Improving upon CCSD(T): ACCSD(T). I. Potential energy surfaces

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Despite the successes of spin-restricted coupled-cluster singles, doubles, and perturbative triples [CCSD(T)], it fails for systems away from equilibria, which might raise questions about transition states, e.g. In an attempt to remedy this failure, we implemented ACCSD(T) in a general purpose form for open and closed shells and with arbitrary single determinant reference functions, and applied it to a wide variety of bond-breaking examples. ACCSD(T) is shown to substantially improve the behavior of CCSD(T) at long bond lengths without significantly affecting the quality of the equilibrium results. Weighted average nonparallelity errors for HF, C2, N2, and H2O are reduced from 22 mhartree for CCSD(T) to 10 mhartree for ACCSD(T). Using ACCSD(T) with a Brueckner reference provides the best single reference coupled-cluster description of N2’s dissociation curve to date. Application of CCSD(T) and ACCSD(T) to the concerted transition state of 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX) indicates that this transition state is well described by either methods, and indicates that the activation barrier is too high for it to be a major pathway of decomposition. © 2008 American Institute of Physics. [DOI: 10.1063/1.2830236]

I. INTRODUCTION

Coupled-cluster theory is preeminent for predictive calculations of moderately sized molecules. To be predictive, a method must have tight error bars for energies, geometries, frequencies, etc., and must be applicable to relatively arbitrary molecular structures.1 For molecules near equilibria, these qualities are best represented within coupled-cluster singles, double, and perturbative triples [CCSD(T)].2,3 CCSD(T) was developed in three stages: The numerically most important term, sometimes called [T], was introduced in 1985 by Urban et al.2 This approximation provided the only fourth-order triples correction that occurs when a Hartree–Fock (HF) reference function is used in CC theory. The next development was by Raghavachari et al.5 who added a single excitation term, which, though much smaller in size (∼5% of the [T] correction), acted in the right direction to improve upon [T]. From the HF perturbation viewpoint, there was no formal reason to add this one-fifth-order term when many other fifth-order terms were also present, but if one chooses to instead count perturbation corrections relative to non-HF cases, where T1 occurs in first order, then this term is a proper fourth-order one, recommending its inclusion. However, once we admit non-HF cases, which are important in providing the wealth of applications of CC theory today, another term that needs to be added occurs in fourth order.3 Finally, to make this generalized CCSD(T) computationally feasible, it is necessary to exploit the freedom that the energy of CCSD(T) is invariant to a semicanonical orbital transformation to retain the ease of application for non-HF reference cases. Together, these steps define CCSD(T), which can be used for any reference determinant: restricted (RHF), restricted open-shell (ROHF), unrestricted (UHF), or quasirestricted (QRHF) Hartree–Fock, Kohn–Sham (KS), Brueckner (B), the first natural determinant (N), etc. ACES II (Ref. 5) provides all as reference functions, to exploit the full flexibility of single-reference CC theory.

CCSD(T) fulfills most of the possible desired properties for an energy model near equilibrium: it is accurate, extensive, orbitally invariant (for rotations among occupied and virtual orbitals), applicable to arbitrary single-determinant reference functions, and analytical derivatives are readily available.1 The computational scaling of CCSD(T) is iteratively O(n^3N^4) with a single non-iterative O(n^3N^4) step. This cost is low enough to allow CCSD(T) to be used for a wide variety of molecules.

Unfortunately, spin-restricted Hartree–Fock (RHF) based CCSD(T) fails significantly away from equilibrium structures because of its perturbative inclusion of triples: the energies produced are far (up to hundreds of millihartree) below the full configuration interaction (full CI) energy. One possible solution is to use spin- and spatial-symmetry broken UHF based CCSD(T). This choice fixes the asymptotic breakdown of CCSD(T). However, it also leads to larger errors in the intermediate “spin recoupling” regime. These failures are not idle problems; if one would like to perform molecular dynamics or Monte Carlo calculations of a system, one’s energy model must be accurate for arbitrary geometries, not solely geometries near equilibria.

Given the potential range of applications, it is not surprising that there have been several attempts to improve upon CCSD(T) for these situations. As of yet, none has reached the widespread acceptance of CCSD(T) itself. This fact is partly due to the stringent requirement that any new method must not disrupt the successes of CCSD(T). There have been many attempts to improve upon CCSD(T), starting with ACCSD(T) introduced by Kucharski and Bartlett,6 and later also studied by Crawford and Stanton.7 Other, later

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ones include the completely renormalized methods of Kowalski and Piecuch \(^8\) and methods based on Löwdin partitioning of the coupled-cluster effective Hamiltonian, such as those introduced by Hirata \textit{et al.} \(^9\) and by Gwaltney and Head-Gordon. \(^10\)

The completely renormalized CCSD(T) [CR-CCSD(T)] method introduces an overlap in the denominator to the triples correction that, while correcting the asymptotic behavior of CCSD(T), introduces a significant error near equilibrium. Also, because of the global nature of the denominator, CR-CCSD(T) is not extensive, violating the rationale for all CC methods. Recent work \(^11\)–\(^14\) has reformulated these methods by utilizing the coupled-cluster left-hand eigenvector, \(L\). Though this newer version is much closer to the earlier (\(L = \Lambda\)) ACCSD(T) mentioned above, unfortunately it also makes the triples correction orbital rotation dependent.

The CCSD(2) method of Gwaltney and Head-Gordon \(^10\) and the CCSD(2)\(_T\) method of Hirata \textit{et al.} \(^9\) both derive from partitioning the coupled-cluster effective Hamiltonian and keeping the lowest order corrections to the energy in perturbation theory. In both cases, the correction is extensive and orbitally invariant, and both methods significantly improve CCSD(T) at long bond distances. In spite of these successes, the results near equilibrium are worse than conventional CCSD(T), and both methods require additional approximations to keep the computational scaling \(O(n^4N^4)\). Both methods also require the entire effective Hamiltonian matrix, which is not as readily available as the bare Hamiltonian, itself.

The actual numerical improvements gained by the above can be largely traced to the older ACCSD(T), which first introduced a left-hand eigenvector, \(\Lambda\), by basing the noniterative (T) correction on the CC functional. \(^3\) The derivation by Crawford and Stanton \(^7\) was from a Löwdin partitioning viewpoint [similar to the justification of CCSD(T) in Ref. \(15\)], though the partitioning is implicit in the functional. \(^1\) As will be shown below, it can also be derived by perturbation theory from CCSD(2)\(_T\). In fact, ACCSD(T) can be viewed as the minimal correction beyond CCSD(T), and since it only requires \(\Lambda\), which has to be obtained in any CC analytical gradient application, it is particularly attractive. Unlike the renormalized approaches above, it is rigorously size extensive, shows occupied-occupied and virtual-virtual orbital invariance, and defines density matrices that are tied to energy derivatives. Without the connection to energy derivatives, any arbitrary operator could be used to left-multiply the CC solution. It also improves CCSD(T) at long bond distances without degrading the equilibrium performance.

One of the areas of chemistry where computation can play the greatest role is in explaining the reactions of energetic materials becomes a task that is well suited for quantum chemistry. One of the prototypical energetic materials is 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX), and there is dispute in the literature about the possible importance of a concerted transition state as a decomposition pathway. Results from density functional theory (DFT) \(\text{B3LYP 6-31(d)}\) indicate that the activation barrier is not the lowest of the potential pathways, \(^16\) but it is close enough in energy to other barriers that higher levels of theory are necessary to verify this conclusion.

Because this transition state is concerted, one might expect that there is significant quasidegenerate character. Therefore, the quality of result that could be expected from CCSD(T) is in doubt. However, this is exactly the type of problem that ACCSD(T) should be capable of handling, and we should be able to determine whether quasidegenerate effects are relevant for this particular transition state, as well as whether the transition state is a significant contributor to the decomposition of RDX.

II. THEORY

A. Derivation of ACCSD(T)

ACCSD(T) is formulated as a noniterative correction to the converged CCSD solution that should approximate CCSDT. For CC, the wave function is approximated by the CC ansatz

\[
|\Psi\rangle = e^T|0\rangle,
\]

where \(|0\rangle\) is a single-determinant reference function. This function is most often a Hartree–Fock wave function, but the generalized CCSD(T) admits any reference function. \(^3\) The \(T\) operator is an excitation operator, which, for CCSDT, is composed of

\[
T = T_1 + T_2 + T_3,
\]

where, using the notation that \(i, j, k\) are occupied orbitals, \(a, b, c\) and \(p, q, r\) are unoccupied (virtual) orbitals, and \(a\) and \(r\) are arbitrary orbitals,

\[
T_n = \left(\frac{1}{n!}\right)^2 \sum_{ijk\cdots} \sum_{abc\cdots} f_{ijk\cdots}^{abc\cdots} (a^\dagger ib^\dagger jc^\dagger k\cdots).
\]

This choice for wave function defines the CCSDT energy functional

\[
\mathcal{E}_{CC} = \langle 0 | (1 + \Lambda) \bar{H} | 0 \rangle,
\]

with the non-Hermitian effective Hamiltonian \(\bar{H}\) defined by the similarity transformation

\[
\bar{H} = e^{-TH}e^T = (He^T)_C
\]

of the normal-ordered bare Hamiltonian

\[
H = \sum_{pq} f_{pq} (p^\dagger q) + \frac{1}{2} \sum_{pqrs} \langle pq || rs \rangle \langle p^\dagger q^\dagger sr \rangle = H^{(0)} + H^{(1)},
\]

where \(f_{pq}\) are Fock matrix elements and \(\langle pq || rs \rangle\) are antisymmetric two-electron integrals, and

\[
H^{(0)} = \sum_{ij} f_{ij} (i^\dagger j) + \sum_{ab} f_{ab} (a^\dagger b) = F_{oo} + F_{eq},
\]

\[
H^{(1)} = \sum_{pq} f_{pq} (p^\dagger q) + \frac{1}{2} \sum_{pqrs} \langle pq || rs \rangle \langle p^\dagger q^\dagger sr \rangle = H^{(0)} + H^{(1)},
\]

\[
H^{(0)} = \sum_{ij} f_{ij} (i^\dagger j) + \sum_{ab} f_{ab} (a^\dagger b) = F_{oo} + F_{eq},
\]

\[
H^{(1)} = \sum_{pq} f_{pq} (p^\dagger q) + \frac{1}{2} \sum_{pqrs} \langle pq || rs \rangle \langle p^\dagger q^\dagger sr \rangle = H^{(0)} + H^{(1)},
\]
\[ H^{(1)} = \sum_{ia} f_{iaa} \langle a^i | + \{ b^i a \} + \frac{1}{2} \sum_{pqrs} \langle pq | rs \rangle \langle p^q | s^r \rangle \]
\[ = F_{ov} + W, \quad (7b) \]
and the off-diagonal \( f_{ij} \) and \( f_{ab} \) terms are eliminated by a semicanonical orbital rotation, if necessary.

The deexcitation operator \( \Lambda \) is, for CSDT,
\[ \Lambda = \Lambda_1 + \Lambda_2 + \Lambda_3, \quad (8) \]
\[ \Lambda_n = \left( \frac{1}{n!} \right) \sum_{abc} \lambda_{abc} \langle a^i | b^j | c \rangle \langle i^a | j^b | c \rangle \cdots. \quad (9) \]

Expanding the CC functional, Eq. (4), to fourth-order contributions and isolating \( \Lambda_3 \) and \( T_3^2 \) gives
\[ \mathcal{E}^{(4)}_{\text{CCSD}} = \mathcal{E}^{(4)}_{\text{CCSD}} + \langle 0 | \Lambda_2 (H^{(1)} T_3^2) | 0 \rangle + \langle 0 | \Lambda_1 (W T_3^2) | 0 \rangle + \langle 0 | \Lambda_3 (H^{(0)} T_3^2) | 0 \rangle + \langle 0 | \Lambda_3 (W T_3^1) | 0 \rangle. \quad (10) \]
One can eliminate \( \Lambda_3 \) by using the equation for \( T_3^2 \),
\[ (H^{(0)} T_3^2) | 0 \rangle + (W T_3^1) | 0 \rangle = 0, \quad (11) \]
which leaves the three terms of Eq. (10) as the definition of ACCSD(T). Furthermore, this is simply the generalized non-HF CCSD(T), \(^3\) except for \( \Lambda_1 \) and \( \Lambda_2 \) replacing \( T_1 \) and \( T_3^2 \).

We can also consider a derivation of ACCSD(T) via partitioning to relate it to other methods that have been suggested. It is straightforward to show that a general functional can be formulated based on the CCSD effective Hamiltonian \( \hat{H}_{SD} \) that is equivalent to full CI,
\[ E_{\text{exact}} = \langle 0 | \mathcal{L} \hat{H}_{SD} \mathcal{R} | 0 \rangle, \quad (12) \]
where \( \mathcal{L} \) and \( \mathcal{R} \) are the left- and right-hand eigenvectors of the non-Hermitian CCSD effective Hamiltonian diagonalized in the space of all determinants, analogous to the equation-of-motion CC (EOM-CC) treatment of excitation energies. \(^{17,18}\) One can then define a projector to the reference and the singly and doubly excited determinants, \( \hat{P} \),
\[ \hat{P} = |0\rangle \langle 0| + \sum_{ia} |a^i \rangle \langle i^a| + \sum_{ijab} |ab^i j^b| \langle ij^a |j^b i \rangle \quad (13) \]
and define its orthogonal projector \( \hat{Q} = \hat{I} - \hat{P} \). These projectors, in turn, define two spaces: the space of determinants in \( \hat{P} \) (P-space), and the space of determinants that span \( \hat{Q} \) (Q-space). Following Löwdin, \(^{19}\) the exact energy can then be written as
\[ E_{\text{exact}} = \langle 0 | \mathcal{L} \hat{P} \hat{H}_{SD} \mathcal{R} | 0 \rangle + \langle 0 | \mathcal{L} \hat{P} \hat{H}_{SD} \hat{Q} (E_{\text{exact}} - \hat{H}_{SD}^{-1} \hat{Q} \hat{H}_{SD} \mathcal{R} | 0 \rangle, \quad (14) \]
where
\[ \mathcal{L}_p = \hat{P} \mathcal{L} \hat{P}, \quad \mathcal{R}_p = \hat{P} \mathcal{R} \hat{P}, \quad \mathcal{L}_p = \hat{P} \mathcal{L} \hat{P}, \quad \mathcal{R}_p = \hat{P} \mathcal{R} \hat{P} \quad (15) \]
are the projections of the exact left- and right-hand eigenstates into the \( P \)-space. We then perturbatively approximate the second term of Eq. (14). The partitioning defined in Eqs. (7a) and (7b) induces a perturbative ordering of the effective Hamiltonian \( \hat{H} \),
\[ \hat{H} = \hat{H}^{[0]} + \hat{H}^{[1]} + \hat{H}^{[2]} + \cdots. \quad (16) \]

By additionally defining the solution of the CCSD equations in the \( P \)-space to be of zeroth order, then
\[ \hat{H}^{[0]} = \hat{P} \hat{H} \hat{P} + \hat{Q} (E_{\text{CCSD}} + F_{vo} + F_{ve}) \hat{Q}, \quad (17) \]
\[ \hat{H}^{[1]} = F_{vo} + W + [F_{vo} + F_{ve}] T_1 | 0 \rangle + [(F_{vo} + F_{ve}) T_2 | 0 \rangle, \quad (18) \]
\[ \hat{E}^{[0]} = (1 + \Lambda) \hat{H} \hat{P} | 0 \rangle = E_{\text{CCSD}}, \quad (22) \]
and the lowest order nonvanishing correction to \( E_{\text{CCSD}} \) is
\[ E^{[3]} = \Delta E_{\text{CCSD}(T)} = \left( \frac{1}{3!} \right)^2 \sum_{ijkl} \Lambda_{ijkl} \langle ab \rangle \langle ab \rangle | H^{[0]} |_{\text{Hart}}^{-1} \langle ab \rangle \langle ab \rangle | H^{[2]} |_{\text{Hart}} | 0 \rangle. \quad (23) \]

The energy expression in Eq. (23) is invariant to any rotation within either the occupied or the virtual space, as the infinite-order CCSD method is. However, to make the ACCSD(T) noniterative, one must choose the Fock operator to be diagonal within the occupied and virtual spaces, which means (semi-)canonical orbitals. Then the inverse in Eq. (23) is trivial, and this expression can be simplified to
\[ \Delta E_{\text{CCSD(T)}} = \left( \frac{1}{3!} \right)^2 \sum_{ijkl} \Lambda_{ijkl} \langle ab \rangle \langle ab \rangle | F_{vo} + W |_{\text{Hart}} \langle ab \rangle \langle ab \rangle \times \frac{1}{\epsilon_{ijkl}^{ab}} \langle ab \rangle \langle ab \rangle | W T_2 | 0 \rangle, \quad (24) \]
where
\[ \epsilon_{ijkl}^{ab} = f_{ii} + f_{jj} + f_{kk} - f_{aa} - f_{bb} - f_{cc}, \quad (25) \]
which is equivalent to Eq. (10). If one needs to keep the orbitals noncanonical, e.g., in the case of localized orbitals, then one can only apply Eq. (23), which must be solved iteratively to maintain orbital invariance.
B. Comparison to other methods

As mentioned in the Introduction, there have been several different attempts to improve CCSD(T) so that it better handles bond-breaking and other quasidegenerate situations. These methods include completely renormalized CCSD(T) [CR-CCSD(T)], its recent extensive modification CR-CCSD(T)C, and CCSD(2)T. All of these methods are \(O(n^3N^4)\) noniterative and improve upon CCSD(T) bond breaking (vide infra), but not all satisfy the desiderata that one would like for a general purpose method.

In CR-CCSD(T), a global overlap denominator is introduced into the CCSD(T) energy expression to temper the overcorrection of CCSD(T) at long bond distances. Unfortunately, the presence of this global denominator immediately breaks extensivity for the correction, making the method more like CI than CC.

A recent modification to CR-CCSD(T) is the rigorously extensive CR-CCSD(T)C. In this method, as in \(\Lambda\)CCSD(T) and CCSD(2)T, the left-hand CCSD eigenvector \(\Lambda\) is used to moderate the overcorrection of CCSD(T). The CR-CCSD(T)C energy correction can be written as

\[
\Delta E_{\text{CR-CCSD(T)C}} = \left(\frac{1}{3!}\right)^2 \sum_{ij} \langle 0|\bar{H}_{SD}\rangle_{ij}^{abc} \frac{1}{\tilde{e}_{ijk}^{abc}} \langle \bar{H}_{SD}\rangle_0, \tag{26}
\]

where \(\tilde{e}_{ijk}^{abc} = E_{\text{CCSD}} - \langle \bar{H}_{ijk} \rangle_{ij}^{abc}. \tag{27}\)

Unlike the bare denominator \(e_{ijk}^{abc}\), the new denominator \(\tilde{e}_{ijk}^{abc}\) is not occupied-occupied and virtual-virtual orbitally invariant. It is similar to the choice of Epstein–Nesbet partitioning for second-order perturbation theory. Therefore, due to arbitrary rotations among the virtual orbitals, for example, the energy correction could change, particularly as a function of geometry, making it unsuitable for potential energy surfaces. Infinite-order coupled-cluster methods are independent of occupied-occupied and virtual-virtual orbital rotations, and one would prefer that to be the case for a perturbative approximation as well, as has been the case for the non-HF generalization of CCSD(T) (Ref. 3) for sometime.

Both the CCSD(2)T (Ref. 9) and CCSD(2) (Ref. 10) methods are based on Löwdin partitioning of the effective Hamiltonian. In both cases, the effective Hamiltonian is split into two:

\[
\bar{H} = \bar{H}^{[0]} + \bar{H}^{[1]}, \tag{28}
\]

For CCSD(2)T, \(\bar{H}^{[0]}\) is chosen to be the same as for \(\Lambda\)CCSD(T), while for CCSD(2), \(\bar{H}^{[0]}\) is chosen to be

\[
\bar{H}^{[0]}_{SD} + \hat{Q}(E_{\text{CCSD}} + \bar{H} + \bar{H}_{1,oo} + \bar{H}_{1,oo}/Q, \tag{29}
\]

where \(\bar{H}_{1}\) is the one-particle part of the effective Hamiltonian. Because the effective Hamiltonian is split into only two pieces [rather than a perturbation series as is done in \(\Lambda\)CCSD(T)], the correction to CCSD in both cases includes contributions from quadruple excitations. Calculating quadruples adds significant computational expense to these methods causing a \(O(n^5N^5)\) scaling. To avoid this expense these approaches use additional approximations. In the case of CCSD(2), the approximate factorization of the quadruples term, introduced by Kucharski and Bartlett, 20 is used, which drops the computational complexity from \(O(n^5N^5)\) to \(O(n^3N^4)\). However, there is also an additional \(O(N^6)\) term [conventional CCSD(T)—and \(\Lambda\)CCSD(T)—scale as \(O(n^5N^5)\)]. Because of this scaling, it is more reasonable to compare CCSD(2) with methods such as CCSD(TQ) that also have an \(O(N^6)\) term and explicitly include quadruple excitations.

On the other hand, the most closely related method to \(\Lambda\)CCSD(T) is CCSD(2)T. (This method was first introduced under the name CC(2)PT(2) in Ref. 21.) The full energy correction from the CCSD(2)T partitioning is actually CCSD(2)TQ and includes a triples and quadruples term

\[
\Delta E_{\text{CCSD(2)T}} = \left(\frac{1}{3!}\right)^2 \sum_{ijk} \langle 0|\bar{H}_{SD}\rangle_{ij}^{abc} \frac{1}{\tilde{e}_{ijk}^{abc}} \langle \bar{H}_{SD}\rangle_0, \tag{30}
\]

\[
\Delta E_{\text{CCSD(2)T}} = \left(\frac{1}{4!}\right)^2 \sum_{ijkl} \langle 0|\bar{H}_{SD}\rangle_{ijkl}^{abcd} \frac{1}{\tilde{e}_{ijkl}^{abcd}} \langle \bar{H}_{SD}\rangle_0. \tag{31}
\]

The quadruples term is discarded to keep the computational complexity \(O(n^3N^4)\) and, therefore, CCSD(2)T does not correspond to a well-defined perturbation order. However, if one perturbatively expands this energy using the partitioning defined above, then the lowest nonvanishing term is the \(\Lambda\)CCSD(T) correction. Therefore, it is reasonable to call \(\Lambda\)CCSD(T) the minimal extension of CCSD(T). It costs twice as much as CCSD(T), but as a byproduct of a CC gradient calculation, that factor of 2 is required, anyway.

III. IMPLEMENTATION

\(\Lambda\)CCSD(T) has been implemented within the ACES II program system by adding to the capabilities of the pre-existing CCSD(T) code. Utilizing the direct product formulation of symmetry, our implementation takes advantage of real Abelian point group symmetry to accelerate calculations. Currently we calculate the correction by forming for each set of \(\{i < j < k\}\) the corresponding \(t^{abc}_{ijk}\) and \(\chi^{abc}_{ijk}\) for all \(\{a < b < c\}\). Then, to calculate the energy correction, the contraction

\[
\delta E_{ij} = \sum_{a < b < c} \lambda^{a}[2]_{abc} \tilde{e}_{ijk}^{abc} \tag{32}
\]

is performed, where, in spin-orbital form, the relevant amplitudes are defined as

\[
t^{abc}_{ijk} = \frac{1}{\tilde{e}_{ijk}^{abc}} \left[ P(a|bc|k|ij) \sum_{d} \langle bc | dk \rangle \rho_{ad}^{pd} \rho_{ad}^{pd} - P(c|ab|i|jk) \sum_{l} \langle lc | jk \rangle \rho_{bl}^{ld} \rho_{bl}^{ld} \right]. \tag{33}
\]
\[
\lambda_{abc}^{[2]} = \frac{1}{\epsilon_{ijk}^{bc}} \left[ P(a/bc|ij) \sum_d (bc\|dk)\lambda_{ad}^{ij} 
- P(c/ab|ijk) \sum_l (le\|jk)\lambda_{bl}^{ik} 
+ P(i/jk)P(ab/c)\lambda_{jk}^{bc} 
+ P(i/jk)P(ab/c)f_{ia}\lambda_{jk}^{bc} \right].
\]

The total energy correction can then be constructed as
\[
\Delta E_{\text{AccSD}(T)} = \sum_{i<j<k} \delta E_{ijk}.
\]

This approach is more memory intensive than an implementation that would not form \(\lambda_{abc}^{[2]}\) explicitly, however, it maintains the most similarity to conventional CCSD(T) and is useful for the implementation of gradients.

For non-Hartree–Fock calculations, the same formulas are used. However, to avoid needing to solve these equations iteratively, and thus needing to store \(\gamma_{ij}^{[2]}\) and \(\Lambda_{ij}^{[2]}\), the occupied-occupied and virtual-virtual blocks of the Fock matrix must be diagonal. This requirement is achieved by rotating among these blocks individually, which defines semicanonical non-Hartree–Fock orbitals.

### IV. RESULTS AND DISCUSSION

#### A. Bond breaking

To judge the \(\Delta\text{CCSD}(T)\) method as it pertains to bond breaking, we applied \(\Delta\text{CCSD}(T)\) to a variety of molecules where \(\text{CCSD}(T)\) fails. Whenever possible we used combinations of molecules and basis sets where there was a full CI reference so that we could unambiguously determine the quality of various methods across potential energy surfaces. Calculations were performed with core orbitals frozen during the correlation procedure. It becomes difficult to stay on the proper energy surface at long bond lengths due to problems converging the self-consistent field and CC equations. Therefore, orbitals and \(T\) amplitudes from prior geometry steps are used as initial guesses for the succeeding geometries. In all cases, the energies are displayed as functions of bond length in units of the equilibrium bond length. For UHF calculations, the symmetry is not enforced at all, and we follow all Hartree–Fock instabilities to remain in a local minimum.

1. **Single bond breaking**

   Single bond breaking should, in principle, be the easiest test of bond breaking. However, as is shown in Fig. 1, RHF \(\text{CCSD}(T)\) is completely unsuitable for reaching the dissociation limit of even these relatively simple cases. In this figure, errors from full CI (Ref. 22) for bond breaking of HF are shown. The restricted Hartree–Fock solution for HF bond breaking approaches the ionized \(\text{H}^+\text{F}^-\) state rather than \(\text{H}^+\text{F}\). Therefore, correlation is attempting to bring the asymptotic behavior from the ions to the neutrals. Neither \(\text{CCSD}(T)\) or \(\Delta\text{CCSD}(T)\) is sufficient in this case to be predictive along the entire potential energy surface. However, rather than errors of tens of millihartrees, \(\Delta\text{CCSD}(T)\) stays within 10 mhartree of the full CI result across the entire range of bond lengths.

Figure 2 is a comparison of four of the alternative triple correction methods for bond breaking in \(\text{F}_2\) in a cc-pVDZ basis.\(^{23}\) The reference for these calculations is CCSD(T), which for a single bond should be an excellent approximation to the full CI. For all four methods, the improvement over CCSD(T) is substantial; however, there are significant differences. At equilibrium, \(\Delta\text{CCSD}(T)\) is the best method and most closely matches CCSD(T). For CR-CCSD(T), CCSD(2)\(_T\), and \(\Delta\text{CCSD}(T)\), the errors from CCSDT (Ref. 24) are more negative the further along the potential energy surface one goes. Of those three, \(\Delta\text{CCSD}(T)\) stays closest to CCSDT over the range considered. Qualitatively, it appears that CR-CCSD(T)\(_L\) is the best method for this molecule at all bond distances beyond \(2R_e\); after that point the errors are effectively distance independent. Interestingly, however, the energy at equilibrium is below that of CCSDT.

![Figure 1](image1.png)  
**FIG. 1.** Errors (in millihartree) from full CI for RHF CCSD(T) and RHF \(\Delta\text{CCSD}(T)\) for HF bond breaking in a 6-31G\(^*\) basis. The horizontal axis is in units of the equilibrium bond length of HF, \(R_e=0.9\) Å, and only valence electrons are correlated. Full CI results are from Ref. 22.

![Figure 2](image2.png)  
**FIG. 2.** Errors (in millihartree) from RHF CCSD(T) for RHF CCSD(T), RHF \(\Delta\text{CCSD}(T)\), and RHF CR-CCSD(T)\(_L\) for \(\text{F}_2\) bond breaking in cc-pVDZ basis. The horizontal axis is in units of the equilibrium bond length of \(\text{F}_2\), \(R_e=2.668\) 16 a.u., and only valence electrons are correlated. CCSDT and CCSD(2)\(_T\) results are from Ref. 24 and CR-CCSD(T)\(_L\) results are from Ref. 13.
CR-CCSD stretching is shown in the left panel of Fig. 5. By twisting the potential energy surface, the total energy curve for this bond becomes much more difficult to describe the farther one is along the range, but the biradical nature would make the equilibrium bond breaking of ethylene more easily described at long range. The planar ethylene molecule has a smaller potential energy curve than that for single bond breaking because of the symmetrized quasidegenerate nature of the 90° state, that is not available, it is known that the interconversion should not display a cusp as it passes through 90°, but rather be smooth. Therefore, it is slightly surprising, given the assumed quasidegenerate nature of the 90° state, that ACCSD(T) apparently performs slightly worse than CCSD(T) for this torsion.

2. Double bond breaking

The quality of double bond breaking results is more instructive than that for single bond breaking because of the corresponding increased difficulty of describing these molecules. Dicarbide is a notoriously difficult molecule. Recent full CI results\(^2^5\) allow for direct comparison with the correct answer in the reasonably large 6-31G* basis set, as shown in Fig. 3. CCSD(T), ACCSD(T), and CR-CCSD(T) (Ref. 25) all display error maxima at approximately 1.0\(R_e\). Though CCSD(T) is the best choice near equilibrium, ACCSD(T) is only a couple of millihartrees more in error, and unlike CCSD(T), can still yield qualitatively correct results up to 2\(R_e\) and beyond. CR-CCSD(T) behaves best at long bond lengths, but is 10 mhartree in error at equilibrium.

One of the paradigmatic examples of “double bond breaking” is the symmetric stretch of H\(_2\)O. In the left panel of Fig. 4, errors from full CI (Ref. 26) in a cc-pVDZ basis are shown for RHF CCSD(T), ACCSD(T), CR-CCSD(T), CCSD(2)\(_T\), and CR-CCSD(T)\(_C\).\(^{9,13}\) ACCSD(T) and CR-CCSD(T)\(_C\) perform equivalently for this example—errors differ by less than 2 mhartree across the potential energy curve. CCSD(2)\(_T\) is slightly better asymptotically, with errors reduced by a few millihartree relative to ACCSD(T), but slightly worse at 2\(R_e\).

For a more chemically interesting example, we look at the bond breaking of ethylene. The planar ethylene molecule is doubly bonded and, subject to a RHF reference, should be much more difficult to describe the farther one is along the potential energy surface. The total energy curve for this bond stretching is shown in the left panel of Fig. 5. By twisting the two methylene groups 90° out of plane from each other, ethylene becomes a singly bonded biradical. In this case, because the bond is only an effective single bond, one would expect that bond breaking would be more easily described at long range, but the biradical nature would make the equilibrium bond breaking more difficult to describe. Results for this case are shown in the right panel of Fig. 5. In both cases, it is clear that for bond breaking \(\Delta\text{CCSD(T)}\) performs significantly better than does CCSD(T). For the case of a closed-shell equilibrium structure (nontwisted ethylene) CCSD(T) and ACCSD(T) are the same at equilibrium, and only begin to disagree at roughly 2\(R_e\). On the other hand, for the biradical twisted ethylene case, \(\Delta\text{CCSD(T)}\) is 7 mhartree higher in energy.

The interconversion between these two conformations of the molecule is plotted in Fig. 6. Though a full CI reference is not available, it is known that the interconversion should not display a cusp as it passes through 90°, but rather be smooth. Therefore, it is slightly surprising, given the assumed quasidegenerate nature of the 90° state, that \(\Delta\text{CCSD(T)}\) apparently performs slightly worse than CCSD(T) for this torsion.

3. Triple bond breaking

Comparing the results for CO in a cc-pVTZ basis set\(^2^3\) shown in Fig. 7 between RHF CCSD, CCSD(T), and ACCSD(T), what is striking is how poorly CCSD(T) behaves. It does not simply variationally collapse, but rather approaches a completely wrong asymptote and introduces an
artificial maximum on the potential energy curve. CCSD, on the other hand, is at least not a complete qualitative failure, and ACCSD(T) maintains that property.

To judge the asymptotic quality of RHF and UHF CCSD(T) and ACCSD(T) results for CO, we calculate the dissociation energies from these methods in two ways. To calculate the “direct” dissociation energy, the UHF-CC energies of the C and O atoms are calculated and the equilibrium energy of the appropriate method subtracted. The extrapolated dissociation energy is then obtained by taking the energy for each method at 4\(R_e\) as that of the dissociated atoms. Longer bond distances were not used because of difficulties converging the RHF CCSD equations. Because the extrapolated results are taken at only 4\(R_e\), there is still residual interaction between the two atoms. A gauge of that residual interaction is given by the UHF CCSD(T) and UHF ACCSD(T) results, which show that there is still 7 mhartree of interaction energy between the atoms. Using these results as a reference, any energy difference greater than 7 mhartree can be traced to improper treatment of the asymptotic region of the potential energy curve.

The results in Table I show that the RHF CCSD(T) are completely unusable for the calculation of dissociation energies, as would be expected from looking at the potential energy curve in Fig. 7. However, the RHF ACCSD(T) results are still in error by more than 20 mhartree.\(^{27}\)

In any examination of bond breaking, one must consider the case of \(\text{N}_2\). In Fig. 8, the full CI data\(^{28}\) for \(\text{N}_2\) in a cc-pVDZ basis are plotted along with several of the different

**TABLE I. CO dissociation energies (in millihartree) calculated using two methods (see text) in a cc-pVTZ basis and the difference between these two results for CCSD(T) and ACCSD(T).\(^{27}\)**

<table>
<thead>
<tr>
<th>Method</th>
<th>(D_e) (direct)</th>
<th>(D_e) (extrap)</th>
<th>(\Delta D_e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF</td>
<td>CCSD(T)</td>
<td>445.1</td>
<td>42.8</td>
</tr>
<tr>
<td></td>
<td>ACCSD(T)</td>
<td>399.0</td>
<td>419.5</td>
</tr>
<tr>
<td>UHF</td>
<td>CCSD(T)</td>
<td>399.1</td>
<td>406.2</td>
</tr>
<tr>
<td></td>
<td>ACCSD(T)</td>
<td>399.1</td>
<td>406.1</td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td></td>
<td>408.2</td>
</tr>
</tbody>
</table>

\(^{27}\)Experimental estimate of dissociation energy from Ref. 27.
triples correction methods. From these data points, none of the methods look particularly bad. Even CCSD(T) remains reasonably well behaved. However, in Table II, the longer range behavior of N2 is shown for CCSD(T), ACCSD(T), and CCSDT. In this case, it is clear that CCSD(T) fails utterly at 2Rc. ACCSD(T) improves this result significantly, and even outperforms CCSDT. However, errors are still on the order of 100 mhartree—clearly not chemical accuracy!

In Fig. 9, a comparison of the nonparallelity errors is made between CCSD, CCSD(T), and ACCSD(T) for HF, C2, N2, and H2O. To compensate for the fact that these potential energy curves are of different lengths for the different molecules, the average nonparallelity has been calculated using a weighting factor depending on the length of the curve computed

\[ \langle E_{\text{NPE}} \rangle = \frac{1}{M} \sum_{A=1}^{M} E_{\text{NPE}}(A) \frac{R_{\text{max}}(A)}{R_c(A)}. \]  

These average nonparallelity errors and their corresponding standard deviations are fitted to Gaussian functions to give a pictorial representation of the spread of results over multiple molecules. Of course, all of these methods perform more poorly the more complex the bonding situation, but ACCSD(T) has both a smaller average error as well as a tighter distribution of errors than CCSD or CCSD(T). The practical effect of the CCSD(T) failure at long bond distances is illustrated by the fact that CCSD is a better choice for minimizing nonparallelity errors than is CCSD(T).

### 4. UHF bond breaking

Most of the results presented above are for RHF references. Due to the nature of the underlying symmetry of the problem and computational advantages, one would prefer to use RHF if possible. However, as the example for CO dissociation energies showed (cf. Table I), UHF can potentially improve things considerably. What is interesting is comparing the UHF CCSD(T) results and UHF results for ACCSD(T) and CCSD(T). In Table I, the results for UHF CCSD(T) and UHF ACCSD(T) are within 1 mhartree of each other. Even more striking is the right panel of Fig. 4 that compares the UHF bond breaking for H2O symmetric stretch—the errors for CCSD(T), ACCSD(T), and CCSD(T) all virtually on top of one another. This result is not isolated. Further examinations show that UHF CCSD(T) and UHF ACCSD(T) are almost identical in all cases. This result stands in sharp contrast to RHF comparisons, necessitating the question of why this might be the case.

To simplify the discussion, we will focus on the components that arise purely from doubles: this corresponds to CCSD(T) or the similar variant ACCSD(T), where terms that involve \( T_1 \) or \( \Lambda_1 \) are dropped. In the Hartree–Fock case, we define

\[ \bar{T}_3 = (T_2 W)_{C} \quad \bar{\Lambda}_3 = (\Lambda_2 W)_{C}. \]  

Then, the energy expressions (for the brackets variants) can be written as

\[ \Delta E_{\text{CCSD[T]}} = \sum_{ijk,abc} \frac{\eta_{ijk} \eta_{abc}}{\epsilon_{ijk}} \]  

\[ \Delta E_{\text{ACCSD[T]}} = \sum_{ijk,abc} \frac{\tilde{\eta}_{ijk} \eta_{abc}}{\epsilon_{ijk}}. \]  

Taking a cue from the analyses of bond breaking in MBPT(2), where \( \epsilon_{\text{HOMO}} = \epsilon_{\text{LUMO}} \) at large separation, it would be reasonable to expect that the causes of failure of RHF CCSD(T) are small denominators \( \epsilon_{ijk} \). If one assumes that generally the magnitude of \( \eta_{ijk} \) is independent of the magnitude of \( \epsilon_{ijk} \), then the problematic terms should be those for which \( \tilde{\eta}_{ijk} \) happens to be large and \( \eta_{abc} \) happens to be small. Therefore, for ACCSD(T) to improve things, it must
be true that when $t_{ij}^{abc}$ is large and $e_{ij}^{abc}$ is small, that $\lambda_{abc}$ must be small enough to moderate that term. In the UHF case, however, one would expect there to be no small denominators, and, therefore, the differing magnitudes of $\tilde{T}$ and $\tilde{\Lambda}$ would be inconsequential.

This simple explanation turns out to be false. An analysis of the $\tilde{T}$ and $\tilde{\Lambda}$ amplitudes shows that the biggest difference between RHF CCSD(T) and RHF ACCSD(T) is not due to moderation of small denominators, rather, it is the actual magnitude of $\tilde{T}_3$ that is the source of the failure. For the case of $F_2$ in a cc-pVDZ basis at $R_{eq}=5.336$ a.u., these results are shown in Table III, ordered by their relative importance to the CCSD(T) correction. In the RHF case, the biggest contributions to $\Delta E_{\text{CCSD(T)}}$ are from large $\tilde{T}_3$ amplitudes. Comparing to the UHF case, while the denominators have not changed significantly (focusing on the $\beta \alpha \alpha$ spin case, for example) the magnitude of $T_3$ has become much smaller. In both the RHF and UHF cases, the $\tilde{\Lambda}$ amplitudes are the same magnitude. Therefore, the reason that RHF ACCSD(T) is significantly better than CCSD(T) at long bond distances is that RHF $\tilde{\Lambda}$ is much closer to UHF $\tilde{\Lambda}$ than is $\tilde{T}$.

In none of the cases analyzed is a small $T_3$ denominator a relevant concern to the turnover of CCSD(T). In cases where RHF ACCSD(T) continues to turnover, e.g., $N_2$, both the $T_3$ and $\Lambda_3$ values diverge significantly from their UHF counterparts, and the denominator still remains approximately the same for both RHF and UHF.

Fundamentally, these results can be summarized succinctly: although the RHF CCSD energy is qualitatively adequate, the RHF CCSD wave function is qualitatively wrong at bond-breaking separations, and this can be traced to small $e_{ij}^{ab}$ denominators. This failure of the RHF CCSD wave function explains why methods such as ACCSD(T) and CCSD(2)$_T$ improve upon CCSD(T); the inclusion of the left-hand eigenvector $\Lambda$, which due to its CI nature is “less wrong,” corrects for some of the failures of the CCSD wave function. On the other, in the UHF case, the UHF CCSD wave function and its $\Lambda$ counterpart are good descriptions at long bond distances. They are both equally poor descriptions in the spin recoupling region, which is why these methods fail there. Of course, the failure of the CCSD wave function has a minimal impact unlesstriples are included perturbatively.

5. Non-Hartree–Fock bond breaking

By explicitly including the contraction of $\Lambda$ with $F_{\alpha\alpha}$ into $\tilde{T}_3$, no-Hartree–Fock reference functions can be handled just as well as Hartree–Fock reference functions. This flexibility allows us to examine bond breaking in high-spin open-shell systems using ROHF references. In Table IV the dependence on bond length for NH$_2$ in a double-zeta with polarization (DZP) basis for two electronic states of different symmetries is summarized.

The difference between ACCSD(T) and CCSD(T) is small for both ROHF and UHF references at all geometries; errors only differ by at most 3 mhartree for ROHF and by less than a millihartree for UHF. In the second to last row of Table IV, the multiplicity of the UHF CCSD state is determined via the projected form of the spin expectation value. As has been pointed out previously for ROHF cases, the projected spin value is trivially satisfied, but not the $S^2$

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**Table III.** The most significant [as judged by their contribution to the CCSD(T) energy] $t_{ij}^{abc}$ amplitudes for $F_2$ in a cc-pVDZ basis (valence electrons are correlated). $R_{eq}$=5.336 a.u. ($\approx 2R_e$).

<table>
<thead>
<tr>
<th>Method</th>
<th>$\delta E$ (mhartree)</th>
<th>$t_{ij}^{abc}$</th>
<th>$\lambda_{abc}$</th>
<th>$e_{ij}^{abc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-4.76</td>
<td>-0.166</td>
<td>-0.056</td>
<td>-1.96</td>
</tr>
<tr>
<td>ACCSD(T)</td>
<td>-4.76</td>
<td>-0.165</td>
<td>-0.056</td>
<td>-1.96</td>
</tr>
<tr>
<td>UHF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROHF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UHF ACCSD(T)</td>
<td>-2.14</td>
<td>-0.141</td>
<td>-0.050</td>
<td>-3.31</td>
</tr>
<tr>
<td></td>
<td>-0.62</td>
<td>-0.074</td>
<td>-0.028</td>
<td>-3.36</td>
</tr>
<tr>
<td></td>
<td>-0.62</td>
<td>-0.074</td>
<td>-0.028</td>
<td>-3.36</td>
</tr>
<tr>
<td>UHF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.09</td>
<td>-0.022</td>
<td>-0.022</td>
<td>-5.15</td>
</tr>
<tr>
<td></td>
<td>-0.09</td>
<td>-0.022</td>
<td>-0.022</td>
<td>-5.15</td>
</tr>
<tr>
<td></td>
<td>-0.07</td>
<td>-0.019</td>
<td>-0.018</td>
<td>-5.20</td>
</tr>
<tr>
<td></td>
<td>-0.03</td>
<td>0.014</td>
<td>0.014</td>
<td>-6.53</td>
</tr>
<tr>
<td></td>
<td>-0.03</td>
<td>0.015</td>
<td>0.015</td>
<td>-6.43</td>
</tr>
</tbody>
</table>

**Table IV.** Errors from full CI (Ref. 44) for NH$_2$ ROHF bond breaking in a DZP basis (in millihartree). Geometry from Ref. 44.

<table>
<thead>
<tr>
<th>Method</th>
<th>$2B_1^1$</th>
<th>$2A_1^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_e$</td>
<td>1.5$R_e$</td>
</tr>
<tr>
<td>ROHF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>0.569</td>
<td>1.734</td>
</tr>
<tr>
<td>ACCSD(T)</td>
<td>0.623</td>
<td>2.12</td>
</tr>
<tr>
<td>UHF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROHF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>0.546</td>
<td>3.774</td>
</tr>
<tr>
<td>UHF ACCSD(T)</td>
<td>0.599</td>
<td>4.085</td>
</tr>
<tr>
<td>$2S+1$</td>
<td>2.000</td>
<td>2.127</td>
</tr>
</tbody>
</table>

| Full CI (H) | -55.743  | -55.605  | -55.505  | -55.689  | -55.518  | -55.415  |

$^a$Results from Ref. 3.
expectation value. Therefore, it is important to not overinterpret the difference in spin contamination between the UHF and ROHF results. However, with that caveat, at the level of the spin projection, it appears that the ROHF based methods better represent the state at \(2R_e\).

A similar example is illustrated in Table V, where results for bond breaking of the doublet CH\(_3\) radical in a DZP basis illustrate the accuracy of \(\Delta\text{CCSD(T)}\) for bond breaking of an open-shell system. The conclusions are similar—ROHF and UHF results for \(\text{CCSD(T)}\) and \(\Delta\text{CCSD(T)}\) are very close to each other. Also, at long bond distances, the spin multiplicity of the UHF-CCSD wave function is far from that of the ROHF-CCSD wave function (as evaluated using the projected expectation value).

One consideration that may be confusing is that \(\text{CCSD(T)}\) fails for RHF bond breaking and \(\Delta\text{CCSD(T)}\) improves that behavior; then why is it that ROHF \(\text{CCSD(T)}\) bond breaking is much more accurate and ROHF \(\Delta\text{CCSD(T)}\) does not improve upon it? In the normal ROHF-coupled-cluster implementation, while the ROHF reference function is spin restricted, the excitation operators are spin unrestricted, i.e., they can be different for \(\alpha\) and \(\beta\) spins. Therefore, ROHF-CC is much more similar to UHF-CC than it is to RHF-CC, and the discussion above of RHF CCSD(T) versus UHF CCSD(T) applies. However, if one were to apply the \(\Delta\text{CCSD(T)}\) derivation and methodology to the recent spin-restricted coupled-cluster methods of Szalay and co-workers (SR-CC), then we conjecture that a \(\Delta\text{CCSD(T)}\) variant would perform significantly better than a CCSD(T) correction to SR-CCSD. Recent work has shown improvements for \(F_2^2\) bond breaking using a different ROHF CR-CCSD(T) as well.

To compare \(\Delta\text{CCSD(T)}\) for some open-shell systems to other methods that have been published in the literature, we examine errors from full CI for the lowest states of each symmetry for H\(_2\)O\(^+\), as is shown in Table VI. These states are mildly multireference, with varying percentages of importance of the underlying HF state, in the case of the UHF results. All of the \(O(N^7)\) methods are within 1 mhartree of the full CI results for these total energies. However, it is also clear that \(\Delta\text{CCSD(T)}\) is better than both of the other alternatives at representing all three of these states. The ability to apply this method to a ROHF reference function also shows clearly that spin contamination of the underlying function is not an important factor at equilibrium for this molecule.

### 6. Brueckner orbitals

One potentially powerful use of non-Hartree–Fock orbitals are the Brueckner orbitals. These are the orbitals whose single determinant maximally overlaps with a correlated wave function, and, therefore, can in some sense encode the effect of correlation into the orbitals themselves. In coupled-cluster theory, the Brueckner orbital condition is equivalent to requiring that the \(T_1\) equation be satisfied and \(T_1 = 0\). Because the Brueckner orbitals modify the structure of the CC equations with the additional \(T_1\) constraint, the \(\Lambda\) equations are slightly different (they include effects of Brueckner orbital relaxation). However, to a first approximation, one can assume that the same \(\Lambda\) equations hold. We implemented the Brueckner instability condition as described by Paldus et al. to determine when there is a symmetry-broken Brueckner solution that had higher overlap with the exact wave function.

In Fig. 10, we plot the errors from full CI for N\(_2\) bond breaking for UHF and unrestricted Brueckner results for \(\text{CCSD(T)}\) and \(\Delta\text{CCSD(T)}\). Symmetry is broken for the UHF case by 1.1\(R_e\), while for the unrestricted Brueckner case, it remains symmetry restricted until 2\(R_e\). The delay of symmetry breaking in the Brueckner orbitals is well known. The combination of \(\Delta\text{CCSD(T)}\) and Brueckner orbitals is able to

**TABLE V.** Errors from full CI (Ref. 45) for CH\(_3\) \(^2A_1^\text{g}\) bond breaking in a DZP basis (in mhartree). \(R_e=2.06\) a.u., HCH=120°, \(C_3v\) symmetry.

<table>
<thead>
<tr>
<th>Method</th>
<th>(R_e)</th>
<th>1.5(R_e)</th>
<th>2(R_e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROHF</td>
<td>0.518</td>
<td>2.113</td>
<td>10.985</td>
</tr>
<tr>
<td>(\Delta\text{CCSD(T)})</td>
<td>0.572</td>
<td>2.450</td>
<td>17.432</td>
</tr>
<tr>
<td>UHF</td>
<td>0.499</td>
<td>2.669</td>
<td>15.720</td>
</tr>
<tr>
<td>(\Delta\text{CCSD(T)})</td>
<td>0.551</td>
<td>2.970</td>
<td>16.267</td>
</tr>
<tr>
<td>2(S^+_1)</td>
<td>2.001</td>
<td>2.026</td>
<td>3.345</td>
</tr>
<tr>
<td>Full CI (H)</td>
<td>(-39.721)</td>
<td>(-39.483)</td>
<td>(-39.303)</td>
</tr>
</tbody>
</table>

**TABLE VI.** Errors from full CI (Ref. 26) for lowest H\(_2\)O\(^+\) states of each symmetry. Geometry from Ref. 26.

<table>
<thead>
<tr>
<th>Method</th>
<th>(^2A_1)</th>
<th>(^2B_1)</th>
<th>(^2B_2)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROHF</td>
<td>0.46</td>
<td>0.53</td>
<td>0.45</td>
<td>0.48</td>
</tr>
<tr>
<td>(\Delta\text{CCSD(T)})</td>
<td>0.47</td>
<td>0.55</td>
<td>0.48</td>
<td>0.50</td>
</tr>
<tr>
<td>UHF</td>
<td>0.48</td>
<td>0.56</td>
<td>0.48</td>
<td>0.50</td>
</tr>
<tr>
<td>(\Delta\text{CCSD(T)})</td>
<td>0.58</td>
<td>0.68</td>
<td>0.58</td>
<td>0.61</td>
</tr>
<tr>
<td>CR-CCSD(T)</td>
<td>0.66</td>
<td>0.76</td>
<td>0.65</td>
<td>0.69</td>
</tr>
<tr>
<td>Full CI (H)</td>
<td>(-75.732\ 91)</td>
<td>(-75.558\ 23)</td>
<td>(-75.806\ 89)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^a\)Results from Ref. 26.

\(^b\)Results from Ref. 9.
corrections will be forthcoming in future papers.

between error of only 5.7 mhartree. Further studies of the synergy between MG3 basis,37–39 and open-shell molecules were calculated using a ROHF reference. The results are collected in Table VII. The difference between CCSD(T) and ACCSD(T) is remarkably small. Overall, the average absolute error difference is less than 0.05 kcal/mol. Recent reduced multireference coupled-cluster [RMR-CCSD(T)] results of Li and Paldus40 similarly show agreement with CCSD(T) numbers.

B. Activation energies

Though surprising, the failures of CCSD(T) away from equilibria appear not to extend to energies of transition states, at least for most well-characterized transition states. To compare the impact of ACCSD(T) on these transition states, we applied both CCSD(T) and ACCSD(T) to the set of reactions with reliable experimental barrier heights of Truhlar and co-workers.35,36 All calculations were performed in the MG3 basis,37–39 and open-shell molecules were calculated using a ROHF reference. The results are collected in Table VII. The difference between CCSD(T) and ACCSD(T) is remarkably small. Overall, the average absolute error difference is less than 0.05 kcal/mol. Recent reduced multireference coupled-cluster [RMR-CCSD(T)] results of Li and Paldus40 similarly show agreement with CCSD(T) numbers.

C. RDX concerted transition state

The proposed concerted “triple whammy” transition state, illustrated in Fig. 11, breaks RDX into three methyl-ene nitramine fragments.16 Because of the size of RDX and the necessity to do a full transition state search using ACCSD(T) is computationally infeasible at this time, we use the geometries optimized at the B3LYP 6-31(d) level.16 Cal-

describe N2 bond breaking out to 2Rc with a nonparallelity error of only 5.7 mhartree. Further studies of the synergy between A-based theory and Brueckner orbitals with triples corrections will be forthcoming in future papers.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Barrier height</th>
<th>Error from best estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+NO\rightarrow OH+N2</td>
<td>18.80</td>
<td>0.66</td>
</tr>
<tr>
<td>H+NO\rightarrow OH+N2</td>
<td>18.80</td>
<td>0.66</td>
</tr>
<tr>
<td>H+FH\rightarrow HF+H</td>
<td>43.57</td>
<td>1.39</td>
</tr>
<tr>
<td>H+CH3\rightarrow H+CH3</td>
<td>19.63</td>
<td>1.63</td>
</tr>
<tr>
<td>H+FCH3\rightarrow HF+CH3</td>
<td>31.92</td>
<td>1.54</td>
</tr>
<tr>
<td>H+FCH3\rightarrow HF+CH3</td>
<td>57.69</td>
<td>0.67</td>
</tr>
<tr>
<td>H+F2\rightarrow HF+H</td>
<td>2.37</td>
<td>0.10</td>
</tr>
<tr>
<td>CH3+Cl\rightarrow CH2F+Cl</td>
<td>6.46</td>
<td>-0.97</td>
</tr>
<tr>
<td>F+CH3\rightarrow FCH3</td>
<td>-1.29</td>
<td>-0.95</td>
</tr>
<tr>
<td>F+CH3\rightarrow FCH3</td>
<td>-1.29</td>
<td>-0.95</td>
</tr>
<tr>
<td>Cl+CH3\rightarrow ClCH3</td>
<td>2.37</td>
<td>-0.73</td>
</tr>
<tr>
<td>Cl+CH3\rightarrow ClCH3</td>
<td>2.37</td>
<td>-0.73</td>
</tr>
<tr>
<td>F+CH3\rightarrow FCH3</td>
<td>-14.50</td>
<td>-1.96</td>
</tr>
<tr>
<td>F+CH3\rightarrow FCH3</td>
<td>22.28</td>
<td>2.17</td>
</tr>
<tr>
<td>F+CH3\rightarrow FCH3</td>
<td>31.70</td>
<td>2.08</td>
</tr>
<tr>
<td>OH+CH3\rightarrow HOCH3</td>
<td>-3.89</td>
<td>-1.11</td>
</tr>
<tr>
<td>OH+CH3\rightarrow HOCH3</td>
<td>16.23</td>
<td>-1.10</td>
</tr>
<tr>
<td>OH+CH3\rightarrow HOCH3</td>
<td>10.67</td>
<td>-0.29</td>
</tr>
<tr>
<td>OH+CH3\rightarrow HOCH3</td>
<td>47.86</td>
<td>0.66</td>
</tr>
<tr>
<td>H+CO\rightarrow HCO</td>
<td>4.07</td>
<td>0.90</td>
</tr>
<tr>
<td>H+CO\rightarrow HCO</td>
<td>4.07</td>
<td>0.90</td>
</tr>
<tr>
<td>H+CH4\rightarrow CH2CH2</td>
<td>21.99</td>
<td>-0.69</td>
</tr>
<tr>
<td>H+CH4\rightarrow CH2CH2</td>
<td>21.99</td>
<td>-0.69</td>
</tr>
<tr>
<td>CH4+CH4\rightarrow CH2CH2</td>
<td>41.75</td>
<td>0.00</td>
</tr>
<tr>
<td>CH4+CH4\rightarrow CH2CH2</td>
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<td>0.00</td>
</tr>
<tr>
<td>CH4+CH4\rightarrow CH2CH2</td>
<td>32.50</td>
<td>-0.47</td>
</tr>
<tr>
<td>CH4+CH4\rightarrow CH2CH2</td>
<td>32.50</td>
<td>-0.47</td>
</tr>
<tr>
<td>HCN+HNC</td>
<td>48.47</td>
<td>0.31</td>
</tr>
<tr>
<td>HCN+HNC</td>
<td>48.47</td>
<td>0.31</td>
</tr>
<tr>
<td>HCN+HNC</td>
<td>33.56</td>
<td>0.45</td>
</tr>
<tr>
<td>Average absolute error</td>
<td>0.85</td>
<td>0.89</td>
</tr>
</tbody>
</table>
calculations are performed at RHF CCSD(T) and RHF ACCSD(T) in a frozen core DZ basis set truncated using frozen natural orbitals to 60% of the virtual space. For the RDX equilibrium and the concerted transition state, these choices lead to 42 active occupied orbitals and 120 active virtual orbitals, for methylidenitramine it is 14 active occupied orbitals and 40 active virtual orbitals.

The results of these calculations are summarized in Table VIII and shown graphically in Fig. 12. All results are offset so that RDX equilibrium energies are set to be 0. There are two firm conclusions that can be made from these results: First, despite the concerted nature of this transition state, CCSD(T) and ACCSD(T) agree to within 0.5 kcal/mol. Therefore, one can trust the CCSD(T) energies for this transition state. Second, the coupled-cluster results indicate that the activation barrier of this pathway is higher for this transition state. Second, the coupled-cluster results have items to recommend it. Recent work has shown that the failure of RHF CCSD(T) over UHF CCSD(T), and the relatively surprising lack of improvement for UHF ACCSD(T) over UHF CCSD(T), we have shown that the failure of RHF CCSD(T) at long bond distances is more complicated than one might initially expect. It is not simply the presence of small denominators due to quasidegeneracy in the (T) correction that leads to collapse of the CCSD(T) energy. Rather, it is the $T_2$ contraction that is overweighted at these bond lengths. The underlying cause of the large $T_2$ values does derive from a small denominator, but rather than a small $e_{ikj}^{abc}$, it is the implicit $e_{ij}^{abc}$ denominator within $T_2$ that becomes too small. Therefore, to fundamentally remedy the failure of triples methods at long bond distances one cannot focus solely on the triples correction, but must also take into account the

**TABLE VIII.** RDX concerted reaction pathway critical point energies in kcal/mol for B3LYP in a 6-31(d) basis (Ref. 16) and CCSD(T) and ACCSD(T) calculations in a 60% truncated DZP basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta E_{act}$ (kcal/mol)</th>
<th>$\Delta E_{rxn}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>59.4</td>
<td>45.9</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>65.8</td>
<td>43.6</td>
</tr>
<tr>
<td>ACCSD(T)</td>
<td>66.2</td>
<td>43.8</td>
</tr>
</tbody>
</table>

**FIG. 11.** Pictorial representation of the RDX concerted dissociation “triple whammy” transition state.

**FIG. 12.** RDX reaction profile comparison for concerted transition state.
misbehavior of the RHF CCSD wave function, though the RHF CCSD energy appears adequate.

It should be noted that the ACCSD(T) method is generalizable to higher orders in various ways.\textsuperscript{6,42,43} In light of the results presented here, it is likely that methods such as ACCSDT\( ^{(Q)} \), etc., could be excellent choices for high-accuracy descriptions of potential energy surfaces while retaining the advantages of single-reference coupled-cluster theory.

Further work is necessary to definitely determine whether the RDX concerted transition state is a possibly important decomposition pathway. Based on the calculation thus far it seems unlikely.

ACKNOWLEDGMENTS

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5 J. F. Stanton, J. Gauss, J. D. Watts \textit{et al.}, \textit{ACES II} is a program product of the Quantum Theory Project, University of Florida. Integral packages included are \textit{VMD} (J. Almlof and P. R. Taylor); \textit{VPcaps} (P. Taylor); \textit{AABACS} (T. Helgaker, H. J. Aa. Jensen, P. Jorgensen, J. Olsen, and P. R. Taylor).