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Extension of the method of moments of coupled-cluster equations to a multireference wave operator formalism☆

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Abstract

The recently proposed method of moments of coupled-cluster equations (MMCC) is extended to a multireference wave operator formalism. After reviewing the single-reference MMCC theory and its performance in calculations of potential energy surfaces involving bond breaking, we introduce the method of moments of the generalized Bloch equation and the method of moments of the state-universal coupled-cluster equations (MM-SUCC). The main idea of the MM-SUCC theory is that of the noniterative energy corrections that, when added to the ground- and excited-state energies obtained in approximate SUCC calculations, recover the exact energies. Approximate variants of the MM-SUCC formalism that may lead to significant improvements in the results of the standard SUCC calculations are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Very few papers have had larger impact on theory of molecular electronic structure than the pioneering works by Jiri Čížek and Joe Paldus [1–5]. In these and many subsequent papers, Jiri Čížek and Joe Paldus introduced the coupled-cluster (CC) theory to chemistry. Since then, the CC method has assumed a prominent place in the field of quantum chemistry, as can be demonstrated by a large number of review articles that were written on this topic (cf., e.g., Refs. [6–14] for some examples) and by countless applications of various CC approaches to problems of chemical interest. As stated by Joe Paldus and his co-worker, Xiangzhu Li, in their recent review article in *Advances of Chemical Physics* [12], 'the methodological developments, computer implementations, and practical applications of various versions of CC theory that have taken place since its inception in the 1960s leave little doubt about the fruitfulness of the exponential cluster *Ansatz* for the wave function and the formalism that ensued. The standard CCSD and CCSD(T) methods, in either spin-orbital or spin-adapted form, are presently available in most quantum chemical software packages and are routinely used in diverse applications in which a highly correlated approach is called for and can be carried out.'

☆ In honour of Josef Paldus on the occasion of his 65th birthday.

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One of the most challenging problems in CC theory is extension of the single-reference CC approach to quasi-degenerate and excited electronic states. The genuine multireference CC (MRCC) theories of the valence-universal (VU) or Fock-space type (see Refs. [10,12,15,16]) and state-universal (SU) or Hilbert-space type (see Refs. [10,12,17–41]) that are based on the generalized Bloch equation and the concept of an effective Hamiltonian acting in a multidimensional model or reference space [42–44] (cf. also Ref. [29]) have been proposed and investigated. The senior author of the present paper was fortunate to be a member of the Paldus Waterloo group and to work with Joe Paldus on various aspects of the multireference SUCC formalism [21–27] (cf. also, Refs. [40,41]). This effort has resulted in a diagrammatic formulation [21,26] and subsequent general-purpose computer implementation [26] of the complete orthogonally spin-adapted two-reference SUCCSD (SUCC singles and doubles) approach that together with earlier variants of the SUCCSD method [19,20,22–25] was successfully applied to potential energy surfaces of the ground and excited states of small hydrogen clusters [22–27] and methylene [40,41], and to property functions of quasi-degenerate molecular systems [27]. Together with Joe Paldus and other members of his Waterloo group, the senior author of this article systematically explored the limits of applicability of the two-reference SUCCSD method and the role of various terms [22–24,26] and higher-than-doubly excited clusters [25] in calculations based on the SUCC formalism of Jeziorski and Monkhorst [17]. These studies, performed under the leadership of Joe Paldus in the late 80s and early 90s, continue to stimulate a considerable research activity in our Michigan group, aimed at the development of new MRCC approaches and serial as well as parallel computer codes that are based on the SUCC wave function ansatz [28–31].

It is clear from all these earlier studies that the SUCC theory can be extremely successful, as is probably best illustrated by the calculations of the singlet–triplet ($A\,^1A_1$–$X\,^3B_1$) [40,41] and singlet–singlet ($2\,^1A_1$–$1\,^1A_1$; $1\,^1A_1 \equiv A\,^1A_1$) [26,30,31] energy separations in methylene with the orthogonally spin-adapted two-reference SUCCSD method including cubic and quartic coupling terms [26]. The SUCC theory that, unlike the VUCC approaches, does not require a simultaneous consideration of different sectors of the Fock space, is much better suited for potential energy surface scans than the VUCC formalism. Unfortunately, as these types of calculations are performed with the existing orthogonally spin-adapted [19–27,30,31] and spin-orbital or spin-free [18,32–39] SUCCSD methods, several new problems are encountered. The list of problems encountered in the SUCCSD calculations and the list of problems encountered in the related calculations employing the approximate CI-like methods based on the generalized Bloch equation [29] include the existence of multiple [23,28,29] and singular [20,22–25,28] solutions, intruder states [23,24,28], and the existence of the so-called intruder solutions [28,29]. The latter solutions are related to a specific algebraic nature of the generalized Bloch and SUCC equations. Small errors relative to full CI in the energies calculated with the SUCCSD approach in the region of nuclear geometries where the electronic states of interest are quasi-degenerate become large as we start exploring regions where the electronic states of interest are not clearly separated from the rest of the electronic spectrum [23–26,28].

It is evident from Ref. [25] and from the remarks made in Ref. [29] that some form of inclusion of higher-than-doubly excited clusters should help to eliminate the problems observed in the SUCC calculations. Unfortunately, there is no clear way how to proceed here, since the SUCC formalism becomes very complicated as we start considering various higher-order terms. The use of the standard multireference many-body perturbation theory (MRMBPT) [45–47] to estimate higher-order corrections of the SUCC formalism, although potentially useful (cf., e.g., Ref. [48]), may not be the best idea, since the MRMBPT approach suffers from intruder states [49–56] in regions where the SUCCSD approach fails. The existence of multiple and pathological solutions of the SUCCSD equations is largely related to an asymmetric treatment of the excitation manifolds corresponding to different reference configurations and to a nonlinear nature of the generalized Bloch equation [28,29], so that simple estimates of higher-order corrections may not help at all or make things even more complicated. The MRMBPT formalism alone does not provide us with a tool that would allow us to clearly resolve problems encountered in the SUCC and CI-like calculations based on the generalized Bloch equation. It is, therefore, important that we understand the relationship between the approximate and exact SUCC formalisms. Since many problems of the SUCC approach are related to the use of the generalized Bloch equation, it is also essential that we precisely formulate the mathematical relationship between the solutions of truncated and exact forms of the generalized Bloch equation.

Trying to deal with the remanent errors that occur in approximate calculations has been a long-standing problem in mathematics and science since the development of expansions in the 17th century. The problem of finding simple ways of estimating the errors made in approximate electronic structure calculations is one of the 'holy grails' of quantum chemistry. In particular, it would be highly desirable to develop a new MRCC approach that allowed us to systematically correct the results of SUCC calculations (making sure that we are improving them relative to full CI and not making them worse), particularly in all these difficult cases where the conventional MRMBPT-like arguments fail. This would be somewhat analogous to the well-known Davidson corrections [57,58] and their quasi-degenerate extensions [7,59–62] that are often used to correct the results of the limited single- and multi-reference CI (MRCI) calculations. In analogy to the Davidson corrections, we would like to be able to correct the results of approximate SUCC calculations solely on the basis of information that can be extracted from these approximate SUCC calculations. It would also be highly desirable to have a formalism that allowed us to correct the energies of electronic states obtained in the SUCC calculations in a state-selective manner, that is to correct one or more SUCC energies independent of energies of other states.

The present study suggests an approach that has the desired characteristics. The main idea of the proposed formalism, termed the *method of moments of the state-universal multireference coupled-cluster equations* (*MM-SUCC*), and of the related *method of moments of the generalized Bloch equation* is that of the non-iterative energy corrections δ_μ, $\mu = 1, \ldots, M$, that, when added to the corresponding energies obtained by solving the approximate SUCC (e.g. SUCCSD) equations, recover the exact energies E_μ of the M electronic states of interest. Each correction δ_μ is a nontrivial functional of the corresponding exact electronic wave function $|\Psi_\mu\rangle$ and the *generalized moments of the SUCC* (*or approximate Bloch*) *equations* (the SUCC or Bloch equations corresponding to projections of these equations on the excited configurations whose excitation level exceeds that defining a given SUCC or other Bloch-equation-based multireference approximation). By approximating the exact formulas for the energy corrections δ_μ (which can be done by using subsets of all generalized moments of the SUCC equations and by replacing wave functions $|\Psi_\mu\rangle$ in the formulas for δ_μ by simple estimates of $|\Psi_\mu\rangle$ provided by inexpensive *ab initio* methods), we can determine the approximate values of corrections δ_μ that, when added to energies obtained in approximate SUCC calculations, provide energy values that are very close to the exact energies. The proposed MM-SUCC approach differs from the standard multireference approaches in that, in computing corrections δ_μ, we rely on the explicit and rigorous relationship between the energies obtained in approximate multireference calculations and the exact energy values. In the standard multireference approaches, which do not rely on the explicit relationship between the approximate and exact energies, we can only hope that by adding sufficiently many higher-order terms to equations representing low-order approaches, we obtain better results; the problem is that in all conventional approaches the control over the choice of higher-order terms is limited by the fact that we must use the MRMBPT or similar arguments and these are not sufficiently transparent in situations where the MRMBPT series poorly converges due to intruder states.

The MM-SUCC approach described in this paper represents a multireference extension of the recently developed method of moments of the single-reference coupled-cluster equations (MMCC) [13,63,64]. In analogy to a multireference formalism discussed in this paper, the main idea of the single-reference MMCC theory is that of a simple, noniterative correction δ that, when added to the energy obtained in the standard approximate single-reference CC calculations, such as CCSD (CC singles and doubles) or CCSDT (CC singles, doubles, and triples), recovers the exact (full CI) result. The energy correction δ is a functional of the ground-state wave function $|\Psi\rangle$ and the generalized moments of the single-reference CC equations, i.e. the single-reference CC equations corresponding to projections of these equations on the excited configurations whose excitation level exceeds that defining a given single-reference CC approximation (e.g. the CCSD equations projected on triples, quadruples, etc.). As demonstrated in Refs. [13,63–65], the use of simple perturbative approximations for $|\Psi\rangle$ in the MMCC energy formula and the use of the generalized moments of the single-reference CCSD equations, corresponding to projections of these equations on triply and quadruply excited configurations, allows us to 'renormalize' the popular and widely used noniterative CC approximations, such as CCSD(T) [66], CCSD[T] [67,68], and CCSD(TQ$_f$) [69], in which the effects due to connected triples and quadruples are estimated using the single-reference MBPT. The resulting *completely renormalized CCSD(T), CCSD[T], and CCSD(TQ) methods*, which represent the MMCC-based extensions of the existing CCSD(T), CCSD[T], and CCSD(TQ$_f$) approaches, remove the pervasive failing of the CCSD(T), CCSD[T], and CCSD(TQ$_f$) ground-state methods, when chemical bonds are stretched or broken, while retaining the simplicity and the 'black-box' character of the noniterative perturbative CC approximations [13,63–65]. This shows how powerful the idea of using the generalized moments of CC equations is in the single-reference case. By extending the MMCC formalism to a multireference case, we should be able to eliminate many of the problems encountered in SUCC calculations.

2. The overview of the method of moments of the single-reference coupled-cluster equations

We begin our considerations by overviewing the recently proposed single-reference MMCC formalism [13,63,64], since the MM-SUCC approach described in a later part of this paper represents its multi-reference generalization.

In the single-reference CC theory, the ground-state wave function of an N-electron system is written in the exponential form $e^T|\Phi\rangle$, where T is the cluster operator and $|\Phi\rangle$ is an independent-particle-model reference configuration (usually, the Hartree–Fock determinant). Let us consider the standard single-reference CC approximation (hereafter referred to as method A), in which the cluster operator T is approximated as follows:

$$T \approx T_A = \sum_{n=1}^{m_A} T_n, \tag{1}$$

where T_n, $n = 1, \ldots, m_A$, are the many-body components of T included in the calculations and $m_A < N$ ($m_A = 2$ defines the CCSD method, $m_A = 3$ defines the CCSDT method, etc.). The equations for cluster amplitudes defining T_A form a system of nonlinear, energy-independent equations, namely,

$$Q_n(H_N\, e^{T_A})_C|\Phi\rangle = 0 \qquad (n = 1, \ldots, m_A), \tag{2}$$

where $H_N = H - \langle\Phi|H|\Phi\rangle$ is the electronic Hamiltonian in the normal-ordered (normal-product) form, Q_n is a projection operator onto the subspace spanned by all n-tuply excited configurations relative to $|\Phi\rangle$, and subscript C designates the connected part of the corresponding operator expression. Once the system of equations, Eq. (2), is solved for T_A, the energy is calculated as follows:

$$E^A = \langle\Phi|H|\Phi\rangle + \langle\Phi|(H_N\, e^{T_A})_C|\Phi\rangle = \langle\Phi|(H\, e^{T_A})_C|\Phi\rangle. \tag{3}$$

We have recently derived the formula for the non-iterative correction δ that, when added to the energy obtained in approximate single-reference CC calculations, E^A, Eq. (3), recovers the exact (full CI) energy E. We obtain [13,63,64],

$$\delta \equiv E - E^A = \sum_{n=m_A+1}^{N} \sum_{m=m_A+1}^{n} \langle\Psi|Q_n(e^{T_A})_{n-m}M_m(m_A)|\Phi\rangle / \langle\Psi|e^{T_A}|\Phi\rangle, \tag{4}$$

where $|\Psi\rangle$ is the full CI state and

$$M_m(m_A)|\Phi\rangle = (H_N\, e^{T_A})_{C,m}|\Phi\rangle = Q_m(H_N\, e^{T_A})_C|\Phi\rangle \tag{5}$$

are the single-reference CC equations, in which $T = T_A$, projected onto the m-tuply excited configurations relative to $|\Phi\rangle$. In general, O_m is the m-body component of operator O (for example, $(e^{T_A})_{n-m}$ is the $(n-m)$-particle component of the single-reference CC wave operator e^{T_A} defining method A). The proof of formula (4) is based on the Fundamental Theorem of the Formalism of β-Nested Equations [13], which describes mathematical relationships between multiple solutions of the single-reference CC equations representing different levels of theory (CCSD, CCSDT, etc.). An alternative derivation of Eq. (4), based on the MMCC functional $\Lambda[\Psi]$, has been given in Ref. [63].

Eq. (4) represents the basic equation of the single-reference MMCC theory. The main element of Eq. (4) is the presence in it of quantities $M_m(m_A)|\Phi\rangle$ that represent CC equations, in which $T = T_A$, projected on the m-tuply excited configurations with $m > m_A$. These readily available quantities represent the *generalized moments of coupled-cluster equations* [70,71]. For example, if we want to correct the CCSD results (the $m_A = 2$ case) and recover the full CI energy, we need to calculate the generalized moments of the CCSD equations, i.e. the CCSD equations projected on triples, quadruples, pentuples, and hextuples or $M_m(2)|\Phi\rangle = Q_m(H_N \, e^{T_1+T_2})_C|\Phi\rangle$, where T_1 and T_2 are the singly and doubly excited clusters resulting from the CCSD calculations and $m = 3$–6 (the $M_m(2)|\Phi\rangle$ moments with $m > 6$ vanish). The energy correction δ is also a functional of the exact wave function $|\Psi\rangle$. We can, however, use simple guesses for $|\Psi\rangle$ and calculate approximate values of δ. In this way, we can correct the results of approximate single-reference CC calculations and obtain energies that are much closer to the exact energy than energy E^A. The only requirement that Eq. (4) imposes on $|\Psi\rangle$ is the presence of some higher-than-m_A-tuply excited configurations in $|\Psi\rangle$. These can be easily estimated by performing inexpensive CI or MBPT calculations.

The completely renormalized CCSD(T) and CCSD(TQ) methods mentioned in Section 1 are obtained by using the MBPT-like expressions to define $|\Psi\rangle$ in Eq. (4). For example, the completely renormalized CCSD(T) [CR-CCSD(T)] approach is obtained by replacing $|\Psi\rangle$ in Eq. (4) by [13,63–65]

$$|\Psi^{\mathrm{CCSD(T)}}\rangle = \Big(1 + T_1 + T_2 + R_0^{(3)}(V_N T_2)_C + R_0^{(3)} V_N T_1\Big)|\Phi\rangle, \quad (6)$$

where T_1 and T_2 are the singly and doubly excited clusters obtained in the CCSD calculations, $R_0^{(3)}$ is the three-body part of the MBPT reduced resolvent, and V_N is the two-body part of H_N, and by invoking the so-called MMCC(2,3) approximation, in which the formula for correction δ is approximated as follows [13,63,64]:

$$\delta \approx \delta^{\mathrm{MMCC(2,3)}} = \langle\Psi|Q_3 M_3(2)|\Phi\rangle / \langle\Psi|e^{T_1+T_2}|\Phi\rangle, \quad (7)$$

where $M_3(2)|\Phi\rangle = Q_3(H_N \, e^{T_1+T_2})_C|\Phi\rangle$ are the CCSD equations projected on triples. The CR-CCSD(T) energy formula is [13,63–65]

$$E^{\mathrm{CR-CCSD(T)}} = E^{\mathrm{CCSD}} + \langle\Psi^{\mathrm{CCSD(T)}}|Q_3 M_3(2)|\Phi\rangle / \langle\Psi^{\mathrm{CCSD(T)}}|e^{T_1+T_2}|\Phi\rangle, \quad (8)$$

where E^{CCSD} is the CCSD energy. If we replace $M_3(2)$ in Eq. (8) by the lowest-order $(V_N T_2)_{C,3}$ term (the three-body part of the connected product of V_N and T_2) and replace the denominator $\langle\Psi^{\mathrm{CCSD(T)}}|e^{T_1+T_2}|\Phi\rangle$ by 1.0, Eq. (8) reduces to the well-known energy expression of the CCSD(T) method [13,63]. In a very similar fashion, we can use the formula for correction δ, Eq. (4), to define the completely renormalized CCSD[T] (CR-CCSD[T]) and completely renormalized CCSD(TQ) [CR-CCSD(TQ)] methods that represent simple, MMCC-based extensions of the existing noniterative CCSD[T] and CCSD(TQ$_f$) approaches [13,63–65]. The MMCC(2,3) approximation, Eq. (7), and its higher-order analogs can also be used to define methods, in which the wave function $|\Psi\rangle$ that enters the MMCC energy formula, Eq. (4) is replaced by inexpensive CI approximations, such as CISDt [13], in which triples of the single-reference CI method are selected using active orbitals (to mimic MRCI).

Our test calculations [13,63–65] indicate that the MMCC formalism represents a powerful approach to the many-electron correlation problem. The most intriguing result is the fact that unlike the standard CCSD[T], CCSD(T), and CCSD(TQ$_f$) methods, their completely renormalized CR-CCSD[T], CR-CCSD(T), and CR-CCSD(TQ) counterparts are capable of describing bond breaking and providing highly accurate results at large internuclear separations, in spite of the apparent presence of elements of MBPT in the CR-CCSD[T], CR-CCSD(T), and CR-CCSD(TQ) energy expressions (cf. Eqs. (6) and (8)). This should be confronted with the well-known

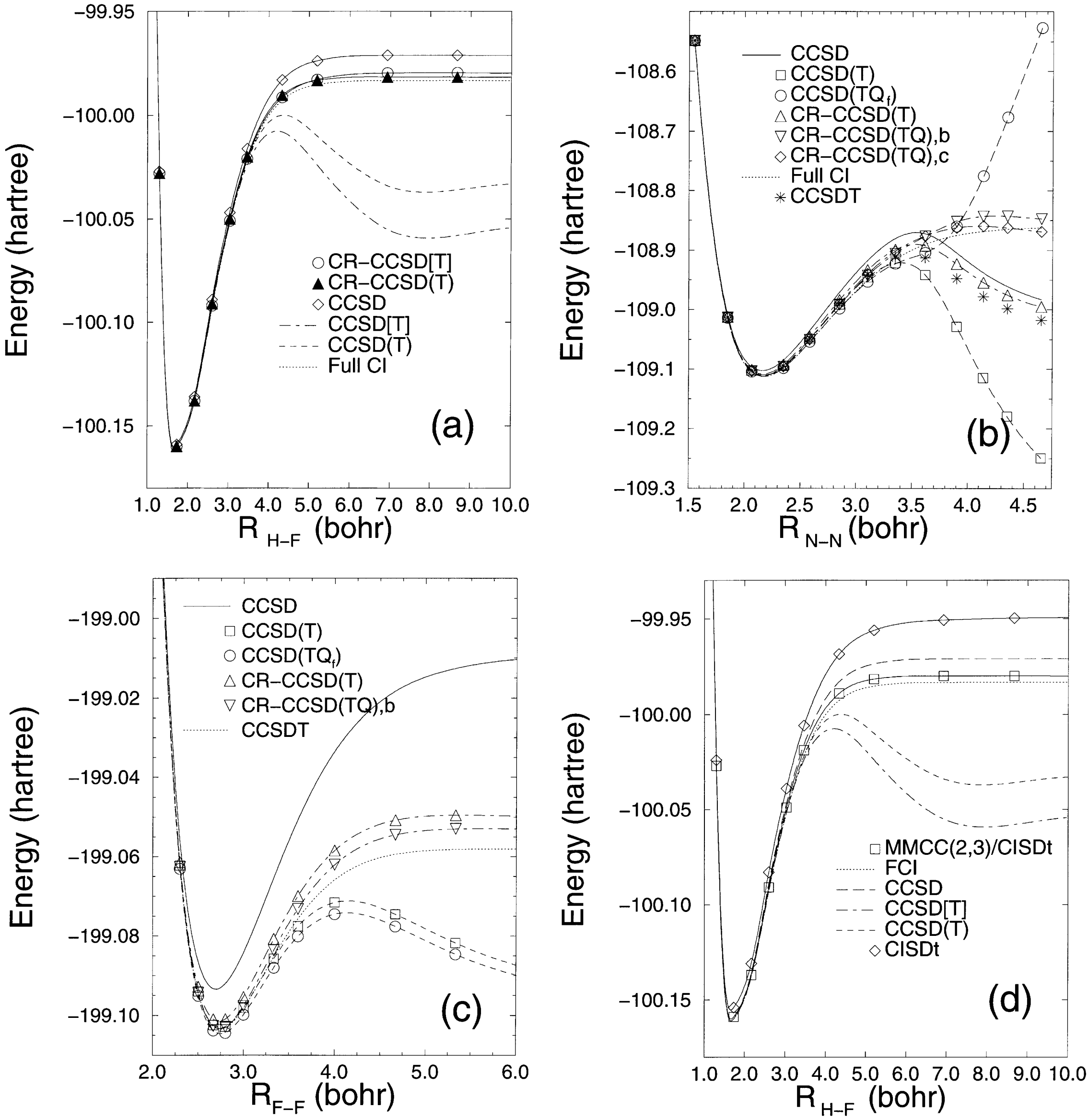

Fig. 1. Potential energy curves for the double-zeta (DZ) HF ((a) and (d)) and N_2 (b) molecules, and the cc-pVDZ F_2 molecule (c) (see Refs. [13,63–65] for the numerical data and see the text for further details).

fact that the presence of the MBPT-like terms in the standard CCSD[T], CCSD(T), and CCSD(TQ$_f$) expressions leads to completely unphysical potential energy surfaces due to divergent behavior of the MBPT series at large internuclear separations (cf., e.g., Refs. [13,63–65], and references therein). The results of the CR-CCSD[T], CR-CCSD(T), and CR-CCSD(TQ) calculations for geometries near the equilibrium, where the standard perturbative CC approximations work fine, are virtually identical to the results obtained with the CCSD[T], CCSD(T), and CCSD(TQ$_f$) schemes, respectively. As shown in Fig. 1(a), in spite of using elements of MBPT and in spite of its noniterative character, the MMCC-based

CR-CCSD(T) method eliminates the unphysical hump on the potential energy curve for the HF molecule produced by the CCSD(T) approach at intermediate internuclear distances R. The CR-CCSD(T) curve for HF is located above the exact (full CI) curve and the errors in the CR-CCSD(T) energies relative to full CI do not exceed 2 mhartree over the entire range of R values [13,63]. The CR-CCSD(T) results for geometries near the equilibrium ($R \approx R_e$), where the CCSD(T) method works great, are practically identical to those obtained with the CCSD(T) approach. As shown in Fig. 1(b), variants 'b' and 'c' of the CR-CCSD(TQ) method [64], which is a simple modification of the CCSD(TQ_f) approach and which, as the latter method, uses elements of MBPT to estimate higher-order effects, provide the potential energy curves for N_2, which are almost identical to the exact curve. A large positive 334.985 mhartree error relative to full CI at $R = 2.25R_e$, obtained with CCSD(TQ_f), and a large negative -387.448 mhartree error obtained with CCSD(T), reduce to as little as 14.796 and 6.708 mhartree, when variants 'b' and 'c' of the CR-CCSD(TQ) method are employed [64] (in this case, even the full CCSDT approach fails at larger internuclear separations; cf. Fig. 1(b)). For another challenging case of the F_2 molecule, the CCSD method produces a minimum, which is nearly twice as deep as the minimum on the realistic CCSDT curve. The CCSD(T) and CCSD(TQ_f) calculations produce humps for intermediate values of R and the energies that at large R values are almost identical to the energy at the equilibrium geometry. The MMCC-based CR-CCSD(T) and CR-CCSD(TQ) methods provide the potential energy curves, which are very close to the CCSDT one [65] (see Fig. 1(c)). Excellent description of bond breaking can also be obtained if we use the MMCC(2,3)/CISDt method, in which instead of relying on the MBPT guesses for $|\Psi\rangle$, we use the inexpensive CISDt approximation. As shown in Fig. 1(d), the CISDt method itself using the valence and σ and σ^* orbitals as active orbitals provides poor potential energy curve for HF. The CCSD potential energy curve is poor, too. However, inclusion of the CISDt wave function $|\Psi\rangle$ into the MMCC(2,3) energy formula, Eq. (7), gives an excellent potential energy curve (see Fig. 1(d)). The 12.291 and 33.642 mhartree errors relative to full CI, produced by the CCSD and CISDt methods, respectively, at $R = 5R_e$, reduce to 3.264 mhartree in the MMCC(2,3)/CISDt calculations [13].

The above examples show that the single-reference MMCC theory is a robust formalism that preserves the simplicity of the popular black-box methods, such as CCSD(T), while providing excellent results. The results of the approximate MMCC calculations, in which the exact formula for the correction δ, Eq. (4), is approximated by using low-order moments of truncated CC equations and simple guesses for $|\Psi\rangle$, represent significant improvements compared to the results obtained with standard CC approximations. Indeed, the MMCC results obtained by adding one of the approximate corrections δ, that we described above, to the CCSD energy are invariably much closer to the results of full CI calculations than the CCSD energy, even when the difference between the CCSD and full CI results is large, as in the case of potential energy curves of N_2 and F_2 (cf. Fig. 1(b) and (c) and Refs. [64,65]).

The success of the single-reference MMCC approach has encouraged us to extend the MMCC formalism to a multireference case. The multireference generalization of the MMCC theory is described in the next three sections.

3. The multireference wave operator formalism

All genuine multireference theories involve two fundamental concepts, namely, that of the *model* or *reference* space $\mathscr{M}_0$ and that of the *wave operator* U. The model space $\mathscr{M}_0$

$$\mathscr{M}_0 = ls\{|\Phi_p\rangle\}_{p=1}^{M}, \tag{9}$$

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

$$\mathscr{M} = ls\{|\Psi_\mu\rangle\}_{\mu=1}^{M}, \tag{10}$$

spanned by M quasidegenerate eigenstates $|\Psi_\mu\rangle$, $\mu = 1,\ldots M$, of the electronic Hamiltonian H,

$$H|\Psi_\mu\rangle = E_\mu|\Psi_\mu\rangle \qquad (\mu = 1,\ldots,M). \tag{11}$$

In order to define reference configurations $|\Phi_p\rangle$, one partitions the employed molecular orbital set into *core*, *active*, and *virtual* orbitals. The core orbitals are occupied and the virtual ones are unoccupied in the references. The references $|\Phi_p\rangle$ differ in the occupancies of active orbitals. All possible distributions of active electrons among the active orbitals result in a *complete model* (or active) *space* (CAS). The use of CAS is essential to obtain size extensive results.

The wave operator $U: \mathscr{M}_0 \rightarrow \mathscr{M}$ is defined as a one-to-one mapping between $\mathscr{M}_0$ and $\mathscr{M}$ that satisfies the *intermediate normalization* condition,

$$PU = P, \tag{12}$$

and the relation determining its kernel, i.e.,

$$UQ = 0. \tag{13}$$

Here, P and Q are the projection operators onto, respectively, model space $\mathscr{M}_0$ and its orthogonal complement $\mathscr{M}_0^{\perp}$ in the N-electron Hilbert space H_N,

$$P = \sum_{p=1}^{M} P^{(p)}, \qquad P^{(p)} = |\Phi_p\rangle\langle\Phi_p|, \tag{14}$$

$$Q = 1 - P. \tag{15}$$

Based on Eqs. (12) and (13), one can show that $U^2 = U$, although, unlike P and Q, the wave operator U is not Hermitian, $U \neq U^{\dagger}$.

The wave operator U satisfies the energy-independent equation

$$HU = UHU, \tag{16}$$

which is referred to as the *generalized Bloch equation* [10,12,42–44]. Once the wave operator is determined by solving Eq. (16), the energies E_μ, $\mu = 1, \ldots, M$, are obtained by diagonalizing the *effective Hamiltonian*,

$$H^{\text{eff}} \equiv H^{\text{eff}}(U) = PHU = PHUP, \tag{17}$$

within the model space $\mathscr{M}_0$. The corresponding wave functions $|\Psi_\mu\rangle$, $\mu = 1, \ldots, M$, are obtained from the formula,

$$|\Psi_\mu\rangle = U|\chi_\mu\rangle \qquad (\mu = 1, \ldots, M), \tag{18}$$

where the zero-order vectors $|\chi_\mu\rangle = P|\Psi_\mu\rangle \in \mathscr{M}_0$ are the right eigenvectors of the effective Hamiltonian,

$$H^{\text{eff}}|\chi_\mu\rangle = E_\mu|\chi_\mu\rangle \qquad (\mu = 1, \ldots, M). \tag{19}$$

Let us assume that the exact wave operator U can be parametrized by a set of M excitation operators $S^{(p)}$, $p = 1, \ldots, M$, i.e.,

$$U = U(S^{(1)}, \ldots, S^{(p)}, \ldots, S^{(M)}), \tag{20}$$

where each operator $S^{(p)}$ is a sum of its many-body components $S_n^{(p)}$,

$$S^{(p)} = \sum_{n=1}^{N} S_n^{(p)} \qquad (p = 1, \ldots, M). \tag{21}$$

We assume that the n-body operator $S_n^{(p)}$, when acting on the reference configuration $|\Phi_p\rangle$, generates the n-tuply excited configurations relative to $|\Phi_p\rangle$ and belonging to $\mathscr{M}_0^{\perp}$. Two ways of parametrizing the wave operator U according to Eq. (20) are particularly important: the linear parametrization with the CI-like excitation operators $S^{(p)} = C^{(p)}$, and the exponential parametrization with the cluster operators $S^{(p)} = T^{(p)}$. In the former case, the formula for U is

$$U = \sum_{p=1}^{M} (1 + C^{(p)})P^{(p)}. \tag{22}$$

In the latter case ($S^{(p)} = T^{(p)}$), the formula for U is

$$U = \sum_{p=1}^{M} \mathrm{e}^{T^{(p)}} P^{(p)}. \tag{23}$$

The use of Eq. (22), in conjunction with the generalized Bloch equation, leads to the Bloch CI (BCI) formalism, explored in Ref. [29]. The use of Eqs. (16) and (23) leads to the multireference SUCC formalism of Jeziorski and Monkhorst [17] (see also Refs. [10,12,18–41]).

The working equations for the many-body components $S_n^{(p)}$, defining U through Eqs. (20) and (21) ($C_n^{(p)}$, when Eq. (22) is employed, and $T_n^{(p)}$, when Eq. (23) is used), are obtained by projecting the generalized Bloch equation, Eq. (16), on the right on $|\Phi_p\rangle$ and on the left on the excited configurations relative to $|\Phi_p\rangle$ that belong to $\mathscr{M}_0^{\perp}$. We obtain,

$$Q^{(p)}HU|\Phi_p\rangle = Q^{(p)}UHU|\Phi_p\rangle \qquad (p = 1, \ldots, M), \tag{24}$$

where

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

with $Q_n^{(p)}$ representing a projection operator onto the subspace of $\mathscr{M}_0^{\perp(p)} \equiv Q^{(p)}\mathscr{M}_0^{\perp}$ spanned by the n-tuply excited configurations relative to $|\Phi_p\rangle$ that belong to $\mathscr{M}_0^{\perp}$. As in the case of the original Bloch equation, Eq. (16), once the system of equations, Eq. (24), is solved for the many-body components $S_n^{(p)}$ defining U, the energies E_μ are obtained by diagonalizing H^{eff}, Eq. (17).

Eqs. (20), (21), (24), and (25) can be used to design a hierarchy of approximate multireference formalisms. Typically, the exact wave operator U is replaced by the approximate operator U_{A},

$$U_{\text{A}} = U_{\text{A}}(S_{\text{A}}^{(1)}, \ldots, S_{\text{A}}^{(p)}, \ldots, S_{\text{A}}^{(M)}), \tag{26}$$

which is obtained by truncating the many-body expansion for each excitation operator $S^{(p)}$ at the conveniently chosen excitation level $m_{\text{A}} < N$. The formula for the operators $S_{\text{A}}^{(p)}$ that are used to parametrize the approximate wave operator U_{A}, Eq. (26), is

$$S_{\text{A}}^{(p)} = \sum_{n=1}^{m_{\text{A}}} S_n^{(p)} \qquad (p = 1, \ldots, M). \tag{27}$$

In the standard approximations based on Eqs. (26) and (27), the system of equations for the exact wave operator U, Eq. (24), is replaced by a truncated system of equations for U_{A}

$$Q_{\text{A}}^{(p)}(HU_{\text{A}} - U_{\text{A}}HU_{\text{A}})|\Phi_p\rangle = 0 \qquad (p = 1, \ldots, M), \tag{28}$$

where $Q_{\text{A}}^{(p)}$ is a projection operator onto the excited configurations used to define $S_{\text{A}}^{(p)}$, i.e.,

$$Q_{\text{A}}^{(p)} = \sum_{n=1}^{m_{\text{A}}} Q_n^{(p)}. \tag{29}$$

For $m_{\text{A}} = 2$ and $S^{(p)} = C^{(p)}$, so that $S_{\text{A}}^{(p)} = C_1^{(p)} + C_2^{(p)}$ (cf. Eq. (22)), we obtain the truncated BCI formalism, referred to as the BCISD approach [29]. For $m_{\text{A}} = 2$ and $S^{(p)} = T^{(p)}$, so that $S_{\text{A}}^{(p)} = T_1^{(p)} + T_2^{(p)}$ (cf. Eq. (23)), we obtain the SUCCSD approach [10,12,19–27,30–41].

Once the approximate wave operator U_{A}, Eq. (26), is determined by solving the nonlinear system of equations, Eq. (28), the approximate energies E_μ^{A} and the corresponding approximate wave functions $|\Psi_\mu^{\text{A}}\rangle = U_{\text{A}}|\chi_\mu^{\text{A}}\rangle$ are obtained by diagonalizing the effective Hamiltonian

$$H_{\text{A}}^{\text{eff}} = PHU_{\text{A}}P \tag{30}$$

in $\mathscr{M}_0$. The system of equations for U_{A} and $H_{\text{A}}^{\text{eff}}$, Eqs. (28) and (30), can be given the following form:

$$P(HU_{\text{A}} - U_{\text{A}}H_{\text{A}}^{\text{eff}})|\Phi_p\rangle = 0 \qquad (p = 1, \ldots, M), \tag{31}$$

$$Q_{\text{A}}^{(p)}(HU_{\text{A}} - U_{\text{A}}H_{\text{A}}^{\text{eff}})|\Phi_p\rangle = 0 \qquad (p = 1, \ldots, M). \tag{32}$$

Eqs. (31) and (32) are particularly useful in the context of extending the MMCC approach of Refs. [13,63,64] to a multireference case (see Sections 4 and 5).

Before describing the extension of the single-reference MMCC method to a multireference case, we would like to emphasize the fundamental difference between the exact schemes, based on Eqs. (17), (20), (21), (24), and (25), and the standard multireference approximations, based on Eqs. (31) and (32) (or Eqs. (26)–(30)). In the exact multireference schemes, based on the generalized Bloch equation, all manifolds of excitations $\mathscr{M}_0^{\perp(p)} = Q^{(p)}\mathscr{M}_0^{\perp}$, used to define operators $S^{(p)}$, are identical, i.e., $\mathscr{M}_0^{\perp(p)} = \mathscr{M}_0^{\perp}$ for all $p = 1, \ldots, M$. This is a consequence of the fact that

$$\sum_{n=1}^{N} Q_n^{(p)} \equiv Q^{(p)} = Q, \tag{33}$$

independent of the value of p. As a result, the exact multireference schemes (e.g. the BFCI approach of Ref. [29] based on Eq. (22) or the exact SUCC method based on Eq. (23)) are completely equivalent to an eigenvalue problem for eigenstates $|\Psi_\mu\rangle$, $\mu = 1, \ldots, M$ [29]. In approximate multireference schemes based on Eqs. (31) and (32) or Eqs. (26)–(30) (e.g. the BCISD approach [29] employing Eq. (22), in which $C^{(p)} = C_1^{(p)} + C_2^{(p)}$, or the SUCCSD approach [10,12,19–27,30–41] employing Eq. (23), in which $T^{(p)} = T_1^{(p)} + T_2^{(p)}$), the manifolds of excitations $\mathscr{M}_{0,\text{A}}^{\perp(p)} \equiv Q_{\text{A}}^{(p)}\mathscr{M}_0^{\perp} \subset \mathscr{M}_0^{\perp}$ used to define truncated operators $S_{\text{A}}^{(p)}$, Eq. (27), are usually different for different references $|\Phi_p\rangle$. This asymmetric treatment of manifolds of excitations corresponding to different references causes that approximate multireference schemes based on Eqs. (31) and (32) or Eqs. (26)–(30) are not equivalent to any Hermitian eigenvalue problem. This significant distortion of the exact Bloch wave operator formalism, resulting from the truncation of the many-body expansions of all operators $S^{(p)}$ at *the same excitation level* $m_{\rm A}$, leads to a number of pathologies in approximate calculations based on Eqs. (31) and (32) or Eqs. (26)–(30). These pathologies (the existence of numerous and complex solutions of Eqs. (31) and (32), the intruder solution problem, etc.) have been discussed in our recent papers [28,29]. As demonstrated below, the extension of the single-reference MMCC approach to a multireference case offers a possibility of reducing the severity of problems encountered in genuine multireference (BCISD, SUCCSD, etc.) calculations.

4. Extension of the method of moments of coupled-cluster equations to a genuine multireference formalism

In analogy to the single-reference formalism [13,63,64], the main idea of the multireference extension of the MMCC theory is that of the noniterative corrections δ_μ that, when added to the energies $E_\mu^{\rm A}$, obtained by solving Eq. (32) and by diagonalizing the effective Hamiltonian $H_{\rm A}^{\rm eff}$, Eq. (30), recover the exact (full CI) energies E_μ, $\mu = 1,\ldots,M$. The state-specific nature of the proposed formalism needs to be emphasized. The formulas for the energy corrections δ_μ, derived in this and in the next section, allow us to correct each of the M eigenvalues $E_\mu^{\rm A}$ *independent* of other eigenvalues. We can correct the energy of a single state or we can correct all energies $E_\mu^{\rm A}$, $\mu = 1,\ldots,M$, of quasidegenerate states $|\Psi_\mu\rangle$.

In this section, we describe the most general formulation of the method of moments of multireference Bloch equations, in which we do not specify the actual form of the parametrization used to define $U_{\rm A}$. We only assume that the approximate wave operator $U_{\rm A}$ is parametrized by excitation operators $S_{\rm A}^{(p)}$, $p = 1,\ldots,M$, according to Eq. (26).

In order to derive the formulas for the energy corrections δ_μ, we consider the functional

$$\Lambda[\Psi,\chi] = \langle\Psi|(HU_{\rm A} - U_{\rm A}HU_{\rm A})|\chi\rangle/\langle\Psi|U_{\rm A}|\chi\rangle$$
$$= \langle\Psi|(HU_{\rm A} - U_{\rm A}H_{\rm A}^{\rm eff})|\chi\rangle/\langle\Psi|U_{\rm A}|\chi\rangle, \quad (34)$$

where $U_{\rm A}$ is an approximate wave operator obtained by solving Eq. (32), $H_{\rm A}^{\rm eff}$ is the corresponding effective Hamiltonian, Eq. (30), $|\chi\rangle$ is a state belonging to $\mathscr{M}_0$, and $|\Psi\rangle$ is an N-electron wave function. For $|\Psi\rangle$ equal to the exact wave function $|\Psi_\mu\rangle$ and for $|\chi\rangle$ equal to the corresponding eigenstate $|\chi_\mu^{\rm A}\rangle$ of the approximate effective Hamiltonian $H_{\rm A}^{\rm eff}$, so that

$$H|\Psi_\mu\rangle = E_\mu|\Psi_\mu\rangle \quad (35)$$

and

$$H_{\rm A}^{\rm eff}|\chi_\mu^{\rm A}\rangle = E_\mu^{\rm A}|\chi_\mu^{\rm A}\rangle, \quad (36)$$

where E_μ and $E_\mu^{\rm A}$ are, respectively, the exact and approximate energies of state $|\Psi_\mu\rangle$, we obtain,

$$\Lambda[\Psi_\mu,\chi_\mu^{\rm A}] = E_\mu - E_\mu^{\rm A} \equiv \delta_\mu. \quad (37)$$

Thus, the value of the functional $\Lambda[\Psi,\chi]$ at $|\Psi\rangle = |\Psi_\mu\rangle$ and $|\chi\rangle = |\chi_\mu^{\rm A}\rangle$ is equal to the error in determining the energy of state $|\Psi_\mu\rangle$ made in the calculation employing the approximate Bloch equation, Eq. (32). The functional $\Lambda[\Psi,\chi]$ represents a rather straightforward generalization of the functional $\Lambda[\Psi]$ used in the single-reference MMCC formalism [63].

In order to obtain the explicit formulas for corrections δ_μ, we first write the model-space state $|\chi\rangle$ as a linear combination of reference configurations $|\Phi_p\rangle$ that span $\mathscr{M}_0$,

$$|\chi\rangle = \sum_{p=1}^{M} |\Phi_p\rangle\langle\Phi_p|\chi\rangle, \quad (38)$$

and insert the resulting expansion into the numerator of Eq. (34). We obtain,

$$\Lambda[\Psi,\chi] = \sum_{p=1}^{M} \langle\Psi|(HU_{\rm A} - U_{\rm A}H_{\rm A}^{\rm eff})|\Phi_p\rangle\langle\Phi_p|\chi\rangle/\langle\Psi|U_{\rm A}|\chi\rangle. \quad (39)$$

Next, in analogy to the single-reference MMCC formalism [13,63,64], we define the generalized moments of the Bloch equation for the approximate wave operator $U_{\rm A}$, namely,

$$M_n^{(p)}(m_{\rm A})|\Phi_p\rangle = Q_n^{(p)}(HU_{\rm A} - U_{\rm A}H_{\rm A}^{\rm eff})|\Phi_p\rangle$$
$$(n = 1,\ldots,N; p = 1,\ldots,M), \quad (40)$$

where, according to our notation, $m_{\rm A}$ designates the highest excitation level characterizing the many-body expansions of operators $S_{\rm A}^{(p)}$ that parametrize the wave operator U_{A} (cf. Eqs. (26) and (27)). Since the approximate wave operator U_{A} is determined by solving the system of equations represented by Eq. (32), we can write

$$M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle = 0 \qquad (n = 1, \ldots, m_{\mathrm{A}};\ p = 1, \ldots, M). \tag{41}$$

In other words, the approximate wave operator U_{A} is determined by imposing a requirement that the first m_{A} moments $M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$ of the generalized Bloch equation, in which U is replaced by U_{A}, vanish for each p. This emphasizes the fundamental role of the generalized moments $M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$, Eq. (40), in formulating the multireference wave operator formalism.

Let us now insert the resolution of identity (cf. Eq. (33)),

$$P + Q = P + \sum_{n=1}^{N} Q_n^{(p)} = \mathbf{1}, \tag{42}$$

into Eq. (39). Because of Eq. (31), we can write,

$$\begin{aligned}\Lambda[\Psi, \chi] &= \sum_{p=1}^{M}\sum_{n=1}^{N} \langle\Psi|Q_n^{(p)}\big(HU_{\mathrm{A}} - U_{\mathrm{A}}H_{\mathrm{A}}^{\mathrm{eff}}\big)|\Phi_p\rangle\langle\Phi_p|\chi\rangle/\langle\Psi|U_{\mathrm{A}}|\chi\rangle \\ &= \sum_{p=1}^{M}\sum_{n=1}^{N} \langle\Psi|M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle\langle\Phi_p|\chi\rangle/\langle\Psi|U_{\mathrm{A}}|\chi\rangle.\end{aligned} \tag{43}$$

Since the first m_{A} moments $M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$, $n = 1, \ldots, m_{\mathrm{A}}$, vanish (cf. Eq. (41)), we immediately obtain the following result:

$$\Lambda[\Psi, \chi] = \sum_{p=1}^{M}\sum_{n=m_{\mathrm{A}}+1}^{N} \langle\Psi|M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle\langle\Phi_p|\chi\rangle/\langle\Psi|U_{\mathrm{A}}|\chi\rangle. \tag{44}$$

The final formulas for the energy corrections δ_μ are obtained by setting $|\Psi\rangle = |\Psi_\mu\rangle$ and $|\chi\rangle = |\chi_\mu^{\mathrm{A}}\rangle$ in Eq. (44). We obtain,

$$\begin{aligned}\delta_\mu &= E_\mu - E_\mu^{\mathrm{A}} = \Lambda[\Psi_\mu, \chi_\mu^{\mathrm{A}}] \\ &= \sum_{p=1}^{M}\sum_{n=m_{\mathrm{A}}+1}^{N} \langle\Psi_\mu|M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle\langle\Phi_p|\chi_\mu^{\mathrm{A}}\rangle/\langle\Psi_\mu|U_{\mathrm{A}}|\chi_\mu^{\mathrm{A}}\rangle\end{aligned} \tag{45}$$

or

$$\begin{aligned}\delta_\mu &= E_\mu - E_\mu^{\mathrm{A}} \\ &= \sum_{p=1}^{M}\sum_{n=m_{\mathrm{A}}+1}^{N} \langle\Psi_\mu|M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle\langle\Phi_p|\chi_\mu^{\mathrm{A}}\rangle/\langle\Psi_\mu|\Psi_\mu^{\mathrm{A}}\rangle,\end{aligned} \tag{46}$$

where

$$|\Psi_\mu^{\mathrm{A}}\rangle \equiv U_{\mathrm{A}}|\chi_\mu^{\mathrm{A}}\rangle \tag{47}$$

is the approximate wave function of the μth state generated by the approximate wave operator U_{A} (cf. Eq. (18)).

Eqs. (45) or (46) are the fundamental equations of the *method of moments of the generalized Bloch equation*. It is clear from Eqs. (45) or (46) that corrections δ_μ can be calculated independent of one another. Once the approximate wave operator U_{A} is determined by solving the system of equations represented by Eq. (32), and once all higher generalized moments $M_n^{(p)}(m_A)|\Phi_p\rangle$, $n = m_{\mathrm{A}} + 1, \ldots, N$, are determined for this U_{A}, we can recover the exact energy E_μ of a given state $|\Psi_\mu\rangle$ by correcting the approximate energy E_μ^{A}, resulting from the diagonalization of $H_{\mathrm{A}}^{\mathrm{eff}}$, Eq. (30), according to Eqs. (45) or (46). Clearly, Eqs. (45) or (46) rely on the knowledge of the exact (full CI) wave function $|\Psi_\mu\rangle$ and, as such, cannot be used in practical calculations. However, we can use a simple estimate of $|\Psi_\mu\rangle$, provided by one of the relatively inexpensive *ab initio* methods, and calculate an approximate value of the energy correction δ_μ that needs to be added to E_μ^{A} to improve the results of multireference calculations based on Eqs. (31) and (32). This and the state-specific nature of corrections δ_μ, Eqs. (45) or (46), combined with the presence of the higher generalized moments of the approximate Bloch equation in Eqs. (45) and (46), are the most essential elements of the new formalism.

Before discussing various ways of using Eqs. (45) and (46) in actual calculations, we consider an important variant of the new theory, based on the Jeziorski–Monkhorst ansatz for the wave operator U, Eq. (23). This new method of improving the SUCC results, referred to as the MM-SUCC approach, is discussed in Section 5.

5. Method of moments of the state-universal multireference coupled-cluster equations

One of the most important applications of the Bloch wave operator formalism is the Jeziorski–Monkhorst SUCC theory, in which the wave operator U is represented as a superposition of exponential operators corresponding to different reference configurations $|\Phi_p\rangle$. In the exact SUCC formalism, the operator U is defined by Eq. (23), where $T^{(p)}$'s are cluster operators corresponding to individual references $|\Phi_p\rangle$. As in the general case of the operator U parametrized by excitation operators $S^{(p)}$ (see Eq. (20)), the cluster operators $T^{(p)}$ are defined as sums of the many-body components $T_m^{(p)}$,

$$T^{(p)} = \sum_{m=1}^{N} T_m^{(p)}, \tag{48}$$

where $T_m^{(p)}$generates the m-tuply excited configurations relative to $|\Phi_p\rangle$ belonging to $\mathscr{M}_0^{\perp}$. The latter requirement is a consequence of the intermediate normalization, Eq. (12). As in the more general multireference theory described in Section 3, the standard approximations are obtained by truncating the many-body expansion for each cluster operator $T^{(p)}$ at the suitably chosen excitation level $m_{\rm A}$ (the value of $m_{\rm A}$ is the same for all values of p). We obtain,

$$U_{\rm A} = \sum_{p=1}^{M} {\rm e}^{T_{\rm A}^{(p)}} P^{(p)}, \tag{49}$$

where

$$T_{\rm A}^{(p)} = \sum_{m=1}^{m_{\rm A}} T_m^{(p)}. \tag{50}$$

The system of nonlinear equations for cluster operators $T_m^{(p)}$, characterizing the exact SUCC theory, is obtained by replacing U in Eq. (24) by Eq. (23). The formula for the effective Hamiltonian $H^{\rm eff}$, characterizing the exact SUCC theory, is obtained by inserting Eq. (23) into Eq. (17). We obtain,

$$P\Big(H\,{\rm e}^{T^{(p)}} - H^{\rm eff}\Big)|\Phi_p\rangle = 0 \qquad (p = 1,\ldots,M), \tag{51}$$

$$Q^{(p)}\left(H\,{\rm e}^{T^{(p)}} - \sum_{q=1}^{M} {\rm e}^{T^{(q)}} P^{(q)} H^{\rm eff}\right)|\Phi_p\rangle = 0 \tag{52}$$

$(p = 1,\ldots,M)$.

An alternative set of equations for $T_m^{(p)}$ and $H^{\rm eff}$, defining the exact SUCC theory, is obtained by replacing Eq. (16) by the equation $HU|\Phi_p\rangle = UHU|\Phi_p\rangle$, where U is defined by Eq. (23), premultiplying this equation on the left by ${\rm e}^{-T^{(p)}}$, and projecting the resulting equation on the excited configurations relative to $|\Phi_p\rangle$ belonging to $\mathscr{M}_0^{\perp}$. We obtain,

$$P\Big[\Big(H\,{\rm e}^{T^{(p)}}\Big)_{\rm C} - H^{\rm eff}\Big]|\Phi_p\rangle = 0 \qquad (p = 1,\ldots,M), \tag{53}$$

$$Q^{(p)}\left[\Big(H\,{\rm e}^{T^{(p)}}\Big)_{\rm C} - \sum_{q=1(q\neq p)}^{M} {\rm e}^{-T^{(p)}}\,{\rm e}^{T^{(q)}} P^{(q)} H^{\rm eff}\right]|\Phi_p\rangle = 0$$

$(p = 1,\ldots,M)$, (54)

where we used the well-known fact that [10,12,13]

$${\rm e}^{-T^{(p)}} H\,{\rm e}^{T^{(p)}}|\Phi_p\rangle = \Big(H\,{\rm e}^{T^{(p)}}\Big)_{\rm C}|\Phi_p\rangle \tag{55}$$

and where subscript C designates the connected part of the corresponding operator expression. Eqs. (53) and (54) were presented in the original paper by Jeziorski and Monkhorst [17].

The system of equations characterizing the approximate SUCC theory defined by Eqs. (49) and (50) is obtained by replacing $U_{\rm A}$ in Eqs. (31) and (32) by Eq. (49). This is equivalent to replacing all operators $T^{(p)}$, $p = 1,\ldots,M$ in Eqs. (51) and (52) by $T_{\rm A}^{(p)}$, Eq. (50), and $Q^{(p)}$ by $Q_{\rm A}^{(p)}$, Eq. (29). We obtain,

$$P\Big(H\,{\rm e}^{T_{\rm A}^{(p)}} - H_A^{\rm eff}\Big)|\Phi_p\rangle = 0 \qquad (p = 1,\ldots,M), \tag{56}$$

$$Q_{\rm A}^{(p)}\left(H\,{\rm e}^{T_{\rm A}^{(p)}} - \sum_{q=1}^{M} {\rm e}^{T_{\rm A}^{(q)}} P^{(q)} H_{\rm A}^{\rm eff}\right)|\Phi_p\rangle = 0 \tag{57}$$

$(p = 1,\ldots,M)$.

Alternatively, we can replace operators $T^{(p)}$ and $Q^{(p)}$ in Eqs. (53) and (54) by $T_{\rm A}^{(p)}$ and $Q_{\rm A}^{(p)}$, respectively. This leads to the most familiar form of the approximate SUCC equations, i.e.

$$P\Big[\Big(H\,{\rm e}^{T_{\rm A}^{(p)}}\Big)_{\rm C} - H_{\rm A}^{\rm eff}\Big]|\Phi_p\rangle = 0 \qquad (p = 1,\ldots,M), \tag{58}$$

$$Q_{\mathrm{A}}^{(p)}\left[\left(H\,\mathrm{e}^{T_{\mathrm{A}}^{(p)}}\right)_{\mathrm{C}}-\sum_{q=1(q\neq p)}^{M}\mathrm{e}^{-T_{\mathrm{A}}^{(p)}}\,\mathrm{e}^{T_{\mathrm{A}}^{(q)}}P^{(q)}H_{\mathrm{A}}^{\mathrm{eff}}\right]|\Phi_p\rangle=0$$
$$(p=1,\ldots,M). \quad (59)$$

Here and elsewhere in the present paper, the approximate SUCC formalism defined by Eqs. (56)–(59), with $T_{\mathrm{A}}^{(p)}$ and $Q_{\mathrm{A}}^{(p)}$ defined by Eqs. (50) and (29), respectively, is referred to as the SUCC-A method. The SUCCSD method [10,12,19–27,30–41] is the SUCC-A approach with $m_{\mathrm{A}}=2$.

In order to determine the energy correction $\delta_\mu = E_\mu - E_\mu^{\mathrm{A}}$ for the approximate SUCC-A approach, we can proceed in two different ways. In the first method, we simply insert the wave operator U_{A}, Eq. (49), into Eq. (39), in which $|\Psi\rangle=|\Psi_\mu\rangle$ and $|\chi\rangle=|\chi_\mu^{\mathrm{A}}\rangle$ ($|\chi_\mu^{\mathrm{A}}\rangle$ is an eigenvector of the operator $H_{\mathrm{A}}^{\mathrm{eff}}$ defined by Eq. (56)), insert the resolution of identity, Eq. (42), between $\langle\Psi_\mu|$ and $(HU_{\mathrm{A}}-U_{\mathrm{A}}H_{\mathrm{A}}^{\mathrm{eff}})$, and take the advantage of the intermediate normalization ($PU_{\mathrm{A}}=P$) and Eqs. (56) and (57). This is equivalent to using Eq. (45), in which $M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$ represents one of the two definitions of the generalized moments of the SUCC-A equations, i.e.,

$$M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle = Q_n^{(p)}\left(H\,\mathrm{e}^{T_{\mathrm{A}}^{(p)}}-\sum_{q=1}^{M}\mathrm{e}^{T_{\mathrm{A}}^{(q)}}P^{(q)}H_{\mathrm{A}}^{\mathrm{eff}}\right)|\Phi_p\rangle$$
$$(n=1,\ldots,N;\;\; p=1,\ldots,M). \quad (60)$$

The resulting formula for δ_μ that allows us to correct the results of the approximate SUCC-A calculations has the following form:

$$\delta_\mu = E_\mu - E_\mu^{\mathrm{A}} = \sum_{p=1}^{M}\sum_{n=m_{\mathrm{A}}+1}^{N} \quad (61)$$
$$\langle\Psi_\mu|M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle\langle\Phi_p|\chi_\mu^{\mathrm{A}}\rangle/\langle\Psi_\mu|\Psi_\mu^{\text{SUCC-A}}\rangle,$$

where

$$|\Psi_\mu^{\text{SUCC-A}}\rangle=\sum_{p=1}^{M}\langle\Phi_p|\chi_\mu^{\mathrm{A}}\rangle\mathrm{e}^{T_{\mathrm{A}}^{(p)}}|\Phi_p\rangle \quad (62)$$

is the wave function resulting from the SUCC-A calculations and where the generalized moments of the SUCC-A equations, $M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$, are defined by Eq. (60). Clearly, once cluster operators $T_{\mathrm{A}}^{(p)}$ are determined by solving the truncated SUCC equations and once the generalized moments $M_n^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$ of the SUCC-A method with $n>m_{\mathrm{A}}$ are calculated using cluster operators $T_{\mathrm{A}}^{(p)}$, one can estimate the value of the energy correction δ_μ by using some approximate form of $|\Psi_\mu\rangle$ in Eq. (61).

Since the state-of-the-art serial and parallel computer implementations of the SUCC method are based on Eqs. (58) and (59) rather than Eqs. (56) and (57) [26,30], it is very important that we derive an alternative formula for the energy corrections δ_μ, which is directly expressed in terms of the generalized moments of the SUCC equations written in the form used by Jeziorski and Monkhorst [17]. We define the generalized moments of the SUCC equations used by Jeziorski and Monkhorst that are evidently related to Eqs. (54) or (59) in the following manner:

$$\Gamma_m^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$$
$$= Q_m^{(p)}\left[\left(H\,\mathrm{e}^{T_{\mathrm{A}}^{(p)}}\right)_{\mathrm{C}}-\sum_{q=1}^{M}\mathrm{e}^{-T_{\mathrm{A}}^{(p)}}\,\mathrm{e}^{T_{\mathrm{A}}^{(q)}}P^{(q)}H_{\mathrm{A}}^{\mathrm{eff}}\right]|\Phi_p\rangle$$
$$= Q_m^{(p)}\left[\left(H\,\mathrm{e}^{T_{\mathrm{A}}^{(p)}}\right)_{\mathrm{C}}-\sum_{q=1(q\neq p)}^{M}\mathrm{e}^{-T_{\mathrm{A}}^{(p)}}\,\mathrm{e}^{T_{\mathrm{A}}^{(q)}}P^{(q)}H_{\mathrm{A}}^{\mathrm{eff}}\right]|\Phi_p\rangle$$
$$\equiv \left[\left(H\,\mathrm{e}^{T_{\mathrm{A}}^{(p)}}\right)_{\mathrm{C}}-\sum_{q=1(q\neq p)}^{M}\mathrm{e}^{-T_{\mathrm{A}}^{(p)}}\mathrm{e}^{T_{\mathrm{A}}^{(q)}}P^{(q)}H_{\mathrm{A}}^{\mathrm{eff}}\right]_m|\Phi_p\rangle$$
$$(m=1,\ldots,N;\;\; p=1,\ldots,M), \quad (63)$$

where $[\ldots]_m$ designates the m-body component of the corresponding operator expression. The generalized moments $\Gamma_m^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$, Eq. (63), are the fundamental quantities of the Jeziorski–Monkhorst formalism, as defined by Eqs. (53) and (54) or (58) and (59). Indeed, the system of equations for the many-body components of cluster operators $T_{\mathrm{A}}^{(p)}$, $p=1,\ldots,M$, Eq. (59), can be obtained by imposing a requirement that the lowest moments $\Gamma_m^{(p)}(m_{\mathrm{A}})|\Phi_p\rangle$, with $m=1,\ldots,m_{\mathrm{A}}$, vanish, i.e.,

$$\Gamma_m^{(p)}(m_A)|\Phi_p\rangle = 0 \qquad (m = 1,\dots,m_A;\ p = 1,\dots,M). \tag{64}$$

In order to express corrections δ_μ in terms of moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, we replace moments $M_n^{(p)}(m_A)|\Phi_p\rangle$, Eq. (60), in Eq. (61) by the formula

$$M_n^{(p)}(m_A)|\Phi_p\rangle = \sum_{m=1}^{n} \left(e^{T_A^{(p)}}\right)_{n-m} \Gamma_m^{(p)}(m_A)|\Phi_p\rangle, \tag{65}$$

where, according to our notation, $(e^{T_A^{(p)}})_{n-m}$ represents an $(n-m)$-body component of $e^{T_A^{(p)}}$. We obtain,

$$\delta_\mu = E_\mu - E_\mu^A = \sum_{p=1}^{M} \sum_{n=m_A+1}^{N} \sum_{m=m_A+1}^{n} \langle\Psi_\mu| \left(e^{T_A^{(p)}}\right)_{n-m} \Gamma_m^{(p)}(m_A)|\Phi_p\rangle\langle\Phi_p|\chi_\mu^A\rangle / \langle\Psi_\mu|\Psi_\mu^{\text{SUCC-A}}\rangle. \tag{66}$$

We used Eq. (64), so that the summation over m was replaced by $\sum_{m=m_A+1}^{n}$. Eq. (66) represents our final formula for the energy corrections δ_μ, expressed in terms of the generalized moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ that are defined by Eq. (63). Eq. (65) that was used to obtain formula (66) is a consequence of the well-known property of the CC exponential ansatz, namely [10,12,13] (cf. Eq. (55)),

$$He^{T_A^{(p)}}|\Phi_p\rangle = e^{T_A^{(p)}}\left(H\, e^{T_A^{(p)}}\right)_C|\Phi_p\rangle. \tag{67}$$

Indeed, by inserting Eq. (67) into Eq. (60) and multiplying the summation over q in Eq. (60) by $e^{T_A^{(p)}}\, e^{-T_A^{(p)}} = \mathbf{1}$, we obtain,

$$\begin{aligned} &M_n^{(p)}(m_A)|\Phi_p\rangle \\ &= Q_n^{(p)}\left[e^{T_A^{(p)}}\left(H\, e^{T_A^{(p)}}\right)_C - e^{T_A^{(p)}}\sum_{q=1}^{M} e^{-T_A^{(p)}}\, e^{T_A^{(q)}} P^{(q)} H_A^{\text{eff}}\right]|\Phi_p\rangle \\ &= Q_n^{(p)}\left\{e^{T_A^{(p)}}\left[\left(H\, e^{T_A^{(p)}}\right)_C - \sum_{q=1}^{M} e^{-T_A^{(p)}}\, e^{T_A^{(q)}} P^{(q)} H_A^{\text{eff}}\right]\right\}|\Phi_p\rangle. \end{aligned} \tag{68}$$

In order to convert Eq. (68) into Eq. (65), we insert the resolution of identity, Eq. (42), between $e^{T_A^{(p)}}$ and the expression between square brackets in Eq. (68), and use the fact that for a complete model space $\mathscr{M}_0$,

$$\begin{aligned} &P\left[\left(H\, e^{T_A^{(p)}}\right)_C - \sum_{q=1}^{M} e^{-T_A^{(p)}}\, e^{T_A^{(q)}} P^{(q)} H_A^{\text{eff}}\right]|\Phi_p\rangle \\ &= P\left[\left(H\, e^{T_A^{(p)}}\right)_C - H_A^{\text{eff}}\right]|\Phi_p\rangle = 0 \end{aligned} \tag{69}$$

(see Eq. (58); we used the fact that $(e^{-T_A^{(p)}})^\dagger|\Phi_q\rangle = |\Phi_q\rangle$ for all $p,q = 1,\dots,M$, when $\mathscr{M}_0$ is complete). This allows us to rewrite Eq. (68) in the following way:

$$\begin{aligned} M_n^{(p)}(m_A)|\Phi_p\rangle &= Q_n^{(p)}\left\{\sum_{m=1}^{N} e^{T_A^{(p)}} Q_m^{(p)}\left[(H\, e^{T_A^{(p)}})_C - \sum_{q=1}^{M} e^{-T_A^{(p)}}\, e^{T_A^{(q)}} P^{(q)} H_A^{\text{eff}}\right]\right\}|\Phi_p\rangle \\ &= Q_n^{(p)}\left\{\sum_{m=1}^{n} (e^{T_A^{(p)}})_{n-m} Q_m^{(p)}\left[(H\, e^{T_A^{(p)}})_C - \sum_{q=1(q\neq p)}^{M} e^{-T_A^{(p)}} e^{T_A^{(q)}} P^{(q)} H_A^{\text{eff}}\right]\right\}|\Phi_p\rangle \\ &= \sum_{m=1}^{n} (e^{T_A^{(p)}})_{n-m} \Gamma_m^{(p)}(m_A)|\Phi_p\rangle, \end{aligned} \tag{70}$$

where we used the definition of moments $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$, Eq. (63), and dropped $Q_n^{(p)}$ in the final expression, since operators $(e^{T_A^{(p)}})_{n-m}$ and $\Gamma_m^{(p)}(m_A)$ entering Eq. (70) and acting on $|\Phi_p\rangle$ are the $(n-m)$-body and m-body excitation operators relative to $|\Phi_p\rangle$, respectively.

Eq. (66) is the fundamental equation of the new formalism of the *method of moments of the SUCC equations* (*MM-SUCC*). This equation gives us a recipe how to improve the results of approximate SUCC calculations. In order to calculate corrections δ_μ, we first solve the equations of the approximate SUCC-A method, Eqs. (58) and (59). Once all cluster operators $T_A^{(p)}$ and the effective Hamiltonian of the SUCC-A method are determined, we construct the corresponding higher generalized moments

$\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ with $m > m_A$, Eq. (63), and calculate corrections δ_μ using Eq. (66), or, more precisely, one of the approximate forms of this equation discussed in Section 6.

Before discussing various ways of approximating Eq. (66), we should mention that Eq. (66) represents an extension of Eq. (4), defining the single-reference MMCC theory, to a multireference case. This can be seen by setting $M = 1$ in Eq. (66) and by using the fact that in the single-reference ($p = M = 1$) case the generalized moments of the SUCC equations, Eq. (63), simplify to

$$\Gamma_m^{(1)}(m_A)|\Phi_1\rangle = Q_m^{(1)}\Big(H\,e^{T_A^{(1)}}\Big)_C|\Phi_1\rangle, \qquad (71)$$

where $|\Phi_1\rangle$ and $T_A^{(1)}$ are the reference configuration and cluster operator of the single-reference CC method, respectively ($|\Phi\rangle$ and T_A in Section 2). Clearly, Eq. (71) represents the generalized moments of the single-reference CC equations defined by Eq. (5). When $M = 1$, the $\langle\Psi_\mu|\Psi_\mu^{\text{SUCC-A}}\rangle$ term in Eq. (66) reduces to $\langle\Psi_\mu|e^{T_A^{(1)}}|\chi_\mu^A\rangle$ and the model-space state $|\chi_\mu^A\rangle$ becomes proportional to the reference configuration $|\Phi_1\rangle$. Thus, the $M = 1$ variant of formula (66) is identical with Eq. (4) defining the single-reference MMCC approach.

6. Discussion of the results: Approximate variants of the method of moments of SUCC equations

Both formulas for the energy corrections δ_μ shown in Section 5, Eqs. (61) and (66), depend on the exact wave functions $|\Psi_\mu\rangle$ and, as such, cannot be calculated without first solving the full CI problem. We can, however, think of using some simple estimates for $|\Psi_\mu\rangle$ obtained in inexpensive (low-order MBPT or MRMBPT, limited CI or MRCI) calculations.

For example, we can use the wave function(s) $|\Psi_\mu\rangle$ obtained in truncated MRCI calculations (using, e.g. the popular MRCISD method or its relatively inexpensive MRDCI [72,73] variant) or, perhaps even better, in calculations employing the active space single-reference limited CI methods, such as our CISDt or CISDtq approaches, in which triples and quadruples of the single-reference CI method are selected using active orbitals [13]. In this way, we should be able to improve the results of both the approximate SUCC (e.g. SUCCSD) calculations and limited CI calculations used to define $|\Psi_\mu\rangle$ by combining the wave function(s) $|\Psi_\mu\rangle$ obtained in the CI calculations with the generalized moments of the approximate SUCC theory (for example, the generalized moments $\Gamma_m^{(p)}(2)|\Phi_p\rangle$ of the SUCCSD formalism with $m > 2$). In particular, we should be able to eliminate the problem of an asymmetric treatment of manifolds of excitations corresponding to different references from approximate SUCC calculations. As mentioned earlier, the $\mathscr{M}_{0,A}^{\perp(p)} = Q_A^{(p)}\mathscr{M}_0^\perp \subset \mathscr{M}_0^\perp$ subspaces, spanned by the $\mathscr{M}_0^\perp$ configurations that are excited relative to $|\Phi_p\rangle$ and that are used to write the truncated SUCC-A equations (cf. Eqs. (57) and (59)), are usually different for different values of p when $m_A < N$. This asymmetry leads to various problems in approximate SUCC (e.g., SUCCSD) calculations (cf. Section 3 and Ref. [29]). However, if we do not truncate the summations over n and m in Eqs. (61) and (66) in any arbitrary manner and if we use the projection onto $|\Psi_\mu\rangle$ in the numerators of Eqs. (61) or (66) as a natural method of selecting terms in the summations over p, n, and m in Eqs. (61) and (66), we will obtain a fully symmetric treatment of manifolds of excitations corresponding to different references $|\Phi_p\rangle$ (assuming, of course, that the CI expansion of $|\Psi_\mu\rangle$ contains some $\mathscr{M}_0^\perp$ configurations whose excitation level relative to at least one of the M references $|\Phi_p\rangle$ exceeds m_A). The projection onto $|\Psi_\mu\rangle$ in the numerators of Eqs. (61) or (66) will select precisely those subsets of higher generalized moments $M_n^{(p)}(m_A)|\Phi_p\rangle$ or $\Gamma_m^{(p)}(m_A)|\Phi_p\rangle$ (different sets of $M^{(p)}$'s or $\Gamma^{(p)}$'s for different values of p) that are needed to restore a fully symmetric treatment of manifolds of excitations in the approximate SUCC calculations. As a matter of fact, the same remark applies to a more general multireference scheme based on Eqs. (31), (32), and (45). We can, in particular, reinforce a fully symmetric treatment of the $\mathscr{M}_{0,A}^{\perp(p)}$ manifolds in calculations employing the BCISD approach discussed in Ref. [29] (cf. Eq. (22)) by letting a suitably chosen approximate wave function $|\Psi_\mu\rangle$ select terms in the summations over p and n in Eqs. (45) or

(46) through projection onto this $|\Psi_\mu\rangle$. As in the SUCC case, the resulting correction δ_μ, when added to the BCISD energy, should lead to significantly improved results that correspond to a symmetric treatment of all $\mathscr{M}_{0,\mathrm{A}}^{\perp(p)}$ $(p = 1, \ldots, M)$ subspaces.

An alternative approach to improving the results of approximate SUCC calculations is to calculate the energy corrections δ_μ using a subset of all higher moments $\Gamma_m^{(p)}(m_\mathrm{A})|\Phi_p\rangle$ with $m = m_\mathrm{A} + 1, \ldots, m_\mathrm{B}$, where $m_\mathrm{A} < m_\mathrm{B} < N$. This is equivalent to truncating the summation over n in Eq. (66) to $\sum_{n=m_\mathrm{A}+1}^{m_\mathrm{B}}$, so that the exact expression (66) is approximated in the following way:

$$\delta_\mu \approx \delta_\mu(m_\mathrm{A}, m_\mathrm{B}) = \sum_{p=1}^{M} \sum_{n=m_\mathrm{A}+1}^{m_\mathrm{B}} \sum_{m=m_\mathrm{A}+1}^{n} \langle\Psi_\mu|\left(\mathrm{e}^{T_\mathrm{A}^{(p)}}\right)_{n-m} \Gamma_m^{(p)}(m_\mathrm{A})|\Phi_p\rangle\langle\Phi_p|\chi_\mu^\mathrm{A}\rangle / \langle\Psi_\mu|\Psi_\mu^{\text{SUCC-A}}\rangle, \tag{72}$$

Eq. (72) defines a multireference analog of the single-reference MMCC(m_A,m_B) approximation introduced in Refs. [13,63,64]. An alternative expression for $\delta_\mu(m_\mathrm{A}, m_\mathrm{B})$ is obtained if we truncate the summation over n in Eq. (61) at $n = m_\mathrm{B}$. The resulting formula for $\delta_\mu(m_\mathrm{A}, m_\mathrm{B})$, i.e.,

$$\delta_\mu(m_\mathrm{A}, m_\mathrm{B}) = \sum_{p=1}^{M} \sum_{n=m_\mathrm{A}+1}^{m_\mathrm{B}} \langle\Psi_\mu|M_n^{(p)}(m_\mathrm{A})|\Phi_p\rangle\langle\Phi_p|\chi_\mu^\mathrm{A}\rangle / \langle\Psi_\mu|\Psi_\mu^{\text{SUCC-A}}\rangle, \tag{73}$$

uses a subset of higher moments $M_n^{(p)}(m_\mathrm{A})|\Phi_p\rangle$, as defined by Eq. (60), rather than the generalized moments $\Gamma_m^{(p)}(m_\mathrm{A})|\Phi_p\rangle$, Eq. (63).

Eqs. (72) or (73) define the hierarchy of the MM-SUCC(m_A,m_B) approximations, in which energies E_μ are obtained by adding corrections $\delta_\mu(m_\mathrm{A}, m_\mathrm{B})$ to energies E_μ^A resulting from SUCC-A calculations. The simplest example of the MM-SUCC(m_A,m_B) scheme is the MM-SUCC(2,3) approach, in which we use Eqs. (72) or (73) to selectively correct one or more SU-CCSD energies (the $m_\mathrm{A} = 2$ case) using the generalized moments of the SUCCSD theory corresponding to projections of the SUCCSD equations on triply excited configurations relative to $|\Phi_p\rangle$, i.e. (cf. Eqs. (60) and (63)–(65)),

$$\begin{aligned}\Gamma_3^{(p)}(2)|\Phi_p\rangle &= M_3^{(p)}(2)|\Phi_p\rangle \\ &= Q_3^{(p)}\left[\left((H\,\mathrm{e}^{T_1^{(p)}+T_2^{(p)}}\right)_\mathrm{C}|\Phi_p\rangle \right. \\ &\quad \left. - \sum_{q=1(q\neq p)}^{M} \mathrm{e}^{-(T_1^{(p)}+T_2^{(p)})}\,\mathrm{e}^{T_1^{(q)}+T_2^{(q)}}|\Phi_q\rangle H_{qp}^\mathrm{eff}(2)\right],\end{aligned} \tag{74}$$

with $H_{qp}^\mathrm{eff}(2) = \langle\Phi_q|(H\,\mathrm{e}^{T_1^{(p)}+T_2^{(p)}})_\mathrm{C}|\Phi_p\rangle$ representing matrix elements of the SUCCSD effective Hamiltonian. The fact that the $\Gamma_3^{(p)}(2)$ and $M_3^{(p)}(2)$ moments are identical is a consequence of Eq. (65), the fact that the first $m_\mathrm{A} = 2$ moments, $\Gamma_1^{(p)}(2)|\Phi_p\rangle$ and $\Gamma_2^{(p)}(2)|\Phi_p\rangle$, vanish, when cluster operators $T_\mathrm{A}^{(p)} = T_1^{(p)} + T_2^{(p)}$ satisfy the SUCCSD equations, and the fact that the 0-body component of $\mathrm{e}^{T_\mathrm{A}^{(p)}}$ equals 1. The energy formula defining the MM-SUCC(2,3) scheme is obtained by setting $m_\mathrm{A} = 2$ and $m_\mathrm{B} = 3$ in Eqs. (72) or (73). We obtain,

$$E_\mu^{\text{MM-SUCC(2,3)}} = E_\mu^{\text{SUCCSD}} + \delta_\mu(2,3) \quad (\mu = 1, \ldots, M), \tag{75}$$

where

$$\delta_\mu(2,3) = \sum_{p=1}^{M} \langle\Psi_\mu|\Gamma_3^{(p)}(2)|\Phi_p\rangle\langle\Phi_p|\chi_\mu^{\text{SUCCSD}}\rangle / \langle\Psi_\mu|\Psi_\mu^{\text{SUCCSD}}\rangle, \tag{76}$$

with $|\chi_\mu^{\text{SUCCSD}}\rangle$ and $|\Psi_\mu^{\text{SUCCSD}}\rangle$ representing the SUCCSD states $|\chi_\mu\rangle$ and $|\Psi_\mu\rangle$, respectively (E_μ^{SUCCSD} is the SUCCSD energy of the μth state).

The MM-SUCC(2,3) scheme is an analog of the single-reference MMCC(2,3) method proposed and fully developed in Refs. [13,63,64] and discussed in Section 2 (cf. Eq. (7)). As in the single-reference MMCC(2,3) method, we have to suggest approximate forms of $|\Psi_\mu\rangle$ that might be used to calculate the energy corrections δ_μ(2,3). Our positive experience with the completely renormalized single-reference CCSD(T) [CR-CCSD(T)] method [13,63–65], which is obtained by using the CC analog of the second-order MBPT wave function instead of $|\Psi\rangle$ in the MMCC(2,3) formula (see Eqs. (6)–(8)), suggests that the wave function $|\Psi_\mu\rangle$ in Eq. (76) could be replaced by the second-order MRMBPT wave function or, as in the CR-CCSD(T) case, by the analog of the MRMBPT(2) wave function obtained by replacing the lowest-order $T_1^{(p)}$ and $T_2^{(p)}$ estimates entering the MRMBPT(2) formula by their SUCCSD values. This would lead to a completely renormalized SUCCSD(T) scheme that might be viewed as an MM-SUCC extension of the SUCCSD(T) method of Ref. [48] and a multireference extension of the single-reference CR-CCSD(T) approach discussed in Section 2 [13,63–65]. In a complete analogy to the single-reference case, where the popular CCSD(T) approach fails to describe quasidegenerate states [13,63–65] (cf. Section 2), the use of the low-order MRMBPT to estimate higher-order (e.g., $T_3^{(p)}$) effects of the SUCC theory, as is done in the SUCCSD(T) method of Ref. [48], may lead to severe problems due to intruder states. The completely renormalized SUCCSD procedure, resulting from the MM-SUCC(2,3) approximation, Eqs. (74)–(76), should improve the SUCCSD(T) results in such cases. The mechanism of this improvement would be similar to the way in which the single-reference CR-CCSD(T) approach improves poor CCSD(T) results in quasi-degenerate situations.

Clearly, the ideas described in this paper need numerical testing. Work is under way in our group towards implementing the approximate variants of the method of moments of the SUCCSD equations discussed in this section.

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