Theor Chem Acc (2006) 116: 621–636
DOI 10.1007/s00214-006-0108-2

REGULAR ARTICLE

Dola Pahari · Pradipta Ghosh · Debashis Mukherjee
Sudip Chattopadhyay

Towards the development and applications of manifestly spin-free multi-reference coupled electron-pair approximation-like methods: a state specific approach

Received: 27 December 2004 / Accepted: 24 March 2005 / Published online: 21 February 2006

Abstract As a practical tool of being applicable to bigger molecules, a full-blown state-specific multi-reference coupled cluster formalism developed by us (Mahapatra et al. in J Chem Phys 110:6171, 1999) would be rather demanding computationally, and it is worthwhile to look for physically motivated approximation schemes which capture a substantial portion of the correlation of the full-blown theory. In this spirit, we have recently proposed coupled electron-pair approximation (CEPA)-like various approximants to the parent spin-adapted state-specific multi-reference coupled cluster (SS-MRCC) theory which depend on the inclusion of EPV terms to various degree. Here, the space of excitations is confined to the first order interactive virtual space generated by the cluster operator, but the EPV terms are included exactly. We call them spin-free state specific multi-reference CERA (SS-MRCEPA) theories. They work within the complete active space (CAS) and have been found to be very effective in bypassing the intruders, similar in performance to that of the parent SS-MRCC theory. The spin-adaptation of the working equations of both the SS-MRCC and the CEPA-like approximants is a non-trivial exercise. In this paper, we delineate briefly the essentials of a spin-free formulation of the SS-MRCC and SS-MRCEPA theories. This allows us to include open-shell configuration state functions (CSF) in the CAS. We consider three variants of SS-MRCEPA method. Two are explicitly orbital invariant: (1) SS-MRCEPA(0), a purely lineralized version of the SS-MRCC theory, (2) SS-MRCEPA(I), which includes all the EPV terms explicitly and exactly in an orbital invariant manner and (3) the SS-MRCEPA(D), which emerges when we keep only the diagonal terms of a set of dressed operators in the working equations. Unlike the first two, the third version is not invariant under the orbital transformation within the set of doubly occupied core, valence and virtual orbitals. The SS-MRCEPA methods produce very encouraging results as was evidenced in the applications on the computation of potential energy surfaces for the ground states of LiH and HF molecules.

Keywords Potential energy surface · State – specific · Multi – reference · Coupled cluster · Coupled electron – pair approximation · Spin – adaptation / Spin - free · Size extensivity

D. Pahari · P. Ghosh · D. Mukherjee
Department of Physical Chemistry,
Indian Association for the Cultivation of Science,
Calcutta 700032, India

D. Mukherjee (✉)
Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore 560064, India
Fax: +91-33-24836561
E-mail: pcdm@iacs.res.in

S. Chattopadhyay
Department of Chemistry,
Bengal Engineering and Science University,
Shibpur, Howrah 711103, India

1 Introduction

Prior to the advent of single-reference (SR) coupled cluster (SRCC) method [1–5], which is very effective and the most sophisticated for treating dynamical correlations in a size-extensive manner, Meyer suggested a very useful and simple non-perturbative size-extensive correlated method known as coupled electron-pair approximation (CEPA) [6]. The CEPA method [6–14] can be described as one of the more modest and physically motivated approximations of the corresponding full-blown CC method among the various coupled pair theories. Although the CEPA method was originally obtained as a result of modification of the size-inextensive configuration interaction (CI) with the single and double (SD) excitation (CISD) equations to an extensive form, it can be derived from the CC equations as well by selecting certain terms from the quadratic part of the working equation. The CEPA emerges from the CC method if most of the computationally demanding nonlinear terms in the CC method are neglected, barring the exclusion principle violating (EPV) terms to various degrees, neglect of which has serious deleterious effects. The CEPA method can be viewed either

as extensivity-corrected CISD or as a special size-extensive truncation of CCSD. Because of its computational simplicity, CEPA can be effectively exploited to treat rather large systems. The CEPA methods are more accurate generally as compared to low order MBPT such as MP2 [15]. There are several variants of CEPA, such as CEPA(n)(n=0,1 and 2) [6–8], Kelly's version [9,10], and the closely allied formulations like ACPF [11] and AQCC [16,17]. The latter two have the advantage of using the extrema of some energy functional, and are thus computationally more convenient for getting gradients. This feature, however, comes with the price of approximating the EPV terms quite drastically. In another line of development, Malrieu and co-workers [12] proposed a dressed CI approach, which includes the EPV terms exactly in the working equations of CISD via dressing of either diagonal or the columns of the CI matrix. This leads to a computationally very appealing procedure since the full machinery of the CISD programmes can be effectively utilized. For extensive survey of SR-based CEPA, we refer to articles by Kutzelnigg [18], Ahlrichs [19] and also by Szalay [20].

The multi-reference (MR)-based approach is superior to that of SR-based theories to handle strong quasi-degeneracy, as in situations involving bond-breaking and direct or avoided curve crossings. For the states in the bond breaking region, cross-over region of the PESs, or for excited states, the interplay of dynamical and non-dynamical correlation effects makes the reference wave functions MR in nature. Under such circumstances, the performance of the SR-based CC methods go down unless rather high-body cluster operators are included [21–29]. The MR-based approaches have the advantage over such SR counterparts in providing the flexibility needed to describe important molecular characteristics, such as bond breaking pathways, excited states, and transition states, within a few-body truncation scheme.

Considerable effort has been devoted for more than two decades to formulate MR methods for both ground and excited electronic states that would have most or all of the following characteristics: (1) size extensivity and size consistency, (2) applicability to both closed- and open-shell systems, (3) ability to accommodate all kinds of multi-dimensional reference spaces for different states, geometries, etc., (4) low computer cost and high accuracy, (5) uniform accuracy in regions of real and/or avoided curve-crossings and in non-degenerate regimes, and (6) fast convergence. The MR-based valence-universal (VU) [30–34] and state-universal (SU) [35,36] coupled cluster (MRCC) methods truncated at the singly and doubly excited cluster level were deemed to be capable of providing very good description for both the dynamical and non-dynamical correlations [30–36]. In particular, it was thought that the SUMR-based methods would be very useful for generating the potential energy surfaces (PES) of a system over a wide range of nuclear geometries. In this method, all the states with constant number of valence electrons corresponding to the different linear combinations of reference functions are treated democratically. Both the VU-MRCC and the SU-MRCC methods are based on effective Hamiltonian formalism. They were successfully applied to the study of direct computation of energy differences and of excited state energies. Unfortunately, although the cluster expansion method has several attractive features of a good many body methods such as size-extensivity, orbital invariance, etc., its efficacy for PES studies has not yet been fully established in the context of effective Hamiltonians till date due to some pitfalls. In the traditional effective Hamiltonian-based MR methods, all the roots are obtained via diagonalizing the effective Hamiltonian, H_{eff} in the reference space in a blanket manner. It now seems to be generally recognized that the simultaneous calculation of all the roots generated by an H_{eff} is seriously hampered when some virtual functions come very close in energy to some high-lying model functions. Owing to the coupling of all the eigenvalues via the H_{eff}, all the roots become poorly described as a consequence. This is the notorious intruder problem [37,38]. Actually the coupling between the model space and those of the complementary virtual space may be too large with respect to the energy denominators and the series will diverge. Thus, the discontinuity of the computed PES appears as a function of nuclear distortions in the presence of intruder states which prevents the computation of the entire PESs over a wide range of geometries in a smooth manner. Sometimes one can even observe that the SR-based theory performs very well, but not the MR-based one due to the intruder effects.

One way out of the problem of intruder effects is to develop theories based on MR scheme but to partition the model space into two sub-spaces – primary and secondary – where the functions of latter space may be energetically close in proximity to the functions of virtual space. The idea is to define a pseudo-wave operator which acts on the entire model space, but generates exact states which are equal in number to the dimension of the primary model subspace and are dominated by the model functions spanning this subspace. This approach was first proposed by Kirtman [39], and developed fully by Malrieu et al. [40,41] in the perturbative context, who termed this the intermediate Hamiltonian (IH) approach. In this formulation, the rather stringent requirement of the effective Hamiltonian approach of having to generate N eigenvalues from an N-dimensional model space is abandoned in favour of generating fewer roots M ($M \leq N$) from an N-dimensional model space. In other words, in this theory, only the subset of the roots of the dressed Hamiltonian, which are dominated by the primary functions, are exact eigen values of the full-blown Hamiltonian. This flexibility is in fact exploited to bypass intruders which might plague the higher roots of an effective Hamiltonian. There have also been important innovations by Hoffmann [42–44], and Khait and Hoffmann [45]. The latter method generates the optimal primary subspace in an iterative manner, which improves the performance of the IH considerably.

Coupled cluster-based IH formalisms [46–48], which are size-extensive, were also developed. While the method advocated by Mukherjee and co-workers [46,47] is general, that put forth by Kaldor and co-workers [48] is approximate. Since the combining coefficients of the model functions are obtained via diagonalization, they are relaxed in the presence

of dynamical correlations. Another approach to circumvent the difficulty is to abandon the partitioning of the MS into primary and secondary subspace, and define a wave operator which acts on just one MR reference function, which is a linear combination of all the functions of the MS. In other words, the emphasis in this approach is on developing a theory which targets only one state rather than several states at the same time. This is thus a state-specific approach. In this strategy, it is not necessary that the exact function be dominated by only certain model functions (which are taken to form the primary subspace in the IH methods).

We have been concerned in recent years in developing state-specific multi-reference CC (SS-MRCC) method, working in both complete [49–52] and incomplete [53] model spaces, which generate rigorously extensive energies via the diagonalization of an effective operator in the model space. Several approximants to the fully developed MRCC theory were also studied, which include spin-adapted state-specific multi-reference CEPA (SS-MRCEPA) [54–59] and perturbative versions (SS-MRPT) [60–62]. For a recent survey, we refer to a forthcoming article [63]. Further studies using the SS-MRCEPA methods, and development of spin-adapted versions thereof–thereby enabling us to have open-shell CSFs is the subject matter of the present paper. The explicit spin-adaptation of open-shell configurations and formulating a general viable theory of electron correlation has been a daunting task. Attempts have been made to utilize the simple exponential Ansatz for the wave-operator in the spin orbital basis [64–67], containing excitations from the reference determinant taken as the vacuum as one of the most naive approaches towards a spin-free solution. Although, this leads to a spin-broken situation, it otherwise retains the compactness and simplicity of the closed-shell SRCC method in generating the CC equations. The symmetry-adapted CC expansion generates a pure spin state, but the corresponding spin-adapted expressions are unwieldy [68]. The spin-contamination problem can be partially resolved via certain suitable constraints on the expectation value of the S^2 operator [69]. Jansen and Schaefer [70] have pointed out the necessity of retaining the exact spin symmetry and spanning the full spin-space by the use of explicitly spin-free cluster operators containing spectator excitations on top of the usual operators inducing excitations. This feature of spin adaptation has been explored in many later developments of spin-free theories [71–74] with mixed success. A highly sophisticated and explicitly spin-free formulation, suggested recently by our group [75,76], employs a cluster Ansatz, different from either a simple exponential, or the more widely used normal-ordered exponential for open-shells, allowing contractions among the cluster operators via the orbitals inducing manifest spectator excitations. This is not only a simple spin-free treatment, but is also terminating in the sense of having terms which are at most quartic – akin to the purely closed-shell SRCC theory [1–5]. In the present paper, we shall explore both the full-blown exponential Ansatz as well as its quasi-linearized analogue.

Several state specific MRCC methods to tackle intruders have been developed in recent times [49–52,77–82]. An MR version of the dressed CI-based approach was developed by Malrieu and co-workers [77–79], which is quite analogous to our SS-MRCEPA methods. A single root Brillouin-Wigner inspired MRCC approach of Hubač and co-workers [80–82] has also been suggested, which is, however, not rigorously extensive. The development of Mukherjee and co-workers [49–52] and Hubač and co-workers [80–82] are both based on the full Jeziorski-Monkhorst (JM) Ansatz [35,36]. Very recently, Pittner [83] showed an analysis for the transition from the SU theory of Jeziorski and Monkhorst [35,36] to the state-specific theories of Hubač and co-workers [80–82] and of Mukherjee and co-workers [49–52]. Malrieu and co-workers [77–79] formulated their state-specific methods, using certain low order quasi-linearized truncation schemes of the JM wave operator, and their emphasis was on incorporating all the EPV terms.

The MR-based perturbation theory (MRPT) [40–44, 60–63, 84–95] is another widely used MR theory for many years. The past few decades have witnessed significant progress in the formulation of MR perturbation theories, even though incorporation of all the desirable features are yet to be completely realized. The state-specific MR (SSMR) perturbative methods [42–44,60–63,86–94] have been developed to bypass the intruder state problem by focusing on one state at a time. There have been two distinct courses of development of the SSMR-based PT. In one, the coefficients of the model functions forming the initial reference functions are fixed by a prior diagonalization in the model space, and they are not revised or updated as a consequence of mixing with the virtual functions [42–44,86–94]: frozen coefficients variety. In contrast, in the SS-MRPT approach of Mukherjee and co-workers [60–63], derived from SS-MRCC, the combining coefficients are iteratively updated, which lends an intrinsic accuracy to the perturbed function: termed as relaxed coefficient variety.

Obviously, the most popular and the simplest MR reference approach is the MR configuration interaction (MRCI) method [96–98]. It is, however, not rigorously extensive in a truncated CI space. Much effort has been expended towards developing the method to make it applicable to large systems and to remove the lack of size-extensive, in a way exactly analogous to the SR-based CI strategies [11,16,17,20, 99–102]. For recent review and analysis of the various state-specific CEPA, ACPF and AQCC methods, we refer to the article by Szalay [20]. In the framework of effective Hamiltonians, Tanaka and co-workers [103–105] have proposed SU-like MRCEPA methods derived from an effective Hamiltonian formalism. We have already emphasized earlier the potential danger of the intruder problem in an effective Hamiltonian-based formalism.

In this paper, we will present a set of explicitly CAS-based spin-free SS version of MR-CEPA (SS-MRCEPA) methods based on the manifestly spin-free SS-MRCC theory. We will describe three variants of spin-free SS-MRCEPA method starting from full-blown explicitly spin-free SS-MRCC method. Among the three, two are invariant with respect to the restricted rotations of core, active and virtual

orbitals : (1) SS-MRCEPA(0), a purely liberalized version of the SS-MRCC theory, (2) SS-MRCEPA(I), which includes all the EPV terms explicitly and exactly in an orbital invariant manner. Another variant is termed as SS-MRCEPA(D), which arises by keeping only the diagonal terms of a set of dressed operators in the working equations. The formulation of SS-MRCEPA(D) is inspired by a previous formulation of CEPA-like variant of Malrieu and co-workers [12–14]. The SS-MRCEPA methods will be applied to compute PES of states of LiH and HF involving open-shell functions. In all the states studied, there are potential intruders in the effective Hamiltonian-based formalisms at some region of the PES and there is quasi-degeneracy at some other region of the PES.

This paper is organized as follows: in Sect. 2.1 we will first describe the formulation of the spin-free SS-MRCC theory. We will discuss the spin-free formulation of SS-MRCEPA methods starting from the CAS-based SS-MRCC theory in Sect. 2.2, respectively. Section 3 covers the discussion of numerical implementation. In Sect. 4, we will present the illustrative numerical applications, along with discussions. Finally, Sect. 5 will summarize our presentation.

2 Theoretical background

We begin this section by emphasizing the basic issues related to our formulation of the SS-MRCC theory [49–52] formulated by us.

2.1 The SS-MRCC formalism with the complete model space

In the SS-MRCC approach, the exact wave function of a given spin is expressed as:

$$\psi = \sum_{\mu} \exp\left(T^{\mu}\right) \phi_{\mu} c_{\mu}. \tag{1}$$

Each model space function, $\{\phi_{\mu}\}$ is a CSF, in a given spin-coupling scheme and together spans a CAS (equivalently called CMS). In our earlier presentations [49–52], we did not address the theoretical aspects of spin-adaptation of the SS-MRCC equations, since we always worked previously with model functions which were closed-shell singlets. The CSFs thereby reduce to closed shell determinants. The spin-adaptation of the equations in such cases is straightforward and trivial, entirely analogous to the one for the case of closed-shell SRCC. Recently, we have developed a spin-adapted version of the SS-MRCC theory [63], where the model functions are neither necessarily singlets nor single determinants. The model functions are, in the general formalism, genuine multi-determinant CSFs. We briefly discuss here the general formalism of the SS-MRCC method, since we want to generate a spin-adapted SS-MRCEPA formalism from the parent spin-adapted SS-MRCC method. The detailed nature of the coupling scheme is not important as long as each CSF is generated with respect to some base CSF by excitation via spin-free unitary generators.

Following the standard terminology, we will call 'inactive holes' the inactive occupied orbitals, doubly filled in every model CSF. The 'inactive particles' will refer to all the orbitals unoccupied in every CSF. Orbitals which are occupied in some (singly or doubly) but unoccupied in others are the 'active' orbitals. In our spin-free form, the labels are for orbitals only, and not for spin orbitals. By the very definition, no active orbital can be doubly occupied in every model CSF. We want to express the cluster operator T^{μ}, inducing excitations to the virtual functions, in terms of excitations of minimum excitation rank, and at the same time wish to represent them in a manifestly spin-free form. To accomplish this, we take as the vacuum – for excitations out of ϕ_{μ} – the largest closed-shell portion of it, $\phi_{0\mu}$. For each such vacuum, we redefine the holes and particles, respectively, as ones which are doubly occupied and unoccupied in $\phi_{0\mu}$. The holes are denoted by the labels $i_{\mu}, j_{\mu}, \ldots$ etc, and the particle orbitals are denoted as $a_{\mu}, b_{\mu}, \ldots$ etc. The particle orbitals are totally unoccupied in any ϕ_{μ}, or are necessarily active orbitals which are singly occupied in ϕ_{μ}. When we want to distinguish these singly occupied active orbitals, we shall denote them by $u_{\mu}, v_{\mu}, \ldots$ etc. We note here that the holes in $\phi_{0\mu}$ include not only the doubly occupied inactive orbitals but also doubly occupied active orbitals of ϕ_{μ}. We will be using the terminology 'active' and 'valence' often interchangeably. In most of our discussions, we will often be discussing the various terms generated by the SS-MRCC theory referred to a particular vacuum $\phi_{0\mu}$, and we then drop the subscript μ from the orbital labels when it is clear which vacuum we are dealing with.

At this point, we would like to emphasize one of the non-trivial circumstances that emerges during the development of completely spin-free SS-MR theory. It was generally mentioned that in the development of such a theory for the closed-shell situations, the use of ϕ_{μ} as the vacuum is not a problem, since the spin-adaptation in such cases is a trivial issue. However, the general spin-adaptation of open-shell states of arbitrary multiplicity is not an easy task. For non-singlet, or even an open-shell singlet ϕ_{μ}, we cannot use this as the vacuum, since either it would lead to a spin-broken solution or to a rather complicated situation, since ϕ_{μ} is a CSF rather than a determinant. In an attempt to maintain the generality of the approach and simultaneously develop a viable theory suited to deal with arbitrary spin situations, we put forth an alternative scheme which uses specific closed-shell vacuum and suitable spin-free unitary generators. Actually, we choose the highest doubly occupied portion of a function ϕ_{μ}, which we represent as $\phi_{0\mu}$, as the vacuum for every ϕ_{μ}. We define all excitations with respect to this only. We would further show that the choice of such a definition makes the mathematical manipulation of the resulting equations easy. It has emphasized earlier that to maintain the size-extensivity of our theory, we need to treat T^{μ}s and T^{ν}s democratically in the coupling term of the cluster finding equation. However, the foregoing discussion on the latest definition of vacuum might give an apparent feeling that the cluster excitation operators are not being treated on the same footing. But we

would soon show that once they are written with respect to the core as vacuum, this apparent problem would be alleviated. Once the cluster amplitudes are defined with respect to $\phi_{0\mu}$ as the vacuum, one can also rewrite all the requisite excitations in normal order with respect to the core being taken as the vacuum. In fact it will transpire that the spin-free operators , written in terms of Unitary generators, involve only spectator excitations with respect to $\phi_{0\mu}$ as vacuum. They are 'particles' both with respect to $\phi_{0\mu}$ and the core, and hence, if we rewrite the cluster operators with respect to the core, then the normal ordering remians unaltered. Hence

$$\{E\}_{0\mu} \equiv \{E\}_{\text{core}}$$

where $\{\ldots\}$ represents the normal ordering.

The general problem of spin-adaptation using multiple vacuua $\phi_{0\mu}$, depending upon the model function ϕ_μ the component of the wave operator $\exp(T^\mu)$ acts upon, is quite a nontrivial and rather involved exercise. Here, we will consider the simplest yet physically the most natural truncation scheme in the rank of cluster operators T^μ, where each such operator is truncated at the excitation rank two. For generating the working equations for the spin-adapted theory in this case, it is useful to classify the various types of excitation operators leading to various virtual CSFs as:

One-body:
(A) hole $\rightarrow$ particle ($h\rightarrow p$): $t^{\mu a}_{\ i}\{E^a_i\}$
(B) hole $\rightarrow$ valence ($h\rightarrow v$): $t^{\mu u}_{\ i}\{E^u_i\}$
(C) valence $\rightarrow$ particle ($v-p$): $t^{\mu a}_{\ u}\{E^a_u\}$
Two-body:
(D) $2h \rightarrow 2p$: $t^{\mu ab}_{\ ij}\{E^{ab}_{ij}\}$
(E) $h,v \rightarrow 2p$: $t^{\mu ab}_{\ iu}\{E^{ab}_{iu}\}$
(F) $2h \rightarrow p,v$: $t^{\mu au}_{\ ij}\{E^{au}_{ij}\}$
(G) $2v \rightarrow 2p$: $t^{\mu ab}_{\ uv}\{E^{ab}_{uv}\}$
(H) $h,v \rightarrow p,v$: $t^{\mu av}_{\ iu}\{E^{av}_{iu}\}$ and $t^{\mu va}_{\ iu}\{E^{va}_{iu}\}$
(I) $2v \rightarrow p,v$: $t^{\mu wa}_{\ uv}\{E^{wa}_{uv}\}$
(J) $2h \rightarrow 2v$: $t^{\mu uv}_{\ ij}\{E^{uv}_{ij}\}$
(K) $h,v \rightarrow 2v$: $t^{\mu wx}_{\ iu}\{E^{wx}_{iu}\}$

In all the excitations above, the operators E in curly brackets denote the normal ordering with respect to $\phi_{0\mu}$, and the 'local' holes, valence and particles are all defined with respect to this vacuum. Interestingly, the two-body operators of the type $\{E^{Xu}_{Yu}\}$ for arbitrary labels X, Y generate the same excitation as the one-body operator $\{E^X_Y\}$ on ϕ_μ, since $\{E^u_u\}$ is the number operator with occupancy 1 for ϕ_μ for singly occupied active orbitals. This can be easily verified:

$$\{E^{Xu}_{Yu}\}\phi_\mu = \{E^X_Y\}\{E^u_u\}\phi_\mu \tag{2}$$

$$= \{E^X_Y\}\phi_\mu \tag{3}$$

Hence, we should include only one of them in our T^μ. We choose the strategy that T^μ will never have excitations of the type $\{E^{Xu}_{Yu}\}$, which we will, henceforth, term as excitations with direct spectators u. However, in contrast, the excitations of the type $\{E^{uX}_{Yu}\}$, involving exchange type of spectator excitations are linearly independent of $\{E^X_Y\}$, as far as their respective actions on ϕ_μ are concerned, and we should keep both such operators in T^μ. Moreover, while considering excitations inducing $Y \rightarrow X$ from ϕ_μ, we will add together contributions from both the one-body and the two-body excitations $\{E^X_Y\}$ and $\{E^{Xu}_{Yu}\}$ for all u singly occupied in ϕ_μ. Although the Ansatz for the wave operator has a superficial resemblance to the JM Ansatz [35], unlike the JM Ansatz, it is in spin-free form, and also has non-commuting operators involving exchange spectators. The detailed algebraic structure of our spin-free SS-MRCC formalism would thus be different from the more special case involving closed-shell model functions only.

For a function ψ with a given spin-multiplicity $(2S+1)$, we shall consider all the CSFs with $M_s = (2S+1)$, generated from some 'base' or 'fiducial' CSF ϕ_R, with inactive occupied orbitals doubly filled, some active orbitals doubly filled, a set n_s of active orbitals with up-spin, a set n_s of orbitals with down-spin, coupled to a singlet, and another set of active orbitals, all with up-spin such that $M_s = (2S+1)$. With this generation scheme, every model CSF can be written as some spin-free excitation operator acting on the base function ϕ_R.

In the SS-MRCC formalism, there is a redundancy in the cluster amplitudes of T^μ, in the sense that each virtual CSF, χ_l, can be generated from several model CSFs. We will impose suitable supplementary sufficiency conditions with the twin objectives of avoiding intruders and maintaining size-extensivity.

To derive the spin-adapted SS-MRCC equations in the SD truncation scheme of the cluster operators, we rewrite the Schrödinger equation for ψ as follows:

$$H\sum_\mu \exp(T^\mu)|\phi_\mu\rangle c_\mu = \sum_\mu \exp(T^\mu)\overline{H_\mu}|\phi_\mu\rangle c_\mu$$
$$= E\sum_\mu \exp(T^\mu)|\phi_\mu\rangle c_\mu, \tag{4}$$

where $\overline{H}_\mu$ is the similarity-transformed Hamiltonian $\exp(-T^\mu)H\exp(T^\mu)$. Introducing the projectors P and Q, respectively, for the model and the virtual spaces, and noting the resolution of identity $I = (P+Q)$, we can write the above equation in long hand as:

$$\sum_\mu \exp(T^\mu)Q\overline{H_\mu}|\phi_\mu\rangle + \sum_{\mu,\nu}\exp(T^\mu)|\phi_\nu\rangle\langle\phi_\nu|\overline{H}|\phi_\mu\rangle c_\mu$$
$$= E\sum_\mu \exp(T^\mu)(P+Q)|\phi_\mu\rangle c_\mu. \tag{5}$$

Using the same insight gleaned from our earlier SS-MRCC formulation in the spin orbital basis in terms of determinants, we interchange the dummy arguments in the second term on the left hand side of the above equation, and get

$$\sum_\mu \exp(T^\mu)Q\overline{H_\mu}|\phi_\mu\rangle + \sum_{\mu,\nu}\exp T^\nu|\phi_\mu\rangle\langle\phi_\mu|\overline{H}_\nu|\phi_\nu\rangle c_\nu$$
$$= E\sum_\mu \exp(T^\mu)(P+Q)|\phi_\mu\rangle c_\mu. \tag{6}$$

We now equate the Q projections on both sides of the above equation for each μ, and premultiplying with $\langle\chi_l|\exp(-T^\mu)$

$\forall\, l$, we get

$$\langle\chi_l|\overline{H}_\mu|\phi_\mu\rangle c_\mu + \sum_\nu \langle\chi_l|\exp(-T^\mu)\exp(T^\nu)|\phi_\mu\rangle \widetilde{H}_{\mu\nu}c_\nu = 0 \quad \forall\, l,\mu, \tag{7}$$

where $\widetilde{H}_{\mu\nu} = \langle\phi_\mu|\overline{H}_\nu|\phi_\nu\rangle$. The equations derived above are our principal working equations for the cluster amplitudes of T^μ, inducing single and double excitations out of each ϕ_μ to all possible χ_l. As we have emphasized earlier, for every single excitation of the type $\{E^X_Y\}$, with $Y \neq u$, we take both the one-body and the two-body excitations $\{E^X_Y\}$ and $\{E^{Xu}_{Yu}\}$ that are generated by $\{\overline{H_\mu}\}$ and $[\exp(-T^\mu)\exp(T^\nu)]$ in the above equation. The equation determining the model space coefficients $\{c_\mu\}$ and the target state energy is given by:

$$\sum_\nu \widetilde{H}_{\mu\nu}c_\nu = Ec_\mu. \tag{8}$$

For computing all the matrix-elements, we rewrite H in normal order with respect to the corresponding $\phi_{0\mu}$ as the vacuum:

$$H = \langle\phi_{0\mu}|H|\phi_{0\mu}\rangle + \{F\} + \{V\}, \tag{9}$$

where

$$\{F\} = \sum_{\mu,\nu} f_0^{XY}\{E^X_Y\} \tag{10}$$

and

$$f_0^{XY} = f_c^{XY} + \sum_{u_d}\left[2V^{Xu_d}_{Yu_d} - V^{u_dX}_{Yu_d}\right]. \tag{11}$$

In the equation above, f_c is the core Fock operator, and sum over u_d runs over all the doubly occupied active orbitals of ϕ_μ. $\{V\}$ is the two-body portion of H in normal order with respect to $\phi_{0\mu}$. We do not explicitly indicate here and later which $\phi_{0\mu}$ has been used as the vacuum, since it would be clear from the functions the operators act upon.

The proof of the size-extensivity of the cluster amplitudes of T^μ follows essentially the same steps as had been taken earlier by us in the spin orbital-based formulation with determinants. We briefly recapitulate the steps here, both for the sake of completeness and for setting the scenario for the SS-MRCEPA developments to follow.

If the cluster operator T^μ is connected, one can easily verify that the dressed Hamiltonian $\overline{H}_\mu$ and the matrix elements $\widetilde{H}_{\mu\nu}$ are also connected via multi-commutator expansion. The proof of the connectedness of the first term of Eq. (7) is thus quite straightforward. But this is nontrivial for the second term. The term $\langle\chi_l|\exp(-T^\mu)\exp(T^\nu)|\phi_\mu\rangle$ can be written as: $\langle\chi_l|\exp\{(T^\nu - T^\mu) + \frac{1}{2}[T^\nu, T^\mu] + \cdots\}|\phi_\mu\rangle$. All the terms involving commutators $[T^\mu, T^\nu]$ are non-vanishing when some active orbitals are occupied in ϕ_μ and unoccupied in ϕ_ν and vice versa, and thus must be labelled by orbitals distinguishing ϕ_μ and ϕ_ν. Since $\widetilde{H}_{\mu\nu}$ is labelled by all the active orbitals distinguishing ϕ_μ and ϕ_ν, its products with the terms involving the multi-commutators have common active labels and are all connected. Demonstrating the connectivity of the term containing $(T^\nu - T^\mu)$ is, however, rather tricky. Since, in the SS-MRCC theory, all the model space functions are treated on the same footing, all being generated from the base function ϕ_R in the same manner, 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 $\widetilde{H}_{\mu\nu}$. As a result of this, the second term of Eq. (7) is connected as a whole. This aspect is very important while formulating size-extensive approximate methods, such as SS-MRCEPA, from the parent SS-MRCC theory.

We will now derive the size-extensive SS-MRCEPA-like approximants from the spin-free SS-MRCC equations presented above.

2.2 Emergence of the SS-MRCEPA methods from SS-MRCC

Before the presentation of the theoretical development of our recently developed explicitly spin-free SS-MRCEPA methods, we discuss certain theoretical issues of SR-CEPA methods which are essential to understand the physical motivation of various approximations needed to generate the SS-MRCEPA scheme from the full-blown SS-MRCC theory.

2.2.1 An overview of SRCEPA method

In this section, we underline the approximations invoked to generate the SR-based CEPA schemes from the parent SRCC equations. For the sake of easier understanding of basic relations, we neglect the single excitation for now, i.e. we consider the CCD model. We start with a Restricted Hartree–Fock (RHF) 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). After simple manipulation, we obtain the following equations:

$$E = \langle\phi_0|H|\phi_0\rangle + \sum_b \langle\phi_0|HT_b|\phi_0\rangle t_b \tag{12}$$

$$Et_a = \langle\chi_a|H|\phi_0\rangle + \sum_b \langle\chi_a|HT_b|\phi_0\rangle t_b + \frac{1}{2}\sum_{b,\,b'}^{b\neq b'} \langle\chi_a|HT_bT_{b'}|\phi_0\rangle t_b t_{b'}. \tag{13}$$

Combining the above two equations results in the following expression:

$$\langle\chi_a|H|\phi_0\rangle = \sum_b [\langle\phi_0|H|\phi_0\rangle\delta_{ab} - \langle\chi_a|HT_b|\phi_0\rangle]t_b + \sum_b \langle\phi_0|HT_b|\phi_0\rangle t_b t_a + \frac{1}{2}\sum_{b,\,b'}^{b\neq b'} \langle\chi_a|HT_bT_{b'}|\phi_0\rangle t_b t_{b'}. \tag{14}$$

After the cancellation of the disconnected terms in the last two terms of the above equation, the rest of the CCD equations have connected terms only, in the sense that no term can be factorized into two components having no orbitals in common. One set of such terms originate from quadruple excitations via power of cluster operators, while the other stems from double excitations. These latter are the EPV terms. All CEPA methods neglect the terms with multiple excitations, but retain the EPV terms. The above equation can be written as follows:

$$\langle\chi_a|H|\phi_0\rangle = \sum_b [(\langle\phi_0|H|\phi_0\rangle + \Delta_b)\delta_{ab} - \langle\chi_a|HT_b|\phi_0\rangle]. \tag{15}$$

Several methods have been suggested to include EPV terms, Δ, to various degrees. These form the suite of the SR-CEPA methods [18]. The CEPA(0) corresponds to ignoring entirely the term Δ in Eq. (15), CEPA(0) approximation is equivalent to linearized CCD. The CEPA(0) method is not exact for the two-electron problem. The 'diagonal dressing' of Malrieu and co-workers [12–14] (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, 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 reference [12–14]. When the singles are included, the CEPA-like approximations are modified by including all the linear and quadratic powers of T_1. The MR-CEPA formulation using the same concept within the SS framework would be presented in the next section.

2.2.2 Theoretical development of SS-MRCEPA methods

While considering the aspects of spin-adaptation for the general SS-MRCC case – where the spin-free excitations containing exchange spectator scattering of the singly occupied active orbitals of a CSF ϕ_μ have to be included in the cluster operators of T^μ, and the blocks inducing the same scattering by their actions on ϕ_μ have to be added together, we will have to do exactly the same thing to generate the spin-free expressions for SS-MRCEPA methods. In fact, the SS-MRCEPA methods follow from some low order truncation of the spin-free versions of the SS-MRCC theory, so all the considerations discussed for the general SS-MRCC case remain operative and valid for the SS-MRCEPA case.

For the development of various CEPA-like approximants starting from the full-blown SS-MRCC equations (Eq. 7), we present the leading terms of the Eq. (7) explicitly in the following form:

$$\underset{\text{I}}{[\langle\chi_l|H|\phi_\mu\rangle} + \underset{\text{II}}{\langle\chi_l|[H, T^\mu]|\phi_\mu\rangle} + \underset{\text{III}}{\frac{1}{2}\langle\chi_l|[[H, T^\mu], T^\mu]|\phi_\mu\rangle]c_\mu} + \underset{\text{IV}}{\sum_\nu \langle\chi_l|(T^\nu - T^\mu)|\phi_\mu\rangle \widetilde{H}_{\mu\nu}c_\nu} + \text{other terms} = 0. \tag{16}$$

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 SR-CEPA, the χ_ls in the Eq. (16) must be doubly excited for each ϕ_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.

The simplest CEPA-like approximation will follow from Eq. (16) if we keep only the linear terms in the cluster amplitudes. This CEPA has been called by us as the SS-MRCEPA(0) 54. Written in long hand, it amounts to:

$$\langle\chi_l|H|\phi_\mu\rangle c_\mu + \sum_m \langle\chi_l|\left(H - H_{\mu\mu}\right)|\chi_m\rangle t_\mu^m c_\mu + \sum_\nu \langle\chi_l|\left(T^\nu - T^\mu\right)|\phi_\mu\rangle H_{\mu\nu}c_\nu = 0, \tag{17}$$

where the sum over m covers all the SD functions with respect to ϕ_μ, and $H_{\mu\mu} = \langle\phi_\mu|H|\phi_\mu\rangle$. If we start from a CAS-SCF energy E_0, with coefficients $\{c_\mu\}$ ($\sum_\nu H_{\mu\nu}c_\nu = E_0c_\mu$), then Eq. (17) can be simplified to:

$$\langle\chi_l|H|\phi_\mu\rangle c_\mu + \sum_m \langle\chi_l|\left(H - E_0\right)|\chi_m\rangle t_\mu^m c_\mu + \sum_{\nu\neq\mu} t_\mu^l(\nu) H_{\mu\nu}c_\nu = 0, \tag{18}$$

where $t_\mu^l(\nu)$ denotes the amplitude of the specific excitation present in T^ν, which excites to χ_l by its action on ϕ_μ. We have also used in the above equation the simplified notation t_μ^l for $t_\mu^l(\mu)$. The second term indicates that t_μ^l will be dominated (in the perturbative sense) by the ratio $\langle\chi_l|H|\phi_\mu\rangle/(E_0 - H_{ll})$ and will be intruder-free if the CAS energy E_0 is away from the virtual function energies $H_{ll} \equiv \langle\chi_l|H|\chi_l\rangle$. On the other hand, an equation containing only the first two terms for determining t_μ^l will have entailed disconnected non-EPV (NEPV) terms. Concretely speaking, the term $E_0t_\mu^lc_\mu$ can be written as:

$$E_0t_\mu^lc_\mu = \sum_\nu t_\mu^l H_{\mu\nu}c_\nu. \tag{19}$$

If this excitation $\mu \rightarrow l$ on ϕ_μ is also an allowed process on ϕ_ν by Pauli exclusion principle, then the corresponding excitation involves orbitals which are not among those distinguishing ϕ_μ and ϕ_ν. Such terms are then disconnected. However, for every such ϕ_ν where this is true, there is a counter term in $t^l_\mu(\nu)\, H_{\mu\nu} c_\nu$, which together leads to $\left(t^l_\mu(\nu) - t^l_\mu\right) H_{\mu\nu} c_\nu$ for all such ϕ_μ's, and – as explained in Sect. 2.1 – since the difference $\left(t^l_\mu(\nu) - t^l_\mu\right)$ is labeled by some or all orbitals distinguishing ϕ_μ and ϕ_ν, $\left(t^l_\mu(\nu) - t^l_\mu\right) H_{\mu\nu} c_\nu$ is a connected term. Hence, such an approximation, termed as SS-MRCEPA(0) by us, is the simplest among the CEPA-like approximants to the SS-MRCC theory which is extensive and also avoids intruders. However, the appearance of the CAS energy E_0, rather than the ground state energy E itself renders it rather approximate. As we already mentioned, the complete linearity of the SS-MRCEPA(0) equations in the cluster amplitudes lends the same invariance property to it as in the MR-CISD. This parallels the situation in the single reference CEPA(0), which also possesses the invariance. In our earlier papers [54–59], we suggested other schemes where E appears which, however, did not have the orbital invariance property as that of the SS-MRCEPA(0).

We will now go on to present an SS version of MRCEPA method starting from the Eq. (7) using the same spirit of Malrieu and co-workers as done in the SR [12–14]. The method is termed by us as SS-MRCEPA(D)[D stands for 'diagonal dressing']. The SS-MRCEPA(D) [56–59] has close resemblance to the MR-$(SC)^2$CI method of Malrieu and co-workers [77–79]. Since we adopt the same philosophy as that of SR-CEPA(D) of Malrieu and co-workers [12–14] (usually termed as the $(SC)^2$CISD), the EPV terms coming from term III in the Eq. (16), must include the product of the cluster operators in such a way that the excitation involved in one T^μ_l has at least one orbital in common with those involved in the other T^μ_l. Thus, we present the leading terms of Eq. (16) explicitly in the following form:

$$
\begin{aligned}
&[\langle\chi_l|H|\phi_\mu\rangle + \sum_m (H_{lm} - H_{\mu\mu}\delta_{lm}) t^\mu_m - \Delta_\mu t^\mu_l \\
&\quad \text{I} \qquad\qquad \text{II} \qquad\qquad \text{III(a)} \\
&+\tfrac{1}{2} \sum_{m,n}{}' g^l_{m,n} t^\mu_m t^\mu_n] c_\mu \;+ \sum_\nu \langle\chi_l|T^\nu|\phi_\mu\rangle \widetilde{H}_{\mu\nu} c_\nu \\
&\quad \text{III(b)} \qquad\qquad \text{IV(a)} \\
&+ \text{other terms} = \mathcal{E} t^\mu_l c_\mu . \\
&\qquad\qquad \text{IV(b)}
\end{aligned}
\tag{20}
$$

The negative sign of the term Δ_μ is the EPV correction in III(a) in Eq. (20) to keep conformity with the analogous SR term. The term III(b) confined to the product of two singles (which is indicated by the prime in the sum) leads to the doubles. The two pieces IV(a) and IV(b) serve two specific and distinct purposes. A portion of the term in IV(a) for $\nu = \mu$:

$$
\widetilde{H}_{\mu\mu} = H_{\mu\mu} + \Delta^l_\mu + D^l_{\mu\text{NEPV}} \tag{21}
$$

cancels both $H_{\mu\mu}\delta_{lm}$ and $\Delta_\mu t^\mu_l$ terms of II and III(a), while the rest of the expression for $\nu \neq \mu$ of IV(a) corrects for the lack of extensivity coming from the terms appearing in $\mathcal{E} t^\mu_l c_\mu$. As Malrieu and co-workers [12–14] have done in $(SC)^2$CI method, we approximate Δ_μ by the terms containing all T^μs with at least one orbital in common with those appearing in t^μ_l. Δ_μ in each equation for t^μ_l is thus l-dependent, and we indicate this by Δ^l_μ. Denoting the energy $\mathcal{E}$ as $\mathcal{E}_{\text{CEPA(D)}}$, Eq. (20) for this scheme, referred to as SS-MRCEPA(D), takes the form:

$$
\begin{aligned}
&[\langle\chi_l|H|\phi_\mu\rangle + \sum_m [H_{lm} - (\mathcal{E}_{\text{CEPA(D)}} + D^l_{\mu\text{NEPV}})\delta_{lm}] t^\mu_m \\
&+\frac{1}{2} \sum_{m,n}{}' g^l_{m,n} t^\mu_m t^\mu_n] c_\mu \;+ \sum_{\nu\neq\mu} \langle\chi_l|T^\nu|\phi_\mu\rangle \widetilde{H}_{\mu\nu} c_\nu = 0,
\end{aligned}
\tag{22}
$$

where $\mathcal{E}$ satisfies the equation

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

The diagonal matrix element of $\widetilde{H}$, used to find the energy has the following form:

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

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

$$
\begin{aligned}
\widetilde{H}_{\nu\mu} = \langle\phi_\nu|(H + \overline{HT^\mu_1} + \overline{HT^\mu_2} + \frac{1}{2}\sum_{m,n} g^l_{m,n} t^\mu_{1m} t^\mu_{1n} \\
+\frac{1}{2}\sum_{m,n} g^l_{m,n} t^\mu_{2m} t^\mu_{2n})|\phi_\mu\rangle .
\end{aligned}
$$

We have not considered the quadratic terms in our preliminary applications of SS-MRCEPA(D) method in this paper.

We now discuss the most recent version of SS-MRCEPA [54,55] that has the state energy E, rather than the CAS energy E_0 in the working equation, but – unlike in SS-MRCEPA(D) – this has the orbital invariance property. We call this as the SS-MRCEPA(I), with 'I' indicating the orbital invariance property of the formulation. The interesting aspect of this formalism lies in the presence of a set of nonlinear terms in the cluster amplitudes having a special structure which ultimately leads to the desired orbital invariance property. In this, $\overline{H_\mu}$ appearing in $\langle\chi_l|\overline{H}_\mu|\phi_\mu\rangle c_\mu$ is approximated by all of those terms that lead to single and double excitations out of ϕ_μ. Thus the expansion gets naturally truncated at the double commutator for T^μ_1 for the singles, and at the single commutator for T^μ_2 for the doubles. These terms bear a striking resemblance with those corresponding to an MR-CISD formulation and would retain the orbital invariance. For the coupling term, $\langle\chi_l|\exp(-T^\mu)\exp(T^\nu)|\phi_\mu\rangle \widetilde{H}_{\mu\nu} c_\nu$, the first factor is approximated by all terms that lead to χ_l from ϕ_μ via single and double excitations. Thus, for single excitations, the first factor is $\langle\chi_l|\left(T^\nu_1 - T^\mu_1\right)|\phi_\mu\rangle$, while for the double excitations it is $\langle\chi_l|\left(\frac{1}{2}T^{\nu^2}_1 + \frac{1}{2}T^{\mu^2}_1 + T^\nu_2 - T^\mu_2 - T^\mu_1 T^\nu_1\right)|\phi_\mu\rangle$. This factor would thus preserve its form upon rotations of the active orbitals, because the transformed functions in the

model and virtual spaces continue to remain connected through the single and double excitations only. In our previous formulations of the SS-MRCEPA [56–59], the second factor in the coupling term was $\widetilde{H}_{\mu\nu}$ where only the diagonal parts of the dressed operator $\bar{H}_\mu$ were included. This then amounted to the lack of invariance of this factor with respect to the orbital transformations. In the present formulation, we exclude all such terms and approximate $\widetilde{H}_{\mu\nu}$ in a way analogous to the first term of Eq. (7). Thus, we have $\widetilde{H}_{\mu\nu}$ expressed as:

$$\widetilde{H}_{\mu\nu} = \langle\phi_\mu|H + \{[H, T^\nu] + \frac{1}{2}[[H, T^\nu], T^\nu]\}_{\mathrm{SD}\nu}|\phi_\nu\rangle, \quad (23)$$

where $\{\quad\}_{\mathrm{SD}\nu}$ denotes single and double excitations out of ϕ_ν. The invariance of the second factor of the coupling term is preserved, as is evident from the structural equivalence of this with those of the model projections of an MR-CISD equations. Collecting all the terms, the SS-MRCEPA(I) can be written as:

$$\underset{\mathrm{I}}{\langle\chi_l|H|\phi_\mu\rangle c_\mu} + \underset{\mathrm{II}}{\langle\chi_l|\{[H, T^\mu] + \tfrac{1}{2}[[H, T^\mu], T^\mu]\}_{\mathrm{SD}\mu}|\phi_\mu\rangle c_\mu}$$
$$+ \sum_\nu \underset{\mathrm{III}}{\langle\chi_l|\{(T^\nu - T^\mu) + \tfrac{1}{2}(T^\nu - T^\mu)^2}$$
$$+ \frac{1}{2}[T^\nu, T^\mu]\}_{\mathrm{SD}\mu}|\phi_\mu\rangle \widetilde{H}_{\mu\nu} c_\nu = 0$$

with

$$\sum_\nu \widetilde{H}_{\mu\nu} c_\nu = E c_\mu. \quad (24)$$

All the components of III with only T^μ operator can be compactly written as:

$$X = \langle\chi_l|\{-T^\mu + \frac{1}{2}T^{\mu^2}\}_{\mathrm{SD}\mu}|\phi_\mu\rangle E c_\mu \quad (25)$$

X contains both the EPV terms and the disconnected non-EPV terms. We now classify the non-EPV terms as: (1) those belonging to the CISD space relative to the CAS, induced by products of powers of T^μ and T^ν, acting on ϕ_ν itself, and (2) those which are outside the CISD space and are disconnected, again induced by similar products of operators as in (1). Interestingly enough, the entire term III in Eq. (24) is a connected quantity, ensuring extensivity by eliminating the inextensivity arising from the term X by the counter-terms containing at least one T^ν. The terms I and II are invariant under the restricted orbital transformations as have been emphasized earlier. The full term III is also invariant as it involves a total sum over all the functions ϕ_ν of the CAS. This approach thus uses the dressed Hamiltonian $\widetilde{H}_{\mu\nu}$, unlike the SS-MRCEPA(0) which uses the bare $H_{\mu\nu}$ and hence might be viewed as a minimal extension of the SS-MRCEPA(0). Moreover, SS-MRCEPA(I) is a step forward since it uses a self-correcting set of terms in $\langle\chi_l|\exp(-T^\mu)\exp(T^\nu)|\phi_\mu\rangle\widetilde{H}_{\mu\nu}$ which leaves not only the EPV terms but also cancels the inextensivity in an orbital invariant manner arising out of the non-EPV terms. We also note that the non-EPV terms outside the CISD space, mentioned in (b) above, generated in the term III of Eq. (24) are not fully eliminated; rather, their size-inextensive component is eliminated. This, in effect, is the minimal expasion beyond the MR-CISD space that is crucial to preserve the orbital invariance. With Eq. (24) we define SS-MRCEPA(I) scheme to the full-blown SS-MRCC. The aspect of size-extensivity is retained in all our SS-MRCEPA methods since T^μ and T^ν are treated on the same footing while truncating $[\exp(-T^\mu)\exp(T^\nu)]$.

In the SS-MRCEPA theories, all the reference functions are treated democratically. They are thus quite useful for the computation of the energies of states associated with varying degrees of degeneracy among the the model space functions over wide range of geometries. Our SS-MRCEPA methods are free from the objections of the instability of working equations due to the intruder state effects akin to the parent SS-MRCC method. The analysis follows the same route as was taken to show avoidance of intruders in the parent SS-MRCC theory [49–52]. The denominator of the leading terms of the cluster finding operator of the SS-MRCEPA method involves a difference of the target state energy itself and the energy of the virtual functions which are closely spaced with the reference space functions. It is important to mention the fact that our theories are free from the intruder effects as long as the target state is energetically well separated from the virtual functions. Thus the SS-MRCEPA theories are very effective to generate the PES over a wide range of nuclear geometries.

Let us now discuss certain general features of our SS-MRCEPA formalisms in order to put them in a proper perspective in relation to other allied formalisms. Unlike MR-ACPF [11] and MR-AQCC methods [16,17], which use an MR starting function with frozen coefficients, our methods have the flexibility of either using frozen coefficients or – as is usually done – the relaxed ones obtained on diagonalization of the effective operator. The real advantage of the SSMR theories over the unrelaxed theories in vogue may be understood if we consider the case of mixed states, e.g. those electronic states which have different contributions of the valence and Rydberg components, or have varying covalent and ionic characters, which change strongly as a function of nuclear coordinate. The relative importance of different configuration types depends sensitively on the coupling of the dynamical and non-dynamical correlations, thereby revising the frozen coefficients of the starting functions considerably. Clearly a formalism allowing relaxation of the model space coefficients in the correlated treatment provides the conceptually correct description of this mixing. Except the SS-MRCEPA(0) method, all the other versions of SS-MRCEPA proceed via iterative update of the reference space coefficients and thereby energy is computed via the diagonalization of the dressed Hamiltonian within the model space. Hence, the coefficients are completely relaxed. Even the SS-MRCEPA(0) which is devoid of iteratively explicit relaxation of the coefficients, incorporates the effect of relaxation during the course of diagonalization of the dressed Hamiltonian constructed within the model space to get the energy of the target state.

The multi-reference dressed CISD methods of Malrieu and co-workers [77–79] are conceptually akin to our

SS-MRCEPA methods. As we have discussed, the CEPA methods can be viewed either as extensivity corrected CI or as truncated versions of CC retaining only the EPV terms. In the dressed CI formalism the space of the dressed MR-CISD matrix is the same as in the ordinary MR-CISD method. This is in contrast to our SS-MRCEPA methods where, due to the redundancy of the cluster amplitudes, the same virtual function may be reached from various model functions ϕ_μ through the respective cluster operators in T^μ. In the method of Malrieu and co-workers [77–79] the redundancy is eliminated by way of introducing suitable weight factors ρ_l^μ. This emphasizes the genealogy of the coefficient c_l of a virtual function χ_l, as a weighted sum

$$c_l = \sum_\mu t_l^\mu c_\mu \equiv \sum_\mu \rho_l^\mu c_l \quad \text{with} \quad \rho_l^\mu = \frac{t_l^\mu c_\mu}{\sum_\nu t_l^\nu c_\nu}. \qquad (26)$$

As we have commented in an earlier paper 54–59, we can envision generating an SS-MRCEPA(D) formalism where the weight factors can be introduced to eliminate the redundancy. However, as emphasized there, the kind of counterterms automatically entering the SS-MRCEPA theory are such that the dressing would have to be a column dressing, rather than diagonal dressing. In fact, the diagonal dressing used by Malrieu and co-workers [77–79] stems from an empirical elimination of the disconnected non-EPV terms. For an extensive discussion we refer to one of our earlier papers [54–59].

It is interesting to discuss at this stage how the different SS-MRCEPA schemes introduced here reduce to the corresponding SR-CEPA schemes in the limit when there is only one function in the model space. It is obvious that the SS-MRCEPA(0) would go over to the SR-CEPA(0) or LCCSD if only the linear cluster operators are retained in our SS-MRCEPA(0). The orbital invariance of the SS-MRCEPA(0) thus carries over to the SR-CEPA(0) in a straightforward manner. The SS-MRCEPA(I) has the set of orbitally invariant terms III in Eq. (24). When there is only one model function ϕ_μ, the SS-MRCEPA(I) reduces to

$$\langle\chi_l \,|\, H \,|\, \phi_\mu\rangle + \langle\chi_l \,|\, \left\{\left[H, T^\mu\right] + \frac{1}{2}\left[\left[H, T^\mu\right], T^\mu\right]\right\}_{\mathrm{SD}\mu} |\, \phi_\mu\rangle = 0,$$

which is again just the SR-CEPA(0) in the CI language. Again, the orbital invariance property is manifest. In the presence of strong quasi-degeneracy, however, SS-MRCEPA(I) is more flexible and incorporates more physical effects as compared to the SS-MRCEPA(D), and hence, would be a more appropriate choice in such a situation. The SS-MRCEPA(D) reduces in the SR limit to just the SR-CEPA with all EPV terms included, analogous to the $(SC)^2$CISD method of Malrieu and co-workers [12], which is not orbitally invariant.

3 Numerical implementation

We now discuss the computational strategy leading to the numerical implementation of SS-MRCEPA methods.

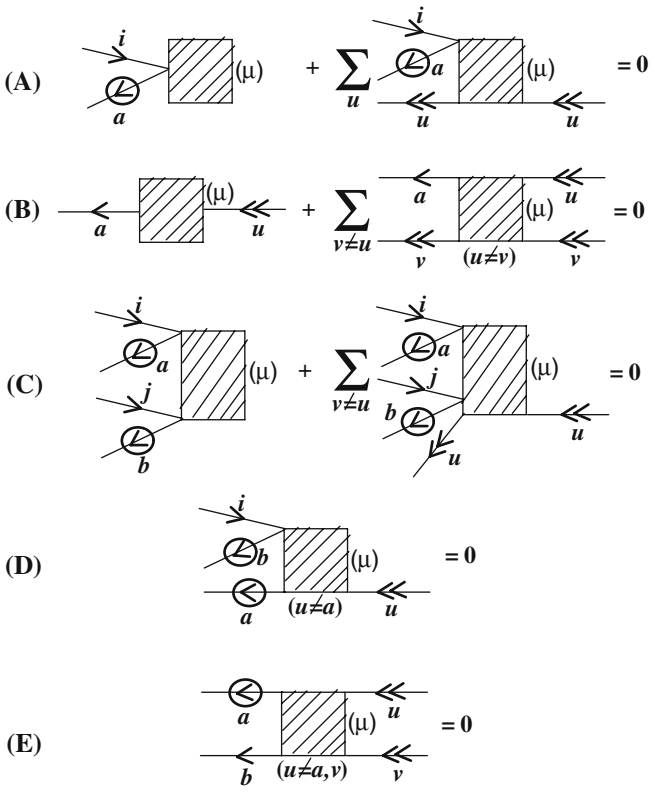

Fig. 1 In the above diagrammatic equations, i represents the set of inactive core orbitals, $a, b, \ldots$ are members of the set of either an active or a virtual orbital (represented by an *encircled arrow*), and $u, v, \ldots \in \{\phi_\mu\}$ denote purely active set of orbitals inducing the spectator excitations

Two sets of variables, the cluster operators, T^μs and the combining coefficients, c_μs constitute the SS-MRCEPA equations in a coupled form. For every ϕ_μ, there are two sets of operators in T^μ: (a) pure excitation operators without spectators and (b) excitation operators with exchange spectators. Generally, the working equations are of the form as shown in Fig. 1.

In the diagrammatic equations in Fig. 1, the hatched blocks correspond to the various connected composites of the SS-MRCEPA methods, and Eqs. (A)–(C) show that the block containing the direct spectators are to be added to a lower rank block without the spectators, since both lead to the same excitations to ϕ_μ and hence are linearly dependent. The Eq. (D) is for the term with exchange spectator only, and there is no lower rank block which is linearly dependent. Equation (E) represents the pure ladders with exchange spectator excitations from ϕ_μ.

We now discuss the organizational strategy for solving the equations in a stable and rapidly convergent manner. Two levels of nested iterations are used for this purpose. The outermost loop (macro-iteration cycle) updates the coefficients c_μ by diagonalizing the effective operator obtained from the converged cluster amplitudes of the inner (micro) iteration. In the micro-iteration, with fixed coefficients, a loop is initiated over μ to compute the amplitudes of T^μ, keeping the

amplitudes of all T^{ν}s, $\nu \neq \mu$ frozen. The macro-iteration updates the coefficients only after the local convergence of all the cluster amplitudes is reached. We emphasize here that the couplings between the various cluster amplitudes in the SS-MRCEPA 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}. Let us also note that there is no macro-iteration for SS-MRCEPA(0). However, the energy is obtained via the diagonalization of the effective operator and hence uses relaxed coefficients with the cluster amplitudes being obtained from initial coefficients of the reference functions.

In our implementation, we use the same tolerance, $\eta(\mu)$ (10^{-8}) for different cluster amplitudes t_i^{μ}. When the $\delta(\mu) = \mid t_{\mu}^{i}(\text{new}) - t_{\mu}^{i}(\text{old}) \mid \ \forall\, l, \mu$ 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_{μ}^{i}, the t_{μ}^{i} amplitude is frozen, while the iteration process is started for the other cluster amplitude t_{ν}^{i}, with $\mu \neq \nu$, till the condition $\delta(\nu) \leq \eta(\nu)$ is attained.

4 Results and discussions

Calculations are presented in this section for the LiH and HF molecules using medium size basis sets. Comparison are made with the results of other methods along with the full CI values if available. Spectroscopic constants are computed from the PES obtained from CEPA methods, and compared with the FCI counterparts.

Since we do not have the results for the spin-free full-blown SS-MRCC as yet, we are unable at this stage to illustrate the extent to which the various approximants to it can capture electron correlation in the general situation relative to the SS-MRCC where open-shell model functions are present. However, in cases where the model functions are of the closed-shell type, the spin-adaptation of the SS-MRCC is straightforward. However, comparison with the FCI benchmark exact results in a given basis will always be done to estimate the absolute accuracy of the numbers in a given theory. In all calculations, we use the CASSCF orbitals corresponding to the lowest energy state of a (3×3) CAS, generated by GAMESS, with a set of natural MOs for the doubly occupied and active orbitals, augmented by a set of canonical orbitals for the virtual functions. In this paper, we have presented only the results of relaxed description of SS-MRCEPA methods obtained via a diagonalization of the effective operator, as well as via the calculation of the corresponding expectation values, which are essentially unrelaxed. The latter has been denoted by $\langle \cdots \rangle$. The use of CASSCF orbitals in lieu of the RHF orbitals improves the performance of our SS-MRCEPA methods appreciably while computing the full PESs. We would illustrate this aspect numerically through the PES of LiH molecule.

In our preliminary applications of the SS-MRCEPA(I) and SS-MRCEPA(D) method in this article as applied to model spaces with open-shell functions, we have not included the quadratic terms of the cluster operators. This does not affect the extensivity of our formalism. A comprehensive account considering the quadratic terms with the open-shell model functions will also be communicated in due course.

4.1 LiH molecule

The study of ground state PES of LiH molecule 106–111 is a good test case in the sense that: (1) The reference space (CASSCF) includes the following configurations: $\phi_1 = 1\sigma^2 2\sigma^2$, $\phi_2 = 1\sigma^2 3\sigma^2$ and $\phi_3 = 1\sigma^2 2\sigma 3\sigma$. The last CSF is an open-shell function, (2) A proper spin-adapted state-specific theory is called for since one of the CSFs is an open-shell singlet. (3) Near the equilibrium region the doubly excited Σ states described by the excited roots of the H_{eff} would be close in energy to some virtual functions, and hence would be intruder-prone. As a consequence, the effective Hamiltonian-based methods would fail to describe the PES very well.

In our calculations of the entire PES, we have used the natural CASSCF orbitals of ground state from the three-dimensional CAS. The basis used is the standard 6-311G* [112]. To judge the quality of the PES, the performance of the various SS-MRCEPA methods is assessed via a comparison with the corresponding FCI values.

In Fig. 2 we present the deviations of various SS-MRCEPA methods from the FCI values for the ground state energies of LiH system. We have presented the deviations for the relaxed and the frozen coefficient varieties.

We now discuss the performance of the SS-MRCEPA methods. Some of the preliminary results could be found in one of our forthcoming articles 63, nevertheless we additionally include the SS-MRCEPA(D) in the present work. The deviations of relaxed and unrelaxed values of various SS-MRCEPA methods from the FCI values are nearly the same. From Fig. 2, performances of the SS-MRCEPA(0) and SS-MRCEPA(D) are seen to be better than the SS-MRCEPA(I) method. The energies obtained via SS-MRCEPA(0) and SS-MRCEPA(D) methods are pretty close to the corresponding FCI values over the entire PES. The minimum and maximum deviations from FCI values for SS-MRCEPA(0) are –0.093 and –0.216 mH, respectively, whereas for the SS-MRCEPA(I) case these values are –4.392 and –7.339 mH, respectively. In the case of SS-MRCEPA(D) method, the minimum deviation from FCI is –0.118 mH whereas the maximum deviation is –0.468 mH. The deviation from the FCI values decreases with increase in internuclear separations for SS-MRCEPA methods. This is also true for the corresponding CEPA(I) scheme. At shorter nuclear distances, the deviation of the relaxed description is slightly smaller than that of the unrelaxed one [e.g. at $R = 2.0$ a.u. for relaxed values deviations for SS-MRCEPA(0) = –0.211 mH, SS-MRCEPA(D) = –0.325 mH and SS-MRCEPA(I) = –6.868 mH whereas for the unrelaxed cases, $\langle$SS-MRCEPA(0)$\rangle$ = –0.260 mH, $\langle$SS-MRCEPA(D)$\rangle$ = –0.335 mH, $\langle$SS-MRCEPA(I)$\rangle$ = –6.869 mH]. The deviations for the relaxed and unrelaxed schemely are

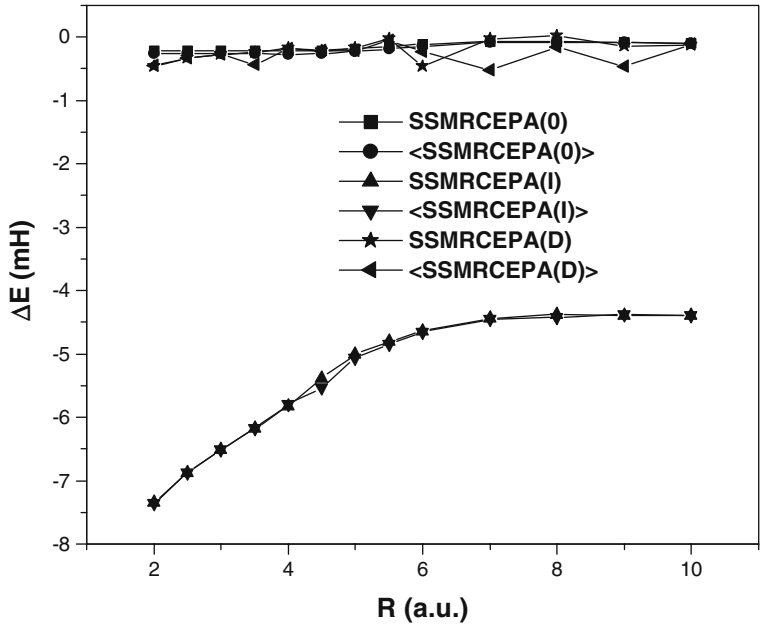

Fig. 2 Plot of energy difference $[E_{\mathrm{FCI}} - E_{\mathrm{Method}}]$ (mH) for the ground state of LiH molecule using the CASSCF orbitals for the lowest root of the (3×3) CAS

almost identical at large bond length [e.g. at $R = 10.0$ a.u., for relaxed values, the deviations for SS-MRCEPA(0) = –0.093 mH, SS-MRCEPA(D) = –0.113 mH and SS-MRCEPA(I) = –4.392 mH whereas for unrelaxed cases, ⟨SS-MRCEPA(0)⟩ = –0.093 mH, ⟨SS-MRCEPA(D)⟩ = –0.118 mH, ⟨SS-MRCEPA(I)⟩ = –4.392 mH]. From the above numerical discussion & regarding the performances of our SS-MRCEPA methods, we may conclude these methods are quite effective in generating the PES of LiH molecule over the wide range of geometries.

The behaviour of the different SS-MRCEPA methods are quite dramatically different if RHF, rather than the CASSCF orbitals, are used in computing the PES. We show the behavior of these methods using RHF orbitals of the ground state for LiH in Fig. 3. Around the equilibrium geometry, where the RHF function dominates (thus approaching the SR limit), the behavior of the SS-MRCEPA(0) and SS-MRCEPA(I) are very similar. SS-MRCEPA(D) behaves quite differently in this region. All the results are, however, poorer as compared with those obtained with CASSCF orbitals, but this figure is displayed only to underline the relative asymptotic limits of the SS-MRCEPA methods in the SR limit.

Since the SS-MRCEPA methods perform very well to compute the PES, we have also calculated the equilibrium geometry r_{e}, harmonic vibrational frequency ω_{e}, anharmonicity constant $\omega_{\mathrm{e}}x_{\mathrm{e}}$, rotational constant B_{e}, rovibronic constant α_{e}, and centrifugal distortion constant $\overline{D}_{\mathrm{e}}$. Table 1 contains the spectroscopic constants for LiH system obtained via different SS-MRCEPA methods using CASSCF orbitals. From the table it is clear that the various spectroscopic constants of LiH molecule computed via various SS-MRCEPA methods are quite encouraging.

4.2 HF molecule

Our next test case is the HF molecule. This molecule possesses pronounced multi-reference character even around the equilibrium geometry [111, 113–118]. Hence the computation of the ground PES of HF molecule over the entire range of geometries is a challenging task for any MR-based method.

Just as in LiH, the three-dimensional reference space of HF contains one open-shell CSF, apart from the two closed-

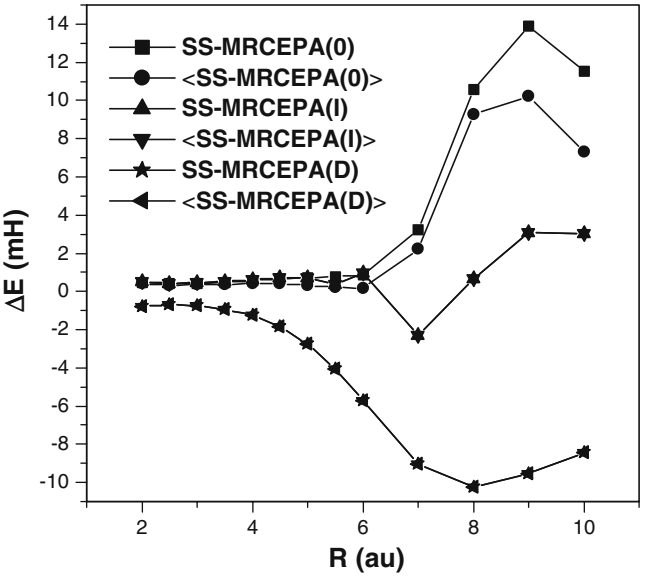

Fig. 3 Plot of energy difference $[E_{\mathrm{FCI}} - E_{\mathrm{Method}}]$ (mH) for the ground state of LiH molecule using the Hartree–Fock orbitals

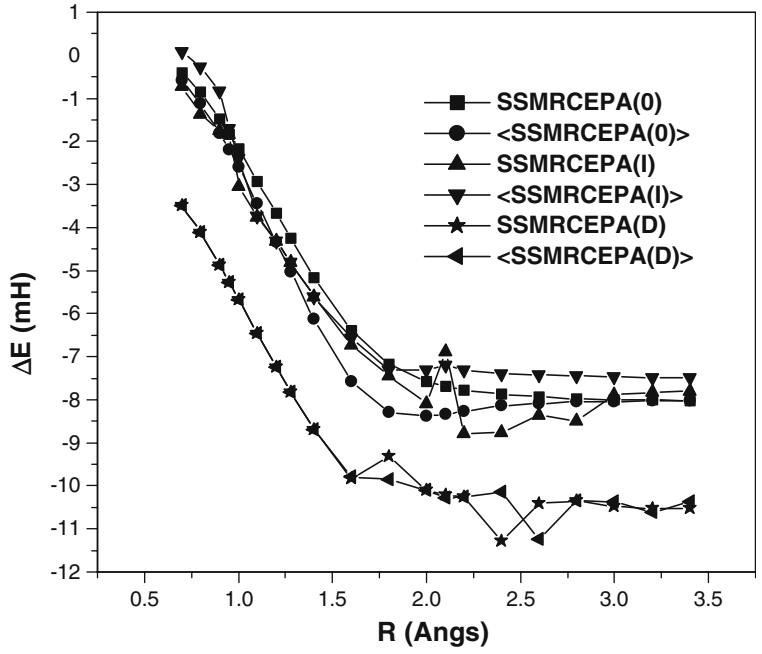

Fig. 4 Plot of energy difference $[E_{\mathrm{FCI}} - E_{\mathrm{Method}}]$ (mH) for the ground state of HF molecule using the 6-31G basis and the CASSCF orbitals for the lowest root of the (3×3) CAS

Table 1 Spectroscopic constants of LiH (using CASSCF orbitals)

Method	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	$D_e \times 10^{-3}$ (cm^{-1})
SS-MRCEPA(0)	1.621	1477.55	20.93	7.238	0.149	0.694
SS-MRCEPA(I)	1.621	1467.08	22.16	7.238	0.161	0.705
SS-MRCEPA(D)	1.631	1376.24	31.10	7.145	0.242	0.770
FCI	1.624	1406.25	28.97	7.215	0.223	0.760
Experiment[a]	1.596	1405.65	23.20	7.513	0.213	0.861

[a] K. P. Huber, G. Herzberg, Constants of diatomic of molecules (Van Norstrand, NY, 1979)

shell functions. The reference configurations are: $\phi_1 = [\mathrm{core}]\sigma^2$, $\phi_2 = [\mathrm{core}]\sigma^{\star 2}$ and $\phi_3 = [\mathrm{core}]\sigma\sigma^\star$. We use the orbitals obtained from CASSCF calculation corresponding to the lowest root of the (3×3) CAS reference function.

For this system we have used two sets of basis viz. standard 6-31G basis, set [119] and cc-pVDZ basis set [112]. Although the present basis sets are not large enough, they are adequate to enable us to draw useful conclusions regarding the applicability of the SS-MRCEPA methods in computing the energies over a wide range of nuclear geometries.

We have used the standard 6-31G basis set [119] for the calculations, since we have the flexibility to compare our results with those obtained by Krylov and co-workers [113–120]. We have calculated both the PES and also compared their relative performance with the standard FCI results in the same basis. To get a better feeling regarding the efficacy of our recently developed explicitly spin-free SS-MRCEPA methods, we also quoted the values of various spin flip approaches of CIS methods [113–120].

Figure 4 depicts the results for the different versions of the SS-MRCEPA methods. A comparison of the figures clearly point out that the performance of the SS-MRCEPA(0) is very close to that of the SS-MRCEPA(I) counterpart. At large distance, SS-MRCEPA(I) performs slightly better than SS-MRCEPA(0). On the other hand, the SS-MRCEPA(0) and SS-MRCEPA(I) methods perform better than the corresponding CEPA(D) version. In this system, the minimum and maximum deviations (mH) of SS-MRCEPA(0) from the FCI values are −0.399 and −8.016, respectively. These deviations (mH) for the SS-MRCEPA(D) method are −3.497 and −10.518. In contrast to the LiH system, the deviation of results of the SS-MRCEPA methods from FCI ones increases gradually with the H–F bond distances. As that of the LiH case, the performance of relaxed description of various SS-MRCEPA methods is slightly better than the unrelaxed one. We now discuss the performance of spin flip-like methods 113–120. In the case of SF-CIS and SC-SF-CIS methods, the deviations from the FCI values are quite large, the minimum and maximum values are −86.101 and −113.270 mH respectively for SC-SF-CIS methods whereas these values for SF-CIS method are −86.697 and −168.229 mH, respectively. To improve the quality of results, proper treatment of the dynamical correlation is essential.

We will now discuss the performance of our SS-MRCEPA methods for the second basis set: cc-pVDZ. In Fig. 5, we present the ground state energies over the entire PES computed explicitly via spin-free SS-MRCEPA methods for the HF system using cc-pVDZ basis. As that of the 6-31G basis, the performance of relaxed scheme of various SS-MRCEPA methods is slightly better than the corresponding unrelaxed version. The relaxed version of SS-MRCEPA(I) performs better over the unrelaxed one at short distances whereas at a large distance (beyond 1.2 Angstroms), the two schemes

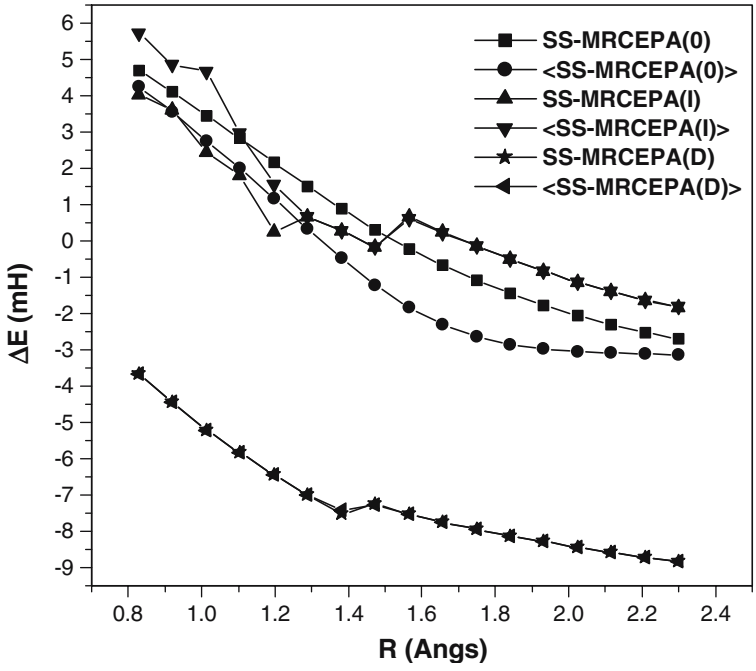

Fig. 5 Plot of energy difference $[E_{\mathrm{FCI}} - E_{\mathrm{Method}}]$ (mH) for the ground state of HF molecule using the cc-pVDZ basis and the CASSCF orbitals for the lowest root of the (3×3) CAS

show similar performance with respect to the FCI values. On the other hand, the performance of SS-MRCEPA(0) and SS-MRCEPA(I) are comparable at a short distance while at a large distance, SS-MRCEPA(I) performs slightly better over SS-MRCEPA(0). The performance of SS-MRCEPA(0) and SS-MRCEPA(I) using cc-pVDZ basis set is better than that of the corresponding CEPA(D) version as also seen for the 6-31G basis set. The maximum deviations for the relaxed schemes of the SS-MRCEPA(0), SS-MRCEPA(I) and SS-MRCEPA(D) are 4.68, 4.04 and −8.84 mH, respectively, and the corresponding minimum deviations are −0.21, −0.14 and −3.67 mH, respectively.

With only a few example applications discussed here, we feel that it may not be fair at this stage to conclude definitively about the relative performance of SS-MRCEPA(0), SS-MRCEPA(D) and SS-MRCEPA(I) methods. From the foregoing discussion, it is clear that the performance of the SS-MRCEPA(0) is usually better than the other variants. At times CEPA(D) performs better than CEPA(I), and vice versa. More exhaustive calculations of various SS-MRCEPA are needed, to come to a definitive conclusion, which are on the way.

5 Summary

In this paper, we have presented a new formulation of manifestly spin-free state-specific multi-reference CEPA theories (SS-MRCEPA) based on a CAS, which are designed to bypass intruders. The method is derived as a CEPA like approximant from our size-extensive SS-MRCC theory. The use of the entire portion $\phi_{0\mu}$ of the highest closed-shell component of ϕ_μ as the vacuum to define all the excitations on ϕ_μ in normal order is rather powerful, and offers a simple yet convenient access not only to define the various excitation operators but also to simplify the resulting working equations in the spin-free formulation. Because of the generally non-commuting nature of the spin-free generator, the working equations are more involved. However, we have presented a scheme which makes it possible to get a simple solution to it in an efficient way. We have discussed in this article, the theory of the spin-free SS-MRCEPA methods generated from the SS-MRCC method and also illustrated the numerical efficacy of its various approximants by applying them in the systems where not only closed-shell but also open-shell functions are present in the model space. These systems possess quasi-degeneracy at some points on the PES and there are potential intruders at some other points. In our applications the CASSCF method is used to account for the non-dynamical behavior which arises for near degeneracies between different electronic configurations. This wave function is then used as the reference in a non-perturbative CEPA-like treatment of remaining dynamical correlation effects. From the above discussion, we can say that the suite of SS-MRCEPA methods perform very well. Unlike most of the CAS-based CEPA like state-specific methods, all of our SS-CEPA counterparts are rigorously size-extensive and intruder-free in nature. Hence, they are very effective in studying the PES over the wide range of geometrical distortions. We have illustrated this by applying them to study the PES of LiH and HF. Of course, the most stringent tests for the generality of our SS-MRCC formalism and its various CEPA-like approximants would be in situations where the orbitals change very rapidly as a function of the minor geometrical distortions, as happens in

weakly avoided crossings. We have shown the effectiveness of our formalisms in one such difficult test system in another paper 63. More extensive applications of the method are under way and will be reported in our forthcoming publications.

Acknowledgements It is a pleasure to dedicate this paper to Jean Paul Malrieu on the happy occasion of his reaching sixty five. DM cherishes the memory of many stimulating discussions with JPM whose friendship, wit, wisdom, originality and erudition have added sparkle to his life.

References

1. Čížek J (1966) J Chem Phys 45:4256
2. Čížek J (1969) Adv Chem Phys 14:35
3. Čížek J, Paldus J (1975) Adv Chem Phys 9:105
4. Bartlett RJ (1989) J Phys Chem 93:1697
5. Bartlett RJ (1995) In: Yarkony DR (ed) Modern electronic structure theory. World Scientific, Singapore
6. Meyer WJ (1973) Chem Phys 58:1017
7. Meyer WJ (1989) Theor Chim Acta 35:277
8. Meyer W (1977) In: Schaeffer HF III (ed) Methods of electronic structure theory. Plenum Press, New York
9. Kelly HP, Sessler AM (1963) Phys Rev 132:2091
10. Kelly HP (1964) Phys Rev 134:1450
11. Gdanitz RJ, Ahlrich R (1988) Chem Phys Lett 143:413
12. Daudey JP, Heully JL, Malrieu JP (1993) J Chem Phys 99:1240
13. Nebot-Gil I, Sanchez-Marin J, Malrieu JP, Heully J-L, Maynau DJ (1995) J Chem Phys 103:2576
14. Malrieu JP, Nebot-Gil I, Sanchez-Marin J (1994) J Chem Phys 100:1440
15. Bartlett RJ, Silver WD (1975) Int J Quantum Chem S9:183
16. Szalay PG, Bartlett RJ (1995) Chem Phys Lett 214:481
17. Fusti-Molnar L, Szalay PG (1996) J Phys Chem 100:6288
18. Kutzelnigg W (1997) In: Schaefer HF III (ed) Methods of electronic structure theory. Plenum Press, New York
19. Ahlrichs R (1983) In: Diercksen GHF, Wilson S (eds) Methods in computational molecular physics. Dordrecht
20. Szalay PG (1997) In: Bartlett RJ (ed) Recent advances in coupled-cluster methods. World Scientific, Singapore
21. Urban M, Noga J, Cole SJ, Bartlett RJ (1985) J Chem Phys 83:4041
22. Watts JD (2001) In: Leszczynski J (ed) Computational chemistry: reviews of current trend. World Scientific, Singapore 7:89 and references therein
23. Scuseria GE, Schafer HF III (1988) Chem Phys Lett 152:382
24. Koch H, Christiansen O, Jørgensen P, Sanchez de MA, Helgaker T (1997) J Chem Phys 106:1808
25. Oliphant N, Adamowicz L (1991) J Chem Phys 94:1229
26. Oliphant N, Adamowicz L (1992) J Chem Phys 96:3739
27. Ivanov VV, Adamowicz L (2000) J Chem Phys 112:9258
28. Piecuch P, Kucharski SA, Bartlett RJ (1999) J Chem Phys 110:6103
29. Piecuch P, Kowalski K, Pimienta I, Kucharski SA (2002) In: Hoffmann MR, Dyall KG (eds) Low-lying potential energy surfaces. ACS Symposium Series No. 828, Washington, DC and references therein
30. Mukherjee D, Moitra RK, Mukhopadhyay A (1975) Mol Phys 30:1861
31. Mukherjee D, Moitra RK, Mukhopadhyay A (1977) Mol Phys 33:955
32. Lindgren I (1978) Int J Quantum Chem S12:33
33. Lindgren I, Mukherjee D (1987) Phys Rep 151:93
34. Mukherjee D, Pal S (1989) Adv Quantum Chem 20:561
35. Jeziorski B, Monkhorst HJ (1981) Phys Rev A 24:1668
36. Jeziorski B, Paldus J (1988) J Chem Phys 88:5673
37. Schucan TH, Weidenmüller HA (1972) Ann Phys 73:108
38. Hose G, Kaldor U (1979) J Phys B 12:3827
39. Kirtman B (1981) J Chem Phys 75:798
40. Malrieu JP, Durand Ph, Daudey JP (1985) J Phys A Math Gen 18:809
41. Durand Ph, Malrieu JP (1987) Adv Chem Phys 67:321 and references therein
42. Hoffmann MR (1992) Chem Phys Lett 195:127
43. Hoffmann MR (1993)Chem Phys Lett 210:193
44. Hoffmann MR (1996) J Chem Phys 100:6125
45. Khait YG, Hoffmann MR (1998) J Chem Phys 108:8317
46. Mukhopadhyay D, Datta B, Mukherjee D (1992) Chem Phys Lett 197:236
47. Datta B, Chaudhuri R, Mukherjee D (1996) J Mol Structure (Theochem) 361:21
48. Landau A, Eliav E, Ishikawa Y, Kaldor U (2000) J Chem Phys 113:9905
49. Mahapatra US, Datta B, Bandyopadhyay B, Mukherjee D (1998) Adv Quantum Chem 30:163
50. Mahapatra US, Datta B, Mukherjee D (1998) Mol Phys 94:157
51. Mahapatra US, Datta B, Mukherjee D (1999) J Chem Phys 110:6171
52. Chattopadhya S, Mahapatra US, Datta B, Mukherjee D (1999) J Chem Phys 111:3820
53. Pahari D, Chattopadhyay S, Das S, Mukherjee D (2003) Chem Phys Lett 381:223
54. Pahari D, Chattopadhyay S, Dev A, Mukherjee D (2004) Chem Phys Lett 386:307
55. Chattopadhyay S, Pahari D, Mukherjee D, Mahapatra US (2004) J Chem Phys 120:5968
56. Chattopadhyay S, Mahapatra US, Datta B, Mukherjee D (2002) Chem Phys Lett 357:426
57. Chattopadhyay S, Mahapatra US, Ghosh P, Mukherjee D (2002) In: Hoffmann MR, Dyall KG (eds) Low-lying potential energy surfaces. ACS symposium series no. 828, Washington, p 109
58. Chattopadhyay S (2004) J Phys B 37:1783
59. Chattopadhyay S, Mahapatra US (2004) J Phys Chem A 108:11664
60. Mahapatra US, Datta B, Mukherjee D (1999) Chem Phys Lett 110:42
61. Mahapatra US, Datta B, Mukherjee D (1999) J Phys Chem A 103:1822
62. Ghosh P, Chattopadhyay S, Jana D, Mukherjee D (2002) Int J Mol Sci 3:733
63. Pahari D, Chattopadhyay S, Das S, Mukherjee D, Mahapatra US (2006) In: Dytkstra CE, Kim KS, Frenking G, Scuseria GE (eds) Theory and applications of computational chemistry: the first 40 years Elsevier, Amsterdam, Chapter–22
64. Rittby M, Bartlett RJ (1988) J Phys Chem 92:3033
65. Scuseria GE (1991) Chem Phys Lett 176:27
66. Lee TJ, Jayatilaka D (1993) Chem Phys Lett 201:1
67. Jayatilaka D, Lee TJ (1993) J Chem Phys 98:9734
68. Nakatsuji H, Hirao K (1978) J Chem Phys 68:2053
69. Szalay PG, Gauss J (1997) 107:9028
70. Jansen CL, Schaefer HF III (1991) Theor Chim Acta 79:1
71. Li X, Paldus J (1994) J Chem Phys 101:8812
72. Li X, Paldus J (1997) In: Bartlett RJ (ed) Modern ideas in coupled cluster methods. World Scientific, Singapore
73. Jeziorski B, Paldus J, Jankowski P (1995) Int J Quantum Chem 56:129
74. Mukhopadhyay D, Mukherjee D (1992) In: Mukherjee D (ed) Applied many-body methods in spectroscopy and electronic structure. Plenum Press, New York
75. Jana D, Bandyopadhyay B, Mukherjee D (1999) Theor Chem Acc 102:317
76. Jana D, Mahapatra US, Mukherjee D (2002) Chem Phys Lett 353:100
77. Meller J, Malrieu JP, Caballol R (1996) J Chem Phys 104:4068
78. Malrieu JP, Daudey JP, Caballol RJ (1994) Chem Phys 101:8908
79. Meller J, Malrieu JP, Heully JL (1995) Chem Phys Lett 244:440

80. Mášik J, Hubač I (1997) In: McWeeny R et al. (eds) Quantum systems in chemistry and physics: trends in methods and applications. KA, Dordrecht
81. Màšik J, Hubač I, Mach P (1998) J Chem Phys 108:6571
82. Hubač I, Pittner J, Čàrsky P (2000) J Chem Phys 112:8779
83. Pittner J (2003) J Chem Phys 118:10876
84. Brandow B (1967) Rev Mod Phys 39:771
85. Lindgren I (1974) J Phys B 7:2441
86. Andersson K, Malmqvist P-A, Roos BO, Sadlej AJ, Wolinski K (1990) J Phys Chem 94:5483
87. Andersson K, Malmqvist P-A, Roos BO (1992) J Chem Phys 96:1218
88. Hirao K (1992) Chem Phys Lett 190:374
89. Hirao K (1992) Chem Phys Lett 196:397
90. Hirao K (1993) Chem Phys Lett 201:59
91. Nakano H (1993) J Chem Phys 99:7983
92. Rolik Z, Szabados A, Surján P (2003) J Chem Phys 119:1922
93. Freed KF (1989) Lecture notes in chemistry, vol 52. Springer, Berlin Heidelberg Newyork, 1 and references therein
94. Chaudhuri RK, Freed KF (1996) J Chem Phys 107:6699 and references therein
95. Angeli C, Cimiraglia R, Malrieu JP (2002) J Chem Phys 117:9138
96. Buenker RJ, Peyerimhoff SD (1974) Theor Chim Acta 35:33
97. Siegbahn PEMJ (1980) Chem Phys 72:1674
98. Buenker RJ, Krebs S (1999) In: Hirao K (ed) Recent advances in multi-reference methods. World Scientific, Singapore and references therein
99. Ruttink PJA, van Lenthe JH, Zwaans R, Groenenboom GC (1991) J Chem Phys 94:7212
100. Szalay PG, Bartlett RJ (1995) J Chem Phys 103:3600
101. Fulde P, Stoll H (1992) J Chem Phys 97:4185
102. Fink R, Staemmler V (1993) Theor Chim Acta 87:129
103. Tanaka K, Sakai T, Mochizuki Y (1999) In: Hirao K (ed) Recent advances in multireference methods. World Scientific, Singapore
104. Tanaka K, Sakai T, Terashima H (1989) Theor Chim Acta 76:213
105. Sakai T, Tanaka K (1992) Theor Chim Acta 85:451
106. Jönsson B , Roos BO, Yalor PR, Siegbahn PEM (1981) J Chem Phys 74:4566
107. Liu S, Daskalakis MF, Dykstra CE (1986) J Chem Phys 85:5877
108. Ben-Shlomo S, Kaldor U (1988) J Chem Phys 89:956
109. Noga J, Tunega D, Kolpper W, Kutzelnigg W (1995) J Chem Phys 1003:309
110. Li X, Paldus J (2003) J Chem Phys 119:5346
111. Scuseria GE, Hamilton TP, Schaefer HF III (1990) J Chem Phys 92:568
112. www.emsl.pnl.gov/forms/basisform.html
113. Sears JS, Sherill CD, Krylov AI (2003) J Chem Phys 118:9084
114. Olsen J, Christiansen O, Koch H, Jørgensen P (1996) J Chem Phys 105:5082
115. Li X, Paldus J (1997) J Chem Phys 108:637
116. Müller H, Franke R, Vogtner S, Jaquet R, Kutzelingg W (1998) Theor Chem Acc 100:85
117. Rosta E, Surján P (2001) J Chem Phys 116:878
118. Abrams ML, Sherrill CD (2003) J Phys Chem A 107:5611
119. Hehre W, Ditchfield R, Pople J (1972) J Chem Phys 56:2257
120. Krylov AI, Sherill CD, Head-Gordon M (2000) J Chem Phys 113:6509