

## INVITED ARTICLE

# Comparison of the completely renormalized equation-of-motion coupled-cluster and Quantum Monte Carlo results for the low-lying electronic states of methylene

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The left-eigenstate completely renormalized (CR) equation-of-motion (EOM) coupled-cluster (CC) method with singles, doubles, and non-iterative triples, abbreviated as CR-EOMCC(2,3) [M. Włoch *et al.*, *Mol. Phys.* **104**, 2149 (2006); P. Piecuch *et al.*, *Int. J. Quantum Chem.* **109**, 3268 (2009)], and the companion ground-state CR-CC(2,3) methodology [P. Piecuch and M. Włoch, *J. Chem. Phys.* **123**, 224105 (2005); P. Piecuch *et al.*, *Chem. Phys. Lett.* **418**, 467 (2006)] are used to determine the total electronic and adiabatic excitation energies corresponding to the ground and lowest three excited states of methylene. The emphasis is on comparing the CR-CC(2,3)/CR-EOMCC(2,3) results obtained with the large correlation-consistent basis sets of the aug-cc-pCV  $xZ$  ( $x = T, Q, 5$ ) quality and the corresponding complete basis set (CBS) limits with the recently published variational and diffusion Quantum Monte Carlo (QMC) data [P. Zimmerman *et al.*, *J. Chem. Phys.* **131**, 124103 (2009)]. It is demonstrated that the CBS CR-CC(2,3)/CR-EOMCC(2,3) results are in very good agreement with the best QMC, i.e. diffusion MC (DMC) data, with errors in the total and adiabatic excitation energies of all calculated states on the order of a few millihartree and less than 0.1 eV, respectively, even for the challenging, strongly multi-reference  $C^1A_1$  state for which the basic EOMCC approach with singles and doubles completely fails. The agreement between the CBS CR-CC(2,3)/CR-EOMCC(2,3) and variational MC (VMC) results for the total energies is not as good as in the DMC case, but the excitation energies resulting from the CBS CR-CC(2,3)/CR-EOMCC(2,3) and VMC calculations agree very well.

**Keywords:** equation-of-motion coupled-cluster method; completely renormalized coupled-cluster approaches; Quantum Monte Carlo; methylene; excited states

## 1. Introduction

Tremendous progress in photochemistry in recent years, where increasingly precise experimental techniques can be used to examine a wide variety of light-driven molecular phenomena, has led to a rapidly growing need for the development and benchmarking of new *ab initio* methods for predictive, high accuracy calculations for excited electronic states. This, in particular, applies to methods exploiting the exponential wave function ansatz of coupled-cluster (CC) theory [1–5], which offer a possibility of achieving the best compromise between computer cost and accuracy, and fastest convergence to the exact results when compared to other *ab initio* techniques (see [6–9] for representative reviews).

Among the most promising and increasingly popular extensions of the CC formalism to excited states, which retain the intrinsic simplicity and ‘black-box’ character of the ground-state single-reference CC

calculations, are the equation-of-motion CC (EOMCC) methodology [10–14] and its symmetry-adapted-cluster configuration-interaction [15–22] and linear-response CC [23–28] counterparts. Indeed, the basic EOMCCSD (EOMCC with singles and doubles) approach [11–13] and the analogous linear response CCSD approximation [27–28] (equivalent to EOMCCSD when excitation energies are considered), which are characterized by the relatively low computer costs of the standard ground-state CCSD scheme [29–32], defined by the iterative steps that scale as  $n_o^2 n_u^4$  and the storage requirements of the  $\sim n_o^2 n_u^2$  type ( $n_o$  and  $n_u$  are the numbers of occupied and unoccupied orbitals, respectively, used in the correlated calculations), often provide an excellent description of excited states dominated by one-electron transitions. Unfortunately, this success does not automatically extend to the more complicated, more multi-reference, excited electronic states, such as those characterized

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by a significant two-electron excitation nature. There also are cases of excited states dominated by singles, where the EOMCCSD theory level is insufficient to obtain high-quality results (see, e.g., [33–34]). In order to describe such challenging states, one must include the effects of triple excitations in the EOMCC method, as is done in the full EOMCCSDT (EOMCC with singles, doubles, and triples) scheme [35–37]. In fact, there are cases where even this may be insufficient and the explicit inclusion of quadruple excitations, in addition to triples, as in the full EOMCCSDTQ (EOMCC with singles, doubles, triples, and quadruples) approach [38–39], is called for if we want to avoid a fundamentally more complex and more expert multi-reference description. The full EOMCCSDT and EOMCCSDTQ methods substantially improve the description of excited states dominated by two-electron transitions, leading to the virtually perfect description of such states [35–41], but this success comes at a very high price and a steep increase of the CPU time and storage requirements that scale as  $n_o^3 n_u^5$  and  $\sim n_o^3 n_u^3$ , respectively, in the EOMCCSDT case, and  $n_o^4 n_u^6$  and  $\sim n_o^4 n_u^4$ , respectively, in the case of EOMCCSDTQ, restricting the applicability of EOMCCSDT and EOMCCSDTQ to small systems with up to a dozen or so correlated electrons and, usually, relatively small basis sets. In order to extend the applicability of the EOMCC formalism to excited states dominated by double excitations, without requiring prohibitive levels of computer effort and without turning to expert, genuine multi-reference methodologies, the last two decades have witnessed the development of a large variety of low-cost EOMCC schemes that account for the effects of triples or triples and quadruples in an approximate manner. In this paper, we focus on the approximate treatment of triple excitations within the EOMCC formalism.

One way to reduce the computer costs of the full EOMCCSDT and other higher-level EOMCC calculations is to select higher-than-doubly excited components of the cluster operator  $T$  that defines the underlying ground-state CC calculations and higher-than-two-body components of the linear excitation operator  $R$  of EOMCC through the use of a small subset of active orbitals, as is done in the so-called active-space EOMCC methods [35,36,42–44] (see [45–50] for the corresponding active-space CC methods for the ground electronic states). In particular, the resulting EOMCCSDt [35,36,42] approximation offers considerable savings in computer effort while preserving high accuracies of the parent EOMCCSDT approach, including extreme cases of electronic quasi-degeneracies, where one has to deal with large numbers of densely spaced excited states

dominated by two-electron transitions [51,52]. Methods that are even easier to use and that do not require the *a priori* selection of higher-than-two-body components of the  $T$  and  $R$  operators are those resulting from various ways of correcting the EOMCCSD energies through the proper identification of the leading terms of higher-order EOMCC schemes due to higher-than-double excitations, while eliminating terms that do not contribute too much. The non-iterative EOMCC methods, such as those of the type of the triples correction of EOM-CC(2)PT(2) [53] and its size intensive [28,54] EOM-CCSD(2) $\tau$  [55] analogue, CCSDR3 [56,57], EOMCCSD(T) [58], EOMCCSD( $\tilde{T}$ ) [59], EOMCCSD(T') [59], CR-EOMCCSD(T) [40,41,60,61] and the related N-EOMCCSD(T) approach [62], and CR-EOMCC(2,3) [63–65] and the spin-flip variant of the CR-EOMCC(2,3) approach of [63–65] considered in [66], as well as their iterative EOMCCSDT- $n$  [58,59] and CC3 [56,57,67,68] counterparts are particularly promising in this regard, since they represent computational black boxes with costs similar to those of the popular CCSD(T) ground-state approach [69] or its CR-CC(2,3) extension [70–72], which eliminates failures of CCSD(T) in situations involving single bond breaking and biradicals. All of the above methods greatly reduce the computer costs of full EOMCCSDT calculations, while improving the EOMCCSD results in situations involving excited states characterized by significant double-excitation components. For example, the most promising EOMCCSD(2) $\tau$ , CCSDR3, EOMCCSD( $\tilde{T}$ ), CR-EOMCCSD(T), N-EOMCCSD(T), and CR-EOMCC(2,3) approaches are characterized by the iterative  $n_o^2 n_u^4$  steps of EOMCCSD and the non-iterative  $n_o^3 n_u^4$  steps needed to construct the triples corrections to the EOMCCSD energies, while eliminating the need for storing the  $\sim n_o^3 n_u^3$  triply excited amplitudes defining the  $T$  and  $R$  operators. This makes these methods applicable to relatively large atomic and molecular problems, including, for example, the electronic excitations in molecules of biological significance [34,73], electronic excitations in ionic crystals [74], electronic excitations and decay pathways in DNA bases [75–80], and photo-induced isomerizations in organic systems [33]. At the same time, methods such as CR-EOMCCSD(T) and its more recent CR-EOMCC(2,3) analogue can be very effective in describing excited states dominated by two-electron transitions [40,41,51,52,60–65,81], and the present paper provides further strong evidence that this is indeed the case.

In this paper, we focus on a previously unexplored way of benchmarking the left-eigenstate CR-EOMCC(2,3) approach of [63–65], which is based on

the biorthogonal formulation [70,71] of the method of moments of the CC/EOMCC equations [40,41,82–85] and which represents the natural and rigorous extension of the ground-state CR-CC(2,3) theory of [70–72] to excited electronic states. As its CR-EOMCCSD(T) predecessor [40,41,60,61] derived from the original formulation of the method of moments of the CC/EOMCC equations [40,41,82–85], the CR-EOMCC(2,3) approach is based on the idea of adding state-specific, non-iterative corrections to the EOMCCSD energies, expressed in terms of the generalized moments of the EOMCCSD equations corresponding to projections of these equations on triply excited determinants. As demonstrated in our earlier work [63–65], in which we compared the CR-EOMCC(2,3) results obtained with the small or medium basis sets of the double- and triple-zeta quality with the corresponding full EOMCCSDT, full configuration interaction (CI), and other high accuracy *ab initio* data, the most complete implementation of the CR-EOMCC(2,3) approach, which is referred to as variant D of CR-EOMCC(2,3), abbreviated as CR-EOMCC(2,3), D (see the next section and [63,65] for further information), significantly improves the EOMCCSD energies while providing the results which are at least as accurate as those obtained with CR-EOMCCSD(T) and noticeably more accurate than those employing the triples correction of the EOM-CC(2)PT(2) method of [53,55] (the latter being equivalent to the approximate variant A of CR-EOMCC(2,3) [63,65]). This is particularly true for the electronically excited states dominated by two-electron transitions. The question emerges if the excellent performance of the CR-EOMCC(2,3),D method holds for large basis sets approaching the infinite basis set regime.

Thus, unlike the earlier benchmark studies of the CR-EOMCC(2,3) approach [63–65], which utilized relatively small basis sets, the main objective of this work is an analysis of the results of larger basis set, all-electron CR-EOMCC(2,3) calculations employing the correlation-consistent basis sets of the aug-cc-pCV $x$ Z quality, in which the cardinal number  $x$  is as large as 5, and the corresponding complete basis set (CBS) limit extrapolations (cf. e.g. [86–90]). The recent Quantum Monte Carlo (QMC) [91–93] study of the ground and three low-lying excited states of methylene by Zimmerman *et al.* [94] offers an excellent opportunity for such an investigation of the CR-EOMCC(2,3) approach, enabling us to compare the CBS CR-EOMCC(2,3) data with the results that at least formally correspond to the numerically exact solutions of the electronic Schrödinger equation in the limit of an infinite basis set.

Although this is a benchmark paper, where our interest in methylene is dictated by the availability of the QMC data [94], let us recall that a few decades ago, methylene was the subject of significant controversies between theory and experiment regarding the geometry of its triplet ground state ( $X^3B_1$ ) and the small gap between the lowest triplet and singlet ( $A^1A_1$ ) states [95–99] (see [100] for a recent review). The year 1970 was particularly important in the fascinating methylene story, as that year provided a definitive *ab initio* theoretical prediction by Bender and Schaefer of the bent structure of CH<sub>2</sub> [101], confirming the earlier findings of Foster and Boys [102] and Harrison and Allen [103], to challenge directly the experimental findings that were initially suggesting the linear structure [104] (see [98] for Professor Henry F. Schaefer III's personal account). Over the years, methylene has become an important benchmark for electronic structure methods due to its small size, which permits all kinds of electronic structure calculations, including the aforementioned full CI and QMC techniques, and a variety of approximate methods, and because some of its excited states are very difficult to describe in an accurate and balanced manner (see, e.g. [72,94,105–136] for selected examples, out of many, of *ab initio* calculations for ground and excited states of methylene, which by no means represent an exhaustive list). In particular, while the ground  $X^3B_1$  state of CH<sub>2</sub> and its second excited state ( $B^1B_1$ ) have largely a single-reference character dominated by dynamical correlations and as such can be adequately represented by a dominant configuration  $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1)$ , the first excited  $A^1A_1$  state and the third excited  $C^1A_1$  state have a significant multi-reference character with considerable admixture of the  $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$  and  $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$  configurations, and are, therefore, challenging to many quantum chemistry approaches. The  $C^1A_1$  state is particularly difficult in this regard. To achieve an accurate and balanced description of total and excitation energies, both static and dynamic electron correlations must be treated accurately, which in the case of the EOMCC methods that treat all correlation effects dynamically through excitations from a single reference determinant means the explicit inclusion of higher-order components of the  $T$  and  $R$  operators, such as triples. As a result, methylene is an excellent test case for benchmarking the excited-state CR-EOMCC(2,3) methodology. Since the QMC methodology used in the recent methylene study [94] relies on a first quantized formulation, and so does not utilize the concept of a basis set, it provides us with an ideal benchmark against which to analyse the large basis set and CBS CR-EOMCC(2,3) results.

## 2. Methods and computational details

In order to compare the CCSD/EOMCCSD and CR-CC(2,3)/CR-EOMCC(2,3) data for the ground and lowest three excited states of methylene with the corresponding QMC results reported in [94] in a meaningful manner, we performed a sequence of all-electron CCSD/EOMCCSD and CR-CC(2,3)/CR-EOMCC(2,3) calculations using the aug-cc-pCV $x$ Z ( $x = T, Q$ , and 5) basis sets [86,137,138], which we subsequently extrapolated to the CBS limit, as described below. The theoretical details of the CR-EOMCC(2,3) approach and its ground-state CR-CC(2,3) analogue can be found in [63–65,70–72], and will not be repeated here. We would only like to mention that, as already pointed out in the Introduction, the CR-CC(2,3) and CR-EOMCC(2,3) methods are based on adding state specific, non-iterative corrections due to triply excited clusters to the total CCSD and EOMCCSD energies of the target electronic states. As in all approaches based on the method of moments of the CC/EOMCC equations [40,41,82–85], including its most recent biorthogonal formulation [70,71] on which the CR-CC(2,3) and CR-EOMCC(2,3) schemes are based, these corrections are constructed through the use of the generalized moments of the appropriate CC/EOMCC equations. In the case of the CR-CC(2,3) and CR-EOMCC(2,3) approaches that interest us in this study, we use the triply excited moments of the CCSD and EOMCCSD equations, which correspond to the projections of these equations on the triply excited determinants  $|\Phi_{ijk}^{abc}\rangle$ , and the left eigenstates of the similarity-transformed Hamiltonian of CCSD theory,  $\bar{H}^{\text{CCSD}} = e^{-T_1 - T_2} \times H e^{T_1 + T_2}$ , where  $T_1$  and  $T_2$  are the singly and doubly excited cluster operators obtained in the CCSD calculations, to construct the relevant triples corrections to the CCSD and EOMCCSD energies. In addition to the CCSD/EOMCCSD moments and left eigenstates of  $\bar{H}^{\text{CCSD}}$ , the triples corrections of CR-CC(2,3)/CR-EOMCC(2,3) require the determination of the diagonal matrix elements  $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$ , which enter the relevant perturbative energy denominators [63,65,70–72]. In the full CR-CC(2,3)/CR-EOMCC(2,3) method, which is generally referred to as variant D of CR-CC(2,3)/CR-EOMCC(2,3), the complete expression for the diagonal elements  $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$ , which involves up to three-body components of  $\bar{H}^{\text{CCSD}}$ , is used in the definition of these perturbative denominators. By applying systematic approximations to the definition of  $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$ , several additional variants of the CR-CC(2,3)/CR-EOMCC(2,3) theory can be obtained. In particular, by replacing  $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$  with its

zeroth-order approximation given by the orbital energy difference  $(\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)$ , we obtain variant A, which is equivalent to the triples correction of the CCSD(2) approach of [53], referred to as the CCSD(2)<sub>T</sub> method [139], in the ground-state case, and to the triples correction of the EOM-CC(2)PT(2) approach of [53] when excited states are considered. Other variants of CR-CC(2,3)/CR-EOMCC(2,3), obtained by neglecting selected many-body terms in  $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$ , are possible as well [63,65,72]. In this work, we focus on the most complete and most accurate variant D of CR-CC(2,3)/CR-EOMCC(2,3), although some information about the performance of variant A is given as well.

In the QMC calculations performed by Zimmerman *et al.* [94], the results of which are reproduced here to facilitate the direct comparison with the CR-CC(2,3)/CR-EOMCC(2,3) results obtained in this study, two different variants of QMC were used, namely variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC). The trial functions for both variants consisted of the Jastrow–Slater multi-determinant complete-active-space (CAS) wave functions which, as explained in [94], were optimized using the linear optimization method [140–142]. Three different active spaces were used to generate CAS trial functions for the QMC calculations reported in [94], namely, the (2,2), (4,4), and (6,6) active spaces (as in [94],  $(n, m)$  denotes an active space of  $n$  electrons and  $m$  orbitals).

In this work, rather than restricting ourselves to the ground  $X^3B_1$  and first excited  $A^1A_1$  states, as was done in our group’s previous small basis set CR-CC calculations for methylene (cf. e.g. [72,134]), we followed the calculations of Zimmerman and co-workers [94] and computed the higher-energy  $B^1B_1$  and  $C^1A_1$  states as well (in making comparisons of the CC/EOMCC data presented in this article with the QMC results reported in [94], it should be mentioned that the authors of [94] use symbol  $B_2$  for the states that are classified here as the  $B_1$  states). It should be noted that since the  $X^3B_1$  and  $A^1A_1$  states are the lowest-energy states of their respective symmetries, they can be obtained with the ground-state CR-CC(2,3) formalism in which one uses the restricted open-shell Hartree–Fock (ROHF) determinant as a reference for the triplet ground state  $X^3B_1$  and the restricted Hartree–Fock (RHF) determinant as a reference for the first-excited  $A^1A_1$  state. This is exactly what we did in this work. One cannot, however, apply the same recipe to all other states. Thus, the remaining  $B^1B_1$  and  $C^1A_1$  states examined in this study were calculated in an intrinsic manner, using the excited-state CR-EOMCC(2,3) approach, with the previously obtained  $A^1A_1$  wave function acting

as the correlated ground state for the EOMCC ansatz for the excited-state  $B^1B_1$  and  $C^1A_1$  wave functions. The  $C^1A_1$  state is particularly important in this context, since this is a strongly multi-reference state of the same symmetry as the  $A^1A_1$  state (i.e. ‘true’ excited state that cannot be captured through ground-state calculations). In both the CC/EOMCC calculations reported in this article and the QMC calculations of [94], the geometries for each state were taken from [108], where they were generated using the full CI calculations with the [5s3p/2s] triple zeta basis set of Dunning [143] augmented with two sets of polarization functions (TZ2P).

As already alluded to above, the CBS limits of the CCSD/EOMCCSD and CR-CC(2,3)/CR-EOMCC(2,3) results were determined through extrapolation from the aug-cc-pCV $x$ Z data (cf. e.g. [86–90]). In order to verify the numerical stability of the CBS results, two different extrapolation schemes were utilized in this work. In the first scheme, referred to here and elsewhere in this paper as the CBS-A scheme, the CBS energy of the  $X^3B_1$  state was determined by first extrapolating the correlation energy [CCSD or CR-CC(2,3), as appropriate] using the well-known formula [87]

$$\Delta E(x) = \Delta E_\infty + Ax^{-3}, \quad (1)$$

where  $x=3, 4, 5$  represents the cardinal number of the aug-cc-pCV $x$ Z basis set ( $x=3$  for aug-cc-pCVTZ,  $x=4$  for aug-cc-pCVQZ, and  $x=5$  for aug-cc-pCV5Z),  $\Delta E(x)$  is the correlation energy obtained with the aug-cc-pCV $x$ Z basis, and  $\Delta E_\infty$  is the correlation energy in the CBS limit. The resulting extrapolated correlation energy was then added to the ROHF/aug-cc-pCV5Z reference energy of the  $X^3B_1$  state, which, due to the well-known fast (exponential) convergence of the ROHF/RHF energies with respect to the basis set, is equivalent to the CBS reference energy to an extremely high (0.1 millihartree) accuracy (we verified this level of accuracy in the ROHF energy of the  $X^3B_1$  state by comparing the corresponding ROHF/aug-cc-pCV5Z and ROHF/aug-cc-pCVQZ data). Once the CBS limit of the total correlated [CCSD or CR-CC(2,3)] energy of the  $X^3B_1$  ground state was determined, the CBS limits of the total energies of the remaining three states were estimated by adding the appropriate aug-cc-pCV5Z excitation energies to the extrapolated total energy of the  $X^3B_1$  ground state. This particular method of estimating the CBS values of the total electronic energies of the  $X^3B_1$ ,  $A^1A_1$ ,  $B^1B_1$ , and  $C^1A_1$  states of methylene is based on the assumption that with aug-cc-pCV5Z the excitation energies are essentially converged with respect to the basis set, so all one has to do is to obtain the CBS limit

of the ground-state energy and add the aug-cc-pCV5Z excitation energies to the resulting ground-state energy value to estimate the CBS energies of the remaining three states. The validity of this assumption is discussed in the next section.

In the second extrapolation scheme, referred to as the CBS-B approach, the CBS total energy of each state of interest was directly extrapolated using the formula [86]

$$E(x) = E_\infty + Be^{-(x-1)} + Ce^{-(x-1)^2}, \quad (2)$$

with  $x=3, 4, 5$ , where  $x$  is again the cardinal number of the aug-cc-pCV $x$ Z basis set,  $E(x)$  is the total energy of the state as computed with the aug-cc-pCV $x$ Z basis, and  $E_\infty$  is the total energy of the state in the CBS limit. The difference between the CBS-A and CBS-B extrapolation schemes lies in the fact that the latter scheme extrapolates the total energy of each electronic state separately, using Equation (2), whereas the former approach extrapolates the ground-state energy only using Equation (1) while making an assumption that the excitation energies converge faster with the basis set than the total energies, so that one can obtain their essentially converged values by performing the calculations with a sufficiently large basis set (in our case, aug-cc-pCV5Z). A comparison of both extrapolation schemes in Section 3 will tell us how accurate this assumption is.

In addition to the large basis set and CBS-limit EOMCCSD and CR-EOMCC(2,3) calculations that are compared with the QMC results reported in [94], we also carried out the CR-CC(2,3)/CR-EOMCC(2,3) and the corresponding CCSD/EOMCCSD calculations using the TZ2P basis set [143], so that we could make a preliminary assessment of the CR-CC(2,3)/CR-EOMCC(2,3) methodology by comparing the resulting total and adiabatic excitation energies with those obtained using full CI [108]. Following the details of [108], these calculations used the same geometries as the aug-cc-pCV $x$ Z CC/EOMCC calculations that form the main focus of this work (recall that these geometries were the full CI geometries taken from [108]), and in all correlated calculations the lowest-energy core orbital was frozen and the highest-energy virtual orbital was deleted.

Although the present work focuses on a comparison of the large basis set and CBS-limit CR-EOMCC(2,3) results with the results of the QMC calculations described in [94], a comparison of the CR-EOMCC(2,3) results with the available experimental data for the  $A^1A_1$ – $X^3B_1$  and  $B^1B_1$ – $X^3B_1$  energy gaps is provided as well. In the former case, the experimental estimate of the non-relativistic, purely

electronic, adiabatic excitation energy corresponding to the  $X^3B_1 \rightarrow A^1A_1$  transition, of 0.406 eV, was obtained by correcting the experimentally derived vibrationless adiabatic excitation energy reported in [144] for the relativistic and non-adiabatic (Born–Oppenheimer diagonal correction) effects calculated in [145] and [146], respectively (as was done earlier in [115]). In the latter case, the experimentally derived value of the purely electronic adiabatic excitation energy corresponding to the  $X^3B_1 \rightarrow B^1B_1$  transition, of 1.415 eV, was taken from [94], where the authors corrected the adiabatic separation between the  $v=0$  vibronic levels of the  $B^1B_1$  and  $X^3B_1$  states, obtained using the information about the relevant  $B^1B_1 - A^1A_1$  and  $A^1A_1 - X^3B_1$  gaps provided in [110] and [144], respectively, for the zero-point vibrational energies obtained in the full CI/TZ2P calculations in [108]. Experimental information about the  $C^1A_1 - X^3B_1$  gap is not available.

All CC and EOMCC calculations reported in this article were performed using the routines described in [72,147] for the CCSD calculations, [60] for the EOMCCSD calculations, [70,72] for the CR-CC(2,3) calculations, and [63,65] for the CR-EOMCC(2,3) calculations that are part of the GAMESS package [148,149]. As a result, since the integral routines in GAMESS are currently restricted to g functions, the h functions of the aug-cc-pCV5Z basis set were omitted in the calculations. As already alluded to above, the RHF reference corresponding to the  $A^1A_1$  state was used in the calculations for all singlet states, whereas the  $X^3B_1$  ground state utilized the triplet ROHF reference. Finally, the spherical components of the d, f, and g basis functions were employed in all of our calculations.

### 3. Results

In order to assess the accuracy of the CR-EOMCC(2,3) approach in calculations for the ground  $X^3B_1$  state and the excited  $A^1A_1$ ,  $B^1B_1$ , and  $C^1A_1$  states of methylene prior to the comparison of the large basis set and CBS-limit CR-EOMCC(2,3) and QMC data, we first examine the results of the CR-EOMCC(2,3) calculations using the TZ2P basis set, which we compare with the available full CI data reported in [108] [from now on, whenever we refer to EOMCCSD and CR-EOMCC(2,3), we imply the ground-state CCSD and CR-CC(2,3) calculations for the  $X^3B_1$  and  $A^1A_1$  states, which are the lowest-energy states in their respective symmetries, and the excited-state EOMCCSD and CR-EOMCC(2,3) calculations exploiting the  $A^1A_1$  wave function as a correlated

ground state in the EOMCC ansatz for the  $B^1B_1$  and  $C^1A_1$  states; cf. the previous section]. The results of this comparison are presented in Table 1.

Focusing first on the total energies, we see that for the ground  $X^3B_1$  state and the excited  $A^1A_1$  and  $B^1B_1$  states, the basic EOMCCSD approach performs reasonably well, with errors relative to full CI of 3.39–5.19 millihartree. This is related to the fact that the ground  $X^3B_1$  state and the second excited  $B^1B_1$  state have a single-reference character dominated by dynamical correlations which the EOMCCSD approach can capture in an accurate manner. The  $A^1A_1$  state, which is more multi-reference than the  $X^3B_1$  and  $B^1B_1$  states, having some admixture of the  $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$  configuration in the zeroth-order description, is still largely single-reference and dominated by the RHF  $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$  determinant, which makes it tractable by EOMCCSD in an adequate manner. The nice performance of EOMCCSD observed in the calculations for the  $X^3B_1$ ,  $A^1A_1$ , and  $B^1B_1$  states does not mean, however, that one cannot improve these results any further. Indeed, the inclusion of the triples effects through the CR-EOMCC(2,3) approach offers additional non-trivial improvements in the total energies for the  $X^3B_1$ ,  $A^1A_1$ , and  $B^1B_1$  states. In particular, the most complete CR-EOMCC(2,3),D scheme reduces the reasonable EOMCCSD errors relative to full CI down to 0.04–1.78 millihartree, which represents an excellent level of agreement with full CI, particularly considering the relatively low costs of the CR-EOMCC(2,3) calculations. Interestingly, the approximate variant A of CR-EOMCC(2,3) is not as accurate as the full variant D in describing the  $X^3B_1$ ,  $A^1A_1$ , and  $B^1B_1$  states, but the discrepancy between the results of the two methods is less than 1 millihartree, since none of the three states has significant contributions from two-electron transitions [65].

Turning to the considerably more multi-reference  $C^1A_1$  state, which is largely dominated by the two-electron transitions from the  $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$  reference, we see that an entirely different picture emerges. Indeed, unlike in the case of the  $X^3B_1$ ,  $A^1A_1$ , and  $B^1B_1$  states, EOMCCSD is no longer capable of providing an accurate total energy for the  $C^1A_1$  state, producing a large error relative to full CI of 44.95 millihartree. Accounting for the effects of triples through the CR-EOMCC(2,3),A approach significantly improves the situation, but the resulting error of 9.08 millihartree is still larger than one would like it to be. As was the case for the  $X^3B_1$ ,  $A^1A_1$ , and  $B^1B_1$  states, the most complete variant D of CR-EOMCC(2,3) provides superior accuracy when compared to the approximate variant A, but unlike

Table 1. Total energies (in hartree) and adiabatic excitation energies (in eV) for the low-lying states of CH<sub>2</sub>, as obtained with the full CI, EOMCCSD, CR-EOMCC(2,3), A, and CR-EOMCC(2,3),D approaches and the TZ2P basis set<sup>a</sup>.

| Method               | Total energy (hartree) |            |            |            | Adiabatic excitation energy (eV) |                 |                 |
|----------------------|------------------------|------------|------------|------------|----------------------------------|-----------------|-----------------|
|                      | $X^3B_1$               | $A^1A_1$   | $B^1B_1$   | $C^1A_1$   | $A^1A_1-X^3B_1$                  | $B^1B_1-X^3B_1$ | $C^1A_1-X^3B_1$ |
| Full CI <sup>a</sup> | -39.066738             | -39.048984 | -39.010059 | -38.968471 | 0.483                            | 1.542           | 2.674           |
| EOMCCSD              | -39.063351             | -39.043791 | -39.005609 | -38.923521 | 0.532                            | 1.571           | 3.805           |
| CR-EOMCC(2,3),A      | -39.066097             | -39.047631 | -39.007791 | -38.959394 | 0.502                            | 1.587           | 2.904           |
| CR-EOMCC(2,3),D      | -39.066699             | -39.048509 | -39.008283 | -38.971988 | 0.495                            | 1.590           | 2.577           |

Note: <sup>a</sup>The basis set, geometries, and full CI energies were taken from [108]. The geometries used here were generated using full CI with the TZ2P basis set. In all correlated calculations, the lowest occupied orbital was frozen, the highest virtual orbital was deleted, and the spherical components of the carbon d orbital were employed.

what was observed for the  $X^3B_1$ ,  $A^1A_1$ , and  $B^1B_1$  states, where the improvement offered by variant D was less than 1 millihartree, for the  $C^1A_1$  state variant D of CR-EOMCC(2,3) reduces the magnitude of the CR-EOMCC(2,3),A error by as much as 5.56 millihartree. As a result, the CR-EOMCC(2,3),D approach produces a highly accurate result for the total energy of the challenging  $C^1A_1$  state that differs from full CI by only 3.52 millihartree.

Moving on to the adiabatic excitation energies obtained with the TZ2P basis set, we see that a similar pattern emerges. Indeed, for the less challenging  $A^1A_1$  and  $B^1B_1$  states, EOMCCSD performs quite well, producing errors relative to full CI of 0.05 and 0.03 eV, respectively. Furthermore, the incorporation of triples has a relatively small impact on the results, with the CR-EOMCC(2,3),A method producing errors relative to full CI of 0.02 and 0.05 eV for the  $A^1A_1$  and  $B^1B_1$  states, respectively, and CR-EOMCC(2,3),D offering additional small improvements. As was the case for the total energies, however, the effect of triple excitations is much larger in the case of the  $C^1A_1$  state, for which the difference between the EOMCCSD and full CI excitation energies is 1.13 eV. The CR-EOMCC(2,3),A approach reduces this discrepancy down to the more acceptable level of 0.23 eV, and the full CR-EOMCC(2,3),D scheme further reduces the error relative to full CI down to 0.10 eV, which is a considerable improvement compared to EOMCCSD and CR-EOMCC(2,3),A. Thus, for both total and adiabatic excitation energies, the full variant D of CR-EOMCC(2,3) provides the most accurate results, which are in excellent agreement with the results of the exact, full CI diagonalization. Similarly superb performance of CR-EOMCC(2,3),D has been observed in our other benchmark studies using finite basis sets (cf. e.g. [63–65]).

We now turn to the main objective of the present study, which is the comparison of the EOMCCSD, CR-EOMCC(2,3), and QMC data, as shown in Table 2. Because of our earlier observation that the complete variant D of CR-EOMCC(2,3) is more accurate than variant A, from now on we only consider the results obtained with variant D of CR-EOMCC(2,3) [referred to for the rest of this discussion as CR-EOMCC(2,3), with no additional labels]. We begin the examination of the EOMCCSD and CR-EOMCC(2,3) data in Table 2 by analysing the numerical stability of the CBS extrapolations. As explained in Section 2, the CBS-A extrapolation scheme is based on an assumption that although the total EOMCC energies are not converged to the CBS limit with the aug-cc-pCV5Z basis, the excitation energies are. An analysis of Table 2 reveals that this

is indeed a valid assumption, as the EOMCCSD and CR-EOMCC(2,3) excitation energies do not significantly change when moving from the aug-cc-pCVQZ to aug-cc-pCV5Z basis sets, with the largest change of 0.02 eV occurring for the most challenging  $C^1A_1$  state. Moving on to a direct comparison of the two types of CBS CR-EOMCC(2,3) total energies for each state, resulting from the CBS-A and CBS-B approaches, we see that the two extrapolation schemes produce results that are in reasonably good agreement with each other. Indeed, the discrepancies between the two sets of CBS CR-EOMCC(2,3) results do not exceed 2.8 millihartree, independent of the electronic state considered. The situation for the EOMCCSD total energies is essentially identical. The agreement between the two different CBS extrapolation schemes for the adiabatic excitation energies is even better. For the  $X^3B_1 \rightarrow A^1A_1$  and  $X^3B_1 \rightarrow B^1B_1$  excitation energies, the two CBS CR-EOMCC(2,3) values differ by 0.001 eV or less, while in the case of the  $C^1A_1$  state, the discrepancy in the excitation energies resulting from the CBS-A and CBS-B extrapolations is 0.013 eV. Again, similar observations apply to the EOMCCSD approach. We can conclude that the CBS EOMCCSD and CR-EOMCC(2,3) values are stable to the level of approximately 2 millihartree for total energies and approximately 0.01 eV for excitation energies, i.e. we can regard them as essentially converged. This is more than sufficient to make a meaningful comparison with the DMC and VMC calculations of [94], which are characterized by a larger scatter of data when different QMC methods are compared with one another (cf. Table 2).

Let us then compare the CBS EOMCCSD and CR-EOMCC(2,3) results with the QMC data. Beginning with the basic EOMCCSD calculations, we see that the resulting  $A^1A_1 - X^3B_1$  and  $B^1B_1 - X^3B_1$  gaps are in reasonably good agreement with the various QMC results, not only in the CBS limit, but also for the finite aug-cc-pCV $x$ Z basis sets with  $x=T, Q,$  and  $5$ . Furthermore, as observed in the preliminary analysis using the TZ2P basis set, accounting for the effects of triples through CR-EOMCC(2,3) does not significantly alter the values for these gaps, changing the excitation energies for the  $A^1A_1$  and  $B^1B_1$  states in the CBS limit by only about 0.03–0.04 eV. In analogy to the TZ2P results discussed above, the situation is quite a bit different for the  $X^3B_1 \rightarrow C^1A_1$  excitation energy. In this case, the EOMCCSD excitation energies differ from those generated by CR-EOMCC(2,3) and the various QMC approaches by roughly 1.4–1.5 eV, confirming that this is by far the most challenging state considered here, which is characterized by a significant multi-reference or two-electron excitation nature that



Table 2. Comparison of the total energies (in hartree) and adiabatic excitation energies (in eV) for the low-lying states of CH<sub>2</sub>, as obtained with the EOMCCSD and CR-EOMCC(2,3) approaches using the aug-cc-pCV<sub>x</sub>Z ( $x = T, Q, 5$ ) basis sets and extrapolating to the CBS limit, with the various QMC results<sup>a</sup>.

| Method        | Basis Set | Total energy (hartree) |             |             |             | Adiabatic excitation energy (eV) |                    |                   |
|---------------|-----------|------------------------|-------------|-------------|-------------|----------------------------------|--------------------|-------------------|
|               |           | $X^3B_1$               | $A^1A_1$    | $B^1B_1$    | $C^1A_1$    | $A^1A_1 - X^3B_1$                | $B^1B_1 - X^3B_1$  | $C^1A_1 - X^3B_1$ |
| EOMCCSD       | $x=T$     | -39.126182             | -39.108786  | -39.072643  | -38.978950  | 0.473                            | 1.457              | 4.006             |
|               | $x=Q$     | -39.137932             | -39.120739  | -39.085176  | -38.988201  | 0.468                            | 1.436              | 4.074             |
|               | $x=5$     | -39.140567             | -39.123385  | -39.087917  | -38.990384  | 0.468                            | 1.433              | 4.087             |
|               | CBS-A     | -39.144329             | -39.127147  | -39.091680  | -38.994146  | 0.468                            | 1.433              | 4.087             |
|               | CBS-B     | -39.142082             | -39.124905  | -39.089492  | -38.991641  | 0.467                            | 1.431              | 4.094             |
| CR-EOMCC(2,3) | $x=T$     | -39.130497             | -39.114493  | -39.075964  | -39.034496  | 0.435                            | 1.484              | 2.612             |
|               | $x=Q$     | -39.142544             | -39.126736  | -39.088654  | -39.046556  | 0.430                            | 1.466              | 2.612             |
|               | $x=5$     | -39.145196             | -39.129390  | -39.091392  | -39.048426  | 0.430                            | 1.464              | 2.633             |
|               | CBS-A     | -39.149079             | -39.133273  | -39.095275  | -39.052309  | 0.430                            | 1.464              | 2.633             |
|               | CBS-B     | -39.146720             | -39.130914  | -39.092964  | -39.049486  | 0.430                            | 1.463              | 2.646             |
| DMC: CAS(2,2) |           | -39.1406(1)            | -39.1255(1) | -39.0890(1) | -39.0451(1) | 0.412(4)                         | 1.405(4)           | 2.600(4)          |
| DMC: CAS(4,4) |           | -39.1408(1)            | -39.1257(1) | -39.0891(1) | -39.0465(1) | 0.412(4)                         | 1.408(4)           | 2.566(4)          |
| DMC: CAS(6,6) |           | -39.1428(1)            | -39.1279(1) | -39.0908(1) | -39.0501(1) | 0.406(4)                         | 1.416(4)           | 2.524(4)          |
| VMC: CAS(2,2) |           | -39.1273(2)            | -39.1124(2) | -39.0755(2) | -39.0311(2) | 0.407(8)                         | 1.411(8)           | 2.620(8)          |
| VMC: CAS(4,4) |           | -39.1279(2)            | -39.1126(2) | -39.0758(2) | -39.0334(2) | 0.416(8)                         | 1.417(8)           | 2.573(8)          |
| VMC: CAS(6,6) |           | -39.1327(2)            | -39.1169(2) | -39.0790(2) | -39.0389(2) | 0.430(8)                         | 1.460(8)           | 2.550(8)          |
| Experiment    |           |                        |             |             |             | 0.406 <sup>b</sup>               | 1.415 <sup>c</sup> |                   |

Notes: <sup>a</sup>The geometries were taken from [108] and were generated using full CI with the TZ2P basis set. In all CC/EOMCC calculations, all electrons were correlated and the spherical components of the d, f, and g basis functions were employed. Since the integral routines in GAMESS used in the CC/EOMCC calculations are currently restricted to g functions, the h functions of the aug-cc-pCV<sub>5</sub>Z basis set were omitted. All DMC and VMC results are taken from [94]. The CR-EOMCC(2,3) acronym stands for the complete variant D of CR-EOMCC(2,3).

<sup>b</sup>Obtained by correcting the experimentally derived value of the vibrationless adiabatic  $A^1A_1 - X^3B_1$  energy gap reported in [144] for the relativistic and non-adiabatic (Born–Oppenheimer diagonal correction) effects calculated in [145] and [146], respectively (as described in [115]).

<sup>c</sup>Obtained by correcting the adiabatic separation between the  $v=0$  vibronic levels of the  $B^1B_1$  and  $X^3B_1$  states, based on the information about the  $B^1B_1 - A^1A_1$  and  $A^1A_1 - X^3B_1$  gaps provided in [110] and [144], respectively, for the zero-point vibrational energies obtained in the full CI/TZ2P calculations in [108] (as described in [94]).

the EOMCCSD approach cannot capture. Looking at the total energies of each state listed in Table 2, we see that for the  $X^3B_1$ ,  $A^1A_1$ , and  $B^1B_1$  states, for which the corresponding EOMCCSD excitation energies are reasonable, the EOMCCSD approach produces errors relative to CR-EOMCC(2,3) on the order of 3.3 to 6.1 millihartree, i.e. errors which are relatively small, for both the aug-cc-pCVxZ basis sets with  $x = T, Q$ , and 5, and in the CBS limit. However, the EOMCCSD calculations for the  $C^1A_1$  state generate a huge error relative to CR-EOMCC(2,3), which in the CBS limit is on the order of 58 millihartree, illustrating once again the much larger role of triply excited clusters in the description of this multi-reference state.

Moving on, it can be seen from Table 2 that the CR-EOMCC(2,3) results for the adiabatic excitation energies, obtained with the aug-cc-pCVxZ basis sets with  $x = T, Q$ , and 5, and in the CBS limit, are in very good agreement with the various QMC results and the available experimental data. In particular, depending on the size of the CAS for the trial functions used in the QMC calculations, the discrepancies between the DMC excitation energies and the corresponding CBS-extrapolated CR-EOMCC(2,3) values range from 0.018–0.024, 0.047–0.059, and 0.033–0.122 eV for the  $A^1A_1$ ,  $B^1B_1$ , and  $C^1A_1$  states, respectively. Interestingly, the agreement of the CR-EOMCC(2,3) excitation energies with the corresponding VMC data is even better, with the discrepancy ranges reducing to 0.000–0.023, 0.003–0.053, and 0.025–0.096 eV for the  $A^1A_1$ ,  $B^1B_1$ , and  $C^1A_1$  states, respectively, when the CBS CR-EOMCC(2,3) and VMC data are compared with one another. It is worth noting, however, that the changes in the excitation energies when going from DMC to VMC are not dramatic, and so we can conclude that the two QMC variants produce comparable results in this regard. The same can be seen when comparing the CR-EOMCC(2,3), DMC, and VMC results with the experimentally derived data for the adiabatic  $A^1A_1 - X^3B_1$  and  $B^1B_1 - X^3B_1$  gaps. It is quite clear from Table 2 that both variants of QMC and the CBS-extrapolated CR-EOMCC(2,3) approach provide excitation energies which are in excellent agreement with one another and with experiment.

The total energies of the  $X^3B_1$ ,  $A^1A_1$ ,  $B^1B_1$ , and  $C^1A_1$  states, however, paint a different picture. The discrepancies between the VMC and DMC results are now on the order of 10 millihartree, which is a rather substantial disagreement within the QMC methodology. Looking at the CBS-extrapolated CR-EOMCC(2,3) total energies listed in Table 2, it is quite clear that they agree much more strongly with the DMC results than with the VMC results. If we focus on the largest CAS(6,6) QMC calculations, then the

CBS-A CR-EOMCC(2,3) energies differ from the DMC results by 2.2–6.3 millihartree, while the corresponding CBS-B energies, in which the CR-EOMCC(2,3) energy of each state is extrapolated to the CBS limit separately using Equation (2), differ by only 0.6–3.9 millihartree. This is an excellent level of agreement, particularly when we realize the entirely different nature of the CR-EOMCC(2,3) and QMC calculations and the fact that we are examining four different electronic states, not just the ground state. The discrepancy with the VMC energies, on the other hand, is an order of magnitude worse, ranging from 13.4 to 16.4 millihartree for the CBS-A CR-EOMCC(2,3) results and 10.6 to 14.0 millihartree for the CBS-B CR-EOMCC(2,3) values. Given the excellent agreement between the independent CR-EOMCC(2,3) and DMC results, and the excellent performance of the CR-EOMCC(2,3) approach relative to full CI in the TZ2P calculations, it is safe to conclude that the VMC results are the ones in larger error, producing total energies that are too high. On the other hand, given the fact that the increase in the VMC energies relative to the CR-EOMCC(2,3) and DMC approaches is nearly constant for all four states, the resulting adiabatic excitation energies are still highly accurate and in very good agreement with those of the latter two methods.

#### 4. Summary and concluding remarks

We used the CR-EOMCC(2,3) approach and the associated ground-state CR-CC(2,3) methodology to determine the total electronic and adiabatic excitation energies corresponding to the ground and lowest three excited states of methylene. We focused on comparing the CR-CC(2,3)/CR-EOMCC(2,3) results, obtained with the larger correlation-consistent basis sets of the aug-cc-pCVxZ ( $x = T, Q, 5$ ) quality and the corresponding CBS limits, with the VMC and DMC data for the  $X^3B_1$ ,  $A^1A_1$ ,  $B^1B_1$ , and  $C^1A_1$  states reported in [94], although a comparison of the CR-CC(2,3)/CR-EOMCC(2,3) and full CI data, using the full CI results obtained with the TZ2P basis set in [108], and a comparison of the CR-CC(2,3)/CR-EOMCC(2,3) adiabatic  $X^3B_1 \rightarrow A^1A_1$  and  $X^3B_1 \rightarrow B^1B_1$  excitation energies with the available experimentally derived data were made as well.

We demonstrated that the CBS-extrapolated CR-CC(2,3)/CR-EOMCC(2,3) results, based on the full implementation of CR-CC(2,3)/CR-EOMCC(2,3) defining variant D of the CR-CC(2,3)/CR-EOMCC(2,3) methodology, are in excellent agreement with the best DMC data, both for the total energies and

the adiabatic excitation energies. Indeed, the CBS values of the CR-EOMCC(2,3),D energies, in which the energy of each state of interest is extrapolated separately, differ from the corresponding CAS(6,6) DMC data reported in [94] by only 0.6–3.9 millihartree, while the discrepancies between the  $X^3B_1 \rightarrow A^1A_1$ ,  $X^3B_1 \rightarrow B^1B_1$ , and  $X^3B_1 \rightarrow C^1A_1$  adiabatic excitation energies resulting from the independent CBS CR-EOMCC(2,3) and CAS(6,6) DMC calculations are 0.024, 0.047, and 0.122 eV, respectively. The agreement between the CBS CR-CC(2,3)/CR-EOMCC(2,3) and VMC results for the total energies is not as good as in the DMC case, indicating that the VMC results are the ones in larger error, but the excitation energies resulting from the CBS CR-CC(2,3)/CR-EOMCC(2,3) and VMC calculations agree very well, independent of the electronic state considered. The CR-CC(2,3)/CR-EOMCC(2,3) adiabatic excitation energies obtained with the larger aug-cc-pCVxZ basis sets and in the CBS limit are in excellent agreement with the available experimentally derived data for the  $A^1A_1 - X^3B_1$  and  $B^1B_1 - X^3B_1$  gaps.

We demonstrated that the full variant D of CR-EOMCC(2,3) provides significantly more accurate results than the EOMCCSD and CR-EOMCC(2,3), A or EOM-CC(2)PT(2) calculations, particularly when the multi-reference states dominated by two-electron transitions, such as the  $C^1A_1$  state of methylene, are examined, independent of the basis set employed, confirming the earlier findings in this regard when other molecular systems were studied [63–65]. The novelty of the present findings in this regard lies in the fact that we demonstrated their validity in the large basis set and CBS-limit calculations. In particular, the CBS-extrapolated CR-EOMCC(2,3),D approach reduces the huge, 60 millihartree and  $\sim 1.6$  eV errors in the CBS EOMCCSD total and excitation energies, relative to the corresponding CAS(6,6) DMC data for the most challenging, doubly excited  $C^1A_1$  state to less than 1 millihartree and about 0.1 eV, respectively.

To conclude, we showed that by using the correlation-consistent basis sets to extrapolate the CBS limit of the CR-CC(2,3)/CR-EOMCC(2,3) energies, we can obtain the total and excitation energies, including excited states dominated by two-electron transitions, that match the highly accurate results of the computationally demanding QMC calculations, which produce the CBS-quality results in an intrinsic manner. This very encouraging finding illustrates the considerable potential of the CR-EOMCC(2,3) methodology and its ground-state CR-CC(2,3) counterpart in applications involving low-lying electronic states of molecular species, and, with the help of CBS extrapolations, in testing different QMC approaches,

particularly in situations involving challenging excited states dominated by two-electron transitions.

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