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Extension of the Renormalized Coupled-Cluster Methods Exploiting Left Eigenstates of the Similarity-Transformed Hamiltonian to Open-Shell Systems: A Benchmark Study[†]

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The recently formulated completely renormalized coupled-cluster method with singles, doubles, and noniterative triples, exploiting the biorthogonal form of the method of moments of coupled-cluster equations (Piecuch, P.; Włoch, M. *J. Chem. Phys.* **2005**, *123*, 224105; Piecuch, P.; Włoch, M.; Gour, J. R.; Kinal, A. *Chem. Phys. Lett.* **2006**, *418*, 467), termed CR-CC(2,3), is extended to open-shell systems. Test calculations for bond breaking in the OH radical and the F_2^+ ion and singlet−triplet gaps in the CH_2, HHeH, and $(HFH)^-$ biradical systems indicate that the CR-CC(2,3) approach employing the restricted open-shell Hartree−Fock (ROHF) reference is significantly more accurate than the widely used CCSD(T) method and other noniterative triples coupled-cluster approximations without making the calculations substantially more expensive. A few molecular examples, including the activation energies of the $C_2H_4 + H \rightarrow C_2H_5$ forward and reverse reactions and the triplet states of the CH_2 and $H_2Si_2O_2$ biradicals, are used to show that the dependence of the ROHF-based CR-CC(2,3) energies on the method of canonicalization of the ROHF orbitals is, for all practical purposes, negligible.

I. Introduction

Coupled-cluster (CC) theory[1−5] has become one of the most important techniques of contemporary quantum chemistry. The method that often symbolizes the success of CC theory is the widely used CCSD(T) approach (CC approach with singles, doubles, and noniterative triples),[6] in which the noniterative (T) correction due to triply excited clusters is added to the CCSD (CC singles and doubles)[7−9] energy. The CCSD(T) method, which from the technical point of view can be regarded as a straightforward modification of the earlier CCSD + T(CCSD) = CCSD[T] approach,[10,11] offers several appealing features that contribute to its popularity. First of all, CCSD(T) is a single-reference (meaning black-box) approach that can easily be used by experts as well as nonexperts. Second of all, CCSD(T) provides a size extensive and accurate description of the nondegenerate ground states of molecular systems with the computer costs that can be characterized as relatively low, considering the resulting accuracies.[12−19] These costs are defined by the iterative steps of the underlying CCSD calculation that scale as $n_o^2 n_u^4$ and the noniterative $n_o^3 n_u^4$ steps that are needed to determine the (T) energy correction, where n_o and n_u are the numbers of occupied and unoccupied orbitals, respectively, that are included in the correlated calculations. Thanks to these relatively low costs and advances in computer architectures, the CCSD(T) approach can nowadays be routinely applied to molecular systems with up to about 100 correlated electrons and a few hundred basis functions when a canonical formulation of CCSD(T) is used and hundreds of correlated electrons and over 1000 basis functions when the local correlation formalism[20] is exploited.[21−23]

There is, however, one major problem with the CCSD(T) and similar single-reference CC methods; namely, all of these methods fail or become very inaccurate when biradicals, bond breaking, and other situations involving large nondynamical correlation effects are examined (cf., e.g., refs 17 and 19 for reviews). Traditionally, the adequate treatment of reaction pathways involving bond breaking and other cases of electronic quasi-degeneracies has been the domain of expert multireference methods, and a great deal of progress has been achieved in the area of multireference calculations over the years. Unfortunately, even the most successful multireference approaches are not without limitations. For example, the low-order multireference perturbation theory methods (cf., e.g., refs 24, 25, and references therein), such as CASPT2,[26−29] may encounter severe difficulties with balancing dynamical and nondynamical correlations in studies of reaction pathways and relative energetics of systems characterized by a varying degree of biradical character,[30−33] while the more robust multireference configuration interaction (MRCI) approaches, including the successful and widely used internally contracted MRCI approach with quasi-degenerate Davidson corrections (the MRCI(Q) method[34,35]), are often prohibitively expensive and lack size extensivity. (CASPT2 is not size extensive either.[36]) One should also keep in mind that all multireference theories require a great deal of expertise and experience, because the user of such methods has to specify a number of additional parameters that do not enter single-reference calculations, such as active orbitals or multiple reference determinants and, particularly in the case of MRCI, numerical thresholds for neglecting the less important electron configurations that all affect the results, in addition to the appropriate choice of the basis set that enters all quantum chemistry calculations based on molecular orbital theory. Thus, it is useful to explore the possibility of attempting to solve at least some classes of chemical problems involving larger nondynamical correlation effects without resorting to multireference calcula-

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tions. This has been the motivation behind the recent development of the noniterative CC approaches based on the partitioning of the similarity-transformed Hamiltonian pursued by Head-Gordon and co-workers[37−41] (see ref 42 for the original idea), adopted in a slightly modified form by Hirata et al.,[43,44] and commonly labeled as the CCSD(2) approximations, the spin-flip CC methods of Krylov and co-workers,[45−47] the iterative and noniterative methods[18,19,40,41,48−51] based on the extended CC theories of Arponen and Bishop[52−58] and Piecuch and Bartlett,[59] and the renormalized and other CC approaches based on the method of moments of CC equations (MMCC).[17−19,50,51,60−76]

In this paper, we focus on the renormalized CC methods for ground electronic states,[17−19,50,51,60−62,65−68,74,76] which represent a new generation of noniterative single-reference CC approaches that are designed to improve the performance of CCSD(T) and similar methods in the bond-breaking/biradical regions of molecular potential energy surfaces, while preserving the ease of use, the relatively low computer costs, and the general philosophy of the CCSD(T) approach. Among the most promising developments in this area is the recently proposed[66−68] CR-CC(2,3) approach, in which, in analogy to CCSD(T), a noniterative correction due to triply excited clusters is added to the CCSD energy. On the basis of the initial benchmark studies[66−68] and several applications,[30,31,33,67,76,77] in which CR-CC(2,3) was used to study bond-breaking and reaction pathways on singlet potential energy surfaces, particularly those involving biradical species, the CR-CC(2,3) method offers the following advantages: (i) is as accurate as CCSD(T) for nondegenerate ground states, (ii) provides accurate results of the full CCSDT (CC singles, doubles, and triples)[78,79] quality for single bond breaking on singlet potential energy surfaces and biradicals with the relatively inexpensive $n_o^3 n_u^4$ steps similar to those of CCSD(T), (iii) is more accurate than the original variant of the completely renormalized (CR) CCSD(T) theory, termed CR-CCSD(T),[17−19,60−62] its newer locally renormalized (LR) LR-CCSD(T) extension,[65] and the CCSD(2)$_T$ approach of ref 44, which all aim at improving the performance of CCSD(T) in the biradical/bond breaking situations, and (iv) is rigorously size extensive without the need to localize orbitals as in the LR-CCSD(T) case (LR-CCSD(T) becomes size extensive only when the orbitals used in the calculations are properly localized on the fragments;[65] otherwise, LR-CCSD(T) is characterized by small inextensivity errors, on the order of 0.5% of the changes in the total correlation energy along a reaction pathway, similar to those present in the CR-CCSD(T) calculations[17,67]). The CR-CC(2,3) approximation belongs to a wider class of the CR-CC(m_A,m_B) approaches, all derived from the biorthogonal formulation of the MMCC theory discussed in refs 66 and 67 (cf. refs 75 and 76 for reviews), that are labeled by the excitation level m_A, defining the CC method that we want to correct, and the excitation level m_B, defining the noniterative correction to CC energy. Let us also recall that the CR-CCSD(T) approach is the lead CR-CC approximation based on the original formulation of the MMCC theory[60,61,70] (cf. refs 17−19 and 74−76 for reviews), whereas LR-CCSD(T) is the noniterative triples CR-CC approximation resulting from the so-called numerator−denominator-connected form of the MMCC formalism.[65] The CCSD(2)$_T$ approach of ref 44 is obtained by ignoring the contributions due to quadruply excited clusters in the CCSD(2) method of ref 43, reducing larger costs of the CCSD(2) calculations, which, depending on the details of the computer implementation, are n_u^6 (refs 37 and 39) or $n_o^4 n_u^5$ (refs 43 and 44), to the much more practical $n_o^3 n_u^4$ steps of the CCSD(T) type. As shown in refs 66−68, when canonical Hartree−Fock orbitals are employed, CCSD(2)$_T$ is also equivalent to what we refer to as variant A of the CR-CC(2,3) approach, in which the diagonal matrix elements of the similarity-transformed Hamiltonian of CCSD involving triply excited determinants, which enter the CR-CC(2,3) triples correction, are replaced by the orbital energy differences characterizing triple excitations. The triples correction of the CCSD(2) method of refs 37 and 39 is, up to small details, equivalent to variant B of the CR-CC(2,3) approach, which is yet another approximation to the full CR-CC(2,3) method discussed in section IIB. As demonstrated in this paper, the full CR-CC(2,3) approach is more accurate than its approximate forms represented by variants A and B.

The successes of the CR-CC(2,3) method in applications involving single bond breaking and biradical structures on singlet potential energy surfaces[30,31,33,66−68,76,77] prompt the question of whether CR-CC(2,3) can be similarly effective in calculations involving open-shell systems. The open-shell problems that are of particular interest to us are bond breaking in radicals and doublet ground states in general as well as singlet−triplet energy gaps in biradical systems. To be more specific, we would like to know if the CR-CC(2,3) approach can provide improvements in the CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ results in calculations for radicals and singlet−triplet gaps in biradicals. This paper represents our first attempt to address this question by testing the recently developed, highly efficient, general-purpose CR-CC(2,3) computer code for nonsinglet electronic states, which we overview in this paper and which will be described in further detail elsewhere,[80] on a few molecular examples, namely, bond breaking in the OH radical and the challenging F_2^+ ion, and singlet−triplet energy gaps in the CH_2, HHeH, and $(HFH)^-$ biradicals. The OH radical is a prototype of many radical species encountered in various areas of chemistry, whereas F_2^+ is known to pose very interesting and challenging problems to single-reference methods.[19,81−83] Methylene represents a classic case of a small gap between the first excited singlet state and the triplet ground state[84−88] that can cause serious difficulties for many electronic structure methods and that normally requires an MRCI[89−94] or multireference CC (MRCC)[95−97] treatment or the use of expensive high-order iterative single-reference CC methods, such as CCSDT,[94,98] to obtain an accurate description. The HHeH system has been used to demonstrate the effectiveness of the density matrix renormalization group approach[99,100] in handling singlet−triplet gaps in magnetic systems,[101] where other methods, including, for example, QCISD(T) (quadratic CI with singles, doubles, and noniterative triples)[6] and a number of density functional theory approaches have serious difficulties with balancing many-electron correlation effects in the close-lying singlet and triplet states.[102,103] The $(HFH)^-$ system is in the same category as the HHeH system. $(HFH)^-$ represents another example of a challenging biradical/magnetic system, where the two paramagnetic centers, each containing an unpaired spin, are linked via a diamagnetic bridge. The additional challenge that $(HFH)^-$ creates to standard single-reference methods, compared to HHeH, is the presence of a polarizable diamagnetic entity in the center,[102] which also has a larger number of electrons compared to a two-electron He atom.

At this time, the open-shell CR-CC(2,3) code used in this work has been interfaced with the restricted open-shell Hartree−Fock (ROHF) and integral routines available in the GAMESS package.[104] It will become part of the official GAMESS distribution in the near future. The benchmark calculations reported in this work are also used as an opportunity to review the theoretical concepts behind the CR-CC(2,3) approach and the most essential characteristics of our newly developed open-shell CR-CC(2,3) code. In particular, by analyzing the activation energies for the $C_2H_4 + H \rightarrow C_2H_5$ forward and reverse reactions, which proceed on a doublet potential energy surface,[105] and triplet states of the CH_2 and $H_2Si_2O_2$ (ref 106) biradicals, we demonstrate that the dependence of the ROHF-based CR-CC(2,3) energies on the method of canonicalization of the ROHF orbitals is, for all practical purposes, negligible.

II. Theory and Computational Details

The CR-CC(2,3) method and the underlying biorthogonal MMCC formalism represent relatively new developments. Thus, we begin our discussion with the key elements of the biorthogonal MMCC theory that are relevant for designing the triples correction to the CCSD energy defining the CR-CC(2,3) approach (section IIA). The most essential equations of the CR-CC(2,3) method are discussed in section IIB, and the remaining algorithmic and computational details that are particularly relevant to the open-shell CR-CC(2,3) code used in this work are described in section IIC.

A. Synopsis of the Biorthogonal MMCC Formalism for Ground Electronic States. As in the case of the original CR-CCSD(T) method,[17−19,60−62] the CR-CC(2,3) approximation discussed in this work is derived from the rigorous formula for the noniterative correction δ_0, which, when added to the ground-state energy obtained in the conventional CC calculations, such as CCSD, recovers the corresponding exact, i.e., full CI, ground-state energy E_0. If we aim at correcting the CCSD energy $E_0^{(\mathrm{CCSD})}$, which is what one does in the CR-CC(2,3) calculations, the relevant expression for

$$\delta_0 = E_0 - E_0^{(\mathrm{CCSD})} \tag{1}$$

resulting from the application of the biorthogonal MMCC formalism of refs 66 and 67 to the Hamiltonian with pairwise interactions is

$$\delta_0 = \sum_{n=3}^{6} \sum_{\substack{i_1<\cdots<i_n \\ a_1<\cdots<a_n}} \ell_{i_1\ldots i_n}^{a_1\ldots a_n} \mathscr{M}_{a_1\ldots a_n}^{i_1\ldots i_n}(2) \tag{2}$$

where

$$\mathscr{M}_{a_1\ldots a_n}^{i_1\ldots i_n}(2) = \langle \Phi_{i_1\ldots i_n}^{a_1\ldots a_n} | \bar{H}^{(\mathrm{CCSD})} | \Phi \rangle \tag{3}$$

are the generalized moments of the CCSD equations, defined as projections of the CCSD equations on the excited determinants $|\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\rangle \equiv a^{a_1}\cdots a^{a_n} a_{i_n}\cdots a_{i_1}|\Phi\rangle$, with $n > 2$, that are normally disregarded in the CCSD calculations, and the coefficients $\ell_{i_1\ldots i_n}^{a_1\ldots a_n}$ are the amplitudes defining the de-excitation operator $\mathscr{L}$, which parametrizes the full CI bra ground state $\langle\Psi_0|$ via the formula

$$\langle\Psi_0| = \langle\Phi|\mathscr{L}\, \mathrm{e}^{-T_1-T_2} \tag{4}$$

The operator

$$\bar{H}^{(\mathrm{CCSD})} = \mathrm{e}^{-T_1-T_2}\, H\, \mathrm{e}^{T_1+T_2} = (H\, \mathrm{e}^{T_1+T_2})_C \tag{5}$$

is the similarity-transformed Hamiltonian of the CCSD method, with

$$T_1 = \sum_{\substack{i \\ a}} t_a^i a^a a_i \tag{6}$$

and

$$T_2 = \sum_{\substack{i<j \\ a<b}} t_{ab}^{ij} a^a a^b a_j a_i \tag{7}$$

representing the singly and doubly excited cluster operators, respectively, and the subscript C designates the connected part of the corresponding operator expression. To guarantee that eq 2 represents the exact difference between the full CI and CCSD energies, eq 1, one must require that the full CI bra state $\langle\Psi_0|$, eq 4, is normalized as

$$\langle\Psi_0|\Psi_0^{(\mathrm{CCSD})}\rangle = 1 \tag{8}$$

where $|\Psi_0^{(\mathrm{CCSD})}\rangle = \mathrm{e}^{T_1+T_2}|\Phi\rangle$ is the CCSD wave function. In the above equations and elsewhere in this article, we use the usual notation where i_1, i_2, ... or i, j, ... are the spin-orbitals occupied in the reference determinant $|\Phi\rangle$ and a_1, a_2, ... or a, b, ... are the unoccupied spin-orbitals. The a^p (a_p) operators are the creation (annihilation) operators associated with the spin-orbitals $|p\rangle$.

The de-excitation operator $\mathscr{L}$, parametrizing the exact bra ground state $\langle\Psi_0|$ according to eq 4, is defined as

$$\mathscr{L} = \sum_{n=0}^{N} \mathscr{L}_n \tag{9}$$

where N is the number of electrons in the system and

$$\mathscr{L}_n = \sum_{\substack{i_1<\cdots<i_n \\ a_1<\cdots<a_n}} \ell_{i_1\ldots i_n}^{a_1\ldots a_n} a^{i_1}\cdots a^{i_n} a_{a_n}\cdots a_{a_1} \tag{10}$$

are the n-body components of $\mathscr{L}$. Formally, the $\ell_{i_1\ldots i_n}^{a_1\ldots a_n}$ amplitudes defining the exact operator $\mathscr{L}$ and, through eq 4, the full CI bra ground state $\langle\Psi_0|$ can be obtained by solving the bra eigenvalue problem[66,67] (cf. also refs 75 and 76)

$$\langle\Phi|\mathscr{L}\bar{H}^{(\mathrm{CCSD})} = E_0\, \langle\Phi|\mathscr{L} \tag{11}$$

which is equivalent to the adjoint form of the Schrödinger equation, $\langle\Psi_0|H = E_0\langle\Psi_0|$, in the entire N-electron Hilbert space. It is interesting to note though that the noniterative correction $\delta_0^{(\mathrm{CCSD})}$, eq 2, is defined in terms of the n-body components of $\mathscr{L}$ with $n > 2$. These components originate from the decomposition of the operator $\mathscr{L}$ into the sum of the CCSD part

$$\mathscr{L}^{(\mathrm{CCSD})} = \mathscr{L}_0 + \mathscr{L}_1 + \mathscr{L}_2 \tag{12}$$

and the remainder term

$$\delta\mathscr{L}^{(\mathrm{CCSD})} = \sum_{n=3}^{N} \mathscr{L}_n \tag{13}$$

The normalization condition defined by eq 8 is then equivalent to

$$\langle\Phi|\mathscr{L}^{(\mathrm{CCSD})}|\Phi\rangle = 1 \tag{14}$$

so that the zero-body component

$$\mathscr{L}_0 = \mathbf{1} \tag{15}$$

where **1** is a unit operator. It should also be noted that although the exact $\ell_{i_1 \ldots i_n}^{a_1 \ldots a_n}$ amplitudes originate from solving the left eigenvalue problem for $\langle\Phi|\mathscr{L}$ in the entire N-electron Hilbert space, eq 11, we do not have to use all many-body components $\mathscr{L}_n$ with $n > 2$ to construct the exact energy correction $\delta_0^{(\mathrm{CCSD})}$, eq 2. We only need to know the components $\mathscr{L}_n$ with $n = 3-6$, independent of the number of electrons in a system. This interesting feature of the biorthogonal MMCC formalism of refs 66 and 67, which distinguishes it from the original[60,61,70] and numerator−denominator-connected[65] MMCC energy expansions, is a consequence of the fact that for Hamiltonians with pairwise interactions, as used in quantum chemistry, the generalized moments of the CCSD equations, $\mathscr{M}_{a_1 \ldots a_n}^{i_1 \ldots i_n}(2)$, eq 3, with $n > 6$ vanish. They also vanish for $n = 1$ and 2, because the ground-state CCSD equations that are used to determine the corresponding T_1 and T_2 clusters are obtained by zeroing moments $\mathscr{M}_{a_1 \ldots a_n}^{i_1 \ldots i_n}(2)$ with $n = 1$ or 2. This is why the range of n values in the definition of the exact correction $\delta_0^{(\mathrm{CCSD})}$, eq 2, is $n = 3-6$.

Because of the normalization condition given by eq 15, the CCSD part of the operator $\mathscr{L}$, defined by eq 12, is similar to the de-excitation operator

$$L^{(\mathrm{CCSD})} = \mathbf{1} + \Lambda^{(\mathrm{CCSD})} \tag{16}$$

which defines the bra or left CCSD state, $\langle\tilde{\Psi}_0^{(\mathrm{CCSD})}| = \langle\Phi|L^{(\mathrm{CCSD})} \mathrm{e}^{-T_1-T_2}$, that matches the ket CCSD ground state $|\Psi_0^{(\mathrm{CCSD})}\rangle = \mathrm{e}^{T_1+T_2}|\Phi\rangle$.[59,107] The operator $\Lambda^{(\mathrm{CCSD})}$ in eq 16 is the standard "lambda" operator of the analytic gradient CCSD theory[12,13,108]

$$\Lambda^{(\mathrm{CCSD})} = \Lambda_1 + \Lambda_2 \tag{17}$$

where

$$\Lambda_1 = \sum_{\substack{i\\a}} \lambda_a^i a^i a_a \tag{18}$$

and

$$\Lambda_2 = \sum_{\substack{i<j\\a<b}} \lambda_{ab}^{ij} a^i a^j a_b a_a \tag{19}$$

are the corresponding one- and two-body components obtained by solving the left ground-state eigenvalue problem involving $\bar{H}^{(\mathrm{CCSD})}$, similar to eq 11, in which $\mathscr{L}$ is replaced by $L^{(\mathrm{CCSD})}$, eq 16, and E_0 by $E_0^{(\mathrm{CCSD})}$ in the subspace of the N-electron Hilbert space spanned by the reference determinant $|\Phi\rangle$ and the singly and doubly excited determinants, $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$, respectively. There obviously is a difference between the CCSD part of the exact operator $\mathscr{L}$, $\mathscr{L}^{(\mathrm{CCSD})}$, eq 12, which is obtained by solving eq 11 in the entire N-electron Hilbert space, and $L^{(\mathrm{CCSD})}$, eq 16, obtained by solving a similar equation in the subspace spanned by $|\Phi\rangle$, $|\Phi_i^a\rangle$, and $|\Phi_{ij}^{ab}\rangle$ (cf., e.g., refs 66, 67, 75, and 76 for a discussion). However, the operators $\mathscr{L}^{(\mathrm{CCSD})}$, eq 12, and $L^{(\mathrm{CCSD})}$, eq 16, have enough in common for formulating useful approximate schemes based on the biorthogonal MMCC formalism, such as CR-CC(2,3), in which the three-body component of $\mathscr{L}$ that defines the lead, $n = 3$, term in the noniterative correction $\delta_0^{(\mathrm{CCSD})}$, eq 2, is related to the corresponding one- and two-body components, $\mathscr{L}_1$ and $\mathscr{L}_2$, approximated by the Λ_1 and Λ_2 components of $L^{(\mathrm{CCSD})}$. Further details of the CR-CC(2,3) approach are discussed next.

B. CR-CC(2,3) Method. In the CR-CC(2,3) method of refs 66−68, which belongs to a larger family of the MMCC(m_A,m_B)$_\mathscr{L}$ and CR-CC(m_A,m_B) approximations resulting from the biorthogonal MMCC theory,[66−68,75,76] we correct the results of the CCSD calculations by adding the triples correction

$$\delta_0(2{,}3) = \sum_{\substack{i<j<k\\a<b<c}} \ell_{ijk}^{abc} \mathscr{M}_{abc}^{ijk}(2) \tag{20}$$

to the CCSD energy $E_0^{(\mathrm{CCSD})}$. The correction $\delta_0(2,3)$, eq 20, is obtained by considering the lead, $n = 3$, term in eq 2 and by neglecting the remaining $n > 3$ contributions that describe the effects of higher-than-triply excited clusters. In analogy to the original CR-CCSD(T) approach,[17−19,60−62] the only moments of the CCSD equations that are needed in the CR-CC(2,3) calculations are moments $\mathscr{M}_{abc}^{ijk}(2)$, which correspond to projections of the CCSD equations on triply excited determinants. We can calculate these moments using the following expression[19]

$$\mathscr{M}_{abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \left[H \left(T_2 + T_1 T_2 + \frac{1}{2} T_2{}^2 + \frac{1}{2} T_1{}^2 T_2 + \frac{1}{2} T_1 T_2{}^2 + \frac{1}{6} T_1{}^3 T_2 \right) \right]_\mathrm{C} \middle| \Phi \right\rangle \tag{21}$$

We refer the reader to refs 73 and 75 for the factorized, computationally efficient expression for $\mathscr{M}_{abc}^{ijk}(2)$ in terms of the singly and doubly excited cluster amplitudes, t_a^i and t_{ab}^{ij}, respectively, and molecular integrals defining the Hamiltonian in the second quantized form. The highly efficient, fully vectorized, open-shell implementation of the CR-CC(2,3) approach tested in this work is based on integrating the spin-orbital expressions for $\mathscr{M}_{abc}^{ijk}(2)$ and the corresponding recursively generated intermediates over the relevant spin variables. (Further technical details will be provided in a separate paper.[80])

The ℓ_{ijk}^{abc} amplitudes entering the CR-CC(2,3) triples correction $\delta_0(2,3)$, eq 20, are determined as follows[66−68,75,76]

$$\begin{aligned}\ell_{ijk}^{abc} &= \langle\Phi|\Lambda^{(\mathrm{CCSD})}\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle / D_{abc}^{ijk} \\ &= \langle\Phi|[(\Lambda_1 \bar{H}_2^{(\mathrm{CCSD})})_\mathrm{DC} + (\Lambda_2 \bar{H}_1^{(\mathrm{CCSD})})_\mathrm{DC} + (\Lambda_2 \bar{H}_2^{(\mathrm{CCSD})})_\mathrm{C}]|\Phi_{ijk}^{abc}\rangle / D_{abc}^{ijk}\end{aligned} \tag{22}$$

where Λ_1 and Λ_2 are the one- and two-body components of the "lambda" operator $\Lambda^{(\mathrm{CCSD})}$ of the analytic gradient CCSD theory,[12,13,108] and

$$\begin{aligned}D_{abc}^{ijk} &= E_0^{(\mathrm{CCSD})} - \langle\Phi_{ijk}^{abc}|\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle \\ &= -\langle\Phi_{ijk}^{abc}|\bar{H}_1^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle - \langle\Phi_{ijk}^{abc}|\bar{H}_2^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle - \langle\Phi_{ijk}^{abc}|\bar{H}_3^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle\end{aligned} \tag{23}$$

where $\bar{H}_1^{(\mathrm{CCSD})}$, $\bar{H}_2^{(\mathrm{CCSD})}$, and $\bar{H}_3^{(\mathrm{CCSD})}$ are the one-, two-, and three-body components of the similarity-transformed Hamiltonian $\bar{H}^{(\mathrm{CCSD})}$ of the CCSD theory, eq 5, and the subscript DC designates the disconnected part of the corresponding operator product. The final formula for the ground-state CR-CC(2,3) energy is

$$E_0^{(\mathrm{CR-CC(2,3)})} = E_0^{(\mathrm{CCSD})} + \delta_0(2{,}3) \tag{24}$$

where the triples correction $\delta_0(2,3)$ is defined by eq 20, with $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc} given by eqs 21 and 22, respectively.

As explained in refs 66 and 67 (cf. also refs 75 and 76), eq 22 can be derived by considering the bra form of the similarity-transformed Schrödinger equation, eq 11, which we right-project on the triply excited determinants $|\Phi_{ijk}^{abc}\rangle$ to obtain

$$\langle\Phi|\mathscr{L}\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle = E_0\,\ell_{ijk}^{abc} \tag{25}$$

Based on the similarity between the CCSD part of the operator $\mathscr{L}$, i.e. $\mathscr{L}^{(\mathrm{CCSD})}$, eq 12, and the de-excitation operator $L^{(\mathrm{CCSD})}$, eq 16, defining the left CCSD state, discussed in section IIA, we approximate the exact operator $\mathscr{L}$ in eq 25 by $\mathbf{1} + \Lambda^{(\mathrm{CCSD})} + \mathscr{L}_3$. We also replace the exact energy E_0 in eq 25 by the CCSD energy $E_0^{(\mathrm{CCSD})}$. This leads to the following system of equations for the ℓ_{ijk}^{abc} amplitudes[66,67]

$$E_0^{(\mathrm{CCSD})}\ell_{ijk}^{abc} - \sum_{\substack{l<m<n\\ d<e<f}} \langle\Phi_{lmn}^{def}|\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle\,\ell_{lmn}^{def} = \langle\Phi|\Lambda^{(\mathrm{CCSD})}\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle \tag{26}$$

The desired eq 22 is obtained by approximating the triples−triples block of the matrix representing $\bar{H}^{(\mathrm{CCSD})}$ in the second term on the left-hand side of eq 26 by its diagonal part.[66,67]

Before discussing different variants of the CR-CC(2,3) method and the remaining computational details associated with the calculations performed in this work, we should mention that the above expression for the ℓ_{ijk}^{abc} amplitudes, eq 22, may have to be modified somewhat if one of the indices i, j, k, a, b, or c corresponds to an orbital that is degenerate with some other orbitals. In that case, at least in principle, one should replace eq 22 by a more elaborate expression in which, instead of using the diagonal matrix elements $\langle\Phi_{ijk}^{abc}|\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ that enter the Epstein−Nesbet-like denominator D_{abc}^{ijk}, eq 23, one solves a small system of linear equations, similar to eq 26, where all amplitudes ℓ_{ijk}^{abc} involving indices of degenerate spin-orbitals are coupled together through the off-diagonal matrix elements $\langle\Phi_{lmn}^{def}|\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ involving the triply excited determinants that carry the indices of degenerate spin-orbitals.[76] Without taking care of this issue, the CR-CC(2,3) energy correction $\delta_0(2,3)$ is not strictly invariant with respect to the rotations among degenerate orbitals, although the dependence of the $\delta_0(2,3)$ correction employing eq 22 to determine the ℓ_{ijk}^{abc} amplitudes on the rotations among degenerate orbitals is minimal. Indeed, all of our numerous tests indicate that changes in the values of $\delta_0(2,3)$ due to the rotations among degenerate orbitals do not exceed 0.1 millihartree when we use eq 22 to determine all amplitudes ℓ_{ijk}^{abc}.[76] Thus, the issue of the lack of invariance of the CR-CC(2,3) correction $\delta_0(2,3)$ employing eq 22 with respect to the rotations among degenerate orbitals is more of a formal problem than a practical one for the vast majority of applications, where one seeks accurate energetics, which the CR-CC(2,3) method provides. Clearly, if the molecule has at most an Abelian symmetry or if the orbitals employed break the non-Abelian symmetry, so that there are no orbital degeneracies, then one can apply eq 22 to all amplitudes ℓ_{ijk}^{abc}.

Equations 20−24 describe the most complete variant of the CR-CC(2,3) approach that, in analogy to some of our earlier publications on the original CR-CC methods, such as refs 19, 72, and 73, can also be designated by an additional letter D (e.g., CR-CC(2,3),D). Other variants can be suggested by considering approximate forms of the denominator D_{abc}^{ijk}, eq 23 (cf. ref 68). Thus, variant C is obtained by ignoring the last, three-body term in eq 23, and variant B is obtained by ignoring the last two terms, leaving the one-body contribution $-\langle\Phi_{ijk}^{abc}|\bar{H}_1^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ in D_{abc}^{ijk} only. Finally, variant A of the CR-CC(2,3) approach is obtained by replacing the denominator D_{abc}^{ijk}, eq 23, by the Møller−Plesset-like denominator for triple excitations, $(\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)$, where ϵ_p's are the spin-orbital energies (diagonal elements of the Fock matrix). Numerically, variant A is often not much different than variant B. This is related to the fact that the denominator D_{abc}^{ijk} used in the CR-CC(2,3),B approximation has the form $-\langle\Phi_{ijk}^{abc}|\bar{H}_1^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle = \bar{h}_i^i + \bar{h}_j^j + \bar{h}_k^k - \bar{h}_a^a - \bar{h}_b^b - \bar{h}_c^c$ where, in general, $\bar{h}_p^q$'s are matrix elements defining the second quantized form of the one-body component of $\bar{H}^{(\mathrm{CCSD})}$, $\bar{H}_1^{(\mathrm{CCSD})} = \sum_{p,q} \bar{h}_p^q a^p a_q$. The diagonal matrix elements $\bar{h}_p^p$ can be regarded as the dressed forms of the usual spin-orbital energies ϵ_p. Similarly, variant C, in which the $\langle\Phi_{ijk}^{abc}|\bar{H}_3^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ contribution to D_{abc}^{ijk} is neglected, is, in most cases, not much different than the complete variant D, because the three-body $\langle\Phi_{ijk}^{abc}|\bar{H}_3^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ terms are often not very important (the two-body $\langle\Phi_{ijk}^{abc}|\bar{H}_2^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ terms are). Although variant C may, on occasion, be slightly more accurate than the full variant D, variant D using the most complete, Epstein−Nesbet-like form of the denominator D_{abc}^{ijk}, eq 23, is generally the most robust one when compared to the other variants. This can be understood if we realize that eq 23 for D_{abc}^{ijk} defining the CR-CC(2,3),D approach is obtained by approximating the triples−triples block of the matrix representing $\bar{H}^{(\mathrm{CCSD})}$, $\bar{\mathbf{H}}_{\mathrm{TT}}^{(\mathrm{CCSD})}$, by its diagonal part, which is kept in its entirety, whereas other variants of CR-CC(2,3) are obtained from variant D by dropping terms in the diagonal part of $\bar{\mathbf{H}}_{\mathrm{TT}}^{(\mathrm{CCSD})}$.

In this paper, we mainly focus on the most complete variant D, for which we do not use any additional letter unless necessary, and the simplest variant A, although we provide the results of the CR-CC(2,3),B and CR-CC(2,3),C calculations in a few initial examples as well. As mentioned in the Introduction, the CR-CC(2,3),A approximation to full CR-CC(2,3) (or CR-CC(2,3),D) is equivalent to the CCSD(2)$_\mathrm{T}$ method of ref 44 when the canonical Hartree−Fock orbitals are employed. Although this is no longer exactly true for the ROHF case, the differences between the ROHF-based CCSD(2)$_\mathrm{T}$ and CR-CC(2,3),A methods are so small that we use the acronym CCSD(2)$_\mathrm{T}$ interchangably with CR-CC(2,3),A. On the basis of the above remarks about the relationships between different variants of CR-CC(2,3), we expect the full CR-CC(2,3) approach to be more accurate than the CCSD(2)$_\mathrm{T}$ method of ref 44, represented here by the CR-CC(2,3),A approximation, and the numerical evidence presented in this work and in the earlier papers[66−68,76,77] confirms this. An analogous relationship exists between the CR-CC(2,3) method and the CCSD(2) approach of refs 37−41 if we neglect the contributions due to quadruples in the latter approach. Specifically, the CCSD(2) method of refs 37−41 in its triples contribution part is, up to small details, equivalent to variant B of the CR-CC(2,3) approach. As in the case of variant A, variant B of CR-CC(2,3), being quite similar to variant A, is considerably less accurate than the full CR-CC(2,3) (i.e., CR-CC(2,3),D) method or variant C of CR-CC(2,3). Again, numerical evidence provided in section III confirms this.

Interestingly, the CR-CC(2,3) approach also reduces to other previously formulated noniterative CC methods of the (T) type if we make additional approximations in eqs 20−24 (see refs 66 and 67). For example, the CR-CC(2,3) approach reduces to the conventional CCSD(T) method if we replace the denominator D_{abc}^{ijk}, eq 23, in eq 22 by the spin-orbital energy difference

$(\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)$ (as is done in the CR-CC(2,3),A approximation), neglect the $(\Lambda_2 \bar{H}_1^{(\text{CCSD})})_{\text{DC}}$ term in eq 22, which is at least a fourth-order term in many-body perturbation theory (MBPT) if the Hartree−Fock reference is employed, replace the $(\Lambda_1 \bar{H}_2^{(\text{CCSD})})_{\text{DC}}$ and $(\Lambda_2 \bar{H}_2^{(\text{CCSD})})_{\text{C}}$ terms in the resulting expression, which appear in the third and second orders of MBPT, respectively, by $(T_1^\dagger V_N)_{\text{DC}}$ and$(T_2^\dagger V_N)_{\text{C}}$, where T_1 and T_2 are obtained in the CCSD calculations and V_N is a two-body part of $H - \langle\Phi|H|\Phi\rangle$, and approximate moment $\mathscr{M}_{abc}^{ijk}(2)$, eq 21, by the lead term $\langle\Phi_{ijk}^{abc}|(V_N T_2)_{\text{C}}|\Phi\rangle$. Just like CCSD(2)$_{\text{T}}$ and CCSD(T), the CR-CC(2,3) method is rigorously size extensive. This has been illustrated numerically in ref 67.

There also is an interesting formal relationship between the CR-CC(2,3) approach examined here and the original CR-CCSD(T) approach of refs 60−62. In particular, one can show (see ref 80 for details) that in addition to the linear terms in the triply excited moments $\mathscr{M}_{abc}^{ijk}(2)$ present in CR-CCSD(T) the CR-CC(2,3) method sums the disconnected product contributions involving $\mathscr{M}_{abc}^{ijk}(2)$ and the various many-body components of $e^{T_1+T_2}$ (the one-body T_1 component, the two-body $(T_2 + (1/2)T_1^2)$ component, etc.) to all orders. This allows one to absorb the renormalizing overlap denominator term $\langle\Psi_0|\Psi_0^{(\text{CCSD})}\rangle$, where $|\Psi_0^{(\text{CCSD})}\rangle$ is a CCSD wave function, which enters the triples correction of CR-CCSD(T), such that the resulting correction to the CCSD energy gains the transparent form of eq 20. The absorption of the overlap denominator term $\langle\Psi_0|\Psi_0^{(\text{CCSD})}\rangle$ through the use of the de-excitation amplitudes ℓ_{ijk}^{abc} in the CR-CC(2,3) approach eliminates the small extensivity errors from the CR-CCSD(T) calculations, while the additional product terms involving $\mathscr{M}_{abc}^{ijk}(2)$ and many-body components of $e^{T_1+T_2}$, which are effectively summed up to all orders in the CR-CC(2,3) expressions, improve the accuracy compared to the results of the CR-CCSD(T) calculations.[66,67] We will discuss the details of the relationship between the CR-CC(2,3) approach and the other methods derived from the biorthogonal MMCC formalism of refs 66 and 67, on the one hand, and CR-CCSD(T) and other methods derived from the original MMCC theory of refs 60, 61, and 70, on the other hand, in a separate work.[80]

Let us, finally, return to the advantages and consequences of using eq 23 for the denominator D_{abc}^{ijk} in the definition of the CR-CC(2,3) triples correction $\delta_0(2,3)$. As already pointed out above, the D_{abc}^{ijk} denominator, eq 23, is expressed in terms of the diagonal elements of the triples−triples block of the matrix representing the CCSD similarity-transformed Hamiltonian $\bar{H}^{(\text{CCSD})}$ rather than the more usual MBPT-like differences of bare spin-orbital energies that are used in the CCSD(T), CCSD(2)$_{\text{T}}$, and CR-CCSD(T) approaches. This is particularly useful in the CR-CC(2,3) calculations for open-shell systems employing the ROHF orbitals, such as those discussed in section III, because the use of the conventional spin-orbital energy differences $(\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)$ instead of the complete form of the diagonal matrix elements of $\bar{H}^{(\text{CCSD})}$ involving triply excited determinants to define the denominator D_{abc}^{ijk}, eq 23, leads to additional formal and practical difficulties related to the choice of the unperturbed Hamiltonian to define the orbital energies and the presence of the off-diagonal matrix elements in the spin-orbital form of the Fock matrix written for the ROHF orbitals (cf., e.g., refs 109−112 for a discussion of these issues in the context of the ROHF-based implementations of the conventional perturbative CCSD(T) and CC3 methods). We do not have to deal with those kinds of issues in the full CR-CC(2,3) calculations, which do not rely on a decomposition of the Hamiltonian into unperturbed and perturbed parts. Thus, the use of the complete form of the triply excited moments $\mathscr{M}_{abc}^{ijk}(2)$, eq 21, and the use of the complete form of the denominator D_{abc}^{ijk}, eq 23, in which all terms resulting from $\langle\Phi_{ijk}^{abc}|\bar{H}^{(\text{CCSD})}|\Phi_{ijk}^{abc}\rangle$ are retained, as in the full CR-CC(2,3) ≡ CR-CC(2,3),D approach, enable us to avoid at least some of the problems complicating the ROHF-based implementations of CCSD(T) (refs 109−111) and CC3 (ref 112), because we never have to determine what terms in the Hamiltonian are regarded as the zeroth-order terms. This, combined with the high accuracies and robustness that the CR-CC(2,3),D method offers in applications involving radicals, biradicals, and single bond breaking, is one of the main advantages of the complete CR-CC(2,3),D approach.

The price that we have to pay for all of these advantages of the CR-CC(2,3),D method is the slight dependence of the ROHF-based CR-CC(2,3),D energies on the method of canonicalization of the ROHF orbitals. Several methods of obtaining the canonical ROHF orbitals exist in the literature,[113−118] which differ in the way the diagonal doubly occupied, singly occupied, and unoccupied blocks of the Fock matrix are constructed (see the documentation of GAMESS[104] for a very instructive overview and useful details). As shown in section III, changes in the CR-CC(2,3),D energies due to different ways of obtaining the ROHF orbitals are on the order of tens of microhartrees or 0.01 kcal/mol, so again, as in the case of orbital degeneracies, this is more of a formal issue than a practical one. We should also keep in mind that even the basic CCSD approach, which is strictly invariant with respect to the canonicalization of the ROHF orbitals, is not invariant with respect to orbital rotations among the occupied orbitals and among the unoccupied orbitals when one freezes core orbitals (which is what one usually does). In fact, as shown in section III, changes in the CR-CC(2,3) energies due to different ways of obtaining the canonical ROHF orbitals are often on the same order as changes in the CCSD energies when core electrons are frozen in post-ROHF calculations. Moreover, with a given canonicalization scheme for the ROHF orbitals, each variant of CR-CC(2,3) is a well-defined and fully reproducible computational procedure. Given the fact that the dependence of the ROHF-based CR-CC(2,3),D energies on the way of producing the ROHF orbitals is, for most practical purposes, negligible and given the excellent accuracies and other advantages that the full CR-CC(2,3) approach employing the ROHF orbitals offers compared to other noniterative triples CC models, we believe that the ROHF-based implementation of the CR-CC(2,3) method tested in this work, which we have incorporated in the widely used GAMESS package, will find good use in quantum chemistry. One of the big advantages of GAMESS is that the user can choose a particular ROHF canonicalization method in the input (with Roothaan's scheme[113] being the default[104]). Thus, anybody interested in implementing the CR-CC(2,3) approach using the ROHF reference, as discussed in this work, can verify the correctness of their implementation by selecting the suitable ROHF canonicalization scheme in the GAMESS input to the ROHF-based CR-CC(2,3) calculations.

C. Remaining Computational Details. The straightforward formal relationships between the CR-CC(2,3), CCSD(2)$_{\text{T}}$, CCSD(T), and CR-CCSD(T) methods imply that computer costs characterizing all of these methods are very similar. Indeed, when properly implemented, the CCSD(T), CR-CCSD(T), CCSD(2)$_{\text{T}}$, and CR-CC(2,3) approaches are $n_o^2 n_u^4$ schemes in the iterative CCSD steps and $n_o^3 n_u^4$ procedures in the noniterative steps needed to construct the relevant triples corrections, where n_o and n_u are the numbers of occupied and unoccupied orbitals, respectively, used in the correlated calculations. Specifically, in analogy to CCSD(2)$_T$, the CR-CC(2,3) approach is an $n_o^2n_u^4$ method in the iterative CCSD steps that generate the T_1 and T_2 clusters and in the additional iterative steps that are needed to obtain the Λ_1 and Λ_2 components of the left CCSD state (needed to construct the ℓ_{ijk}^{abc} amplitudes, eq 22). Because the iterative computational steps needed to calculate Λ_1 and Λ_2 no longer require recalculating the matrix elements of $\bar{H}^{(\mathrm{CCSD})}$ or other intermediates of CCSD in every iteration, in many cases the time spent on generating Λ_1 and Λ_2 is less than the time spent on the CCSD iterations for T_1 and T_2. In general, the time spent on the left CCSD iterations that produce Λ_1 and Λ_2 does not exceed the time spent on the standard CCSD iterations that yield T_1 and T_2. In other words, the iterative part of the CR-CC(2,3) calculation does not use more than twice the time spent on the iterative parts of the CCSD(T) and CR-CCSD(T) calculations, which do not need Λ_1 and Λ_2 to construct the relevant triples energy corrections and which are solely based on the usual CCSD iterations. In analogy to the CCSD(2)$_T$ and CR-CCSD(T) methods (cf., e.g., refs 44 and 119 for a discussion), the noniterative steps required to calculate the triples correction $\delta_0(2,3)$ of CR-CC(2,3) are only twice as expensive as the noniterative $n_o^3n_u^4$ steps used to construct the (T) correction of CCSD(T). This factor of 2 is related to the need for the $n_o^3n_u^4$ steps in constructing the triexcited moments $\mathscr{M}_{abc}^{ijk}(2)$, eq 21, and the additional $n_o^3n_u^4$ steps that are needed to construct the $\langle\Phi|(\Lambda_2\bar{H}_2^{(\mathrm{CCSD})})_C|\Phi_{ijk}^{abc}\rangle$ contribution to the ℓ_{ijk}^{abc} amplitudes, eq 22, which enter the expression for $\delta_0(2,3)$, eq 20. In summary, the CR-CC(2,3) approach, being at most twice as expensive as CCSD(T) when the CPU time requirements are examined, is essentially as practical as the CCSD(T), CCSD(2)$_T$, and CR-CCSD(T) approaches. Similar remarks apply to memory requirements and disk usage. In particular, in analogy to CCSD(T) and similar methods, we can completely eliminate the need for storing the three-body quantities of the $n_o^3n_u^3$ type (the $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc} quantities are in this category) and determine the energy correction $\delta_0(2,3)$ by computing the relevant $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc} contributions on the fly. As we have done in the past when coding other CR-CC methods,[72,73,75,119] in constructing the individual $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc} terms, which have to be multiplied and summed up to produce the correction $\delta_0(2,3)$ following eq 20, we use explicit loops over i, j, and k only (see, for example, refs 73 and 75 for the overall loop structure defining the calculations of noniterative triples corrections in our other efficient CR-CC codes). As in refs 73 and 75, we do not use explicit loops over a, b, and c to determine $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc} and calculate first the corresponding partially antisymmetric six-index quantities that are antisymmetric with respect to i, j, and k but not with respect to a, b, and c. These partially antisymmetric six-index quantities are antisymmetrized with respect to indices a, b, and c to produce the final values of $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc} for a given set of $i < j < k$ and $a < b < c$ only at the very end when one needs to multiply $\mathscr{M}_{abc}^{ijk}(2)$ by ℓ_{ijk}^{abc} to form a particular contribution to $\delta_0(2,3)$. By avoiding the explicit loops over a, b, and c in the most essential and most computationally intensive part of the code that calculates $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc}, we maximize the benefits of using fast matrix multiplication routines, while eliminating the need for storing large $\mathscr{M}_{abc}^{ijk}(2)$ and ℓ_{ijk}^{abc} vectors of the $n_o^3n_u^3$ type.

The efficient open-shell implementation of the CR-CC(2,3) code used in this work has been written such that it can work with any high-spin reference $|\Phi\rangle$, including the ROHF and unrestricted Hartree−Fock (UHF) reference determinants. However, at this time, the CR-CC(2,3) code is intimately interfaced with the ROHF integral routines from GAMESS;[104] i.e., after the ROHF calculation performed by GAMESS, we call the efficient integral transformation routines, also taken from GAMESS, and then sort the resulting molecular integrals, using the routines written by Dr. Michael W. Schmidt, according to the number of occupied and unoccupied orbital indices that label them and according to the spin type of each orbital index (α or β) in a usual way. Once this is done, we go through the CCSD iterations to calculate T_1 and T_2, left CCSD iterations to calculate Λ_1 and Λ_2, and noniterative steps needed to determine the triples corrections $\delta_0(2,3)$ of the CR-CC(2,3),A−D approaches. As in the case of the earlier closed-shell CR-CC(2,3) codes (and other CC programs) interfaced with the RHF routines from GAMESS,[66,72,119] the CCSD nonlinear equations for the t_a^i and t_{ab}^{ij} cluster amplitudes and the left CCSD linear equations for λ_i^a and λ_{ij}^{ab} de-excitation amplitudes are solved using the usual DIIS algorithm.[120−123] By determining the λ_i^a and λ_{ij}^{ab} amplitudes that define the Λ_1 and Λ_2 operators of the left CCSD state, we automatically gain access to the one-electron density matrix of the CCSD ground-state wave function,[12,13,59,107] $\gamma_q^p = \langle\Phi|(\mathbf{1} + \Lambda_1 + \Lambda_2)\overline{a^pa_\mathrm{q}}|\Phi\rangle$, where $\overline{a^pa_\mathrm{q}} = \mathrm{e}^{-T_1-T_2}\,a^pa_q\,\mathrm{e}^{T_1+T_2}$, and the corresponding one-electron properties[12,13,59,107,108] in addition to corrections $\delta_0(2,3)$ of the CR-CC(2,3),A−D methods. This is yet another advantage of the CR-CC(2,3) methodology, which produces accurate triples corrections to CCSD energies along with one-electron properties calculated at the CCSD level. Although we plan to work on the UHF-based CR-CC(2,3) code in the long-term future, once the suitable molecular integral infrastructure for the UHF basis is developed within GAMESS, the use of the spin- and symmetry-adapted ROHF reference in the CR-CC(2,3) calculations has a very important advantage of eliminating, to a large extent, the issues of symmetry breaking and spin contamination that plague the UHF-based correlated calculations. Theoretically, there may be some problems in cases where ROHF incorrectly favors localizing the unpaired electrons, but we have not encountered anything unusual in our CR-CC(2,3) calculations that would indicate the significance of such problems in the context of CR-CC(2,3) considerations. The CR-CC(2,3) approach seems robust enough to work well with the ROHF references. In general, the overall benefits of using the spin-adapted ROHF reference functions in the CR-CC(2,3) calculations are, in our view, much more important than any of the potential formal or numerical complications that the use of such references may lead to, particularly because the ROHF-based CR-CC(2,3) method is very accurate and capable of eliminating the deficiencies of the reference determinant. Indeed, one of the major advantages of the CR-CC(2,3) and other CR-CC approaches, particularly in cases involving stronger quasi-degeneracies that occur in bond breaking and biradical situations, is that unlike the conventional CC methods of the CCSD(T) type the CR-CC(2,3) and other CR-CC approaches work well with the spin- and symmetry-adapted references of the restricted type.[17−19,25,30,31,33,44,50,51,60−62,64−68,72−77,119,124−146] The present paper shows that the same is true in open-shell cases employing the ROHF references.

The triply excited moments of the CCSD equations, $\mathscr{M}_{abc}^{ijk}(2)$, eq 21, which are the key quantities for the CR-CC(2,3) calculations, have been coded by integrating the factorized, computationally efficient expressions, exploiting the idea of recursively generated intermediates, which we obtained with the diagrammatic method and presented in refs 73 and 75, over the relevant spin variables. Similar spin-integrated spin-orbital expressions have been developed for the ℓ_{ijk}^{abc} amplitudes, eq 22, and other elements of the CR-CC(2,3) calculations. One of the most characteristic features of our approach to coding moments $\mathscr{M}_{abc}^{ijk}(2)$ and other quantities that are present in the CR-CC(2,3) expressions is the maximum use of the one- and two-body matrix elements of the similarity-transformed Hamiltonian of CCSD, $\bar{H}^{(\mathrm{CCSD})}$, eq 5, which we use as natural intermediates for all CCSD-based CC calculations.

The results obtained with the ROHF-based CR-CC(2,3) code used in this work reduce to those obtained with the RHF-based CR-CC(2,3) code of ref 66, exploited in a number of earlier studies,[30,31,33,66−68,76,77] when the calculations are performed for the singlet electronic states. Because the number of triple excitations in the spin-integrated spin-orbital formulation is twice the number of triples in the corresponding closed-shell case (we have to consider the $\alpha\beta\beta \rightarrow \alpha\beta\beta$ and $\beta\beta\beta \rightarrow \beta\beta\beta$ spin cases for triple excitations $i,j,k \rightarrow a,b,c$, in addition to the $\alpha\alpha\alpha \rightarrow \alpha\alpha\alpha$ and $\alpha\alpha\beta \rightarrow \alpha\alpha\beta$ cases present in the closed-shell case), the CPU time spent on computing the CR-CC(2,3) correction $\delta_0(2,3)$ in the open-shell formulation should be twice the time needed for the computation of $\delta_0(2,3)$ in the spin-free (or nonorthogonally spin-adapted) closed-shell formulation. On the basis of a large number of tests, where we have run the present ROHF-based CR-CC(2,3) code and the earlier, highly efficient RHF-based CR-CC(2,3) code side by side for a variety of singlet ground states, we can state that the open-shell computer implementation of the CR-CC(2,3) method tested in this study satisfies this condition. Further details of the open-shell CR-CC(2,3) code benchmarked in this work will be provided elsewhere.[80]

III. Numerical Examples and Discussion

To demonstrate the types of improvements that the CR-CC(2,3) method can offer in applications involving open-shell problems, when compared to other noniterative triples methods, including CCSD(T), CCSD(2)$_T$, and CR-CCSD(T), and the underlying CCSD approach, we consider the following five molecular examples, grouped into two categories: (i) the potential energy curves of the OH radical and F_2^+ ion and (ii) the singlet−triplet energy gaps in the CH_2, HHeH, and $(HFH)^-$ biradical systems. In all of the CC calculations performed in this work, we used the symmetry-adapted ROHF references for the doublet and triplet states and symmetry-adapted RHF references for the singlet states. Unless otherwise indicated, Roothaan's variant of the ROHF approach,[113] which is a default in GAMESS, was employed. With the exception of tests dealing with the dependence of the CR-CC(2,3) energies on the method of canonicalization of the ROHF orbitals, in all correlated calculations reported in this work, the lowest-energy molecular orbitals that correlate with the 1s orbitals of the C and F atoms were kept frozen. Unless otherwise stated, the spherical components of the d and f orbitals were employed.

In addition to the above examples, we use the activation energies of the $C_2H_4 + H \rightarrow C_2H_5$ forward and reverse reactions, which proceed on a doublet potential energy surface, the corresponding total electronic energies of the C_2H_5 product and transition-state species, and the lowest triplet states of the CH_2 (ref 94) and $H_2Si_2O_2$ (ref 106) biradicals to examine the dependence of the CR-CC(2,3) energies on the method of canonicalization of the ROHF orbitals. We tested six different ways of performing the ROHF calculations using the canonicalization approaches of Roothaan,[113] McWeeny and Diercksen,[114] Guest and Saunders,[115] Faegri and Manne,[116] Davidson,[117] and Binkley, Pople, and Dobosh.[118] The activation energies for the $C_2H_4 + H \rightarrow C_2H_5$ reaction are part of the databases used to assess the performance of electronic structure methods in thermochemical kinetics studies.[105] Thus, the $C_2H_4 + H \rightarrow C_2H_5$ reaction gives us an opportunity to comment on the potential applicability of the CR-CC(2,3) approach in the calculations of barrier heights characterizing chemical reactions involving radical species. Each calculation examining the dependence of the CR-CC(2,3) energies on the method of obtaining the ROHF orbitals was performed in two different ways, namely, with frozen-core orbitals and with all electrons correlated in the CC steps. In the former case, no CC method is invariant with respect to the rotation of occupied and unoccupied orbitals. In the latter case, the CCSD energies are independent of the method of canonicalization of the ROHF orbitals.

The calculations for OH, which is a good representative of radical species studied in various areas of chemistry, were performed with the 6-31G(d,p) basis set,[147−149] for which we could perform the exact, full CI calculations using GAMESS, enabling us to assess the accuracy of various CC approximations. In the case of bond breaking in F_2^+, which is a very challenging problem for the single-reference methods, we performed two sets of CC calculations. In the first set of calculations, we used the 6-31G basis set,[147,148] which is small enough to enable the exact, full CI calculations, which we performed with MOLPRO.[150] In the second set of calculations, we used the aug-cc-pVTZ basis set.[147,151,152] In this case, we were unable to perform full CI calculations due to the enormous costs that such calculations would require, so we used the MRCI(Q) approach of refs 34 and 35, as implemented in MOLPRO, instead to provide reference energy values for assessing the relative performance of various noniterative triples CC methods. We also carried out the MRCI(Q) calculations for the 6-31G basis set, which we could compare with full CI, to make sure that MRCI(Q) provides a reasonable benchmark for comparing the CCSD, CCSD(T), CCSD(2)$_T$ (i.e., CR-CC(2,3),A), CR-CCSD(T), and full CR-CC(2,3) methods. The MRCI(Q) calculations were performed in the usual way, using the complete-active-space self-consistent-field (CASSCF) reference and active orbitals that correlate with the 2s and 2p shells of both F atoms. The calculations for OH and F_2^+ were performed for a number of internuclear separations, $R_{\mathrm{O-H}}$ and $R_{\mathrm{F-F}}$, respectively, stretching the bonds in each case by a factor of 3 (approximately 3 in the OH case), which is more or less equivalent, to within a millihartree or so, to reaching the relevant asymptotes. The corresponding equilibrium bond lengths for OH and F_2^+ were taken from ref 153.

The CCSD, CCSD(T), CCSD(2)$_T$ (i.e., CR-CC(2,3),A), CR-CCSD(T), and CR-CC(2,3) calculations of the adiabatic singlet−triplet ($A^1A_1-X^3B_1$) energy gap in the CH_2 biradical, which is a classic test case that requires the precise and well-balanced incorporation of electron correlation effects and an accurate description of the ground and excited states of different symmetries and multiplicities, were performed in two different ways. In the first set of calculations, we used the geometries of the X^3B_1 and A^1A_1 states of CH_2 given in ref 89 and Dunning's[154] [4s2p/2s] double-ζ (DZ) basis set, scaled for the H atoms, and augmented with one set of polarization functions (DZP), also described in ref 89. The corresponding full CI results were taken from ref 89 as well. As in ref 89, the six Cartesian components of the carbon d orbital were used in the calculations. In the second set of calculations, we used the [5s3p/3s] triple-ζ (TZ) basis set of Dunning,[155] augmented with two sets of polarization functions (TZ2P), as described in ref 94, and the full CI geometries of the X^3B_1 and A^1A_1 states of CH_2 determined for this basis set in ref 94. The corresponding full CI energies were taken from ref 94 as well. Following ref 94, in the calculations for CH_2 using a TZ2P basis set, in addition to freezing one core orbital (as in the DZP case), we dropped the highest-energy virtual orbital from the correlated calculations.

The CCSD, CCSD(T), $CCSD(2)_T$, CR-CCSD(T), and CR-CC(2,3) calculations of the energy gap between the triplet excited state ($A^3\Sigma_u^+$) and singlet ground state ($X^1\Sigma_g^+$) of the linear HHeH system, which was used in the earlier studies to examine the effectiveness of various ab initio and density functional theory methods in modeling magnetic exchange coupling constants,[101−103] were performed with the 6-311G(d,p) basis set.[147,156] The analogous calculations for the linear $(HFH)^-$ system, which, in addition to being a biradical, has a polarizable diamagnetic entity in the center,[102] have been performed with the 6-31G(d,p) basis set.[147−149] In both cases, 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−He and H−F distances, R_{H-He} and R_{H-F}, respectively, defining the linear, $D_{\infty h}$-symmetric HHeH and $(HFH)^-$ systems, in which the terminal H atoms are linked via the diamagnetic central atom (He in the HHeH case and F^- in the $(HFH)^-$ case). The R_{H-He} distances in HHeH were varied from $R_{H-He} = 1.25$ Å to $R_{H-He} = 5.0$ Å. The R_{H-F} distances in $(HFH)^-$ were varied from $R_{H-F} = 1.5$ Å to $R_{H-F} = 4.0$ Å. Shorter R_{H-He} and R_{H-F} distances correspond to moderately strong biradicals. Longer R_{H-He} and R_{H-F} distances correspond to essentially pure biradicals, where the H atoms separated by a very large distance weakly interact via a diamagnetic bridge, giving rise to nearly degenerate singlet and triplet states. The RHF/ROHF-based CCSD, CCSD(T), $CCSD(2)_T$, CR-CCSD(T), and CR-CC(2,3) results for the HHeH and $(HFH)^-$ systems are compared with the full CI data, obtained with GAMESS and MOLPRO, and with the UHF-based CCSD, CCSD(T), QCISD,[157] and QCISD(T) results obtained with Gaussian 98.[158]

The calculations for the $C_2H_4 + H \rightarrow C_2H_5$, CH_2, and $H_2Si_2O_2$ systems, which are used to examine the effect of the method of canonicalization of the ROHF orbitals on the CR-CC(2,3) results, were performed with the aug-cc-pVTZ (frozen-core) and aug-cc-pCVTZ (all-electron) basis sets[147,151,152] in the case of the $C_2H_4 + H \rightarrow C_2H_5$ reaction, the TZ2P basis set[94,155] in the case of CH_2, and the 6-311G(d,p) basis set[147,156,159] in the $H_2Si_2O_2$ case. In the case of the $C_2H_4 + H \rightarrow C_2H_5$ reaction, the relevant nuclear geometries of the C_2H_4 and C_2H_5 species were taken from ref 105. In the case of the triplet ground state of CH_2, the relevant nuclear geometry determined with full CI was taken from ref 94. The calculations for the lowest triplet state of $H_2Si_2O_2$ were performed using the geometry of the corresponding singlet structure determined with the two-configurational SCF approach in ref 106.

We begin our discussion with the potential energy curves of the OH and F_2^+ systems (section IIIA). The results obtained for the singlet−triplet gaps in the CH_2, HHeH, and $(HFH)^-$ systems are discussed in section IIIB. The effect of the method of canonicalization of the ROHF orbitals on the CR-CC(2,3) results for the energetics of the $C_2H_4 + H \rightarrow C_2H_5$ reaction and triplet states of CH_2 and $H_2Si_2O_2$ is discussed in section IIIC.

A. Potential Energy Curves of OH and F_2^+. We first examine the ground-state potential energy curve of the "easier" OH system, which is typical of many radical species. The results of our calculations for OH are collected in Table 1. Because

TABLE 1: Ground-State Energies of the OH Radical, as Described by the 6-31G(d,p) Basis Set,[147−149] Obtained with the Full CI and CC Methods at the Representative Internuclear Separations R_{O-H}, and the MUE and NPE Values Relative to Full CI Characterizing the CC Results[a]

	R_{O-H}									
method	0.77	0.96966[b]	1.07	1.27	1.50	1.75	2.00	2.50	3.00	MUE	NPE
full CI	−75.481036	−75.546516	−75.540195	−75.505499	−75.462404	−75.428354	−75.409100	−75.396165	−75.393798		
CCSD	1.732	2.113	2.401	3.303	5.153	8.257	10.935	6.059	2.656	10.935	9.203
CCSD(T)	0.334	0.466	0.555	0.804	1.242	1.789	2.095	3.122	1.596	3.122	2.788
CR-CCSD(T)	0.456	0.619	0.734	1.080	1.805	3.144	4.854	4.389	1.915	4.854	4.398
$CCSD(2)_T$[c]	0.381	0.539	0.649	0.978	1.654	2.856	4.385	3.399	0.939	4.385	4.004
CR-CC(2,3),B[d]	0.416	0.586	0.707	1.075	1.843	3.230	4.940	3.649	1.084	4.940	4.524
CR-CC(2,3),C	0.057	0.161	0.217	0.343	0.580	1.058	2.224	2.884	0.595	2.884	2.827
CR-CC(2,3)[e]	0.062	0.168	0.227	0.366	0.643	1.204	2.437	2.909	0.608	2.909	2.847

[a] The full CI energies are in hartree. The CC energies and the corresponding MUE and NPE values are in millihartree. The O−H distances R_{O-H} are in angstroms. In all correlated calculations, the lowest occupied 1σ orbital was kept frozen. [b] The equilibrium bond length taken from ref 153. [c] Defined as the approximate variant A of CR-CC(2,3) described in the text. [d] Equivalent, up to small details, to the triples part of the (2) correction of the CCSD(2) method of refs 37 and 39. [e] Equivalent to the full variant D of CR-CC(2,3) described in the text.

the dissociation of OH is a process that is formally somewhat simpler than a single bond breaking and because one of the two dissociation fragments, the hydrogen atom, is a one-electron system that is described by any of the methods used in this work exactly, the CCSD approach provides a qualitatively correct description of the bond breaking in OH. This is reflected in the relatively small values of the maximum unsigned error (MUE) and nonparallelity error (NPE; NPE is defined as the difference between the most positive and most negative signed errors along a given potential energy curve) relative to full CI, characterizing the CCSD results for OH shown in Table 1, which are 10.935 and 9.203 millihartree, respectively. The conventional CCSD(T) method further improves the CCSD results, reducing the MUE and NPE values resulting from the CCSD calculations to the relatively small values of 3.122 and 2.788 millihartree, respectively. Very similar improvements in the CCSD results are observed when instead of CCSD(T) one uses the triples corrections of the CR-CCSD(T) and CCSD(2)$_\mathrm{T}$ approaches.

One might think that it is virtually impossible to improve these already very good results any further using the idea of the relatively inexpensive noniterative corrections to the CCSD energies due to triple excitations, but our CR-CC(2,3) calculations indicate that additional improvements in the CCSD(T), CR-CCSD(T), and CCSD(2)$_\mathrm{T}$ results are still possible. Indeed, the most complete variant of the CR-CC(2,3) approach (variant D) reduces the already relatively small MUE and NPE values characterizing the CCSD(T), CR-CCSD(T), and CCSD(2)$_\mathrm{T}$ results for OH to as little as 2.909 and 2.847 millihartree, respectively. What is most encouraging here is the fact that the CR-CC(2,3) method is more accurate than CCSD(T) at all internuclear separations $R_{\mathrm{O-H}}$, including the equilibrium region, where CCSD(T) performs very well. In particular, the full CR-CC(2,3) approach reduces the 0.466 millihartree error at the equilibrium geometry of OH resulting from the CCSD(T) calculations to 0.168 millihartree. The CR-CCSD(T) and CCSD(2)$_\mathrm{T}$ methods are slightly less accurate than CCSD(T) in the equilibrium region, which is consistent with the earlier calculations for closed-shell systems. The CR-CCSD(T) and CCSD(2)$_\mathrm{T}$ methods provide virtually identical results at all values of $R_{\mathrm{O-H}}$, which agrees with the earlier studies of single bond breaking on singlet potential energy surfaces.[44,66−68,76,77] The full CR-CC(2,3) approach behaves in a different manner, reducing the errors observed in the CR-CCSD(T) and CCSD(2)$_\mathrm{T}$ (i.e., CR-CC(2,3),A) calculations by a substantial factor, which in the case of bond breaking in OH is usually between 2 and 3. Again, this parallels some of our earlier observations when we studied bond breaking on singlet potentials.[66−68,76,77]

Interestingly, variant B of the CR-CC(2,3) method, which is practically identical to the triples correction of the CCSD(2) approach of Gwaltney and Head-Gordon,[37,39] is less accurate than variant A of CR-CC(2,3). In fact, the CR-CC(2,3),B approximation is characterized by larger MUE and NPE values than those characterizing the CR-CCSD(T) results. Clearly, the use of the one-body term $\langle \Phi_{ijk}^{abc} | \bar{H}_1^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle = \bar{h}_a^a + \bar{h}_b^b + \bar{h}_c^c - \bar{h}_i^i - \bar{h}_j^j - \bar{h}_k^k$ alone in the definition of the D_{abc}^{ijk} denominator, as is done in variant B of CR-CC(2,3), is not sufficient to improve the CCSD(2)$_\mathrm{T}$ or CR-CCSD(T) results. One needs to go beyond the one-body components of $\bar{H}_1^{(\mathrm{CCSD})}$ in defining D_{abc}^{ijk}, as is done in variants C and D of CR-CC(2,3), to improve the results of the CCSD(2)$_\mathrm{T}$ or CR-CCSD(T) calculations. The CR-CC(2,3),C results in Table 1 are slightly more accurate than the results of the full CR-CC(2,3) calculations with variant D, but the differences between these two variants of the CR-CC(2,3) theory are practically none, implying the negligible role of the three-body $\langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$ contributions to the denominator D_{abc}^{ijk}. In conclusion, the full CR-CC(2,3) method provides a highly accurate description of bond breaking in the OH radical, improving the results of the CCSD(T), CR-CCSD(T), and CCSD(2)$_\mathrm{T}$ calculations at all O−H separations and providing a more accurate description of the equilibrium region than the widely used CCSD(T) approach.

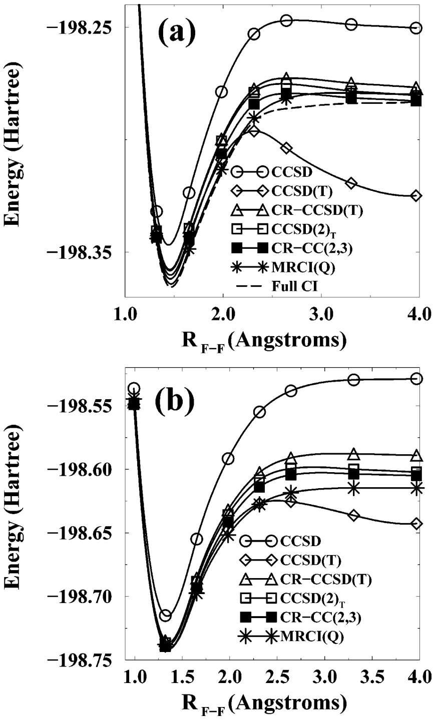

Figure 1. Comparison of the potential energy curves of F_2^+ resulting from the CCSD, CCSD(T), CR-CCSD(T), CCSD(2)$_\mathrm{T}$ (approximated by CR-CC(2,3),A), and CR-CC(2,3) calculations, employing the D_{2h}-adapted ROHF reference and the (a) 6-31G and (b) aug-cc-pVTZ basis sets with the corresponding potential energy curves obtained in the (a) full CI and MRCI(Q) and (b) MRCI(Q) calculations.

The excellent performance of the CR-CC(2,3) method in the case of OH is clearly very encouraging from the point of view of the future applications of this method to reaction pathways involving radicals, so let us examine now what happens when the CR-CC(2,3) approach and other noniterative triples CC approximations are applied to a different kind of a problem, the highly demanding F_2^+ system. We chose this particular example for several reasons. First of all, the nature of the F_2^+ system is such that we cannot expect perfect performance of any CCSD(T)-like approximation, including CR-CC(2,3), in this case. In analogy to the neutral F_2 molecule (cf., e.g., refs 124 and 137), the dissociation of the F_2^+ ion is a very complicated multireference problem, characterized by a rapid increase of the nondynamical correlation effects as the F−F bond stretches, which is difficult to capture with single-reference methods.[81−83] As in the case of the F_2 molecule, an accurate description of the F_2^+ dissociation with the single-reference CC methods that exploit the spin- and symmetry-adapted Hartree−Fock reference of the restricted type may require an explicit incorporation of quadruply excited clusters. The CR-CC(2,3) method ignores the T_4 clusters altogether, so the results of the CR-CC(2,3) calculations based on the symmetry-adapted ROHF reference cannot be as good as in the OH case, but it is still quite interesting to investigate if the CR-CC(2,3) approach can provide improvements in the results obtained with other noniterative triples CC

TABLE 2: Comparison of Various CC Ground-State Energies with the Corresponding Full CI and MRCI(Q) Results Obtained for a Few Geometries of the F_2^+ Molecule with the 6-31G[147,148] and aug-cc-pVTZ[147,151,152] Basis Sets, and the MUE and NPE Values Characterizing the CC and MRCI(Q) Results Relative to Full CI in the 6-31G Case and the CC Results Relative to MRCI(Q) in the aug-cc-pVTZ Case[a]

method	$0.75R_e$	R_e[b]	$1.25R_e$	$1.5R_e$	$1.75R_e$
		6-31G			
full CI[c]	−198.059252	−198.345407	−198.350097	−198.314945	−198.291842
CCSD	3.897	13.478	26.445	36.182	38.799
CCSD(T)	0.905	3.722	7.037	6.103	−4.291
CR-CCSD(T)	1.279	5.288	11.229	15.283	14.444
CCSD(2)$_T$[d]	1.134	4.889	10.584	14.379	12.865
CR-CC(2,3),B[e]	1.224	5.598	12.681	18.129	17.831
CR-CC(2,3),C	0.397	1.727	4.078	5.342	4.163
CR-CC(2,3)[f]	0.414	2.139	5.787	8.637	7.614
MRCI(Q)[g]	1.938	1.419	1.491	1.672	1.561
		aug-cc-pVTZ			
MRCI(Q)[g]	−198.544634	−198.737808	−198.697538	−198.651729	−198.627569
CCSD	8.192	22.789	42.694	60.088	72.611
CCSD(T)	−4.190	−1.102	3.173	4.296	0.552
CR-CCSD(T)	−2.520	3.076	11.980	19.879	25.108
CCSD(2)$_T$[d]	−3.240	1.458	9.376	16.128	19.376
CR-CC(2,3),B[e]	−2.931	2.621	12.431	21.545	27.030
CR-CC(2,3),C	−4.421	−1.885	3.000	7.218	9.072
CR-CC(2,3)[f]	−4.412	−1.660	4.261	10.214	13.698

method	$2R_e$	$2.5R_e$	$3R_e$	MUE	NPE
		6-31G			
full CI[c]	−198.286194	−198.283840	−198.283050		
CCSD	39.152	35.051	32.691	39.152	35.255
CCSD(T)	−17.510	−35.460	−41.834	41.834	48.871
CR-CCSD(T)	13.531	8.985	6.306	15.283	14.004
CCSD(2)$_T$[d]	10.943	5.503	2.666	14.379	13.245
CR-CC(2,3),B[e]	16.407	11.431	8.925	18.129	16.905
CR-CC(2,3),C	4.367	0.747	−1.524	5.342	6.866
CR-CC(2,3)[f]	6.714	2.494	0.249	8.637	8.388
MRCI(Q)[g]	4.465	4.558	3.150	4.558	3.139
		aug-cc-pVTZ			
MRCI(Q)[g]	−198.618418	−198.614724	−198.614744		
CCSD	80.086	85.063	85.999	85.999	77.807
CCSD(T)	−7.123	−21.562	−27.980	27.980	32.276
CR-CCSD(T)	27.375	26.925	25.787	27.375	29.895
CCSD(2)$_T$[d]	18.976	14.846	12.490	19.376	22.616
CR-CC(2,3),B[e]	28.411	26.342	24.934	28.411	31.342
CR-CC(2,3),C	8.436	5.160	3.694	9.072	13.493
CR-CC(2,3)[f]	13.964	11.128	9.759	13.964	18.376

[a] The full CI energies for the 6-31G basis set and the MRCI(Q) energies for the aug-cc-pVTZ basis set are in hartree. The CC and MRCI(Q) energies relative to full CI for the 6-31G basis set, the CC energies relative to MRCI(Q) for the aug-cc-pVTZ basis set, and the corresponding MUE and NPE values are in millihartree. In all correlated calculations, the lowest two occupied 1σ orbitals were kept frozen. [b] $R_e = 1.322$ Å is the equilibrium value of the internuclear distance R_{F-F} taken from ref 153. [c] Due to convergence problems at the internuclear distances $R_{F-F} = 2R_e$, $2.5R_e$, and $3R_e$, when the ROHF orbitals were used in the full CI calculations, the reported full CI energies were obtained by performing the CASSCF calculations, in which all orbitals in a molecular orbital basis set other than the lowest two core orbitals were chosen as active orbitals. The differences between the full CI results obtained in this way and the results of full CI calculations employing the ROHF orbitals at the F−F distances $R_{F-F} = 0.75R_e$, R_e, $1.25R_e$, $1.5R_e$, and $1.75R_e$, where no convergence problems occcur, are −14, −11, −14, −11, and −9 microhartree, respectively. [d] Defined as the approximate variant A of CR-CC(2,3) described in the text. [e] Equivalent, up to small details, to the triples part of the (2) correction of the CCSD(2) method of refs 37 and 39. [f] Equivalent to the full variant D of CR-CC(2,3) described in the text. [g] The active space consisted of the molecular orbitals correlating with the 2s and 2p shells of the F atoms.

approaches in the case of F_2^+. One of the most challenging problems that the single-reference methods face, when bond breaking in F_2^+ is examined, is the possibility of the breakdown of the inversion symmetry (lowering of the symmetry from $D_{\infty h}$ to $C_{\infty v}$ or D_{2h} to C_{2v}) by the UHF or ROHF calculations, which may significantly impact the results of the correlated single-reference calculations employing the UHF or ROHF references.[82,83] The spin- and symmetry-adapted multireference methods employing the CASSCF and other properly constructed multideterminantal references do not have such problems (cf., e.g., the MRCI calculations for F_2^+, employing the generalized valence bond (GVB) references[160] or our MRCI(Q) results in Table 2 and Figure 1), but in the single-reference calculations one must proceed with extra caution. In the case of F_2^+, the single-reference methods that impose the $D_{\infty h}$ or D_{2h} symmetry on the reference determinant (preserving, in particular, the inversion symmetry) may experience severe difficulties in describing the dissociation of the ground-state F_2^+ molecule into F(2p^5 ^{2}P) + F$^+$(2p^4 ^{3}P). As in the case of bond breaking of closed-shell molecules into open-shell fragments, the description of bond breaking in F_2^+ by the single-reference CC methods may benefit from using the spin- and symmetry-broken UHF references. This has been demonstrated by Watts and Bartlett,[83] who showed that one may obtain a reasonable description of the entire potential energy curve of F_2^+ with the single-reference CC methods employing the spin- and symmetry-broken (C_{2v}-adapted) UHF reference. This is not possible if one employs a single-determinantal reference configuration adapted to the spin and spatial ($D_{\infty h}$ or D_{2h}) symmetries of the Hamiltonian of F_2^+.

Indeed, the use of the symmetry-adapted single-determinantal references creates a situation where the nondynamic correlation effects become very large and difficult to describe by the conventional single-reference methods, even in the region of the intermediate stretches of the F−F bond in F_2^+. This can be seen in Table 2 and Figure 1, where we compare the results of the CCSD, CCSD(T), CR-CCSD(T), CCSD(2)$_T$ (i.e., CR-CC(2,3),A), and full CR-CC(2,3) calculations for F_2^+, employing the D_{2h}-adapted ROHF reference, with the exact, full CI results and the results of the accurate MRCI(Q) calculations. Indeed, the errors in the CCSD results relative to full CI and MRCI(Q) are large already at the equilibrium geometry, exceeding 10 millihartree in the case of the 6-31G basis set and 20 millihartree in the case of the aug-cc-pVTZ basis set, and it is sufficient to stretch the F−F separation by 25% to double these errors. The MUE and NPE values relative to full CI characterizing the CCSD results for the small 6-31G basis set in the entire $R_{F-F} = 0.75R_e - 3R_e$ region, where R_e is the equilibrium bond length in F_2^+, are 39.152 and 35.255 millihartree, respectively (similar values would be obtained if we used the MRCI(Q) energies as reference energies in determining MUE and NPE; cf. Table 2). The MUE and NPE values relative to MRCI(Q) characterizing the CCSD results obtained with the aug-cc-pVTZ basis set of 85.999 and 77.807 millihartree, respectively, are so large that the CCSD approach produces a potential well that is approximately 50% deeper than that obtained with the MRCI(Q) approach (cf. Figure 1b). Indeed, if we calculate the binding energy D_e as the difference of energies obtained at $R_{F-F} = 3R_e$ and $R_{F-F} = R_e$, then the MRCI(Q)/aug-cc-pVTZ approach gives $D_e = 3.35$ eV, which compares very well with the experimental D_e value of 3.41 eV[153,161] and the GVB-based MRCI value of D_e of 3.00 eV reported in ref 160. The CCSD method employing the aug-cc-pVTZ basis set and the symmetry-adapted ROHF reference gives 5.07 eV, which clearly is a much worse result. As one might expect, the standard CCSD(T) approach, employing the D_{2h}-adapted ROHF reference, fails too, producing a well-pronounced unphysical hump at the intermediate values of R_{F-F} (Figure 1). Consequently, the CCSD(T) energies display a strongly nonvariational behavior at larger F−F separations. At $R_{F-F} = 3R_e$, the CCSD(T) energy is already 41.834 millihartree below the corresponding full CI energy when the 6-31G basis set is employed. When one uses the aug-cc-pVTZ basis set, the CCSD(T) energy is 27.980 millihartree below the corresponding MRCI(Q) energy at $R_{F-F} = 3R_e$. These large negative values should be compared to the much smaller errors relative to full CI or MRCI(Q) at $R_{F-F} = R_e$, which are 3.722 millihartree in the 6-31G case and −1.102 millihartree in the aug-cc-pVTZ case. These significant changes in the error values characterizing the CCSD(T) energies, the strongly nonvariational behavior of CCSD(T) at larger F−F separations, and the presence of the hump on the CCSD(T) potential energy curve result in the large NPE values relative to full CI or MRCI(Q) characterizing the CCSD(T) results in the entire $R_{F-F} = 0.75R_e - 3R_e$ region, which are almost 50 millihartree in the 6-31G case and more than 30 millihartree in the aug-cc-pVTZ case.

TABLE 3: Adiabatic $A^1A_1-X^3B_1$ Splitting in CH_2 Obtained with Full CI and Various CC Approaches and the DZP Basis Set[a]

method	$E(X^3B_1)$ (hartree)	$E(A^1A_1)$ (hartree)	$E(A^1A_1) - E(X^3B_1)$ (kcal/mol)
full CI[a]	−39.046 260	−39.027 183	11.97
CCSD	−39.044 111	−39.023 639	12.85
CCSD(T)	−39.045 893	−39.026 310	12.29
CR-CCSD(T)	−39.045 744	−39.025 970	12.41
CCSD(2)$_T$[b]	−39.045 791	−39.026 058	12.38
CR-CC(2,3),B[c]	−39.045 743	−39.025 960	12.41
CR-CC(2,3),C	−39.046 267	−39.026 864	12.18
CR-CC(2,3)[d]	−39.046 261	−39.026 850	12.18

[a] The basis sets, geometries, and full CI energies were taken from ref 89. As in ref 89, in all correlated calculations, the lowest occupied orbital was kept frozen, and Cartesian components of the carbon d orbital were employed. [b] Defined as the approximate variant A of CR-CC(2,3) described in the text. [c] Equivalent, up to small details, to the triples part of the (2) correction of the CCSD(2) method of refs 37 and 39. [d] Equivalent to the full variant D of CR-CC(2,3) described in the text.

As shown in Table 2 and Figure 1, the CR-CCSD(T) and CCSD(2)$_T$ methods provide considerable improvements in the poor CCSD and CCSD(T) results for F_2^+, particularly at larger internuclear separations. The CR-CCSD(T) and CCSD(2)$_T$ approaches reduce the very large errors in the CCSD results at all F−F separations by a substantial factor. This is clearly reflected in the MUE values, which in the case of the 6-31G basis set are 39.152 millihartree for CCSD and 15.283 and 14.379 millihartree for CR-CCSD(T) and CCSD(2)$_T$ (i.e., CR-CC(2,3),A), respectively. In the case of the aug-cc-pVTZ basis set, where MUE values are calculated relative to the MRCI(Q) energies, the CR-CCSD(T) and CCSD(2)$_T$ approaches reduce the huge MUE value of 85.999 millihartree to 27.375 and 19.376 millihartree, respectively. The ROHF-based CR-CCSD(T) and CCSD(2)$_T$ approaches replace the well-pronounced humps on the CCSD(T) curves at the intermediate F−F distances by the tiny humps, which in the case of the aug-cc-pVTZ basis set are about 1 millihartree for CR-CCSD(T), with a maximum on the corresponding potential curve defining the hump reached at $R_{F-F} \approx 2.5R_e$, and about 3 millihartree for CCSD(2)$_T$ (i.e., CR-CC(2,3),A), with a similar maximum on the CCSD(2)$_T$ potential energy curve found at $R_{F-F} \approx 2R_e$ (cf. Figure 1b). Clearly, these are major improvements compared to CCSD(T), which in the case of the aug-cc-pVTZ basis set produces a 17 millihartree hump, if we subtract the CCSD(T) energy at $R_{F-F} = 3R_e$ from the CCSD(T) energy at the maximum on the corresponding potential energy curve defining the hump. As shown in Table 2 and Figure 1, the CR-CCSD(T) and CCSD(2)$_T$ methods reduce the large negative errors in the CCSD(T) energies at larger values of R_{F-F} to smaller positive errors. For example, the large negative errors in the CCSD(T) results relative to full CI at $R_{F-F} = 2R_e$ and $3R_e$ of −17.510 and −41.834 millihartree, respectively, obtained with the 6-31G basis set, reduce to much smaller positive errors of 13.531 and 6.306 millihartree when the CR-CCSD(T) approach is employed and 10.943 and 2.666 millihartree when the CCSD(2)$_T$ (i.e., CR-CC(2,3),A) method is used. If we attempt to measure the quality of the CR-CCSD(T) and CCSD(2)$_T$ curves by calculating the corresponding approximate binding energies D_e as differences of energies obtained at the R_{F-F} values where the CR-CCSD(T) and CCSD(2)$_T$ potentials have maxima associated with tiny humps and at $R_{F-F} = R_e$, then we obtain 4.00 eV for CR-CCSD(T) and 3.73 eV for CCSD(2)$_T$, (i.e., CR-CC(2,3),A), when the aug-cc-pVTZ basis set is employed. Although these results are not as good as the MRCI(Q)/aug-cc-pVTZ D_e value of 3.35 eV, which is closer to the experimental D_e value of 3.41 eV, the CR-CCSD(T) and CCSD(2)$_T$ estimates of D_e are clearly much better than the

TABLE 4: Adiabatic $A^1A_1-X^3B_1$ Splitting in CH_2 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)
full CI[a]	−39.066 738	−39.048 984	11.14
CCSD[b]	−39.063 313	−39.043 791	12.25
CCSD[c]	−39.063 351	−39.043 791	12.27
CCSD(T)[b]	−39.066 192	−39.048 005	11.41
CCSD(T)[c]	−39.066 276	−39.048 005	11.47
CR-CCSD(T)[b]	−39.065 931	−39.047 475	11.58
CR-CCSD(T)[c]	−39.066 011	−39.047 475	11.63
CCSD(2)$_T$[b,d]	−39.066 015	−39.047 631	11.54
CCSD(2)$_T$[c,d]	−39.066 097	−39.047 631	11.59
CR-CC(2,3)[b,e]	−39.066 601	−39.048 509	11.35
CR-CC(2,3)[c,e]	−39.066 699	−39.048 509	11.41

[a] The basis set, geometries, and full CI energies were taken from ref 94. As in ref 94, in all correlated calculations, the lowest occupied orbital was kept frozen, the highest unoccupied orbital was deleted, and spherical components of the carbon d orbital were employed. All calculations were performed at the full CI equilibrium geometries computed in ref 94, and they are as follows: for X^3B_1, $r_e = 1.0775$ Å and $\theta_e = 133.29°$; for A^1A_1, $r_e = 1.1089$ Å and $\theta_e = 101.89°$. [b] Triplet calculations were performed using the ROHF canonicalization procedure of Guest and Saunders.[115] [c] Triplet calculations were performed using the Roothaan single matrix ROHF canonicalization procedure.[113] [d] Defined as the approximate variant A of CR-CC(2,3) described in the text. [e] Equivalent to the full variant D of CR-CC(2,3) described in the text.

CCSD/aug-cc-pVTZ result of 5.07 eV. We realize that we cannot treat these D_e estimates too rigorously, but we are mentioning them here to indicate the types of improvements that the CR-CCSD(T) and CCSD(2)$_T$ methods can offer when the problem is as challenging as F_2^+.

As in the case of OH, one might think that further improvements in the results for F_2^+ at the relatively simple level offered by a single-reference CC theory, where the CCSD energies are corrected through the use of noniterative corrections due to triples, are no longer possible. The CR-CC(2,3) results in Table 2 and Figure 1 provide information to the contrary. In fact, the full CR-CC(2,3) approach offers substantial improvements in the results of the CR-CCSD(T) and CCSD(2)$_T$ calculations at all values of R_{F-F}, while correcting the unphysical behavior of the conventional CCSD(T) approach at larger F−F distances. The MUE values of 15.283 and 14.379 millihartree resulting from the CR-CCSD(T) and CR-CC(2,3),A calculations with the 6-31G basis set reduce to 8.637 millihartree, when the full CR-CC(2,3) method is employed. A similar error reduction is observed when we examine the corresponding NPE values. The MUE value of 8.637 millihartree obtained in the simple, single-reference, ROHF-based CR-CC(2,3) calculations, which neglect higher-than-triple excitations, for a system with large nondynamical and dynamical correlation effects can actually be regarded as a reasonably good result. For example, the much more complex MRCI(Q) approach designed to handle large nondynamical correlation effects gives the MUE value relative to full CI of 4.558 millihartree, when the 6-31G basis set is employed. Although we do not have access to the full CI data in the case of the aug-cc-pVTZ basis set and can only rely on comparisons with the MRCI(Q) energies, which obviously carry their own errors, the overall improvements in the CCSD, CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ results offered by the full CR-CC(2,3) method in the calculations employing the aug-cc-pVTZ basis set are similar to those observed in the calculations with the 6-31G basis. For example, the 27.375 and 18.976 millihartree errors in the CR-CCSD(T) and CCSD(2)$_T$ (i.e., CR-CC(2,3),A) results relative to MRCI(Q) at $R_{F-F} = 2R_e$ reduce to 13.964 millihartree, when the full CR-CC(2,3) method is employed. The huge positive error in the CCSD energy at $R_{F-F} = 3R_e$ of 85.999 millihartree and the relatively large negative error in the CCSD(T) energy at the same F−F distance of −27.980 millihartree reduce to a relatively small positive error of 9.759 millihartree, which is also less than the 25.787 and 12.490 millihartree errors relative to MRCI(Q) obtained with the CR-CCSD(T) and CCSD(2)$_T$ (i.e., CR-CC(2,3),A) approaches, when the full CR-CC(2,3) approach is used. The CR-CC(2,3) potential energy curves have tiny remanent humps, on the order of 3 and 1 millihartree, with maxima reached at $R_{F-F} \approx 2R_e$ and $2.5R_e$, respectively, when the 6-31G and aug-cc-pVTZ basis sets are employed, but clearly the CR-CC(2,3) curves are orders of magnitude better than the corresponding CCSD(T) potentials, which are characterized by the well-pronounced humps of about 29 and 17 millihartree, when we limit ourselves to the F−F distances not exceeding $3R_e$ (cf. Figure 1). If we try to estimate the approximate binding energy resulting from the full CR-CC(2,3) calculations by forming a difference of the CR-CC(2,3)/aug-cc-pVTZ energy at the R_{F-F} value where the CR-CC(2,3)/aug-cc-pVTZ potential has a maximum associated with the tiny hump ($2.5R_e$) and the CR-CC(2,3)/aug-cc-pVTZ energy at $R_{F-F} = R_e$, then we obtain 3.70 eV. This is an improvement over the CR-CCSD(T) and CR-CC(2,3),A values of 4.00 and 3.73 eV, respectively, and also not a bad result, when compared to the MRCI(Q)/aug-cc-pVTZ D_e value of 3.35 eV or the experimental D_e value of 3.41 eV, particularly if we take into consideration the black-box nature of the CR-CC(2,3) calculations and their relatively low cost comparable to CCSD(T).

As in the case of the OH radical, the CCSD(2)$_T$ method of Hirata el al.,[44] which is represented here by variant A of the CR-CC(2,3) approach, is more accurate than variant B of CR-CC(2,3), which is, up to small details, equivalent to the triples correction of the CCSD(2) method of Gwaltney and Head-Gordon.[37,39] The CR-CC(2,3),B results are also worse than those obtained with the CR-CCSD(T) approach. This can be seen by comparing the CCSD(2)$_T$, CR-CC(2,3),B, and CR-CCSD(T) MUE values in Table 2, which are 14.379, 18.129, and 15.283 millihartree, respectively, for the 6-31G basis set, where all errors are calculated relative to full CI, and 19.376, 28.411, and 27.375 millihartree, respectively, for the aug-cc-pVTZ basis set, where all errors are calculated relative to MRCI(Q). Thus, the sole use of the one-body $\langle \Phi_{ijk}^{abc} | \bar{H}_1^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$ contribution to the D_{abc}^{ijk} denominator in eq 23, as is done in the CR-CC(2,3),B calculations, is not sufficient to improve the CCSD(2)$_T$ or CR-CCSD(T) results. As in the case of OH, one needs to incorporate the two-body $\langle \Phi_{ijk}^{abc} | \bar{H}_2^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$ terms in D_{abc}^{ijk}, as is done in variant C, or two- and three-body terms, $\langle \Phi_{ijk}^{abc} | \bar{H}_2^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$ and $\langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$, respectively, as in the full variant D, to obtain improvements in the results of the CCSD(2)$_T$ and CR-CCSD(T) calculations. Interestingly, the CR-CC(2,3),C results for F_2^+ appear to be more accurate than the results of the full CR-CC(2,3) calculations using variant D, but this is not a general rule, and it is hard to justify dropping the three-body $\langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$ contribution from the complete form of the denominator D_{abc}^{ijk} given by eq 23. Thus, we continue to favor the full CR-CC(2,3) approach, represented by variant D, in which all many-body contributions to D_{abc}^{ijk} that result from considering the diagonal part of the triples−triples block of the matrix representing $\bar{H}^{(\mathrm{CCSD})}$ are included in the calculations. The full CR-CC(2,3) approach is accurate and robust enough to justify this. It is interesting, though, to observe the significant improvements, compared to variants A and B of CR-CC(2,3), when the two-body $\langle\Phi_{ijk}^{abc}|\bar{H}_2^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ contributions are incorporated in the D_{abc}^{ijk} denominator.

Last but not least, we would also like to emphasize once again that, unlike CR-CCSD(T) and CCSD(2)$_T$ or CR-CC(2,3),B, the full CR-CC(2,3) approach is capable of offering improvements over CCSD(T) or providing the results of the CCSD(T) quality in the equilibrium region, where CCSD(T) works well. This can be clearly seen by examining the results for F_2^+ in Table 2. For example, the full CR-CC(2,3) approach reduces the 0.905, 3.722, and 7.037 millihartree errors at $R_{F-F} = 0.75R_e$, R_e, and $1.25R_e$, respectively, obtained in the CCSD(T)/6-31G calculations, to 0.414, 2.139, ad 5.787 millihartree, respectively. The analogous errors resulting from the CR-CCSD(T) and CCSD(2)$_T$ (i.e., CR-CC(2,3),A) calculations with the 6-31G basis set are visibly larger (1.279, 5.288, and 11.229 millihartree, respectively, when the CR-CCSD(T) approach is used, and 1.134, 4.889, and 10.584 millihartree, when the CCSD(2)$_T$ method is employed). Variant B of CR-CC(2,3), which is equivalent to the triples correction of the CCSD(2) theory developed in refs 37 and 39, is even less accurate. In the case of the aug-cc-pVTZ basis set, the differences between CCSD(T) and MRCI(Q) energies at $R_{F-F} = 0.75R_e$, R_e, and $1.25R_e$ are −4.190, −1.102, and 3.173 millihartree, respectively, and full CR-CC(2,3) gives −4.412, −1.660, and 4.261 millihartree for the analogous energy differences with MRCI(Q), which shows that the quality of the CR-CC(2,3) and CCSD(T) data in the equilibrium region of F_2^+ is more or less the same. (We have to keep in mind that MRCI(Q) is not the exact theory and carries its own errors, which, based on the results obtained with the 6-31G basis set, can easily be on the order of 1 millihartree.) We can conclude this subsection by stating that the CR-CC(2,3) method provides the best overall description of the potential energy curve of F_2^+, when compared with other noniterative triples single-reference CC approximations that have similar computer costs and ease of use. As in the case of bond breaking in F_2, which proceeds on the singlet potential energy curve and which we studied in our earlier CR-CC(2,3) work,[66−68] the open-shell variant of full CR-CC(2,3) employing the spin- and symmetry-adapted ROHF reference provides an accurate description of the equilibrium region of the challenging F_2^+ system, which can compete with that offered by the conventional CCSD(T) approach, while providing substantial improvements in the CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ results at larger internuclear separations of F_2^+.

B. Singlet−Triplet Splittings in CH_2, HHeH, and $(HFH)^-$. The previous subsection dealt with bond breaking on doublet potentials. In this subsection, we deal with another important class of open-shell problems, namely, with the single−triplet gaps in biradical systems. Our first example is the seminal case of the relatively small $A^1A_1-X^3B_1$ gap in methylene, which has been the subject of controversies between theory and experiment (cf., e.g., refs 84−88 and references therein) and which is very sensitive to the quality of the electronic structure calculations.[25,89−98] One of the biggest challenges that one encounters in determining the $A^1A_1-X^3B_1$ gap in methylene is the fact that the X^3B_1 ground state is a nondegenerate high-spin state, which can be reasonably well-described by single-reference methods, but the first excited A^1A_1 state has a significant degree of biradical character and nondynamical correlation, which normally requires a genuine multireference treatment. An accurate determination of the gap between two electronic states that have such different characteristics requires a well-balanced and precise assessment of both dynamical and nondynamical correlation effects, and very few electronic structure methods are capable of doing this. For example, even the highly successful multireference perturbation theory methods, including the widely used CASPT2 approach, give large (∼30%) errors in the results for the singlet−triplet gap in methylene (see, e.g., refs 24 and 25). The genuine multireference methods of the MRCI and MRCC type provide excellent results for the $A^1A_1-X^3B_1$ gap in CH_2,[89−97] but the question is if we can obtain reasonable results for the same gap when we apply the single-reference CR-CC(2,3) approach, using the ROHF reference for the X^3B_1 state and the RHF reference for the A^1A_1 state. As in the previous subsection, we are particularly interested in answering the question of whether the CR-CC(2,3) approach examined in this work can improve the results of the CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ calculations.

The results of the CCSD, CCSD(T), CR-CCSD(T), CCSD(2)$_T$ (i.e., CR-CC(2,3),A), and CR-CC(2,3) calculations for the X^3B_1 and A^1A_1 states and the adiabatic energy gap between them using the same DZP-type basis sets and geometries as used in the well-known benchmark study by Bauschlicher and Taylor,[89] who provided the exact, full CI results, are listed in Table 3. It is immediately obvious from this table that the full CR-CC(2,3) approach provides the best results when compared to the CCSD and other noniterative triples methods, reducing the 0.88, 0.32, 0.44, and 0.41 kcal/mol errors relative to full CI in the CCSD, CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ (i.e., CR-CC(2,3),A) values of the $A^1A_1-X^3B_1$ gap in methylene to 0.21 kcal/mol. The 2.149, 0.367, 0.516, and 0.469 millihartree errors in the CCSD, CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ results for the easier, largely single-reference X^3B_1 state reduce to −0.001 millihartree when the full CR-CC(2,3) method is employed. The 3.544, 0.873, 1.213, and 1.125 millihartree errors in the CCSD, CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ results for the more challenging and more multideterminantal A^1A_1 state reduce to 0.333 millihartree, when the full CR-CC(2,3) method is used. Thus, the CR-CC(2,3) approach provides improvements both in the total energies of the X^3B_1 and A^1A_1 electronic states and in the difference between them, offering a well-balanced and accurate description that can only compete with the most accurate MRCI and MRCC work[89,93,95] or with the calculations using the expensive single-reference full CCSDT method employing the UHF reference, which gives 12.09 kcal/mol for the $A^1A_1-X^3B_1$ gap in methylene.[98] Interestingly, our CR-CC(2,3) result for the singlet−triplet gap in CH_2 of 12.18 kcal/mol, which compares rather well with the full CI value of 11.97 kcal/mol, is more accurate than the results of the approximate CCSDT calculations using the iterative CCSDT-*n* models, which are considerably more expensive than our noniterative CR-CC(2,3) approach and give 12.28−12.33 kcal/mol (see ref 98 for further details). In analogy to the OH and F_2^+ cases, variant B of the CR-CC(2,3) approach, which is almost the same as the triples correction of the CCSD(2) method of refs 37 and 39, is slightly less accurate than the CR-CC(2,3),A and CR-CCSD(T) methods and considerably less accurate than variants C and D of the CR-CC(2,3) theory, illustrating once again the benefits of incorporating higher-than-one-body components of $\langle\Phi_{ijk}^{abc}|\bar{H}^{(\mathrm{CCSD})}|\Phi_{ijk}^{abc}\rangle$ in the definition of the denominator D_{abc}^{ijk}, eq 23.

The results in Table 4 show that all of the observations about the relative performance of various noniterative triples CC methods, including CCSD(T), CR-CCSD(T), CCSD(2)$_T$, and full CR-CC(2,3), in calculations of the $A^1A_1-X^3B_1$ energy gap

TABLE 5: $A^3\Sigma_u^+-X^1\Sigma_g^+$ Gap for the Linear, $D_{\infty h}$-Symmetric HHeH System (in cm^{-1}) Described by the 6-311G(d,p) Basis Set[147,156] as a Function of the H−He Distance R_{H-He} (in Å)

	RHF reference							UHF reference					
R_{H-He}	full CI	SCF	CCSD	CCSD(T)	CR-CCSD(T)	CCSD(2)$_T$[a]	CR-CC(2,3)[b]	SCF	CCSD	CCSD(T)	QCISD	QCISD(T)	$\lvert c_2/c_0\rvert$[c]
1.250	4859	−21285	4224	4938	4746	4731	4845	1947	3994	4549	3943	4519	0.5248
1.500	1168	−34648	630	1433	1105	1072	1166	450	785	902	781	896	0.7416
1.625	544	−39081	113	833	506	471	546	210	335	376	334	374	0.8175
1.750	249	−42406	−77	517	229	197	253	97	144	157	143	156	0.8732
1.875	113	−44900	−124	337	103	77	118	44	62	66	62	66	0.9130
2.000	51	−46790	−117	225	47	27	55	20	27	28	27	28	0.9408
2.125	23	−48248	−94	153	22	7	27	9	12	12	12	12	0.9601
2.250	10	−49399	−71	104	11	0	13	4	5	5	5	5	0.9734
2.500	2	−51108	−36	49	3	−2	4	1	1	1	1	1	0.9884
2.750	0	−52340	−18	23	1	−1	2	0	0	0	0	0	0.9951
3.000	0	−53298	−9	11	0	−1	1	0	0	0	0	0	0.9980
5.000	0	−57247	0	0	0	0	0	0	0	0	0	0	1.0000

[a] Defined as the approximate variant A of CR-CC(2,3) described in the text. [b] Equivalent to the full variant D of CR-CC(2,3) described in the text. [c] The absolute value of the ratio of the coefficients at the doubly excited (HOMO)^2 → (LUMO)^2 determinant (c_2) and the RHF ground-state determinant (c_0) characterizing the full CI expansion of the $X^1\Sigma_g^+$ state.

in methylene remain valid when the larger, TZ2P basis set, used in ref 94, is employed. As in the case of the DZP basis set, the full CR-CC(2,3) approach is more accurate than the CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ methods, giving an excellent result for the singlet−triplet gap of 11.35−11.41 kcal/mol, where the full CI result is 11.14 kcal/mol. The differences between the CR-CC(2,3) and full CI energies are very small as well, namely, 39−137 microhartree for the X^3B_1 state and 475 microhartree for the A^1A_1 state. No other noniterative triples CC method can provide equally good results. In particular, the widely used CCSD(T) approach gives the 462−546 microhartree errors for the X^3B_1 state and the 979 microhartree error for the A^1A_1 state. These are considerably larger errors than those obtained with full CR-CC(2,3). Another interesting feature of CR-CC(2,3) is the remarkable agreement between the full CR-CC(2,3) energy for the A^1A_1 state and the corresponding full CCSDT energy reported in ref 94. The difference between the full CR-CC(2,3) and CCSDT energies for this state is only 267 microhartree. The analogous difference between the CCSD(T) and the CCSDT energies of 771 microhartree is clearly much higher, confirming the earlier observations[66−68] that, unlike CCSD(T), the CR-CC(2,3) energies are always very close to the corresponding full CCSDT energies.

The results in Table 4 also show that the method used to obtain the canonical ROHF orbitals has virtually no effect on the CR-CC(2,3) energies for the X^3B_1 state. The Roothaan canonicalization of ROHF,[113] which is a default in GAMESS, and the Guest−Saunders canonicalization scheme,[115] used in ref 94, give the full CR-CC(2,3) energies of the X^3B_1 state that differ by as little as 98 microhartree. Part of this 98 microhartree difference must be due to freezing the core and dropping the virtual orbitals in the CR-CC(2,3) calculations. Indeed, the difference between the underlying CCSD energies obtained with the Roothaan and Guest−Saunders canonicalization schemes is 38 microhartree. The CCSD energies are invariant with respect to orbital rotations, but only when none of the orbitals is dropped from the correlated calculations. The tiny change in the CR-CC(2,3) energy for the X^3B_1 state translates into the very small, 0.06 kcal/mol, difference between the CR-CC(2,3) values of the $A^1A_1-X^3B_1$ gap obtained with the Roothaan and Guest−Saunders canonicalization procedures. All of this shows the robustness of the CR-CC(2,3) theory, which is not only very accurate but also virtually insensitive to the way the canonical ROHF orbitals are obtained. We will return to the issue of the impact of the ROHF canonicalization procedure on the CR-CC(2,3) energies in section IIIC.

Balancing two electronic states of different spatial and spin symmetries becomes even more challenging when the HHeH and (HFH)$^-$ linear systems are examined. The HHeH and (HFH)$^-$ systems are model magnetic systems, where two paramagnetic centers each carrying an unpaired spin, represented in this case by the terminal hydrogen atoms, are linked via a diamagnetic bridge constituted by the He (the HHeH case) or F$^-$ (the (HFH)$^-$ case) atom.[101−103] The spins of the two 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 gaps between these states, which provide information about the magnetic exchange coupling constants J, as functions of the H−He and H−F distances, R_{H-He} and R_{H-F}, respectively, in the D_{2h}-symmetric linear HHeH and (HFH)$^-$ systems, have been studied in refs 102 and 103 using full CI and a variety of approximate ab initio and density functional theory methods (see also ref 101). These studies show that, not surprisingly, the majority of electronic structure methods, including the widely used density functional theory and QCISD(T) approaches, have severe problems with describing the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps in the HHeH and (HFH)$^-$ systems and their dependencies on the corresponding H−He and H−F distances, which should smoothly approach zero as these distances approach ∞.

In analogy to methylene, balancing and accurately describing the electron correlation effects in the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states of the HHeH and (HFH)$^-$ systems is a major challenge to many methods. What is even more challenging here is the fact that unlike methylene, which is a relatively weak biradical, both HHeH and (HFH)$^-$ systems are strong biradicals, particularly in the region of larger R_{H-He} and R_{H-F} distances. This can be seen in Tables 5 and 6, which show the absolute values of the ratios of the coefficients at the doubly excited (HOMO)^2 → (LUMO)^2 determinant (c_2) and the RHF ground-state determinant (c_0) characterizing the full CI expansions of the $X^1\Sigma_g^+$ wave functions of the HHeH (Table 5) and (HFH)$^-$ (Table 6) systems as functions of the relevant R_{H-He} and R_{H-F} coordinates. As in the classic case of the H_2 molecule, the symmetry of the HOMO in the HHeH and (HFH)$^-$ systems is σ_g, the symmetry of the LUMO is σ_u, and the ratio of the full CI expansion coefficients at the (HOMO)^2 → (LUMO)^2 and RHF configurations, c_2/c_0, characterizing the $X^1\Sigma_g^+$ state is equivalent to the full CI value of the T_2 cluster amplitude corresponding to the (HOMO)^2 → (LUMO)^2 double excitation. (The corresponding

TABLE 6: $A^3\Sigma_u^+-X^1\Sigma_g^+$ Gap for the Linear, $D_{\infty h}$-Symmetric (HFH)$^-$ System (in cm^{-1}) Described by the 6-31G(d,p) Basis Set[147−149] as a Function of the H−F Distance $R_{\mathrm{H-F}}$ (in Å)

	RHF reference							UHF reference			
$R_{\mathrm{H-F}}$	full CI	SCF	CCSD	CCSD(T)	CR-CCSD(T)	CCSD(2)$_T$[a]	CR-CC(2,3)[b]	SCF	CCSD	CCSD(T)	$\|c_2/c_0\|$[c]
1.500	9525	−7169	7320	9468	8916	8886	9355	3024	7398	8418	0.3768
1.625	7008	−12006	4372	7066	6319	6279	6834	1641	4981	5776	0.4274
1.750	4911	−16708	1838	5179	4169	4117	4752	718	3156	3693	0.4846
1.875	3304	−21135	−172	3902	2553	2482	3183	186	1913	2244	0.5458
2.000	2147	−25229	−1656	3212	1444	1345	2087	−67	1122	1323	0.6082
2.125	1353	−28970	−2668	3023	758	615	1370	−151	638	766	0.6698
2.250	827	−32363	−3282	3225	393	182	916	−150	350	438	0.7292
2.375	488	−35424	−3572	3714	259	−54	628	−118	182	247	0.7858
2.500	277	−38172	−3605	4394	280	−171	435	−81	88	137	0.8392
3.000	17	−46460	−2369	7370	943	−230	43	−8	1	10	1.0174
4.000	0	−53986	−230	8899	1741	−34	−33	0	0	0	1.1727

[a] Defined as the approximate variant A of CR-CC(2,3) described in the text. [b] Equivalent to the full variant D of CR-CC(2,3) described in the text. [c] The absolute value of the ratio of the coefficients at the doubly excited (HOMO)^2 → (LUMO)^2 determinant (c_2) and the RHF ground-state determinant (c_0) characterizing the full CI expansion of the $X^1\Sigma_g^+$ state.

TABLE 7: Comparison of the Total Energies Obtained with Various Electronic Structure Methods for the $X^1\Sigma_g^+$ State of the Linear $D_{\infty h}$-Symmetric HHeH System Described by the 6-311G(d,p) Basis Set[147,156] as a Function of the H−He Distance $R_{\mathrm{H-He}}$ (in Å)[a]

	RHF reference							UHF reference				
$R_{\mathrm{H-He}}$	full CI	SCF	CCSD	CCSD(T)	CR-CCSD(T)	CCSD(2)$_T$[b]	CR-CC(2,3)[c]	SCF	CCSD	CCSD(T)	QCISD	QCISD(T)
1.250	−3.831731	156.305	3.083	−0.316	0.558	0.626	0.072	49.534	4.125	1.455	4.352	1.591
1.500	−3.857318	196.930	2.546	−1.185	0.311	0.462	0.015	36.623	1.836	1.234	1.852	1.262
1.625	−3.866631	213.259	2.025	−1.302	0.189	0.347	−0.005	34.001	1.013	0.782	1.016	0.790
1.750	−3.873695	226.367	1.524	−1.212	0.103	0.247	−0.015	32.569	0.521	0.432	0.521	0.434
1.875	−3.878850	236.642	1.104	−1.014	0.050	0.169	−0.019	31.780	0.257	0.220	0.257	0.220
2.000	−3.882507	244.662	0.780	−0.791	0.020	0.112	−0.018	31.337	0.124	0.107	0.124	0.107
2.125	−3.885048	250.982	0.543	−0.589	0.005	0.073	−0.016	31.084	0.060	0.051	0.059	0.051
2.250	−3.886787	256.049	0.375	−0.426	−0.001	0.047	−0.014	30.936	0.029	0.024	0.029	0.024
2.500	−3.888750	263.669	0.177	−0.212	−0.004	0.020	−0.009	30.795	0.007	0.005	0.007	0.005
2.750	−3.889612	269.222	0.084	−0.102	−0.002	0.008	−0.005	30.739	0.002	0.001	0.002	0.001
3.000	−3.889974	273.558	0.041	−0.049	−0.001	0.004	−0.003	30.713	0.001	0.000	0.001	0.000
5.000	−3.890192	291.514	0.001	−0.001	0.000	0.000	0.000	30.677	0.000	0.000	0.000	0.000

[a] The full CI energies are given in hartree, while the remaining energies are given in millihartree relative to the corresponding full CI values. [b] Defined as the approximate variant A of CR-CC(2,3) described in the text. [c] Equivalent to the full variant D of CR-CC(2,3) described in the text.

T_1 amplitude vanishes because the HOMO and the LUMO have different symmetries.) In analogy to the bare H_2 system, the absolute values of this amplitude are small in the weakly biradical region of small H−H distances, but they become large, approaching values around 1.0, when the H−H distance becomes large and the $X^1\Sigma_g^+$ state gains a strongly biradical character. In other words, the $|c_2/c_0|$ ratio provides us with a measure of the degree of the biradical character in the HHeH and (HFH)$^-$ systems. As indicated by the $|c_2/c_0|$ values in Tables 5 and 6, which vary between 0.52 and 1.00, when $R_{\mathrm{H-He}}$ varies between 1.25 and 5.0 Å in HHeH, and between 0.38 and 1.17, when $R_{\mathrm{H-F}}$ varies between 1.5 and 4.0 Å in (HFH)$^-$, the HHeH and (HFH)$^-$ systems have a significant biradical character already at the relatively short H−He and H−F distances, while becoming essentially pure biradicals when these distances exceed 2.5 Å. Because of the significant biradical nature of the HHeH and (HFH)$^-$ systems at almost all H−He and H−F distances shown in Tables 5 and 6, the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps in these systems are already relatively small and sensitive to the electron correlation treatment used in the calculations of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states in the regions of shorter H−He and H−F distances, while rapidly approaching zero as $R_{\mathrm{H-He}}$ and $R_{\mathrm{H-F}}$ become large, as the full CI results presented in Tables 5 and 6 clearly indicate.

The sensitivity of the results for the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps in the HHeH and (HFH)$^-$ systems to the way that the electron correlation effects are treated can be seen by analyzing the data shown in Tables 5 and 6. The corresponding full CI and various CC electronic energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states as functions of the relevant H−He and H−F distances are shown in Tables 7 and 8 for the HHeH system and Tables 9 and 10 for the (HFH)$^-$ system. It is clear from these tables that the basic CCSD approximation is not sufficient to provide an accurate description, which means that one needs to go beyond the CCSD level and include the effects of triply excited clusters. Indeed, as shown in Table 5, at $R_{\mathrm{H-He}} = 1.25$ Å, the error in the CCSD result for the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap in the HHeH system is 635 cm^{-1} or 13.1%, and the RHF/ROHF-based CCSD approach behaves erratically when we increase the value of $R_{\mathrm{H-He}}$, such that the triplet state goes below the singlet state in the 1.75 Å ≤ $R_{\mathrm{H-He}}$ ≤ 3.0 Å region, which is a qualitatively incorrect result. The problem of state reversal is particularly dramatic in the $R_{\mathrm{H-He}}$ = 1.75−2.25 Å region, where, for example, the positive values of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap at $R_{\mathrm{H-He}}$ = 1.75, 2.0, and 2.25 Å, which in the full CI calculations are 249, 51, and 10 cm^{-1}, become −77, −117, and −71 cm^{-1}, respectively, when the ROHF/RHF-based CCSD method is employed. One might think that the use of the UHF rather than RHF/ROHF references in the CCSD calculations helps, but this is not the case. As shown in Table 5, the UHF-based CCSD calculations make the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap positive in the entire $R_{\mathrm{H-He}}$ region, but errors in the UHF-based CCSD results for this gap are as large as 865 cm^{-1} or 17.8% at $R_{\mathrm{H-He}}$ = 1.25 Å, 209 cm^{-1} or 38.4% at $R_{\mathrm{H-He}}$ = 1.625 Å, and 24 cm^{-1} or 47.1% at $R_{\mathrm{H-He}}$ = 2.0 Å. The frequently used UHF-based QCISD approach provides similarly large errors.

TABLE 8: Comparison of the Total Energies Obtained with Various Electronic Structure Methods for the $A^3\Sigma_u^+$ State of the Linear $D_{\infty h}$-Symmetric HHeH System Described by the 6-311G(d,p) Basis Set[147,156] as a Function of the H−He Distance R_{H-He} (in Å)[a]

	RHF reference							UHF reference				
R_{H-He}	full CI	SCF	CCSD	CCSD(T)	CR-CCSD(T)	CCSD(2)$_T$[b]	CR-CC(2,3)[c]	SCF	CCSD	CCSD(T)	QCISD	QCISD(T)
1.250	−3.809590	37.185	0.190	0.041	0.042	0.042	0.008	36.265	0.183	0.042	0.176	0.039
1.500	−3.851994	33.738	0.092	0.021	0.021	0.021	0.005	33.348	0.090	0.021	0.087	0.020
1.625	−3.864150	32.713	0.061	0.014	0.014	0.014	0.004	32.477	0.060	0.014	0.058	0.013
1.750	−3.872559	32.013	0.039	0.009	0.009	0.009	0.003	31.875	0.039	0.009	0.037	0.009
1.875	−3.878335	31.547	0.025	0.006	0.006	0.006	0.002	31.468	0.024	0.006	0.024	0.005
2.000	−3.882275	31.242	0.015	0.004	0.004	0.004	0.001	31.197	0.015	0.004	0.015	0.003
2.125	−3.884944	31.046	0.010	0.002	0.002	0.002	0.001	31.021	0.010	0.002	0.009	0.002
2.250	−3.886740	30.922	0.006	0.001	0.001	0.001	0.001	30.908	0.006	0.001	0.006	0.001
2.500	−3.888741	30.793	0.003	0.001	0.001	0.001	0.000	30.789	0.003	0.001	0.002	0.001
2.750	−3.889610	30.739	0.001	0.000	0.000	0.000	0.000	30.738	0.001	0.000	0.001	0.000
3.000	−3.889974	30.713	0.001	0.000	0.000	0.000	0.000	30.713	0.001	0.000	0.001	0.000
5.000	−3.890192	30.677	0.000	0.000	0.000	0.000	0.000	30.677	0.000	0.000	0.000	0.000

[a] The full CI energies are given in hartree, while the remaining energies are given in millihartree relative to the corresponding full CI values. [b] Defined as to the approximate variant A of CR-CC(2,3) described in the text. [c] Equivalent to the full variant D of CR-CC(2,3) described in the text.

The results in Table 6 show that the performance of the CCSD approach in the calculations for the $(HFH)^-$ system is even more erratic. The errors in the RHF/ROHF- and UHF-based CCSD calculations are extremely large, and the RHF/ROHF-based CCSD values of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap, which should be positive for all R_{H-F} values, become very negative in the 1.875 Å $\leq R_{H-F} \leq$ 4.0 Å region. Indeed, errors in the RHF/ROHF-based CCSD results 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 and remain large for the remaining H−F distances. 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. As in the HHeH case, the UHF-based CCSD approach makes the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap positive at all H−F distances, but the problem of large errors relative to full CI remains. This can be illustrated by the 2127 cm^{-1} or 22.3%, 1025 cm^{-1} or 47.7%, and 189 cm^{-1} or 68.2% errors in the UHF-based CCSD results for the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap at R_{H-F} = 1.5, 2.0, and 2.5 Å, respectively. Clearly, one needs to include the effects of triply excited clusters to improve the poor results of the CCSD calculations for the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps in the HHeH and $(HFH)^-$ systems. The CCSD approach is incapable of providing reasonable $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps, particularly for the $(HFH)^-$ system, because it fails to balance the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, describing the $A^3\Sigma_u^+$ state more accurately than the corresponding $X^1\Sigma_g^+$ state. This can be seen by inspecting the errors in the CCSD energies of the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, particularly in the $(HFH)^-$ case. In the case of $(HFH)^-$, the errors in describing the $X^1\Sigma_g^+$ state in the R_{H-F} = 1.5−3.0 Å region range between 12.346 and 20.546 millihartree, whereas the errors in describing the $A^3\Sigma_u^+$ state in the same region range between 1.476 and 2.628 millihartree. The fact that CCSD is so much less accurate for the $X^1\Sigma_g^+$ state is a consequence of the multireference nature of this state, which requires at least two determinants (the RHF and the $(HOMO)^2 \rightarrow (LUMO)^2$ configurations) to obtain a reasonable zero-order description, particularly at larger R_{H-F} values. The $A^3\Sigma_u^+$ state is largely dominated by the triplet ROHF configuration for all H−F separations and, as such, is easier to describe by the single-reference CC methods, including CCSD.

The inclusion of triples through the CCSD(T) approach improves the situation but only to some extent. The RHF/ROHF-based CCSD(T) calculations for the $(HFH)^-$ system are even more erratic at larger H−F distances than the corresponding CCSD calculations, and the errors in the calculated $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps for the HHeH and $(HFH)^-$ systems with both the restricted and the unrestricted references are too large to be acceptable in accurate studies. The fact that the $X^1\Sigma_g^+$ state obtained in the CCSD(T) calculations remains a ground state at all H−He and H−F distances examined in Tables 5−10 is an improvement compared to CCSD but only to some extent, because, for example, the RHF-based CCSD(T) method completely fails for the $X^1\Sigma_g^+$ state of the $(HFH)^-$ system at larger H−F distances, artificially lowering its energy, so that the $X^1\Sigma_g^+$ state becomes the ground state, as it should, but for entirely unphysical reasons. For example, as shown in Tables 9 and 10, the signed errors in the RHF-based CCSD(T) energy of the $X^1\Sigma_g^+$ state and the ROHF-based CCSD(T) energy of the $A^3\Sigma_u^+$ state at R_{H-F} = 4.0 Å, where both states are practically degenerate, are −40.115 and 0.434 millihartree, respectively. The large, ∼40 millihartree, lowering of the energy of the $X^1\Sigma_g^+$ state at R_{H-F} = 4.0 Å by the RHF-based CCSD(T) approach and, in general, the large negative errors relative to full CI obtained with the RHF-based CCSD(T) method in the $R_{H-F} \geq$ 2.25 Å region, which exceed, in absolute value, 10 millihartree, are a consequence of an inability of this approach to describe singlet biradicals, for which the triples (T) correction of the restricted CCSD(T) always becomes too negative. This artificial energy lowering helps to reverse 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 $R_{H-F} \geq$ 1.875 Å region, but errors in the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap calculated with the CCSD(T) approach employing restricted references in this region are huge, ranging from 598 cm^{-1} or 18.1% at R_{H-F} = 1.875 Å to 1065 cm^{-1} or 49.6% at R_{H-F} = 2.0 Å, 4117 cm^{-1} or 1486.3% at R_{H-F} = 2.5 Å, and 8899 cm^{-1} at R_{H-F} = 4.0 Å, where the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap should be numerically 0. We do not observe anything like this in the HHeH case, where the CCSD(T) approach employing restricted references is practically exact at large H−He distances (Tables 7 and 8), because the $X^1\Sigma_g^+$ state of the HHeH system at large values of R_{H-He} is equivalent to the significantly stretched H_2 molecule and the He atom, which are both described exactly at the CCSD and CCSD(T) levels. There are, however, other problems with the CCSD(T) results for the HHeH system. For example, the relatively small, 78 cm^{-1} or 1.6%, error in the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap obtained with the RHF/ROHF-based CCSD(T) approach at R_{H-He} = 1.25 Å

TABLE 9: Comparison of the Total Energies Obtained with Various Electronic Structure Methods for the $X^1\Sigma_g^+$ State of the Linear, $D_{\infty h}$-Symmetric $(HFH)^-$ System Described by the 6-31G(d,p) Basis Set[147−149] as a Function of the H−F Distance R_{H-F} (in Å)[a]

	RHF reference							UHF reference		
R_{H-F}	full CI	SCF	CCSD	CCSD(T)	CR-CCSD(T)	CCSD(2)$_T$[b]	CR-CC(2,3)[c]	SCF	CCSD	CCSD(T)
1.500	−100.589392	277.056	12.674	0.827	3.578	3.471	0.919	226.127	12.240	5.580
1.625	−100.584704	285.951	14.501	0.330	3.951	3.881	0.967	219.120	11.667	6.165
1.750	−100.577669	296.141	16.351	−0.594	4.199	4.178	0.927	212.251	10.319	6.116
1.875	−100.570151	307.260	18.045	−2.071	4.243	4.291	0.768	206.070	8.554	5.408
2.000	−100.563055	318.849	19.398	−4.177	4.027	4.185	0.491	200.817	6.789	4.354
2.125	−100.556686	330.443	20.261	−6.914	3.535	3.876	0.143	196.486	5.276	3.292
2.250	−100.551083	341.671	20.546	−10.225	2.790	3.432	−0.192	192.950	4.089	2.405
2.375	−100.546222	352.284	20.224	−14.003	1.841	2.944	−0.432	190.056	3.208	1.739
2.500	−100.542059	362.150	19.328	−18.084	0.755	2.500	−0.524	187.679	2.578	1.274
3.000	−100.531336	393.748	12.346	−32.964	−3.573	1.558	0.060	181.950	1.579	0.568
4.000	−100.526513	425.698	2.518	−40.115	−7.388	0.585	0.321	179.720	1.472	0.433

[a] The full CI energies are given in hartree, while the remaining energies are given in millihartree relative to the corresponding full CI values. [b] Defined as the approximate variant A of CR-CC(2,3) described in the text. [c] Equivalent to the full variant D of CR-CC(2,3) described in the text.

TABLE 10: Comparison of the Total Energies Obtained with Various Electronic Structure Methods for the $A^3\Sigma_u^+$ State of the Linear, $D_{\infty h}$-Symmetric $(HFH)^-$ System Described by the 6-31G(d,p) Basis Set[147−149] as a Function of the H−F Distance R_{H-F} (in Å)[a]

	RHF reference							UHF reference		
R_{H-F}	full CI	SCF	CCSD	CCSD(T)	CR-CCSD(T)	CCSD(2)$_T$[b]	CR-CC(2,3)[c]	SCF	CCSD	CCSD(T)
1.500	−100.545993	200.994	2.628	0.569	0.803	0.559	0.143	196.505	2.547	0.537
1.625	−100.552773	199.318	2.492	0.595	0.810	0.561	0.175	194.668	2.430	0.549
1.750	−100.555291	197.638	2.349	0.624	0.816	0.557	0.202	193.145	2.320	0.564
1.875	−100.555097	195.908	2.206	0.652	0.821	0.546	0.216	191.865	2.216	0.580
2.000	−100.553271	194.114	2.068	0.677	0.823	0.531	0.218	190.730	2.117	0.598
2.125	−100.550520	192.280	1.940	0.694	0.820	0.512	0.219	189.633	2.017	0.616
2.250	−100.547315	190.446	1.824	0.699	0.811	0.492	0.213	188.498	1.914	0.630
2.375	−100.543996	188.656	1.722	0.692	0.793	0.473	0.202	187.293	1.812	0.638
2.500	−100.540796	186.962	1.637	0.672	0.769	0.457	0.193	186.047	1.717	0.634
3.000	−100.531257	181.982	1.476	0.537	0.642	0.430	0.178	181.834	1.503	0.534
4.000	−100.526513	179.722	1.472	0.434	0.547	0.431	0.169	179.720	1.473	0.434

[a] The full CI energies are given in hartree, while the remaining energies are given in millihartree relative to the corresponding full CI values. [b] Defined as the approximate variant A of CR-CC(2,3) described in the text. [c] Equivalent to the full variant D of CR-CC(2,3) described in the text.

increases to 265 cm^{-1} or 22.7% at R_{H-He} = 1.5 Å, 289 cm^{-1} or 53.1% at R_{H-He} = 1.625 Å, 268 cm^{-1} or 107.6% at R_{H-He} = 1.75 Å, and 174 cm^{-1} or 341.2% at R_{H-He} = 2.0 Å. These errors indicate that the decay of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap resulting from the CCSD(T) calculations employing restricted references with the H−He distance is much too slow compared to full CI. For example, the RHF/ROHF-based CCSD(T) value of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap at R_{H-He} = 2.5 Å of 49 cm^{-1} is considerably larger than the corresponding full CI value of 2 cm^{-1}. The CCSD(T) values of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap in the HHeH system decay much faster with the H−He distance when one uses the UHF reference in the calculations instead of the RHF and ROHF references, but then the decay becomes too fast due to mixing of singlet and triplet contributions in the spin-contaminated UHF-based CCSD(T) calculations, and the results obtained at short H−He distances are not as good as those obtained with the CCSD(T) method using restricted, spin-adapted references. The same is, in fact, true for the $(HFH)^-$ system, where the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap obtained with the UHF-based CCSD(T) approach decays too fast, compared to full CI, with the H−F distance and where the errors in the UHF-based CCSD(T) results for the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap at small values of R_{H-F} are considerably larger than those obtained in the CCSD(T) calculations employing restricted references. For example, the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps obtained in the full CI calculations for the HHeH and $(HFH)^-$ systems at the H−He (the HHeH case) and H−F (the $(HFH)^-$ case) distances of 2.0 Å are 51 and 2147 cm^{-1}, respectively. The UHF-based CCSD(T) calculations give 28 and 1323 cm^{-1}, respectively, i.e., values that are much too low, whereas the CCSD(T) calculations employing restricted references give 225 and 3212 cm^{-1}, respectively, i.e., values that are much too high. When we look at the gap values at shorter H−He and H−F distances, we learn, for example, that the UHF-based CCSD(T) value of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap in the HHeH system calculated at R_{H-He} = 1.25 Å of 4549 cm^{-1} is not nearly as accurate as the value obtained in the RHF/ROHF-based CCSD(T) calculations, which give 4938 cm^{-1}. (The full CI result is 4859 cm^{-1}.) Similarly, the UHF-based CCSD(T) value of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap in the $(HFH)^-$ system at R_{H-F} = 1.5 Å of 8418 cm^{-1} is not nearly as accurate as the result of the CCSD(T) calculations employing restricted references, which is 9468 cm^{-1}. (The full CI result is 9525 cm^{-1}.) As shown in Table 5, the UHF-based QCISD(T) results are very similar to those obtained with the UHF-based CCSD(T) approach. In particular, the QCISD(T)/UHF gap in the HHeH system decays much too fast with the H−He distance and is rather inaccurate at shorter H−He distances, when compared with the corresponding full CI data.

The above discussion illustrates the considerable challenges that the HHeH and $(HFH)^-$ systems create for the standard CCSD and CCSD(T) approaches and their QCISD and QCISD(T) analogues. It is, therefore, interesting to examine how effective our CR-CC(2,3) approach is in addressing these challenges, particularly when compared to other noniterative triples CC methods, including the CCSD(T) approach discussed above and the CR-CCSD(T) and CCSD(2)$_T$ schemes. As shown in Tables 5 and 6, the CR-CC(2,3) approach (meaning variant D of CR-CC(2,3)) employing restricted references, developed in this work, provides a virtually exact description of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap for the HHeH system and a highly accurate description of the analogous gap in the $(HFH)^-$ system. In fact, no other noniterative triples CC approach that has computer costs similar to those of CR-CC(2,3), listed in Tables 5−10, is capable of producing similar accuracies. Indeed, the CR-CC(2,3) approach gives very small errors in the calculated $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps for the HHeH system, which are 14 cm^{-1} for the gap of 4859 cm^{-1} at $R_{H-He} = 1.25$ Å, 2 cm^{-1} for the gap of 1168 cm^{-1} at $R_{H-He} = 1.5$ Å, 2 cm^{-1} for the gap of 544 cm^{-1} at $R_{H-He} = 1.625$ Å, 4 cm^{-1} for the gap of 249 cm^{-1} at $R_{H-He} = 1.75$ Å, 4 cm^{-1} for the gap of 51 cm^{-1} at $R_{H-He} = 2.0$ Å, and 3 cm^{-1} for the gap of 10 cm^{-1} at $R_{H-He} = 2.25$ Å. This should be compared with the 78, 265, 289, 268, 174, and 94 cm^{-1} errors, respectively, obtained with the CCSD(T) method employing restricted references, 310, 266, 169, 93, 23, and 5 cm^{-1} errors, respectively, obtained with the UHF-based CCSD(T) approach, 113, 63, 38, 21, 4, and 1 cm^{-1} errors, respectively, obtained with CR-CCSD(T), and 128, 97, 73, 52, 24, and 10 cm^{-1} errors, respectively, obtained with CCSD(2)$_T$, defined as CR-CC(2,3),A.

As is often the case, the CR-CCSD(T) and CCSD(2)$_T$ methods, particularly the former approach, provide considerable improvements in the RHF/ROHF-based CCSD(T) results in the strongly biradical region (in this case, the H−He distances of 1.5 Å or more), but they are somewhat less accurate than the CCSD(T) approach, employing restricted references at $R_{H-He} = 1.25$ Å, where the degree of the biradical character is not too large. The RHF/ROHF-based CR-CC(2,3) approach provides considerable improvements in the CCSD(T) results employing restricted as well as unrestricted references in the entire region of R_{H-He} values, not only at larger H−He distances, improving at the same time the CR-CCSD(T) and CCSD(2)$_T$ (i.e., CR-CC(2,3),A) results at all H−He distances, particularly at the shorter ones. This can be seen by analyzing the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap values, as discussed above, or by looking at the errors in the description of the individual $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states shown in Tables 7 and 8. For example, the errors in describing the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states at $R_{H-He} = 1.25$ Å, which are 3.083 and 0.190 millihartree, respectively, when the RHF/ROHF-based CCSD method is employed, 4.125 and 0.183 millihartree, respectively, when the UHF-based CCSD approach is exploited, 0.316 and 0.041 millihartree, respectively, when the RHF/ROHF-based CCSD(T) approach is used, 1.455 and 0.042 millihartree, respectively, when the UHF-based CCSD(T) method is applied, 0.558 and 0.042 millihartree, respectively, when the RHF/ROHF-based CR-CCSD(T) approach is employed, and 0.626 and 0.042 millihartree, respectively, when the RHF/ROHF-based CCSD(2)$_T$ (i.e., CR-CC(2,3),A) method is used, reduce to 0.072 and 0.008 millihartree, respectively, when the full CR-CC(2,3) approach exploiting the RHF and ROHF references is employed. As desired, the CR-CC(2,3) values of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap for the HHeH system correctly approach 0 when the H−He distance becomes large. Although all CC methods shown in Table 5 behave in a similar manner in the asymptotic region of the HHeH case, none of the other CC approaches examined in this work can compete with the extremely high accuracy that the CR-CC(2,3) approach offers in the calculations for the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states and $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap of the HHeH system.

Much of the above analysis remains valid when the $(HFH)^-$ system is examined. The $(HFH)^-$ system is more complex than HHeH, so one cannot expect the microhartree-type or cm^{-1}-type accuracies observed in the CR-CC(2,3) calculations for the latter system, but the improvements in the CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ (i.e., CR-CC(2,3),A) results for $(HFH)^-$ offered by the CR-CC(2,3) approach are equally impressive. For example, as shown in Tables 9 and 10, the errors in describing the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states at $R_{H-F} = 2.0$ Å, which are 19.398 and 2.068 millihartree, respectively, when the RHF/ROHF-based CCSD method is employed, 6.789 and 2.117 millihartree, respectively, when the UHF-based CCSD approach is exploited, 4.177 and 0.677 millihartree, respectively, when the RHF/ROHF-based CCSD(T) approach is used, 4.354 and 0.598 millihartree, respectively, when the UHF-based CCSD(T) method is applied, 4.027 and 0.823 millihartree, respectively, when the RHF/ROHF-based CR-CCSD(T) approach is employed, and 4.185 and 0.531 millihartree, respectively, when the RHF/ROHF-based CCSD(2)$_T$ (i.e., CR-CC(2,3),A) method is used, reduce to 0.491 and 0.218 millihartree, respectively, when the CR-CC(2,3) approach exploiting the RHF and ROHF references is employed. The errors in the CR-CC(2,3) calculations for the $X^1\Sigma_g^+$ state of the $(HFH)^-$ system do not exceed 0.967 millihartree in the entire $R_{H-F} = 1.5-4.0$ Å region and are often much smaller than this, which is a clear demonstration of the superiority of the CR-CC(2,3) approach over other noniterative triples methods, particularly when we realize that the unsigned errors in the CCSD(T) calculations using restricted references become as large as 40.115 millihartree at $R_{H-F} = 4.0$ Å. (The corresponding error in the CR-CC(2,3) result is only 0.321 millihartree.) The UHF-based CCSD(T) approach behaves much better than the RHF-based CCSD(T) method, reducing the large maximum error in the description of the $X^1\Sigma_g^+$ state by the latter method to 6.165 millihartree, but this is not enough to provide the results that could compete with those obtained with the CR-CC(2,3) approach. As shown in Table 9, the CR-CCSD(T) and CCSD(2)$_T$ methods considerably improve the RHF-based CCSD(T) results for the $X^1\Sigma_g^+$ state at larger H−F distances, but none of these approaches can provide the results of the CR-CC(2,3) quality. Moreover, the CR-CCSD(T) and CCSD(2)$_T$ approaches worsen the results of the RHF-based CCSD(T) calculations at shorter H−F distances ($R_{H-F} < 2.0$Å), whereas the CR-CC(2,3) method provides the results of the CCSD(T) or better quality in this region and a uniformly accurate description of the $X^1\Sigma_g^+$ state at all R_{H-F} values, which no other CC method considered in this study can offer. Although the $A^3\Sigma_u^+$ state is much easier to describe by the single-reference CC approaches, even in this case the CR-CC(2,3) results are by far the most accurate ones. Indeed, as shown in Table 10, the errors in the CR-CC(2,3) results for the $A^3\Sigma_u^+$ state of $(HFH)^-$ do not exceed 0.219 millihartree in the entire $R_{H-F} = 1.5-4.0$ Å region. The maximum errors resulting from the ROHF-based CCSD(T), UHF-based CCSD(T), ROHF-based CR-CCSD(T), and ROHF-based CCSD(2)$_T$ (i.e., CR-CC(2,3),A) calculations are 0.699, 0.638, 0.823, and 0.561 millihartree, respectively.

The very good performance of the CR-CC(2,3) approach in the calculations of the individual $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states of $(HFH)^-$, and, what is particularly important, a well-balanced description of both states by the CR-CC(2,3) method are reflected by the accurate values of the $A^3\Sigma_u^+-X^1\Sigma_g^+$ gap of the $(HFH)^-$ system provided by the CR-CC(2,3) approach in the practically entire $R_{H-F} = 1.5-4.0$ Å region. Indeed, as shown in Table 6, the CR-CC(2,3) approach gives the relatively small errors in the calculated $A^3\Sigma_u^+-X^1\Sigma_g^+$ gaps for the $(HFH)^-$

system, which are 170 cm^{-1} for the gap of 9525 cm^{-1} at $R_{H-F} = 1.5$ Å, 174 cm^{-1} for the gap of 7008 cm^{-1} at $R_{H-F} = 1.625$ Å, 159 cm^{-1} for the gap of 4911 cm^{-1} at $R_{H-F} = 1.75$ Å, 121 cm^{-1} for the gap of 3304 cm^{-1} at $R_{H-F} = 1.875$ Å, 60 cm^{-1} for the gap of 2147 cm^{-1} at $R_{H-F} = 2.0$ Å, 17 cm^{-1} for the gap of 1353 cm^{-1} at $R_{H-F} = 2.125$ Å, and 89 cm^{-1} for the gap of 827 cm^{-1} at $R_{H-F} = 2.25$ Å. This should be compared with the 57, 58, 267, 598, 1065, 1670, and 2398 cm^{-1} errors, respectively, obtained with the CCSD(T) method employing restricted references, 1107, 1232, 1219, 1060, 824, 587, and 389 cm^{-1} errors, respectively, obtained with the UHF-based CCSD(T) approach, 609, 689, 743, 751, 703, 596, and 434 cm^{-1} errors, respectively, obtained with CR-CCSD(T), and 639, 729, 795, 822, 802, 738, and 645 cm^{-1} errors, respectively, obtained with CCSD(2)$_T$ (CR-CC(2,3),A). We can see once again that the CR-CCSD(T) and CCSD(2)$_T$ methods, particularly the former approach, provide considerable improvements in the RHF/ROHF-based CCSD(T) results when the H−F distance becomes larger but are less accurate than the CCSD(T) approach employing restricted references in the $R_{H-F} \leq 1.75$ Å region, where the $|c_2/c_0|$ ratio shown in Table 6 does not exceed 0.5, i.e., when the degree of the biradical character is not too large yet. The CR-CC(2,3) approach provides the results, which are competitive with the results of the RHF/ROHF-based CCSD(T) calculations and much better than the results of the UHF-based CCSD(T) calculations in the $R_{H-F} \leq 1.75$ Å region, while reducing the errors in the results of the CCSD(T) calculations employing restricted references in the $R_{H-F} > 1.75$ Å region, where the RHF/ROHF-based CCSD(T) method fails, by orders of magnitude. There is a slight increase of errors in the RHF/ROHF-based CR-CC(2,3) results for the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap of $(HFH)^-$ at $R_{H-F} = 2.375$ and 2.5 Å to 139 and 157 cm^{-1}, respectively, where the corresponding full CI values are 488 and 277 cm^{-1}, but this is still an overall better performance than that offered by other noniterative triples CC methods. For example, the RHF/ROHF-based CCSD(2)$_T$ (i.e., CR-CC(2,3),A) approach gives the 542 and 448 cm^{-1} errors, respectively, at these two values of R_{H-F}. The UHF-based CCSD(T) method, which is expected to perform reasonably well in this region, gives the 242 and 140 cm^{-1} errors, respectively. The RHF/ROHF-based CCSD(T) approach completely fails, giving the 3225 and 4117 cm^{-1} errors in the calculated $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap of the $(HFH)^-$ system at $R_{H-F} = 2.375$ and 2.5 Å, respectively. We can conclude that the CR-CC(2,3) approach provides the overall best description of the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ gap of $(HFH)^-$ at all H−F distances when compared to other single-reference CC approximations that have similar computer costs and that are based on the idea of correcting the CCSD energies for the effects of triples via noniterative energy corrections.

C. Effect of Canonicalization of ROHF Orbitals on the CR-CC(2,3) Energies. The ROHF-based CR-CC(2,3) approach, as implemented in this work, provides high accuracies in applications involving radicals, biradicals, and single bond breaking, but, as mentioned in section IIB, the ROHF-based CR-CC(2,3) energies of open-shell states may display a slight dependence on the method of canonicalization of the ROHF orbitals. In this subsection, we demonstrate that changes in the full CR-CC(2,3) (i.e., CR-CC(2,3),D) energies due to different ways of obtaining the ROHF orbitals are on the order of tens of microhartree or 0.01 kcal/mol, so that lack of the strict invariance of the CR-CC(2,3) energies on the method of canonicalization of the ROHF orbitals is more of a formal issue than a practical one, particularly that for a given canonicalization scheme the CR-CC(2,3) method is a uniquely defined computational procedure. As shown below, changes in the CR-CC(2,3) energies due to different ways of obtaining the canonical ROHF orbitals are often on the same order as or not much greater than the tiny changes in the CCSD energies when core electrons are frozen in post-ROHF calculations.

We have, in fact, already discussed an example illustrating the above statements in section IIIB, when we analyzed the performance of the CR-CC(2,3) approach in the calculations of the triplet ground state of methylene employing the TZ2P basis set used in ref 94 (Table 4). As shown in Table 4, two popular canonicalization schemes of Roothaan[113] (default in GAMESS) and Guest and Saunders[115] give the full CR-CC(2,3) energies of the X^3B_1 state of methylene that differ by 98 microhartree, where the difference between the underlying CCSD energies due to freezing the core and dropping the highest-energy virtual orbital in these calculations is 38 microhartree. (Recall that the CCSD energies are invariant with respect to ROHF canonicalization but only when none of the orbitals is dropped from the CCSD calculations.) As pointed out in subsection IIIB, this tiny change in the CR-CC(2,3) energy for the X^3B_1 state caused by using different canonicalization schemes translates into the 0.06 kcal/mol difference between the CR-CC(2,3) values of the $A^1A_1 - X^3B_1$ gap obtained with the Roothaan and Guest−Saunders procedures for generating ROHF orbitals.

We have tested hundreds of open-shell cases in a similar manner, examining up to six different ways of performing the ROHF calculations using the canonicalization approaches of Roothaan,[113] McWeeny and Diercksen,[114] Guest and Saunders,[115] Faegri and Manne,[116] Davidson,[117] and Binkley, Pople, and Dobosh.[118] (See the documentation for GAMESS[104] for an overview and information about how to perform these different types of ROHF calculations with GAMESS.) All of these examples show similar patterns to those observed in the above methylene case, i.e., the insignificant dependencies of the calculated CR-CC(2,3) energies on the canonicalization procedure that are on the order of a few tens of microhartree. Methylene represents a small molecular system and a weak biradical. Let us, therefore, examine the lowest triplet state of the larger $H_2Si_2O_2$ system, which also is a relatively strong biradical investigated earlier by Schmidt et al.[106] The results of the CCSD and CR-CC(2,3) calculations for this system, using the 6-311G(d,p) basis set,[147,156,159] the nuclear geometry of the corresponding singlet structure determined with the two-configurational SCF approach in ref 106, and six different ROHF canonicalization procedures listed above, are given in Table 11. As one can see, the differences between the CR-CC(2,3) energies of the lowest triplet state of the $H_2Si_2O_2$ biradical do not exceed 35 microhartree in the frozen-core case, where 12 lowest-energy core orbitals were dropped from the CC calculations, and 31 microhartree, when all electrons were correlated. If we limit ourselves to the popular canonicalization methods of Roothaan and Guest and Saunders, then the differences between the CR-CC(2,3) energies of the lowest triplet state of $H_2Si_2O_2$ are even smaller, namely, 19 microhartree in the frozen-core case and 14 microhartree when all electrons are correlated. In the all-electron case, the CCSD energies do not depend on the ROHF canonicalization scheme, but they do depend on it when core orbitals are frozen. The difference between the CCSD energies obtained with the Roothaan-type and Guest−Saunders-type canonical ROHF orbitals, when 12 lowest-energy core orbitals are frozen in the CCSD calculations, is 4 microhartree. Thus, changes in the CR-CC(2,3) energies due to different ways of obtaining ROHF

TABLE 11: Effect of the Method of Canonicalization of the ROHF Orbitals on the CCSD and CR-CC(2,3) Energies (in hartree) Obtained in the Frozen-Core and All-Electron Calculations of the Lowest Triplet State of the $H_2Si_2O_2$ Biradical, as Described by the 6-311G(d,p) Basis Set,[147,156,159] Using the Geometry of the Corresponding Singlet Structure Determined with the Two-Configurational SCF Approach[106]

ROHF canonicalization method[a]	frozen-core (12 orbitals)	all electrons correlated
	CCSD	
R	−729.41091969	−729.69529140
MD	−729.41091624	−729.69529140
GS	−729.41091552	−729.69529140
FM	−729.41091552	−729.69529140
D	−729.41091552	−729.69529140
BPD	−729.41091552	−729.69529140
	CR-CC(2,3)	
R	−729.43012120	−729.71613811
MD	−729.43010820	−729.71612921
GS	−729.43010216	−729.71612421
FM	−729.43010216	−729.71612421
D	−729.43011804	−729.71613986
BPD	−729.43008670	−729.71610896

[a] R, MD, GS, FM, D, and BPD stand for the canonicalization approaches of Roothaan,[113] McWeeny and Diercksen,[114] Guest and Saunders,[115] Faegri and Manne,[116] Davidson,[117] and Binkley, Pople, and Dobosh,[118] respectively.

orbitals are not only very small but also not hugely different than changes in the CCSD energies due to freezing core orbitals. This is an important observation, because the majority of CC calculations are performed with frozen-core orbitals, where the results will always depend on how ROHF orbitals are rotated during canonicalization.

The above two examples involve triplet states. Let us, therefore, conclude this section by examining the effect of the ROHF canonicalization procedure on the CR-CC(2,3) results for the activation energies of the $C_2H_4 + H \rightarrow C_2H_5$ forward and reverse reactions, which proceed on a doublet potential energy surface, and the corresponding total electronic energies of the C_2H_5 product and transition-state species. The results of the CCSD and CR-CC(2,3) calculations, employing the aug-cc-pVTZ (the frozen-core case) and aug-cc-pCVTZ (the all-electron case) basis sets,[147,151,152] the nuclear geometries of the relevant molecular species taken from ref 105, and the same six canonicalization methods as used in the $H_2Si_2O_2$ case, are summarized in Table 12. As one can see, the differences between the CR-CC(2,3) energies of the C_2H_5 product species due to different methods of obtaining the ROHF orbitals do not exceed 133 microhartree in the frozen-core case and 120 microhartree in the all-electron case. If we limit ourselves to the popular canonicalization schemes of Roothaan and Guest and Saunders, then the differences between the corresponding CR-CC(2,3) energies of the C_2H_5 product molecule are 94 microhartree in the frozen-core case and 82 microhartree in the all-electron case. The difference between the CCSD energies of the C_2H_5 product species obtained in the frozen-core calculations using the Roothaan-type and Guest−Saunders-type canonical ROHF orbitals is 15 microhartree. The differences between the CR-CC(2,3) energies of the C_2H_5 transition-state species due to different methods of obtaining the ROHF orbitals are even smaller than those in the case of the C_2H_5 product molecule. They do not exceed 49 microhartree in the frozen-core case and 52 microhartree in the all-electron case, and if we limit ourselves to only two canonicalization schemes of Roothaan and Guest and Saunders, then they are 32 and 38 microhartree, respectively.

TABLE 12: Effect of the Method of Canonicalization of the ROHF Orbitals on the Activation Energies of the $C_2H_4 + H \rightarrow C_2H_5$ Forward ($V_f^\dagger$) and Reverse ($V_r^\dagger$) Reactions (in kcal/mol) and the Corresponding Total Electronic Energies (in hartree) of the C_2H_5 Product and Transition-State Species Obtained in the Frozen-Core and All-Electron CCSD and CR-CC(2,3) Calculations Employing the aug-cc-pVTZ and aug-cc-pCVTZ Basis Sets[147,151,152]

ROHF canonicalization method[a]	C_2H_5 transition state[b]	C_2H_5 product[b]	$V_f^\dagger/V_r^\dagger$ [b,c]
	aug-cc-pVTZ, frozen-core (2 orbitals)		
	CCSD		
R	−78.92408390	−78.99532551	2.49/44.70
MD	−78.92408297	−78.99531306	2.49/44.70
GS	−78.92408278	−78.99531036	2.49/44.70
FM	−78.92408278	−78.99531036	2.49/44.70
D	−78.92408278	−78.99531036	2.49/44.70
BPD	−78.92408278	−78.99531036	2.49/44.70
	CR-CC(2,3)		
R	−78.93981497	−79.00793943	2.06/42.75
MD	−78.93979160	−79.00785969	2.07/42.71
GS	−78.93978279	−79.00784537	2.08/42.71
FM	−78.93978279	−79.00784537	2.08/42.71
D	−78.93980619	−79.00788043	2.06/42.72
BPD	−78.93976561	−79.00780692	2.09/42.70
	aug-cc-pCVTZ, all electron		
	CCSD		
R	−79.02476229	−79.09599752	2.55/44.70
MD	−79.02476229	−79.09599752	2.55/44.70
GS	−79.02476229	−79.09599752	2.55/44.70
FM	−79.02476229	−79.09599752	2.55/44.70
D	−79.02476229	−79.09599752	2.55/44.70
BPD	−79.02476229	−79.09599752	2.55/44.70
	CR-CC(2,3)		
R	−79.04135899	−79.10936685	2.12/42.68
MD	−79.04133112	−79.10929705	2.14/42.65
GS	−79.04132138	−79.10928466	2.14/42.65
FM	−79.04132138	−79.10928466	2.14/42.65
D	−79.04134916	−79.10932364	2.12/42.65
BPD	−79.04130671	−79.10924660	2.15/42.63
UABH6/DBH24[d]			1.72/41.75

[a] R, MD, GS, FM, D, and BPD stand for the canonicalization approaches of Roothaan,[113] McWeeny and Diercksen,[114] Guest and Saunders,[115] Faegri and Manne,[116] Davidson,[117] and Binkley, Pople, and Dobosh,[118] respectively. [b] The geometries of the C_2H_5 transition state and product and the C_2H_4 reactant are taken from ref 105. [c] The RHF-based CCSD and CR-CC(2,3) energies of the C_2H_4 reactant needed to calculate the activation barriers are −78.42822424 and −78.44327344 hartree for the aug-cc-pVTZ frozen-core case and −78.52901035 and −78.54491349 hartree for the aug-cc-pCVTZ all-electron case. In both cases, the ROHF energy of the H atom is −0.49982118 hartree. [d] The empirical activation barriers are taken from the UABH6 subset of the DBH24 database of ref 105.

The above analysis indicates that the dependence of the CR-CC(2,3) energies on the way of obtaining ROHF orbitals is, for all practical purposes, negligible. Consequently, important properties, such as the activation energies characterizing chemical reactions proceeding on nonsinglet potential energy surfaces obtained with the ROHF-based CR-CC(2,3) approach, are virtually independent of the ROHF canonicalization procedure. This is shown in Table 12 for the forward and reverse $C_2H_4 + H \rightarrow C_2H_5$ reactions. As one can see, the differences between the CR-CC(2,3) activation energies due to different methods of obtaining the ROHF orbitals do not exceed 0.03 kcal/mol or about 1% for the forward reaction, which is characterized, according to CR-CC(2,3) calculations, by a barrier of about 2.1 kcal/mol, and 0.05 kcal/mol or about 0.1% for the reverse reaction, which is characterized, according to CR-CC(2,3) calculations, by a barrier of about 42.7 kcal/mol.

The recommended empirical estimates of the activation barriers characterizing the forward ($V_f^\dagger$) and reverse ($V_r^\dagger$) $C_2H_4 + H \rightarrow C_2H_5$ reactions, which are part of the DBH24 database of ref 105, are $V_f^\dagger = 1.72$ kcal/mol and $V_r^\dagger = 41.75$ kcal/mol, respectively. The CCSD approach employing basis sets of aug-cc-p(C)VTZ quality gives $V_f^\dagger \approx 2.5$ kcal/mol and $V_r^\dagger = 44.7$ kcal/mol. As one can see, the CR-CC(2,3) approach reduces the ~0.8 kcal/mol or 47% and ~3.0 kcal/mol or 7% errors in the CCSD results for $V_f^\dagger$ and $V_r^\dagger$ to ~0.3−0.4 kcal/mol or 20% and 0.9−1.0 kcal/mol or 2%, respectively. This shows that the CR-CC(2,3) method has a potential for becoming a method of choice in the accurate calculations of the activation barriers, in addition to being very useful in studies of single bond breaking, reaction pathways involving radicals and biradicals, and singlet−triplet gaps in biradical or magnetic systems, as shown in the earlier sections of this paper and some of our earlier studies.[30,31,33,66−68,76,77] A more systematic study of the performance of the CR-CC(2,3) approach in calculations of reaction barriers, employing the 24 reactions constituting the DBH24 database of ref 105 and several different basis sets, will be published elsewhere.[162]

IV. Summary

In this study, we have extended the recently formulated CR-CC(2,3) approach,[66−68] in which the suitably designed, size extensive, renormalized corrections due to triply excited clusters are added to the CCSD energies, to open-shell systems. After describing the CR-CC(2,3) method and its most important formal and computational characteristics and overviewing the key elements of the underlying biorthogonal MMCC theory[66,67] (cf. refs 75 and 76 for reviews), which leads to a new generation of the successful CC approximations, such as CR-CC(2,3), we have discussed the most essential steps that we had to undertake to develop the highly efficient computer programs that enable us to perform the CR-CC(2,3) calculations for nonsinglet electronic ground states. Although in developing our CR-CC(2,3) codes for open-shell systems we have not limited ourselves to any particular form of the high-spin reference state, the actual programs used in this study have been intimately interfaced with the ROHF routines from the GAMESS package. Although we plan to work on extending our present open-shell CR-CC(2,3) code to UHF references, once the suitable integral infrastructure for the UHF basis is developed, the use of the spin- and symmetry-adapted ROHF references in the CR-CC(2,3) calculations is, in our view, a preferred option, which has an advantage of eliminating, to a large extent, the issues of symmetry breaking and spin contamination that enter the UHF-based CC considerations. As shown in this paper using a number of open-shell problems as examples and as demonstrated in our earlier work,[30,31,33,66−68,76,77] where we used the CR-CC(2,3) method to examine reaction pathways on singlet potential energy surfaces, the CR-CC(2,3) method is much more robust than the conventional CCSD(T) approach when the spin- and symmetry-adapted references of the restricted type are employed.

Further technical details related to our highly efficient, fully factorized implementation of the CR-CC(2,3) approach used in the present study will be provided elsewhere.[80] In this work, we have focused on testing the open-shell CR-CC(2,3) codes on several typical open-shell problems of varying difficulty, including those where the standard CCSD and CCSD(T) approaches completely break down. One of the main objectives of this work has been to show that the complete CR-CC(2,3) approach is more accurate than other noniterative triples CC approximations, which have similar computer costs, including CCSD(T), CR-CCSD(T), and CCSD(2)$_T$ (represented in this work by CR-CC(2,3),A), in calculations involving open-shell systems. Thus, we have examined a relatively simple problem of bond breaking in the OH radical, which is typical of many radical studies, where the conventional CCSD(T) approach works reasonably well, and the most challenging case of bond breaking in the F_2^+ ion, where CCSD and CCSD(T) completely fail. We have studied the classic problem of the singlet−triplet energy gap in methylene, which is a relatively weak biradical system in which the CCSD(T) method, although not the most accurate, behaves in a reasonable manner, and much more challenging problems of the singlet−triplet gaps in the linear HHeH and $(HFH)^-$ systems, which are model magnetic systems with a significant and rapidly varying degree of biradical character, where the CCSD(T) and related QCISD(T) approaches employing restricted and unrestricted Hartree−Fock references face considerable difficulties.

In all cases examined in this study, the CR-CC(2,3) approach turned out to be the most accurate one. We have demonstrated that CR-CC(2,3) eliminates the failures of CCSD(T) in calculations involving the open-shell systems that display a multireference character, while being at least as accurate as CCSD(T) in calculations involving nondegenerate open-shell states for which CCSD(T) is sufficiently good. We have also demonstrated that the full CR-CC(2,3) approach examined in this study improves the results of the CR-CCSD(T) and CCSD(2)$_T$ (i.e., CR-CC(2,3),A) calculations, which just like CR-CC(2,3) aim at eliminating the failures of CCSD(T) in situations characterized by larger nondynamical correlation effects. This applies to situations where the nondynamical correlation effects are strong, as in the case of the F_2^+, HHeH, and $(HFH)^-$ systems, and cases where the accurate treatment of dynamical correlations through the CC wave function ansatz is sufficient to obtain reasonable accuracies, such as the equilibrium region of the OH radical or singlet−triplet gap in methylene.

A few examples, including the activation energies of the $C_2H_4 + H \rightarrow C_2H_5$ forward and reverse reactions, which proceed on a doublet potential energy surface, and the corresponding total electronic energies of the C_2H_5 product and transition-state open-shell species, as well as the lowest-energy triplet states of the CH_2 and $H_2Si_2O_2$ biradicals, have been used to demonstrate that the dependence of the ROHF-based CR-CC(2,3) energies on the method of canonicalization of the ROHF orbitals is, for all practical purposes, negligible, typically at the level of tens of microhartree or 0.01 kcal/mol when activation barriers are examined. By analyzing the energetics of the forward and reverse $C_2H_4 + H \rightarrow C_2H_5$ reactions, we have shown that the ROHF-based CR-CC(2,3) approach may become useful in accurate calculations of the activation energies in addition to being successful in studies of single bond breaking, reaction pathways involving radicals and biradicals, and singlet−triplet gaps in biradical/magnetic systems.

The benchmark results involving a few typical open-shell problems described in this work, combined with the earlier studies of closed-shell systems,[30,31,33,66−68,76,77] clearly indicate that the recently developed CR-CC(2,3) approximation provides an excellent alternative to the existing noniterative CC methods of the CCSD(T) type and that the biorthogonal MMCC formalism, on which the CR-CC(2,3) method is based, is a promising theoretical framework for designing new generations of relatively inexpensive and robust single-reference CC methods that can be used in various areas of chemistry.

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References and Notes

(1) Coester, F. *Nucl. Phys.* **1958**, *7*, 421.

(2) Coester, F.; Kümmel, H. *Nucl. Phys.* **1960**, *17*, 477.

(3) Čížek, J. *J. Chem. Phys.* **1966**, *45*, 4256.

(4) Čížek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(5) Čížek, J.; Paldus, J. *Int. J. Quantum Chem.* **1971**, *5*, 359.

(6) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(7) Purvis, G. D., III.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(8) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1987**, *86*, 2881.

(9) Piecuch, P.; Paldus, J. *Int. J. Quantum Chem.* **1989**, *36*, 429.

(10) Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, *83*, 4041.

(11) Piecuch, P.; Paldus, J. *Theor. Chim. Acta* **1990**, *78*, 65.

(12) Bartlett, R. J. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; Vol. 1, p 1047

(13) Gauss, J. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III., Schreiner, P. R., Eds.; Wiley: Chichester, U. K., 1998; Vol. 1, p 615.

(14) Paldus, J.; Li, X. *Adv. Chem. Phys.* **1999**, *110*, 1.

(15) Crawford, T. D.; Schaefer, H. F., III. *Rev. Comput. Chem.* **2000**, *14*, 33.

(16) Paldus, J. In *Handbook of Molecular Physics and Quantum Chemistry*; Wilson, S., Bernath, P. F., McWeeny, R., Eds.; Wiley: Chichester, U. K., 2003; Vol. 2, p 272.

(17) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; McGuire, M. J. *Int. Rev. Phys. Chem.* **2002**, *21*, 527.

(18) Piecuch, P.; Kowalski, K.; Fan, P.-D.; Pimienta, I. S. O. In *Advanced Topics in Theoretical Chemical Physics*; Maruani, J., Lefebvre, R., Brändas, E., Eds.; Progress in Theoretical Chemistry and Physics 12; Kluwer Academic: Dordrecht, The Netherlands, 2003; p 119.

(19) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; Fan, P.-D.; Lodriguito, M.; McGuire, M. J.; Kucharski, S. A.; Kuś, T.; Musiał, M. *Theor. Chem. Acc.* **2004**, *112*, 349.

(20) Saebø, S.; Pulay, P. *Annu. Rev. Phys. Chem.* **1993**, *44*, 213.

(21) Schütz, M. *J. Chem. Phys.* **2000**, *113*, 9986.

(22) Schütz, M.; Werner, H. J. *Chem. Phys. Lett.* **2000**, *318*, 370.

(23) Schütz, M. *J. Chem. Phys.* **2002**, *116*, 8772.

(24) Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233.

(25) Chaudhuri, R. K.; Freed, K. F.; Hose, G.; Piecuch, P.; Kowalski, K.; Włoch, M.; Chattopadhyay, S.; Mukherjee, D.; Rolik, Z.; Szabados, Á.; Tóth, G.; Surján, P. R. *J. Chem. Phys.* **2005**, *122*, 134105.

(26) Roos, B. O.; Linse, P.; Siegbahn, P. E. M.; Blomberg, M. R. A. *Chem. Phys.* **1982**, *66*, 197.

(27) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Woliński, K. *J. Phys. Chem.* **1990**, *94*, 5483.

(28) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(29) Andersson, K.; Roos, B. O. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; Advanced Series in Physical Chemistry 2; World Scientific: Singapore, 1995; p 55.

(30) Cramer, C. J.; Włoch, M.; Piecuch, P.; Puzzarini, C.; Gagliardi, L. *J. Phys. Chem. A* **2006**, *110*, 1991.

(31) Cramer, C. J.; Kinal, A.; Włoch, M.; Piecuch, P.; Gagliardi, L. *J. Phys. Chem. A* **2006**, *110*, 11557.

(32) Rode, M. F.; Werner, H.-J. *Theor. Chem. Acc.* **2005**, *114*, 309.

(33) Kinal, A.; Piecuch, P. *J. Phys. Chem. A* **2007**, *111*, 734.

(34) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.

(35) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514.

(36) Rintelman, J. M.; Adamovic, I.; Varganov, S.; Gordon, M. S. *J. Chem. Phys.* **2005**, *122*, 044105.

(37) Gwaltney, S. R.; Head-Gordon, M. *Chem. Phys. Lett.* **2000**, *323*, 21.

(38) Gwaltney, S. R.; Sherrill, C. D.; Head-Gordon, M.; Krylov, A. I. *J. Chem. Phys.* **2000**, *113*, 3548.

(39) Gwaltney, S. R.; Head-Gordon, M. *J. Chem. Phys.* **2001**, *115*, 2014.

(40) Gwaltney, S. R.; Byrd, E. F. C.; Van Voorhis, T.; Head-Gordon, M. *Chem. Phys. Lett.* **2002**, *353*, 359.

(41) Head-Gordon, M.; Van Voorhis, T.; Gwaltney, S. R.; Byrd, E. F. C. In *Low-Lying Potential Energy Surfaces*; Hoffmann, M. R., Dyall, K. G., Eds.; ACS Symposium Series 828; American Chemical Society: Washington, DC, 2002; p 93.

(42) Stanton, J. F. *Chem. Phys. Lett.* **1997**, *281*, 130.

(43) (a) Hirata, S.; Nooijen, M.; Grabowski, I.; Bartlett, R. J. *J. Chem. Phys.* **2001**, *114*, 3919. (b) Hirata, S.; Nooijen, M.; Grabowski, I.; Bartlett, R. J. *J. Chem. Phys.* **2001**, *115*, 3967 (erratum).

(44) Hirata, S.; Fan, P.-D.; Auer, A. A.; Nooijen, M.; Piecuch, P. *J. Chem. Phys.* **2004**, *121*, 12197.

(45) Krylov, A. I. *Chem. Phys. Lett.* **2001**, *338*, 375.

(46) Krylov, A. I.; Sherrill, C. D. *J. Chem. Phys.* **2002**, *116*, 3194.

(47) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2002**, *117*, 4694.

(48) Van, Voorhis, T.; Head-Gordon, M. *Chem. Phys. Lett.* **2000**, *330*, 585.

(49) Byrd, E. F. C.; Van Voorhis, T.; Head-Gordon, M. *J. Phys. Chem. B* **2002**, *106*, 8070.

(50) Fan, P.-D.; Kowalski, K.; Piecuch, P. *Mol. Phys.* **2005**, *103*, 2191.

(51) Fan, P.-D.; Piecuch, P. *Adv. Quantum Chem.* **2006**, *51*, 1.

(52) Arponen, J. S. *Ann. Phys.* **1983**, *151*, 311.

(53) Arponen, J. S.; Bishop, R. F.; Pajanne, E. *Phys. Rev. A* **1987**, *36*, 2519.

(54) Bishop, R. F.; Arponen, J. S. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1990**, *24*, 197.

(55) Arponen, J. S.; Bishop, R. F. *Ann. Phys.* **1991**, *207*, 171.

(56) Bishop, R. F. *Theor. Chim. Acta* **1991**, *80*, 95.

(57) Arponen, J. *Phys. Rev. A* **1997**, *55*, 2686.

(58) Arponen, J. S.; Bishop, R. F.; Pajanne, E. *Phys. Rev. A* **1987**, *36*, 2539.

(59) Piecuch, P.; Bartlett, R. J. *Adv. Quantum Chem.* **1999**, *34*, 295.

(60) Piecuch, P.; Kowalski, K. In *Computational Chemistry: Reviews of Current Trends*; Leszczyński, J., Ed.; World Scientific: Singapore, 2000; Vol. 5, p 1.

(61) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 18.

(62) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 5644.

(63) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O. *Int. J. Mol. Sci.* **2002**, *3*, 475.

(64) Pimienta, I. S. O.; Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2003**, *119*, 2951.

(65) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 074107.

(66) Piecuch, P.; Włoch, M. *J. Chem. Phys.* **2005**, *123*, 224105.

(67) Piecuch, P.; Włoch, M.; Gour, J. R.; Kinal, A. *Chem. Phys. Lett.* **2006**, *418*, 467.

(68) Włoch, M.; Lodriguito, M. D.; Piecuch, P.; Gour, J. R. *Mol. Phys.* **2006**, *104*, 2149.

(69) Lodriguito, M. D.; Kowalski, K.; Włoch, M.; Piecuch, P. *J. Mol. Struct: THEOCHEM* **2006**, *771*, 89.

(70) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2001**, *115*, 2966.

(71) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2002**, *116*, 7411.

(72) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2004**, *120*, 1715.

(73) Włoch, M.; Gour, J. R.; Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 214107.

(74) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; Kucharski, S. A. In *Low-Lying Potential Energy Surfaces*; Hoffmann, M. R., Dyall, K. G., Eds.; ACS Symposium Series 828; American Chemical Society: Washington, DC, 2002; p 31.

(75) Piecuch, P.; Włoch, M.; Lodriguito, M. D.; Gour, J. R. In *Recent Advances in the Theory of Chemical and Physical Systems*; Julien, J.-P., Maruani, J., Mayou, D., Wilson, S., Delgado-Barrio, G., Eds.; Progress in Theoretical Chemistry and Physics 15; Springer: Dordrecht, The Netherlands, 2006; p 45.

(76) Piecuch, P.; Włoch, M.; Varandas, A. J. C. In *Topics in the Theory of Chemical and Physical Systems*; Lahmar, S., Maruani, J., Wilson, S., Delgado-Barrio, G., Eds.; Progress in Theoretical Chemistry and Physics 16; Springer: Dordrecht, The Netherlands, 2007; p 63.

(77) Piecuch, P.; Włoch, M.; Varandas, A. J. C. *Theor. Chem. Acc.* [Online early access]. DOI: 10.1007/s00214-007-0297-3. Published Online: May 15, 2007.

(78) (a) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041. (b) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3401 (erratum).

(79) Scuseria, G. E.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1988**, *152*, 382.

(80) Włoch, M.; Gour, J. R.; Piecuch, P. Unpublished work.

(81) Farnell, L.; Pople, J. A.; Radom, L. *J. Phys. Chem.* **1983**, *87*, 79.

(82) Murphy, R.; Schaefer, H. F., III.; Nobes, R. H.; Radom, L.; Pitzer, R. S. *Int. Rev. Phys. Chem.* **1986**, *5*, 229.

(83) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 6652.

(84) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531.

(85) Goddard, W. A., III. *Science* **1985**, *227*, 917.

(86) Schaefer, H. F., III. *Science* **1986**, *231*, 1100.

(87) Bunker, P. R. In *Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules: The State of the Art*; Bartlett R. J., Ed.; Reidel: Dordrecht, The Netherlands, 1985; p 141.

(88) Jensen, P.; Bunker, P. R. *J. Chem. Phys.* **1988**, *89*, 1327.

(89) Bauschlicher, C. W.; Taylor, P. R. *J. Chem. Phys.* **1986**, *85*, 6510.

(90) Bauschlicher, C. W.; Langhoff, S. R.; Taylor, P. R. *J. Chem. Phys.* **1987**, *87*, 387.

(91) Comeau, D. C.; Shavitt, I.; Jensen, P.; Bunker, P. R. *J. Chem. Phys.* **1989**, *90*, 6491.

(92) McLean, A. D.; Bunker, P. R.; Escribano, R. M.; Jensen, P. *J. Chem. Phys.* **1987**, *87*, 2166.

(93) Knowles, D. B.; Alvarez-Collado, J. R.; Hirsch, G.; Buenker, R. J. *J. Chem. Phys.* **1990**, *92*, 585.

(94) Sherrill, C. D.; Leininger, M. L.; van Huis, T. J.; Schaefer, H. F., III. *J. Chem. Phys.* **1998**, *108*, 1040.

(95) Li, X.; Piecuch, P.; Paldus, J. *Chem. Phys. Lett.* **1994**, *224*, 267.

(96) Piecuch, P.; Li, X.; Paldus, J. *Chem. Phys. Lett.* **1994**, *230*, 377.

(97) Balková, A.; Bartlett, R. J. *J. Chem. Phys.* **1995**, *102*, 7116.

(98) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1990**, *93*, 6104.

(99) White, S. R. *Phys. Rev. Lett.* **1992**, *69*, 2863.

(100) White, S. R. *Phys. Rev. B* **1993**, *48*, 10345.

(101) Daul, S.; Ciofini, I.; Daul, C.; White, S. R. *Int. J. Quantum Chem.* **2000**, *79*, 331.

(102) Hart, J. R.; Rappe, A. K.; Gorun, S. M.; Upton, T. H. *J. Phys. Chem.* **1992**, *96*, 6264.

(103) Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone, V. *Inorg. Chem.* **1997**, *36*, 5022.

(104) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(105) Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 569.

(106) Schmidt, M. W.; Nguyen, K. A.; Gordon, M. S.; Montgomery, J. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 5998.

(107) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029.

(108) Salter, E. A.; Trucks, G. W.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 1752.

(109) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(110) Gauss, J.; Lauderdale, W. J.; Stanton, J. F.; Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1991**, *182*, 207.

(111) Crawford, T. D.; Schaefer, H. F., III. *J. Chem. Phys.* **1996**, *104*, 6259.

(112) Smith, C. E.; King, R. A.; Crawford, T. D. *J. Chem. Phys.* **2005**, *122*, 054110.

(113) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(114) McWeeny, R.; Diercksen, G. *J. Chem. Phys.* **1968**, *49*, 4852.

(115) Guest, M. F.; Saunders, V. R. *Mol. Phys.* **1974**, *28*, 819.

(116) Faegri, K., Jr.; Manne, R. *Mol. Phys.* **1976**, *31*, 1037.

(117) Davidson, E. R. *Chem. Phys. Lett.* **1973**, *21*, 565.

(118) Binkley, J. S.; Pople, J. A.; Dobosh, P. A. *Mol. Phys.* **1974**, *28*, 1423.

(119) Piecuch, P.; Kucharski, S. A.; Kowalski, K.; Musiał, M. *Comput. Phys. Commun.* **2002**, *149*, 71.

(120) Pulay, P. *Chem. Phys. Lett.* **1980**, *73*, 393.

(121) Pulay, P. *J. Comput. Chem.* **1982**, *3*, 556.

(122) Hamilton, T. P.; Pulay, P. *J. Chem. Phys.* **1986**, *84*, 5728.

(123) Scuseria, G. E.; Lee, T. J.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1986**, *130*, 236.

(124) Kowalski, K.; Piecuch, P. *Chem. Phys. Lett.* **2001**, *344*, 165.

(125) Piecuch, P.; Kucharski, S. A.; Špirko, V.; Kowalski, K. *J. Chem. Phys.* **2001**, *115*, 5796.

(126) McGuire, M. J.; Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2002**, *117*, 3617.

(127) McGuire, M. J.; Kowalski, K.; Piecuch, P.; Kucharski, S. A.; Musiał, M. *J. Phys. Chem. A* **2004**, *108*, 8878.

(128) McGuire, M. J.; Piecuch, P. *J. Am. Chem. Soc.* **2005**, *127*, 2608.

(129) Özkan, I.; Kinal, A.; Balci, M. *J. Phys. Chem. A* **2004**, *108*, 507.

(130) Kinal, A.; Piecuch, P. *J. Phys. Chem. A* **2006**, *110*, 367.

(131) DeKock, R. L.; McGuire, M. J.; Piecuch, P.; Allen, W. D.; Schaefer, H. F., III.; Kowalski, K.; Kucharski, S. A.; Musiał, M.; Bonner, A. R.; Spronk, S. A.; Lawson, D. B.; Laursen, S. L. *J. Phys. Chem. A* **2004**, *108*, 2893.

(132) Kowalski, K. *J. Chem. Phys.* **2005**, *123*, 014102.

(133) Piecuch, P.; Hirata, S.; Kowalski, K.; Fan, P.-D.; Windus, T. L. *Int. J. Quantum Chem.* **2006**, *106*, 79.

(134) Nangia, S.; Truhlar, D. G.; McGuire, M. J.; Piecuch, P. *J. Phys. Chem. A* **2005**, *109*, 11643.

(135) Coussan, S.; Ferro, Y.; Trivella, A.; Roubin, P.; Wieczorek, R.; Manca, C.; Piecuch, P.; Kowalski, K.; Włoch, M.; Kucharski, S. A.; Musiał, M. *J. Phys. Chem. A* **2006**, *110*, 3920.

(136) Varandas, A. J. C.; Piecuch, P. *Chem. Phys. Lett.* **2006**, *430*, 448.

(137) Musiał, M.; Bartlett, R. J. *J. Chem. Phys.* **2005**, *122*, 224102.

(138) Li, X.; Paldus, J. *J. Chem. Phys.* **2006**, *124*, 174101.

(139) Li, X.; Paldus, J. *J. Chem. Phys.* **2006**, *125*, 164107.

(140) Chipman, D. M. *J. Chem. Phys.* **2006**, *124*, 044305.

(141) Sarker, M. I. M.; Kim, C. S.; Choi, C. H. *Chem. Phys. Lett.* **2005**, *411*, 297.

(142) Avramov, P. V.; Adamovic, I.; Ho, K. M.; Wang, C. Z.; Lu, W. C.; Gordon, M. S. *J. Phys. Chem. A* **2005**, *109*, 6294.

(143) Zgierski, M. Z.; Patchkovskii, S.; Lim, S. *J. Chem. Phys.* **2005**, *123*, 081101.

(144) Zgierski, M. Z.; Patchkovskii, S.; Fujiwara, T.; Lim, S. *J. Phys. Chem. A* **2005**, *109*, 9384.

(145) Zgierski, M. Z.; Patchkovskii, S.; Lim, E. C. *Can. J. Chem.* **2007**, *85*, 124.

(146) Pimienta, I. S. O.; Elzey, S.; Boatz, J. A.; Gordon, M. S. *J. Phys. Chem. A* **2007**, *111*, 691.

(147) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U. S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U. S. Department of Energy under Contract No. DE-AC06-76RLO-1830. Contact David Feller or Karen Schuchardt for further information.

(148) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(149) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(150) Amos, R. D.; Bernhardsson, A.; Berning, A; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J. *MOLPRO*, a package of ab initio programs, version 2002.6.

(151) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(152) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769.

(153) Huber, K. P.; Herzberg, G. Constants of diatomic molecules In *NIST Chemistry WebBook*; Linstrom, P. J., Mallard, W. G., Eds.; NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, 2005 (data prepared by J. W. Gallagher and R. D. Johnson, III). http://webbook.nist.gov.

(154) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(155) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(156) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(157) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(158) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(159) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(160) Cartwright, D. C.; Hay, P. J. *Chem. Phys.* **1987**, *114*, 305.

(161) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: New York, 1979; Vol. 4.

(162) Zheng, J.; Gour, J. R.; Lutz, J. J.; Włoch, M.; Piecuch, P.; Truhlar, D. G. *J. Chem. Phys.*, submitted for publication.