dressing method involving both the linked and unlinked contributions from the outer space [known as TD1)]. The most sophisticated version takes into account the higher-order EPV terms in a self-consistent manner in addition to the linked and unlinked contributions. This has been called the TD1EPV method by Malrieu and co-workers.[10] From Figure 1, it is clear that the values of (SC)^{2}CI are diverging in nature at the region of near degeneracy. However, the corresponding TD1 and TD1EPV values show considerable improvement. This includes linked triples and quadruples with respect to the determinant ϕ_1 as well as full EPV terms. In contrast, our two-determinants model space approach captures most of the nondynamical correlations and a substantial amount of dynamical correlations at all points of the PEC. At larger distances, the ground state is essentially SR in nature and our SS-MRCEPA(D), which has full EPV and linked SD excitations out of the model space, should behave very similarly to (SC)^{2}CI, which also includes SD excitations in a SR setting and keeps only the EPV terms. We can conclude that our SS-MRCEPA methods are quite efficient approximations of the parent SS-MRCC method to compute the ground-state PEC of the P4 model.

(b) H4 Model. The ground state of the H4 model[50,51] can be described completely by $\phi_1 = 1a_1^2 1b_2^2$ and $\phi_2 = 1a_1^2 2a_1^2$. We apply a DZP[51] basis for this model. The H4 system consists of two stretched H_2 in a trapezoidal geometry where all the nearest neighbor internuclear separations are fixed (2 au). The range of degeneracy is completely described by a single parameter α [0.0−0.5]. α = 0.0 and α = 0.5 correspond to the completely degenerate and nondegenerate situations, respectively. The C_{2v} symmetry has been used at each stage of the calculation of this model system. The orbitals are used for the lowest root of the (2 × 2) CAS.

Table 1 displays the deviations of the theoretically computed ground-state energies by the SS-MRCEPA(D) method as well as other results with respect to the FCI values available in the literature. When we have considered the SUCCSD method, the results are not so good in comparison to the other full-blown CC methods. Li and Paldus[25] have very recently shown that the inclusion of the higher-than-pair cluster in the SU-MRCC method [referred to as CI-*corrected* SUCCSD] can improve the results of the SUCCSD method and intruder state problem. The results of the CI-*corrected* SUCCSD represent a definite improvement over the SUCCSD results in the nondegenerate region of geometries, but not so in the degenerate region. The performance of the SS-MRCEPA(0) method is quite good among the various (quasi)linearized forms of the various CC methods. A comparison with the results of the FCI and other methods indicates that SS-MRCEPA(D) is numerically stable and bypasses the difficulties of the intruder states in a stable manner, while at the same time generating very encouraging ground- and corresponding excited-state energies over a wide range of the geometries.

2. H_8 Model. The eight-electron model system H_8[52] consists of four H_2 molecules with internuclear separation fixed at 2.0 au, arranged in the octagonal D_{2h} configuration, and its geometry is uniquely determined by a single parameter α. α = 0 corresponds to the regular octagonal (D_{8h}) geometry. The broad spectrum of configurations, α [0,1], provides an opportunity to study the performance of the SS-MRCEPA(D) method from highly degenerate situations to practically nondegenerate ones in a continuous way.

Our model space consists of two functions, $\phi_1 = a_g^2\, b_{3u}^2\, b_{2u}^2\, a_g^2$ and $\phi_2 = a_g^2\, b_{3u}^2\, b_{2u}^2\, b_{1g}^2$. A strong interaction between ϕ_1 and ϕ_2 can be seen by examining the FCI coefficients of the ground state. Coefficients associated with the two reference functions in the two lowest-lying FCI indicate that this two-dimensional reference space is also appropriate in the degenerate, quasi-degenerate, and nondegenerate situations for both the ground and excited states. In our calculations, we used the minimal basis set (MBS). The CASSCF orbitals corresponding to the lowest root of the (2 × 2) CAS are used for our ground and the corresponding first excited state.

The ground (1^1A_1) state and the excited (2^1A_1) state computed via the SS-MRCEPA(D) method are shown in Table 2 and Table 3, respectively. To get a better conclusion regarding the performance of the SS-MRCEPA(D) method, we have also quoted the results of other methods and indicated the relative energies of the various methods with respect to the corresponding FCI values within the bracket. From both the tables, it is clear that the deviation of the SS-MRCEPA(D) from the FCI values is very close to the full-blown parent SS-MRCC theory. For the ground state, the results of the SS-MRCEPA(D) method are better than the corresponding CEPA(0) version, while for the excited state the quality of results of SS-MRCEPA(0) is strikingly very good. For the excited state, the performance of the SS-MRCC, the SSCCSD(T),[53] and the SS-MRCEPA(D) is very close and they perform slightly better than the SU-MRCC and the CASCCSD.[54] The better quality of the results for the ground state in comparison to the corresponding lowest singlet

TABLE 1: Relative Correlation Energies (mH) with Respect to the FCI Values, [$E_{FCI} - E_{method}$], of the Ground State of the H4 Model for Different Values of α

	α							
	0.0	0.01	0.02	0.1	0.2	0.3	0.4	0.5
MRMBPT3[b]	−2.172	−2.295	−2.386	−2.155	−2.079	−2.136	−2.161	−2.166
MRCISD[b]		−1.771	−1.706	−1.277	−1.039			−0.895
MRL-CCSD[b]	3.685	3.610	3.436	5.027	*	*	*	*
MRL-BWCCSD[b]	−3.942	−3.961	−3.863	−3.212	−3.071	−3.092	−3.136	−3.151
SS-MRCEPA(0)	0.011	0.076	0.227	0.227	−0.110	−0.270	−0.347	−0.371
SS-MRCEPA(D)	−2.195	−2.468	−2.360	−1.91	−1.637	−1.554	−1.596	−0.283
SS-MRCC	0.156	0.102	−0.030	−0.398	−0.353	−0.309	−0.289	−0.283
sr-MRBWCCSD[b]	0.100	0.012	−0.146	−0.582	−0.579	−0.559	−0.551	−0.548
SUCCSD[c]	0.686	0.594		0.173	1.187	1.998	2.308	2.379
CI-*corrected* SUCCSD[c]	−1.528	−1.499		−1.077	−0.848	−0.784	−0.797	−0.808

[a] MRCISD and SUCCSD: missing values were not present. * denotes that no convergence is achieved. [b] Reference 24. [c] Reference 25.

TABLE 2: Total Energies (au) of the Ground State (1^1A_1) of the H_8 Model[a]

	α						
	0.0001	0.001	0.01	0.06	0.1	0.5	1.0
SRCCSD	−4.199769 (−5.034)	−4.199885 (−5.03)	−4.198280 (−7.49)	−4.209147 (−3.02)	−4.216649 (−2.11)	−4.292535 (−6.86)	−4.352445 (−4.45)
SSCCSD(T)[b]	−4.211119 (6.32)	−4.211128 (6.24)	−4.211304 (5.54)	−4.214785 (2.62)	4.220106 (1.34)	−4.292907 (−0.31)	−4.352691 (−0.30)
SSCCSD(TQ)[b]	−4.203722 (−1.08)	−4.203809 (−1.08)	−4.204728 (−1.04)	−4.211350 (−0.82)	−4.218096 (−0.67)	−4.292914 (−0.31)	−4.352730 (−0.26)
SU-MRCC[b]	−4.207640 (2.84)	−4.207725 (2.84)	−4.205069 (−0.70)	−4.214866 (2.70)	−4.221149 (2.39)	−4.293765 (0.54)	−4.353555 (0.66)
SS-MRCEPA(0)	−4.210300 (5.49)	−4.210388 (5.50)	−4.211283 (5.51)	−4.217405 (5.24)	−4.223742 (4.98)	−4.294248 (1.03)	−4.354840 (1.85)
SS-MRCEPA(D)	−4.200584 (−4.22)	−4.200946 (−3.94)	−4.201347 (−4.22)	−4.207690 (−4.47)	−4.214155 (−4.61)	−4.288770 (−4.45)	−4.348842 (4.15)
SS-MRCC	−4.206429 (1.63)	−4.206513 (1.63)	−4.207397 (1.63)	−4.213R668 (1.49)	−4.220020 (1.25)	−4.293847 (0.626)	−4.351823 (−1.67)
FCI	−4.204803	−4.204886	−4.205769	−4.212169	−4.218767	−4.293221	−4.352990

[a] Values (mH) within the parentheses indicate the deviation from the FCI values, [$E_{FCI} - E_{method}$]. [b] Reference 53.

TABLE 3: Total Energies (au) of the Lowest Singlet Excited State (2^1A_1) of the H_8 Model[a]

	α				
	0.0001	0.001	0.01	0.06	0.1
SRCCSD[b]	−4.118353 (−25.647)	−4.118594 (−25.51)	−4.120809 (−23.98)	−4.128224 (−18.11)	−4.129853 (−15.32)
SU-MRCC[b]	−4.135637 (−8.39)	−4.135707 (−8.40)	−4.136340 (−8.45)	−4.137793 (−8.54)	−4.136717 (−8.45)
CASCCSD[b]	−4.135711 (−8.32)	−4.135802 (−8.30)	−4.136401 (−8.39)	−4.137813 (−8.52)	−4.136832 (−8.34)
F-CASCCSD[b]	−4.140076 (−3.95)	−4.140083 (−4.02)	−4.140230 (−4.56)	−4.140281 (−6.05)	−4.139390 (−5.78)
SSCCSD(T)[b]	−4.137306 (−6.72)	−4.137502 (−6.60)	−4.138924 (−5.88)	−4.143823 (−2.51)	−4.143428 (−1.74)
SSCCSD(TQ)[b]	−4.142368 (−1.66)	−4.142449 (−1.65)	−4.143192 (−1.60)	−4.144964 (−1.37)	−4.143895 (−1.28)
SS-MRCEPA(0)	−4.145839 (1.81)	−4.145918 (1.82)	−4.146698 (1.91)	−4.149320 (2.98)	4.148999 (3.27)
SS-MRCEPA(D)	−4.136805 (−7.22)	−4.136601 (−7.50)	−4.137756 (−7.04)	−4.139481 (−6.85)	−4.138333 (−6.84)
SS-MRCC	−4.137071 (−6.96)	−4.137144 (−6.96)	−4.137797 (−6.99)	−4.139257 (−7.08)	−4.136138 (−9.03)
FCI	−4.144027	−4.144103	−4.144791	−4.146335	−4.145172

[a] Values (mH) within the parentheses indicate the deviation from the FCI values, [$E_{FCI} - E_{method}$]. [b] Reference 54.

excited state, 2^1A_1, obtained via SS-MRCC and SS-MRCEPA(D) methods is due to the intervention of higher-lying states that act as intruders for the 2^1A_1 state. The results given in the tables show that the CEPA(D)-like approximations in the parent SS-MRCC theory are potentially very convenient to compute the energies for the degenerate, nondegenerate, and also intruder-prone regions for the ground as well as the corresponding lowest singlet excited state.

3. Li_2 System. The ground-state PEC of the Li_2 molecule is a rather good test case[23,55,56] for assessing the performance of any SR or MR theory. The ground state of the Li_2 molecule requires a two-determinantal description in the zeroth order: ϕ_1

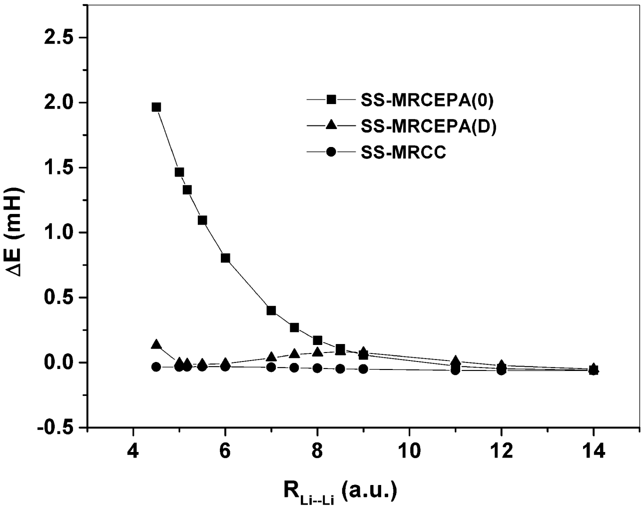

Figure 2. PEC (relative energies with respect to FCI) of the Li_2 molecule (DZ basis).

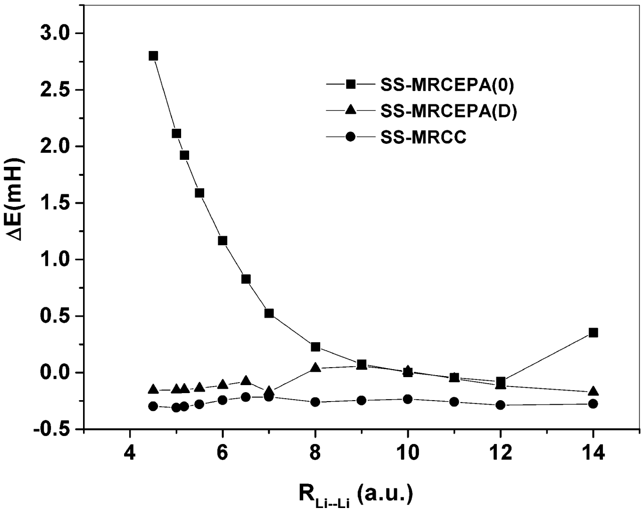

Figure 3. PEC (relative energies with respect to CISDTQ) of the Li_2 molecule (6-311G** basis).

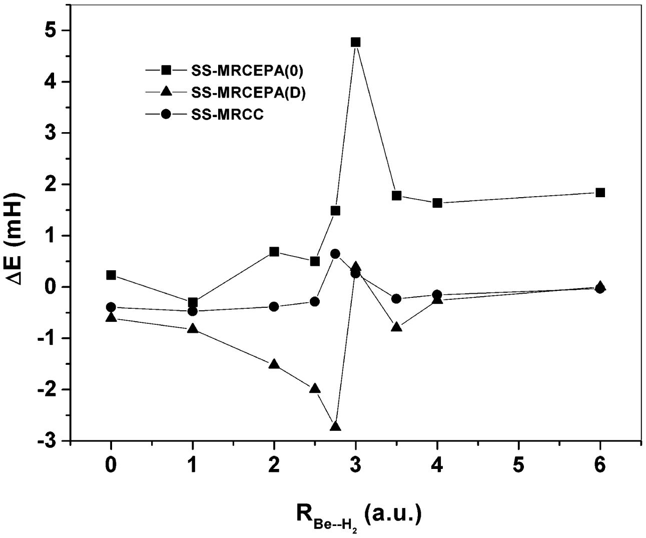

Figure 4. PEC (relative energies with respect to FCI) of insertion of Be into H_2.

$= 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$ and $\phi_2 = 1\sigma_g^2 1\sigma_u^2 2\sigma_u^2$. We have used both a small DZ basis[57] and a somewhat larger (6-311G**) basis, taken from the GAMESS basis library, for the study of the ground-state PEC using the SS-MRCEPA(D) theory. In all our calculations, we have used the D_{2h} point group.

The results obtained with the DZ and 6-311G** basis sets are plotted in Figure 2 and Figure 3, respectively (as a deviation from the FCI and CISDTQ values). The figures display the fact that the performance of the SS-MRCEPA(D) is very close in agreement to the parent SS-MRCC method. The good numerical agreement of our SS-MRCEPA values with the corresponding standard results (FCI/CISDTQ), coupled with the fact that the SS-MRCEPA(D) is able to reproduce the full PEC of the system with small deviation from the FCI values, again indicates the efficacy of the approximations. The deviation of the SS-MRCEPA(0) from the FCI/CISTDQ values is slightly higher than the corresponding SS-MRCEPA(D) and SS-MRCC methods at smaller values of Li−Li distances. From the figure, it is evident that our methods show encouraging results in computing the PECs.

4. Insertion of Be into H_2: BeH_2 Model. The C_{2v} insertion reaction of Be into H_2 to form the BeH_2 complex[58] is a very often used model to test the performance of various MR methods.[23,59−62] The Be atom approaches the H_2 molecule from the direction perpendicular to the bond, and the bond is stretched to enhance the nondynamical correlation effect as the distance of approach becomes shorter. This system poses a serious challenge to any theory where both nondynamical and dynamical correlations are important in varying degrees along the PEC, the active orbitals cross along the distance of approach, thus necessitating theories which treat all model functions on the same footing, and the two active orbitals face intruder orbitals at the two extreme geometries, viz., the large distance of approach and short distance of approach. State-specific formalism should handle this situation for the ground-state PEC.

It is observed from the coefficients of the FCI results that in the regions of the points A−C and G−I the dominant configurations are $\phi_1 = 1a_1^2 2a_1^2 1b_2^2$ and $\phi_2 = 1a_1^2 2a_1^2 3a_1^2$, respectively. At the transition points D−F, both configurations are equally important: *a quasi-degenerate reaction region*. Hence these two configurations constituting the CAS are sufficient for an accurate description of the reference function of the ground-state PEC of the BeH_2 system. From a close study of the CI coefficients, one can infer that the system shows strong configurational degeneracy at geometries D, E, and F and faces intruders at geometries B, C, H, and I. Therefore this model tests how well the method performs with a strongly changing reference function and in the presence of the intruders.

In Figure 4, we have presented the lowest $^1A_1$ state energies obtained via the SS-MRCEPA(D) method along with FCI and SS-MRCEPA(0) values as a function of the R(Be−H_2) distance. The comparison with the FCI results shows that the performance of the SS-MRCEPA(D) method is good. In addition, we reported some numbers for particular geometries (D, E, and F) along with other available results in Table 4. Around the region D−F, the unperturbed energy of the “excited” orthogonal complement of the function with the same two model functions comes close to that for the ground state, and the exact extent of splitting of the two states as well as the barrier height generated due to the weakly avoided crossing becomes very sensitive to the accuracy of the formalism used. The full-blown SS-MRCC theory performs very well in handling both the intruders and in predicting good barrier height.[23] Inspection of the table also leads to the conclusion that the SS-MRCEPA(D) performs pretty well with respect to the FCI values even at these three important reaction points. Very recently Pittner et al.[62] have applied the MRBWCCSD method of Hubač and co-workers[24] which is not

TABLE 4: Relative Energies (mH) with Respect to the FCI Values, [$E_{FCI} - E_{method}$], of the 1^1A_1 State of BeH_2[a]

	geometry		
	D	E	F
FCI[a]	−15.622883	−15.602919	−15.624981
MCSCF[b]	−53.31	−64.35	−66.68
MRCI[b]	−0.84	−2.01	−3.08
MRLCCM[b]	2.62	2.40	5.50
MRCEPA(0)[c]	3.28	4.30	5.50
MRACPF[c]	0.90	0.90	0.53
MRAQCC[d]	−0.29	−1.11	−1.98
MRAQCC-mc[d]	0.19	−0.57	−0.36
MRAQCC-v[d]	−0.45	−1.37	−2.29
MRAQCC-vmc[d]	−0.02	−0.87	−1.11
MRCEPA[e]	1.65	2.55	5.88
MCCEPA[f]	−0.20	−0.15	−0.54
QDVPT[g]	2.9	4.7	5.5
MRCEPA(2)[h]	1.2	3.5	4.5
QDVPT+APC[i]	0.91	1.03	0.53
MRBWCCSD (uncorrected)[j]	−0.68	0.26	0.48
MRBWCCSD (corrected)[j]	−0.44	0.60	1.96
SS-MRCEPA(0)	0.503	1.487	4.77
SS-MRCEPA(D)	−1.994	−2.735	0.381
SS-MRCC	0.08	−0.85	−0.37

[a] Values in a.u. [b] Reference 59. [c] Reference 8. [d] Reference 41. [e] Reference 42. [f] Reference 43. [g] Reference 44. [h] Reference 46. [i] Reference 63. [j] Reference 62.

rigorously size-extensive to study the perpendicular insertion reaction of Be into H_2 to form the BeH_2 complex. They observed that the performance of the MRBWCCSD method is promising, although the size-extensive correction of the method does not necessarily improve the results relative to the FCI values.[62]

5. F_2 System. The study of the potential energy curve for F_2 is a quite challenging test for any *multireference* method due to the high contribution of dynamical and nondynamical correlation effects. We investigate here the performance of the SS-MRCEPA methods in describing the ground-state PEC of the F_2 molecule. It is now a well-known fact that RHF- or UHF-based SR methods are not able to describe the PEC of the F_2 molecule. F_2 has a ground electronic configuration of $\phi_1 = 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_g^4 1\pi_u^4 3\sigma_g^2$ and a large nondynamical correlation arising from the $\phi_2 = 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_g^4 1\pi_u^4 3\sigma_u^2$ configuration. Since the $3\sigma_g$ and $3\sigma_u$ belong to different symmetries, the functions $i\phi_1$ and phi_2 constitute the CAS. The $3\sigma_g$ orbital plays the role of HOMO in the dissociation region, while near the equilibrium domain this role is played by the $1\pi_g$ orbital. Then the $1\pi_g \rightarrow 3\sigma_u$ excitations obviously act as intruders. However, if one wishes to increase the dimension of the active space by the inclusion of $1\pi_g$ orbitals, even more intruders will be encountered. Thus our choice of a two-dimensional reference space with two active orbitals, $3\sigma_g$ and $3\sigma_u$, is optimal. Straightforward application of the conventional two-dimensional Hilbert space MR method is not applicable in this case because of several crossings between model and outer zero-order levels near the equilibrium geometry. There have been many studies on this PEC, both in the realm of perturbative and nonperturbative approaches in recent times.[64−69] The pronounced nondynamical character coupled with the intruder states warrants a SSMR description of the system to study the complete PEC. In this paper, we present the calculations performed on the F_2 molecule employing the same scheme and basis (DZP) as used by Laidig et al.[64] for comparing with the literature data of various previous calculations. Since the SS-MR formalisms treat both these configurations (ϕ_1 and ϕ_2) on an equal footing, we could have chosen either of the two determinants to generate the HF orbitals. For the applications in this paper, molecular orbitals are taken from the RHF solutions corresponding to the configuration ϕ_1.

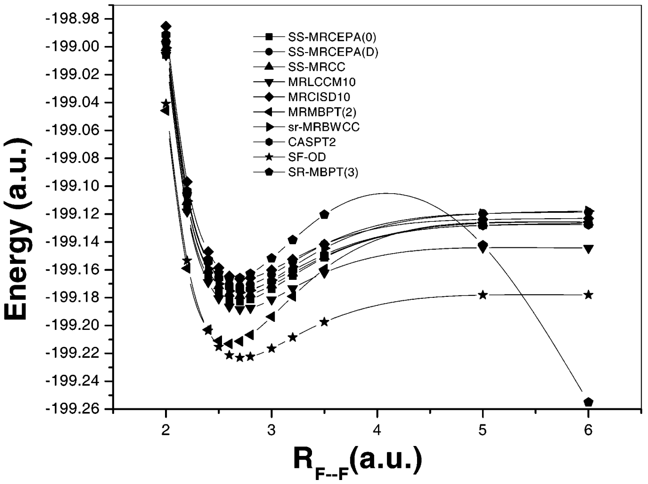

Figure 5. PEC of the F_2 molecule.

In Figure 5, we plot the entire PEC calculated by our SS-MRCEPA methods and compare them with the parent SS-MRCC and other available results, viz., (i) MRCISD10 and MRLCCM10,[64] (ii) sr-MRBWCCSD and MRMBPT(2),[66,67] (iii) CASPT2, and (iv) VOO-CCD(2) and SF-OD.[68] We also present the results of various SR-based MBPT methods reported by Laidig et al.[64] The suffix associated with the MRCISD and MRLCCM denotes the reference space consisting of 10 configurations considered in these calculations. The sr-MRBWCCSD[66] of Hubač's group used the same active space as we have considered here, and they start from the RHF wave function for their calculations of the PEC of the F_2 molecule. The sr-MRBWCCSD method is not fully size-extensive. To compute the PEC of the F_2 molecule via the MRMBPT(2) method using full-valence space, Hubač and co-workers[67] have used various types of shifting techniques to avoid the problem of intruders, since it is an effective Hamiltonian based method. The results reported against CASPT2[20] have been carried out using active space of full valence. The valence optimized orbitals coupled cluster doubles (VOO-CCD) is an alternative computationally cost effective way for a full valence complete active space SCF (CASSFC) model for single bond dissociation and diradicals. Dynamical correlation is incorporated into the VOO-CCD function via usual second-order perturbation theory which leads to the VOO-CCD(2) model. The method is size-consistent in nature. In the SF-OD method optimized orbitals (OO) coupled cluster double (CCD) model, the constituting reference state and the target state are then generated via single double spin-flip (SF) excitations. The VOO-CCD(2) and SF-based methods are quite promising while describing single bond breaking within the SR framework. The energies computed via either MRCISD10 or MRLCCM10 of Laidig et al.[64] are not size-extensive in nature. Here it is important to mention the fact that MRLCCM is quite different from the linear SU-MRCC method,[19] which gives size-extensive energies. The SS-MRCEPA method is rigorously size-extensive and also intruder free as long as the target state is well separated from the virtual functions. Here we present only the relaxed values of the SS-MR methods, since the relaxed description of the SS-MR is essential for a proper description of the F−F bonding. Figure 5 shows that the energies computed via the SR-MBPT method go down in the region of dissociation which explains the singular behavior of the method in the case of the HOMO−LUMO degeneracy. Energetically MRMBPT(2) and SF-OD are close to each other. The potential

TABLE 5: Spectroscopic Constants of F_2

method	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (eV)
(SC)^2-SDCI[a]	1.407	947	10.87	2.306
MRCISD10[a]	1.435	821	15.2	1.222
MRLCCM10[a]	1.439	842	15.3	1.221
MRCISD32[a]	1.436			1.275
MRLCCM32[a]	1.439			1.257
CASPT2 [a]	1.442	819	13.9	1.275
sr-MRBWCCSD[a]	1.421	888	13.8	1.703
MRMBPT(2)[b]				
simple averaging	1.374	1054	10.8	2.348
double averaging	1.377	1040	10.8	2.196
VOO−CCD(2)[c]	1.417			1.51
SF−CIS(D)[c]	1.429			1.14
SF−OD[c]	1.437			1.24
SS-MRCEPA(0)	1.417	909	11.09	1.547
SS-MRCEPA(D)	1.417	862	16.76	1.466
SS-MRCC	1.420	876	14.27	1.430
experiment[d]	1.411	917.000	11.2	1.659

[a] Reference 66. [b] Reference 67. [c] Reference 68, 116, 3194. [d] Experiment: Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; VNR: New York, 1979.

energy curves of the MRMBPT(2) and CASPT2 are not smooth over the wide range of nuclear distances. These two methods show a very narrow unphysical barrier around the nuclear distance of 6.0 au.[67] From the figure, it is clear that the SS-MRCEPA methods reproduce the pattern of the ground-state PEC of the F_2 molecule in a well-behaved and balanced manner over the wide range of internuclear distances as that of other MR methods as well as the parent full-blown SS-MRCC method and the SF-based method.

Since the energies computed via different methods are not very close to one another, it is natural to test the efficacy of the various methods to generate the PEC in a very accurate manner via the computation of the various spectroscopic constants. Thus, to proceed toward testing the quality of the PEC generated via different methods, we have presented the ground-state spectroscopic constants in Table 5. Since the corresponding FCI values using the same basis are not available, we compare these values with experimental ones. The various spectroscopic constants presented in the table are equilibrium distance r_e (Å), harmonic vibrational frequency ω_e (cm^{-1}), anharmonicity constant $\omega_e x_e$ (cm^{-1}), and dissociation energy D_e (eV). Table 5 shows that each of the SS-MRCEPA methods shows good numerical agreement with the corresponding SS-MRCC, other available results, and the experimental values. The equilibrium distances calculated via different methods except the MRMBPT(2) method are comparable and agree with experimental results closely. From the table, it is evident that the dissociation energy given by the VOO-CCD(2) and CEPA(0) methods is quite close to the experimental value. Among the other methods, the D_e value of the SS-MRCEPA(D) and SS-MRCC methods is in good agreement with the experimental results. The table also depicts that the spectroscopic constants of the MRCISD and MRLCCM methods do not improve much on going from the reference space consisting of 10 configurations to the reference space consisting of 32 configurations, although the calculations involved in MRCISD32 and MRLCCM32 are much more computationally demanding than those of MRCISD10 and MRLCCM10. Unfortunately the basis set saturation limiting values of spectroscopic constants of this system are still not known; it is thus not fair to conclude which method gives us more accurate spectroscopic constants and PECs of high quality in this basis set. However, from the foregoing comparative study of the shape of PECs (Figure 5) and the spectroscopic constants (Table 5) we may conclude that the SS-MRCEPA method gives us the PEC with a correct shape over the wide range of geometries in an intruder-free manner although the two configurations considered here are not sufficient for an accurate zeroth-order description of the ground PEC of the F_2 molecule.

TABLE 6: Relative Energies (mH) with Respect to the XCI Values, [$E_{XCI} - E_{method}$], of the 1^1A_1 State of CH_2 Using the DZP and TZ2P Basis Sets, Where XCI Stands for FCI and CISDTQ for DZP and TZ2P, Respectively

method	DZP	TZ2P	method	DZP	TZ2P
MRCI[a]	−5.03		MRAQCC-v[a]	−2.91	
MRLCCM[a]	1.27		MRAQCC-vmc[a]	−2.73	
MRCEPA(0)[a]	1.27		SS-MRCEPA(0)	−1.58	1.01
MRCEPA[a]	1.19		SS-MRCEPA(D)	−3.48	2.85
MRACPF[a]	−1.01		SS-MRCC	−2.54	1.69
MRACPF-mc[a]	−0.61		SS-MRCEPA(0)[b]	−0.56	−1.17
MRAQCC[a]	−2.69		SS-MRCEPA(D)[b]	−2.43	−2.06
MRAQCC-mc[a]	−2.51		SS-MRCC [b]	−1.92	−1.11

[a] Reference 11. [b] Calculations using CASSCF orbitals.

6. Lowest Singlet of the CH_2 System. Historically, the determination of the ground states of CH_2 represented one of the first significant successes of quantum chemistry. Even today, this molecule is often used as a benchmark for testing new theoretical developments.[23,32,70−72] To gain further insight into the performance of the SS-MRCEPA(D) method, we decided to compute the energy of the two lowest $^1A_1$ states of the CH_2 system at equilibrium geometry, because earlier calculations showed that at least the $^1A_1$ requires a MR description. To be able to compare with FCI results, we use the same geometry, basis (DZP), and scheme of Bauschlicher and Taylor.[70] Using the same scheme and geometry, we have also used another basis set: TZ2P.[72] The TZ2P basis is the standard triple ζ[73] plus two sets of polarization functions: d functions on carbon and p functions on hydrogen. Although the present basis sets are not large enough, they are nevertheless adequate to enable us to draw useful conclusions regarding the applicability of the SS-MRCEPA(D) method while computing the energies. For the TZ2P basis, we were unable to get the FCI values with our limited computer facilities. Thus for comparison we choose the CISDTQ results for this basis set. Here we constitute the required CAS using the configurations $\phi_1 = 1a_1^2 2a_1^2 1b_2^2 3a_1^2$ and $\phi_2 = 1a_1^2 2a_1^2 1b_2^2 1b_1^2$. In this calculation, we have used two sets of orbitals for both the states: (a) HF orbitals of the function ϕ_1 and (b) CASSCF orbitals corresponding to the lowest energy of the above (2 × 2) CAS.

The results relative to the FCI/CISDTQ values for the 1^1A_1 state of our SS-MRCEPA(D) methods and other available methods are presented in Table 6 for DZP and TZ2P basis sets.

We conclude the following for the DZP basis:

(i) The MRCI method does not give satisfactory results.

(ii) The performance of the SS-MRCEPA(D) method toward computing the energy of the 1^1A_1 state is quite encouraging as compared to the other methods reported.

(iii) The performance of the SS-MRCEPA(0) and MRACPF-mc results is rather close to the FCI in comparison to other methods reported.

(iv) The performance of the SS-MRCEPA(D) method is comparable to that of the various MRAQCC methods.

We will now discuss the performance of our SS-MRCEPA method using the TZ2P basis. We have already pointed out that FCI values are not available for this basis. Hence we compare the results generated via SS-MRCEPA and SS-MRCC methods with the CISDTQ values. The deviation of SS-MRCEPA and SS-MRCC values using HF orbitals from CISDTQ is slightly smaller than the corresponding values obtained using CASSCF

TABLE 7: [$2^1A_1-1^1A_1$] Excitation Energies (eV) for CH_2 Using the DZP and TZ2P Basis[a]

method	DZP	TZ2P	method	DZP	TZ2P
$(SC)^2$CISD[b]	5.79		SS-MRCEPA(0)	4.33	4.15
$(SC)^2$CISDT[b]	4.44		SS-MRCEPA(D)	4.39	4.28
$(SC)^2$CISDTQ[b]	4.64		SS-MRCC	4.61	4.65
MRCI[b]	4.65		CISDTQ	4.59	4.54
MRCI+Q[b]	4.58		FCI	4.60	
EOM-CCSDT[c]	4.69				

[a] Orbitals: HF of $\mathbf{1a_1^2 2a_1^2 1b_2^2 3a_1^2}$ function. [b] Reference 74. [c] Reference 75.

orbitals. The deviation of SS-MRCEPA(D) with respect to the CISDTQ values is very close in proximity to the deviation of the parent full-blown SS-MRCC method.

To test the performance of the formalism for excitation energies, we have chosen deliberately the excited root while we diagonalize the matrix of the dressed Hamiltonian $\tilde{H}$.

In Table 7, we summarize the excitation energies between the two lowest $^1A_1$ states obtained by the SS-MRCEPA(D) and other methods using the DZP and TZ2P basis sets. From the table, it is clear that the excitation energies obtained from our SS-MRCEPA(D) method are quite credible, in comparison to the FCI/CISDTQ results. The SS-MRCEPA(0) and MRCI+Q values are the same and are seen to compare quite well with the FCI results. Although the results of the $(SC)^2$CISDT or $(SC)^2$CISDTQ approach are comparable, our SS-MRCEPA method is less demanding from the computational point of view. On the other hand, the dimension of the diagonalization space used in our SS-MRCEPA method is much smaller than that in the MRCI+Q calculations. These issues may make the SS-MRCEPA method computationally more attractive. The inclusion of triples involves including a plethora of diagrams, which also makes the EOM-CCSDT method computationally demanding. The computed values of excitation energy using the TZ2P basis via our SS-MRCEPA method are very close to those of the parent SS-MRCC method.

Finally we make a comment that the most stringent test for the generality of the CEPA method would be in situations where the orbitals change very rapidly as a function of the minor geometrical distortions. Unfortunately we are unable to test the SS-MRCEPA(D) method immediately for such cases. If we consider explicitly the behavior of the SS-MRCEPA method as a function of rotation of the orbitals, in general open-shell model functions will be generated. Our current programs for the SS-MRCEPA method cannot at present handle such open-shell model functions. Actually the invariant methods show lesser dependence on the nature of the orbitals than the noninvariant ones.

VI. Conclusions

The recently developed SS-MRCEPA(D) is a quite promising method for treating the correlations of both dynamical and nondynamical types, in the presence of quasi-degeneracy in an intruder-free manner over the whole range of the potential energy curve as that of its full-blown mother SS-MRCC theory. The above-presented results for simple but interesting systems, which enable a comparison with the energies of the FCI (or large scale CI) and other CC- as well as CEPA-type methods, clearly demonstrate the potentiality of the SS-MRCEPA(D) method in describing the ground PEC of various molecular systems. We emphasize that the SS-MRCEPA calculations require smaller CPU time than the corresponding SS-MRCC methods although there is no significant loss of accuracy despite the rather drastic but physically motivated approximations. Thus, the SS-MRCEPA(D) method may represent a desirable alternative for calculating the PEC over a wide range of geometries. The SS-MRCEPA(D) method is size-extensive. The SS-MRCEPA(D) method using CAS is not invariant under separate unitary transformations of the core, active, and virtual orbitals. Hence we have also discussed the aspect of size-consistency which is a nontrivial issue for the SS-MRCEPA(D) method.

More extensive work is needed to fully access the accuracy and utility of this method on a larger scale of ground-state calculations involving closed as well as open-shell reference space functions. The number of cluster amplitudes of the method considered can be reduced using a contracted description of the ansatz of the starting wave function as that of the contracted MRCI method.

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