

# NONITERATIVE COUPLED-CLUSTER METHODS FOR EXCITED ELECTRONIC STATES

PIOTR PIECUCH<sup>1,2</sup>, MARTA WLOCH, MARICRIS  
LODRIGUITO AND JEFFREY R. GOUR  
*Department of Chemistry, Michigan State University,  
East Lansing, MI 48824, USA*

**Abstract.** New classes of noniterative coupled-cluster (CC) methods, which improve the results of the standard equation-of-motion (EOM) and response CC calculations for excited states dominated by two-electron transitions and excited-state potential energy surfaces along bond breaking coordinates, are reviewed. All of the methods discussed in this article are derived from the method of moments of CC equations (MMCC) and all of them are characterized by the relatively low computer costs which are similar to those characterizing the popular ground-state CCSD(T) theory. Three types of approaches are discussed: (i) the externally corrected MMCC approaches employing the configuration interaction and multi-reference perturbation theory wave functions, (ii) the completely renormalized EOMCC methods, including their most recent extension to excited states of radicals and other open-shell systems, and (iii) the new classes of MMCC and completely renormalized EOMCC theories employing the left eigenstates of the similarity-transformed Hamiltonian used in CC/EOMCC theory.

## 1. Introduction

The single-reference coupled cluster (CC) theory [1–5] has become a standard computational tool for studying ground-state molecular properties [6–10]. The basic approximations, such as CCSD (coupled cluster singles and doubles approach) [11–15], and the noniterative CCSD[T] [16, 17] and CCSD(T) [18] methods, in which the cleverly designed corrections due to

<sup>1</sup>Corresponding author. E-mail address: piecuch@cem.msu.edu.

<sup>2</sup>Also at: Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA.

triple excitations are added to the CCSD energy, can be routinely applied to molecules containing dozens of light atoms, several transition metal atoms, hundreds of electrons, and hundreds or even thousands of basis functions (see, e.g., Refs. [19, 20]). The CCSD(T) method is currently available in the majority of popular quantum chemistry software packages, enabling highly accurate *ab initio* calculations of useful molecular properties by experts as well as non-experts.

One of the biggest challenges in CC theory is the development of highly accurate and affordable methods for excited electronic states that would match the ease of applicability characterizing the ground-state CCSD and CCSD(T) approaches. The most promising candidates in this area are the linear-response CC theory [21–25] and the closely related equation-of-motion CC (EOMCC) [26–29] and symmetry-adapted cluster configuration interaction (SAC-CI) [30–34] methods. For example, the linear response CCSD [24, 25] and EOMCCSD [26–28] approximations, which are characterized by the manageable computational steps that scale as  $\mathcal{N}^6$  with the system size, provide reliable information about excited states dominated by one-electron transitions. The problem is that the linear response CCSD and EOMCCSD methods cannot describe excited states having significant double excitation components and excited-state potential energy surfaces along bond breaking coordinates [35–54]. High-level EOMCC methods including higher-than-double excitations, such as the recently implemented full EOMCCSDT (EOMCC singles, doubles, and triples) [43, 44, 55, 56] and EOMCCSDTQ (EOMCC singles, doubles, triples, and quadruples) [46, 57] approaches, provide an excellent description of excited states dominated by doubles [43, 44, 46, 49] and excited-state potential energy surfaces [44], but large costs of the EOMCCSDT and EOMCCSDTQ calculations, which are defined by the iterative steps that scale as  $\mathcal{N}^8$  and  $\mathcal{N}^{10}$  with the system size, respectively, limit their applicability to small molecules with 2–3 light atoms and relatively small basis sets (the EOMCC schemes with up to pentuple and even hextuple excitations have been implemented too [57], but the  $\mathcal{N}^{12}$  and  $\mathcal{N}^{14}$  scalings of the resulting EOMCCSDTQP and EOMCCSDTQPH methods with the system size make these approaches completely impractical, since problems that one can tackle with such approaches are of the type of problems that can be handled by the full configuration interaction theory; moreover, the role of higher-than-quadruple excitations in the EOMCC calculations of interest in chemistry is virtually none [57]). Other, less expensive, ways of incorporating triple or triple and quadruple excitations in the EOMCC or linear response CC formalisms must be developed in order to make these methods applicable to a wide range of molecular problems and excited states dominated by either one- or two-electron transitions.

In order to improve the accuracy of EOMCCSD or linear response CCSD calculations in applications involving states having significant doubly excited contributions, while keeping the computer costs at the reasonably low level, a few iterative and noniterative EOMCC and linear response CC approximations including triple excitations have been proposed. The examples are the iterative EOMCCSDT- $n$  approaches and their noniterative EOMCCSD(T), EOMCCSD( $\tilde{T}$ ), and EOMCCSD(T') counterparts [35, 36] or the linear-response CC methods such as CC3 [38–41] and CCSDR(3) [40, 41], which use elements of many-body perturbation theory (MBPT) to estimate triples effects. All of these methods are characterized by the relatively inexpensive  $\mathcal{N}^7$  steps and all of them improve the EOMCCSD/linear response CCSD results for excited states dominated by two-electron transitions, but there are many cases where the results of EOMCCSDT- $n$ , EOMCCSD(T), CC3, and similar calculations are far from satisfactory. This can be illustrated by the large 0.4–0.5 and 0.9 eV errors in the description of the lowest  $^1\Pi_g$  and  $^1\Delta_g$  states of the  $C_2$  molecule, respectively, by the EOMCCSDT-1 and CC3 approaches [41] or the failure of the CC3 and CCSDR(3) methods to provide accurate information about excited-state potential energy surfaces along bond breaking coordinates [58] (cf., also, Ref. 51 for an additional analysis). Problems encountered in the EOMCCSDT- $n$ , EOMCCSD(T), CC3, and similar calculations, when excited states dominated by doubles and excited-state potential energy surfaces are examined, should not come as a surprise. Similar failures are observed in the ground-state CCSD(T) calculations. The CCSD(T) method works well for closed-shell molecules near the equilibrium geometries, but it completely fails when chemical bonds are stretched or broken (see, e.g., Refs. 8, 49, 50, 52, and references therein). As is the case with the ground-state CCSD(T) approach, the EOMCC/response CC methods of the EOMCCSDT- $n$ , EOMCCSD(T), or CC3 type are based on the conventional arguments originating from MBPT and these arguments do not apply to quasi-degenerate situations, such as bond breaking or excited states dominated by two-electron transitions. We can improve the results for excited states dominated by doubles and excited-state potential energy surfaces by switching to the recently developed active-space variant of the full EOMCCSDT approach, in which the leading triples contributions of the EOMCCSDT method are selected with the help of active orbitals, reducing the computer costs of full EOMCCSDT calculations quite substantially if the number of active orbitals is small [42–44], but it is desirable to explore alternative approaches, which would combine the ease-of-use of the noniterative single-reference CC/EOMCC approximations, such as CCSD(T) or EOMCCSD(T), with the effectiveness with which the expensive full EOMCCSDT or EOMCCSDTQ approaches handle excited states dominated by doubles and excited-state potential energy surfaces.

In the last three years, we have demonstrated that an excellent description of excited states dominated by double excitations and, to a large extent, excited-state potential energy surfaces along bond breaking coordinates can be obtained by using the completely renormalized (CR) EOM-CCSD(T) approaches [49, 51–53, 59, 60] or one of the externally corrected variants of the excited-state generalization of the method of moments of CC equations (MMCC) [47–50, 52] (see Refs. [61–63] for the original papers on MMCC theory for ground electronic states). The CR-EOMCCSD(T) and other MMCC methods are based on a simple idea of improving the EOMCCSD or other EOMCC energies through the use of the suitably designed noniterative corrections due to triples or triples and quadruples that utilize the concept of the generalized moments of CC/EOMCC equations rather than the usual MBPT arguments exploited in the standard CCSD(T)/EOMCCSD(T), EOMCCSDT- $n$ , CC3, and similar approaches. The CR-EOMCCSD(T) and other excited-state MMCC methods preserve the relatively low,  $\mathcal{N}^6 - \mathcal{N}^7$ -like, costs of the noniterative methods of the CCSD(T)/EOMCCSD(T) type, while providing considerable improvements in the EOMCCSD results and in the results of the EOMCCSDT- $n$ , EOMCCSD(T), CC3, and similar calculations [47–53, 59, 60, 64]. As in the case of the ground-state MMCC and CR-CC methods [49, 50, 52, 61–63, 65–77], the key to a successful description of excited states by the CR-EOMCCSD(T) and other MMCC methods is the very good control of accuracy that all of these methods offer by directly addressing the quantity of interest, which is the difference between the exact, full CI, and EOMCC (e.g., EOMCCSD) energies. The MMCC formalism provides us with precise information about the many-body structure of these differences, suggesting several useful types of noniterative corrections to EOMCCSD or other EOMCC energies.

The purpose of the present paper is to review the most essential elements of the excited-state MMCC theory and various approximate methods that result from it, including the aforementioned CR-EOMCCSD(T) [49, 51, 52, 59] and externally corrected MMCC [47–50, 52] approaches. In the discussion of approximate methods, we focus on the MMCC corrections to EOMCCSD energies due to triple excitations, since these corrections lead to the most practical computational schemes. Although some of the excited-state MMCC methods have already been described in our earlier reviews [49, 50, 52], it is important that we update our earlier work by the highly promising new developments that have not been mentioned before. For example, since the last review [52], we have successfully extended the CR-EOMCCSD(T) methods to excited states of radicals and other open-shell systems [59]. We have also developed a new type of the externally cor-

rected excited-state MMCC methods employing inexpensive multi-reference MBPT (MRMBPT) wave functions in the design of noniterative corrections to EOMCCSD energies [78]. Finally, we have started exploring an entirely new idea of utilizing the left eigenstates of the CC/EOMCC similarity-transformed Hamiltonian (the CC/EOMCC “bra” wave functions) in the process of designing the noniterative MMCC corrections [79] and obtained the first evidence how accurate the CR-EOMCCSD(T) methods are in calculations of properties other than energy [59]. All of these new developments are discussed in the present review, along with the systematic description of other, more established, excited-state MMCC methods described in the earlier work.

## 2. Generalization of the method of moments of coupled-cluster equations to excited electronic states: Exact formalism

The key idea of the single-reference MMCC formalism [47–50, 52, 61–63] (cf. Refs. [80–82] for a multi-reference extension) is that of the state-selective, noniterative energy corrections

$$\delta_\mu^{(A)} \equiv E_\mu - E_\mu^{(A)}, \quad (1)$$

which, when added to the energies of ground ( $\mu = 0$ ) and excited ( $\mu > 0$ ) states,  $E_\mu^{(A)}$ , obtained in the standard CC/EOMCC calculations, such as CCSD/EOMCCSD, CCSDT/EOMCCSDT, etc. (designated here as method  $A$ ), recover the corresponding exact, i.e. full CI, energies  $E_\mu$ . The main goal of all approximate MMCC calculations, including the CR-EOMCCSD(T) [49, 51, 52, 59] approaches, the MMCC and CR-EOMCCSD(T) methods employing the left eigenstates of the similarity-transformed Hamiltonian [79], and the CI-corrected [47–50, 52] and MRMBPT-corrected [78] MMCC methods for excited electronic states discussed in this work, is to approximate corrections  $\delta_\mu^{(A)}$ , such that the resulting MMCC energies, defined as

$$E_\mu^{(\text{MMCC})} = E_\mu^{(A)} + \delta_\mu^{(A)}, \quad (2)$$

are close to the corresponding full CI energies  $E_\mu$ .

All ground- and excited-state MMCC approximations are obtained from the rigorous formulas for the exact corrections  $\delta_\mu^{(A)}$  in terms of the generalized moments of CC/EOMCC equations, derived by Kowalski and Piecuch in Refs. [47, 61, 62] (cf., also, Refs. 49, 79). Since the proper introduction of these formulas requires an understanding of the underlying CC/EOMCC theory, we begin the discussion of the excited-state MMCC formalism with the key ingredients of the single-reference CC/EOMCC theory.

## 2.1. BASIC ELEMENTS OF COUPLED-CLUSTER AND EQUATION-OF-MOTION COUPLED-CLUSTER METHODS

The single-reference CC theory is based on the exponential ansatz for the ground-state wave function,

$$|\Psi_0\rangle = |\Psi_0^{(\text{CC})}\rangle \equiv e^T |\Phi\rangle, \quad (3)$$

where  $T$  is the cluster operator (a particle-hole excitation operator) and  $|\Phi\rangle$  is the reference determinant (often, the Hartree-Fock determinant). In all standard CC approximations, we truncate the many-body expansion for the cluster operator  $T$  at a given excitation level  $m_A < N$ , where  $N$  is the number of correlated electrons in a system. An example of the standard CC approximation is the CCSD method. In this case,  $m_A = 2$  and the cluster operator  $T$  is approximated by

$$T^{(\text{CCSD})} = T_1 + T_2, \quad (4)$$

where

$$T_1 = t_a^i a^a a_i \quad (5)$$

and

$$T_2 = \frac{1}{4} t_{ab}^{ij} a^a a^b a_j a_i \quad (6)$$

are the singly and doubly excited cluster components,  $t_a^i$  and  $t_{ab}^{ij}$  are the corresponding singly and doubly excited cluster amplitudes,  $i, j, \dots$  ( $a, b, \dots$ ) are the single-particle states (spin-orbitals) occupied (unoccupied) in the reference determinant  $|\Phi\rangle$ , and  $a^p$  ( $a_p$ ) are the usual creation (annihilation) operators associated with the orthonormal spin-orbitals  $|p\rangle$ . Here and elsewhere in the present paper, we use the Einstein summation convention over repeated upper and lower indices, so that the summation symbols corresponding to unrestricted summations over occupied and/or unoccupied spin-orbitals are omitted. The general form of the truncated cluster operator defining a standard CC approximation  $A$ , characterized by the excitation level  $m_A$ , is

$$T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad (7)$$

where

$$T_n = \left(\frac{1}{n!}\right)^2 t_{a_1 \dots a_n}^{i_1 \dots i_n} a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} \quad (8)$$

( $n = 1, \dots, m_A$ ) are the many-body components of  $T^{(A)}$  and  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  are the corresponding cluster amplitudes. The cluster amplitudes  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  are determined by solving a coupled system of nonlinear and energy-independent

algebraic equations of the form:

$$\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \bar{H}^{(A)} | \Phi \rangle = 0, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad (9)$$

where  $n = 1, \dots, m_A$ ,

$$\bar{H}^{(A)} = e^{-T^{(A)}} H e^{T^{(A)}} = (H e^{T^{(A)}})_C \quad (10)$$

is the similarity-transformed Hamiltonian of the CC/EOMCC theory, subscript  $C$  designates the connected part of the corresponding operator expression, and  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle \equiv a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} |\Phi\rangle$  are the  $n$ -tuply excited determinants relative to  $|\Phi\rangle$ . In particular, the standard CCSD equations for the singly and doubly excited cluster amplitudes  $t_a^i$  and  $t_{ab}^{ij}$ , defining  $T_1$  and  $T_2$ , respectively, can be written as

$$\langle \Phi_i^a | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad (11)$$

$$\langle \Phi_{ij}^{ab} | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad i < j, \quad a < b, \quad (12)$$

where

$$\bar{H}^{(\text{CCSD})} = e^{-T^{(\text{CCSD})}} H e^{T^{(\text{CCSD})}} = (H e^{T^{(\text{CCSD})}})_C \quad (13)$$

is the similarity-transformed Hamiltonian of the CCSD/EOMCCSD approach. The explicit and computationally efficient form of these and other equations used in CC calculations, in terms of one- and two-body matrix elements of the Hamiltonian in the normal-ordered form,  $f_p^q \equiv \langle p | f | q \rangle$  and  $v_{pq}^{rs} \equiv \langle pq | v | rs \rangle - \langle pq | v | sr \rangle$ , respectively, where  $f$  is the Fock operator and  $v$  is the electron-electron repulsion term, and cluster amplitudes  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  or, in the CCSD ( $m_A = 2$ ) case,  $t_a^i$  and  $t_{ab}^{ij}$ , can be derived by applying diagrammatic techniques of many-body theory combined with diagram factorization methods which yield highly vectorized computer codes [59, 70, 83]. Once the system of equations, Eq. (9), is solved for  $T^{(A)}$  or  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  (or Eqs. (11) and (12) are solved for  $T_1$  and  $T_2$  or  $t_a^i$  and  $t_{ab}^{ij}$ ), the CC energy corresponding to the standard method  $A$  is calculated using the equation

$$E_0^{(A)} = \langle \Phi | \bar{H}^{(A)} | \Phi \rangle \equiv \langle \Phi | \bar{H}_{\text{closed}}^{(A)} | \Phi \rangle, \quad (14)$$

where  $\bar{H}_{\text{closed}}^{(A)}$  is a “closed” part of  $\bar{H}^{(A)}$  which is represented by those diagrams contributing to  $\bar{H}^{(A)}$  that have no external (uncontracted) Fermion lines (as opposed to the “open” part of  $\bar{H}^{(A)}$  which is represented by the diagrams having external or uncontracted Fermion lines).

The ground-state CC theory has a natural extension to excited electronic states  $|\Psi_\mu\rangle$  via the EOMCC or linear response CC method, in which we write

$$|\Psi_\mu\rangle = |\Psi_\mu^{(\text{CC})}\rangle \equiv R_\mu e^T |\Phi\rangle, \quad (15)$$

where  $T$  is obtained in the ground-state CC calculations and  $R_\mu$  is a linear particle-hole excitation operator similar to  $T$  obtained by diagonalizing the similarity-transformed Hamiltonian  $\bar{H} = e^{-T} H e^T$ . As in the ground-state case, the standard EOMCC approximations are obtained by truncating the many-body expansion for the excitation operator  $R_\mu$  at a given excitation level  $m_A < N$ , which is the same as the excitation level used to define the truncated form of  $T$ . Thus, in the EOMCCSD theory, which is a basic EOMCC approximation where  $m_A$  is set at 2, we write

$$R_\mu^{(\text{CCSD})} = R_{\mu,0} + R_{\mu,1} + R_{\mu,2}, \quad (16)$$

where

$$R_{0,\mu} = r_0(\mu) \mathbf{1}, \quad (17)$$

$$R_{\mu,1} = r_a^i(\mu) a^a a_i, \quad (18)$$

and

$$R_{\mu,2} = \frac{1}{4} r_{ab}^{ij}(\mu) a^a a^b a_j a_i \quad (19)$$

are the reference, one-body, and two-body components of  $R_\mu^{(\text{CCSD})}$ , and  $r_0(\mu)$ ,  $r_a^i(\mu)$ , and  $r_{ab}^{ij}(\mu)$  are the corresponding excitation amplitudes ( $\mathbf{1}$  in Eq. (17) is a unit operator). In general, when  $T$  is approximated by  $T^{(A)}$ , Eq. (7), the corresponding excitation operator  $R_\mu$  defining the EOMCC method  $A$  is approximated by

$$R_\mu^{(A)} = R_{\mu,0}^{(A)} + R_{\mu,\text{open}}^{(A)}, \quad (20)$$

where the “open” part of  $R_\mu^{(A)}$  is defined as

$$R_{\mu,\text{open}}^{(A)} = \sum_{n=1}^{m_A} R_{\mu,n}, \quad (21)$$

with

$$R_{\mu,n} = \left( \frac{1}{n!} \right)^2 r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu) a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} \quad (22)$$

representing the  $n$ -body components of  $R_\mu^{(A)}$ . The excitation amplitudes  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$  defining  $R_{\mu,\text{open}}^{(A)}$  are obtained by solving the eigenvalue problem involving the similarity-transformed Hamiltonian  $\bar{H}^{(A)}$  in the space spanned by the excited determinants  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$  with  $n = 1, \dots, m_A$ , i.e.

$$\begin{aligned} \langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | (\bar{H}_{\text{open}}^{(A)} R_{\mu,\text{open}}^{(A)})_C | \Phi \rangle &= \omega_\mu^{(A)} r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu), \\ i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \end{aligned} \quad (23)$$



where

$$\bar{H}_{\text{open}}^{(A)} = \bar{H}^{(A)} - \bar{H}_{\text{closed}}^{(A)} = \bar{H}^{(A)} - E_0^{(A)} \mathbf{1} \quad (24)$$

is the “open” part of  $\bar{H}^{(A)}$ , represented by the diagrams of  $\bar{H}^{(A)}$  that have external Fermion lines, and

$$\omega_\mu^{(A)} = E_\mu^{(A)} - E_0^{(A)} \quad (25)$$

is the vertical excitation energy obtained with the EOMCC method A. In particular, the  $r_a^i(\mu)$ , and  $r_{ab}^{ij}(\mu)$  amplitudes of the EOMCCSD theory and the corresponding excitation energies  $\omega_\mu^{(\text{CCSD})}$  are obtained by diagonalizing the similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$ , Eq. (13), in the relatively small space of singly and doubly excited determinants  $|\Phi_i^a\rangle$  and  $|\Phi_{ij}^{ab}\rangle$ . Equation (23) alone does not provide information about the coefficient  $r_0(\mu)$  at the reference determinant  $|\Phi\rangle$  in the corresponding EOMCC wave function  $R_\mu^{(A)} e^{T^{(A)}} |\Phi\rangle$ . This coefficient can be determined *a posteriori* using the equation

$$r_0(\mu) = \langle \Phi | (\bar{H}_{\text{open}}^{(A)} R_{\mu, \text{open}}^{(A)})_C | \Phi \rangle / \omega_\mu^{(A)}, \quad (26)$$

once the excitation amplitudes  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$  defining  $R_{\mu, \text{open}}^{(A)}$  are known. For consistency of our presentation, we use the notation in which  $\mu > 0$  means that we are dealing with excited states, whereas  $\mu = 0$  corresponds to the ground-state problem. In particular, the excitation operator  $R_\mu^{(A)}$  is formally defined as a unit operator when  $\mu = 0$ , i.e.  $r_0(\mu = 0) = 1$  and  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu = 0) = 0$  for  $n \geq 1$ , so that the EOMCC ansatz, Eq. (15), reduces to the ground-state CC ansatz, Eq. (3), in the ground-state,  $\mu = 0$ , case. With this definition of  $R_{\mu=0}^{(A)}$ , the EOMCC system of equations, Eq. (23), formally reduces to the standard system of the ground-state CC equations, Eq. (9), although we must, of course, remember that in the EOMCC calculations of excited states employing Eq. (23) we only solve for the excitation operator  $R_\mu^{(A)}$  (or, for the corresponding excitation amplitudes  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$ ) using the given values of cluster amplitudes  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  defining the cluster operator  $T^{(A)}$ , obtained in the corresponding ground-state CC calculations that precede the excited-state EOMCC calculations.

The similarity-transformed Hamiltonians  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$  are not hermitian, so that in addition to the right eigenstates  $R_\mu^{(A)} |\Phi\rangle$  or  $R_\mu^{(\text{CCSD})} |\Phi\rangle$ , which define the “ket” CC/EOMCC or CCSD/EOMCCSD wave functions, we can also determine the left eigenstates of  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$ ,  $\langle \Phi | L_\mu^{(A)}$  or  $\langle \Phi | L_\mu^{(\text{CCSD})}$ , respectively, which define the corresponding “bra” CC/EOMCC or CCSD/EOMCCSD wave functions

$$\langle \tilde{\Psi}_\mu^{(\text{CC})} | = \langle \Phi | L_\mu e^{-T} \quad (27)$$

that match the “ket” states given by Eq. (15). Here,  $L_\mu$  (in approximate methods,  $L_\mu^{(A)}$  or  $L_\mu^{(\text{CCSD})}$ ) is a hole-particle deexcitation operator, so that, for example,

$$L_\mu^{(\text{CCSD})} = L_{\mu,0} + L_{\mu,1} + L_{\mu,2}, \quad (28)$$

where

$$L_{0,\mu} = l_0(\mu) \mathbf{1}, \quad (29)$$

$$L_{\mu,1} = l_i^a(\mu) a^i a_a, \quad (30)$$

and

$$L_{\mu,2} = \frac{1}{4} l_{ij}^{ab}(\mu) a^i a^j a_b a_a \quad (31)$$

are the reference, one-body, and two-body components of  $L_\mu^{(\text{CCSD})}$ , and  $l_0(\mu)$ ,  $l_i^a(\mu)$ , and  $l_{ij}^{ab}(\mu)$  are the corresponding deexcitation amplitudes. The right and left eigenstates of  $\bar{H}^{(\text{CCSD})}$  form a biorthonormal set,

$$\langle \Phi | L_\mu^{(\text{CCSD})} R_\nu^{(\text{CCSD})} | \Phi \rangle = \delta_{\mu,\nu}, \quad (32)$$

where  $\delta_{\mu,\nu}$  is the usual Kronecker delta, so that the coefficient  $l_0(\mu)$  at  $\langle \Phi |$  in the left CCSD/EOMCCSD eigenstate  $\langle \Phi | L_\mu^{(\text{CCSD})}$  satisfies

$$l_0(\mu) = \delta_{\mu,0}, \quad (33)$$

meaning that  $l_0(\mu) = 0$  in the excited-state ( $\mu > 0$ ) case. In general, the deexcitation operators  $L_\mu^{(A)}$  generating the left eigenstates of the similarity-transformed Hamiltonian  $\bar{H}^{(A)}$ ,  $\langle \Phi | L_\mu^{(A)}$ , can be written as

$$L_\mu^{(A)} = L_{\mu,0}^{(A)} + L_{\mu,\text{open}}^{(A)}, \quad (34)$$

where the “open” part of  $L_\mu^{(A)}$  is defined as

$$L_{\mu,\text{open}}^{(A)} = \sum_{n=1}^{m_A} L_{\mu,n}, \quad (35)$$

with

$$L_{\mu,n} = \left( \frac{1}{n!} \right)^2 l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu) a^{i_1} \dots a^{i_n} a_{a_n} \dots a_{a_1} \quad (36)$$

representing the  $n$ -body components of  $L_\mu^{(A)}$ . As in the CCSD case, the left and right eigenstates of  $\bar{H}^{(A)}$ ,  $\langle \Phi | L_\mu^{(A)}$  and  $R_\nu^{(A)} | \Phi \rangle$ , respectively, form a biorthonormal set,

$$\langle \Phi | L_\mu^{(A)} R_\nu^{(A)} | \Phi \rangle = \delta_{\mu,\nu}, \quad (37)$$

and the zero-body part of  $L_\mu^{(A)}$  satisfies

$$L_{\mu,0}^{(A)} = \delta_{\mu,0} \mathbf{1}, \quad (38)$$

i.e.  $L_{\mu,0}^{(A)}$  vanishes for excited states ( $\mu > 0$ ), while being equal to the unit operator in the ground-state ( $\mu = 0$ ) case. The deexcitation amplitudes  $l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu)$  defining  $L_{\mu, \text{open}}^{(A)}$  are obtained by solving the left eigenvalue problem involving the similarity-transformed Hamiltonian  $\bar{H}^{(A)}$  in the space spanned by the excited determinants  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$  with  $n = 1, \dots, m_A$ ,

$$\delta_{\mu,0} \langle \Phi | \bar{H}_{\text{open}}^{(A)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle + \langle \Phi | L_{\mu, \text{open}}^{(A)} \bar{H}_{\text{open}}^{(A)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle = \omega_\mu^{(A)} l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu), \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad (39)$$

where  $\omega_\mu^{(A)}$  is the vertical excitation energy, Eq. (25), and where we already used Eq. (38). In particular,

$$\langle \Phi | L_{\mu, \text{open}}^{(A)} \bar{H}_{\text{open}}^{(A)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle = \omega_\mu^{(A)} l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu), \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad (40)$$

in the excited-state ( $\mu > 0$ ) case. When the ground-state ( $\mu = 0$ ) case is considered, we usually write

$$L_0^{(A)} = \mathbf{1} + \Lambda^{(A)}, \quad (41)$$

where

$$\Lambda^{(A)} = \sum_{n=1}^{m_A} \Lambda_n \equiv L_{0, \text{open}}^{(A)}, \quad (42)$$

with

$$\Lambda_n = \left( \frac{1}{n!} \right)^2 \lambda_{i_1 \dots i_n}^{a_1 \dots a_n} a^{i_1} \dots a^{i_n} a_{a_n} \dots a_{a_1}, \quad (43)$$

represents the well-known “lambda” operator of the analytic gradient CC theory [84]. The ground-state deexcitation amplitudes  $\lambda_{i_1 \dots i_n}^{a_1 \dots a_n} \equiv l_{i_1 \dots i_n}^{a_1 \dots a_n}(0)$  that define the  $\Lambda^{(A)}$  operator are obtained by solving the following system of linear equations (cf. Eq. (39)):

$$\langle \Phi | \bar{H}_{\text{open}}^{(A)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle + \langle \Phi | \Lambda^{(A)} \bar{H}_{\text{open}}^{(A)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle = 0, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n. \quad (44)$$

The CCSD/EOMCCSD equations for the deexcitation amplitudes  $l_i^a(\mu)$ ,  $l_{ij}^{ab}(\mu)$ ,  $\lambda_i^a \equiv l_i^a(0)$ , and  $\lambda_{ij}^{ab} \equiv l_{ij}^{ab}(0)$  are obtained by setting  $m_A = 2$  in Eqs. (40) and (44).

If the only purpose of the calculation is to obtain energies  $E_\mu^{(A)}$  or vertical excitation energies  $\omega_\mu^{(A)}$  (in the  $m_A = 2$  case, the EOMCCSD energies  $E_\mu^{(\text{CCSD})}$  and vertical excitation energies  $\omega_\mu^{(\text{CCSD})}$ ), the left eigenstates of  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$ ,  $\langle \Phi | L_\mu^{(A)}$  or  $\langle \Phi | L_\mu^{(\text{CCSD})}$ , respectively, are not needed and it is sufficient to solve the right eigenvalue problem involving  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$ , Eq. (23). However, if one has to calculate properties other than energy, such as the expectation values and transition matrix elements involving the CC/EOMCC states  $\langle \tilde{\Psi}_\mu |$  and  $|\Psi_\nu\rangle$ , both right and left eigenstates of  $\bar{H}^{(A)}$  (or  $\bar{H}^{(\text{CCSD})}$ ) are important. Indeed, if  $\theta$  is a property operator, we obtain

$$\langle \tilde{\Psi}_\mu^{(\text{CC})} | \theta | \Psi_\nu^{(\text{CC})} \rangle = \langle \Phi | L_\mu \bar{\theta} R_\nu | \Phi \rangle, \quad (45)$$

where  $\bar{\theta} = e^{-T} \theta e^T = (\theta e^T)_C$ . In particular, when  $\theta = a^p a_q$  in Eq. (45), we can determine the CCSD or EOMCCSD one-body reduced density matrices in the CC/EOMCC electronic states  $|\Psi_\mu\rangle$ , designated by  $\gamma_q^p(\mu) \equiv \gamma_q^p(\mu, \mu)$ , or the corresponding transition one-body reduced density matrices  $\gamma_q^p(\mu, \nu)$ ,  $\mu \neq \nu$ . We obtain,

$$\gamma_q^p(\mu, \nu) = \langle \Phi | L_\mu \overline{a^p a_q} R_\nu | \Phi \rangle. \quad (46)$$

We can use the above expressions to calculate electron densities and various (transition) one-body properties, including, for example, dipole and transition dipole moments,

$$\langle \tilde{\Psi}_\mu^{(\text{CC})} | \theta | \Psi_\nu^{(\text{CC})} \rangle = \theta_p^q \gamma_q^p(\mu, \nu), \quad (47)$$

where  $\theta_p^q \equiv \langle p | \theta | q \rangle$  are matrix elements of the one-electron property operator  $\theta$  and  $\gamma_q^p(\mu, \nu)$  is defined by Eq. (46). In approximate CC/EOMCC calculations, the cluster operator  $T$  and the excitation and deexcitation operators  $R_\mu$  and  $L_\mu$  are, of course, replaced by their truncated forms ( $T^{(A)}$ ,  $R_\mu^{(A)}$ , and  $L_\mu^{(A)}$ , respectively).

Although the main use of the left eigenstates of  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$  is the calculation of properties other than energy and analytic energy gradients (cf., e.g., Refs. [6, 7, 28, 29, 84–90]), other uses of  $L_\mu^{(A)}$  are possible. In particular, as mentioned in the Introduction, the left eigenstates of  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$  (or the corresponding “bra” CC/EOMCC wave functions  $\langle \tilde{\Psi}_\mu |$ ) can be used to design new types of noniterative MMCC corrections to standard CC/EOMCC energies. These new types of MMCC corrections exploiting the left eigenstates of the CC/EOMCC similarity-transformed Hamiltonians as well as other types of MMCC approaches to excited electronic states and their performance in benchmark calculations are reviewed in Section 3. The basic ideas behind the underlying MMCC theory are discussed in the next subsection.

## 2.2. NONITERATIVE CORRECTIONS TO COUPLED-CLUSTER AND EQUATION-OF-MOTION COUPLED-CLUSTER ENERGIES DEFINING THE EXACT METHOD OF MOMENTS OF COUPLED-CLUSTER EQUATIONS

We are now equipped with all of the basic concepts of the CC/EOMCC theory which are necessary to explain the noniterative MMCC approaches to ground and excited electronic states. In this section, we focus on the exact MMCC theory. The approximate MMCC schemes for excited electronic states, including the externally corrected MMCC approaches and the CR-EOMCCSD(T) theory, and their most recent analog based on the left eigenstates of the similarity-transformed Hamiltonian, are discussed in Section 3.

As described in Section 2.1, the standard CC and EOMCC equations are obtained by projecting  $\bar{H}^{(A)}|\Phi\rangle$  and  $\bar{H}^{(A)}R_\mu^{(A)}|\Phi\rangle$  on the excited determinants  $|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle$  with  $n = 1, \dots, m_A$  that correspond to the particle-hole excitations included in the cluster operator  $T^{(A)}$  and linear excitation operator  $R_\mu^{(A)}$ . The corresponding ground-state CC energy is obtained by projecting  $\bar{H}^{(A)}|\Phi\rangle$  on the reference determinant  $|\Phi\rangle$ . It is, therefore, quite natural to expect that in order to correct the results of the standard CC/EOMCC calculations employing the cluster and excitation operators truncated at  $m_A$ -body terms, we have to consider the projections of  $\bar{H}^{(A)}|\Phi\rangle$  and  $\bar{H}^{(A)}R_\mu^{(A)}|\Phi\rangle$  on the excited determinants  $|\Phi_{i_1\dots i_k}^{a_1\dots a_k}\rangle$  with  $k > m_A$ , which span the orthogonal complement of the subspace spanned by the reference determinant  $|\Phi\rangle$  and the excited determinants  $|\Phi_{i_1\dots i_k}^{a_1\dots a_k}\rangle$  with  $k = 1, \dots, m_A$ . These projections, designated by  $\mathfrak{M}_{\mu, a_1\dots a_k}^{i_1\dots i_k}(m_A)$ , define the generalized moments of the CC/EOMCC equations corresponding to method A. We obtain [47–52, 61–63, 72, 74],

$$\mathfrak{M}_{\mu, a_1\dots a_k}^{i_1\dots i_k}(m_A) = \langle \Phi_{i_1\dots i_k}^{a_1\dots a_k} | (\bar{H}^{(A)} R_\mu^{(A)}) | \Phi \rangle, \quad (48)$$

where  $k > m_A$ . Because of our convention in which  $R_{\mu=0}^{(A)} = \mathbf{1}$ , Eq. (48) includes the ground-state,  $\mu = 0$ , case. Indeed, when  $\mu = 0$ , moments  $\mathfrak{M}_{\mu, a_1\dots a_k}^{i_1\dots i_k}(m_A)$ , Eq. (48), reduce to the generalized moments of CC equations  $\mathfrak{M}_{a_1\dots a_k}^{i_1\dots i_k}(m_A)$  defining approximation A [49, 50, 52, 61–63, 72, 74],

$$\mathfrak{M}_{0, a_1\dots a_k}^{i_1\dots i_k}(m_A) \equiv \mathfrak{M}_{a_1\dots a_k}^{i_1\dots i_k}(m_A) = \langle \Phi_{i_1\dots i_k}^{a_1\dots a_k} | \bar{H}^{(A)} | \Phi \rangle. \quad (49)$$

It can be demonstrated that once the cluster and excitation operators,  $T^{(A)}$  and  $R_\mu^{(A)}$ , respectively, and the ground- and excited-state energies  $E_\mu^{(A)}$  are determined by solving the relevant CC/EOMCC equations, Eqs. (9), (23), and (26), we can obtain the exact, full CI, energies  $E_\mu$  by adding the

following state-selective corrections  $\delta_\mu^{(A)}$  to energies  $E_\mu^{(A)}$  [47–52, 61–63, 72]:

$$\begin{aligned}\delta_\mu^{(A)} &\equiv E_\mu - E_\mu^{(A)} \\ &= \sum_{n=m_A+1}^N \sum_{k=m_A+1}^n \langle \Psi_\mu | C_{n-k}(m_A) M_{\mu,k}(m_A) | \Phi \rangle / \\ &\quad \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle.\end{aligned}\quad (50)$$

Here,

$$C_{n-k}(m_A) = (e^{T^{(A)}})_{n-k} \quad (51)$$

is the  $(n - k)$ -body component of the exponential wave operator  $e^{T^{(A)}}$ , defining the CC method  $A$ ,  $|\Psi_\mu\rangle$  is the full CI wave function of the  $\mu$ -th electronic state, and

$$M_{\mu,k}(m_A) = \left(\frac{1}{k!}\right)^2 \mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(m_A) a^{a_1} \dots a^{a_k} a_{i_k} \dots a_{i_1}, \quad (52)$$

where  $\mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(m_A)$ ,  $k > m_A$ , represent the generalized moments of the CC/EOMCC equations corresponding to the approximate method  $A$ , as defined by Eq. (48). In particular, if we want to recover the full CI energies  $E_\mu$  from the CCSD/EOMCCSD energies  $E_\mu^{(\text{CCSD})}$  (the  $m_A = 2$  case), we have to add the following corrections  $\delta_\mu^{(\text{CCSD})}$  to energies  $E_\mu^{(\text{CCSD})}$ :

$$\delta_\mu^{(\text{CCSD})} = \sum_{n=3}^N \sum_{k=3}^n \langle \Psi_\mu | C_{n-k}(2) M_{\mu,k}(2) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle. \quad (53)$$

Here,  $T^{(\text{CCSD})}$  and  $R_\mu^{(\text{CCSD})}$  are the cluster and excitation operators obtained in the CCSD and EOMCCSD calculations, Eqs. (4) and (16), respectively,  $C_{n-k}(2)$  is the  $(n - k)$ -body component of  $e^{T^{(\text{CCSD})}}$ , and

$$M_{\mu,k}(2) = \left(\frac{1}{k!}\right)^2 \mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(2) a^{a_1} \dots a^{a_k} a_{i_k} \dots a_{i_1}, \quad (54)$$

where

$$\mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(2) = \langle \Phi_{i_1\dots i_k}^{a_1\dots a_k} | (\bar{H}^{(\text{CCSD})} R_\mu^{(\text{CCSD})}) | \Phi \rangle, \quad (55)$$

with  $k \geq 3$ , are the generalized moments of the CCSD ( $\mu = 0$ ) or EOM-CCSD ( $\mu > 0$ ) equations. The above equations for  $\delta_\mu^{(A)}$  and  $\delta_\mu^{(\text{CCSD})}$ , in terms of the generalized moments  $\mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(m_A)$  and  $\mathfrak{M}_{\mu,a_1\dots a_k}^{i_1\dots i_k}(2)$ , respectively, can be obtained by considering the asymmetric energy expression,

$$\Lambda[\Psi] = \langle \Psi | (H - E_\mu^{(A)}) R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle / \langle \Psi | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle, \quad (56)$$

referred to as the MMCC functional [47, 49, 50, 62, 72]. This expression satisfies the important property

$$\Lambda[\Psi_\mu] = E_\mu - E_\mu^{(A)}, \quad (57)$$

where  $E_\mu$  is the exact, full CI, energy, if  $|\Psi_\mu\rangle$  is a full CI state. We refer the reader to the original work by Kowalski and Piecuch [47, 62] and Appendices in Ref. [49] for the details of the derivation of Eq. (50) using functional  $\Lambda[\Psi]$ , Eq. (56). It is worth mentioning here that the applicability of the MMCC functional, Eq. (56), introduced by Kowalski and Piecuch for the ground-state problem in 2000 [62] and extended to excited states in 2001 [47], in direct calculations of the noniterative correction  $\delta_0^{(\text{CCSD})}$  to standard CCSD energy has been examined by Li and Paldus [91, 92]. These authors showed that the asymmetric energy expression represented by Eq. (56) is capable of improving the results of standard CC calculations at larger internuclear separations. The only problem with applying Eq. (56) “as is” is the fact that direct calculations of corrections  $\delta_\mu^{(A)}$  using the MMCC functional are prohibitively expensive. After rewriting the MMCC functional, Eq. (56), in terms of the generalized moments of CC/EOMCC equations, as is done in Eqs. (50) and (53), one can propose a variety of relatively inexpensive CC/EOMCC approximations that the direct application of Eq. (56) cannot lead to. Li and Paldus have realized this and in subsequent papers (see, e.g., Ref. 93, 94) they used the expressions for the ground-state correction  $\delta_0^{(\text{CCSD})}$  which are identical to our Eq. (53). They have not studied the excited-state corrections  $\delta_\mu^{(A)}$  though.

Equation (50) (or its CCSD/EOMCCSD-based analog, Eq. (53)) defines the exact MMCC formalism for ground and excited states. This equation allows us to improve the CC/EOMCC (e.g. CCSD/EOMCCSD) results, in a state-selective manner, by adding the noniterative corrections  $\delta_\mu^{(A)}$  (in practice, one of the approximate forms of  $\delta_\mu^{(A)}$  or  $\delta_\mu^{(\text{CCSD})}$ ), obtained using the information that can be directly extracted from the standard CC/EOMCC calculations, such as operators  $T^{(A)}$  and  $R_\mu^{(A)}$ , matrix elements of  $\bar{H}^{(A)}$ , and generalized moments of the CC/EOMCC equations  $\mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$ , to the CC/EOMCC energies  $E_\mu^{(A)}$ . The key quantities in Eq. (50) that require more attention and that are essential for designing the approximate forms of the MMCC corrections  $\delta_\mu^{(A)}$  are the generalized moments  $\mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$ , Eq. (48), and the many-body components of  $e^{T^{(A)}}$  defining the  $C_{n-k}(m_A)$  operators, Eq. (51). The  $C_{n-k}(m_A)$  terms are very easy to calculate. The zero-body term,  $C_0(m_A)$ , equals 1; the one-body term,  $C_1(m_A)$ , equals  $T_1$ ; the two-body term,  $C_2(m_A)$ , equals  $T_2 + \frac{1}{2}T_1^2$  if  $m_A \geq 2$ ; the three-body term  $C_3(m_A)$  equals  $T_1T_2 + \frac{1}{6}T_1^3$  if  $m_A = 2$  and  $T_3 + T_1T_2 + \frac{1}{6}T_1^3$  if  $m_A \geq 3$ ,

etc. The determination of the generalized moments  $\mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$  is relatively straightforward too, particularly for the lower-order CC/EOMCC methods, such as CCSD and EOMCCSD (the  $m_A = 2$  case). Indeed, the formula for the leading moment  $\mathfrak{M}_{\mu, abc}^{ijk}(2)$ , entering the basic MMCC(2,3) approximation discussed in Section 3 and corresponding to the projection of the CCSD/EOMCCSD equations on triply excited determinants  $|\Phi_{ijk}^{abc}\rangle$ , in terms of the many-body components of the CCSD/EOMCCSD similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$ , Eq. (13), and the EOMCCSD excitation operator  $R_\mu^{(\text{CCSD})}$ , Eq. (16), which enables us to correct the CCSD and EOMCCSD energies by considering the leading term in correction  $\delta_\mu^{(\text{CCSD})}$ , Eq. (53), is [47–49, 51, 52, 59]

$$\begin{aligned} \mathfrak{M}_{\mu, abc}^{ijk}(2) &= \langle \Phi_{ijk}^{abc} | (\bar{H}_2^{(\text{CCSD})} R_{\mu, 2})_C | \Phi \rangle \\ &+ \langle \Phi_{ijk}^{abc} | [\bar{H}_3^{(\text{CCSD})} (R_{\mu, 1} + R_{\mu, 2})]_C | \Phi \rangle \\ &+ \langle \Phi_{ijk}^{abc} | (\bar{H}_4^{(\text{CCSD})} R_{\mu, 1})_C | \Phi \rangle + r_0(\mu) \mathfrak{M}_{abc}^{ijk}(2), \end{aligned} \quad (58)$$

where the ground-state moment  $\mathfrak{M}_{abc}^{ijk}(2)$ , obtained by projecting the CCSD equations on triply excited determinants, is given by [51, 52]

$$\begin{aligned} \mathfrak{M}_{abc}^{ijk}(2) &= \langle \Phi_{ijk}^{abc} | [H_N (T_2 + T_1 T_2 + \tfrac{1}{2} T_2^2 + \tfrac{1}{2} T_1^2 T_2 \\ &+ \tfrac{1}{2} T_1 T_2^2 + \tfrac{1}{6} T_1^3 T_2)]_C | \Phi \rangle. \end{aligned} \quad (59)$$

In the above equations, the operators  $\bar{H}_p^{(\text{CCSD})}$  represent the  $p$ -body components of  $\bar{H}^{(\text{CCSD})}$  and  $H_N = H - \langle \Phi | H | \Phi \rangle$  is the Hamiltonian in the normal-ordered form. The fully factorized expression for the triply excited moments of the CCSD/EOMCCSD equations  $\mathfrak{M}_{\mu, abc}^{ijk}(2)$ , in terms of the amplitudes defining the CCSD/EOMCCSD cluster and excitation operators,  $T_1$ ,  $T_2$ ,  $R_{\mu, 0}$ ,  $R_{\mu, 1}$ , and  $R_{\mu, 2}$ , and molecular integrals  $f_p^q$  and  $v_{pq}^{rs}$ , which can be used in the efficient computer implementations of all MMCC(2,3) approximations, including the externally corrected MMCC(2,3) and CR-EOMCCSD(T) schemes, has the following form [59]:

$$\begin{aligned} \mathfrak{M}_{\mu, abc}^{ijk}(2) &= \mathcal{A}_{abc} \mathfrak{T}_{\mu, abc}^{ijk}(2) \\ &= \mathcal{A}_{abc} \{ \mathcal{A}^{i/jk} [ (\tfrac{1}{2} \bar{h}_{ab}^{ie} r_{ec}^{jk} - \tfrac{1}{2} \bar{h}_{mc}^{jk} r_{ab}^{im} - \tfrac{1}{2} I_{mc}^{jk} t_{ab}^{im} + I_{ab}^{ie} t_{ec}^{jk}) \\ &+ \tfrac{1}{2} r_0 (\bar{h}_{ab}^{ie} t_{ec}^{jk} - I_{mc}^{jk} t_{ab}^{im}) ] \}, \end{aligned} \quad (60)$$

where, for simplicity, we dropped the symbol  $\mu$  in the amplitudes  $r_{ec}^{jk}(\mu)$ ,  $r_{ab}^{im}(\mu)$ , and  $r_0(\mu)$ . The antisymmetrizers  $\mathcal{A}_{pqr}$ ,  $\mathcal{A}_{p/qr}$ , and  $\mathcal{A}_{pq}$ , which enter Eq. (60) directly or through the matrix elements of  $\bar{H}^{(\text{CCSD})}$ , and other



intermediates that are needed to construct Eq. (60) and that are listed in Table 1, are defined in a usual way,

$$\mathcal{A}_{pqr} \equiv \mathcal{A}^{pqr} = 1 - (pq) - (pr) - (qr) + (pqr) + (prq), \quad (61)$$

$$\mathcal{A}_{p/qr} \equiv \mathcal{A}^{p/qr} = 1 - (pq) - (pr), \quad (62)$$

and

$$\mathcal{A}_{pq} \equiv \mathcal{A}^{pq} = 1 - (pq), \quad (63)$$

with  $(pq)$  and  $(pqr)$  representing the cyclic permutations of two and three indices, respectively. The explicit spin-orbital expressions for one- and two-body matrix elements of  $\bar{H}^{\text{CCSD}}$ ,  $\bar{h}_p^q$  and  $\bar{h}_{pq}^{rs}$ , respectively, and other recursively generated intermediates entering Eq. (60), in terms of cluster amplitudes  $t_a^i$  and  $t_{ab}^{ij}$ , excitation amplitudes  $r_a^i \equiv r_a^i(\mu)$  and  $r_{ab}^{ij} \equiv r_{ab}^{ij}(\mu)$ , and molecular integrals  $f_p^q$  and  $v_{pq}^{rs}$ , are given in Table 1. Similar expressions can be given for the EOMCCSD moments  $\mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(2)$  with  $k \geq 4$  that enter the MMCC(2,4) and other higher-order MMCC schemes. In general, the generalized moments  $\mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$  corresponding to the CC/EOMCC approximation  $A$  can be calculated using the formula [47–52]:

$$\begin{aligned} \mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A) &= \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | (\bar{H}_{\text{open}}^{(A)} R_{\mu, \text{open}}^{(A)})_C | \Phi \rangle \\ &+ \sum_{p=m_A+1}^{k-1} \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | (\bar{H}_p^{(A)} R_{\mu, k-p}^{(A)})_{DC} | \Phi \rangle \\ &+ r_0(\mu) \mathfrak{M}_{a_1 \dots a_k}^{i_1 \dots i_k}(m_A), \end{aligned} \quad (64)$$

where  $r_0(\mu)$  is the coefficient at the reference determinant  $|\Phi\rangle$  in the many-body expansion of  $R_\mu^{(A)}|\Phi\rangle$ , Eq. (20) (cf. Eq. (26) for the formula for  $r_0(\mu)$ ), subscripts “open,”  $C$ , and  $DC$  refer to open (i.e. having external lines), connected, and disconnected parts of a given operator expression,  $O_j$  represents the  $j$ -body component of operator  $O$ , and  $\mathfrak{M}_{a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$  are the generalized moments of the single-reference CC equations defined by Eq. (49).

In order to use Eqs. (50) and (53) in practical calculations, the following two issues must be addressed. First, the exact MMCC corrections  $\delta_\mu^{(A)}$ , Eq. (50), or  $\delta_\mu^{(\text{CCSD})}$ , Eq. (53), are represented by complete many-body expansions including the  $N$ -body contributions, where  $N$  is the number of electrons in a system, corresponding to all many-body components of the wave functions  $|\Psi_\mu\rangle$  that enter Eqs. (50) and (53) (cf. the summations over  $n$  in Eqs. (50) and (53)). In order to develop practical MMCC methods, we must truncate the many-body expansions for  $\delta_\mu^{(A)}$  or  $\delta_\mu^{(\text{CCSD})}$ , given by Eqs. (50) or (53), at some, preferably low, excitation level  $m_B > m_A$ . This leads to the MMCC( $m_A, m_B$ ) schemes [47–52, 61–63, 72]. Examples of these schemes are

TABLE 1. Explicit algebraic expressions for the matrix elements elements of  $\bar{H}^{\text{CCSD}}$  (designated by  $\bar{h}$ ) and other intermediates (designated by  $I$  or  $\vartheta$ ) used to construct the triply excited moments of the CCSD/EOMCCSD equations,  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , Eq. (60).

<i>Intermediate</i>	<i>Expression<sup>a</sup></i>
$\bar{h}_i^a$	$f_i^a + t_e^m v_{im}^{ae}$
$I_i^a$	$-r_e^m v_{mi}^{ae}$
$\bar{h}_{ai}^{bc}$	$v_{ai}^{bc} - t_a^m v_{mi}^{bc}$
$\bar{h}_{ij}^{ka}$	$v_{ij}^{ka} + t_e^k v_{ij}^{ea}$
$\bar{h}_{ab}^{cd}$	$v_{ab}^{cd} + \frac{1}{2} t_{ab}^{mn} v_{mn}^{cd} - t_b^m \bar{h}_{am}^{cd} + t_a^m v_{bm}^{cd}$
$\bar{h}_{ij}^{kl}$	$v_{ij}^{kl} + \frac{1}{2} t_{ef}^{kl} v_{ij}^{ef} - t_e^k \bar{h}_{ij}^{le} + t_e^l v_{ij}^{ke}$
$\bar{h}_{ia}^{jb}$	$\vartheta_{ia}^{jb} - t_{ea}^j v_{im}^{eb} - t_a^m \bar{h}_{im}^{jb}$
$\bar{h}_{ab}^{ic}$	$v_{ab}^{ic} + t_e^i v_{ab}^{ec} - t_a^m \bar{h}_{mb}^{ic} + t_b^m \vartheta_{ma}^{ic} - t_{ab}^{im} \bar{h}_m^c + t_{ae}^{im} \bar{h}_{bm}^{ce} - t_{be}^{im} v_{am}^{ce} + \frac{1}{2} t_{ab}^{nm} \bar{h}_{nm}^{ic}$
$\bar{h}_{ia}^{jk}$	$v_{ia}^{jk} + t_a^m \bar{h}_{mi}^{jk} - t_e^j v_{ia}^{ke} + \mathcal{A}^{jk} t_{ae}^{km} \bar{h}_{im}^{je} + t_{ea}^{jk} \bar{h}_i^e + t_e^k \vartheta_{ia}^{je} - \frac{1}{2} t_{ef}^{jk} v_{ai}^{ef}$
$I_{ab}^{ic}$	$\frac{1}{2} \bar{h}_{ab}^{ec} r_e^i - \bar{h}_{bm}^{ec} r_{ae}^{im} + \frac{1}{4} \bar{h}_{mn}^{ic} r_{ab}^{mn} - \bar{h}_{mb}^{ic} r_a^m$
$I_{ia}^{jk}$	$I_i^{ej} t_{ae}^{kj} + \frac{1}{2} \bar{h}_{ai}^{ef} r_{ef}^{kj} - \bar{h}_{im}^{jk} r_a^m + \mathcal{A}^{jk} (\bar{h}_{im}^{je} r_{ae}^{km} + \bar{h}_{ia}^{je} r_e^k)$
$I_{ia}^{'jk}$	$\bar{h}_{ia}^{jk} - t_{ea}^j \bar{h}_i^e$
$\vartheta_{ia}^{jb}$	$v_{ia}^{jb} + t_e^j v_{ia}^{eb}$

<sup>a</sup> Summation over repeated upper and lower indices is assumed;  $f_p^q = \langle p|f|q \rangle$  and  $v_{pq}^{rs} = \langle pq|v|rs \rangle - \langle pq|v|sr \rangle$  are the one- and two-electron integrals in a molecular spin-orbital basis  $\{p\}$  corresponding to the Fock operator ( $f$ ) and the two-body part of the Hamiltonian ( $v$ ).

the CI- and MRMBPT-corrected MMCC(2,3) methods [47, 49, 50, 52, 78] and the CR-EOMCCSD(T) approach [49, 51, 52, 59] discussed in Section 3, in which the suitably designed corrections  $\delta_\mu^{(\text{CCSD})}$ , based on the exact Eq. (53), are added to the CCSD/EOMCCSD energies. Alternatives to the MMCC( $m_A, m_B$ ) schemes are the approximate MMCC methods employing the left eigenstates of the similarity-transformed Hamiltonian  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$  [79], in which the MMCC corrections  $\delta_\mu^{(A)}$  or  $\delta_\mu^{(\text{CCSD})}$  are first rewritten in a computationally convenient form that does not use the overlap denominators  $\langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$  or  $\langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle$  entering Eqs. (50) and (53) (also discussed in Section 3). The second issue that needs to be addressed is the fact that the wave functions  $|\Psi_\mu\rangle$  that enter the exact

Eqs. (50) and (53) are the full CI states. Thus, we must approximate wave functions  $|\Psi_\mu\rangle$  in some way. A few different methods of approximating  $|\Psi_\mu\rangle$  in Eq. (53), leading to the aforementioned externally corrected MMCC(2,3) approaches and CR-EOMCCSD(T) schemes, and their analogs exploiting the left eigenstates of  $\bar{H}^{(\text{CCSD})}$ , and the performance of all of these methods in actual calculations of excited electronic states are discussed in the next section.

### 3. Approximate MMCC methods for excited states and their performance

There are two, essentially different, ways of approximating the MMCC corrections  $\delta_\mu^{(A)}$ , Eq. (50), that lead to relatively inexpensive, and therefore practical, computational schemes. In the first method, we assume that the CI expansions of the ground- and excited-state wave functions  $|\Psi_\mu\rangle$  entering Eq. (50) are relatively short and do not contain higher-than- $m_B$ -tuply excited components relative to the reference determinant  $|\Phi\rangle$ , where the excitation level  $m_B$  is not much higher than the excitation level  $m_A$  defining the CC/EOMCC approximation we are trying to improve. This leads to the externally (CI or MRMBPT) corrected MMCC( $m_A, m_B$ ) schemes [47–50, 52, 78] and the CR-EOMCCSD(T) method [49, 51, 52, 59]. We discuss these approaches first, focusing on the MMCC( $m_A, m_B$ ) methods with  $m_A = 2$  and  $m_B = 3$ , which enable us to improve the results of the CCSD/EOMCCSD calculations by terms that represent the leading triples effects (see Section 3.1). In the second approach, discussed in Section 3.2, which leads to the MMCC( $m_A, m_B$ ) $_{\mathcal{L}}$  schemes, including the recently formulated [79] and promising CR-EOMCCSD(T) $_{\mathcal{L}}$  approximation, we rewrite the “bra” wave functions  $\langle\Psi_\mu|$  in Eq. (50) in terms of the left eigenstates of  $\bar{H}^{(A)}$ . The main difference between the regular MMCC( $m_A, m_B$ ) approaches and the MMCC( $m_A, m_B$ ) $_{\mathcal{L}}$  methods is the absence of the overlap denominator  $\langle\Psi_\mu|R_\mu^{(A)}e^{T^{(A)}}|\Phi\rangle$  in the MMCC( $m_A, m_B$ ) $_{\mathcal{L}}$  energy corrections. The information about this denominator, which enters the regular MMCC energy formula, Eq. (50), and which helps to improve the results for doubly excited states and excited-state potential energy surfaces along bond breaking coordinates, is incorporated in the MMCC( $m_A, m_B$ ) $_{\mathcal{L}}$  methods through the use of the left eigenstates of  $\bar{H}^{(A)}$  ( $\bar{H}^{(\text{CCSD})}$  in the CR-EOMCCSD(T) $_{\mathcal{L}}$  case).

### 3.1. EXTERNALLY CORRECTED MMCC(2,3) SCHEMES AND THE CR-EOMCCSD(T) APPROACH

The MMCC(2,3), CR-EOMCCSD(T), and other MMCC( $m_A, m_B$ ) methods are obtained by assuming that the CI expansions of the ground- and excited-state wave functions  $|\Psi_\mu\rangle$  entering Eq. (50) do not contain higher-than- $m_B$ -tuply excited components relative to the reference  $|\Phi\rangle$ , where  $m_A < m_B < N$ . In all MMCC( $m_A, m_B$ ) approximations, we calculate the ground- and excited-state energies as follows [47–52, 61–63, 72]:

$$E_\mu^{(\text{MMCC})}(m_A, m_B) = E_\mu^{(A)} + \delta_\mu(m_A, m_B), \quad (65)$$

where  $E_\mu^{(A)}$  is the energy of the  $\mu$ -th electronic state, obtained with some standard EOMCC method  $A$ , and

$$\begin{aligned} \delta_\mu(m_A, m_B) = & \sum_{n=m_A+1}^{m_B} \sum_{k=m_A+1}^n \langle \Psi_\mu | C_{n-k}(m_A) \\ & \times M_{\mu,k}(m_A) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle \end{aligned} \quad (66)$$

is the relevant MMCC correction to  $E_\mu^{(A)}$ . As in the exact theory defined by Eq. (50), the generalized moments of the CC/EOMCC equations,  $\mathfrak{M}_{\mu, a_1 \dots a_k}^{i_1 \dots i_k}(m_A)$ , Eqs. (48) and (64), enter Eqs. (65) and (66) through quantities  $M_{\mu,k}(m_A)|\Phi\rangle$ , Eq. (52), and  $C_{n-k}(m_A)$  are the many-body components of  $e^{T^{(A)}}$ , defined by Eq. (51), where  $T^{(A)}$  is the cluster operator defining (along with the excitation operator  $R_\mu^{(A)}$ ) the CC/EOMCC calculations  $A$ , whose results we are trying to correct.

We limit our discussion to the low-order MMCC( $m_A, m_B$ ) schemes with  $m_A = 2$  and  $m_B = 3$ , which can be used to correct the results of the CCSD/EOMCCSD calculations for the effects of triple excitations (for the description of the MMCC(2,4) and other higher-order MMCC( $m_A, m_B$ ) methods, see Refs. [48–50, 52, 61–63, 72]). The MMCC(2,3) energy expression is as follows [47–52, 61–63, 72]:

$$E_\mu^{(\text{MMCC})}(2, 3) = E_\mu^{(\text{CCSD})} + \langle \Psi_\mu | M_{\mu,3}(2) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle, \quad (67)$$

where  $E_\mu^{(\text{CCSD})}$  is the CCSD ( $\mu = 0$ ) or EOMCCSD ( $\mu > 0$ ) energy,  $T^{(\text{CCSD})}$  is the cluster operator obtained in the CCSD calculations (cf. Eq. (4)),  $R_\mu^{(\text{CCSD})}$  is the corresponding excitation operator (cf. Eq. (16); when  $\mu = 0$ ,  $R_\mu^{(\text{CCSD})} = \mathbf{1}$ ), and

$$M_{\mu,3}(2) = \frac{1}{36} \mathfrak{M}_{\mu,abc}^{ijk}(2) a^a a^b a^c a_k a_j a_i, \quad (68)$$

with  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  representing the triply excited moments of the CCSD/EOMCCSD equations defined by Eqs. (58) and (59). These moments are easy to calculate. As implied by Eqs. (58) and (59), their determination requires the explicit consideration of the triples-reference, triples-singles, and triples-doubles blocks of the matrix representing the CCSD/EOMCCSD similarity-transformed Hamiltonian  $\bar{H}^{\text{CCSD}}$ , Eq. (13). In consequence, the most expensive steps of the ground- and excited-state calculations using methods based on the MMCC(2,3) approximation are essentially identical to the  $n_o^3 n_u^4$  noniterative steps of the ground-state CCSD(T) calculations ( $n_o$  and  $n_u$  are the numbers of occupied and unoccupied correlated orbitals, respectively). Similar remarks apply to the memory and disk-space requirements. Clearly, these are great simplifications in the computer effort, compared to the higher-level EOMCC approaches, such as EOMCCSDT [43, 44, 55, 56], particularly if we realize that we only have to use the  $T_1$  and  $T_2$  clusters, obtained in the CCSD calculations, to construct matrix elements of  $\bar{H}^{(\text{CCSD})}$  that enter  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , Eqs. (58) and (59). In practical implementations of all MMCC(2,3) methods, the simplifications are even greater, since, as shown by Eq. (60) and Table 1, we can calculate moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  in a highly efficient manner, which leads to noniterative  $n_o^3 n_u^4$  procedures, by using recursively generated intermediates and one- and two-body matrix elements of  $\bar{H}^{(\text{CCSD})}$ ,  $\bar{h}_p^q$  and  $\bar{h}_{pq}^{rs}$ , respectively, expressed in terms of the CCSD cluster amplitudes  $t_a^i$  and  $t_{ab}^{ij}$ , EOMCCSD excitation amplitudes  $r_a^i(\mu)$  and  $r_{ab}^{ij}(\mu)$ , and molecular integrals  $f_p^q$  and  $v_{pq}^{rs}$ .

Depending on the form of the wave function  $|\Psi_\mu\rangle$  in Eq. (67), we can distinguish between the externally corrected MMCC(2,3) approaches for excited states, which employ the inexpensive CI or MRMBPT (in general, non-CC) wave functions to approximate  $|\Psi_\mu\rangle$  [47–50, 52, 61, 68, 78], and CR-EOMCCSD(T) methods, which are based on the perturbative analysis of the full EOMCCSDT problem to provide the approximate form of  $|\Psi_\mu\rangle$  for MMCC(2,3) calculations [49, 51, 52, 59]. The CR-EOMCCSD(T) approaches can be viewed as the excited-state extensions of the ground-state CR-CCSD(T) method introduced in Refs. [61, 62] (see, also, Refs. [49, 50, 52, 63, 65, 67, 69, 70, 72, 73, 75, 76]). Externally corrected MMCC methods are very similar, in the overall idea, to the large class of the externally corrected CC methods pioneered by Paldus and collaborators, in which CC and non-CC concepts are combined together to improve CC results in the presence of quasi-degeneracies [8, 17, 95–102]. In particular, the CI-corrected MMCC methods discussed in this work, which were originally introduced in the context of the ground-state calculations by Piecuch and Kowalski in Ref. 61, are very similar to the so-called energy-corrected CC approaches of Li and Paldus [91–94]. We begin the discussion of MMCC(2,3) methods with the externally corrected approaches.

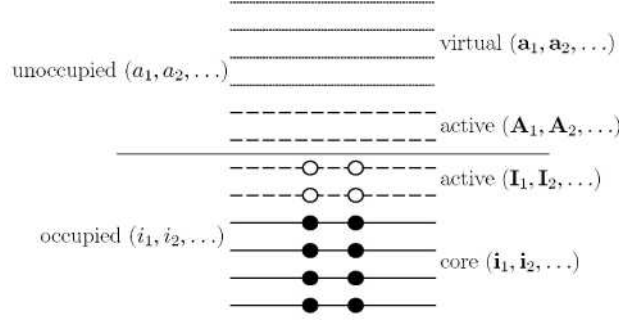


Figure 1. The orbital classification used in the active-space CI, MRMBPT, and the CI- and MRMBPT-corrected MMCC methods, such as MMCC(2,3)/CI and MMCC(2,3)/PT. Core, active, and virtual orbitals are represented by solid, dashed, and dotted lines, respectively. Full and open circles represent core and active electrons of the reference determinant  $|\Phi\rangle$  (the closed-shell reference  $|\Phi\rangle$  is assumed).

### 3.1.1. The CI- and MRMBPT-corrected MMCC(2,3) methods

In the CI-corrected MMCC(2,3) approach and other CI-corrected MMCC( $m_A, m_B$ ) methods for excited states, originally introduced in Refs. [47, 48], we replace the wave functions  $|\Psi_\mu\rangle$  in Eqs. (66) and (67) by the wave functions obtained in inexpensive CI calculations that provide a qualitatively correct description of the ground and excited states of interest. One of the best choices of the CI wave functions  $|\Psi_\mu\rangle$  for such calculations is provided by the multi-reference-like, active-space CI approaches, such as CISDt. In this case, following the philosophy of multi-reference calculations, we divide the available spin-orbitals into four groups (see Figure 1) of core spin-orbitals ( $\mathbf{i}_1, \mathbf{i}_2, \dots$  or  $\mathbf{i}, \mathbf{j}, \dots$ ), active spin-orbitals occupied in reference  $|\Phi\rangle$  ( $\mathbf{I}_1, \mathbf{I}_2, \dots$  or  $\mathbf{I}, \mathbf{J}, \dots$ ), active spin-orbitals unoccupied in reference  $|\Phi\rangle$  ( $\mathbf{A}_1, \mathbf{A}_2, \dots$  or  $\mathbf{A}, \mathbf{B}, \dots$ ), and virtual spin-orbitals ( $\mathbf{a}_1, \mathbf{a}_2, \dots$  or  $\mathbf{a}, \mathbf{b}, \dots$ ). The choice of active spin-orbitals (typically, a few highest-energy occupied spin-orbitals and a few lowest-energy unoccupied spin-orbitals) is dictated by the dominant orbital excitations in the ground and excited states that we would like to calculate. An example of the good choice of active orbitals for the calculations of the valence excited states of  $\text{CH}^+$  can be found in Table 2.

In the specific case of the CI-corrected MMCC(2,3) approach, very good results are obtained when the wave function  $|\Psi_\mu\rangle$  in Eq. (67) is replaced by the wave function obtained in the active-space CISDt calculations, which

is defined as follows:

$$|\Psi_\mu^{(\text{CISDt})}\rangle = (C_{\mu,0} + C_{\mu,1} + C_{\mu,2} + c_{\mu,3})|\Phi\rangle, \quad (69)$$

where

$$C_{\mu,0} = c_0(\mu) \mathbf{1}, \quad (70)$$

$$C_{\mu,1}|\Phi\rangle = c_a^i(\mu) a^a a_i = \sum_{i,a} c_a^i(\mu) a^a a_i, \quad (71)$$

and

$$C_{\mu,2} = \frac{1}{4} c_{ab}^{ij}(\mu) a^a a^b a_j a_i = \sum_{i<j, a<b} c_{ab}^{ij}(\mu) a^a a^b a_j a_i \quad (72)$$

are the excitation operators defining the reference, singly excited, and doubly excited contributions to  $|\Psi_\mu^{(\text{CISDt})}\rangle$ , and

$$c_{\mu,3} = \sum_{i<j<\mathbf{K}, \mathbf{A}<b<c} c_{\mathbf{A}bc}^{ij\mathbf{K}}(\mu) a^{\mathbf{A}} a^b a^c a_{\mathbf{K}} a_j a_i \quad (73)$$

are the internal and semi-internal triples containing at least one active occupied and one active unoccupied spin-orbital indices, designated by  $\mathbf{K}$  and  $\mathbf{A}$ , respectively. The CISDt method can be viewed as an inexpensive variant of the CI singles, doubles, and triples (CISDT) approximation, in which the complete set of triple excitations is replaced by a relatively small set of triples defined by Eq. (73). The final energy expression defining the CISDt-corrected MMCC(2,3) method, referred to as the MMCC(2,3)/CI approximation, is:

$$E_\mu^{(\text{MMCC/CI})}(2,3) = E_\mu^{(\text{EOMCCSD})} + \sum_{i<j<\mathbf{K}, \mathbf{A}<b<c} [c_{\mathbf{A}bc}^{ij\mathbf{K}}(\mu)]^* \mathfrak{M}_{\mu, \mathbf{A}bc}^{ij\mathbf{K}}(2) / D_\mu^{(\text{CISDt})}, \quad (74)$$

where  $\mathfrak{M}_{\mu, \mathbf{A}bc}^{ij\mathbf{K}}(2)$  represent the subset of all triply excited moments of the CCSD/EOMCCSD equations defined by Eqs. (58) and (59) and

$$D_\mu^{(\text{CISDt})} \equiv \langle \Psi_\mu^{(\text{CISDt})} | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle = \Delta_{\mu,0}^{(\text{CISDt})} + \Delta_{\mu,1}^{(\text{CISDt})} + \Delta_{\mu,2}^{(\text{CISDt})} + \Delta_{\mu,3}^{(\text{CISDt})} \quad (75)$$

is the overlap denominator  $\langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle$  appearing in the general Eq. (67), written for the wave function  $|\Psi_\mu\rangle = |\Psi_\mu^{(\text{CISDt})}\rangle$ , Eq. (69). The  $\Delta_{\mu,0}^{(\text{CISDt})}$ ,  $\Delta_{\mu,1}^{(\text{CISDt})}$ ,  $\Delta_{\mu,2}^{(\text{CISDt})}$ , and  $\Delta_{\mu,3}^{(\text{CISDt})}$  terms that contribute to the denominator  $D_\mu^{(\text{CISDt})}$ , Eq. (75), are defined as

$$\Delta_{\mu,0}^{(\text{CISDt})} = [c_0(\mu)]^* r_0(\mu), \quad (76)$$

$$\Delta_{\mu,1}^{\text{CISDt}} = \sum_{i,a} [c_a^i(\mu)]^* \beta_a^i(\mu), \quad (77)$$

$$\Delta_{\mu,2}^{\text{CISDt}} = \sum_{i < j, a < b} [c_{ab}^{ij}(\mu)]^* \beta_{ab}^{ij}(\mu), \quad (78)$$

and

$$\Delta_{\mu,3}^{\text{CISDt}} = \sum_{i < j < \mathbf{K}, \mathbf{A} < b < c} [c_{\mathbf{A}bc}^{ij\mathbf{K}}(\mu)]^* \beta_{\mathbf{A}bc}^{ij\mathbf{K}}(\mu), \quad (79)$$

where  $c_0(\mu)$ ,  $c_a^i(\mu)$ ,  $c_{ab}^{ij}(\mu)$ , and  $c_{\mathbf{A}bc}^{ij\mathbf{K}}(\mu)$  are the CI coefficients obtained in the variational CISDt calculations for the  $\mu$ -th electronic state and  $r_0(\mu)$ ,

$$\beta_a^i(\mu) = \langle \Phi_i^a | (R_{\mu,1} + R_{\mu,0}T_1) | \Phi \rangle, \quad (80)$$

$$\beta_{ab}^{ij}(\mu) = \langle \Phi_{ij}^{ab} | [R_{\mu,2} + R_{\mu,1}T_1 + R_{\mu,0}(T_2 + \frac{1}{2}T_1^2)] | \Phi \rangle, \quad (81)$$

and

$$\beta_{abc}^{ijk}(\mu) = \langle \Phi_{ijk}^{abc} | [R_{\mu,2}T_1 + R_{\mu,1}(T_2 + \frac{1}{2}T_1^2) + R_{\mu,0}(T_1T_2 + \frac{1}{6}T_1^3)] | \Phi \rangle \quad (82)$$

are the coefficients at the reference determinant  $|\Phi\rangle$  and singly, doubly, and triply excited determinants,  $|\Phi_i^a\rangle$ ,  $|\Phi_{ij}^{ab}\rangle$ , and  $|\Phi_{ijk}^{abc}\rangle$  respectively, in the CI expansion of the CCSD/EOMCCSD wave function  $R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} |\Phi\rangle$ , which can be easily determined using the CCSD/EOMCCSD cluster and excitation amplitudes  $t_a^i$ ,  $t_{ab}^{ij}$ ,  $r_0(\mu)$ ,  $r_a^i(\mu)$ , and  $r_{ab}^{ij}(\mu)$ . As in the case of moments  $\mathfrak{M}_{\mu, \mathbf{A}bc}^{ij\mathbf{K}}(2)$ , we only need a subset of all triexcited coefficients  $\beta_{abc}^{ijk}(\mu)$ , Eq. (82), defined through active spin-orbital indices as  $\beta_{\mathbf{A}bc}^{ij\mathbf{K}}(\mu)$ , to calculate the triply excited contribution  $\Delta_{\mu,3}^{\text{CISDt}}$ , Eq. (79), to the denominator  $D_\mu^{\text{CISDt}}$ . One can easily extend the above MMCC(2,3)/CI approximation to higher-order CI-corrected MMCC( $m_A, m_B$ ) schemes, such as MMCC(2,4)/CI, which describes the combined effect of triple and quadruple excitations that are defined through active orbitals in a similar way as the triple excitations of the CISDt wave functions (see, e.g., Refs. [48, 49, 52]).

One of the main advantages of the CI-corrected MMCC schemes, including MMCC(2,3)/CI, is a very good control of the quality of wave functions  $|\Psi_\mu\rangle$  used to construct the noniterative corrections  $\delta_\mu(m_A, m_B)$ , which is accomplished through the judicious choice of active orbitals that can always be adjusted to excited states of a given type or, when the potential energy surfaces are examined, to a given type of bond breaking. Another advantage of the CI-corrected MMCC methods is their relatively low computer cost, which is a consequence of the fact that it is usually sufficient to use very small active orbital spaces to obtain good results (cf., e.g., Table 2 and Figure 2). The relatively low cost of the CI-corrected MMCC



calculations can be explained by using the CISDt-corrected MMCC(2,3) approach, defined by Eq. (74), as an example. As one can see, we do not have to determine the entire set of the triexcited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  in the MMCC(2,3)/CI calculations. This alone leads to considerable savings in the computer effort, since we only have to construct  $\sim N_o N_u n_o^2 n_u^2$  moments  $\mathfrak{M}_{\mu,\mathbf{A}bc}^{ij\mathbf{K}}(2)$ , where  $N_o$  ( $N_u$ ) is the number of active orbitals occupied (unoccupied) in  $|\Phi\rangle$ , which is a small fraction of all  $\sim n_o^3 n_u^3$  moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  when  $N_o \ll n_o$  and  $N_u \ll n_u$ . Moreover, the  $\sim n_o^3 n_u^4$  steps related to the construction of moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  reduce to the  $\mathcal{N}^5$ -like  $N_o N_u n_o^2 n_u^3$  steps in the MMCC(2,3)/CI calculations. There is an additional cost related to the CISDt calculations, needed to generate the  $|\Psi_\mu^{\text{CISDt}}\rangle$  wave functions, but again the usual  $n_o^3 n_u^5$  steps of the parent CISDT calculations reduce to the considerably less expensive  $N_o N_u n_o^2 n_u^4$  steps in the CISDt case. All these factors contribute to the relatively low cost of the MMCC(2,3)/CI calculations. The number of triples used in the CISDt-corrected MMCC(2,3) calculations is usually very small (no more than  $\sim 30\%$  of all triples; sometimes even less than that [47–49, 52, 68]). The CPU times required to construct the relevant corrections  $\delta_\mu(2,3)$  to CCSD/EOMCCSD energies are often on the order of the CPU time of a single CCSD/EOMCCSD iteration [47–49, 52, 68].

We illustrate the performance of the CISDt-corrected MMCC(2,3) approach using excited states of the  $\text{CH}^+$  ion as an example (see Table 2 and Figure 2). We are comparing the MMCC(2,3)/CI results for a few low-lying excited states of  $\text{CH}^+$  of the  $^1\Sigma^+$ ,  $^1\Pi$ , and  $^1\Delta$  symmetries, obtained with the  $[5s3p1d/3s1p]$  basis set described in Ref. [103] and the ground-state restricted Hartree-Fock (RHF) orbitals, with the results of the corresponding full CI calculations reported in Refs. [45, 103]. Along with the MMCC(2,3)/CI and full CI data, we show the EOMCCSD and full EOMCCSDT results (the latter ones obtained in Ref. [44]) and the results obtained with the perturbative triples CC3 model [39] (see Table 2). In addition, in Figure 2, we compare the potential energy curves for excited states of  $\text{CH}^+$ , obtained with the MMCC(2,3)/CI approach, with the corresponding EOMCCSD and full CI curves on the one hand and the potential energy curves resulting from the CISDt calculations, which are used to generate wave functions  $|\Psi_\mu\rangle$  for the MMCC(2,3)/CI method, on the other hand. In calculating the CISDt wave functions  $|\Psi_\mu^{\text{CISDt}}\rangle$  and in calculating the final MMCC(2,3)/CI energies, we used a small active space consisting of the highest-energy occupied orbital,  $3\sigma$ , and three lowest-energy unoccupied orbitals,  $1\pi_x \equiv 1\pi$ ,  $1\pi_y \equiv 2\pi$ , and  $4\sigma$ . This choice of active space reflects the nature of orbital excitations defining the valence excited states of  $\text{CH}^+$  shown in Table 2 and Figure 2 (see Refs. [42, 43, 47] for details).

TABLE 2. A comparison of the MMCC(2,3)/CI, MMCC(2,3)/PT, CR-EOMCCSD(T), and CR-EOMCCSD(T) $_{\mathcal{L}}$  vertical excitation energies of the CH<sup>+</sup> ion, as described by the [5s3p1d/3s1p] basis set of Olsen *et al.* [103], at the equilibrium geometry, with the exact, full CI, data and other CC results.<sup>a</sup>

State	Full CI <sup>b</sup>	EOMCCSD <sup>c</sup>	CC <sup>gd</sup>	EOMCCSDT <sup>e</sup>	MMCC(2,3)/CF <sup>e,f</sup>	MMCC(2,3)/PT <sup>f,g</sup>	CR-EOMCCSD(T) <sup>h</sup>	CR-EOMCCSD(T) $_{\mathcal{L}}$ <sup>i</sup>
2 <sup>1</sup> Σ <sup>+</sup>	8.549	0.560	0.230	0.074	0.084	0.102	0.117	0.106
3 <sup>1</sup> Σ <sup>+</sup>	13.525	0.055	0.016	0.001	0.000	0.052	0.011	0.020
4 <sup>1</sup> Σ <sup>+</sup>	17.217	0.099	0.026	-0.002	0.015		0.025	0.022
1 <sup>1</sup> Π	3.230	0.031	0.012	-0.003	0.007	0.015	0.007	0.017
2 <sup>1</sup> Π	14.127	0.327	0.219	0.060	0.105	-0.176	0.113	0.135
1 <sup>1</sup> Δ	6.964	0.924	0.318	0.040	0.051	0.090	0.027	0.032
2 <sup>1</sup> Δ	16.833	0.856	0.261	-0.038	0.006		-0.002	-0.030

<sup>a</sup> The full CI values are the excitation energies. All other values are the deviations from the full CI results. The  $n$  <sup>1</sup>Y energy is the vertical excitation energy from the ground state ( $X$  <sup>1</sup>Σ<sup>+</sup>  $\equiv$  1 <sup>1</sup>Σ<sup>+</sup>) to the  $n$ -th singlet state of symmetry Y. All energies are in eV. The equilibrium bond length in CH<sup>+</sup> is 2.13713 bohr.

<sup>b</sup> From Ref. [103].

<sup>c</sup> From Ref. [44].

<sup>d</sup> From Ref. [39].

<sup>e</sup> From Refs. [47, 48].

<sup>f</sup> The active space consisted of the 3σ, 1π<sub>x</sub>  $\equiv$  1π, 1π<sub>y</sub>  $\equiv$  2π, and 4σ orbitals.

<sup>g</sup> From Ref. [78].

<sup>h</sup> The CR-EOMCCSD(T)<sub>ID</sub> result taken from Ref. [51].

<sup>i</sup> From Ref. [79].

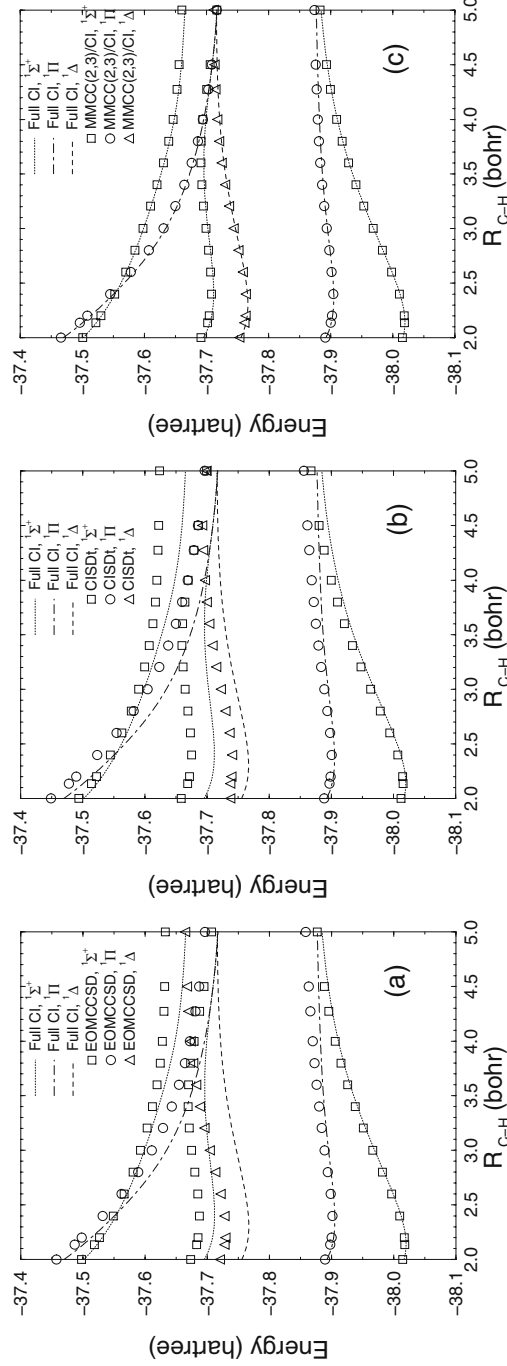


Figure 2. Potential energy curves for the  $\text{CH}^+$  ion (energies in hartree and the C-H distance in bohr; see Refs. [44, 47] for the EOMCCSD and MMCC(2,3)/CI data; see Refs. [45, 103] for the full CI data). The results include the ground state and the two lowest excited states of the  $1\Sigma^+$  symmetry (the full CI curves are indicated by the dotted lines and other results are represented by  $\square$ ), the lowest two  $1\Pi$  states (the full CI curves are indicated by the dashed-dotted lines and other results are represented by  $\circ$ ), and the lowest  $1\Delta$  state (the full CI curve is indicated by the dashed line and other results are indicated by  $\triangle$ ). (a) A comparison of the EOMCCSD and full CI results. (b) A comparison of the CISDt and full CI results. (c) A comparison of the MMCC(2,3)/CI and full CI results.

We begin our discussion with the vertical excitation energies at the equilibrium geometry,  $R_{C-H} = R_e = 2.13713$  bohr, shown in Table 2. In this case, the doubly excited nature of the first-excited  $^1\Sigma^+$  ( $2\ ^1\Sigma^+$ ) state and of the lowest two  $^1\Delta$  states  $1\ ^1\Delta$  and  $2\ ^1\Delta$ , and the partially biexcited character of the second  $^1\Pi$  state  $2\ ^1\Pi$  (cf. Refs. [42, 43, 47, 103]) cause significant problems for the EOMCCSD approach. The errors in the EOMCCSD excitation energies for these four states, relative to the corresponding full CI values, are 0.560, 0.924, 0.856, and 0.327 eV, respectively. The CC3 method reduces these large errors to 0.219–0.318 eV, but if we want to obtain errors which are less than 0.1 eV with the standard EOMCC methodology, we must use the full EOMCCSDT approach (or its active-space EOMCCSDt variant [43, 44]). The full EOMCCSDT approach reduces the relatively large unsigned errors in the EOMCCSD results for the  $2\ ^1\Sigma^+$ ,  $1\ ^1\Delta$ ,  $2\ ^1\Delta$ , and  $2\ ^1\Pi$  states to 0.074, 0.040, 0.038, and 0.060 eV, respectively.

As shown in Table 2, the inexpensive MMCC(2,3)/CI approach is capable of providing the results of full EOMCCSDT quality. Indeed, the errors in the vertical excitation energies for the  $2\ ^1\Sigma^+$ ,  $1\ ^1\Delta$ ,  $2\ ^1\Delta$ , and  $2\ ^1\Pi$  states of  $\text{CH}^+$  that have large double excitation components, obtained with the noniterative MMCC(2,3)/CI approximation, are 0.006–0.105 eV. This should be compared to the 0.327–0.924 eV errors in the EOMCCSD results, the 0.219–0.318 eV errors obtained with the CC3 method, and the 0.504–0.882 eV errors obtained with the CISDt approach used to construct wave functions  $|\Psi_\mu\rangle$  for the MMCC(2,3)/CI calculations [47, 48]. For the remaining states shown in Table 2 (the third and fourth  $^1\Sigma^+$  states and the lowest-energy  $^1\Pi$  state), the errors in the CISDt-corrected MMCC(2,3) results, relative to full CI, are 0.000–0.015 eV. Again, the only standard EOMCC method that can compete with the MMCC(2,3)/CI approach is the expensive full EOMCCSDT approximation.

The excellent performance of the CISDt-corrected MMCC(2,3) approximation is not limited to vertical excitation energies at the equilibrium geometry. As shown in Figure 2 (c), the MMCC(2,3)/CI method is capable of providing a highly accurate description of entire excited-state potentials of  $\text{CH}^+$ . The very large (often  $> 1$  eV) errors in the EOMCCSD and CISDt results for the excited-state potential energy curves, relative to the corresponding full CI curves (cf. Figures 2 (a) and (b)) are reduced in the MMCC(2,3)/CI calculations to 0.00–0.10 eV. For example, the errors in the EOMCCSD excitation energies, relative to full CI, for the three lowest excited states of the  $^1\Sigma^+$  symmetry, the two lowest  $^1\Pi$  states, and the two lowest  $^1\Delta$  states are 0.668, 0.124, 0.256, 0.109, 0.564, 1.114, and 2.095 eV, respectively, at  $R_{C-H} = 1.5R_e$ , and 0.299, 0.532, 0.771, 0.234, 0.467, 1.178, and 3.950 eV, respectively, at  $R_{C-H} = 2R_e$  [44]. Our

MMCC(2,3)/CI method reduces these large unsigned errors to 0.072, 0.005, 0.025, 0.024, 0.059, 0.065, and 0.086 eV, respectively, at  $R_{C-H} = 1.5R_e$ , and 0.074, 0.048, 0.046, 0.045, 0.007, 0.079, and 0.029 eV, respectively, at  $R_{C-H} = 2R_e$  [47,48]. As in the  $R_{C-H} = R_e$  case, the only standard EOMCC approach that can provide the results of this high quality is the expensive full EOMCCSDT method [44]. Interestingly enough, the MMCC(2,3)/CI approximation is capable of providing the reasonably correct description of the asymptotic region of the potential energy curves of  $CH^+$ , restoring almost perfectly, for example, the degeneracy of the  $2^1\Sigma^+$ ,  $2^1\Pi$ , and  $1^1\Delta$  states in the  $R_{C-H} = \infty$  limit, which is severely broken by all EOMCC/response CC doubles models, including the standard EOM-CCSD approach (cf. Figures 2 (a) and (c); see, also, Refs. [45,47]). There is no need to reoptimize orbitals to obtain an accurate description of excited states of  $CH^+$  in the MMCC(2,3)/CI calculations (the ordinary RHF orbitals are sufficient) and the required computer effort is small. For example, the fraction of all triples used in the MMCC(2,3)/CISDt calculations discussed here was, depending of state's symmetry, 26–29 % [47,48].

The CI-corrected MMCC methods provide us with an excellent description of excited states dominated by double excitations and excited-state potentials along bond breaking coordinates, but one may think of reducing the costs of the CISDt-corrected MMCC(2,3) and similar calculations even further by replacing the CI wave functions  $|\Psi_\mu\rangle$  in the MMCC( $m_A, m_B$ ) energy expressions, Eqs. (65) and (66), by the wave functions obtained with low-order MRMBPT approaches. We have recently implemented the pilot version of one of the possible MRMBPT-corrected MMCC(2,3) approaches, referred here and elsewhere in this article to as the MMCC(2,3)/PT method [78], in which we proceed as follows: First, as in all multi-reference calculations, and in analogy to the CISDt calculations discussed above, we divide the available spin-orbitals into core, active, and virtual categories, as shown in Figure 1. By distributing active electrons among active spin-orbitals in all possible ways, we produce a certain number (designated here by  $M$ ) of reference determinants  $|\Phi_p\rangle$ , which span the complete model space or  $P$ -space  $\mathcal{M}_0$ . With the judicious choice of active spin-orbitals, we can assume that the linear combinations of reference determinants  $|\Phi_p\rangle$ ,  $p = 1, \dots, M$ ,

$$|\bar{\Psi}_\mu^{(P)}\rangle = \sum_{p=1}^M \bar{c}_{p\mu} |\Phi_p\rangle, \quad (83)$$

where the coefficients  $\bar{c}_{p\mu}$  and the corresponding eigenvalues  $\bar{E}_\mu$  are obtained by diagonalizing the Hamiltonian in the model space  $\mathcal{M}_0$ , represent reasonable zero-order approximations to the ground- and excited states

$|\Psi_\mu\rangle$  and energies  $E_\mu$  of interest. Once the model space  $\mathcal{M}_0$  is defined, we consider all singly and doubly excited determinants with respect to each reference  $|\Phi_p\rangle$ ,  $p = 1, \dots, M$ , which span the  $Q$ -space (a subspace of the orthogonal complement  $\mathcal{M}_0^\perp$ ), as is often done in multi-reference CISD calculations, and define the wave functions  $|\Psi_\mu\rangle$ , which will eventually be used to design the MMCC/PT (e.g. MMCC(2,3)/PT) energy corrections, as

$$|\Psi_\mu\rangle = \sum_{p=1}^M c_{p\mu} |\Phi_p\rangle + \sum_{q=M+1}^R c_{q\mu} |\Phi_q\rangle, \quad (84)$$

where  $|\Phi_p\rangle$ ,  $p = 1, \dots, M$ , are the reference determinants and  $|\Phi_q\rangle$ ,  $q = M+1, \dots, R$ , are the  $Q$ -space determinants, as defined above. We estimate the values of the coefficients  $c_{p\mu}$ ,  $p = 1, \dots, M$ , and  $c_{q\mu}$ ,  $q = M+1, \dots, R$ , in Eq. (84) by applying the partitioning technique to the Hamiltonian matrix in the space spanned by the  $P$ -space and  $Q$ -space determinants  $|\Phi_p\rangle$  and  $|\Phi_q\rangle$ , respectively. Thus, if  $\mathbf{C}_{P\mu}$  and  $\mathbf{C}_{Q\mu}$  are the column vectors of coefficients  $c_{p\mu}$  with  $p = 1, \dots, M$  and  $c_{q\mu}$  with  $q = M+1, \dots, R$ , respectively, and if  $\mathbf{H}_{PP}$ ,  $\mathbf{H}_{PQ}$ ,  $\mathbf{H}_{QP}$ , and  $\mathbf{H}_{QQ}$  are the corresponding  $PP$ ,  $PQ$ ,  $QP$ , and  $QQ$  blocks of the Hamiltonian, we can write the Hamiltonian eigenvalue problem for the wave functions  $|\Psi_\mu\rangle$ , Eq. (84), as follows:

$$\begin{pmatrix} \mathbf{H}_{PP} & \mathbf{H}_{PQ} \\ \mathbf{H}_{QP} & \mathbf{H}_{QQ} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{P\mu} \\ \mathbf{C}_{Q\mu} \end{pmatrix} = E_\mu \begin{pmatrix} \mathbf{C}_{P\mu} \\ \mathbf{C}_{Q\mu} \end{pmatrix}. \quad (85)$$

If we approximate the  $QQ$  block of the Hamiltonian,  $\mathbf{H}_{QQ}$ , by the diagonal matrix elements  $\langle \Phi_q | H | \Phi_q \rangle$ , we can immediately write

$$\mathbf{C}_{Q\mu} \approx (E_\mu \mathbf{1} - \mathbf{D}_Q)^{-1} \mathbf{H}_{QP} \mathbf{C}_{P\mu}, \quad (86)$$

or, more explicitly,

$$c_{q\mu} \approx \sum_{p=1}^M (E_\mu - \langle \Phi_q | H | \Phi_q \rangle)^{-1} \langle \Phi_q | H | \Phi_p \rangle c_{p\mu}, \quad (q = M+1, \dots, R), \quad (87)$$

where  $\mathbf{D}_Q$  in Eq. (86) is the diagonal part of  $\mathbf{H}_{QQ}$ . In the MRMBPT scheme used in our pilot implementation of the MMCC(2,3)/PT method [78], we obtain the approximate values of the coefficients  $c_{q\mu}$ ,  $q = M+1, \dots, R$ , by replacing the energies  $E_\mu$  and coefficients  $c_{p\mu}$ ,  $p = 1, \dots, M$ , in Eq. (87) by the zero-order energies  $\bar{E}_\mu$  and coefficients  $\bar{c}_{p\mu}$ , respectively, resulting from the diagonalization of the Hamiltonian in the model space  $\mathcal{M}_0$  (diagonalization of  $\mathbf{H}_{PP}$ ). We use the resulting approximate values of the coefficients  $c_{q\mu}$ ,

$$\bar{c}_{q\mu} = \sum_{p=1}^M (\bar{E}_\mu - \langle \Phi_q | H | \Phi_q \rangle)^{-1} \langle \Phi_q | H | \Phi_p \rangle \bar{c}_{p\mu}, \quad (q = M+1, \dots, R), \quad (88)$$

along with the coefficients  $\bar{c}_{p\mu}$  obtained by diagonalizing  $\mathbf{H}_{PP}$ , to define the wave functions

$$|\bar{\Psi}_\mu\rangle = \sum_{p=1}^M \bar{c}_{p\mu} |\Phi_p\rangle + \sum_{q=M+1}^R \bar{c}_{q\mu} |\Phi_q\rangle, \quad (89)$$

which can be used instead of the wave functions  $|\Psi_\mu\rangle$  in the MMCC( $m_A, m_B$ ) energy expressions, Eqs. (65) and (66), to define the MMCC( $m_A, m_B$ )/PT approximations.

In the specific case of the MMCC(2,3)/PT approximation, we go one step further and, after rewriting each  $|\bar{\Psi}_\mu\rangle$ , Eq. (89), in the form of the CI expansion relative to the reference determinant  $|\Phi\rangle$  used in the CCSD and EOMCCSD calculations whose results we want to improve,

$$|\bar{\Psi}_\mu\rangle = (\bar{C}_{\mu,0} + \bar{C}_{\mu,1} + \bar{C}_{\mu,2} + \bar{C}_{\mu,3} + \cdots)|\Phi\rangle, \quad (90)$$

where

$$\bar{C}_{\mu,0} = \bar{c}_0(\mu) \mathbf{1}, \quad (91)$$

$$\bar{C}_{\mu,1}|\Phi\rangle = \bar{c}_a^i(\mu) a^a a_i = \sum_{i,a} \bar{c}_a^i(\mu) a^a a_i, \quad (92)$$

$$\bar{C}_{\mu,2} = \frac{1}{4} \bar{c}_{ab}^{ij}(\mu) a^a a^b a_j a_i = \sum_{i<j, a<b} \bar{c}_{ab}^{ij}(\mu) a^a a^b a_j a_i, \quad (93)$$

and

$$\bar{C}_{\mu,3} = \frac{1}{36} \bar{c}_{abc}^{ijk}(\mu) a^a a^b a^c a_k a_j a_i = \sum_{i<j<k, a<b<c} \bar{c}_{abc}^{ijk}(\mu) a^a a^b a^c a_k a_j a_i \quad (94)$$

are the corresponding particle-hole excitation operators relative to  $|\Phi\rangle$  defining the reference, singly excited, doubly excited, and triply excited contributions to  $|\bar{\Psi}_\mu\rangle$ , we truncate the CI expansion for the MRMBPT wave function  $|\bar{\Psi}_\mu\rangle$ , Eq. (90), at triply excited determinants (the  $\bar{C}_{\mu,3}|\Phi\rangle$  term). As a result, the final energy formula for the MMCC(2,3)/PT energy, obtained by replacing  $|\Psi_\mu\rangle$  in Eq. (67) by  $|\bar{\Psi}_\mu\rangle$ , Eq. (90), truncated at triply excited determinants relative to  $|\Phi\rangle$ , is

$$E_\mu^{(\text{MMCC/PT})}(2,3) = E_\mu^{(\text{EOMCCSD})} + \sum_{i<j<k, a<b<c} [\bar{c}_{abc}^{ijk}(\mu)]^* \mathfrak{M}_{\mu,abc}^{ijk}(2) / \bar{D}_\mu, \quad (95)$$

where the triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  are defined by Eqs. (58) and (59) (and calculated using Eq. (60)), and

$$\bar{D}_\mu \equiv \langle \bar{\Psi}_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle = \bar{\Delta}_{\mu,0} + \bar{\Delta}_{\mu,1} + \bar{\Delta}_{\mu,2} + \bar{\Delta}_{\mu,3} \quad (96)$$

is the overlap denominator  $\langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T(\text{CCSD})} | \Phi \rangle$  entering Eq. (67), written for the wave function  $|\Psi_\mu\rangle = |\bar{\Psi}_\mu\rangle$ , Eq. (90), truncated at triples. The  $\bar{\Delta}_{\mu,0}$ ,  $\bar{\Delta}_{\mu,1}$ ,  $\bar{\Delta}_{\mu,2}$ , and  $\bar{\Delta}_{\mu,3}$  contributions to the denominator  $\bar{D}_\mu$ , Eq. (96), are calculated as

$$\bar{\Delta}_{\mu,0} = [\bar{c}_0(\mu)]^* r_0(\mu), \quad (97)$$

$$\bar{\Delta}_{\mu,1} = \sum_{i,a} [\bar{c}_a^i(\mu)]^* \beta_a^i(\mu), \quad (98)$$

$$\bar{\Delta}_{\mu,2} = \sum_{i<j, a<b} [\bar{c}_{ab}^{ij}(\mu)]^* \beta_{ab}^{ij}(\mu), \quad (99)$$

and

$$\bar{\Delta}_{\mu,3} = \sum_{i<j<k, a<b<c} [\bar{c}_{abc}^{ijk}(\mu)]^* \beta_{abc}^{ijk}(\mu), \quad (100)$$

where  $\bar{c}_0(\mu)$ ,  $\bar{c}_a^i(\mu)$ ,  $\bar{c}_{ab}^{ij}(\mu)$ , and  $\bar{c}_{abc}^{ijk}(\mu)$  are the CI coefficients obtained by rewriting the MRMBPT wave function,  $|\bar{\Psi}_\mu\rangle$ , Eq. (89), in the single-reference CI form of Eq. (90), and  $r_0(\mu)$ ,  $\beta_a^i(\mu)$ ,  $\beta_{ab}^{ij}(\mu)$ , and  $\beta_{abc}^{ijk}(\mu)$  are the coefficients at the reference determinant  $|\Phi\rangle$  and singly, doubly, and triply excited determinants,  $|\Phi_i^a\rangle$ ,  $|\Phi_{ij}^{ab}\rangle$ , and  $|\Phi_{ijk}^{abc}\rangle$  respectively, in the CI expansion of the CCSD/EOMCCSD wave function  $R_\mu^{(\text{CCSD})} e^{T(\text{CCSD})} |\Phi\rangle$  (for the formulas for the coefficients  $\beta_a^i(\mu)$ ,  $\beta_{ab}^{ij}(\mu)$ , and  $\beta_{abc}^{ijk}(\mu)$ , see Eqs. (80)–(82), respectively). Although the summations over  $i, j, k, a, b, c$  in Eqs. (95) and (100) have the form of the complete summations over triples, in reality the wave functions  $|\bar{\Psi}_\mu\rangle$ , Eq. (89), contain only a small subset of all triples, once we rewrite each  $|\bar{\Psi}_\mu\rangle$  in the form of the single-reference CI expansion, Eq. (90). This is a consequence of using active orbitals in designing the model space  $\mathcal{M}_0$ , which limit triple excitations relative to the reference  $|\Phi\rangle$  to a small class of triple excitations that carry a certain number of active spin-orbital indices. Although the actual number of triples in  $|\bar{\Psi}_\mu\rangle$  depends on the dimension of the active space used in the MRMBPT calculations, in analogy to the MMCC(2,3)/CI calculations, we only need a subset of all triexcited coefficients  $\beta_{abc}^{ijk}(\mu)$ , Eq. (82), and a subset of triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , Eqs. (58)–(60), which match the nonzero coefficients  $\bar{c}_{abc}^{ijk}(\mu)$ , to calculate the MMCC(2,3)/PT energy, Eq. (95). Again, as in the MMCC(2,3)/CI case, one can easily extend the above MMCC(2,3)/PT approximation to higher-order MRMBPT-corrected MMCC( $m_A, m_B$ ) schemes, such as the MMCC(2,4)/PT approach which describes the combined effect of selected triple and quadruple excitations introduced by the MRMBPT wave functions [78].

One of the main advantages of the MRMBPT-corrected MMCC schemes, such as MMCC(2,3)/PT, is their low cost, compared to the already rather



inexpensive CI-corrected MMCC methods. As in the case of the CI-corrected MMCC approaches, such as MMCC(2,3)/CI, in the MMCC(2,3)/PT method and other MRMBPT-corrected MMCC approximations we have a very good control of accuracy through active orbitals defining model space  $\mathcal{M}_0$ , which can always be adjusted to the excited states or the bond breaking problem of interest, but unlike in the MMCC/CI schemes, we do not have to solve the iterative CISDt or other CI-like equations to generate the wave functions  $|\Psi_\mu\rangle$  that enter the corrections  $\delta_\mu(m_A, m_B)$  of the MRMBPT-corrected MMCC theories. We calculate the relevant CI-like coefficients, such as  $\bar{c}_0(\mu)$ ,  $\bar{c}_a^i(\mu)$ ,  $\bar{c}_{ab}^{ij}(\mu)$ , and  $\bar{c}_{abc}^{ijk}(\mu)$ , by converting the relatively simple expressions that define the MRMBPT wave functions  $|\bar{\Psi}_\mu\rangle$ , Eq. (89), into the single-reference CI form defined by Eq. (90). Thus, the main computer effort goes into the calculations of a small subset of triexcited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , leading to the significant reduction of the  $n_o^3 n_u^4$  steps that are normally needed to calculate all moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ .

We illustrate the performance of the MMCC(2,3)/PT approach using selected excited states of the  $\text{CH}^+$  ion, as described by the  $[5s3p1d/3s1p]$  basis set of Ref. [103] (see Table 2). As in the case of the MMCC(2,3)/CI approach, we compare the MMCC(2,3)/PT results with the full CI vertical excitation energies at the equilibrium geometry  $R_{\text{C-H}} = R_e = 2.13713$  bohr, reported in Ref. [103], and the corresponding EOMCCSD, EOMCCSDT, and CC3 results reported in Refs. [39, 44]. In calculating the MRMBPT wave functions  $|\bar{\Psi}_\mu\rangle$ , Eqs. (89) and (90), we used the same small set of active orbitals consisting of the  $3\sigma$ ,  $1\pi_x \equiv 1\pi$ ,  $1\pi_y \equiv 2\pi$ , and  $4\sigma$  orbitals as employed in the MMCC(2,3)/CI calculations.

As shown in Table 2, the inexpensive MMCC(2,3)/PT approach is capable of providing the results which are practically as good as the excellent MMCC(2,3)/CI results. In the case of the  $2^1\Sigma^+$  and  $1^1\Delta$  states, which have a strong double excitation character, causing the EOMCCSD approach to fail, the MMCC(2,3)/PT corrections to CCSD/EOMCCSD energies produce the results of the EOMCCSDT quality, reducing the 0.560 and 0.924 eV errors in the EOMCCSD results to 0.102 and 0.090 eV, respectively. For these two states, the errors relative to full CI obtained with the noniterative MMCC(2,3)/PT approach are 2–3 times smaller than the errors obtained with the much more expensive and iterative CC3 method. For states such as  $2^1\Pi$ , which have a partially biexcited character, and for states dominated by single excitations ( $3^1\Sigma^+$ ,  $1^1\Pi$ ), the MMCC(2,3)/PT results are as good as the CC3 results. Although in this pilot study, we could not find the MRMBPT wave functions that would have a significant overlap with the EOMCCSD wave functions for the higher-energy  $4^1\Sigma^+$  and  $2^1\Delta$  states,

so that we could not obtain the complete set of MMCC(2,3)/PT energies, we can conclude that the MMCC(2,3)/PT method is as accurate as the MMCC(2,3)/CI approximation. This is good news, since MMCC(2,3)/PT calculations are less expensive than MMCC(2,3)/CI calculations, as explained above. We have, in fact, the preliminary results for the excitation energies corresponding to stretched geometries of the  $\text{CH}^+$  ion [78]. For example, the MMCC(2,3)/PT approach reduces the large, 0.299, 0.532, 0.234, 0.467, and 1.178 eV errors in the EOMCCSD results for the  $2^1\Sigma^+$ ,  $3^1\Sigma^+$ ,  $1^1\Pi$ ,  $2^1\Pi$ , and  $1^1\Delta$  states at  $R_{\text{C-H}} = 2R_e$  to  $-0.079$ ,  $-0.021$ ,  $0.133$ ,  $-0.123$ , and  $0.005$  eV, respectively. The MMCC(2,3)/CI approach offers a very similar error reduction, but we need to solve the iterative CISDt equations to obtain the wave functions  $|\Psi_\mu^{(\text{CISDt})}\rangle$ , Eq. (69), to calculate the MMCC(2,3)/CI corrections. This is not needed in the MMCC(2,3)/PT calculations, which rely on the less expensive MRMBPT-like wave functions  $|\bar{\Psi}_\mu\rangle$ , Eq. (89), in the process of constructing the  $\delta_\mu(2,3)$  corrections to the CCSD/EOMCCSD energies.

The CI- and MRMBPT-corrected MMCC approximations lead to significant improvements of the EOMCC excitation energies by constructing corrections  $\delta_\mu(m_A, m_B)$  with the help of the wave functions  $|\Psi_\mu\rangle$  obtained in the non-CC calculations that provide a reasonable, qualitatively correct description of the ground and excited states of interest. The question arises if we can achieve the same goal and similar accuracies by designing the MMCC corrections  $\delta_\mu(m_A, m_B)$  using nothing else than the cluster and excitation operators obtained in the CC/EOMCC calculations. This question is addressed in the next subsection.

### 3.1.2. The CR-EOMCCSD(T) approach: The “black-box” MMCC method for molecular excited states

An interesting alternative to the externally corrected MMCC methods, discussed in Section 3.1.1, is offered by the CR-EOMCCSD(T) approach [49, 51, 52, 59]. The CR-EOMCCSD(T) method can be viewed as an extension of the ground-state CR-CCSD(T) approach of Refs. [61, 62], which overcomes the failures of the standard CCSD(T) approximations when diradicals [76, 104, 105] and potential energy surfaces involving single bond breaking and single bond insertion [49, 50, 52, 60–62, 65, 67, 69, 70, 72, 73] are examined, to excited states.

The CR-EOMCCSD(T) approach is a purely single-reference, “black-box” method based on the MMCC(2,3) approximation, in which the wave function  $|\Psi_\mu\rangle$  entering Eq. (67) is designed by using the singly and doubly excited cluster amplitudes  $t_a^i$  and  $t_{ab}^{ij}$ , defining  $T_1$  and  $T_2$ , respectively, obtained in the CCSD calculations, and the zero-, one- and two-body amplitudes  $r_0(\mu)$ ,  $r_a^i(\mu)$  and  $r_{ab}^{ij}(\mu)$ , defining  $R_{\mu,0}$ ,  $R_{\mu,1}$ , and  $R_{\mu,2}$ , respectively,

obtained in the EOMCCSD calculations. As with all MMCC(2,3) methods, the CR-EOMCCSD(T) approach enables us to correct the results of the CCSD/EOMCCSD calculations through noniterative energy corrections due to triples.

The wave functions  $|\Psi_\mu\rangle$  that are used to design triples corrections of the CR-EOMCCSD(T) theory are obtained by analyzing the EOMCCSDT eigenvalue problem, in which the most expensive triples-triples block of the CCSDT/EOMCCSDT similarity-transformed Hamiltonian matrix is approximated by its diagonal and in which the  $T_3$  cluster contributions to matrix elements of the CCSDT/EOMCCSDT similarity-transformed Hamiltonian are neglected. Depending on additional approximations in the resulting wave functions  $|\Psi_\mu\rangle$ , we can propose several variants of the CR-EOMCCSD(T) theory [51, 52]. In the following, we focus on variant ID (the CR-EOMCCSD(T),ID method), which represents one of the most complete versions of the CR-EOMCCSD(T) approach and which often provides the most accurate description of excited states when compared to the remaining CR-EOMCCSD(T) approximations [51–53]. Since we discuss here only one variant of the CR-EOMCCSD(T) theory, namely, the CR-EOMCCSD(T),ID method, we drop “ID” from the acronym CR-EOMCCSD(T),ID, remembering that from now on CR-EOMCCSD(T) will stand in this paper for the CR-EOMCCSD(T),ID approach. In the CR-EOMCCSD(T)  $\equiv$  CR-EOMCCSD(T),ID method, the wave function  $|\Psi_\mu\rangle$  that enters Eq. (67), designated as  $|\Psi_\mu^{(\text{CR-EOMCCSD(T)})}\rangle$ , is defined as follows [51, 52, 59]:

$$\begin{aligned} |\Psi_\mu^{(\text{CR-EOMCCSD(T)})}\rangle &= \bar{P}(R_{\mu,0} + R_{\mu,1} + R_{\mu,2} + \tilde{R}_{\mu,3})e^{T_1+T_2}|\Phi\rangle \\ &= \{R_{\mu,0} + (R_{\mu,1} + R_{\mu,0}T_1) \\ &\quad + [R_{\mu,2} + R_{\mu,1}T_1 + R_{\mu,0}(T_2 + \tfrac{1}{2}T_1^2)] \\ &\quad + [\tilde{R}_{\mu,3} + R_{\mu,2}T_1 + R_{\mu,1}(T_2 + \tfrac{1}{2}T_1^2) \\ &\quad + R_{\mu,0}(T_1T_2 + \tfrac{1}{6}T_1^3)]\}|\Phi\rangle, \end{aligned} \quad (101)$$

where  $\bar{P}$  is a projection operator on the subspace spanned by the reference  $|\Phi\rangle$  and all singly, doubly, and triply excited determinants. The triple excitation operator  $\tilde{R}_{\mu,3}$ , entering Eq. (101), is calculated as

$$\tilde{R}_{\mu,3} = \frac{1}{36} \tilde{r}_{abc}^{ijk}(\mu) a^a a^b a^c a_k a_j a_i, \quad (102)$$

where

$$\tilde{r}_{abc}^{ijk}(\mu) = \mathfrak{M}_{\mu,abc}^{ijk}(2)/D_{\mu,abc}^{ijk} \quad (103)$$

are the approximate values of the triple excitation amplitudes  $r_{abc}^{ijk}(\mu)$  resulting from the analysis of the full EOMCCSDT eigenvalue problem [51]. As

one can see, we calculate the approximate amplitudes  $\tilde{r}_{abc}^{ijk}(\mu)$  using exactly the same set of triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  of the CCSD/EOMCCSD equations that enters the MMCC(2,3) energy expression, Eq. (67). The  $D_{\mu,abc}^{ijk}$  quantities that enter Eq. (103) represent the perturbative denominators for triple excitations, which are defined as follows [51, 52, 59]:

$$\begin{aligned} D_{\mu,abc}^{ijk} &= E_{\mu}^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \\ &= \omega_{\mu}^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}_1^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \\ &\quad - \langle \Phi_{ijk}^{abc} | \bar{H}_2^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \\ &\quad - \langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle, \end{aligned} \quad (104)$$

where  $\bar{H}_p^{(\text{CCSD})}$ ,  $p = 1 - 3$ , are the one-, two-, and three-body components of the CCSD/EOMCCSD similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$ , respectively, and  $\omega_{\mu}^{(\text{CCSD})}$  is the EOMCCSD vertical excitation energy.

The use of the diagonal elements of the triples-triples block of the  $\bar{H}^{(\text{CCSD})}$  matrix rather than the more usual MBPT-like differences of bare spin-orbital energies ( $\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k$ ) in the definition of the denominators  $D_{\mu,abc}^{ijk}$ , which are needed to define the approximate triexcited amplitudes  $\tilde{r}_{abc}^{ijk}(\mu)$ , has a positive effect on the overall accuracies of the CR-EOMCCSD(T) calculations, while facilitating the open-shell implementation of the CR-EOMCCSD(T) method employing the restricted open-shell Hartree-Fock (ROHF) orbitals [59]. Indeed, the use of spin-orbital energy differences ( $\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k$ ) instead of the complete form of the diagonal matrix elements of  $\bar{H}^{(\text{CCSD})}$  involving triply excited determinants to define the denominator  $D_{\mu,abc}^{ijk}$ , Eq. (104), would lead to formal and practical difficulties related to the choice of the unperturbed Hamiltonian to define orbital energies because of the presence of the off-diagonal matrix elements in the spin-orbital form of the Fock matrix written for the ROHF orbitals (see Refs. [54, 85, 86, 106] for a discussion of serious problems that appear in the ROHF-based implementations of the CCSD(T) and CC3 methods). The use of the complete form of triexcited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , as defined by Eqs. (58)–(60), and the use of the complete form of the denominator  $D_{\mu,abc}^{ijk}$ , Eq. (104), in which all terms resulting from  $\langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$  are retained, as is done in the CR-EOMCCSD(T) approach discussed here, enables us to avoid these problems, which complicate the ROHF-based implementations of the CCSD(T) [85, 86, 106] and CC3 [54] methods, since we never have to worry about what terms in the Hamiltonian should be regarded as the zero-order terms to calculate the approximate triple excitation operator  $\tilde{R}_{\mu,3}$ , Eq. (102). This is one of the many advantages of the

MMCC-based CR-EOMCCSD(T) theory over the conventional treatment of triple excitations, such as CCSD(T) and CC3.

The above equations enable us to calculate the CR-EOMCCSD(T) energies by replacing  $|\Psi_\mu\rangle$  in Eq. (67) by  $|\Psi_\mu^{(\text{CR-EOMCCSD(T)})}\rangle$ , Eq. (101). The resulting energy formula,

$$E_\mu^{(\text{CR-EOMCCSD(T)})} = E_\mu^{(\text{CCSD})} + \langle \Psi_\mu^{(\text{CR-EOMCCSD(T)})} | M_{\mu,3}(2) | \Phi \rangle / \langle \Psi_\mu^{(\text{CR-EOMCCSD(T)})} | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle, \quad (105)$$

applies to ground and excited states (ground states when  $\mu = 0$  and excited states when  $\mu > 0$ ). In particular, we obtain the ground-state CR-EOMCCSD(T) energies by replacing  $R_{\mu,0}$ ,  $R_{\mu,1}$ , and  $R_{\mu,2}$  in Eq. (101) by  $\mathbf{1}$ ,  $0$ , and  $0$ , respectively, and  $\tilde{R}_{\mu,3}$ , Eq. (102), by  $\tilde{R}_{0,3} = \frac{1}{36} \tilde{r}_{abc}^{ijk}(0) a^a a^b a^c a_k a_j a_i$ , where  $\tilde{r}_{abc}^{ijk}(0) = \mathfrak{M}_{abc}^{ijk}(2)/D_{0,abc}^{ijk}$ , with  $\mathfrak{M}_{abc}^{ijk}(2)$  representing the triply excited moments of the CCSD equations, Eq. (59), and  $D_{0,abc}^{ijk}$  given by Eq. (104) in which  $\mu = 0$  and  $\omega_0^{(\text{CCSD})} = 0$ . The state-selective nature of the CR-EOMCCSD(T) method, in which the ground- and excited-state energies are obtained in separate, yet related, calculations using Eq. (105) and wave functions  $|\Psi_\mu^{(\text{CR-EOMCCSD(T)})}\rangle$  that result from the analysis of the EOMCCSDT equations including the ground-state problem, leads to a much better balance between the energies of ground and excited states compared to the standard EOMCCSD(T), EOMCCSD( $\tilde{T}$ ), EOMCCSD(T') [35, 36], and CCSDR(3) [40, 41] calculations [51, 52]. In the standard approaches of the EOMCCSD(T) type, one focuses on directly improving the EOMCCSD vertical excitation energies and this leads to large discrepancies between the accuracies of the excited-state energies obtained from the EOMCCSD(T), EOMCCSD( $\tilde{T}$ ), EOMCCSD(T'), and CCSDR(3) calculations and the ground-state energies calculated with the CCSD or CCSD(T) approaches (see Ref. [51] for a detailed discussion). Moreover, as shown, for example, in Refs. [51, 58], the standard noniterative methods of the EOMCCSD(T) type and their iterative analogs of the EOMCCSDT- $n$  or CC3 type cannot be used to study excited-state potentials along bond breaking coordinates. As shown below, the CR-EOMCCSD(T) method is more robust in this regard, allowing one to explore large fragments of excited-state potential energy surfaces, even when the ground state is characterized by a large degree of nondynamic correlation.

The above Eq. (105) is a general expression. Let us briefly discuss the more explicit formulas for the CR-EOMCCSD(T) energies  $E_\mu^{(\text{CR-EOMCCSD(T)})}$ . In the most efficient implementations of the CR-EOMCCSD(T) approach reported in Refs. [51, 59], we rewrite Eq. (105)

as follows [59]:

$$E_{\mu}^{(\text{CR-EOMCCSD(T)})} = E_{\mu}^{(\text{CCSD})} + N_{\mu}^{\text{CR(T)}} / D_{\mu}^{\text{CR(T)}}, \quad (106)$$

where

$$N_{\mu}^{\text{CR(T)}} = \sum_{i < j < k, a < b < c} [\gamma_{abc}^{ijk}(\mu)]^* \mathfrak{M}_{\mu,abc}^{ijk}(2) \quad (107)$$

and

$$D_{\mu}^{\text{CR(T)}} = \Delta_{\mu,0}^{\text{CR(T)}} + \Delta_{\mu,1}^{\text{CR(T)}} + \Delta_{\mu,2}^{\text{CR(T)}} + \Delta_{\mu,3}^{\text{CR(T)}} \quad (108)$$

are the numerator ( $\langle \Psi_{\mu}^{(\text{CR-EOMCCSD(T)})} | M_{\mu,3}(2) | \Phi \rangle$ ) and denominator ( $\langle \Psi_{\mu}^{(\text{CR-EOMCCSD(T)})} | R_{\mu}^{(\text{CCSD})} e^{T(\text{CCSD})} | \Phi \rangle$ ) terms appearing in Eq. (105). As already explained, the triply excited moments of the CCSD/EOMCCSD equations,  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , are most efficiently calculated with the help of Eq. (60). The  $\gamma_{abc}^{ijk}(\mu)$  amplitudes that enter the numerator term  $N_{\mu}^{\text{CR(T)}}$ , Eq. (107), represent the coefficients at the triply excited determinants  $|\Phi_{ijk}^{abc}\rangle$  in the CI expansion of  $|\Psi_{\mu}^{(\text{CR-EOMCCSD(T)})}\rangle$ ,

$$\gamma_{abc}^{ijk}(\mu) = \langle \Phi_{ijk}^{abc} | \Psi_{\mu}^{(\text{CR-EOMCCSD(T)})} \rangle = \tilde{r}_{abc}^{ijk}(\mu) + \beta_{abc}^{ijk}(\mu), \quad (109)$$

where  $\tilde{r}_{abc}^{ijk}(\mu)$  and  $\beta_{abc}^{ijk}(\mu)$  are given by Eqs. (103) and (82), respectively. The  $\Delta_{\mu,0}^{\text{CR(T)}}$ ,  $\Delta_{\mu,1}^{\text{CR(T)}}$ ,  $\Delta_{\mu,2}^{\text{CR(T)}}$ , and  $\Delta_{\mu,3}^{\text{CR(T)}}$  terms that contribute to the denominator  $D_{\mu}^{\text{CR(T)}}$ , Eq. (108), are defined as

$$\Delta_{\mu,0}^{\text{CR(T)}} = |r_0(\mu)|^2, \quad (110)$$

$$\Delta_{\mu,1}^{\text{CR(T)}} = \sum_{i,a} |\beta_a^i(\mu)|^2, \quad (111)$$

$$\Delta_{\mu,2}^{\text{CR(T)}} = \sum_{i < j, a < b} |\beta_{ab}^{ij}(\mu)|^2, \quad (112)$$

and

$$\Delta_{\mu,3}^{\text{CR(T)}} = \sum_{i < j < k, a < b < c} [\gamma_{abc}^{ijk}(\mu)]^* \beta_{abc}^{ijk}(\mu), \quad (113)$$

where  $r_0(\mu)$ ,  $\beta_a^i(\mu)$ , and  $\beta_{ab}^{ij}(\mu)$  are the coefficients at the reference determinant  $|\Phi\rangle$  and singly and doubly excited determinants,  $|\Phi_i^a\rangle$  and  $|\Phi_{ij}^{ab}\rangle$ , respectively, in the CI expansion of the CCSD or EOMCCSD wave functions  $R_{\mu}^{(\text{CCSD})} e^{T(\text{CCSD})} |\Phi\rangle$  (for the formulas for  $\beta_a^i(\mu)$  and  $\beta_{ab}^{ij}(\mu)$ , see Eqs. (80) and (81), respectively). The key elements of the algorithm that leads

to the highly efficient general-purpose computer implementation of the CR-EOMCCSD(T) approach, based on Eq. (106), are shown in Figure 3. As one can read from Figure 3, we calculate moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  “on the fly” in the explicit loop over  $i < j < k$  and there is no explicit loop over  $a < b < c$ . Instead, we calculate the entire set of moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  corresponding to all values of  $a, b, c$  and fixed values of indices  $i, j, k$  from the  $i < j < k$  loop, which are stored in a relatively small array of dimension  $n_u^3$ . This is done to achieve a high efficiency of the resulting CR-EOMCCSD(T) code. Indeed, we could choose an alternative coding strategy and calculate moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  for  $i < j < k$  and  $a < b < c$  only, but this would have to be done at the expense of the high degree of vectorization characterizing Eq. (60) and the algorithm shown in Figure 3, which significantly benefits from the use of fast matrix multiplication routines from the BLAS library in determining  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ . For example, if we used the explicit  $i < j < k$  and  $a < b < c$  loops, the calculation of the  $\frac{1}{2}\bar{h}_{ab}^{ie}r_{ec}^{jk}$  term in Eq. (60), which is one of the terms that defines the  $n_o^3n_u^4$  scaling of the CR-EOMCCSD(T) theory, would split into a very large number of  $\sim \frac{1}{36}n_o^3n_u^3$  very short matrix multiplications, each involving the summation over a single index  $e$  only. Each of these matrix multiplications is fast, but we would have to repeat them as many times as the number of elements in the  $i < j < k$  and  $a < b < c$  loops and this would result in a much slower code. By having the explicit loop over  $i < j < k$  only, the summation over  $e$  for the entire set of all  $a, b, c$  values entering the  $\bar{h}_{ab}^{ie}r_{ec}^{jk}$  term is performed with a single call to the BLAS matrix multiplication routine, which is a much more efficient use of fast matrix multipliers. At the same time, by calculating moments  $\mathfrak{M}_{K,abc}^{ijk}(2)$  in the explicit loop over  $i < j < k$ , we keep the memory requirements at the relatively low level that does not exceed  $n_u^3$  words when we execute Eq. (60). As a result, the memory requirements of the CR-EOMCCSD(T) calculations are defined by the  $t_{ae}^{im}\bar{h}_{mb}^{ec}$ ,  $-t_{be}^{im}v_{ma}^{ec}$ , and  $-\bar{h}_{bm}^{ec}r_{ae}^{im}$  terms that enter the definitions of  $\bar{h}_{ab}^{ic}$  and  $I_{ab}^{ic}$  in Table 1. These memory requirements are  $2n_on_u^3$  words. The calculation of moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  in the explicit loop over  $i < j < k$  and for all values of  $a, b, c$  to achieve a high degree of vectorization creates an impression that the operation count in our algorithm is artificially increased by a factor of 6, compared to the use of the explicit  $i < j < k$  and  $a < b < c$  loops, but this is a false impression. To avoid over-computing, which the calculation involving all  $a, b, c$  values seems to imply, while enhancing, at the same time, the performance through a highly efficient use of the BLAS matrix multiplication routines, instead of enforcing the correct symmetry of  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  with respect to permutations of indices  $a, b, c$  during the determination of  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , we first calculate the nonsym-



metric quantity  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  for the given  $i, j, k$  values from the  $i < j < k$  loop and for all  $a, b, c$  values (see Eq. (60)). Once this is done, we have at our disposal all of the relevant  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  values that are needed to construct the final  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  moment, which is obtained by simply adding the six values of  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  that correspond to six permutations of indices  $a, b, c$ , with the appropriate permutation signs, as in the definition of the antisymmetrizer  $\mathcal{A}_{abc}$ , Eq. (61). In other words, the antisymmetrization over  $a, b, c$  is done at the very end, once all six numerical values of  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  that correspond to six permutations of indices  $a, b, c$  are determined.

By following the algorithm described in Figure 3 and by using the idea of recursively generated intermediates in the calculation of the triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  (cf. Eq. (60) and Table 1) and the CR-EOMCCSD(T) corrections  $\delta_{\mu}^{\text{CR(T)}} = N_{\mu}^{\text{CR(T)}}/D_{\mu}^{\text{CR(T)}}$  to CCSD/EOMCCSD energies, we achieve a very high degree of efficiency of the CR-EOMCCSD(T) computer codes. In particular, the most expensive steps of the CR-EOMCCSD(T) codes based on the algorithm described in Figure 3 scale as  $n_o^2 n_u^4$  in the iterative CCSD and EOMCCSD parts and  $n_o^3 n_u^4$  in the noniterative part associated with the determination of the CR-EOMCCSD(T) corrections  $\delta_{\mu}^{\text{CR(T)}}$ . Specifically, the CPU time required to calculate the triples correction  $\delta_{\mu}^{\text{CR(T)}}$  for a given excited state is twice or three times the CPU time required to calculate the standard (T) correction of the ground-state CCSD(T) method (for the ground state, the timings of CR-EOMCCSD(T) and CCSD(T) calculations are essentially the same). For comparison, the full EOMCCSDT approach involves a lot more expensive and iterative  $n_o^3 n_u^5$  steps. The CC3 method, with its iterative  $n_o^3 n_u^4$  steps, is less time-consuming compared to EOMCCSDT, but the need to perform iterative  $\mathcal{N}^7$ -like calculations makes the CC3 approach considerably more expensive than the CR-EOMCCSD(T) method. At the same time, as shown in Table 2, the CR-EOMCCSD(T) results are more accurate than the corresponding CC3 results. In fact, they are almost as good as the results of full EOMCCSDT calculations (see Tables 2 and 3; see Refs. [49, 51, 52] for other examples).

Let us, therefore, illustrate the performance of the CR-EOMCCSD(T) approach by a few examples of benchmark calculations (for the realistic applications of the CR-EOMCCSD(T) approach, see, for example, Refs. [51, 52, 64]). As in the case of the MMCC(2,3)/CI and MMCC(2,3)/PT methods, we begin our discussion with the electronic excitations in the  $\text{CH}^+$  ion, as described by the  $[5s3p1d/3s1p]$  basis set of Ref. [103] (see Table 2). A comparison of the vertical excitation energies, corresponding to the three lowest-energy excited states of the  $^1\Sigma^+$  symmetry and two lowest-energy states of the  $^1\Pi$  and  $^1\Delta$  symmetries, obtained at the equilibrium geometry



Solve the CCSD/EOMCCSD equations

LOOP OVER  $\mu$

Compute the CCSD/EOMCCSD total energy  $E_\mu^{(\text{CCSD})}$

Compute  $\Delta_{\mu,0}^{\text{CR(T)}}$ ,  $\Delta_{\mu,1}^{\text{CR(T)}}$ , and  $\Delta_{\mu,2}^{\text{CR(T)}}$ , Eqs. (110)–(112), respectively

DENOM =  $\Delta_{\mu,0}^{\text{CR(T)}} + \Delta_{\mu,1}^{\text{CR(T)}} + \Delta_{\mu,2}^{\text{CR(T)}}$

SUM = 0.0

LOOP OVER  $i < j < k$

Calculate  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  for all values of  $a, b, c$  using Eq. (60)

Calculate  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  by antisymmetrizing  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$ , as in Eq. (60)

LOOP OVER  $a < b < c$

Calculate  $D_{\mu,abc}^{ijk}$ , Eq. (104)

Calculate  $\tilde{r}_{abc}^{ijk}(\mu)$ , Eq. (103)

Calculate  $\beta_{abc}^{ijk}(\mu)$ , Eq. (82)

Calculate  $\gamma_{abc}^{ijk}(\mu)$ , Eq. (109)

SUM = SUM +  $\gamma_{abc}^{ijk}(\mu) * \mathfrak{M}_{\mu,abc}^{ijk}(2)$

DENOM = DENOM +  $\gamma_{abc}^{ijk}(\mu) * \beta_{abc}^{ijk}(\mu)$

END OF LOOP OVER  $a < b < c$

END OF LOOP OVER  $i < j < k$

CORR = SUM/DENOM

$E_\mu^{(\text{CR-EOMCCSD(T)})} = E_\mu^{(\text{CCSD})} + \text{CORR}$

END OF LOOP OVER  $\mu$

Figure 3. The key elements of the algorithm used to calculate the CR-EOMCCSD(T) energy, Eq. (106).

$R_{\text{C-H}} = R_e = 2.13713$  bohr with the CR-EOMCCSD(T) approach, with the analogous results obtained in the EOMCCSD, CC3, EOMCCSDT, and full CI calculations reported in Refs. [39, 44, 103] is given in Table 2. As one can see, the relatively inexpensive CR-EOMCCSD(T) method, which has the ease-of-use of the standard ground-state CCSD(T) approach, pro-

vides the results of the EOMCCSDT quality, particularly for the  $2^1\Sigma^+$ ,  $1^1\Delta$ , and  $2^1\Delta$  states that are dominated by double excitations, for which the standard EOMCCSD approach fails. Indeed, the CR-EOMCCSD(T) approach reduces the 0.560, 0.924, and 0.856 eV errors obtained with the EOMCCSD method for the  $2^1\Sigma^+$ ,  $1^1\Delta$ , and  $2^1\Delta$  states of  $\text{CH}^+$  to 0.117, 0.027, and  $-0.002$  eV, respectively. In fact, the CR-EOMCCSD(T) results for the  $2^1\Sigma^+$ ,  $1^1\Delta$ , and  $2^1\Delta$  states are considerably better than the results of the iterative triples CC3 calculations, which give 0.230–0.318 eV errors in this case. Similar remarks apply to the  $2^1\Pi$  state, which has a partially biexcited character (see Table 2). For the remaining three states that are dominated by singles (the  $3^1\Sigma^+$ ,  $4^1\Sigma^+$ , and  $1^1\Pi$  states), the CR-EOMCCSD(T) method improves the relatively good EOMCCSD results, reducing the 0.031–0.099 eV errors obtained with the EOMCCSD approach to 0.007–0.025 eV, which is more or less the same level of accuracy as observed in the CC3 calculations. The overall accuracy of the CR-EOMCCSD(T) approach, which is a relatively inexpensive “black-box” method, is as good as the accuracy of the MMCC(2,3)/CI approximation, which requires choosing active orbitals and performing additional CISDt calculations.

As shown in Refs. [51, 52], the excellent performance of the CR-EOMCCSD(T) approach is not limited to the equilibrium geometry. For example, the CR-EOMCCSD(T) method is capable of reducing the large unsigned errors of 0.299, 0.532, 0.234, 0.467, and 1.178 eV, obtained in the EOMCCSD calculations for  $\text{CH}^+$  at  $R_{\text{C-H}} = 2R_e$  for the  $2^1\Sigma^+$ ,  $3^1\Sigma^+$ ,  $1^1\Pi$ ,  $2^1\Pi$ , and  $1^1\Delta$  states, to 0.093, 0.084, 0.061, 0.018, and 0.009 eV, respectively [51, 52]. At the significantly stretched nuclear geometries of  $\text{CH}^+$ , such as  $R_{\text{C-H}} = 2R_e$ , the CR-EOMCCSD(T) approach has some problems with the higher-energy  $4^1\Sigma^+$  and  $2^1\Delta$  states, but even in this case we observe considerable improvements in the poor EOMCCSD results when the CR-EOMCCSD(T) method is employed (see Refs. [51, 52] for further details). Similar remarks apply to excited-state potential energy surfaces along bond breaking coordinates of other molecules, including strongly multi-reference systems, such as ozone [107] and  $\text{C}_2$  [53]. For example, in a recent study [53], we have examined the performance of the CR-EOMCCSD(T) method employing RHF orbitals in the calculations of ground- and excited-state potential energy curves of  $\text{C}_2$ , as described by the 6-31G\* basis set [108]. In addition to the ground-state ( $X^1\Sigma_g^+$ ) curve, we have examined two lowest-energy excited states of the  $^1\Delta_g$  and  $^1\Sigma_g^+$  symmetries, designated as the  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states, respectively. The CR-EOMCCSD(T) results have been compared with the full CI curves for the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$ , and  $B'^1\Sigma_g^+$  states of the  $\text{C}_2/6\text{-}31\text{G}^*$  molecule reported by Abrams and Sherrill [109]. Our findings are summarized in Figure 4. As

one can see, the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$ , and  $B'^1\Sigma_g^+$  potential curves of  $C_2$  create a significant challenge for the standard CCSD and EOMCCSD approaches. If we focus on the C–C distances ranging between 1.1 and 1.8 Å, the errors in the CCSD and EOMCCSD results for the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$ , and  $B'^1\Sigma_g^+$  states are 0.76–1.52 eV, 2.77–3.48 eV, and 2.43–3.18 eV, respectively. In particular, the error in the EOMCCSD vertical excitation energy corresponding to the  $X^1\Sigma_g^+ \rightarrow B^1\Delta_g$  transition at the approximate equilibrium geometry  $R_{C-C} = 1.25$  Å, relative to the full CI value of 2.43 eV, is 1.98 eV. A similarly large error in the EOMCCSD result for the  $X^1\Sigma_g^+ \rightarrow B^1\Delta_g$  vertical transition in  $C_2$  was observed earlier by Christiansen *et al.* [41]. These authors used a modified version of the aug-cc-pVDZ basis set [110, 111] and noted that even the iterative CC3 and EOMCCSDT-1 methods, which account for the triples effects, produce large errors on the order of 0.9 eV, when the  $B^1\Delta_g$  state is examined. In fact, in a more recent study [49], Piecuch *et al.* showed that the lowest  $^1\Delta_g$  state of  $C_2$  cannot be accurately described by the full EOMCCSDT approach, which gives an error on the order of 0.4 eV, when the modified variant of the aug-cc-pVDZ basis set used by Christiansen *et al.* is employed. The only standard EOMCC method, which is capable of providing an accurate description of the  $B^1\Delta_g$  state of  $C_2$ , is the prohibitively expensive full EOMCCSDTQ approach [46].

As shown in Figure 4, the CCSD and EOMCCSD potentials are not only characterized by huge errors, as described above; they are also qualitatively incorrect. For example, the  $B^1\Delta_g$  potential curve is shifted to higher energies so much that it crosses the  $B'^1\Sigma_g^+$  curve; this is completely wrong since the full CI calculations show that the  $B^1\Delta_g$  curve should cross the  $X^1\Sigma_g^+$  potential, not the  $B'^1\Sigma_g^+$  curve. In addition, the small,  $\sim 0.4$  eV energy gap corresponding to an avoided crossing of the  $X^1\Sigma_g^+$  and  $B'^1\Sigma_g^+$  full CI states at  $R \approx 1.7$  Å is absent in the CCSD/EOMCCSD calculations. The extremely poor performance of the standard EOMCCSD approach for the  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states of  $C_2$  confirms the well-known fact that the EOMCCSD method cannot describe excited-state potential energy surfaces along bond-breaking coordinates and excited states dominated by two-electron transitions (in this case, the  $1\pi_u^2 \rightarrow 3\sigma_g^2$  double excitations relative to the RHF reference determinant).

The CR-EOMCCSD(T) approach dramatically improves the poor CCSD/EOMCCSD results. This can be seen by comparing the CCSD/EOMCCSD and full CI potential energy curves with the CR-EOMCCSD(T) potential curves shown in Figure 4. Although the CR-EOMCCSD(T) method cannot accurately describe the  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  excited states in the asymptotic region [53] (not shown in Figure 4), the CR-EOMCCSD(T) results for the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states in the

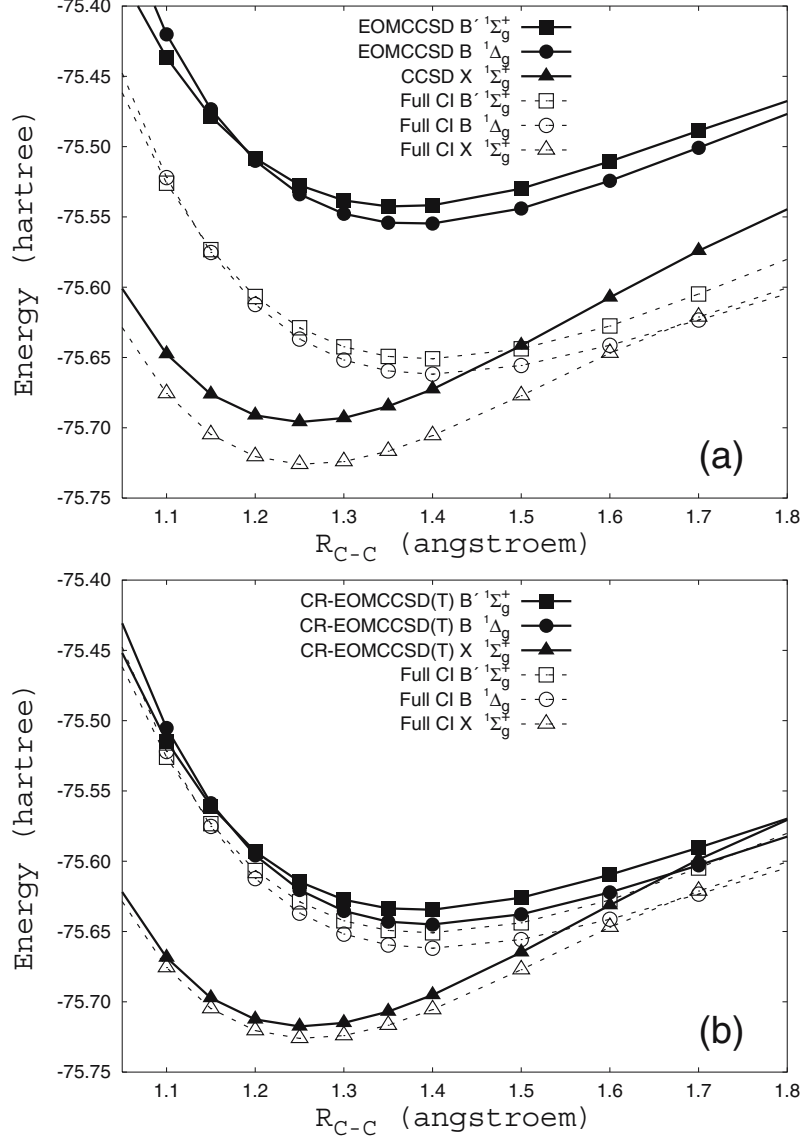


Figure 4. Potential energy curves for the  $C_2$  molecule (energies in hartree and the C-C distance in Å; the CCSD/EOMCCSD and full CI data taken from Refs. [53, 109]; the CR-EOMCCSD(T)≡CR-EOMCCSD(T),ID data has not been published before). The results include the ground state,  $X \ ^1\Sigma_g^+$ , and the lowest excited states of the  $^1\Delta_g$  and  $^1\Sigma_g^+$  symmetries,  $B \ ^1\Delta_g$  and  $B' \ ^1\Sigma_g^+$ . The full CI curves are indicated by the dashed lines and open symbols and the CC/EOMCC curves are indicated by the solid lines and filled symbols. (a) A comparison of the CCSD/EOMCCSD and full CI results. (b) A comparison of the CR-EOMCCSD(T) and full CI results.

spectroscopic  $1.1 \text{ \AA} \leq R_{C-C} \leq 1.8 \text{ \AA}$  region are quite good, particularly if we take into consideration the single-reference character and the relatively low cost of the CR-EOMCCSD(T) calculations and the challenge that the low-lying electronic states of  $C_2$  create for single-reference methods [53, 109]. The CR-EOMCCSD(T) approach reduces the 0.76–1.52 eV, 2.77–3.48 eV, and 2.43–3.18 eV errors obtained in the CCSD/EOMCCSD calculations for the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states of  $C_2$  in the  $1.1 \text{ \AA} \leq R_{C-C} \leq 1.8 \text{ \AA}$  region to 0.19–0.81 eV, 0.45–0.61 eV, and 0.28–0.49 eV, respectively. In particular, the large, 1.98 eV, error in the EOMCCSD vertical excitation energy corresponding to the  $X^1\Sigma_g^+ \rightarrow B^1\Delta_g$  transition at the approximate equilibrium geometry  $R_{C-C} = 1.25 \text{ \AA}$  reduces to 0.22 eV, when the CR-EOMCCSD(T) method is employed. A similarly impressive error reduction in the EOMCCSD results for the  $X^1\Sigma_g^+ \rightarrow B^1\Delta_g$  vertical transition in  $C_2$  was observed in our recent CR-EOMCCSD(T), MMCC(2,3)/CI, and MMCC(2,4)/CI calculations employing the modified aug-cc-pVDZ basis set of Christiansen *et al.* [48, 49, 51, 52].

The CR-EOMCCSD(T) curves for the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states of  $C_2$  are almost parallel to the corresponding full CI curves. Indeed, the nonparallelity errors (NPE's; NPE is defined as the difference between the maximum and minimum errors along a potential energy curve) obtained with the CR-EOMCCSD(T) approach in the  $1.1 \text{ \AA} \leq R_{C-C} \leq 1.8 \text{ \AA}$  region are 0.62, 0.16, and 0.21 eV for the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states, respectively. This should be compared to the NPE values of 0.76, 0.71, and 0.75 eV, respectively, obtained in the EOMCCSD calculations. We can reduce the NPE values obtained with the CR-EOMCCSD(T), ID method discussed here even further if we employ variant III of the CR-EOMCCSD(T) approach [51, 52]. As shown in Ref. [53], the NPE values obtained with variant III of the CR-EOMCCSD(T) method for the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states in the  $1.1 \text{ \AA} \leq R_{C-C} \leq 1.8 \text{ \AA}$  region are 0.36, 0.06, and 0.16 eV, respectively.

As shown in Figure 4, the CR-EOMCCSD(T) approach restores the crossing of the  $X^1\Sigma_g^+$  and  $B^1\Delta_g$  states in the  $R \approx 1.7 \text{ \AA}$  region. It also brings the  $X^1\Sigma_g^+$  and  $B'^1\Sigma_g^+$  states much closer to each other in the  $R = 1.6 - 1.8 \text{ \AA}$  region, trying to mimic the existence of an avoided crossing between these two states that the standard CCSD/EOMCCSD methods fail to describe. The only problem is that variant ID of the CR-EOMCCSD(T) theory brings the nearly degenerate  $X^1\Sigma_g^+$  and  $B'^1\Sigma_g^+$  states too close to each other, so that they become virtually degenerate. As shown in Ref. [53], this problem can be eliminated by replacing the denominators  $D_{\mu,abc}^{ijk}$ , Eq. (104), that are used to define the approximate triexcited amplitudes  $\tilde{r}_{abc}^{ijk}(\mu)$  by the MBPT-like energy differences  $[\omega_{\mu}^{(\text{CCSD})} - (\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)]$ ,

but then one loses some of the high accuracy of the CR-EOMCCSD(T),ID and CR-EOMCCSD(T),III results. This problem will have to be addressed in the future.

Finally, before discussing our recent attempt to formulate the MMCC methods employing left eigenstates of the CC/EOMCC similarity-transformed Hamiltonian [79], let us mention that the very good performance of the CR-EOMCCSD(T) approach is not limited to singlet electronic states or closed-shell molecules. We have recently developed the highly efficient computer codes for the CR-EOMCCSD(T) calculations for non-singlet electronic states of radical and other open-shell systems, as described by the ROHF orbitals [59]. We have tested these codes on excited states of several open shell systems, including the CH radical, which poses a serious challenge to standard EOMCC and response CC methods, such as EOMCCSD and CC3 [54], since some of the low-lying states of CH have a large double excitation character which requires a highly accurate determination of the triples effects ( $T_3$  and  $R_{\mu,3}$ ) in CC/EOMCC calculations. This can be seen in Table 3, where we characterize the low-lying excited states of CH by the reduced excitation level (REL) defined as [59]

$$\text{REL} = \sum_{n=0}^2 n \langle \Phi | (R_{\mu,n})^\dagger R_{\mu,n} | \Phi \rangle / \sum_{n=0}^2 \langle \Phi | (R_{\mu,n})^\dagger R_{\mu,n} | \Phi \rangle, \quad (114)$$

where  $R_{\mu,n}$ ,  $n = 0 - 2$ , are the zero-, one-, and two-body components of the excitation operator  $R_\mu^{(\text{CCSD})}$  obtained in the EOMCCSD calculations. The  $\text{REL} \approx 1.0$  value implies that a given excited state is dominated by singles and  $\text{REL} \approx 2.0$  for excited states dominated by doubles. As shown in Table 3, the  $a^4\Sigma^-$  and  $A^2\Delta$  states of CH are dominated by single excitations, whereas the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states have a considerable multi-reference character [112] and significant contributions from double excitations.

Shown in Table 3 are the total and adiabatic excitation energies  $T_e$ , obtained with the aug-cc-pVTZ basis set [110,111], and the dipole moments  $\mu$ , obtained with the aug-cc-pVDZ basis set [110,111], in various electronic states of CH. We compare the CR-EOMCCSD(T) results for the total and adiabatic excitation energies and dipole moments with the corresponding results of the CCSD/EOMCCSD calculations and the recently reported [46] results of the full CCSDT/EOMCCSDT calculations employing the unrestricted Hartree-Fock (UHF) reference. The relevant experimental data, including the  $T_e$  and  $\mu$  values and the equilibrium bond lengths used in the CC/EOMCC calculations, were taken from Refs. [113–119]. The CCSD/EOMCCSD and CCSDT/EOMCCSDT values of the dipole moments were obtained analytically, using the right and left eigenstates of the relevant similarity-transformed Hamiltonians, as described in Section

2.1 (see Eqs. (45)–(47)). The CR-EOMCCSD(T) values of  $\mu$  were obtained numerically using the finite-field method.

As shown in Table 3, the CR-EOMCCSD(T) approach provides a uniformly accurate description of the excited states of CH, independent of their (singly or doubly excited, doublet or quartet) character. The CR-EOMCCSD(T) adiabatic excitation energies  $T_e$  obtained with the aug-cc-pVTZ basis set are within 0.07–0.33 eV from experiment. This includes the  $B\ ^2\Sigma^-$  and  $C\ ^2\Sigma^+$  states dominated by two-electron transitions, for which the EOMCCSD approach fails, producing the 1.19 and 1.42 eV errors, respectively, when the aug-cc-pVTZ basis set is employed. The CR-EOMCCSD(T) approach reduces these large errors to 0.07 and 0.15 eV, respectively, which is a considerable improvement. The overall description of the excited states of CH listed in Table 3 by the CR-EOMCCSD(T) approach is almost as good as that obtained with the full CCSDT/EOMCCSDT method, particularly for the most challenging  $B\ ^2\Sigma^-$  and  $C\ ^2\Sigma^+$  states dominated by doubles. In general, the differences between the CR-EOMCCSD(T) and CCSDT/EOMCCSDT values of  $T_e$  obtained here with the aug-cc-pVTZ basis set range between 0.06 eV for the  $C\ ^2\Sigma^+$  state and 0.26 eV for the  $A\ ^2\Delta$  state, which is a very good agreement, particularly if we realize that the CR-EOMCCSD(T) method employs the iterative  $n_o^2n_u^4$  and noniterative  $n_o^3n_u^4$  steps, which are much less expensive than the iterative  $n_o^3n_u^5$  steps of the full CCSDT/EOMCCSDT approach.

The above similarities between the results of the CR-EOMCCSD(T) and CCSDT/EOMCCSDT calculations can also be observed when we examine the total energies of various excited states of CH listed in Table 3. The differences between the CR-EOMCCSD(T) and the corresponding EOMCCSDT total energies of the excited states of CH given in Table 3 range between 2.7 and 9.8 millihartree (the difference between the CCSDT and CR-EOMCCSD(T) ground-state energies is only 0.5 millihartree). This is very encouraging, particularly when we realize that a few millihartree differences between the CR-EOMCCSD(T) and EOMCCSDT energies are very small when compared to the magnitude of triples effects in the excited-state calculations. These effects, as measured by the differences between the EOMCCSDT and EOMCCSD energies, can be on the order of 50 millihartree (cf., e.g., the 46.6 and 53.3 millihartree differences between the EOMCCSDT and EOMCCSD energies for the  $B\ ^2\Sigma^-$  and  $C\ ^2\Sigma^+$  states, respectively, in Table 3). Finally, it is quite encouraging to observe that the CR-EOMCCSD(T) method is capable of substantially improving the CCSD/EOMCCSD results for the dipole moments in ground and excited states. For the  $X\ ^2\Pi$ ,  $a\ ^4\Sigma^-$ , and  $A\ ^2\Delta$  states, the agreement between the EOMCCSDT and CR-EOMCCSD(T) values of  $\mu$  shown in Table 3 is virtually perfect. For the most challenging  $B\ ^2\Sigma^-$ , and  $C\ ^2\Sigma^+$  states dominated



TABLE 3. Total energies ( $E$ ), adiabatic excitation energies ( $T_e$ ), reduced excitations level (REL) values, and dipole moments ( $\mu$ ) of the ground and low-lying excited states of the CH radical, as obtained with the aug-cc-pVTZ ( $E$ ,  $T_e$ , and REL) and aug-cc-pVDZ ( $\mu$ ) basis sets [110, 111]. Experimental data and nuclear geometries used in the CC/EOMCC calculations<sup>a</sup> are taken from Refs. [113–119].

<i>State</i>	<i>Method</i>	<i>E/hartree</i>	<i>T<sub>e</sub>/eV</i>	<i>REL</i>	<i>μ/debye</i>
$X\ ^2\Pi$	CCSD	-38.409232			1.39
	CCSDT <sup>b</sup>	-38.413493			1.37
	CR-EOMCCSD(T)	-38.412954			1.37
	Experiment				$1.46 \pm 0.06^c$
$a\ ^4\Sigma^-$	EOMCCSD	-38.372480	1.00	1.15	0.66
	EOMCCSDT <sup>b</sup>	-38.386466	0.74		0.65
	CR-EOMCCSD(T)	-38.379436	0.91		0.64
	Experiment		$0.74^d$		
$A\ ^2\Delta$	EOMCCSD	-38.289817	3.25	1.12	0.82
	EOMCCSDT <sup>b</sup>	-38.305291	2.94		0.81
	CR-EOMCCSD(T)	-38.295500	3.20		0.81
	Experiment		$2.87^e$		$0.77 \pm 0.07^f$
$B\ ^2\Sigma^-$	EOMCCSD	-38.246634	4.42	1.81	0.97
	EOMCCSDT <sup>b</sup>	-38.293254	3.27		1.27
	CR-EOMCCSD(T)	-38.296665	3.16		1.14
	Experiment		$3.23^g$		
$C\ ^2\Sigma^+$	EOMCCSD	-38.212223	5.36	1.89	0.76
	EOMCCSDT <sup>b</sup>	-38.265474	4.03		0.87
	CR-EOMCCSD(T)	-38.262752	4.09		0.85
	Experiment		$3.94^h$		

<sup>a</sup> The equilibrium geometries used in the CC/EOMCC calculations were taken from experiment. They are:  $r_e = 1.1197868\ \text{\AA}$  for the  $X\ ^2\Pi$  state [113],  $r_0 = 1.0977\ \text{\AA}$  for the  $a\ ^4\Sigma^-$  state [114],  $r_e = 1.1031\ \text{\AA}$  for the  $A\ ^2\Delta$  state [113],  $r_e = 1.1640\ \text{\AA}$  for the  $B\ ^2\Sigma^-$  state [115], and  $r_e = 1.1143\ \text{\AA}$  for the  $C\ ^2\Sigma^+$  state [116].

<sup>b</sup> The UHF-based CCSDT/EOMCCSDT results reported in Ref. [46].

<sup>c</sup> From Ref. [117].

<sup>d</sup> From Ref. [118].

<sup>e</sup> From Ref. [113].

<sup>f</sup> From Ref. [119].

<sup>g</sup> From Ref. [115].

<sup>h</sup> From Ref. [116].

by double excitations, the CR-EOMCCSD(T) approach provides substantial improvements in the EOMCCSD dipole moment values, reducing the



0.30 and 0.11 debye errors relative to the corresponding full EOMCCSDT results to 0.13 and 0.02 debye, respectively.

All of the above examples show that the externally corrected MMCC(2,3) approaches and the more “black-box” CR-EOMCCSD(T) method offer considerable improvements in the EOMCCSD results, particularly when the excited states of interest are dominated by two-electron transitions or when the excited-state potential energy surfaces along bond breaking coordinates are examined. The CR-EOMCCSD(T) approach and other MMCC(2,3) schemes are capable of improving the results of CC3 and other standard EOMCC/response CC calculations that incorporate triples effects in an approximate way, bringing the excitation energies closer to the corresponding full EOMCCSDT and full CI values. Other examples of the successful applications of the excited-state MMCC(2,3) and CR-EOMCCSD(T) methods can be found elsewhere [48, 49, 51, 52, 60, 64, 107]. In the next section, we focus on one of the most recent advances in the excited-state MMCC theory, which is the development of MMCC and CR-EOMCC approximations that use the left eigenstates of the CC/EOMCC similarity-transformed Hamiltonian.

### 3.2. THE MMCC SCHEMES EXPLOITING THE LEFT EIGENSTATES OF THE SIMILARITY-TRANSFORMED HAMILTONIAN: THE CR-EOMCCSD(T)<sub>ℒ</sub> APPROACH

All MMCC methods discussed in the previous section are obtained by extracting the leading terms from the exact MMCC expressions for the noniterative corrections  $\delta_\mu^{(A)}$ , Eq. (50), or  $\delta_\mu^{(\text{CCSD})}$ , Eq. (53), which, when added to the energies obtained in the standard CC/EOMCC calculations,  $E_\mu^{(A)}$  or  $E_\mu^{(\text{CCSD})}$ , respectively, recover the exact (i.e. full CI) energies  $E_\mu$  of the electronic states of interest. The resulting MMCC( $m_A, m_B$ ) methods are characterized by the presence of the denominator terms  $\langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$  or  $\langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle$  that renormalize the resulting corrections  $\delta_\mu(m_A, m_B)$  to provide the desired improvements in the CC/EOMCC results for the excited states dominated by double excitations and for the molecular potential energy surfaces along bond breaking coordinates (see, e.g., Refs. [61–63, 66, 76] for a detailed discussion of the role of the  $\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle$  and  $\langle \Psi_0 | e^{T^{(\text{CCSD})}} | \Phi \rangle$  denominator terms in improving the ground-state CC results). The calculation of these overlap denominator terms for the wave functions  $|\Psi_\mu\rangle$  defining the externally corrected MMCC( $m_A, m_B$ ) methods and the CR-EOMCCSD(T) approach constitutes a very small fraction of the total computer effort related to the determination of the  $\delta_\mu(m_A, m_B)$  corrections, but usually these denominators introduce small size extensivity errors, estimated at  $\sim 0.5\%$  of the total

correlation energy in the ground-state calculations [49, 77] (size extensivity is defined here as the absence of disconnected diagrams in the MBPT expansion of the electronic energy; this is not necessarily the same as the ability of a given method to describe bond breaking or separation of a given system into noninteracting fragments; for example, size inextensive methods, such as MRCI, can describe all kinds of system fragmentations, while some size extensive approaches, such as CCSD(T), fail to describe bond breaking). The size extensivity errors in the externally corrected MMCC( $m_A, m_B$ ) and CR-EOMCCSD(T) calculations are much smaller than the errors obtained with the standard CCSD, CCSD(T), EOMCCSD, and similar methods when potential energy surfaces along bond breaking coordinates and reaction pathways are examined [49, 105], but it is always interesting to look for new alternatives that might eliminate the size extensivity problem from approximate MMCC calculations. Kowalski and Piecuch have recently developed the rigorously size extensive extension of the ground-state CR-CC methods, such as CR-CCSD(T), by introducing a new concept of the numerator-denominator connected MMCC expansions and the idea of local renormalization [77], but it is quite difficult to extend these considerations to excited states at this time. Moreover, the problem of size extensivity of the EOMCC results for excited states is much more complicated than the extensivity of the ground-state CC calculations, since approximate EOMCC methods, such as EOMCCSD, whose results we are trying to improve here, are not size extensive [25, 59, 120–122]. The EOM-CCSD method is only size intensive, meaning that it can provide the correct description of an idealized separation of a given many-electron system into two noninteracting fragments, in which only one of the two separated fragments is singly excited [25] (as shown later by Meissner [122], the EOM-CCSD approach can also describe one-electron charge-transfer excitations between separated fragments). Unfortunately, this property of EOMCCSD does not eliminate the size extensivity error from the EOMCCSD and other truncated EOMCC calculations. Although we cannot address all of these issues here, it may be worth contemplating new classes of MMCC methods that might potentially reduce the extensivity errors through the elimination of the overlap denominators  $\langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$  or  $\langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle$  from the noniterative corrections  $\delta_\mu^{(A)}$  or  $\delta_\mu^{(\text{CCSD})}$ .

We have recently started exploring MMCC methods which are based on the new forms of the expressions for the corrections  $\delta_\mu^{(A)}$  or  $\delta_\mu^{(\text{CCSD})}$  that do not use the overlap denominator terms  $\langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$  and  $\langle \Psi_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle$  [79]. The key to such methods is the use of the left eigenstates of the similarity-transformed Hamiltonians  $\bar{H}^{(A)}$  or  $\bar{H}^{(\text{CCSD})}$ . This is based on an observation that the CC/EOMCC “bra” state  $\langle \tilde{\Psi}_\mu^{(\text{CC})} |$ ,

Eq. (27), and the “ket” CC/EOMCC state  $|\Psi_\mu^{(\text{CC})}\rangle$ , Eq. (15), satisfy (cf. Eq. (37))

$$\langle \tilde{\Psi}_\mu^{(\text{CC})} | \Psi_\mu^{(\text{CC})} \rangle = 1, \quad (115)$$

so that in the exact, full CI, limit the  $\langle \tilde{\Psi}_\mu^{(\text{CC})} |$  “bra” state represents the renormalized form of the “ket” state  $|\Psi_\mu^{(\text{CC})}\rangle$  (this should be contrasted with the fact that, in general,  $\langle \Psi_\mu^{(\text{CC})} | \Psi_\mu^{(\text{CC})} \rangle \neq 1$ ).

The main idea of the MMCC methods exploiting the left eigenstates of  $\bar{H}^{(A)}$  is the following representation of the exact, full CI “bra” state  $\langle \Psi_\mu |$  entering Eqs. (50) and (53) [79]:

$$\langle \Psi_\mu | = \langle \Phi | \mathcal{L}_\mu e^{-T^{(A)}}. \quad (116)$$

Here,  $T^{(A)}$  is the cluster operator for the CC method  $A$ , whose results we would like to improve (cf. Eq. (7)), and

$$\mathcal{L}_\mu = \sum_{n=0}^N \mathcal{L}_{\mu,n}, \quad (117)$$

where

$$\mathcal{L}_{\mu,n} = \left( \frac{1}{n!} \right)^2 \ell_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu) a^{i_1} \dots a^{i_n} a_{a_n} \dots a_{a_1} \quad (118)$$

is the  $n$ -body component of  $\mathcal{L}_\mu$ , is the suitably chosen deexcitation operator such that  $\langle \Phi | \mathcal{L}_\mu = \langle \Psi_\mu | e^{T^{(A)}}$  (obviously, such operator always exists). We can further decompose the operator  $\mathcal{L}_\mu$  into  $\mathcal{L}_\mu^{(A)}$  and  $\delta \mathcal{L}_\mu^{(A)}$ ,

$$\mathcal{L}_\mu = \mathcal{L}_\mu^{(A)} + \delta \mathcal{L}_\mu^{(A)}, \quad (119)$$

where

$$\mathcal{L}_\mu^{(A)} = \sum_{n=0}^{m_A} \mathcal{L}_{\mu,n} \quad (120)$$

and

$$\delta \mathcal{L}_\mu^{(A)} = \sum_{n=m_A+1}^N \mathcal{L}_{\mu,n}, \quad (121)$$

with  $m_A$  representing the excitation level defining the CC/EOMCC method  $A$ . Since we can always normalize the full CI “bra” state  $\langle \Psi_\mu |$ , which enters Eqs. (50) and (53), in an arbitrary manner without changing the values of corrections  $\delta_\mu^{(A)}$  and  $\delta_\mu^{(\text{CCSD})}$ , we choose the normalization of  $\langle \Psi_\mu |$ , Eq. (116), such that

$$\langle \Phi | \mathcal{L}_\mu^{(A)} R_\mu^{(A)} | \Phi \rangle = 1. \quad (122)$$

Equation (122) looks like Eq. (37), but this is where the similarities between  $\langle \Phi | \mathcal{L}_\mu^{(A)}$  and the left eigenstate  $\langle \Phi | L_\mu^{(A)}$ , corresponding to the right eigenstate  $R_\mu^{(A)} | \Phi \rangle$  of  $\bar{H}^{(A)}$ , end. The  $\langle \Phi | \mathcal{L}_\mu^{(A)}$  state is only one of the two contributions to  $\langle \Phi | \mathcal{L}_\mu = \langle \Psi_\mu | e^{T^{(A)}}$ , as defined by Eq. (119), whereas  $\langle \Phi | L_\mu^{(A)}$  is the true left eigenstate of  $\bar{H}^{(A)}$  corresponding to  $R_\mu^{(A)} | \Phi \rangle$ . The  $\langle \Phi | \mathcal{L}_\mu^{(A)}$  and  $\langle \Phi | L_\mu^{(A)}$  states can be numerically similar, but they are formally not identical unless  $m_A = N$  and  $\delta \mathcal{L}_\mu^{(A)} = 0$ .

With the above representation of the full CI “bra” state  $\langle \Psi_\mu |$ , Eq. (116), and with the normalization of  $\langle \Psi_\mu |$  defined by Eq. (122), we can rewrite Eq. (50) for the exact value of the correction  $\delta_\mu^{(A)}$  in the following way [79]:

$$\delta_\mu^{(A)} \equiv E_\mu - E_\mu^{(A)} = \sum_{n=m_A+1}^N \langle \Phi | \mathcal{L}_{\mu,n} M_{\mu,n}(m_A) | \Phi \rangle, \quad (123)$$

where the operators  $M_{\mu,n}(m_A)$  are defined in terms of the generalized moments of CC/EOMCC equations of method  $A$ ,  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$ , via Eq. (52). By using Eqs. (52) and (118), we can immediately write

$$\delta_\mu^{(A)} = \sum_{n=m_A+1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} \ell_{i_1\dots i_n}^{a_1\dots a_n}(\mu) \mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A), \quad (124)$$

where the generalized moments of CC/EOMCC equations are defined by Eqs. (48) and (49) and  $\ell_{i_1\dots i_n}^{a_1\dots a_n}(\mu)$  are the deexcitation amplitudes defining the  $n$ -body components of  $\mathcal{L}_\mu$ . We only need the amplitudes  $\ell_{i_1\dots i_n}^{a_1\dots a_n}(\mu)$  and moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  with  $n > m_A$  to construct Eq. (124).

As one can see, the main difference between the new MMCC expression for the exact correction  $\delta_\mu^{(A)}$ , given by Eqs. (123) and (124), and the original MMCC formula, Eq. (50), is the absence of the overlap denominator term  $\langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$  in Eqs. (123) and (124). This may be a useful feature in calculating the approximate values of corrections  $\delta_\mu^{(A)}$ , particularly when the lack of rigorous size extensivity of the MMCC( $m_A, m_B$ ) methods discussed in the previous section becomes an issue. Another difference is the absence of the  $C_{n-k}(m_A)$  terms representing the  $(n-k)$ -body components of  $e^{T^{(A)}}$  in Eqs. (123) and (124). One can rather easily show [79] that these terms can be summed over to  $e^{T^{(A)}}$ , which cancels out the  $e^{-T^{(A)}}$  operator entering the formula for  $\langle \Psi_\mu |$ , Eq. (116).

The details of the derivation of Eqs. (123) and (124) will be described elsewhere [79]. Let us only mention that one can derive Eqs. (123) and (124) by using the original MMCC formula for the correction  $\delta_\mu^{(A)}$ , Eq. (50), in

which the exact “bra” state  $\langle \Psi_\mu |$  is replaced by Eq. (116), or by replacing the wave function  $\langle \Psi |$  in the MMCC functional, Eq. (56), by  $\langle \Psi_\mu |$ , Eq. (116), and by exploiting the resolution of identity in the  $N$ -electron Hilbert space in a manner which is analogous to the original derivation of the MMCC energy expressions [47, 62] (see, also, Ref. [49]). The overlap denominator term  $\langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$  entering Eqs. (50) and (56) disappears from the resulting expressions for  $\delta_\mu^{(A)}$ , since

$$\langle \Phi | \mathcal{L}_\mu R_\mu^{(A)} | \Phi \rangle = \langle \Phi | \mathcal{L}_\mu^{(A)} R_\mu^{(A)} | \Phi \rangle + \langle \Phi | (\delta \mathcal{L}_\mu^{(A)}) R_\mu^{(A)} | \Phi \rangle = 1. \quad (125)$$

In arriving at Eq. (125), we used Eqs. (119) and (122), and the obvious fact that  $\langle \Phi | (\delta \mathcal{L}_\mu^{(A)}) R_\mu^{(A)} | \Phi \rangle = 0$  (cf. the definition of  $\delta \mathcal{L}_\mu^{(A)}$ , Eq. (121);  $\delta \mathcal{L}_\mu^{(A)}$  contains  $n$ -body components with  $n > m_A$ , whereas the  $n$ -body components of  $R_\mu^{(A)}$  have  $n \leq m_A$ ).

The question arises how to use Eqs. (123) and (124) in practice. In analogy to the MMCC( $m_A, m_B$ ) schemes defined by Eqs. (65) and (66), we can introduce the MMCC( $m_A, m_B$ ) $_{\mathcal{L}}$  methods in which we calculate the energy as follows [79]:

$$E_\mu^{(\text{MMCC})}(m_A, m_B)_{\mathcal{L}} = E_\mu^{(A)} + \delta_\mu(m_A, m_B)_{\mathcal{L}}, \quad (126)$$

where  $m_B > m_A$  and where

$$\begin{aligned} \delta_\mu(m_A, m_B)_{\mathcal{L}} &= \sum_{n=m_A+1}^{m_B} \langle \Phi | \mathcal{L}_{\mu,n} M_{\mu,n}(m_A) | \Phi \rangle \\ &= \sum_{n=m_A+1}^{m_B} \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} \ell_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu) \mathfrak{M}_{\mu, a_1 \dots a_n}^{i_1 \dots i_n}(m_A) \end{aligned} \quad (127)$$

is the relevant correction to the CC/EOMCC energy  $E_\mu^{(A)}$ . An example of the MMCC( $m_A, m_B$ ) $_{\mathcal{L}}$  method might be the MMCC(2,3) $_{\mathcal{L}}$  approximation, in which, in analogy to the MMCC(2,3) methods discussed in the previous section, we correct the results of the CCSD/EOMCCSD calculations by adding the corrections

$$\delta_\mu(2, 3)_{\mathcal{L}} = \langle \Phi | \mathcal{L}_{\mu,3} M_{\mu,3}(m_A) | \Phi \rangle = \sum_{i < j < k, a < b < c} \ell_{ijk}^{abc}(\mu) \mathfrak{M}_{\mu, abc}^{ijk}(2) \quad (128)$$

to the CCSD/EOMCCSD energies  $E_\mu^{(\text{CCSD})}$ .

As in the case of the MMCC(2,3) schemes, discussed in Section 2, we can use Eq. (128) to design the analog of the CR-EOMCCSD(T) method employing the left eigenstates of  $\bar{H}^{(\text{CCSD})}$ . In order to accomplish this and formulate the resulting CR-EOMCCSD(T) $_{\mathcal{L}}$  approximation, we have to come

up with the approximate form of the three-body operator  $\mathcal{L}_{\mu,3}$ , which uses the standard elements of the CCSD/EOMCCSD theory, such the CCSD cluster operators  $T_1$  and  $T_2$  and the zero-, one- and two-body components of the left eigenstate  $\langle\Phi|L_\mu^{(\text{CCSD})}$  of the CCSD/EOMCCSD similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$ . The desired approximate form of  $\mathcal{L}_{\mu,3}$  that can be used to formulate the CR-EOMCCSD(T) $\mathcal{L}$  approximation can be obtained by analyzing the equation

$$\langle\Phi|\mathcal{L}_\mu\bar{H}^{(\text{CCSD})} = E_\mu\langle\Phi|\mathcal{L}_\mu, \quad (129)$$

which is equivalent to the Schrödinger equation  $H|\Psi_\mu\rangle = E_\mu|\Psi_\mu\rangle$  or, more precisely, to its adjoint form  $\langle\Psi_\mu|H = E_\mu\langle\Psi_\mu|$  if  $\langle\Phi|\mathcal{L}_\mu e^{-T^{(\text{CCSD})}}$  is the exact, full CI “bra” state  $\langle\Psi_\mu|$ . By right-projecting Eq. (129) on the triply excited determinants  $|\Phi_{ijk}^{abc}\rangle$ , while approximating the operator  $\mathcal{L}_\mu$  by  $L_\mu^{(\text{CCSD})} + \tilde{\mathcal{L}}_{\mu,3}$ , where  $\langle\Phi|L_\mu^{(\text{CCSD})}$  is the left eigenstate of the  $\bar{H}^{(\text{CCSD})}$  obtained in the CCSD/EOMCCSD calculations and  $\tilde{\mathcal{L}}_{\mu,3}$  is an approximate form of the three-body component  $\mathcal{L}_{\mu,3}$ , and by replacing the exact energy  $E_\mu$  in the resulting equation by the CCSD/EOMCCSD energy  $E_\mu^{(\text{CCSD})}$ , while approximating the triples-triples block of the matrix representing  $\bar{H}^{(\text{CCSD})}$  by its diagonal, we obtain

$$\mathcal{L}_{\mu,3} \approx \tilde{\mathcal{L}}_{\mu,3} = \frac{1}{36} \tilde{\ell}_{ijk}^{abc}(\mu) a^i a^j a^k a_c a_b a_a, \quad (130)$$

where

$$\tilde{\ell}_{ijk}^{abc}(\mu) = \langle\Phi|L_\mu^{(\text{CCSD})}\bar{H}^{(\text{CCSD})}|\Phi_{ijk}^{abc}\rangle/D_{\mu,abc}^{ijk}, \quad (131)$$

with  $D_{\mu,abc}^{ijk}$  defined by Eq. (104). An elementary diagrammatic analysis of Eq. (131) shows that

$$\begin{aligned} \tilde{\ell}_{ijk}^{abc}(\mu) &= \langle\Phi|[L_{\mu,1}\bar{H}_2^{(\text{CCSD})} + L_{\mu,2}\bar{H}_1^{(\text{CCSD})} \\ &\quad + (L_{\mu,2}\bar{H}_2^{(\text{CCSD})})_C]|\Phi_{ijk}^{abc}\rangle/D_{\mu,abc}^{ijk}, \end{aligned} \quad (132)$$

where  $L_{\mu,1}$  and  $L_{\mu,2}$  are the one- and two-body components of  $L_\mu^{(\text{CCSD})}$  obtained by solving the left CCSD ( $\mu = 0$ ) and EOMCCSD ( $\mu > 0$ ) equations (Eqs. (44) and (40), respectively, where  $m_A = 2$ ) and  $\bar{H}_1^{(\text{CCSD})}$  and  $\bar{H}_2^{(\text{CCSD})}$  are the one and two-body components of  $\bar{H}^{(\text{CCSD})}$ . The final CR-EOMCCSD(T) $\mathcal{L}$  energy is calculated as [79]

$$E_\mu^{(\text{CR-EOMCCSD(T)}\mathcal{L})} = E_\mu^{(\text{CCSD})} + \sum_{i < j < k, a < b < c} \tilde{\ell}_{ijk}^{abc}(\mu) \mathfrak{M}_{\mu,abc}^{ijk}(2), \quad (133)$$

where  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  are the triply excited moments of the CCSD ( $\mu = 0$ ) or EOMCCSD ( $\mu > 0$ ) equations that one can calculate using Eq. (60) and  $\tilde{\ell}_{ijk}^{abc}(\mu)$  is defined by Eq. (132). The above expression applies to ground ( $\mu = 0$ ) and excited ( $\mu > 0$ ) states. In the former case, we simply replace the one- and two-body components of  $L_{\mu}^{(\text{CCSD})}$  in Eq. (132) by the one- and two-body operators  $\Lambda_1$  and  $\Lambda_2$  obtained by solving the linear system of the CCSD “lambda” equations, Eq. (44), where  $A = \text{CCSD}$  and  $m_A = 2$ . One can easily verify that the ground-state CR-EOMCCSD(T) $_{\mathcal{L}}$  energy reduces to the energy expression defining the CCSD(2) $_T$  approach of Refs. [75, 123] if the denominator  $D_{0,abc}^{ijk}$  in Eq. (132) written for the  $\mu = 0$  case is replaced by the usual MBPT-like difference of bare spin-orbital energies for triples,  $(\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)$  (see Refs. [124–131] for the related approaches).

The CR-EOMCCSD(T) $_{\mathcal{L}}$  method is essentially as inexpensive as the CR-EOMCCSD(T) approach of Refs. [49, 51, 52, 59], discussed in Section 3.1.2. Thus, the most expensive steps of the CR-EOMCCSD(T) $_{\mathcal{L}}$  approach scale as  $n_o^2 n_u^4$  in the iterative CCSD and EOMCCSD parts and  $n_o^3 n_u^4$  in the noniterative part associated with the determination of the triples correction  $\sum_{i<j<k, a<b<c} \tilde{\ell}_{ijk}^{abc}(\mu) \mathfrak{M}_{\mu,abc}^{ijk}(2)$ . The only essential difference between the CR-EOMCCSD(T) and CR-EOMCCSD(T) $_{\mathcal{L}}$  methods is the need to solve the CCSD “lambda” equations and the left EOMCCSD equations, in addition to solving the usual CCSD equations and right EOMCCSD equations, in the CR-EOMCCSD(T) $_{\mathcal{L}}$  calculations. The CCSD “lambda” equations and the left EOMCCSD equations are characterized by the  $n_o^2 n_u^4$  steps which are similar to the usual  $n_o^2 n_u^4$  steps of CCSD/EOMCCSD. Thus, the costs of the CR-EOMCCSD(T) $_{\mathcal{L}}$  and CR-EOMCCSD(T) calculations are not much different.

The CR-EOMCCSD(T) $_{\mathcal{L}}$  method is currently under development, so that we cannot show too many examples of the actual applications yet. However, we have already tested the CR-EOMCCSD(T) $_{\mathcal{L}}$  approach using the electronic excitations in the  $\text{CH}^+$  ion as an example. The CR-EOMCCSD(T) $_{\mathcal{L}}$  results for the three lowest-energy excited states of the  $^1\Sigma^+$  symmetry and two lowest-energy states of the  $^1\Pi$  and  $^1\Delta$  symmetries, obtained at the equilibrium geometry  $R_{\text{C-H}} = R_e = 2.13713$  bohr and the same  $[5s3p1d/3s1p]$  basis set of Ref. [103] as used in the MMCC(2,3)/CI, MMCC(2,3)/PT, and CR-EOMCCSD(T) calculations discussed in Section 3.1, are shown in Table 2. As one can see, the CR-EOMCCSD(T) $_{\mathcal{L}}$  approach is as effective in improving the EOMCCSD results as the CR-EOMCCSD(T) method analyzed in Section 3.1.2. This is particularly true for the  $2\ ^1\Sigma^+$ ,  $1\ ^1\Delta$ , and  $2\ ^1\Delta$  states that are dominated by double excitations, for which the CR-EOMCCSD(T) $_{\mathcal{L}}$  approach provides the results of the full EOMCCSDT quality, reducing the large 0.560, 0.924, and 0.856



eV errors in the EOMCCSD calculations for the  $2^1\Sigma^+$ ,  $1^1\Delta$ , and  $2^1\Delta$  states to 0.106, 0.032, and  $-0.030$  eV, respectively. As in the case of the externally corrected MMCC(2,3) methods and CR-EOMCCSD(T) approach, the CR-EOMCCSD(T) $_{\mathcal{L}}$  results for the  $2^1\Sigma^+$ ,  $1^1\Delta$ , and  $2^1\Delta$  states are considerably better than the results of the iterative CC3 calculations. A similar superiority of the CR-EOMCCSD(T) $_{\mathcal{L}}$  approach over the CC3 method is observed for the partially biexcited  $2^1\Pi$  state, for which the 0.327 and 0.219 eV errors obtained with the EOMCCSD and CC3 approaches, respectively, reduce to 0.135 eV, when the CR-EOMCCSD(T) $_{\mathcal{L}}$  method is employed. For the remaining excited states listed in Table 2 that are dominated by one-electron transitions (the  $3^1\Sigma^+$ ,  $4^1\Sigma^+$ , and  $1^1\Pi$  states), the CR-EOMCCSD(T) $_{\mathcal{L}}$  approach is as accurate as the CC3 method, i.e. only slightly less accurate than the full EOMCCSDT approach. The overall accuracy of the CR-EOMCCSD(T) $_{\mathcal{L}}$  approach, which represents a new type of “black-box” MMCC approximation, is very similar to the accuracy of the externally corrected MMCC(2,3) methods and CR-EOMCCSD(T) approach.

The performance of the CR-EOMCCSD(T) $_{\mathcal{L}}$  method, which is based on the modified form of the MMCC formalism that no longer needs the overlap denominators of the  $\langle\Psi_\mu|R_\mu^{(\text{CCSD})}e^{T^{(\text{CCSD})}}|\Phi\rangle$  type to improve the EOMCCSD energies, is very encouraging. However, we have to perform a larger number of calculations to see if CR-EOMCCSD(T) $_{\mathcal{L}}$  offers the same level of consistency in applications involving singly and doubly excited states as other MMCC approximations. The results of our findings will be reported elsewhere [79].

#### 4. Summary and concluding remarks

We have provided a comprehensive discussion of new classes of noniterative CC/EOMCC methods, developed by our group, that can provide an accurate description of excited electronic states, particularly the most challenging excited states dominated by two-electron transitions and excited-state potential energy surfaces along bond breaking coordinates which require a well-balanced description of dynamic and nondynamic correlation effects. All of the methods discussed in this article are derived from the more general MMCC formalism, which is based on the idea of correcting standard CC/EOMCC results, originating, for example, from CCSD and EOMCCSD calculations, through the *a posteriori* noniterative energy corrections that in the exact limit of the MMCC theory recover the exact, full CI energies of the electronic states of interest. The key elements in designing the MMCC corrections to CC/EOMCC energies are the generalized moments of the CC/EOMCC equations, which can be rather easily extracted from



the approximate CC/EOMCC calculations whose results we would like to improve, particularly when one is interested in correcting the results of basic CCSD/EOMCCSD calculations.

We have discussed three classes of excited-state MMCC methods: (i) the externally corrected MMCC approaches employing the configuration interaction and multi-reference perturbation theory wave functions, (ii) the CR-EOMCC methods, such as CR-EOMCCSD(T), and (iii) the new classes of MMCC and CR-EOMCC theories employing the left eigenstates of the similarity-transformed Hamiltonian used in the CC/EOMCC theory. The first class of externally corrected MMCC theories is based on the idea of combining the information that originates from the CC/EOMCC calculations (the cluster and excitation amplitudes that define a given CC/EOMCC approximation and the corresponding generalized moments) with the approximate wave functions obtained in some low-order non-CC calculations that can provide a qualitatively correct description of the bond breaking process or excited states of interest. In our discussion of the externally corrected MMCC methods, we have focused on the MMCC(2,3)/CI and MMCC(2,3)/PT methods that can be used to correct the results of the CCSD/EOMCCSD calculations for the effects of triple excitations, as described by combining the triply excited moments of the CCSD/EOMCCSD equations with the wave functions originating from the low-order CISDt and MRMBPT calculations.

The idea of CR-EOMCC methods, such as CR-EOMCCSD(T), is entirely different. In this case, we design the MMCC corrections to the CC/EOMCC energies due to higher-order excitations without resorting to any non-CC calculations. For example, in the CR-EOMCCSD(T) approach discussed in this article, we design the corrections to the CCSD/EOMCCSD energies due to triples using the singly and doubly excited clusters obtained in the CCSD calculations, the zero-, one-, and two-body components of the linear excitation operator defining the EOMCCSD approach, and the triply excited moments of the CCSD/EOMCCSD equations. Thus, the CR-EOMCCSD(T) approach and other CR-EOMCC approximations are similar in spirit to the popular computational “black-box” methods, such as CCSD(T). In particular, the computer costs of the CR-EOMCCSD(T) method per single electronic state are more or less the same as the costs of the CCSD(T) calculations: both are the relatively inexpensive iterative  $\mathcal{N}^6$  and noniterative  $\mathcal{N}^7$  procedures. The same remark applies to the externally corrected MMCC(2,3)/CI and MMCC(2,3)/PT methods, although one has to perform the additional CISDt and low-order MRMBPT calculations, in addition to the CCSD and EOMCCSD calculations, to obtain the MMCC(2,3)/CI and MMCC(2,3)/PT triples corrections. Moreover, one has to select active orbitals to carry out the MMCC(2,3)/CI

and MMCC(2,3)/PT calculations, so that the externally corrected MMCC methods are not as easy to use as the purely single-reference CR-EOMCCSD(T) approach. On the other hand, the choice of active orbital space for the MMCC(2,3)/CI and MMCC(2,3)/PT calculations is often obvious if we have some *a priori* knowledge of the orbital excitations that dominate the electronic excitations of interest.

The third and the most recent group of the MMCC and CR-EOMCC methods is based on the idea of renormalizing the triples and other higher-order corrections to CCSD/EOMCCSD or other CC/EOMCC energies in situations involving two-electron excitations and excited-state potential energy surfaces along bond breaking coordinates through the left eigenstates of the similarity-transformed Hamiltonian used in the CC/EOMCC calculations. The left eigenstates of the similarity-transformed Hamiltonian used in the CC/EOMCC theory enable us to eliminate the overlap denominators that are present in other methods based on the original MMCC theory. This may have some advantages in situations where the presence of disconnected diagrams in the CR-EOMCCSD(T) triples corrections resulting from the use of the overlap denominators creates a potential problem. One of the approximations in this category, which we discussed in greater detail, is the CR-EOMCCSD(T)<sub>ℒ</sub> approach, which is a promising candidate for the “black-box” method for the calculations of excited states dominated by single or double excitations that has computer costs similar to those of CCSD(T) or CR-EOMCCSD(T).

In a few numerical examples, we have demonstrated that all of the above MMCC and CR-EOMCC methods provide considerable improvements in the EOMCCSD results, particularly when the excited states of interest gain a significant double excitation or multi-reference character. The MMCC(2,3)/CI, MMCC(2,3)/PT, CR-EOMCCSD(T), and CR-EOMCCSD(T)<sub>ℒ</sub> methods can often compete with the much more expensive EOMCCSDT approach. In fact, there are cases, such as the lowest-energy  $^1\Delta_g$  state of the  $C_2$  molecule, where the MMCC(2,3)/CI and CR-EOMCCSD(T) methods balance the ground and excited state correlation effects better than full EOMCCSDT. Even if this particular case is a result of the fortuitous cancellation of errors, it is very encouraging to see that the low-cost and easy-to-use MMCC(2,3)/CI, MMCC(2,3)/PT, CR-EOMCCSD(T), and CR-EOMCCSD(T)<sub>ℒ</sub> methods can be as accurate as the high-level and very expensive EOMCC methods, such as EOMCCSDT.

## Acknowledgements

One of us (P.P.) would like to thank Professors Jean-Pierre Julien and Jean Maruani for inviting him to give a talk at the Ninth European Workshop

on Quantum Systems in Chemistry and Physics (QSCP-IX), where some of the results discussed in this contribution were presented. P.P. would like to thank Dr. Stephen Wilson and Professor Jean Maruani for encouraging him to write this review article. This work has been supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (Grant No. DE-FG02-01ER15228) and the National Science Foundation (Grant No. CHE-0309517; both awards provided to P.P.). Additional support has been provided by the National Science Foundation REU Program in the Department of Chemistry at Michigan State University (J.R.G.).

## References

1. F. Coester, *Nucl. Phys.* **7**, 421 (1958).
2. F. Coester and H. Kümmel, *Nucl. Phys.* **17**, 477 (1960).
3. J. Čížek, *J. Chem. Phys.* **45**, 4256 (1966).
4. J. Čížek, *Adv. Chem. Phys.* **14**, 35 (1969).
5. J. Čížek and J. Paldus, *Int. J. Quantum Chem.* **5**, 359 (1971).
6. R.J. Bartlett, in: *Modern Electronic Structure Theory*, Part I, edited by D.R. Yarkony (World Scientific, Singapore, 1995), pp. 1047-1131.
7. J. Gauss, in: *Encyclopedia of Computational Chemistry*, edited by P.v.R. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer III, and P.R. Schreiner (Wiley, Chichester, U.K., 1998), Vol. 1, pp. 615-636.
8. J. Paldus and X. Li, *Adv. Chem. Phys.* **110**, 1 (1999).
9. T.D. Crawford and H.F. Schaefer III, *Rev. Comp. Chem.* **14**, 33 (2000).
10. J. Paldus, in: *Handbook of Molecular Physics and Quantum Chemistry*, edited by S. Wilson (Wiley, Chichester, 2003), Vol. 2, pp. 272-313.
11. G.D. Purvis III and R.J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
12. G.E. Scuseria, A.C. Scheiner, T.J. Lee, J.E. Rice, and H.F. Schaefer III, *J. Chem. Phys.* **86**, 2881 (1987).
13. G.E. Scuseria, C.L. Janssen, and H.F. Schaefer III, *J. Chem. Phys.* **89**, 7382 (1988).
14. T.J. Lee and J.E. Rice, *Chem. Phys. Lett.* **150**, 406 (1988).
15. P. Piecuch and J. Paldus, *Int. J. Quantum Chem.* **36**, 429 (1989).
16. M. Urban, J. Noga, S.J. Cole, and R.J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985).
17. P. Piecuch and J. Paldus, *Theor. Chim. Acta* **78**, 65 (1990).
18. K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
19. M. Schütz, *J. Chem. Phys.* **116**, 8772 (2002).
20. R.M. Olson, S. Varganov, M.S. Gordon, S. Chretien, H. Metiu, P. Piecuch, K. Kowalski, S.A. Kucharski, and M. Musiał, *J. Am. Chem. Soc.* **127**, 1049 (2005).
21. H. Monkhorst, *Int. J. Quantum Chem. Symp.* **11**, 421 (1977).
22. E. Dalgaard and H. Monkhorst, *Phys. Rev. A* **28**, 1217 (1983).
23. M. Takahashi and J. Paldus, *J. Chem. Phys.* **85**, 1486 (1986).
24. H. Koch and P. Jørgensen, *J. Chem. Phys.* **93**, 3333 (1990).
25. H. Koch, H.J.Aa. Jensen, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **93**, 3345 (1990).
26. J. Geertsen, M. Rittby, and R.J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989).
27. D.C. Comeau and R.J. Bartlett, *Chem. Phys. Lett.* **207**, 414 (1993).
28. J.F. Stanton and R.J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).
29. P. Piecuch and R.J. Bartlett, *Adv. Quantum Chem.* **34**, 295 (1999).
30. H. Nakatsuji and K. Hirao, *Chem. Phys. Lett.* **47**, 569 (1977).

31. H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053, 4279 (1978).
32. H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978).
33. H. Nakatsuji, *Chem. Phys. Lett.* **67**, 329, 334 (1979).
34. H. Nakatsuji, in: *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczyński (World Scientific, Singapore, 1997), Vol. 2, pp. 62-124.
35. J.D. Watts and R.J. Bartlett, *Chem. Phys. Lett.* **233**, 81 (1995).
36. J.D. Watts and R.J. Bartlett, *Chem. Phys. Lett.* **258**, 581 (1996).
37. J.D. Watts and R.J. Bartlett, *J. Chem. Phys.* **101**, 3073 (1994).
38. H. Koch, O. Christiansen, P. Jørgensen, and J. Olsen, *Chem. Phys. Lett.* **244**, 75 (1995).
39. O. Christiansen, H. Koch, and P. Jørgensen, *J. Chem. Phys.* **103**, 7429 (1995).
40. O. Christiansen, H. Koch, and P. Jørgensen, *J. Chem. Phys.* **105**, 1451 (1996).
41. O. Christiansen, H. Koch, P. Jørgensen, and J. Olsen, *Chem. Phys. Lett.* **256**, 185 (1996).
42. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 8490 (2000).
43. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **115**, 643 (2001).
44. K. Kowalski and P. Piecuch, *Chem. Phys. Lett.* **347**, 237 (2001).
45. A.I. Krylov, C.D. Sherrill, and M. Head-Gordon, *J. Chem. Phys.* **113**, 6509 (2000).
46. S. Hirata, *J. Chem. Phys.* **121**, 51 (2004).
47. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **115**, 2966 (2001).
48. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **116**, 7411 (2002).
49. P. Piecuch, K. Kowalski, I.S.O. Pimienta and M.J. McGuire, *Int. Rev. Phys. Chem.* **21**, 527 (2002).
50. P. Piecuch, K. Kowalski, I.S.O. Pimienta, and S.A. Kucharski, in: *Low-Lying Potential Energy Surfaces*, ACS Symposium Series, Vol. 828, edited by M.R. Hoffmann and K.G. Dyall (American Chemical Society: Washington, D.C., 2002), pp. 31-64.
51. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **120**, 1715 (2004).
52. P. Piecuch, K. Kowalski, I.S.O. Pimienta, P.-D. Fan, M. Lodriguito, M.J. McGuire, S.A. Kucharski, T. Kuś, and M. Musiał, *Theor. Chem. Acc.* **112**, 349 (2004).
53. C.D. Sherrill and P. Piecuch, *J. Chem. Phys.* **122**, XXX (2005), in press [to appear in April 1, 2005 issue].
54. C.E. Smith, R.A. King, and T.D. Crawford, *J. Chem. Phys.* **122**, 054110 (2005).
55. M. Włoch, M. Musiał, and S.A. Kucharski, *Ann. Pol. Chem. Soc.* **1**, 255 (2001).
56. S.A. Kucharski, M. Włoch, M. Musiał, and R.J. Bartlett, *J. Chem. Phys.* **115**, 8263 (2001).
57. M. Kállay and J. Gauss, *J. Chem. Phys.* **121**, 9257 (2004).
58. H. Larsen, J. Olsen, P. Jørgensen, and O. Christiansen, *J. Chem. Phys.* **113**, 6677 (2000); **114**, 10985 (2001) [Erratum].
59. M. Włoch, J.R. Gour, K. Kowalski, and P. Piecuch, *J. Chem. Phys.*, in press.
60. R.K. Chaudhuri, K.F. Freed, G. Hose, P. Piecuch, K. Kowalski, M. Włoch, S. Chattopadhyay, D. Mukherjee, Z. Rolik, Á. Szabados, G. Tóth, and P.R. Surján, *J. Chem. Phys.* **122**, XXX (2005), in press [to appear in April 1, 2005 issue].
61. P. Piecuch and K. Kowalski, in: *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczyński (World Scientific, Singapore, 2000), Vol. 5, pp. 1-104.
62. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 18 (2000).
63. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 5644 (2000).
64. S. Coussan, Y. Ferro, M. Rajzmann, A. Trivella, P. Roubin, R. Wieczorek, P. Piecuch, K. Kowalski, M. Włoch, S.A. Kucharski, and M. Musiał, in preparation for *J. Phys. Chem. A*.
65. K. Kowalski and P. Piecuch, *Chem. Phys. Lett.* **344**, 165 (2001).
66. P. Piecuch, S.A. Kucharski, and K. Kowalski, *Chem. Phys. Lett.* **344**, 176 (2001).
67. P. Piecuch, S.A. Kucharski, V. Špirko, and K. Kowalski, *J. Chem. Phys.* **115**, 5796 (2001).

68. P. Piecuch, K. Kowalski, and I.S.O. Pimienta, *Int. J. Mol. Sci.* **3**, 475 (2002).
69. M.J. McGuire, K. Kowalski, and P. Piecuch, *J. Chem. Phys.* **117**, 3617 (2002).
70. P. Piecuch, S.A. Kucharski, K. Kowalski, and M. Musiał, *Comp. Phys. Commun.* **149**, 71 (2002).
71. I.S.O. Pimienta, K. Kowalski, and P. Piecuch, *J. Chem. Phys.* **119**, 2951 (2003).
72. P. Piecuch, K. Kowalski, P.-D. Fan, and I.S.O. Pimienta, in: *Advanced Topics in Theoretical Chemical Physics*, Vol. 12 of *Progress in Theoretical Chemistry and Physics*, edited by J. Maruani, R. Lefebvre, and E. Brändas (Kluwer, Dordrecht, 2003), pp. 119-206.
73. M.J. McGuire, K. Kowalski, P. Piecuch, S.A. Kucharski, and M. Musiał, *J. Phys. Chem. A* **108**, 8878 (2004).
74. P.-D. Fan, K. Kowalski, and P. Piecuch, *Mol. Phys.*, in press.
75. S. Hirata, P.-D. Fan, A.A. Auer, M. Nooijen, and P. Piecuch, *J. Chem. Phys.* **121**, 12197 (2004).
76. M.J. McGuire and P. Piecuch, *J. Am. Chem. Soc.* **127**, 2608 (2005).
77. K. Kowalski and P. Piecuch, *J. Chem. Phys.* **122**, 074107 (2005).
78. M. Lodriguito, K. Kowalski, M. Włoch, and P. Piecuch, in preparation for *J. Chem. Phys.*
79. P. Piecuch, M. Włoch, and J.R. Gour, in preparation for *J. Chem. Phys.*
80. K. Kowalski and P. Piecuch, *J. Mol. Struct.: THEOCHEM* **547**, 191 (2001).
81. P. Piecuch and K. Kowalski, *Int. J. Mol. Sci.* **3**, 676 (2002).
82. K. Kowalski and P. Piecuch, *Mol. Phys.* **102**, 2425 (2004).
83. S.A. Kucharski and R.J. Bartlett, *Theor. Chim. Acta* **80**, 387 (1991).
84. E.A. Salter, G.W. Trucks, and R.J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989).
85. J.D. Watts, J. Gauss, and R.J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
86. J. Gauss, W.J. Lauderdale, J.F. Stanton, J.D. Watts, and R.J. Bartlett, *Chem. Phys. Lett.* **182**, 207 (1991).
87. J. Gauss, J.F. Stanton, and R.J. Bartlett, *J. Chem. Phys.* **95**, 2623 (1991).
88. J. Gauss, J.F. Stanton, and R.J. Bartlett, *J. Chem. Phys.* **95**, 2639 (1991).
89. J. Gauss and J.F. Stanton, *Phys. Chem. Chem. Phys.* **2**, 2047 (2000).
90. J. Gauss and J.F. Stanton, *J. Chem. Phys.* **116**, 1773 (2002).
91. X. Li and J. Paldus, *J. Chem. Phys.* **115**, 5759 (2001).
92. X. Li and J. Paldus, *J. Chem. Phys.* **115**, 5774 (2001).
93. X. Li and J. Paldus, *J. Chem. Phys.* **117**, 1941 (2002).
94. X. Li and J. Paldus, *J. Chem. Phys.* **118**, 2470 (2003).
95. J. Paldus, J. Čížek, and M. Takahashi, *Phys. Rev. A* **30**, 2193 (1984).
96. P. Piecuch, R. Toboła, and J. Paldus, *Phys. Rev. A* **54**, 1210 (1996).
97. J. Paldus and J. Planelles, *Theor. Chim. Acta* **89**, 13 (1994).
98. G. Peris, J. Planelles, and J. Paldus, *Int. J. Quantum Chem.* **62**, 137 (1997).
99. L. Stolarczyk, *Chem. Phys. Lett.* **217**, 1 (1994).
100. X. Li and J. Paldus, *J. Chem. Phys.* **107**, 6257 (1997).
101. X. Li and J. Paldus, *J. Chem. Phys.* **108**, 637 (1998).
102. X. Li and J. Paldus, *Chem. Phys. Lett.* **286**, 145 (1998).
103. J. Olsen, A.M. Sánchez de Merás, H.J.Aa. Jensen, and P. Jørgensen, *Chem. Phys. Lett.* **154**, 380 (1989).
104. I. Özkan, A. Kinal, and M. Balci, *J. Phys. Chem. A* **108**, 507 (2004).
105. A. Kinal and P. Piecuch, *J. Am. Chem. Soc.*, submitted.
106. T.D. Crawford and H.F. Schaefer III, *J. Chem. Phys.* **104**, 6259 (1996).
107. K. Kowalski and P. Piecuch, unpublished.
108. W.J. Hehre, R. Ditchfield, and J.A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).
109. M. L. Abrams and C. D. Sherrill, *J. Chem. Phys.* **121**, 9211 (2004).
110. T.H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
111. R.A. Kendall, T.H. Dunning Jr., and R.J. Harrison, *J. Chem. Phys.* **96**, 6769 (1992).

- 112. A. Kalamos, A. Mavridis, and A. Metropoulos, *J. Chem. Phys.* **111**, 9536 (1999).
- 113. M. Zachwieja, *J. Mol. Spectrosc.* **170**, 285 (1995).
- 114. T. Nelis, J.M. Brown, and K.M. Evenson, *J. Chem. Phys.* **92**, 4067 (1990).
- 115. R. Kepa, A. Para, M. Rytel, and M. Zachwieja, *J. Mol. Spectrosc.* **178**, 189 (1996).
- 116. K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- 117. D.H. Phelps and F.W. Dalby, *Phys. Rev. Lett.* **16**, 3 (1966).
- 118. A. Kasdan, E. Herbst, and W.C. Lineberger, *Chem. Phys. Lett.* **31**, 78 (1975).
- 119. T.C. Steimle, D.F. Nachman, D.A. Fletcher, and J.M. Brown, *J. Mol. Spectrosc.* **138**, 222 (1989).
- 120. D. Mukhopadhyay, S. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, *Theor. Chim. Acta* **80**, 441 (1991).
- 121. L. Meissner and R.J. Bartlett, *J. Chem. Phys.* **94**, 6670 (1991).
- 122. L. Meissner and R.J. Bartlett, *J. Chem. Phys.* **102**, 7490 (1995).
- 123. S. Hirata, M. Nooijen, I. Grabowski and R.J. Bartlett, *J. Chem. Phys.* **114**, 3919 (2001); **115**, 3967 (2001) [Erratum].
- 124. S.R. Gwaltney and M. Head-Gordon, *Chem. Phys. Lett.* **323**, 21 (2000).
- 125. S.R. Gwaltney, C.D. Sherrill, M. Head-Gordon, and A.I. Krylov, *J. Chem. Phys.* **113**, 3548 (2000).
- 126. S.R. Gwaltney and M. Head-Gordon, *J. Chem. Phys.* **115**, 2014 (2001).
- 127. S.R. Gwaltney, E.F.C. Byrd, T. Van Voorhis, and M. Head-Gordon, *Chem. Phys. Lett.* **353**, 359 (2002).
- 128. M. Head-Gordon, T. Van Voorhis, S.R. Gwaltney, and E.F.C. Byrd, in: *Low-Lying Potential Energy Surfaces*, ACS Symposium Series, Vol. 828, edited by M.R. Hoffmann and K.G. Dyall (American Chemical Society, Washington, D.C., 2002), pp. 93-108.
- 129. J.F. Stanton, *Chem. Phys. Lett.* **281**, 130 (1997).
- 130. D.T. Crawford and J.F. Stanton, *Int. J. Quantum Chem.* **70**, 601 (1998).
- 131. S.A. Kucharski and R.J. Bartlett, *J. Chem. Phys.* **108**, 5243 (1998).