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State-specific multi-reference coupled electron-pair approximation like methods: formulation and molecular applications ☆

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Received 18 January 2002; in final form 27 March 2002

Abstract

We present two variants of state-specific multi-reference coupled electron-pair type approximants (SS-MRCEPA) of our recently formulated state-specific multi-reference coupled-cluster (SS-MRCC) theory. Just like the parent SS-MRCC theory, these are formulated with a complete active space, and are rigorously size-extensive and size-consistent. They also bypass the intruder problem very efficiently. The efficacy of the methods is illustrated with the computation of the ground state potential energy surface of the trapezoidal H4 model, where the ground state requires a two-determinantal model space and the effective hamiltonian methods face intruders. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The single-reference (SR) coupled-cluster (CC) method in varying degrees of truncation is now well established as a very successful tool for treating electron correlation of closed-shell sys-tems to a high degree of accuracy [1–3]. The main advantage of the SRCC method lies in the main-tenance of extensivity at any level of truncation of the rank of the cluster operator and also in the omission of certain terms from the SRCC equa-tions. In a truncated CI, in contrast, the lack of extensivity is quite serious and manifest for even a few electron system and the error increases rapidly with the size of the system. Prior to the widespread use of the SRCC method, Meyer [4,5] analyzed carefully the aspect of inextensivity in a doubles CI (DCI). He corrected the inextensivity of the working equations by dropping the terms in the equations which are manifestly inextensive, and approximating the exclusion principle violating (EPV) terms suitably, leading to the CEPA(n)

approximations $(n = 0\text{–}2)$. The connection of CEPA with certain specific approximations of SRCC method was established by Hurley [6] and Kutzelnigg and co-workers [7,8]. From the vantage point of today, the CEPA-like methods may be viewed either as specific approximations of the singles–doubles SRCC (SR-CCSD) equations or as certain modifications of the singles–doubles CI (CISD) equations to restore extensivity. Both lead in general to a set of coupled equations for the cluster amplitudes or for the expansion coefficients of the virtual functions. An alternative way to restore extensivity of a CISD, while retaining its eigenvalue equation form is to dress the CISD matrix suitably by some EPV terms, as was pursued by Malrieu and co-workers [9]. Despite the huge success of the SR-CCSD method, the CEPA-like methods are still very popular and useful, since they capture the leading terms of inextensivity correction in a non-perturbative manner, yet remaining rather simple in structure.

It is now well known that the closed-shell determinants are not adequate to describe bond dissociation. As a result, breakdown of SR theory is expected for long or weak bonds, or in avoided crossings along the potential energy surfaces (PES), etc. In addition, states of some systems require more than one determinant for its proper description. This warrants the use of multi-reference (MR) approaches. The generalization of CC to the multi-reference cases is not straightforward. Most of the widely used MRCC methods [10–13] are based on effective hamiltonians (H_{eff}), and face the ubiquitous intruder problem [14,15] while describing PES. Thus it is natural to develop a theory based on the MR approach which is free from the intruder state problem. It now seems to be generally recognized that the simultaneous calculation of all the roots, obtained by diagonalization of an $(N \times N)$ matrix of H_{eff} in the model space to generate N eigenvalues of the hamiltonian H, targeted by an H_{eff} is at the heart of the problem. If some higher lying roots are affected by intruders, the entire set of N eigenvalues becomes poor. If one abandons this constraint, and demands that only the roots unaffected by intruders are the target states, then intruders can be avoided naturally [16,17]. One

can even focus on only one target state of interest, but work with an $(N \times N)$ MR model space. This leads to the *state-specific multi-reference* (SSMR) methods. The recent SSMR developments in the context of CC formulation are by Malrieu and co-workers [18,19], Mukherjee and co-workers [20–24], and Masik et al. [25,26]. The state-specific multi-reference CC (SS-MRCC) method of Mahapatra et al. [20–22] is rigorously size-extensive, and works with a complete active space (CAS). Its efficacy [21–24] has been tested on the computation of PESs of several electronic states with strong multi-reference character, and which are invaded by intruders in the effective hamiltonian-based theories. Perturbative versions of the method have also been developed and their usefulness has also been demonstrated [23,24,27,28].

It seems worthwhile at this stage to generate physically motivated MR approximations similar to CEPA method, starting from an MRCC theory. Such methods have been suggested recently [29–31]. A CI-like CEPA method via a dressed hamiltonian [32] has also been developed. We will explore in this Letter the efficacy of the CEPA-like approximations of the SS-MRCC method of Mukherjee and co-workers [21–24]. We will henceforth refer to them as SS-MRCEPA methods. These are yet much simpler and more flexible in structure as compared to the other MR-CEPA methods [29–31], and are manifestly extensive.

In Section 2 we will emphasize the theoretical underpinnings of CEPA-like approximations in the SR-based correlation theories. After a brief discussion of the structure of the parent SS-MRCC method, we will indicate the types of approximations one should make to arrive at the SS-MRCEPA-like equations – following largely the lead from the SR-CEPA methods. We will also discuss in Section 2 the new features that emerge in the SS-MRCEPA equations. In Section 3 we will present an illustrative application by applying the methods to the PES of the ground state of the H4 system at the trapezoidal geometry [33] which has strong quasi-degeneracy. It also poses the difficulty of intruders if effective hamiltonian-based methods are used [21–24].

2. Theoretical developments

2.1. Preliminaries

Before embarking on a discussion of the parent SS-MRCC method and the CEPA-like approximants thereof, we digress a bit to introduce the CEPA approximants in the single-reference case. This will motivate us towards the types of approximations needed in generating the analogous MR-CEPA equations starting from the SS-MRCC equations.

We will discuss the emergence of the CEPA approximations from both CI and the SRCC equations. We start out from the Hartree-Foch (HF) reference function ϕ_0, and superpose on it the virtual functions χ_l to include correlations. The virtual space projections of the CI equations are of the form

$$\langle \chi_l | H | \phi_0 \rangle + \sum_m \langle \chi_l | H | \chi_m \rangle c_m = E c_l = (E_{HF} + \Delta) c_l, \tag{1}$$

where Δ is the correlation energy. The analogous virtual space projections in the SRCC equations are given by

$$\langle \chi_l | \exp(-T) H \exp(T) | \phi_0 \rangle = 0. \tag{2}$$

In the CEPA suite of methods, the space of the projection manifold is confined to single and double excitations from ϕ_0. Thus all the virtual functions in Eqs. (1) and (2) are confined to this virtual subspace. All the CEPA methods try to eliminate the disconnected terms on the RHS of Eq. (1). This always corresponds to retaining only certain special EPV terms in Δ in the CISD equations. It should be emphasized that historically the CEPA methods were developed within the pair correlation theories in the framework of a DCI. The equivalent CEPA approximations in the SR-CCD equations are also well defined as specific subsets. Once the essentials of the CEPA-like approximations are laid down, the inclusion of singles becomes a rather straightforward exercise. We thus discuss first the DCI and the SR-CCD in the context of CEPA.

The CEPA(0) corresponds to ignoring entirely the Δ term of Eq. (1). This corresponds to ignoring not only the disconnected terms in a DCI, but also all the EPV terms. In the SR-CCD equations, this translates as keeping only up to the linear terms of T_2, leading to CCD. The more accurate CEPA(2), approximates the EPV terms Δ in the projection onto the double $\chi_{\alpha\beta}^{pq}$ corresponding to excitations from occupied orbitals α and β to virtuals p and q as

$$\Delta = \epsilon_{\alpha\beta}, \tag{3}$$

where $\epsilon_{\alpha\beta}$ is the pair correlation energy for the occupied pair (α, β). This in the SR-CCD equation would imply retaining only those quadratic terms of T_2 which are labeled by $\alpha, \beta \to p, q$ for one T_2 and $\alpha, \beta \to$ all virtuals for the other T_2. The 'diagonal dressing' of Malrieu and co-workers [9] (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 $\chi_{\alpha\beta}^{pq}$ which have at least one orbital in common with α, β, p and q. In the SR-CCD context, this amounts to keeping in the quadratic terms, one T_2 amplitude with the labels α, β, p, 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 [9]. When the singles are included, the CEPA-like approximations are modified by including all the linear and quadratic powers of T_1. We will use the MR analogue of the CEPA(0) and the CEPA(D) approximations in our present studies.

2.2. Resumé of the SS-MRCC method

We will now discuss the essential ingredients and the theoretical issues leading to the development of the SS-MRCC formalism. This will form the starting point for the SS-MRCEPA-like approximations to follow.

The SS-MRCC method is based on a CAS, spanned by the model functions $\{\phi_\mu\}$. The target state ψ is formed via the use of a multiple cluster expansion ansatz:

$$\psi = \sum_\mu \exp(T^\mu) \phi_\mu c_\mu, \tag{4}$$

where c_μs are the combining coefficients of the model functions, and T^μ excites to all the virtual

functions $\{\chi_l\}$ by its action on ϕ_μ. It is possible that some virtual function χ_l is generated more than once as a result of excitation from various ϕ_μs, and there is thus a redundancy of the cluster amplitudes. The SS-MRCC equations are obtained via the use of appropriate sufficiency conditions which satisfy the twin desirable goals: (a) avoidance of intruders and (b) maintenance of extensivity. It is convenient to present the working equations for the amplitudes of T^μ by defining the corresponding ϕ_μ as the vacuum. T^μ then consists of various n hole–n particle excitations from ϕ_μ.

We present below, without the detailed derivation [20–22], the form of the working equations for the cluster amplitudes of the parent SS-MRCC theory

$$\langle\chi_l|\overline{H}_\mu|\phi_\mu\rangle c_\mu + \sum_v \langle\chi_l|\exp(-T^\mu)\exp(T^v)|\phi_\mu\rangle\tilde{H}_{\mu v}c_v$$

$$= 0 \quad \forall l, \mu, \tag{5}$$

where $\overline{H}_\mu = \overline{H\exp(T^\mu)}$ and $\tilde{H}_{\mu v} = \langle\phi_\mu|\overline{H}_v|\phi_v\rangle$. χ_ls are all the excited states reached by the action of T^μ on ϕ_μ.

The equations determining the model space coefficients $\{c_\mu\}$ are given by

$$\sum_v \tilde{H}_{\mu v}c_v = Ec_\mu. \tag{6}$$

We note that the set $\{c_\mu\}$ and $\{T_\mu\}$ are coupled through Eqs. (5) and (6). Solving these coupled set of equations we obtain both the cluster amplitudes and the converged coefficients from the diagonalization.

The detailed discussions of the SS-MRCC theory regarding the derivation, the proof of the extensivity and the analytic presentation of the avoidance of intruders are discussed at length in our previous papers for SS-MRCC [20–22].

We now focus on the development of linearized and quasi-linearized approximations of our SS-MRCC theory leading to the SS-MRCEPA methods.

2.3. The SS-MRCEPA schemes

To arrive at the CEPA-like approximations from the SS-MRCC equations we rewrite them in a quasi-linearized form:

$$[\langle\chi_l|H|\phi_\mu\rangle + \langle\chi_l|[H,T^\mu]|\phi_\mu\rangle + \tfrac{1}{2}\langle\chi_l|[[H,T^\mu],T^\mu]|\phi_\mu\rangle]c_\mu$$
$$\text{I} \qquad\qquad \text{II} \qquad\qquad\qquad \text{III}$$
$$+ \sum_v \langle\chi_l|(T^v - T^\mu)|\phi_\mu\rangle\tilde{H}_{\mu v}c_v + \text{other terms} = 0. \tag{7}$$
$$\text{IV}$$

There are several features of the equations which should be emphasized here: (a) the combining coefficients $\{c_\mu\}$ are not frozen at some preassigned values, but are iteratively updated to their relaxed values; (b) the first three terms have explicitly connected algebraic structure in case T^μ is connected; (c) among the quadratic terms appearing in III, the terms with one-body excitations are still doubles while the product of doubles or of singles and doubles lead to virtual functions χ_l which are more than doubly excited with respect to ϕ_μ; (d) the fourth term contains two pieces, one containing T^v and the other containing T^μ, which may be individually disconnected but the *entire term* containing the matrix element $\langle\chi_l|(T^v - T^\mu)|\phi_\mu\rangle\tilde{H}_{\mu v}$ is a connected entity [21,22]. The aspect (d) is very important for our purpose, since in any approximation or truncation scheme, each term of the two pieces *must be treated on the same footing*. Thus the term IV has to be computed in a manner which uses the same approximation for the matrix elements $\tilde{H}_{\mu v}$.

Using the same kind of considerations as were used to generate the various CEPA-like approximations from the SR-CCSD equations, we confine the rank of cluster operators T^μ to at most two-body excitations. Thus for each ϕ_μ, the χ_ls used in the projection in Eq. (7) must be at most doubly excited with respect to ϕ_μ. Moreover, the term III should include product of single excitations leading to doubles, and should exclude all other product terms which are more than doubly excited with respect to ϕ_μ. However, depending on the sophistication of the CEPA-like approximation, we will include the EPV terms of III coming from the product of doubles and singles and doubles to various degrees. For every χ_l reached by a T_l^μ from ϕ_μ, these EPV terms of III must include at least one T_l^μ operator while the other T^μ can be any one of the possible excitations which have at least one orbital in common with those involved in T_l^μ. To show this, we express the leading terms of Eq. (7) explicitly in the following form:

$$\left[\langle \chi_l | H | \phi_\mu \rangle + \sum_m (H_{lm} - H_{\mu\mu}\delta_{lm})t_m^\mu - \Delta_\mu t_l^\mu. \right.$$

$$\qquad \text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{III(a)}$$

$$\left. + \frac{1}{2} \sum_{m,n}{}' g_{m,n}^l t_m^\mu t_n^\mu \right] c_\mu + \sum_v \langle \chi_l | T^v | \phi_\mu \rangle \tilde{H}_{\mu v} c_v$$

$$\qquad\qquad \text{III(b)} \qquad\qquad\qquad \text{IV(a)}$$

$$+ \text{ other terms} = \mathscr{E} t_l^\mu c_\mu, \tag{8}$$

$$\qquad\qquad \text{IV(b)}$$

where we have shown the genesis of all the terms by the same labels by which they were indicated in Eq. (7). All CEPA schemes neglect the terms not explicitly shown in Eq. (8). The two pieces of the term IV containing T^v and T^μ are now separately indicated as IV(a) and IV(b), respectively. The 'energy' $\mathscr{E}$ is taken as a parameter, whose actual value depends on the approximation used in $\tilde{H}_{\mu v}$. Δ_μ is the EPV correction in III(a) coming from product of doubles, whose actual form again depends on the approximation used in our SS-MRCEPA. The negative sign of this term in Eq. (8) is to keep conformity with the analogous SR term. The term III(b) denotes the doubles contribution confined to the product of two singles (which is indicated by the prime in the sum). We note at this stage that the terms I–III are entirely similar to those in the SR-CEPA. In fact if we neglect the terms IV(a) and IV(b), then we get precisely SR-CEPA-like approximations for each ϕ_μ. But this approximation is too drastic in the sense that it entails intruders (because of the implicit presence of $(H_{ll} - H_{\mu\mu})$ in Eq. (8)), and thus belies one of the very basic goal which motivated our state-specific developments. We recall the feature which we highlighted earlier: while two pieces of IV, i.e., IV(a) and IV(b) may be disconnected, the entire term IV taken together is a connected entity. The two pieces IV(a) and IV(b) serve two specific and distinct purposes in this regard. A portion of the term in IV(a) for $v = \mu$ cancels both $H_{\mu\mu}\delta_{lm}$ and $\Delta_\mu t_l^\mu$ terms of II and III(a), while the rest of the expressions for $v \neq \mu$ of IV(a) corrects for the lack of extensivity coming from the terms appearing in $\mathscr{E} t_l^\mu c_\mu$. The details of this cancellation for each of the two SS-MRCEPA methods suggested by us are discussed below.

We now introduce the two specific types of CEPA-like approximations which we want to propose in this Letter. Entirely in line with the CEPA(0) scheme for the SR case, if we ignore Δ_μ entirely in Eq. (8), then we should start generating an analogous SS-MRCEPA scheme. We still have the freedom of approximating $\tilde{H}_{\mu v}$ independently, but in the spirit of quasi-linearization, we now approximate $\tilde{H}_{\mu v}$ as just $H_{\mu v}$. Then $\mathscr{E}$ becomes just E_0, the CAS energy itself. This set of approximations leads to what we call the SS-MRCEPA(0). Written in long hand it takes the form

$$\left[\langle \chi_l | H | \phi_\mu \rangle + \sum_m (H_{lm} - E_0\delta_{lm})t_m^\mu + \frac{1}{2} \sum_{m,n}{}' g_{m,n}^l t_m^\mu t_n^\mu \right] c_\mu$$

$$+ \sum_{v \neq \mu} \langle \chi_l | T^v | \phi_\mu \rangle H_{\mu v} c_v = 0. \tag{9}$$

We now discuss the most sophisticated approximation of Δ_μ, analogous to what was done in CEPA(D) in the SR case [9]. We approximate Δ_μ by all the terms containing all T^μs 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. As emphasized earlier, we have to treat the two pieces of IV on the same footing in their handling of $\tilde{H}_{\mu v}$. We approximate this by its quadratic expansion. The diagonal term $\tilde{H}_{\mu\mu}$ appearing in IV(a) of Eq. (8) for a given l can be written as

$$\tilde{H}_{\mu\mu} = H_{\mu\mu} + \Delta_\mu^l + D_{\mu \text{NEPV}}^l, \tag{10}$$

where Δ_μ^l is the correction for T^μ with at least one orbital in common with those labeling t_l^μ. The rest of the term has no orbital in common with those appearing in t_l^μ. With this observation, it is clear that the term $(H_{\mu\mu} + \Delta_\mu^l)\delta_{lm}$ in Eq. (8) is cancelled by the first two terms of Eq. (10). Denoting the energy $\mathscr{E}$ as $\mathscr{E}_{\text{CEPA(D)}}$, Eq. (8) for this scheme, referred to as SS-MRCEPA(D), takes the form:

$$\left[\langle \chi_l | H | \phi_\mu \rangle + \sum_m [H_{lm} - (\mathscr{E}_{\text{CEPA(D)}} + D_{\mu \text{NEPV}}^l)\delta_{lm}]t_m^\mu \right.$$

$$\left. + \frac{1}{2} \sum_{m,n}{}' g_{m,n}^l t_m^\mu t_n^\mu \right] c_\mu + \sum_{v \neq \mu} \langle \chi_l | T^v | \phi_\mu \rangle \tilde{H}_{\mu v} c_v = 0. \tag{11}$$

To see the avoidance of the intruders, we re-write both the two SS-MRCEPA equations in the following form:

$$
t_l^\mu = \frac{1}{(\varepsilon - H_{ll} - D_\mu^l)} \left[\langle \chi_l | H | \phi_\mu \rangle + \frac{1}{2} \sum_{m,n}' g_{m,n}^l t_m^\mu t_n^\mu \right.
$$
$$
\left. + \sum_{m \neq l} H_{lm} t_m^\mu + \sum_{v \neq \mu} \langle \chi_l | T^v | \phi_\mu \rangle \tilde{H}_{\mu v}(c_v/c_\mu) \right]
$$
(12)

$\tilde{H}_{\mu v} = H_{\mu v}$ for SS-MRCEPA(0), and has a multi-commutator structure for SS-MRCEPA(D). $\mathscr{E} = E_0$ for SS-MRCEPA(0), and is $\mathscr{E}_{CEPA(D)}$ for SS-MRCEPA(D). $D_\mu^l = 0$ for SS-MRCEPA(0) and has the value as given by Eq. (10) for SS-MRCEPA (D), D_μ^l is usually rather small. Unlike in the effective hamiltonian-based theories, $(\mathscr{E} - H_{ll} - D_\mu^l)$ will always be robust if $\mathscr{E}$ is well removed, far from any H_{ll}, even when $H_{\mu\mu}$ is close to this H_{ll}. Intruders are thus avoided naturally. Also, from the mode of derivations, it is quite clear that these are both *size-extensive* and *size-consistent*.

Structurally, the SS-MRCEPA(0) and the SS-MRCEPA(D) bear close resemblance with our state-specific multi-reference perturbation theory [27,28] of the Rayleigh–Schrödinger (SS-MRPT (RS)) and the Brillouin–Wigner (SS-MRPT (BW)) types, respectively.

There is a real advantage of approximating the SS-MRCC theory in the SS-MRCEPA form if we can retain the bulk of the correlation energy captured by the full-blown SS-MRCC theory, while we save a lot of computer time since we neglect a host of non-linear terms. Our results, discussed in the section to follow, will amply demonstrate the accuracy of the SS-MRCEPA schemes.

3. Applications

In order to examine the efficacy and performance of our SS-MRCEPA methods, we have applied them to study the ground state PES of trapezoidal H4 model system (H4 model). The H4 model system was first introduced by Jankowski and Paldus [33]. It is a rather well-studied system [21,22,25,28,34,35] to test the efficiency of different SR and MR based many-body theories. As we have already pointed out that the ground state of H4 model possesses quasi-degeneracy at some point of the PES and there are potential intruders at some other geometries, and hence serves as a stringent test case for the SS-MRCEPA methods. In our calculations we have used a DZV basis on top of which a p function with an exponent of 1.0 on each hydrogen atom is added. This is taken from GAMESS library. We apply the C_{2v} symmetry at each stage of calculation for this model system.

In C_{2v} symmetry, the H4 model has a ground state electronic configuration of $\phi_1 = 1a_1^2 1b_2^2$ and a varying degree of non-dynamical correlation contribution originating from the $\phi_2 = 1a_1^2 2a_1^2$. Hence the ground state of H4 model is well described by a two-determinantal active space. The active orbitals ($2a_1$ and $1b_2$) belong to two different symmetries and thus the active space describing the ground state is complete. The degree of quasi-degeneracy of the model functions of the H4 model can be effectively tuned by changing a single parameter α. At $\alpha = 0.0$, the conformation is square and ϕ_1 and ϕ_2 are equally important. Around $\alpha = 0.0$ is thus the region of strong degeneracy. At $\alpha = 0.5$ both ϕs are practically non-degenerate. We encounter an intruder around $\alpha = 0.3$, where ϕ_2 crosses a virtual function. Our theories treat all the reference determinants on the same footing. Thus we can use the HF orbitals corresponding to any one of the model space functions, ϕ_1 or ϕ_2, in our calculations. Here we have used HF orbitals corresponding to the function ϕ_1 throughout the PES.

In Fig. 1 we plot the energies of the ground state of the H4 model as a function of α, obtained by the SS-MRCEPA methods along with the SS-MRCC and FCI values obtained using the same basis set. We have also plotted (inset in Fig. 1) the H_{11}, H_{22} and the diagonal element H_{33} of the intruding virtual function ($\chi = 1a_1 1b_2^2 2a_1$) to give an idea of both the quasi-degeneracy of ϕ_1 and ϕ_2 and the appearance of the intruder problem. The figure clearly demonstrates that both our SS-MRCEPA
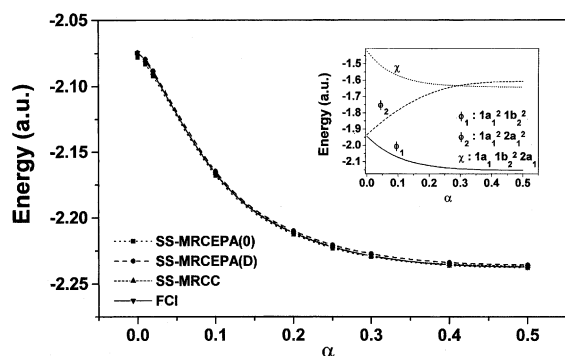
Fig. 1. The ground state PES of H4 model (inset: plot of CSF energies).

methods pretty closely approximate the FCI PES for the ground state of the H4 model, akin to the parent SS-MRCC method. From the given figure it is also clear that similar to the SS-MRCC method, both the SS-MRCEPA approaches do not encounter intruders at all and their performance over a wide range of geometries, including the points of quasi-degeneracy and intruders, are very good. In an attempt to make a clear representation of the performance of our newly formulated state-specific multi-reference CEPA methods, we provide, in Table 1, the deviation from FCI values of the results obtained by using the SS-MRCEPA and the parent SS-MRCC methods. From the table, it is evident that the SS-MRCC performs quite well throughout the range of the PES. Also the numerical accuracy achieved by the SS-MRCEPA methods is quite close to that

of the parent SS-MRCC approach. This indicates that SS-MRCEPA is a good approximation to the SS-MRCC method.

4. Summary

In this Letter, we have focused our attention on the formulation and numerical applications of CEPA-like counterparts (SS-MRCEPA) of our SS-MRCC theory based on a CAS. It neglects most of the complicated non-linear terms of the parent SS-MRCC method using a series of physically motivated graded approximation schemes, by including appropriate EPV terms. Our SS-MRCEPA methods are rigorously size-extensive and size-consistent. From the very mode of formulation of our SS-MRCEPA theories, it is clear that the combining coefficients are iteratively updated to the values that they should have in an exact state ψ. Hence our formulation provides a completely relaxed form of ψ. The SS-MRCEPA theories bypass the intruder problem by focusing on only one specific state. Also, they treat all the reference determinants on the same footing and is thus well suited to describe wide ranges of molecular geometry possessing varying degrees of quasi-degeneracy along with the presence of potential intruder states. This is borne out by the example application of the PES of the ground state of the H4 model. Also, this indicates that the SS-MRCEPA methods are useful and good approximations of the SS-MRCC theory.

Table 1
Relative energies (mH) with respect to the FCI values (a.u.), $(E_{FCI} - E_{method})$, of the ground state of the H4 model for different values of α

α	SS-MRCEPA(0)	SS-MRCEPA(D)	SS-MRCC	FCI
0.00	3.560	−0.101	0.349	−2.074481
0.01	2.991	−0.813	0.239	−2.080156
0.02	2.455	−1.476	0.046	−2.089648
0.10	1.533	−1.919	−0.453	−2.166511
0.20	0.990	−1.771	−0.459	−2.211612
0.25	0.844	−1.706	−0.445	−2.222221
0.30	0.709	−1.693	0.065	−2.228826
0.40	0.555	−1.694	−0.431	−2.235418
0.50	0.528	−1.685	−0.433	−2.237165

Acknowledgements

References

[1] J. Cizek, J. Chem. Phys. 45 (1966) 4256.
[2] J. Paldus, J. Cizek, I. Shavitt, Phys. Rev. A 5 (1972) 50.
[3] R.J. Bartlett, in: D.R. Yarkony (Ed.), Modern Electronic Structure Theory, World Scientific, Singapore, 1995.
[4] W. Meyer, J. Chem. Phys. 58 (1973) 1017.
[5] W. Meyer, Theor. Chim. Acta 35 (1989) 277.
[6] A.C. Hurley, in: Electron Correlation in Small Molecules, Academic Press, London, 1976.
[7] R. Ahlrichs, H. Lischka, V. Staemmler, W. Kutzelnigg, J. Chem. Phys. 62 (1975) 1225.
[8] W. Kutzelnigg, in: H.F. Schaefer III (Ed.), Methods of Electronic Structure Theory, Plenum Press, NY, 1977.
[9] J.P. Daudey, J.L. Heully, J.P. Malrieu, J. Chem. Phys. 99 (1993) 1240.
[10] I. Lindgren, D. Mukherjee, Phys. Rep. 151 (1987) 93.
[11] D. Mukherjee, S. Pal, Adv. Quantum Chem. 20 (1989) 561.
[12] B. Jeziorski, H.J. Monkhorst, Phys. Rev. A 24 (1981) 1668.
[13] B. Jeziorski, J. Paldus, J. Chem. Phys. 88 (1988) 5673.
[14] T.H. Schucan, H.A. Weidenmüller, Ann. Phys. 73 (1972) 108.
[15] G. Hose, U. Kaldor, J. Phys. B 12 (1979) 3827.
[16] B. Kirtman, J. Chem. Phys. 75 (1981) 798.
[17] J.P. Malrieu, Ph. Durand, J.P. Daudey, J. Phys. A (Math. Gen.) 18 (1985) 809.
[18] I. Nebot-Gil, J. Sanchez-Marin, J. Malrieu, J.-L. Heully, D.J. Maynau, J. Chem. Phys. 103 (1995) 2576.
[19] J. Meller, J.P. Malrieu, R. Caballol, J. Chem. Phys. 104 (1996) 4068.
[20] U.S. Mahapatra, B. Datta, B. Bandyopadhyay, D. Mukherjee, in: D. Hanstrop, H. Persson (Eds.), Advances in Quantum Chemistry, vol. 30, Academic Press Inc., San Diego, 1998.
[21] U.S. Mahapatra, B. Datta, D. Mukherjee, Mol. Phys. 94 (1998) 157.
[22] U.S. Mahapatra, B. Datta, D. Mukherjee, J. Chem. Phys. 110 (1999) 6171.
[23] S. Chattopadhyay, U.S. Mahapatra, D. Mukherjee, J. Chem. Phys. 111 (1999) 3820.
[24] S. Chattopadhyay, U.S. Mahapatra, P. Ghosh, D. Mukherjee, in: M.R. Hoffmann, K.G. Dyall (Eds.), Low-Lying Potential Energy Surfaces, ACS Symposium Series No. 828, ACS, Washington, DC, 2002.
[25] J. Masik, I. Hubac, in: R. McWeeny, et al. (Eds.), Quantum Systems in Chemistry and Physics: Trends in Methods and Applications, Kluwer Academic, Dordrecht, 1997.
[26] J. Masik, I. Hubac, P. Mach, J. Chem. Phys. 108 (1998) 6571.
[27] U.S. Mahapatra, B. Datta, D. Mukherjee, Chem. Phys. Lett. 299 (1999) 42.
[28] U.S. Mahapatra, B. Datta, D. Mukherjee, J. Phys. Chem. A 103 (1999) 1822.
[29] P.J.A. Ruttink, J.H. van Lenthe, R. Zwaans, G.C. Groenenboom, J. Chem. Phys. 94 (1991) 7212.
[30] R. Fink, V. Staemmler, Theor. Chim. Acta 87 (1993) 129.
[31] P.G. Szalay, in: R.J. Bartlett (Ed.), Recent Advances in Coupled-Cluster Methods, World Scientific, Singapore, 1997, and references therein.
[32] J.P. Malrieu, J.P. Daudey, J.L. Heully, Chem. Phys. Lett. 244 (1995) 440.
[33] K. Jankowski, J. Paldus, Int. J. Quantum Chem. 18 (1983) 1243.
[34] S. Zarrabian, J. Paldus, Int. J. Quantum Chem. 38 (1990) 761.
[35] K. Jankowski, J. Paldus, J. Wasilewski, J. Chem. Phys. 95 (1991) 3549.