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**Method of Moments for the Continuous Transition
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Method of Moments for the Continuous Transition Between the Brillouin-Wigner-Type and Rayleigh-Schrödinger-Type Multireference Coupled Cluster Theories *

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Abstract

We apply the method of moments to the multireference (MR) coupled cluster (CC) formalism representing the continuous transition between the Brillouin-Wigner-type and Rayleigh-Schrödinger-type theories based on the Jeziorski-Monkhorst wave function ansatz and de-

*We dedicate this paper to Professor Henry F. Schaefer III on the occasion of his 65th birthday.

rive the formula for the noniterative energy corrections to the corresponding MRCC energies that recover the exact, full configuration interaction energies in the general model space case, including complete and incomplete model spaces. We also extend the relationship between the generalized moments of the state-universal (SU) MRCC equations within the Jeziorski-Monkhorst and Kucharski-Bartlett formulations of the SUMRCC theory to the general model space case. Finally, we argue that in the complete model space case, the relationship between moments of the SUMRCC equations corresponding to the Jeziorski-Monkhorst and Kucharski-Bartlett formulations of the SUMRCC theory, derived in this work, implies an equivalence of these two formulations of the SUMRCC approach, provided that the disconnected linked terms are included in the Kucharski-Bartlett formulation, and verify this statement numerically.

Keywords:

multireference coupled cluster theory, method of moments of coupled cluster equations, state-universal multireference coupled cluster approach, Brillouin-Wigner multireference coupled cluster approach, generalized Bloch equation, effective Hamiltonian, size extensivity, size consistency, C-conditions, complete and incomplete model spaces

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1 Introduction

1 The single-reference version of the standard coupled-cluster (CC) method [1] (for selected re-
2 views, see [2–11]) is nowadays routinely exploited in computational chemistry via several success-
3 ful approximations and general-purpose electronic structure packages. Recently, the quantum-
4 chemistry inspired single-reference CC methods have also been successfully employed in accurate
5 calculations of nuclear structure (cf., e.g., [12–18]). In particular, the widely used and compu-
6 tationally affordable CCSD(T) method [19, 20] that accounts perturbatively for the connected
7 triply excited clusters via noniterative corrections to the CCSD (CC singles and doubles) [21–24]
8 energies has proved to be very reliable and accurate in applications involving nondegenerate
9 ground states of molecular systems. Its main drawback – the inability to describe bond breaking
10 and biradicals – has been, to a large extent, remedied by the noniterative corrections defining
11 the method of moments of CC (MMCC) equations introduced by Piecuch and Kowalski [25, 26]
12 (see [27, 28] for representative reviews). The single-reference MMCC formalism exploits the
13 projections of the similarity transformed Hamiltonian of CC theory acting on the reference de-
14 terminant on the Slater determinants whose excitation rank is higher than the ranks of the
15 excited determinants that are used to solve the corresponding CC equations. When combined
16 with a full configuration interaction (FCI) bra wave function, the MMCC energy correction
17 recovers the exact, FCI energy from the energy and cluster amplitudes corresponding to the
18 truncated CC (e.g., CCSD) wave function. This alone would be formally interesting but of
19 not much use in practice. Thus, Piecuch et al. have replaced the FCI wave function in the
20 MMCC energy expressions by all kinds of approximate wave functions, and in this way de-
21 veloped a wide variety of approximate MMCC approaches, including, among others, the com-
22 pletely renormalized (CR) CCSD(T) and CCSD(TQ) methods, which substantially improve the
23 behavior of the non-iterative approximations of the CCSD(T) or CCSD(TQ) type in the bond
24 breaking region with an effort similar to that of the corresponding CCSD(T) and CCSD(TQ)
25 calculations [25–28]. The recently developed size extensive extensions of the CR-CCSD(T) and
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CR-CCSD(TQ) methods [29–32], especially the noniterative triples corrections to the CCSD energies based on the biorthogonal formulation of the MMCC theory [30, 31] defining the CR-CC(2,3) approach [30–32], seem particularly promising in applications involving single bond breaking, reaction mechanisms in organic and bioinorganic chemistry involving biradicals, and singlet-triplet gaps in magnetic/biradical systems (see, e.g., [30–39]). The original CR-CCSD(T) and CR-CCSD(TQ) approaches can be useful and successful as well, particularly in studies of potential energy surfaces and reaction mechanisms [27, 28, 33, 35–37, 39–42]. As pointed out in [30–32], the CR-CC(2,3) approach encompasses other possible ways of handling non-iterative triples corrections to CCSD energy, including, in addition to CCSD(T), the triples corrections of the CCSD(2) approaches [43–48] (see [49, 50] for the original ideas) and the so-called Lambda CCSD(T) methods [51, 52], which all improve the CCSD(T) results in the bond breaking and biradical regions, but not as effectively as CR-CC(2,3) ((CR-CC(2,3) is also more accurate in the equilibrium and closed-shell regions [30–32]).

There are, however, situations where nondynamic correlation effects arise when the single reference configuration becomes degenerate or quasidegenerate with some nearby lying state, in which case the use of a single determinant as a reference leads to difficulties, such as symmetry breaking and lack of a balanced description of a number of quasi-degenerate states. This occurs when, for example, one of the reaction products is in a low-spin open-shell state, which requires a genuine multi-determinantal description, or when dealing with quasi-degenerate excited states, potential energy surface crossings, and poly-radical species, to mention a few typical situations. One can extend the idea of single-reference MMCC corrections and CR-CC methods to excited states by combining them with the equation-of-motion (EOM) CC theory [53, 54], as in, for example, [27, 28, 31, 55–57], but there are cases of electronic quasi-degeneracies where this is not sufficient (cf., e.g., [58, 59]). Such cases require – at least in principle – a multireference (MR) version of the CC theory with a sufficiently large model space that guarantees the size-consistent description of the studied system.

There are basically two types of genuine MRCC methods, where the word “genuine” implies

the use of the truly multi-root Bloch wave operator formalism, namely, the Fock-space or valence universal MRCC approaches (see, e.g., [60, 61], and references therein) and the Hilbert-space or state-universal (SU) MRCC schemes [62–71], which are based on the Jeziorski-Monkhorst ansatz [62]. In this paper, we focus on methods that utilize the Jeziorski-Monkhorst wave function ansatz, which relies on the use of multiple cluster operators that are assigned to individual reference determinants spanning the multi-dimensional reference or model space.

There exist two formulations of the SUMRCC theory which depend on whether one premultiplies the amplitude equations by $e^{-T(\mu)}$, where $T(\mu)$ is the cluster operator associated with the reference determinant $|\Phi_\mu\rangle$, prior to the projection on the excited determinants, as suggested in the original Jeziorski-Monkhorst paper [62] and as exploited in the early work by Paldus, Piecuch, and their co-workers (cf., e.g., [63–66]), or whether one projects the amplitude equations on the excited determinants without premultiplying them first by $e^{-T(\mu)}$, as suggested by Kucharski and Bartlett [67] (see, e.g., [68, 69] for the follow-up work and representative applications). It is worth mentioning that Kowalski and Piecuch extended the MMCC approach to the SUMRCC case, enabling one to correct the results of the low-order SUMRCC calculations, such as SUMRCCSD, by the effects of higher-order (e.g., triple) excitations using the noniterative corrections to the SUMRCC energies expressed in terms of the generalized moments of the SUMRCC equations (projections of the SUMRCC equations on the higher-order excited determinants that are normally disregarded in the SUMRCC calculations) [70, 71].

Unfortunately, independent of the formulation, the SUMRCC formalisms suffer from convergence difficulties caused by intruder states or intruder multiple solutions [64, 65, 72]. Unlike in the perturbation theory, where intruders are inevitable from the theoretical point of view, in the genuine MRCC methods, such as SUMRCC, they are a consequence of the polynomial character of amplitude equations resulting from the use of the exponential ansatz for the wave function, which is further complicated by the nonlinear character of the generalized Bloch equation on which the genuine MRCC methods are based [72, 73], manifesting themselves in the existence of multiple, often singular, unphysical solutions that lead to convergence difficulties and large

inaccuracies when one iteratively solves the MRCC equations. Clearly, intruders are a serious obstacle on the way toward routine applications of the SUMRCC methods. The same is generally true for other genuine MRCC approaches exploiting the multi-root Bloch wave operator formalism, although significant progress has been accomplished toward eliminating intruders within the valence-universal MRCC approach by Meissner [74–76] who has replaced the conventional multi-root method of solving the valence-universal MRCC equations employing the effective Hamiltonian formulation that leads to convergence problems by the alternative, intermediate Hamiltonian formulation that enables the one-root calculations of the valence-universal MRCC type.

One can eliminate intruders from the SUMRCC considerations by turning to methods that abandon the idea of multiple cluster operators characterizing the Jeziorski-Monkhorst ansatz altogether, as in, for example, the state-specific MRCC techniques and the analogous active-space CC/EOMCC approaches employing a single-reference formalism, which incorporate the key ingredients of MRCC theory, such as the concept of active orbitals, into the otherwise single-reference CC or EOMCC considerations. In these methods, pioneered by Adamowicz, Oliphant, and Piecuch in the early 1990s [77–81] and revisited by Piecuch, Kucharski, and Bartlett in the late 1990s [82, 83], and their subsequent extensions, including, for example, excited and open-shell states, by the Adamowicz and Piecuch groups (cf., e.g., [84–93]), one combines the ordinary single-reference CC or EOMCC formalism with a multi-reference concept of active orbitals, which are used to select a relatively small subset of the dominant triply and other higher-than-doubly excited clusters that reflect the nature of the electronic quasi-degeneracy or excited states of interest. Although methods of this type can be very successful in applications involving single and multiple bond breaking, excited states dominated by many-electron transitions, and ground and excited states of radicals, one has to be able to identify the appropriate dominant determinant, which is regarded as a formal reference state and Fermi vacuum, to design them. This may not always be straightforward, particularly if several reference determinants contribute more or less equally to the wave function. The important question emerges if one can address the issue of

intruders within the Jeziorski-Monkhorst MRCC ansatz that treats all reference determinants on equal footing.

One promising approach to avoid the intruder state problem within the Jeziorski-Monkhorst SUMRCC ansatz is the state-specific MRCC theory proposed by Mukherjee et al. [94–97], which has recently been efficiently implemented including triple excitations by the Schaefer [98–100] and Pittner [101] groups. In particular, a new “linked” formulation of the Mukherjee’s theory, which has simpler coupling terms in the amplitude equations, has been recently derived and its equivalence with the original “connected” formulation within the complete model space (CMS) has been established by mathematical techniques that are similar to those exploited in the present paper [102].

Another interesting MRCC formalism that should be mentioned in this context is that proposed by Hanrath [103–105]. Hanrath’s MRCC removes the inherent redundancy of the Jeziorski-Monkhorst wave operator ansatz by means of determinant-based amplitude indexing [103–105]. This approach has the advantage of eliminating the need for non-unique “sufficiency conditions” of the Hilbert space MRCC theory, which resolve the underdetermined character of the equations due to possibly multiple paths leading from different reference determinants to a given excited determinant in the framework of the Jeziorski-Monkhorst ansatz, at the expense of a more complicated form of amplitude equations.

Yet another MRCC approach exploiting the Jeziorski-Monkhorst ansatz and aimed at eliminating intruders is the (size-extensivity corrected) MR Brillouin-Wigner CC (MRBWCC) method [106–110], in which the BW energy denominator shift improves the convergence properties by avoiding intruder states altogether. The basic MRBWCCSD method has been shown to yield reasonably accurate results for systems where the nondynamic correlation plays a significant role [111–123]. Recently, the connected triple excitations have been included in the MRBWCC theory [124–126], resulting in a considerable increase in the accuracy of the method thanks to the more precise description of dynamic correlation effects, similar to the single-reference case, where one has to incorporate connected triply excited clusters, at least approximately, to obtain

a quantitative description.

1 Generally, the occurrence of intruder states in the genuine MRCC methods can be attributed
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3 to the small separation between the energies associated with the model space configurations and
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5 energies of the excited configurations that do not belong to the model space. This is particularly
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7 likely to happen when the CMS is employed. In the CMS case, one often encounters excited
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9 configurations whose energies become very close to the energies of some reference configurations,
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11 particularly when the dimension of CMS becomes large due to the use of the larger numbers of
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13 active orbitals and electrons. In fact, it often happens that the emergence of intruders is tied
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15 to relatively few reference configurations that are not essential for achieving an accurate and
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17 size-consistent description, and may, therefore, be safely eliminated, assuming that the use of
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19 the resulting incomplete model space does not lead to other problems, such as departure from
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21 strict size extensivity that might cause a significant loss of accuracy when the many-electron
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23 system of interest becomes large (normally, one has to use CMS in order for the genuine MRCC
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25 theories to be rigorously size extensive; cf., e.g., [62]).
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30 There have been several suggestions about how to eliminate the need for the use of CMS in
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32 genuine MRCC calculations which abandon the intermediate normalization requirement of the
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34 MRCC wave functions (see, e.g., [127–133]). In the resulting incomplete model space MRCC
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36 theories, which are often cumbersome and which in some cases enforce extensivity at the ex-
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38 pense of accuracy, the intermediate normalization requirement is given up in order to eliminate
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40 the disconnected energy diagrams that automatically show up in genuine MRCC considerations
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42 when the CMS assumption is abandoned and the intermediate normalization condition is main-
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44 tained (cf., e.g., [62]). Recently, Li and Paldus have introduced a much more transparent and
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46 very elegant solution to the problem, resulting in the general model space (GMS) SUMRCC
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48 theory [134–136]. The GMS SUMRCC theory uses the so-called C-conditions, which enable
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50 one to employ incomplete model spaces in the SUMRCC calculations in a straightforward and
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52 rather routine fashion while retaining the intermediate normalization requirement and clarity
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54 of the resulting equations [134–136]. This idea has actually been touched upon in the original
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Jeziorski-Monkhorst paper [62], but has not been pursued in detail until Li and Paldus published their recent work. As shown in [134–136], when the model space and cluster amplitudes are defined in a suitable manner, the GMS SUMRCC method satisfying the C-conditions is exactly size-consistent [136] in the sense of additive separability of the resulting energies, although it does not fulfill the strict connected-diagrams-only requirement defining the recently discussed concept of generalized extensivity [137]. In collaboration with Li and Paldus, the aforementioned MRBWCC method has been generalized to the incomplete model space case as well [138]. As in the SUMRCC case discussed in [134–136], the C-conditions have been exploited. We should point out, however, that in the case of the MRBWCC theory the intruder state problem is not the reason for employing incomplete model spaces, since MRBWCC is a state specific, intruder-free theory. The primary motivation behind the use of incomplete model spaces in the MRBWCC calculations is the considerable saving in the computer effort resulting from the elimination of unimportant reference configurations.

In the present work, we combine the MRBWCC theory with the MMCC approach and with the treatment of general model spaces via the C-conditions. Thus, in Section 2.1, we derive the MMCC energy correction formula for the generalized form of the MRCC formalism that describes the continuous transition between the BWMRCC theory and the Rayleigh-Schrödinger (RS)-type SUMRCC theory of Jeziorski and Monkhorst. Then, in Section 2.2, we extend the original Kowalski-Piecuch formula for the relationship between moments of the Jeziorski-Monkhorst-style and Kucharski-Bartlett-style SUMRCC equations [70, 71] to the general incomplete model space case. Next, in Section 3, we show that in the CMS case, the two alternative formulations of the SUMRCC theory, with and without the premultiplication by $e^{-T(\mu)}$, which result, respectively, in the explicitly connected Jeziorski-Monkhorst-style SUMRCC equations used in [62–66] and the Kucharski-Bartlett-style SUMRCC equations in which the disconnected terms are retained (so that they might be canceled out or eliminated later for computational reasons, if need be), exploited in [67–69], i.e., the SUMRCC methods that employ two different definitions of moments of MRCC equations, are equivalent (while in the incomplete model space case they are not) and

support this formal finding by a numerical evidence. Finally, in Section 4, we summarize the

results.

2 Method of Moments of Coupled Cluster Equations for the Brillouin-Wigner-Type and Rayleigh-Schrödinger-Type Multireference Coupled Theories Based on the Jeziorski-Monkhorst Ansatz

2.1 The energy correction formula for the continuous transition between the Brillouin-Wigner-type and Rayleigh-Schrödinger-type multireference coupled cluster theories employing the Jeziorski-Monkhorst ansatz

As usual in the MRCC literature, we define the model space \mathcal{M} spanned by a number of reference configurations $|\Phi_\mu\rangle$, although we do not require \mathcal{M} to be complete. We introduce the projection operators on the model space \mathcal{M} and its orthogonal complement \mathcal{M}^\perp , P and Q , respectively, which are defined as

$$P = \sum_{\mu=1}^M |\Phi_\mu\rangle\langle\Phi_\mu| \quad (1)$$

and

$$Q = \mathbf{1} - P, \quad (2)$$

where M is the dimension of \mathcal{M} and $\mathbf{1}$ represents the identity operator in the relevant N -electron Hilbert space. The operators P and Q , Eqs. (1) and (2), respectively, satisfy the well-known properties of all projection operators, i.e., they are idempotent and hermitian, and $PQ = QP = 0$. We confine ourselves to the MRCC theories employing the Jeziorski-Monkhorst

ansatz [62] for the wave operator,

$$\Omega_\alpha = \sum_{\mu=1}^M e^{T(\mu)} |\Phi_\mu\rangle \langle \Phi_\mu|, \quad (3)$$

where $T(\mu)$ are the cluster operators associated with the model space configurations $|\Phi_\mu\rangle$. In general, the Ω_α operators generate the wave functions $|\Psi_\alpha\rangle$ of the target states α of interest from their respective projections onto the model space,

$$|\Psi_\alpha\rangle = \Omega_\alpha P |\Psi_\alpha\rangle \equiv \Omega_\alpha |\Psi_\alpha^P\rangle. \quad (4)$$

The wave operator Ω_α , which produces a given target state $|\Psi_\alpha\rangle$ from the corresponding zero-order model state $|\Psi_\alpha^P\rangle$, is, in general, state specific, so that we label it with the additional index α [in the original SUMRCC theory of Jeziorski and Monkhorst [62], the wave operator Ω is state universal and cluster operators $T(\mu)$ are not geared toward one particular state $|\Psi_\alpha\rangle$ but, rather, to a family of quasi-degenerate states whose number is the same as the dimension of the model space \mathcal{M} , so that one can drop subscript α at Ω in that case; there are, however, various ways of determining cluster operators $T(\mu)$, including the MRBWCC theory considered in this work, that may be state specific, so in the general case the wave operator Ω should be labeled by the index defining the target state it generates, as in Eq. (4)]. The intermediate normalization,

$$P\Omega_\alpha = P, \quad (5)$$

is assumed throughout all of the derivations discussed in this paper.

The determination of the wave operator Ω_α starts by writing the equation, which is equivalent to the Schrödinger equation, $H\Omega_\alpha P |\Psi_\alpha\rangle = E_\alpha \Omega_\alpha P |\Psi_\alpha\rangle$, and which one can regard as the generalized form of the Bloch equation for a λ -scaled continuous transition between the BW-type and RS-type MRCC theories [109] applied to the wave function $|\Psi_\alpha\rangle$,

$$H\Omega_\alpha P |\Psi_\alpha\rangle = \lambda E_\alpha \Omega_\alpha P |\Psi_\alpha\rangle + (1 - \lambda) \Omega_\alpha P H \Omega_\alpha P |\Psi_\alpha\rangle, \quad (6)$$

where $\lambda = 0$ corresponds to the RS case and $\lambda = 1$ corresponds to the BW case. As usual, we introduce the (non-hermitian) effective Hamiltonian,

$$H^{\text{eff}} = P H \Omega_\alpha P, \quad (7)$$

which acts only within the model space \mathcal{M} and which yields the MRCC energy E_α of the α -th

state $|\Psi_\alpha\rangle$ as its eigenvalue,

$$H^{\text{eff}}|\Psi_\alpha^P\rangle = E_\alpha|\Psi_\alpha^P\rangle. \quad (8)$$

The corresponding eigenvector $|\Psi_\alpha^P\rangle$ provides the coefficients defining the expansion of the MRCC wave function $|\Psi_\alpha\rangle$ projected onto the model space \mathcal{M} (or the zero-order component of $|\Psi_\alpha\rangle$),

$$|\Psi_\alpha^P\rangle = \sum_{\mu=1}^M c_\alpha^\mu |\Phi_\mu\rangle. \quad (9)$$

The amplitude equations for the λ -scaled transition from the MRBWCC theory to the Kucharski-Bartlett formulation of the RS-style SUMRCC method corresponding to the truncated scheme in which

$$T(\mu) = \sum_{n=1}^{m_A} T_n(\mu), \quad (10)$$

where $T_n(\mu)$ is the n -body component of $T(\mu)$ and $m_A \leq N$ is the excitation level defining the truncated calculation of interest (e.g., $m_A = 2$ in the MRCCSD case), can be given the following compact form [109]:

$$G_n(\mu)|\Phi_\mu\rangle = 0 \quad (n = 1, \dots, m_A; \mu = 1, \dots, M), \quad (11)$$

where the generalized G -moments, $G_n(\mu)|\Phi_\mu\rangle$, are simply a linear combination of the BW-type and RS-type moments of the MRCC equations employing the Jeziorski-Monkhorst ansatz, $B_n(\mu)|\Phi_\mu\rangle$ and $M_n(\mu)|\Phi_\mu\rangle$, respectively, as in the following expression in terms of the operators $G_n(\mu)$, $B_n(\mu)$, and $M_n(\mu)$ that define these moments,

$$G_n(\mu) = \lambda B_n(\mu) + (1 - \lambda)M_n(\mu). \quad (12)$$

The B - and M - moments entering Eq. (12) are defined as

$$B_n(\mu)|\Phi_\mu\rangle = Q_n(\mu) \left[(He^{T(\mu)})_{C+DC,L} - (E_\alpha - H_{\mu\mu}^{\text{eff}})e^{T(\mu)} \right] |\Phi_\mu\rangle \quad (13)$$

and

$$M_n(\mu)|\Phi_\mu\rangle = Q_n(\mu) \left[(He^{T(\mu)})_{C+DC,L} - \sum_{\nu(\neq\mu)} e^{T(\nu)} |\Phi_\nu\rangle \langle \Phi_\nu| H^{\text{eff}} \right] |\Phi_\mu\rangle, \quad (14)$$

respectively, where, for simplicity, the truncation of each cluster operator $T(\mu)$, $\mu = 1, \dots, M$, at the m_A -tuple excitations, as in Eq. (10), is assumed throughout without displaying the index m_A explicitly. The M -moments, Eq. (14), correspond to the Kucharski-Bartlett formulation of the RS-style SUMRCC theory [67] in a form where the disconnected linked terms are retained (in their original work [67], Kucharski and Bartlett dropped the disconnected linked terms from the final amplitude equations). On the other hand, the original Jeziorski-Monkhorst formulation of the RS-style SUMRCC theory [62], exploited over the years by Paldus, Piecuch, and their co-workers (cf., e.g., [63–66, 70–72, 134–136]), is defined in terms of the following moments:

$$\Gamma_n(\mu)|\Phi_\mu\rangle = Q_n(\mu) \left[(He^{T(\mu)})_C - \sum_{\nu(\neq\mu)} e^{-T(\mu)} e^{T(\nu)} |\Phi_\nu\rangle \langle \Phi_\nu| H^{\text{eff}} \right] |\Phi_\mu\rangle. \quad (15)$$

For example, the amplitude equations defining the Jeziorski-Monkhorst formulation of the SUMRCC theory, corresponding to the approximate scheme in which each $T(\mu)$ is truncated at the m_A -tuply excited clusters, as in Eq. (10), are obtained by zeroing the Γ -moments $\Gamma_n(\mu)|\Phi_\mu\rangle$ with $n = 1, \dots, m_A$ and $\mu = 1, \dots, M$,

$$\Gamma_n(\mu)|\Phi_\mu\rangle = 0 \quad (n = 1, \dots, m_A; \mu = 1, \dots, M). \quad (16)$$

In the above formulas, the subscript C designates the connected diagrams only, while DC, L stands for the disconnected, but linked diagrams. The $Q_n(\mu)$ operator is a projector onto the manifold spanned by the n -tuply excited determinants with respect to the μ -th Fermi vacuum $|\Phi_\mu\rangle$.

In order to derive the MMCC energy correction for the λ -scaled transition from the MRB-WCC approach to the Kucharski-Bartlett formulation of the RS-type SUMRCC method corresponding to Eq. (11), we follow the general philosophy of all MMCC considerations [26, 27, 29–31, 55, 70] and exploit the asymmetric energy expression

$$E_\alpha[\Xi] \equiv \frac{\langle \Xi | H \Omega_\alpha | \Psi_\alpha^P \rangle}{\langle \Xi | \Omega_\alpha | \Psi_\alpha^P \rangle}, \quad (17)$$

where $|\Xi\rangle$ is a “trial” state, which has a nonzero overlap with the target state α , and $|\Psi_\alpha^P\rangle = P|\Psi_\alpha\rangle$ is the projection of the approximate wave function $|\Psi_\alpha\rangle$, corresponding to the target state

α and obtained in the MRCC calculations based on Eq. (11) in which each cluster operator $T(\mu)$

is truncated at the m_A -tuply excited component, onto the model space \mathcal{M} . The usefulness of Eq. (17) stems from the fact that $E_\alpha[\Xi]$ gives the exact, FCI energy of the target state α , independent of the truncation level m_A used in the MRCC calculations, if $\langle \Xi |$ is the corresponding FCI bra wave function. Clearly, we can also write

$$E_\alpha = \frac{\langle \Xi | \Omega_\alpha [(1 - \lambda) H^{\text{eff}} + \lambda E_\alpha] | \Psi_\alpha^P \rangle}{\langle \Xi | \Omega_\alpha | \Psi_\alpha^P \rangle}, \quad (18)$$

where E_α is the energy obtained by solving the system of MRCC equations represented by Eq. (11), corresponding to the truncation of each $T(\mu)$ operator at the m_A -body component, and by diagonalizing the resulting effective Hamiltonian H^{eff} , Eq. (7), in the model space \mathcal{M} . Based on Eqs. (4), (7), (17), and (18), we can introduce the energy correction functional

$$\Delta E_\alpha[\Xi] \equiv E_\alpha[\Xi] - E_\alpha = \frac{\langle \Xi | H \Omega_\alpha - \lambda E_\alpha \Omega_\alpha - (1 - \lambda) \Omega_\alpha P H \Omega_\alpha | \Psi_\alpha^P \rangle}{\langle \Xi | \Omega_\alpha | \Psi_\alpha^P \rangle}, \quad (19)$$

which defines the difference between the exact, FCI energy of the target state α of interest and the corresponding MRCC energy E_α , obtained by solving Eq. (11) and diagonalizing the corresponding effective Hamiltonian in \mathcal{M} , if $\langle \Xi |$ is the FCI bra wave function representing state α . The appearance of the generalized Bloch equation applied to $|\Psi_\alpha\rangle$, Eq. (6), in the numerator of Eq. (19) should be noted.

We now introduce the resolution of identity with respect to the μ -th Fermi vacuum $|\Phi_\mu\rangle$,

$$\mathbf{1} = P + \sum_{n=1}^N Q_n(\mu), \quad (20)$$

into the numerator of the right-hand-side (rhs) of Eq. (19) and expand the zero-order state $|\Psi_\alpha^P\rangle$ according to Eq. (9). We assume that the amplitude equations, Eq. (11), have been solved, i.e., the projections of the corresponding generalized Bloch equation applied to $|\Psi_\alpha\rangle$ on the excited determinants with the excitation rank relative to $|\Phi_\mu\rangle$ not exceeding m_A vanish, so that [cf. Eqs. (6) and (7)],

$$Q_n(\mu)[H \Omega_\alpha P - \lambda E_\alpha \Omega_\alpha P - (1 - \lambda) \Omega_\alpha H^{\text{eff}}] |\Phi_\mu\rangle = 0 \quad (n = 1, \dots, m_A; \mu = 1, \dots, M). \quad (21)$$

We obtain,

$$\Delta E_\alpha[\Xi] = \frac{\sum_\mu c_\alpha^\mu \{ \lambda \langle \Xi | H^{\text{eff}} - E_\alpha | \Phi_\mu \rangle + \sum_{n>m_A} \langle \Xi | Q_n(\mu) [H\Omega_\alpha P - \lambda E_\alpha \Omega_\alpha P - (1-\lambda)\Omega_\alpha H^{\text{eff}}] | \Phi_\mu \rangle \}}{\langle \Xi | \Omega_\alpha | \Psi_\alpha^P \rangle}, \quad (22)$$

where we used the following identity

$$P[H\Omega_\alpha P - \lambda E_\alpha \Omega_\alpha P - (1-\lambda)\Omega_\alpha H^{\text{eff}}] | \Phi_\mu \rangle = \lambda(H^{\text{eff}} - E_\alpha) | \Phi_\mu \rangle. \quad (23)$$

Since E_α is the eigenvalue of H^{eff} and since the c_α^μ coefficients form the corresponding eigenvector, we have

$$\sum_\mu c_\alpha^\mu (H^{\text{eff}} - E_\alpha) | \Phi_\mu \rangle = 0, \quad (24)$$

so that the first term in the numerator of the rhs of Eq. (22) vanishes. By reinserting the Jeziorski-Monkhorst ansatz for the wave operator Ω_α , Eq. (3), back into the resulting expression, we obtain the desired MMCC formula for the energy correction $\Delta E_\alpha[\Xi]$ corresponding to a continuous transition from the BW-style to the RS-style MRCC theory exploiting the Jeziorski-Monkhorst ansatz, namely,

$$\Delta E_\alpha[\Xi] = \frac{\sum_\mu c_\alpha^\mu \sum_{n>m_A} \langle \Xi | G_n(\mu) | \Phi_\mu \rangle}{\sum_\mu c_\alpha^\mu \langle \Xi | e^{T(\mu)} | \Phi_\mu \rangle}, \quad (25)$$

where the $G_n(\mu) | \Phi_\mu \rangle$ moments are defined by Eqs. (12)–(14). Note that the $G_n(\mu) | \Phi_\mu \rangle$ moments that contribute to Eq. (25) have the excitation rank $n > m_A$, since we assume that the truncated cluster operators $T(\mu)$ that are needed to determine these moments have been obtained by solving the amplitude equations given by Eq. (11).

When $\langle \Xi |$ is the FCI bra wave function representing state α , the $\Delta E_\alpha[\Xi]$ correction added to the MRCC energy E_α , obtained by solving the MRCC system of equations represented by Eq. (11) and diagonalizing the corresponding effective Hamiltonian in the model space \mathcal{M} , recovers the exact, FCI energy of state α . By employing approximate forms of $\langle \Xi |$, we can obtain a variety of approximate MRMMCC models based on Eq. (11), similar to those discussed in [70, 71]. We should emphasize the state-specific character of the noniterative corrections $\Delta E_\alpha[\Xi]$. The most useful new feature of Eq. (25), when compared to the earlier MRMMCC considerations reported

in [70, 71], is its applicability to both the SUMRCC and MRBWCC methods, which are simply the two limiting cases in the λ -scaled continuous transition between the BW-type and RS-type MRCC theories corresponding to $\lambda = 0$ and 1, respectively. We should also point out that we have never had to assume the completeness of the model space in the above derivation, although we have employed the intermediate normalization condition, Eq. (5), since the generalized Bloch equation, Eq. (6), as well as the construction of the effective Hamiltonian, Eq. (7), rely on it. Since it is possible to satisfy the intermediate normalization requirement in both the incomplete model space SUMRCC and incomplete model space MRBWCC considerations with the help of the C-conditions, as discussed in [134–136, 138], the MMCC energy corrections $\Delta E_\alpha[\Xi]$ given by Eq. (25), which enable us to correct energies E_α obtained in the truncated MRCC calculations based on Eq. (11), are also suitable for the calculations involving incomplete model spaces.

2.2 Formula for the conversion between the M - and Γ -moments

Kowalski and Piecuch [70, 71] expressed their MMCC correction $\Delta E_\alpha[\Xi]$ for the case of the RS-style SUMRCC theory (the $\lambda = 0$ limit in our considerations) in terms of moments $\Gamma_n(\mu)|\Phi_\mu\rangle$, Eq. (15), rather than moments $M_n(\mu)|\Phi_\mu\rangle$, Eq. (14), that enter the definition of the generalized moments $G_n(\mu)|\Phi_\mu\rangle$, as in Eq. (12), used in our formula for $\Delta E_\alpha[\Xi]$, Eq. (25). They did this by deriving a formula that directly relates the M - and Γ -moments [70]. In the following, we generalize the relationship between the M - and Γ -moments obtained in [70] to the important case of incomplete model spaces.

Let us begin with the derivation of an auxiliary formula

$$P \left[(He^{T(\mu)})_C - \sum_{\nu \in \mathcal{M}} e^{-T(\mu)} e^{T(\nu)} |\Phi_\nu\rangle \langle \Phi_\nu| H^{\text{eff}} \right] |\Phi_\mu\rangle = -P \left[(He^{T(\mu)})_{DC,L} + (e^{-T(\mu)} - 1) H^{\text{eff}} \right] |\Phi_\mu\rangle, \quad (26)$$

valid for the general model space case, including complete and incomplete model spaces. Notice that in the former case, the rhs of Eq. (26) vanishes.

First, we write the following identity:

$$\begin{aligned}
 P \left[(He^{T(\mu)})_C - \sum_{\nu \in \mathcal{M}} e^{-T(\mu)} e^{T(\nu)} |\Phi_\nu\rangle \langle \Phi_\nu| H^{\text{eff}} \right] |\Phi_\mu\rangle \\
 = P(He^{T(\mu)})_C - \sum_{\tau, \rho, \nu \in \mathcal{M}} |\Phi_\rho\rangle \langle \Phi_\rho| e^{-T(\mu)} |\Phi_\tau\rangle \langle \Phi_\tau| e^{T(\nu)} |\Phi_\nu\rangle \langle \Phi_\nu| H^{\text{eff}} |\Phi_\mu\rangle, \quad (27)
 \end{aligned}$$

where we have inserted the resolution of identity, $P + Q = \mathbf{1}$, between $e^{-T(\mu)}$ and $e^{T(\nu)}$, while exploiting the property

$$Qe^{-T(\mu)} |\Phi_\rho\rangle = 0. \quad (28)$$

We can simplify the rhs of Eq. (27) by exploiting the condition

$$\langle \Phi_\tau | e^{T(\nu)} | \Phi_\nu \rangle = \delta_{\tau\nu}, \quad (29)$$

resulting from the assumption of intermediate normalization, since the intermediate normalization is preserved in the general model space case examined in this work thanks to the use of the C-conditions [134, 138]. In consequence, we obtain the following formula for the rhs of Eq. (27):

$$P(He^{T(\mu)})_C - \sum_{\rho, \nu \in \mathcal{M}} |\Phi_\rho\rangle \langle \Phi_\rho| e^{-T(\mu)} |\Phi_\nu\rangle \langle \Phi_\nu| H^{\text{eff}} |\Phi_\mu\rangle \quad (30)$$

or, using the definition of the P projector, Eq. (1), and the trivial identity $PH^{\text{eff}} = H^{\text{eff}}$,

$$P[(He^{T(\mu)})_C - e^{-T(\mu)} H^{\text{eff}}] |\Phi_\mu\rangle. \quad (31)$$

Next, we split the term containing $e^{-T(\mu)}$ in Eq. (31), obtaining the following form of the rhs of Eq. (27):

$$[P(He^{T(\mu)})_C - H^{\text{eff}}] |\Phi_\mu\rangle - P(e^{-T(\mu)} - 1) H^{\text{eff}} |\Phi_\mu\rangle. \quad (32)$$

The definition of the effective Hamiltonian, Eq. (7), and the Jeziorski-Monkhorst ansatz, Eq. (3), imply that

$$P \left[(He^{T(\mu)})_{C+DC,L} - H^{\text{eff}} \right] |\Phi_\mu\rangle = 0. \quad (33)$$

By combining Eqs. (32) and (33), we arrive at the desired auxiliary formula, Eq. (26).

The derivation of the relationship between the M - and Γ -moments starts from the following well-known property of the exponential wave function ansatz:

$$He^{T(\mu)} |\Phi_\mu\rangle = e^{T(\mu)} (He^{T(\mu)})_C |\Phi_\mu\rangle. \quad (34)$$

Inserting Eq. (34) into the definition of the M -moments, Eq. (14), and using the identity

$e^{T(\mu)}e^{-T(\mu)} = \mathbf{1}$, we obtain

$$M_n(\mu)|\Phi_\mu\rangle = Q_n(\mu)e^{T(\mu)} \left[(He^{T(\mu)})_C - \sum_{\nu \in \mathcal{M}} e^{-T(\mu)}e^{T(\nu)}|\Phi_\nu\rangle\langle\Phi_\nu|H^{\text{eff}} \right] |\Phi_\mu\rangle. \quad (35)$$

We now insert the resolution of identity, Eq. (20), between $e^{T(\mu)}$ and the expression between square brackets in Eq. (35), and use the previously derived auxiliary formula, Eq. (26),

$$\begin{aligned} M_n(\mu)|\Phi_\mu\rangle &= -Q_n(\mu)e^{T(\mu)}P \left[(He^{T(\mu)})_{DC,L} + (e^{-T(\mu)} - 1)H^{\text{eff}} \right] |\Phi_\mu\rangle \\ &\quad + Q_n(\mu)e^{T(\mu)} \left\{ \sum_{m=1}^N Q_m(\mu) \left[(He^{T(\mu)})_C \right. \right. \\ &\quad \left. \left. - \sum_{\nu \in \mathcal{M}} e^{-T(\mu)}e^{T(\nu)}|\Phi_\nu\rangle\langle\Phi_\nu|H^{\text{eff}} \right] \right\} |\Phi_\mu\rangle \\ &= -Q_n(\mu)e^{T(\mu)}P \left[(He^{T(\mu)})_{DC,L} + (e^{-T(\mu)} - 1)H^{\text{eff}} \right] |\Phi_\mu\rangle \\ &\quad + Q_n(\mu) \sum_{m=1}^N \left\{ (e^{T(\mu)})_{(n-m)} Q_m(\mu) \left[(He^{T(\mu)})_C \right. \right. \\ &\quad \left. \left. - \sum_{\nu \in \mathcal{M}} e^{-T(\mu)}e^{T(\nu)}|\Phi_\nu\rangle\langle\Phi_\nu|H^{\text{eff}} \right] \right\} |\Phi_\mu\rangle, \end{aligned} \quad (36)$$

where $(e^{T(\mu)})_{(n-m)}$ designates the $(n-m)$ -body part of $e^{T(\mu)}$. Using the definition of the Γ -moments, Eq. (15), and dropping the $Q_n(\mu)$ projector from the second rhs term in Eq. (37) [one can do it since the product of $(e^{T(\mu)})_{(n-m)}$ and $\Gamma_m(\mu)$ is the n -body excitation operator relative to $|\Phi_\mu\rangle$], and realizing that the $\nu = \mu$ term in the summation over ν in Eq. (37) vanishes since $Q_m(\mu)|\Phi_\mu\rangle = 0$, we obtain the following final formula relating the two types of moments:

$$M_n(\mu)|\Phi_\mu\rangle = -Q_n(\mu)e^{T(\mu)}P \left[(He^{T(\mu)})_{DC,L} + (e^{-T(\mu)} - 1)H^{\text{eff}} \right] |\Phi_\mu\rangle + \sum_{m=1}^n (e^{T(\mu)})_{n-m} \Gamma_m(\mu)|\Phi_\mu\rangle. \quad (38)$$

As already pointed out, the above relationship between the M - and Γ -moments is valid for both the complete and incomplete model space cases. If the model space is complete, the first part of the rhs of Eq. (38) vanishes and the relationship between the M - and Γ -moments simplifies to

$$M_n(\mu)|\Phi_\mu\rangle = \sum_{m=1}^n (e^{T(\mu)})_{n-m} \Gamma_m(\mu)|\Phi_\mu\rangle, \quad (39)$$

which is precisely the expression derived by Kowalski and Piecuch in [70]. In other words, Eq.

(38) provides us with the natural extension of the earlier work [70], where the authors assumed that the model space is complete, to the general case of incomplete model spaces.

3 Relationship Between the Jeziorski-Monkhorst and Kucharski-Bartlett Formulations of the State-Universal Multireference Coupled Cluster Theory

According to Eq. (38) or, better, Eq. (39), we can write the following relationships between the $M_n(\mu)$ and $\Gamma_m(\mu)$ operators that generate the M - and Γ -moments when the model space is complete:

$$M_1(\mu) = \Gamma_1(\mu), \quad (40)$$

$$M_2(\mu) = \Gamma_2(\mu) + \Gamma_1(\mu)(e^{T(\mu)})_1, \quad (41)$$

$$M_3(\mu) = \Gamma_3(\mu) + \Gamma_2(\mu)(e^{T(\mu)})_1 + \Gamma_1(\mu)(e^{T(\mu)})_2, \text{ etc.} \quad (42)$$

Assuming that cluster amplitudes have been converged within the Jeziorski-Monkhorst formulation of the SUMRCC scheme [62], so that the $T(\mu)$ operators satisfy the system of equations represented by Eq. (16), which is obtained by zeroing the $\Gamma_n(\mu)|\Phi_\mu\rangle$ moments with $n = 1, \dots, m_A$, one automatically obtains the amplitude equations used in the Kucharski-Bartlett formulation of the SUMRCC theory [67],

$$M_n(\mu)|\Phi_\mu\rangle = 0 \quad (n = 1, \dots, m_A; \mu = 1, \dots, M). \quad (43)$$

Conversely, assuming that the $T(\mu)$ operators satisfy the system of equations represented by Eq. (43), we immediately obtain (by a trivial back substitution) the system of equations represented by Eq. (16). Thus, the Jeziorski-Monkhorst and Kucharski-Bartlett formulations of the SUMRCC theory are equivalent in the CMS case and, as shown below, give identical numerical results, as long as one does not remove any terms from the definition of the $M_n(\mu)|\Phi_\mu\rangle$

moments, Eq. (14) [as mentioned in Section 2.1, in the development of practical SUMRCC schemes, Kucharski and Bartlett dropped the disconnected linked terms from the definition of the $M_n(\mu)|\Phi_\mu\rangle$ moments given by Eq. (14)]. They are no longer equivalent, however, when incomplete model spaces are employed (and $m_A < N$), even when C-conditions are exploited, due to the presence of the $-Q_n e^{T(\mu)} P[\dots]|\Phi_\mu\rangle$ term on the rhs of Eq. (38) that does not cancel out.

The equivalence of the Jeziorski-Monkhorst and Kucharski-Bartlett SUMRCCSD approaches in the CMS case was tested by us numerically using, as an example, the lowest 1A_1 state of the CH_2 biradical. The standard cc-pVDZ basis set [139] (with the Cartesian components of the d orbitals) was employed and the core orbital that correlates with the $1s$ orbital of the C atom was frozen in the SUMRCCSD calculations. The model space consisted of two closed-shell reference determinants, namely, the ground-state restricted Hartree-Fock (RHF) determinant and the determinant corresponding to the HOMO \rightarrow LUMO double excitation. The RHF orbitals were employed throughout. This model space, which corresponds to two active electrons and two active orbitals, is complete due to the fact that HOMO and LUMO belong to different symmetry species of the C_{2v} group used in the calculations. The SUMRCCSD calculations using the Kucharski-Bartlett formulation of SUMRCC, resulting from solving the system of amplitude equations represented by Eq. (43) in which $m_A = 2$, were performed using Pittner's implementation of the λ -scaled transition between the BW-type and RS-type MRCCSD theories employing the Jeziorski-Monkhorst ansatz, defined by Eq. (11) with $m_A = 2$ and λ set at 0, interfaced with ACES II [140]. The SUMRCCSD calculations using the Jeziorski-Monkhorst formulation of SUMRCC, resulting from solving the system of amplitude equations represented by Eq. (16) in which $m_A = 2$, were performed using the Piecuch-Paldus implementation of the orthogonally spin-adapted two-reference SUMRCCSD approach [66] interfaced with the RHF and integral transformation routines available in GAMESS [141].

The results of our comparative calculations for the three representative geometries of CH_2 are summarized in Table 1. They clearly demonstrate the equivalence of the Jeziorski-Monkhorst

Table 1: The energies of the lowest 1A_1 state of methylene, as described by the cc-pVDZ basis set and the two-dimensional model space consisting of the ground-state RHF determinant and the closed-shell determinant obtained via HOMO \rightarrow LUMO double excitation, obtained with the Jeziorski-Monkhorst (JM) and Kucharski-Bartlett (KB) formulations of the SUMRCCSD approach (see the text for the remaining computational details).

r_{CH}	α_{HCH}	E(KB-MRCCSD)	E(JM-MRCCSD)
Å	degs	hartree	hartree
1.1	130	-39.0045923428	-39.0045923428
1.6	130	-38.8919360582	-38.8919360582
1.1	170	-38.9741688837	-38.9741688837

and Kucharski-Bartlett SUMRCCSD approaches.

4 Summary

In this paper, we applied idea of the method of moments to the continuous transition between the BW-type and RS-type formulations of the MRCC theory employing the Jeziorski-Monkhorst ansatz. This allowed us to derive the formula for the state-specific, noniterative MMCC corrections which, when added to the energies obtained in the BW-type and RS-type MRCC calculations, or the MRCC calculations corresponding to a continuous transition between the BW-type and RS-type limits of the MRCC theory, recover the exact, FCI energies of the electronic states of interest. We considered the complete and incomplete model space cases. In the latter case, to maintain intermediate normalization, we exploited the C-conditions technique of Li and Paldus. In particular, we extended the previously reported formula relating moments of the SUMRCC equations in the Jeziorski-Monkhorst and Kucharski-Bartlett formulations of the SUMRCC theory in the case of the complete model space to incomplete model spaces. We demonstrated that

in the complete model space case, the two formulations of the SUMRCC theory are equivalent, provided that the disconnected linked terms are retained in the Kucharski-Bartlett amplitude equations, and verified this formal finding numerically using the two-reference SUMRCCSD calculations for CH₂.

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