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Combining active-space coupled-cluster methods with moment energy corrections via the CC($P;Q$) methodology, with benchmark calculations for biradical transition states

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We have recently suggested the CC($P;Q$) methodology that can correct energies obtained in the active-space coupled-cluster (CC) or equation-of-motion (EOM) CC calculations, which recover much of the nondynamical and some dynamical electron correlation effects, for the higher-order, mostly dynamical, correlations missing in the active-space CC/EOMCC considerations. It is shown that one can greatly improve the description of biradical transition states, both in terms of the resulting energy barriers and total energies, by combining the CC approach with singles, doubles, and active-space triples, termed CCSDt, with the CC($P;Q$)-style correction due to missing triple excitations defining the CC($t;3$) approximation. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3700802>]

I. INTRODUCTION

The success of coupled-cluster (CC) theory¹ is often associated with the popularity of the noniterative correction due to triply excited clusters² added to the CC singles and doubles (CCSD) energy,³ abbreviated as CCSD(T). This stems from the fact that CCSD(T), which is a modification of the earlier CCSD[T] approach,⁴ provides a highly accurate and size-extensive description of dynamical electron correlation effects characterizing nondegenerate ground states of molecules near the equilibrium geometries, with an ease characterizing all single-reference (SR) calculations and with relatively low computer costs defined by the iterative $n_o^2 n_u^4$ and noniterative $n_o^3 n_u^4$ CPU steps (n_o and n_u are the numbers of occupied and unoccupied orbitals, respectively). Unfortunately, the standard SRCC methods, such as CCSD and CCSD(T), and their various excited state equation-of-motion (EOM; Ref. 5) or response⁶ extensions have difficulties with capturing nondynamical correlation effects characterizing chemical reaction profiles involving bond breaking, biradicals, and excited states having significant two- or other many-electron contributions.

There are two most widely explored ways of extending the CC approach to situations involving stronger nondynamical correlation effects. The first one is to turn to the multi-reference (MR) CC methods, including, for example, the state-universal (SU; Refs. 7–26) and state-specific (SS; Refs. 27–34) approaches based on the Jeziorski-Monkhorst ansatz⁷ (cf. Refs. 35–47 for representative most recent advances). Some other examples of the SSMRCC methods include, to some extent, the active-space CC/EOMCC approaches exploited in this work^{48–58} (see Ref. 59 for a recent review), the related complete active space CC (CASCC) schemes,^{60–62} the block-correlated CC (BCCC; Refs. 63 and

64) theories, the internally contracted MRCC approaches (see, e.g., Refs. 65–70), and methods combining the CC and non-CC (e.g., configuration interaction (CI)) concepts,^{71–81} with the reduced MRCC (RMRCC; Refs. 79–81) and tailored CC (TCC) schemes^{76–78} being particularly promising. If the main goal is an examination of open-shell systems that differ by one or more electrons from the corresponding closed-shell species, one may also benefit from the valence-universal MRCC theories, pioneered in the mid-1970s (Refs. 82–88; see Refs. 89–92 for selected recent advances) or from the related electron-attached (EA; Refs. 57, 58, and 93–95) and ionized (IP; Refs. 57, 58, and 95–99) EOMCC theories, and their multiply attached/ionized extensions.^{100–102} A variety of open-shell variants^{103–105} of the symmetry-adapted-cluster CI methodology,^{106,107} similar to EA/IP EOMCC and useful in some MR applications, such as electronic states of radicals, as well as the canonical transformation theory,^{108–110} similar to the internally contracted SSMRCC, and the related anti-Hermitian contracted Schrödinger equation (ACSE) approach^{111,112} are worth mentioning too.

The second way of handling stronger nondynamical correlation effects within the CC framework, which is the subject of this study, is to recover these effects dynamically through higher-order components of the cluster operator T , such as the tri- and tetra-excited clusters, T_3 and T_4 , respectively, in the ground-state SRCC wave function ansatz $|\Psi_0\rangle = e^T|\Phi\rangle$ and, in the case of excited states, through the inclusion of the analogous higher-order components of the linear excitation operator R_μ (e.g., $R_{\mu,3}$ and $R_{\mu,4}$) in the EOMCC ansatz $|\Psi_\mu\rangle = R_\mu e^T|\Phi\rangle$ ($\mu = 0$ designates the ground state, $\mu > 0$ labels excited states, and $|\Phi\rangle$ is the reference determinant). An advantage of the SRCC-like description is the fact that methods of this type are characterized by an ease of application and implementation that cannot be matched by the MRCC theories. The main challenge of the SRCC methods with higher-than-double excitations is the fact that a full incorporation of T_3 , T_4 , $R_{\mu,3}$, $R_{\mu,4}$, etc. components in the CC/EOMCC formalism,

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although possible,^{51,55,56,113–122} is computationally too expensive for the majority of applications, whereas the conventional ways of approximating the resulting CC singles, doubles, and triples (CCSDT),^{113,114} CC singles, doubles, triples, and quadruples (CCSDTQ),^{51,115,116} EOMCCSDT,^{55,56,120} EOMCCSDTQ,^{121,122} etc. methods, as in the CCSD(T), CCSDT-1,^{123,124} and other iterative or noniterative CC/EOMCC schemes that rely on many-body perturbation theory (MBPT) to estimate the effects of higher-than-double excitations, fail to describe electronic quasi-degeneracies.

An effort to come up with approximate CC and EOMCC approaches that can handle stronger nondynamical correlation effects within the SR framework, without running into the prohibitive costs of the full CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, and similar calculations, has become a significant part of the CC/EOMCC development work in recent two decades. Among methods that have emerged from this effort are the new generations of noniterative corrections to the energies resulting from the lower-order SRCC/EOMCC calculations, including, for example, CCSD(T)_Λ,^{125,126} Λ-CCSD(T),^{127,128} Λ-CCSD(TQ)_F,¹²⁹ CCSD(2)_T,¹³⁰ and CCSD(2),^{130–134} and their EOMCC-based, excited-state extensions,^{134,135} the completely renormalized (CR) CC and EOMCC schemes, and other approaches resulting from the method of moments of CC (MMCC) equations,^{136–152} and the spin-flip (SF) CC/EOMCC techniques.^{153–156} The aforementioned active-space CC/EOMCC theories,^{48–59} which are often abbreviated, following Refs. 52 and 54, as the “little t” (CCSDt, EOMCCSDt), “little tq” (CCSDtq, EOMCCSDtq), etc. approaches and which rely on selecting higher-than-two-body components of T and R_{μ} relevant to the quasi-degeneracy problem of interest should be listed here, too. Although the active-space CC/EOMCC methods are not the black boxes of the CCSD(T), Λ-CCSD(T), CCSD(2), CR-CC/EOMCC, or SF-CC/EOMCC type, since one has to choose active orbitals to define the T and R_{μ} operators, they use a single Slater determinant as a reference defining the Fermi vacuum and, as such, fall into the category of SR methods that are easier to use than typical MRCC methods relying on multi-determinantal reference states or multiple Fermi vacua. The MMCC-based CR-CC and active-space CC approaches are particularly relevant to this work.

The CR-CC/EOMCC and active-space CC/EOMCC methods have their respective advantages, but they also have weaknesses that require further development work. For example, none of the most practical CR-CC or CR-EOMCC approaches, including CR-CC(2,3),^{145–148} CR-EOMCC(2,3),^{147,149,157} and CR-EOMCCSD(T),^{141,158} which correct the CCSD/EOMCCSD energies for the effects of triple excitations, are applicable to all MR situations. This in itself is not the biggest problem, since, at the cost of running more expensive calculations, one can utilize the CR-CC/EOMCC schemes that account for higher-than-triple excitations,^{136–139,150–152,159,160} use the MMCC methods exploiting the extended CC (Refs. 161–163) rather than the normal CC theory,^{143,151,164} or turn to the externally corrected MMCC approaches that use non-CC wave functions to approximate the bra states that enter the MMCC energy

corrections.^{136,140,144,147,150,151,165–167} There is, however, a more fundamental problem, which is addressed in this study, namely, the CR-CC/EOMCC and, in general, all noniterative CC/EOMCC methods always rely on a specific *a priori*-defined CC (e.g., CCSD) or EOMCC (e.g., EOMCCSD) calculation, so there is no natural mechanism to adjust the lower-order cluster components, such as the singly and doubly excited clusters, T_1 and T_2 , respectively, that define the SRCC ground-state energy formula, or their excited-state $R_{\mu,1}$ and $R_{\mu,2}$ analogs, in the presence of the larger T_n and $R_{\mu,n}$ components with $n \geq 3$ that characterize stronger nondynamical correlations. As shown in this work, this problem may sometimes become quite disturbing, particularly when one examines certain classes of chemical reaction profiles involving biradical transition states. The active-space CC and EOMCC approaches are iterative and, as such, capable of adjusting the lower-order T_1 and T_2 components, or their excited-state $R_{\mu,1}$ and $R_{\mu,2}$ counterparts, to the effects due to higher-than-double excitations, while allowing one to select higher-than-two-body excitations, relevant to the quasi-degeneracy problem of interest, via a suitable choice of active orbitals to substantially reduce computer costs of the parent CC/EOMCC schemes, but they are not as efficient in capturing dynamical correlations as the CCSD(T), CR-CC(2,3), and similar approaches, particularly near the equilibrium geometries, where the active orbitals used in the CCSDt, CCSDtq, and similar calculations are often no longer meaningful.

In response to this unsatisfactory situation and encouraged by the recent RMRCCSD(T) (Refs. 80 and 81) and CCSD(T)-h (Refs. 168–171) work, in which one incorporates the dynamical correlation effects due to triple excitations missing in RMRCCSD and CCSDt using perturbative CCSD(T)-style expressions, we have recently suggested, as part of the broader review,¹⁵² the generalization of the existing biorthogonal MMCC theory,^{145–147,149} which enables one to correct the CC/EOMCC energies obtained with the arbitrary, i.e., conventional (e.g., CCSD/EOMCCSD or CCSDT/EOMCCSDT) as well as unconventional (e.g., CCSDt/EOMCCSDt or CCSDtq/EOMCCSDtq) truncations in T and R_{μ} for essentially any subset of the missing many-electron correlation effects of interest. The resulting moment expansions, defining the Flexible MMCC (Flex-MMCC) and CC($P;Q$) formalisms discussed in this work, which can be regarded as a companion study to the review presented in Ref. 152, enable one to contemplate a variety of new schemes. Among them is the CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. hierarchy, in which the energies obtained in the active-space CC/EOMCC calculations, such as CCSDt, CCSDtq, or CCSDTq, are corrected for the effects of higher-order, primarily dynamical, correlations, such as triples (3) or triples and quadruples (3,4) missing in the active-space CC/EOMCC considerations using the noniterative corrections similar to those of CR-CC/EOMCC.

The potential advantages of the Flex-MMCC and CC($P;Q$) formalisms have been illustrated in Ref. 152 by the preliminary CC(t;3) calculations for the bond breaking in the HF, F₂, and F₂⁺ molecules, as described by the aug-cc-pVTZ (Refs. 172 and 173; HF) and cc-pVTZ (Ref. 172; F₂ and F₂⁺) basis sets and employing the restricted Hartree-Fock (RHF) or

TABLE I. The maximum unsigned error (MUE) and non-parallelity error (NPE) values (in millihartree) characterizing the results of various CC calculations for the potential energy curves of the HF, F₂, and F₂⁺ molecules, relative to the corresponding CCSDT energies, reported in Ref. 152.

Molecular system ^a	CCSD	CCSD(T)	CR-CC(2,3)	CCSDt	CCSD(T)-h	CC(t;3)
MUE						
HF($R/R_e = 0.75 - 5.0$)	36.029	71.762	1.553	3.779	0.350	0.187
F ₂ ($R/R_e = 0.75 - 5.0$)	69.103	47.179	4.254	2.290	0.524	0.162
F ₂ ⁺ ($R/R_e = 0.75 - 3.0$)	89.240	22.032	14.305	1.840	0.727	0.254
NPE						
HF($R/R_e = 0.75 - 5.0$)	29.733	71.770	1.433	1.385	0.330	0.202
F ₂ ($R/R_e = 0.75 - 5.0$)	57.742	47.200	4.618	0.732	0.410	0.110
F ₂ ⁺ ($R/R_e = 0.75 - 3.0$)	77.510	22.132	15.262	0.717	0.604	0.081

^aIn each case, R/R_e designates the range of internuclear separations, in multiples of the equilibrium distance, which was used in the MUE and NPE evaluation. The active spaces used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of the $N_o = 3$ highest-energy occupied and $N_u = 10$ lowest-energy unoccupied orbitals that correlate with the 1s, 2s, and 2p shells of the H atom and the 2p, 3s, 3p, and 4s shells of the F atom in the HF case, and the $N_o = 5$ highest occupied and $N_u = 9$ lowest unoccupied orbitals that correlate with the 2p, 3s, and 3p shells of the F atoms in the case of F₂ and F₂⁺. See Ref. 152 for further details.

restricted open-shell Hartree-Fock (ROHF) references. These results are summarized in Table I. As we can see, CC(t;3) improves the CCSDt and CR-CC(2,3) results, as well as the results of the CCSD(T) and CCSD(T)-h calculations, providing potential energy surfaces (PESs) that agree with those obtained with the parent CCSDT approach to within small fractions of a millihartree, both in terms of the maximum unsigned errors (MUEs) and the non-parallelity errors (NPEs) relative to CCSDT. All of this is accomplished at the small fraction of the costs of the CCSDT calculations, which are characterized by the iterative $n_o^3 n_u^5$ steps, since the most expensive steps of CC(t;3) scale as $N_o N_u n_o^2 n_u^4$ in the underlying CCSDt calculations and $n_o^3 n_u^4$ in the triples correction part similar to CR-CC(2,3), where N_o ($< n_o$ or $\ll n_o$) and N_u ($\ll n_u$) are the numbers of active occupied and active unoccupied orbitals, respectively.

The improvements offered by CC(t;3), when compared to CCSD(T), CR-CC(2,3), CCSDt, and CCSD(T)-h, in cases involving single bond breaking are significant. One can also show that CC(t;3) is more robust than CCSDt and CCSD(T)-h, when we replace the full CCSDt approach by one of its simplified forms, in which the spin-orbital indices defining triples are more severely constrained compared to the original CCSDt ansatz of Refs. 49–56 (see Ref. 152 for the details). There is, however, another category of important applications, where neither CCSD(T) nor CR-CC(2,3), nor any other existing noniterative triples CC approach based on CCSD (Λ -CCSD(T), CCSD(2)_T, etc.) provide the desired improvements. This category includes certain classes of biradical transition states, such as, for example, the transition state characterizing the challenging and frequently studied^{22,35,37,64,68,78,174–185} automerization of cyclobutadiene or the equally challenging transition state defining the disrotatory pathway for the isomerization of bicyclo[1.1.0]butane (abbreviated as *bicbut*) to *trans*-buta-1,3-diene (abbreviated as *t-but*), which is one of the two lowest-energy pathways that we^{186,187} and subsequently others^{188,189} examined in recent years in the context of the electronic structure development work (see Refs. 190–198 for the earlier experimental and theoretical work relevant to the *bicbut*→*t-but* isomerization). The purpose of the present study is to show that the CC(t;3) approach is ro-

bust enough to provide substantial improvements in the CCSD(T), Λ -CCSD(T), CCSD(2)_T, CR-CC(2,3), CCSDt, and CCSD(T)-h results, for total as well as relative energies, in cases involving biradical transition states, represented here by the cyclobutadiene and *bicbut*→*t-but* isomerizations.

We have chosen the above molecular examples, since they have been examined before with many SRCC and MRCC methods, since they are small enough to obtain the accurate full CCSDT information, and since they clearly show the types of errors the existing noniterative CCSD(T)-type or CR-CC-type methods based on the conventional CCSD may produce in biradical situations. Indeed, as demonstrated in the present work and as emphasized in Ref. 78, the standard CCSD(T) approach as well as the CR-CC and other approaches with a noniterative treatment of triple excitations on top of CCSD, including CR-CC(2,3), CR-CCSD(T),^{136,137} Λ -CCSD(T), and CCSD(2)_T, overestimate the small barrier for the automerization of cyclobutadiene, which should not exceed 10 kcal/mol,¹⁷⁴ by more than 5 and, in some calculations, by almost 10 kcal/mol. This is a situation, where CCSD(T) does not yet display the all-too-familiar, excessively negative, triples correction, which is often seen for biradicals and bond breaking, producing the transition-state energy considerably above that of full CCSDT, but none of the new generations of triples corrections, including CR-CC(2,3), CR-CCSD(T), Λ -CCSD(T), and CCSD(2)_T, improve the CCSD(T) results. In the case of the strongly biradical disrotatory pathway for the *bicbut*→*t-but* isomerization, where CCSD(T) fails, placing the corresponding transition state about 20 kcal/mol below the lowest-energy conrotatory transition state, and where CR-CC(2,3) restores the correct pathway ordering while providing an excellent description of the conrotatory path,^{186,187} for which the experimental activation energy is well established,¹⁹⁰ one observes a rather significant error in the CR-CC(2,3) description of the disrotatory transition state. As shown in this work, the CCSD(2)_T approach, although similar to CR-CC(2,3),^{145–148} does not help, worsening the CR-CC(2,3) results for both pathways. The disrotatory activation barrier resulting from the CR-CC(2,3) calculations with the cc-pVTZ and cc-pVQZ basis sets, reported in Refs. 186 and 187, and its analog obtained using the complete basis set limit (CBS) extrapolation (there is

almost no difference between the CR-CC(2,3)/cc-pVTZ, CR-CC(2,3)/cc-pVQZ, and CR-CC(2,3)/CBS results¹⁸⁷) is about 7 kcal/mol higher than the result of the carefully executed diffusion quantum Monte Carlo (DMC; Refs. 199–201) calculations,¹⁸⁹ and about 10 kcal/mol higher than the ACSE,¹⁸⁸ MRMBPT,^{186,188,198} and MRCI (Ref. 198) results. Although there is no experimental information about the disrotatory pathway and it is hard to know if other calculations, particularly MRMBPT, MRCI, or ACSE, provide the correct values, we know from the full CCSDT/cc-pVDZ calculations performed in this study that the CR-CC(2,3) result for the disrotatory transition state for the *bicbut*→*t-but* isomerization is too high by about 5 kcal/mol. Thus, although we cannot entirely agree with the statement in Ref. 188 that “the CR-CC method may be missing some multireference correlation that would lower the energy of the biradical disrotatory transition state by about 15 millihartree or 9.5 kcal/mol,” since, based on the accurate DMC calculations reported in Ref. 189 and our own CCSDT data, the error is in the 5–7 kcal/mol range, we agree that, in analogy to the automerization of cyclobutadiene, CR-CC(2,3) does not capture all of the relevant electron correlations effects, producing errors in the activation energies characterizing some biradical transition states on the order of a few kcal/mol. In all of the above and similar cases, the main problem lies in substantial errors in the description of the transition-state energies, which can be, as shown in this study, on the order of 10 millihartree at the CCSD(T), CCSD(2)_T, CR-CC(2,3), and similar levels, when compared to a reliable full CCSDT treatment. This should be contrasted by the behavior of the active-space CCSDt approach, which, as shown in this work, provides excellent barrier heights in situations involving biradical transition states, consistent with the small NPE values observed in Table I, but rather substantial errors in the calculated total energies relative to full CCSDT at the reactant, product, and transition-state structures, which can be as large as 10–30 millihartree.

The above discussion illustrates the key points which motivate our work on the CC(*P*;*Q*) formalism and approximations such as CC(t;3). The noniterative triples CC methods exploiting the CCSD values of T_1 and T_2 are not flexible enough to provide accurate relative energetics in all biradical situations due to their inability to couple the T_1 , T_2 , and T_3 (in general, T_n with $n \geq 3$) clusters needed to describe the strongly quasi-degenerate transition-state regions. The active-space CC approaches, such as CCSDt, which produce very good relative energetics in biradical cases, may fail to provide an accurate description of dynamical correlation effects associated with the T_3 clusters. These kinds of problems are often used to advocate a MR treatment, including MRCC or MRCC-like theories that were previously applied to the automerization of cyclobutadiene,^{22,35,37,64,68,184} but, as shown in this study, none of the above molecular examples involving biradical transition states require a genuine MRCC approach. One can obtain excellent results by using full SRCCSDT and, what is most important from the practical point of view, the inexpensive CC(t;3) approximation to CCSDT utilizing the Flex-MMCC and CC(*P*;*Q*) formalisms.

II. THEORY AND ALGORITHMIC DETAILS

A. Basic elements of the CC(*P*;*Q*) methodology

The CC(*P*;*Q*) and the underlying Flex-MMCC formalisms are obtained by generalizing the existing biorthogonal MMCC theory.^{145–147,149} Normally, one uses MMCC to correct the ground- and excited-state energies resulting from the conventional CC/EOMCC calculations truncated at m_A -fold excitations, such as CCSD/EOMCCSD where $m_A = 2$ or CCSDT/EOMCCSDT where $m_A = 3$, for the remaining correlation effects that correspond to the excited determinants $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle = E_{i_1 \dots i_n}^{a_1 \dots a_n} |\Phi\rangle$ with $n > m_A$. The Flex-MMCC and CC(*P*;*Q*) formalisms go one step further and enable one to correct the CC/EOMCC energies obtained with the arbitrary, conventional as well as unconventional, truncations in the cluster and excitation operators T and R_μ for the missing electron correlation effects of interest. Those could be the usual corrections due to all triples in the case of CCSD/EOMCCSD or all quadruples in the CCSDT/EOMCCSDT case, or the less conventional corrections due to the subsets of triples or triples and quadruples neglected in the active-space CCSDt/EOMCCSDt and CCSDtq/EOMCCSDtq considerations. As usual, i_1, i_2, \dots or i, j, \dots and a_1, a_2, \dots or a, b, \dots are the occupied and unoccupied spin-orbitals, respectively, in the reference determinant $|\Phi\rangle$ and $E_{i_1 \dots i_n}^{a_1 \dots a_n} = \prod_{k=1}^n a^{a_k} a_{i_k}$, with a^p and a_p designating the creation and annihilation operators associated with the spin-orbitals p , are the n -body particle-hole excitation operators. Because of the utilization of the active-space CC ideas in this work, we also adopt the notation in which bold capital-case indices represent active spin-orbitals (**I**, **J**, ... for the active occupied and **A**, **B**, ... for the active unoccupied ones) and bold lower-case indices designate the inactive spin-orbitals outside the active subset (**i**, **j**, ... for the core or inactive occupied spin-orbitals and **a**, **b**, ... for the virtual or inactive unoccupied spin-orbitals).

To introduce the Flex-MMCC and CC(*P*;*Q*) methodologies more formally, let $\mathcal{H}^{(P)}$ designate the subspace of the N -electron Hilbert space \mathcal{H} of interest, referred to as the P -space and spanned by the excited determinants $|\Phi_K\rangle = E_K |\Phi\rangle$, where E_K is the elementary excitation operator generating $|\Phi_K\rangle$ from the reference $|\Phi\rangle$, and let

$$T^{(P)} = \sum_{|\Phi_K\rangle \in \mathcal{H}^{(P)}} t_K E_K \quad (1)$$

and

$$R_\mu^{(P)} = R_{\mu,0}^{(P)} + R_{\mu,\text{open}}^{(P)} = r_{\mu,0} \mathbf{1} + \sum_{|\Phi_K\rangle \in \mathcal{H}^{(P)}} r_{\mu,K} E_K \quad (2)$$

be the truncated forms of T and R_μ in which t_K and $r_{\mu,K}$ are the cluster and excitation amplitudes obtained in the CC/EOMCC calculations in $\mathcal{H}^{(P)}$, which we subsequently want to correct for the correlation effects involving the excited determinants $|\Phi_K\rangle$ from the Q -space $\mathcal{H}^{(Q)} \subseteq (\mathcal{H}^{(0)} \oplus \mathcal{H}^{(P)})^\perp$ ($\mathcal{H}^{(0)}$ is a one-dimensional subspace spanned by $|\Phi\rangle$, which is accounted for in the P -space CC/EOMCC calculations, $\mathbf{1}$ is a unit operator, and to incorporate the ground-state ($\mu = 0$) and excited-state ($\mu > 0$) cases within a single set of formulas, we define $R_{\mu=0}^{(P)} = \mathbf{1}$). For example, $\mathcal{H}^{(P)}$ could be spanned by all $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ determinants with $n \leq m_A$ and

$\mathcal{H}^{(Q)}$ by those with $m_A < n \leq m_B$, where $m_B \leq N$. In this case, the Flex-MMCC formalism would reduce to the existing biorthogonal MMCC schemes, which include the CR-CC(m_A, m_B) (e.g., CR-CC(2,3)) and CR-EOMCC(m_A, m_B) (e.g., CR-EOMCC(2,3)) approximations that correct the results of the CC/EOMCC calculations truncated at the m_A -fold excitations for the effects of n -fold excitations with $m_A < n \leq m_B$. But we could also consider unconventional choices of the P - and Q -spaces. For example, after performing the active-space CCSDt/EOMCCSDt calculations, in which

$$T \approx T^{(\text{CCSDt})} = T_1 + T_2 + t_3 \quad (3)$$

and

$$R_\mu \approx R_\mu^{(\text{CCSDt})} = r_{\mu,0} \mathbf{1} + R_{\mu,1} + R_{\mu,2} + r_{\mu,3}, \quad (4)$$

where T_1 and T_2 , and their excited-state $R_{\mu,1}$ and $R_{\mu,2}$ analogs are the normal singly and doubly excited components of T and R_μ , defined using all correlated spin-orbitals, and

$$t_3 = \sum_{\mathbf{I} > j > k, a > b > c} t_{abC}^{\mathbf{I}jk} E_{\mathbf{I}jk}^{abC} \quad (5)$$

and

$$r_{\mu,3} = \sum_{\mathbf{I} > j > k, a > b > c} r_{\mu,abC}^{\mathbf{I}jk} E_{\mathbf{I}jk}^{abC} \quad (6)$$

are the ‘‘little t’’ components of T and R_μ , defined with the help of active orbitals, we may want to correct the resulting $E_\mu^{(\text{CCSDt})}$ energies for the triple-excitation effects missing in CCSDt/EOMCCSDt. In this case, the $\mathcal{H}^{(P)}$ subspace used in the Flex-MMCC and CC($P;Q$) considerations is spanned by the $|\Phi_i^a\rangle$, $|\Phi_{ij}^{ab}\rangle$, and $|\Phi_{\mathbf{I}jk}^{abc}\rangle$ determinants and the corresponding subspace $\mathcal{H}^{(Q)}$ is spanned by the $|\Phi_{\mathbf{I}jk}^{abc}\rangle$, $|\Phi_{\mathbf{I}jk}^{abC}\rangle$, $|\Phi_{\mathbf{I}jk}^{aBC}\rangle$, $|\Phi_{\mathbf{I}jk}^{ABC}\rangle$, $|\Phi_{\mathbf{I}jk}^{abc}\rangle$, $|\Phi_{\mathbf{I}jk}^{abC}\rangle$, and $|\Phi_{\mathbf{I}jk}^{aBC}\rangle$ determinants that have no active indices among either i, j , and k or a, b , and c . This is what we do in the CC(t;3) calculations reported in this work. We are also assuming that the P -space CC calculations are performed by solving the non-linear system

$$\langle \Phi_K | \bar{H}_{\text{open}}^{(P)} | \Phi \rangle = 0, \quad |\Phi_K\rangle \in \mathcal{H}^{(P)}, \quad (7)$$

to obtain the cluster amplitudes t_K defining $T^{(P)}$ and the corresponding ground-state energy

$$E_0^{(P)} = \langle \Phi | \bar{H}^{(P)} | \Phi \rangle, \quad (8)$$

where

$$\bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}} = (H e^{T^{(P)}})_C \quad (9)$$

is the relevant similarity-transformed Hamiltonian (with C representing the connected operator product) and $\bar{H}_{\text{open}}^{(A)} = \bar{H}^{(A)} - E_0^{(A)} \mathbf{1}$ is the open part of $\bar{H}^{(A)}$ defined by diagrams having external Fermion lines. If we are interested in excited states (the amplitudes $r_{\mu,K}$ defining $R_\mu^{(P)}$ and the corresponding energies $E_\mu^{(P)}$), we diagonalize $\bar{H}^{(P)}$ in $\mathcal{H}^{(P)}$ by solving

$$\langle \Phi_K | (\bar{H}_{\text{open}}^{(P)} R_{\mu,\text{open}}^{(P)})_C | \Phi \rangle = \omega_\mu^{(P)} r_{\mu,K}, \quad |\Phi_K\rangle \in \mathcal{H}^{(P)}, \quad (10)$$

where $\omega_\mu^{(P)} = E_\mu^{(P)} - E_0^{(P)}$. Because of the non-Hermiticity of $\bar{H}^{(P)}$, if we further want to calculate properties other than energy, i.e., in addition to the ket CC/EOMCC states

$$|\Psi_\mu^{(P)}\rangle = R_\mu^{(P)} |\Psi_0^{(P)}\rangle = R_\mu^{(P)} e^{T^{(P)}} |\Phi\rangle, \quad (11)$$

we want to know the corresponding bra states

$$\langle \tilde{\Psi}_\mu^{(P)} | = \langle \Phi | L_\mu^{(P)} e^{-T^{(P)}}, \quad (12)$$

where

$$L_\mu^{(P)} = L_{\mu,0}^{(P)} + L_{\mu,\text{open}}^{(P)} \equiv \delta_{\mu,0} \mathbf{1} + \sum_{|\Phi_K\rangle \in \mathcal{H}^{(P)}} l_{\mu,K} (E_K)^{\dagger}, \quad (13)$$

we must solve the P -space variant of the left CC/EOMCC eigenvalue problem,

$$\delta_{\mu,0} \langle \Phi | \bar{H}_{\text{open}}^{(P)} | \Phi_K \rangle + \langle \Phi | L_{\mu,\text{open}}^{(P)} \bar{H}_{\text{open}}^{(P)} | \Phi_K \rangle = \omega_\mu^{(P)} l_{\mu,K}, \quad |\Phi_K\rangle \in \mathcal{H}^{(P)}. \quad (14)$$

According to the Flex-MMCC formalism, once the P -space CC/EOMCC equations are solved and the corresponding energies $E_\mu^{(P)}$ determined, we correct energies $E_\mu^{(P)}$ for the correlation effects due to the Q -space excitations using the following formula:

$$E_\mu^{(P+Q)} \equiv E_\mu^{(P)} + \delta_\mu(P; Q), \quad (15)$$

where

$$\delta_\mu(P; Q) = \sum_{\substack{|\Phi_K\rangle \in \mathcal{H}^{(Q)} \\ \text{rank}(|\Phi_K\rangle) \leq \min(N_\mu^{(P)}, \Xi^{(Q)})}} \ell_{\mu,K}(P) \mathfrak{M}_{\mu,K}(P), \quad (16)$$

with

$$\mathfrak{M}_{\mu,K}(P) = \langle \Phi_K | (\bar{H}^{(P)} R_\mu^{(P)}) | \Phi \rangle \quad (17)$$

representing the generalized moments of the CC ($\mu = 0$; $R_{\mu=0}^{(P)} = \mathbf{1}$) or EOMCC ($\mu > 0$) equations corresponding to the calculations with $T = T^{(P)}$ and $R_\mu = R_\mu^{(P)}$, associated with the projections of these equations on the $|\Phi_K\rangle$ determinants from the Q -space $\mathcal{H}^{(Q)}$. The $N_\mu^{(P)}$ symbol that enters Eq. (16) is the highest many-body rank of the excited determinant $|\Phi_K\rangle$ relative to the $|\Phi\rangle$ vacuum, designated by $\text{rank}(|\Phi_K\rangle)$, for which the generalized moment $\mathfrak{M}_{\mu,K}(P)$ of the P -space CC/EOMCC equations calculated using Eq. (17) is still non-zero. The $\Xi^{(Q)}$ symbol in Eq. (16) is the highest many-body rank of the excited determinant(s) $|\Phi_K\rangle$ included in $\mathcal{H}^{(Q)}$. For example, if we want to use Eq. (17) to correct the CCSDt/EOMCCSDt energies for triples missing in CCSDt and EOMCCSDt, $N_\mu^{(P)} = 10$, but $\Xi^{(Q)} = 3$, so that, as expected, $\min(N_\mu^{(P)}, \Xi^{(Q)}) = 3$.

In analogy to other MMCC expansions formulated to date,^{136,137,140,142,145,146,150–152} Eq. (15) can be derived by considering the asymmetric expression for the full CI energies E_μ ,

$$E_\mu = \langle \Psi_\mu | H R_\mu^{(P)} e^{T^{(P)}} | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(P)} e^{T^{(P)}} | \Phi \rangle, \quad (18)$$

in which we replace the exact bra states $\langle \Psi_\mu |$ by

$$\langle \Psi_\mu | = \langle \Phi | \mathcal{L}_\mu e^{-T^{(P)}}, \quad (19)$$

where

$$\mathcal{L}_\mu = \delta_{\mu,0} \mathbf{1} + \mathcal{L}_\mu^{(P)} + \delta\mathcal{L}_\mu^{(P)}, \quad (20)$$

with

$$\mathcal{L}_\mu^{(P)} = \sum_{|\Phi_K\rangle \in \mathcal{H}^{(P)}} \ell_{\mu,K} (E_K)^\dagger \quad (21)$$

and

$$\delta\mathcal{L}_\mu^{(P)} = \sum_{|\Phi_K\rangle \in (\mathcal{H}^{(0)} \oplus \mathcal{H}^{(P)})^\perp} \ell_{\mu,K} (E_K)^\dagger. \quad (22)$$

The final form of Eqs. (15) and (16), with moments $\mathfrak{M}_{\mu,K}(P)$ defined by Eq. (17), emerges when, after inserting the resolution of identity in the N -electron Hilbert space \mathcal{H} , expressed as $|\Phi\rangle\langle\Phi| + P + P^\perp = \mathbf{1}$, where P and P^\perp are the projection operators on $\mathcal{H}^{(P)}$ and $(\mathcal{H}^{(0)} \oplus \mathcal{H}^{(P)})^\perp$, in the numerator of Eq. (18), one limits the summation over the excited determinants $|\Phi_K\rangle \in (\mathcal{H}^{(0)} \oplus \mathcal{H}^{(P)})^\perp$ to those that belong to $\mathcal{H}^{(Q)}$, while replacing the exact $\ell_{\mu,K}$ de-excitation amplitudes, which satisfy the left eigenvalue problem

$$\langle\Phi|\mathcal{L}_\mu\bar{H}^{(P)} = E_\mu\langle\Phi|\mathcal{L}_\mu, \quad (23)$$

in the entire N -electron Hilbert space \mathcal{H} , by their approximate $\ell_{\mu,K}(P)$ values. One obtains the latter values by restricting the eigenvalue problem represented by Eq. (23) to the subspace of interest, i.e., $\mathcal{H}^{(0)} \oplus \mathcal{H}^{(P)} \oplus \mathcal{H}^{(Q)}$, based on the information obtained in the preceding P -space CC/EOMCC calculations. Different ways of handling the $\ell_{\mu,K}(P)$ amplitudes entering the correction $\delta_\mu(P;Q)$, Eq. (16), lead to different Flex-MMCC approximations. The CC($P;Q$) hierarchy is one such procedure.

In the CC($P;Q$) approaches, we approximate the de-excitation operator \mathcal{L}_μ by splitting it into the known, *a priori* determined, P -space component $L_\mu^{(P)}$, defined by Eq. (13) and obtained by solving the left CC/EOMCC eigenvalue problem given by Eq. (14), and the unknown component $\mathcal{L}_\mu^{(Q)}$ that provides information about the $\ell_{\mu,K}(P)$ amplitudes corresponding to $|\Phi_K\rangle \in \mathcal{H}^{(Q)}$, which enter $\delta_\mu(P;Q)$, Eq. (16). Thus, we write

$$\mathcal{L}_\mu \approx L_\mu^{(P)} + \mathcal{L}_\mu^{(Q)}, \quad (24)$$

where

$$\mathcal{L}_\mu^{(Q)} = \sum_{|\Phi_K\rangle \in \mathcal{H}^{(Q)}} \ell_{\mu,K}(P) (E_K)^\dagger. \quad (25)$$

By replacing the exact \mathcal{L}_μ operator in Eq. (23) by its approximate form given by Eq. (24), followed by right projecting the resulting equation on the $|\Phi_K\rangle$ determinants from $\mathcal{H}^{(Q)}$ while approximating the exact energy E_μ by $E_\mu^{(P)}$, and applying the Epstein-Nesbet-like partitioning to the linear system that emerges from these considerations, we obtain

$$\begin{aligned} &\langle\Phi|L_\mu^{(P)}\bar{H}^{(P)}|\Phi_K\rangle + \sum_{|\Phi_{K'}\rangle \in \mathcal{H}^{(Q)}, K' \neq K} \langle\Phi_{K'}|\bar{H}^{(P)}|\Phi_K\rangle \ell_{\mu,K'}(P) \\ &= D_{\mu,K}(P) \ell_{\mu,K}(P), \quad |\Phi_K\rangle \in \mathcal{H}^{(Q)}, \end{aligned} \quad (26)$$

where

$$D_{\mu,K}(P) = E_\mu^{(P)} - \langle\Phi_K|\bar{H}^{(P)}|\Phi_K\rangle. \quad (27)$$

We may attempt to solve the above system iteratively or ignore the off-diagonal elements of $\bar{H}^{(P)}$ in the Q -space, obtaining the noniterative CR-CC-style formula

$$\ell_{\mu,K}(P) = \langle\Phi|L_\mu^{(P)}\bar{H}^{(P)}|\Phi_K\rangle/D_{\mu,K}(P), \quad (28)$$

limiting the use of Eq. (26) to small blocks of the $\bar{H}^{(P)}$ matrix involving the degenerate Q -space determinants $|\Phi_K\rangle$ if we want to enforce the strict invariance of the resulting energies $E_\mu^{(P+Q)}$ with respect to rotations among degenerate orbitals. Here, we focus on the simplified CC($P;Q$) approaches in which the $\ell_{\mu,K}(P)$ amplitudes are determined using Eq. (28).

Equation (15) for the energies $E_\mu^{(P+Q)}$, in which one determines the $\delta_\mu(P;Q)$ corrections using Eq. (16), with moments $\mathfrak{M}_{\mu,K}(P)$ and amplitudes $\ell_{\mu,K}(P)$ calculated using Eqs. (17) and (28), defines the CC($P;Q$) hierarchy that interests us in this work. This hierarchy contains all of the previously formulated CR-CC(m_A, m_B) and CR-EOMCC(m_A, m_B) methods, including CR-CC(2,3) and CR-EOMCC(2,3), as special cases. Indeed, the CR-CC(2,3) and CR-EOMCC(2,3) methods are obtained by solving the right and left CCSD and EOMCCSD equations in the P -space spanned by the singly and doubly excited determinants, and by defining the Q -space as the subspace spanned by all triply excited determinants to determine the corrections $\delta_\mu(P;Q)$ to the CCSD and EOMCCSD energies. However, one can go beyond reconstructing the existing CR-CC(m_A, m_B) and CR-EOMCC(m_A, m_B) approximations from the above formulas and use the CC($P;Q$) methodology to introduce novel, unconventional schemes, such as the CC(t;3), CC(t,q;3), CC(t,q;3,4), and CC(q;4) methods suggested in Ref. 152. The key elements of the CC(t;3) approach are summarized next.

B. The CC(t;3) approach

The CC(t;3) calculations begin by solving the CCSDt equations, obtained by replacing $\bar{H}^{(P)}$ in Eq. (7) by the similarity-transformed Hamiltonian of CCSDt,

$$\bar{H}^{(\text{CCSDt})} = e^{-T^{(\text{CCSDt})}} H e^{T^{(\text{CCSDt})}} = (H e^{T^{(\text{CCSDt})}})_C, \quad (29)$$

and the P -space determinants $|\Phi_K\rangle$ entering the resulting nonlinear system by the $|\Phi_i^a\rangle$, $|\Phi_{ij}^{ab}\rangle$, and $|\Phi_{ijk}^{abc}\rangle$ determinants, to obtain the T_1 , T_2 , and t_3 components of $T^{(\text{CCSDt})}$, Eq. (3). The ground-state CCSDt energy is determined in an usual way using Eq. (8), in which $\bar{H}^{(P)}$ is replaced by $\bar{H}^{(\text{CCSDt})}$, Eq. (29). If we are interested in the EOMCCSDt information about excited states, we diagonalize $\bar{H}^{(\text{CCSDt})}$ in the P -space spanned by the $|\Phi_i^a\rangle$, $|\Phi_{ij}^{ab}\rangle$, and $|\Phi_{ijk}^{abc}\rangle$ determinants. Once the ground- and excited-state energies $E_\mu^{(\text{CCSDt})}$ of interest are determined, we calculate the CC(t;3) energies $E_\mu^{(\text{CC}(t;3))}$ as

$$E_\mu^{(\text{CC}(t;3))} = E_\mu^{(\text{CCSDt})} + \delta_\mu(t;3), \quad (30)$$

where, according to the CC($P;Q$) equations presented in Sec. II A, the correction $\delta_\mu(t;3)$ due to triples missing in the CCSDt/EOMCCSDt considerations is calculated using

$$\delta_\mu(t;3) = \sum_{|\Phi_{ijk}^{abc}\rangle \in \mathcal{H}^{(T)} \ominus \mathcal{H}^{(0)}} \ell_{\mu,ijk}^{abc}(\text{CCSDt}) \mathfrak{M}_{\mu,abc}^{ijk}(\text{CCSDt}), \quad (31)$$

with the CCSDt ($\mu = 0$) or EOMCCSDt ($\mu > 0$) moments entering Eq. (31) defined by

$$\mathfrak{M}_{\mu,abc}^{ijk}(\text{CCSDt}) = \langle \Phi_{ijk}^{abc} | (\bar{H}^{(\text{CCSDt})} R_{\mu}^{(\text{CCSDt})}) | \Phi \rangle, \quad (32)$$

and the $\ell_{\mu,ijk}^{abc}(\text{CCSDt})$ amplitudes that multiply these moments in Eq. (31) calculated as

$$\ell_{\mu,ijk}^{abc}(\text{CCSDt}) = \langle \Phi | L_{\mu}^{(\text{CCSDt})} \bar{H}^{(\text{CCSDt})} | \Phi_{ijk}^{abc} \rangle / D_{\mu,abc}^{ijk}(\text{CCSDt}). \quad (33)$$

The summation over the triply excited determinants $|\Phi_{ijk}^{abc}\rangle$ in Eq. (31), which in methods such as CR-CC(2,3) or CR-EOMCC(2,3) would span the subspace of all triples, designated by $\mathcal{H}^{(\text{T})}$ ($\mathcal{H}^{(\text{T})} = \text{span}\{|\Phi_{ijk}^{abc}\rangle, i > j > k, a > b > c\}$), excludes those determinants $|\Phi_{ijk}^{abc}\rangle$ that are already included in CCSDt/EOMCCSDt, designated by $\mathcal{H}^{(\text{l})} = \text{span}\{|\Phi_{\mathbf{I}jk}^{abc}\rangle, \mathbf{I} > j > k, a > b > c\}$. The $L_{\mu}^{(\text{CCSDt})}$ de-excitation operator, entering Eq. (33) and defined as

$$L_{\mu}^{(\text{CCSDt})} = \delta_{\mu,0} \mathbf{1} + L_{\mu,1} + L_{\mu,2} + l_{\mu,3}, \quad (34)$$

where $L_{\mu,1}$ and $L_{\mu,2}$ are the corresponding one- and two-body components, and

$$l_{\mu,3} = \sum_{\mathbf{I} > j > k, a > b > c} l_{\mu,\mathbf{I}jk}^{abc} E_{abc}^{\mathbf{I}jk} \quad (35)$$

is obtained by solving the left eigenvalue problem of CCSDt/EOMCCSDt (Eq. (14) in which $T^{(P)} = T^{(\text{CCSDt})}$ and $\mathcal{H}^{(P)} = \mathcal{H}^{(\text{CCSDt})}$). Finally, the Epstein-Nesbet-style $D_{\mu,abc}^{ijk}(\text{CCSDt})$ denominator, needed in Eq. (33) as well, is calculated using (cf. Eq. (27))

$$D_{\mu,abc}^{ijk}(\text{CCSDt}) = E_{\mu}^{(\text{CCSDt})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSDt})} | \Phi_{ijk}^{abc} \rangle. \quad (36)$$

If one wants to be more explicit about the summation over triples defining the $\mathcal{H}^{(\text{T})} \ominus \mathcal{H}^{(\text{l})}$ subspace in Eq. (31), we can also write

$$\begin{aligned} \delta_{\mu}(t;3) &= \sum_{i>j>k,a>b>c} \ell_{\mu,ijk}^{abc}(\text{CCSDt}) \mathfrak{M}_{\mu,abc}^{ijk}(\text{CCSDt}) \\ &+ \sum_{\mathbf{I} > j > k, a > b > c} \ell_{\mu,\mathbf{I}jk}^{abc}(\text{CCSDt}) \mathfrak{M}_{\mu,abc}^{\mathbf{I}jk}(\text{CCSDt}). \end{aligned} \quad (37)$$

We refer the reader to Ref. 152 for the formulas for other types of the CC(t;3) approximations, in which we constrain triple excitations in CCSDt/EOMCCSDt in a different way than the one exploited here. One can develop similar equations for other approximations resulting from the CC(P;Q) formalism, where one corrects the results of the CCSDtq/EOMCCSDtq or CCSDTq/EOMCCSDTq calculations for the missing triples (CC(t,q;3)), triples and quadruples (CC(t,q;3,4)), and quadruples (CC(q;4)).¹⁵²

The CC(t;3) method offers considerable savings in the computer effort compared to the parent CCSDT/EOMCCSDT approach, replacing the expensive, iterative, $n_o^3 n_u^5$ steps of CCSDT/EOMCCSDT by the $N_o N_u n_o^2 n_u^4$ steps of CCSDt/EOMCCSDt, equivalent to the costs of CCSD calculations multiplied by a small prefactor equal to the number of single excitations in the active space, and the noniterative $n_o^3 n_u^4$ steps similar to the costs of the CCSD(T) or CR-CC(2,3) calculations. Similar applies to disk storage, which is reduced from the $\sim n_o^3 n_u^3$ requirements

of CCSDT/EOMCCSDT, related to the need to store all triply excited amplitudes, to the much more manageable $\sim N_o N_u n_o^2 n_u^2$ requirements of CC(t;3).

So far, we have implemented the ground-state CC(t;3) method, which we have interfaced with the RHF, ROHF, and integral transformation routines available in the GAMESS package.^{202,203} Since we have not yet developed the codes that could solve the left-eigenstate CCSDt equations, which would normally be needed to determine the $\ell_{0,ijk}^{abc}(\text{CCSDt})$ amplitudes for the ground-state correction $\delta_0(t;3)$, we have introduced a few simplifications in the CC(t;3) routines exploited in this work. Thus, we have approximated the similarity-transformed Hamiltonian of CCSDt, Eq. (29), which enters the ground-state moments $\mathfrak{M}_{0,abc}^{ijk}(\text{CCSDt}) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSDt})} | \Phi \rangle$ and amplitudes $\ell_{0,ijk}^{abc}(\text{CCSDt})$, by the CCSD-like

$$\bar{H}^{(\text{CCSDt})}(2) = e^{-T_1 - T_2} H e^{T_1 + T_2} = (H e^{T_1 + T_2})_C, \quad (38)$$

in which the t_3 component of $T^{(\text{CCSDt})}$ is neglected, although—and this needs to be emphasized—the T_1 and T_2 amplitudes entering Eq. (38) originate from the true CCSDt calculations. Moreover, we have replaced $L_0^{(\text{CCSDt})}$, Eq. (34), that enters $\ell_{0,ijk}^{abc}(\text{CCSDt})$ by

$$L_0^{(\text{CCSDt})}(2) = \mathbf{1} + L_{0,1} + L_{0,2}, \quad (39)$$

in which the $l_{0,3}$ component of $L_0^{(\text{CCSDt})}$ is neglected and the one- and two-body components, $L_{0,1}$ and $L_{0,2}$, respectively, are obtained by solving the left eigenvalue problem involving $\bar{H}^{(\text{CCSDt})}(2)$, Eq. (38), in the space of single and double excitations. In this way, we account for the relaxation of the T_1 , T_2 , $L_{0,1}$, and $L_{0,2}$ amplitudes in the presence of the t_3 component of the CCSDt cluster operator $T^{(\text{CCSDt})}$, which becomes significant when t_3 is larger, as is the case in the biradical and bond breaking regions of the PES, while taking advantage of our efficient CR-CC(2,3) codes^{145,148} in calculations of the relevant $\mathfrak{M}_{0,abc}^{ijk}(\text{CCSDt})$ moments and $\ell_{0,ijk}^{abc}(\text{CCSDt})$ amplitudes. We followed a similar computational strategy in the initial numerical tests presented in Ref. 152 and summarized in Table I. Since the CC(t;3) results match the total and relative energetics of full CCSDT almost exactly, the changes in the ground-state CC(t;3) energies resulting from replacing the true similarity-transformed Hamiltonian of CCSDt by $\bar{H}^{(\text{CCSDt})}(2)$ and the true de-excitation operator $L_0^{(\text{CCSDt})}$ by $L_0^{(\text{CCSDt})}(2)$ cannot be substantial, although we will examine this aspect of CC(t;3) in the future.

III. NUMERICAL RESULTS

In order to demonstrate the benefits offered by combining the active-space CCSDt methodology with the CR-CC(2,3)-style corrections defining the CC(t;3) approach in MR situations involving biradical transition states, we applied the CC(t;3) method to the automerization of cyclobutadiene and the conrotatory and disrotatory isomerization pathways of bicyclobutane to butadiene. In each case, we used the cc-pVDZ and cc-pVTZ basis sets, employed in the earlier CC calculations for the same systems,^{35,37,64,68,78,186,187} which enabled us to perform the reference CCSDT calculation in the

former case and a number of other SRCC calculations in both cases. The CCSDT total and relative energies are particularly important, since they allow us to make judgments regarding various approximate triples SRCC approaches, including the CCSD(T), CCSD(2)_T, CR-CC(2,3), CCSDt, CCSD(T)-h, and CC(t;3) methods used in our calculations. Moreover, as shown in this work, full CCSDT provides a highly accurate description of the above isomerization reactions, so that any affordable approximate triples CC approach that matches the quality of the CCSDT results has a potential to become valuable in practice. The CCSDT/cc-pVTZ calculations for the isomerization pathways of bicyclobutane to butadiene turned out to be too expensive for us, but we managed to perform the CCSDT/cc-pVDZ calculations for this system, again needed to define the reference energy values for other SRCC triples methods, while carrying out the CCSD(T), CCSD(2)_T, CR-CC(2,3), CCSDt, CCSD(T)-h, and CC(t;3) calculations with both basis sets employed in this study. As shown, for example, in Refs. 184 and 187, the cc-pVTZ basis set is large enough to provide the results which are reasonably converged (to within a fraction of kcal/mol) with the basis as far as the relative energetics are concerned, so that the results of the CC(t;3)/cc-pVTZ calculations presented in this work are quite realistic. The CCSD, CCSD(T), CCSD(2)_T, and CR-CC(2,3) calculations were performed using the CC routines developed in Refs. 145, 148, 158, and 204, available in GAMESS, whereas the CCSDt, CCSD(T)-h, and CCSDT calculations were carried out by adopting the codes described in Ref. 168, interfaced with the GAMESS RHF/ROHF and integral transformation routines. The CC(t;3) calculations were performed with the computer programs developed in this and the earlier¹⁵² work, described in Sec. II and interfaced with GAMESS as well. In all of the SRCC calculations carried out in this study, which relied on the RHF reference, the core orbitals correlating with the 1s shells of the carbon atoms were kept frozen and the spherical components of the *d* and *f* functions were employed throughout.

A. Automerization of cyclobutadiene

We begin our discussion with the CC(t;3) and other CC results obtained for the frequently studied^{22,35,37,64,68,78,174-185} case of the automerization of cyclobutadiene (see Tables II and III). This prototypical anti-aromatic, π -electron, and highly reactive system (see

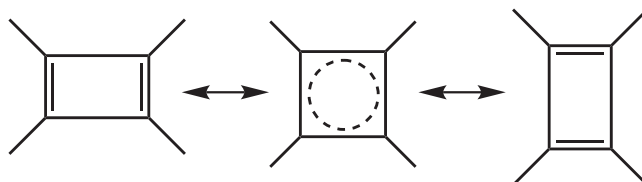


FIG. 1. Automerization of cyclobutadiene. The leftmost and rightmost structures correspond to the degenerate reactant/product minima, whereas the structure in the middle represents the transition state.

Fig. 1) represents a significant challenge for both experiment and theory. In particular, in order for a given electronic structure method to be useful in this case, it has to provide an accurate description of the strongly quasi-degenerate, biradical transition state (a square configuration in Fig. 1), which has to be balanced with the description of the nondegenerate closed-shell reactant (or product) region of the PES. According to the available experimental data, the activation energy for the automerization of cyclobutadiene falls into the 1.6–10 kcal/mol range.^{174,175} The results collected in Tables II and III clearly indicate that the requirement of producing a balanced description of the reactant/product and transition-state regions that would lead to reasonable values of the activation energy is far from trivial, particularly when the SR approaches are employed. Indeed, the most practical black-box SRCC approaches, such as CCSD, CCSD(T), Δ -CCSD(T), and CR-CC(2,3), produce activation energies that are much too high, even when one includes the best estimates of the zero-point vibrational energy (Δ ZPVE), such as that given in Ref. 184 (−2.5 kcal/mol). This is exactly the problem this paper is trying to address.

Because of the apparently MR character of the transition state, which involves, in the minimum-level description, two reference determinants corresponding to two active molecular orbitals (MOs), namely, the highest-energy occupied MO (HOMO) and the lowest-energy unoccupied MO (LUMO), and two active electrons spanning the (2,2) complete active space (CAS), which in the language of active-space CC approaches examined in this study would correspond to choosing $N_o = 1$ and $N_u = 1$, the automerization of cyclobutadiene is often regarded as a problem that must be treated with MR methods. This includes methods based on CC theory and, in fact, several MRCC approaches have already been applied to examine it. Table III provides some of the most representative examples, including SUMRCC,⁷⁻²⁶ abbreviated in

TABLE II. A comparison of various CC ground-state energies for the reactant and transition-state species defining the automerization of cyclobutadiene, based on the geometries optimized in the MR-AQCC calculations reported in Ref. 184.^a

Species	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CCSD(T)-h	CC(t;3)	CCSDT
cc-pVDZ								
Reactant	26.827	1.123	4.764	0.848	20.786	−0.371	−0.137	−154.244157
Transition state	47.979	14.198	20.080	14.636	20.274	−4.548	0.071	−154.232002
cc-pVTZ								
Reactant	36.016	0.278	4.813	0.941	30.007	−1.232	−0.141	−154.390763
Transition state	55.205	12.291	18.741	13.793	28.259	−7.298	−1.038	−154.373902

^aThe CCSDT values are total energies, in hartree. The remaining energies represent errors relative to CCSDT, in millihartree. The active space used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of the one highest-energy occupied and one lowest-energy unoccupied orbitals.

TABLE III. Purely electronic barrier heights (in kcal/mol) for the automerization of cyclobutadiene resulting from various SRCC and MRCC calculations.

Method	cc-pVDZ	cc-pVTZ
CCSD	20.9	22.6
CCSD(T)	15.8	18.1
CCSD(2) _T	17.2	19.3
CR-CC(2,3)	16.3	18.6
CCSDt	7.3	9.5
CCSD(T)-h	5.0	6.8
CC(t;3)	7.8	10.0
CCSDT	7.6	10.6
Λ CCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7
SUCCSD ^c	7.0	8.7
MkCCSD ^c	7.8	9.6
RMRCCSD ^c	10.4	13.0
SUCCSD(T) ^c	4.8	5.9
RMRCCSD(T) ^c	7.2	9.5
SUCCSD/mcscf ^c	7.2	8.9
MkCCSD/mcscf ^c	7.9	9.7
RMRCCSD/mcscf ^c	9.5	11.4
SUCCSD(T)/mcscf ^c	5.7	7.2
RMRCCSD(T)/mcscf ^c	5.9	7.5
TD MRCCSD(T) ^d	6.6	
MR BWCCSD(a.c.) ^e	6.5	7.6
MR BWCCSD(i.c.) ^e	6.2	7.4
MR BWCCSD(T)(a.c.) ^e	6.1	7.0
MR BWCCSD(T)(i.c.) ^e	5.7	6.8
MR MkCCSD ^e	7.8	9.1
MR MkCCSD(T) ^e	7.8	8.9
MRAQCC/SS-CASSCF ^f	7.7	8.9
MRAQCC/SA-2-CASSCF ^f	7.3	8.4
DIP-EOM-CCSD ^a	8.3	10.7
SS-EOM-CCSD[+2] ^g	8.3	9.5
Experimental range ^h	1.6–10	
Δ ZPVE ⁱ	-2.5	

^aFrom Ref. 78.^bFrom Ref. 64.^cFrom Ref. 37.^dFrom Ref. 22, using a split-valence[3s2p1d/1s] basis set.^eFrom Ref. 35; “a.c.” stands for the *a posteriori* size-extensivity correction and “i.c.” for the iterative one.^fFrom Ref. 184.^gFrom Ref. 68.^hFrom Ref. 174.ⁱ Δ ZPVE is the zero-point vibrational energy correction, as estimated in Ref. 184.

Table III, following Refs. 22 and 37 where the calculations of this type were reported, as SUCC (Ref. 37) and TD MRCC,²² Mukherjee’s SSMRCC,^{27,28} designated in Table III, following Refs. 35 and 37 where such calculations were performed, by MR MkCC or MkCC, Brillouin-Wigner MRCC,^{29–32} abbreviated in Table III, following Ref. 35 where such calculations were carried out, as MR BWCC, the internally contracted SSMRCC approach employing elements of EOMCC exploited in Ref. 68, designated in Ref. 68 and Table III by SS-EOM-CCSD[+2], and the BCCC theory,⁶³ abbreviated in Ref. 64 where such calculations were reported, as CAS-BCCC4. In addition to the purely MRCC approaches,

a variety of hybrid CC methods mixing the SR and MR concepts, including the MRCI-corrected RMRC theory^{79–81} and the CASSCF-based TCC formalism,^{76–78} have been used to examine the automerization of cyclobutadiene.^{37,78} Last, but not least, the automerization of cyclobutadiene has been examined⁷⁸ with the doubly ionized (DIP) EOMCC approach,^{100–102} which can be regarded as an “easy way” of introducing MR concepts into the CC theory,¹⁰² and the MR average-quadratic CC (MR-AQCC) method,¹⁸⁴ which is a MRCI-like diagonalization scheme designed using elements of CC to approximately restore size extensivity.^{205,206}

Not surprisingly, several of the above MRCC-level studies report information about the poorly performing SRCC methods, such as CCSD,^{22,37,78} CCSD(T),^{22,37,78} Λ -CCSD(T),⁷⁸ and CR-CCSD(T),⁷⁸ often to argue the need for a MR treatment of the automerization of cyclobutadiene. It is clear, however, from a comprehensive study involving a variety of SRCC and MRCC methods by Balková and Bartlett²² that one can obtain a reasonable description of the activation energy characterizing the automerization of cyclobutadiene with full CCSDT. It is apparent from Table III that the activation energies resulting from the CCSDT calculations are not only within the experimental range but also in almost perfect agreement (to within 1 kcal/mol or so) with the results of the best MRCC or MRCC-level calculations, such as those performed using the MkCCSD(T),³⁵ CAS-BCCC4,⁶⁴ RMRCCSD(T),³⁷ MRAQCC,¹⁸⁴ and SS-EOM-CCSD[+2] (Ref. 68) approaches, to mention a few examples. The only problem with CCSDT is that it is too expensive for the majority of applications. An approximate treatment of triples that would reduce the costs of the CCSDT calculations, while preserving the accuracy of CCSDT for both the relative and total energies, would clearly be useful in this case. We show that CC(t;3) is such an approach.

The information about the performance of a variety of SRCC approaches, including our own CCSD, CCSD(T), CCSD(2)_T, CR-CC(2,3), CCSDt, CCSD(T)-h, CC(t;3), and CCSDT calculations and the Λ -CCSD(T) calculations reported in Ref. 78, can be found in Tables II (total energies) and III (electronic barrier heights). Since our main objective is to make comparisons with full CCSDT, regarded in the present study as a benchmark and parent method for CCSD(T), CCSD(2)_T, CR-CC(2,3), Λ -CCSD(T), CCSDt, CCSD(T)-h, and CC(t;3), which also provides a reasonable description, and in analogy to some of the earlier papers on the same topic, we rely on the reactant/product and transition-state geometries optimized elsewhere. As in Ref. 64, we use the MRAQCC geometries reported in Ref. 184.

It is clear from Table II that the main reason for the failure of methods employing the CCSD values of T_1 and T_2 , when determining the *a posteriori* corrections due to triples, such as CCSD(T), or its newer CCSD(2)_T, CR-CC(2,3), and Λ -CCSD(T) analogs, is the neglect of the coupling between the T_3 clusters and their lower-order T_1 and T_2 counterparts, which is present in full CCSDT but absent in the noniterative methods such as CCSD(T). This results in the rather large, $\sim 12 - 20$ millihartree, errors relative to the CCSDT energies in the quasi-degenerate transition-state region that do not balance the much smaller errors, ranging from less than

1 millihartree in the case of CCSD(T) and CR-CC(2,3) to about 5 millihartree in the case of CCSD(2)_T, in the reactant/product closed-shell regions.

The CCSDt approach works in a different way. Like full CCSDT, it couples the T_1 and T_2 clusters with their triply excited t_3 counterparts, selected via active orbitals, as in Eq. (3), adjusting their values accordingly when solving the CCSDt equations, which greatly helps the relative energetics, but the selection of triples characterizing CCSDt may lead to substantial errors in total energies relative to the corresponding full CCSDT energies. As shown in Tables II and III, the CCSDt calculations employing one active occupied and one active unoccupied orbitals relevant to the problem of the automerization of cyclobutadiene, corresponding to HOMO and LUMO ($N_o = 1$ and $N_u = 1$), provide an excellent description of the barrier heights, which agree with those obtained with full CCSDT to within 0.3 kcal/mol in the cc-pVDZ case and 1.1 kcal/mol in the case of cc-pVTZ, but it is clear, when examining Table II, that these small differences between the CCSDt and CCSDT activation energies are a result of the cancellation of the uncomfortably large errors due to the triple excitations missing in the CCSDt calculations. The differences between the CCSDt and CCSDT total energies, although almost independent of the nuclear geometry, are on the order of 20–21 millihartree in the case of the cc-pVDZ basis set and approximately 28–30 millihartree in the cc-pVTZ case. In other words, quite a bit of information about triples, particularly of the dynamical type, is still missing when the CCSDt approach relying on small number of active orbitals is employed. We could increase the number of active orbitals in the CCSDt calculations to bring the resulting total energies closer to their CCSDT values, but this would make the CCSDt calculations a lot more expensive.

The CCSD(T)-h approach, which corrects the CCSDt energies for the missing triples using the conventional (T) correction of CCSD(T), improves the above situation but not as effectively as CC(t;3). The CCSD(T)-h calculations bring the total energies at the reactant/product and transition-state structures to a better agreement with full CCSDT than in the CCSDt case, and improve the CCSD(T), CCSD(2)_T, and CR-CC(2,3) energies in the transition-state region at the same time, but the total and activation energies obtained with CCSD(T)-h, shown in Tables II and III, are not as accurate as those produced by CC(t;3). Indeed, the differences between the CCSD(T)-h and CCSDT energies in the transition-state region are -4.548 millihartree, when the cc-pVDZ basis set is used, and -7.298 millihartree, when the cc-pVTZ basis is employed, as compared to only 0.071 and -1.038 millihartree, respectively, obtained with CC(t;3). This is a consequence of adopting a robust, CR-CC(2,3)-style, form of the triples correction in the CC(t;3) considerations instead of the (T) correction of CCSD(T) exploited in CCSD(T)-h. It is possible that the activation energy lowering when going from TCCSD to TCCSD(T), as reported in Ref. 78, by almost 5 kcal/mol in the cc-pVDZ case and by nearly 6 kcal/mol in the case of the cc-pVTZ basis set, is too large as well because of the use of the (T)-style correction in the TCCSD(T) design.

Unlike CC(t;3), the CCSD(T)-h approach does not provide a uniformly accurate description of the stationary point

energetics, since the differences between the CCSD(T)-h and CCSDT energies at the reactant/product geometries, which are -0.371 millihartree in the cc-pVDZ case and -1.232 millihartree in the case of the cc-pVTZ basis, are much smaller than the corresponding differences in the transition-state region. This affects the quality of the activation energies resulting from the CCSD(T)-h calculations, which instead of going up relative to CCSDt toward the corresponding CCSDT barrier heights, go down, by 2.3 kcal/mol when the cc-pVDZ basis set is employed and 2.7 kcal/mol when the cc-pVTZ basis is used. As in the case of CCSDt, we could try to improve the CCSD(T)-h results by increasing the number of active orbitals used in the underlying CCSDt calculations, but this would again diminish the computational advantages of CCSD(T)-h when compared to the parent full CCSDT approach. The CC(t;3) method addresses all of these concerns by providing a highly and uniformly accurate description of the reactant/product and transition-state regions that guarantees that the CC(t;3) total and activation energies match those resulting from the full CCSDT calculations almost perfectly in spite of the use of the very small active space in the underlying CCSDt calculations. As already mentioned, the CC(t;3) method provides very small errors relative to full CCSDT in the total energies characterizing the transition-state region. The errors in the reactant/product region, which are on the order of 0.1 millihartree, are very small as well. As a result, the CC(t;3) calculations bring the CCSDt activation energies closer to their CCSDT counterparts, which is a desired behavior. Indeed, the CC(t;3) values of the barrier heights, of 7.8 kcal/mol in the case of the cc-pVDZ basis set and 10.0 kcal/mol, when the cc-pVTZ basis set is used, are in excellent agreement with the corresponding CCSDT activation energies of 7.6 and 10.6 kcal/mol, respectively. After correcting the CC(t;3)/cc-pVTZ electronic barrier height for the ZPVE contributions, estimated in Ref. 184 at -2.5 kcal/mol, we obtain 7.5 kcal/mol, in almost perfect agreement with the best MRCC data, which place it around 6–7 kcal/mol when the MkCCSD(T), CAS-BCCC4, RMRCCSD(T), MRAQCC, and SS-EOM-CCSD[+2] calculations are performed.

B. Isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene

Our second example is the pericyclic rearrangement of bicyclo[1.1.0]butane (*bicbut*) to *trans*-buta-1,3-diene (*t-but*). The early experimental studies of the *bicbut*→*t-but* isomerization^{190–194} suggested that this process proceeds by concerted conrotatory movement of the methylene groups,^{193,194} in agreement with the Woodward-Hoffman symmetry rules.²⁰⁷ Computational studies using the MR approaches of the MRMBPT (Refs. 186, 188, and 198) and MRCI (Ref. 198) types, the SRCC methods of the CR-CC type, including CR-CCSD(T) and CR-CC(2,3),^{186,187} and, most recently, the ACSE (Ref. 188) and DMC (Ref. 189) methodologies, have all confirmed this, while demonstrating that near the end the reaction pathway passes through the *gauche*-buta-1,3-diene intermediate (abbreviated as *g-but*) before reaching the final *t-but* configuration.^{186,187,189,198} Theoretical studies have also considered the concerted

disrotatory^{186–189,197,198} and nonconcerted^{196,198} pathways, finding the concerted disrotatory transition state (abbreviated as *dis_TS*) to be $\sim 15 - 25$ kcal/mol higher in energy than the conrotatory transition state (abbreviated as *con_TS*), and placing the nonconcerted pathway even higher than that. Thus, the current consensus, reconfirmed by the CCSDt, CC(t;3), and CCSDT calculations performed in this work, is that the *bicbut* \rightarrow *t-but* isomerization proceeds along the conrotatory concerted path, characterized, according to the available experimental data, by the activation enthalpy of 40.6 ± 2.5 kcal/mol,¹⁹⁰ and that both concerted pathways, after passing through the corresponding conrotatory and disrotatory transition states, *con_TS* and *dis_TS*, respectively, converge at the local minimum defining the intermediate *g-but* configuration. The *g-but* intermediate isomerizes via a low-energy rotational barrier, defined by the transition-state *gt_TS* structure, before the *t-but* product is finally reached.

The conrotatory and disrotatory concerted pathways for the *bicbut* \rightarrow *t-but* isomerization, as described above, are shown in Fig. 2. The corresponding numerical data relevant to the objectives of the present work, including the total electronic and ZPVE-corrected activation energies (i.e., enthalpies at 0 K) obtained in the CCSDt, CC(t;3), and full CCSDT calculations, as well as the corresponding CCSD, CCSD(T), CCSD(2)_T, and CR-CC(2,3) results, can be found in Tables IV and V. As in the case of the automerization of cyclobutadiene, we used the cc-pVDZ (all methods) and cc-pVTZ (all methods but CCSDT) basis sets. We compare the SRCC calculations among themselves, with the full CCSDT energies serving as benchmark values, and with the ZPVE-corrected activation energies resulting from the most recent optimized MR DMC (OMR-DMC) calculations based on the CASSCF(10,10)-type guide functions,¹⁸⁹ focusing on the highest-level OMR3-DMC data. We also compare our CC(t;3) results with the recent ACSE calculations reported in Ref. 188, which are in good agreement with the MRMBPT (Refs. 186, 188, and 198) and MRCI (Ref. 198) calculations (listed in Table V as well), but in some disagreement with our previously reported^{186,187} CR-CC(2,3) data, questioning the accuracy of CR-CC(2,3) in describing the disrotatory pathway. As in our earlier CR-CC studies,^{186,187} the geometries of the stationary points defining the conrotatory and disrotatory pathways of the *bicbut* \rightarrow *t-but* isomerization and the corresponding ZPVE values were taken from the CASSCF(10,10)

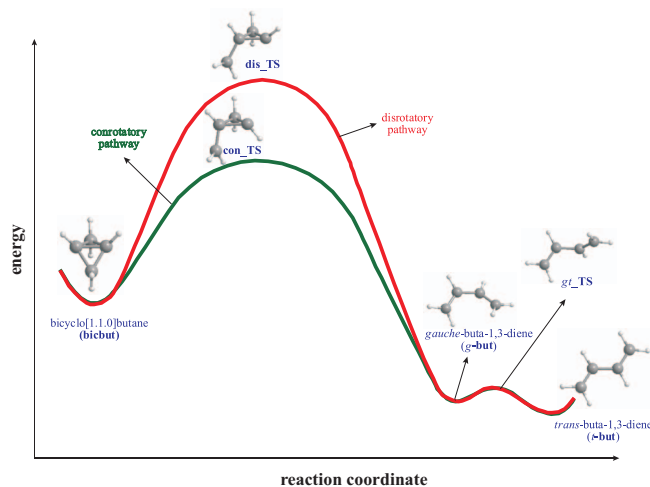


FIG. 2. Schematic representation of the conrotatory and disrotatory pathways describing the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene.

calculations performed in Ref. 186, employing five doubly occupied MOs and the corresponding five antibonding MOs involved in the bond rearrangements characterizing these pathways. The OMR3-DMC calculations reported in Ref. 189, used in this work to judge the accuracy of other methods in determining relative energies, utilized the same geometries and ZPVEs. The ACSE calculations reported in Ref. 188 utilized the CASSCF(10,10) geometries and ZPVE values as well, but they were obtained independently. To be consistent with the choice of the active space in the above CASSCF calculations, the active orbitals used in obtaining the CCSDt, CCSD(T)-h, and CC(t;3) results included the $N_o = 5$ highest occupied and $N_u = 5$ lowest unoccupied MOs.

As emphasized in the Introduction, the *bicbut* \rightarrow *t-but* isomerization creates a number of challenges for theory. This is particularly true in the case of the higher-energy disrotatory pathway characterized by the strongly biradical transition-state *dis_TS*. According to Ref. 186, the *dis_TS* structure has a $\sim 90\%$ biradical character, as opposed to only $\sim 24\%$ for the conrotatory transition state, and less than 10% for the remaining stationary points along the lowest two isomerization pathways shown in Fig. 2. As a result and as demonstrated in Ref. 186 (see, also, Table V), the conventional CCSD(T) approach fails, placing the disrotatory transition state about

TABLE IV. A comparison of various CC ground-state energies for the stationary points that define the conrotatory and disrotatory pathways characterizing the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene, obtained in the calculations with the cc-pVDZ basis set.^a

Species ^b	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3) ^c	CCSDt	CCSD(T)-h	CC(t;3)	CCSDT
bicbut	21.863	0.450	3.107	0.134	14.427	-0.200	-0.263	-155.493418
con_TS	30.130	0.573	5.305	0.968	14.024	-0.826	-0.418	-155.425760
dis_TS	50.760	-69.648	14.052	7.345	11.487	-5.918	-0.491	-155.395697
g-but	23.259	1.009	3.786	0.794	11.377	-0.183	-0.065	-155.533880
gt_TS	22.836	0.964	3.658	0.782	11.402	-0.139	-0.028	-155.528927
t-but	23.396	1.036	3.837	0.840	10.963	-0.192	-0.056	-155.538628

^aThe CCSDT values are total energies, in hartree. The remaining energies represent errors relative to CCSDT, in millihartree. The active spaces used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of the $N_o = 5$ highest-energy occupied and $N_u = 5$ lowest-energy unoccupied orbitals.

^bGeometries of all species, as optimized in the CASSCF(10,10)/cc-pVDZ calculations, were taken from Ref. 186.

^cFrom Ref. 187.

TABLE V. The electronic energies corrected for the zero-point vibrational energies taken from Ref. 186 (i.e., enthalpies at 0 K) of the conrotatory and disrotatory transition states, *con_TS* and *dis_TS*, respectively, the *g-but* intermediate, the transition state connecting *g-but* and *t-but* (*gt_TS*), and the *t-but* final product, relative to the *bicbut* reactant, at several levels of theory.

Method	con_TS	dis_TS	g-but	gt_TS	t-but
cc-pVDZ					
CCSD	45.0	75.7	-25.6	-23.1	-28.5
CCSD(T)	39.9	13.5	-26.1	-23.4	-29.0
CCSD(2) _T	43.9	68.3	-25.0	-22.0	-28.0
CR-CC(2,3) ^a	40.3	62.1	-26.1	-23.3	-29.0
CCSDt	39.5	55.7	-28.4	-25.6	-31.6
CCSD(T)-h	39.4	53.9	-26.5	-23.7	-29.4
CC(t;3)	39.7	57.4	-26.4	-23.6	-29.3
CCSDT	39.8	57.5	-26.5	-23.7	-29.4
MCQDPT2 ^b	37.0	53.7	-26.4	-23.4	-29.4
cc-pVTZ					
CCSD	45.6	78.9	-24.8	-22.2	-27.6
CCSD(T) ^a	40.4	21.8	-25.1	-22.3	-28.0
CCSD(2) _T	41.7	67.8	-25.0	-22.3	-27.9
CR-CC(2,3) ^{a,b}	41.1	66.1	-24.9	-22.1	-27.9
CCSDt	40.1	59.0	-27.2	-25.3	-31.1
CCSD(T)-h	39.7	53.6	-25.4	-22.6	-28.4
CC(t;3)	40.2	60.1	-25.3	-22.6	-28.3
MRMP2/6-31G(d) ^c	38.0	54.0	-26.6		
MRMP2/6-311G(d,p) ^c	35.7	52.2	-27.0		
CASPT2/6-31G(d) ^d	41.5	56.3	-23.2		-26.0
MRCI(Q)/6-31G(d) ^d	41.5	56.7	-29.8		-32.4
ACSE/6-31G(d) ^c	41.8	56.4	-24.2		
ACSE/6-311G(d,p) ^c	41.2	55.7	-23.8		
OMR3-DMC ^e	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)
Experiment	40.6 ± 2.5 ^f				-25.9 ± 0.4 ^g

^aFrom Ref. 187.

^bFrom Ref. 186.

^cFrom Ref. 188.

^dFrom Ref. 198.

^eFrom Ref. 189.

^fFrom Ref. 190.

^gThe reaction enthalpy at 298 K based on the enthalpies of formation of bicyclo[1.1.0]butane and buta-1,3-diene reported in Ref. 195.

20 kcal/mol below the conrotatory one. The MRMBPT approaches of the CASPT2,^{208,209} MRMP2,^{210,211} and MCQDPT2 (Refs. 212 and 213) types, used in Refs. 186, 188, and 198, the MRCI(Q) method^{214,215} used in Ref. 198, and the CR-CC(2,3) approach exploited in our earlier work,^{186,187} as well as the ACSE (Ref. 188) and DMC (Ref. 189) calculations restore the correct pathway ordering, while providing, in most cases, an accurate description of the conrotatory path (see Table V), but, as noted in the Introduction, claims have been made in the literature regarding the accuracy of the CR-CC(2,3) description of the disrotatory transition state,¹⁸⁸ which seems higher in energy than the available CASPT2,^{188,198} MRMP2,¹⁸⁸ MCQDPT2,¹⁸⁶ MRCI(Q),¹⁹⁸ and ACSE (Ref. 188) data by about 10 kcal/mol.

Normally, it would be hard to reconcile such differences in the absence of the experimental information, which is only available for the lowest-energy conrotatory pathway (cf., e.g., Table V). However, Berner and Lüchow have recently published the definitive and well-converged OMR-DMC results for the stationary point energetics of the conrotatory

and disrotatory pathways,¹⁸⁹ with the aforementioned OMR3-DMC calculations, summarized in Table V, representing the highest-level results. We use their results as well as our own CC(t;3) calculations, which almost perfectly reproduce the total and relative energetics of the high-level full CCSDT approach, when the cc-pVDZ basis set is employed, and the relative energetics of the OMR3-DMC method of Berner and Lüchow, when the cc-pVTZ basis set is used in the CC(t;3) calculations, to claim that while CR-CC(2,3) overestimates the activation energy characterizing the biradical disrotatory transition state by about 5–7 kcal/mol, the recent ACSE and the previously reported MRMBPT and MRCI activation energies characterizing the same transition state are somewhat too low.

Indeed, as shown in Table IV, the CC(t;3) approach yields a uniformly and highly accurate description of both pathways, reproducing the corresponding full CCSDT energies at the six stationary points defining the conrotatory and disrotatory *bicbut*→*t-but* isomerization paths to within less than 0.5 millihartree, when the cc-pVDZ basis set is used. This is an outstanding result, particularly when compared with other SRCC methods with an approximate treatment of triple excitations, including CCSD(2)_T, CR-CC(2,3), CCSDt, and CCSD(T)-h, which successfully address an issue of the incorrect energy ordering of the conrotatory and disrotatory transition states by the CCSD(T) approach but are not as effective in capturing the relevant correlation effects as CC(t;3). In particular, the CR-CC(2,3) method works very well in the PES regions characterized by the small to moderate biradical character, represented by the *bicbut*, *con_TS*, *g-but*, *gt_TS*, and *t-but* structures, reducing the ~3–5 millihartree errors relative to CCSDT obtained in the corresponding CCSD(2)_T calculations to less than 1 millihartree, but the ~7 millihartree difference between the CR-CC(2,3) and CCSDT energies at the *dis_TS* geometry, although much smaller than ~14 millihartree obtained with CCSD(2)_T, is far from the CC(t;3) level. It is exactly this difference that makes the CR-CC(2,3) estimate of the disrotatory activation energy too high, by almost 5 kcal/mol relative to the corresponding full CCSDT energy when the cc-pVDZ basis set is employed, and by about 7 kcal/mol relative to OMR3-DMC, when the CR-CC(2,3)/cc-pVTZ calculations are performed (see Table V; as already pointed out, the use of basis sets larger than cc-pVTZ has very small effect on the relative energetics of the stationary points characterizing the conrotatory and disrotatory pathways of the *bicbut*→*t-but* isomerization^{186,187}).

As shown in Table V, the active-space CCSDt calculations provide the relative energetics of both *bicbut*→*t-but* isomerization pathways examined here, which is in very good agreement with the full CCSDT data, when the cc-pVDZ basis set is examined, and with the OMR3-DMC results, when the cc-pVTZ basis set is used, improving the CR-CC(2,3) description of the disrotatory transition state, but this is a result of the cancellation of the rather large errors due to the triple excitations missing in the CCSDt considerations, which range from 10.963 to 14.427 millihartree in the cc-pVDZ case (see Table IV). Although these large errors in the calculated total energies cancel out quite well, often to within a fraction of kcal/mol, there are a few cases, such as the *g-but*, *gt_TS*, and

t-but structures, where the relative energies resulting from the CCSDt/cc-pVDZ and CCSDT/cc-pVDZ or CCSDt/cc-pVTZ and OMR3-DMC calculations differ by about 2–3 kcal/mol. Clearly, one cannot expect that the active-space CC methods, such as CCSDt, using smaller numbers of active orbitals, will always guarantee perfect error cancellation in determining the relative energetics, when the dynamical correlation effects due to neglected excitations (missing triples in the CCSDt case) exceed 10 millihartree. One can, of course, address this concern, at the cost of making the CCSDt calculations more expensive, by using larger numbers of active orbitals, but our preferred solution is to correct the CCSDt energies, obtained with smaller numbers of active orbitals, for the missing triples using the CC(t;3) corrections.

As already explained, the CC(t;3)/cc-pVDZ approach using only five highest-energy occupied MOs and five lowest-energy unoccupied MOs in the underlying CCSDt calculations reproduces the corresponding CCSDT/cc-pVDZ total energies at all six stationary points defining the conrotatory and disrotatory pathways of the *bicbut*→*t-but* isomerization to within 0.5 millihartree. As a result and as shown in Table V, the relative energies characterizing all these points, obtained in the CC(t;3) and CCSDT calculations with the cc-pVDZ basis set, agree to within 0.1 kcal/mol. For comparison, the analogous attempt to improve the total and relative energetics of CCSDt via the CCSD(T)-h approach produces errors relative to CCSDT that are in some cases much larger. This is particularly true in the case of the disrotatory transition state, where the difference between the CCSD(T)-h and CCSDT energies obtained with the cc-pVDZ basis set is –5.918 millihartree, as opposed to only –0.491 millihartree obtained with CC(t;3) (see Table IV). In consequence, the CCSD(T)-h approach, instead of bringing the CCSDt result for the disrotatory activation barrier closer to the corresponding CCSDT value, changes the CCSDt energy in an opposite direction, resulting in a 3.6 kcal/mol difference between the disrotatory activation barriers obtained in the CCSDT and CCSD(T)-h calculations with the cc-pVDZ basis set. The CC(t;3) method, which relies on a more robust form of the correction due to triples missing in CCSDt, when compared to CCSD(T)-h, reduces this difference to 0.1 kcal/mol. The same applies to comparisons of the CCSD(T)-h and CC(t;3) relative energies, resulting from the calculations with the larger cc-pVTZ basis set, with the OMR3-DMC data. Again, as shown in Table V, the CCSD(T)-h approach, instead of bringing the CCSDt result for the ZPVE-corrected disrotatory activation barrier of 59.0 kcal/mol closer to the OMR3-DMC value of 58.6(5) kcal/mol, moves it away from the latter value, to 53.6 kcal/mol. CC(t;3) does not do it, producing 60.1 kcal/mol, in excellent agreement with OMR3-DMC.

In general, the CC(t;3)/cc-pVTZ values of the relative energies characterizing the stationary points along the conrotatory and disrotatory pathways of the *bicbut*→*t-but* isomerization agree with the OMR3-DMC calculations of Ref. 189 to within 0.1–0.4 kcal/mol for the *con_TS*, *g-but*, *gt_TS*, and *t-but* points and 1.5 kcal/mol for the challenging *dis_TS* structure. No other calculation performed to date has accomplished such accuracy level. For example, the most accurate ACSE/6-311G(d,p) calculations reported in Ref. 188

produce errors relative to OMR3-DMC that range from 0.8 kcal/mol in the case of the *con_TS* structure to 2.9 kcal/mol in the *dis_TS* case. Similar errors are obtained when the previously reported^{186,188,198} MRMBPT and MRCI data are analyzed (see Table V). Our earlier CR-CC(2,3) studies using the cc-pVTZ and cc-pVQZ bases, and CBS extrapolations¹⁸⁷ suggest that the CC(t;3)/cc-pVTZ relative energies are within 1 kcal/mol from their CBS analogs.

It is also encouraging to see the agreement between our best CC(t;3)/cc-pVTZ and the available experimental data. As shown in Table V, the activation enthalpy resulting from the CC(t;3)/cc-pVTZ calculations corresponding to the conrotatory transition state is 40.2 kcal/mol, in excellent agreement with the experimental value of 40.6 ± 2.5 kcal/mol. Although the experimental error bars are relatively large in this case, making all of the approximate triples SRCC methods examined in this work look reasonable, CC(t;3) is the only method among the approximate triples SRCC approaches examined here that provides an excellent agreement with both the total and relative energies resulting from the full CCSDT calculations, independent of the stationary point on the PES. The CC(t;3)/cc-pVTZ value of the enthalpy of isomerization of bicyclo[1.1.0]butane to buta-1,3-diene, the experimental estimate of which is -25.9 ± 0.4 kcal/mol,¹⁹⁵ -28.3 kcal/mol, when the *t-but* structure is used as a product, and -25.3 kcal/mol, when the nearly isoenergetic *g-but* rotamer is used instead. Both of these results are very accurate. They agree with the corresponding OMR3-DMC data to within the numerical accuracy of the OMR3-DMC calculations.

IV. CONCLUSIONS

The conventional, MBPT-based, noniterative SRCC methods, including CCSD(T) and its various higher-order and excited-state, EOMCC-based, extensions, have difficulties with handling MR electronic states. The newer generations of such methods, including Λ -CCSD(T), CCSD(2)_T, and CR-CC(2,3), and their higher-order and excited-state analogs, alleviate some of these problems, but all noniterative SRCC/EOMCC methods have one fundamental flaw, namely, they always rely on a specific, *a priori*-defined SRCC (e.g., CCSD) or EOMCC (e.g., EOMCCSD) calculation, so there is no mechanism to adjust the lower-order cluster components, such as T_1 and T_2 , in the presence of the larger T_n components with $n \geq 3$ that characterize systems with stronger nondynamical electron correlation effects. By neglecting the coupling of the higher-order T_n components with $n \geq 3$ with their lower-order T_1 and T_2 counterparts, the noniterative SRCC methods, even those belonging to the more robust Λ -CCSD(T), CCSD(2), and CR-CC categories, may not be flexible enough to provide an accurate description of certain classes of chemical reaction profiles involving biradical transition states. The active-space SRCC approaches, such as CCSDt, CCSDtq, etc., which describe the coupling of the higher-order T_n components with $n \geq 3$, selected with the help of active orbitals, with the lower-order T_1 and T_2 clusters, provide reasonable relative energetics in many biradical cases, but they usually fail to provide accurate total energies relative to the parent SRCC approximations, such as CCSDT, CCSDTQ, etc., due

to the neglect of higher-order T_n components that do not involve active orbitals. These kinds of problems are often used to advocate a genuine MR (e.g., MRCC) treatment.

This paper has discussed a different and, in our view, simpler solution by exploring the recently suggested $CC(P;Q)$ hierarchy and the underlying Flex-MMCC formalism that enable one to contemplate a variety of novel low-cost SRCC and EOMCC schemes, such as $CC(t;3)$. In the ground-state $CC(t;3)$ method, the energies obtained in the active-space CCSDt calculations are corrected for the effects of triples missing in the CCSDt considerations using the robust noniterative corrections derived from the $CC(P;Q)$ expansions, which are similar to those defining the existing CR-CC(2,3) theory. We have discussed the key elements of the $CC(P;Q)$ and $CC(t;3)$ approaches and, by examining the automerization of cyclobutadiene and the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene, which involve biradical transition states and which pose serious challenges to the CCSD(T), Λ -CCSD(T), CCSD(2)_T, and CR-CC(2,3) methods, demonstrated that one can recover the total and relative energies of full CCSDT to within less than 1 millihartree and a fraction of kcal/mol, respectively, with a relatively small effort compared to CCSDT. For comparison, the CCSD(T), CCSD(2)_T, CR-CC(2,3), and similar levels produce substantial errors in the description of the transition-state energies, on the order of 10 millihartree for total energies and several kcal/mol for relative energies. We have also demonstrated that the $CC(t;3)$ approach improves the results of the active-space CCSDt calculations, which produce accurate barrier heights in situations involving biradical transition states, but which are also characterized by rather substantial errors, on the order of 10–30 millihartree, in the calculated total energies relative to CCSDT. The $CC(t;3)$ -style corrections to the CCSDt energies reduce these errors to less than 1 millihartree, further improving the relative energetics. We have shown that the $CC(t;3)$ approach, which employs the robust corrections derived from the $CC(P;Q)$ considerations, resembling the triples corrections of CR-CC(2,3), is a lot more effective in capturing the effects due to the triple excitations missing in CCSDt than the CCSD(T)-h method that attempts to do the same through the use of the conventional (T) expressions. In fact, the conventional (T) correction applied within the CCSD(T)-h framework can worsen the CCSDt results, when the automerization of cyclobutadiene and the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene are examined, moving them away from the corresponding CCSDT energies.

Finally, based on the excellent agreement between the $CC(t;3)$ and CCSDT total and relative energies obtained with the cc-pVDZ basis set, and the $CC(t;3)/cc$ -pVTZ relative energies obtained in this work and their OMR3-DMC counterparts obtained in Ref. 189, we have resolved the issues raised in Ref. 188 related to the relative performance of the ACSE and CR-CC(2,3) approaches in describing the concerted disrotatory pathway of the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene. We have provided evidence that while CR-CC(2,3) overestimates the activation energy characterizing the biradical disrotatory transition state of this isomerization, the ACSE and the previously reported MRMBPT and

MRCI activation energies characterizing the same transition state are somewhat too low.

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