

Merging Active-Space and Renormalized Coupled-Cluster Methods via the CC($P;Q$) Formalism, with Benchmark Calculations for Singlet–Triplet Gaps in Biradical Systems

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ABSTRACT: We have recently developed a flexible form of the method of moments of coupled-cluster (CC) equations and the CC($P;Q$) hierarchy, which enable one to correct the CC and equation-of-motion CC energies obtained with unconventional truncations in the cluster and excitation operators [Shen, J.; Piecuch, P. *Chem. Phys.* **2012**, 401, 180; *J. Chem. Phys.* **2012**, 136, 144104]. One of the CC($P;Q$) methods is a novel hybrid scheme, abbreviated as CC($t;3$), in which the results of CC calculations with singles, doubles, and active-space triples, termed CCSD t , are corrected for the triple excitations missing in CCSD t using the expressions that are reminiscent of the completely renormalized (CR) CC approach known as CR-CC(2,3). We demonstrate that the total electronic energies of the lowest singlet and triplet states, and the singlet–triplet gaps in biradical systems, including methylene, (HFH) $^-$, and trimethylenemethane, resulting from the CC($t;3$) calculations agree with those obtained with the full CC approach with singles, doubles, and triples to within fractions of a millihartree, improving the results of the noniterative triples CCSD(T), CCSD(2) $_T$, and CR-CC(2,3) and hybrid CCSD(T)-h calculations, and competing with the best multireference CC data.

1. INTRODUCTION

It is often stated that molecular problems involving bond breaking and biradicals require a genuine multireference (MR) description. This, in particular, applies to methods based on the exponential wave function ansatz of coupled-cluster (CC) theory^{1–4} (see refs 5 and 6 for selected reviews). Indeed, the standard single-reference (SR) CC approaches, such as the CC method with singles and doubles (CCSD)^{7,8} and the popular CCSD(T) approximation,⁹ or the predecessor of CCSD(T) abbreviated as CCSD+ T (CCSD) or CCSD[T],¹⁰ in which one corrects the CCSD energy for the dominant effects due to triply excited clusters, have difficulties with capturing nondynamical electron correlations characterizing reaction profiles involving bond breaking and biradicals. This includes applications involving singlet–triplet gaps in biradical systems examined in this work, in which one has to provide an accurate and balanced description of the quasi-degenerate low-spin and high-spin electronic states, where the former state is poorly represented by a single Slater determinant.

Unfortunately, even the most successful MR or multi-configurational (MC) methods that are designed to capture the dominant dynamical and nondynamical correlation effects, including, for example, the widely used MR many-body perturbation theory (MBPT) approaches of the CASPT2,^{11,12} MRMP2,^{13,14} and MCQDPT2^{15,16} types (cf. refs 17 and 18 for review information), or the equally popular internally contracted MR configuration interaction (CI) approach with the quasi-degenerate Davidson corrections, abbreviated as MRCI(Q),^{19,20} and other MRCI-type diagonalization techniques (see ref 18 for a recent review), which typically employ the complete-active-space self-consistent-field (CASSCF) references,²¹ are not without limitations. For example, the low-order MRMBPT methods may encounter problems with balancing dynamical and nondynamical correlation effects in studies of reaction pathways characterized by a varying degree of biradical character as a

consequence of difficulties with determining the adequate and computationally manageable active spaces (cf., e.g., refs 22–24). The MRCI-type methodologies are more robust in this regard, but they are often prohibitively expensive and lack size extensivity (the “diagonalize-then-perturb” MRMBPT methods, including, for example, CASPT2, are not size extensive either²⁵). The situation with the multitude of MRCC methodologies formulated to date is even more complex, and we refer the reader to the recent analyses of the topic, such as refs 26 and 27, for a detailed discussion. Here, we only mention that one can use the genuine, state-universal (SU)^{28–51} and state-specific (SS)^{52–62} MRCC approaches that exploit multiple cluster operators, multiple Fermi vacua, and the Jeziorski–Monkhorst wave function ansatz²⁸ (cf. refs 63–82 for representative recent studies), but there also are SSMRCC methods that do not rely on this ansatz. Among them are the active-space CC approaches exploited in this work that utilize the SRCC formalism^{83–103} (see ref 104 for a recent review), the related CASC schemes,^{105–107} the block-correlated CC (BCCC)^{108,109} theories, and the internally contracted MRCC approaches.^{110–116} One can also extend the applicability of SRCC methods to MR situations by mixing the SRCC and non-CC (e.g., MRCI and CASSCF) ideas,^{117–127} with the reduced MRCC (RMRCC)^{125–127} and tailored CC (TCC) schemes^{122–124} being particularly promising. Finally, if one is interested in open-shell systems obtained by adding electron(s) to or removing electron(s) from closed-shell species, one may utilize the valence-universal MRCC theories^{128–134} (cf. refs 135–138 for selected recent advances) or the closely related electron-attached (EA)^{101,103,139–141} and ionized (IP)^{101,103,141–145}

Special Issue: Berny Schlegel Festschrift

Received: September 2, 2012

equation-of-motion CC (EOMCC)^{146–148} theories, their symmetry-adapted-cluster CI^{149,150} counterparts,^{151–154} and their multiply attached/ionized extensions.^{155–157}

One would hope that after more than three decades of intense development, we should nowadays be able to perform routine MRCC calculations for arbitrary multidimensional reference spaces. Unfortunately, this is not the case. As pointed out in ref 27, all of the MRCC methods formulated to date, in spite of their sophistication and complexity, continue facing various formal and practical challenges, compromising one or more fundamental features that the high-level *ab initio* theories of this type are expected to preserve. For example, the genuine, multiroot, SUMRCC methods based on the Jeziorski–Monkhorst ansatz suffer from intruder states^{32,34} or, considering the polynomial character of CC equations, intruder, often singular, unphysical multiple solutions.³⁷ Such solutions emerge as a consequence of the nonlinear character of the underlying generalized Bloch equation,¹⁵⁸ which is further enhanced by the exponential parametrization of the wave operator that maps the multidimensional reference space into the target space spanned by a group of quasi-degenerate eigenstates of the Hamiltonian one is trying to determine. The SSMRCC methods based on the same wave function ansatz and originally proposed by Mukherjee and co-workers,^{52,53} often abbreviated as the Mk-MRCC approaches, although free from intruders, suffer from convergence problems, particularly in excited-state considerations and especially when one or more coefficients at the reference determinants become small.^{66,74} Furthermore, it is hard to obtain the Mk-MRCC results that can compete with those obtained in the size-extensivity corrected MRCI calculations, particularly when the MRAQCC^{159,160} and MRACPF¹⁶¹ approaches are employed, without the explicit inclusion of higher-than-doubly excited clusters that make the resulting Mk-MRCC approximations prohibitively expensive in the majority of molecular applications (see, e.g., refs 73, 74, and 162). In fact, as pointed out in ref 66, by utilizing the multiroot Jeziorski–Monkhorst ansatz in the SSMRCC considerations, the Mk-MRCC methods become more expensive than the analogous SUMRCC approaches if one is interested in determining multiple electronic states without resorting to a linear-response formalism. On the other hand, the use of the linear-response formalism in the Mk-MRCC context results in artificial splittings of excited states and an incorrect pole structure of dynamical polarizabilities,^{163–165} which is a consequence of the redundancies that emerge when the intrinsically multiroot Jeziorski–Monkhorst ansatz is applied to a single electronic state. The Brillouin–Wigner (BW) alternative to the Mk-MRCC theory developed by Hubač, Masik, Pittner, Čarský, and co-workers,^{57–60} which utilizes the Jeziorski–Monkhorst ansatz as well, although free from intruders and not having the convergence problems observed in the Mk-MRCC considerations, lacks size extensivity and, in analogy to Mk-MRCC and SUMRCC, the results obtained without the explicit inclusion of higher-than-doubly excited clusters are often less accurate than those obtained with MRAQCC or MRACPF (cf., e.g., ref 166). The MRexpT theory of Hanrath^{61,62} provides high-accuracy results, while addressing the redundancy issues plaguing other SSMRCC approaches based on the Jeziorski–Monkhorst ansatz, but this is done at the expense of violating size extensivity and introducing a rather complex formalism, which is difficult to implement in a computationally efficient manner. It is also difficult to extend the genuine MRCC methods that rely on the explicit use of multiple reference determinants to larger model spaces, although considerable progress has been made in this direction thanks to

the massively parallel implementation efforts by Kowalski, Pittner, and their collaborators.⁷⁷

The above are only a few selected examples from the much longer list of conceptual as well as computational problems facing MRCC methodologies. While there is no doubt that the genuine MRCC approaches employing multideterminantal reference states are worth further investigation, it is useful, at the same time, to explore alternative strategies to the MR problem in quantum chemistry within the CC framework. The simplest and certainly most pragmatic idea in this category is to capture the dynamical and nondynamical correlations relevant to the electronic near-degeneracies of interest dynamically through particle-hole excitations out of a single Slater determinant, as in the SRCC and EOMCC theories, relying on the well-established ability of the SRCC and EOMCC theories with a full treatment of higher-than-double excitations to rapidly converge toward the exact, full CI, limit. An obvious 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 genuine MRCC theories. Unfortunately, the SRCC methods with a complete, fully iterative, treatment of higher-than-double excitations, which would be appropriate for typical MR situations, including bond breaking, biradicals, and excited states dominated by two-electron transitions, such as CCSDT (CC singles, doubles, and triples),^{167,168} CCSDTQ (CC singles, doubles, triples, and quadruples),^{87,169,170} EOMCCSDT,^{97,98,171} and EOMCCSDTQ,^{172,173} are computationally too expensive for the majority of molecular systems of interest. At the same time, traditional ways of reducing the costs of high-level SRCC/EOMCC calculations through the CCSD(T), CCSDT-1,^{174,175} and other similar approximations that utilize MBPT to estimate the effects of higher-than-double excitations (cf., e.g., refs 6 and 104 for more complete lists of such approximations) are usually inapplicable to electronic near-degeneracies.

The idea of approximating the high-level SRCC/EOMCC approaches with a complete treatment of higher-than-double excitations such that one could accurately describe at least some of the typical MR problems within the SRCC/EOMCC framework at the small fraction of the computer costs of the CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, and similar methods has led to the development of new generations of the non-iterative, CCSD(T)-like, corrections to the energies resulting from the lower-order SRCC/EOMCC calculations. Among them are the CCSD(T)_Λ,^{176,177} Λ-CCSD(T),^{178,179} Λ-CCSD(TQ)_Λ,¹⁸⁰ CCSD(2)_T,¹⁸¹ and CCSD(2)_Λ^{181–185} schemes and their EOMCC-based, excited-state, extensions,^{185,186} and a variety of the completely renormalized (CR) CC/EOMCC and other approaches resulting from the energy expansions that define the method of moments of CC (MMCC) equations.^{187–205} All of these methods aim at preserving the ease of use, the relatively low computer costs, and the overall philosophy of CCSD(T) and similar approximations, while offering improvements over CCSD(T) in typical MR situations, such as single bond breaking, biradicals, and excited states having substantial double excitation components, where the conventional CCSD(T)-type corrections to the CCSD or EOMCCSD energies fail. Other relatively inexpensive and easy to use SRCC/EOMCC techniques that work well in MR situations include the spin-flip (SF) CC/EOMCC methods^{206–209} and the aforementioned active-space CC/EOMCC theories.^{83–104} The latter theories, which are nowadays abbreviated, following refs 94 and 96, as the CCSDt/EOMCCSDt, CCSDtq/EOMCCSDtq, etc. approaches, are based on selecting higher-than-two-body

components of the cluster operator T and EOM excitation operator R_μ relevant to the quasi-degeneracy problem of interest using active orbitals.

In an effort toward formulating the SRCC-like methods for MR problems, we have been primarily interested in developing the MMCC, CR-CC/EOMCC, and active-space CC/EOMCC methodologies. In particular, inspired by the RMRCCSD(T)^{126,127} and CCSD(T)-h^{210–213} work, in which one corrects the RMRCCSD energies in the former case and the CCSDt energies in the latter case for the dynamical correlation effects due to connected triple excitations missing in RMRCCSD and CCSDt using the (T) corrections of CCSD(T), we have recently proposed the Flexible MMCC (Flex-MMCC) and CC(P;Q) formalisms.^{205,214} These novel quantum-chemical frameworks can be viewed as generalizations of the existing biorthogonal MMCC theory^{198–200,202} and its older versions.^{187–189,191,192,195–197,203,204} The biorthogonal MMCC formalism and its earlier variants provide compact expressions for the differences between the full CI and CC/EOMCC energies obtained using conventional truncations in the cluster operator T and EOM excitation operator R_μ that have, for example, resulted in the noniterative triples CR-CC(2,3)^{198–201} CR-EOMCC(2,3),^{200,202,215} and CR-EOMCCSD(T)^{193,194} corrections to the standard CCSD and EOMCCSD energies, and their various higher-order analogs.^{187–190,192,195–197,203,204,216,217} The Flex-MMCC and CC(P;Q) formalisms of refs 205 and 214 go one step further and enable one to correct the CC/EOMCC energies obtained with the 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 some or all of the many-electron correlation effects that the truncated T and R_μ do not describe. As a result, one can now contemplate a variety of unconventional corrections to the ground-state CC and excited-state EOMCC energies, including, in particular, the CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. hierarchy discussed in refs 205 and 214. In this hierarchy, the energies obtained in the active-space CC/EOMCC calculations, such as CCSDt/EOMCCSDt, CCSDtq/EOMCCSDtq, or CCSDTq/EOMCCSDTq, are corrected for the effects of higher-order, primarily dynamical, correlations, such as triples (3), triples and quadruples (3,4), or quadruples (4) missing in the active-space CC/EOMCC considerations using the noniterative corrections that are formally similar to those defining the CR-CC/EOMCC methods. In particular, as elaborated on in refs 205 and 214 and as further demonstrated in this work, the ground-state variant of the CC(t;3) approach can be viewed as an improvement over the CCSD(T)-h method of refs 210–213, in which the (T) correction of conventional CCSD(T) used in CCSD(T)-h to correct the CCSDt energies for the triples effects missing in CCSDt is replaced by the more robust CR-CC(2,3)-type expression. Similarly, the recently implemented CCSD(T)q-h approach, in which one uses the (T) correction of CCSD(T) to correct the CCSDtq energies,²¹⁸ can be regarded as an approximation to the ground-state CC(t,q;3) method proposed in ref 205. It should be emphasized that the systematically improvable CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. hierarchy developed in refs 205 and 214 results from the rigorous moment energy expansions defining the Flex-MMCC and CC(P;Q) frameworks rather than from the more intuitive *ad hoc* considerations used in the design of the RMRCCSD(T), CCSD(T)-h, and CCSD(T)q-h schemes. It should also be pointed out that unlike RMRCCSD(T), CCSD(T)-h, and CCSD(T)q-h, which apply to the ground-state problem only, the

CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. hierarchy and the underlying Flex-MMCC and CC(P;Q) formalisms apply to ground and excited states.

Our interest in pursuing the CC(P;Q) formalism of refs 205 and 214 stems from the fact that the noniterative corrections to the active-space CCSDt and CCSDtq energies that this formalism leads to provide us with a transparent and inexpensive mechanism for relaxing the singly and doubly excited clusters, T_1 and T_2 , respectively, which in methods such as CR-CC(2,3) or CR-CC(2,4) are taken from the CCSD calculations, in the presence of higher-than-doubly excited clusters, without having to resort to the prohibitively expensive CCSDT or CCSDTQ methods. Indeed, as shown in refs 205 and 214, the neglect of the coupling between the lower-order T_1 and T_2 components and their higher-order T_n analogs with $n \geq 3$ may lead to substantial errors in the results of the CR-CC(2,3), Λ -CCSD(T), CCSD(2)_T, and similar calculations for certain classes of chemical reaction profiles involving biradical transition states and for some bond dissociation curves. The CC(P;Q)-inspired CC(t;3) method that incorporates the information about the coupling among the singly, doubly, and triply excited (T_3) clusters through the use of the higher-quality T_1 and T_2 amplitudes obtained in the CCSDt rather than CCSD calculations in determining the relevant triples corrections addresses this issue. Indeed, as demonstrated in refs 205 and 214, CC(t;3) offers great improvements in the CR-CC(2,3), Λ -CCSD(T), and CCSD(2)_T results in the bond breaking and biradical situations by producing total as well as relative energies that typically are within small fractions of a millihartree from the corresponding CCSDT data without making the calculations much more expensive. This study provides evidence that the same is also true when the singlet–triplet gaps in biradical species are examined. The active-space SRCC approaches, such as CCSDt, which capture the coupling of the higher-order T_n components with $n \geq 3$, selected with the help of active orbitals, with the T_1 and T_2 clusters, provide excellent relative energetics in many biradical and bond breaking cases as well, but they often fail to provide accurate total energies relative to the parent SRCC approximations due to the neglect of the higher-order T_n components of the primarily dynamical character that do not involve active orbitals. As shown in this study and refs 205 and 214, the CC(t;3) method addresses this issue, too, by correcting the CCSDt energies for the triple excitation effects neglected in CCSDt using the CR-CC(2,3)-like expressions derived with the help of the CC(P;Q) formalism.

As implied by the above remarks, the present study extends the earlier CC(t;3) work^{205,214} to another important category of molecular applications, where having a robust, easy to use, and relatively inexpensive SRCC methodology, capable of improving the CCSD(T), CCSD(2)_T, CR-CC(2,3), and similar results on the one hand and the results of the active-space CCSDt and CCSDt-based CCSD(T)-h calculations on the other hand, is desired, namely, the singlet–triplet gaps in biradical systems. Molecular examples that are used in this work to illustrate the utility of the CC(t;3) approach in calculations of the singlet–triplet gaps in biradicals include the weakly biradical methylene system, the more challenging (HFH)[−] ion, where the degree of biradical character can be continuously varied by simultaneously stretching both H–F bonds, and the strongly biradical trimethylenemethane (TMM) species. Methylene represents a classic case of a small gap between the first excited singlet state, A^1A_1 , and triplet ground state, X^3B_1 (see refs 219–223), which can cause severe difficulties for many electronic structure methods. Normally, an accurate description of this gap requires a MRCI^{224–229}

or MRCC^{230–233} treatment, or the use of the expensive, higher-order, SRCC approaches, such as CCSDT^{229,234} or the SF variant of the EOMCC(2,3) method²³⁵ with a full treatment of triple excitations in the EOM operator R_{μ} , which has computer costs similar to those characterizing CCSDT, referred to as EOM-SF-CC(2,3)²⁰⁹ (see ref 236 for a more complete list of references, including methods other than MRCC, MRCI, CCSDT, and EOM-SF-CC(2,3)). We have previously investigated the singlet–triplet gap in methylene using the CR-CC(2,3) approach, improving the results of the CCSD(T) and CCSD(2)_T calculations and bringing the total energies of the X^3B_1 and A^1A_1 states and the adiabatic energy separation between them to very good agreement with the CCSDT,^{229,234} full CI,^{224,229} and, after extrapolating to the complete basis set (CBS) limit, Quantum Monte Carlo (QMC)²³⁷ data.^{201,236} The question remains if one can improve the already accurate CR-CC(2,3) energies and the results of the active-space CCSDt calculations even further, especially for total energies, by turning to the CC(t;3) methodology. We have examined the $D_{\infty h}$ -symmetric (HFH)[−] ion, which can be viewed as a prototype magnetic system,²³⁸ using the CR-CC(2,3) approach as well,^{201,239} demonstrating once again that the CR-CC(2,3) method improves the CCSD(T) and CCSD(2)_T results, both for the total energies of the $X^1\Sigma_g^+$ ground state and the $A^3\Sigma_u^+$ first excited state, and the gap between them, which should approach zero as both H–F bonds are stretched to infinity. However, the behavior of CR-CC(2,3) and, as demonstrated in this study, CCSDt, particularly at larger H–F separations, where the $X^1\Sigma_g^+$ state of (HFH)[−] becomes a very strong biradical, is not as good as in the methylene case. As shown in ref 212, the CCSD(T)-h approach, which attempts to capture the effects due to the triple excitations missing in CCSDt through the use of the conventional (T) correction, improves the total energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states and the gap between them resulting from the CR-CC(2,3) and CCSDt calculations, but the question remains if our CC(t;3) approach can improve the CCSD(T)-h results even further, particularly when compared to the full CCSDT data, which both CCSD(T)-h and CC(t;3) are trying to approximate. The third example, TMM, is probably chemically most interesting. TMM is an example of a non-Kekulé hydrocarbon, in which four electrons are delocalized over four π molecular orbitals (MOs). Since the original analyses pointing to its unusual electronic structure reported more than 60 years ago,^{240,241} TMM has attracted a lot of attention among theorists^{109,208,209,233,242–272} and experimentalists.^{273–286} In particular, in accordance with the Hund rule, it has a D_{3h} -symmetric triplet ground state, X^3A_2' , which was confirmed by the EPR experiment in 1976,²⁷⁴ and two low-lying and nearly degenerate closed-shell and open-shell singlet states, stabilized by the Jahn–Teller²⁸⁷ distortion and having a manifestly MR, biradical, character, namely, the approximately C_{2v} -symmetric A^1B_1 state and the C_{2v} -symmetric B^1A_1 state (see, e.g., refs 208, 268, and 271 for a thorough discussion). As a result, a lot of theoretical effort has been dedicated to an accurate determination of the relevant singlet–triplet splittings,^{109,208,209,233,253–269,271,272} with the best recent results obtained using the sophisticated MRCC^{109,233,272} and EOM-SF-CC(2,3)²⁰⁹ approaches, which reproduce the experimentally determined $B^1A_1 - X^3A_2'$ gap using photoelectron spectroscopy²⁷⁹ to within ~ 1 –3 kcal/mol (as explained in refs 268 and 279, the lower-energy B^1A_1 state could not be observed in the photoelectron spectrum recorded in ref 279 because of the unfavorable Franck–Condon factors). The $B^1A_1 - X^3A_2'$ separation in TMM has also been examined with the SR CCSD(T) and CR-CC(2,3) methods.²³³ As shown in ref 233 and as further elaborated on in this study, the CCSD(T), CCSD(2)_T,

and CR-CC(2,3) approaches, which are all based on a noniterative treatment of triple excitations on top of CCSD, overestimate the adiabatic $B^1A_1 - X^3A_2'$ gap in TMM by about 10–15 kcal/mol (~ 50 –85%). This is a disappointing result, providing arguments in favor of the MRCC methodologies, which work a lot better in this case.^{109,233,272} The active-space CCSDt approach offers great improvements, bringing the $B^1A_1 - X^3A_2'$ separation in TMM, as shown in this study, to an excellent agreement with full CCSDT, which works well in this case in spite of its SR character, but the total electronic energies of the X^3A_2' and B^1A_1 states of TMM obtained with CCSDt possess large, >10 millihartree, errors relative to the corresponding CCSDT energies, which is a disappointment, too. It is interesting to investigate how the CC(t;3) approach and its CCSD(T)-h analog cope with these challenges. The key questions that we will address are as follows:

- How accurate are the total energies of the X^3A_2' and B^1A_1 states of TMM resulting from the CC(t;3) and CCSD(T)-h calculations relative to the full CCSDT data, which both of these methods are trying to approximate?
- Are the total energies of the X^3A_2' and B^1A_1 states obtained with CC(t;3) and CCSD(T)-h closer to their CCSDT counterparts than the energies resulting from the CCSDt calculations?
- Are the CC(t;3) and CCSD(T)-h values of the $B^1A_1 - X^3A_2'$ gap in TMM more accurate than those resulting from the CCSD(T), CCSD(2)_T, and CR-CC(2,3) calculations, when compared with the CCSDT and other *ab initio* results as well as with the available experimental data?
- Does the CC(P;Q)-inspired CC(t;3) methodology provide improvements in the description of the total energies of the X^3A_2' and B^1A_1 states of TMM and the gap between them, relative to the corresponding CCSDT data, when compared with the analogous CCSD(T)-h results?

The main objective of this study, after reviewing the relevant theoretical and algorithmic details, is to examine the performance of the CC(t;3) approach in calculations of the lowest singlet and triplet states of methylene, (HFH)[−], and TMM, and the energy separations between them, as compared to other CC results, particularly to other practical ways of handling T_3 clusters in the SRCC theory.

2. THEORY: THE CC(t;3) METHOD

The CC(t;3) approach that interests us in this work is a novel *ab initio* hybrid scheme derived from the CC(P;Q) framework introduced in refs 205 and 214. In a nutshell, the CC(P;Q) formalism and the underlying Flex-MMCC theory are obtained by generalizing the biorthogonal moment expansions of refs 198–200 and 202, so that, in addition to being able to correct the ground- and excited-state energies obtained in the standard CC/EOMCC calculations, such as CCSD or EOMCCSD, for the higher-order correlation effects, such as, for example, triples, we can also correct the energies resulting from the unconventional truncations in the cluster operator T and EOM excitation operator R_{μ} , including those that characterize the active-space CC/EOMCC methods. In particular, in the CC(t;3) approach, one uses the CC(P;Q) expressions of refs 205 and 214 to correct the CCSDt or EOMCCSDt energies for the effects of those triple excitations that are not captured by CCSDt/EOMCCSDt. In analogy to the earlier MMCC methods,^{187–205} we determine the corrections to the CCSDt or EOMCCSDt energies using the generalized moments of the CCSDt/EOMCCSDt equations that are obtained by projecting these equations on the subset of

triply excited determinants which is disregarded in the CCSDt/EOMCCSDt considerations. Since the goal of this study is to examine the performance of CC(t;3) in applications involving the lowest singlet and triplet states, in the following description we focus on the ground-state CC(t;3) theory.

The CC(t;3) calculations are initiated by solving the SRCC-like system of the nonlinear, energy-independent, equations for the cluster operator

$$T^{(\text{CCSDt})} = T_1 + T_2 + t_3 \quad (1)$$

defining the ground-state CCSDt wave function

$$|\Psi_0^{(\text{CCSDt})}\rangle = e^{T^{(\text{CCSDt})}}|\Phi\rangle \quad (2)$$

where the singly, doubly, and triply excited components of $T^{(\text{CCSDt})}$ are given by

$$T_1 = \sum_{i,a} t_{ia}^i E_i^a \quad (3)$$

$$T_2 = \sum_{i>j,a>b} t_{ab}^{ij} E_{ij}^{ab} \quad (4)$$

and

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

respectively, which can be given the following compact form:^{84,85,87,94,95,104}

$$\langle\Phi_K|\bar{H}^{(\text{CCSDt})}|\Phi\rangle = 0, |\Phi_K\rangle \in \mathcal{H}^{(\text{CCSDt})} \quad (6)$$

Here,

$$\bar{H}^{(\text{CCSDt})} = e^{-T^{(\text{CCSDt})}} H e^{T^{(\text{CCSDt})}} = (H e^{T^{(\text{CCSDt})}})_C \quad (7)$$

is the similarity-transformed Hamiltonian of CCSDt (with C designating the connected operator product) and $\mathcal{H}^{(\text{CCSDt})}$ is a subspace of the many-electron Hilbert space spanned by the singly excited determinants $|\Phi_i^a\rangle = E_i^a|\Phi\rangle$, doubly excited determinants $|\Phi_{ij}^{ab}\rangle = E_{ij}^{ab}|\Phi\rangle$ (with $i > j$ and $a > b$), and selected triply excited determinants $|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle = E_{\mathbf{ijk}}^{\mathbf{abc}}|\Phi\rangle$ (with $\mathbf{I} > \mathbf{j} > \mathbf{k}$ and $\mathbf{a} > \mathbf{b} > \mathbf{c}$) that correspond to the excitations included in $T^{(\text{CCSDt})}$. As in all of our earlier papers on the active-space methods, we adopt a notation in which $|\Phi\rangle$ is the reference determinant, which in all calculations reported in this work is the restricted Hartree–Fock (RHF) or restricted open-shell Hartree–Fock (ROHF) state, i,j,\dots are the spin–orbitals occupied in $|\Phi\rangle$, with $\mathbf{I},\mathbf{J},\dots$ designating the active ones, $\mathbf{a},\mathbf{b},\dots$ are the unoccupied spin–orbitals, with $\mathbf{A},\mathbf{B},\dots$ labeling those that are active, and $E_{i_1\dots i_n}^{a_1\dots a_n} = \prod_{\kappa=1}^n a_{i_\kappa}^{a_\kappa}$ are the elementary excitation operators defined in terms of the creation (a^p) and annihilation (a_p) operators associated with the spin–orbital basis $\{p\}$. Once the cluster amplitude equations represented by eq 6 are solved for t_{ia}^i , t_{ab}^{ij} , and $t_{\mathbf{abc}}^{\mathbf{Ijk}}$, we determine the ground-state CCSDt energy, $E_0^{(\text{CCSDt})}$, in a usual manner by using the SRCC-like expression

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

After obtaining $E_0^{(\text{CCSDt})}$, we calculate the desired CC(t;3) ground-state energy $E_0^{(\text{CC}(t;3))}$ as

$$E_0^{(\text{CC}(t;3))} = E_0^{(\text{CCSDt})} + \delta_0(t;3) \quad (9)$$

where, following the general CC(P;Q) recipe, the noniterative correction $\delta_0(t;3)$ due to the triples missing in the CCSDt considerations is determined using the formula^{205,214}

$$\delta_0(t;3) = \sum_{|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle \in \mathcal{H}^{(T)} \ominus \mathcal{H}^{(t)}} I_{0,\mathbf{ijk}}^{\mathbf{abc}}(\text{CCSDt}) \mathcal{M}_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt}) \quad (10)$$

The $\mathcal{M}_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt})$ quantities entering eq 10 are the aforementioned moments of the CCSDt equations corresponding to projections of these equations on the subset of triply excited determinants ignored in CCSDt, i.e.,

$$\mathcal{M}_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt}) = \langle\Phi_{\mathbf{ijk}}^{\mathbf{abc}}|\bar{H}^{(\text{CCSDt})}|\Phi\rangle \quad (11)$$

The $I_{0,\mathbf{ijk}}^{\mathbf{abc}}(\text{CCSDt})$ amplitudes that multiply moments $\mathcal{M}_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt})$ in eq 10 are calculated as

$$I_{0,\mathbf{ijk}}^{\mathbf{abc}}(\text{CCSDt}) = \langle\Phi|L_0^{(\text{CCSDt})}\bar{H}^{(\text{CCSDt})}|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle/D_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt}) \quad (12)$$

The de-excitation operator $L_0^{(\text{CCSDt})}$ entering eq 12, which is defined as

$$L_0^{(\text{CCSDt})} = \mathbf{1} + L_{0,1} + L_{0,2} + l_{0,3} \quad (13)$$

where $\mathbf{1}$ is the unit operator, $L_{0,1}$ and $L_{0,2}$ are the regular one- and two-body components of $L_0^{(\text{CCSDt})}$ defined using all correlated spin–orbitals, and

$$l_{0,3} = \sum_{\mathbf{I}>\mathbf{j}>\mathbf{k},\mathbf{a}>\mathbf{b}>\mathbf{c}} l_{0,\mathbf{ijk}}^{\mathbf{abc}} E_{\mathbf{abc}}^{\mathbf{Ijk}} \quad (14)$$

is the “little l ” three-body component defined, in analogy to t_3 , eq 5, with the help of active orbitals, and which defines the bra CCSDt ground state

$$\langle\tilde{\Psi}_0^{(\text{CCSDt})}| = \langle\Phi|L_0^{(\text{CCSDt})} e^{-T^{(\text{CCSDt})}} \quad (15)$$

is obtained by solving the left-eigenstate CCSDt equations. The $D_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt})$ denominator entering eq 12 is the Epstein–Nesbet-style expression, which looks as follows:

$$D_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt}) = E_0^{(\text{CCSDt})} - \langle\Phi_{\mathbf{ijk}}^{\mathbf{abc}}|\bar{H}^{(\text{CCSDt})}|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle \quad (16)$$

The summation over the triply excited determinants $|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle$ in eq 10, which in the previously developed MMCC-type methods, such as CR-CC(2,3), would span the subspace of all triexcited determinants, $\mathcal{H}^{(T)} = \text{span}\{|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle, \mathbf{i} > \mathbf{j} > \mathbf{k}, \mathbf{a} > \mathbf{b} > \mathbf{c}\}$, excludes those determinants $|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle$ which are already included in the CCSDt/EOMCCSDt calculations, designated here by $\mathcal{H}^{(t)} = \text{span}\{|\Phi_{\mathbf{ijk}}^{\mathbf{abc}}\rangle, \mathbf{I} > \mathbf{j} > \mathbf{k}, \mathbf{a} > \mathbf{b} > \mathbf{c}\}$. If one desires to be explicit about the summation over the triply excited determinants included in eq 10, we can write

$$\delta_0(t;3) = \sum_{\mathbf{i}>\mathbf{j}>\mathbf{k},\mathbf{a}>\mathbf{b}>\mathbf{c}} I_{0,\mathbf{ijk}}^{\mathbf{abc}}(\text{CCSDt}) \mathcal{M}_{0,\mathbf{abc}}^{\mathbf{ijk}}(\text{CCSDt}) + \sum_{\mathbf{I}>\mathbf{j}>\mathbf{k},\mathbf{a}>\mathbf{b}>\mathbf{c}} I_{0,\mathbf{Ijk}}^{\mathbf{abc}}(\text{CCSDt}) \mathcal{M}_{0,\mathbf{abc}}^{\mathbf{Ijk}}(\text{CCSDt}) \quad (17)$$

where the bold lower-case indices designate the inactive spin–orbitals outside the active subset ($\mathbf{i},\mathbf{j},\dots$ for the core/inactive occupied ones and $\mathbf{a},\mathbf{b},\dots$ for the virtual/inactive unoccupied ones).

We refer the reader to ref 205 for further details, including the excited-state extension of the CC(t;3) theory and other types of the CC(P;Q)-inspired corrections to the active-space CC/EOMCC energies. Our focus in this work is on two variants of the ground-state CC(t;3) formalism, abbreviated as the CC(t;3)_A and CC(t;3)_D approaches, which are obtained by two different ways of treating the perturbative denominator $D_{0,abc}^{ijk}$ (CCSDt) entering eq 12 and which are analogous to the MMCC-based CR-CC(2,3)_A and CR-CC(2,3)_D corrections to the CCSD energies explored in our earlier work (see, e.g., refs 200–202 and 239). Thus, in analogy to the most complete and, as shown in many papers (cf. refs 198–202, 239, and 288 for the selected examples), most accurate level D of CR-CC(2,3), the CC(t;3)_D method uses the Epstein–Nesbet-like treatment of the $D_{0,abc}^{ijk}$ (CCSDt) denominator, as given by eq 16. On the other hand, the CC(t;3)_A approach replaces eq 16 for $D_{0,abc}^{ijk}$ (CCSDt), which can also be written as^{198–202,239} $(-\sum_{n=1}^3 \langle \Phi_{ijk}^{abc} | \bar{H}_n^{(\text{CCSDt})} | \Phi_{ijk}^{abc} \rangle)$, where $\bar{H}_n^{(\text{CCSDt})}$ is the n -body component of $\bar{H}_n^{(\text{CCSDt})}$, by the Møller–Plesset-like expression $(\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c)$, with ε_p 's representing the single-particle energies associated with spin-orbitals p (diagonal elements of the Fock matrix). As emphasized in our earlier work,^{198–202,239} variant A of the ground-state CR-CC(2,3) theory is equivalent to the CCSD(2)_T approach of ref 181. Thus, we can regard the CC(t;3)_A correction to the CCSDt energy as the CC(t;3) analog of the CCSD(2)_T correction to the CCSD energy. Similarly, the CC(t;3)_D correction to the CCSDt energy based on the complete treatment of the $D_{0,abc}^{ijk}$ (CCSDt) denominator, as given by eq 16, can be regarded as the CC(t;3) analog of the CR-CC(2,3)_D triples correction to CCSD.

As explained in refs 198–201, variant A of the CR-CC(2,3) method can be approximated further by neglecting selected higher-order terms in the CCSD analogs of moments $M_{0,abc}^{ijk}$ (CCSDt) and de-excitation amplitudes $I_{0,ijk}^{abc}$ (CCSDt), resulting in the CCSD(T) approach. Thus, the CCSD(T)-h scheme of refs 210–213, which we examine in this work as well and in which the (T) correction of conventional CCSD(T) is used to correct the ground-state CCSDt energies for the triples effects missing in CCSDt, can be viewed as an approximation to CC(t;3) as well. The key difference between the CCSD(T)-h and CC(t;3) methods is the utilization of the standard CCSD(T) triples correction, added to the CCSDt energy in an *ad hoc* manner, in the former case and the use of the more robust, CR-CC(2,3)-type, correction, derived from the Flex-MMCC and CC(P;Q) formalisms, in the latter case. Because of the above relationships between the CCSD(T)-h, CC(t;3)_A, and CC(t;3)_D approaches, it is interesting to compare them side by side, examining which of the three methods offers the best representation of the full CCSDT total and relative energies, including the total electronic energies of the lowest singlet and triplet states, and singlet–triplet gaps in biradical systems. Such a comparison is one of the main objectives of this study.

Although the CC(t;3) formalism of refs 205 and 214 applies to ground as well as excited states, which is another advantage of CC(t;3) over the CCSD(T)-h approach of refs 210–213 that has no natural extension to excited states, so far we have implemented the ground-state CC(t;3) method, interfacing the resulting computer codes with the RHF, ROHF, and integral transformation routines available in the GAMESS package.²⁸⁹ We refer the reader to refs 205 and 214 for more information. Here, we only mention that the CC(t;3) approach, including the A and D variants of it examined in this work, offers considerable

savings in computer effort compared to the parent CCSDT methodology. Indeed, CC(t;3) replaces the expensive, iterative, $n_o^3 n_u^5$ steps of CCSDT with the $N_o N_u n_o^2 n_u^4$ steps of CCSDt, where n_o and n_u are the numbers of occupied and unoccupied orbitals, respectively, and N_o ($< n_o$ or $\ll n_o$) and N_u ($\ll n_u$) are the numbers of the active occupied and active unoccupied orbitals, followed by the noniterative $n_o^3 n_u^4$ steps similar to those of CCSD(T) or CR-CC(2,3). In other words, the CC(t;3) schemes replace the iterative and computationally demanding CPU steps of full CCSDT, which scale as \mathcal{N}^8 with the system size \mathcal{N} , by the iterative \mathcal{N}^6 -like CCSDt steps and noniterative \mathcal{N}^7 -type corrections. Similar remarks apply to disk storage, which is reduced from the $\sim n_o^3 n_u^3$ (\mathcal{N}^6 -type) requirements of CCSDT, related to the need to store all triply excited cluster amplitudes, to the much more manageable $\sim N_o N_u n_o^2 n_u^2$ (\mathcal{N}^4 -like) requirements of CC(t;3), where we only have to store the small subset of triply excited amplitudes included in the CCSDt calculations. It is, therefore, interesting to examine if the CC(t;3) method, which is an inexpensive approximation to CCSDT, is capable of producing total electronic energies of the lowest singlet and triplet states, and singlet–triplet gaps in biradical systems that match the corresponding CCSDT data.

3. RESULTS

To demonstrate the types of improvements the CC(t;3) method (particularly, its most complete variant D) can offer in applications involving the lowest-energy singlet and triplet states, and singlet–triplet gaps in biradical species, when compared to the CCSD(T), CCSD(2)_T or CR-CC(2,3)_A and CR-CC(2,3)_D corrections to the CCSD energies, the active-space CCSDt calculations, and the CCSD(T)-h correction to CCSDt, we consider the following three examples: methylene, the linear (HFH)[−] ion, and TMM. As already alluded to above, we used the RHF orbitals in the calculations for the singlet states and the ROHF orbitals, obtained using the canonicalization approach due to Roothaan,²⁹⁰ which is a default in GAMESS, in the calculations for the triplet states. As demonstrated in ref 201, the effect of the procedure used to produce canonical ROHF orbitals on the noniterative triples corrections of the CCSD(T), CCSD(2)_T, or CR-CC(2,3) type is on the order of tens of microhartree at worst, i.e., negligible from the point of view of the objectives of this work, where changes in the results due to the use of different CC methods are much larger. The spherical components of the d and f basis functions were employed throughout.

In the case of methylene, we performed two sets of calculations. In the first set, we adopted the exactly solvable TZ2P model employing the [5s3p/3s] triple- ζ basis set of Dunning²⁹¹ augmented with two sets of polarization functions, as described in ref 229, where the authors determined the geometries and energies of the X ³B₁ and A ¹A₁ states of CH₂ using full CI. We used the same basis set and geometries in the CCSD, CCSD(T), CR-CC(2,3)_A, CR-CC(2,3)_D, CCSDt, CCSD(T)-h, CC(t;3)_A, CC(t;3)_D, and CCSDT calculations reported in this study (the CCSD, CCSD(T), CR-CC(2,3)_A, and CR-CC(2,3)_D results, used here for comparison purposes, can also be found in ref 201). Following ref 229, the lowest-energy occupied and highest-energy unoccupied MOs were frozen in these calculations. In addition to comparisons of various SRCC approaches with an approximate treatment of triple excitations with CCSDT and full CI using the TZ2P basis set, we also examined the performance of the CC(t;3) methodology in calculations using the larger aug-cc-pVTZ and aug-cc-pVQZ basis sets^{292,293} and extrapolations to

the CBS limit, so that we could compare the resulting $A^1A_1-X^3B_1$ gap values with the available experimental data. In analogy to our earlier work on methylene,^{231,236} the relevant experimental estimate of the nonrelativistic, purely electronic, adiabatic excitation energy corresponding to the $X^3B_1 \rightarrow A^1A_1$ transition was obtained by correcting the experimentally derived vibrationless adiabatic excitation energy reported in ref 294 for the relativistic and nonadiabatic (Born–Oppenheimer diagonal correction) effects calculated in refs 295 and 296, respectively. In determining the CBS energy values corresponding to various SRCC methods, we used the well-known formula²⁹⁷ $\Delta E(x) = \Delta E_\infty + Ax^{-3}$, where x represents the cardinal number of the aug-cc-pV x Z basis set ($x = 3$ for aug-cc-pVTZ and $x = 4$ for aug-cc-pVQZ), $\Delta E(x)$ is the correlation energy obtained with the aug-cc-pV x Z basis, and ΔE_∞ is the correlation energy in the CBS limit. The resulting extrapolated correlation energies for the X^3B_1 and A^1A_1 states were subsequently added to the corresponding ROHF and RHF energies obtained in the calculations using the aug-cc-pVSZ basis to determine the CBS values of total energies (due to the fast, i.e., exponential, convergence of the SCF energies with the basis set, the aug-cc-pVSZ values of the ROHF and RHF energies of methylene are, for all practical purposes, equivalent to the CBS limits of these energies²³⁶). We were unable to perform the full CCSDT calculations for the aug-cc-pVQZ basis set, i.e., we cannot provide the CBS CCSDT information, but we managed to determine the CCSDT/aug-cc-pVTZ energies of the X^3B_1 and A^1A_1 states, allowing us to verify if the conclusions regarding comparisons of the various SRCC methods with approximate treatments of triples with full CCSDT, reached using the TZ2P basis set, remain valid in the aug-cc-pVTZ case. As in the recent studies of methylene using large correlation-consistent basis sets²³⁶ and QMC,²³⁷ in performing the CC(t;3) and other SRCC calculations using the aug-cc-pVTZ and aug-cc-pVQZ bases, we adopted the same full CI/TZ2P geometries of the X^3B_1 and A^1A_1 states, obtained in ref 229, as those used in the TZ2P calculations. Finally, because of the partly MR character of the A^1A_1 state of methylene, which involves the highest-energy occupied MO (HOMO) and the lowest-energy unoccupied MO (LUMO), the CCSDt calculations and the subsequent CCSD(T)-h, CC(t;3)_A, and CC(t;3)_D computations in all three basis sets used in our calculations for CH₂ employed the minimum active space consisting of two active electrons and two active orbitals corresponding to HOMO and LUMO.

In the case of the $D_{\infty h}$ -symmetric (HFH)[−] system, where two paramagnetic centers, each carrying an unpaired spin, represented by the terminal hydrogen atoms, are linked via a polarizable diamagnetic bridge constituted by the F[−] ion,²³⁸ we used the 6-31G(d,p) basis set,^{298,299} so that we could compare our CC(t;3)_A and CC(t;3)_D results, along with the corresponding CCSD, CCSD(T), CR-CC(2,3)_A, CR-CC(2,3)_D, CCSDt, and CCSD(T)-h data, with the full CI/6-31G(d,p) energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, and the gap between them obtained in ref 201. At the same time, the use of the relatively small 6-31G(d,p) basis set enabled us to perform the relevant RHF-based and ROHF-based full CCSDT calculations, which are most important for the present study, since they allow us to directly judge how good various approximate triples SRCC approaches examined in this work are in capturing the combined effect of T_1 , T_2 , and T_3 clusters. Following ref 201, in order to vary the degree of biradical character and the magnitude of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap, we used several values of the H–F distance R_{H-F} defining the linear, $D_{\infty h}$ -symmetric, (HFH)[−] system, ranging from $R_{H-F} = 1.5$ Å to

$R_{H-F} = 4.0$ Å. As explained in ref 201, the shorter H–F distances correspond to a moderately strong biradical character, whereas the longer ones result in the (HFH)[−] system becoming essentially a pure biradical in which the weakly interacting unpaired electrons of the terminal H atoms separated by a very large distance give rise to the nearly degenerate singlet and triplet states. The CCSD, CCSD(T), CR-CC(2,3)_A, and CR-CC(2,3)_D energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, and the gap between them as functions of R_{H-F} , included in this work for comparison purposes, can also be found in refs 201 and 239. At the same time, the full CCSDT values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in (HFH)[−] and the corresponding CCSD(T)-h values can be found in ref 212. We did, however, recalculate the CCSD(T)-h $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap values and the corresponding total energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, since we wanted to compare the CCSD(T)-h results with their CC(t;3)_A and CC(t;3)_D counterparts using exactly the same small active space as that used in our CCSDt and CC(t;3) calculations (the CCSD(T)-h calculations reported in ref 212 relied on different active orbitals than those employed in this study). In analogy to methylene, the zeroth-order description of the $X^1\Sigma_g^+$ state of the (HFH)[−] system involves only two orbitals, HOMO and LUMO, which become asymptotically degenerate. Thus, in performing the CCSDt, CCSD(T)-h, CC(t;3)_A, and CC(t;3)_D calculations for (HFH)[−], we used the minimum, two-electron/two-orbital, active space corresponding to HOMO and LUMO. Following ref 201, the lowest-energy core orbital was frozen in the post-SCF calculations.

In the challenging case of the TMM system, where we focused on the examination of the total electronic energies of the D_{3h} -symmetric X^3A_2' ground state, which has a largely SR nature, and the C_{2v} -symmetric B^1A_1 excited state, which has a biradical-type MR character, and the adiabatic gap between them, we used the cc-pVDZ and cc-pVTZ²⁹² basis sets that were employed in a number of the earlier SRCC and MRCC calculations.^{208,209,233,271,272} The cc-pVDZ basis set is small enough to allow us to carry out the reference full CCSDT calculations, which are, as already mentioned, particularly important in this work, where we judge the performance of the CC(t;3)_D approach, along with the corresponding CC(t;3)_A data, by comparing them with a number of other approximate treatments of connected triple excitations in the SRCC theory, including CCSD(T), CR-CC(2,3)_A, CR-CC(2,3)_D, CCSDt, and CCSD(T)-h. Moreover, as shown in this work, the full CCSDT method, in spite of its SR character, provides a reasonable description of the $B^1A_1 - X^3A_2'$ gap in TMM, so that any approximate triples CC approach that matches the quality of the CCSDT results at a fraction of the latter method's computer costs has a potential to become very valuable in practice. The CCSDT/cc-pVTZ calculations for TMM turned out to be too expensive for us, but we had no problem whatsoever with generating the corresponding CCSD, CCSD(T), CR-CC(2,3)_A, CR-CC(2,3)_D, CCSDt, CCSD(T)-h, CC(t;3)_A, and CC(t;3)_D results, which we could subsequently compare with the other SRCC and MRCC data obtained using the cc-pVTZ basis set reported in refs 208, 209, 233, 271, and 272. As observed in refs 208, 209, 233, 271, and 272 and as confirmed in the present study, the increase of the basis set from the valence double- ζ plus polarization (i.e., cc-pVDZ-type) quality to cc-pVTZ has little effect on the calculated adiabatic $B^1A_1 - X^3A_2'$ gap in TMM. Thus, we also compare our CC(t;3)/cc-pVTZ results with the realistic estimate of the purely electronic $B^1A_1 - X^3A_2'$ gap value reported in ref 208, which is often used in the literature to assess the accuracy of various quantum-chemistry methods and which is

obtained by subtracting the theoretical zero-point vibrational energy correction ($\Delta ZPVE$) resulting from the SF-DFT/6-31G(d) calculations²⁰⁸ from the experimental singlet–triplet separation determined in ref 279. In producing the reference CCSDT/cc-pVDZ results and the CCSD, CCSD(T), CR-CC(2,3)_A, CR-CC(2,3)_D, CCSDt, CCSD(T)-h, CC(t;3)_A, and CC(t;3)_D energies obtained with the cc-pVDZ and cc-pVTZ basis sets, we used the geometries of the X^3A_2' and B^1A_1 states of TMM obtained in the SF-DFT/6-31G(d) optimizations described in ref 208. As explained in ref 209 and as re-emphasized in ref 109, the unusual electronic structure of TMM, in which four π electrons are delocalized over the network of four π -type MOs, and an adequate description of the B^1A_1 – X^3A_2' gap in TMM require the use of the four-electron/four-orbital active space, which in the case of the B^1A_1 state consists of the two highest-energy occupied and two lowest-energy unoccupied MOs. Following the earlier SRCC and MRCC work for TMM reported in refs 109, 208, 209, 233, 271, and 272, the lowest-energy occupied MOs correlating with the 1s shells of the carbon atoms were frozen in all of the CC calculations performed in this study.

The most essential CC computations carried out in this work were performed using our own computer codes. In particular, the CC(t;3)_A and CC(t;3)_D calculations were carried out using the computer programs developed in refs 205 and 214, which are interfaced with the GAMESS RHF/ROHF and integral transformation routines and which take advantage of the CCSDt codes described in ref 210 and the suitably modified CR-CC(2,3) routines described in refs 198 and 201. The CCSD, CCSD(T), CR-CC(2,3)_A (i.e., CCSD(2)_T), and CR-CC(2,3)_D calculations were performed using the CC programs developed in refs 194, 198, 201, and 300, available in the GAMESS package, whereas the CCSDt, CCSD(T)-h, and full CCSDT calculations were carried out using the appropriate modifications in the codes described in ref 210, interfaced with the GAMESS RHF/ROHF and integral transformation routines as well.

3.1. Methylene. We begin our discussion with the CC(t;3) and other CC results, focusing on the SRCC methods with up to triply excited clusters, obtained for the TZ2P model of methylene, examined with the full CI approach in ref 229 (see Table 1). Methylene is known for its very small adiabatic A^1A_1 – X^3B_1 energy gap, which in the past was the subject of controversies between theory and experiment (cf., e.g., refs 219–223 and references therein). The A^1A_1 – X^3B_1 gap in methylene is highly sensitive to the quality of the electronic structure treatment, which has to provide an accurate and balanced description of the non-degenerate X^3B_1 ground state and quasi-degenerate first-excited A^1A_1 state that normally requires the use of the MRCI^{224–229} or MRCC^{230–233} methodologies, or the expensive SRCC approaches with an iterative account of higher-than-double excitations, such as CCSDT^{229,234} or EOM-SF-CC(2,3),²⁰⁹ to mention a few examples (see ref 236 for a more complete list of references). Indeed, as shown in Table 1, the full CCSDT approach produces a highly accurate A^1A_1 – X^3B_1 energy separation, which differs from its exact, full CI, counterpart by only 0.11 kcal/mol when the TZ2P basis set is employed. This is a result of the very accurate description of the X^3B_1 and A^1A_1 states by the CCSDT method. Indeed, as demonstrated in Table 1, the total electronic energies of the X^3B_1 and A^1A_1 states of CH₂ obtained in the CCSDT/TZ2P calculations differ from those resulting from the analogous full CI calculations by only 0.035 and 0.208 millihartree, respectively, which is a major improvement over the basic CCSD approximation that gives the 3.387 and 5.193 millihartree errors for the same two states.

Table 1. The Adiabatic A^1A_1 – X^3B_1 Splitting in CH₂, along with the Corresponding Total Electronic Energies of the X^3B_1 and A^1A_1 States, Obtained with Full CI and Various CC Approaches and the TZ2P Basis Set^a

method	$E(X^3B_1)$ (hartree)	$E(A^1A_1)$ (hartree)	$E(A^1A_1) - E(X^3B_1)$ (kcal/mol)
CCSD	–39.063351	–39.043791	12.27
CCSD(T)	–39.066276	–39.048005	11.47
CR-CC(2,3) _A ^b	–39.066097	–39.047631	11.59
CR-CC(2,3) _D	–39.066699	–39.048509	11.41
CCSDt	–39.063837	–39.045231	11.68
CCSD(T)-h	–39.066390	–39.048417	11.28
CC(t;3) _A	–39.066235	–39.048120	11.37
CC(t;3) _D	–39.066721	–39.048699	11.31
CCSDT	–39.066703	–39.048776	11.25
full CI ^a	–39.066738	–39.048984	11.14

^aThe basis set, geometries, and full CI energies were taken from ref 229. As in ref 229, the lowest occupied orbital and the highest unoccupied orbital were frozen in post-SCF calculations, and the spherical components of the carbon *d* orbital were employed throughout. The active space used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of two active electrons and two active orbitals corresponding to HOMO and LUMO. ^bCR-CC(2,3)_A is equivalent to the CCSD(2)_T approach of ref 181.

The approximate inclusion of the connected triply excited clusters via the noniterative CCSD(T), CR-CC(2,3)_A (i.e., CCSD(2)_T), and CR-CC(2,3)_D approaches or the iterative, but similarly inexpensive CCSDt treatment using only two active orbitals to select T_3 cluster amplitudes improves the CCSD results, bringing the total electronic energies of the X^3B_1 and A^1A_1 states and the gap between them to a much better agreement with full CCSDT or full CI, with variant D of the CR-CC(2,3) method being particularly successful, but it is quite clear from the results collected in Table 1 that further improvements in the results may be desired. Indeed, the most accurate noniterative triples CR-CC(2,3)_D approach reduces the 0.427 and 0.606 millihartree errors in the CCSD(T) and CR-CC(2,3)_A results relative to full CCSDT for the “easier” X^3B_1 state to 4 microhartree, which is a great result, but the 0.267 millihartree difference between the CR-CC(2,3)_D and CCSDT energies for the more challenging A^1A_1 state remains. Although the 0.267 millihartree difference between the CR-CC(2,3)_D and CCSDT energies is much smaller than the analogous 0.771 and 1.145 millihartree differences characterizing the CCSD(T) and CR-CC(2,3)_A data, confirming the utility of the most complete variant D of the CR-CC(2,3) approach in calculations involving biradical states when compared to the conventional CCSD(T) treatment or the CCSD(2)_T (i.e., CR-CC(2,3)_A) approximation, it is worth exploring the possibility of making further improvements in the results. This becomes particularly evident in the CCSDt case, where the differences between the resulting total electronic energies of the X^3B_1 and A^1A_1 states, and the gap between them with the corresponding full CCSDT data are 2.866 millihartree, 3.545 millihartree, and 0.43 kcal/mol, respectively, i.e., considerably larger than in the case of the CR-CC(2,3)_D calculations.

The CCSD(T)-h method, which corrects the CCSDt energies for the missing triples using the conventional (T) correction of CCSD(T), improves the above situation in a substantial manner, particularly in the case of the A^1A_1 – X^3B_1 gap, which differs from that resulting from the full CCSDT calculations by only 0.03 kcal/mol when the CCSD(T)-h approach is employed and

the TZ2P basis set is used, but the overall performance of the CCSD(T)-h scheme in describing the total electronic energies of the X^3B_1 and A^1A_1 states is not as good as in the case of the $CC(t;3)_D$ correction to CCSDt resulting from the $CC(P;Q)$ considerations. Indeed, as shown in Table 1, the tiny differences between the $CC(t;3)_D$ and full CCSDT energies of the X^3B_1 and A^1A_1 states, of 0.018 and 0.077 millihartree, respectively, are a lot smaller than the 0.313 and 0.359 millihartree differences with the CCSDT energy values for the same two states obtained using the CCSD(T)-h method. The CCSD(T)-h/TZ2P value of the $A^1A_1-X^3B_1$ gap is marginally more accurate than that resulting from the analogous $CC(t;3)_D$ /TZ2P calculations (by 0.03 kcal/mol), but this clearly is a result of the fortuitous cancellation of errors, since the CCSD(T)-h total energies are not as accurate as those obtained with $CC(t;3)_D$. In fact, the total electronic energies of the X^3B_1 and A^1A_1 states obtained with the CCSD(T)-h approach are less accurate than those resulting from the more black-box CR-CC(2,3)_D calculations (by 0.309 and 0.092 millihartree, respectively, when the TZ2P basis set is employed), whereas the $CC(t;3)_D$ approach is as accurate as CR-CC(2,3)_D for the X^3B_1 state, which has a SR character, and more accurate than CR-CC(2,3)_D when the more quasi-degenerate A^1A_1 state is examined, while improving the CR-CC(2,3)_D value of the $A^1A_1-X^3B_1$ gap (by 0.10 kcal/mol in the TZ2P case). As desired, the $CC(t;3)_D$ corrections to the CCSDt energies are very effective in improving the CCSDt results. When the TZ2P basis set is used in the calculations, they reduce the 2.866 millihartree, 3.545 millihartree, and 0.43 kcal/mol errors in the CCSDt values of the total energies of the X^3B_1 and A^1A_1 states, and the adiabatic gap between them, relative to full CCSDT, to 0.018 millihartree, 0.077 millihartree, and 0.06 kcal/mol, respectively. The $CC(t;3)_D$ approach is, for all practical purposes, as accurate in describing the total energies of the X^3B_1 and A^1A_1 states of methylene, and the gap between them as CCSDT, which provides the results of the nearly full CI quality, but is a lot more expensive than $CC(t;3)_D$.

The $CC(t;3)_D$ method is also more accurate than the A variant of $CC(t;3)$, designated as $CC(t;3)_A$, which replaces the Epstein–Nesbet-like $D_{0,abc}^{ijk}$ (CCSDt) denominator entering the $CC(t;3)$ correction to the CCSDt energy, eq 16, by the Møller–Plesset form of it discussed in the previous section. As pointed out in section 2, the $CC(t;3)_A$ correction to the CCSDt energy can be regarded as the $CC(t;3)$ analog of the CR-CC(2,3)_A or CCSD(2)_T approach, whereas the similar $CC(t;3)_D$ correction using the more complete form of the $D_{0,abc}^{ijk}$ (CCSDt) denominator can be viewed as the $CC(t;3)$ analog of the CR-CC(2,3)_D method. As shown in Table 1 and as indicated above, the triples correction to the CCSD energy defining the CR-CC(2,3)_D approach is considerably more accurate than the analogous triples correction of CR-CC(2,3)_A or CCSD(2)_T. It is, therefore, not surprising that the $CC(t;3)_D$ method performs better than its $CC(t;3)_A$ counterpart, reducing the 0.468 and 0.656 millihartree errors relative to the energies of the X^3B_1 and A^1A_1 states obtained with full CCSDT to 0.018 and 0.077 millihartree, respectively, and improving the $CC(t;3)_A$ value of the $A^1A_1-X^3B_1$ gap by 0.06 kcal, when the TZ2P basis set is used. Both variants of the $CC(t;3)$ theory examined in this work improve the results of the CCSDt calculations, bringing them to a closer agreement with CCSDT, but variant D is more effective. Unlike the $CC(t;3)_D$ approach, the $CC(t;3)_A$ approximation does not seem to offer any advantages over the CCSD(T)-h method in the case of the lowest singlet and triplet states of methylene, but, as shown in the next two subsections, this

observation is not generally true, particularly when the degree of biradical character substantially increases. In cases involving stronger biradicals, the CCSD(T)-h approach may worsen the singlet–triplet gap values compared to CCSDt, in a sense of moving them away from the full CCSDT values, whereas both the $CC(t;3)_D$ method and its approximate $CC(t;3)_A$ variant always improve the CCSDt results, bringing them to a closer agreement with CCSDT, which is a desired behavior. 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, which is safe to use only when the electronic quasi-degeneracy is small.

All of the essential observations regarding a comparison of the CCSD(T), CCSD(2)_T (i.e., CR-CC(2,3)_A), CR-CC(2,3)_D, CCSDt, CCSD(T)-h, $CC(t;3)_A$, and $CC(t;3)_D$ results with those obtained with full CCSDT remain valid when the TZ2P basis set is replaced by the larger aug-cc-pVTZ basis. Indeed, the most complete variant D of the CR-CC(2,3) approach brings the CCSD(T) and CR-CC(2,3)_A energies of the X^3B_1 and A^1A_1 states obtained with the aug-cc-pVTZ basis set to a closer agreement with the corresponding CCSDT data, but as shown in Table 2, the analogous variant D of $CC(t;3)$ offers greater improvements. For example, the CR-CC(2,3)_D method reduces the 0.448 and 0.823 millihartree differences between the CCSD(T)/aug-cc-pVTZ and CCSDT/aug-cc-pVTZ energies of the X^3B_1 and A^1A_1 states to 0.177 and 0.657 millihartree, but $CC(t;3)_D$ reduces these differences to 0.130 and 0.409 millihartree, respectively. As a result, the $CC(t;3)_D$ approach employing the aug-cc-pVTZ basis set improves the $A^1A_1-X^3B_1$ gap values obtained in the corresponding CCSD(T), CR-CC(2,3)_A, and CR-CC(2,3)_D calculations, reducing the 0.23, 0.37, and 0.30 kcal/mol errors relative to the CCSDT/aug-cc-pVTZ value of 9.52 kcal/mol to 0.17 kcal/mol. The $CC(t;3)_D$ method also remains effective in improving the CCSDt results. Indeed, the differences between the CCSDt/aug-cc-pVTZ energies of the X^3B_1 and A^1A_1 states and the gap between them and the corresponding CCSDT data are 3.510 and 4.723 millihartree and 0.76 kcal/mol, as opposed to 0.130 and 0.409 millihartree and 0.17 kcal/mol, respectively, obtained in the $CC(t;3)_D$ /aug-cc-pVTZ calculations. Although, as in the TZ2P case, the CCSD(T)-h approach employing the aug-cc-pVTZ basis set is marginally more accurate in describing the $A^1A_1-X^3B_1$ gap in methylene than the corresponding $CC(t;3)_D$ /aug-cc-pVTZ calculations (by 0.06 kcal/mol), $CC(t;3)_D$ remains more effective than CCSD(T)-h in capturing the triples missing in CCSDt when the total energies of the X^3B_1 and A^1A_1 states are examined. Indeed, as shown in Table 2, the CCSD(T)-h approach using the aug-cc-pVTZ basis set gives the 0.284 and 0.459 millihartree errors relative to CCSDT for the total energies of the X^3B_1 and A^1A_1 states, which should be compared to 0.130 and 0.409 millihartree, respectively, obtained in the $CC(t;3)_D$ /aug-cc-pVTZ calculations. Finally, in analogy to the TZ2P case, variant D of $CC(t;3)$ is more effective than variant A, which gives the 0.490 and 0.867 millihartree differences with the total energies of the X^3B_1 and A^1A_1 states obtained in the CCSDT calculations, when the aug-cc-pVTZ basis set is employed.

Although we have no access to the full CCSDT (or full CI) data for basis sets larger than aug-cc-pVTZ, the results in Tables 1 and 2 suggest that the $CC(t;3)_D$ approach advocated in the present study provides similarly accurate results for other basis sets, including aug-cc-pVQZ and the CBS limit explored in Table 2. Indeed, as shown in Table 2, the $CC(t;3)_D$ values of the nonrelativistic, purely electronic, adiabatic $A^1A_1-X^3B_1$ gap in

Table 2. The Adiabatic Singlet–Triplet Separation, $\Delta E_{S-T} = E(A^1A_1) - E(X^3B_1)$ (in kcal/mol), in CH_2 , along with the Corresponding Total Electronic Energies of the X^3B_1 and A^1A_1 States (in hartree), Obtained with Various CC Approaches Using the aug-cc-pVTZ and aug-cc-pVQZ Basis Sets and the CBS Extrapolations^a

method	aug-cc-pVTZ			aug-cc-pVQZ			CBS		
	$E(X^3B_1)$	$E(A^1A_1)$	ΔE_{S-T}	$E(X^3B_1)$	$E(A^1A_1)$	ΔE_{S-T}	$E(X^3B_1)$	$E(A^1A_1)$	ΔE_{S-T}
CCSD	−39.076387	−39.059493	10.60	−39.084024	−39.067547	10.34	−39.088557	−39.072419	10.13
CCSD(T)	−39.080127	−39.064588	9.75	−39.088107	−39.073004	9.48	−39.092889	−39.078140	9.26
CR-CC(2,3) _A ^b	−39.079904	−39.064151	9.89	−39.087874	−39.072559	9.61	−39.092649	−39.077690	9.39
CR-CC(2,3) _D	−39.080398	−39.064754	9.82	−39.088282	−39.073028	9.57	−39.092995	−39.078061	9.37
CCSDt	−39.077065	−39.060688	10.28	−39.084737	−39.068710	10.06	−39.089295	−39.073558	9.87
CCSD(T)-h	−39.080291	−39.064952	9.63	−39.088275	−39.073359	9.36	−39.093061	−39.078489	9.14
CC(t;3) _A	−39.080085	−39.064544	9.75	−39.088058	−39.072932	9.49	−39.092835	−39.078048	9.28
CC(t;3) _D	−39.080445	−39.065002	9.69	−39.088341	−39.073291	9.44	−39.093063	−39.078334	9.24
CCSDT	−39.080575	−39.065411	9.52						
experiment ^c									9.37

^aThe geometries, generated in the full CI calculations using the TZ2P basis set, were taken from ref 229. The spherical components of the d , f , and g basis functions were employed throughout and in all CC calculations the lowest occupied orbital was kept frozen. The active space used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of two active electrons and two active orbitals corresponding to HOMO and LUMO.

^bCR-CC(2,3)_A is equivalent to the CCSD(2)_T approach of ref 181. ^cObtained by correcting the experimentally derived value of the vibrationless adiabatic $A^1A_1 - X^3B_1$ energy gap reported in ref 294 for the relativistic and nonadiabatic (Born–Oppenheimer diagonal correction) effects calculated in refs 295 and 296, respectively (as described in ref 231).

methylene resulting from the calculations using the aug-cc-pVQZ basis set and the subsequent CBS extrapolations, of 9.44 and 9.24 kcal/mol, respectively, are in excellent agreement with the experimental estimate of 9.37 kcal/mol. At the same time, the CC(t;3)_D approach is capable of improving the CBS-extrapolated CCSDt and CCSD(T)-h gap values, which are 9.87 and 9.14 kcal/mol, respectively. It is true that the CC(t;3)_D value of the $A^1A_1 - X^3B_1$ gap in methylene resulting from the CBS extrapolations is no longer more accurate than the corresponding CBS-limit CCSD(T), CR-CC(2,3)_A, CR-CC(2,3)_D, and CC(t;3)_A results. We must keep in mind, however, that CC(t;3)_D also provides excellent total energies of the X^3B_1 and A^1A_1 states, which for every finite basis set, seem to agree with the corresponding full CCSDT data to within small fractions of a millihartree. None of the other triples corrections to the CCSD or CCSDt energies is equally effective. It is, therefore, interesting to examine if the analogous observations remain true for the stronger biradical systems, such as (HFH)[−] and TMM.

3.2. (HFH)[−]. Obtaining an accurate and balanced description of the lowest-energy singlet and triplet states becomes considerably more challenging when the (HFH)[−] system is examined. As mentioned in the Introduction, the $D_{\infty h}$ -symmetric (HFH)[−] molecule, in which both H–F bonds are simultaneously stretched, has been used in the literature as a prototype magnetic system, where two paramagnetic centers, each carrying an unpaired spin, represented by the terminal hydrogen atoms, are linked via a polarizable diamagnetic bridge constituted by the F[−] ion.²³⁸ The spins of the paramagnetic electrons of the H atoms can be parallel or antiparallel, yielding two different spin states, namely, a singlet, $X^1\Sigma_g^+$, which is a ground state, and a triplet, $A^3\Sigma_u^+$, which is the first excited state. The total electronic energies of these two states and the gap between them, which should approach zero as both H–F bonds are stretched to infinity and which provides information about the magnetic exchange coupling constant J as a function of the H–F distance R_{H-F} , have been studied using a variety of *ab initio* and density functional theory methods in refs 201, 212, 238, and 239. All of these studies show that the majority of electronic structure approaches encounter considerable problems with describing the $A^3\Sigma_u^+ - X^1\Sigma_g^+$

gap in the (HFH)[−] system. This also applies to methods based on CC theory, including the restricted as well as unrestricted CCSD and CCSD(T) approaches examined in refs 201 and 239, which provide an erratic description of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in (HFH)[−]. The restricted CCSD and CCSD(T) methods, which use the RHF reference for the $X^1\Sigma_g^+$ ground state and the ROHF reference for the $A^3\Sigma_u^+$ state, perform particularly poorly at larger H–F separations, whereas their unrestricted counterparts employing the UHF reference for both states, which improve the results in the asymptotic region, provide large errors in the description of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in (HFH)[−] at shorter H–F distances. In this work, where our main goal is the assessment of the effectiveness of the CC(t;3) methodology in reproducing total electronic energies of the lowest singlet and triplet states of biradical systems, and gaps between them resulting from the CCSDT calculations, rather than the discussion of issues related to the optimum choice of the reference determinants, we focus, for consistency reasons, on the restricted SRCC methods. We refer the reader to ref 201 for a discussion of the UHF-based SRCC calculations.

As shown in Tables 3 and 4, the main challenge for the CC theory, if we are to rely on the SRCC formalism and utilize the spin- and symmetry-adapted RHF/ROHF references, is in an accurate inclusion of higher-than-doubly excited clusters, particularly triples and particularly in the case of the $X^1\Sigma_g^+$ state, which has a manifestly MR character involving the doubly excited (HOMO)² → (LUMO)² determinant, in addition to the RHF configuration. As demonstrated in ref 201, the ratio of the full CI expansion coefficients at the (HOMO)² → (LUMO)² and RHF configuration state functions characterizing the $X^1\Sigma_g^+$ state, which is equivalent to the T_2 cluster amplitude corresponding to the (HOMO)² → (LUMO)² excitation, since HOMO and LUMO have different symmetries, increases, in absolute value, from 0.38 to 1.17 as R_{H-F} is varied between 1.5 and 4.0 Å. Thus, the moderately biradical (HFH)[−] system at shorter H–F separations becomes a strong biradical at larger H–F distances. Because of the significant biradical character of the (HFH)[−] ion at almost all H–F separations shown in Tables 3 and 4, the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in this system is already quite small and sensitive to the electron correlation treatment used in the determination of the $X^1\Sigma_g^+$

Table 3. A Comparison of the Total Energies Obtained with Various CC and Full CI Methods for the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ States of the Linear, $D_{\infty h}$ -Symmetric (HFH) $^-$ System Described by the 6-31G(d,p) Basis Set As a Function of the H–F Distance R_{H-F} (in Å)^a

R_{H-F}	CCSD	CCSD(T)	CR-CC(2,3) _A ^b	CR-CC(2,3) _D	CCSDt	CCSD(T)-h	CC(t;3) _A	CC(t;3) _D	CCSDT	full CI ^c
$X^1\Sigma_g^+$										
1.500	11.411	−0.435	2.208	−0.343	2.531	−0.322	0.261	−0.197	−100.588130	−100.589392
1.625	13.067	−1.104	2.447	−0.467	2.541	−0.397	0.293	−0.164	−100.583270	−100.584704
1.750	14.738	−2.206	2.566	−0.686	2.557	−0.481	0.323	−0.135	−100.576056	−100.577669
1.875	16.259	−3.858	2.505	−1.018	2.575	−0.576	0.346	−0.113	−100.568365	−100.570151
2.000	17.453	−6.122	2.240	−1.454	2.583	−0.686	0.358	−0.097	−100.561110	−100.563055
2.125	18.181	−8.994	1.795	−1.937	2.566	−0.813	0.354	−0.087	−100.554605	−100.556686
2.250	18.360	−12.410	1.246	−2.377	2.513	−0.953	0.333	−0.082	−100.548898	−100.551083
2.375	17.971	−16.256	0.692	−2.685	2.418	−1.096	0.296	−0.088	−100.543969	−100.546222
2.500	17.051	−20.360	0.224	−2.800	2.283	−1.223	0.244	−0.108	−100.539783	−100.542059
3.000	10.449	−34.862	−0.340	−1.837	1.618	−1.251	−0.021	−0.335	−100.529438	−100.531336
4.000	1.907	−40.726	−0.026	−0.290	0.768	0.146	−0.063	−0.243	−100.525901	−100.526513
MUE ^d	18.360	40.726	2.566	2.800	2.583	1.251	0.358	0.335		
NPE ^e	16.453	40.291	2.906	2.509	1.814	1.397	0.421	0.253		
$A^3\Sigma_u^+$										
1.500	2.268	0.240	0.199	−0.217	1.894	0.169	0.130	−0.207	−100.545633	−100.545993
1.625	2.119	0.253	0.188	−0.198	1.755	0.190	0.121	−0.189	−100.552401	−100.552773
1.750	1.966	0.269	0.174	−0.181	1.615	0.217	0.109	−0.175	−100.554908	−100.555291
1.875	1.817	0.288	0.158	−0.173	1.479	0.248	0.095	−0.168	−100.554708	−100.555097
2.000	1.678	0.308	0.141	−0.172	1.352	0.280	0.080	−0.167	−100.552882	−100.553271
2.125	1.554	0.326	0.127	−0.166	1.241	0.310	0.068	−0.162	−100.550135	−100.550520
2.250	1.446	0.335	0.115	−0.165	1.149	0.331	0.059	−0.160	−100.546938	−100.547315
2.375	1.354	0.333	0.104	−0.167	1.081	0.339	0.052	−0.162	−100.543628	−100.543996
2.500	1.277	0.319	0.097	−0.167	1.035	0.332	0.050	−0.162	−100.540435	−100.540796
3.000	1.130	0.192	0.085	−0.168	1.031	0.207	0.066	−0.166	−100.530911	−100.531257
4.000	1.123	0.084	0.082	−0.180	1.121	0.085	0.082	−0.180	−100.526164	−100.526513
MUE ^d	2.268	0.335	0.199	0.217	1.894	0.339	0.130	0.207		
NPE ^e	1.145	0.251	0.117	0.053	0.863	0.254	0.080	0.046		

^aThe CCSDT and full CI values are total energies, in hartree. The remaining energies are errors relative to CCSDT, in millihartree. The lowest-energy occupied orbital was frozen in post-SCF calculations and the spherical components of the fluorine *d* orbital were employed throughout. The active space used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of two active electrons and two active orbitals corresponding to HOMO and LUMO. ^bCR-CC(2,3)_A is equivalent to the CCSD(2)_T approach of ref 181. ^cFrom ref 201. ^dThe maximum unsigned error relative to CCSDT (in millihartree). ^eThe nonparallelity error relative to CCSDT (in millihartree).

and $A^3\Sigma_u^+$ states in the region of shorter H–F distances, while rapidly decreasing as R_{H-F} becomes larger, causing troubles to the standard CCSD and CCSD(T) approaches, which are incapable of handling such a challenging situation. Indeed, the errors in the RHF/ROHF-based CCSD values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in (HFH) $^-$, as described by the 6-31G(d,p) basis set, increase from 2205 cm^{−1} or 23.1% at $R_{H-F} = 1.5$ Å to 4109 cm^{−1} or 496.9% at $R_{H-F} = 2.25$ Å, being generally large at practically all of the remaining H–F distances. According to the full CI calculations, the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ separation in (HFH) $^-$ should be positive at all R_{H-F} values, but the RHF/ROHF-based CCSD calculations make it negative in the $1.875 \text{ Å} \leq R_{H-F} \leq 4.0 \text{ Å}$ region. For example, the positive values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap at $R_{H-F} = 2.0, 2.25,$ and 2.5 Å , which in the full CI calculations are 2147, 827, and 277 cm^{−1}, become −1656, −3282, and −3605 cm^{−1}, respectively, when the ROHF/RHF-based CCSD method is employed. Clearly, one needs to include the effects of T_3 clusters to improve the poor CCSD results, since CCSD cannot balance the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, describing the largely single-configurational $A^3\Sigma_u^+$ state a lot more accurately than the quasi-degenerate $X^1\Sigma_g^+$ state. This can be seen by comparing the CCSD and CCSDT energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states shown in Table 3. The full treatment of T_3 clusters offered by CCSDT reduces the large errors in the CCSD results for the $X^1\Sigma_g^+$ state, relative to full CI, which in the $R_{H-F} = 1.5\text{--}3.0 \text{ Å}$ region range between 12.346 and 20.546 millihartree, to 1.262–2.276 millihartree,

which obviously is a much better description. In the case of the $A^3\Sigma_u^+$ state, which the CCSD approach describes more accurately, giving the 1.472–2.628 millihartree errors in the entire $R_{H-F} = 1.5 - 4.0 \text{ Å}$ region, full CCSDT becomes virtually exact, providing errors relative to full CI that do not exceed 0.389 millihartree. As a result and as shown in Table 4, the erratic description of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in the (HFH) $^-$ system by the CCSD approach becomes a lot more reasonable when the CCSDT method is employed. Some small errors due to the use of restricted references and the neglect of higher–than–triply excited clusters, particularly T_4 , remain when the RHF/ROHF-based CCSDT approach is employed, and we will examine this aspect of theory in the future work, but we can certainly treat the restricted CCSDT results for the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states of (HFH) $^-$ listed in Tables 3 and 4 as accurate enough for benchmarking the SRCC methods with approximate treatments of T_3 clusters, such as CC(t;3).

As already alluded to above, the popular CCSD(T) approach, which uses arguments originating from MBPT to estimate the T_3 effects, is incapable of handling the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in (HFH) $^-$. In fact, the RHF/ROHF-based CCSD(T) results for the (HFH) $^-$ system become even more erratic at larger H–F distances than the corresponding CCSD results. For example, as shown in Tables 3 and 4, the absolute values of the differences between the RHF-based CCSD(T) energies of the $X^1\Sigma_g^+$ state and their CCSDT or full CI counterparts exceed 10 millihartree when $R_{H-F} \geq 2.25 \text{ Å}$, reaching more than 40 millihartree at

Table 4. The $A^3\Sigma_u^+ - X^1\Sigma_g^+$ Gap for the Linear, $D_{\infty h}$ -Symmetric (HFH) $^-$ System (in cm^{-1}) Described by the 6-31G(d,p) Basis Set As a Function of the H–F Distance $R_{\text{H-F}}$ (in Å)^a

$R_{\text{H-F}}$	CCSD	CCSD(T)	CR-CC(2,3) _A ^b	CR-CC(2,3) _D	CCSDt	CCSD(T)-h	CC(t;3) _A	CC(t;3) _D	CCSDT	full CI ^c
1.500	7320	9468	8886	9355	9187	9435	9298	9325	9327	9525
1.625	4372	7066	6279	6834	6602	6904	6737	6770	6775	7008
1.750	1838	5179	4117	4752	4435	4795	4595	4633	4642	4911
1.875	−172	3902	2482	3183	2757	3178	2942	2985	2997	3304
2.000	−1656	3212	1345	2087	1536	2018	1745	1791	1806	2147
2.125	−2668	3023	615	1370	690	1228	919	965	981	1353
2.250	−3282	3225	182	916	131	712	370	413	430	827
2.375	−3572	3714	−54	628	−219	390	22	59	75	488
2.500	−3605	4394	−171	435	−417	198	−186	−155	−143	277
3.000	−2369	7370	−230	43	−452	−3	−304	−286	−323	17
4.000	−230	8899	−34	−33	20	−71	−26	−44	−58	0

^aThe lowest-energy occupied orbital was frozen in post-SCF calculations and the spherical components of the fluorine *d* orbital were employed throughout. The active space used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of two active electrons and two active orbitals corresponding to HOMO and LUMO. ^bCR-CC(2,3)_A is equivalent to the CCSD(2)_T approach of ref 181. ^cFrom ref 201.

$R_{\text{H-F}} = 4.0$ Å, where, according to the full CI and CCSDT calculations, the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states should be practically degenerate and where the analogous differences between the ROHF-based CCSD(T) and CCSDT or full CI energies characterizing the $A^3\Sigma_u^+$ state do not exceed small fractions of a millihartree. The huge lowering of the energy of the $X^1\Sigma_g^+$ state at larger H–F separations, which exceeds ~ 40 millihartree when $R_{\text{H-F}} = 4.0$ Å, reverses the incorrect ordering of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states of (HFH) $^-$ observed in the RHF/ROHF-based CCSD calculations in the $1.875 \text{ Å} \leq R_{\text{H-F}} \leq 4.0 \text{ Å}$ region, but this does not help anything. Indeed, the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap calculated with the CCSD(T) approach employing restricted references becomes larger and larger rather than smaller and smaller as the H–F distances increase, reaching completely unphysical values, such as 8899 cm^{-1} at $R_{\text{H-F}} = 4.0$ Å, where full CI gives the numerical zero and full CCSDT -58 cm^{-1} only. The UHF-based CCSD(T) approach would alleviate this problem, restoring the asymptotic degeneracy of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, but, as demonstrated in ref 201, the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in the (HFH) $^-$ system obtained in the UHF-based CCSD(T) calculations decays too fast with $R_{\text{H-F}}$ compared to full CI, and the errors in the UHF-based CCSD(T) results for the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap at shorter H–F distances are much larger than those obtained in the CCSD(T) calculations employing restricted references. In other words, neither restricted nor unrestricted CCSD(T) provide an adequate description of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in (HFH) $^-$, since one cannot rely on the conventional (T) correction to obtain a reasonable and balanced representation of the T_3 correlation effects on the SRCC energies over a wider range of the H–F separations. Alternative and more robust ways of handling connected triple excitations in the SRCC formalism are needed to reproduce the full CCSDT-quality data for the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states in the (HFH) $^-$ system and the gap between them.

As shown in refs 201 and 239, the CR-CC(2,3) methodology, including variants A and D of CR-CC(2,3) examined in Tables 3 and 4, offers great improvements in the results compared to CCSD(T), particularly for the quasi-degenerate $X^1\Sigma_g^+$ state and particularly at larger H–F separations. Indeed, the large maximum unsigned error (MUE) and nonparallelity error (NPE) values relative to full CCSDT characterizing the CCSD(T) energies of the $X^1\Sigma_g^+$ state in the $R_{\text{H-F}} = 1.5\text{--}4.0$ Å region, of 40.726 and 40.291 millihartree, reduce to 2.566 and 2.906 millihartree, respectively, when the CR-CC(2,3)_A approach is employed, and 2.800 and 2.509 millihartree, respectively, when

the CR-CC(2,3)_D approximation is utilized. Although CCSD(T) works well for the $A^3\Sigma_u^+$ state, producing small MUE and NPE values relative to full CCSDT of only 0.335 and 0.251 millihartree, respectively, both variants of CR-CC(2,3) improve the CCSD(T) results for the $A^3\Sigma_u^+$ state as well, so that the overall performance of the CR-CC(2,3)_A and CR-CC(2,3)_D methods in describing the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in (HFH) $^-$ is a lot better than the performance of CCSD(T). This is particularly true for the CR-CC(2,3)_D approach, which improves the CCSD(T) results for the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap, when compared to the parent CCSDT theory, at all H–F separations, not only at the larger ones. Indeed, the CR-CC(2,3)_D method reduces the 141, 537, and 1406 cm^{-1} differences between the CCSD(T) and CCSDT values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap at $R_{\text{H-F}} = 1.5, 1.75,$ and 2.0 Å to 28, 110, and 281 cm^{-1} , respectively, while replacing the massive errors in the CCSD(T) description of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap at larger H–F distances, which are, for example, 4537, 7693, and 8957 cm^{-1} at $R_{\text{H-F}} = 2.5, 3.0,$ and 4.0 Å , respectively, by the more acceptable errors on the order of dozens or hundreds of cm^{-1} . However, in spite of these improvements, neither the CR-CC(2,3)_D results nor their CR-CC(2,3)_A counterparts can be viewed as completely satisfactory. It is, for example, difficult to treat the 486 cm^{-1} difference between the CR-CC(2,3)_D and CCSDT values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap at $R_{\text{H-F}} = 2.25 \text{ Å}$, where the CCSDT gap value is 430 cm^{-1} , as a good result. It is equally difficult to accept the fact that CR-CC(2,3)_D provides opposite signs of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in the $R_{\text{H-F}} = 2.5\text{--}3.0 \text{ Å}$ region when compared to its full CCSDT counterpart. Variant A of CR-CC(2,3) behaves better in this regard, providing $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap values that have the same signs as those resulting from the CCSDT calculations in the $R_{\text{H-F}} = 2.5\text{--}3.0 \text{ Å}$ region, but the CR-CC(2,3)_A approach is considerably less accurate than its CR-CC(2,3)_D analog at shorter H–F distances, increasing, for example, the 28, 110, and 281 cm^{-1} errors in the CR-CC(2,3)_D gap values relative to CCSDT at $R_{\text{H-F}} = 1.5, 1.75,$ and 2.0 Å to 441, 525, and 461 cm^{-1} , respectively. It is quite clear that non-iterative triples corrections to the CCSD energies, even the CR-CC(2,3) ones, are not entirely satisfactory.

The active-space treatment of triples via the CCSDt approach, although providing more uniform errors at various H–F separations relative to full CCSDT, when compared to the CR-CC(2,3)_A and CR-CC(2,3)_D calculations, both for the total energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states and the gap between them, is not completely satisfactory either. Indeed, the differences

between the CCSDt and CCSDT gaps increase from 140 cm^{-1} at $R_{\text{H-F}} = 1.5\text{ Å}$ to 299 cm^{-1} at $R_{\text{H-F}} = 2.25\text{ Å}$, to decrease again to 78 cm^{-1} at $R_{\text{H-F}} = 4.0\text{ Å}$. These differences do not appear to be very large, but we must remember that the 299 and 78 cm^{-1} differences between the CCSDt and CCSDT values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap at $R_{\text{H-F}} = 2.25$ and 4.0 Å are comparable, in absolute value, to the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gaps resulting from the CCSDT calculations, which are 430 and -58 cm^{-1} , respectively. Moreover, the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap values obtained with CCSDt at $R_{\text{H-F}} = 2.375$ and 4.0 Å have different signs than their CCSDT counterparts. On the basis of the results in Tables 3 and 4, we can conclude that the inability of the CCSDt approach to reproduce the full CCSDT singlet–triplet gap values in the $(\text{HFH})^-$ system as precisely as one would like must be directly related to the rather significant differences between the total energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states resulting from the CCSDt and CCSDT calculations, which are as large as 2.583 millihartree in the case of the $X^1\Sigma_g^+$ state and 1.894 millihartree in the $A^3\Sigma_u^+$ case. We could reduce the differences between the CCSDt and CCSDT total energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states by using larger numbers of active orbitals in the CCSDt calculations, but this would make these calculations more expensive. In our view, it is more interesting to examine an alternative strategy, where instead of using larger active spaces, one attempts to improve the quality of the CCSDt results, obtained with a minimum active space of only two orbitals exploited in the present work, by correcting the CCSDt energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states of $(\text{HFH})^-$ for the effects of triple excitations missing in the CCSDt considerations.

All three approaches that correct the CCSDt energies for the missing triple excitations, examined in this study, i.e., CCSD(T)-h, $\text{CC}(t;3)_A$, and $\text{CC}(t;3)_D$, improve the total energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states of $(\text{HFH})^-$, when compared to the $\text{CR-CC}(2,3)_A$, $\text{CR-CC}(2,3)_D$, and CCSDt calculations, bringing the results to a closer agreement with the full CCSDT data, but the $\text{CC}(t;3)_D$ method is by far most effective. Indeed, the CCSD(T)-h approach reduces the MUE values relative to full CCSDT characterizing the $\text{CR-CC}(2,3)_A$, $\text{CR-CC}(2,3)_D$, and CCSDt energies of the $X^1\Sigma_g^+$ state along the $R_{\text{H-F}}$ coordinate, of 2.566, 2.800, and 2.583 millihartree, respectively, to 1.251 millihartree, but this is nowhere near the 0.335 millihartree MUE value obtained with $\text{CC}(t;3)_D$. Similar remarks apply to the corresponding NPE values, which in the $\text{CR-CC}(2,3)_A$, $\text{CR-CC}(2,3)_D$, CCSDt, and CCSD(T)-h calculations for the $X^1\Sigma_g^+$ state are 2.906, 2.509, 1.814, and 1.397 millihartree, respectively, and as little as 0.253 millihartree in the case of $\text{CC}(t;3)_D$. The situation for the “easier,” largely single-configurational, $A^3\Sigma_u^+$ state is somewhat different, since the $\text{CR-CC}(2,3)_A$, $\text{CR-CC}(2,3)_D$, CCSD(T)-h, and $\text{CC}(t;3)_D$ corrections lead to very small MUE and NPE values relative to full CCSDT, on the order of 0.1–0.3 millihartree, but once again the $\text{CC}(t;3)_D$ approach improves the results of the CCSD(T)-h calculations, reducing the MUE and NPE values relative to CCSDT characterizing the CCSD(T)-h energies, of 0.339 and 0.254 millihartree, to 0.207 and 0.046 millihartree, respectively.

The above observations have major consequences on the results obtained for the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap. Indeed, the $\text{CC}(t;3)_D$ approach reduces the rather significant errors in the $\text{CR-CC}(2,3)_A$, $\text{CR-CC}(2,3)_D$, and CCSDt values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap relative to the corresponding full CCSDT data, which are as large as 525 cm^{-1} in the $\text{CR-CC}(2,3)_A$ case, 578 cm^{-1} in the case of $\text{CR-CC}(2,3)_D$, and 299 cm^{-1} in the CCSDt case, to $2\text{--}37\text{ cm}^{-1}$ when the entire $R_{\text{H-F}} = 1.5\text{--}4.0\text{ Å}$ region is examined. This should be contrasted with the CCSD(T)-h approach, which improves total energies resulting from the CCSDt calculations and, at several H–F distances, the

$\text{CR-CC}(2,3)_A$ and $\text{CR-CC}(2,3)_D$ energies, particularly in the case of the $X^1\Sigma_g^+$ state, but does not offer substantial improvements in the description of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap compared to the $\text{CR-CC}(2,3)_A$, $\text{CR-CC}(2,3)_D$, and CCSDt calculations, providing errors relative to full CCSDT that can be as large as 341 cm^{-1} . Perhaps more importantly, the CCSD(T)-h method does not always bring the CCSDt results for the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in $(\text{HFH})^-$ to a closer agreement with CCSDT (cf. the CCSD(T)-h and CCSDt values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in the $R_{\text{H-F}} = 2.375\text{--}3.0\text{ Å}$ region), which is an undesired behavior, since the purpose of the CCSD(T)-h calculations is to correct the CCSDt results for the missing triple excitations. In fact, the CCSD(T)-h value of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in $(\text{HFH})^-$ at $R_{\text{H-F}} = 2.5\text{ Å}$ is positive, where full CCSDT produces a negative gap value. On the basis of the results in Tables 3 and 4, one might make a claim that CCSD(T)-h improves the results of the CCSDt calculations compared to full CI, but this is not a proper way of judging the performance of the CCSD(T)-h method, which by design aims at approximating total energies obtained with CCSDT. We could make similar claims about the $\text{CR-CC}(2,3)_D$ approximation, which was compared with full CI in refs 201 and 239, where we could, for example, observe the sub-millihartree differences between the $\text{CR-CC}(2,3)_D$ and full CI energies of the $X^1\Sigma_g^+$ state at all H–F distances shown in Tables 3 and 4, but we must pay closer attention to the more important fact that the differences between the $\text{CR-CC}(2,3)_D$ and CCSDT energies for this state can be as large as 2.800 millihartree. It is quite clear that the use of the conventional (T) expressions to correct the results of the CCSDt calculations for the triple excitations missing in CCSDt in an *ad hoc* manner, as in the CCSD(T)-h approach, is not as robust as the use of the $\text{CR-CC}(2,3)$ -style corrections to the CCSDt energies defining the $\text{CC}(t;3)$ methodology, derived with the help of the rigorous $\text{CC}(P;Q)$ formalism. The tiny, $2\text{--}37\text{ cm}^{-1}$, differences between the $\text{CC}(t;3)_D$ and full CCSDT values of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap in $(\text{HFH})^-$ in the entire $R_{\text{H-F}} = 1.5\text{--}4.0\text{ Å}$ region, combined with the observation that the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gaps resulting from the $\text{CC}(t;3)_D$ and CCSDT calculations have always the same sign and with the fact that the MUE and NPE values relative to full CCSDT characterizing the $\text{CC}(t;3)_D$ energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states do not exceed 0.2–0.3 millihartree, are very promising from the point of view of future applications of the $\text{CC}(t;3)_D$ approach.

As in the case of methylene, the $\text{CC}(t;3)_D$ method, which uses the more complete, Epstein–Nesbet-like, form of the $D_{0,abc}^{ijk}(\text{CCSDt})$ denominator entering the $\text{CC}(t;3)$ expressions, is more effective in improving the CCSDt results than the $\text{CC}(t;3)_A$ approach, which relies on the Møller–Plesset form of $D_{0,abc}^{ijk}(\text{CCSDt})$. On the other hand, unlike in the methylene case, the $\text{CC}(t;3)_A$ approach is considerably more accurate than the CCSD(T)-h correction to CCSDt. This applies to the total energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, where the $\text{CC}(t;3)_A$ and $\text{CC}(t;3)_D$ results are often quite similar and much better than those obtained with CCSD(T)-h, as well as to the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap. In the latter case, the differences between the $\text{CC}(t;3)_A$ and CCSDT values range between 19 and 62 cm^{-1} , which is a major improvement over CCSD(T)-h that gives errors relative to CCSDT as large as 341 cm^{-1} . Once again though, the $19\text{--}62\text{ cm}^{-1}$ differences between the $\text{CC}(t;3)_A$ and full CCSDT gap values are not as good as the $2\text{--}37\text{ cm}^{-1}$ differences obtained with $\text{CC}(t;3)_D$. The fact that both variants of the $\text{CC}(t;3)$ methodology, not only the somewhat more sophisticated $\text{CC}(t;3)_D$ approach but also the simplified $\text{CC}(t;3)_A$ approximation, are much more accurate than

Table 5. A comparison of Various CC Energies for the X^3A_2' and B^1A_1 States of TMM Obtained in the Calculations with the cc-pVDZ Basis Set Using the SF-DFT/6-31G(d) Geometries Reported in Ref 208^a

state	CCSD	CCSD(T)	CR-CC(2,3) _A ^b	CR-CC(2,3) _D	CCSDt	CCSD(T)-h	CC(t;3) _A	CC(t;3) _D	CCSDT
X^3A_2'	19.167	0.960	2.977	0.391	12.500	0.115	1.568	0.015	−155.466207
B^1A_1	58.053	5.160	19.780	13.372	12.236	−2.886	0.790	−0.780	−155.431597

^aThe CCSDT values are total energies, in hartree. The remaining energies are errors relative to CCSDT, in millihartree. The lowest-energy occupied orbitals correlating with the 1s shells of the carbon atoms were frozen in post-SCF calculations and the spherical components of the *d* orbitals were employed throughout. The active space used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of four active electrons and four active orbitals corresponding to the valence π system of TMM. ^bCR-CC(2,3)_A is equivalent to the CCSD(2)_T approach of ref 181.

the CCSD(T)-h approach in the case of the (HFH)[−] system is related to the strongly biradical character of (HFH)[−], which is much stronger than in the methylene case. By exploiting a more robust form of the triples correction in the CC(t;3) considerations compared to the standard CCSD(T) correction used in CCSD(T)-h, which is safe to use when the degree of electronic quasi-degeneracy is small but not appropriate when quasi-degeneracies become more substantial, one should observe improvements in the CCSD(T)-h results when using the CC(t;3) methodology, which become particularly significant in the strongly biradical situations. This is exactly what we observe when we compare the performance of the CC(t;3) and CCSD(T)-h methods in calculations for the weakly biradical methylene molecule and strongly biradical (HFH)[−] system.

3.3. Trimethylenemethane. Our final example is the TMM molecule, a fascinating non-Kekulé hydrocarbon characterized by the delocalization of four π electrons over four closely spaced π -type MOs, which results in a triplet ground state and the low-lying quasi-degenerate singlet excited states that have a largely biradical nature.^{208,268,271} In this case, as explained in the Introduction and in the beginning of this section, we focused on the performance of the CC(t;3) methodology, as compared to other treatments of the connected triple excitations within the SRCC framework, in determining the total energies of the D_{3h} -symmetric X^3A_2' ground state, the C_{2v} -symmetric B^1A_1 excited state, and the adiabatic gap between them (see Tables 5 and 6). As explained in refs 208, 268, and 271, the triplet ground state is largely single-configurational, the B^1A_1 excited state is strongly biradical, having a manifestly MR character, and the main challenge is in obtaining an accurate and balanced description of the many-electron correlation effects characterizing both states, which are mostly dynamical in the case of the former state and substantially nondynamical in the latter case.

As pointed out in the Introduction, a great deal of theoretical effort has been dedicated to responding to this challenge.^{109,208,209,233,253–269,271,272} If we limit ourselves to the CC work, the most accurate recent results were obtained using the high-level MRCC approaches of the SU²³³ as well as SS types,^{109,233,272} the MRCI-corrected RMRC methods,²³³ and the sophisticated SR-type EOM-SF-CC approach with a full treatment of triple excitations in the EOM operator R_{μ} , referred to as EOM-SF-CC(2,3).²⁰⁹ By capturing the relevant higher-order correlation effects, the best genuine MRCC theories employing the Jeziorski–Monkhorst ansatz, including the size-extensivity corrected BWMRCCSD method, abbreviated as BWCCSD-it,²⁷² the two approximate ways of handling the triply excited clusters in the BWMRCC theory, abbreviated as BWCCSDT-1 α and BWCCSDT- α ,²⁷² and the SUMRCCSD approach, abbreviated in ref 233, where the calculations of this type were reported, as SUCCSD, reproduce the experimentally derived estimate of the purely electronic B^1A_1 – X^3A_2' gap in TMM reported in ref 208, of 18.1 kcal/mol, to within ~ 1 –3 kcal/mol,

when the cc-pVDZ and cc-pVTZ basis sets are employed (see Table 6). As shown in ref 109, the BCCC variant of the SSMRCC theory, abbreviated in ref 109 as CAS-BCCC4, gives equally good results (19.0 kcal/mol, when the basis set of the double- ζ plus polarization quality is employed). The RMRCSSD(T) approach, in which one corrects the MRCI-corrected RMRCSSD energies for the triples corrections missing in RMRCSSD using the (T)-like expressions, works well, too, although the results of the RMRCSSD(T) calculations are not entirely satisfactory. As shown in ref 233 and Table 6, the most accurate RMRCSSD(T) calculations to date, performed using the cc-pVTZ basis set, the MCSCF orbitals, and the (T)_{se} variant of the (T) correction, in which the nondiagonal nature of the Fock matrix in calculations for the triplet ground state is ignored to regain size extensivity, give 22.6 kcal/mol. This is telling us that even the best MRCC-type theories, which are designed to handle electronic quasi-degeneracies, such as those characterizing the B^1A_1 state, through the use of multidimensional reference spaces, face challenges when handling problems as complex as the B^1A_1 – X^3A_2' gap in TMM.

Indeed, if we carefully analyze the results of various earlier calculations summarized in Table 6, we can see that none of the MRCC-type results can be viewed as perfectly converged. For example, the RMRCSSD approach, which uses MRCI to provide information about the triply and quadruply excited clusters missing in the CCSD calculations, gives a poor gap value of 30.6 kcal/mol, when the RHF/ROHF orbitals are employed, but a much better result of 23.8 kcal/mol, when the MCSCF orbitals are employed. The BWCCSD-it approach, which ignores the triply excited clusters altogether, gives the vibrationless B^1A_1 – X^3A_2' gap values of about 18 kcal/mol, in excellent agreement with the experimentally derived result of 18.1 kcal/mol, but the BWCCSDT-1 α and BWCCSDT- α calculations, which incorporate the T_3 clusters within the BWMRCC framework, worsen the results, lowering the gap to 14.9 kcal/mol in the BWCCSDT-1 α case. In other words, the use of multidimensional reference spaces and sophisticated MRCC-style formalisms does not necessarily guarantee good results. As a matter of fact, practically none of the MRCC calculations performed to date have produced the B^1A_1 – X^3A_2' gap in TMM, which would be as accurate as the EOM-SF-CC(2,3)/cc-pVTZ value of 18.2 kcal/mol obtained in ref 209. Thus, in at least some applications involving singlet–triplet gaps in biradical systems, one may be better off by capturing the relevant dynamical and nondynamical correlation effects dynamically by including the higher-order components of the cluster operator T and, if appropriate, the EOM excitation operator R_{μ} , such as triples, within the SRCC or EOMCC framework, which are conceptually and algorithmically much simpler than the genuine MRCC considerations. The EOM-SF-CC(2,3)/cc-pVTZ result listed in Table 6, taken from ref 209, conveys this message in a very transparent manner.

Table 6. The Singlet–Triplet Separation, $\Delta E_{S-T} = E(B^1A_1) - E(X^3A_2')$ (in kcal/mol), for TMM, As Obtained with Various CC and CI Methods, and the cc-pVDZ and cc-pVTZ Basis Sets

method	cc-pVDZ	cc-pVTZ
CCSD ^{a,b}	46.1	46.9
CCSD(T) ^{a,b}	24.4	27.1
CR-CC(2,3) _A ^{a,b,c}	32.3	33.6
CR-CC(2,3) _D ^{a,b}	29.9	31.8
CCSDt ^{a,b}	21.6	22.6
CCSD(T)-h ^{a,b}	19.8	19.3
CC(t;3) _A ^{a,b}	21.2	21.8
CC(t;3) _D ^{a,b}	21.2	21.7
CCSDT ^{a,b}	21.7	
2R SUCCSD/RHF ^d		19.9
2R SUCCSD/MCSCF ^d		16.1
2R RMRCCSD/RHF ^d		30.6
2R RMRCCSD/MCSCF ^d		23.8
2R RMRCCSD(T) _f /RHF ^d		25.8
2R RMRCCSD(T) _f /MCSCF ^d		23.6
2R RMRCCSD(T) _{se} /RHF ^d		23.8
2R RMRCCSD(T) _{se} /MCSCF ^d		22.6
SF-CIS ^{b,e}		20.4
SF-CIS(D) ^{b,e}		20.6
SF-OD ^{b,e}		21.7
EOM-SF-CCSD ^{b,f}		21.5
EOM-SF-CC(2,3) ^{b,f}		18.2
4R BWCCSD it ^g	18.2	17.8
4R BWCCSDT-1 α ^g	14.9	
4R BWCCSDT- α ^g	15.6	
exptl. ^h	16.0 \pm 0.1	
exptl. – $\Delta ZPVE$ ⁱ	18.1	

^aThis work. The lowest-energy occupied orbitals correlating with the 1s shells of the carbon atoms were frozen in post-SCF calculations and the spherical components of the *d* and *f* orbitals were employed throughout. The active space used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of four active electrons and four active orbitals corresponding to the valence π system of TMM. ^bThe result obtained using the single-point calculations at the SF-DFT/6-31G(d) geometries reported in ref 208. ^cCR-CC(2,3)_A is equivalent to the CCSD(2)_T approach of ref 181. ^dThe two-reference (2R) SUCCSD and RMRCC results using RHF and MCSCF orbitals, reported in ref 233. The (T) corrections to the 2R RMRCCSD energies were calculated in two different ways. In the “size-extensive” (T)_{se} case, the nondiagonal nature of the Fock matrix was ignored, and only the diagonal elements were accounted for, so that the resulting triples correction is size extensive. In the “full” (T)_f variant, the off-diagonal Fock matrix elements were included. ^eFrom ref 208. ^fFrom ref 209. ^gThe four-reference (4R) BWCC results using CASSCF orbitals taken from ref 272, including the 4R BWCCSD calculations with the iterative size-extensivity correction, abbreviated as 4R BWCCSD-it, and the results obtained with two types of the approximate 4R BWCCSDT approaches, referred to in ref 272 as the 4R BWCCSDT-1 α and 4R BWCCSDT- α methods. ^hFrom ref 279. ⁱThe estimate of the purely electronic ΔE_{S-T} gap obtained by subtracting the zero-point vibrational energy correction $\Delta ZPVE$ resulting from the SF-DFT/6-31G(d) calculations reported in ref 208 from the experimental singlet–triplet separation determined in ref 279.

The SRCCSDT calculations using the ROHF reference for the X^3A_2' state, the RHF reference for the B^1A_1 state, and the cc-pVDZ basis set, which we performed in this study and which produce a reasonably accurate value of the purely electronic $B^1A_1-X^3A_2'$ gap in TMM of 21.7 kcal/mol, are proving the

same point, too. Although the CCSDT/cc-pVDZ value of the $B^1A_1-X^3A_2'$ gap in TMM obtained in the present work is not as impressive as the EOM-SF-CC(2,3)/cc-pVTZ result obtained in ref 209, which may be a consequence of using the relatively poor RHF reference in the calculations for the quasi-degenerate B^1A_1 state and, perhaps, of the non-negligible role of the basis set and T_4 effects, the CCSDT/cc-pVDZ data in Tables 5 and 6 are certainly accurate enough to provide reliable information for assessing the performance of the approximate treatments of triple excitations within the SRCC framework in calculations for TMM. As explained in the beginning of this section, the CCSDT/cc-pVTZ calculations for the X^3A_2' and B^1A_1 states of TMM turned out to be prohibitively expensive for us, but, judging by the rather weak dependence of the $B^1A_1-X^3A_2'$ gap in TMM on the basis set, observed, for example, in the well-behaved CCSDt and CC(t;3) calculations, which we could perform using the cc-pVDZ and cc-pVTZ bases, we should be able to treat the CCSDT/cc-pVDZ energies as reliable enough for judging the accuracy of the CCSD(T), CCSD(2)_T or CR-CC(2,3)_A, CR-CC(2,3)_D, CCSDt, CCSD(T)-h, CC(t;3)_A, and CC(t;3)_D calculations. All of these calculations replace the expensive iterative CPU steps of CCSDT that scale as N^8 with the system size N by the much more manageable iterative N^6 -type and noniterative N^7 -type calculations, so it is very useful to learn which of these approximate treatments of triple excitations within the SRCC theory works best in the challenging TMM case.

It is clear from the results in Tables 5 and 6 that none of the noniterative corrections to the CCSD energies provide an accurate description of the $B^1A_1-X^3A_2'$ gap in TMM. It is true that for each basis set used in this study both CCSD(T) and its CR-CC(2,3)_A (i.e., CCSD(2)_T) and CR-CC(2,3)_D analogs improve the extremely poor CCSD results, but neither CCSD(T) nor CCSD(2)_T, and not even variant D of CR-CC(2,3), which is usually more accurate than the former two methods, offer a satisfactory performance. As in the previously examined (HFH)[−] case and as in the case of biradical reaction pathways considered in ref 214, one can attribute the failure of the CCSD(T), CCSD(2)_T or CR-CC(2,3)_A, and CR-CC(2,3)_D approaches to the use of the CCSD values of the T_1 and T_2 clusters, when determining the *a posteriori* corrections due to triples, and to 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 CCSD(T)-type approximations. Indeed, as shown in Table 5, the neglect of the coupling among the T_1 , T_2 , and T_3 clusters in the CCSD(T), CCSD(2)_T or CR-CC(2,3)_A, and CR-CC(2,3)_D calculations results in the rather large, 5.160–19.780 millihartree, errors relative to the CCSDT energies for the quasi-degenerate B^1A_1 state that do not balance the much smaller errors, ranging from 0.391 millihartree in the CR-CC(2,3)_D case to 2.977 millihartree in the case of the CCSD(2)_T or CR-CC(2,3)_A calculations for the X^3A_2' state. The CR-CC(2,3)_D method provides substantial improvements in the CCSD(T) description of the triplet ground state and the CCSD(2)_T or CR-CC(2,3)_A description of the B^1A_1 state, but this is not sufficient to produce an accurate $B^1A_1-X^3A_2'$ gap value, which differs from the corresponding CCSDT result by 8.2 kcal/mol when the cc-pVDZ basis set is employed.

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 5, adjusting their values accordingly when solving the CCSDt equations, eq 6, which greatly helps the results for the $B^1A_1-X^3A_2'$ gap (relative

energetics in general^{88,89,94–100,104,205,214}), but the selection of triples characterizing CCSDt may lead to substantial errors in total energies relative to the corresponding full CCSDT energies. Indeed, as shown in Table 6, the CCSDt calculations employing the smallest, chemically sensible, four-electron/four-orbital active space, which in the case of the quasi-degenerate B^1A_1 state translates into two highest-energy occupied and two lowest-energy unoccupied MOs, provide an excellent description of the $B^1A_1-X^3A_2'$ gap, which agrees with that obtained with full CCSDT to within 0.1 kcal/mol when the cc-pVDZ basis set is employed. It is clear, however, based on the results in Table 5, that this small difference between the CCSDt and CCSDT values of the $B^1A_1-X^3A_2'$ energy separation in TMM is a consequence of the cancellation of the rather large errors due to the triple excitations missing in the CCSDt considerations. The differences between the CCSDt and CCSDT total energies obtained with the cc-pVDZ basis set, although almost independent of the electronic state, exceed 12 millihartree. In other words, quite a bit of information about triples, particularly of the dynamical type, is missing when the CCSDt approach relying on a small number of active orbitals is employed. Obviously, we could increase the active space used in the CCSDt calculations to bring the total energies of the X^3A_2' and B^1A_1 states closer to their CCSDT values, but this would make the CCSDt calculations more expensive.

As in the other molecular examples examined in this work, the CCSD(T)-h method, which corrects the CCSDt energies for the missing triple excitations using the conventional (T) expressions exploited in CCSD(T), improves the above situation, bringing the total energies of the X^3A_2' and B^1A_1 states to a much better agreement with full CCSDT than in the CCSDt case, while improving the results of the CCSD-based CCSD(T), CCSD(2)_T or CR-CC(2,3)_A, and CR-CC(2,3)_D calculations, but the overall performance of CCSD(T)-h is substantially worse than the performance of our best CC(t;3)_D correction. Indeed, as shown in Table 5, the differences between the CCSD(T)-h and CCSDT energies obtained with the cc-pVDZ basis set are 0.115 millihartree in the case of the X^3A_2' state and −2.886 millihartree when the B^1A_1 state is examined. The analogous differences between the CC(t;3)_D and CCSDT energies, of 0.015 and −0.780 millihartree, are considerably smaller. As a result, the CC(t;3)_D value of the $B^1A_1-X^3A_2'$ gap obtained with the cc-pVDZ basis set is within 0.5 kcal/mol from the corresponding full CCSDT result, as opposed to 1.9 kcal/mol obtained with CCSD(T)-h. This is yet another example demonstrating that one greatly benefits from adopting a robust, CR-CC(2,3)-style, form of the triples correction in the CC(t;3) considerations instead of the conventional (T) correction of CCSD(T) exploited in CCSD(T)-h. In fact, even the simplified CC(t;3)_A approach, which replaces the Epstein–Nesbet-like $D_{0,abc}^{ijk}$ (CCSDt) denominator, eq 16, used in the CC(t;3)_D calculations by its Møller–Plesset analog, produces an overall better description than the CCSD(T)-h methodology. Indeed, the CC(t;3)_A approximation reduces the absolute value of the difference between the CCSD(T)-h and CCSDT energies for the quasi-degenerate B^1A_1 state from 2.886 to 0.790 millihartree and the 1.9 kcal/mol difference between the CCSD(T)-h and CCSDT $B^1A_1-X^3A_2'$ gap values to 0.5 kcal/mol when the cc-pVDZ basis set is used. The CCSD(T)-h approach is noticeably more accurate than its CC(t;3)_A counterpart in describing the single-configurational X^3A_2' state, which is not entirely surprising, since in this case the use of the (T) correction, which works well in SR situations, should suffice, but neither CCSD(T)-h nor CC(t;3)_A are as accurate as the CC(t;3)_D approximation.

As in the case of the (HFH)[−] system, one may get a false impression that CCSD(T)-h outperforms the CC(t;3) methodology in the description of the $B^1A_1-X^3A_2'$ gap, bringing the CCSDt results to a closer agreement with experiment than in the CC(t;3)_D (or CC(t;3)_A) case, but this would be a completely misleading interpretation of our results. The purpose of the CCSD(T)-h and CC(t;3) calculations, which correct the CCSDt energies for the triple excitations missing in the CCSDt considerations, is to bring the CCSDt results, both for the total energies and for the corresponding relative energies, such as those characterizing the stationary points along the reaction pathways examined in our earlier work²¹⁴ or the singlet–triplet gaps examined in the present study, to a reasonable agreement with the corresponding CCSDT data. The CC(t;3) methodology, particularly its most complete variant D, satisfies this condition, but CCSD(T)-h does not, when the degree of the biradical character becomes significant. We have observed this behavior of CCSD(T)-h vs CC(t;3) in our earlier studies of bond breaking²⁰⁵ and biradical reaction pathways,²¹⁴ and we see a similar behavior here in the context of singlet–triplet gaps. It is encouraging to see that the CC(t;3)_D methodology provides the results of the full CCSDT quality, both for the individual electronic states and for the energy gaps between them, in situations which normally require a genuine MR treatment, and at a fraction of the cost of the CCSDT calculations.

4. SUMMARY

The traditional, MBPT-based, noniterative SRCC approaches, including the widely used CCSD(T) approximation, have difficulties with handling biradicals and other MR situations. The newer generations of such methods, including CR-CC(2,3) or its CCSD(2)_T and Λ -CCSD(T) analogs, as well as their various higher-order and excited-state extensions, help to address this problem, but they have their limitations, too. In particular, none of the existing noniterative approaches that correct the results of the standard SRCC calculations for the effects of higher-order excitations enable one 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 many-electron correlation effects, including biradicals. As a result, the noniterative SRCC methods of the conventional CCSD(T) type or their more robust Λ -CCSD(T), CCSD(2), and CR-CC analogs are not always flexible enough to provide an accurate description of chemical reaction profiles involving biradical transition states, which we examined in our previous study,²¹⁴ or the singlet–triplet gaps in biradical systems considered in this work. The active-space SRCC approaches, such as the CCSDt method exploited in the present paper and its higher-order extensions, describe the coupling of the T_n components with $n \geq 3$, selected via active orbitals, with the T_1 and T_2 clusters, providing accurate relative energetics in biradical situations, including, as shown in this work, the gaps between the lowest-energy singlet and triplet states, but they may fail to produce accurate total energies relative to the parent SRCC approximations (in the case of CCSDt, full CCSDT).

We have recently developed the novel CC(P;Q) hierarchy and the underlying Flex-MMCC formalism, which allow us to address the above challenges. The CC(P;Q) methodology is general enough to enable us to correct the SRCC or EOMCC energies obtained with both the conventional (e.g., CCSD/EOMCCSD) and unconventional (e.g., CCSDt/EOMCCSDt) truncations in the cluster operator T and the EOM excitation operator R_μ for some or all of the many-electron correlation

effects that the truncated T and R_μ cannot normally describe.^{205,214} One of the methods that has emerged from the $CC(P;Q)$ considerations is the low cost $CC(t;3)$ hybrid scheme examined in the present study, in which the results of the CCSDt calculations are corrected for the triple excitations missing in CCSDt using the expressions that are reminiscent of the CR-CC(2,3) approach.

In this work, after summarizing the key elements of the ground-state $CC(t;3)$ methodology, we have applied it, along with a number of other approximate treatments of triple excitations in the SRCC theory, including CCSD(T), CCSD(2)_T, CR-CC(2,3), CCSDt, and CCSD(T)-h, and the full CCSDT approach, to the total electronic energies of the lowest singlet and triplet states, and the singlet–triplet gaps in selected biradical systems. The species examined in this article have included the weakly biradical methylene molecule, the more challenging linear (HFH)[−] ion, where the degree of biradical character can be continuously varied by simultaneously stretching both H–F bonds, and the strongly biradical TMM species. In the case of methylene, which represents a well-known example of a small adiabatic gap between the somewhat biradical A^1A_1 state and almost purely single-configurational X^3B_1 state, the CCSD(T), CCSD(2)_T, and CR-CC(2,3) approaches, especially CR-CC(2,3)_D, and the CCSDt and CCSD(T)-h methods work well, although further improvements in the results, particularly in the description of the total electronic energy of the quasi-degenerate A^1A_1 state by the CCSD(T) and CR-CC(2,3)_A (i.e., CCSD(2)_T) approaches and in the description of the total energies of both states by CCSDt and CCSD(T)-h, are desired. In the case of the (HFH)[−] system, the CR-CC(2,3)_A, CR-CC(2,3)_D, CCSDt, and CCSD(T)-h approaches improve the erratic CCSD(T) data, but further improvements in the results for the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, and the gap between them, particularly when compared to the parent CCSDT calculations, are needed, too. Finally, the TMM molecule, where the X^3A_2' ground state is largely single-configurational and the low-lying B^1A_1 excited state is strongly biradical, the main challenge is in obtaining an accurate and well-balanced description of the mostly dynamical many-electron correlation effects in the X^3A_2' state and the substantially non-dynamical correlation effects in the B^1A_1 state. This is a case where even the most sophisticated MRCC theories have difficulties with providing reasonably converged results that would agree with the experimentally derived adiabatic $B^1A_1-X^3A_2'$ gap value. This is also the case where all of the noniterative corrections to the CCSD energies work poorly, giving the $B^1A_1-X^3A_2'$ gap values that can be in substantial error, on the order of 10–15 kcal/mol, when compared to the reasonably accurate full CCSDT calculations or experimental data. The CCSDt approach works extremely well for the $B^1A_1-X^3A_2'$ gap in TMM, producing the value within 0.1 kcal/mol from the corresponding full CCSDT result, when the cc-pVDZ basis set is employed, but it gives large errors relative to the CCSDT energies of the individual X^3A_2' and B^1A_1 states that exceed 12 millihartree with the same basis. The CCSD(T)-h corrections to the CCSDt energies move the $B^1A_1-X^3A_2'$ gap resulting from the CCSDt calculations away from full CCSDT, while having difficulties with bringing the error in the total energy of the quasi-degenerate B^1A_1 state relative to CCSDT to a submillihartree range.

As demonstrated in this work, the $CC(t;3)$ methodology, particularly its $CC(t;3)_D$ variant, which replaces the expensive iterative CPU steps of CCSDT that scale with the system size as N^8 by the iterative N^6 -type and noniterative N^7 -type calculations, addresses all of the above issues. The total electronic

energies of the lowest singlet and triplet states, and the gaps between them resulting from the $CC(t;3)_D$ calculations, agree with those obtained with full CCSDT to within fractions (in most cases, small fractions) of a millihartree. In the case of the TZ2P model of methylene, the $CC(t;3)_D$ total energies of the X^3B_1 and A^1A_1 states, and the adiabatic gap between them agree with those obtained with CCSDT to within 0.018 millihartree, 0.077 millihartree, and 0.06 kcal/mol, respectively. When the TZ2P basis set is replaced by the substantially larger aug-cc-pVTZ basis, the differences between the $CC(t;3)_D$ and CCSDT values of the total energies of the X^3B_1 and A^1A_1 states, and the adiabatic gap between them remain small (0.130 and 0.409 millihartree, and 0.17 kcal/mol, respectively), and the CBS-extrapolated $A^1A_1-X^3B_1$ gap resulting from the $CC(t;3)_D$ /aug-cc-pVTZ and $CC(t;3)_D$ /aug-cc-pVQZ calculations, of 9.24 kcal/mol, is in excellent agreement with the experimentally derived value of 9.37 kcal/mol. In the case of the linear (HFH)[−] system, as described by the 6-31G(d,p) basis set, the differences between the $CC(t;3)_D$ and CCSDT total energies of the quasi-degenerate $X^1\Sigma_g^+$ and single-configurational $A^3\Sigma_u^+$ states, and the gap between them in the entire $R_{H-F} = 1.5\text{--}4.0$ Å region do not exceed 0.335 millihartree, 0.207 millihartree, and 37 cm^{−1}, respectively, while being usually even smaller (on the order of 0.1 millihartree in the case of total energies and 10 cm^{−1} in the case of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap).

The superb performance of the $CC(t;3)_D$ approach is also observed when the TMM system is examined. In this case, the differences between the $CC(t;3)_D$ and full CCSDT energies of the X^3A_2' and B^1A_1 states are 0.015 and −0.780 millihartree, when the cc-pVDZ basis set is employed. The corresponding $B^1A_1-X^3A_2'$ gap value, resulting from the $CC(t;3)_D$ calculations, of 21.2 kcal/mol, is within 0.5 kcal/mol from the full CCSDT result. The $CC(t;3)_D$ /cc-pVTZ value of the adiabatic $B^1A_1-X^3A_2'$ gap in TMM, of 21.7 kcal/mol, is in reasonable agreement with the experimentally derived result of 18.1 kcal/mol and the best values resulting from the sophisticated MRCC and RMRC calculations that fall into the 15–23 kcal/mol range. None of the other noniterative triples corrections to the CCSD or CCSDt energies can deliver a similarly impressive performance. The slightly simplified form of the $CC(t;3)$ methodology, represented by the $CC(t;3)_A$ approach, works well, too, being almost as good as the more complete $CC(t;3)_D$ approach in the strongly biradical situations, but $CC(t;3)_A$ is less effective than $CC(t;3)_D$ in the weakly biradical cases. The $CC(t;3)$ methodology, particularly its $CC(t;3)_D$ variant, which employs the robust energy corrections derived from the $CC(P;Q)$ considerations, resembling the triples corrections of CR-CC(2,3), is also more effective in capturing 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. This seems particularly true in the case of stronger biradicals, such as (HFH)[−] and TMM.

On the basis of the results obtained in this work, we can recommend the $CC(t;3)_D$ approach for applications involving singlet–triplet gaps and associated total energies in biradical species as long as the T_4 clusters do not play a major role. Other ways of correcting the CCSDt energies, such as $CC(t;3)_A$ and CCSD(T)-h, are useful, too, but none of the other corrections to CCSD or CCSDt is as effective as $CC(t;3)_D$. Encouraged by the excellent performance of the $CC(t;3)$ approach, we will continue developing the $CC(P;Q)$ theory. We will, in particular, examine the $CC(t;q;3)$ and $CC(t;q;3,4)$ methods proposed in ref 205, in which energies obtained in the active-space CCSDtq calculations are corrected for the effects of triples or triples and quadruples

missing in CCSDtq. The CC(t,q;3) and CC(t,q;3,4) methods should be particularly useful in the more complicated MR situations, such as double bond breaking, where the appropriate SRCC level is CCSDTQ.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by the U.S. Department of Energy (Grant No. DE-FG02-01ER15228).

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