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# Left-Eigenstate Completely Renormalized Equation-of-Motion Coupled-Cluster Methods: Review of Key Concepts, Extension to Excited States of Open-Shell Systems, and Comparison With Electron-Attached and Ionized Approaches

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**ABSTRACT:** The recently proposed left-eigenstate completely renormalized (CR) coupled-cluster (CC) method with singles, doubles, and noniterative triples, termed CR-CC(2,3) [Piecuch and Włoch, *J Chem Phys*, 2005, 123, 224105; Piecuch et al. *Chem Phys Lett*, 2006, 418, 467] and the companion CR-EOMCC(2,3) methodology, which has been previously applied to singlet excited states of closed-shell molecular systems [Włoch et al. *Mol Phys*, 2006, 104, 2149] and in which relatively inexpensive noniterative corrections due to triple excitations derived from the biorthogonal method of moments of CC equations

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(MMCC) are added to the CC singles and doubles (CCSD) or equation-of-motion (EOM) CCSD energies, have been extended to excited states of open-shell species. The resulting highly efficient computer codes for the open-shell CR-EOMCC(2,3) approach exploiting the recursively generated intermediates and fast matrix multiplication routines have been developed and interfaced with the GAMESS package, enabling CR-EOMCC(2,3) calculations for singlet as well as nonsinglet ground and excited states of closed- and open-shell systems using the restricted Hartree–Fock or restricted open-shell Hartree–Fock references. A number of important mathematical and algorithmic details related to formal aspects and computer implementation of the CR-EOMCC(2,3) method have been discussed, in addition to overviewing the key concepts behind the CR-EOMCC(2,3) and biorthogonal MMCC methodologies for ground and excited states, and the numerical results involving low-lying states of the CH, CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO species, including states dominated by two-electron transitions, have been presented. The results of the CR-EOMCC(2,3) calculations have been compared with other CC/EOMCC approaches, including the EOMCCSD and EOMCC singles, doubles, and triples methods, and their full and active-space valence counterparts based on the electron-attached and ionized EOMCC methodologies, and the predecessor of CR-EOMCC(2,3) termed CR-EOMCCSD(T) [Kowalski and Piecuch, *J Chem Phys*, 2004, 120, 1715]. © 2009 Wiley Periodicals, Inc. *Int J Quantum Chem* 109: 3268–3304, 2009

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## 1. Introductory Remarks: Overview of the Noniterative Triples Coupled-Cluster and Equation-of-Motion Coupled-Cluster Methods and the Objectives of the Present Study

In 1989, Raghavachari et al. published a seminal article [1] in which they introduced an interesting type of noniterative correction due to triply excited clusters to the CCSD (coupled-cluster singles and doubles) [2–5] energy which defines the CCSD(T) method. Over the years, the CCSD(T) approach has become the most widely used approximation based on the coupled-cluster (CC) exponential wave function ansatz [6–10] which symbolizes the success of CC theory in quantum chemistry. The popularity of the CCSD(T) approach stems from the fact that CCSD(T) provides a highly accurate and size-extensive description of the many-electron correlation effects for nondegenerate ground states of molecules near the equilibrium geometries with the relatively low computer costs defined by the iterative  $n_o^2 n_u^4$  or  $\mathcal{N}^6$  steps of CCSD and the noniterative  $n_o^3 n_u^4$  or  $\mathcal{N}^7$  steps of the triples (T) correction ( $n_o$  and  $n_u$  are the numbers of occupied and unoccupied orbitals, respectively, used in post-Hartree–Fock or other post-self-consistent-field calculations, and  $\mathcal{N}$  is a general measure of the system size).

With the computational steps of this type, which in realistic applications involving larger basis sets are orders of magnitude less expensive than the iterative  $n_o^3 n_u^5$  (or  $\mathcal{N}^8$ ) steps of the parent full CCSDT (CC singles, doubles, and triples) method [11, 12], one can nowadays perform routine CCSD(T) calculations for systems with up to about 100 correlated electrons and a few hundred basis functions. This should be contrasted with the small systems consisting of up to a dozen or so correlated electrons that are tractable by the full CCSDT approach, which in most applications does not offer any significant advantages as far as the accuracy is concerned when one focuses on molecular properties near the equilibrium geometries, while making the calculations a lot more expensive. Another factor that greatly contributes to the popularity of the CCSD(T) method among nonexperts is the fact that CCSD(T) is a single-reference approach of the black-box type. Also, immediately after the discovery of the CCSD(T) approach, it was noticed [13–15] that the triples correction of CCSD(T), which mixes fourth-order-type and selected fifth-order-type terms in the many-body perturbation theory (MBPT) energy expansion in a manner that at the time of the discovery of CCSD(T) was unconventional and not very well understood, is generally more accurate and robust than the previously developed triples corrections of the  $\text{CCD} + \text{ST} = \text{CCD}[\text{ST}]$  (Ref. [16]) and  $\text{CCSD} + \text{T} = \text{CCSD}[\text{T}]$  (Ref. [17]) approaches

(see Ref. [18] for the orthogonally spin-adapted formulation of CCD[ST] and CCSD[T]) that define the corrections due to triples in a conventional manner by analyzing the fourth order of MBPT only, which is where the connected triply excited clusters appear for the first time. The superiority of CCSD(T) over CCSD[T] was eventually formally explained by Stanton [19] and, more recently, by us [20, 21]. As shown in Refs. [19–21], we need to augment the CCSD[T] energy by one specific fifth-order-type term that distinguishes CCSD(T) from its CCSD[T] predecessor to describe the leading energy contributions due to triply excited clusters toward the exact, full configuration interaction (CI) energy in a consistent manner. Finally, the relatively simple formal structure of the CCSD(T) equations makes it possible to extend CCSD(T) to large molecular systems with hundreds of correlated electrons and thousands of basis functions through the use of the local correlation formalism [22, 23] that leads to the near linear scaling CCSD(T) algorithms which recover practically all of the canonical CCSD(T) energy at a small fraction of the computer effort required by the conventional CCSD(T) calculations employing the delocalized Hartree–Fock orbitals, as shown, for example, in Refs. [24–28].

The spectacular success of CCSD(T) in calculations involving the nondegenerate ground states of molecular systems has inspired considerable activity toward extending the idea of noniterative triples corrections to single-reference CCSD energies to some of the most frequent multireference situations, such as bond breaking and biradicals, where the standard CCSD(T) approach of Ref. [1] encounters problems, and to excited electronic states that interest us in this work. An effort to extend the applicability of CCSD(T) to bond breaking and biradicals has resulted in the new generations of noniterative corrections to single-reference CC (e.g., CCSD) energies which eliminate, at least to some extent, the failures of CCSD(T) in such situations while preserving its relatively low costs and ease of use, i.e., methods that can effectively capture larger nondynamical correlation effects in an intrinsically single-reference manner through the suitably defined corrections to conventional CC energies. Those include the noniterative CC approaches based on the Löwdin-style [29] partitioning of the similarity-transformed Hamiltonian, pursued primarily by Head-Gordon and co-workers [30–33], and in a slightly modified form by Hirata et al. [34, 35], which are commonly labeled as the CCSD(2) approximations and which are closely related to the ideas

presented in Refs. [19, 36–39], and the renormalized CC approaches, including, for example, the completely renormalized (CR) CCSD(T) approach (Refs. [40–44]) and its more recent locally renormalized (LR) CCSD(T) (Refs. [45, 46]) and left-eigenstate CR-CCSD(T)<sub>ℒ</sub> ≡ CR-CC(2,3) (Refs. [20, 21, 47–49]) analogs that address the issue of small size extensivity errors, on the order of 0.5–1% of the total correlation energy, in the CR-CCSD(T) calculations. The CR-CCSD(T) approach and other CR-CC approximations in that category are based on the asymmetric energy expressions and the ensuing moment expansions of the exact, full CI energy that define the more general theoretical framework termed the method of moments of CC equations (MMCC) (Refs. [40–44, 50, 51]). The LR-CCSD(T) and other LR-CC approaches are based on the numerator-denominator-connected variant of the MMCC energy expansion [45] and the analogous considerations presented in Ref. [52], where the authors developed the so-called extensively renormalized (XR) CC approximations. The CR-CC(2,3) and other CR-CC( $m_A, m_B$ ) schemes are based on yet another form of the moment expansion of the full CI energy that defines the biorthogonal MMCC formalism [20, 21, 49]. As in the case of CCSD(T), the most expensive computational steps that characterize the triples correction of CCSD(2), which defines the CCSD(2)<sub>T</sub> method [35], and the triples corrections of CR-CCSD(T), LR-CCSD(T), XR-CCSD(T), and CR-CC(2,3) scale as  $n_o^3 n_u^4$  with  $n_o$  and  $n_u$  or  $\mathcal{N}^7$  with the size of the system. Of all of these approximations, the CR-CC(2,3) approach of Refs. [20, 21, 47–49] seems to be generally the most accurate and robust, particularly in applications involving single bond breaking [20, 21, 47, 48, 53–57], mechanistic studies involving biradicals [20, 21, 58–62], and singlet-triplet gaps in biradical/magnetic systems [48, 49, 60]. Very recently, the Piecuch Michigan State University group has managed to extend the CR-CC(2,3) method to large systems with hundreds of correlated electrons and thousands of basis functions by developing the local correlation, linear scaling, and naturally parallel CR-CC(2,3) algorithm which recovers the canonical CR-CC(2,3) correlation energies to within 0.1–0.5% or so and the corresponding relative energies to within ~1 kcal/mol or better at a small fraction of the computer time required by the canonical CR-CC(2,3) calculations using the delocalized Hartree–Fock basis [26–28].

Encouraged by the excellent performance of the CR-CC(2,3) [or CR-CCSD(T)<sub>ℒ</sub>] approach in applications involving ground electronic states, we have decided to investigate the possibility of extending

the idea of the noniterative triples corrections of the CR-CC(2,3) type, which have the relatively low computer costs defined by the  $n_o^3 n_u^4$  steps, to excited electronic states. The general theoretical framework of the biorthogonal MMCC formalism that leads to the entire class of the resulting CR-EOMCC(2,3) and similar corrections to the excited-state energies obtained in the equation-of-motion CCSD (EOMCCSD) [63] and other EOMCC [63–67] or the equivalent linear-response or time-dependent CC [68–73] calculations, has been established in Ref. [21]. The initial computer implementation and testing of the CR-EOMCC(2,3) approach, originally abbreviated as CR-EOMCCSD(T)<sub>∞</sub> [47, 74], for the excited singlet states of closed-shell species, in which the suitably defined corrections due to triples derived from the biorthogonal MMCC theory of Ref. [21] are added to the EOMCCSD energies, have been discussed in Refs. [47, 74], demonstrating a considerable promise, particularly in the applications involving excited states dominated by two-electron transitions that normally require higher and often prohibitively expensive levels of the EOMCC theory, such as full EOM-CCSDT [75–79], or expert multireference methods to obtain an accurate description. As shown in Refs. [47, 74], the vertical excitation energies resulting from the CR-EOMCC(2,3)  $\equiv$  CR-EOMCCSD(T)<sub>∞</sub> calculations for singlet excited states of closed-shell molecules can be as accurate as those resulting from the full EOMCCSDT calculations and at least as accurate as those obtained with the well-established predecessor of CR-EOMCC(2,3), termed CR-EOMCCSD(T) (Refs. [43, 44, 80, 81]), which is based on the original MMCC formalism for excited electronic states developed in Refs. [50, 51] (cf., also, Refs. [43, 44]) and which has been in frequent use in molecular applications involving electronic excitations in recent years (cf. Refs. [43, 44, 47, 74, 80–107] for the selected examples). Based on the initial benchmark calculations reported in Refs. [47, 74], the performance of the CR-EOMCC(2,3) approach is particularly good for the excited states dominated by double excitations, where the errors in the calculated excitation energies obtained with EOMCCSD often exceed 1 eV and where CR-EOMCC(2,3) reduces these large errors to the level of 0.1 eV or better.

The main objective of this article is to complete the initial stage of the CR-EOMCC(2,3) development and testing by examining if the CR-EOMCC(2,3) approach of Refs. [47, 74] based on the biorthogonal formulation of the excited-state MMCC theory [21] can be equally effective in describing the

nonsinglet excited states of open-shell (e.g., radical) species, including, as in the aforementioned case of singlet states, the challenging excited states of open-shell systems dominated by two-electron transitions. To accomplish this, we had to extend the CR-EOMCC(2,3) computer program exploited earlier in the calculations for the singlet states of closed-shell systems [47, 74], based on the restricted Hartree–Fock (RHF) reference, to the excited states of open-shell molecules. The resulting open-shell CR-EOMCC(2,3) code, which is as a natural extension of the ground-state CR-CC(2,3) program reported in Ref. [48] and the RHF-based, closed-shell CR-EOMCC(2,3) code used in Refs. [47, 74], and which is described in this article, uses the restricted open-shell Hartree–Fock (ROHF) determinant as a reference and is interfaced with the integral and ROHF routines available in the GAMESS package [108]. The development of the open-shell CR-EOMCC(2,3) approach gives us an opportunity to describe various mathematical and algorithmic details related to computer implementation of the CR-EOMCC(2,3) method, which have not been discussed in the earlier work [47, 74], in addition to overviewing the basic concepts behind the CR-EOMCC(2,3) theory and the underlying biorthogonal MMCC methodology for ground and excited states. The description of the key ideas behind the biorthogonal MMCC and CR-EOMCC(2,3) approaches for ground and excited states, and the mathematical and computational details that are relevant to the efficient implementation of the CR-EOMCC(2,3) method for ground and excited states of closed- and open-shell systems is one of the important goals of this work.

It should be mentioned that the CR-EOMCC(2,3) approach that we proposed in Refs. [47, 74] has recently been implemented by Krylov and co-workers [109], using the spin-conserving as well as spin-flip [110–112] formulations of the EOMCC theory [regrettably and without justification, the authors of Ref. [109] have also renamed the so-called variants A and D of the CR-EOMCC(2,3)  $\equiv$  CR-EOMCCSD(T)<sub>∞</sub> approach, which we introduced 2 years earlier in Ref. [47], as “EOM-CCSD(ft)” and “EOM-CCSD(dT),” respectively]. In particular, the authors of Ref. [109] have tested the CR-EOMCC(2,3) triples corrections proposed in Refs. [47, 74] for the interesting case of the adiabatically nearly degenerate doublet states of the 1,2,3-tri-dehydrobenzene radical, obtaining encouraging results. Unfortunately, none of the excited states of radical species examined in Ref. [109] has a significant doubly excited character that would result in

large triples corrections to the EOMCCSD energies or larger variations among the excitation energies obtained with different ways of treating the perturbative denominators that enter the triples corrections of CR-EOMCC(2,3). This article provides the convincing examples of the challenging excited states of open-shell species where the triples corrections of CR-EOMCC(2,3) become very large (as large as 1–2.5 eV) and where it becomes critical to use the complete treatment of the perturbative denominators that enter the CR-EOMCC(2,3) triples corrections offered by the so-called variant D of CR-EOMCC(2,3) [the CR-EOMCC(2,3),D approach; cf., e.g., Ref. [47]]. As shown in this study, the less complete treatments of the perturbative denominators that enter the CR-EOMCC(2,3) triples corrections offered by variants A and B [the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B approaches], while improving the EOMCCSD energies, may lead to substantial error increases in the resulting excitation energies, which in the examples examined in this work are as large as 0.4–1 eV, when compared to the CR-EOMCC(2,3),D calculations.

When mentioning various types of the CR-EOMCC(2,3) approximations, one should point out that in analogy to the ground state considerations, where variants A and B of CR-CC(2,3) are equivalent, at least for the case of the Hartree–Fock reference, to the triples corrections of the CCSD(2) methods of Refs. [30–35], the excited-state CR-EOMCC(2,3) approach introduced in Refs. [47, 74] and examined in the present study is closely related to the triples corrections to the EOMCCSD energies described in Refs. [34, 113]. As in the case of the ground-state CCSD(2) approach, the noniterative corrections to the EOMCC energies discussed in Refs. [34, 113] are obtained via partitioning of the similarity-transformed Hamiltonian of the CC theory and the ensuing perturbation theory analysis, following the ideas originally laid down by Stanton and Gauss [114, 115], Stanton [19], and Crawford and Stanton [36]. In particular, the aforementioned variant A of CR-EOMCC(2,3) [the CR-EOMCC(2,3),A method] is identical to the triples correction of the EOM-CC(2)PT(2) approach discussed in Refs. [34, 113]. Unfortunately, the authors of Ref. [113] have failed to recognize this, while trying to criticize the successful CR-EOMCCSD(T) approach for the lack of the correct size dependence of the resulting energies, a feature shared by the EOM-CC(2)PT(2) approach, which is also less accurate than the CR-EOMCCSD(T) method and the CR-EOMCC(2,3) approach examined in this

work. As explained in the earlier articles on the CR-CC(2,3) and CR-EOMCC(2,3) methods [47–49] and as already alluded to above, the main difference between the approximate variant A and the complete variant D of CR-CC(2,3) and CR-EOMCC(2,3) is in the form of the perturbative denominator used to define the relevant triples corrections, which is of the Møller–Plesset type in the case of variant A and of the Epstein–Nesbet type in the case of variant D. As shown in Refs. [20, 21, 47–49, 55, 56] the use of the Epstein–Nesbet-style perturbative denominator in defining the triples corrections of CR-CC(2,3) leads to better (in many cases substantially better) results in the ground-state CR-CC(2,3) calculations. It has also been demonstrated that the use of the Epstein–Nesbet-style rather than Møller–Plesset-style perturbative denominators in defining the triples corrections to EOMCCSD energies leads to considerable improvements in the results of the excited-state CR-EOMCCSD(T) calculations [44, 74, 80, 82], bringing them closer to the parent EOM-CCSDT approach. One of the important objectives of this article is to demonstrate that the same remains true in the excited-state CR-EOMCC(2,3) calculations, particularly in cases of the excited states of open-shell systems dominated by two-electron processes where, as already mentioned, the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B approaches may worsen the results by as much as 1 eV when compared to the more complete CR-EOMCC(2,3),C and CR-EOMCC(2,3),D approximations, which have the same costs as the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B calculations.

We should also mention that the straightforward modification of the CR-EOMCC(2,3) energy expressions of Refs. [47, 74], following the recipe described in Ref. [113], would enable us to formulate the CR-EOMCC(2,3) corrections that restore strict size intensivity [73, 116] of the resulting excitation energies, which the EOMCCSD approach preserves but the CR-EOMCC(2,3) approach and other noniterative EOMCC methods of this type, including EOM-CC(2)PT(2) and CR-EOMCCSD(T), violate (see Refs. [81, 113] for an analysis). In this case, the modified CR-EOMCC(2,3),A approximation would become equivalent to the EOMCCSD(2)<sub>T</sub> approach of Ref. [113]. One can show that the reason for the violation of size intensivity of excitation energies by the CR-EOMCC(2,3) [and the analogous EOM-CC(2)PT(2) or equivalent CR-EOMCC(2,3),A] corrections is related to the presence of the size-extensive ( $r_{\mu,0} = 0$ ) or approximately size-extensive (non-zero  $r_{\mu,0}$ ) contribution

$\beta_\mu(2,3) = \sum_{\substack{i < j < k \\ a < b < c}} (r_{\mu,0} \ell_{\mu,ijk}^{abc} - \ell_{0,ijk}^{abc}) \mathfrak{M}_{0,abc}^{ijk}(2)$ , where

using the notation introduced in Section 2,  $r_{\mu,0}$  is the amplitude defining the zero-body component  $R_{\mu,0}$  of the EOMCCSD linear excitation operator  $R_\mu^{(\text{CCSD})}$ ,  $\ell_{\mu,ijk}^{abc}$  are the de-excitation amplitudes entering the triples correction  $\delta_\mu(2,3)$  of CR-EOMCC(2,3),  $\ell_{0,ijk}^{abc}$  are the ground-state counterparts of the  $\ell_{\mu,ijk}^{abc}$  amplitudes defining the ground-state triples correction  $\delta_0(2,3)$  of CR-CC(2,3), and  $\mathfrak{M}_{0,abc}^{ijk}(2)$  are the triply excited moments of the ground-state CCSD equations, in the vertical excitation energy  $\omega_\mu^{(\text{CR-EOMCC}(2,3))} = E_\mu^{(\text{CR-EOMCC}(2,3))} - E_0^{(\text{CR-CC}(2,3))}$ . Using the equations presented in Section 2.2, we can write  $\omega_\mu^{(\text{CR-EOMCC}(2,3))} = \omega_\mu^{(\text{CCSD})} + \alpha_\mu(2,3) + \beta_\mu(2,3)$ , where  $\omega_\mu^{(\text{CCSD})}$  is the vertical excitation energy of EOMCCSD,  $\alpha_\mu(2,3) = \sum_{\substack{i < j < k \\ a < b < c}} \ell_{\mu,ijk}^{abc} \tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2)$ , with

$\tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2}) | \Phi \rangle$  representing the contribution to the triply excited moment  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  of EOMCCSD due to the one- and two-body components of  $R_\mu^{(\text{CCSD})}$ , and  $\beta_\mu(2,3)$  is the quantity defined above [it should be noted that the complete moment  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  of EOMCCSD is a sum of  $\tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2)$  and  $r_{\mu,0} \mathfrak{M}_{0,abc}^{ijk}(2)$ , where the latter term represents the contribution due to the zero-body component of  $R_\mu^{(\text{CCSD})}$ ]. Since the EOMCCSD approach is rigorously size intensive and the  $\alpha_\mu(2,3)$  term is size intensive as well, the  $\omega_\mu^{(\text{CCSD})} + \alpha_\mu(2,3)$  part of the CR-EOMCC(2,3) excitation energy  $\omega_\mu^{(\text{CR-EOMCC}(2,3))}$  is the size-intensive quantity. Unfortunately, the  $\beta_\mu(2,3)$  term, being a rigorously or approximately size-extensive contribution that cannot be eliminated from  $\omega_\mu^{(\text{CR-EOMCC}(2,3))}$ , grows with the size of the system, destroying the size intensity of  $\omega_\mu^{(\text{CR-EOMCC}(2,3))}$ . In fact, when the symmetry of the excited state  $\mu$  is different from that of the ground state, the zero-body, reference component  $R_{\mu,0}$  of the corresponding excitation operator  $R_\mu^{(\text{CCSD})}$  is zero, yielding the vanishing contribution from  $R_{\mu,0}$  to the CR-EOMCC(2,3) triples correction  $\delta_\mu(2,3)$  to this excited state in a situation where the corresponding contribution to the ground-state CR-CC(2,3) triples correction  $\delta_0(2,3)$  in which formally  $R_{\mu=0,0} = \mathbf{1}$ , where  $\mathbf{1}$  is the unit operator, is non-zero, growing with the size of the system as a size-extensive quantity. We investigated this numerically already in 2006 using the noninteracting  $\text{C}_2 + n\text{Ne}$  systems which we examined earlier in Ref. [81]. For example, the CR-EOMCC(2,3) energy of the excited state of  $\text{C}_2 + \text{Ne}$  that corresponds to the  $X^1\Sigma_g^+ \rightarrow$

$B^1\Delta_g$  excitation in  $\text{C}_2$ , in which the Ne atom remains in its ground state,  $E_\mu^{(\text{CR-EOMCC}(2,3))}(\text{C}_2 + \text{Ne})$ , equals the sum of the CR-EOMCC(2,3) energy of the  $B^1\Delta_g$  state of  $\text{C}_2$  and the CCSD [rather than CR-CC(2,3)] ground-state energy of Ne, i.e.,  $E_\mu^{(\text{CR-EOMCC}(2,3))}(\text{C}_2 + \text{Ne}) = E_\mu^{(\text{CR-EOMCC}(2,3))}(\text{C}_2) + E_0^{(\text{CCSD})}(\text{Ne})$ , since the zero-body component of the  $R_\mu^{(\text{CCSD})}$  operator corresponding to the excited state of the noninteracting  $\text{C}_2 + \text{Ne}$  system, which correlates with the  $B^1\Delta_g$  state of  $\text{C}_2$  and the ground state of Ne, and which has a different symmetry than the ground state of the  $\text{C}_2 + \text{Ne}$  system, is zero. The corresponding ground-state energy of  $\text{C}_2 + \text{Ne}$ ,  $E_0^{(\text{CR-CC}(2,3))}(\text{C}_2 + \text{Ne})$ , obtained with the size-extensive CR-CC(2,3) method, equals the sum of the CR-CC(2,3) energies of the ground states of  $\text{C}_2$  and Ne, i.e.,  $E_0^{(\text{CR-CC}(2,3))}(\text{C}_2 + \text{Ne}) = E_0^{(\text{CR-CC}(2,3))}(\text{C}_2) + E_0^{(\text{CR-CC}(2,3))}(\text{Ne})$ . In consequence, the vertical excitation energy of the noninteracting  $\text{C}_2 + \text{Ne}$  system corresponding to the  $X^1\Sigma_g^+ \rightarrow B^1\Delta_g$  excitation in the  $\text{C}_2$  fragment within  $\text{C}_2 + \text{Ne}$ ,  $\omega_\mu^{(\text{CR-EOMCC}(2,3))}(\text{C}_2 + \text{Ne}) = E_\mu^{(\text{CR-EOMCC}(2,3))}(\text{C}_2 + \text{Ne}) - E_0^{(\text{CR-CC}(2,3))}(\text{C}_2 + \text{Ne})$ , equals the vertical excitation energy  $\omega_\mu^{(\text{CR-EOMCC}(2,3))}(\text{C}_2)$  of  $\text{C}_2$  corresponding to the  $X^1\Sigma_g^+ \rightarrow B^1\Delta_g$  transition minus the ground-state CR-CC(2,3) triples correction for Ne,  $\delta_0(2,3)(\text{Ne})$ , rather than  $\omega_\mu^{(\text{CR-EOMCC}(2,3))}(\text{C}_2)$  only, as would be required by the rigorously size-intensive theory. One can try to address the problem by enforcing the cancellation of the term which contributes to the CR-EOMCC(2,3) triples correction  $\delta_\mu(2,3)$  to the excited-state energy  $E_\mu^{(\text{CR-EOMCC}(2,3))}$  and which originates from the presence of the zero-body component of the corresponding  $R_\mu^{(\text{CCSD})}$  operator of EOMCCSD in the triply excited moments of EOMCCSD with the analogous term that contributes to the triples correction  $\delta_0(2,3)$  of the CR-CC(2,3) ground-state energy  $E_0^{(\text{CR-CC}(2,3))}$ , restoring the size-intensivity of the resulting excitation energies  $\omega_\mu$ , but, using the words of the authors of Ref. [113], such cancellation is “neither rigorous nor accurate.” Although we have been aware of this rather obvious possibility of restoring size intensivity of the CR-EOMCC(2,3) approach along the lines described in Ref. [113] from the very beginning, i.e., from the time CR-EOMCC(2,3) was proposed in early 2006 [47, 74], we do not pursue the topic of size intensivity or the lack thereof in this article, since for smaller and medium size molecules, where one typically correlates up to 30–50 electrons, the issue of the departure from strict size intensivity in the CR-EOMCC calculations of vertical and adiabatic excitation energies is of relatively minor significance when compared to

other sources of errors [81], and the recipe to restore size intensivity discussed in Ref. [113] is, as the authors of Ref. [113] acknowledge, completely *ad hoc*, worsening the calculated excitation energies in many cases. For the time being, i.e., until the issue of the lack of size intensivity of the CR-EOMCCSD(T), CR-EOMCC(2,3), and EOM-CC(2)PT(2) corrections is addressed in a formal manner—and we must acknowledge that we do not have a satisfactory, rigorous, and generally applicable mathematical solution of this problem at hand yet—we will continue examining various other aspects of the CR-EOMCCSD(T) and CR-EOMCC(2,3) calculations. It is worth mentioning though that the spin-flip variant of our CR-EOMCC(2,3) theory seems to retain the size-intensive feature of EOMCCSD without making any changes in the CR-EOMCC(2,3) triples correction formulas of Refs. [47, 74], as implied by the remarks made in Ref. [109], which is undoubtedly an interesting observation and a potentially promising development.

Before summarizing the plan of this work and proceeding to the most essential mathematical and computational details of the CR-EOMCC(2,3) approach relevant to the present study, it is important to mention that prior to the introduction of the CR-EOMCCSD(T) (Refs. [43, 44, 80, 81]) and CR-EOMCC(2,3) (Refs. [47, 74]) approaches, and the related EOM-CC(2)PT(2) and EOMCCSD(2)<sub>T</sub> (Refs. [34, 113]) methods, there have been several earlier attempts to formulate the iterative as well as non-iterative EOMCC and linear response CC schemes that avoid the prohibitive  $n_o^3 n_u^5$  ( $\mathcal{N}^8$ -like) costs of the full EOMCCSDT calculations while accounting for the leading effects due to triple excitations in an approximate manner. The representative examples include the iterative EOMCCSDT-1 approach and its noniterative EOMCCSD(T) counterpart [117], or the approximate triples linear-response CC methods, such as CC3 [118–122] and CCSDR(3) [120–122], which are all characterized by the relatively inexpensive  $\mathcal{N}^7$  steps and which all rely on the MBPT-like analysis to estimate the effects due to triples on the vertical excitation energies. One can also use the somewhat more expensive and yet affordable EOMCCSDT-3 method and its noniterative EOMCCSD( $\tilde{T}$ ) and EOMCCSD(T') counterparts [123], with the EOMCCSD( $\tilde{T}$ ) scheme being particularly successful (cf., e.g., Refs. [124–126]). Interestingly, as noted in Ref. [80], one can recognize the elements of the triples corrections to the EOMCCSD excitation energies

defining EOMCCSD( $\tilde{T}$ ) in the equations defining the CR-EOMCCSD(T) approach of Refs. [43, 44, 80, 81], which, as mentioned above, was derived from the original version of the excited-state MMCC formalism [50, 51]. In fact, the similarities between the EOMCCSD( $\tilde{T}$ ) approach and the more recent types of the triples corrections to EOMCCSD energies go beyond this. For example, the authors of Ref. [113] pointed out that the size-intensive parts of the triples corrections to the excitation energies of EOMCCSD defining the EOM-CC(2)PT(2) method of Refs. [34, 113] or the EOMCCSD(2)<sub>T</sub> approach of Ref. [113], which were obtained through the use of the partitioning of the similarity-transformed Hamiltonian and the resulting perturbation theory analysis originally suggested in Refs. [19, 36, 114, 115], are identical to the triples corrections to the excitation energies defining the EOMCCSD( $\tilde{T}$ ) approach. These formal similarities between the EOM-CC(2)PT(2) or EOMCCSD(2)<sub>T</sub> and CR-EOMCCSD(T) methods, which are more robust than the traditional methods of the EOMCCSD(T) type, and the EOMCCSD( $\tilde{T}$ ) scheme, may explain, at least in part, the successes of the latter scheme in actual molecular applications, including those reported in the aforementioned Refs. [124–126]. Unfortunately, although the EOMCCSD( $\tilde{T}$ ) approach and other approximate triples EOMCC or linear-response CC methods developed in the 1990s improve the EOMCCSD results for the excited states dominated by two-electron transitions, there remain too many cases where the results of EOMCCSDT-*n*, EOMCCSD(T), CC3, and similar calculations are less than satisfactory, and not as good as those provided by the EOM-CC(2)PT(2), EOMCCSD(2)<sub>T</sub>, CR-EOMCCSD(T), and CR-EOMCC(2,3) calculations (cf., e.g., Refs. [43, 44, 47, 74, 80, 81, 113]). 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<sub>2</sub> molecule, respectively, by the EOMCCSDT-1 and CC3 approaches [121], which variant ID of the CR-EOMCCSD(T) approach reduces to 0.054 and 0.283 eV, respectively, the relatively large 0.318 and 0.261 eV errors in the description of the two lowest-energy  $^1\Delta_g$  states of CH<sup>+</sup>, which the CR-EOMCC(2,3),D approach reduces to 0.025 and 0.030 eV, respectively, or the failure of the CC3 and CCSDR(3) methods to provide accurate and well-balanced information about excited-state potential energy surfaces along bond breaking coordinates [127], which the CR-EOMCC methods can handle

quite well (see Refs. [44, 80] for analysis and direct comparisons; cf., also, Ref. [113] for the analogous results at the related EOMCCSD(2)<sub>T</sub> level).

In discussing various approximate ways of describing triple excitation effects within the EOMCC framework, we cannot overlook the fact that one can also improve the EOMCC results for the excited states dominated by doubles and excited-state potential energy surfaces in a relatively inexpensive manner by turning to the active-space variant of the EOMCCSDT approach, which significantly reduces the costs of full EOMCCSDT calculations through the suitable selection of the dominant triply excited cluster and excitation amplitudes exploiting the concept of active orbitals rather than through the use of perturbative arguments. In analogy to the corresponding ground-state active-space CC methods [128–133], the resulting EOMCCSDt approach [75, 76, 134] belongs to a category of iterative approximations that combine the single-reference EOMCC formalism with multireference concepts, although one can classify EOMCCSDt as a largely single-reference theory, since the EOMCCSDt calculations rely on the use of a single Fermi vacuum and utilize a modified form of the single-reference CCSDT and EOMCCSDT equations. In the case of open-shell radical species that interest us in this work, one can also utilize methods based on the electron-attached (EA) (Refs. [135–143]) and ionized (IP) (Refs. [114, 115, 138–150]) EOMCC formalisms (cf. Ref. [67] for an overview of the relevant mathematical concepts), or their EA and IP counterparts [142, 151–156] based on the more general SAC-CI framework [151–163]. In these methods, one obtains the electronic states of radicals by applying the electron attaching or ionizing operator  $R$  with the 1-particle (1p) or 1-hole (1h), 2-particle–1-hole (2p-1h) or 2-hole–1-particle (2h-1p), etc. components to the ground state of the related closed-shell reference system provided by the conventional single-reference CC calculation, relying on the intuitive idea that a radical can be viewed as a system obtained by attaching an electron to or removing an electron from the related closed-shell molecule, followed by relaxation of the remaining electrons. As clearly demonstrated in Refs. [138–140, 142], the minimum levels of truncation that lead to an accurate description of the ground and excited states of radicals, at least in the spectroscopic region, are 3p-2h in the EA-EOMCC case and 3h-2p in the IP-EOMCC case. The EA- and IP-EOMCC methods that use these

truncation levels are EA-EOMCCSD(3p-2h) (Refs. [138–140]), IP-EOMCCSD(3h-2p) (Refs. [138–140]), EA-EOMCCSDT [137], and IP-EOMCCSDT [148, 149]. The former two approaches are particularly attractive, since they combine the  $n_o^2 n_u^5$  and  $n_o^3 n_u^4$  ( $\mathcal{N}^7$ -like) steps in the diagonalization of the similarity-transformed Hamiltonian, with the  $n_o^2 n_u^4$  ( $\mathcal{N}^6$ -like) steps of the underlying ground-state CCSD calculation rather than the much more expensive  $n_o^3 n_u^5$  ( $\mathcal{N}^8$ -like) steps of CCSDT used in the EA-EOMCCSDT and IP-EOMCCSDT methods. Further reduction of the computer costs of the EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) approaches can be obtained by combining the aforementioned idea of active-space CC and EOMCC methods with the EA- and IP-EOMCC methodologies, as described in Refs. [138–140, 142]. In the specific case of the EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) methods, one uses a small set of active orbitals to select the dominant 3p-2h and 3h-2p components of the electron attaching and ionizing operators  $R$ , which reduces the  $\mathcal{N}^7$ -like steps of the parent EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) calculations to the inexpensive steps of the  $n_o^2 n_u^4$  type that differ from the underlying CCSD calculations only by a small prefactor equal to the number of active unoccupied [the EA-EOMCCSD(3p-2h) case] or occupied [the IP-EOMCCSD(3h-2p) case] orbitals. As shown in Refs. [138–140, 142] (see, also, Ref. [143] for additional examples), the active-space EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) methods provide the results that are practically identical to those obtained with the full EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) approaches at a small fraction of the computer cost. Although this article focuses on the extension of the noniterative CR-EOMCC(2,3) method to the excited states of radicals, which is a more black-box methodology when compared to the active-space EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p), we are mentioning the full and active-space EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) methods here, since one of our goals is to compare the results of the CR-EOMCC(2,3) calculations with the corresponding full and active-space EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) calculations. All of these methods aim at the computationally efficient inclusion of triple excitations within the EOMCC formalism, so their direct comparison is certainly quite useful for the future practical applications of these kinds of approaches.



In conclusion of this introductory review section, the main goals of the present work are the overview of the key ideas behind the biorthogonal MMCC theory and the CR-EOMCC(2,3) approach that results from it, the thorough description of the mathematical and algorithmic details that lead to the efficient computer implementation of the CR-EOMCC(2,3) theory for ground and excited states of closed and open-shell systems, and the examination of the accuracy of the CR-EOMCC(2,3) triples corrections of Refs. [47, 74] in applications involving challenging excited states of open-shell molecules and the types of improvements that can be offered by switching from the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B models to their CR-EOMCC(2,3),C and CR-EOMCC(2,3),D extensions which use a more complete representation of the diagonal matrix elements of the similarity-transformed Hamiltonian that enter the perturbation theory denominators of the CR-EOMCC(2,3) corrections. The numerical examples investigated in this study include the low-lying valence excited states of the CH, CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO systems. The valence excited states of CH, CNC and C<sub>2</sub>N are particularly interesting, since a significant fraction of these states has a predominantly two-electron excitation nature that creates a significant challenge to the EOMCC methodologies. The CR-EOMCC(2,3),A–D adiabatic excitation energies of the above open-shell systems are compared with one another and with the available EOM-CCSD, EOMCCSDT, and full and active-space EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) data, as well as with the experimental values, so that we can offer a thorough assessment of the performance of four different variants of the CR-EOMCC(2,3) approach in studies of excited states of challenging open-shell molecules.

## 2. Theory and Computational Details

### 2.1. BIORTHOGONAL MMCC THEORY FOR GROUND AND EXCITED STATES

As explained in the introductory review section, the ground-state CR-CC(2,3) method and its excited-state CR-EOMCC(2,3) extension are based on the idea of adding the *a posteriori* noniterative corrections due to triple excitations, which originate from the more general biorthogonal MMCC formalism [20, 21, 47, 49, 74], to the CCSD and EOMCCSD energies, respectively. In analogy to the original MMCC

theory [40–44, 50, 51], the biorthogonal formulation of MMCC developed in Refs. [20, 21, 47, 49, 74] provides the formal basis for deriving the many-body expansions for the state-selective, noniterative energy corrections

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

where  $E_{\mu}^{(A)}$  is the ground-state ( $\mu = 0$ ) or excited-state ( $\mu > 0$ ) energy obtained in the standard CC or EOMCC calculations with some approximate method  $A$ , such as CCSD or EOMCCSD, which we want to correct, and  $E_{\mu}$  is the corresponding exact, i.e., full CI energy. Specifically, if

$$T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad (2)$$

with

$$T_n = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} t_{a_1 \dots a_n}^{i_1 \dots i_n} a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1}, \quad (3)$$

and

$$R_{\mu}^{(A)} = R_{\mu,0}^{(A)} + R_{\mu,\text{open}}^{(A)} \equiv r_{\mu,0} \mathbf{1} + \sum_{n=1}^{m_A} R_{\mu,n}, \quad (4)$$

with

$$R_{\mu,n} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} r_{\mu,a_1 \dots a_n}^{i_1 \dots i_n} a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} \quad (n \geq 1), \quad (5)$$

where  $i_1, i_2, i_3, \dots$  or  $i, j, k, \dots$  ( $a_1, a_2, a_3, \dots$  or  $a, b, c, \dots$ ) are the spin-orbitals occupied (unoccupied) in the reference determinant  $|\Phi\rangle$ ,  $a^p$  ( $a_p$ ) are the creation (annihilation) operators associated with the orthonormal spin-orbital basis set  $\{|p\rangle\}$ , and  $\mathbf{1}$  is the unit operator, represent the cluster and linear excitation operators defining the ground-state CC and excited-state EOMCC wave functions,

$$|\Psi_0^{(A)}\rangle = e^{T^{(A)}} |\Phi\rangle \quad (6)$$

and

$$|\Psi_{\mu}^{(A)}\rangle = R_{\mu}^{(A)} |\Psi_0^{(A)}\rangle = R_{\mu}^{(A)} e^{T^{(A)}} |\Phi\rangle, \quad (7)$$

respectively, of an  $N$ -electron system corresponding to the approximate method  $A$  defined by the truncation level  $m_A < N$  (in CCSD and EOMCCSD,  $m_A = 2$ ), we can write [20, 21, 47, 49, 74]

$$\begin{aligned}\delta_\mu^{(A)} &= \sum_{n=m_A+1}^{N_{\mu,A}} \langle \Phi | \mathcal{L}_{\mu,n} M_{\mu,n}(m_A) | \Phi \rangle \\ &= \sum_{n=m_A+1}^{N_{\mu,A}} \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} \ell_{\mu,i_1\dots i_n}^{a_1\dots a_n} \mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A). \quad (8)\end{aligned}$$

Here,

$$M_{\mu,n} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} \mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A) a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} \quad (n \geq 1) \quad (9)$$

is the particle-hole excitation operator defined in terms of the generalized moments of the CC ( $\mu = 0$ ) or EOMCC ( $\mu > 0$ ) equations,

$$\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A) = \langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | (\bar{H}^{(A)} R_\mu^{(A)}) | \Phi \rangle, \quad (10)$$

which represent the projections of these equations written for the CC/EOMCC approximation  $A$  on the excited determinants  $|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle$  with  $n > m_A$  that are normally disregarded in the standard CC/EOMCC calculations (e.g., triples, quadruples, etc. in the  $m_A = 2$  CCSD/EOMCCSD case). The above formula for the generalized moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$ , Eq. (10), includes both the ground- and excited-state cases, since one can formally define the  $\mu = 0$  excitation operator  $R_{\mu=0}^{(A)}$  in Eq. (7) as a unit operator to obtain the ground-state CC wave function, Eq. (6). In this case, moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$ , Eq. (10), reduce to the generalized moments of the ground-state CC equations corresponding to approximation  $A$ ,

$$\mathfrak{M}_{0,a_1\dots a_n}^{i_1\dots i_n}(m_A) = \langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | \bar{H}^{(A)} | \Phi \rangle. \quad (11)$$

The  $\bar{H}^{(A)}$  operator in the above equations is the usual similarity-transformed Hamiltonian of the CC/EOMCC theory corresponding to approximation  $A$ ,

$$\bar{H}^{(A)} = e^{-T^{(A)}} H e^{T^{(A)}} = (H e^{T^{(A)}})_C, \quad (12)$$

where subscript  $C$  designates the connected operator product. It is worth mentioning that the ground-state moments  $\mathfrak{M}_{0,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  are not only useful for the calculations of the ground-state correction  $\delta_0^{(A)}$ . They are also important for determining the corresponding excited-state moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  when the ground and excited states of interest have the same spin and spatial symmetry, i.e., when the  $r_{\mu,0}$  amplitude defining the reference contribution to  $R_\mu^{(A)}$  in Eq. (4) is nonzero. Indeed, by splitting  $R_\mu^{(A)}$  into the zero-body reference part and the open part containing  $n$ -body components of  $R_\mu^{(A)}$  with  $n \geq 1$ , as in Eq. (4), one can rewrite Eq. (10) as follows [44, 50, 51]

$$\begin{aligned}\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A) &= \langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | (\bar{H}_{\text{open}}^{(A)} R_{\mu,\text{open}}^{(A)})_C | \Phi \rangle \\ &+ \sum_{p=m_A+1}^{n-1} \langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | (\bar{H}_p^{(A)} R_{\mu,n-p}^{(A)})_{DC} | \Phi \rangle + r_{\mu,0}^{(A)} \mathfrak{M}_{0,a_1\dots a_n}^{i_1\dots i_n}(m_A),\end{aligned} \quad (13)$$

where subscripts “open” and  $DC$  refer to open (i.e., having external Fermion lines) and disconnected parts of a given operator expression, and  $O_j$  represents the  $j$ -body component of operator  $O$ . In particular,

$$\bar{H}_{\text{open}}^{(A)} = \bar{H}^{(A)} - \bar{H}_{\text{closed}}^{(A)} = \bar{H}^{(A)} - E_0^{(A)} \mathbf{1} \quad (14)$$

is the open part of  $\bar{H}^{(A)}$  defined by the diagrams of  $\bar{H}^{(A)}$  that have external Fermion lines. The closed (or vacuum) part of  $\bar{H}^{(A)}$  that has no external lines is simply the ground-state CC energy,

$$E_0^{(A)} = \langle \Phi | \bar{H}^{(A)} | \Phi \rangle = \langle \Phi | \bar{H}_{\text{closed}}^{(A)} | \Phi \rangle. \quad (15)$$

We can also write

$$\mathfrak{M}_{0,a_1\dots a_n}^{i_1\dots i_n}(m_A) = \langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | \bar{H}_n^{(A)} | \Phi \rangle = \bar{h}_{a_1\dots a_n}^{i_1\dots i_n}(m_A), \quad (16)$$

where  $\bar{h}_{a_1\dots a_n}^{i_1\dots i_n}(m_A)$  are the antisymmetrized matrix elements of the particle-hole type defining, along with the analogous matrix elements that involve other types of spin-orbital indices, the second-quantized form of the  $n$ -body components of  $\bar{H}^{(A)}$  with  $n \geq 1$ ,

$$\bar{H}_n^{(A)} = \sum_{\substack{q_1 < \dots < q_n \\ p_1 < \dots < p_n}} \bar{h}_{p_1\dots p_n}^{q_1\dots q_n}(m_A) a^{p_1} \dots a^{p_n} a_{q_n} \dots a_{q_1}. \quad (17)$$

It should be noted that the exact biorthogonal MMCC expansion for the noniterative corrections  $\delta_\mu^{(A)}$  in terms of the generalized moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$ , given by Eq. (8), is finite, independent of the number of electrons  $N$  in a system. This is emphasized by the upper summation limit  $N_{\mu,A}$  in Eq. (8) which defines the highest value of  $n$  for which the corresponding moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  are nonzero or, for small, few-electron systems, the number of correlated electrons, whichever is smaller. For example, the generalized moments of the ground-state CCSD equations (the  $m_A = 2$  case) vanish when  $n > 6$  if the Hamiltonian contains at most two-body interactions, as is the case in quantum chemistry. Similarly, the generalized moments of the EOMCCSD equations vanish when  $n > 8$ . Thus, the exact corrections

$$\delta_\mu^{(\text{CCSD})} = E_\mu - E_\mu^{(\text{CCSD})} \quad (18)$$

to the CCSD ( $\mu = 0$ ) or EOMCCSD ( $\mu > 0$ ) energies  $E_\mu^{(\text{CCSD})}$ , which enable us to determine the differences between the CCSD or EOMCCSD energies and the corresponding full CI energies, simplify to

$$\begin{aligned} \delta_\mu^{(\text{CCSD})} &= \sum_{n=3}^{N_{\mu,\text{CCSD}}} \langle \Phi | \mathcal{L}_{\mu,n} M_{\mu,n}(2) | \Phi \rangle \\ &= \sum_{n=3}^{N_{\mu,\text{CCSD}}} \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} \ell_{\mu,i_1\dots i_n}^{a_1\dots a_n} \mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(2), \end{aligned} \quad (19)$$

where

$$\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(2) = \langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | [\bar{H}^{(\text{CCSD})}(R_{\mu,0} + R_{\mu,1} + R_{\mu,2})] | \Phi \rangle, \quad (20)$$

with

$$\bar{H}^{(\text{CCSD})} = e^{-T_1-T_2} H e^{T_1+T_2} = (H e^{T_1+T_2})_C, \quad (21)$$

are the generalized moments of the CCSD ( $\mu = 0$ ) or EOMCCSD ( $\mu > 0$ ) equations and

$$N_{\mu,\text{CCSD}} = \begin{cases} \min(6, N) & \text{if } \mu = 0 \\ \min(8, N) & \text{if } \mu > 0 \end{cases}, \quad (22)$$

independent of the number of electrons  $N$  in the system. This finite nature of the biorthogonal MMCC

energy expansions distinguishes them from the original MMCC theory of Refs. [40–42, 50, 51] in which the formulas for the exact corrections  $\delta_\mu^{(A)}$  or  $\delta_\mu^{(\text{CCSD})}$  in terms of the generalized moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  have the form of complete, full-CI-like expansions whose length grows with the system size. The explicit resummation and subsequent elimination of the many-body components of the exponential wave operator of CC theory that appear at the individual generalized moment contributions in the MMCC energy expansions of Refs. [40–42, 50, 51], which enable one to transform the full-CI-like energy expansions characterizing the original MMCC theory into the finite expansions given by Eqs. (8) and (19) whose lengths are determined by the highest value of  $n$  for which the corresponding moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  and  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(2)$  are nonzero rather than by the number of electrons  $N$ , has been presented in Ref. [49].

The  $\mathcal{L}_{\mu,n}$  operators which appear in Eq. (8) are the  $n$ -body components of the hole-particle deexcitation operator  $\mathcal{L}_\mu$  that parameterizes the exact, full CI bra state  $\langle \Psi_\mu |$  according to the following ansatz [20, 21, 47, 49, 74]:

$$\langle \Psi_\mu | = \langle \Phi | \mathcal{L}_\mu e^{-T^{(A)}}, \quad (23)$$

where

$$\mathcal{L}_\mu = \sum_{n=0}^N \mathcal{L}_{\mu,n}, \quad (24)$$

with

$$\mathcal{L}_{\mu,n} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} \ell_{\mu,i_1\dots i_n}^{a_1\dots a_n} a^{i_1} \dots a^{i_n} a_{a_1} \dots a_{a_n}. \quad (25)$$

The noniterative corrections  $\delta_\mu^{(A)}$ , Eq. (8), are expressed in terms of the  $n$ -body components  $\mathcal{L}_{\mu,n}$  and the corresponding deexcitation amplitudes  $\ell_{\mu,i_1\dots i_n}^{a_1\dots a_n}$  with  $m_A < n \leq N_{\mu,A}$ . As shown in Ref. [21], the  $\mathcal{L}_{\mu,n}$  components with  $n \leq m_A$  do not enter Eq. (8), since after decomposing the operator  $\mathcal{L}_\mu$  defining the exact bra state  $\langle \Psi_\mu |$  via Eq. (23) into the  $A$  part

$$\mathcal{L}_\mu^{(A)} = \sum_{n=0}^{m_A} \mathcal{L}_{\mu,n} \quad (26)$$

and the reminder

$$\delta \mathcal{L}_\mu^{(A)} = \sum_{n=m_A+1}^N \mathcal{L}_{\mu,n}, \quad (27)$$

i.e., after rewriting  $\mathcal{L}_\mu$  as

$$\mathcal{L}_\mu = \mathcal{L}_\mu^{(A)} + \delta\mathcal{L}_\mu^{(A)}, \quad (28)$$

the  $\mathcal{L}_\mu^{(A)}$  component of  $\mathcal{L}_\mu$  does not contribute to  $\delta_\mu^{(A)}$  if the  $T^{(A)}$  and  $R_\mu^{(A)}$  operators satisfy the corresponding CC and EOMCC equations of method  $A$ , which are

$$\mathfrak{M}_{0,a_1\dots a_n}^{i_1\dots i_n}(m_A) = 0, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad n = 1, \dots, m_A, \quad (29)$$

where  $\mathfrak{M}_{0,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  is defined by Eq. (11), in the ground-state CC ( $\mu = 0$ ) case, and

$$\langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | (\bar{H}_{\text{open}}^{(A)} R_{\mu,\text{open}}^{(A)})_C | \Phi \rangle = \omega_\mu^{(A)} r_{\mu,\mu_1\dots \mu_n}^{i_1\dots i_n}, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad n = 1, \dots, m_A, \quad (30)$$

combined with

$$r_{\mu,0} = \langle \Phi | (\bar{H}_{\text{open}}^{(A)} R_{\mu,\text{open}}^{(A)})_C | \Phi \rangle / \omega_\mu^{(A)}, \quad (31)$$

where

$$\omega_\mu^{(A)} = E_\mu^{(A)} - E_0^{(A)} \quad (32)$$

is the vertical excitation energy, in the excited-state EOMCC ( $\mu > 0$ ) case. As already explained, the  $\mathcal{L}_{\mu,n}$  components with  $n > N_{\mu,A}$  do not contribute to  $\delta_\mu^{(A)}$  either, since the corresponding moments  $\mathfrak{M}_{\mu,a_1\dots a_n}^{i_1\dots i_n}(m_A)$  with  $n > N_{\mu,A}$  vanish.

To guarantee that Eq. (8) represents the exact difference between the full CI energy  $E_\mu$  and the corresponding CC/EOMCC energy  $E_\mu^{(A)}$ , we must impose the normalization condition

$$\langle \Phi | \mathcal{L}_\mu^{(A)} R_\mu^{(A)} | \Phi \rangle = 1. \quad (33)$$

Although Eq. (33) resembles the familiar biorthonormality condition

$$\langle \Phi | L_\mu^{(A)} R_\nu^{(A)} | \Phi \rangle = \delta_{\mu,\nu}, \quad (34)$$

that characterizes the CC/EOMCC bra or left states

$$\langle \tilde{\Psi}_\mu^{(A)} | = \langle \Phi | L_\mu^{(A)} e^{-T^{(A)}} \quad (35)$$

(see, e.g., Refs. [63, 67]), where  $L_\mu^{(A)}$  is a deexcitation counterpart of the EOMCC excitation operator  $R_\mu^{(A)}$ , Eq. (4), defined as

$$L_\mu^{(A)} = L_{\mu,0}^{(A)} + L_{\mu,\text{open}}^{(A)} \equiv \delta_{\mu,0} \mathbf{1} + \sum_{n=1}^{m_A} L_{\mu,n}, \quad (36)$$

with

$$L_{\mu,n} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} l_{\mu,i_1\dots i_n}^{a_1\dots a_n} a^{i_1} \dots a^{i_n} a_{a_n} \dots a_{a_1} \quad (37)$$

representing the  $n$ -body components of  $L_\mu^{(A)}$  and  $l_{\mu,i_1\dots i_n}^{a_1\dots a_n}$  the corresponding deexcitation amplitudes, the left eigenstates of  $\bar{H}^{(A)}$ ,  $\langle \Phi | L_\mu^{(A)}$ , and the bra states  $\langle \Phi | \mathcal{L}_\mu^{(A)}$ , which are defined through the  $n$ -body components of the operator  $\mathcal{L}_\mu$  with  $n \leq m_A$ , are formally different objects. Indeed,  $\langle \Phi | L_\mu^{(A)}$  is the left eigenstate of  $\bar{H}^{(A)}$  corresponding to the right eigenstate  $R_\mu^{(A)} | \Phi \rangle$ , which is obtained by solving the truncated left CC/EOMCC eigenvalue problem

$$\delta_{\mu,0} \langle \Phi | \bar{H}_{\text{open}}^{(A)} | \Phi_{i_1\dots i_n}^{a_1\dots a_n} \rangle + \langle \Phi | L_{\mu,\text{open}}^{(A)} \bar{H}_{\text{open}}^{(A)} | \Phi_{i_1\dots i_n}^{a_1\dots a_n} \rangle = \omega_\mu^{(A)} l_{\mu,i_1\dots i_n}^{a_1\dots a_n}, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad (38)$$

for the deexcitation amplitudes  $l_{\mu,i_1\dots i_n}^{a_1\dots a_n}$  in the subspace of the  $N$ -electron Hilbert space spanned by the excited determinants  $|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle$  with  $n = 1, \dots, m_A$ . For comparison, the  $\langle \Phi | \mathcal{L}_\mu^{(A)}$  state is only one of the two contributions to the similarity-transformed form of the exact left state  $\langle \Psi_\mu |$ , i.e.  $\langle \Phi | \mathcal{L}_\mu = \langle \Psi_\mu | e^{T^{(A)}}$  [cf. Eqs. (26)–(27)] and the corresponding exact  $l_{\mu,i_1\dots i_n}^{a_1\dots a_n}$  amplitudes defining the operator  $\mathcal{L}_\mu$  and, through Eq. (23), the full CI bra state  $\langle \Psi_\mu |$ , satisfy the equation

$$\langle \Phi | \mathcal{L}_\mu \bar{H}^{(A)} = E_\mu \langle \Phi | \mathcal{L}_\mu, \quad (39)$$

which is equivalent to the adjoint form of the electronic Schrödinger equation,  $\langle \Psi_\mu | H = E_\mu \langle \Psi_\mu |$ , for the exact wave functions and energies in the entire  $N$ -electron Hilbert space, if  $\langle \Phi | \mathcal{L}_\mu e^{-T^{(A)}}$  is the exact, full CI bra state  $\langle \Psi_\mu |$  corresponding to energy  $E_\mu$ . Thus, the  $L_\mu^{(A)}$  and  $\mathcal{L}_\mu^{(A)}$  operators become identical only when  $m_A = N$ , while being different when  $m_A < N$ . On the other hand, there are sufficiently many similarities between  $L_\mu^{(A)}$  and  $\mathcal{L}_\mu^{(A)}$  which one can exploit to design practical computational methods based on the biorthogonal MMCC theory defined by Eq. (8), in which one adds approximate forms of the non-iterative corrections  $\delta_\mu^{(A)}$ , Eq. (8), to the energies  $E_\mu^{(A)}$  obtained in truncated CC/EOMCC calculations. The CR-EOMCC(2,3) approach described in the next subsection, in which one adds the approximate form

of the noniterative correction  $\delta_\mu^{(\text{CCSD})}$ , Eq. (19), truncated at triples excitations, to the CCSD/EOMCCSD energies  $E_\mu^{(\text{CCSD})}$  is one such method.

## 2.2. THE CR-EOMCC(2,3) APPROACH

The CR-EOMCC(2,3) approach, originally abbreviated as the CR-EOMCCSD(T)<sub>ℒ</sub> theory [47, 74], is an example of a truncated MMCC( $m_A, m_B$ ) scheme based on the biorthogonal MMCC formalism in which we set the upper limit for the summation over  $n$  in Eq. (8) at  $n = m_B$ , where the maximum excitation level  $m_B$  allowed in the moment expansion for the noniterative correction  $\delta_\mu^{(A)}$  satisfies the condition  $m_A < m_B \leq N_{\mu,A}$  [20, 21, 47] (for the truncated MMCC( $m_A, m_B$ ) schemes resulting from the original MMCC formalism of Kowalski and Piecuch, see Refs. [40–44, 50, 51]). To be specific, the CR-EOMCC(2,3) method is a biorthogonal MMCC( $m_A, m_B$ ) scheme with  $m_A = 2$  and  $m_B = 3$ , i.e., a scheme based on truncating the summation over  $n$  in the formula for the noniterative corrections  $\delta_\mu^{(\text{CCSD})}$ , Eq. (19), to the CCSD/EOMCCSD energies  $E_\mu^{(\text{CCSD})}$  at the  $n = 3$  term, which is the leading term on top of CCSD/EOMCCSD toward full CI describing the corrections due to triple excitations. As is the case for all biorthogonal MMCC(2,3) energies, the CR-EOMCC(2,3) energies  $E_\mu(2, 3)$  for the ground ( $\mu = 0$ ) or excited ( $\mu > 0$ ) states are calculated in the following manner (see Ref. [47]):

$$E_\mu(2, 3) = E_\mu^{(\text{CCSD})} + \delta_\mu(2, 3), \quad (40)$$

where

$$\delta_\mu(2, 3) = \langle \Phi | \mathcal{L}_{\mu,3} M_{\mu,3}(2) | \Phi \rangle = \sum_{\substack{i < j < k \\ a < b < c}} \ell_{\mu,ijk}^{abc} \mathfrak{M}_{\mu,abc}^{ijk}(2), \quad (41)$$

with  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  representing the triply excited moments of the CCSD ( $\mu = 0$ ) or EOMCCSD ( $\mu > 0$ ) equations defined by Eq. (20) [in the  $\mu = 0$  case, Eq. (20) simplifies further, since the EOMCCSD linear excitation operator ( $R_{\mu,0} + R_{\mu,1} + R_{\mu,2}$ ) is then replaced by the unit operator; cf. Eq. (11)]. Since the triply excited moments of the CCSD/EOMCCSD equations are well-defined and relatively easy to determine using the expression [see Refs. [43, 44, 50, 51]; cf. also, Eqs. (13) and (20)]

$$\begin{aligned} \mathfrak{M}_{\mu,abc}^{ijk}(2) &= \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} (R_{\mu,0} + R_{\mu,1} + R_{\mu,2}) | \Phi \rangle \\ &= \langle \Phi_{ijk}^{abc} | (\bar{H}_2^{(\text{CCSD})} R_{\mu,2})_C | \Phi \rangle \\ &\quad + \langle \Phi_{ijk}^{abc} | [\bar{H}_3^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2})]_C | \Phi \rangle \\ &\quad + \langle \Phi_{ijk}^{abc} | (\bar{H}_4^{(\text{CCSD})} R_{\mu,1})_C | \Phi \rangle + r_{\mu,0} \langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\text{CCSD})} | \Phi \rangle, \end{aligned} \quad (42)$$

where  $\bar{H}_n^{(\text{CCSD})}$  represents the  $n$ -body component of the similarity-transformed Hamiltonian of the CCSD theory, Eq. (21), once the CCSD and EOMCCSD equations are solved (see Section 2.3 for further discussion), the main issue in developing practical computational schemes based on Eqs. (40) and (41) is a method of approximating the exact deexcitation amplitudes  $\ell_{\mu,ijk}^{abc}$  that define the three-body component  $\mathcal{L}_{\mu,3}$  of the operator  $\mathcal{L}_\mu$  defining the bra wave function ansatz, Eq. (23), used in the biorthogonal MMCC theory.

The desired expressions for the approximate form of  $\mathcal{L}_{\mu,3}$  or  $\ell_{\mu,ijk}^{abc}$  that lead to the CR-EOMCC(2,3) approach are obtained by exploiting the similarity between the CCSD part of the exact operator  $\mathcal{L}_\mu$ , i.e.  $\mathcal{L}_\mu^{(\text{CCSD})}$ , defined by Eq. (26) where  $m_A$  is set at 2, and the CCSD/EOMCCSD deexcitation operator  $L_\mu^{(\text{CCSD})}$ , given by Eq. (36) in which  $m_A = 2$ , that can be easily obtained by solving the linear system of the left CCSD/EOMCCSD equations, Eq. (38), where  $m_A = 2$ , once the singly and doubly excited cluster amplitudes,  $t_a^i$  and  $t_{ab}^{ij}$ , respectively, and (in the  $\mu > 0$  case) the EOMCCSD excitation energies,

$$\omega_\mu^{(\text{CCSD})} = E_\mu^{(\text{CCSD})} - E_0^{(\text{CCSD})}, \quad (43)$$

are determined by solving the corresponding CCSD and right EOMCCSD equations [Eqs. (29) and (30), respectively, where  $m_A$  is set at 2]. This similarity between  $\mathcal{L}_\mu^{(\text{CCSD})}$  and  $L_\mu^{(\text{CCSD})}$  (or  $\mathcal{L}_\mu^{(A)}$  and  $L_\mu^{(A)}$  when  $m_A$  is not necessarily 2) has been discussed in the previous subsection. Thus, we approximate the exact operator  $\mathcal{L}_\mu$  defining the bra state  $\langle \Psi_\mu |$  via Eq. (23) as follows [cf. Eq. (28)]:

$$\mathcal{L}_\mu \approx L_\mu^{(\text{CCSD})} + \mathcal{L}_{\mu,3}, \quad (44)$$

where  $L_\mu^{(\text{CCSD})}$  defines the left eigenstate  $\langle \Phi | L_\mu^{(\text{CCSD})}$  of the similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$  of CCSD, obtained by solving Eq. (38) where  $m_A = 2$ , and  $\mathcal{L}_{\mu,3}$  is the approximate form of the three-body

component of  $\mathcal{L}_\mu$  we would like to determine, given by [cf. Eq. (25)]

$$\mathcal{L}_{\mu,3} = \sum_{\substack{i < j < k \\ a < b < c}} \ell_{\mu,ijk}^{abc} a^i a^j a^k a_c a_b a_a, \quad (45)$$

with  $\ell_{\mu,ijk}^{abc}$  representing the relevant triply deexcited amplitudes.

Having decided on the mathematical form of the approximate operator  $\mathcal{L}_\mu$ , we obtain the explicit, computationally tractable expression for the approximate  $\ell_{\mu,ijk}^{abc}$  amplitudes that enter the CR-EOMCC(2,3) triples correction formula, Eq. (41), by substituting the approximate expression for  $\mathcal{L}_\mu$  given by Eq. (44) into the exact form of the similarity-transformed bra eigenvalue problem for  $\mathcal{L}_\mu$ , Eq. (39), where  $A$  is set at CCSD (and  $m_A$  at 2), right-project the resulting equation on the triply excited determinants  $|\Phi_{ijk}^{abc}\rangle$  to obtain

$$\langle \Phi | L_\mu^{(\text{CCSD})} \tilde{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle + \sum_{\substack{l < m < n \\ d < e < f}} \langle \Phi_{lmn}^{def} | \tilde{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \ell_{\mu,lmn}^{def} = E_\mu \ell_{\mu,ijk}^{abc}, \quad (46)$$

replace the exact energy  $E_\mu$  in Eq. (46) by the corresponding CCSD/EOMCCSD energy  $E_\mu^{(\text{CCSD})}$ , and, finally, approximate the triples–triples block of the matrix representing  $\tilde{H}^{(\text{CCSD})}$  in the second term on the left-hand side of Eq. (46) by its diagonal, as in the Epstein–Nesbet partitioning. The result of all of these operations is the following formula for the approximate  $\ell_{\mu,ijk}^{abc}$  amplitudes in terms of the many-body components of the similarity-transformed Hamiltonian of CCSD, one- and two-body components of  $L_\mu^{(\text{CCSD})}$ , and, in the  $\mu > 0$  case, the EOMCCSD excitation energies  $\omega_\mu^{(\text{CCSD})}$  (see, e.g., Ref. [47]):

$$\ell_{\mu,ijk}^{abc} = N_{\mu,ijk}^{abc} / D_{\mu,abc}^{ijk}, \quad (47)$$

where the numerator  $N_{\mu,ijk}^{abc}$  and denominator  $D_{\mu,abc}^{ijk}$  are defined as follows:

$$N_{\mu,ijk}^{abc} = \langle \Phi | L_\mu^{(\text{CCSD})} \tilde{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle = \langle \Phi | [(L_{\mu,1} \tilde{H}_2^{(\text{CCSD})})_{DC} + (L_{\mu,2} \tilde{H}_1^{(\text{CCSD})})_{DC} + (L_{\mu,2} \tilde{H}_2^{(\text{CCSD})})_C] | \Phi_{ijk}^{abc} \rangle, \quad (48)$$

$$D_{\mu,abc}^{ijk} = E_\mu^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \tilde{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle = \omega_\mu^{(\text{CCSD})} - \sum_{n=1}^3 \langle \Phi_{ijk}^{abc} | \tilde{H}_n^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle. \quad (49)$$

The CR-EOMCC(2,3) approach is obtained by substituting Eq. (42) for  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and Eq. (47) for  $\ell_{\mu,ijk}^{abc}$ , where  $N_{\mu,ijk}^{abc}$  and  $D_{\mu,abc}^{ijk}$  are given by Eqs. (48) and (49), respectively, into the triples correction formula, Eq. (41), which is subsequently added to the CCSD ( $\mu = 0$ ) or EOMCCSD ( $\mu > 0$ ) energy  $E_\mu^{(\text{CCSD})}$  to obtain the total energy  $E_\mu(2,3)$ , Eq. (40).

When  $\mu = 0$ , the CR-EOMCC(2,3) equations reduce to the equations defining the ground-state CR-CC(2,3) calculations, presented in Refs. [20, 21, 47–49]. Indeed, when  $\mu = 0$ , the formal excitation energy  $\omega_{\mu=0}^{(\text{CCSD})}$ , Eq. (43), vanishes, the reference coefficient defining the zero-body component of the EOMCCSD excitation operator  $R_\mu$ , i.e.,  $r_{\mu,0}$ , becomes 1, the one- and two-body components of  $R_\mu$ ,  $R_{\mu,1}$  and  $R_{\mu,2}$ , respectively, vanish, and the one- and two-body components of the EOMCCSD deexcitation operator  $L_\mu^{(\text{CCSD})}$ , i.e.,  $L_{\mu,1}$  and  $L_{\mu,2}$ , become equivalent to the one- and two-body components of the “lambda” operator of the analytic gradient CCSD theory [164],  $\Lambda_1$  and  $\Lambda_2$ , respectively, which are obtained by solving the linear system of equations represented by Eq. (38) in which  $\mu = 0$ ,  $A = \text{CCSD}$ ,  $L_{\mu=0,\text{open}}^{(\text{CCSD})} = \Lambda_1 + \Lambda_2$ ,  $\omega_{\mu=0}^{(A)} = 0$ , and  $n = 1, 2$ . As a result, when  $\mu = 0$ , the CR-EOMCC(2,3) triples correction  $\delta_\mu(2,3)$  reduces to

$$\delta_0(2,3) = \sum_{\substack{i < j < k \\ a < b < c}} \ell_{0,ijk}^{abc} \mathfrak{M}_{0,abc}^{ijk}(2), \quad (50)$$

where the triply excited moments of the CCSD equations,  $\mathfrak{M}_{0,abc}^{ijk}(2)$ , and the corresponding deexcitation amplitudes  $\ell_{0,ijk}^{abc}$  are given by [cf. Eqs. (42) and (47)–(49)]

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \tilde{H}_3^{(\text{CCSD})} | \Phi \rangle = \langle \Phi_{ijk}^{abc} | \left[ H \left( T_2 + T_1 T_2 + \frac{1}{2} T_2^2 + \frac{1}{2} T_1^2 T_2 + \frac{1}{2} T_1 T_2^2 + \frac{1}{6} T_1^3 T_2 \right) \right]_C | \Phi \rangle \quad (51)$$

and

$$\ell_{0,ijk}^{abc} = N_{0,ijk}^{abc} / D_{0,abc}^{ijk}, \quad (52)$$

respectively, with

$$N_{0,ijk}^{abc} = \langle \Phi | (1 + \Lambda_1 + \Lambda_2) \tilde{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle \\ = \langle \Phi | [(\Lambda_1 \tilde{H}_2^{(CCSD)})_{DC} + (\Lambda_2 \tilde{H}_1^{(CCSD)})_{DC} \\ + (\Lambda_2 \tilde{H}_2^{(CCSD)})_C] | \Phi_{ijk}^{abc} \rangle \quad (53)$$

and

$$D_{0,abc}^{ijk} = E_0^{(CCSD)} - \langle \Phi_{ijk}^{abc} | \tilde{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle \\ = - \sum_{n=1}^3 \langle \Phi_{ijk}^{abc} | \tilde{H}_n^{(CCSD)} | \Phi_{ijk}^{abc} \rangle. \quad (54)$$

Equations (50)–(54) are exactly the same as the equations defining the ground-state triples correction of CR-CC(2,3) reported in Refs. [20, 21, 47–49]. Thus, the CR-EOMCC(2,3) approach is the most natural extension of the ground-state CR-CC(2,3) theory to excited states.

We should point out that the above expression for the  $\ell_{\mu,ijk}^{abc}$  amplitudes, Eq. (47), may have to be modified if one of the indices  $i, j, k, a, b, c$  corresponds to an orbital which is degenerate with some other orbitals (see Ref. [48] for the analogous remarks about the ground-state  $\ell_{0,ijk}^{abc}$  amplitudes defining the CR-CC(2,3) calculations). In that case, to make sure that the CR-EOMCC(2,3) energies remain invariant with respect to rotations among degenerate orbitals, one should replace Eq. (47) by a more elaborate expression in which, instead of using the diagonal matrix elements  $\langle \Phi_{ijk}^{abc} | \tilde{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle$  that enter the Epstein–Nesbet-like denominator  $D_{\mu,abc}^{ijk}$ , Eq. (49), one solves a small system of linear equations, similar to Eq. (46), where all amplitudes  $\ell_{\mu,ijk}^{abc}$  involving indices of degenerate spin-orbitals are coupled together through the off-diagonal matrix elements  $\langle \Phi_{lmn}^{def} | \tilde{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle$  involving the triply excited determinants that carry the indices of degenerate spin-orbitals [48]. Without taking care of this issue, the CR-EOMCC(2,3) energy correction  $\delta_\mu(2,3)$  is not strictly invariant with respect to the rotations among degenerate orbitals, although the dependence of the  $\delta_\mu(2,3)$  correction using Eq. (47) to determine the  $\ell_{\mu,ijk}^{abc}$  amplitudes on the rotations among degenerate orbitals is minimal. Indeed, as shown in Ref. [48], changes in the values of triples corrections due to the rotations among degenerate orbitals do not exceed 0.1 millihartree when one uses Eq. (47) to determine amplitudes  $\ell_{\mu,ijk}^{abc}$ . Thus, the issue of the lack of invariance of the CR-EOMCC(2,3) correction  $\delta_\mu(2,3)$  using Eq. (47) with respect to the rotations among degenerate orbitals is more of a formal problem than the practical one as long as one does not calculate energy

derivatives for systems with orbital degeneracies. If the molecule has at most an Abelian symmetry or if the orbitals used break the non-Abelian symmetry (for example, due to the use of symmetry-broken reference determinant or external fields), so that there are no orbital degeneracies, one can apply Eq. (47) to all amplitudes  $\ell_{\mu,ijk}^{abc}$  as is. All of these remarks regarding the invariance properties of the CR-EOMCC(2,3) energies with respect to rotations among degenerate orbitals in calculations involving non-Abelian symmetries through the suitable modification of Eq. (47) for  $\ell_{\mu,ijk}^{abc}$ , as described above, and the analogous remarks about the ground-state CR-CC(2,3) energies made in Ref. [48] are important for a number of reasons. For example, the authors of Ref. [38], who have implemented the rotationally invariant approximation to the ground-state CR-CC(2,3) approach, have not realized that one can restore the invariance of the CR-CC(2,3) energies with respect to rotations among degenerate orbitals, as described above and in Ref. [48], making, as a result, incorrect remarks about invariance properties of CR-CC(2,3) in their work [38]. The authors of Ref. [109], who have implemented our CR-EOMCC(2,3) corrections, characterized the orbital invariance properties of CR-CC(2,3) and CR-EOMCC(2,3) in a correct manner.

In analogy to the ground-state CR-CC(2,3) theory (cf., e.g., Ref. [48]) and following the naming convention initiated in our earlier publications on the CR-EOMCCSD(T) [44, 80, 81] and CR-EOMCC(2,3) [47] approaches, the above equations, with the exact treatment of moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , as in Eqs. (42) and (51), and the exact treatment of the Epstein–Nesbet-like denominator  $D_{\mu,abc}^{ijk}$ , as in Eqs. (49) and (54), where no terms in  $D_{\mu,abc}^{ijk}$  are neglected, describe the most complete variant of the CR-EOMCC(2,3) approach designated as CR-EOMCC(2,3),D. By neglecting selected terms in Eq. (49) for  $D_{\mu,abc}^{ijk}$ , we obtain approximate CR-EOMCC(2,3) schemes. For example, variant C of the CR-EOMCC(2,3) theory, designated as the CR-EOMCC(2,3),C approach, is obtained by ignoring the three-body component of  $\tilde{H}^{(CCSD)}$  in Eq. (49), i.e., the  $\langle \Phi_{ijk}^{abc} | \tilde{H}_3^{(CCSD)} | \Phi_{ijk}^{abc} \rangle$  term, while keeping the contributions to  $D_{\mu,abc}^{ijk}$  from the one- and two-body components of  $\tilde{H}^{(CCSD)}$  intact. The CR-EOMCC(2,3),B approach is obtained by ignoring the two- and three-body components of  $\tilde{H}^{(CCSD)}$  in Eq. (49), leaving only the one-body contribution  $\langle \Phi_{ijk}^{abc} | \tilde{H}_1^{(CCSD)} | \Phi_{ijk}^{abc} \rangle$  in  $D_{\mu,abc}^{ijk}$ . Finally, variant A of the CR-EOMCC(2,3) approach is obtained by replacing

the Epstein–Nesbet-like denominator  $D_{\mu,abc}^{ijk}$ , Eq. (49), by the Møller–Plesset-like denominator for triple excitations,  $\omega_{\mu}^{(\text{CCSD})} - (\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)$ , where  $\epsilon_p$ 's are the single-particle energies associated with spin-orbitals  $p$  (diagonal elements of the Fock matrix). Numerically, variant A of CR-EOMCC(2,3) is often not much different than variant B and the results shown in Section 3 will illustrate this in a transparent manner. This is related to the fact that the  $D_{\mu,abc}^{ijk}$  denominator utilized in the CR-EOMCC(2,3),B approximation has the form  $\omega_{\mu}^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \tilde{H}_1^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle = \omega_{\mu}^{(\text{CCSD})} - (\bar{h}_a^a + \bar{h}_b^b + \bar{h}_c^c - \bar{h}_i^i - \bar{h}_j^j - \bar{h}_k^k)$ , where, in general,  $\bar{h}_p^q \equiv \bar{h}_p^q(2)$  are matrix elements defining the second-quantized form of the one-body component of  $\tilde{H}^{(\text{CCSD})}$ , i.e. [cf. Eq. (17)],  $\tilde{H}_1^{(\text{CCSD})} = \sum_{p,q} \bar{h}_p^q a^p a_q$ . The diagonal matrix elements  $\bar{h}_p^p$  can be viewed as the dressed spin-orbital energies  $\epsilon_p$ , which are not much different than the  $\epsilon_p$  values when the singly and doubly excited cluster amplitudes,  $t_{ab}^i$  and  $t_{ab}^{ij}$ , respectively, are not too large. Similarly, the CR-EOMCC(2,3),C approach, in which the  $\langle \Phi_{ijk}^{abc} | \tilde{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$  contribution to  $D_{\mu,abc}^{ijk}$  is neglected, is, in most cases, not much different than the complete variant D of CR-EOMCC(2,3), since the three-body  $\langle \Phi_{ijk}^{abc} | \tilde{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$  terms are usually not too important (the two-body  $\langle \Phi_{ijk}^{abc} | \tilde{H}_2^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$  terms are). We will see the similarity between the CR-EOMCC(2,3),C and CR-EOMCC(2,3),D results in Section 3.

As mentioned in the Introduction section, the CR-EOMCC(2,3),A approximation is identical to the triples correction of the EOM-CC(2)PT(2) approach discussed in Refs. [34, 113]. The spin-conserving variant of the EOM-CCSD(fT) method examined in Ref. [109] is equivalent to the CR-EOMCC(2,3),A approximation, too. The spin-conserving variant of the EOM-CCSD(dT) method, also discussed in Ref. [109], is based on our most complete CR-EOMCC(2,3),D theory. The spin-flip EOM-CCSD(fT) and EOM-CCSD(dT) methods of Ref. [109] rely on our CR-EOMCC(2,3),A and CR-EOMCC(2,3),D expressions for the energy corrections due to triples as well. As explained in our earlier articles on the ground-state CR-CC(2,3) approach [20, 21, 47–49], the CR-CC(2,3),A approximation, i.e., the CR-EOMCC(2,3),A approach adopted to the ground-state,  $\mu = 0$ , case, is equivalent to the CCSD(2)<sub>T</sub> method of Ref. [35]. The analogous relationship exists between the CR-CC(2,3) method and the CCSD(2) approach of Refs. [30–33] if we neglect the contributions due to quadruples in the latter

approach. Specifically, the CCSD(2) method of Refs. [30–33] in its triples contribution part is equivalent to variant B of the CR-CC(2,3) approach, which we obtain by setting up  $\mu = 0$  in the CR-EOMCC(2,3),B equations. In fact, if necessary, we could account for quadruple excitations in the biorthogonal MMCC theory through the use of the higher-level CR-CC(2,4)/CR-EOMCC(2,4) and CR-CC(3,4)/CR-EOMCC(3,4) schemes, which correct the results of CCSD/EOMCCSD and CCSDT/EOMCCSDT calculations, respectively, for the effects of quadruples through the noniterative corrections of the  $\sum_{\substack{i < j < k < l \\ a < b < c < d}} \ell_{\mu,ijkl}^{abcd} \mathfrak{M}_{\mu,abcd}^{ijkl}(2)$

and  $\sum_{\substack{i < j < k < l \\ a < b < c < d}} \ell_{\mu,ijkl}^{abcd} \mathfrak{M}_{\mu,abcd}^{ijkl}(3)$  types [see, e.g., Refs. [165, 166] for the examples of the applications of the CR-CC(2,4) and CR-EOMCC(2,4) methods]. As discussed in detail in Refs. [20, 21, 47–49], by systematically neglecting higher-order terms in the CR-CC(2,3),A, i.e.,  $\mu = 0$  CR-EOMCC(2,3),A expressions, one can obtain the widely used CCSD(T) approach. Thus, one can view the CR-EOMCC(2,3),A–D approximations considered in this and the earlier [47] work as the natural extensions of the CCSD(T) method to excited electronic states, which also remove the well-known deficiencies of CCSD(T) in applications involving biradical ground states and bond breaking in the ground-state calculations, as mentioned in the Introduction section. One can also obtain the variety of triples corrections to the ground-state CCSD energies, calculated with the help of the left CCSD eigenstates and discussed in Refs. [19, 36–39] by neglecting higher-order terms in the CR-CC(2,3),A triples correction formula [particularly, the higher-order contributions to the triply excited moments  $\mathfrak{M}_{0,abc}^{ijk}(2)$ , Eq. (51)].

Although this might be less obvious, there also is a formal relationship between the CR-EOMCC(2,3) approaches examined here and the original CR-EOMCCSD(T) methods of Refs. [43, 44, 80, 81]. One can show [49] that in addition to the linear terms in the triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  present in CR-EOMCCSD(T), the MMCC(2,3) truncation scheme defined by Eq. (41), on which the CR-EOMCC(2,3) method is based, sums up the disconnected product contributions involving  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and various many-body components of the CCSD wave operator  $e^{T_1+T_2}$  present in the CR-EOMCCSD(T) triples correction [the one-body  $T_1$  component, the two-body  $(T_2 + \frac{1}{2}T_1^2)$  component, etc.] to all orders. In consequence, one can absorb the overlap



denominator  $\langle \Psi_\mu | \Psi_\mu^{(\text{CCSD})} \rangle$ , where  $|\Psi_\mu^{(\text{CCSD})}\rangle$  is the EOMCCSD wave function, which renormalized the triples correction of CR-EOMCCSD(T), such that the resulting correction to the CCSD/EOMCCSD energy gains the transparent form of Eq. (41) without such a denominator. As pointed out in Refs. [47, 49], the absorption of the overlap denominator term  $\langle \Psi_\mu | \Psi_\mu^{(\text{CCSD})} \rangle$  through the use of the deexcitation amplitudes  $\ell_{\mu,ijk}^{abc}$  in the CR-EOMCC(2,3) approach eliminates the small extensivity errors from the ground-state CR-EOMCCSD(T) or CR-CCSD(T) calculations, while the additional product terms involving  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and many-body components of  $e^{T_1+T_2}$ , which are summed up to all orders in the CR-EOMCC(2,3) triples correction, may improve the accuracy compared to the results of the CR-EOMCCSD(T) calculations, as shown in Section 3. As discussed in Refs. [47–49] and references cited therein, the analogous remarks apply to the relative accuracies of the ground-state CR-CC(2,3) and CR-CCSD(T) calculations, where CR-CC(2,3) is always somewhat more accurate.

Unfortunately, as explained in detail in the Introduction section, unlike the ground-state CR-CC(2,3) or  $\mu = 0$  CR-EOMCC(2,3) theory, which is a rigorously size-extensive formalism, the excited-state ( $\mu > 0$ ) CR-EOMCC(2,3) approach is neither size extensive nor preserves the size intensivity of the EOMCCSD excitation energies. One can try to restore the size intensivity of the CR-EOMCC(2,3) excitation energies by the *ad hoc* modifications of the type used in Ref. [113] or by adopting the more sophisticated spin-flip ideas, as in Ref. [109], but none of these options is of interest in this article since none of them addresses the extensivity/intensivity issues in a complete, formally satisfactory manner. The *ad hoc* modifications in the CR-EOMCC(2,3), A-like expressions discussed in Ref. [113] (cf., also, the Introduction section for the additional comments) are not only questionable and arbitrary, but they also attempt to restore the intensivity of the resulting excitation energies at the expense of increasing errors and producing less robust results (for example, excitation energies which are considerably below the exact ones). The use of the spin-flip variants of the CR-EOMCC(2,3) corrections seems to lead to size-intensive results for the vertical excitation energies, but the underlying ground-state spin-flip CCSD theory does not appear to be rigorously size extensive, although this might be a rather unimportant issue in the actual molecular applications. The numerical evidence presented in

Section 3 shows that the total and excitation energies resulting from the CR-EOMCC(2,3) calculations, particularly when the complete CR-EOMCC(2,3),D variant is used, are very accurate when compared to the available full EOMCCSDT and experimental data, while being very competitive with the CR-EOMCCSD(T), EA-EOMCCSD(3p-2h), and IP-EOMCCSD(3h-2p) calculations, which work very well in applications involving excitation energies in open-shell species. This suggests that the departure from the strict size intensivity may not be a major issue for the types of molecular sizes (up to about 50 correlated electrons; cf., e.g., Ref. [81] for an analysis) and the types of applications the CR-EOMCC(2,3) can handle at this time (vertical and adiabatic excitation energies, potential energy surfaces of excited states along bond breaking coordinates that do not involve very large stretches of the relevant chemical bonds).

Before discussing the key algorithmic details of the efficient computer implementation of the CR-EOMCC(2,3) approach, applicable to both the singlet and nonsinglet electronic states (see Section 2.3), let us add a few comments on the advantages and consequences of exploiting the complete form of Eq. (49) for the denominator  $D_{\mu,abc}^{ijk}$  in the definition of the CR-EOMCC(2,3) triples correction  $\delta_\mu(2,3)$ , used in the full CR-EOMCC(2,3),D scheme, particularly those that are relevant to the open-shell implementation of the CR-EOMCC(2,3) methods discussed in this work. As already alluded to above and as shown in Section 3, the use of the complete form of the  $D_{\mu,abc}^{ijk}$  denominator, Eq. (49), which is expressed in terms of the diagonal elements of the triples–triples block of the matrix representing the CCSD similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$  that involve one-, two-, and three-body components of  $\bar{H}^{(\text{CCSD})}$ , rather than the more usual MBPT-like differences of bare spin-orbital energies or their dressed form involving the one-body components of  $\bar{H}^{(\text{CCSD})}$  only, exploited in the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B approximations and their EOM-CC(2)PT(2) and CCSD(2)<sub>T</sub>/EOMCCSD(2)<sub>T</sub> analogs, results in improved accuracies in the description of the excited-state energies. There also are formal and algorithmic benefits of using the complete  $D_{\mu,abc}^{ijk}$  denominator in the CR-EOMCC(2,3) considerations, particularly in the calculations for open-shell systems using the ROHF orbitals, such as those discussed in Section 3. Indeed, the use of the conventional 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. (49), leads to a number of formal and practical difficulties related to the choice of the unperturbed Hamiltonian to define the orbital energies and the presence of the off-diagonal matrix elements in the spin-orbital form of the Fock matrix written for the ROHF orbitals (cf., e.g., Refs. [167–170] for a discussion of these issues in the context of the ROHF-based implementations of the conventional perturbative CCSD(T) and CC3 methods). We do not have to worry about those kinds of issues in the full CR-EOMCC(2,3),D calculations, which do not rely on a decomposition of the Hamiltonian into unperturbed and perturbed parts. In other words, the use of the complete form of the triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , Eqs. (42) and (51), and the use of the complete form of the denominator  $D_{\mu,abc}^{ijk}$ , Eq. (49), in which all terms resulting from  $\langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$  are retained, as in the full CR-EOMCC(2,3),D approach, enables us to avoid at least some of the problems complicating the ROHF-based implementations of the analogous CCSD(T) (Refs. [167–169]) and CC3 (Ref. [170]) methods, since we never have to determine what terms in the Hamiltonian are regarded as the zeroth-order terms. This, combined with the high accuracies and robustness the CR-EOMCC(2,3),D approach in applications involving electronically excited states of the closed-shell [47, 74] as well as open-shell (Section 3) systems, and the analogously high accuracies of the corresponding ground-state CR-CC(2,3),D approach in applications involving single bond breaking [20, 21, 47, 48, 53–57], including large systems with hundreds of correlated electrons [26–28], mechanistic studies involving biradicals [20, 21, 58–62], and singlet-triplet gaps in biradical/magnetic systems [48, 49, 60], is one of the main advantages of the complete CR-EOMCC(2,3),D approach. As in the open-shell ground-state CR-CC(2,3),D case discussed in Ref. [48], the price we must pay for the above advantages of the CR-EOMCC(2,3),D method over other noniterative EOMCC approximations is the slight dependence of the ROHF-based CR-EOMCC(2,3),D energies on the method of canonicalization of the ROHF orbitals, but changes in the CR-EOMCC(2,3),D energies due to different ways of obtaining the ROHF orbitals (see, e.g., Refs. [171–176] for some of the best known formulations of ROHF) are on the order of tens of microhartree, so again, as in the case of orbital degeneracies,

this is more of a formal issue than a practical one. One should also point out that in an analogy to the ground-state CR-CC(2,3) theory using the ROHF reference [48], for a given canonicalization procedure of obtaining the ROHF orbitals, each variant of the CR-EOMCC(2,3) method, including the most accurate and most complete CR-EOMCC(2,3),D scheme, is an unambiguously defined and fully reproducible computational procedure.

### 2.3. THE KEY ALGORITHMIC DETAILS OF THE OPEN-SHELL IMPLEMENTATION OF CR-EOMCC(2,3)

The general-purpose open-shell CR-EOMCC(2,3) code discussed and tested in this work, which is interfaced with the integral and ROHF routines available in the GAMESS package [108], consists of three segments. First, we solve the ground-state CCSD equations to obtain the singly and doubly excited cluster amplitudes,  $t_a^i$  and  $t_{ab}^{ij}$ , respectively. Then, in the second step, we use the converged  $t_a^i$  and  $t_{ab}^{ij}$  amplitudes to construct the EOMCCSD equations, which are solved using the Hirao-Nakatsuji extension [177] of the Davidson diagonalization algorithm [178] to non-hermitian eigenvalue problems. Since the noniterative triples correction  $\delta_\mu(2,3)$  of each of the CR-EOMCC(2,3),A–D schemes requires access to the one- and two-body components of the EOM-CCSD deexcitation operator  $L_\mu^{(\text{CCSD})}$ ,  $L_{\mu,1}$  and  $L_{\mu,2}$ , respectively, and the amplitudes  $l_{\mu,i}^a$  and  $l_{\mu,ij}^{ab}$  that define them, which enter the definition of the deexcitation amplitudes  $\rho_{\mu,ijk}^{abc}$ , Eq. (47), via the numerator quantities  $N_{\mu,ijk}^{abc}$ , Eq. (48), along with the zero-, one-, and two-body components of the excitation operator  $R_\mu^{(\text{CCSD})}$  and the corresponding amplitudes  $r_{\mu,0}$ ,  $r_{\mu,a}^i$ , and  $r_{\mu,ab}^{ij}$ , which enter the  $\mu > 0$  moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , as in Eq. (42), we solve the EOMCCSD eigenvalue problem both for the right eigenstates  $R_\mu^{(\text{CCSD})}|\Phi\rangle$  [Eqs. (30) and (31)] and for their left analogs  $\langle\Phi|L_\mu^{(\text{CCSD})}$  [Eq. (38)]. In practice, we solve the EOMCCSD right eigenvalue problem, Eqs. (30) and (31) where  $m_A = 2$ , first, to obtain  $r_{\mu,0}$ ,  $r_{\mu,a}^i$ ,  $r_{\mu,ab}^{ij}$ , and  $\omega_\mu^{(\text{CCSD})}$ , and use the resulting excitation energies  $\omega_\mu^{(\text{CCSD})}$  to convert the corresponding left eigenvalue problem, Eq. (38) where  $m_A = 2$ , into the system of linear equations for the  $l_{\mu,i}^a$  and  $l_{\mu,ij}^{ab}$  amplitudes. As in the case of the earlier CR-CC(2,3) codes for the ground electronic states of the closed- and open-shell systems [20, 48], CR-EOMCC(2,3) codes for singlet excited states [47], and other CC and EOMCC programs interfaced with

the RHF and ROHF routines from GAMESS [80, 81, 140, 179], the CCSD nonlinear equations for the  $t_a^i$  and  $t_{ab}^{ij}$  cluster amplitudes and the left EOMCCSD linear equations for the  $l_{\mu,i}^a$  and  $l_{\mu,ij}^{ab}$  deexcitation amplitudes are solved using the DIIS algorithm [180–183]. It is worth mentioning that by determining the  $l_{\mu,i}^a$  and  $l_{\mu,ij}^{ab}$  amplitudes that define the  $L_{\mu,1}$  and  $L_{\mu,2}$  operators of the left CCSD/EOMCCSD states, we automatically gain access to the one-electron density matrices of the CCSD/EOMCCSD wave functions and the corresponding transition density matrices,

$$\gamma_q^p(\mu, \nu) = \langle \tilde{\Psi}_\mu^{(\text{CCSD})} | a^p a_q | \Psi_\nu^{(\text{CCSD})} \rangle, \quad (55)$$

which are calculated as [63, 67, 164]

$$\gamma_q^p(\mu, \nu) = \langle \Phi | L_\mu^{(\text{CCSD})} \overline{a^p a_q} R_\nu^{(\text{CCSD})} | \Phi \rangle, \quad (56)$$

where

$$\overline{a^p a_q} = e^{-T_1 - T_2} a^p a_q e^{T_1 + T_2} = (a^p a_q e^{T_1 + T_2})_C, \quad (57)$$

and to all kinds of one-electron properties and transition matrix elements

$$\langle \tilde{\Psi}_\mu^{(\text{CCSD})} | \theta | \Psi_\nu^{(\text{CCSD})} \rangle = \sum_{p,q} \theta_p^q \gamma_q^p(\mu, \nu), \quad (58)$$

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. (56). This is yet another advantage of the CR-EOMCC(2,3) methodology, which produces accurate triples corrections to the CCSD/EOMCCSD energies along with one-electron properties calculated at the CCSD/EOMCCSD level at no extra effort. In this article, we focus on the noniterative triples corrections  $\delta_\mu(2,3)$  to the EOMCCSD energies of closed- and open-shell systems obtained with the RHF/ROHF references defining the CR-EOMCC(2,3) theory, so that no further details of our efficient implementation of the CCSD and EOM-CCSD methods for closed- and open-shell systems, which uses the well-known ideas of diagram factorization, recursively generated intermediates [184], and fast matrix multiplication routines from the BLAS library, and exploited throughout much of our entire CC/EOMCC programming work to date, are discussed here.

To obtain the working equations for the CR-EOMCC(2,3) corrections  $\delta_\mu(2,3)$  that lead to efficient, fully vectorized computer codes, we must rewrite the key elements of Eq. (41), which are the triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , Eqs. (42) and (51), and

the numerator and denominator contributions,  $N_{\mu,ijk}^{abc}$ , Eq. (48), and  $D_{\mu,abc}^{ijk}$ , Eq. (49), respectively, to the deexcitation amplitudes  $\ell_{\mu,ijk}^{abc}$ , Eq. (47), in terms of the cluster and excitation amplitudes defining  $T_1$ ,  $T_2$ ,  $R_{\mu,0}$ ,  $R_{\mu,1}$ , and  $R_{\mu,2}$ , the deexcitation amplitudes defining  $L_{\mu,1}$  and  $L_{\mu,2}$ , and the one- and two-electron molecular integrals,  $f_p^q = \langle p | f | q \rangle$  ( $f$  is the Fock operator) and  $v_{pq}^{rs} = \langle pq | v | rs \rangle - \langle pq | v | sr \rangle$ , respectively, defining the normal-product form of the Hamiltonian,  $H_N = H - \langle \Phi | H | \Phi \rangle = \sum_{p,q} f_p^q N[a^p a_q] + \frac{1}{4} \sum_{p,q,r,s} v_{pq}^{rs} N[a^p a^q a_s a_r]$ , where  $N[\dots]$  stands for the normal product of operators. We obtain,

$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \mathcal{A}_{abc} \mathfrak{T}_{\mu,abc}^{ijk}(2), \quad (59)$$

$$N_{\mu,ijk}^{abc} = \mathcal{A}_{abc} \Gamma_{\mu,ijk}^{abc}, \quad (60)$$

and

$$D_{\mu,abc}^{ijk} = \omega_\mu^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}_1^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle - \langle \Phi_{ijk}^{abc} | \bar{H}_2^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle - \langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle, \quad (61)$$

where the partly antisymmetrized quantities  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  and  $\Gamma_{\mu,ijk}^{abc}$ , entering  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $N_{\mu,ijk}^{abc}$ , are defined as

$$\mathfrak{T}_{\mu,abc}^{ijk}(2) = \mathcal{A}^{i/jk} \left[ \left( \frac{1}{2} \bar{h}_{ab}^{ie} t_{ec}^{jk} - \frac{1}{2} \bar{h}_{mc}^{jk} r_{ab}^{im} - \frac{1}{2} I_{mc}^{jk} t_{ab}^{im} + I_{ab}^{ie} t_{ec}^{jk} \right) + \frac{1}{2} r_0 (\bar{h}_{ab}^{ie} t_{ec}^{jk} - I_{mc}^{jk} t_{ab}^{im}) \right] \quad (62)$$

and

$$\Gamma_{\mu,ijk}^{abc} = \mathcal{A}^{i/jk} \left[ \frac{1}{2} I_i^a v_{jk}^{bc} + \frac{1}{2} I_{jk}^{bc} \bar{h}_i^a + \frac{1}{2} I_{jk}^{ec} \bar{h}_{ie}^{ab} - \frac{1}{2} I_{im}^{ab} \bar{h}_{jk}^{mc} \right], \quad (63)$$

respectively, and

$$\langle \Phi_{ijk}^{abc} | \bar{H}_1^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle = -\bar{h}_i^i - \bar{h}_j^j - \bar{h}_k^k + \bar{h}_a^a + \bar{h}_b^b + \bar{h}_c^c, \quad (64)$$

$$\begin{aligned} \langle \Phi_{ijk}^{abc} | \bar{H}_2^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle = & -\bar{h}_{ai}^{ai} - \bar{h}_{bi}^{bi} - \bar{h}_{ci}^{ci} \\ & -\bar{h}_{aj}^{aj} - \bar{h}_{bj}^{bj} - \bar{h}_{cj}^{cj} \\ & -\bar{h}_{ak}^{ak} - \bar{h}_{bk}^{bk} - \bar{h}_{ck}^{ck} \\ & +\bar{h}_{ij}^{ij} + \bar{h}_{ik}^{ik} + \bar{h}_{jk}^{jk} \\ & +\bar{h}_{ab}^{ab} + \bar{h}_{ac}^{ac} + \bar{h}_{bc}^{bc}, \end{aligned} \quad (65)$$

and

$$\begin{aligned} \langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle = & -\bar{h}_{aij}^{iaj} - \bar{h}_{aik}^{iak} - \bar{h}_{ajk}^{jak} \\ & -\bar{h}_{bij}^{ibj} - \bar{h}_{bik}^{ibk} - \bar{h}_{bjk}^{jbk} \\ & -\bar{h}_{cij}^{icj} - \bar{h}_{cik}^{ick} - \bar{h}_{cjk}^{jck} \\ & +\bar{h}_{aib}^{iab} + \bar{h}_{aic}^{iac} + \bar{h}_{bic}^{ibc} \\ & +\bar{h}_{ajb}^{jab} + \bar{h}_{ajc}^{jac} + \bar{h}_{bjc}^{jbc} \\ & +\bar{h}_{akb}^{kab} + \bar{h}_{akc}^{kac} + \bar{h}_{bkc}^{kbc}, \quad (66) \end{aligned}$$

with

$$\bar{h}_{aib}^{iab} = -v_{im}^{ab} t_{ab}^{im} \quad (67)$$

and

$$\bar{h}_{aij}^{iaj} = v_{ij}^{ae} t_{ae}^{ij}. \quad (68)$$

In the above equations, particularly in Eqs. (62), (63), (67), and (68), we use the Einstein summation convention over repeated upper and lower indices. The Einstein summation convention over repeated upper and lower indices is also exploited in Table I. This table provides the explicit spin-orbital expressions for the one- and two-body matrix elements of  $\bar{H}^{(\text{CCSD})}$ ,  $\bar{h}_p^q \equiv \bar{h}_p^q(2)$  and  $\bar{h}_{pq}^{rs} \equiv \bar{h}_{pq}^{rs}(2)$ , defining  $\bar{H}_1^{(\text{CCSD})}$  and  $\bar{H}_2^{(\text{CCSD})}$ , respectively, as in Eq. (17), and other recursively generated intermediates entering Eqs. (62)–(65), in terms of the CCSD cluster amplitudes  $t_a^i$  and  $t_{ab}^{ij}$ , EOMCCSD excitation amplitudes  $r_a^i$  and  $r_{ab}^{ij}$ , and molecular integrals  $f_p^q$  and  $v_{pq}^{rs}$  [the trivially factorizable matrix elements  $\bar{h}_{aib}^{iab}$  and  $\bar{h}_{aij}^{iaj}$  that enter the three-body contribution  $\langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$  to  $D_{\mu,abc}^{ijk}$  are outside Table I, in the form of Eqs. (67) and (68), respectively]. It should be noted that we dropped the symbol  $\mu$  representing the electronic state of interest from  $r_{\mu,0}$ ,  $r_{\mu,a}^i$ ,  $r_{\mu,ab}^{ij}$ ,  $l_{\mu,i}^a$ , and  $l_{\mu,ij}^{ab}$  in the above equations and in the expressions collected in Table I. The antisymmetrizers  $\mathcal{A}_{pqr}$ ,  $\mathcal{A}_{p/qr}$ , and  $\mathcal{A}_{pq}$ , which enter Eqs. (59), (60), (62), and (63) directly or via the matrix elements of  $\bar{H}^{(\text{CCSD})}$  and other intermediates listed in Table I, are defined as

$$\mathcal{A}_{pqr} \equiv \mathcal{A}^{pqr} = 1 - (pq) - (pr) - (qr) + (pqr) + (prq), \quad (69)$$

$$\mathcal{A}_{p/qr} \equiv \mathcal{A}^{p/qr} = 1 - (pq) - (pr), \quad (70)$$

and

$$\mathcal{A}_{pq} \equiv \mathcal{A}^{pq} = 1 - (pq), \quad (71)$$

TABLE I

Explicit algebraic expressions for the matrix elements of  $\bar{H}^{(\text{CCSD})}$  (designated by  $\bar{h}$ ) and other intermediates (designated by  $l$  or  $\vartheta$ ) used to construct the triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and the numerator and denominator contributions,  $N_{\mu,ijk}^{abc}$  and  $D_{\mu,abc}^{ijk}$ , respectively, via Eqs. (59)–(68), which are needed to calculate the CR-EOMCC(2,3) corrections  $\delta_\mu(2,3)$ .

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

<sup>a</sup> Summation over repeated upper and lower spin-orbital indices is assumed;  $t_p^q = \langle p|f|q \rangle$  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 ( $v$ ) of the Hamiltonian in the normal ordered form.

where  $(pq)$  and  $(pqr)$  represent the cyclic permutations of two and three indices, respectively.

By exploiting the idea of recursively generated intermediates and by reusing the one- and two-body matrix elements of  $\bar{H}^{(\text{CCSD})}$ , which are generated in the CCSD/EOMCCSD calculations that precede the calculations of moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ , numerators  $N_{\mu,ijk}^{abc}$ , denominators  $D_{\mu,abc}^{ijk}$ , deexcitation amplitudes

$\ell_{\mu,ijk}^{abc}$ , and, ultimately, triples corrections  $\delta_\mu(2,3)$ , we achieve a high degree of code vectorization, while avoiding the explicit construction and storing of the expensive three- and four-body matrix elements of  $\bar{H}^{(\text{CCSD})}$  that formally contribute to  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  [cf. Eq. (42)]. The three-body matrix elements of  $\bar{H}^{(\text{CCSD})}$  contribute to the denominator  $D_{\mu,abc}^{ijk}$  as well [cf. Eqs (49) and (66)], but, as shown in Eqs. (67) and (68), the three-body matrix elements  $\bar{h}_{aib}^{iab}$  and  $\bar{h}_{aij}^{iaj}$  that enter Eq. (66) can be represented as binary contractions of two-body objects that can be easily handled by fast matrix multiplication routines.

Thanks to the efficient use of recursively generated intermediates and matrix elements of  $\bar{H}^{(\text{CCSD})}$ , the most expensive steps of our open-shell CR-EOMCC(2,3) code 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  $\delta_\mu(2,3)$  part. Specifically, the CR-EOMCC(2,3) approach is an  $n_o^2 n_u^4$  method in the iterative CCSD steps that generate the  $T_1$  and  $T_2$  clusters, the iterative EOMCCSD steps that generate the  $R_{\mu,1}$  and  $R_{\mu,2}$  components, and in the additional iterative steps that are needed to obtain the  $L_{\mu,1}$  and  $L_{\mu,2}$  components of the left CCSD/EOMCCSD states of interest [needed to construct the  $\ell_{\mu,ijk}^{abc}$  amplitudes, Eq. (47)]. Since the iterative steps needed to solve the EOMCCSD equations for excited states and to determine  $L_{\mu,1}$  and  $L_{\mu,2}$  no longer require recalculating the matrix elements of  $\bar{H}^{(\text{CCSD})}$  or other intermediates of CCSD in every iteration, the time spent on solving the right and left EOMCCSD eigenvalue problems is less than the time spent on the CCSD iterations for  $T_1$  and  $T_2$ . In general, one can make a conservative statement that the CPU time spent on the left CCSD/EOMCCSD iterations that produce the  $L_{\mu,1}$  and  $L_{\mu,2}$  components for the determination of the  $N_{\mu,ijk}^{abc}$  and, subsequently,  $\ell_{\mu,ijk}^{abc}$  coefficients, does not exceed the time spent on the standard CCSD and right EOMCCSD iterations that yield  $T_1$  and  $T_2$  (CCSD), and  $R_{\mu,1}$  and  $R_{\mu,2}$  (EOMCCSD). In other words, the iterative part of the CR-EOMCC(2,3) calculation does not use more than twice the time spent on solving the CCSD equations and the right eigenvalue problem of EOMCCSD.

The noniterative steps required to calculate the triples correction  $\delta_\mu(2,3)$  of CR-EOMCC(2,3) for a specific electronic state  $\mu$  are only twice or three times as expensive as the  $n_o^3 n_u^4$  steps that are used to construct the conventional ground-state (T) correction of conventional CCSD(T). The approximate factor of two in the increase of the CPU time spent on determining the triples correction  $\delta_\mu(2,3)$  of CR-EOMCC(2,3) compared to the (T) correction of

CCSD(T) applies to the  $\mu = 0$  ground-state case. This is a consequence of the presence of the  $n_o^3 n_u^4$  steps in constructing the triexcited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  when  $\mu = 0$ , i.e., when  $r_0 = 1$  and  $r_a^i = r_{ab}^{ij} = 0$  [see Eq. (62)], and the additional  $n_o^3 n_u^4$  steps that are needed to construct the  $N_{\mu,ijk}^{abc}$  coefficients [see Eq. (63)] that define the  $\ell_{\mu,ijk}^{abc}$  amplitudes, Eq. (47). The approximate factor of three in the increase of the CPU time spent on calculating  $\delta_\mu(2,3)$  compared to the (T) correction of CCSD(T) applies to excited states. This is a consequence of the presence of two  $n_o^3 n_u^4$  steps in constructing the triexcited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  when  $\mu > 0$ , i.e., when the EOMCCSD excitation amplitudes  $r_a^i$  and  $r_{ab}^{ij}$  are not all zero [see Eq. (62)], and the additional  $n_o^3 n_u^4$  steps that are needed to construct the  $N_{\mu,ijk}^{abc}$  coefficients [see Eq. (63)]. In summary, the CR-EOMCC(2,3) approach, being a noniterative triples, single-reference, black-box approach which is only twice or three times as expensive as CCSD(T) per single electronic state when the CPU time requirements are examined, is essentially as practical and as easy to use as the CCSD(T) approach. For comparison, the full EOMCCSDT calculations involve a lot more expensive and iterative  $n_o^3 n_u^5$  steps. The full EA-EOMCCSD(3p-2h) (Refs. [138–140]), IP-EOMCCSD(3h-2p) (Refs. [138–140]), EA-EOMCCSDT [137], and IP-EOMCCSDT [148, 149] approaches mentioned in the Introduction section, which provide accurate results for the excited states of open-shell systems as well, invoke the iterative  $n_o^2 n_u^5$  (the EA cases) and  $n_o^3 n_u^4$  (the IP cases) steps, which are also more expensive than the noniterative  $n_o^3 n_u^4$  steps of CR-EOMCC(2,3). Yet, as shown in the next section, the CR-EOMCC(2,3) results for the challenging open-shell excited states dominated by two-electron transitions are practically as good as those obtained with the full EOMCCSDT, EA-EOMCCSD(3p-2h), and IP-EOMCCSD(3h-2p) methods.

The similarly encouraging remarks about the computer costs of the CR-EOMCC(2,3) calculations apply to memory requirements, which are proportional to  $n_o n_u^3$  words, and disk usage that scales as the fourth power of the number of orbitals in a basis set corresponding to the two-electron integrals  $v_{pq}^{rs}$  and the analogous two-body matrix elements  $\bar{h}_{pq}^{rs}$ . In particular, in analogy to the ground-state CCSD(T) approach and similar methods, we can completely eliminate the need for storing the three-body quantities of the  $n_o^3 n_u^3$  type [the  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ ,  $N_{\mu,ijk}^{abc}$ ,  $D_{\mu,abc}^{ijk}$  and  $\ell_{\mu,ijk}^{abc}$  quantities are in this category] and determine

the energy corrections  $\delta_\mu(2,3)$  by computing the relevant  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ ,  $N_{\mu,ijk}^{abc}$ ,  $D_{\mu,abc}^{ijk}$ , and  $\ell_{\mu,ijk}^{abc}$  contributions on the fly, as shown in the algorithm below. The key elements of our algorithm to calculate the triples correction  $\delta_\mu(2,3)$  of the CR-EOMCC(2,3) theory can be summarized as follows:

```
SUM = 0.0
LOOP OVER i<j<k
    Calculate  $\Gamma_{\mu,ijk}^{abc}$  for all values of  $a, b, c$  using
        Eq. (63)
    Calculate  $N_{\mu,ijk}^{abc}$  by antisymmetrizing  $\Gamma_{\mu,ijk}^{abc}$ ,
        as in Eq. (60)
    Calculate  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  for all values of  $a, b, c$  using
        Eq. (62)
    Calculate  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  by antisymmetrizing
         $\mathfrak{T}_{\mu,abc}^{ijk}(2)$ , as in Eq. (59)
    LOOP OVER a<b<c
        Calculate  $D_{\mu,abc}^{ijk}$ , Eqs. (61) and (64)–(66)
        Calculate  $\ell_{\mu,ijk}^{abc}$ , Eq. (47)
        SUM = SUM +  $\ell_{\mu,ijk}^{abc} * \mathfrak{M}_{\mu,abc}^{ijk}(2)$ 
    END OF LOOP OVER a<b<c
END OF LOOP OVER i<j<k
 $\delta_\mu(2,3) = \text{SUM}$ 
```

As one can see from the above algorithm and as we did it in the past when coding other CR-CC and CR-EOMCC methods [20, 48, 74, 80, 81, 179], in constructing the individual  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $\ell_{\mu,ijk}^{abc}$  terms, which have to be multiplied and summed up to produce the correction  $\delta_\mu(2,3)$  following Eq. (41), we use explicit loops over the occupied labels  $i < j < k$  only. We do not use explicit loops over the unoccupied indices  $a < b < c$  to determine  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $\ell_{\mu,ijk}^{abc}$ . Instead, we first calculate the entire set of the partially antisymmetric six-index quantities  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  and  $\Gamma_{\mu,ijk}^{abc}$ , which are antisymmetric with respect to  $i, j$ , and  $k$  but not with respect to  $a, b$ , and  $c$ , for a given set of occupied indices  $i < j < k$  and all values of  $a, b$ , and  $c$ , which we subsequently antisymmetrize with respect to  $a, b$ , and  $c$  in a trivial manner using Eqs. (59) and (60), respectively, to produce the final  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $N_{\mu,ijk}^{abc}$  values that can be stored in relatively small arrays of dimension  $n_u^3$ , since we are at this point inside the loop over  $i < j < k$ . Once the values of  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $N_{\mu,ijk}^{abc}$  are determined for a given set of occupied indices  $i, j$ , and  $k$ , within a loop over  $i < j < k$ , and all values of  $a, b$ , and  $c$ , we open the loop over  $a < b < c$  only to multiply  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  by  $\ell_{\mu,ijk}^{abc}$  (the latter originating from  $N_{\mu,ijk}^{abc}$ ) to

form a contribution to  $\delta_\mu(2,3)$  from a particular set of  $i < j < k$  and  $a < b < c$  values. By avoiding the explicit loops over  $a, b$ , and  $c$  in the most essential and most computationally intensive part of the code that calculates moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and numerator coefficients  $N_{\mu,ijk}^{abc}$  that define the deexcitation amplitudes  $\ell_{\mu,ijk}^{abc}$ , we maximize the benefits of using fast matrix multiplication routines, while eliminating the need for storing large  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $\ell_{\mu,ijk}^{abc}$  vectors of the  $n_o^3 n_u^3$  type. For example, if we used the explicit  $i < j < k$  and  $a < b < c$  loops throughout the entire algorithm of constructing  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$ ,  $\ell_{\mu,ijk}^{abc}$ , and  $\delta_\mu(2,3)$ , the calculation of the  $\frac{1}{2} \bar{h}_{ab}^{ie} r_{ec}^{jk}$  term in Eq. (62), which is one of the terms that defines the  $n_o^3 n_u^4$  scaling of the CR-EOMCC(2,3) theory, would split into a very large number of  $\sim 1/36 n_o^3 n_u^3$  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  $\frac{1}{2} \bar{h}_{ab}^{ie} r_{ec}^{jk}$  term is performed with a single call to the BLAS matrix multiplication routine, which is a much more efficient use of fast matrix multipliers. Similar remarks apply to other terms in  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $N_{\mu,ijk}^{abc}$ . The calculations of the triply excited moments  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and of the coefficients  $N_{\mu,ijk}^{abc}$  that define the deexcitation amplitudes  $\ell_{\mu,ijk}^{abc}$  in the explicit loop over  $i < j < k$  and for all values of  $a, b, c$  to achieve a high degree of vectorization may create 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 overcomputing, 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  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $N_{\mu,ijk}^{abc}$  with respect to permutations of indices  $a, b, c$  during the determination of  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  and  $N_{\mu,ijk}^{abc}$ , we first calculate the nonsymmetric quantities  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  and  $\Gamma_{\mu,ijk}^{abc}$  for the given  $i, j, k$  values from the  $i < j < k$  loop and for all  $a, b, c$  values using Eqs. (62) and (63). Once this is done, we have at our disposal all of the relevant  $\mathfrak{T}_{\mu,abc}^{ijk}(2)$  and  $\Gamma_{\mu,ijk}^{abc}$  values that are needed to construct the final  $\mathfrak{M}_{\mu,abc}^{ijk}(2)$  moments and  $N_{\mu,ijk}^{abc}$  coefficients, which are 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, to obtain  $\mathfrak{M}_{\mu,abc}^{ijk}$  (2) and the analogous six values of  $\Gamma_{\mu,ijk}^{abc}$ , again with the appropriate permutation signs, to obtain  $N_{\mu,ijk}^{abc}$ , as in the definition of the antisymmetrizer  $\mathcal{A}_{abc}$ , Eq. (69). 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) and  $\Gamma_{\mu,ijk}^{abc}$  that correspond to permutations of indices  $a, b, c$ , when  $i, j$ , and  $k$  are fixed inside the  $i < j < k$  loop, are determined.

Before discussing the results of a few benchmark calculations, we would like to mention that the remaining details of the present open-shell implementation of the CR-EOMCC(2,3),A–D methods are quite similar to those described, for example, in Refs. [167–170] for the CCSD(T) [167–169], CR-CC(2,3) [48], CC3 [170], and CR-EOMCCSD(T) [81] approaches. In particular, in coding the CR-EOMCC(2,3),A–D methods, we relied on the usual spin-orbital/spin-factored approach, which applies to CC and EOMCC calculations for ground and excited states with either the unrestricted Hartree–Fock (UHF) or ROHF reference wave functions. Although our CR-EOMCC(2,3) computer codes are developed in such a way that they can be applied to any high-spin reference determinant  $|\Phi\rangle$ , they are interfaced at this time with the ROHF integral routines from GAMESS [108]. Thus, after the ROHF calculation performed by GAMESS, we call the appropriate and highly efficient integral transformation routines, also taken from GAMESS, and then sort the resulting molecular integrals, using the program written by Dr. Michael W. Schmidt on the occasion of incorporating the ROHF-based ground-state CR-CC(2,3) code in the GAMESS package [48], according to the number of occupied and unoccupied orbital indices that label them and according to the spin type of each orbital index ( $\alpha$  or  $\beta$ ) in a usual manner. Although it may be worthwhile to examine the performance of the CR-EOMCC(2,3) methods in calculations exploiting UHF references, the comparison of the results of the ROHF- and UHF-based EOMCCSD and CC3 calculations for radical systems suggests that the use of the ROHF reference functions in the EOMCC or response CC calculations of excited states leads to better results, particularly when the spin contamination becomes more significant [170]. Thus, we expect that the use of the ROHF references in the present computer implementation of the CR-EOMCC(2,3),A–D approaches may have a positive impact on the calculated excitation energies.

### 3. Numerical Examples

To test the performance of the open-shell extension of the CR-EOMCC(2,3),A–D approaches and computer codes discussed in the previous section, we calculated the ground and the low-lying doublet and quartet excited states of the CH radical (Tables II and III) and the valence doublet excited states of the CNC (Table IV), C<sub>2</sub>N (Table IV), N<sub>3</sub> (Table V), and NCO (Table V) systems. The valence excited states of the CH, CNC and C<sub>2</sub>N species are especially interesting since a number of them have a predominantly two-electron excitation character, which requires a highly accurate determination of the triples effects in the CC/EOMCC calculations. Indeed, as implied by the reduced excitation level (REL) diagnostics introduced in Ref. [81], which is designed to give values around 1.0 for excited states dominated by one-electron transitions and 2.0 for excited states dominated by two-electron processes, the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states of CH, the  $B^2\Sigma_u^+$  state of CNC, and the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states of C<sub>2</sub>N are dominated by two-electron transitions, resulting in the extremely poor description of these states by the basic EOMCCSD approach and the EA-EOMCCSD method truncated at  $2p$ - $1h$  excitations [135, 136], referred to here and elsewhere in this article as the EA-EOMCCSD( $2p$ - $1h$ ) approach [138–140, 142] (see Tables II–IV). For this reason, it is essential to include triple excitations in the EOMCC considerations if we are to obtain a reasonable description of these states. As implied by the values of the REL diagnostics in Tables II–V, the remaining states of CH, CNC, and C<sub>2</sub>N and the low-lying states of N<sub>3</sub> and NCO are dominated by one-electron transitions and, as such, are reasonably well described by the basic EOMCCSD approach, with the EA-EOMCCSD( $2p$ - $1h$ ) and IP-EOMCCSD( $2h$ - $1p$ )  $\equiv$  IP-EOMCCSD [144–147] levels working well for the singly excited states of the CH radical and the N<sub>3</sub> and NCO systems, but it is useful to examine if the EOMCC methods with triple excitations and their EA and IP valence counterparts with  $3p$ - $2h$  and  $3h$ - $2p$  excitations can provide further small improvements in the already good EOMCCSD, EA-EOMCCSD( $2p$ - $1h$ ), and IP-EOMCCSD( $2h$ - $1p$ ) results for the states dominated by single,  $1p$ , and  $1h$  excitations.

Clearly, one can always include triple excitations in the EOMCC considerations by turning to the full EOMCCSDT approach [75–79] or its valence EA-EOMCCSD( $3p$ - $2h$ ) and IP-EOMCCSD( $3h$ - $2p$ ) analogs [138–140] mentioned in the Introduction section.

TABLE II

Total energies ( $E$ ), adiabatic excitation energies ( $T_e$ ), and reduced excitation level (REL) values of the ground  $X^2\Pi$  and excited  $a^4\Sigma^-$  and  $A^2\Delta$  states of the CH radical, as obtained with the aug-cc-pVDZ basis set.

| Theory                        | $E$ /Hartree | $T_e$ /eV | REL  |
|-------------------------------|--------------|-----------|------|
| $X^2\Pi$                      |              |           |      |
| CCSD                          | -38.384 762  |           |      |
| CCSDT <sup>a</sup>            | -38.387 721  |           |      |
| EA-EOMCCSD(2p-1h)             | -38.385 027  |           |      |
| EA-EOMCCSD(3p-2h)             | -38.386 710  |           |      |
| EA-EOMCCSD(3p-2h){3}          | -38.385 058  |           |      |
| CR-CCSD(T),ID <sup>b</sup>    | -38.387 333  |           |      |
| CR-CC(2,3),A                  | -38.386 970  |           |      |
| CR-CC(2,3),B                  | -38.386 882  |           |      |
| CR-CC(2,3),C                  | -38.387 525  |           |      |
| CR-CC(2,3),D                  | -38.387 517  |           |      |
| $a^4\Sigma^-$                 |              |           |      |
| EOMCCSD                       | -38.351 024  | 0.918     | 1.17 |
| EOMCCSDT <sup>a</sup>         | -38.363 501  | 0.659     |      |
| EA-EOMCCSD(2p-1h)             | -38.297 982  | 2.369     |      |
| EA-EOMCCSD(3p-2h)             | -38.362 222  | 0.666     |      |
| EA-EOMCCSD(3p-2h){3}          | -38.361 486  | 0.641     |      |
| CR-EOMCCSD(T),ID <sup>b</sup> | -38.357 877  | 0.802     |      |
| CR-EOMCC(2,3),A               | -38.356 275  | 0.835     |      |
| CR-EOMCC(2,3),B               | -38.356 026  | 0.840     |      |
| CR-EOMCC(2,3),C               | -38.358 617  | 0.787     |      |
| CR-EOMCC(2,3),D               | -38.358 586  | 0.787     |      |
| Experiment <sup>c</sup>       |              | 0.74      |      |
| $A^2\Delta$                   |              |           |      |
| EOMCCSD                       | -38.263 296  | 3.305     | 1.14 |
| EOMCCSDT <sup>a</sup>         | -38.276 613  | 3.023     |      |
| EA-EOMCCSD(2p-1h)             | -38.205 024  | 4.898     |      |
| EA-EOMCCSD(3p-2h)             | -38.275 098  | 3.037     |      |
| EA-EOMCCSD(3p-2h){3}          | -38.274 268  | 3.015     |      |
| CR-EOMCCSD(T),ID <sup>b</sup> | -38.268 079  | 3.245     |      |
| CR-EOMCC(2,3),A               | -38.267 562  | 3.249     |      |
| CR-EOMCC(2,3),B               | -38.267 353  | 3.253     |      |
| CR-EOMCC(2,3),C               | -38.269 067  | 3.223     |      |
| CR-EOMCC(2,3),D               | -38.269 043  | 3.224     |      |
| Experiment <sup>d</sup>       |              | 2.87      |      |

Experimental excitation energies and nuclear geometries used in the CC/EOMCC calculations were taken from Refs. [185–187]. The equilibrium bond lengths used in the CC/EOMCC calculations were taken from experiment and they are the same as used by Hirata in Ref. [78]. They are:  $r_e = 1.1197868$  Å for the  $X^2\Pi$  state (Ref. [185]),  $r_0 = 1.0977$  Å for the  $a^4\Sigma^-$  state (Ref. [186]), and  $r_e = 1.1031$  Å for the  $A^2\Delta$  state (Ref. [185]). In all correlated calculations the lowest energy core orbital was frozen.

<sup>a</sup> The UHF-based results reported in Ref. [78].

<sup>b</sup> The ROHF-based results reported in Ref. [81].

<sup>c</sup> From Ref. [187].

<sup>d</sup> From Ref. [185].

Let us recall that in the case of EOMCCSDT, we approximate the cluster and EOMCC linear excitation operators as  $T^{(\text{CCSDT})} = T_1 + T_2 + T_3$  and  $R^{(\text{CCSDT})} = R_{\mu,0} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3}$ , respectively, and solve the CC and EOMCC equations, Eqs. (29) and (30), in the space spanned by all singly, doubly, and triply excited determinants,  $|\Phi_i^a\rangle$ ,  $|\Phi_{ij}^{ab}\rangle$ , and  $|\Phi_{ijk}^{abc}\rangle$ , respectively. In the EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) cases, we solve the

TABLE III

Total energies ( $E$ ), adiabatic excitation energies ( $T_e$ ), and reduced excitation level (REL) values of the excited  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states of the CH radical, as obtained with the aug-cc-pVDZ basis set.

| Theory                        | $E$ /Hartree | $T_e$ /eV | REL  |
|-------------------------------|--------------|-----------|------|
| $B^2\Sigma^-$                 |              |           |      |
| EOMCCSD                       | -38.228 924  | 4.241     | 1.79 |
| EOMCCSDT <sup>a</sup>         | -38.267 435  | 3.273     |      |
| EA-EOMCCSD(2p-1h)             | -38.160 687  | 6.105     |      |
| EA-EOMCCSD(3p-2h)             | -38.262 600  | 3.377     |      |
| EA-EOMCCSD(3p-2h){3}          | -38.261 677  | 3.357     |      |
| CR-EOMCCSD(T),ID <sup>b</sup> | -38.270 424  | 3.181     |      |
| CR-EOMCC(2,3),A               | -38.257 269  | 3.529     |      |
| CR-EOMCC(2,3),B               | -38.255 709  | 3.569     |      |
| CR-EOMCC(2,3),C               | -38.272 744  | 3.123     |      |
| CR-EOMCC(2,3),D               | -38.272 498  | 3.130     |      |
| Experiment <sup>c</sup>       |              | 3.23      |      |
| $C^2\Sigma^+$                 |              |           |      |
| EOMCCSD                       | -38.194 213  | 5.185     | 1.87 |
| EOMCCSDT <sup>a</sup>         | -38.238 031  | 4.073     |      |
| EA-EOMCCSD(2p-1h)             | -38.180 332  | 5.570     |      |
| EA-EOMCCSD(3p-2h)             | -38.236 024  | 4.100     |      |
| EA-EOMCCSD(3p-2h){3}          | -38.234 680  | 4.092     |      |
| CR-EOMCCSD(T),ID <sup>b</sup> | -38.236 048  | 4.117     |      |
| CR-EOMCC(2,3),A               | -38.224 449  | 4.422     |      |
| CR-EOMCC(2,3),B               | -38.222 634  | 4.469     |      |
| CR-EOMCC(2,3),C               | -38.238 514  | 4.055     |      |
| CR-EOMCC(2,3),D               | -38.238 118  | 4.065     |      |
| Experiment <sup>d</sup>       |              | 3.94      |      |

Experimental excitation energies and nuclear geometries used in the CC/EOMCC calculations were taken from Refs. [185, 188, 189]. The equilibrium bond lengths used in the CC/EOMCC calculations were taken from experiment and they are the same as used by Hirata in Ref. [78]. They are:  $r_e = 1.1197868$  Å for the  $X^2\Pi$  state (Ref. [185]),  $r_e = 1.1640$  Å for the  $B^2\Sigma^-$  state (Ref. [188]), and  $r_e = 1.1143$  Å for the  $C^2\Sigma^+$  state (Ref. [189]). In all correlated calculations the lowest energy core orbital was frozen.

<sup>a</sup> The UHF-based results reported in Ref. [78].

<sup>b</sup> The ROHF-based results reported in Ref. [81].

<sup>c</sup> From Ref. [188].

<sup>d</sup> From Ref. [189].



TABLE IV

Adiabatic excitation energies (eV) and reduced excitation level (REL) values of the low-lying valence excited states of CNC and C<sub>2</sub>N.

| Molecule         | State           | REL   | EA-EOMCCSD |         |                |         | CR-EOMCCSD<br>(T), ID | CR-EOMCC(2,3) |       |       |       | Experiment <sup>a</sup> |
|------------------|-----------------|-------|------------|---------|----------------|---------|-----------------------|---------------|-------|-------|-------|-------------------------|
|                  |                 |       | (2p-1h)    | (3p-2h) | (3p-2h)<br>{4} | EOMCCSD |                       | A             | B     | C     | D     |                         |
| CNC              | $A^2\Delta_u$   | 1.099 | 7.206      | 4.105   | 4.085          | 4.291   | 4.339                 | 4.400         | 4.397 | 4.395 | 4.395 | 3.761                   |
|                  | $B^2\Sigma_u^+$ | 1.979 | 7.639      | 4.718   | 4.704          | 7.123   | 4.675                 | 5.432         | 5.595 | 4.582 | 4.599 | 4.315                   |
| C <sub>2</sub> N | $A^2\Delta$     | 1.090 | 6.190      | 3.055   | 3.028          | 3.191   | 3.344                 | 3.377         | 3.368 | 3.389 | 3.388 | 2.636                   |
|                  | $B^2\Sigma^-$   | 1.856 | 7.856      | 3.677   | 3.648          | 5.514   | 3.351                 | 4.018         | 4.160 | 3.091 | 3.110 | 2.779                   |
|                  | $C^2\Sigma^+$   | 1.897 | 6.722      | 3.809   | 3.788          | 6.358   | 4.023                 | 4.741         | 4.901 | 3.799 | 3.824 | 3.306                   |

The nuclear geometries used in the CC/EOMCC calculations are the same as used in Ref. [195]. For CNC a linear  $D_{2h}$  geometry was used, whereas for C<sub>2</sub>N a linear  $C_{2v}$  geometry was adopted. The optimized bond lengths for each molecule and state were determined using the SAC-CI SDT- $R$  approach and are as follows. For CNC,  $R_{CN} = 1.253$  Å for the ground  $X^2\Pi_g$  state,  $R_{CN} = 1.256$  Å for the  $A^2\Delta_u$  state, and  $R_{CN} = 1.259$  Å for the  $B^2\Sigma_u^+$  state. For C<sub>2</sub>N,  $R_{CC} = 1.400$  Å,  $R_{CN} = 1.185$  Å for the ground  $X^2\Pi$  state,  $R_{CC} = 1.315$  Å,  $R_{CN} = 1.207$  Å for the  $A^2\Delta$  state,  $R_{CC} = 1.302$  Å,  $R_{CN} = 1.223$  Å for the  $B^2\Sigma^-$  state, and  $R_{CC} = 1.311$  Å,  $R_{CN} = 1.214$  Å for the  $C^2\Sigma^+$  state.

<sup>a</sup> Taken from Ref. [190].

CCSD equations for the related closed-shell system with  $(N - 1)$  (the EA case) or  $(N + 1)$  (the IP case) electrons and, after constructing the similarity-transformed Hamiltonian of the closed-shell CCSD calculation for the appropriate  $(N \mp 1)$ -electron reference system, we diagonalize it in the space spanned by the  $1p$ ,  $2p-1h$ , and  $3p-2h$  determinants,  $|\Phi^a\rangle = a^a|\Phi^{(N-1)}\rangle$ ,  $|\Phi_j^{ab}\rangle = a^a a^b a_j |\Phi^{(N-1)}\rangle$ , and  $|\Phi_{jk}^{abc}\rangle = a^a a^b a^c a_k a_j |\Phi^{(N-1)}\rangle$ , respectively, in the EA case, and the space spanned by the  $1h$ ,  $2h-1p$ , and  $3h-2p$  determinants,  $|\Phi_i\rangle = a_i|\Phi^{(N+1)}\rangle$ ,  $|\Phi_{ij}^b\rangle = a^b a_j a_i |\Phi^{(N+1)}\rangle$ , and  $|\Phi_{ijk}^{bc}\rangle = a^b a^c a_k a_j a_i |\Phi^{(N+1)}\rangle$ , respectively, in the IP case, where  $|\Phi^{(N\mp 1)}\rangle$  is the reference determinant for the relevant closed-shell CCSD calculation for the  $(N \mp 1)$ -electron system [the aforementioned

EA-EOMCCSD( $2p-1h$ ) and IP-EOMCCSD( $2h-1p$ ) calculations use similar ideas, but they neglect the  $3p-2h/3h-2p$  excitations]. Unfortunately, as already alluded to above, the full EOMCCSDT approach is a very expensive procedure characterized by the  $n_o^3 n_u^5$  iterative steps and very large memory and disk requirements, since one must store the very long triply excited  $T_3$  and  $R_{\mu,3}$  vectors, each containing  $\sim n_o^3 n_u^3$  elements. The EA-EOMCCSD( $3p-2h$ ) and IP-EOMCCSD( $3h-2p$ ) approaches are less expensive than EOMCCSDT (for example, one only has to solve the ground-state CCSD equations for the related  $(N \mp 1)$ -electron systems instead of solving the full CCSDT equations for the  $N$ -electron target system of interest that are required by EOMCCSDT),

TABLE V

Adiabatic excitation energies (eV) and reduced excitation level (REL) values of the low-lying valence excited states of N<sub>3</sub> and NCO.

| Molecule       | State           | REL   | IP-EOMCCSD |         |                |         | CR-EOMCCSD<br>(T), ID | CR-EOMCC(2,3) |       |       |       | Experiment <sup>a</sup> |
|----------------|-----------------|-------|------------|---------|----------------|---------|-----------------------|---------------|-------|-------|-------|-------------------------|
|                |                 |       | (2p-1h)    | (3p-2h) | (3h-2p)<br>{2} | EOMCCSD |                       | A             | B     | C     | D     |                         |
| N <sub>3</sub> | $B^2\Sigma_u^+$ | 1.087 | 4.640      | 4.598   | 4.729          | 4.804   | 4.915                 | 4.948         | 4.941 | 4.971 | 4.968 | 4.555                   |
| NCO            | $A^2\Sigma^+$   | 1.060 | 2.900      | 2.864   | 3.078          | 2.931   | 3.087                 | 3.123         | 3.111 | 3.161 | 3.158 | 2.821                   |
|                | $B^2\Pi$        | 1.073 | 4.199      | 3.911   | 3.904          | 4.053   | 4.011                 | 4.093         | 4.106 | 4.061 | 4.068 | 3.937                   |

The nuclear geometries used in the CC/EOMCC calculations are the same as used in Ref. [195]. For N<sub>3</sub> a linear  $D_{2h}$  geometry was used, whereas for NCO a linear  $C_{2v}$  geometry was adopted. The optimized bond lengths for each molecule and state were determined using the SAC-CI SDT- $R$  approach and are as follows. For N<sub>3</sub>,  $R_{NN} = 1.188$  Å for the ground  $X^2\Pi_g$  state, and  $R_{NN} = 1.185$  Å for the  $B^2\Sigma_u^+$  state. For NCO,  $R_{NC} = 1.230$  Å,  $R_{CO} = 1.193$  Å for the ground  $X^2\Pi$  state,  $R_{NC} = 1.191$  Å,  $R_{CO} = 1.190$  Å for the  $A^2\Sigma^+$  state, and  $R_{NC} = 1.220$  Å,  $R_{CO} = 1.309$  Å for the  $B^2\Pi$  state.

<sup>a</sup> Taken from Ref. [190].

but the iterative  $n_o^2 n_u^5$  steps of EA-EOMCCSD( $3p-2h$ ) and iterative  $n_o^3 n_u^4$  steps of IP-EOMCCSD( $3h-2p$ ) required by the corresponding diagonalizations of the similarity-transformed Hamiltonian (particularly, the former ones) are still relatively time consuming. As pointed out in the Introduction section, one can reduce the computer costs of the full EA-EOMCCSD( $3p-2h$ ) and IP-EOMCCSD( $3h-2p$ ) calculations by selecting the dominant  $3p-2h$  and  $3h-2p$  components of the relevant electron attaching and ionizing EOMCC operators  $R_\mu$  with the help of active orbitals, obtaining the active-space EA-EOMCCSD( $3p-2h$ ) and IP-EOMCCSD( $3h-2p$ ) methods that require relatively inexpensive steps of the  $n_o^2 n_u^4$  type [138–140], and this is done in this work as well, with a great deal of success, but the main point of this study is the examination of whether one can obtain results comparable to the accurate full EOM-CCSDT and full and active-space EA-EOMCCSD( $3p-2h$ ) and IP-EOMCCSD( $3h-2p$ ) data for the open-shell systems of interest by using the purely black-box CR-EOMCC(2,3) methodology, which relies on the relatively inexpensive noniterative steps of the  $n_o^3 n_u^4$  type in determining the triples corrections to the EOMCCSD energies and which does not require choosing active orbitals to select triple excitations. A comparison of the CR-EOMCC(2,3) results, particularly those obtained with the complete variant D discussed in the previous section, with those obtained with the more established and already quite successful CR-EOMCCSD(T) methodology [43, 44, 80, 81] [for compatibility of this comparison, we use the CR-EOMCCSD(T)<sub>ID</sub> approach of Refs. [80, 81] in our calculations] will tell us if the CR-EOMCC(2,3)<sub>D</sub> approach that interests us most is at least as effective in describing electronic excitations in open-shell systems as the CR-EOMCCSD(T)<sub>ID</sub> method. A comparison of the CR-EOMCC(2,3)<sub>A–D</sub> results among themselves, particularly for excited states dominated by two-electron transitions, will allow us to appreciate the benefits of using the complete variant D of the CR-EOMCC(2,3) theory.

To facilitate comparisons with the results of the expensive full EOMCCSDT, EA-EOMCCSD( $3p-2h$ ), and IP-EOMCCSD( $3h-2p$ ) calculations, the EOM-CCSD and CR-EOMCC(2,3) calculations for CH were performed using the aug-cc-pVDZ basis set [191, 192], whereas the calculations for CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO were performed with the DZP [4s2p1d] basis set of Refs. [193, 194]. The relevant UHF-based EOMCCSDT data for CH, obtained using the aug-cc-pVDZ basis set, were taken from Ref. [78]. The

corresponding EA-EOMCCSD( $2p-1h$ ) and full and active-space EA-EOMCCSD( $3p-2h$ ) calculations, in which one uses the closed-shell CH<sup>+</sup> ion as a reference 6-electron system for describing the 7-electron CH radical through electron attachment, were performed with the system of highly efficient EA/IP-EOMCC codes described in Ref. [140]. We note that the analogous EA-EOMCCSD( $2p-1h$ ), EA-EOMCCSD( $3p-2h$ ), and active-space EA-EOMCCSD( $3p-2h$ ) calculations were reported earlier [140], but we have improved our EA/IP EOMCC codes since then and recalculated all of the total (*E*) and adiabatic excitation (*T<sub>e</sub>*) energies for CH listed in Tables II and III for the purpose of this study with these improved codes. The active orbital space for the active-space EA-EOMCCSD( $3p-2h$ ) calculations consisted of the three unoccupied valence orbitals of the CH<sup>+</sup> ion (the  $1\pi_x$ ,  $1\pi_y$ , and  $4\sigma$  orbitals of CH<sup>+</sup>), which is indicated in Tables III and IV by the additional symbol {3} at the relevant EA-EOMCCSD( $3p-2h$ ) acronym. The same EA/IP EOMCC program suite was used to obtain the EA-EOMCCSD( $2p-1h$ ), EA-EOMCCSD( $3p-2h$ ), and active-space EA-EOMCCSD( $3p-2h$ ) results for the 19-electron CNC and C<sub>2</sub>N species, where the 18-electron, closed-shell, reference systems for the EA-EOMCC calculations are the CNC<sup>+</sup> and C<sub>2</sub>N<sup>+</sup> ions, and the IP-EOMCCSD( $2h-1p$ ), full IP-EOMCCSD( $3h-2p$ ), and active-space IP-EOMCCSD( $3h-2p$ ) results for the 21-electron N<sub>3</sub> and NCO species, where the 22-electron, closed-shell, reference systems for the IP-EOMCC calculations are the N<sub>3</sub><sup>−</sup> and NCO<sup>−</sup> ions. We elaborate some more on the full and active space EA-EOMCCSD( $3p-2h$ ) and IP-EOMCCSD( $3h-2p$ ) calculations for CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO and their comparison with the analogous EA and IP SAC-CI calculations with up to  $3p-2h/3h-2p$  excitations in Ref. [195]. The active orbital spaces for the active-space EA-EOMCCSD( $3p-2h$ ) calculations for CNC and C<sub>2</sub>N consisted of the two lowest-energy pairs of unoccupied  $\pi$  molecular orbitals of CNC<sup>+</sup> and C<sub>2</sub>N<sup>+</sup>, respectively, while the active space for N<sub>3</sub> and the active space for NCO each consisted of the highest-energy pair of occupied orbitals of N<sub>3</sub><sup>−</sup> and NCO<sup>−</sup>, respectively. We designate the resulting active-space EA-EOMCCSD( $3p-2h$ ) and IP-EOMCCSD( $3h-2p$ ) calculations as EA-EOMCCSD( $3p-2h$ ){4} and IP-EOMCCSD( $3h-2p$ ){2}, where {4} and {2} emphasize the numbers of active orbitals used to select the relevant  $3p-2h$  and  $3h-2p$  excitations, respectively, following the relevant amplitude selection procedures introduced in Refs. [138–140]. All EA-EOMCC and IP-EOMCC

calculations used the ground-state RHF orbitals of the corresponding reference ions, whereas the EOMCCSD and CR-EOMCC(2,3) calculations used the ROHF orbitals resulting from the Roothaan's canonicalization scheme [171] which is a default in GAMESS, with which our CC/EOMCC codes are interfaced. In all of the calculations reported in this article, the lowest core orbitals corresponding to the C, N, and O atoms were frozen in all post-Hartree-Fock calculations and the spherical  $d$  orbitals were used throughout.

In addition to comparing our CR-EOMCC(2,3) results with those obtained with the accurate EOM-CCSDT, EA-EOMCCSD(3 $p$ -2 $h$ ), and IP-EOMCCSD(3 $h$ -2 $p$ ) levels, we make comparisons with the available experimental data. The experimental data for the CH radical, including the adiabatic excitation energies and the equilibrium bond lengths that were used in the CC/EOMCC calculations, were taken from Refs. [185–189] (the same values were used in the EOMCCSDT calculations reported in Ref. [78]). The experimental adiabatic excitation energies for the CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO species were taken from Ref. [190]. The relevant nuclear geometries of the ground and excited states of CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO that were used in the CC/EOMCC calculations for these systems were taken from Ref. [195], where Professor Masahiro Ehara and two of us (J.R.G. and P.P.) exploited the analytic gradients of the EA/IP SAC-CI SDT-R method [196–198] to obtain them. As shown in Ref. [195], the EA-SAC-CI SDT-R geometries of the ground and excited states of CNC and C<sub>2</sub>N and the IP-SAC-CI SDT-R geometries of the ground and excited states of N<sub>3</sub> and NCO that interest us in this work are almost identical, to within 0.01–0.03 Å or better, to the available experimental data. We used the theoretical geometries rather than the experimental ones in our adiabatic excitation energy calculations for CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO since information about the experimental geometries for the low-lying states of C<sub>2</sub>N and for the  $B^2\Pi$  state of NCO is not available. It should also be pointed out that the EA/IP SAC-CI SDT-R approaches are, up to small and rather unimportant details, equivalent to the EA-EOMCCSD(3 $p$ -2 $h$ ) and IP-EOMCCSD(3 $h$ -2 $p$ ) approaches used in this article to compute the adiabatic excitation energies (see Ref. [142] for a thorough discussion). Thus, the use of the geometries optimized with the EA/IP SAC-CI SDT-R approaches is consistent with the highest level of the EA/IP EOMCC theory employed in this work [in principle, we should use the EA-EOMCCSD(3 $p$ -2 $h$ ) and IP-EOMCCSD(3 $h$ -2 $p$ ) methods to optimize geometries,

but the analytic gradients of EA-EOMCCSD(3 $p$ -2 $h$ ) and IP-EOMCCSD(3 $h$ -2 $p$ ) have not been developed yet]. The information about the available experimental adiabatic excitation energies for the CH, CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO systems and nuclear geometries used in the various CC and EOMCC calculations discussed in this article can be found in Tables II–V.

We now proceed to the discussion of the results of the CR-EOMCC(2,3),A–D calculations for the low-lying states of the CH, CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO species, and their comparison with other CC/EOMCC and experimental data.

### 3.1. THE CH RADICAL

As already mentioned, the  $a^4\Sigma^-$  and  $A^2\Delta$  states of the CH radical are dominated by single excitations, whereas the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states have a considerable multireference character and significant contributions from double excitations. The detailed information about electron configurations that dominate the CI expansions of the  $a^4\Sigma^-$ ,  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states of CH can be found in Ref. [199]. The results in Tables II and III clearly demonstrate that the complete CR-EOMCC(2,3),D approach provides a uniformly and highly accurate description of the excited states of CH, independent of their (singly or doubly excited, doublet or quartet) character. The CR-EOMCC(2,3),D values of the adiabatic excitation energies  $T_e$  obtained with the aug-cc-pVDZ basis set are within 0.05–0.35 eV from experiment. This includes the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states dominated by two-electron transitions, for which the EOMCCSD and EA-EOMCCSD(2 $p$ -1 $h$ ) approaches completely fail, producing the 1.01 and 1.25 eV errors, respectively, in the EOMCCSD case and 2.88 and 1.63 eV errors, respectively, in the EA-EOMCCSD(2 $p$ -1 $h$ ) case, when the aug-cc-pVDZ basis set is used. The CR-EOMCC(2,3),D approach reduces these large errors in the EOMCCSD and EA-EOMCCSD(2 $p$ -1 $h$ )  $T_e$  values for the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states of CH to 0.10 and 0.13 eV, respectively. Variant C of CR-EOMCC(2,3) is as accurate as variant D, confirming the remarks made in Section 2 that the contributions to the  $D_{\mu,abc}^{ijk}$  denominator, Eq. (49), due to the three-body component of  $\bar{H}^{(\text{CCSD})}$ , neglected in the CR-EOMCC(2,3),C approach, are unimportant. However, neither variant A, equivalent to the EOM-CC(2)PT(2) method discussed in Refs. [34, 113], which uses the Møller–Plesset-like denominator for triple excitations,  $\omega_{\mu}^{(\text{CCSD})} - (\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)$  instead of the Epstein–Nesbet form of  $D_{\mu,abc}^{ijk}$

involving up to three-body components of  $\bar{H}^{(\text{CCSD})}$ , nor variant B, which uses the one-body matrix elements  $\bar{h}_p^p$  instead of the bare orbital energies  $\epsilon_p$  in the definition of  $D_{\mu,abc}^{ijk}$ , work as well as the CR-EOMCC(2,3),C and CR-EOMCC(2,3),D approaches. The differences between the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B values of  $T_e$  on the one hand and the CR-EOMCC(2,3),C and CR-EOMCC(2,3),D  $T_e$  values on the other hand are particularly significant, in favor of the latter two approaches, for the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states, which are dominated by doubles. Indeed, the small 0.10–0.11 and 0.12–0.13 eV errors in describing the adiabatic excitation energies corresponding to these two states of CH resulting from the CR-EOMCC(2,3),C and CR-EOMCC(2,3),D calculations increase to 0.30–0.34 and 0.48–0.53 eV, respectively. This shows that it is essential to use the complete treatment of the  $D_{\mu,abc}^{ijk}$  denominator, as in the CR-EOMCC(2,3),D approach, rather than its approximate forms represented by variants A and B, if we aim at the high-quality description of the excited states of the CH radical.

As explained earlier, a reliable description of excited states dominated by double excitations requires an accurate determination of the triples effects and these are best described by the full CCSDT/EOMCCSDT and full and active-space EA-EOMCCSD(3p-2h) methods. It is, therefore, interesting to compare the results of the CR-EOMCC(2,3),D calculations with the corresponding EOMCCSDT and EA-EOMCCSD(3p-2h) data. As shown in Tables II and III, the UHF-based EOMCCSDT approach provides a very accurate description of the excited states of CH. For the states listed in Tables II and III, the errors in the EOMCCSDT  $T_e$  values obtained with the aug-cc-pVDZ basis set, relative to experiment, do not exceed 0.15 eV. The full and active-space EA-EOMCCSD(3p-2h) methods provide similarly small errors that do not exceed 0.17 eV, with the results of the active-space EA-EOMCCSD(3p-2h){3} calculations being virtually identical to their parent EA-EOMCCSD(3p-2h) counterparts. This is somewhat better than the 0.05–0.35 eV errors obtained in the CR-EOMCC(2,3),D/aug-cc-pVDZ calculations, but we must remember that iterative  $n_o^3n_u^5$  and  $n_o^2n_u^5$  steps of the EOMCCSDT and EA-EOMCCSD(3p-2h) approaches, respectively, make the EOMCCSDT and EA-EOMCCSD(3p-2h) calculations a lot more expensive than the CR-EOMCC(2,3) calculations that use the iterative  $n_o^2n_u^4$  and noniterative  $n_o^3n_u^4$  steps. The active-space EA-EOMCCSD(3p-2h){3} calculations reduce the iterative  $n_o^2n_u^5$  steps to the inexpensive steps of the  $n_o^2n_u^4$  type that differ from the underlying

CCSD calculations only by a small prefactor equal to the number of active unoccupied orbitals, making the active-space EA-EOMCCSD(3p-2h) approach very competitive with CR-EOMCC(2,3) from the point of view of the computer costs, but we must keep in mind that the CR-EOMCC(2,3) approach is a black-box method that does not require selecting active orbitals on a molecule-by-molecule basis. It is interesting to observe that the two inexpensive CR-EOMCC(2,3),D and EA-EOMCCSD(3p-2h){3} approaches work so well for the adiabatic excitation energies of the CH radical, independent of the one- or two-electron nature of the calculated excited states.

It is also very encouraging to observe that the CR-EOMCC(2,3),D method provides results which for the most challenging  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states are almost as accurate as the results of the expensive full EOMCCSDT calculations, both in terms of the calculated excitation energies and when the total electronic energies resulting from the CR-EOMCC(2,3),D and EOMCCSDT calculations are compared with one another. The differences between the CR-EOMCC(2,3),D and EOMCCSDT values of  $T_e$  shown in Tables II and III are 0.13 eV for the  $a^4\Sigma^-$  state, 0.20 eV for the  $A^2\Delta$  state, 0.14 eV for the  $B^2\Sigma^-$  state, and 0.01 eV for the  $C^2\Sigma^+$  state. Again, variants A and B of CR-EOMCC(2,3) are not as accurate. For example, the CR-EOMCC(2,3),A approach, which is equivalent to the EOM-CC(2)PT(2) method of Hirata et al. [34, 113], produces the 0.18, 0.23, 0.26, and 0.35 eV differences with the EOMCCSDT  $T_e$  values for the  $a^4\Sigma^-$ ,  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states, respectively, which are substantially larger than those obtained with CR-EOMCC(2,3),D, particularly for the states dominated by double excitations. The older and more established CR-EOMCCSD(T),ID approach works considerably better than the CR-EOMCC(2,3),A  $\equiv$  EOM-CC(2)PT(2) and CR-EOMCC(2,3),B schemes as well, reducing the differences with the EOMCCSDT values of  $T_e$  for the  $a^4\Sigma^-$ ,  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states to 0.14, 0.22, 0.09, and 0.04 eV, respectively, and is only slightly less accurate, on average, than the CR-EOMCC(2,3),D method. In general, the performance of the CR-EOMCC(2,3),D and CR-EOMCCSD(T),ID approaches is very similar, although it is encouraging to observe that the CR-EOMCC(2,3),D method is capable of providing small improvements when compared to the already very accurate CR-EOMCCSD(T),ID data.

Similar remarks apply to the total electronic energies. The differences between the total energies

obtained in the CR-CC(2,3),D/CR-EOMCC(2,3),D and CCSDT/EOMCCSDT calculations for the  $X^2\Pi$ ,  $a^4\Sigma^-$ ,  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states are 0.204, 4.915, 7.570, 5.063, and 0.087 millihartree, respectively. Variant C of CR-CC(2,3)/CR-EOMCC(2,3) gives virtually identical results. The CR-EOMCC(2,3),A  $\equiv$  EOM-CC(2)PT(2) calculations increase these differences to 0.751, 7.226, 9.051, 10.166, and 13.582 millihartree, respectively, which is a significant error increase. Variant B of CR-CC(2,3)/CR-EOMCC(2,3) is even worse, although the differences between the CR-CC(2,3),B/CR-EOMCC(2,3),B and CR-CC(2,3),A/CR-EOMCC(2,3),A energies are quite small. The CR-CCSD(T),ID/CR-EOMCCSD(T),ID method works almost as well as the CR-CC(2,3),D/CR-EOMCC(2,3),D approach, producing the 0.388, 5.624, 8.534, 2.989, and 1.983 millihartree errors relative to CCSDT/EOMCCSDT when the total energies of the  $X^2\Pi$ ,  $a^4\Sigma^-$ ,  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states resulting from the CR-CCSD(T),ID/CR-EOMCCSD(T),ID and CCSDT/EOMCCSDT calculations are compared. Thus, although the overall performance of the CR-CCSD(T),ID/CR-EOMCCSD(T),ID and CR-CC(2,3),D/CR-EOMCC(2,3),D methods is excellent and quite similar, the CR-CC(2,3),D/CR-EOMCC(2,3),D approach offers additional error reductions when compared to the full CCSDT/EOMCCSDT data. This demonstrates that the CR-CC(2,3),D/CR-EOMCC(2,3),D calculations provide the results which are, to a large extent, a faithful representation of the full CCSDT/EOMCCSDT data, a feature observed earlier in the ground-state CR-CC(2,3),D calculations [20, 21, 47].

In conclusion, the results of the CR-EOMCC(2,3) calculations for the low-lying states of the CH radical show that the complete variant D of CR-EOMCC(2,3) provides excellent adiabatic excitation and total energies which are in very good agreement with the full EOMCCSDT and EA-EOMCCSD(3p-2h) data. The use of the complete Epstein–Nesbet form of the  $D_{\mu,abc}^{ijk}$  denominator defining the CR-CC(2,3)/CR-EOMCC(2,3) triples corrections is essential to obtain a highly accurate description, particularly when the excited states of interest are dominated by two-electron transitions. The use of the Møller–Plesset-like form of the  $D_{\mu,abc}^{ijk}$  denominator, as is done in variant A of CR-EOMCC(2,3) or the EOM-CC(2)PT(2) method of Refs. [34, 113], is insufficient, increasing the  $\sim 0.1$  eV errors to as much as 0.5 eV. The only other inexpensive methods that work as well as CR-EOMCC(2,3),D are the CR-EOMCCSD(T),ID and active-space EA-EOMCCSD(3p-2h) approaches,

although the CR-EOMCC(2,3),D scheme offers slight improvements in the overall description of the low-lying states of CH when compared to the CR-EOMCCSD(T),ID data. The high quality of the CR-EOMCC(2,3),D results matches that of the active-space EA-EOMCCSD(3p-2h) calculations, which is very encouraging since just like its CR-EOMCCSD(T),ID predecessor, CR-EOMCC(2,3),D is a black-box procedure that does not require choosing active orbitals.

### 3.2. THE CNC, C<sub>2</sub>N, N<sub>3</sub>, AND NCO MOLECULES

As mentioned in the beginning of this section, the CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO systems are interesting, since some of their low-lying excited states are dominated by two-electron transitions, where triples effects are of major significance, while some other states have a predominantly one-electron nature which the basic EOMCC methods of the EOM-CCSD type can handle quite well. We do not have access to the full EOMCCSDT data for the low-lying excited states of the CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO species, but, judging by the performance of the EA-EOMCCSD(3p-2h) approach in the CH case, where the adiabatic excitation energies resulting from the full and active-space EA-EOMCCSD(3p-2h) and EOMCCSDT calculations are very similar, we can obtain reasonable insights into the performance of the CR-EOMCC(2,3),A–D methods by comparing the CR-EOMCC(2,3),A–D excitation energies with those obtained with the full and active-space EA-EOMCCSD(3p-2h) (the CNC and C<sub>2</sub>N systems) and IP-EOMCCSD(3h-2p) (the N<sub>3</sub> and NCO systems) approaches. As in the CH case, we can also compare the results of the CR-EOMCC(2,3),A–D calculations for the adiabatic excitation energies of CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO with the CR-EOMCCSD(T),ID and experimental data.

We begin with the CNC molecule (Table IV). The ground  $X^2\Pi_g$  state of CNC is dominated by 1p excitations out of the closed-shell ground state of CNC<sup>+</sup> which, as explained in the beginning of this section, serves as a reference system for the EA-EOMCC calculations, while the  $A^2\Delta_u$  and  $B^2\Sigma_u^+$  excited states of CNC, particularly the latter state, show significant contributions from two-electron excitation processes, resulting in large 2p-1h contributions relative to the ground state of CNC<sup>+</sup> that dominate the corresponding wave functions [195] and, in the case of the  $B^2\Sigma_u^+$  state, a large REL value of 1.979 which indicates that this state is dominated by double excitations relative to the ground

$X^2\Pi_g$  state of CNC. Because of the large  $2p-1h$  contributions relative to the ground state of  $\text{CNC}^+$  characterizing the  $A^2\Delta_u$  and  $B^2\Sigma_u^+$  states, the basic EA-EOMCCSD( $2p-1h$ ) approach produces very poor values of the corresponding adiabatic excitation energies  $T_e$ , of 7.206 and 7.639 eV, respectively, which deviate from the experimental values by as much as 3.3–3.5 eV. The EOMCCSD approach works quite well for the  $A^2\Delta_u$  state, which is characterized by the REL value of 1.099 (implying that this state is largely dominated by single excitations relative to the ground state of CNC), but the adiabatic excitation energy corresponding to the  $X^2\Pi_g \rightarrow B^2\Sigma_u^+$  excitation obtained in the EOMCCSD calculations, of 7.123 eV, is almost as poor as its EA-EOMCCSD( $2p-1h$ ) counterpart due to the predominantly two-electron character of the  $B^2\Sigma_u^+$  state. The full and active-space EA-EOMCCSD( $3p-2h$ ) methods drastically improve these poor EA-EOMCCSD( $2p-1h$ ) and EOMCCSD results, reducing the large errors obtained with EA-EOMCCSD( $2p-1h$ ) for the  $A^2\Delta_u$  and  $B^2\Sigma_u^+$  states and the large error resulting from the EOMCCSD calculations for the  $B^2\Sigma_u^+$  state to about 0.3–0.4 eV. This substantial improvement in the description of the  $A^2\Delta_u$  and  $B^2\Sigma_u^+$  states of CNC resulting from the inclusion of the  $3p-2h$  excitations in the EA-EOMCC calculations reflects on the two-electron excitation character of the  $B^2\Sigma_u^+$  state and the fact that the corresponding wave functions of both states are largely dominated by  $2p-1h$  contributions relative to the ground state of the reference  $\text{CNC}^+$  ion. As already pointed out, the full inclusion of the  $3p-2h$  excitations in the EA-EOMCC calculations is quite demanding, resulting in the iterative  $n_o^2 n_u^5$  steps. For this reason, it is important to note that the active-space EA-EOMCCSD( $3p-2h$ ){4} method with only four orbitals in the active space reproduces the results of the full EA-EOMCCSD( $3p-2h$ ) calculations within an accuracy of 0.01–0.02 eV for the  $A^2\Delta_u$  and  $B^2\Sigma_u^+$  states of CNC, while requiring only a small fraction of the CPU time, memory, and disk.

Let us then analyze the CR-EOMCC(2,3) data. As shown in Table IV, the CR-EOMCC(2,3),D results for the  $A^2\Delta_u$  and  $B^2\Sigma_u^+$  states of CNC are almost as good as the high-quality EA-EOMCCSD( $3p-2h$ ) data. Indeed, the CR-EOMCC(2,3),D approach reduces the 2.81 and 3.32 eV errors, relative to experiment, in the EOMCCSD and EA-EOMCCSD( $2p-1h$ ) results for the  $B^2\Sigma_u^+$  state dominated by doubles to 0.28 eV. The CR-EOMCC(2,3),D method does not offer any improvements over the already reasonable EOMCCSD result for the  $A^2\Delta_u$  state, which is a consequence of a REL value for this state of 1.099

(as compared to 1.979 for the  $B^2\Sigma_u^+$  state), but the CR-EOMCC(2,3),D value of  $T_e$  for the  $A^2\Delta_u$  state, of 4.395 eV, is in much better agreement with the experimental  $T_e$  value of 3.761 eV than the EA-EOMCCSD( $2p-1h$ ) result of 7.206 eV. The CR-EOMCC(2,3),D results for the  $A^2\Delta_u$  and  $B^2\Sigma_u^+$  states of CNC are of the same overall quality as the results of the CR-EOMCC(2,3),ID calculations, although CR-EOMCC(2,3),D improves the adiabatic excitation energy of the  $B^2\Sigma_u^+$  state by 0.08 eV. As in the CH case, variants C and D of CR-EOMCC(2,3) yield virtually identical results. The results of the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B calculations are very similar as well. However, there is a substantial difference between the  $T_e$  values resulting from the CR-EOMCC(2,3),A or CR-EOMCC(2,3),B and CR-EOMCC(2,3),C or CR-EOMCC(2,3),D calculations for the  $B^2\Sigma_u^+$  state dominated by double excitations. For example, the CR-EOMCC(2,3),A approach, which is equivalent to the EOM-CC(2)PT(2) method of Refs. [34, 113], gives a substantial error relative to experiment, of 1.12 eV, for the  $T_e$  value characterizing the  $B^2\Sigma_u^+$  state, which should be compared to a much smaller error of 0.28 eV obtained with the CR-EOMCC(2,3),D scheme. There is almost no difference between the CR-EOMCC(2,3),A-D results for the  $A^2\Delta_u$  state, which is a consequence of a predominantly single excitation nature of this state relative to the ground state of CNC and the smallness of triples corrections. One has to examine challenging excited states of the type of the  $B^2\Sigma_u^+$  state to appreciate the significant improvements in the results of the CR-EOMCC(2,3) calculations when going from variant A to D.

For  $\text{C}_2\text{N}$ , the  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  excited states examined in this work are all characterized by significant  $2p-1h$  components relative to the ground state of the reference  $\text{C}_2\text{N}^+$  ion [195], and, as implied by the REL values of about 1.9, the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states are dominated by two-electron processes relative to  $\text{C}_2\text{N}$ 's ground state (see Table IV; as pointed out in Ref. [195], the  $B^2\Sigma^-$  state of  $\text{C}_2\text{N}$  also has non-negligible  $3p-2h$  contributions). Once again, the basic EA-EOMCCSD( $2p-1h$ ) approach fails to accurately describe the adiabatic excitation energies characterizing the low-lying excited states of  $\text{C}_2\text{N}$ , producing errors relative to experiment of 3.55, 5.08, and 3.42 eV for the  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states, respectively. The EOMCCSD results for the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states, which are dominated by doubles, are almost as bad, with errors in the corresponding  $T_e$  values of 2.74 and 3.05 eV, respectively. As is the case for CNC, the explicit inclusion of

3p-2h excitations through the use of the full and active-space EA-EOMCCSD(3p-2h) approaches significantly improves the  $T_e$  values relative to the poor EA-EOMCCSD(2p-1h) (all three states) and EOMCCSD (the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states) results. Indeed, the  $T_e$  values resulting from the full EA-EOMCCSD(3p-2h) calculations for the  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states of 3.055, 3.677, and 3.809 eV, respectively, are in much better agreement with the experimental values of 2.636, 2.779, and 3.306 eV than the poor EA-EOMCCSD(2p-1h) (all states) and EOMCCSD (the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states only) energies. Unfortunately, in spite of these significant improvements, as well as the relatively accurate results for the  $A^2\Delta$  and  $C^2\Sigma^+$  states, the EA-EOMCCSD(3p-2h) method has problems with describing the  $B^2\Sigma^-$  state, producing the  $T_e$  value which is in relatively large error, of about 0.9 eV, relative to the corresponding experimental value of  $T_e$ . This is, most likely, a consequence of the presence of non-negligible contributions from the 3p-2h excitations in the wave function of the  $B^2\Sigma^-$  state of  $C_2N$  which normally requires the higher-level EA-EOMCC treatment with 4p-3h excitations [142, 195]. On the other hand, the main purpose of the present calculations is to compare the CR-EOMCC(2,3) results with the accurate treatment of triple excitations, which the EA-EOMCCSD(3p-2h) certainly offers. Thus, larger error relative to experiment, of about 0.9 eV, observed in the EA-EOMCCSD(3p-2h) calculations for the  $B^2\Sigma^-$  state of  $C_2N$ , is not detrimental to our analysis. We should also note that once again the active-space EA-EOMCCSD(3p-2h){4} scheme performs extremely well, producing discrepancies relative to its more expensive parent EA-EOMCCSD(3p-2h) analog of only 0.02–0.03 eV.

In analogy to the CNC system, the CR-EOMCC(2,3),D results for the  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states of  $C_2N$  are as good, in the overall quality, as the EA-EOMCCSD(3p-2h) data. Indeed, the CR-EOMCC(2,3),D approach reduces the 5.08 and 3.42 eV errors in the EA-EOMCCSD(2p-1h) results for the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states and the 2.74 and 3.05 eV errors for the same two states obtained with EOMCCSD to 0.33 and 0.52 eV, respectively. The CR-EOMCC(2,3),D method does not offer any improvements over the already reasonable EOMCCSD result for the  $A^2\Delta$  state, which is a consequence of the predominantly one-electron nature of this state relative to the ground state of  $C_2N$ , but the CR-EOMCC(2,3),D  $T_e$  value for the  $A^2\Delta$  state, of 3.388 eV, is in much better agreement with the experimental  $T_e$  value of 2.636 eV than

the EA-EOMCCSD(2p-1h) result of 6.190 eV. Interestingly, the CR-EOMCC(2,3),D approach provides improvements in the description of the  $B^2\Sigma^-$  state by the high-level EA-EOMCCSD(3p-2h) approach, reducing the 0.90 eV error obtained with EA-EOMCCSD(3p-2h) to 0.33 eV. The CR-EOMCC(2,3),D results for the  $A^2\Delta$ ,  $B^2\Sigma^-$ , and  $C^2\Sigma^+$  states of  $C_2N$  are of similar quality as the results of the CR-EOMCCSD(T),ID calculations, although the CR-EOMCC(2,3),D method improves the adiabatic excitation energies of the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states, which are dominated by doubles, by 0.24 and 0.20 eV, respectively. Other patterns observed in the CR-EOMCC(2,3) calculations for the CH and CNC systems, such as the similarity of the results obtained with variants C and D, the similarity of the results obtained with variants A and B, and the superiority of the CR-EOMCC(2,3),D approach over the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B methods, are observed in the  $C_2N$  case as well. For example, the CR-EOMCC(2,3),A approach, which uses the simplified, Møller–Plesset-like form of the  $D_{\mu,abc}^{ijk}$  denominator, gives the 1.24 and 1.44 eV errors in the adiabatic excitation energies characterizing the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states of  $C_2N$ , respectively. The complete treatment of the  $D_{\mu,abc}^{ijk}$  denominator offered by the CR-EOMCC(2,3),D approach reduces these substantial errors to as little as 0.33 and 0.52 eV, respectively. Again, there is no difference among the CR-EOMCC(2,3),A–D results for the predominantly singly excited  $A^2\Delta$  state, i.e., one has to consider the more challenging excited states of the type of the  $B^2\Sigma^-$  and  $C^2\Sigma^+$  states to appreciate the benefits of using the most complete CR-EOMCC(2,3),D method.

Let us finally examine the results of the CR-EOMCC(2,3),A–D calculations for the  $N_3$  and NCO systems, as compared to the IP-EOMCCSD(2h-1p), IP-EOMCCSD(3h-2p), EOMCCSD, and CR-EOMCCSD(T),ID data (see Table V). The valence excited states of these two systems are dominated by 1h excitations from the ground states of the reference  $N_3^-$  and  $NCO^-$  ions and show a predominantly one-electron excitation nature relative to the corresponding ground states of  $N_3$  and NCO, with only tiny contributions from 2h-1p excitations and two-electron excitation processes. As a result, the valence excited states of  $N_3$  and NCO examined in Table V are much easier to describe, and the basic IP-EOMCCSD(2h-1p) and EOMCCSD approaches perform quite well. Indeed, the discrepancies between the IP-EOMCCSD(2h-1p) and experimental results

are only 0.08–0.26 eV for the  $B^2\Sigma_u^+$  state of  $N_3$  and the  $A^2\Sigma^+$  and  $B^2\Pi$  states of NCO. The analogous discrepancies between EOMCCSD and experiment are 0.11–0.25 eV. The inclusion of the higher-order  $3h$ - $2p$  correlation effects through the IP-EOMCCSD( $3h$ - $2p$ ) approach, although not absolutely necessary, provides additional small improvements, reducing the 0.08–0.26 and 0.11–0.25 eV errors in the IP-EOMCCSD( $2h$ - $1p$ ) and EOMCCSD results to 0.03–0.04 eV. The active-space IP-EOMCCSD( $2h$ - $1p$ ){2} method, with only two active orbitals in the definition of  $3h$ - $2p$  excitations, gives similar values as its more expensive parent IP-EOMCCSD( $3h$ - $2p$ ) counterpart, although the deviations between the active-space and full IP-EOMCCSD( $3h$ - $2p$ ) results are somewhat larger than those observed for CNC and  $C_2N$ , particularly for the  $B^2\Sigma_u^+$  state of  $N_3$  and  $A^2\Sigma^+$  state of NCO, where the discrepancies are 0.13 eV and 0.21 eV, respectively. This may be a consequence of using a very small active space and of changes in the character of the orbitals when going from  $N_3$  to the  $N_3^-$  reference ion and from NCO to the  $NCO^-$  reference system. Putting aside these technical aspects of the active-space IP-EOMCCSD( $3h$ - $2p$ ) calculations, which may require further separate study, we can certainly state that both the basic EOMCCSD and IP-EOMCCSD( $2h$ - $1p$ ) methods and the higher-level IP-EOMCCSD( $3h$ - $2p$ ) approach provide highly accurate  $T_e$  values for the low-lying states of the  $N_3$  and NCO systems, since these states are dominated by one-electron transitions. In view of the above discussion of the results for the singly excited states of the CH, CNC, and  $C_2N$  systems, it is not at all surprising that all CR-EOMCC(2,3),A–D variants provide similarly high accuracies that are also very similar to those obtained with the CR-EOMCCSD(T),ID scheme, with errors relative to experiment on the order of 0.1–0.4 eV.

In summary, the accuracy patterns observed in the CR-EOMCC(2,3) calculations for the low-lying states of the CNC,  $C_2N$ ,  $N_3$ , and NCO systems are quite similar to those observed for the CH radical. Of all variants of CR-EOMCC(2,3), the CR-EOMCC(2,3),D approach, which relies on the complete, Epstein–Nesbet-like representation of the  $D_{\mu,abc}^{ijk}$  denominator, is generally the most accurate one, providing the results which are in good agreement with the full and active-space EA-EOMCCSD( $3p$ - $2h$ ) and IP-EOMCCSD( $3h$ - $2p$ ) data. The use of the Møller–Plesset-like form of the  $D_{\mu,abc}^{ijk}$  denominator, as is done in the CR-EOMCC(2,3),A approach or EOMCC(2)PT(2) method of Refs. [34, 113], or its dressed

variant based on replacing orbital energies by the one-body matrix elements of  $\tilde{H}^{(CCSD)}$ , is not sufficient when the excited states of interest have significant two-electron contributions, as illustrated by the >1 eV errors in the CR-EOMCC(2,3),A calculations for the CNC and  $C_2N$  systems, which the CR-EOMCC(2,3),D approach reduces to the ~0.3 eV level. The high quality of the CR-EOMCC(2,3),D results matches that of the full and active-space EA-EOMCCSD( $3p$ - $2h$ ) and IP-EOMCCSD( $3h$ - $2p$ ) calculations, and the accuracies of CR-EOMCC(2,3),D and CR-EOMCCSD(T),ID are similar, although there are cases where the CR-EOMCC(2,3),D method is slightly more accurate than its more established CR-EOMCCSD(T),ID predecessor.

## 4. Summary

The recently proposed CR-CC(2,3) approach for ground electronic states [20, 21, 47–49] and the companion CR-EOMCC(2,3) methodology, which has been previously applied to singlet excited states of closed-shell molecular systems [47, 74], have been extended to excited states of open-shell species. The resulting, highly efficient, general-purpose computer codes for the open-shell CR-EOMCC(2,3) approach, in which the relatively inexpensive noniterative corrections due to triple excitations derived from the general theoretical framework defining the biorthogonal MMCC formalism [20, 21, 47–49] are added to the CCSD/EOMCCSD energies, have been developed and interfaced with the GAMESS package, enabling the routine CR-EOMCC(2,3) calculations for singlet as well as nonsinglet ground and excited states of closed- and open-shell systems using the ROHF references. The development of the open-shell CR-EOMCC(2,3) approach has given us an opportunity to describe various important mathematical and algorithmic details related to formal aspects and computer implementation of the CR-EOMCC(2,3) method, which have not been discussed in the earlier work [47, 74], in addition to overviewing the key concepts behind the CR-EOMCC(2,3) theory and the underlying biorthogonal MMCC methodology for ground and excited states.

The numerical results for the low lying doublet and quartet states of the CH radical and the low-lying doublet states of the CNC,  $C_2N$ ,  $N_3$ , and NCO systems, including states that display a manifestly multireference character and a significant role of two-electron transitions, reported in this article, show



that the complete variant D of the ROHF-based CR-EOMCC(2,3) method, in which one uses the Epstein–Nesbet-like partitioning for the triples–triples block of the similarity-transformed Hamiltonian of the CCSD theory to define the deexcitation amplitudes that multiply the triply excited moments of the CCSD/EOMCCSD equations which enter the triples corrections of CR-EOMCC(2,3), provides a uniformly and highly accurate description of the excited states of open-shell systems, independent of their singly or doubly excited and doublet or quartet character. The use of the Møller–Plesset-like form of the  $D_{\mu,abc}^{ijk}$  denominator that enters the CR-EOMCC(2,3) triples correction formula, as is done in the CR-EOMCC(2,3),A approach and the EOM-CC(2)PT(2) method of Refs. [34, 113], or its dressed variant based on replacing bare orbital energies by the one-body matrix elements of the similarity-transformed Hamiltonian of CCSD, is not sufficient when the excited states of interest have significant two-electron contributions, as illustrated by the  $\sim 0.5$  errors in the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B calculations for the CH radical and the  $>1$  eV errors in the CR-EOMCC(2,3),A and CR-EOMCC(2,3),B calculations for the CNC and C<sub>2</sub>N systems, which the more complete CR-EOMCC(2,3),D approach reduces to the 0.1–0.3 eV level.

The results of the CR-EOMCC(2,3) calculations for the low-lying states of the CH, CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO systems demonstrate that the complete variant D of CR-EOMCC(2,3) provides excellent adiabatic excitation and total energies which are in very good agreement with the full EOMCCSDT, EA-EOMCCSD(3p-2h), and IP-EOMCCSD(3h-2p) data. This is an important finding, since the CR-EOMCC(2,3) calculations are much less expensive than the EOMCCSDT, EA-EOMCCSD(3p-2h), and IP-EOMCCSD(3h-2p) calculations. In analogy to the widely used CCSD(T) approach, the CR-EOMCC(2,3) approaches require the relatively inexpensive iterative steps of CCSD/EOMCCSD that scale as  $n_o^2 n_u^4$  and the noniterative steps of the  $n_o^3 n_u^4$  type which are needed to determine the relevant triples corrections to the CCSD/EOMCCSD energies. This should be contrasted with the expensive and iterative  $n_o^3 n_u^5$ ,  $n_o^2 n_u^5$ , and  $n_o^3 n_u^4$  steps of EOMCCSDT, EA-EOMCCSD(3p-2h), and IP-EOMCCSD(3h-2p), respectively. The storage requirements for the CR-EOMCC(2,3) calculations are relatively small too, since one does not have to store quantities other than the one- and two-body molecular integrals and recursively generated intermediates, whose number scales as  $n_o^2 n_u^2$ ,

as opposed to the need to store much larger objects of the  $n_o^3 n_u^3$ ,  $n_o^2 n_u^3$ , and  $n_o^3 n_u^2$  types in the EOMCCSDT, EA-EOMCCSD(3p-2h), and IP-EOMCCSD(3h-2p) calculations. Out of all *ab initio* methods examined in this article, the only other approaches that match the relatively low cost and high accuracy of the CR-EOMCC(2,3),D calculations are the CR-EOMCCSD(T),ID predecessor of CR-EOMCC(2,3),D, originally proposed in Refs. [80, 81] (cf., also, Refs. [43, 44]), and the active-space EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) approaches of Refs. [138–140], in which one uses active orbitals to select the dominant 3p-2h and 3h-2p excitations. It is very encouraging to observe that CR-EOMCC(2,3),D approach, which is a black-box method that does not require selecting active orbitals on a molecule-by-molecule basis, works as well as the active-space EA-EOMCCSD(3p-2h) and IP-EOMCCSD(3h-2p) approaches. It is also very promising to observe that the CR-EOMCC(2,3),D method is at least as accurate as the more established and older CR-EOMCCSD(T),ID methodology in applications involving challenging excited states of open-shell species. Given the robust behavior of the CR-EOMCC(2,3),D and CR-EOMCCSD(T),ID methods in such applications and given the successes of the CR-EOMCC approaches to date in a variety of applications involving simulations of molecular electronic spectra and excited-state potentials (cf., e.g., Refs. [43, 44, 47, 74, 80–107]), the CR-EOMCC methods, including the open-shell CR-EOMCC(2,3),D and CR-EOMCCSD(T),ID approaches discussed in the present work, may offer a useful and easy-to-use single-reference alternative to the popular CASPT2 methodology [200–202] in calculations involving vertical and adiabatic excitation energies in medium size molecular systems, particularly when one considers the fact that CASPT2, being a multireference procedure with a low-level treatment of dynamical correlation effects, may face difficulties in handling larger molecular problems that sometimes require prohibitively large active orbitals spaces [58, 59]. Among other potential issues with CASPT2 is “the known tendency of CASPT2 to slightly underestimate excitation energies” [203]. Similar tendency is observed when the older generations of the approximate triples EOMCC or response CC methods, such as EOMCCSD(T), EOMCCSD( $\tilde{T}$ ), or CCSDR(3), are applied to the more difficult types of excited states or excited-state potential energy surfaces along bond stretching coordinates. The vertical and adiabatic excitation energies resulting from the CR-EOMCC calculations and the CR-EOMCC

excited-state potentials are usually above the experimental or full CI ones, which helps the robustness of the CR-EOMCC results (see, e.g., Ref. [80] for an analysis). The noniterative character of the CR-EOMCC(2,3),D, CR-EOMCCSD(T),ID, and other CR-EOMCC triples corrections, which naturally split into sums of contributions from individual triple excitations, as in Eq. (41), makes these methods well suited for efficient parallel implementations that can help to extend the applicability of these kinds of methods to larger systems with dozens of atoms in the future.

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