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Rigorously extensive orbital-invariant renormalized perturbative triples corrections from quasi-variational coupled cluster theory

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We show that, by making use of the linked tensor objects inherent to the approach, Orbital-optimised Quasi-Variational Coupled Cluster Theory (OQVCCD) leads naturally to a computationally-trivial, rigorously extensive, and orbital-invariant renormalization of the standard (T) correction for the perturbative inclusion of the effects of connected triple excitations. The resulting prototype method, renormalized perturbative triple OQVCCD (R-OQVCCD(T)), is demonstrated to predict potential energy curves for single bond-breaking processes of significantly higher accuracy than OQVCCD with the standard perturbative triple-excitation correction (OQVCCD(T)) itself, and to be in good numerical correspondence with the existing renormalized (R-CCSD(T)) and completely renormalized (CR-CCSD(T)) coupled-cluster singles doubles triples methods, while continuing to provide descriptions of multiple bond-breaking processes of OQVCCD(T) quality. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4791636>]

I. INTRODUCTION

Contemporary molecular electronic structure calculations have become extremely powerful tools for predictive chemistry, but while Kohn-Sham Density Functional Theory^{1,2} (DFT) is often the method of choice for fast and moderately accurate calculations on extended molecular systems, wavefunction-based *ab initio* methods typically achieve extremely high accuracy by seeking controlled approximations to solutions of the Born-Oppenheimer electronic Schrödinger equation.

In the case of the single-reference *ab initio* methods, the Hartree-Fock^{3,4} (HF) approximation is first made, and a scheme with the potential to account for the correlation of the electrons is then applied, a huge number of which have been proposed. These include Many-Body Perturbation Theory⁵ (MBPT), Configuration Interaction⁶ (CI), and electron pair methods such as the Coupled Pair Functional^{7,8} (CPF), the Coupled Electron Pair Approximation⁹⁻¹³ (CEPA), or the Linear Coupled Pair Many-Electron Theory^{13,14} (LCPMET or CEPA(0)), and Traditional Coupled Cluster¹⁵⁻²⁰ (TCC) Theory. TCC, typically truncated to the level of single and double excitations (CCSD) for reasons of computational cost, has become the dominant approach, with the others falling out of widespread use due to the problematic lack of extensivity, the questionable convergence of perturbation series²¹⁻²³ or the lack of invariance to rotations of the underlying orbital spaces, for example.

CCSD can be additionally combined with perturbative estimates of the effects of higher excitations, accounting for more of the omitted correlation energy, and significantly boosting its quantitative accuracy. Modern developments in electronic structure theory such as explicit correlation²⁴ and local correlation²⁵ have even been demonstrated to be highly

successful in mitigating the requirements of large basis sets and the steep scaling of computational cost with system size suffered by the *ab initio* methods, respectively.

Unfortunately, while TCC is highly capable of capturing the dynamic electron correlation omitted by the HF method, there exist certain molecular situations for which no single determinant dominates the description of the electronic structure, and the HF approximation itself breaks down, such that single-reference methods typically perform erratically. This regime of strong non-dynamic (or static) electron correlation occurs commonly in multiple bond dissociations, and multi-radicals, for example. In addition, the breakdown of perturbation theory that occurs as molecular orbitals approach degeneracy makes the treatment of even *single* bond-breaking with hybrid CC-MBPT methods such as CCSD(T)^{26,26} problematic.

For an adequate description of bond-breaking, one may apply, for example, Internally-Contracted Multireference CI,²⁸ along with some *a posteriori* correction for the lack of extensivity, such as that of Davidson,²⁹ or other theories,³⁰⁻³² but multireference schemes commonly suffer from the expensive scaling of computational cost with system size and require the specification of an appropriate active space, making them difficult to deploy on large or chemically-intricate systems, in stark contrast to the highly black-box nature of the single-reference methods.

In recent years, much progress has been made on purely single-reference descriptions of bond-breaking by the renormalization of the perturbative corrections applied to CCSD,³³⁻³⁶ significantly mitigating the effect of the overestimation of the remaining correlation energy by (T) in the bond-breaking regime. This has been further extended to a generating functionals based formulation of the method of moments.³⁷ We also note that the family of variants of CCSD(T) based on the CCSD lagrangian multipliers³⁸⁻⁴¹ can often perform more robustly than CCSD(T) as bonds are

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broken. Unfortunately, these approaches only defer the breakdown of perturbation theory, and the resulting methods are no more robust to the failure of the HF approximation than the electronic structure method to which these renormalized corrections are applied. These problems can be overcome in recently-developed hybrid methods that combine active-space CC with CCSD(T),⁴² but with increased complexity relative to single-determinant reference approaches. We have recently demonstrated that a single-determinant reference CC-like method posed as an approximately variationally bounded functional need not break down so readily in the non-dynamic regime.^{43–45} Furthermore, we have surprisingly discovered that when the essential physics of strong non-dynamic correlation is captured by the underlying electronic structure method, the perturbative corrections for higher excitations also need not break down, and our OQVCCD(T)^{45–47} method has been demonstrated to predict qualitatively correct molecular dissociation curves for dinitrogen⁴⁷ and many other multiply-bonded molecules,⁴⁸ as well as for singlet multiradicals.⁴⁹ However, since the breakdown of perturbation theory remains the principal problem for the dissociation of singly-bonded molecules, this paper discusses the possibility of combining a renormalization scheme for (T) with our quasi-variational functional, exploring to what extent it is possible to obtain a method capable of a unified description of equilibrium phenomena, single bond-breaking and multiple bond-breaking, all within a strictly single-reference framework.

II. THEORY

A. Coupled cluster theories

In contrast to CI, for which the parameterization is linear,

$$|\Phi_{\text{CI}}\rangle = (1 + \hat{T})|\Phi_0\rangle, \quad (1)$$

the CC ansatz is that the molecular wavefunction should be parameterized exponentially,

$$|\Phi_{\text{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle, \quad (2)$$

in terms of all possible determinants that can be generated by the excitation operator, \hat{T} , from the single-determinantal reference wavefunction, $|\Phi_0\rangle$. It is conventional to partition this operator by the order of the excited determinants generated,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots, \quad (3)$$

where \hat{T}_1 generates singly-excited determinants,

$$\hat{T}_1|\Phi_0\rangle = T_a^i a^\dagger i |\Phi_0\rangle = T_a^i |\Phi_i^a\rangle, \quad (4)$$

and \hat{T}_2 generates doubly-excited determinants,

$$\hat{T}_2|\Phi_0\rangle = \frac{1}{4} T_{ab}^{ij} b^\dagger j a^\dagger i |\Phi_0\rangle = \frac{1}{4} T_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \quad (5)$$

for example. The cluster operator is usually truncated to the level of single and double excitations, $\hat{T} = \hat{T}_1 + \hat{T}_2$, for reasons of computational practicality, with the exponential parameterization maintaining the correct separability of the wavefunction, unlike in CI.

The most intuitive way to calculate the ground-state energy associated with the CC wavefunction is to proceed as in

variational CI,⁵⁰

$$E_{\text{CI}} = \frac{\langle \Phi_0 | (1 + \hat{T})^\dagger \hat{H} (1 + \hat{T}) | \Phi_0 \rangle}{\langle \Phi_0 | (1 + \hat{T})^\dagger (1 + \hat{T}) | \Phi_0 \rangle}, \quad (6)$$

and to find the optimal quantum mechanical energy associated with the CC wavefunction as the minimum of the following functional:

$$E_{\text{VCC}} = \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} = \langle \Phi_0 | e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} | \Phi_0 \rangle_L. \quad (7)$$

This is Variational Coupled Cluster (VCC), but is unfortunately of factorial computational complexity, independent of the truncation of \hat{T} , and alternative procedures are instead sought.

The Traditional Coupled Cluster (TCC) method instead inserts the CC ansatz into the electronic Schrödinger Equation, premultiplies it by $e^{-\hat{T}}$,

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E_{\text{TCC}} | \Phi_0 \rangle, \quad (8)$$

and subsequently projects this equation onto the various manifolds of excited determinants in order to determine the energy and equations to be solved for \hat{T} . For example, in the case of $\hat{T} = \hat{T}_1 + \hat{T}_2$, the CCSD method is defined by the following set of equations:

$$\langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E_{\text{CCSD}}, \quad (9)$$

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \quad (10)$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0. \quad (11)$$

In contrast to VCC, the similarity transformed Hamiltonian, $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$, of TCC theory obeys the Baker-Campbell-Hausdorff Theorem,⁵¹ ensuring that TCC calculations are always of polynomial, as opposed to factorial complexity. In light of this, the TCC method has become the *de facto* standard for performing coupled cluster calculations, and commonly achieves exceptional accuracy for the description of a wide variety of molecular phenomena.

It is unfortunate, therefore, that CCSD can perform erratically, or even collapse catastrophically to energies far below the exact ground-state Schrödinger energy eigenvalue when the Hartree-Fock approximation fails. This failure is commonly associated with the non-Hermitian nature of \bar{H} , and the subsequent projective determination of the amplitude equations. A VCC energy, however, is variationally bounded, and a growing body of numerical evidence^{52–58} demonstrates this method to predict physically correct potential energy curves for systems for which TCC is simply wrong. There is therefore significant interest in the development of approximations to the VCC method of practical complexities that might allow the description of strongly non-dynamic processes without resorting to the more expensive (and less easily applicable) multireference methods. Unfortunately, many of the simpler approximations to VCC do not remain faithful to the spirit of a true CC method,⁴⁴ violating properties such as rigorous

TABLE I. Linked $\mathcal{O}(T^3)$ contributions to VCCD along with the equivalent QVCCD terms, where $\langle \hat{T}^\dagger \hat{T} \rangle = \frac{1}{4} T_{ab}^{ij} T_{ij}^{ab}$, and where $\{e, \bar{e}\}$ and $\{h, \bar{h}\}$ are unsummed labels denoting the two spinorbitals occupied and unoccupied in the reference wavefunction, respectively.

Diagram	$\frac{1}{2!} \langle \hat{T}_2^\dagger \hat{H} \hat{T}_2 \rangle_L$ Term	QVCCD Term	2 Electrons	2 Holes
	$-\frac{1}{4} T_{ij}^{ac} T_{cd}^{kl} T_{kl}^{bd} \langle ij ab \rangle$	$-\frac{1}{2} T_{ij}^{ac} \mathcal{A} \eta_c^b \langle ij ab \rangle$	$-T_{e\bar{e}}^{ac} \mathcal{A} \eta_c^b \langle e\bar{e} ab \rangle$	$-T_{ij}^{h\bar{h}} \langle \hat{T}^\dagger \hat{T} \rangle \langle ij h\bar{h} \rangle$
	$-\frac{1}{4} T_{ik}^{ab} T_{cd}^{kl} T_{jl}^{cd} \langle ij ab \rangle$	$-\frac{1}{2} T_{ik}^{ab} \mathcal{B} \eta_j^k \langle ij ab \rangle$	$-T_{e\bar{e}}^{ab} \langle \hat{T}^\dagger \hat{T} \rangle \langle e\bar{e} ab \rangle$	$-T_{ik}^{h\bar{h}} \mathcal{B} \eta_j^k \langle ij h\bar{h} \rangle$
	$+\frac{1}{16} T_{kl}^{ab} T_{cd}^{kl} T_{ij}^{cd} \langle ij ab \rangle$	$+\frac{1}{8} T_{kl}^{ab} \mathcal{C} \eta_{ij}^{kl} \langle ij ab \rangle$	$+\frac{1}{2} T_{e\bar{e}}^{ab} \langle \hat{T}^\dagger \hat{T} \rangle \langle e\bar{e} ab \rangle$	$+\frac{1}{2} T_{ij}^{h\bar{h}} \langle \hat{T}^\dagger \hat{T} \rangle \langle ij h\bar{h} \rangle$
	$+\frac{1}{2} T_{ik}^{ac} T_{cd}^{kl} T_{lj}^{db} \langle ij ab \rangle$	$+\frac{1}{2} T_{ik}^{ac} \mathcal{D} \eta_{lj}^{kb} \langle ij ab \rangle$	$+T_{e\bar{e}}^{ac} \mathcal{A} \eta_c^b \langle e\bar{e} ab \rangle$	$+T_{ik}^{h\bar{h}} \mathcal{B} \eta_j^k \langle ij h\bar{h} \rangle$

extensivity or equivalence to Full CI (FCI) when the cluster operator is complete.

We have recently proposed the Orbital-Optimized⁵⁹ Quasi-Variational Coupled Cluster⁴⁵ (OQVCCD) method, with the goal of remedying this situation; the OQVCCD predicted ground-state energy is defined to be the minimum of the following CEPA(0)-like functional,

$$E_{\text{OQVCCD}} = \langle \hat{H} \rangle + 2 \langle \hat{H} \hat{T}_2 \rangle + \langle {}_1 \hat{T}_2^\dagger (\hat{H} - \langle \hat{H} \rangle) {}_1 \hat{T}_2 \rangle, \quad (12)$$

with respect to both the doubles amplitudes, $\{T_{ab}^{ij}\}$, and the orbitals.⁵⁹ The renormalized cluster operator is defined through

$${}_q \hat{T}_2 |\Phi_0\rangle = \frac{1}{4} {}_q T_{ab}^{ij} b^\dagger j a^\dagger i |\Phi_0\rangle = \frac{1}{4} {}_q T_{ab}^{ij} |\Phi_{ij}^{ab}\rangle \quad (13)$$

with renormalized amplitudes defined as follows:

$$\begin{aligned} {}_q T_{ab}^{ij} = & 2 \left[\frac{1}{2} (1 - \tau_{ab}) \left(\mathcal{A} \mathbf{U}^{-\frac{q}{2}} \right)_a^c T_{cb}^{ij} \right] \\ & + 2 \left[\frac{1}{2} (1 - \tau_{ij}) \left(\mathcal{B} \mathbf{U}^{-\frac{q}{2}} \right)_k^i T_{ab}^{kj} \right] \\ & - 1 \left[\frac{1}{2} \left(\mathcal{C} \mathbf{U}^{-\frac{q}{2}} \right)_{kl}^{ij} T_{ab}^{kl} \right] \\ & - 2 \left[\frac{1}{4} (1 - \tau_{ij})(1 - \tau_{ab}) \left(\mathcal{D} \mathbf{U}^{-\frac{q}{2}} \right)_{ak}^{ic} T_{cb}^{kj} \right], \quad (14) \end{aligned}$$

where,

$$\begin{aligned} \mathcal{A} U_b^a &= \delta_b^a + \mathcal{A} \eta_b^a & \mathcal{C} U_{kl}^{ij} &= \delta_{kl}^{ij} + \mathcal{C} \eta_{kl}^{ij}, \\ \mathcal{B} U_j^i &= \delta_j^i + \mathcal{B} \eta_j^i & \mathcal{D} U_{aj}^{ib} &= \delta_{aj}^{ib} + \mathcal{D} \eta_{aj}^{ib}, \end{aligned} \quad (15)$$

and where,

$$\mathcal{A} \eta_b^a = \langle \hat{T}^\dagger a^\dagger b \hat{T} \rangle = \frac{1}{2} T_{bc}^{ij} T_{ij}^{ac}, \quad (16)$$

$$\mathcal{B} \eta_j^i = \langle \hat{T}^\dagger j i^\dagger \hat{T} \rangle = \frac{1}{2} T_{ab}^{ik} T_{jk}^{ab}, \quad (17)$$

$$\mathcal{C} \eta_{kl}^{ij} = \langle \hat{T}^\dagger k l j^\dagger i^\dagger \hat{T} \rangle = \frac{1}{2} T_{ab}^{ij} T_{kl}^{ab}, \quad (18)$$

$$\mathcal{D} \eta_{aj}^{ib} = \langle \hat{T}^\dagger j b^\dagger a i^\dagger \hat{T} \rangle = T_{ac}^{ik} T_{jk}^{bc}. \quad (19)$$

This theory may be understood from two perspectives. First, the internal mathematical structure of double-excitation VCC (VCCD), consisting of equalities and cancellations between diagrams in the limits of 2 electrons or 2 holes (see Table I), is exploited, such that a both exact and extensive approximation of VCCD can be constructed from only a subset of the total VCCD terms, albeit an infinite one, and the powers of the \mathcal{A} , \mathcal{B} , \mathcal{C} , and \mathcal{D} transformation matrices generate geometric series of linked VCCD terms that are combined as a linear combination to construct such an exact subset. The other perspective, is that in the limit of either 2 electrons or 2 holes,

$${}_q \hat{T}_2 \rightarrow \frac{\hat{T}_2}{(1 + \langle \hat{T}_2^\dagger \hat{T}_2 \rangle)^{q/2}}, \quad (20)$$

such that CI with double excitations (CID), equivalent in this case to FCI, is then recovered. For more complicated systems, the effect of the inverse matrices is to renormalize the functional analogously to division by the CI denominator, but by using only explicitly linked terms from which to construct the functional. More accurately, our theory can be understood to generate a linked approximation to the VCC functional, through the application of Cramer's formula⁶⁰⁻⁶² for the inverse of each \mathbf{U} matrix; the division by $|\mathbf{U}|$ generates an approximation to $\langle e^{\hat{T}^\dagger} e^{\hat{T}} \rangle$, and the cofactor matrix generates the higher numerator terms present in $\langle e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} \rangle$ from the CEPA(0)-like functional. For a more thorough explanation of the workings of this novel electronic structure method, we refer the reader to Ref. 46 in particular.

We have previously demonstrated that the OQVCCD method is more faithful to VCCSD than either CCSD or the related Brueckner Coupled Cluster Doubles⁶³⁻⁶⁵ (BCCD) method,

$$\langle \Phi_0 | \hat{H} e^{\hat{T}_2} | \Phi_0 \rangle = E_{\text{BCCD}}, \quad (21)$$

$$\langle \Phi_i^a | \hat{H} e^{\hat{T}_2} | \Phi_0 \rangle = 0, \quad (22)$$

$$\langle \Phi_{ij}^{ab} | \hat{H} e^{\hat{T}_2} | \Phi_0 \rangle = T_{ij}^{ab} E_{\text{BCCD}}, \quad (23)$$

when non-dynamic correlation becomes strong.⁴⁵ When combined with a perturbative correction for the effects of triple excitations, the subject of Sec. II B, it is particularly powerful for the strictly single-reference description of multiple bond-breaking,⁴⁸ even capable of describing the dissociation of dinitrogen,⁴⁷ and also singlet multiradicals,⁴⁹ for example.

B. Perturbative corrections for the effects of connected triple excitations

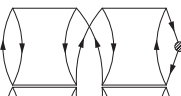
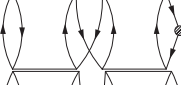
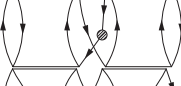

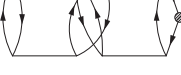
It is well known that a single-reference method must take the effects of at least triple excitations into account in order to achieve chemically-accurate quantitative descriptions of molecular phenomena. Unfortunately, the explicit inclusion of triple excitations into a CC scheme is prohibitively expensive, with the full CCSDT treatment scaling with $\mathcal{O}(N^8)$ complexity, and even the simplest modifications of the CCSD equations, such as CCSDT-1,⁶⁶ scaling with iterative $\mathcal{O}(N^7)$ complexity, significantly more expensive than the $\mathcal{O}(N^6)$ cost of the basic CCSD method. Instead, it is common practice to incorporate triples through a many-body perturbation theory estimate of their energetic effects that may be performed after the completion of the CCSD calculation in a single non-iterative $\mathcal{O}(N^7)$ step, the most common of which are the [T],²⁶ (T),²⁷ and -T⁶⁷ corrections. Of these, [T] is the simplest; an expansion of Full TCC in orders of Møller-Plesset perturbation theory reveals that CCSD is correct to third-order, but omits terms containing triple excitations from fourth-order, so CCSD[T] incorporates also these omitted terms. In CCSD(T), further fifth-order triples-containing terms are added to the energy that have been justified in a variety of ways by different authors.^{27,68,69} CCSD(T) tends to work exceptionally well, but it has been noted that this may be because (T) typically overestimates the correlation energy associated with triples, effectively accounting for some of the quadruples energy.

We have previously applied the [T] correction (which is, of course, equivalent to a (T) correction for vanishing singles), to the OQVCCD method with great success; OQVCCD(T)

has been demonstrated to achieve similar levels of numerical accuracy around equilibria to BCCD(T), and is significantly more robust for multiple bond-breaking processes.^{45–48}

Let us here explain in more detail why [T] is directly applicable to OQVCCD. Since single excitations vanish, we are concerned only with the incorporation of the fourth-order terms omitted by OQVCCD. It has been shown, for example by Kutzelnigg,^{70,71} that CCD and VCCD are equivalent to fourth-order in Møller-Plesset theory, as are CCDT and VCCDT, and the same [T] correction for missing fourth-order terms may therefore be applied to VCCD as CCD. In the case of QVCCD, a Møller-Plesset expansion reveals that all terms through third-order perturbation theory enter from the CEPA(0)-like terms that are included exactly by our functional. The first non-trivial terms are $\langle \hat{T}_2^\dagger \hat{V} \hat{T}_2 \rangle_L$ and $\frac{1}{4} \langle (\hat{T}_2^\dagger)^2 \hat{F} \hat{T}_2 \rangle_L$, which enter at fourth-order. The QVCCD functional has been designed such that $\langle \hat{T}_2^\dagger \hat{V} \hat{T}_2 \rangle_L$ is obtained exactly, as can be verified by an examination of Table I. As a consequence of this construction, $\frac{1}{4} \langle (\hat{T}_2^\dagger)^2 \hat{F} \hat{T}_2 \rangle_L$ is also captured exactly. This can be confirmed similarly by an examination of the 1-electron $\mathcal{O}(T^4)$ terms, for which we have given the subset containing the all-internal elements of the Fock matrix in Table II.⁷² The corresponding all-external elements may be inferred from hole-particle symmetry. QVCCD is therefore equivalent to VCCD, and therefore also to CCD, through fourth-order Møller-Plesset theory. This means that the standard [T] or (T) corrections may be applied to OQVCCD to account for the omitted triples-containing terms at fourth-order. In fact, since OQVCCD omits all terms containing connected triples, any perturbative correction that accounts solely for triples-containing terms may be applied to it, even those derived from a TCC perspective. These can still be expected to work well on the grounds that OQVCCD is, except when non-dynamic correlation becomes strong, almost coincident with the BCCD method, and therefore requires the same energetic correction. Stated another way, for this prototypical investigation, including the higher-order effects of TCC-like triples (as opposed to VCC-like triples) is better than omitting these contributions entirely.

TABLE II. Linked $\mathcal{O}(T^4)$ contributions to VCCD involving the internal-internal Fock matrix elements, $\{f_i^j\}$, along with the equivalent QVCCD terms.

Diagram	$(\frac{1}{2!})^2 \langle (\hat{T}_2^\dagger)^2 \hat{H} \hat{T}_2 \rangle_L$ Term	QVCCD Term	2 Electrons	2 Holes	
A		$+ \frac{1}{2} f_i^j T_{jk}^{ac} T_{ab}^{ik} T_{cd}^{ml} T_{ml}^{bd}$	$+ f_i^j T_{jk}^{ac} T_{ab}^{ik} \mathcal{A} \eta_c^b$	$+ 2 f_e^e T_{ee}^{ac} T_{ab}^{e\bar{e}} \mathcal{A} \eta_c^b$	$+ 2 f_i^j \mathcal{B} \eta_j^i \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$
B1		$+ \frac{1}{4} f_i^j T_{jk}^{ab} T_{ab}^{il} T_{lm}^{cd} T_{cd}^{km}$	$+ \frac{1}{2} f_i^j T_{jk}^{ab} T_{ab}^{il} \mathcal{B} \eta_l^k$	$+ 2 f_e^e \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$+ f_i^j c \eta_{jl}^{ik} \mathcal{B} \eta_k^l$
B2		$+ \frac{1}{4} f_i^j T_{mk}^{ab} T_{ab}^{ik} T_{jl}^{cd} T_{cd}^{ml}$	$+ \frac{1}{2} f_i^j T_{mk}^{ab} T_{ab}^{ik} \mathcal{B} \eta_j^m$	$+ 2 f_e^e \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$+ f_i^j c \eta_{jl}^{ik} \mathcal{B} \eta_k^l$
C		$- \frac{1}{8} f_i^j T_{jk}^{cd} T_{ab}^{ik} T_{cd}^{lm} T_{lm}^{ab}$	$- \frac{1}{4} f_i^j T_{ab}^{ik} T_{lm}^{ab} c \eta_{jk}^{lm}$	$- 2 f_e^e \langle \hat{T}_2^\dagger \hat{T}_2 \rangle \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$	$- f_i^j \mathcal{B} \eta_j^i \langle \hat{T}_2^\dagger \hat{T}_2 \rangle$
D		$- f_i^j T_{jl}^{ac} T_{ab}^{ik} T_{km}^{bd} T_{dc}^{ml}$	$- f_i^j T_{jl}^{ac} T_{ab}^{ik} \mathcal{D} \eta_{kc}^{bl}$	$- 2 f_e^e T_{ee}^{ac} T_{ab}^{e\bar{e}} \mathcal{A} \eta_c^b$	$- 2 f_i^j c \eta_{jl}^{ik} \mathcal{B} \eta_k^l$

However, in light of the form taken by (T),

$$E_{(T)} = \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | \hat{T}_2^\dagger \hat{V} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \quad (24)$$

where singles have been taken to vanish, there exist systems for which the denominator becomes small, and the perturbative correction becomes too large, grossly overestimating the remaining uncaptured correlation energy, and leading to a physically-incorrect description of, for example, the dissociation of simple molecules such as difluorine, F₂. Since this is a problem associated with the breakdown of perturbation theory only, improving the variational boundedness of the underlying electronic structure theory does nothing to alleviate this problem, but can be solved by the renormalization of the perturbative correction.^{33–36}

We now provide a rationale for renormalization, following the arguments developed by Nooijen and LeRoy.⁷³ Consider the Hermitian adjoint of the Full CC Schrödinger Equation,

$$\langle \Phi_0 | e^{\tilde{T}^\dagger} \hat{H} = E_{\text{FCC}} \langle \Phi_0 | e^{\tilde{T}^\dagger}, \quad (25)$$

where \tilde{T} is the full (untruncated and exact) cluster operator,

$$\tilde{T} = \tilde{T}_1 + \tilde{T}_2 + \tilde{T}_3 + \dots \quad (26)$$

Postmultiplying by the CCSD exponential operator,

$$\langle \Phi_0 | e^{\tilde{T}^\dagger} \hat{H} e^{\tilde{T}} = E_{\text{FCC}} \langle \Phi_0 | e^{\tilde{T}^\dagger} e^{\tilde{T}}, \quad (27)$$

where $\hat{T} = \hat{T}_1 + \hat{T}_2$ only, projecting onto the reference wavefunction,

$$\langle \Phi_0 | e^{\tilde{T}^\dagger} \hat{H} e^{\tilde{T}} | \Phi_0 \rangle = E_{\text{FCC}} \langle \Phi_0 | e^{\tilde{T}^\dagger} e^{\tilde{T}} | \Phi_0 \rangle, \quad (28)$$

and rearranging yields the following expression for the FCC energy:

$$E_{\text{FCC}} = \frac{\langle \Phi_0 | e^{\tilde{T}^\dagger} \hat{H} e^{\tilde{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\tilde{T}^\dagger} e^{\tilde{T}} | \Phi_0 \rangle}. \quad (29)$$

By inserting the unit operator, $e^{\hat{T}} e^{-\hat{T}}$,

$$\begin{aligned} E_{\text{FCC}} &= \frac{\langle \Phi_0 | e^{\tilde{T}^\dagger} e^{\hat{T}} e^{-\hat{T}} \hat{H} e^{\tilde{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\tilde{T}^\dagger} e^{\hat{T}} e^{-\hat{T}} | \Phi_0 \rangle} \\ &= \langle \Phi_0 | e^{G[\hat{T}, \tilde{T}^\dagger]} e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle. \end{aligned} \quad (30)$$

In the above, we have introduced Arponen's construction,⁷⁴ where for two connected operators \hat{A} , \hat{B} and a normalised wavefunction ϕ ,

$$\frac{\langle \phi | \exp(\hat{B}) \exp(\hat{A}) | \phi \rangle}{\langle \phi | \exp(\hat{B}) \exp(\hat{A}) | \phi \rangle} = \langle \phi | \exp(G[\hat{A}, \hat{B}]) | \phi \rangle, \quad (31)$$

where $G[\hat{A}, \hat{B}]$ is also a connected operator. Within this notation, for any operator \hat{Q} , expectation values that correspond to physical quantities, i.e., contain only linked parts, can be simplified:

$$\begin{aligned} \langle \phi | \exp(G[\hat{A}, \hat{B}]) \hat{Q} | \phi \rangle &= \frac{\langle \phi | \exp(\hat{B}) \exp(\hat{A}) \hat{Q} | \phi \rangle}{\langle \phi | \exp(\hat{B}) \exp(\hat{A}) | \phi \rangle} \\ &= \langle \phi | \exp(\hat{B}) \exp(\hat{A}) \hat{Q} | \phi \rangle_L \end{aligned} \quad (32)$$

since the linked part of the denominator is unity.

Introducing a resolution of the identity in the basis of all possible determinants, grouped by excitation level,

$$E_{\text{FCC}} = \sum_{K \in \{0, \text{S}, \text{D}, \text{T}, \text{Q}, \dots\}} \langle \Phi_0 | e^{G[\hat{T}, \tilde{T}^\dagger]} | K \rangle \langle K | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle \quad (33)$$

and noting that the CCSD cluster operators satisfy the CCSD equations, Eqs. (9)–(11), we obtain an expression for the optimum correction that should be applied to CCSD to give the FCC energy,

$$E_{\text{FCC}} = E_{\text{CCSD}} + \sum_{K \in \{\text{T}, \text{Q}, \dots\}} \langle \Phi_0 | e^{G[\hat{T}, \tilde{T}^\dagger]} | K \rangle \langle K | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle. \quad (34)$$

We then consider the case that $|\Phi_0\rangle$ is a non-HF reference wavefunction such that all single excitation amplitudes vanish, that is, the correction is of the type that can be applied to BCCD or OQVCCD, and consider the effects of triple excitations in the identity resolution,

$$\delta E = \sum_{K \in \text{T}} \langle \Phi_0 | e^{G[\hat{T}_2, \tilde{T}_2^\dagger + \tilde{T}_3^\dagger]} | K \rangle \langle K | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle. \quad (35)$$

Since the direct evaluation of this correction would be very complex, we now construct a leading-order approximation to it, by taking \tilde{T}_2 to be the converged \hat{T}_2 operator, and approximating \tilde{T}_3 using the usual second-order perturbation theory as $\hat{T}_3^{(2)}$, where

$$\hat{T}_3^{(2)} | \Phi_0 \rangle = \left(\frac{1}{3!}\right)^2 T_{abc}^{ijk(2)} | \Phi_{ijk}^{abc} \rangle, \quad (36)$$

and

$$T_{ijk}^{abc(2)} = \frac{\langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}. \quad (37)$$

This gives

$$\delta E \approx \sum_{K \in \text{T}} \frac{\langle \Phi_0 | e^{\hat{T}_2^\dagger} e^{\hat{T}_3^{(2)\dagger}} e^{\hat{T}_2} | K \rangle \langle K | (\hat{H} e^{\hat{T}_2})_c | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}_2^\dagger} e^{\hat{T}_3^{(2)\dagger}} e^{\hat{T}_2} | \Phi_0 \rangle}. \quad (38)$$

Finally, to obtain a leading-order analysis, we omit the term quadratic in \hat{T}_2 from the triples moment, and truncate the exponential of \hat{T}_3 at first order to give

$$\delta E \approx \sum_{K \in \text{T}} \frac{\langle \Phi_0 | e^{\hat{T}_2^\dagger} \hat{T}_3^{(2)\dagger} e^{\hat{T}_2} | K \rangle \langle K | (\hat{H} \hat{T}_2)_c | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}_2^\dagger} e^{\hat{T}_2} | \Phi_0 \rangle}. \quad (39)$$

This expression is the (T) energy rescaled by division by $\langle \Phi_0 | e^{\hat{T}_2^\dagger} e^{\hat{T}_2} | \Phi_0 \rangle$. What we have done therefore, is to show how (T) emerges from of Eq. (35). However, this indirect approach of constructing a perturbative approximation to Eq. (35) reveals that even the simplest perturbative corrections for triples such as (T) require rescaling by denominator factors, and this does not become apparent solely from an examination of those terms omitted at lowest-order in Møller-Plesset theory. In practice, this denominator is extremely close to unity

around molecular equilibria, such that (T) is then fully recovered. However, the denominator tends to grow large in the bond-breaking regime, and this has the effect of tempering the corresponding growth of (T).

Piecuch *et al.*^{33–36} therefore sought to incorporate the effect of the renormalizing denominator, as well as to add additional terms to the perturbative correction by relaxing some of the approximations made above, in order to achieve both highly accurate and very robust perturbative corrections. While early attempts violated extensivity,³³ or achieved extensivity only in a localized orbital basis,³⁴ more recent work has resulted in the CR-CC(2,3) method³⁵ that is rigorously extensive, and which has been demonstrated to be simply excellent for the description of single bond-breaking processes.³⁶ Despite this, CR-CC(2,3) is not without its problems; the method exploits the left eigenstates of the similarity-transformed Hamiltonian, and therefore requires a full solution of the CCSD \hat{A} equations in addition to the equations that determine \hat{T} , rendering the method roughly *twice* as computationally expensive as a CCSD(T) calculation. Furthermore, we have previously shown CR-CC(2,3) to perform poorly for systems involving strong non-dynamic electron correlation,⁴⁸ due to the failure of the underlying CCSD method, making CR-CC(2,3) inferior to OQVCCD(T) for such problems. A long-term goal would therefore be the development of a renormalized triples correction as powerful as that of CR-CC(2,3) to the OQVCCD method.

Nooijen and LeRoy⁷³ pursued the linked-diagram form of Eqs. (32) and (35), i.e.,

$$\delta E = \sum_{\substack{i < j < k \\ a < b < c}} \langle \Phi_0 | e^{\hat{T}_2^\dagger + \hat{T}_3^\dagger} e^{\hat{T}_2} | \Phi_{ijk}^{abc} \rangle_L \langle \Phi_{ijk}^{abc} | (\hat{H} e^{\hat{T}_2})_c | \Phi_0 \rangle, \quad (40)$$

or, applying the same approximations as described previously,

$$\delta E \approx \sum_{\substack{i < j < k \\ a < b < c}} \langle \Phi_0 | e^{\hat{T}_2^\dagger} \hat{T}_3^{(2)\dagger} e^{\hat{T}_2} | \Phi_{ijk}^{abc} \rangle_L \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle. \quad (41)$$

This is, of course, related to the cancellations that occur between the numerator and denominator in the VCC functional. In contrast to the approach of Piecuch, by performing the exact cancellation first and then seeking an approximation to the explicitly linked expression, Nooijen and LeRoy⁷³ were able to construct a rigorously extensive and orbital-invariant renormalized triples scheme directly. It is then the higher-order terms, or the sum to infinity of the resulting non-terminating series, that has the effect of tempering the leading-order (T) term.

Again, on the grounds that the direct application of Eq. (41) as an *a posteriori* correction is not computationally feasible, Nooijen and LeRoy⁷³ attempted an approximation based on the introduction of a linked tensor, μ_j^i , to account for low-order exclusion-principle violating (EPV) contributions, and then essentially made an educated guess for the function of the renormalizing factor required to account for the higher-order terms. Unfortunately, it is difficult to objectively evaluate the performance of this renormalized triples scheme,

because it is applied only to the extensive singles-doubles configuration interaction (p-XCISD) method proposed in the same paper.⁷³ All that one can say is that the *combination* certainly cannot treat the dissociation of difluorine correctly. It also seems to be implied that the calculation must be performed in the basis that diagonalizes $\hat{\mu}$, and there is no guarantee that this same basis also diagonalizes the Fock operator, a necessity for performing practical (T) calculations with non-HF reference wavefunctions.

However, in light of our work,^{43–46} the μ_j^i tensor may be viewed alternatively as a means of approximating $\langle \Phi_0 | \hat{T}_2^\dagger \hat{T}_3^{(2)\dagger} \hat{T}_2 | \Phi_{ijk}^{abc} \rangle_L$, specifically accounting for one of the many diagrammatic contributions, and is actually directly proportional to our $B\eta_j^i$ tensor. In fact, a large subset of the individual diagrams contributing to this term appear to be nothing more than the quasi-variational coupled cluster positive-semidefinite linked tensors, $A\eta_b^a$, $B\eta_j^i$, $C\eta_{kl}^{ij}$, and $D\eta_{aj}^{ib}$ contracted with the triples vertex, with higher-order terms inevitably containing contractions involving the powers of these objects. Despite this aesthetic connection with our work, we are not proposing some transformation of the triples (analogous to our transformation of the doubles to renormalize the CEPA(0) functional) be performed, on the grounds that doing so either violates the $\mathcal{O}(o^3 v^4)$ -non-iterative complexity criterion, or would require the immense $\mathcal{O}(o^3 v^3)$ storage of the triples, in comparison to the more modest $\mathcal{O}(o^2 v^2)$ memory requirements of a CCSD(T) calculation.

Instead, we propose a pragmatic, but natural alternative; the evaluation of the second-order triples present in the standard (T) correction with the quasi-variational coupled cluster transformed *doubles*,

$$\delta E \approx \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | 2\hat{T}_2^\dagger \hat{V} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \quad (42)$$

where, analogous to common practical implementations of non-Hartree-Fock reference perturbative corrections, for example, BCCD(T), ψ_p , ϵ_p refer to eigenpairs of the Fock matrix with occupied-virtual blocks set to zero. Let us first give a simple explanation for why this could be at all beneficial. The transformed cluster amplitudes, by construction, contain the regular cluster amplitudes coupled to a linked approximation to division by the CI norm, through the negative powers of the matrices defined in Eq. (15). Since the smallest possible eigenvalue of any of these matrices is unity,^{45,46} this has the effect of ensuring that the transformed amplitudes, qT_{ab}^{ij} , are always smaller in magnitude than the regular amplitudes, $\{T_{ab}^{ij}\}$, with the greatest effect at long bond lengths. The introduction of transformed amplitudes therefore has the same qualitative effect as the denominator of Eq. (35), or the sum to infinity of the linked series of Eq. (41). Furthermore, since the transformed amplitudes are themselves explicitly linked tensor objects, this modification of (T) automatically remains both rigorously extensive and invariant to rotations in the underlying orbital spaces.

More rigorously, we can show that Eq. (42) is an explicitly linked approximation to Eq. (35); by omitting the triples contributions to the denominator in Eq. (35) and keeping only

those terms linear in $\hat{T}_3^{(2)}$ in the numerator,

$$\begin{aligned} \delta E &= \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | e^{\hat{T}_2^\dagger + \hat{T}_3^{(2)\dagger}} e^{\hat{T}_2} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | (\hat{H} e^{\hat{T}_2})_c | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}_2^\dagger + \hat{T}_3^{(2)\dagger}} e^{\hat{T}_2} | \Phi_0 \rangle} \\ &\approx \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | e^{\hat{T}_2^\dagger} \hat{T}_3^{(2)\dagger} e^{\hat{T}_2} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | (\hat{H} e^{\hat{T}_2})_c | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}_2^\dagger} e^{\hat{T}_2} | \Phi_0 \rangle}, \quad (43) \end{aligned}$$

then ignoring the term quadratic in \hat{T}_2 from the triples moment, we find that,

$$\delta E \approx \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | e^{\hat{T}_2^\dagger} \hat{T}_3^{(2)\dagger} e^{\hat{T}_2} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}_2^\dagger} e^{\hat{T}_2} | \Phi_0 \rangle}. \quad (44)$$

For a system containing only 3 electrons or 3 holes, the simplest possible systems for which a triples correction can be non-zero, the following simplification occurs:

$$\begin{aligned} \delta E &\rightarrow \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | \hat{T}_3^{(2)\dagger} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle}{1 + \langle \hat{T}_2^\dagger \hat{T}_2 \rangle} \\ &= \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | \hat{T}_2^\dagger \hat{V} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle}{(1 + \langle \hat{T}_2^\dagger \hat{T}_2 \rangle) (\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)}. \quad (45) \end{aligned}$$

In other words, for a 3-electron system, simply dividing (T) by the CI norm is a sensible approximation to Eq. (35). Of course, this expression contains unlinked terms, so an explicitly linked approximation is required, and we have already established that the transformed amplitudes are fit for this purpose.

$$\delta E \approx \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | {}_2\hat{T}_2^\dagger \hat{V} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}. \quad (46)$$

Since it is appropriate in these limiting cases, we propose applying this approximation to arbitrary systems.

It is also possible to understand Eq. (42) as an approximation to Eq. (41), given the alternative perspective that the transformed amplitudes, when inserted into the QVCCD functional of Eq. (12), generate closed-form geometric series of VCCD-like terms that, when combined, yield an excellent infinite-order approximation to $\langle e^{\hat{T}_2^\dagger} \hat{H} e^{\hat{T}_2} \rangle_L$. Similarly, by evaluating (T) with the transformed amplitudes, an infinite-order approximation to Eq. (41) is generated. It can be confirmed that this approximation is sensible by examining the low-order contributions. The leading-order contribution to Eq. (41) is simply (T), and the next lowest-order term involves $\langle \Phi_{ijk}^{abc} | \hat{T}_2^\dagger \hat{T}_3^{(2)\dagger} \hat{T}_2 | \Phi_0 \rangle_L$. Equation (42) may be similarly expanded through application of the binomial theorem to the inverse of the matrices defined in Eq. (15). Clearly, the leading-order contribution to the transformed amplitudes, $\{ {}_q T_{ab}^{ij} \}$, is the regular cluster amplitudes, $\{ T_{ab}^{ij} \}$, such that the leading-order contribution to Eq. (42) is also just (T). The next lowest-

order terms generated, however, contain contractions of the doubles amplitudes with the quasi-variational coupled cluster positive-semidefinite tensors, such as ${}_{\mathcal{B}}\eta_j^i$. This means that, of the individual contributing diagrams, this approximation accounts for $\langle am || ij \rangle T_{ml}^{bc} {}_{\mathcal{B}}\eta_k^l$, for example, where the ${}_{\mathcal{B}}\eta_j^i$ tensor is contracted with the doubles vertex of the second-order triples, but omits terms such as, $\langle am || lj \rangle T_{mk}^{bc} {}_{\mathcal{B}}\eta_l^i$, where this tensor does not connect to the doubles vertex, but instead to the 2-electron integral. The approximation is therefore imperfect, but clearly accounts for more higher-order terms than (T) alone. Finally, we note that Nooijen and LeRoy⁷³ independently achieved a similar effect through their μ_j^i tensor, but we additionally account for terms containing $\mathcal{A}\eta_b^a$, $c\eta_{kl}^{ij}$, and $\mathcal{D}\eta_{aj}^{ib}$ objects, and therefore take the view that our renormalization is both more complete and also more balanced.

Let us now make one small modification to the proposed theory; we note that, to this point, we have been associating the renormalizing denominator solely with the numerator term containing the triples amplitudes in Eq. (35). Given that the denominator cancels solely with the unlinked contributions in this triples-containing term, in light of Eq. (41), this seems to be the correct view, which led us to Eq. (42). However, computationally, this means that *both*,

$$W_{ijk}^{abc} = \langle \Phi_{ijk}^{abc} | \hat{V} \hat{T}_2 | \Phi_0 \rangle, \quad (47)$$

and,

$$V_{ijk}^{abc} = \langle \Phi_{ijk}^{abc} | \hat{V} {}_2\hat{T}_2 | \Phi_0 \rangle, \quad (48)$$

must be evaluated, roughly doubling the cost of the non-iterative step. The same consideration applies to existing variants of CCSD(T) based on the CCSD lagrangian multipliers.^{38–41} Consider, however, the following suggestion for the renormalized triples correction:

$$\delta E \approx \sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | {}_1\hat{T}_2^\dagger \hat{V} | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | \hat{V} {}_1\hat{T}_2 | \Phi_0 \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}. \quad (49)$$

This agrees to at least $\mathcal{O}(\hat{V}^2 \hat{T}_2^4)$, or at least sixth-order in Møller-Plesset theory, with Eq. (42), suggesting only an extremely small numerical discrepancy between the two. However, Eq. (49) requires only the evaluation of,

$$W_{ijk}^{abc} = \langle \Phi_{ijk}^{abc} | \hat{V} {}_1\hat{T}_2 | \Phi_0 \rangle, \quad (50)$$

which can be done at no additional cost over a standard (T) calculation. We take the view that the evaluation of (T), as the limiting step in the calculation, is already hard enough, and that Eq. (49) is therefore the pragmatic choice over Eq. (42), especially since, like Eq. (42), Eq. (49) remains rigorously extensive and orbital-invariant.

III. RESULTS AND DISCUSSION

Our proposed prototype renormalized triples scheme for OQVCCD, hereafter denoted R-OQVCCD(T), now forms part of the MOLPRO quantum chemistry software package,^{75,76} alongside the OQVCCD and OQVCCD(T) methods already in existence. The computational implementation of this new scheme is a trivial extension of (T),

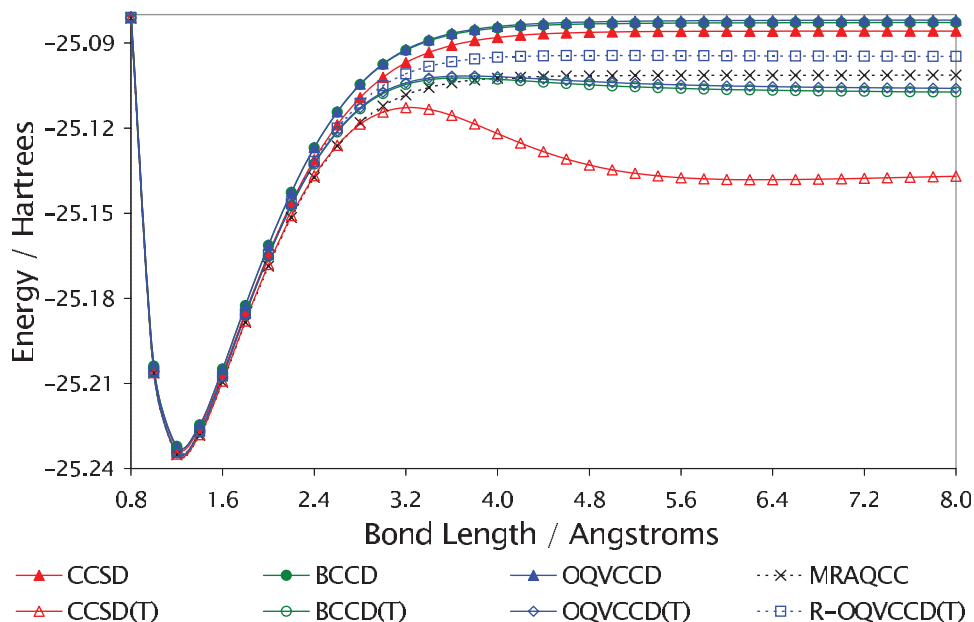


FIG. 1. Calculated potential energy curves for the BH molecule with the aug-cc-pVQZ basis set.

simply involving passing the converged $\{T_{ab}^{ij}\}$ amplitudes into the non-iterative triples subroutine in place of the regular amplitudes, $\{T_{ab}^{ij}\}$. In this section, we turn to the numerical assessment of the capabilities of R-OQVCCD(T). In all cases, we use Multireference Averaged Quadratic Coupled Cluster³² (MRAQCC) as the benchmark for the correct description of the system. We first assess the quality of the improvement of the description of single bond-breaking that is achieved by R-OQVCCD(T), relative to CCSD(T), BCCD(T), and OQVCCD(T).

First, consider the very simple BH molecule, for which complete potential energy curves calculated by each of the methods of interest are given in Figure 1. We have also

supplied, for additional clarity, a plot of the error of each calculated energy relative to MRAQCC in Figure 2. R-OQVCCD(T) is almost coincident with OQVCCD(T) at short bond lengths, suggesting that (T) is recovered, and that our renormalization does not degrade the already highly-accurate description of the equilibrium region. At longer bond lengths, from approximately 2.8 Å, the CCSD(T) method diverges strongly from MRAQCC, subsequently turning over and approaching a spurious dissociation limit. The BCCD(T) and OQVCCD(T) methods, on the other hand, show only a much weaker divergence from MRAQCC, an improvement associated with the use of either Brueckner or variationally optimal orbitals.^{41,48} Nevertheless, these curves still predict a

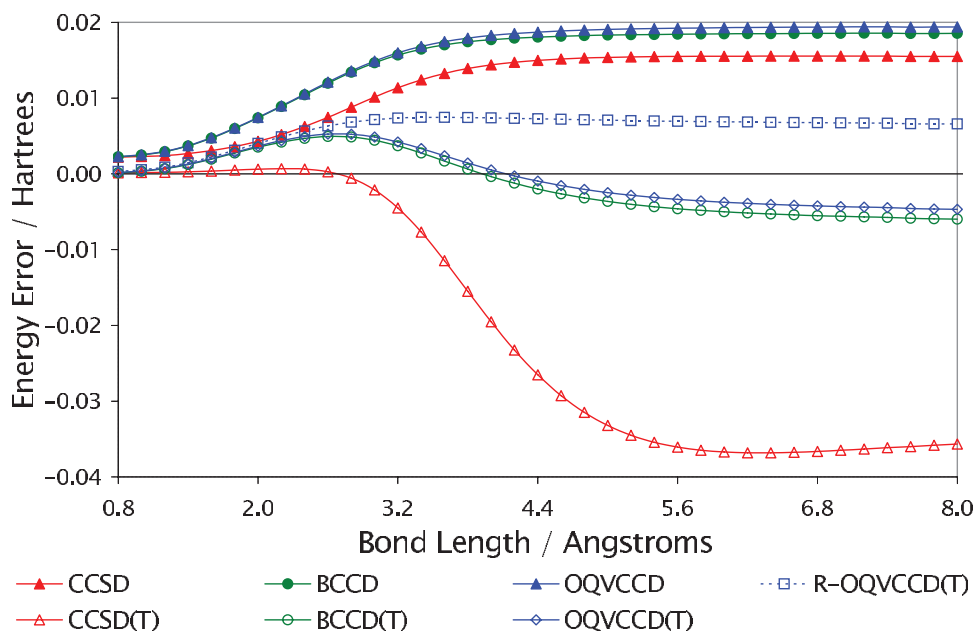


FIG. 2. Errors in calculated potential energies relative to MRAQCC for the BH molecule with the aug-cc-pVQZ basis set.

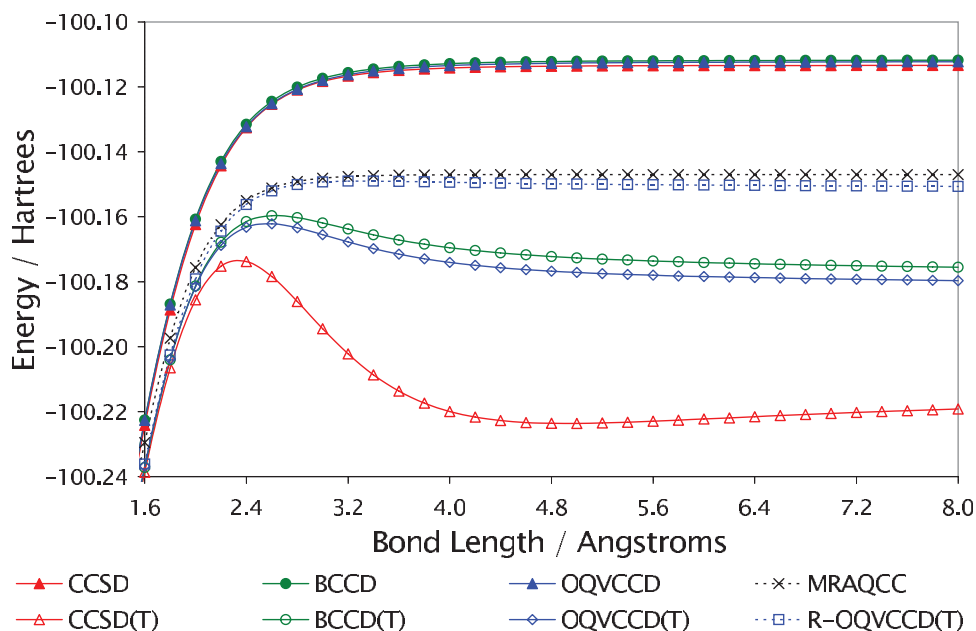


FIG. 3. Calculated potential energy curves for the HF molecule with the aug-cc-pVQZ basis set.

crossing with MRAQCC at approximately 4.0 Å, providing qualitatively incorrect descriptions of the molecular dissociation. In contrast, the R-OQVCCD(T) method does not contain a crossing, and instead maintains a positive error close to the peak OQVCCD(T) error, providing a significantly improved description, despite the very slightly negative slope.

We provide further plots of the potential energy curves for the dissociations of the HF molecule, the OH⁻ anion, and for the abstraction of a single hydrogen from water in Figures 3–5, respectively. All plots are qualitatively similar to each other, and to the BH plot already discussed; the BCCD and OQVCCD curves agree quantitatively to within a very fine tolerance, as do the BCCD(T) and OQVCCD(T)

methods. However, the R-OQVCCD(T) method shows a remarkable improvement to almost MRAQCC quality at long bond lengths, with a slightly negative gradient as the only deficiency, in comparison to the large unphysical maximum present in the curves of the other triples-corrected methods.

Next, we assess the performance of R-OQVCCD(T) relative to some of the well-established renormalized CCSD(T) methods of Piecuch *et al.*, with associated results obtained from the GAMESS package.⁷⁷ We have first chosen to examine F₂ for this purpose, a quintessential example of the failure of CCSD(T) to properly describe single bond-breaking. The calculated potential energy curves for this system are given

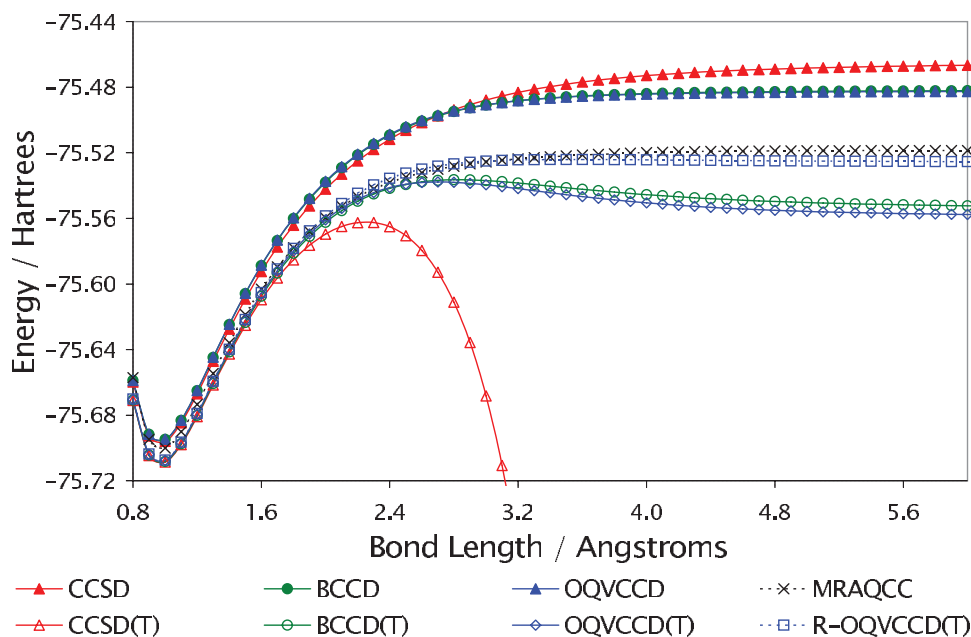


FIG. 4. Calculated potential energy curves for the OH⁻ anion with the aug-cc-pVTZ basis set.

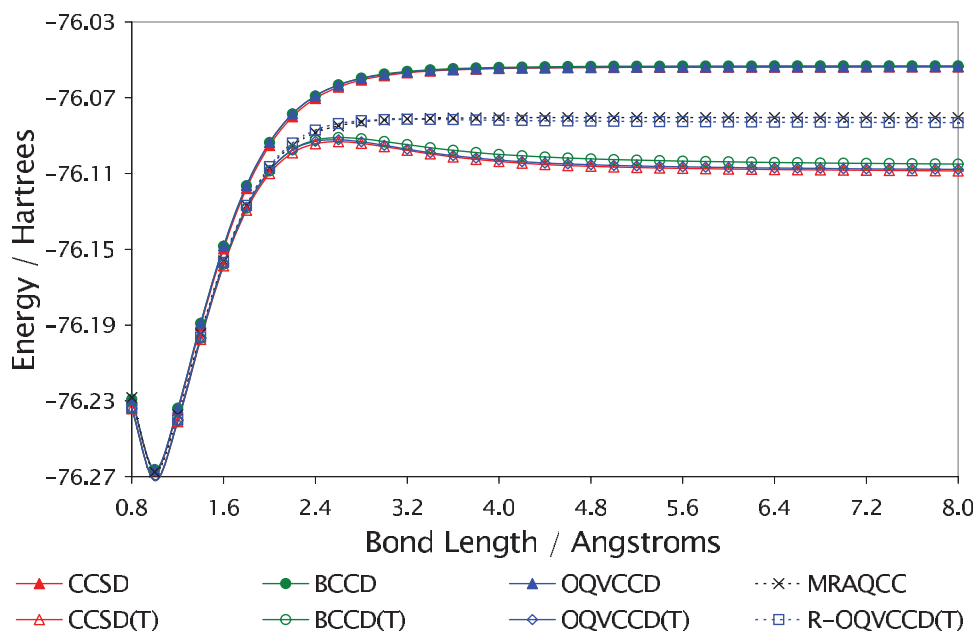


FIG. 5. Calculated potential energy curves for abstracting a single hydrogen atom from the water molecule with the aug-cc-pVDZ basis set.

in Figure 6, and clearly none of the methods employing the standard (T) perturbative correction are capable of describing the dissociation of this molecule. The effect of optimization of the orbitals is also minimal, and hardly mitigates the enormous failure of (T) at all here, as it does in the other systems examined. We therefore find it extremely satisfying that the R-OQVCCD(T) scheme achieves a qualitatively accurate description of the bond-breaking, with the potential energy curve remaining above that of MRAQCC throughout. More astonishing, however, is that this first prototype renormalization of (T) for use with quasi-variational coupled cluster theory appears to achieve a quantitative accuracy somewhere be-

tween the R-CCSD(T) and CR-CCSD(T) levels, while also maintaining rigorous extensivity.

As a further example, consider the abstraction of a single hydrogen atom from methane, for which calculated potential energy curves are supplied in Figure 7. In this case, the BCCD(T) and OQVCCD(T) curves are almost coincident throughout, both crossing the MRAQCC curve at approximately 3.0 Å. The R-CCSD(T) method also predicts a crossing with the MRAQCC energy, though at the longer bond length of 3.6 Å. The CR-CCSD(T) method performs much better, and does not predict such a crossing, and R-OQVCCD(T) remains in very close numerical agreement

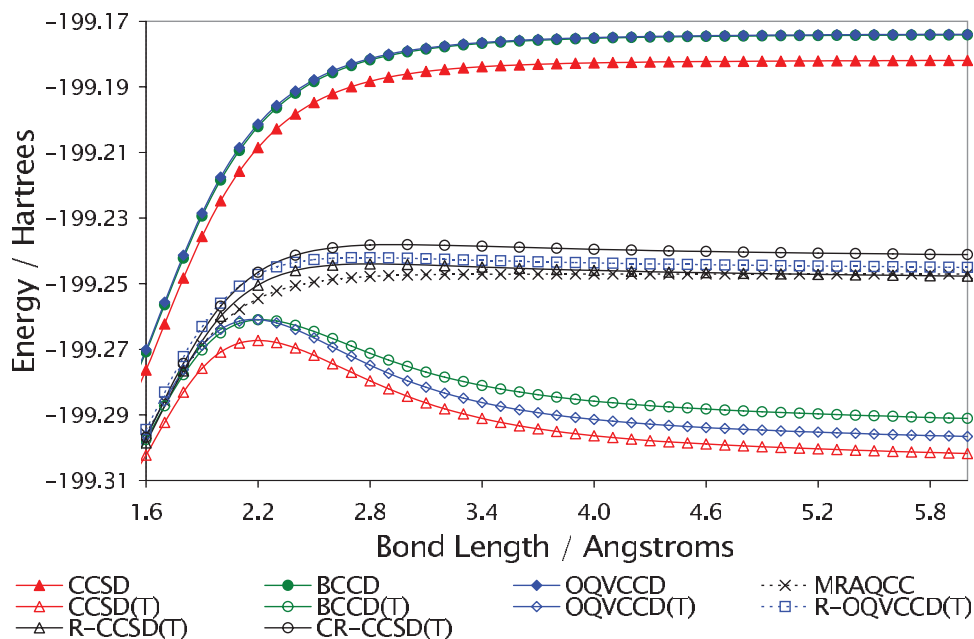


FIG. 6. Calculated potential energy curves for the F_2 molecule with the aug-cc-pVTZ basis set.

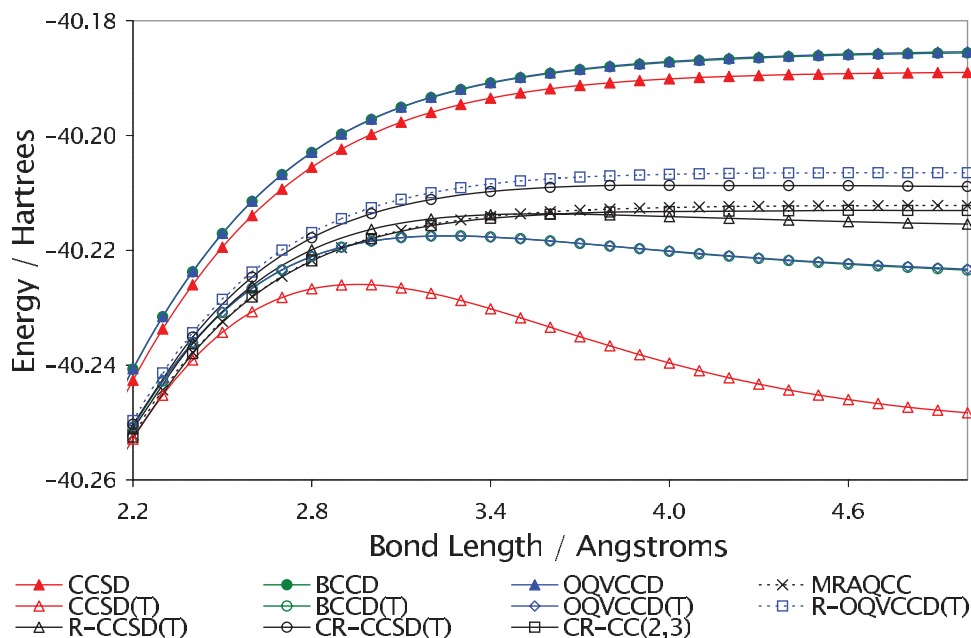


FIG. 7. Calculated potential energy curves for the abstraction of a single hydrogen from the CH_4 molecule with the aug-cc-pVDZ basis set.

with CR-CCSD(T) throughout, with the curve lying only a few milli-Hartrees higher in energy at long bond lengths. The significantly more advanced CR-CC(2,3) method is, of course, significantly superior to the other single-reference methods tested, but, rather than detracting from the quality of the presented results, we view this as an indication of the quality of potential energy curves that might be predicted by quasi-variational coupled cluster, if further improvements to our suggested (and merely proof-of-concept) renormalized triples correction are made.

Finally, let us consider multiple bond-breaking, involving strong non-dynamic correlation. Due to the associated breakdown of the Hartree-Fock approximation, CCSD itself fails to

describe these problematic molecular dissociations, and even the extremely powerful CR-CC(2,3) method, based on CCSD, performs poorly. However, we have recently demonstrated that our approximately variationally-bounded OQVCCD(T) method is significantly more robust to the failure of HF theory.^{47,48} We therefore check that the renormalization of the triples correction does not greatly disrupt the already excellent description of the electronic structure for such molecules.

First, we consider a system involving the simultaneous breaking of several single covalent bonds, for which we have selected the extreme example of the simultaneous stretching of all 4 carbon-hydrogen bonds in ethene, for which calculated potential energy curves are given in Figure 8. All

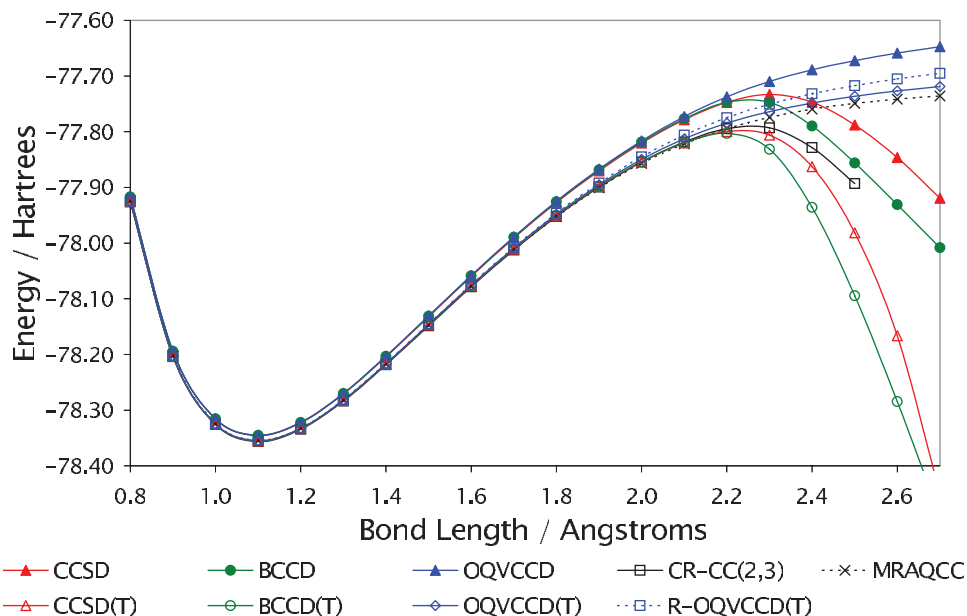


FIG. 8. Calculated potential energy curves for the simultaneous stretching of all C-H bonds in the C_2H_4 molecule with the cc-pVDZ basis set.

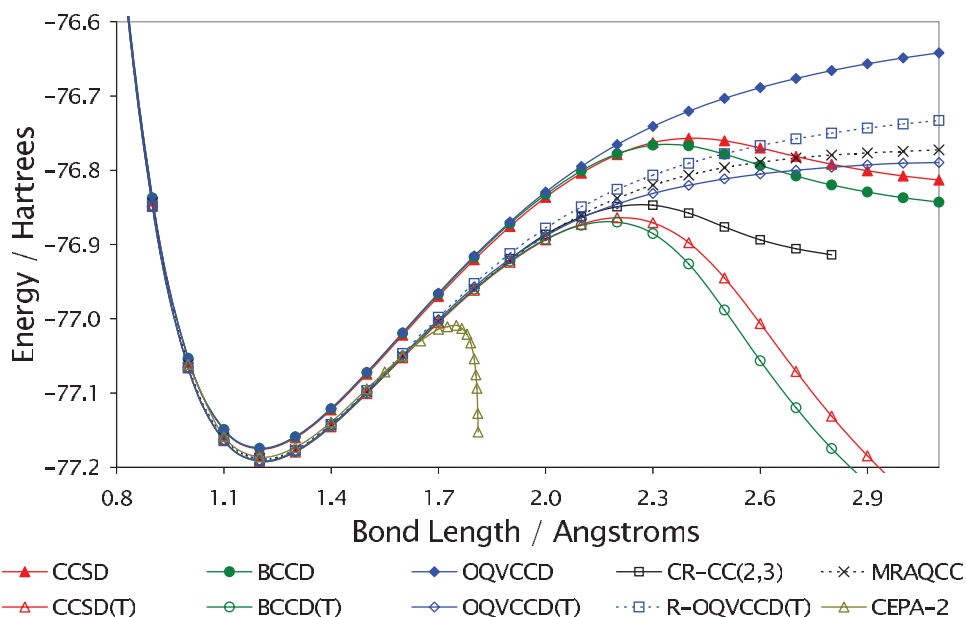


FIG. 9. Calculated potential energy curves for stretching the triple bond in acetylene with the aug-cc-pVTZ basis set and the C-H bond length held fixed at 1.06 Å.

methods tested adequately describe molecular geometries close to equilibrium, but, as the bonds are stretched, the CCSD and BCCD methods turn over from approximately 2.3 Å. Correlated with this is the failure of the CCSD(T) and BCCD(T) methods, and even CR-CC(2,3). OQVCCD, on the other hand, does not predict an unphysical maximum and remains qualitatively valid throughout, with both the OQVCCD(T) and R-OQVCCD(T) methods describing the energetics extremely well. Importantly, R-OQVCCD(T) lies only a few tens of milli-Hartrees higher in energy than OQVCCD(T) at large bond lengths.

Second, we consider breaking the triple bond in acetylene, with results illustrated in Figure 9. Similarly to the previous example, each of the methods performs adequately

around the equilibrium geometry, but the CCSD and BCCD potential energy curves experience a crossing with the MRAQCC energy around 2.6 Å. The OQVCCD curve, however, experiences no such crossing. Upon the addition of triple excitations, the divergence of the TCC-based methods from MRAQCC is magnified, with each of CCSD(T), BCCD(T), and CR-CC(2,3) predicting the characteristic unphysical maximum around 2.6 Å. The OQVCCD(T) method, however, does not predict an unphysical maximum at all and remains quantitatively close to the MRAQCC curve throughout, but slightly below it. Although the absolute error of the R-OQVCCD(T) method is slightly larger than that of OQVCCD(T), the renormalization of the triples reduces the overestimation of the triples energy by (T), such that

TABLE III. Summary of potential energy surface errors.

Maximum absolute deviation from MRAQCC / Hartree							
	CCSD	CCSD(T)	BCCD	BCCD(T)	OQVCCD	OQVCCD(T)	R-OQVCCD(T)
BH	0.0155	0.0368	0.0186	0.0060	0.0194	0.0052	0.0075
HF	0.0336	0.0766	0.0352	0.0285	0.0347	0.0326	0.0066
OH ⁻	0.0522	510.8648	0.0364	0.0340	0.0360	0.0393	0.0131
H ₂ O	0.0267	0.0282	0.0273	0.0246	0.0269	0.0274	0.0056
F ₂	0.0652	0.0547	0.0729	0.0440	0.0731	0.0495	0.0065
CH ₄	0.0232	0.0361	0.0266	0.0113	0.0268	0.0111	0.0058
C ₂ H ₄	0.1836	0.7146	0.2724	0.7543	0.0887	0.0171	0.0406
C ₂ H ₂	0.0588	0.4588	0.0599	0.4793	0.1705	0.0228	0.0795
Non-parallelity error relative to MRAQCC / Hartree							
BH	0.0133	0.0375	0.0163	0.0109	0.0171	0.0099	0.0071
HF	0.0283	0.0675	0.0283	0.0231	0.0279	0.0267	0.0057
OH ⁻	0.0548	510.8583	0.0381	0.0314	0.0377	0.0380	0.0156
H ₂ O	0.0280	0.0256	0.0282	0.0232	0.0277	0.0264	0.0070
F ₂	0.0275	0.0463	0.0289	0.0414	0.0282	0.0480	0.0045
CH ₄	0.0136	0.0356	0.0236	0.0129	0.0238	0.0128	0.0068
C ₂ H ₄	0.2309	0.7175	0.3194	0.7577	0.0813	0.0180	0.0412
C ₂ H ₂	0.0597	0.4571	0.0905	0.4791	0.1659	0.0392	0.0832

R-OQVCCD(T) remains above MRAQCC throughout. For reference, we have additionally included CEPA-2 results, obtained from the ORCA package.⁷⁸ This method diverges even closer to the equilibrium geometry than CCSD, however.

Table III summarises the deviations of each method from MRAQCC for each of the systems discussed above, showing the maximum absolute energy deviation, and the non-parallelity error (NPE), defined as the difference between the maximum and minimum deviations. The performance of R-OQVCCD(T) is seen to be outstanding for all of the singly-bonded molecules, for which its mean NPE is just 0.0078, compared to OQVCCD(T) (0.0270) and BCCD(T) (0.0238). For the breaking of multiple bonds, R-OQVCCD(T) is by this measure slightly worse than OQVCCD(T). We attribute this to a possible partial cancellation of errors in OQVCCD(T) between remaining missing parts of the fifth-order energy in OQVCCD, and the overshooting of the triple excitation contribution. The renormalised (T) correction addresses the second effect but not the first.

IV. CONCLUDING REMARKS

We have shown that quasi-variational coupled cluster theory leads naturally to a new scheme for the renormalization of the (T) perturbative correction for the effects of connected triple excitations. Our approach has been to modify (T) such that it is evaluated simply using the set of transformed cluster amplitudes, $\{T_{ab}^{ij}\}$, as shown in Eq. (42). With *zero* increase in computational cost above standard (T), impressive results already close to the CR-CCSD(T) level for single bond-breaking processes, no deficiency relative to OQVCCD(T) around molecular equilibria, and the advantage of maintaining both rigorous extensivity and orbital invariance, we believe our approach to be highly promising.

We have further confirmed that R-OQVCCD(T) remains of OQVCCD(T) quality for the description of problems involving strong non-dynamic electron correlation, and is still one of the only $\mathcal{O}(\sigma^2 v^4)$ -iterative $\mathcal{O}(\sigma^3 v^4)$ -non-iterative methods capable of correctly describing extreme electronic structure phenomena such as breaking the triple bond in acetylene. Despite this, we have noted R-OQVCCD(T) to yield slightly larger absolute errors relative to MRAQCC than the OQVCCD(T) method. However, our view is that the reason OQVCCD(T) is so good for multiple bond-breaking may be that it benefits from the well-known overestimation of the correlation energy associated with the triples by (T). Our renormalization of (T), however, likely redresses this overestimation, such that R-OQVCCD(T) is, in fact, closer to the level of accuracy that might be obtained from treating the triples explicitly, for example in a hypothetical OQVCCD(T) theory; R-OQVCCD(T) is likely more representative of the true triples energy than OQVCCD(T). Accounting for higher excitations, potentially through a factorized (and renormalized) perturbative correction for quadruples also, R-OQVCCD(TQ₄), therefore can be expected to improve accuracy further.

We do not claim our prototype renormalization of (T) to approach the accuracy of the state-of-the-art CR-CC(2,3) method for single bond-breaking problems, but R-OQVCCD(T) is at least physically correct, and therefore

qualitatively similar to CR-CC(2,3), and since no calculation of the CCSD $\hat{\Lambda}$ operator is required, the application of our renormalization scheme is significantly computationally cheaper. Nevertheless, the existence of more powerful renormalized triples corrections such as CR-CC(2,3) suggests that practical improvements to the non-iterative component of R-OQVCCD(T) must certainly exist. In fact, it is already possible for us to suggest

$$\sum_{\substack{i < j < k \\ a < b < c}} \frac{\langle \Phi_0 | (\hat{H} - \hat{T}_2)_c^\dagger | \Phi_{ijk}^{abc} \rangle \langle \Phi_{ijk}^{abc} | (\hat{H} \hat{T}_2 + \frac{1}{2!} \hat{H} \hat{T}_2^2)_c | \Phi_0 \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \quad (51)$$

as a potential augmentation of the present theory, where Eq. (42) is used in place of the more pragmatic Eq. (49), and the term quadratic in \hat{T}_2 present in the triples moment is retained, resulting in a so-called *Completely Renormalized* correction, which when applied to OQVCCD might be denoted as CR-OQVCCD(T).

Ultimately, however, our goal here has been simply to demonstrate that it is possible to combine the OQVCCD method, highly robust to the non-dynamic breakdown of the HF approximation, with a renormalized correction for the effects of connected triple excitations such that single bond-breaking may also be modelled correctly. As such, we view R-OQVCCD(T) as the first member of a family of quantum-chemical methods capable of treating not only equilibrium phenomena, but also both single and multiple bond-breaking processes, all within a strictly single-reference framework.

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