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The State-Universal Multi-Reference Coupled-Cluster Theory: An Overview of Some Recent Advances

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Abstract: Some recent advances in the area of multi-reference coupled-cluster theory of the state-universal type are overviewed. An emphasis is placed on the following new developments: (i) the idea of combining the state-universal multi-reference coupled-cluster singles and doubles method (SUMRCCSD) with the multi-reference many-body perturbation theory (MRMBPT), in which cluster amplitudes of the SUMRCCSD formalism that carry only core and virtual orbital indices are replaced by their first-order MRMBPT estimates; and (ii) the idea of combining the recently proposed method of moments of coupled-cluster equations with the SUMRCC formalism. It is demonstrated that the new SUMRCCSD(1) method, obtained by approximating the SUMRCCSD cluster amplitudes carrying only core and virtual orbital indices by their first-order MRMBPT values, provides the results that are comparable to those obtained with the complete SUMRCCSD approach.

Keywords: Coupled-cluster theory; Multi-reference formalism; State-universal multi-reference coupled-cluster method; Many-body perturbation theory; Method of moments of coupled-cluster equations

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1 Introduction

One of the most important problems in coupled-cluster (CC) theory [1–7] is extension of the standard single-reference CC approach to quasi-degenerate and excited electronic states. This can be accomplished by developing the multi-reference generalizations of the CC theory. In this paper, we focus on the *genuine* multi-reference CC (MRCC) theories, which are based on the concept of effective Hamiltonian acting in a multi-dimensional reference or model space [4, 6, 8–12] and which use the exponential CC ansatz to parametrize the solutions of the generalized Bloch equation [8]. The *state-specific* (SS) MRCC methods [4, 6], including the active-space CC approaches of Adamowicz, Piecuch, Bartlett, and their collaborators [13–26] and their more recent excited-state extensions [27–29], the SSMRCC approach of Mahapatra *et al.* [30, 31], and the highly promising Brillouin-Wigner MRCC approach [32–37], will not be discussed in this work, although the similarity of the wave function ansatz used in the genuine state-universal MRCC theory [4, 6, 38–59], considered in this paper, and the form of the wave function exploited by the SSMRCC and Brillouin-Wigner MRCC approaches of Refs. 30, 31 and 32–37, respectively, should be noted.

The genuine MRCC theories classify as either the Fock-space or valence-universal (VU) methods [4, 6, 60–99] or the Hilbert-space or state-universal (SU) approaches [4, 6, 38–59]. The VUMRCC methods, which require a simultaneous consideration of ground and excited states of a given many-electron system and its ions (different sectors of the Fock space), are excellent for describing vertical excitation energies, vertical ionization potentials, and vertical electron affinities. Unfortunately, the VUMRCC methods suffer from intruder states and unphysical multiple solutions [98, 99], which, together with the requirement of considering different sectors of the Fock space, make accurate VUMRCC calculations of larger portions of molecular potential energy surfaces (PESs) rather difficult. In spite of these formal and practical complications, the recent large scale applications of the VUMRCC methods to realistic atomic and molecular problems (see, e.g., Refs. 88–92, 94–97) and the interesting new ideas, such as the idea of exploiting similarity transformations to separate eigenvalue problems for different valence sectors of the Fock space [93] and the idea of using the VUMRCC concepts in the so-called similarity transformed equation-of-motion CC theory [100, 101], show a lot of promise.

The SUMRCC approaches, which do not require a consideration of different sectors of the Fock space, seem to be well suited for studies of molecular PESs. Indeed, as shown in Refs. 41, 43, 44, 46–50, 54, the PES and property function scans with the SUMRCC methods can be very successful and highly accurate results can be obtained. The SUMRCC method is also capable of providing an extremely accurate description of electronic energy separations in small molecular systems, as has been illustrated by the calculations of the singlet–triplet ($A\,^1A_1 - X\,^3B_1$) [51, 52]

and singlet–singlet ($2\ ^1A_1 - 1\ ^1A_1$; $1\ ^1A_1 \equiv A\ ^1A_1$) [50] energy gaps in methylene. For example, the orthogonally spin-adapted (OSA) [102–106] two-reference SUMRCCSD (SUMRCC singles and doubles) approach [39, 41, 45–50, 54] including all relevant direct and coupling terms [50], which contrary to the statements made in Ref. 107 represents the most complete formulation of this method to date, combined with the open-shell CCSD approach [108], gives 3133 cm^{-1} for the singlet–triplet separation T_0. This compares extremely well with the spectroscopically derived value of T_0 of 3147 ± 5 cm^{-1} [109]. There are open problems in the SUMRCC theory (cf. the remarks below), but this and other examples show that the SUMRCC theory is a highly promising formalism, which needs to be developed further. Unfortunately, apart from the earlier advances in formulating, implementing, and testing the spin-adapted and spin-orbital SUMRCCSD methods [4, 6, 38–56] and apart from the recent activity in our group (see, e.g., Refs. 57–59) and the group of Pal [110], who formulated the response SUMRCC theory, the development of the genuine SUMRCC method has practically stopped, which is a situation that this paper hopes to change (at least, to some extent).

There are several open problems in the SUMRCC theory that must be addressed if we wish this method to become a useful alternative for routine and accurate *ab initio* calculations of ground and excited-state molecular PESs. There are, for example, problems related to the existence of multiple [47, 57] and singular [41, 46–49, 57] solutions, intruder states [46, 47, 49, 57], and the existence of the so-called intruder solutions [57]. The latter solutions are related to a specific algebraic nature of the generalized Bloch equation, on which the SUMRCC theory is based [111]. The existence of multiple intruder solutions of the SUMRCCSD equations may cause severe convergence problems or, at the very least, a significant decrease in accuracy of the calculated electronic energies in regions of PESs where the electronic states of interest are no longer clearly separated from the rest of the electronic spectrum [47–49, 57]. There is also a long-standing problem of generalizing the existing two-reference OSA SUMRCCSD theory [39, 41, 45–50, 54] and its two electron/two orbital spin-orbital analog [43, 44] to larger reference spaces, which has not been solved yet in a satisfactory manner. Our recent studies of the solutions of the generalized Bloch equation [111] clearly demonstrate that the SUMRCC calculations would benefit from using larger reference spaces. Unfortunately, it is not easy to propose an efficient computational scheme that would allow us to perform routine SUMRCC calculations for larger reference or model spaces. Part of the problem is the fact that the wave function ansatz of Jeziorski and Monkhorst [38], on which all SUMRCC approaches are based, requires that a separate cluster operator $T^{(p)}$ is assigned to each reference configuration $|\Phi_p\rangle$ ($p = 1, \ldots, M$). Aside from various mathematical difficulties that this assumption creates, the requirement of having a separate cluster operator $T^{(p)}$ for each reference configuration $|\Phi_p\rangle$ leads to an excessively large number of cluster amplitudes when the dimension of model space (M) is large and when we are only interested in a few low-lying states.

The present paper reviews some of our recent work that addresses the above problems. It is evident from the results described in Ref. 48 and from the comments made in our recent work [111] that the inclusion of higher–than–doubly excited clusters in the SUMRCC formalism should help to eliminate at least some of the difficulties encountered in the SUMRCCSD calculations. The existence of multiple and pathological solutions of the SUMRCCSD equations is largely related to an asymmetric treatment of the excitation manifolds corresponding to different reference configurations and to a nonlinear nature of the generalized Bloch equation [57, 111], so that the standard corrections due to triply [53] and other higher–than–doubly excited clusters, based on the multi-reference many-body perturbation theory (MRMBPT) [112–114], do not eliminate these problems. As a matter of fact, the use of the standard, MRMBPT-based estimates of higher-order corrections within the SUMRCC formalism is a rather risky procedure, since the MRMBPT approach suffers from intruder states in regions where the SUMRCCSD approach fails. In our view, it is more important to examine first the mathematical relationship between the approximate and exact SUMRCC formalisms, so that one can suggest new ways of systematically correcting the results of the SUMRCC calculations, particularly in all these difficult cases where the conventional MRMBPT arguments fail. Clearly, it would be highly desirable to have a simple method of correcting the energies of electronic states obtained in the SUMRCC calculations in a state-specific and non-iterative manner that would resemble the well-known noniterative *a posteriori* corrections due to triples or triples and quadruples characterizing, for example, the popular CCSD(T) method [115] and its CCSD(TQ_f) analog [116].

We have recently suggested an approach, termed the *method of moments of the state-universal multi-reference coupled-cluster equations* (MM-SUMRCC), which provides us with simple recipes for systematically improving the SUMRCCSD results by adding the state-specific noniterative corrections due to triples and other higher–than–doubly excited clusters to the energies obtained by solving the SUMRCCSD equations [117]. The MM-SUMRCC approach differs from the standard multi-reference approaches in that, in computing the energy corrections due to higher-order clusters, in the MM-SUMRCC theory we rely on the explicit and rigorous relationship between the energies obtained in the SUMRCC (e.g., SUMRCCSD) calculations and the exact energy values. In the standard multi-reference methods, we can only hope that by adding sufficiently many higher-order terms to the equations representing low-order approaches, one obtains better results; the control over the choice of higher-order terms is limited by the fact that we use the MRMBPT or similar arguments, which may not be sufficiently transparent in situations where the MRMBPT approach suffers from intruder states. The MM-SUMRCC theory, which is a multi-reference analog of the recently developed method of moments of the single-reference [7, 118–121] and equation-of-motion [121–123] CC equations, is overviewed in this paper.

We also discuss the recently proposed SUMRCCSD(1) approach, which is based on the idea of combining the SUMRCCSD method with the MRMBPT approach [59]. In the SUMRCCSD(1) method, we approximate the doubly excited cluster amplitudes that carry only core and virtual orbital indices by their first-order MRMBPT estimates. In addition, we assume that the singly excited cluster amplitudes corresponding to core–virtual excitations vanish. As we discuss it in this paper, both assumptions lead to a completely symmetric treatment of the core–virtual cluster amplitudes of the SUMRCCSD theory, which in the SUMRCCSD(1) method no longer depend on the reference label p. The more symmetric treatment of the excitation manifolds corresponding to different reference configurations in the SUMRCCSD(1) method may have a positive effect on the calculated energies, while offering us considerable savings in the computer effort. In the SUMRCCSD theory, each individual core–virtual excitation is represented by as many independent cluster amplitudes as the number of reference configurations, although in the intuitive description we would only use as many independent cluster amplitudes for a given core–virtual excitation as the number of electronic states of interest. In the SUMRCCSD(1) method, we simplify this situation to the utmost by replacing many sets of cluster amplitudes carrying core and virtual orbital indices, each labeled by the corresponding reference label p, by a single set. Moreover, instead of solving for cluster amplitudes carrying only core and virtual indices, in the SUMRCCSD(1) approach we approximate them by the simple first-order MRMBPT expressions. This leads to additional savings in the computer effort. Since core–virtual excitations are known to be rather insensitive to nuclear geometry [124], the molecular PESs resulting from the SUMRCCSD(1) calculations should be virtually parallel to the SUMRCCSD PESs.

Whenever possible, we illustrate our new ideas with the examples of numerical calculations. Some examples are taken from our recent work [59], while some other examples are new. We hope that this overview of our recent efforts in the area of MRCC theory will stimulate further activity aimed at the development of accurate and practical genuine MRCC methods of the state-universal type that may one day be used in routine *ab initio* calculations.

2 The State-Universal Multi-Reference Coupled-Cluster Theory

As mentioned in the Introduction, the SUMRCC theory belongs to a wider category of methods which are referred to as the genuine MRCC approaches. All genuine MRCC methods involve three basic concepts, namely, that of the multi-dimensional *model* or *reference* space $\mathcal{M}_0$, that of the *wave operator* U, and that of the *effective Hamiltonian* $H^{\rm eff}$ [4, 6]. Alternative formulations of genuine multi-reference methods, in which the effective Hamiltonians are obtained by similarity transformations of the Hamiltonian (this frees us from the necessity of solving for the wave operator) can be developed [93, 125] (cf., also, Refs. 9, 10, 40), but we do not use them here, since the

SUMRCC theory of Jeziorski and Monkhorst [38] is based on the exponential parameterization of the wave operator and solving the generalized Bloch equation for the wave operator represented by the Jeziorski-Monkhorst ansatz.

The model space $\mathcal{M}_0$,

$$\mathcal{M}_0 = ls\{|\Phi_p\rangle\}_{p=1}^{M} \ , \tag{1}$$

is spanned by a suitably chosen set of M configuration state functions $|\Phi_p\rangle$, $p = 1, \ldots, M$, that provide a reasonable zero-order description of the *target space*,

$$\mathcal{M} = ls\{|\Psi_\mu\rangle\}_{\mu=1}^{M} \ , \tag{2}$$

spanned by M quasi-degenerate eigenstates $|\Psi_\mu\rangle$, $\mu = 1, \ldots, M$, of the electronic Hamiltonian H. The wave operator $U : \mathcal{M}_0 \to \mathcal{M}$ is defined as a one–to–one mapping between $\mathcal{M}_0$ and $\mathcal{M}$. It is usually assumed that U satisfies the *intermediate normalization* condition,

$$PU = P, \tag{3}$$

where P is the projection operator onto $\mathcal{M}_0$,

$$P = \sum_{p=1}^{M} P^{(p)} \ , \quad P^{(p)} = |\Phi_p\rangle\langle\Phi_p|. \tag{4}$$

It is also assumed that U annihilates states belonging to the orthogonal complement $\mathcal{M}_0^{\perp}$, so that

$$UQ = 0, \tag{5}$$

where

$$Q = 1 - P. \tag{6}$$

Equations (3) and (5) immediately imply that $U^2 = U$, so that the wave operator U, just like operators P and Q, is idempotent. However, unlike P and Q, the wave operator U is not Hermitian, $U \neq U^\dagger$.

The wave operator U is obtained by solving the equation,

$$HU = UHU, \tag{7}$$

which is known in the literature as the *generalized Bloch equation* [4, 6, 8–10, 78]. Once the wave operator is determined, the energies E_μ of the electronic states $|\Psi_\mu\rangle$, $\mu = 1, \ldots, M$, are obtained by diagonalizing the effective Hamiltonian,

$$H^{\text{eff}} \equiv H^{\text{eff}}(U) = PHU = PHUP, \tag{8}$$

within $\mathcal{M}_0$. The corresponding wave functions $|\Psi_\mu\rangle$ are calculated using the formula,

$$|\Psi_\mu\rangle = U|\chi_\mu\rangle \quad (\mu = 1, \ldots, M), \tag{9}$$

where the zero-order states,

$$|\chi_\mu\rangle \equiv P|\Psi_\mu\rangle \in \mathcal{M}_0, \tag{10}$$

are the right eigenstates of H^{eff},

$$H^{\text{eff}}|\chi_\mu\rangle = E_\mu|\chi_\mu\rangle \quad (\mu = 1, \ldots, M). \tag{11}$$

In the SUMRCC formalism, we use the Jeziorski-Monkhorst ansatz for the wave operator U, i.e. [38],

$$U = \sum_{p=1}^{M} e^{T^{(p)}} P^{(p)}, \tag{12}$$

where $T^{(p)}$ is the cluster operator corresponding to reference configuration $|\Phi_p\rangle$. The intermediate normalization condition, Eq. (3), requires that each $T^{(p)}$ generates states belonging to $\mathcal{M}_0^\perp$, when acting on the corresponding $|\Phi_p\rangle$. The wave operator U, Eq. (12), reduces to the well-known wave operator of the single-reference CC theory, $U^{\text{SRCC}} = e^T|\Phi\rangle\langle\Phi|$, when model space $\mathcal{M}_0$ is a one-dimensional space spanned by a single reference configuration $|\Phi\rangle$.

In order to define the remaining elements of the SUMRCC theory, we must specify the method of constructing the model space $\mathcal{M}_0$ and cluster operators $T^{(p)}$. As in all multi-reference *ab initio* methods, in order to define the reference configurations $|\Phi_p\rangle$, we divide all molecular spin-orbitals into the three disjoint subsets of *core, active*, and *virtual* spin-orbitals. The core spin-orbitals (designated by $\mathbf{i}, \mathbf{j}, \ldots$) are occupied and the virtual ones (designated by $\mathbf{a}, \mathbf{b}, \ldots$) are unoccupied in all reference configurations $|\Phi_p\rangle$, $p = 1, \ldots, M$. The reference configurations differ in the occupancies of active spin-orbitals (designated by $\mathbf{I}, \mathbf{J}, \ldots$, for spin-orbitals occupied in a given reference determinant $|\Phi_p\rangle$, and by $\mathbf{A}, \mathbf{B}, \ldots$, for spin-orbitals unoccupied in this $|\Phi_p\rangle$). All possible distributions of active electrons among active spin-orbitals result in a *complete model* (or active) *space* (CAS). The use of CAS is essential to obtain size extensive results [38], although it is possible to formulate the size extensive SUMRCC method employing incomplete model spaces by relaxing the intermediate normalization condition [126, 127]. In this paper, we consider the CAS formulation of the SUMRCC theory.

In analogy to the standard single-reference CC theory, each cluster operator $T^{(p)}$ is a sum of its many-body components $T_n^{(p)}$. In the exact SUMRCC formalism,

$$T^{(p)} = \sum_{m=1}^{N} T_m^{(p)}, \tag{13}$$

where N is the number of electrons in a system under consideration. In the standard SUMRCC approximations, the many-body expansion of each cluster operator $T^{(p)}$ is truncated at some (usually low) excitation level. Thus, if m_A is the excitation level defining a given standard SUMRCC approximation, referred here and elsewhere in this work to as method A, the corresponding cluster operators $T^{(p)}$ have the following form:

$$T_A^{(p)} = \sum_{m=1}^{m_A} T_m^{(p)}. \tag{14}$$

Note that the value of m_A is the same for all values of p. The SUMRCCSD method is obtained by setting $m_A = 2$.

In a conventional SUMRCC theory of Jeziorski and Monkhorst [38], the system of coupled nonlinear equations for the unknown cluster operators $T_m^{(p)}$ is obtained by replacing Eq. (7) by the equation $HU|\Phi_p\rangle = UHU|\Phi_p\rangle$, where U is defined by Eq. (12), premultiplying this equation on the left by $e^{-T^{(p)}}$, and projecting the resulting equation on the excited configurations relative to $|\Phi_p\rangle$ belonging to $\mathcal{M}_0^{\perp}$. The final equations for cluster operators $T_m^{(p)}$ defining the exact SUMRCC theory can be written as follows:

$$\Lambda_d^{(p)}((^{(p)}E_K)^\dagger) = \Lambda_c^{(p)}((^{(p)}E_K)^\dagger) \quad (p = 1, \ldots, M)\,, \tag{15}$$

where the left-hand side *direct term* is defined as

$$\Lambda_d^{(p)}((^{(p)}E_K)^\dagger) \equiv \langle\Phi_p|(^{(p)}E_K)^\dagger\,(e^{-T^{(p)}}He^{T^{(p)}})|\Phi_p\rangle \quad (p = 1, \ldots, M)\,, \tag{16}$$

and the right-hand side *coupling term*, which reflects the multi-reference nature of the SUMRCC theory, takes the form

$$\Lambda_c^{(p)}((^{(p)}E_K)^\dagger) \equiv \sum_{q=1(q\neq p)}^{M} \langle\Phi_p|(^{(p)}E_K)^\dagger\,(e^{-T^{(p)}}e^{T^{(q)}})|\Phi_q\rangle\, H_{qp}^{\mathrm{eff}} \quad (p = 1, \ldots, M). \tag{17}$$

The operators $^{(p)}E_K$ are the excitation operators, generating the excited configurations relative to $|\Phi_p\rangle$ belonging to $\mathcal{M}_0^{\perp}$, when acting on $|\Phi_p\rangle$. These operators are also used to represent cluster operators $T^{(p)}$,

$$T^{(p)} = \sum_K {}^{(p)}t_K\, {}^{(p)}E_K, \tag{18}$$

where coefficients $^{(p)}t_K$ are the corresponding cluster amplitudes. Because of this representation, the system of equations, Eq. (15), represents a system of *coupled nonlinear algebraic equations* for cluster amplitudes $^{(p)}t_K$. For the complete model space $\mathcal{M}_0$, the excitation operators $^{(p)}E_K$ and cluster amplitudes $^{(p)}t_K$ carry at least one inactive (i.e., core or virtual) spin-orbital index [38].

The $H^{\rm eff}_{qp}$ quantities entering the coupling term $\Lambda^{(p)}_c(({}^{(p)}E_K)^\dagger)$, Eq. (17), are the matrix elements of the SUMRCC effective Hamiltonian,

$$H^{\rm eff}_{pq} = \langle\Phi_p|H^{\rm eff}|\Phi_q\rangle = \langle\Phi_p|HU|\Phi_q\rangle = \langle\Phi_p|e^{-T^{(q)}}He^{T^{(q)}}|\Phi_q\rangle. \tag{19}$$

Once the system of equations, Eq. (15), is solved and matrix elements of the effective Hamiltonian are constructed, we calculate the final SUMRCC energies E_μ and the corresponding zero-order states $|\chi_\mu\rangle$, $\mu = 1,\ldots,M$, by diagonalizing the effective Hamiltonian matrix in model space $\mathcal{M}_0$, as described above [cf. Eq. (11)]. The SUMRCC wave functions $|\Psi_\mu\rangle$ are obtained by applying the wave operator U, Eq. (12), to zero-order states $|\chi_\mu\rangle$. We obtain [cf. Eqs. (9) and (12)],

$$|\Psi_\mu\rangle = \sum_{p=1}^{M} c_{p\mu}\, e^{T^{(p)}}|\Phi_p\rangle \quad (\mu = 1,\ldots,M), \tag{20}$$

where coefficients

$$c_{p\mu} = \langle\Phi_p|\chi_\mu\rangle \tag{21}$$

are determined by solving an eigenvalue problem involving $H^{\rm eff}$ in $\mathcal{M}_0$, Eq. (11).

The above equations defining the exact SUMRCC theory, particularly Eqs. (15)–(17) and (19), can be rewritten in a somewhat more symbolic form, namely,

$$P[(He^{T^{(p)}})_C - H^{\rm eff}]|\Phi_p\rangle = 0 \qquad (p = 1,\ldots,M), \tag{22}$$

$$Q^{(p)}[(He^{T^{(p)}})_C - \sum_{q=1(q\neq p)}^{M} e^{-T^{(p)}}e^{T^{(q)}}P^{(q)}H^{\rm eff}]|\Phi_p\rangle = 0 \;\; (p = 1,\ldots,M), \tag{23}$$

where subscript C designates the connected part of the corresponding operator expression. In deriving Eqs. (22) and (23), we used the well-known fact that [4, 6, 7]

$$e^{-T^{(p)}}He^{T^{(p)}}|\Phi_p\rangle = (He^{T^{(p)}})_C|\Phi_p\rangle. \tag{24}$$

Operator P appearing in Eq. (22) is the projection operator onto $\mathcal{M}_0$ defined by Eq. (4), whereas operators $Q^{(p)}$ appearing in Eq. (23) are the projection operators onto the manifolds of excited configurations relative to $|\Phi_p\rangle$ belonging to $\mathcal{M}_0^\perp$ that are generated by excitation operators ${}^{(p)}E_K$. If $Q^{(p)}_n$ designates a projection operator onto the subspace of $\mathcal{M}_0^{\perp(p)} \equiv Q^{(p)}\mathcal{M}_0^\perp$ spanned by the n-tuply excited configurations relative to $|\Phi_p\rangle$ that belong to $\mathcal{M}_0^\perp$, we can write

$$Q^{(p)} = \sum_{n=1}^{N} Q^{(p)}_n. \tag{25}$$

In the exact theory, all manifolds of excitations $\mathcal{M}_0^{\perp(p)}$, used to define cluster operators $T^{(p)}$, are identical, i.e., $\mathcal{M}_0^{\perp(p)} = \mathcal{M}_0^{\perp}$ for all $p = 1, \ldots, M$. This is a consequence of the fact that

$$\sum_{n=1}^{N} Q_n^{(p)} \equiv Q^{(p)} = Q, \tag{26}$$

independent of the value of p. Because of this symmetric treatment of the manifolds of excitations corresponding to different references $|\Phi_p\rangle$, the exact SUMRCC method is completely equivalent to an eigenvalue problem for eigenstates $|\Psi_\mu\rangle$, $\mu = 1, \ldots, M$ [111] (see, also, Ref. 117). This is no longer the case, when cluster operators $T^{(p)}$ are truncated in a standard manner according to Eq. (14). Indeed, in the standard SUMRCC approximations, the system of equations (22) and (23) is replaced by a truncated system of equations for the many-body components $T_m^{(p)}$ of cluster operators $T_A^{(p)}$, namely,

$$P[(He^{T_A^{(p)}})_C - H_A^{\mathrm{eff}}]|\Phi_p\rangle = 0 \quad (p = 1, \ldots, M), \tag{27}$$

$$Q_A^{(p)}[(He^{T_A^{(p)}})_C - \sum_{q=1(q\neq p)}^{M} e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H_A^{\mathrm{eff}}]|\Phi_p\rangle = 0 \;\; (p = 1, \ldots, M), \tag{28}$$

where operators $T_A^{(p)}$ are defined by Eq. (14), H_A^{eff} is the effective Hamiltonian of the approximate SUMRCC method A, and $Q_A^{(p)}$ is a projection operator onto the excited configurations used to define $T_A^{(p)}$, i.e.,

$$Q_A^{(p)} = \sum_{n=1}^{m_A} Q_n^{(p)}. \tag{29}$$

The manifolds of excitations $\mathcal{M}_{0,A}^{\perp(p)} \equiv Q_A^{(p)}\mathcal{M}_0^{\perp} \subset \mathcal{M}_0^{\perp}$, used to define the truncated cluster operators $T_A^{(p)}$, are usually different for different reference configurations $|\Phi_p\rangle$ (cf., e.g., the lists of excitations ${}^{(p)}E_K$, corresponding to different references $|\Phi_p\rangle$ of the OSA SUMRCCSD formalism of Refs. 39, 41, 45–50, 54, given in Ref. 47). As pointed out in Ref. 111, this asymmetric treatment of the manifolds of excitations corresponding to different reference configurations causes that the approximate SUMRCC schemes based on Eqs. (27) and (28) (including the existing SUMRCCSD methods) are not equivalent to any Hermitian eigenvalue problem. This significant distortion of the exact SUMRCC theory, resulting from the truncation of the many-body expansions of all operators $T^{(p)}$ at the same excitation level m_A, leads to a number of pathologies in approximate SUMRCC calculations based on Eqs. (27) and (28). These pathologies include the existence of an excessive number of real and complex solutions that lack physical interpretation and the appearance of the intruder solution problem [57]. The multi-reference extension of the MMCC theory, which we recently suggested in Ref. 117, and which we overview in the next section, offers a possibility of reducing the severity of problems encountered in the standard SUMRCC (e.g.,

SUMRCCSD) calculations by incorporating higher-order effects in the SUMRCC formalism and by reinforcing the symmetric treatment of the $\mathcal{M}_{0,A}^{\perp(p)}$ subspaces.

3 A New Type of the Noniterative Corrections to Multi-Reference Coupled-Cluster Energies: The Method of Moments of the State-Universal Multi-Reference Coupled-Cluster Equations

As mentioned in the Introduction, inclusion of higher–than–doubly excited clusters in the SUMRCC formalism should help to eliminate some pathologies that are encountered in the SUMRCCSD calculations. Although one can suggest ways of improving the SUMRCCSD results by adding the corrections due to triply excited clusters based on the standard MRMBPT theory [53], the use of the MRMBPT arguments in constructing such corrections may, in general, be a risky procedure, since the MRMBPT approach is often plagued by intruder states. Undoubtedly, it would be useful to have an alternative method of correcting the SUMRCCSD results, which does not necessarily rely on the standard MRMBPT arguments.

We have recently introduced a new, nonstandard method of correcting the results of various CC calculations, termed the method of moments of coupled-cluster equations (MMCC) [7, 117–123]. The main idea of the MMCC formalism is that of the noniterative energy corrections which, when added to the energies obtained in approximate CC or equation-of-motion CC (EOMCC) [128–130] calculations, such as CCSD or EOMCCSD, recover the exact (full configuration interaction or full CI) energies of ground or excited states. It has been demonstrated that the MMCC formalism allows us to *renormalize* the existing noniterative single-reference CC approximations, such as CCSD(T) [115], CCSD(TQ$_{\rm f}$) [116], and CCSDT(Q$_{\rm f}$) [116], so that they can correctly describe entire ground-state PESs in situations where the standard arguments based on MBPT, on which the CCSD(T), CCSD(TQ$_{\rm f}$), and similar approximations are based, completely fail [7, 26, 117–121, 131–133] (cf., also, Ref. 134 for a rederivation of the renormalized CCSD(T) expressions, published one year earlier in Refs. 7, 118, 119, and for some additional tests). It has also been demonstrated that the EOMCC-based excited-state MMCC theory allows us to introduce a new hierarchy of simple noniterative EOMCC approximations that remove the pervasive failing of the EOMCCSD and perturbative EOMCCSDT approximations in describing excited-state PESs [122, 123]. Clearly, the MMCC methodology provides us with new ways of systematically improving the CC or EOMCC results by adding simple noniterative corrections to the CC or EOMCC energies. Thus, it might be useful to investigate the possibility of extending the MMCC formalism to a multi-reference case.

Encouraged by the remarkable performance of the single-reference MMCC approximations, we have recently generalized the MMCC formalism to a multi-reference case by proposing the method

of moments of the state-universal multi-reference coupled-cluster equations (MM-SUMRCC) [117]. The main idea of the MM-SUMRCC theory is that of the noniterative, state-specific energy corrections

$$\delta_\mu = E_\mu - E_\mu^A \quad (\mu = 1, \ldots, M), \tag{30}$$

which, when added to energies E_μ^A, obtained by solving the approximate SUMRCC (e.g., SUMR-CCSD) equations, recover the exact (full CI) energies E_μ of the electronic states of interest. The main purpose of the approximate MM-SUMRCC calculations is to estimate corrections δ_μ, so that the resulting energies $E_\mu^A + \delta_\mu$ remain very close to the corresponding exact energies E_μ.

Each correction δ_μ is a nontrivial functional of the corresponding exact electronic wave function $|\Psi_\mu\rangle$ and the *generalized moments of the SUMRCC equations*, i.e., the SUMRCC equations projected on the excited configurations whose excitation level exceeds that defining a given SUMRCC approximation. The precise mathematical definition of the generalized moments of the SUMRCC equations, which is consistent with Eq. (28) and which is used in the MM-SUMRCC formalism of Ref. 117, is as follows:

$$\begin{aligned}\Gamma_m^{(p)}(m_A)|\Phi_p\rangle &= Q_m^{(p)}[(He^{T_A^{(p)}})_C - \sum_{q=1(q\neq p)}^{M} e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H_A^{\rm eff}]|\Phi_p\rangle \equiv [(He^{T_A^{(p)}})_C \\ &\quad - \sum_{q=1(q\neq p)}^{M} e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H_A^{\rm eff}]_m|\Phi_p\rangle \quad (m = 1, \ldots, N\,;\ p = 1, \ldots, M),\end{aligned} \tag{31}$$

where $[\ldots]_m$ designates the m-body component of the corresponding operator expression. The generalized moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, Eq. (31), can be viewed as the most fundamental quantities of the Jeziorski-Monkhorst theory, as defined by Eqs. (27) and (28), since the system of equations for the many-body components of cluster operators $T_A^{(p)}$, $p = 1, \ldots, M$, Eq. (28), is immediately obtained by imposing a requirement that the lowest moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, with $m = 1, \ldots, m_A$, vanish, i.e.,

$$\Gamma_m^{(p)}(m_A)|\Phi_p\rangle = 0 \quad (m = 1, \ldots, m_A;\ p = 1, \ldots, M)\ . \tag{32}$$

The generalized moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, which enter the formula for the noniterative corrections δ_μ, Eq. (30), are those with $m > m_A$. As shown in Ref. 117, the explicit formula for corrections δ_μ, in terms of moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, is as follows:

$$\delta_\mu = E_\mu - E_\mu^A = (d_\mu^A)^{-1} \sum_{p=1}^{M} c_{p\mu}^A \sum_{n=m_A+1}^{N} \sum_{m=m_A+1}^{n} \langle\Psi_\mu|(e^{T_A^{(p)}})_{n-m}\, \Gamma_m^{(p)}(m_A)|\Phi_p\rangle, \tag{33}$$

where $c_{p\mu}^A = \langle\Phi_p|\chi_\mu^A\rangle$ are the coefficients defining the model-space states

$$|\chi_\mu^A\rangle = \sum_{p=1}^{M} c_{p\mu}^A |\Phi_p\rangle, \tag{34}$$

obtained by diagonalizing the effective Hamiltonian of the approximate SUMRCC method A in $\mathcal{M}_0$,

$$d_\mu^A = \langle \Psi_\mu | \Psi_\mu^{\text{SUMRCC-}A} \rangle \tag{35}$$

is an overlap of the exact wave function $|\Psi_\mu\rangle$ and the SUMRCC wave function

$$|\Psi_\mu^{\text{SUMRCC-}A}\rangle = \sum_{p=1}^{M} c_{p\mu}^A \, e^{T_A^{(p)}} |\Phi_p\rangle, \tag{36}$$

obtained with method A, and $(e^{T_A^{(p)}})_{n-m}$ is the $(n-m)$-body component of $e^{T_A^{(p)}}$.

The derivation of Eq. (33) is based on considering the energy functional

$$\Lambda[\Psi,\chi] = \langle \Psi | (HU_A - U_A H U_A) | \chi \rangle / \langle \Psi | U_A | \chi \rangle = \langle \Psi | (HU_A - U_A H_A^{\text{eff}}) | \chi \rangle / \langle \Psi | U_A | \chi \rangle, \tag{37}$$

where [cf. Eq. (12)]

$$U_A = \sum_{p=1}^{M} e^{T_A^{(p)}} P^{(p)} \tag{38}$$

is an approximate wave operator obtained by solving the SUMRCC equations of method A, $|\chi\rangle$ is a state belonging to $\mathcal{M}_0$, and $|\Psi\rangle$ is an N-electron wave function. For $|\Psi\rangle = |\Psi_\mu\rangle$ and for $|\chi\rangle$ equal to the corresponding eigenstate $|\chi_\mu^A\rangle$ of the effective Hamiltonian H_A^{eff}, we immediately obtain

$$\Lambda[\Psi_\mu, \chi_\mu^A] = E_\mu - E_\mu^A \equiv \delta_\mu. \tag{39}$$

The derivation of Eq. (33) proceeds as follows: First, we show the following general relationship [117]:

$$\Lambda[\Psi,\chi] = \sum_{p=1}^{M} \sum_{n=1}^{N} \langle \Psi | M_n^{(p)}(m_A) | \Phi_p \rangle \langle \Phi_p | \chi \rangle / \langle \Psi | U_A | \chi \rangle, \tag{40}$$

where

$$M_n^{(p)}(m_A) | \Phi_p \rangle = Q_n^{(p)} (HU_A - U_A H_A^{\text{eff}}) | \Phi_p \rangle. \tag{41}$$

Next, we prove that quantities $M_n^{(p)}(m_A)|\Phi_p\rangle$ can be expressed in terms of the SUMRCC moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$,

$$M_n^{(p)}(m_A) | \Phi_p \rangle = \sum_{m=1}^{n} (e^{T_A^{(p)}})_{n-m} \, \Gamma_m^{(p)}(m_A) | \Phi_p \rangle. \tag{42}$$

The substitution of Eq. (42) into Eq. (40) and the use of the fact that in method A the lowest moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, with $m = 1, \ldots, m_A$, vanish [cf. Eq. (32)] allow us to write

$$\Lambda[\Psi,\chi] = \sum_{p=1}^{M} \sum_{n=m_A+1}^{N} \sum_{m=m_A+1}^{n} \langle \Psi | (e^{T_A^{(p)}})_{n-m} \, \Gamma_m^{(p)}(m_A) | \Phi_p \rangle \langle \Phi_p | \chi \rangle / \langle \Psi | U_A | \chi \rangle. \tag{43}$$

By setting $|\Psi\rangle = |\Psi_\mu\rangle$ and $|\chi\rangle = |\chi_\mu^A\rangle$ in Eq. (43) and using Eqs. (38) and (39), we obtain the desired Eq. (33).

Equation (33) is the basic equation of the MM-SUMRCC theory. We can use it to improve the results of approximate SUMRCC calculations in the following way: First, we solve the equations of a given SUMRCC method, Eqs. (27) and (28), to determine the cluster operators, $T_A^{(p)}$, $p = 1, \ldots, M$, and the corresponding effective Hamiltonian, $H_A^{\rm eff}$. Next, we construct the generalized moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ with $m > m_A$ using Eq. (31). Finally, we use cluster operators $T_A^{(p)}$, generalized moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, and the right eigenvectors of $H_A^{\rm eff}$, i.e., $\boldsymbol{c}_\mu^A = (c_{1\mu}^A, \ldots, c_{M\mu}^A)$, to calculate corrections δ_μ with the help of Eq. (33).

We should also note the formal similarity of Eq. (33) and the single-reference MMCC energy formula discussed in Refs. 7, 118, 119 (for a review, see Ref. 121). Indeed, in the single-reference ($M = 1$) case, the d_μ^A denominator term in Eq. (33) reduces to $\langle\Psi_\mu|e^{T_A^{(1)}}|\Phi_1\rangle$, since the model-space state $|\chi_\mu^A\rangle$ becomes proportional to the reference configuration $|\Phi_1\rangle$. In addition, when $M = 1$, the generalized moments of the SUMRCC equations, Eq. (31), reduce to the generalized moments of the single-reference CC equations defined in Refs. 7, 118, 119. We obtain [cf. Eq. (31)],

$$\Gamma_m^{(1)}(m_A)|\Phi_1\rangle = Q_m^{(1)}(He^{T_A^{(1)}})_C|\Phi_1\rangle \equiv M_m(m_A)|\Phi_1\rangle, \tag{44}$$

where $M_m(m_A)|\Phi_1\rangle$ are the generalized moments of the single-reference CC equations. The substitution of Eq. (44) into the $M = 1$ variant of Eq. (33) leads to the following result:

$$\delta_\mu = \sum_{n=m_A+1}^{N} \sum_{m=m_A+1}^{n} \langle\Psi_\mu|(e^{T_A^{(1)}})_{n-m}\, M_m(m_A)|\Phi_1\rangle / \langle\Psi_\mu|e^{T_A^{(1)}}|\Phi_1\rangle, \tag{45}$$

which clearly is the single-reference MMCC energy formula, provided that we identify $T_A^{(1)}$ and $|\Phi_1\rangle$ with, respectively, the cluster operator and the reference configuration of the standard single-reference CC method.

The exact form of Eq. (33) cannot be used in practical calculations, since we usually do not know the exact (full CI) wave functions $|\Psi_\mu\rangle$, $\mu = 1, \ldots, M$. However, we can calculate the approximate values of corrections δ_μ which, when added to the SUMRCC energies E_μ^A, may give very good estimates of the exact energies E_μ, if we use simple estimates of wave functions $|\Psi_\mu\rangle$, provided by one of the relatively inexpensive *ab initio* methods. Independent of the approximate form of $|\Psi_\mu\rangle$ chosen for such calculations, corrections δ_μ can be calculated in a state-specific manner. Our belief that simple estimates of wave functions $|\Psi_\mu\rangle$ may be sufficient to obtain accurate δ_μ values is based on the success of the single-reference MMCC methods and their renormalized CC analogs [7, 26, 117–123, 131–134], in which simple perturbative or CI wave functions are used to construct the relevant energy corrections.

For example, we can use wave functions $|\Psi_\mu\rangle$ obtained in truncated multi-reference CI (MRCI) calculations (using, e.g., the popular MRCISD method or one of its approximate variants) and use the resulting corrections δ_μ to improve the results of the SUMRCCSD calculations (the $m_A = 2$ case). We can also think of using the CISDt or CISDtq [7, 120, 122, 123] approaches, in which triply and quadruply excited configurations of the single-reference CI method are selected via active orbitals, to construct wave functions $|\Psi_\mu\rangle$ in Eq. (33). In either case, we should be able to significantly improve the quality of the SUMRCCSD results and reinforce a fully symmetric treatment of the manifolds of excitations corresponding to different reference configurations, which is broken by the SUMRCCSD and other SUMRCC approximations. Indeed, when $m_A < N$, the $\mathcal{M}_{0,A}^{\perp(p)} = Q_A^{(p)}\mathcal{M}_0^\perp \subset \mathcal{M}_0^\perp$ subspaces spanned by the excited configurations relative to $|\Phi_p\rangle$ are usually different for different p values. As mentioned earlier, this asymmetric treatment of manifolds of excitations corresponding to different references $|\Phi_p\rangle$ causes that the conventional SUMRCC approaches based on Eqs. (27) and (28) are not equivalent to any Hermitian eigenvalue problem which, in turn, leads to various problems in SUMRCC calculations. However, if we do not truncate the summations over n and m in Eq. (33) in any arbitrary manner and if we simply let the projection onto a suitably chosen approximate wave function $|\Psi_\mu\rangle$ select terms in the summations over p, n, and m in the numerator of Eq. (33), we will obtain a fully symmetric treatment of the $\mathcal{M}_{0,A}^{\perp(p)}$ subspaces corresponding to different references $|\Phi_p\rangle$. In order for this scheme to work, we only have to assume that the CI expansions of wave functions $|\Psi_\mu\rangle$ contain some $\mathcal{M}_0^\perp$ configurations whose excitation level relative to at least one of the M references $|\Phi_p\rangle$ exceeds m_A. This is certainly true for the MRCISD wave functions and their CISDt and CISDtq analogs if we are interested in correcting the SUMRCCSD results. The projection onto $|\Psi_\mu\rangle$ in the numerator of Eq. (33) will select precisely those subsets of the generalized moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ (usually, different subsets of $\Gamma^{(p)}$'s for different values of p) that are needed to restore a symmetric treatment of the manifolds of excitations in the approximate SUMRCC (e.g., SUMRCCSD) calculations. Although this particular way of improving the SUMRCCSD results by using the MRCISD, CISDt, or CISDtq wave functions $|\Psi_\mu\rangle$ in Eq. (33) has not been tested yet in actual numerical calculations, we believe that we should be able to obtain significant improvements in the calculated SUMRCC energies, particularly in regions plagued by intruder states or intruder solutions, where there is an apparent need to incorporate higher–than–doubly excited clusters and have a more symmetric treatment of the $\mathcal{M}_{0,A}^{\perp(p)}$ subspaces in the SUMRCC calculations.

We can also contemplate other ways of using Eq. (33). We can, for example, introduce the multi-reference analogs of the MMCC(m_A, m_B) approximations suggested in Refs. 7, 118, 119 (see, also, Refs. 120–123). The multi-reference MMCC(m_A, m_B) approximations [referred to as the MM-SUMRCC(m_A, m_B) or MM-SUCC(m_A, m_B) schemes] are obtained by truncating the summation over n in Eq. (33) at $n = m_B$, where $m_A < m_B < N$. The multi-reference MMCC(m_A, m_B)

energy formula can be given the following form [117]:

$$E_\mu(m_A, m_B) = E_\mu^A + \delta_\mu(m_A, m_B), \tag{46}$$

where

$$\delta_\mu(m_A, m_B) = (d_\mu^A)^{-1} \sum_{p=1}^{M} c_{p\mu}^A \sum_{n=m_A+1}^{m_B} \sum_{m=m_A+1}^{n} \langle \Psi_\mu | (e^{T_A^{(p)}})_{n-m} \, \Gamma_m^{(p)}(m_A) | \Phi_p \rangle. \tag{47}$$

As implied by Eq. (46), the MM-SUCC(m_A, m_B) method uses moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ with $m = m_A + 1, \ldots, m_B$. For typical applications of Eq. (46) (e.g., $m_A = 2$ and $m_B = 3$ or 4), the $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ moments with $m = m_A + 1, \ldots, m_B$ form a small subset of all $\Gamma^{(p)}$'s.

The simplest example of the MM-SUCC(m_A, m_B) approximation is the MM-SUCC(2,3) scheme, in which we use Eq. (46) to correct the results of the SUMRCCSD calculations (the $m_A = 2$ case). In this case, the only generalized moments of the SUMRCC equations that need to be considered are the $\Gamma_3^{(p)}(2)|\Phi_p\rangle$ moments. The MM-SUCC(2,3) energy expression is [117]

$$E_\mu(2,3) = E_\mu^A + \delta_\mu(2,3), \tag{48}$$

where

$$\delta_\mu(2,3) = (d_\mu^{\mathrm{SUMRCCSD}})^{-1} \sum_{p=1}^{M} c_{p\mu}^{\mathrm{SUMRCCSD}} \langle \Psi_\mu | \Gamma_3^{(p)}(2) | \Phi_p \rangle, \tag{49}$$

with

$$d_\mu^{\mathrm{SUMRCCSD}} = \langle \Psi_\mu | \Psi_\mu^{\mathrm{SUMRCCSD}} \rangle \tag{50}$$

representing an overlap of the "trial" wave function $|\Psi_\mu\rangle$ and the SUMRCCSD wave function [cf. Eq. (36)]

$$|\Psi_\mu^{\mathrm{SUMRCCSD}}\rangle = \sum_{p=1}^{M} c_{p\mu}^{\mathrm{SUMRCCSD}} e^{T_1^{(p)} + T_2^{(p)}} |\Phi_p\rangle. \tag{51}$$

The coefficients $c_{p\mu}^{\mathrm{SUMRCCSD}}$, $p = 1, \ldots, M$, are the components of the right eigenvector of the SUMRCCSD effective Hamiltonian, whose matrix elements, designated here by $H_{qp}^{\mathrm{eff}}(2)$, are defined as follows [cf. Eqs. (19) and (24)]:

$$H_{qp}^{\mathrm{eff}}(2) = \langle \Phi_q | (H e^{T_1^{(p)} + T_2^{(p)}})_C | \Phi_p \rangle, \tag{52}$$

where $T_1^{(p)}$ and $T_2^{(p)}$ are the singly and doubly excited clusters of the SUMRCCSD approach. The $\Gamma_3^{(p)}(2)|\Phi_p\rangle$ moments that appear in Eq. (49) can be expressed in terms of the projections of the SUMRCCSD equations on the triply excited configurations relative to $|\Phi_p\rangle$. If $i, j, k, \ldots$ $(a, b, c, \ldots)$ represent the spin-orbitals that are occupied (unoccupied) in the reference configuration $|\Phi_p\rangle$ and if ${}^{(p)}E_{ijk}^{abc} = X^a X_i X^b X_j X^c X_k$ are the excitation operators that generate the triply excited

configurations relative to $|\Phi_p\rangle$ (X^a and X_i are the usual creation and annihilation operators, respectively), we can write

$$\Gamma_3^{(p)}(2)|\Phi_p\rangle = \sum_{i>j>k,a>b>c} {}^{(p)}\Gamma_{abc}^{ijk}(2)\ {}^{(p)}E_{ijk}^{abc}|\Phi_p\rangle, \tag{53}$$

where

$${}^{(p)}\Gamma_{abc}^{ijk}(2) = \langle\Phi_p|{}^{(p)}E_{abc}^{ijk}(He^{T_1^{(p)}+T_2^{(p)}})_C|\Phi_p\rangle - \sum_{q=1(q\neq p)}^{M} \langle\Phi_p|{}^{(p)}E_{abc}^{ijk}\, e^{-(T_1^{(p)}+T_2^{(p)})}\, e^{T_1^{(q)}+T_2^{(q)}}|\Phi_q\rangle\, H_{qp}^{\mathrm{eff}}(2) \tag{54}$$

are the projections of the SUMRCCSD equations on triexcited configurations (${}^{(p)}E_{abc}^{ijk}$ represents the hermitian adjoint to ${}^{(p)}E_{ijk}^{abc}$). In the case of the complete model space $\mathcal{M}_0$, considered here, at least one index among i, j, k, a, b, c in Eqs. (53) and (54) must be inactive.

The MM-SUCC(2,3) scheme described above represents a multi-reference analog of the single-reference MMCC(2,3) method introduced in Refs. 7, 118, 119 (cf., also, Refs. 120–123). In analogy to the latter method, it might be useful to consider the second-order MRMBPT [MRMBPT(2)] wave function or, perhaps even better, an analog of the MRMBPT(2) wave function, obtained by replacing the lowest-order $T_1^{(p)}$ and $T_2^{(p)}$ estimates entering the MRMBPT(2) formula by their SUMRCCSD values, as a source of wave function $|\Psi_\mu\rangle$ in the MM-SUCC(2,3) energy expressions, Eqs. (48) and (49). The MRMBPT(2) wave function is the lowest-order MRMBPT wave function that contains information about the $T_3^{(p)}$ cluster components. The use of wave functions $|\Psi_\mu\rangle$ of this type in Eqs. (48) and (49) would lead to a multi-reference extension of the recently proposed completely renormalized CCSD(T) [CR-CCSD(T)] method [7, 26, 117–119, 121, 132, 133]. The spectacular successes of the single-reference CR-CCSD(T) approach in calculations of ground-state PESs involving bond breaking, where the standard CCSD(T) approach completely fails, suggest that the multi-reference analog of the CR-CCSD(T) approach, obtained by inserting the MRMBPT(2)-like wave functions $|\Psi_\mu\rangle$ in Eqs. (48) and (49), may provide excellent results, particularly in difficult situations in which the use of the low-order MRMBPT theory alone to estimate the higher-order (e.g., $T_3^{(p)}$) effects is not entirely appropriate due to the presence of intruder states.

We realize, of course, that using the approximate CI or MBPT methods to calculate wave functions $|\Psi_\mu\rangle$ in Eq. (33) and considering the truncated MM-SUCC(m_A, m_B) schemes will cause the resulting energies to be no longer strictly size extensive (in a sense of introducing the unlinked terms into the MM-SUMRCC energies). However, our experience with the CI-based single-reference MMCC methods [7, 120, 122, 123] and the MBPT-based renormalized CC approaches, such as CR-CCSD(T) [7, 26, 117–119, 121, 132, 133], demonstrates that the presence of unlinked terms in the MMCC approximations does not have an effect on the excellent performance of the

approximate MMCC schemes. In fact, we have recently performed a number of calculations showing that the CR-CCSD(T) approach provides approximately size extensive results, as long as we remain within the range of general applicability of this approach, which is a single bond breaking (cf., e.g., Refs. 133, 135). Moreover, a number of studies by the Paldus Waterloo group involving the so-called reduced MRCCSD (RMRCCSD) approach indicate that using the relatively inexpensive MRCI wave functions to estimate the higher-order contributions of the CC theory [6, 136–141], at the risk of introducing unlinked terms into the calculations, tremendously benefits the CC results. The direct use of the final energy expressions in CC calculations, as is done in our MMCC theory [7, 118–123] and its multi-reference extension discussed here and in Ref. 117, which may result in the introduction of unlinked terms, is also exploited in the Brillouin-Wigner MRCC method [32–37]. As in the approximate MMCC case, the Brillouin-Wigner MRCC approach is not size extensive. However, the Brillouin-Wigner MRCC results are excellent (even for molecular systems containing heavier atoms), which is again suggesting to us that the presence of unlinked terms in the approximate MM-SUMRCC energy expressions may not have a detrimental effect on the final results. We should also keep in mind that all approximate MMCC methods (just like the RMRCCSD approach of Paldus and Li) introduce unlinked terms in very high orders, so that it is quite likely that the results of approximate MM-SUMRCC calculations will be very good, in spite of the presence of unlinked terms in the approximate MM-SUMRCC energy expressions.

Clearly, the new ideas described in this section need to be implemented and tested numerically. Work is under way in our laboratory towards implementing various MM-SUMRCC approximations. The results of this effort will be reported as soon as they become available.

4 The State-Universal Multi-Reference Coupled-Cluster Method with Perturbative Description of Core-Virtual Excitations: The SUMRCCSD(1) Approach

One of the main problems that slows down further development of the SUMRCC method in the direction of extending it to larger reference spaces is the fact that the Jeziorski-Monkhorst ansatz requires that a separate cluster operator $T^{(p)}$ is assigned to each reference configuration $|\Phi_p\rangle$ $(p = 1, \ldots, M)$. This requirement leads to an excessively large number of cluster amplitudes when the number of reference configurations is large. In the Jeziorski-Monkhorst formalism, we are forced to solve for all M $T^{(p)}$ cluster operators, even if we are interested in calculating a few low-lying states. In particular, each individual core–virtual excitation is in the SUMRCC theory represented by as many independent cluster amplitudes as the number of references. This is somewhat counterintuitive, since ideally we should only be required to determine as many cluster amplitudes for a given core–virtual excitation as is the number of electronic states under consideration. For example, in the popular MRCISD approach, we are required to determine as many CI

coefficient vectors as is the number of calculated states. The latter number is usually much smaller than the number of reference configurations used in such calculations. As a matter of fact, at least in the first-order MRMBPT, the values of the core–virtual amplitudes representing the doubly excited clusters $T_2^{(p)}$ do not depend on the reference label p [38]. It is, therefore, quite reasonable to introduce an approximation, in which all core–virtual amplitudes of the SUMRCC theory are approximated by their first-order MRMBPT estimates. This new approximation, referred to as the SUMRCCSD(1) method [59], is discussed in this section.

As shown below, the SUMRCCSD(1) approach provides the results of the SUMRCCSD quality at the fraction of the computer cost associated with the SUMRCCSD calculations. Alternative ways of simplifying the SUMRCCSD scheme are possible by considering the state-selective methods employing the Jeziorski-Monkhorst ansatz (cf., e.g., Refs. 30–37). Although these new methods are highly promising, in this paper we focus on simplifying the original SUMRCC method *within its conventional effective Hamiltonian formulation*, which is exactly what the SUMRCCSD(1) approximation offers by reducing the number of cluster amplitudes that need to be determined by the iterative procedure and by reducing the number of nonlinear equations that need to be solved.

Let ${}^{(p)}E_i^a = X^a X_i$ and ${}^{(p)}E_{ij}^{ab} = X^a X_i X^b X_j$ $(i > j, a > b)$ be the excitation operators generating the singly and doubly excited configurations relative to reference $|\Phi_p\rangle$. In terms of these operators, the singly and doubly excited clusters of the SUMRCCSD approach take the usual form,

$$T_1^{(p)} = \sum_{i,a} {}^{(p)}t_a^i \; {}^{(p)}E_i^a, \tag{55}$$

$$T_2^{(p)} = \sum_{i>j,a>b} {}^{(p)}t_{ab}^{ij} \; {}^{(p)}E_{ij}^{ab}, \tag{56}$$

where ${}^{(p)}t_a^i$ and ${}^{(p)}t_{ab}^{ij}$ are the singly and doubly excited cluster amplitudes obtained by solving the SUMRCCSD equations. Since we are assuming here that $\mathcal{M}_0$ is complete, the operators ${}^{(p)}E_i^a$ and ${}^{(p)}E_{ij}^{ab}$ and the corresponding cluster amplitudes ${}^{(p)}t_a^i$ and ${}^{(p)}t_{ab}^{ij}$ must carry at least one inactive (i.e., core or virtual) spin-orbital label.

In general, the ${}^{(p)}t_a^i$ and ${}^{(p)}t_{ab}^{ij}$ values depend on label p. Indeed, suppose the spin-orbitals i, j, ... and a, b, ... (commonly designated as the ρ, σ, ... spin-orbitals) are obtained in the canonical Hartree-Fock calculations and suppose the reference $|\Phi_1\rangle$ is the ground-state Hartree-Fock determinant. Let us construct the remaining reference configurations $|\Phi_p\rangle$, $p = 2, \ldots, M$, in a usual way by choosing some occupied and some unoccupied spin-orbitals in $|\Phi_1\rangle$ as active spin-orbitals and by promoting active electrons (electrons occupying active spin-orbitals in $|\Phi_1\rangle$) to active spin-orbitals that are unoccupied in $|\Phi_1\rangle$. Let us also introduce the Fock matrix elements

$${}^{(p)}f_\rho^\sigma = z_\rho^\sigma + \sum_{i \in \text{occupied in } |\Phi_p\rangle} v_{\rho i}^{\sigma i}, \tag{57}$$

where $z_\rho^\sigma = \langle\rho|z|\sigma\rangle$ and $v_{\rho\sigma}^{\tau\omega} = \langle\rho\sigma|v|\tau\omega\rangle - \langle\rho\sigma|v|\omega\tau\rangle$ are the one-electron and antisymmetrized two-electron molecular integrals defining the electronic Hamiltonian,

$$H = \sum_{\rho,\sigma} z_\rho^\sigma \, X^\rho X_\sigma + \frac{1}{4} \sum_{\rho,\sigma,\tau,\omega} v_{\rho\sigma}^{\tau\omega} \, X^\rho X^\sigma X_\omega X_\tau, \tag{58}$$

and let us partition the Hamiltonian into the unperturbed operator

$$H_0 = \sum_{\rho,\sigma} {}^{(1)}f_\rho^\sigma \, X^\rho X_\sigma = \sum_\rho \epsilon_\rho \, X^\rho X_\rho \tag{59}$$

and the perturbation

$$W = H - H_0, \tag{60}$$

where

$$\epsilon_\rho = {}^{(1)}f_\rho^\rho \tag{61}$$

in Eq. (59) are the molecular orbital energies obtained in canonical Hartree-Fock calculations. With this partitioning of the Hamiltonian, one can perform the usual MRMBPT analysis of the wave function cluster expansions and show, for example, that the first-order MRMBPT estimates for the singly and doubly excited cluster amplitudes, ${}^{(p)}t_a^i(1)$ and ${}^{(p)}t_{ab}^{ij}(1)$, respectively, are

$${}^{(p)}t_a^i(1) = ({}^{(p)}f_a^i - {}^{(1)}f_a^i)/(\epsilon_i - \epsilon_a) = {}^{(p)}f_a^i/(\epsilon_i - \epsilon_a), \tag{62}$$

$${}^{(p)}t_{ab}^{ij}(1) = v_{ab}^{ij}/(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b), \tag{63}$$

where in Eq. (62) we used the fact that ${}^{(1)}f_a^i = 0$ (in general, for the canonical Hartree-Fock spin-orbitals, the $p = 1$ matrix elements ${}^{(1)}f_\rho^\sigma$ vanish unless $\rho = \sigma$). Clearly, the values of ${}^{(p)}t_a^i(1)$ and ${}^{(p)}t_{ab}^{ij}(1)$ depend on p, since different spin-orbitals are occupied in different reference configurations $|\Phi_p\rangle$. In addition, the ${}^{(p)}t_a^i(1)$ amplitudes vanish for $p = 1$ and are, in general, nonzero for $p > 1$. The order-by-order analysis of the SUMRCCSD method demonstrates that differences between cluster amplitudes associated with different references $|\Phi_p\rangle$ are even larger in higher orders of MRMBPT [38].

Although the ${}^{(p)}t_a^i$ and ${}^{(p)}t_{ab}^{ij}$ amplitudes are, in general, p-dependent and should be treated as independent parameters in the process of solving the SUMRCCSD equations, the first-order core–virtual biexcited amplitudes, ${}^{(p)}t_{\mathbf{ab}}^{\mathbf{ij}}(1)$, do not depend on label p. We have,

$${}^{(p)}t_{\mathbf{ab}}^{\mathbf{ij}}(1) \equiv t_{\mathbf{ab}}^{\mathbf{ij}}(1) = v_{\mathbf{ab}}^{\mathbf{ij}}/(\epsilon_{\mathbf{i}} + \epsilon_{\mathbf{j}} - \epsilon_{\mathbf{a}} - \epsilon_{\mathbf{b}}). \tag{64}$$

This observation suggests an approximation in which, instead of solving for the large number of core–virtual amplitudes ${}^{(p)}t_{\mathbf{ab}}^{\mathbf{ij}}$, we simply estimate their values using the first-order MRMBPT expression, Eq. (64) [59]. The first-order core–virtual monoexcited amplitudes ${}^{(p)}t_{\mathbf{a}}^{\mathbf{i}}(1)$ depend

on p, but they are usually much smaller than the ${}^{(p)}t^{\mathbf{ij}}_{\mathbf{ab}}(1)$ amplitudes, so that we may simply neglect the core–virtual ${}^{(p)}t^{\mathbf{i}}_{\mathbf{a}}(1)$ amplitudes altogether and invoke an additional approximation in which [59]

$$ {}^{(p)}t^{\mathbf{i}}_{\mathbf{a}}(1) \equiv t^{\mathbf{i}}_{\mathbf{a}}(1) = 0. \tag{65} $$

In this way, we can reinforce the fully symmetric treatment of both singly and doubly excited core–virtual cluster amplitudes. The significance of the symmetric treatment of the manifolds of excitations corresponding to different reference configurations $|\Phi_p\rangle$, which are not treated symmetrically in the standard SUMRCCSD scheme, has been discussed in the previous sections.

Equations (64) and (65) define the SUMRCCSD(1) method [59]. Since the core–virtual amplitudes are determined *a priori* by Eqs. (64) and (65), in the SUMRCCSD(1) approach we no longer consider the amplitude equations corresponding to core–virtual excitations. In other words, Eqs. (15)–(17) of the standard SUMRCCSD theory in which ${}^{(p)}E_K = {}^{(p)}E^{\mathbf{a}}_{\mathbf{i}}, {}^{(p)}E^{\mathbf{ab}}_{\mathbf{ij}}$ are simply ignored, so that the number of equations and the number of unknown cluster amplitudes that need to be determined in the iterative procedure are identical. As shown in Table 1, this considerably reduces the computer effort involved, since in the SUMRCCSD(1) method we only consider a relatively small subset of all SUMRCCSD amplitude equations corresponding to single and double excitations that carry at least one active index, i.e., ${}^{(p)}E_K = {}^{(p)}E^{\mathbf{a}}_{\mathbf{I}}, {}^{(p)}E^{\mathbf{A}}_{\mathbf{i}}, {}^{(p)}E^{\mathbf{ab}}_{\mathbf{Ij}}$ $(\mathbf{a} > \mathbf{b})$, ${}^{(p)}E^{\mathbf{aB}}_{\mathbf{ij}}$ $(\mathbf{i} > \mathbf{j})$, ${}^{(p)}E^{\mathbf{ab}}_{\mathbf{IJ}}$ $(\mathbf{I} > \mathbf{J}, \mathbf{a} > \mathbf{b})$, ${}^{(p)}E^{\mathbf{AB}}_{\mathbf{ij}}$ $(\mathbf{i} > \mathbf{j}, \mathbf{A} > \mathbf{B})$, ${}^{(p)}E^{\mathbf{aB}}_{\mathbf{Ij}}$, ${}^{(p)}E^{\mathbf{aB}}_{\mathbf{IJ}}$ $(\mathbf{I} > \mathbf{J})$, ${}^{(p)}E^{\mathbf{AB}}_{\mathbf{Ij}}$ $(\mathbf{A} > \mathbf{B})$. We use these equations to determine the relatively small subset of all ${}^{(p)}t^{i}_{a}$ and ${}^{(p)}t^{ij}_{ab}$ amplitudes that carry at least one active index. Even for small systems, such as the methylene molecule, and even for the simple two-reference ($M = 2$) singlet case, the savings in the computer effort are substantial. For example, the total number of spin- and symmetry-adapted cluster amplitudes used in the two-reference OSA SUMRCCSD calculations for the the lowest two ${}^1A_1$ states of methylene, as described by the double-zeta plus polarization (DZP) basis set of Refs. 142, 143, is 1341 (720 for $|\Phi_1\rangle$ and 621 for $|\Phi_2\rangle$; see Table 1). The number of core–virtual amplitudes for each reference is in this case 318, so that the total number of core–virtual amplitudes considered in the two-reference OSA SUMRCCSD calculations for the DZP methylene molecule is 636. These 636 amplitudes are estimated in the SUMRCCSD(1) method by the first-order MRMBPT expression, Eq. (64), and by Eq. (65), and only the remaining 705 cluster amplitudes that carry at least one active orbital index are determined iteratively by solving the relevant subset of all SUMRCCSD equations. A similar ~ 50 % reduction in the number of amplitudes that have to be determined in the SUMRCCSD(1) iterative procedure characterizes the calculations for methylene employing a larger $[5s4p3d2f1g/3s2p1d]$ basis set of Ref. 144 (cf., also, Ref. 52). In this case, the total number of core–virtual amplitudes considered in the two-reference OSA SUMRCCSD calculations is 10432, while the number of all singly and doubly excited cluster amplitudes is 22611 (see Table 1). The 10432 core–virtual amplitudes are estimated in the SUMRCCSD(1) calculations via Eqs. (64)

and (65), whereas the remaining 12179 amplitudes are determined iteratively. This significant reduction in the number of cluster amplitudes that have to be determined in the SUMRCCSD(1) iterative procedure would be even larger for larger many-electron systems, since the number of core–virtual amplitudes increases with the number of core electrons.

In order to test the SUMRCCSD(1) method, we performed a few benchmark calculations using the two-reference OSA SUMRCCSD(1) approach, which we implemented by modifying the two-reference OSA SUMRCCSD code described in Ref. 50 (see Refs. 58, 145 for a parallel version). Let us recall that in the two-reference OSA SUMRCCSD method of Ref. 50 (see Refs. 39, 41, 45–49 for earlier developments), the model space $\mathcal{M}_0$ is spanned by two closed-shell configurations $|\Phi_1\rangle$ and $|\Phi_2\rangle$ involving two active electrons and two active orbitals that belong to different symmetry species of the spatial symmetry group of the system. The $M = 2$ model space, $\mathcal{M}_0 = \mathrm{span}\{|\Phi_1\rangle, |\Phi_2\rangle\}$, is complete if we are only interested in the totally symmetric singlet eigenstates of the Hamiltonian [39, 41, 45–50, 54]. The explicit equations of the two-reference OSA SUMRCCSD(1) theory, in terms of the OSA mono- and biexcited cluster amplitudes, are a straightforward modification of the two-reference OSA SUMRCCSD equations presented elsewhere [39, 41, 45, 50].

The results of the SUMRCCSD(1) calculations discussed in this section include the lowest two $^1A_1$ states of the DZP H4 model [146, 147] (see Table 2 and Fig. 1), the lowest two $^1\Sigma_g^+$ states of the Li_2 molecule, as described by the double zeta (DZ) basis set of Refs. 148, 149 (see Table 3), and the lowest two $^1A_1$ states of methylene, as described by the DZP basis set [142, 143] and the $[5s4p3d/3s2p]$ [52] and $[5s4p3d2f1g/3s2p1d]$ atomic natural orbital [144] basis sets (see Table 4). The results of the SUMRCCSD(1) calculations for H4 and CH_2 were reported earlier [59]. The results for Li_2 are new.

We compare the SUMRCCSD(1) results with those obtained with the two-reference SUMRCCSD and MRMBPT(2) methods. The MRMBPT(2) results were obtained with the method described in Ref. 150 and implemented in GAMESS [151]. It is useful to compare the MRMBPT(2) and SUMRCCSD(1) results, since both approaches rely on the first-order MRMBPT corrections to the wave function. Whenever possible, we also compare the SUMRCCSD(1) results with the results of full CI calculations. The results of the two-reference SUMRCCSD and full CI calculations for the DZP H4 model can be found in Ref. 50. The SUMRCCSD results for the lowest two $^1A_1$ states of the DZP model of methylene can be found in Refs. 50, 58 (recall that the lowest $^1A_1$ state represents in this case the first-excited state; the ground state of CH_2 is $^3B_1$; cf. the Introduction). The results of the two-reference SUMRCCSD calculations for methylene for the $[5s4p3d/3s2p]$ and $[5s4p3d2f1g/3s2p1d]$ basis sets were reported in Refs. 52, 58.

We begin our discussion with the H4 model, which consists of two slightly stretched H_2 molecules arranged in an isosceles trapezoidal configuration, with all nearest-neighbor H–H separations fixed

at 2.0 bohr. The geometry of the H4 model is determined by a single parameter $\alpha \in [0, \frac{1}{2}]$. The $\alpha = 0$ and $\alpha = \frac{1}{2}$ limits correspond to square and linear conformations, respectively [146].

Table 1. Numbers of the spin- and symmetry-adapted singly and doubly excited cluster amplitudes used in the two-reference OSA SUMRCCSD calculations for molecular systems discussed in this work.[a]

		$p = 1$		$p = 2$		$p = 1$ or 2	
Molecule	Basis set	N_S	N_D	N_S	N_D	$N_{S(CV)}$	$N_{D(CV)}$
H4[b]	DZP[c]	14	229	12	233	6	55
Li_2	DZ[d]	13	279	13	279	8	167
CH_2[e]	$[4s2p1d/2s1p]$[f]	26	694	20	601	16	302
	$[5s4p3d/3s2p]$[g]	57	3294	44	2867	35	1442
	$[5s4p3d2f1g/3s2p1d]$[h]	102	11715	84	10710	64	5152

[a] N_S and N_D designate, respectively, the numbers of all singly and doubly excited cluster amplitudes used in the two-reference OSA SUMRCCSD calculations. $N_{S(CV)}$ and $N_{D(CV)}$ designate, respectively, the numbers of singly and doubly excited cluster amplitudes corresponding to core–virtual excitations.

[b] The H4 model of Ref. 146.

[c] The $[2s1p]$ basis set taken from Ref. 147.

[d] The $[4s2p]$ contraction of the Dunning-Hay basis set of Ref. 148 (see Ref. 149).

[e] The lowest-energy molecular orbital $(1a_1)$ is kept frozen and the Cartesian components of the d and (if present in a basis set) f and g orbitals are employed.

[f] The DZP basis set taken from Refs. 142, 143.

[g] Basis set taken from Ref. 52.

[h] Basis set taken from Refs. 52, 144.

By changing parameter α, we can continuously vary the degree of configurational quasi-degeneracy involving the ground-state RHF (restricted Hartree-Fock) reference configuration

$$|\Phi_1\rangle = |(1a_1)^2(1b_2)^2| \tag{66}$$

and the doubly excited configuration

$$|\Phi_2\rangle = |(1a_1)^2(2a_1)^2|, \tag{67}$$

obtained by promoting two electrons from the highest-energy occupied orbital $(1b_2)$ to the lowest-energy unoccupied orbital $(2a_1)$. Indeed, in the $\alpha = 0$ limit, the absolute values of the coefficients

at configurations $|\Phi_1\rangle$ and $|\Phi_2\rangle$, which dominate the full CI expansions of the lowest two $^1A_1$ states in this region, are identical. For $\alpha = 0.5$, the ground-state wave function becomes essentially non-degenerate, with $|\Phi_1\rangle$ representing the leading configuration in the corresponding full CI expansion.

The results of our SUMRCCSD(1) calculations for the lowest two $^1A_1$ states of the DZP H4 model (the 1 $^1A_1$ and 2 $^1A_1$ states) are shown in Table 2 and Fig. 1. In the SUMRCCSD(1), SUMRCCSD, and MRMBPT(2) calculations, we chose orbitals $1b_2$ and $2a_1$ as active. This choice of active orbitals is justified by the dominant role of the $|\Phi_1\rangle$ and $|\Phi_2\rangle$ configurations, Eqs. (66) and (67), respectively, in the full CI expansions of the lowest two $^1A_1$ states of the H4 system.

As can be seen from Table 2 and Fig. 1, the SUMRCCSD(1) potential energy curves representing the lowest two $^1A_1$ states of are shifted by ~ 1 millihartree or less relative to the corresponding SUMRCCSD curves. The errors in the SUMRCCSD(1) results, relative to full CI, range between 0.5 ($\alpha \approx 0$) and 2.7 ($\alpha \approx 0.5$) millihartree for the ground state and between 4.1 ($\alpha \approx 0$) and 3.0 ($\alpha \approx 0.5$) millihartree for the first-excited $^1A_1$ state. The errors obtained with the SUMRCCSD method are virtually identical to those obtained with the simpler SUMRCCSD(1) approximation. The SUMRCCSD(1) and SUMRCCSD vertical excitation energies Δ corresponding to the 1 $^1A_1 \rightarrow 2$ $^1A_1$ transition agree to within 0.5–1.5 millihartree for all values of α. For comparison, the MRMBPT(2) approach completely fails for $\alpha > 0.15$ due to intruder states. The errors in the MRMBPT(2) results for the 1 $^1A_1 \rightarrow 2$ $^1A_1$ excitation energies, relative to full CI, are as large as 172.8 millihartree in the $\alpha \approx 0.5$ region. Even in the region of small α values, where the MRMBPT(2) approach works best, the errors in the MRMBPT(2) results for the 1 $^1A_1 \rightarrow 2$ $^1A_1$ excitation energies are much larger than those obtained with the SUMRCCSD(1) method (cf., e.g., the 9.4 millihartree error in the MRMBPT(2) value of Δ at $\alpha = 0$ with the 3.6 millihartree error obtained with the SUMRCCSD(1) approach for the same value of α).

The excellent performance of the SUMRCCSD(1) approach is also observed in the calculations for the DZ model of Li_2. We considered three geometries in this case: the equilibrium geometry, $R = R_e = 5.051$ bohr (R is the internuclear separation), and two stretches of the Li–Li bond, $R = 1.5R_e$ and $R = 2R_e$. For larger distances R, the ground and the first-excited states of the $^1\Sigma_g^+$ symmetry are dominated by the RHF configuration

$$|\Phi_1\rangle = |(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2| \tag{68}$$

and the doubly excited configuration

$$|\Phi_2\rangle = |(1\sigma_g)^2(1\sigma_u)^2(2\sigma_u)^2|, \tag{69}$$

so that it is prudent to choose the highest-energy occupied and the lowest-energy unoccupied molecular orbitals, $2\sigma_g$ and $2\sigma_u$, respectively, in our SUMRCCSD(1), SUMRCCSD, and MRMBPT(2) calculations. The results of the two-reference SUMRCCSD(1), SUMRCCSD, and

Table 2. The SUSD(1) ≡ SUMRCCSD(1), SUSD ≡ SUMRCCSD, and full CI energies (in hartree) for the lowest two $^1A_1$ states of the DZP H4 model and the SUMRCCSD(1), SUMRCCSD, MRMBPT(2), and full CI values of the $1\,^1A_1 \rightarrow 2\,^1A_1$ excitation energies (Δ, in millihartree) as functions of the parameter α [59].

	$E(1\,^1A_1)$/hartree			$E(2\,^1A_1)$/hartree			Δ/millihartree			
α	Full CI	SUSD	SUSD(1)	Full CI	SUSD	SUSD(1)	Full CI	SUSD	SUSD(1)	MRMBPT(2)
0.00	-2.063112	-2.063798	-2.062587	-1.981434	-1.978061	-1.977326	81.678	85.737	85.261	91.106
0.01	-2.069401	-2.069995	-2.068761	-1.980637	-1.977338	-1.976662	88.764	92.657	92.099	98.721
0.05	-2.114299	-2.114383	-2.113209	-1.944499	-1.941439	-1.940819	169.800	172.944	172.239	180.908
0.10	-2.160115	-2.160288	-2.159318	-1.900893	-1.897403	-1.896775	259.222	262.885	262.543	277.072
0.15	-2.188929	-2.189551	-2.188914	-1.877185	-1.873723	-1.872963	311.744	315.828	315.951	335.579
0.20	-2.206548	-2.207735	-2.207443	-1.866764	-1.863997	-1.863065	339.784	343.738	344.378	358.148
0.30	-2.224122	-2.226120	-2.226254	-1.861977	-1.860253	-1.859109	362.145	365.867	367.145	323.481
0.40	-2.230887	-2.233195	-2.233458	-1.863818	-1.862164	-1.860944	367.069	371.031	372.514	239.768
0.50	-2.232700	-2.235079	-2.235363	-1.865105	-1.863379	-1.862140	367.595	371.700	373.223	194.819

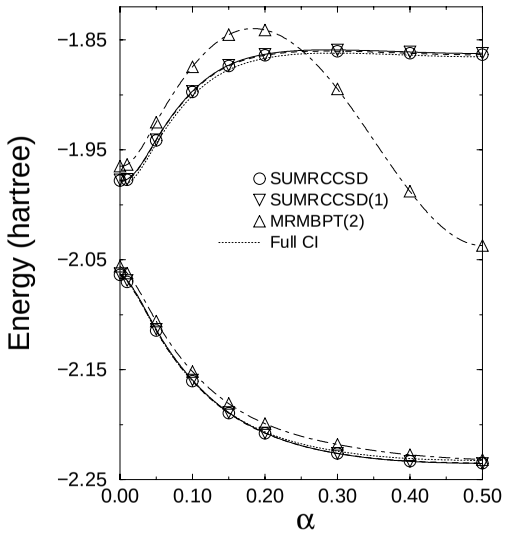

Figure 1. The SUMRCCSD, SUMRCCSD(1), MRMBPT(2), and full CI potential energy curves for the lowest two $^1A_1$ states of the DZP H4 model.

MRMBPT(2) calculations for Li_2, using configurations $|\Phi_1\rangle$, Eq. (68), and $|\Phi_2\rangle$, Eq. (69), as references, along with the corresponding full CI results, are shown in Table 3.

The results in Table 3 show that the SUMRCCSD(1) approach provides the potential energy curves of Li_2 that are in excellent agreement with the high quality curves obtained with the SUMRCCSD method. The SUMRCCSD(1) energies for the lowest two $^1\Sigma_g^+$ states of Li_2 are only slightly above the corresponding SUMRCCSD energies [the difference between the SUMRCCSD(1) and SUMRCCSD energies is ~ 2.5 millihartree, independently of the value of R]. In consequence, the errors in the SUMRCCSD(1) results, relative to full CI, are very small (2.7–2.8 millihartree for the ground state and 3.1–3.2 millihartree for the first-excited $^1\Sigma_g^+$ state). The errors in the $1\ ^1\Sigma_g^+ \rightarrow 2\ ^1\Sigma_g^+$ vertical excitation energies (designated by Δ) obtained with the SUMRCCSD(1) method, relative to full CI, are 0.4–0.5 millihartree, independently of the value of R. The SUMRCCSD results for the $1\ ^1\Sigma_g^+ \rightarrow 2\ ^1\Sigma_g^+$ excitation energies are virtually identical to those obtained with the simpler SUMRCCSD(1) approach. The two-reference MRMBPT(2) method works reasonably well in the quasi-degenerate region corresponding to larger R values, where the lowest two $^1\Sigma_g^+$ states are dominated by configurations (68) and (69), but the SUMRCCSD(1) results are much more accurate [cf., e.g., the 12.8 millihartree error in the MRMBPT(2) result for the vertical excitation energy Δ at $R = 2R_e$ with the 0.3–0.4 millihartree errors obtained at the same value of R with the SUMRCCSD and SUMRCCSD(1) approaches]. In the $R \approx R_e$ region, the ground state is dominated by the RHF configuration $|\Phi_1\rangle$, Eq. (68), but the first-excited state of the $^1\Sigma_g^+$ symmetry has significant contributions from configurations belonging to $\mathcal{M}_0^{\perp}$. As a result, the error in the MRMBPT(2) value for the vertical excitation energy Δ is as large as 54.0 millihartree at $R = R_e$. Remarkably enough, the errors in the SUMRCCSD and SUMRCCSD(1) results for the $1\ ^1\Sigma_g^+ \rightarrow 2\ ^1\Sigma_g^+$ excitation energy are as little as 0.5 millihartree at $R = R_e$. This clearly shows that we can tremendously benefit from incorporating the MRMBPT ideas into the SUMRCCSD scheme.

Our final example is methylene [59]. As mentioned in the Introduction, the OSA SUMRCCSD approach provides excellent ($\sim$ spectroscopic) results for the very small energy gap between the ground state, $X\,^3B_1$, and the lowest excited state of the $^1A_1$ symmetry, $A^1A_1 \equiv 1\ ^1A_1$ [51, 52]. The OSA SUMRCCSD method is also capable of providing the excellent description of the singlet–singlet ($2\ ^1A_1 - 1\ ^1A_1$) energy separation [50]. For example, the full CI value of the singlet–singlet energy gap in the DZP methylene molecule is 168.907 millihartree [143]. The two-reference SUMRCCSD method gives 169.885 millihartree [50], in excellent agreement with full CI.

The success of the two-reference SUMRCCSD method in describing the $2\ ^1A_1 - 1\ ^1A_1$ energy gap in methylene is largely (but not entirely) related to the quasi-degenerate character of the lowest two $^1A_1$ states, which are both dominated by two closed-shell configurations,

$$|\Phi_1\rangle = |(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2| \tag{70}$$

Table 3. The SUSD(1) ≡ SUMRCCSD(1), SUSD ≡ SUMRCCSD, and full CI energies (in hartree) for the lowest two $^1\Sigma_g^+$ states of the DZ model of Li_2 and the SUMRCCSD(1), SUMRCCSD, MRMBPT(2), and full CI values of the $1\ ^1\Sigma_g^+ \rightarrow 2\ ^1\Sigma_g^+$ excitation energies (Δ, in millihartree) for the equilibrium value of the Li–Li separation R ($R = R_e = 5.051$ bohr) and two stretches of the Li–Li bond ($R = 1.5R_e$ and $R = 2R_e$).

	E($1\ ^1\Sigma_g^+$)/hartree			E($2\ ^1\Sigma_g^+$)/hartree			Δ/millihartree			
R	Full CI	SUSD	SUSD(1)	Full CI	SUSD	SUSD(1)	Full CI	SUSD	SUSD(1)	MRMBPT(2)
R_e	-14.913528	-14.913370	-14.910858	-14.763208	-14.762564	-14.760053	150.320	150.806	150.805	204.355
$1.5R_e$	-14.896085	-14.895911	-14.893368	-14.821975	-14.821249	-14.818768	74.110	74.662	74.600	53.536
$2R_e$	-14.883931	-14.883655	-14.881143	-14.816531	-14.815959	-14.813388	67.400	67.696	67.755	80.210

Table 4. The SUSD(1) ≡ SUMRCCSD(1), SUSD ≡ SUMRCCSD, and full CI energies (in hartree) for the lowest two $^1A_1$ states of methylene and the SUMRCCSD(1), SUMRCCSD, MRMBPT(2), and full CI values of the $1\ ^1A_1 \rightarrow 2\ ^1A_1$ excitation energy (Δ, in millihartree).[a]

	$E(1\ ^1A_1)$/hartree			$E(2\ ^1A_1)$/hartree			Δ/millihartree			
Basis set	Full CI	SUSD	SUSD(1)	Full CI	SUSD	SUSD(1)	Full CI	SUSD	SUSD(1)	MRMBPT(2)
$[4s2p1d/2s1p]$[b]	-39.027183	-39.024914	-39.016102	-38.858276	-38.855029	-38.845259	168.907	169.885	170.843	157.563
$[5s4p3d/3s2p]$[c]		-39.052925	-39.044501		-38.885053	-38.875240		167.872	169.261	149.490
$[5s4p3d2f1g/3s2p1d]$[d]		-39.067393	-39.059620		-38.901687	-38.892411		165.706	167.209	147.514

[a] Based on the results reported in Ref. 59. The lowest-energy molecular orbital was kept frozen and the Cartesian components of the d and (if present in a basis set) f and g orbitals were employed.

[b] Basis set, geometries, and full CI results taken from Refs. [142, 143].

[c] Basis set and geometries taken from Ref. [52].

[d] Basis set and geometries taken from Refs. [52, 144].

and

$$|\Phi_2\rangle = |(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2|, \tag{71}$$

involving active orbitals $3a_1$ and $1b_1$. Thus, by choosing orbitals $3a_1$ and $1b_1$ as active orbitals in the SUMRCCSD calculations, we should (and we do) obtain excellent results for the singlet–singlet energy separation. It is interesting to note though that the two-reference MRMBPT(2) method does not provide very good results in this case, in spite of the apparently two-reference character of the lowest two $^1A_1$ states. For example, the error in the $1\ ^1A_1 \rightarrow 2\ ^1A_1$ excitation energy obtained with the MRMBPT(2) approach for the DZP methylene model, relative to full CI, is 11.344 millihartree. This should be compared to a much smaller, 0.978, millihartree error obtained with the two-reference SUMRCCSD method (see Table 4).

The results in Table 4 show that the description of the lowest two $^1A_1$ states of methylene by the two-reference SUMRCCSD(1) approach is almost as good as that provided by its parent SUMRCCSD analog. Although the differences between the SUMRCCSD(1) and SUMRCCSD individual energies are somewhat larger than in the case of the H4 and Li_2 systems, the vertical excitation energies corresponding to the $1\ ^1A_1 \rightarrow 2\ ^1A_1$ transition in methylene (the Δ values in Table 4) obtained in the SUMRCCSD(1) and SUMRCCSD calculations are essentially identical, independent of the basis set employed. Indeed, the differences between the Δ values resulting from the SUMRCCSD(1) and SUMRCCSD calculations are 0.958 millihartree for the DZP basis set, 1.389 millihartree for the $[5s4p3d/3s2p]$ basis set, and 1.503 millihartree for the largest $[5s4p3d2f1g/3s2p1d]$ basis set. The difference between the Δ values obtained in the SUMRCCSD(1) and full CI calculations with the DZP basis set is 1.936 millihartree, which should be compared to a 0.978 millihartree difference between the SUMRCCSD and full CI values of Δ.

Thus, we can summarize this section by stating that the SUMRCCSD(1) approach provides a viable alternative to the SUMRCCSD method. At least for the small molecular systems tested in this work and in our original study [59], the SUMRCCSD(1) approach is capable of providing the results of the SUMRCCSD quality at the fraction of the computer effort associated with the SUMRCCSD calculations. We are encouraged by the preliminary results overviewed in this section and we will work on generalizing the two-reference SUMRCCSD(1) approach of Ref. 59 to larger model spaces.

5 Summary

We overviewed our recent results in the area of the genuine SUMRCC theory. We focused on a new type of the noniterative corrections to the SUMRCC energies, obtained by extending the MMCC formalism of Refs. 7, 117–123 to a multi-reference case, and on combining the SUMRCCSD and MRMBPT approaches by replacing the cluster amplitudes of the SUMRCCSD method that carry

only core and virtual orbital indices by their first-order MRMBPT estimates. We believe that the multi-reference variant of the MMCC theory provides us with a systematic way of improving the SUMRCC results by adding relatively simple, noniterative, state-specific corrections to the SUMRCC energies. In particular, the multi-reference extension of the MMCC formalism suggests simple ways of restoring the symmetric treatment of manifolds of excitations corresponding to different reference configurations, broken by the conventional SUMRCC approximations, and simple ways of incorporating higher–than–double excitations in the SUMRCCSD method. We demonstrated that the SUMRCCSD(1) approach of Ref. 59, in which the core–virtual cluster amplitudes of the SUMRCCSD theory are approximated by the first-order MRMBPT expressions, gives the results of the SUMRCCSD quality at the fraction of the computer effort associated with the SUMRCCSD calculations. We believe that the SUMRCCSD(1) approach may allow us to extend the existing two-orbital/two-electron SUMRCCSD approaches to larger active spaces, since the SUMRCCSD(1) method eliminates one of the main bottlenecks of the SUMRCC theory, which is the requirement of assigning a separate large set of core–virtual cluster amplitudes to each reference configuration. Clearly, there may exist other ways of estimating the SUMRCC cluster amplitudes via low-order MRMBPT expressions. We are currently exploring other MRMBPT-based SUMRCC approximations. The results of these studies will be reported as soon as they become available.

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