

New classes of non-iterative energy corrections to multi-reference coupled-cluster energies

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Two new classes of non-iterative corrections to the ground- and excited-state energies obtained in the state-universal multi-reference coupled-cluster (SUMRCC) calculations have been developed using the multi-reference extension of the method of moments of coupled-cluster equations (MMCC) [KOWALSKI, K., and PIECUCH, P., 2001, *J. molec. Struct. (THEOCHEM)*, **547**, 191]. In the first class of the configuration interaction (CI) corrected multi-reference MMCC (MRMMCC) approximations, the non-iterative corrections due to triply or triply and quadruply excited clusters are constructed with the help of multi-reference CI (MRCI) calculations employing the same active space as used in the SUMRCC calculations. In the second class of the completely renormalized (CR) SUMRCC methods, which can be viewed as the multi-reference extensions of the single-reference CR-CCSD(T) theory [KOWALSKI, K., and PIECUCH, P., 2000, *J. chem. Phys.*, **113**, 18], the non-iterative corrections due to triply excited clusters are constructed with the help of the multi-reference many-body perturbation theory. In both cases, the non-iterative corrections due to higher-order clusters are added to the energies obtained with the SUMRCC method with singles and doubles. It is demonstrated that the newly developed corrections, including the CR-SUMRCC methods, offer considerable improvements in the SUMRCCSD results, reducing, in particular, the large errors in the SUMRCCSD results due to intruders.

1. Introduction

It is generally acknowledged that methods based on the coupled-cluster (CC) theory [1–5] provide the best compromise between high accuracy and relatively low computer cost in applications involving atomic and molecular systems (cf., e.g., [6–11] and references therein). The success of CC theory in atomic and molecular physics and chemistry applications is largely due to the ability of the CC wave function ansatz to capture the bulk of the dynamical correlation effects at the low level of approximation. Unfortunately, severe problems arise when the single-reference CC methods are applied to quasi-degenerate, open-shell, and excited electronic states that are characterized by large non-dynamic correlation effects. The most typical situations in chemistry where non-dynamic correlation effects are of the utmost significance include diradicals, transition states and reaction intermediates, excited states dominated by two-electron and other many-electron

transitions, and ground- and excited-state potential energy surfaces along bond breaking coordinates.

Some of the problems related to the presence of large non-dynamic correlation effects can be successfully resolved by using suitably designed modifications of the single-reference CC methods, including, for example, the renormalized CC approaches employing the formalism of the method of moments of CC equations (MMCC) [11–28], the externally corrected CC methods [8, 29–42], the active-space CC schemes [15, 43–62], and the spin-flip CC models [63–66], but undoubtedly there is a need to develop genuine multi-reference coupled-cluster (MRCC) methods [6, 8] based on the generalized Bloch equation and the concept of an effective Hamiltonian acting in a multidimensional model or reference space [67–69] (cf., also, [70]). By design, the genuine MRCC approaches should be capable of handling all kinds of quasi-degenerate and open-shell states in a computationally convenient and elegant manner.

The genuine MRCC theories classify as either the Fock-space or valence-universal (VU) methods [6, 8, 71–110] or the Hilbert-space or state-universal (SU) approaches [6, 8, 111–139]. The VUMRCC methods, which require a simultaneous consideration of ground

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and excited states of a given many-electron system and its ions (different sectors of the Fock space), can be very useful for calculations of vertical excitation energies, vertical ionization potentials, and vertical electron affinities. Unfortunately, the VUMRCC methods suffer from intruder states and unphysical multiple solutions [109, 110], which, together with the demanding requirement of a simultaneous consideration of different sectors of the Fock space, make accurate VUMRCC calculations of larger portions of molecular potential energy surfaces (PESs) very difficult.

The SUMRCC methods, which are based on the Jeziorski–Monkhorst ansatz [111] and which are probably closest in spirit to the popular multi-reference configuration interaction (MRCI) and multi-reference many-body perturbation theory (MRMBPT) [140–142] methods, do not require a consideration of different sectors of the Fock space. Thus, they are much better suited for studies of molecular PESs. Indeed, as shown in [114, 116–118, 120–124, 128], the PES and property function scans with the SUMRCC methods can be very successful and highly accurate results can be obtained. The SUMRCC methods are also capable of providing the spectroscopically accurate description of electronic energy separations in small molecular systems, as has been illustrated by the calculations of the singlet–triplet ($A^1A_1 - X^3B_1$) [125, 126] and singlet–singlet ($2^1A_1 - 1^1A_1$; $1^1A_1 \equiv A^1A_1$) [124, 132] energy gaps in methylene. Unfortunately, apart from the earlier advances in formulating, implementing, and testing the spin-adapted and spin-orbital SUMRCCSD methods [6, 8, 111–130] and apart from the limited recent activities in our group (see, e.g., [131–134]), the group of Pal [135], who formulated the response SUMRCC theory, and the Paldus Waterloo group [136–139], who introduced the generalized version of the SUMRCC method enabling the systematic use of incomplete model spaces in SUMRCC calculations, the development of the genuine SUMRCC method has practically stopped. We believe that this situation should change, since the SUMRCC theory has the potential of offering an elegant and, at the same time, well balanced description of many classes of ground and excited electronic states, particularly when the quasi-degeneracies and the degree of non-dynamic correlation are too severe to be handled by other CC methods.

There are several open problems in the SUMRCC theory that must be addressed before this method becomes a useful alternative for routine and accurate *ab initio* calculations of ground- and excited-state molecular PESs and related properties. There is, for example, a long-standing problem of generalizing the existing explicitly connected orthogonally spin-adapted two-reference SUMRCCSD (SUMRCC singles and doubles)

theory [112, 114, 119–124, 128] to model spaces of arbitrarily large dimensions and states of arbitrary multiplicity. Our recent studies of the multiple solutions of the generalized Bloch equation [70] clearly demonstrate that the SUMRCC calculations would benefit from using large reference spaces. Unfortunately, it is not easy to propose an efficient computational procedure that would allow one to perform routine SUMRCC calculations for larger model spaces, although recent effort by Li and Paldus [136–139] represents one of the most important advances in this area in many years. Part of the problem with extending the SUMRCC methods to larger model spaces is the fact that the wave function ansatz of Jeziorski and Monkhorst [111], on which all SUMRCC approaches are based, requires that a separate cluster operator $T^{(p)}$ is assigned to each reference configuration $|\Phi_p\rangle$ ($p = 1, \dots, M$). 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 the model space (M) is large, particularly when we are only interested in a few low-lying states whose number is much less than M . We have recently addressed an issue of an excessively large number of cluster amplitudes in the SUMRCCSD theory by proposing the SUMRCCSD(1) approach, which is based on the idea of combining the SUMRCCSD method with the MRMBPT approach [133, 134]. In the SUMRCCSD(1) method, the most numerous doubly excited cluster amplitudes, which carry only core and virtual orbital indices, are approximated by their first-order MRMBPT estimates. As shown in [133, 134], the SUMRCCSD(1) approach offers considerable savings in the computer effort, eliminating the largest block of cluster amplitudes carrying only core and virtual orbital indices, while preserving the accuracy of the complete SUMRCCSD method, in which all cluster amplitudes are determined in the iterative procedure.

The SUMRCCSD(1) method is promising, but it does not solve two other problems that the SUMRCC theory faces: the intruder-state problem and the difficulties with extending the basic SUMRCCSD approximation to account for triply and other higher-than-two-body clusters in a computationally tractable manner. As in the single-reference case, where the appropriate use of higher-than-two-body clusters helps to extend the applicability of the single-reference CC approximations to bond breaking and some types of quasi-degenerate and excited states that cannot be handled by the basic CCSD (CC singles and doubles) approximation [8, 11–55, 60–62], the incorporation of higher-than-two-body clusters in the SUMRCC method may help to reduce the severity of the intruder-state problem in

SUMRCCSD calculations, while improving the description of dynamic correlation effects.

Historically, the intruder-state problem was first discovered in the context of MRMBPT calculations, causing the divergent behaviour of the MRMBPT series when the model spaces were inadequate for the electronic states under consideration [143–148]. In the context of the SUMRCC calculations, the intruder-state problem has been shown to be closely related to the intruder-resolution problem [131] and the existence of multiple [121, 131] and singular [114, 120–123, 131] solutions of SUMRCCSD equations. As shown in [70], the existence of multiple intruder solutions is a consequence of a specific nonlinear nature of the generalized Bloch equation, on which all genuine MRCC methods, including SUMRCC, are based. The exponential parameterization of the Bloch wave operator complicates the situation even further, resulting in the appearance of an excessive number of spurious solutions of nonlinear SUMRCCSD equations that may strongly interact with the model space under consideration [131]. The existence of multiple intruder solutions of the SUMRCCSD equations leads to 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 [121–123, 131].

In the last two decades, a few different ideas have been introduced to eliminate or at least significantly reduce the detrimental impact of the intruder-state problem on the SUMRCC results. Basically, all of the proposed schemes rely on one of the following approaches: (i) the refinement of the model space by eliminating the reference configurations that strongly interact with one or more many-electron states, which are of no interest in the calculations while causing the appearance of intruders, and (ii) the enhancement of the quality of the non-diagonal elements of the effective Hamiltonian matrix or approximate SUMRCC energies by inclusion of terms that correspond to higher-order clusters neglected in the SUMRCCSD approximation. The first approach is equivalent to the use of incomplete model spaces. Normally, we have to use a complete model (or active) space in the SUMRCC theory to obtain the size extensive description [111]. Thus, in order to preserve the size-extensivity of the genuine SUMRCC formalism, while using incomplete model spaces, we may have to abandon the intermediate normalization of the wave operator used in the Jeziorski–Monkhorst formulation of the SUMRCC theory [149, 150]. The problem is that the SUMRCCSD results obtained in this way are not very accurate [118]. Recently, Li and Paldus have introduced a much better, indeed brilliant and very elegant, scheme of preserving the intermediate

normalization of the Jeziorski–Monkhorst wave operator and size extensivity for an arbitrary type of the model space by admitting in the cluster operators $T^{(p)}$ suitably defined classes of internal excitations, which are set to zero in the SUMRCC theory employing complete model spaces [136–139], but which no longer vanish in the incomplete model space calculations.

The use of incomplete model spaces may considerably help to reduce the convergence problems and inaccuracies caused by intruders, but clearly the use of complete model spaces in multi-reference calculations is an appealing idea. The removal of specific references from the complete model space that lead to the appearance of intruders cannot be easily converted into a routine or semi-automatic numerical procedure. We should keep in mind that the success and popularity of quantum chemistry methods among chemists and molecular physicists heavily depend on a balance between high accuracy, computer costs, and ease of applicability. The use of complete model spaces has one major advantage over the use of incomplete model spaces: the user can define the appropriate complete model space in a straightforward fashion by providing only the number of active orbitals and the number of active electrons. These numbers typically correspond to numbers of valence orbitals and valence electrons in a molecular system which can be determined from elementary chemical considerations (cf. [151] for a very instructive review). The ease of using complete model spaces in correlated calculations is probably best illustrated by the popularity of the low-order MRMBPT methods employing the complete active space self-consistent-field references, such as CASPT2 and related approaches [152–161] (cf. [151] for a review). Moreover, the experience with single-reference CC methods is telling us that it is difficult to adequately describe dynamic correlation effects, which are important in all high accuracy calculations, without considering higher-than-doubly excited clusters. Thus, it is prudent to develop new classes of SUMRCC methods that considerably reduce the inaccuracies related to intruders because of the use of complete model spaces and the inaccuracies related to the use of singly and doubly excited clusters only by incorporating the essential information about triply and other higher-than-doubly excited clusters in the SUMRCC formalism in a computationally tractable fashion. Clearly, it is highly desirable to have a simple method of correcting the SUMRCCSD energies in a state-specific and non-iterative manner that would resemble the well-known non-iterative *a posteriori* corrections due to triples or triples and quadruples characterizing, for example, the popular CCSD(T) method [162] and its CCSD(TQ_F) [163] and renormalized [11–18, 20–23, 25, 28] analogs.

The standard ways of handling the effects due to higher-than-doubly excited clusters in the MRCC methods are typically tied to the analysis of the MRMBPT expansions of MRCC energies and wave functions (cf., e.g., [111]). In the form exploited by Balková and Bartlett [127], the triply excited cluster amplitudes are estimated in an *ad hoc* manner by expressing them in terms of one- and two-body clusters and by subsequently using the resulting information to construct the state-selective non-iterative energy corrections to SUMRCCSD energies. In an alternative approach, which no longer has a state-selective character, information about triples or triples and quadruples obtained in the perturbative analysis or extracted from the cluster analysis of MRCI wave functions [164] is used to improve the effective Hamiltonian, which is diagonalized to produce the final energies. Similar ways of improving the effective Hamiltonian to obtain the MRCC energies corrected for the effects due to triples have been used in the context of the VUMRCC calculations [108, 165, 166]. Given the numerical costs of such procedures, the results are disappointing. The diagonalizations of effective Hamiltonians corrected for approximate triples may actually worsen the MRCC results obtained with singles and doubles only [108, 166]. There also are several problems with using MRMBPT in a straightforward fashion to improve the SUMRCCSD results. For example, the inaccuracies and other problems plaguing the SUMRCCSD method are in part related to an asymmetric treatment of the excitation manifolds corresponding to different reference configurations [70, 131] (see [47, 112, 121] for examples). The standard *ad hoc* energy corrections due to triply [127] and other higher-than-doubly excited clusters, based on MRMBPT, do not address this problem. Moreover, 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 important to rely on the rigorous mathematical relationships between the approximate and exact SUMRCC methods rather than on a trivial MRMBPT analysis if we are to suggest effective ways of systematically correcting the results of the SUMRCC calculations addressing the above problems, particularly in all these difficult cases where the conventional MRMBPT arguments fail.

We have recently developed a new theory, termed the method of moments of coupled-cluster equations (MMCC), which provides us with general recipes for systematically improving the results of single- and multi-reference CC calculations by focusing on the quantities of interest, which are the differences between the exact,

full CI, and the corresponding single- or multi-reference CC energies [11–14, 18, 22, 23, 26–28, 134, 167]. In the single-reference case, including the ground-state MMCC methods [11–14, 18, 22, 23, 28], and their more recent extensions to excited states [11, 18, 23, 26–28] via the equation-of-motion CC (EOMCC) formalism [168–171], the MMCC theory enabled us to formulate a variety of very useful and easy to use non-iterative CC/EOMCC approximations, including the CI-corrected MMCC approaches [11, 12, 18, 19, 23, 26, 27], the renormalized CC/EOMCC approaches [11–18, 20–23, 25, 28], and the quasi-variational and quadratic MMCC schemes [11, 22–24]. The CI-corrected MMCC methods and the renormalized CC approaches have already been adopted by others [172–175] and used in several large-scale quantum chemistry [25, 28, 176, 177] and nuclear physics [178] applications. The single-reference MMCC methods are capable of providing excellent results for diradicals [176], vibrational terms values [11, 17, 18, 23, 177], several types of unimolecular dissociations [11–19, 21–24], at least some exchange and bond insertion reactions [11, 20, 22, 23, 25], excited states dominated by two-electron transitions [11, 18, 23, 26–28], and ground- and excited-state potential energy surfaces along bond breaking coordinates [11–28]. Since all of the above MMCC and renormalized CC methods are based on the rigorous relationships between the exact and CC/EOMCC energies, they remove the well-known failures of the standard single-reference CC methods, such as CCSD/EOMCCSD (CC/EOMCC singles and doubles approach), CCSD(T), and CCSD(TQ_r), in cases involving bond breaking and difficult excited states, where the usual MBPT arguments used to design the standard CC/EOMCC approximations fail because of the inadequate information about higher-than-doubly excited clusters and strongly divergent behaviour of the single-reference MBPT expansions in quasi-degenerate situations.

In this paper, we use the genuine multi-reference extension of the MMCC formalism [134, 167] to develop a few approximate and practical SUMRCC schemes, in which relatively simple non-iterative corrections due to triply or triply and quadruply excited clusters are added, in a state-selective fashion, to the ground- and excited-state energies obtained in the SUMRCCSD calculations. In analogy to the single-reference case, the new non-iterative SUMRCC approximations classify as either the CI-corrected multi-reference MMCC (MRMMCC) approximations or as the completely renormalized (CR) SUMRCC methods, which can be viewed as the multi-reference extensions of the single-reference CR-CCSD(T) theory [11–15, 17, 18, 20–23, 25, 28]. As in all MMCC approximations, the MRMMCC and CR-SUMRCC methods are based on

the rigorous understanding of the many-body structure of the differences between the full CI and SUMRCCSD energies, which enables us to identify the leading terms constituting these differences. In analogy to the single-reference MMCC approximations, these differences are expressed in terms of the generalized moments of the SUMRCC equations, which are obtained by projecting the SUMRCC equations on the excited Slater determinants that are not included in solving the SUMRCC equations. In this paper, we provide numerical evidence that the non-iterative SUMRCC approximations, based on the general MRMMCC theory described in [134, 167] offer considerable improvements in the SUMRCCSD results, reducing, in particular, the large errors in the SUMRCCSD results due to intruders and inadequate choices of the model spaces. Thus, the non-iterative corrections to SUMRCCSD energies developed in this work may provide a useful and relatively inexpensive solution to many of the problems encountered in SUMRCC calculations.

The paper is organized as follows: In section 2, we outline the MRMMCC formalism based on the SUMRCC theory and the pertinent approximations, including the basic MRMMCC(2,3) and MRMMCC(2,4) approaches and their specific CI-corrected and completely renormalized variants that account for the effects of triples or triples and quadruples, respectively, in a non-iterative fashion. Next, in section 3, we demonstrate how the resulting CI-corrected MRMMCC(2,3) and MRMMCC(2,4) approaches and their perturbative CR-SUMRCCSD(T) analog work for two benchmark systems: the H8 model [179] and CH₂. In section 4, we summarize the results and provide concluding remarks.

2. Theory and computational details

The main idea of the MRMMCC theory employing the SUMRCC formalism is that of the non-iterative, state-selective energy corrections

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

which, when added to the energies E_{μ}^A , obtained by solving the approximate SUMRCC (e.g., SUMRCCSD) equations, referred here and elsewhere to as method A , recover the exact (full CI) energies E_{μ} of the electronic states $|\Psi_{\mu}\rangle$ of interest [134, 167]. The main purpose of the approximate MRMMCC calculations is to estimate corrections δ_{μ}^A , such that the resulting energies $E_{\mu}^A + \delta_{\mu}^A$ are very close to the corresponding exact energies E_{μ} . This is done with the help of the formula that determines the precise many-body structure of corrections δ_{μ}^A in terms of the generalized moments of the SUMRCC equations defining approximation A . Before describing

this formula and the approximate MRMMCC schemes that result from it, we overview the basic elements of the SUMRCC formalism that are relevant to the MRMMCC methods.

2.1. The SUMRCC formalism

As already stated in the Introduction, all genuine multi-reference approaches, including the SUMRCC formalism of Jeziorski and Monkhorst [111], rely on two fundamental concepts: that of the multi-dimensional *model (or reference) space* \mathcal{M}_0 and that of the *wave operator* U . It is assumed that the model space \mathcal{M}_0 ,

$$\mathcal{M}_0 = \text{ls}\{|\Phi_p\rangle\}_{p=1}^M, \quad (2)$$

spanned by M suitably chosen configuration-state functions $|\Phi_p\rangle$, provides a reasonable zero-order approximation to the *target space*,

$$\mathcal{M} = \text{ls}\{|\Psi_{\mu}\rangle\}_{\mu=1}^M, \quad (3)$$

spanned by M eigenstates $|\Psi_{\mu}\rangle$ of the electronic Hamiltonian H . Typically, in order to define the reference configuration-state functions $|\Phi_p\rangle$, we partition the molecular orbital set employed into the three disjoint subsets of *core*, *active*, and *virtual* orbitals. The core orbitals are occupied and the virtual ones are unoccupied in all references $|\Phi_p\rangle$. The configurations $|\Phi_p\rangle$ differ in the occupancies of active orbitals. All possible distributions of the active electrons among the active orbitals result in a *complete model (or active) space* (CAS). As mentioned in the Introduction, the use of CAS in the SUMRCC theory guarantees the size extensivity of the results [111]. The recent work of Li and Paldus [136–139] shows that one can obtain the rigorously size extensive SUMRCC description with incomplete model spaces if the so-called C-conditions are imposed on the internal cluster amplitudes carrying only active spin-orbital indices, but for the reasons discussed in the Introduction in this paper we focus on complete model spaces. The case of incomplete model spaces will be examined in a future work.

The wave operator $U: \mathcal{M}_0 \rightarrow \mathcal{M}$ is defined as a one-to-one mapping between the \mathcal{M}_0 and \mathcal{M} spaces. The exact eigenstates $|\Psi_{\mu}\rangle$ are obtained by applying the wave operator U to the zero-order states

$$|\chi_{\mu}\rangle \equiv P|\Psi_{\mu}\rangle \in \mathcal{M}_0, \quad (4)$$

where

$$P = \sum_{p=1}^M P^{(p)}, \quad P^{(p)} = |\Phi_p\rangle\langle\Phi_p| \quad (5)$$

is the projection operator onto \mathcal{M}_0 . We obtain

$$|\Psi_\mu\rangle = U|\chi_\mu\rangle \quad (\mu = 1, \dots, M), \quad (6)$$

where $|\chi_\mu\rangle$ is defined by equation (4). It is also assumed that the wave operator U annihilates states belonging to the orthogonal complement \mathcal{M}_0^\perp , so that

$$UQ = 0, \quad (7)$$

where

$$Q = 1 - P. \quad (8)$$

The wave operator U defined in the above manner, referred to as the Bloch wave operator, satisfies the *intermediate normalization condition*,

$$PU = P. \quad (9)$$

Equations (7) and (9) immediately imply that $U^2 = U$, so that the wave operator U , just like projection 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

$$HU = UHU, \quad (10)$$

which is usually referred to as the *generalized Bloch equation* [6, 8, 67–69, 142]. Once the wave operator is obtained by solving equation (10), the energies E_μ of the electronic states $|\Psi_\mu\rangle$, $\mu = 1, \dots, M$, are calculated by diagonalizing the *effective Hamiltonian*,

$$H^{\text{eff}} \equiv H^{\text{eff}}(U) = PHU = PHUP, \quad (11)$$

in the model space \mathcal{M}_0 . The corresponding wave functions $|\Psi_\mu\rangle$ are determined using equation (6), where the zero-order states $|\chi_\mu\rangle$ are the right eigenstates of H^{eff} ,

$$H^{\text{eff}}|\chi_\mu\rangle = E_\mu|\chi_\mu\rangle \quad (\mu = 1, \dots, M). \quad (12)$$

In the SUMRCC formalism of Jeziorski and Monkhorst, we use the following exponential parameterization of the wave operator U

$$U = \sum_{p=1}^M e^{T^{(p)}} P^{(p)}, \quad (13)$$

where $T^{(p)}$ is the cluster operator corresponding to the reference configuration $|\Phi_p\rangle$. The wave operator U , equation (13), reduces to the wave operator of the single-reference CC theory, $U^{\text{SRCC}} = e^T|\Phi\rangle\langle\Phi|$, when \mathcal{M}_0 is a one-dimensional space spanned by a single

Slater determinant $|\Phi\rangle$ (this one-dimensional case is obtained when the set of active spin-orbitals is empty). In analogy to the standard single-reference CC theory, each cluster operator $T^{(p)}$, $p = 1, \dots, M$, is a sum of its many-body components $T_n^{(p)}$, where

$$T_n^{(p)} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} {}^{(p)}t_{a_1 \dots a_n}^{i_1 \dots i_n} {}^{(p)}E_{i_1 \dots i_n}^{a_1 \dots a_n}, \quad (14)$$

with ${}^{(p)}t_{a_1 \dots a_n}^{i_1 \dots i_n}$ and ${}^{(p)}E_{i_1 \dots i_n}^{a_1 \dots a_n}$ representing the corresponding cluster amplitudes and excitation operators generating the n -tuply excited configurations $|{}^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ relative to $|\Phi_p\rangle$ (as usual, indices i_m (a_m) represent the spin-orbitals occupied (unoccupied) in $|\Phi_p\rangle$). The intermediate normalization condition, equation (9), and the completeness of the model space require that each $T_n^{(p)}$ component generates a state belonging to \mathcal{M}_0^\perp when acting on the corresponding reference $|\Phi_p\rangle$. This means that the internal cluster amplitudes ${}^{(p)}t_{a_1 \dots a_n}^{i_1 \dots i_n}$ carrying only active spin-orbital indices vanish.

In the exact SUMRCC formalism

$$T^{(p)} = \sum_{n=1}^N T_n^{(p)} \quad (p = 1, \dots, M), \quad (15)$$

where N is the number of electrons in the system under consideration. In the standard SUMRCC approximations, the many-body expansion of each cluster operator $T^{(p)}$ is truncated at some excitation level. Thus, if m_A is the excitation level defining a given SUMRCC approximation A , the corresponding cluster operators $T^{(p)}$ assume the following form:

$$T_A^{(p)} = \sum_{n=1}^{m_A} T_n^{(p)} \quad (p = 1, \dots, M). \quad (16)$$

Note that the value of m_A is the same for all values of p . The SUMRCCSD approach is obtained by setting $m_A = 2$ in equation (16).

The explicit equations for the unknown cluster operators $T_n^{(p)}$ or cluster amplitudes ${}^{(p)}t_{a_1 \dots a_n}^{i_1 \dots i_n}$ that define them are obtained by replacing the generalized Bloch equation, equation (10), by a system of equations $HU|\Phi_p\rangle = UHU|\Phi_p\rangle$, where U is defined by equation (13) and $p = 1, \dots, M$, premultiplying the p th equation in the resulting system of equations on the left by $e^{-T^{(p)}}$, and projecting the resulting equations on the excited configurations that belong to \mathcal{M}_0^\perp and that are included in the cluster components $T_n^{(p)}$ participating in the calculations (the p th equation is projected on the excited configurations $|{}^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$). In the standard SUMRCC approximation A , in which the many-body expansions of cluster operators $T^{(p)}$ are truncated at the m_A -body

terms (cf. equation (16)), we only consider the projections on the excited configurations $|^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ with $n \leq m_A$. This leads to the final form of the SUMRCC equations for the amplitudes $^{(p)}t_{a_1 \dots a_n}^{i_1 \dots i_n}$ defining $T_A^{(p)}$ clusters

$$\mathcal{Q}_n^{(p)} \left[(H_{N_p} e^{T_A^{(p)}})_C - \sum_{q=1(q \neq p)}^M e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H^{\text{eff}, A} \right] |\Phi_p\rangle = 0$$

$$(p = 1, \dots, M, n = 1, \dots, m_A), \quad (17)$$

or somewhat more explicitly

$$^{(p)}\Lambda_{i_1 \dots i_n}^{a_1 \dots a_n} + ^{(p)}\Xi_{i_1 \dots i_n}^{a_1 \dots a_n} = 0, \quad i_1 < \dots < i_n,$$

$$a_1 < \dots < a_n, \quad n = 1, \dots, m_A, \quad p = 1, \dots, M, \quad (18)$$

where

$$^{(p)}\Lambda_{i_1 \dots i_n}^{a_1 \dots a_n} = \left\langle ^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \left| (H_{N_p} e^{T_A^{(p)}})_C \right| \Phi_p \right\rangle \quad (19)$$

and

$$^{(p)}\Xi_{i_1 \dots i_n}^{a_1 \dots a_n} = - \sum_{q=1(q \neq p)}^M \left\langle ^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \left| e^{-T_A^{(p)}} e^{T_A^{(q)}} \right| \Phi_q \right\rangle H_{qp}^{\text{eff}, A} \quad (20)$$

are the *direct* and *coupling* terms, respectively. In the above equations, $H_{N_p} = H - \langle \Phi_p | H | \Phi_p \rangle$ is the Hamiltonian in the normal-ordered form relative to the Fermi vacuum $|\Phi_p\rangle$, subscript C designates the connected part of a given operator expression,

$$\mathcal{Q}_n^{(p)} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} \left| ^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \right\rangle \left\langle ^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \right| \quad (21)$$

is a projection operator onto the subspace of \mathcal{M}_0^\perp spanned by the n -tuply excited configurations relative to $|\Phi_p\rangle$, and the matrix elements of the effective Hamiltonian, $H_{qp}^{\text{eff}, A}$, entering the coupling term in equations (17) or (18), are defined as

$$H_{qp}^{\text{eff}, A} \equiv \langle \Phi_q | H^{\text{eff}, A} | \Phi_p \rangle = \langle \Phi_q | (H_{N_p} e^{T_A^{(p)}})_C | \Phi_p \rangle + \delta_{qp} \langle \Phi_p | H | \Phi_p \rangle, \quad (22)$$

where δ_{qp} is the usual Kronecker delta. It should be noted that the direct term $^{(p)}\Lambda_{i_1 \dots i_n}^{a_1 \dots a_n}$, equation (19), is analogous to the standard single-reference CC equations written for the reference $|\Phi_p\rangle$. The main difference between the single-reference CC equations and the SUMRCC equations is in the presence of the coupling term $^{(p)}\Xi_{i_1 \dots i_n}^{a_1 \dots a_n}$, equation (20), in the latter equations. In the single-reference case, where $M = 1$, the coupling term vanishes.

Once the system of equations, equation (17) or (18), is solved for cluster operators $T_A^{(p)}$, and the matrix elements of the effective Hamiltonian are constructed with the converged amplitudes $^{(p)}t_{a_1 \dots a_n}^{i_1 \dots i_n}$, the final SUMRCC energies E_μ^A defining approximation A are obtained as eigenvalues of the effective Hamiltonian $H^{\text{eff}, A}$, namely (cf. equation (12))

$$H^{\text{eff}, A} |\chi_\mu^A\rangle = E_\mu^A |\chi_\mu^A\rangle \quad (\mu = 1, \dots, M). \quad (23)$$

The corresponding SUMRCC wave functions $|\Psi_\mu^A\rangle$ are obtained by applying the wave operator U , equation (13), where $T^{(p)} = T_A^{(p)}$, to the zero-order states

$$|\chi_\mu^A\rangle = \sum_{p=1}^M c_{p\mu}^A |\Phi_p\rangle, \quad (24)$$

where coefficients

$$c_{p\mu}^A = \langle \Phi_p | \chi_\mu^A \rangle \quad (25)$$

are determined by diagonalizing $H^{\text{eff}, A}$ in \mathcal{M}_0 . We obtain (cf. equations (6) and (13))

$$|\Psi_\mu^A\rangle = \sum_{p=1}^M c_{p\mu}^A e^{T_A^{(p)}} |\Phi_p\rangle \quad (\mu = 1, \dots, M). \quad (26)$$

Equations (17)–(26), where $T_A^{(p)}$ is given by equation (16), define the SUMRCC approximation A . When $m_A = N$ in the above equations, we obtain the exact theory equivalent to full CI. When $m_A = 2$, we obtain the SUMRCCSD approach. Now, we need the explicit many-body expressions for the energy corrections δ_μ^A , equation (1), that would enable us to design non-iterative SUMRCC approximations, such as CR-SUMRCCSD(T). These expressions, defining the MRMMCC theory, are discussed next.

2.2. The MRMMCC formalism

In analogy to the single-reference CC methods and their extensions to excited states via the EOMCC approach [11–14, 18, 22, 23, 26–28], we can express the differences δ_μ^A between the exact, full CI, energies E_μ and their SUMRCC counterparts E_μ^A , equation (1), in terms of the generalized moments of the SUMRCC equations defining the SUMRCC approximation A whose results we are trying to improve. We obtain [134, 167]

$$\delta_\mu^A \equiv E_\mu - E_\mu^A = (d_\mu^A)^{-1} \sum_{p=1}^M c_{p\mu}^A \sum_{n=m_A+1}^N \sum_{m=m_A+1}^n \langle \Psi_\mu | (e^{T_A^{(p)}})_{n-m} \Gamma_m^{(p)}(m_A) | \Phi_p \rangle, \quad (27)$$

where $c_{p\mu}^A$ are the coefficients defining the zero-order model-space states $|\chi_\mu^A\rangle$, equation (24), obtained by diagonalizing the effective Hamiltonian of the approximate SUMRCC method A in \mathcal{M}_0 ,

$$d_\mu^A = \langle \Psi_\mu | \Psi_\mu^A \rangle \quad (28)$$

is an overlap of the exact wave function $|\Psi_\mu\rangle$ and the corresponding SUMRCC wave function $|\Psi_\mu^A\rangle$, equation (26), obtained with method A , ($e^{T_A^{(p)}}$) $_{n-m}$ is the $(n-m)$ -body component of $e^{T_A^{(p)}}$, and

$$\begin{aligned} \Gamma_m^{(p)}(m_A)|\Phi_p\rangle &= Q_m^{(p)} \left[\left(H_{N_p} e^{T_A^{(p)}} \right)_C - \sum_{q=1(q \neq p)}^M e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H^{\text{eff}, A} \right] |\Phi_p\rangle \\ (m = 1, \dots, N, p = 1, \dots, M) \end{aligned} \quad (29)$$

are the quantities that are directly expressed in terms of the generalized moments of the SUMRCC equations

$$\begin{aligned} {}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) &= \langle {}^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m} | \left[\left(H_{N_p} e^{T_A^{(p)}} \right)_C \right. \\ &\quad \left. - \sum_{q=1(q \neq p)}^M e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H^{\text{eff}, A} \right] |\Phi_p\rangle. \end{aligned} \quad (30)$$

We have

$$\Gamma_m^{(p)}(m_A)|\Phi_p\rangle = \sum_{\substack{i_1 < \dots < i_m \\ a_1 < \dots < a_m}} {}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) |{}^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m}\rangle. \quad (31)$$

As one can see, the generalized moments ${}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A)$, equation (30), which enter the energy corrections δ_μ^A , equation (27), represent the projections of the SUMRCC equations on the excited configurations $|{}^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m}\rangle$ whose excitation level m exceeds that of a given SUMRCC approximation A . For example, if we want to obtain the exact energies E_μ by adding corrections δ_μ^A to the SUMRCCSD energies E_μ^A (the $m_A = 2$ case), we have to consider moments ${}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2)$ with $m > 2$ (projections of the SUMRCCSD equations on triply and other higher-than-doubly excited configurations relative to references $|\Phi_p\rangle$). As a matter of fact, the generalized moments ${}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A)$ or their $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ analogs, equations (29) and (31), are the most fundamental quantities of the Jeziorski–Monkhorst theory. Indeed, the SUMRCC equations for the cluster operators $T_A^{(p)}$, equations (17) and (18), are immediately obtained by imposing a requirement that the lowest moments ${}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A)$ or $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$,

with $m = 1, \dots, m_A$, vanish. For example, we obtain equation (17) by requiring that

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

In analogy to the SUMRCC equations (cf. equation (18)) and to facilitate further discussion, we split the generalized moments ${}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A)$ into direct and coupling contributions,

$${}^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) = \text{I},^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) + \text{II},^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A), \quad (33)$$

where

$$\text{I},^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) = \langle {}^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m} | \left(H_{N_p} e^{T_A^{(p)}} \right)_C | \Phi_p \rangle \quad (34)$$

and

$$\text{II},^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) = - \sum_{q=1(q \neq p)}^M \langle {}^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m} | e^{-T_A^{(p)}} e^{T_A^{(q)}} | \Phi_q \rangle H_{qp}^{\text{eff}, A}. \quad (35)$$

A similar decomposition is possible for the corresponding quantities $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$

$$\Gamma_m^{(p)}(m_A)|\Phi_p\rangle = \Gamma_m^{(p),\text{I}}(m_A)|\Phi_p\rangle + \Gamma_m^{(p),\text{II}}(m_A)|\Phi_p\rangle, \quad (36)$$

where the direct contributions $\Gamma_m^{(p),\text{I}}(m_A)|\Phi_p\rangle$ are given by

$$\begin{aligned} \Gamma_m^{(p),\text{I}}(m_A)|\Phi_p\rangle &= \sum_{\substack{i_1 < \dots < i_m \\ a_1 < \dots < a_m}} \text{I},^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) |{}^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m}\rangle \\ &= Q_m^{(p)} \left(H_{N_p} e^{T_A^{(p)}} \right)_C |\Phi_p\rangle \end{aligned} \quad (37)$$

and the coupling contributions $\Gamma_m^{(p),\text{II}}(m_A)|\Phi_p\rangle$ are defined as

$$\begin{aligned} \Gamma_m^{(p),\text{II}}(m_A)|\Phi_p\rangle &= \sum_{\substack{i_1 < \dots < i_m \\ a_1 < \dots < a_m}} \text{II},^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A) |{}^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m}\rangle \\ &= - \sum_{q=1(q \neq p)}^M Q_m^{(p)} e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H^{\text{eff}, A} |\Phi_p\rangle. \end{aligned} \quad (38)$$

It should be noted that, in the single-reference case, where $M=1$ and where the corresponding coupling contributions to the SUMRCC moments, $\text{II},^{(1)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A)$, vanish, the SUMRCC moments ${}^{(1)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A)$ reduce to the generalized moments of the single-reference CC equations using $|\Phi_1\rangle$ as a reference. In this case, equation (27) reduces to the formula for the difference

between the exact and CC ground-state energies defining the single-reference MMCC theory [11–14, 18, 22, 23] (see [134, 167] for further details). It should also be mentioned that, for a given excitation level m_A , the explicit expressions for the coupling contributions to the SUMRCC moments, ${}^{II,(p)}\gamma_{a_1\dots a_m}^{i_1\dots i_m}(m_A)$, equation (35), in terms of cluster amplitudes ${}^{(p)}t_{a_1\dots a_n}^{i_1\dots i_n}$, $n = 1, \dots, m_A$, defining method A , strongly depend on the model space employed. This should be contrasted with the direct moments ${}^{I,(p)}\gamma_{a_1\dots a_m}^{i_1\dots i_m}(m_A)$, equation (34), which have the same mathematical form for all model spaces.

Equation (27) defines the exact MRMMCC theory. Two issues have to be resolved before using this equation in practice. First of all, the wave functions $|\Psi_\mu\rangle$ that enter the exact equation (27) are the exact, full CI, states. Thus, in order to propose the computationally tractable approaches based on the MRMMCC theory, we must approximate the $|\Psi_\mu\rangle$ wave functions in some way. The basic requirements that all approximate forms of $|\Psi_\mu\rangle$ must satisfy are as follows: (i) all wave functions $|\Psi_\mu\rangle$ must be relatively easy to determine; the cost of determining $|\Psi_\mu\rangle$'s should be less than or comparable to the cost of solving the SUMRCC equations for method A whose results we are trying to improve through corrections δ_μ^A , and (ii) wave functions $|\Psi_\mu\rangle$ must contain higher-than- m_A -tuply excited configurations relative to at least some references $|\Phi_p\rangle$; this is necessary to obtain the non-zero values of corrections δ_μ^A (cf. equation (27)). Second, the exact MRMMCC corrections δ_μ^A , equation (27), have the form of the complete many-body expansions involving all n -tuply excited configurations with $n = m_A, \dots, N$, where N is the number of electrons in a system (see the summation over n in equation (27)). Thus, in order to develop the computationally tractable MRMMCC methods, we must truncate the many-body expansions for δ_μ^A in some way. We can, for example, truncate the summation over n in equation (27) at $n = m_B$, where the excitation level $m_A < m_B < N$. This leads to the MRMMCC (m_A, m_B) schemes [134, 167]. The MRMMCC(2,3), MRMMCC(2,4), and CR-SUMRCCSD(T) schemes discussed in the next subsection are the MRMMCC (m_A, m_B) schemes with $m_A = 2$ and $m_B = 3$ (the MRMMCC(2,3) and CR-SUMRCCSD(T) cases) or $m_B = 4$ (the MRMMCC(2,4) case). We can also use the projection on the wave function $|\Psi_\mu\rangle$ entering equation (27) as a method of selecting the specific many-body terms from the complete many-body expansion defining δ_μ^A . In this case, the specific many-body structure of $|\Psi_\mu\rangle$ determines the nature of truncation in equation (27). All of these methods of approximating equation (27), leading to the CI-corrected MRMMCC and CR-SUMRCC methods, are discussed in section 2.3.

2.3. Approximate variants of the MRMMCC theory

In this paper, we focus on implementing and testing the following two variants of the MRMMCC theory: (i) the CI-corrected MRMMCC methods and (ii) the CR-SUMRCCSD(T) approach. Our main interest is in correcting the results of the SUMRCCSD calculations (equation (27) with $m_A = 2$). We begin our discussion of these methods with the CI-corrected MRMMCC approaches.

2.3.1. The CI-corrected MRMMCC methods

In the CI-corrected MRMMCC methods, we obtain the wave functions $|\Psi_\mu\rangle$ entering equation (27) by performing limited CI calculations. In the $m_A = 2$ case considered in this work, the most natural choice of $|\Psi_\mu\rangle$, which is compatible with the SUMRCCSD calculations whose results we are trying to improve, is provided by the MRCISD (MRCI singles and doubles) approach employing the same active space as used in the SUMRCCSD calculations. If $|\Psi_\mu^{\text{MRCISD}}\rangle$ is the MRCISD wave function, the formula for the CI-corrected MRMMCC energies becomes

$$E_\mu^{\text{MRMMCC/CI}} = E_\mu^{\text{SUMRCCSD}} + \delta_\mu^{\text{MRMMCC/CI}}, \quad (39)$$

where E_μ^{SUMRCCSD} is the SUMRCCSD energy of state $|\Psi_\mu\rangle$ and the corresponding non-iterative correction $\delta_\mu^{\text{MRMMCC/CI}}$ is defined as

$$\begin{aligned} \delta_\mu^{\text{MRMMCC/CI}} &= (d_\mu^{\text{SUMRCCSD/CI}})^{-1} \sum_{p=1}^M c_{p\mu}^{\text{SUMRCCSD}} \sum_{n=3}^{k_p} \\ &\times \sum_{m=3}^n \langle \Psi_\mu^{\text{MRCISD}} | (e^{T_1^{(p)} + T_2^{(p)}})_{n-m} \Gamma_m^{(p)}(2) | \Phi_p \rangle. \end{aligned} \quad (40)$$

Here, $T_1^{(p)}$ and $T_2^{(p)}$ represent the singly and doubly excited cluster components obtained in the SUMRCCSD calculations,

$$c_{p\mu}^{\text{SUMRCCSD}} = \langle \Phi_p | \chi_\mu^{\text{SUMRCCSD}} \rangle \quad (41)$$

are the coefficients defining the zero-order states $|\chi_\mu^{\text{SUMRCCSD}}\rangle$ obtained by diagonalizing the SUMRCCSD effective Hamiltonian $H^{\text{eff, SUMRCCSD}}$, whose matrix elements are calculated as

$$H_{qp}^{\text{eff, SUMRCCSD}} = \langle \Phi_q | (H e^{T_1^{(p)} + T_2^{(p)}})_C | \Phi_p \rangle \quad (42)$$

in the model space \mathcal{M}_0 ,

$$d_\mu^{\text{SUMRCCSD/CI}} = \langle \Psi_\mu^{\text{MRCISD}} | \Psi_\mu^{\text{SUMRCCSD}} \rangle \quad (43)$$

is an overlap of the MRCISD wave function $|\Psi_\mu^{\text{MRCISD}}\rangle$ with the corresponding SUMRCCSD wave function

$$|\Psi_\mu^{\text{SUMRCCSD}}\rangle = \sum_{p=1}^M c_{p\mu}^{\text{SUMRCCSD}} e^{T_1^{(p)}+T_2^{(p)}} |\Phi_p\rangle, \quad (44)$$

and the quantities $\Gamma_m^{(p)}(2)|\Phi_p\rangle$, $p = 1, \dots, M$, $m > 2$, are defined as

$$\Gamma_m^{(p)}(2)|\Phi_p\rangle = \Gamma_m^{(p),I}(2)|\Phi_p\rangle + \Gamma_m^{(p),II}(2)|\Phi_p\rangle, \quad (45)$$

where

$$\Gamma_m^{(p),I}(2)|\Phi_p\rangle = \sum_{\substack{i_1 < \dots < i_m \\ a_1 < \dots < a_m}} I, (p) \gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2) |^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m}\rangle \quad (46)$$

and

$$\Gamma_m^{(p),II}(2)|\Phi_p\rangle = \sum_{\substack{i_1 < \dots < i_m \\ a_1 < \dots < a_m}} II, (p) \gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2) |^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m}\rangle, \quad (47)$$

with

$$I, (p) \gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2) = \langle^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m} | (H_{N_p} e^{T_1^{(p)}+T_2^{(p)}})_C | \Phi_p \rangle \quad (48)$$

and

$$II, (p) \gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2) = - \sum_{q=1(q \neq p)}^M \langle^{(p)}\Phi_{i_1 \dots i_m}^{a_1 \dots a_m} | e^{-T_1^{(p)}-T_2^{(p)}} e^{T_1^{(q)}+T_2^{(q)}} | \Phi_q \rangle \times H_{qp}^{\text{eff}, \text{SUMRCCSD}} \quad (49)$$

representing the direct and coupling contributions to the generalized moments of the SUMRCCSD equations

$$^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2) = I, (p) \gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2) + II, (p) \gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(2). \quad (50)$$

The upper summation limit k_p in equation (40) represents the rank of the highest excitation in the many-body expansion of the MRCISD wave function $|\Psi_\mu^{\text{MRCISD}}\rangle$ relative to the Fermi vacuum $|\Phi_p\rangle$. The values of k_p depend on the choice of the model space \mathcal{M}_0 and, in general, may vary with the reference label p . As long as the model space is multi-dimensional, the values of k_p are greater than 2, since some single and double excitations from references $|\Phi_q\rangle$ with $q \neq p$ become higher-than-double excitations relative to a given $|\Phi_p\rangle$. For example, when the model space is two dimensional and the corresponding references $|\Phi_1\rangle$ and $|\Phi_2\rangle$ differ by a double excitation (the case of two active orbitals of different symmetry and two active electrons [112, 114, 119–124, 128]), the many-body expansions of $|\Psi_\mu^{\text{MRCISD}}\rangle$, $\mu = 1, 2$, may contain up to quadruply

excited determinants relative to each $|\Phi_p\rangle$, $p = 1, 2$ (some singles and doubles relative to one reference become selected triples and quadruples of the semi-internal type relative to the other reference [112]). Thus, the CI-corrected MRMMCC method based on equations (39)–(49) enables us to improve the results of the SUMRCCSD calculations by adding the non-iterative corrections due to selected classes of semi-internal higher-than-doubly excited clusters, which are present in the MRCISD method and absent in the SUMRCCSD approach, to the SUMRCCSD energies.

In addition to improving the accuracies of the SUMRCCSD calculations (see section 3), the CI-corrected MRMMCC approach has one, very important, feature which is worth mentioning here: it reinforces 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 subspaces $\mathcal{M}_{0,A}^{\perp(p)}$ of the \mathcal{Q} -space \mathcal{M}_0^{\perp} spanned by the excited configurations $^{(p)}\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}$ with $n = 1, \dots, m_A$, which are used to construct the truncated SUMRCC equations, equations (18)–(20), are usually different for different values of p (see, e.g., [47, 70, 112, 121]). As explained in [70], this asymmetric treatment of the manifolds of excitations corresponding to different references $|\Phi_p\rangle$, resulting from truncating the many-body expansions of all operators $T^{(p)}$ at exactly the same excitation level m_A , causes the approximate SUMRCC schemes, such as SUMRCCSD, to be not equivalent to any Hermitian eigenvalue problem. This non-Hermitian nature of the SUMRCC approximations, combined with a highly nonlinear character of the SUMRCC equations, lead to a number of pathologies observed in approximate SUMRCC calculations mentioned in the Introduction. The CI-corrected MRMMCC methods enable us to eliminate at least some of these pathologies by restoring the symmetric treatment of the $\mathcal{M}_{0,A}^{\perp(p)}$ subspaces. This is possible, since, in the CI-corrected MRMMCC approaches, we do not truncate the summations over n and m in equation (27) in any arbitrary manner. Instead, we use the projections onto the MRCI wave functions $|\Psi_\mu\rangle$, $\mu = 1, \dots, M$, all employing the same set of determinants to define them, as a natural method of selecting the relevant higher-order terms in the summations over p , n , and m that are present in the numerators of equations (27) and (40) and absent in the truncated SUMRCC calculations. By projecting the numerators of equations (27) and (40) on the MRCI wave functions $|\Psi_\mu\rangle$, we automatically select those subsets of the generalized moments $^{(p)}\gamma_{a_1 \dots a_m}^{i_1 \dots i_m}(m_A)$ or quantities $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ (usually, different $^{(p)}\gamma$'s or $\Gamma^{(p)}$'s for different values of p) that need to be considered to restore a perfectly symmetric treatment of

the manifolds of excitations in the approximate SUMRCC (e.g., SUMRCCSD) calculations. As shown in section 3, this symmetrization of the excitation manifolds $\mathcal{M}_{0,A}^{\perp(p)}$ through corrections δ_μ defining the CI-corrected MRMMCC approach leads to considerable improvements in the SUMRCCSD energies, particularly in regions plagued by intruders, where there is a need to incorporate higher-than-doubly excited clusters in a well-balanced manner.

As mentioned earlier, when the dimension of the model space \mathcal{M}_0 is 2 and the corresponding references $|\Phi_1\rangle$ and $|\Phi_2\rangle$ differ by a double excitation, the many-body expansions of the wave functions $|\Psi_\mu^{\text{MRCISD}}\rangle$, $\mu = 1, 2$, may contain up to quadruply excited determinants relative to each $|\Phi_p\rangle$, $p = 1, 2$. This implies that, in this case, the upper limits for the summation index n in equation (40) satisfy the condition $k_p \leq 4$. When the dimension of the model space is greater than 2, the values of k_p may exceed 4. In this case, in addition to the complete version of the CI-corrected MRMMCC method described by equations (39)–(49), in which values of k_p are determined by the many-body structure of the wave functions $|\Psi_\mu^{\text{MRCISD}}\rangle$, it may be prudent to consider the truncated variants of the CI-corrected MRMMCC schemes, in which the summation over n in equation (40) is limited to the leading terms, such as $n = 3$ or $n = 3, 4$, independent of the dimension of \mathcal{M}_0 . By truncating the many-body expansion (the summation over n) defining the MRMMCC/CI correction $\delta_\mu^{\text{MRMMCC/CI}}$, equation (40), at $n = 3$, we obtain the CI-corrected MRMMCC(2,3) (MRMMCC(2,3)/CI) method. By truncating the summation over n in equation (40) at $n = 4$, we obtain the CI-corrected MRMMCC(2,4) (MRMMCC(2,4)/CI) method. In general, the MRMMCC(2,3)/CI and MRMMCC(2,4)/CI approaches do not restore the perfectly symmetric treatment of the excitation manifolds relative to different references $|\Phi_p\rangle$, but they are worth considering here, since they still bring a lot of information about selected classes of triples and quadruples missing in the SUMRCCSD scheme at a relatively low cost. When \mathcal{M}_0 is two dimensional (the aforementioned case of two active orbitals of different symmetry and two active electrons), the MRMMCC(2,4)/CI approach and the complete CI-corrected MRMMCC method defined by equations (39)–(49) are identical.

2.3.2. The MRMMCC(2,3) and MRMMCC(2,4) approximations and the CR-SUMRCCSD(T) scheme

The idea of the CI-corrected MRMMCC(2,3) and MRMMCC(2,4) approaches can be extended to non-CI choices of the wave functions $|\Psi_\mu\rangle$ that enter equation (27). In general, the MRMMCC(2,3) and MRMMCC(2,4) approximations are defined by setting

$m_A = 2$ in equation (27) and by limiting the summations over n in the resulting equations to $n = 3$ (the MRMMCC(2,3) case) or $\sum_{n=3}^4$ (the MRMMCC(2,4) case). Thus, the formula for the energy defining the general MRMMCC(2,3) scheme is

$$E_\mu^{\text{MRMMCC}}(2, 3) = E_\mu^{\text{SUMRCCSD}} + \delta_\mu(2, 3), \quad (51)$$

where

$$\delta_\mu(2, 3) = (d_\mu^{\text{SUMRCCSD}})^{-1} \sum_{p=1}^M c_{p\mu}^{\text{SUMRCCSD}} \langle \Psi_\mu | \Gamma_3^{(p)}(2) | \Phi_p \rangle, \quad (52)$$

with $c_{p\mu}^{\text{SUMRCCSD}}$ defined by equation (41), d_μ^{SUMRCCSD} defined as an overlap of $|\Psi_\mu\rangle$ with the SUMRCCSD wave function (44), and $\Gamma_3^{(p)}(2)|\Phi_p\rangle$ defined in terms of the generalized moments of the SUMRCCSD equations corresponding to projections of these equations on the triply excited determinants $|^{(p)}\Phi_{i_1 i_2 i_3}^{a_1 a_2 a_3}\rangle$ (see equations (45)–(49) with m set at 3). The general MRMMCC(2,4) energy expression is

$$E_\mu^{\text{MRMMCC}}(2, 4) = E_\mu^{\text{SUMRCCSD}} + \delta_\mu(2, 4), \quad (53)$$

where

$$\delta_\mu(2, 4) = (d_\mu^{\text{SUMRCCSD}})^{-1} \sum_{p=1}^M c_{p\mu}^{\text{SUMRCCSD}} \times \langle \Psi_\mu | [\Gamma_3^{(p)}(2) + T_1^{(p)} \Gamma_3^{(p)}(2) + \Gamma_4^{(p)}(2)] | \Phi_p \rangle, \quad (54)$$

with $\Gamma_3^{(p)}(2)|\Phi_p\rangle$ and $\Gamma_4^{(p)}(2)|\Phi_p\rangle$ defined in terms of the generalized moments of the SUMRCCSD equations corresponding to projections of these equations on the triply and quadruply excited determinants $|^{(p)}\Phi_{i_1 i_2 i_3}^{a_1 a_2 a_3}\rangle$ and $|^{(p)}\Phi_{i_1 i_2 i_3 i_4}^{a_1 a_2 a_3 a_4}\rangle$ (see equations (45)–(49) with m set at 3 and 4, respectively). The MRMMCC(2,3) and MRMMCC(2,4) approximations belong to the general class of the MRMMCC(m_A, m_B) schemes mentioned in section 2.2, in which we calculate corrections δ_μ^A to the SUMRCC energies E_μ^A by truncating the summation over n in equation (27) at the $n = m_B$ term, where $m_A < m_B < N$. The MRMMCC(2,3) and MRMMCC(2,4) approaches reduce to the single-reference MMCC(2,3) and MMCC(2,4) approximations, originally proposed in [12, 13] (cf., also, [11, 14, 18, 22, 23, 26, 27]), when the model space is one dimensional (the $M = 1$ case; see [134, 167] for more information).

The MRMMCC(2,3) and MRMMCC(2,4) approximations defined by equations (51)–(54) can be used to develop the CI-corrected MRMMCC(2,3) and MRMMCC(2,4) methods, described in section 2.3.1, or to propose the CR-SUMRCC approaches in which,

in analogy to the single-reference CR-CCSD(T) theory [11–15, 17, 18, 20–23, 25, 28] and its higher-order extensions [11–18, 22–24], we use the perturbative forms of the wave functions $|\Psi_\mu\rangle$ in equations (52) and (54). In this paper, we focus on the lowest-order CR-SUMRCC approach, termed CR-SUMRCCSD(T), in which perturbative triples corrections based on equation (52), designated as $\delta_\mu(T)$, are added to the SUMRCCSD energies. The CR-SUMRCCSD(T) energy is calculated as follows:

$$E_\mu^{\text{CR-SUMRCCSD(T)}} = E_\mu^{\text{SUMRCCSD}} + \delta_\mu(T), \quad (55)$$

where

$$\delta_\mu(T) = (d_\mu^{(T)})^{-1} \sum_{p=1}^M c_{p\mu}^{\text{SUMRCCSD}} \times \langle \Psi_\mu^{\text{CR-SUMRCCSD(T)}} | \Gamma_3^{(p)}(2) | \Phi_p \rangle \quad (56)$$

is the non-iterative triples correction to the SUMRCCSD energy E_μ^{SUMRCCSD} . The denominator $d_\mu^{(T)}$ entering equation (56) is defined as

$$d_\mu^{(T)} = \langle \Psi_\mu^{\text{CR-SUMRCCSD(T)}} | \Psi_\mu^{\text{SUMRCCSD}} \rangle \quad (57)$$

and the zero-order coefficients $c_{p\mu}^{\text{SUMRCCSD}}$ are defined by equation (41). The wave function $|\Psi_\mu^{\text{CR-SUMRCCSD(T)}}\rangle$ entering equations (56) and (57) is defined as

$$|\Psi_\mu^{\text{CR-SUMRCCSD(T)}}\rangle = \sum_{p=1}^M c_{p\mu}^{\text{SUMRCCSD}} (P^{(p)} + Q_1^{(p)} + Q_2^{(p)} + Q_3^{(p)}) e^{T_1^{(p)} + T_2^{(p)} + \tilde{T}_3^{(p)}} |\Phi_p\rangle, \quad (58)$$

where the $T_1^{(p)}$ and $T_2^{(p)}$ clusters are obtained in the SUMRCCSD calculations and $\tilde{T}_3^{(p)}$ represent the perturbative estimates of the tri-excited cluster components $T_3^{(p)}$. The approximate $\tilde{T}_3^{(p)}$ clusters entering equation (58) are calculated as follows:

$$\tilde{T}_3^{(p)} = \sum_{\substack{i_1 < i_2 < i_3 \\ a_1 < a_2 < a_3}} (p) \tilde{t}_{a_1 a_2 a_3}^{i_1 i_2 i_3} (p) E_{i_1 i_2 i_3}^{a_1 a_2 a_3}, \quad (59)$$

where

$$(p) \tilde{t}_{a_1 a_2 a_3}^{i_1 i_2 i_3} = (p) \gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3} (2) / (p) \Delta_{i_1 i_2 i_3}^{a_1 a_2 a_3}, \quad (60)$$

with $(p) \gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3} = \text{I}, (p) \gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3} + \text{II}, (p) \gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3}$ designating the triply excited moments of the SUMRCCSD equations, defined by equations (48)–(50) in which $m = 3$, and

$$(p) \Delta_{i_1 i_2 i_3}^{a_1 a_2 a_3} = -\langle (p) \Phi_{i_1 i_2 i_3}^{a_1 a_2 a_3} | H_{N_p} | (p) \Phi_{i_1 i_2 i_3}^{a_1 a_2 a_3} \rangle \quad (61)$$

representing the diagonal matrix elements of the Hamiltonian H_{N_p} corresponding to the triply excited determinants $|(p) \Phi_{i_1 i_2 i_3}^{a_1 a_2 a_3}\rangle$ relative to $|\Phi_p\rangle$. It is easy to verify that the CR-SUMRCCSD(T) method is a straightforward generalization of the single-reference CR-CCSD(T) methods, introduced in [12, 13, 28], to the multi-reference case.

Clearly, the wave function $|\Psi_\mu^{\text{CR-SUMRCCSD(T)}}\rangle$, equation (58), defining the CR-SUMRCCSD(T) method, represents an approximate form of the SUMRCCSDT (SUMRCC singles, doubles, and triples) wave function, in which contributions from the higher-than-triply excited determinants relative to references $|\Phi_p\rangle$ are neglected (they are projected out by $P^{(p)} + Q_1^{(p)} + Q_2^{(p)} + Q_3^{(p)}$; cf. equation (58)). In order to obtain the approximate form of $T_3^{(p)}$ clusters defining $|\Psi_\mu^{\text{CR-SUMRCCSD(T)}}\rangle$, given by equations (59)–(61), we have to analyse the triply excited part of the SUMRCCSDT system of equations. The tri-excited part of the SUMRCCSDT system can be given the following form (cf. equation (17)):

$$\begin{aligned} & Q_3^{(p)} \left[(H_{N_p} e^{T_1^{(p)} + T_2^{(p)} + T_3^{(p)}})_C - \sum_{q=1(q \neq p)}^M e^{-T_1^{(p)} - T_2^{(p)} - T_3^{(p)}} \right. \\ & \quad \left. \times e^{T_1^{(q)} + T_2^{(q)} + T_3^{(q)}} P^{(q)} H^{\text{eff, SUMRCCSDT}} \right] |\Phi_p\rangle \\ & = 0 \quad (p = 1, \dots, M), \end{aligned} \quad (62)$$

or, more explicitly (after separating terms containing $T_3^{(p)}$ clusters from terms containing $T_1^{(p)}$ and $T_2^{(p)}$ clusters only),

$$\begin{aligned} & Q_3^{(p)} \left\{ \left[H_{N_p} T_3^{(p)} (1 + T_1^{(p)} + T_2^{(p)} + \frac{1}{2}(T_1^{(p)})^2) \right]_C \right. \\ & \quad \left. + (H_{N_p} e^{T_1^{(p)} + T_2^{(p)}})_C - \sum_{q=1(q \neq p)}^M (e^{-T_1^{(p)} - T_2^{(p)}} e^{T_1^{(q)} + T_2^{(q)}} P^{(q)} \right. \\ & \quad \left. \times H^{\text{eff, SUMRCCSDT}}) - \Omega_3^{(p)} \right\} |\Phi_p\rangle = 0 \\ & (p = 1, \dots, M), \end{aligned} \quad (63)$$

where $H^{\text{eff, SUMRCCSDT}}$ is the effective Hamiltonian of the SUMRCCSDT method and $\Omega_3^{(p)} |\Phi_p\rangle$ are the coupling terms in the SUMRCCSDT system which explicitly depend on the $T_3^{(q)}$ ($q = 1, \dots, M$) clusters.

By neglecting the $\Omega_3^{(p)}|\Phi_p\rangle$ contributions, which are quantities of at least third order in the MRMBPT wave functions, and by replacing the SUMRCCSDT effective Hamiltonian $H^{\text{eff,SUMRCCSDT}}$ by its SUMRCCSD counterpart $H^{\text{eff,SUMRCCSD}}$, equation (42), while ignoring the nonlinear direct terms containing $T_3^{(p)}$, we immediately obtain

$$Q_3^{(p)}(H_{N_p}T_3^{(p)})_C|\Phi_p\rangle = -\Gamma_3^{(p)}(2)|\Phi_p\rangle \quad (p = 1, \dots, M), \quad (64)$$

where $\Gamma_3^{(p)}(2)|\Phi_p\rangle$ are the quantities defined by equations (45)–(49) in which $m = 3$. If we approximate the triples–triples block of the Hamiltonian, $Q_3^{(p)}H_{N_p}Q_3^{(p)}$, by its diagonal part and use the explicit relationship between $\Gamma_3^{(p)}(2)|\Phi_p\rangle$ and the triply excited moments of the SUMRCCSD equations ${}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2)$, i.e.

$$\Gamma_3^{(p)}(2)|\Phi_p\rangle = \sum_{\substack{i_1 < i_2 < i_3 \\ a_1 < a_2 < a_3}} {}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2) |{}^{(p)}\Phi_{i_1i_2i_3}^{a_1a_2a_3}\rangle, \quad (65)$$

we obtain the equation

$$\langle {}^{(p)}\Phi_{i_1i_2i_3}^{a_1a_2a_3} | H_{N_p} | {}^{(p)}\Phi_{i_1i_2i_3}^{a_1a_2a_3} \rangle {}^{(p)}t_{a_1a_2a_3}^{i_1i_2i_3} = -{}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2), \quad (66)$$

which leads to the approximate form of the triply excited amplitudes ${}^{(p)}t_{a_1a_2a_3}^{i_1i_2i_3}$ given by equation (60).

Equations (55)–(61) define the complete variant of the CR-SUMRCCSD(T) theory, referred to as the CR-SUMRCCSD(T),A approach. We can, of course, think of various modifications of the CR-SUMRCCSD(T),A method. One possibility, which we explore in this paper, is the simplification of the expressions for the approximate triply excited cluster amplitudes ${}^{(p)}\tilde{t}_{a_1a_2a_3}^{i_1i_2i_3}$, equation (60), by replacing the diagonal Hamiltonian matrix elements ${}^{(p)}\Delta_{i_1i_2i_3}^{a_1a_2a_3}$, equation (61), by their lowest-order estimates obtained by forming the appropriate orbital energy differences $\epsilon_{i_1} + \epsilon_{i_2} + \epsilon_{i_3} - \epsilon_{a_1} - \epsilon_{a_2} - \epsilon_{a_3}$. This simplification of the CR-SUMRCCSD(T) theory leads to the CR-SUCCSD(T),B approach.

2.3.3. Computer costs of the MRMMCC/CI and CR-SUMRCCSD(T) calculations

From the numerical point of view, the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T) methods offer several advantages. First of all, in all three methods, the effects due to higher-than-doubly excited clusters are estimated in a non-iterative and state-selective fashion, using the singly and doubly excited clusters obtained in the SUMRCCSD calculations. Second, the non-iterative energy corrections δ_μ characterizing the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T) calculations are relatively

inexpensive. The most expensive steps of the MRMMCC(2,3)/CI and CR-SUMRCCSD(T) calculations associated with the determination of the relevant corrections δ_μ are very similar to the most expensive steps of the single-reference CCSD(T) calculations, which scale as $n_o^3 n_u^4$ (n_o and n_u are the numbers of occupied and unoccupied orbitals in each reference $|\Phi_p\rangle$). The CPU operation count characterizing the calculation of a single triples correction $\delta_\mu(T)$ of the CR-SUMRCCSD(T) approach is, roughly, $M \times n_o^3 n_u^4$, since each correction $\delta_\mu(T)$, equation (56), requires the determination of all tri-excited moments ${}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2)$ for all reference configurations $|\Phi_p\rangle$. The MRMMCC(2,3)/CI calculations have scaling of a similar type, but there are some differences with the CR-SUMRCCSD(T) calculations. Because of the use of the MRCISD wave functions $|\Psi_\mu^{\text{MRCISD}}\rangle$ in designing the non-iterative corrections δ_μ , we do not have to consider all tri-excited moments ${}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2)$ in the MRMMCC(2,3)/CI calculations. We only have to consider a relatively small subset of these moments that corresponds to the semi-internal triple excitations selected through the process of projecting quantities $\Gamma_3^{(p)}(2)|\Phi_p\rangle$ in equation (52) on $|\Psi_\mu^{\text{MRCISD}}\rangle$. This leads to some savings in the CPU time compared to the CR-SUMRCCSD(T) calculations. On the other hand, we must solve the MRCISD equations for all electronic states of interest to determine the wave functions $|\Psi_\mu^{\text{MRCISD}}\rangle$ that are used in the MRMMCC(2,3)/CI calculations. This increases the costs of the MRMMCC(2,3)/CI calculations by the iterative $n_o^2 n_u^4$ -like steps associated with the additional MRCISD calculations, which do not have to be performed in the CR-SUMRCCSD(T) case. Thus, the relative costs of the CR-SUMRCCSD(T) versus MRMMCC(2,3)/CI calculations vary from case to case, although both methods are $n_o^3 n_u^4$ -like procedures in the non-iterative steps associated with the determination of the relevant corrections δ_μ . Similar remarks apply to the MRMMCC(2,4)/CI calculations, which have costs similar to the single-reference CCSD(TQ_f) approach. In analogy to the CCSD(TQ_f) method, the most expensive steps of the MRMMCC(2,4)/CI calculations scale as $n_o^2 n_u^5$, although the prefactor determining the actual cost depends on the cost of the additional MRCISD calculations that must be performed to construct the relevant corrections δ_μ and on the number of semi-internal versus all quadruples (again, we do not have to consider all quadruply excited moments ${}^{(p)}\gamma_{a_1a_2a_3a_4}^{i_1i_2i_3i_4}(2)$ in the MRMMCC(2,4)/CI calculations, but, rather, their semi-internal counterparts selected through the process of projecting quantities $\Gamma_4^{(p)}(2)|\Phi_p\rangle$ in equation (54) on $|\Psi_\mu^{\text{MRCISD}}\rangle$).

Clearly, the final cost of the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T)

calculations is largely determined by the iterative SUMRCCSD calculations, which have to be performed first, before calculating the non-iterative δ_μ corrections. The most expensive steps of the SUMRCCSD calculations scale, roughly, as $M \times n_0^2 n_u^4$. This is a consequence of the following two facts: (i) the direct terms ${}^{(p)}\Lambda_{i_1 \dots i_n}^{a_1 \dots a_n}$ of the SUMRCCSD equations (equation (19) where $n = 1, 2$ and $T_A^{(p)} = T_1^{(p)} + T_2^{(p)}$) are identical to the single-reference CCSD equations written for each reference $|\Phi_p\rangle$, and (ii) the costs of calculating the coupling terms ${}^{(p)}\Xi_{i_1 \dots i_n}^{a_1 \dots a_n}$, equation (20), are much smaller than the $n_0^2 n_u^4$ costs of determining the direct term (cf., e.g., [124]). For smaller problems, most of the CPU time is spent on the SUMRCCSD (and, in the MRMMCC/CI case, MRCISD) iterations. For larger problems, the non-iterative steps characterizing the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T) calculations have costs that are often comparable to the costs of all SUMRCCSD iterations.

3. Numerical examples and discussion

In order to test the performance of the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T), X ($X = A, B$) approaches, we carried out a series of pilot calculations for the lowest two 1A_g states of the minimum basis set (MBS) H8 system [179] (see Table 1) and the lowest two 1A_1 states of the CH₂

molecule, as described by the double-zeta (DZ) basis set [180] (see Table 2). Both systems provide us with the situations where the SUMRCCSD method fails due to intruders once the relevant geometrical parameters are allowed to vary. The use of small basis sets enables us to compare the SUMRCCSD, MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T), X ($X = A, B$) results with the exact results obtained with the full CI approach.

All MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T), X ($X = A, B$) calculations discussed in this section were performed with the pilot computer programs that were interfaced with our two-reference orthogonally spin-adapted SUMRCCSD code, initially described in [124] and further enhanced in [132]. The SUMRCCSD code of [124, 132], which is interfaced with the GAMESS package [181], allows for a calculation of two totally symmetric singlet states that correspond to a two-dimensional model space $\mathcal{M}_0 = \text{span}\{|\Phi_1\rangle, |\Phi_2\rangle\}$, where the reference determinants $|\Phi_1\rangle$ and $|\Phi_2\rangle$ differ by a double excitation and are obtained by using two active orbitals of different symmetry and two active electrons [112, 114, 119–124, 128]. The two-dimensional model spaces of this type represent the most natural choices of model spaces for the lowest singlet states of the H8 and CH₂ systems. They are complete if we limit ourselves to two totally symmetric singlet states. In all calculations reported in this paper, we used the

Table 1. A comparison of the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, CR-SUMRCCSD(T),A, and CR-SUMRCCSD(T),B energies of the 1 1A_g and 2 1A_g states of the MBS H8 system [179], E_1 and E_2 , respectively, with the exact energies of these states, obtained with full CI, and the results of the SUMRCCSD, single- and multi-reference CISD, single-reference CISDTQ, and multi-reference $H^{\text{eff,SUMRCCSD}}(T),A$ and $H^{\text{eff,SUMRCCSD}}(T),B$ calculations. The full CI energy values represent total energies in hartree. The remaining energies are in millihartree relative to the corresponding full CI energies. The geometrical parameter α of the H8 model is in bohr. The coefficients at references $|\Phi_1\rangle$ and $|\Phi_2\rangle$, equations (70) and (71), respectively, that characterize the normalized full CI wave functions of the lowest two states of the 1A_g symmetry are shown in the last two rows.

Method	$\alpha = 1.0$		$\alpha = 0.1$		$\alpha = 0.0001$	
	E_1	E_2	E_1	E_2	E_1	E_2
Full CI	-4.352990	-3.998978	-4.218763	-4.145171	-4.204803	-4.144027
CISD	8.396	59.314	14.240	51.602	22.779	42.374
CISDTQ	0.254	1.608	0.316	0.650	0.449	0.435
MRCISD	6.877	21.540	5.582	8.116	5.952	6.657
SUMRCCSD	-0.565	25.927	-2.387	8.454	-2.837	8.390
MRMMCC(2,3)/CI	0.748	8.593	1.335	1.178	1.499	0.794
MRMMCC(2,4)/CI	0.370	4.328	0.448	1.471	0.525	1.245
CR-SUMRCCSD(T),A	0.452	4.101	0.976	-0.205	0.919	-0.228
CR-SUMRCCSD(T),B	0.859	11.140	1.546	-0.036	1.349	0.138
CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$]	0.567	-3.111	1.360	-1.398	1.359	-1.289
CR-SUMRCCSD(T),B/[$d_\mu^{(T)} = 1$]	1.022	6.277	2.001	-1.195	1.845	-0.866
$H^{\text{eff,SUMRCCSD}}(T),A$	1.571	23.791	1.212	4.856	1.341	4.212
$H^{\text{eff,SUMRCCSD}}(T),B$	-1.986	27.348	0.801	5.267	0.554	5.000
$ \Phi_1\rangle$	0.939657	0.074711	0.831984	0.448118	0.668268	0.668203
$ \Phi_2\rangle$	-0.081890	0.788778	-0.440484	0.810218	-0.659121	0.654618

Table 2. A comparison of the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, CR-SUMRCCSD(T),A, and CR-SUMRCCSD(T),B energies of the 1^1A_1 and 2^1A_1 states of the CH_2 molecule, E_1 and E_2 , respectively, as described by the DZ basis set [180], at the equilibrium ($R = R_e$) and two displaced geometries ($R = 1.5R_e$ and $2R_e$), with the exact energies of these states, obtained with full CI, and the results of the SUMRCCSD, single- and multi-reference CISD, single-reference CISDTQ, and multi-reference $H^{\text{eff,SUMRCCSD}}(T),A$ and $H^{\text{eff,SUMRCCSD}}(T),B$ calculations. The full CI energy values represent total energies in hartree. The remaining energies are in millihartree relative to the corresponding full CI energies. The coefficients at references $|\Phi_1\rangle$ and $|\Phi_2\rangle$, equations (72) and (73), respectively, that characterize the normalized full CI wave functions of the lowest two states of the 1A_1 symmetry are shown in the last two rows.

Method	$R = R_e^a$		$R = 1.5R_e$		$R = 2R_e$	
	E_1	E_2	E_1	E_2	E_1	E_2
Full CI	-38.962739	-38.806311	-38.859216	-38.699721	-38.769579	-38.674611
CISD	5.861	82.500	15.338	55.627	42.700	91.325
CISDTQ	0.122	1.612	0.624	5.998	2.891	10.013
MRCISD	4.054	12.617	14.031	26.326	41.217	57.005
SUMRCCSD	1.106	1.741	3.179	8.358	4.792	14.935
MRMMCC(2,3)/CI	1.127	1.416	3.428	7.052	5.218	9.633
MRMMCC(2,4)/CI	1.085	1.441	3.452	6.896	5.599	6.727
CR-SUMRCCSD(T),A	0.243	0.281	0.582	0.214	-0.507	8.255
CR-SUMRCCSD(T),B	0.600	0.294	1.997	1.303	2.101	-49.157
CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$]	0.199	0.064	0.162	-2.518	-3.360	-3.474
CR-SUMRCCSD(T),B/[$d_\mu^{(T)} = 1$]	0.574	0.078	1.805	-1.059	0.796	-159.040
$H^{\text{eff,SUMRCCSD}}(T),A$	1.314	1.532	3.937	7.601	4.298	15.429
$H^{\text{eff,SUMRCCSD}}(T),B$	2.054	0.793	3.582	7.956	4.079	15.648
$ \Phi_1\rangle$	0.959913	0.159122	0.917384	0.038133	0.784768	-0.027831
$ \Phi_2\rangle$	-0.162644	0.910436	-0.068631	0.822510	-0.014952	0.477437

^aThe equilibrium geometry of the 1^1A_1 state taken from [182].

ground-state restricted Hartree–Fock (RHF) orbitals. The MRCISD calculations required to construct the MRMMCC(2,3)/CI and MRMMCC(2,4)/CI corrections and some single-reference CI calculations, such as CISD, were performed with our own computer codes. The full CI calculations were performed with GAMESS.

As mentioned in the previous section, when the model space \mathcal{M}_0 is two dimensional and $|\Phi_1\rangle$ and $|\Phi_2\rangle$ differ by a double excitation, the MRMMCC(2,4)/CI approach is equivalent to the complete CI-corrected MRMMCC method defined by equations (39)–(49). In the pilot implementation of the MRMMCC(2,4)/CI method employed in this study, we used the exact forms of the triply excited moments ${}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2)$ (see equation (50) and equations (48) and (49), where $m = 3$), which enter the MRMMCC(2,4) correction formula, equation (54), through quantities $\Gamma_3^{(p)}|\Phi_p\rangle$, equation (65). In the case of the quadruply excited moments ${}^{(p)}\gamma_{a_1a_2a_3a_4}^{i_1i_2i_3i_4}(2) = {}^I,{}^{(p)}\gamma_{a_1a_2a_3a_4}^{i_1i_2i_3i_4}(2) + {}^{II},{}^{(p)}\gamma_{a_1a_2a_3a_4}^{i_1i_2i_3i_4}(2)$, which enter the MRMMCC(2,4) correction $\delta_\mu(2,4)$, equation (54), through $\Gamma_4^{(p)}|\Phi_p\rangle$ (cf. equations (45)–(49), where $m = 4$), we used the complete formula for the direct moment ${}^I,{}^{(p)}\gamma_{a_1a_2a_3a_4}^{i_1i_2i_3i_4}(2)$, equation (48), and the following approximate form of the coupling moment

${}^{II},{}^{(p)}\gamma_{a_1a_2a_3a_4}^{i_1i_2i_3i_4}(2)$ obtained by retaining the leading terms in equation (49):

$${}^{II},{}^{(p)}\gamma_{a_1a_2a_3a_4}^{i_1i_2i_3i_4}(2) = - \sum_{q=1(q \neq p)}^M \langle {}^{(p)}\Phi_{i_1i_2i_3i_4}^{a_1a_2a_3a_4} | (T_2^{(q)} - T_2^{(p)}) | \Phi_q \rangle \times H_{qp}^{\text{eff,SUMRCCSD}}. \quad (67)$$

In implementing the MRMMCC(2,3)/CI and CR-SUMRCCSD(T) methods, which only rely on the triply excited moments ${}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2)$, we used the exact forms of the direct and coupling contributions to these moments given by equations (48) and (49), respectively, where $m = 3$.

In addition to comparing the SUMRCCSD, MRMMCC(2,3)/CI, and MRMMCC(2,4)/CI results for the H8 and CH_2 systems with the corresponding full CI data, we also tested the idea of incorporating the approximate information about triply excited clusters $T_3^{(p)}$ directly into the effective Hamiltonian, which is diagonalized in \mathcal{M}_0 to produce the final energies. As mentioned in the Introduction, the idea of improving the MRCC results by enriching the effective Hamiltonian with approximate forms of triply and other higher-than-doubly excited clusters was considered earlier in the

context of the SUMRCC [164] and VUMRCC [108, 165, 166] calculations. Having access to the approximate triply excited clusters $\tilde{T}_3^{(p)}$, equations (59)–(61), which we can easily generate using the triply excited moments of the SUMRCCSD equations ${}^{(p)}\gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3}$ (2), we decided to test the idea of correcting the SUMRCCSD results for the effect of triples by diagonalizing the augmented form of the effective Hamiltonian, in which the off-diagonal matrix elements of $H^{\text{eff, SUMRCCSD}}$ are replaced by

$$H_{qp}^{\text{eff, SUMRCCSD}}(T) = \langle \Phi_q | (H e^{T_1^{(p)} + T_2^{(p)} + \tilde{T}_3^{(p)}})_{\text{C}} | \Phi_p \rangle \quad (q \neq p) \quad (68)$$

in the model space \mathcal{M}_0 (the diagonal matrix elements of $H^{\text{eff, SUMRCCSD}}$ do not change when the triply excited cluster components $\tilde{T}_3^{(p)}$ are added to the SUMRCCSD cluster operators $T_1^{(p)} + T_2^{(p)}$). The $T_1^{(p)}$ and $T_2^{(p)}$ clusters in equation (68) represent the singly and doubly excited clusters obtained in the SUMRCCSD calculations and $\tilde{T}_3^{(p)}$ components are calculated using equations (59)–(61). For a specific case of the two-dimensional model space considered in this study, the off-diagonal elements of $H^{\text{eff, SUMRCCSD}}(T)$ have the following form:

$$H_{3-p,p}^{\text{eff, SUMRCCSD}}(T) = H_{3-p,p}^{\text{eff, SUMRCCSD}} + \langle \Phi_{3-p} | [H_{N_p}(\tilde{T}_3^{(p)} + T_1^{(p)}\tilde{T}_3^{(p)})] | \Phi_p \rangle \quad (p = 1, 2), \quad (69)$$

where $H_{3-p,p}^{\text{eff, SUMRCCSD}}$ ($p = 1, 2$) are the off-diagonal matrix elements of the effective Hamiltonian of the two-reference SUMRCCSD approach. As in the case of the CR-SUMRCCSD(T) method, in which we use clusters $\tilde{T}_3^{(p)}$ to calculate the non-iterative corrections $\delta_\mu(T)$ according to equations (56)–(61), we can consider different forms of $\tilde{T}_3^{(p)}$ to define the augmented effective Hamiltonian $H^{\text{eff, SUMRCCSD}}(T)$. We can, for example, simplify the expressions for the approximate triply excited cluster amplitudes ${}^{(p)}\tilde{t}_{a_1 a_2 a_3}^{i_1 i_2 i_3}$, equation (60), by replacing the diagonal matrix elements of the Hamiltonian, ${}^{(p)}\Delta_{i_1 i_2 i_3}^{a_1 a_2 a_3}$, equation (61), by their lowest-order estimates $\epsilon_{i_1} + \epsilon_{i_2} + \epsilon_{i_3} - \epsilon_{a_1} - \epsilon_{a_2} - \epsilon_{a_3}$. This simplification in the definition of $H^{\text{eff, SUMRCCSD}}(T)$ leads to the $H^{\text{eff, SUMRCCSD}}(T)$,B approach. The use of the complete form of the effective Hamiltonian $H^{\text{eff, SUMRCCSD}}(T)$, in which $\tilde{T}_3^{(p)}$ is defined by equations (59)–(61), leads to the $H^{\text{eff, SUMRCCSD}}(T)$,A method.

Earlier attempts to improve the results of the MRCC calculations by augmenting the effective Hamiltonian by triples and other higher-order effects have led to rather disappointing results, since in many cases the results obtained by diagonalizing the effective Hamiltonians

augmented by higher-than-double excitations turned out to be worse than those obtained with singles and doubles only [108, 164–166]. It is interesting to examine if the $H^{\text{eff, SUMRCCSD}}(T)$,A and $H^{\text{eff, SUMRCCSD}}(T)$,B methods described here improve the results of the SUMRCCSD calculations and if the results of diagonalizing $H^{\text{eff, SUMRCCSD}}(T)$, equation (68) or (69), are better than the results of adding the non-iterative corrections δ_μ defining the CR-SUMRCCSD(T) and CI-corrected MRMMCC methods to the SUMRCCSD energies.

3.1. H8 model

We begin our discussion with the results obtained for the MBS H8 system [179], which has been frequently used in testing CC and other many-body approaches. The H8 system consists of four H_2 molecules arranged in a distorted octagonal configuration having the D_{2h} symmetry. The H–H distance in each H_2 molecule is set at 2.0 bohr. The basis set defining the MBS H8 system consists of eight 1s-type atomic orbitals centred on the hydrogen atoms [179].

The geometry of the H8 model is defined by the parameter α , which measures the displacement of the two opposite H_2 molecules from their position in a regular octagon. By changing the value of α , we can continuously vary the level of quasi-degeneracy of the lowest two states of the 1A_g symmetry. According to the full CI calculations, in the $\alpha > 0.1$ bohr region, the ground state of the MBS H8 system ($1 {}^1A_g$) is dominated by the RHF configuration

$$|\Phi_1\rangle = |(1a_g)^2(1b_{3u})^2(1b_{2u})^2(2a_g)^2|. \quad (70)$$

In this region, the first excited 1A_g state ($2 {}^1A_g$) has a significant contribution from the bi-excited $2a_g^2 \rightarrow 1b_{1g}^2$ determinant

$$|\Phi_2\rangle = |(1a_g)^2(1b_{3u})^2(1b_{2u})^2(1b_{1g})^2|. \quad (71)$$

In the $\alpha \leq 0.1$ bohr region, the lowest two 1A_g states become quasi-degenerate and almost completely dominated by the RHF and $2a_g^2 \rightarrow 1b_{1g}^2$ configurations (see table 1 for the values of the coefficients at $|\Phi_1\rangle$, equation (70), and $|\Phi_2\rangle$, equation (71), in the full CI wave function expansions of the $1 {}^1A_g$ and $2 {}^1A_g$ states).

The prominent role of the RHF and $2a_g^2 \rightarrow 1b_{1g}^2$ configurations in describing the lowest two 1A_g states of H8, particularly in the $\alpha \leq 0.1$ bohr region, suggests choosing $|\Phi_1\rangle$, equation (70), and $|\Phi_2\rangle$, equation (71), as reference determinants in the SUMRCCSD calculations (this is equivalent to choosing the valence orbitals $2a_g$ and $1b_{1g}$ and two valence electrons as active). Since the references $|\Phi_1\rangle$ and $|\Phi_2\rangle$, equations (70) and (71),

respectively, dominate the full CI expansions of the lowest two 1A_g states in the $\alpha \leq 0.1$ bohr region, the SUMRCCSD energies in this region are quite accurate. Indeed, the errors in the SUMRCCSD results for $\alpha \leq 0.1$ bohr, relative to full CI, are approximately 2.4–2.8 millihartree for the ground state and 8.4–8.5 millihartree for the first excited 1A_g state (cf. table 1). The situation dramatically changes when α approaches larger values. For example, when $\alpha = 1.0$ bohr, the ground state is entirely dominated by $|\Phi_1\rangle$, but the first-excited 1A_g state is no longer well represented by the model space spanned by $|\Phi_1\rangle$ and $|\Phi_2\rangle$. As shown in table 1, the \mathcal{M}_0^\perp configurations constitute a significant contribution to the $2\ {}^1A_g$ state for $\alpha = 1.0$ bohr. Indeed, when $\alpha = 1.0$ bohr, 37.2% of the square of the norm of the $2\ {}^1A_g$ full CI wave function is due to the \mathcal{M}_0^\perp determinants; this should be compared to 12.5% at $\alpha = 0.0001$ bohr. This leads to a severe intruder-state problem, which affects the results of the SUMRCCSD calculations in the region of larger α values. As shown in table 1, the errors in the SUMRCCSD results for the $2\ {}^1A_g$ state increase from 8.390 millihartree at $\alpha = 0.0001$ bohr to 25.927 millihartree at $\alpha = 1.0$ bohr.

The results in Table 1 clearly indicate that the CI-corrected MRMMCC methods and the CR-SUMRCCSD(T) approach are capable of providing substantial improvements to the poor description of the $2\ {}^1A_g$ state in the $\alpha = 1.0$ bohr region by the SUMRCCSD method. The MRMMCC(2,4)/CI approach, which is equivalent to the complete CI-corrected MRMMCC theory when the model space \mathcal{M}_0 is spanned by the $|\Phi_1\rangle$ and $|\Phi_2\rangle$ configurations defined by equations (70) and (71), reduces the 25.927 millihartree error in the SUMRCCSD energy of the $2\ {}^1A_g$ state to 4.328 millihartree. This shows that the symmetrization of the excitation manifolds relative to references $|\Phi_1\rangle$ and $|\Phi_2\rangle$ through selected classes of triples and quadruples that are brought into the SUMRCC formalism via the non-iterative energy corrections $\delta_\mu^{\text{MRMMCC/CI}}$, equation (40), leads to tremendous improvements in the SUMRCCSD results. Even the simplest MRMMCC(2,3)/CI approach, in which quadruply excited moments of the SUMRCCSD equations are ignored, gives considerable improvements in the poor description of the $2\ {}^1A_g$ state by the SUMRCCSD method, reducing the 25.927 millihartree error in the SUMRCCSD energy at $\alpha = 1.0$ bohr to 8.593 millihartree.

Large improvements in the SUMRCCSD results offered by the MRMMCC(2,3)/CI and MRMMCC(2,4)/CI methods are not limited to the first excited 1A_g state and the $\alpha = 1.0$ bohr region. The non-iterative corrections defining the MRMMCC(2,3)/CI and MRMMCC(2,4)/CI methods work equally effectively in the quasi-degenerate ($\alpha \leq 0.1$ bohr) region and for the

ground state. As shown in table 1, the 2.837 and 8.390 millihartree errors in the SUMRCCSD results for the ground and the first excited 1A_g states at $\alpha = 0.0001$ bohr reduce to 1.499 and 0.794 millihartree, respectively, when the MRMMCC(2,3)/CI approach is employed, and 0.525 and 1.245 millihartree, respectively, when the more complete MRMMCC(2,4)/CI method is used. Thus, the CI-corrected MRMMCC methods provide a very effective way of improving the SUMRCCSD results. This is particularly true for the MRMMCC(2,4)/CI approach, which produces 0.370–0.525 millihartree errors in the entire region of α for the ground state and 1.245–4.328 millihartree errors for the first excited 1A_g state. The latter errors are six to seven times smaller than the errors obtained with the SUMRCCSD method for the $2\ {}^1A_g$ state. Interestingly enough, the MRMMCC(2,3)/CI and MRMMCC(2,4)/CI results are also considerably better than the results of the MRCISD calculations, which provide the $|\Psi^{\text{MRCISD}}\rangle$ wave functions for constructing corrections $\delta_\mu^{\text{MRMMCC/CI}}$ or their $\delta_\mu(2,3)$ and $\delta_\mu(2,4)$ analogs (cf. table 1). This demonstrates the robust nature of the MRMMCC formalism, in which the relatively inaccurate MRCISD approach, providing the $|\Psi^{\text{MRCISD}}\rangle$ wave functions for constructing corrections $\delta_\mu^{\text{MRMMCC/CI}}$, and the relatively inaccurate SUMRCCSD method, providing cluster amplitudes for determining these corrections, are combined together to produce a much better description of the lowest two 1A_g states of the H8 system for all values of α . The only limited CI approach that provides better results for the MBS H8 system than the CI-corrected MRMMCC methods is the very expensive CISDTQ (CI singles, doubles, triples, and quadruples) approximation. Another interesting feature of the CI-corrected MRMMCC methods is the fact that the resulting energies of the $1\ {}^1A_g$ and $2\ {}^1A_g$ states are invariably above the corresponding full CI values. This is not true for the SUMRCCSD results.

An alternative and even more effective way of correcting the SUMRCCSD results, also based on the MRMMCC formalism, is offered by the CR-SUMRCCSD(T) approximations, which we described in section 2.3.2. In this case, the non-iterative triples corrections $\delta_\mu(T)$, equation (56), to SUMRCCSD energies are calculated using the singly and doubly excited clusters obtained in the SUMRCCSD calculations and moments ${}^{(p)}\gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3}(2)$. Unlike the MRMMCC(2,3)/CI and MRMMCC(2,4)/CI methods, the CR-SUMRCCSD(T) approaches do not require any additional non-CC calculations. As shown in table 1, the more complete CR-SUMRCCSD(T),A approximation, in which the approximate $\tilde{T}_3^{(p)}$ clusters entering equation (56) are defined by equations (59)–(61), provides the results that are comparable to the

excellent MRMMCC(2,4)/CI results. In particular, the CR-SUMRCCSD(T),A approximation is capable of reducing the 8.390, 8.454, and 25.927 millihartree errors in the SUMRCCSD results for the first excited 1A_g state at $\alpha = 0.0001$, 0.1, and 1.0 bohr to 0.228, 0.205, and 4.101 millihartree, respectively. The 0.452–0.976 millihartree errors in the CR-SUMRCCSD(T),A results for the ground state are equally impressive. As shown in table 1, the CR-SUMRCCSD(T),A approximation is much more effective in improving the SUMRCCSD results than the analogous CI-corrected MRMMCC (2,3) method (both methods use the triply excited moments ${}^{(p)}\gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3}$ (2) only). This is a consequence of the fact that the MRMMCC(2,3)/CI method uses only a relatively small subset of all ${}^{(p)}\gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3}$ (2) moments, which corresponds to the semi-internal triply excited determinants included in the MRCISD calculations of the $|\Psi_\mu^{\text{MRCISD}}\rangle$ wave functions that are used to construct the relevant $\delta_\mu(2,3)$ corrections. The CR-SUMRCCSD(T),A approach uses all ${}^{(p)}\gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3}$ (2) moments.

The less complete CR-SUMRCCSD(T),B approximation, in which the diagonal Hamiltonian matrix elements ${}^{(p)}\Delta_{i_1 i_2 i_3}^{a_1 a_2 a_3}$ entering the definition of the triply excited cluster amplitudes ${}^{(p)}\tilde{t}_{a_1 a_2 a_3}^{i_1 i_2 i_3}$, equation (60), are replaced by the orbital energy differences $\epsilon_{i_1} + \epsilon_{i_2} + \epsilon_{i_3} - \epsilon_{a_1} - \epsilon_{a_2} - \epsilon_{a_3}$, provide significant improvements in the SUMRCCSD results too, but the 11.140 millihartree error in the CR-SUMRCCSD(T),B energy of the first excited 1A_g state at $\alpha = 1.0$ bohr is not as appealing as the 4.101 millihartree error obtained with the more complete CR-SUMRCCSD(T),A approximation. This shows the importance of using the complete form of the denominator ${}^{(p)}\Delta_{i_1 i_2 i_3}^{a_1 a_2 a_3}$, equation (61), in estimating the triply excited cluster amplitudes ${}^{(p)}\tilde{t}_{a_1 a_2 a_3}^{i_1 i_2 i_3}$ entering the CR-SUMRCCSD(T) triples corrections. The use of the MRMBPT-like orbital energy differences $\epsilon_{i_1} + \epsilon_{i_2} + \epsilon_{i_3} - \epsilon_{a_1} - \epsilon_{a_2} - \epsilon_{a_3}$ in the region where the SUMRCCSD approach has severe problems with describing the first excited 1A_g state due to intruders is a risky procedure and we can see the negative consequences of using these bare orbital energy differences by comparing the CR-SUMRCCSD(T),B versus CR-SUMRCCSD(T),A results.

We can also improve the overall description of the lowest two 1A_g states of the MBS H8 system by the CR-SUMRCCSD(T),B approach by considering the CR-SUMRCCSD(T),B/[$d_\mu^{(T)} = 1$] approximation, in which the overlap denominator $d_\mu^{(T)}$, equation (57), entering the formula for the energy correction $\delta_\mu(T)$, equation (56), is replaced by 1. As shown in table 1, the 11.140 millihartree error in the CR-SUMRCCSD(T),B result for the $2 {}^1A_g$ state of H8 at $\alpha = 1.0$ bohr reduces to 6.277 millihartree when the CR-SUMRCCSD(T),B/[$d_\mu^{(T)} = 1$] approximation is employed. The analogous

CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] method, which is obtained by replacing the $d_\mu^{(T)}$ denominator in the CR-SUMRCCSD(T),A energy expression by 1, works very well too, reducing the 4.101 millihartree error in the CR-SUMRCCSD(T),A result for the $2 {}^1A_g$ state of H8 at $\alpha = 1.0$ bohr to 3.111 millihartree. The CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] results for the smaller values of α are slightly worse than the corresponding CR-SUMRCCSD(T),A results, but the overall description of the lowest two 1A_g states of the MBS H8 system by the CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] method is very good. Unlike CR-SUMRCCSD(T),A, the CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] approach is a fully connected formalism (the overlap denominators $d_\mu^{(T)}$ introduce disconnected terms into the corresponding energy expansions), so it may be worthwhile testing this approach in other cases. One such case is discussed in section 3.2, where we describe the results of the CR-SUMRCCSD(T) and CI-corrected MRMMCC calculations for methylene.

Before discussing the methylene case, let us mention that the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T) results for the lowest two 1A_g states of the MBS H8 model are also much better than the results of the $H^{\text{eff,SUMRCCSD}}(T),A$ and $H^{\text{eff,SUMRCCSD}}(T),B$ calculations, in which we are trying to improve the SUMRCCSD results by diagonalizing the effective Hamiltonian $H^{\text{eff,SUMRCCSD}}(T)$, equation (68) or (69), augmented by the same triply excited cluster components $\tilde{T}_3^{(p)}$ that are used in the CR-SUMRCCSD(T) calculations. The application of the $H^{\text{eff,SUMRCCSD}}(T),A$ and $H^{\text{eff,SUMRCCSD}}(T),B$ methods leads to some improvements in the SUMRCCSD results in the quasi-degenerate, $\alpha \leq 0.1$ bohr, region (errors in the SUMRCCSD results reduce by a factor of 2), but no improvements are observed in the region of larger α values. In fact, the $H^{\text{eff,SUMRCCSD}}(T),B$ results at $\alpha = 1.0$ bohr are worse than the SUMRCCSD results. For example, the $H^{\text{eff,SUMRCCSD}}(T),B$ approach increases the large, 25.927 millihartree, error in the SUMRCCSD energy of the first excited 1A_g state to 27.348 millihartree. The more accurate treatment of the ‘perturbative’ denominators ${}^{(p)}\Delta_{i_1 i_2 i_3}^{a_1 a_2 a_3}$, equation (61), which define the triply excited cluster components $\tilde{T}_3^{(p)}$ that enter the augmented effective Hamiltonian $H^{\text{eff,SUMRCCSD}}(T)$ in the $H^{\text{eff,SUMRCCSD}}(T),A$ approximation, improves the $H^{\text{eff,SUMRCCSD}}(T),B$ result for the first excited 1A_g state at $\alpha = 1.0$ bohr, but the level of this improvement is rather minor (the error reduces from 27.348 to 23.791 millihartree). The $H^{\text{eff,SUMRCCSD}}(T),A$ and $H^{\text{eff,SUMRCCSD}}(T),B$ results are, of course, considerably worse than those obtained with the CR-SUMRCCSD(T) and other MRMMCC approaches. In particular, the $H^{\text{eff,SUMRCCSD}}(T),A$ calculations lead to

a much worse description of the lowest two 1A_g states of the MBS H8 model than that obtained with the CR-SUMRCCSD(T),A approach, in spite of the fact that both approaches rely on exactly the same form of $\tilde{T}_3^{(p)}$ cluster components. It should be noted that the CR-SUMRCCSD(T) methods use the generalized moments of the SUMRCCSD equations, in which the SUMRCCSD effective Hamiltonian $H^{\text{eff,SUMRCCSD}}$ is kept in its original form. All of this clearly shows that the *ad hoc* modification of the SUMRCCSD effective Hamiltonian to account for the effects of triples is a very risky procedure. The non-iterative corrections defining the CR-SUMRCCSD(T) approaches, which use the uncorrected form of the SUMRCCSD effective Hamiltonian, do not carry that risk and provide a much more systematic way of accounting for the triples effects within the SUMRCC formalism. Our observations about the disappointing performance of the $H^{\text{eff,SUMRCCSD}}(T),A$ and $H^{\text{eff,SUMRCCSD}}(T),B$ approaches seem to be in agreement with the earlier attempts to improve the MRCC results by incorporating the approximate information about higher-than-doubly excited clusters directly into the effective Hamiltonian [108, 164–166].

3.2. Methylene

The methylene molecule is known to have a very small energy gap between the lowest singlet and triplet states, $A{}^1A_1 \equiv 1{}^1A_1$ and $X{}^3B_1$, respectively, which has represented a major challenge for *ab initio* methods (cf., e.g., [125, 126] and references therein). It is also rather difficult to obtain the correct value of the vertical singlet–singlet ($2{}^1A_1 - 1{}^1A_1$) energy separation, although the orthogonally spin-adapted two-reference SUMRCCSD method provides very good results in this case [124, 132–134]. The problem with the accurate determination of the energies of the lowest two 1A_1 states of methylene is that both states have a quasi-degenerate character. The two closed-shell configurations,

$$|\Phi_1\rangle = |(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2| \quad (72)$$

and

$$|\Phi_2\rangle = |(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2|, \quad (73)$$

involving two active orbitals, $3a_1$ and $1b_1$, and two active electrons, are required to obtain a reasonable zero-order description of the μ 1A_1 , $\mu = 1, 2$, states. At the equilibrium geometry of the $1{}^1A_1$ state (designated as $R = R_e$, where R is the C–H distance and R_e is the equilibrium value of R ; taken from [182]), the lowest 1A_1 state is dominated by the RHF configuration $|\Phi_1\rangle$, equation (72), although the doubly excited configuration

$|\Phi_2\rangle$, equation (73), has a large contribution too (see table 2). For the second 1A_1 state, the situation is reversed and the full CI expansion of the $2{}^1A_1$ state is largely dominated by the doubly excited configuration $|\Phi_2\rangle$ (cf. table 2).

The prominent role of the $|\Phi_1\rangle$ and $|\Phi_2\rangle$ configurations, equations (72) and (73), respectively, in describing the lowest two 1A_1 states of CH_2 suggests that we choose these two configurations as references in the SUMRCCSD calculations. As in the case of the MBS H8 system, the resulting model space $\mathcal{M}_0 = \text{ls}\{|\Phi_1\rangle, |\Phi_2\rangle\}$ is complete, since active orbitals $3a_1$ and $1b_1$, which are involved in constructing the $|\Phi_1\rangle$ and $|\Phi_2\rangle$ references, belong to different irreducible representations of the C_{2v} group. As shown in table 2, the model space spanned by $|\Phi_1\rangle$, equation (72), and $|\Phi_2\rangle$, equation (73), is perfectly adequate for the SUMRCCSD calculations of the lowest two 1A_1 states of methylene at $R = R_e$. In this region, the errors in the SUMRCCSD energies of the $1{}^1A_1$ and $2{}^1A_1$ states, relative to full CI, are only 1.106 and 1.741 millihartree, respectively, and the MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T) methods provide further improvements in these very good SUMRCCSD results. The results obtained with the more complete variant of the CR-SUMRCCSD(T) approach, termed CR-SUMRCCSD(T),A, are particularly impressive. Indeed, the CR-SUMRCCSD(T),A method reduces the 1.106 and 1.741 millihartree errors in the SUMRCCSD results for the $1{}^1A_1$ and $2{}^1A_1$ states at $R = R_e$ to 0.243 and 0.281 millihartree, respectively. The CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] approximation, in which the overlap denominator $d_\mu^{(T)}$, equation (57), entering the formula for the correction $\delta_\mu(T)$, equation (56), is replaced by 1, provides even better results (cf. table 2).

The $R = R_e$ region does not seem to constitute a serious challenge to the SUMRCCSD, MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T) methods. The situation changes when we simultaneously stretch both C–H bonds in methylene by 50 and 100% (cf. the $R = 1.5R_e$ and $R = 2R_e$ cases, respectively, in table 2). The model space spanned by only two configurations $|\Phi_1\rangle$ and $|\Phi_2\rangle$, equations (72) and (73), respectively, is no longer adequate for the $R = 1.5R_e$ and $R = 2R_e$ geometries (see the values of the coefficients at $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in the full CI expansions of the normalized $1{}^1A_1$ and $2{}^1A_1$ states in table 2). The situation is particularly challenging at $R = 2R_e$ and when the $2{}^1A_1$ state is examined. When $R = 2R_e$, the \mathcal{M}_0^+ configurations constitute more than 50% of the $2{}^1A_1$ wave function. This leads to a severe intruder-state problem and a large, 14.935 millihartree, error in the results of the two-reference SUMRCCSD calculations

for the 2^1A_1 state. When $R = 2R_e$, the model space spanned by $|\Phi_1\rangle$ and $|\Phi_2\rangle$ is also inadequate for describing the 1^1A_1 state. As shown in table 2, 38.4% of the square of the norm of the 1^1A_1 state at $R = 2R_e$ is due to the \mathcal{M}_0^\perp determinants. This should be compared to a much smaller, 5.2%, contribution from the \mathcal{M}_0^\perp configurations to the 1^1A_1 state at $R = R_e$. In consequence, the small, 1.106 millihartree, error in the SUMRCCSD energy of the 1^1A_1 state at $R = R_e$ increases to 4.792 millihartree when $R = 2R_e$. The situation at $R = 1.5R_e$ is somewhat less dramatic, but we still observe sizable errors in the two-reference SUMRCCSD results for the 1^1A_1 and 2^1A_1 states of methylene when both C–H bonds are stretched by 50% (3.179 and 8.358 millihartree, respectively).

As in the case of the MBS H8 model, all MRMMCC methods, including MRMMCC(2,3)/CI, MRMMCC(2,4)/CI, and CR-SUMRCCSD(T),A, provide improvements in the SUMRCCSD results at $R = 1.5R_e$ and $2R_e$. The CR-SUMRCCSD(T),A results are particularly impressive when the ground state is examined and when $R \leq 1.5R_e$. For example, the CR-SUMRCCSD(T),A approach is capable of reducing the 3.179 and 8.358 millihartree errors in the SUMRCCSD results for the 1^1A_1 and 2^1A_1 states at $R = 1.5R_e$ to 0.582 and 0.214 millihartree, respectively. The CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] analog of the CR-SUMRCCSD(T),A method provides very good results too, particularly at $R = 2R_e$, reducing, for example, the 14.935 and 8.255 millihartree errors in the SUMRCCSD and CR-SUMRCCSD(T),A results for the 2^1A_1 state at $R = 2R_e$ to 3.474 millihartree. Interestingly enough, the improvements in the SUMRCCSD energies of the lowest two 1A_1 states obtained with the CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] approach are so great that the $2^1A_1 - 1^1A_1$ energy gap resulting from the CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] calculations differs from the corresponding full CI value only by 0.114 millihartree.

The use of the orbital energy differences $\epsilon_{i_1} + \epsilon_{i_2} + \epsilon_{i_3} - \epsilon_{a_1} - \epsilon_{a_2} - \epsilon_{a_3}$ instead of the diagonal Hamiltonian matrix elements ${}^{(p)}\Delta_{i_1i_2i_3}^{a_1a_2a_3}$ in defining the triply excited cluster amplitudes ${}^{(p)}\tilde{t}_{a_1a_2a_3}^{i_1i_2i_3}$, equation (60), that enter the CR-SUMRCCSD(T) triples corrections $\delta_\mu(T)$ has no detrimental effect on the CR-SUMRCCSD(T) results for $R \leq 1.5R_e$. In this region, the corresponding CR-SUMRCCSD(T),B results are almost as good as those obtained with the CR-SUMRCCSD(T),A approach. The situation changes when the C–H bonds are stretched to $R = 2R_e$. In this case, the intruder-state problem and the inadequacy of the two-dimensional model space are so severe that the use of the bare orbital energy differences instead of the diagonal Hamiltonian matrix elements ${}^{(p)}\Delta_{i_1i_2i_3}^{a_1a_2a_3}$ in the

CR-SUMRCCSD(T) calculations leads to a failure of the CR-SUMRCCSD(T) approximation (see the large negative, -49.157 and -159.040 millihartree, errors in the CR-SUMRCCSD(T),B and CR-SUMRCCSD(T),B/[$d_\mu^{(T)} = 1$] results for the 2^1A_1 state at $R = 2R_e$). The use of the more complete CR-SUMRCCSD(T),A and CR-SUMRCCSD(T),A/[$d_\mu^{(T)} = 1$] approximations, in which the ${}^{(p)}\Delta_{i_1i_2i_3}^{a_1a_2a_3}$ denominators entering the ${}^{(p)}\tilde{t}_{a_1a_2a_3}^{i_1i_2i_3}$ cluster amplitudes are treated in a more accurate manner, is essential to obtain reasonable results for the lowest two 1A_1 states of methylene at $R = 2R_e$. Based on this observation and taking into consideration the overall performance of the CR-SUMRCCSD(T),A versus CR-SUMRCCSD(T),B methods in the H8 and methylene cases, we do not recommend employing bare orbital energies to construct the ${}^{(p)}\Delta_{i_1i_2i_3}^{a_1a_2a_3}$ denominators that are used to define the approximate tri-excited amplitudes entering the CR-SUMRCCSD(T) energy expressions.

In contrast to the MBS H8 model, the overall performance of the CR-SUMRCCSD(T),A method in the calculations for methylene is considerably better than the performance of the CI-corrected MRMMCC(2,4) approach (the CR-SUMRCCSD(T),A method is also better than the CI-corrected MRMMCC(2,3) method, but based on the results for the H8 system this could be expected, since the MRMMCC(2,3)/CI method uses only a relatively small subset of the ${}^{(p)}\gamma_{a_1a_2a_3}^{i_1i_2i_3}(2)$ moments, whereas the CR-SUMRCCSD(T),A approach uses all of them). Indeed, if we exclude the 2^1A_1 state at $R = 2R_e$ from the analysis, the errors in the CR-SUMRCCSD(T),A results for the lowest two 1A_1 states of methylene do not exceed 0.582 millihartree in the entire $R = R_e - 2R_e$ region. This should be compared to the 1.085–6.896 millihartree errors in the MRMMCC(2,4)/CI results. Even for the most complicated case of the 2^1A_1 state at $R = 2R_e$, the 8.255 millihartree error obtained with the CR-SUMRCCSD(T),A approach is comparable to the error resulting from the MRMMCC(2,4)/CI calculations. One can explain this superior performance of the CR-SUMRCCSD(T),A method, when compared to the MRMMCC(2,4)/CI approach, by observing that the two-reference MRCISD wave functions $|\Psi_\mu^{\text{MRCISD}}\rangle$, which are used to construct the non-iterative corrections $\delta_\mu^{\text{MRMMCC/CI}}$, equation (40), are not particularly accurate and do not bring a lot of information about higher-order effects neglected in the SUMRCCSD calculations. For example, the MRCISD energies of the 1^1A_1 state are not much different from the single-reference CISD energies, independent of the value of R (see table 2). The errors in the two-reference MRCISD results for the lowest two states of the 1A_1 symmetry at $R = 2R_e$ are in the 41–57 millihartree range. Thus, it is actually quite

surprising to observe that the MRMMCC(2,4)/CI approach, employing the relatively poor two-reference MRCISD wave functions to calculate the corresponding energy corrections $\delta_\mu(2,4)$, is capable of reducing the 14.935 millihartree error in the SUMRCCSD result for the 2^1A_1 state at $R = 2R_e$ to 6.727 millihartree (this result is much better than the result obtained with the significantly more expensive CISDTQ approach, which produces a 10.013 millihartree error). This is another illustration of the robustness of the MRMMCC formalism, which can provide considerable improvements in the SUMRCCSD results in spite of using rather poor wave functions $|\Psi_\mu\rangle$ in designing the MRMMCC corrections δ_μ . The excellent CR-SUMRCCSD(T),A results illustrate the same, since the wave functions $|\Psi_\mu^{\text{CR-SUMRCCSD(T)}}\rangle$, equation (58), which define the CR-SUMRCCSD(T) approaches, are the low-order approximations to the SUMRCCSDT wave functions.

Before summarizing our findings, let us mention that in analogy to the MBS H8 model, the CR-SUMRCCSD(T),A results for the lowest two 1A_1 states of methylene are much better than the results of the $H^{\text{eff,SUMRCCSD}}(T)$,A calculations, which use the same triply excited cluster components $\tilde{T}_3^{(p)}$ as used in the CR-SUMRCCSD(T) calculations to augment the effective Hamiltonian of the SUMRCCSD method. As shown in table 2, the $H^{\text{eff,SUMRCCSD}}(T)$,A approach and its $H^{\text{eff,SUMRCCSD}}(T)$,B counterpart offer no essential improvements in the SUMRCCSD results or make them even worse (cf., e.g., the $H^{\text{eff,SUMRCCSD}}(T)$,A and $H^{\text{eff,SUMRCCSD}}(T)$,B results for the 2^1A_1 state at $R = 2R_e$). This once again shows that the *ad hoc* modification of the SUMRCCSD effective Hamiltonian to account for the effects of triples, tested in [108,164,165,166] in the context of the SUMRCC and VUMRCC calculations, is an ill-defined procedure. The non-iterative corrections defining the CR-SUMRCCSD(T) approaches, which use the uncorrected form of the SUMRCCSD effective Hamiltonian to define the relevant triply excited moments ${}^{(p)}\gamma_{a_1 a_2 a_3}^{i_1 i_2 i_3}(2)$, and their CI-corrected MRMMCC(2,3) and MRMMCC(2,4) counterparts offer a systematic and a well-defined method of accounting for the triples and other higher-order effects within the SUMRCC formalism.

4. Summary

Among the most serious problems the genuine MRCC methods, such as SUMRCC, face are the intruder-state problem and the difficulties with incorporating the triply and other higher-than-two-body clusters in a computationally tractable manner. In this work, we have demonstrated that one can develop

highly effective non-iterative corrections to the ground- and excited-state energies obtained in the SUMRCCSD calculations, which improve the SUMRCCSD results in the intruder-state region in spite of the use of complete model spaces, by exploiting the multi-reference extension of the MMCC formalism [134, 167]. We may be able to extend the proposed MRMMCC approximations to incomplete model spaces, following, for example, the beautiful ideas laid down in [136–139], but it is encouraging to see that one can obtain significant improvements in the complete active space SUMRCCSD calculations by using the relatively inexpensive MRMMCC energy corrections. As shown in [136–139], the use of incomplete model spaces helps to alleviate the intruder-state problem, but we must keep in mind that the removal of specific references from the complete model spaces that cause the appearance of intruders cannot be easily converted into a routine numerical procedure. Thus, the MRMMCC approaches developed and tested in this work may offer a useful alternative to SUMRCC methods using incomplete model spaces. The MRMMCC corrections to SUMRCCSD energies are also very useful in the quasi-degenerate region, providing further improvements in the SUMRCCSD results and submillihartree accuracies.

Two classes of non-iterative MRMMCC corrections to SUMRCCSD energies have been developed in this work: (i) the CI-corrected MRMMCC approximations, in which non-iterative corrections due to triply and other higher-than-doubly excited clusters are constructed with the help of the MRCISD calculations and (ii) the CR-SUMRCCSD(T) methods in which non-iterative MRMMCC corrections due to triply excited clusters are obtained using the information extracted from the SUMRCCSD calculations, without any input from non-CC calculations. We have demonstrated that the CI-corrected MRMMCC methods and the CR-SUMRCCSD(T) approaches offer considerable improvements in the SUMRCCSD results, even when the model space is inadequate and the intruder-state problem becomes severe. The CI-corrected MRMMCC methods improve the SUMRCCSD results by approximately symmetrizing the manifolds of excitations corresponding to different reference configurations through the suitably designed corrections to SUMRCCSD energies that account for the selected classes of higher-than-double excitations. The CR-SUMRCCSD(T) approaches improve the SUMRCCSD results by providing the information about triply excited clusters neglected in the SUMRCCSD calculations. The CR-SUMRCCSD(T) approaches can be regarded as the multi-reference analogs of the highly successful single-reference CR-CCSD(T) theory, which helps to eliminate

the failure of the standard CCSD(T) method in the bond breaking and diradical cases [11–15, 17, 18, 20–23, 25, 28].

Test calculations for the H8 and CH₂ systems revealed that of all the MRMMCC approximations considered in this study, the CR-SUMRCCSD(T) method offers the best compromise between relatively low computer cost and high accuracy. In particular, the CR-SUMRCCSD(T) approach, which uses the triply excited moments of the SUMRCCSD equations only and which has a CPU operation count similar to that of the single-reference CCSD(T) approach, offers considerable improvements in the SUMRCCSD results when errors in the description of ground and excited states obtained with the SUMRCCSD method are big and corrections due to triply excited clusters are sizable. This should be contrasted with methods in which the effective Hamiltonian of the SUMRCCSD approach is modified in an *ad hoc* manner to account for the effects of triples, without making the appropriate changes in the SUMRCC equations. These *ad hoc* methods fail to provide the expected improvements in the SUMRCCSD results or even worsen the SUMRCCSD results. We have also demonstrated that, in order to obtain good results in the intruder-state region with the CR-SUMRCCSD(T) approach, it is essential to use the diagonal matrix elements of the Hamiltonian in defining the perturbative triples corrections $\delta_{\mu}(T)$ rather than simple orbital energy differences. This is particularly true for calculations of excited states.

The CI-corrected MRMMCC methods, particularly the MRMMCC(2,4)/CI approximation, work very well too, improving the SUMRCCSD results in the quasi-degenerate and intruder-state regions, but they require additional MRCISD calculations to construct the non-iterative corrections to SUMRCCSD energies which increase the computer cost of the MRMMCC calculations. Thus, the CR-SUMRCCSD(T) method is, at this time, our preferred way of correcting the SUMRCCSD results. However, we have to perform further tests and examine the relative performance of the CI-corrected MRMMCC and CR-SUMRCCSD(T) methods in other cases to see if the accuracy patterns observed in the preliminary numerical calculations reported in this paper are generally true. In particular, it will be very important to examine the performance of the CI-corrected MRMMCC and CR-SUMRCCSD(T) methods in calculations involving larger multi-dimensional model spaces. This will require a significant extension of our orthogonally spin-adapted two-reference SUMRCCSD code to larger active orbital spaces.

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