# Linear-Scaling Coupled Cluster with Perturbative Triple Excitations: The Divide−Expand−Consolidate CCSD(T) Model

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ABSTRACT: We propose a reformulation of the traditional (T) triples correction to the coupled cluster singles and doubles (CCSD) energy in terms of local Hartree−Fock (HF) orbitals such that its structural form aligns with our recently developed linear-scaling divide−expand−consolidate (DEC) coupled cluster family of local correlation methods. In a DEC-CCSD(T) calculation, a basis of local occupied and virtual HF orbitals is used to partition the correlated calculation on the full system into a number of independent atomic fragment and pair fragment calculations, each performed within a truncated set of the complete orbital space. In return, this leads to a massively parallel algorithm for the evaluation of the DEC-CCSD(T) correlation energy, which formally scales linearly

with the size of the full system and has a tunable precision with respect to a conventional CCSD(T) calculation via a single energy-based input threshold. The theoretical developments are supported by proof of concept DEC-CCSD(T) calculations on a series of medium-sized molecular systems.
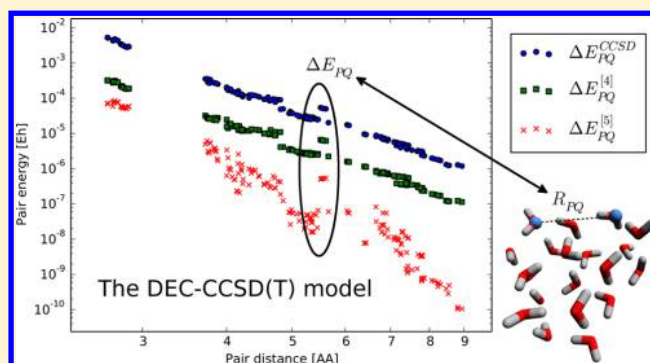
1. INTRODUCTION

In the quest for chemical accuracy in *ab initio* electronic structure calculations, the coupled cluster (CC) singles and doubles model[1] (CCSD) augmented by a perturbative treatment of triple excitations[2] (CCSD(T)) has proven itself the gold standard. However, despite the notable success of the CCSD(T) model in benchmarking electronic energies and other molecular properties for small molecular systems, its seventh-power scaling with system size remains a severe impediment of the model, generally preventing it from large-scale applications and hence from becoming beneficial beyond the niche of modest-sized molecular systems. In standard implementations, the scaling wall of the CCSD(T) model arises because the energy correction is expressed in a basis of highly nonlocal canonical Hartree−Fock (HF) molecular orbitals (MOs), making a local description of electron correlation effects unattainable.

Throughout the years, elaborate attempts have been made at pushing the limits for the CCSD(T) model by devising massively parallel implementations of the standard canonical formulation.[3−11] However, it is evident that such attempts cannot significantly extend the application range of the model as the inherent scaling wall of the model is not overcome. If large molecular systems are to be addressed by the CCSD(T) model, the underlying algorithm is bound to be reformulated such that its implementation becomes not only massively parallel but also linearly scaling. Furthermore, if this alternative algorithm in itself is to be successful as a tool within high-

accuracy *ab initio* quantum chemistry, it is imperative that it possesses a strict error control through the use of a single parameter that directly identifies the precision of the calculation as compared to a standard calculation.

To accommodate the preceding requirements, a plethora of local correlation CCSD(T) methods have been introduced, many of which reduce the computational scaling to one that depends linearly on system size. The first successful of these was the local CCSD(T) method developed by Schütz and Werner,[12] and since then the CCSD(T) model has been implemented within various local correlation schemes such as the incremental scheme,[13] the divide-and-conquer scheme,[14] the cluster-in-molecule scheme,[15,16] and most recently in terms of orbital-specific virtual orbitals[17] as well as pair and triples natural orbitals.[18] Common for all of these methods is the introduction of a set of parameters which regulate the overall accuracy of the calculation as compared to a conventional calculation. However, none of the methods have been designed to determine optimal local orbital spaces in an automated fashion based on a single energy criterion provided by the end user. In the present work, we propose a novel implementation of the CCSD(T) model, which has an error in the final energy that is indeed adjusted by the turn of a single knob, while at the same time being both linearly scaling and massively parallel. These advances are made possible through a reformulation of

the (T) correction to the CCSD energy such that its expression in terms of localized orbitals aligns with our recently developed divide−expand−consolidate (DEC) coupled cluster framework.[19−23]

In a DEC-CC calculation, the inherent locality of the electron correlation problem is efficiently exploited in order to express the correlated wave function calculation on the full molecular system in terms of numerous small and independent fragment calculations that each uses a subset of the total orbital space. Importantly, the local orbital spaces used in the individual fragment calculations are determined in a black-box manner during the calculation to ensure that the calculated final energy is determined to within a predefined precision compared to a conventional calculation. An important prerequisite for the proposed DEC-CCSD(T) model—as for any DEC-CC model—is our recently developed strategy for generating a set of local orthogonal orbitals for both the occupied and virtual orbital spaces,[24] which allows us to describe local electron correlation effects without invoking, e.g., a set of linearly dependent nonorthogonal projected atomic orbitals.

The alternative formulation of the (T) triples energy correction used herein, which forms the basis for the DEC-CCSD(T) method, has a computational cost that is twice that of the standard expression. However, in contrast to the one conventionally used in standard implementations, which is restricted to the canonical HF basis, our alternative formulation may be expressed in any basis of optimized HF orbitals. As a consequence, the (T) correction can be expressed in a basis of localized orbitals, making it possible to take advantage of the locality of the triples amplitudes and, in return, obtain a reduced overall computational scaling of the energy correction.

In section 2, the conventional and alternative formulations of the (T) correction are compared to one another in terms of computational cost and the ability to be expressed in various bases of optimized HF orbitals. In section 3, we show how the coupling of the alternative expression for the (T) correction to the DEC scheme is made for a set of local HF orbitals, while numerical proof of concept DEC-CCSD(T) results are presented in section 4. Finally, section 5 gives some conclusive remarks.

2. CCSD(T) CORRELATION ENERGY

In a basis of spatial (spin-free) HF orbitals, the total CCSD energy for a closed-shell system is given as

$$E_{CCSD} = E^{HF} + E^{CCSD} \tag{2.0.1}$$

In eq 2.0.1, E^{HF} is the HF energy and E^{CCSD} the CCSD correlation energy, which reads[25]

$$E^{CCSD} = \sum_{ab} \sum_{ij} (t_{ij}^{ab} + t_i^a t_j^b) L_{iajb} \tag{2.0.2}$$

where $\{t_i^a\}$ and $\{t_{ij}^{ab}\}$ are the CCSD singles and doubles amplitudes, respectively, and $L_{iajb} = 2g_{iajb} - g_{ibja}$ is an antisymmetrized two-electron integral written in Mulliken notation. In the following, the indices $\{i,j,k,l,m\}$ and $\{a,b,c,d,e\}$ will denote occupied and virtual HF orbitals, respectively.

The CCSD(T) energy is defined as[2]

$$E_{CCSD(T)} = E^{HF} + E^{CCSD} + E^{(T)} \tag{2.0.3}$$

where $E^{(T)}$ is the so-called (T) perturbative correction to the CCSD energy for the effect of triple excitations. The structure of $E^{(T)}$ is defined by two energy contributions rationalized from many-body perturbation theory[26] (MBPT): $E^{[4]}$, a fourth-order term involving CCSD doubles amplitudes, and $E^{[5]}$, a fifth-order term involving CCSD singles amplitudes

$$E^{(T)} = E^{[4]} + E^{[5]} \tag{2.0.4}$$

In a basis of canonical HF spatial orbitals, the expressions for the fourth- and fifth-order contributions may be derived from MBPT as[27]

$$E^{[4]} = \sum_{abc} \sum_{ijk} \tilde{t}_{ijk}^{abc} t_{ijk}^{abc} \varepsilon_{ijk}^{abc} \tag{2.0.5a}$$

$$E^{[5]} = \sum_{abc} \sum_{ijk} \tilde{z}_{ijk}^{abc} t_{ijk}^{abc} \varepsilon_{ijk}^{abc} \tag{2.0.5b}$$

In eqs 2.0.5, the triples amplitudes $\{t_{ijk}^{abc}\}$ are given as

$$t_{ijk}^{abc} = -P_{ijk}^{abc} \frac{\sum_d t_{ij}^{ad} g_{ckbd} - \sum_l t_{il}^{ab} g_{cklj}}{\varepsilon_{ijk}^{abc}} \tag{2.0.6}$$

where ε_{ijk}^{abc} denotes the orbital energy difference between the virtual and occupied orbitals of the excitation

$$\varepsilon_{ijk}^{abc} = \varepsilon_a + \varepsilon_b + \varepsilon_c - (\varepsilon_i + \varepsilon_j + \varepsilon_k) \tag{2.0.7}$$

and P_{ijk}^{abc} is a symmetrization operator

$$P_{ijk}^{abc} x_{ijk}^{abc} = x_{ijk}^{abc} + x_{ikj}^{acb} + x_{jik}^{bac} + x_{jki}^{bca} + x_{kij}^{cab} + x_{kji}^{cba} \tag{2.0.8}$$

The z_{ijk}^{abc} coefficients in eq 2.0.5b are given as

$$z_{ijk}^{abc} = \frac{-(t_i^a g_{jbkc} + t_j^b g_{iakc} + t_k^c g_{iajb})}{\varepsilon_{ijk}^{abc}} \tag{2.0.9}$$

and the tilde notation on an arbitrary six-index quantity $\tilde{x}_{ijk}^{abc}$ in eq 2.0.5 is defined as

$$\tilde{x}_{ijk}^{abc} = 2\left(\frac{2}{3} x_{ijk}^{abc} - x_{ijk}^{acb} + \frac{1}{3} x_{ijk}^{bca}\right) \tag{2.0.10}$$

The expressions for the fourth- and fifth-order contributions in eqs 2.0.5 both contain orbital energy differences, and the evaluation of the (T) energy correction by this conventional formulation will thus be practically restricted to a basis of canonical HF orbitals. If, on the other hand, we were to express the correction in a more general, optimized HF basis (e.g., in terms of localized HF orbitals), the equation for the triples amplitudes in eq 2.0.6 would read

$$\sum_e (t_{ijk}^{ebc} F_{ae} + t_{ijk}^{aec} F_{be} + t_{ijk}^{abe} F_{ce}) - \sum_m (t_{mjk}^{abc} F_{mi} + t_{imk}^{abc} F_{mj} + t_{ijm}^{abc} F_{mk})$$

$$= -P_{ijk}^{abc} \left(\sum_d t_{ij}^{ad} g_{ckbd} - \sum_l t_{il}^{ab} g_{cklj}\right) \tag{2.0.11}$$

Since eq 2.0.11 is expressed in terms of off-diagonal elements of the Fock matrix, which become nonzero in the local HF basis,[28] the total (T) correction would have to be evaluated by means of an expensive iterative scheme, thereby drastically limiting the application range of the CCSD(T) model.

Alternatively, the two correction terms in eq 2.0.4 may be derived from Lagrangian-based CC perturbation theory for a HF reference state[25,29] and expressed as

$$E^{[4]} = 2 \sum_{ab} \sum_{ij} (2t_{ij}^{ab} - t_{ji}^{ab}) T_{ij}^{ab} \qquad (2.0.12a)$$

$$E^{[5]} = 2 \sum_{a} \sum_{i} t_i^a T_i^a \qquad (2.0.12b)$$

In eqs 2.0.12, the fourth- and fifth-order contributions to the (T) correction are formulated in terms of the T_{ij}^{ab} and T_i^a intermediates, respectively

$$T_{ij}^{ab} = \sum_{cd} \sum_{k} (t_{ijk}^{acd} L_{bckd} - t_{kji}^{acd} g_{kdbc})$$
$$- \sum_{c} \sum_{kl} (t_{ikl}^{abc} L_{kjlc} - t_{lki}^{abc} g_{kjlc}) \qquad (2.0.13a)$$

$$T_i^a = \sum_{cd} \sum_{kl} (t_{ikl}^{acd} - t_{lki}^{acd}) L_{kcld} \qquad (2.0.13b)$$

Comparing the evaluation of $E^{(T)}$ from eqs 2.0.5 and 2.0.12/2.0.13, we note that both expressions contain the triples amplitudes of eq 2.0.6, the generation of which scale as o^3v^4 (where o and v denote the number of occupied and virtual orbitals, respectively). The evaluation of the T_{ij}^{ab} intermediates in eq 2.0.13a contains an additional o^3v^4 scaling term, while the conventional expression in eq 2.0.5a contains no such term since each triples amplitude is immediately contracted with either itself or a z coefficient in an o^3v^3 step. As mentioned earlier, the contractions in eqs 2.0.5 are limited to the canonical HF basis. Thus, as the local nature of the triples amplitudes cannot be explored within this highly nonlocal basis, and the use of any other basis but that formed by the canonical HF orbitals will increase the computational cost, locality considerations cannot be used to reduce the overall computational scaling of the (T) energy correction whenever the formulations in eqs 2.0.5 are used. On the other hand, the alternative expressions in eqs 2.0.12 are valid within any basis of optimized HF orbitals, be that a canonical or a local basis. Since the intermediates in eqs 2.0.13 are constructed from triples amplitudes and MO integrals only, it is possible to take advantage of the locality of these two quantities when evaluating $\{T_{ij}^{ab}, T_i^a\}$ and, in return, $E^{(T)}$ in a local basis. As will be shown in section 3.2, eqs 2.0.12 and 2.0.13 thus provide a pathway toward a reduction of the overall computational scaling of the (T) energy correction.

In the present work, we will use the DEC-CC framework for determining the T_i^a and T_{ij}^{ab} intermediates in a basis of local HF orbitals. In practice, the intermediates in a DEC-CCSD(T) calculation will be determined from individual CCSD(T) calculations within local atomic fragment and pair fragment orbital spaces in analogy with the evaluation of CCSD singles and doubles amplitudes in the DEC-CCSD model.[19,20] As we will demonstrate in sections 3 and 4, the alternative expressions for the (T) energy correction in eqs 2.0.12 facilitate a reduction in computational scaling of the $E^{CCSD(T)}$ energy to a linear dependence on system size, while retaining control of the error introduced as compared to a conventional CCSD(T) calculation.

3. DEC PARTITIONING OF THE CCSD AND CCSD(T) CORRELATION ENERGIES

To understand the similarities and differences between the DEC evaluation of the CCSD energy and the (T) energy correction, the foundation for both DEC formulations will be discussed next. In section 3.1, we give formally exact

expressions for both E^{CCSD} and $E^{(T)}$ in terms of DEC atomic fragment and pair interaction energies, while section 3.2 is devoted to the actual approximate evaluation of these.

3.1. Formulation in Terms of Atomic Fragment and Pair Interaction Energies. In the DEC-CC framework,[19−23] we assign local HF orbitals to atomic sites P, Q, R, S, ... and each atomic site P thus gets assigned a set of local occupied, $\underline{P}$, and virtual, $\overline{P}$, HF orbitals. Reformulating the CCSD correlation energy in terms of summations over atomic sites and pair sites, eq 2.0.2 reads[19]

$$E^{CCSD} = \sum_{P} \left[E_P^{CCSD} + \sum_{Q<P} \Delta E_{PQ}^{CCSD} \right] \qquad (3.1.1)$$

where the atomic fragment energy, E_P^{CCSD}, and the pair interaction energy, ΔE_{PQ}^{CCSD}, are given as

$$E_P^{CCSD} = \sum_{ab} \sum_{ij \in \underline{P}} (t_{ij}^{ab} + t_i^a t_j^b) L_{iajb} \qquad (3.1.2a)$$

$$\Delta E_{PQ}^{CCSD} = \sum_{ab} \left(\sum_{i \in \underline{P}} \sum_{j \in \underline{Q}} + \sum_{i \in \underline{Q}} \sum_{j \in \underline{P}} \right)(t_{ij}^{ab} + t_i^a t_j^b) L_{iajb} \quad (3.1.2b)$$

In eqs 3.1.1 and 3.1.2, the CCSD correlation energy is written in such a way that the summations over the two occupied orbitals, $\{i,j\}$, in eq 2.0.2 are replaced by summations over atomic sites P and pair sites P,Q as well as summations over orbitals $\{i,j\}$ assigned to the respective atomic sites.

Since the expression for the (T) correction in eqs 2.0.12 contains similar summations over occupied and virtual orbitals, we may likewise substitute these by summations over atomic sites P and pair sites P,Q as in eq 3.1.1

$$E^{(T)} = \sum_{P} \left[E_P^{(T)} + \sum_{Q<P} \Delta E_{PQ}^{(T)} \right] \qquad (3.1.3)$$

where the triples atomic fragment energy, $E_P^{(T)}$, and triples pair interaction energy, $\Delta E_{PQ}^{(T)}$, are given as

$$E_P^{(T)} = E_P^{[4]} + E_P^{[5]} \qquad (3.1.4a)$$

$$\Delta E_{PQ}^{(T)} = \Delta E_{PQ}^{[4]} + \Delta E_{PQ}^{[5]} \qquad (3.1.4b)$$

The CCSD(T) fourth-order terms become

$$E_P^{[4]} = 2 \sum_{ab} \sum_{ij \in \underline{P}} (2t_{ij}^{ab} - t_{ji}^{ab}) T_{ij}^{ab} \qquad (3.1.5a)$$

$$\Delta E_{PQ}^{[4]} = 2 \sum_{ab} \left(\sum_{i \in \underline{P}} \sum_{j \in \underline{Q}} + \sum_{i \in \underline{Q}} \sum_{j \in \underline{P}} \right)(2t_{ij}^{ab} - t_{ji}^{ab}) T_{ij}^{ab} \quad (3.1.5b)$$

while the fifth-order terms become

$$E_P^{[5]} = 2 \sum_{a \in \overline{P}} \sum_{i \in \underline{P}} t_i^a T_i^a \qquad (3.1.6a)$$

$$\Delta E_{PQ}^{[5]} = 2 \left(\sum_{a \in \overline{P}} \sum_{i \in \underline{Q}} + \sum_{a \in \overline{Q}} \sum_{i \in \underline{P}} \right) t_i^a T_i^a \qquad (3.1.6b)$$

with the T_{ij}^{ab} and T_i^a intermediates given in eqs 2.0.13.

We note how the fourth-order term in eqs 3.1.5 is partitioned in the same way as E^{CCSD} in eq 3.1.2; that is, the summations over occupied orbitals are replaced by summations over the atomic sites and pair sites to which the local HF orbitals have been assigned. For the fifth-order term in eqs 3.1.6, however, we have chosen a partitioning in which both single excitation indices refer to the same atomic site for the atomic fragments,

while for the pair interaction energies, the indices are assigned to different atomic sites.

3.2. Evaluation of Atomic Fragment and Pair Interaction Energies. By replacing the summations over orbitals in E^{CCSD} and $E^{(T)}$ by summations over atomic sites and pair sites as well as orbitals assigned to these sites in eqs 3.1.1 and 3.1.3, no approximations are introduced and no reductions will be obtained with respect to computational requirements. On the other hand, if restrictions can be made in the summations over the space of virtual orbitals in the atomic fragment and pair interaction calculations without compromising the overall accuracy of the calculation, then E^{CCSD} and $E^{(T)}$ may be calculated using an algorithm that scales quadratically with system size. Furthermore, as we will see, many pair contributions may be neglected without compromising the precision of the calculated correlation energy, ultimately leading to a linear-scaling algorithm for the evaluation of the DEC-CCSD(T) energy.

We initially consider E^{CCSD} in eqs 3.1.2 and assume it is expressed in a basis of local HF orbitals. The atomic fragment energy, E_P^{CCSD}, in eq 3.1.2a contains the integrals L_{iajb} where both occupied indices $\{i,j\}$ refer to local orbitals assigned to atomic site P. These integrals will be nonvanishing only if the virtual indices $\{a,b\} \in [\overline{P}]$, where the space $[\overline{P}]$ denotes the virtual HF orbital space that is spatially local to P (including $\overline{P}$); see Figure 1. For the pair interaction energy in eq 3.1.2b, the summations over the virtual orbital space may be restricted in a similar manner using unions of the atomic fragment orbital spaces for the constituent atomic sites, resulting in the
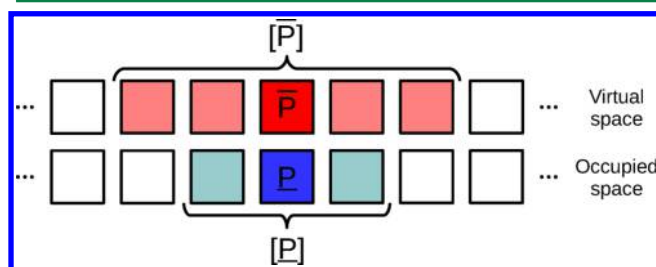
Figure 1. Different orbital spaces for a given atomic fragment P. Each box denotes a set of occupied or virtual orbitals assigned to an atomic site. The CCSD amplitude equations are solved in the $[\underline{P}] \cup [\overline{P}]$ space, and the CCSD atomic fragment energy is evaluated in the $\underline{P} \cup [\overline{P}]$ space.

following DEC-CCSD atomic fragment and pair interaction energies[20]

$$E_P^{CCSD} = \sum_{ab \in [\overline{P}]} \sum_{ij \in \underline{P}} (t_{ij}^{ab} + t_i^a t_j^b) L_{iajb} \tag{3.2.1a}$$

$$\Delta E_{PQ}^{CCSD} = \sum_{ab \in [\overline{P}] \cup [\overline{Q}]} \left(\sum_{i \in \underline{P}} \sum_{j \in \underline{Q}} + \sum_{i \in \underline{Q}} \sum_{j \in \underline{P}} \right)(t_{ij}^{ab} + t_i^a t_j^b) L_{iajb} \tag{3.2.1b}$$

In order to accurately determine the CCSD amplitudes in eq 3.2.1a, it is imperative that certain coupling effects to amplitudes outside the $\underline{P} \cup [\overline{P}]$ space are described. As elaborated upon in ref 20, most of these coupling effects arise from nonvanishing charge distributions in two-electron integrals in addition to the distance decay of the Fock matrix. As a result of these additional effects, the amplitudes of eq 3.2.1a have to be allowed to couple to, e.g., amplitudes t_{kl}^{ab} for which $\{k,l\} \in [\underline{P}]$, where $[\underline{P}]$ denotes the set of occupied orbitals that are spatially local to the atomic site P (including

P); see Figure 1. In practice, the DEC-CCSD atomic fragment energy, E_P^{CCSD}, is thus determined by (i) solving the CCSD amplitude equations in the truncated $[\underline{P}] \cup [\overline{P}]$ space and (ii) extracting the amplitudes of the $\underline{P} \cup [\overline{P}]$ space that are needed for evaluating E_P^{CCSD} using eq 3.2.1a. Similarly, pair fragment energies are determined using unions of spaces in accordance with eq 3.2.1b. The $[\underline{P}]$ and $[\overline{P}]$ spaces are determined dynamically in a black-box manner during the calculation to ensure that the resulting error in the atomic fragment energy, E_P^{CCSD}, is below the so-called fragment optimization threshold (FOT). This procedure will thus account for the coupling effects mentioned earlier. The practical implementation of the fragment optimization procedure is described in ref 20.

Turning our attention to the (T) correction, the orbital spaces entering the expressions for the fourth-order DEC-CCSD(T) atomic fragment and pair interaction energies in eqs 3.1.5 may be truncated in a similar fashion

$$E_P^{[4]} = 2 \sum_{ab \in [\overline{P}]} \sum_{ij \in \underline{P}} (2t_{ij}^{ab} - t_{ji}^{ab}) T_{ij}^{ab} \tag{3.2.2a}$$

$$\Delta E_{PQ}^{[4]} = 2 \sum_{ab \in [\overline{P}] \cup [\overline{Q}]} \left(\sum_{i \in \underline{P}} \sum_{j \in \underline{Q}} + \sum_{i \in \underline{Q}} \sum_{j \in \underline{P}} \right)(2t_{ij}^{ab} - t_{ji}^{ab}) T_{ij}^{ab} \tag{3.2.2b}$$

while the expressions for the fifth-order energies in eqs 3.1.6 remain unchanged. In practice, the actual spaces required for the accurate evaluation of the (T) correction will be constrained to the truncated $[\underline{P}] \cup [\overline{P}]$ spaces used in the preceding calculation of the CCSD correlation energy due to two primary reasons. First, as the fourth- and fifth-order contributions to the (T) correction are constructed from CCSD singles and/or doubles amplitudes, these will only be satisfactorily described within truncated fragment spaces suitable for the CCSD model. Second, the total (T) correction is known from the literature to be roughly an order of magnitude smaller than the CCSD correlation energy,[25] and the errors introduced from reusing the CCSD fragment spaces are thus expected to be minor compared to the intrinsic FOT error. As a result, we will refrain from attempting to improve upon the underlying $[\underline{P}] \cup [\overline{P}]$ spaces obtained for the CCSD model when evaluating the (T) correction. Furthermore, we will also use union spaces in the calculation of (T) pair interaction energies. Both of these assumptions will be numerically justified from the DEC-CCSD(T) results in section 4.

In ref 21, it was illustrated how the dominating contributions to the CCSD pair interaction energies in eq 3.2.1b, that is, those that arise from the CCSD doubles amplitudes, decay asymptotically as r_{PQ}^{-6} (where r_{PQ} is the interatomic distance between atomic sites P and Q), thereby exhibiting a decay rate in accordance with that of regular dispersion energies. In short, the origin of this decay rate may be traced back to the fact that both the CCSD doubles amplitudes and the integrals entering eq 3.2.1b decay as r_{PQ}^{-3} whenever $i \in \underline{P}$ and $j \in \underline{Q}$. For this reason, we may neglect pair interaction energies beyond a certain interatomic distance, again without compromising the precision of the total correlation energy. Neglecting contributions to E^{CCSD} from distant pairs thus reduces the total scaling into one that formally depends only linearly on the size of the system.

For the fourth- and fifth-order (T) pair interaction energies in eqs 3.2.2b and 3.1.6b, respectively, we initially note how the fifth-order contributions will typically be an order of magnitude smaller than the corresponding fourth-order contributions.[25]

For this reason, the actual (T) correction for a pair at a large interatomic separation will be determined almost exclusively by the dominant fourth-order contributions, and when analyzing the distance decay of the (T) pair interaction energies, we may limit our analysis to these. In order to conduct a similar analysis for the (T) pair interaction energies as the one done for the CCSD counterparts, it is instructive to turn to an alternative formulation of the fourth-order contribution. From coupled cluster perturbation theory,[25,29] this contribution may be written in terms of the Møller–Plesset fluctuation potential, $\hat{\Phi}$, as

$$E^{[4]} = \langle \mathrm{HF}|[\hat{\Phi}, \tilde{T}_2^{[3]}]|\mathrm{HF}\rangle \qquad (3.2.3)$$

where $\tilde{T}_2^{[3]} = \sum_{\mu_2} \tilde{t}_{\mu_2}^{[3]} \hat{\tau}_{\mu_2}$ is a double excitation operator built from the following third-order doubles amplitudes

$$\tilde{t}_{\mu_2}^{[3]} = -\varepsilon_{\mu_2}^{-1}\langle \mu_2|[\hat{\Phi}, T_3]|\mathrm{HF}\rangle \qquad (3.2.4)$$

In eq 3.2.4, ε_{μ_2} is the orbital energy difference between the virtual and occupied orbitals of double excitation μ_2 (cf. eq 2.0.7), while T_3 is a triple excitation operator built from the amplitudes in eq 2.0.6.

Writing out the fourth-order contribution to the (T) correction in eq 3.2.3, we arrive at the following expression

$$E^{[4]} = \sum_{ab} \sum_{ij} \tilde{t}_{ij}^{ab,[3]} L_{iajb} \qquad (3.2.5)$$

Comparing eq 3.2.5 to the corresponding expression for the doubles contribution to the CCSD energy in eq 2.0.2, we note how these greatly resemble one another. Since the third-order doubles amplitudes in eq 3.2.4 represent the lowest-order relaxation contribution from triple excitations to the doubles amplitudes in the coupled cluster singles, doubles, and triples model[30] (CCSDT), which decay with the interatomic distance between atomic sites P and Q in the same way as the CCSD doubles amplitudes, i.e., as r_{PQ}^{-3}, the fourth-order contribution to the (T) correction, and thus the total (T) correction, will decay as r_{PQ}^{-6}. For this reason, we may neglect contributions to $E^{(\mathrm{T})}$ from distant pairs following the same line of arguments that led to a reduction in the computational scaling of the CCSD energy and, in return, obtain an algorithm for the evaluation of the CCSD(T) energy that scales only linearly with the size of the system.

In outlining the final DEC-CCSD(T) algorithm, we note that two levels of approximations have been introduced for the fourth-order contributions in eqs 3.2.2 compared to the exact expressions in eq 2.0.12a, while only one of these have been introduced for the fifth-order contributions in eqs 3.1.6 compared to eq 2.0.12b. For the fourth-order contributions, the summations over the virtual space have been truncated (approximation i), and the CCSD amplitudes t_{ij}^{ab} as well as the T_{ij}^{ab} intermediates have been determined within a truncated set of localized HF orbitals (approximation ii). For example, the $[\underline{P}]$ and $[\overline{P}]$ spaces have been used for atomic fragment P (see Figure 1). For the fifth-order contributions, only approximation ii has been invoked; i.e., truncated spaces have been used in the determination of the CCSD singles amplitudes t_i^a and the T_i^a intermediates.

The DEC-CCSD(T) algorithm can now be summarized as follows:

(i) Determine localized occupied and virtual HF MOs.

(ii) For each atomic site P, determine the optimized orbital spaces $[\underline{P}]$ and $[\overline{P}]$ as detailed in ref 20.

(iii) Solve the CCSD amplitude equations in the $[\underline{P}] \cup [\overline{P}]$ space and evaluate the CCSD atomic fragment energy, E_P^{CCSD}, using eq 3.2.1a.

(iv) Transform the local HF orbitals of the $[\underline{P}] \cup [\overline{P}]$ space into a pseudocanonical basis in order to generate triples amplitudes on the fly using eq 2.0.6 (thus avoiding their storage) and evaluate the T_{ij}^{ab} and T_i^a intermediates (eqs 2.0.13) in this basis.

(v) Transform T_{ij}^{ab} and T_i^a back into the local basis and evaluate $E_P^{(\mathrm{T})}$ in this basis using eqs 3.2.2a and 3.1.6a, recalling that the contractions between cluster amplitudes and intermediates are limited to the restricted sets of local orbitals $i,j \in \underline{P}$ and $a,b \in [\overline{P}]$.

(vi) Repeat steps iii–v for the pair fragments PQ using unions of atomic fragment orbital spaces; see eqs 3.2.1b, 3.2.2b, and 3.1.6b; pair fragments with large interatomic distances (small energy contributions) may be neglected.

(vii) Add up the CCSD and (T) atomic fragment and pair interaction energies to get the total DEC-CCSD(T) energy using eqs 3.1.1 and 3.1.3.

Finally, we stress how the intermediate transformations to and from a pseudocanonical fragment basis are collectively nothing but a computationally efficient way of evaluating the (T) correction in the local HF basis. By solving the equations for the T_{ij}^{ab} and T_i^a intermediates in a diagonal rather than a local basis, we are capable of generating individual triples amplitudes on demand, thereby circumventing the physical storage of the complete six-dimensional tensor of triples amplitudes. The actual summations over the occupied space in eqs 3.2.2 and 3.1.6, however, must be restricted to only those local orbitals that belong to the $\underline{P}$ and $\underline{Q}$ spaces, which is why we subsequently need to back-transform T_{ij}^{ab} and T_i^a to the original local basis.

4. NUMERICAL RESULTS

In the present section, we demonstrate how the DEC-CCSD(T) model—via a single input parameter (the FOT)—allows for error control and systematic convergence toward results obtained with the CCSD(T) model in its conventional canonical formulation. Proof of concept investigations are performed on a set of medium-sized molecules for which the conventional CCSD(T) model can be applied for a direct comparison. We will consider a test set consisting of the following molecules/systems:

(i) two water clusters—one with 12 water molecules (system 1a) and one with 20 (system 1b)

(ii) two linear, saturated fatty acids—$C_{12}H_{24}O_2$ (system 2a) and $C_{16}H_{32}O_2$ (system 2b)

(iii) two α-helix structures—one with three glycine residues (system 3a) and one with four (system 3b)

(iv) two conjugated hydrocarbons—$C_{12}H_{14}$ (system 4a) and $C_{16}H_{18}$ (system 4b)

All calculations are performed using the Dunning correlation-consistent cc-pVDZ and cc-pVTZ basis sets[31] with the frozen-core approximation invoked.

While systems 1a, 2a, 3a, and 4a are small enough for conventional CCSD(T)/cc-pVTZ calculations to be performed, the calculations on the larger systems 1b, 2b, 3b, and 4b have only been carried out within the smaller cc-pVDZ basis set. All calculations—conventional as well as DEC calculations

Table 1. Conventional Canonical Correlation Energies (a.u.) Calculated within the cc-pVTZ Basis Set for Systems 1a, 2a, 3a, and 4a and the cc-pVDZ Basis Set for Systems 1b, 2b, 3b, and 4b

model	MP2	CCSD	[4]	[5]	(T)	CCSD(T)
System 1a	−3.22086	−3.27285	−0.10832	0.00313	−0.10519	−3.37803
System 2a	−2.54756	−2.66321	−0.11362	0.00348	−0.11014	−2.77350
System 3a	−2.53798	−2.57194	−0.12294	0.00618	−0.11676	−2.68870
System 4a	−1.91519	−1.99236	−0.10457	0.00228	−0.10230	−2.09466
System 1b	−4.19401	−4.34508	−0.08606	0.00381	−0.08225	−4.42733
System 2b	−2.64643	−2.85048	−0.09245	0.00302	−0.08943	−2.93991
System 3b	−2.64774	−2.73911	−0.10103	0.00709	−0.09394	−2.83305
System 4b	−2.09819	−2.23745	−0.09706	0.00228	−0.09478	−2.33223

for the MP2, CCSD, and CCSD(T) models—have been performed using a local version of the LSDALTON program[32,33] (the DEC-CCSD(T) model in a pilot implementation), and for all of the presented proof of concept DEC calculations, regardless of the CC model, we have used atomic fragment orbital spaces optimized at the MP2 level of theory.[20]

In section 4.1, we compare DEC-CC and conventional CC correlation energies for all of the eight test systems, while the decaying behavior of the DEC-CCSD(T) triples pair interaction energies with respect to interatomic distance is investigated in section 4.2.

4.1. DEC-CCSD(T) Correlation Energy. In this section, we compare DEC-CCSD(T) correlation energies calculated using FOT values of 10^{-3}, 10^{-4}, and 10^{-5} a.u. to conventional CCSD(T) results. In the following analyses, the total CCSD(T) correlation energy will be decomposed into the CCSD correlation energy and the (T) correction, which is further partitioned into the fourth- and fifth-order contributions of eq 2.0.4. The results for the CCSD correlation energy and the (T) correction will be reported alongside DEC-MP2 and conventional MP2 correlation energies for comparison. Table 1 gives conventional CC correlation energies for the systems of the test set. In Table 2, we investigate the performance of the DEC-MP2, DEC-CCSD, and DEC-CCSD(T) models by reporting the total error in the DEC-CC correlation energy, i.e., the difference between the DEC-CC correlation energy (E^{DEC-CC}) and the conventional CC correlation energy for the full molecule (E^{CC}),

$$\delta CC = E^{DEC-CC} - E^{CC} \qquad (4.1.1)$$

as well as the DEC recovery of the full correlation energy,

$$\Delta CC = \frac{E^{DEC-CC}}{E^{CC}} \qquad (4.1.2)$$

From the results in Table 2, we observe a reduction of the total error in the correlation energy (δCC) by roughly an order of magnitude whenever the FOT is reduced by an equal amount. This behavior is observed across all of the models and even holds for the (T) energy correction alone. For all of the test systems, the DEC recovery (ΔCC) for a given FOT is independent of the nature of the system in question (homo- or heterogeneous, saturated or unsaturated, one- or three-dimensional overall structure, dominated by covalent or hydrogen bonds, etc.). At a FOT of 10^{-4} a.u., for example, the DEC-CCSD(T) model succeeds in recovering between 99.83% and 99.96% of the conventional CCSD(T) result. Furthermore, we observe the same pattern for the relative errors in moving from a double-ζ to a triple-ζ basis set.

Upon inspecting the individual entries of Table 2, we notice how the CCSD and (T) total errors in the correlation energy

are of similar magnitude, indicating that neither of the two dominates the total CCSD(T) error. Phrased differently, no unnecessary efforts have been made at determining any of the two contributions to the total CCSD(T) correlation energy at a higher level of precision than the other. This is found to be true for both loose and tight FOT values. The smaller recoveries for the (T) correction, i.e., larger relative errors, in particular at lower FOT values, naturally arise due to the fact that the (T) correction is more than an order of magnitude smaller than the CCSD correlation energy. The total CCSD errors, however, appear at times to be artificially low; compare, e.g., the MP2 and CCSD errors for systems 1a and 2a at a FOT of 10^{-4} a.u. These low CCSD errors are due to cancellations of errors between the individual CCSD atomic fragment and pair fragment errors, which can have different signs. For the MP2 model and the (T) correction, the dominant fragment errors are positive, and such error cancellations are therefore much less prominent. Finally, we focus on the fourth- and fifth-order contributions to the (T) correction. As mentioned in section 3, the fourth-order contribution to the (T) energy correction is typically an order of magnitude larger in size than the fifth-order contribution, and from Table 2, we notice how this relationship holds for the total DEC errors as well. For this reason, both the total and relative DEC errors for the (T) correction will be entirely dominated by those for the fourth-order contribution. For the fifth-order contribution, we generally observe smaller total errors, but larger relative errors, than for the fourth-order contribution, due to the fact that the reference fifth-order contributions in Table 1 themselves are smaller. However, upon tightening the FOT, the relative fifth-order errors begin to close in on the same level of accuracy as observed for all of the other relative quantities in Table 2.

4.2. CCSD(T) Triples Pair Interaction Energies. As previously discussed for the MP2 and CCSD models,[20,21] the decay of the pair interaction energies in eq 3.2.1b with interatomic distance is an integral part of the DEC method as it allows for a screening of negligible contributions from distant pairs. As mentioned in section 3.2, this screening reduces the scaling of the method from one that depends quadratically on system size to one that depends only linearly. In this section, we provide numerical results that support the theoretical investigations of section 3.2 on the rapid decay of the CCSD(T) triples pair interaction energies in eqs 3.2.2b and 3.1.6b with interatomic pair distance. In Figure 2, we plot the CCSD as well as the fourth- and fifth-order (T) pair interaction energies as a function of interatomic pair distance for system 1b. The results in Figure 2 have been obtained by carrying out a CCSD(T) calculation on the full water cluster and subsequently extracting the pair interaction energies using eqs 3.1.5b and 3.1.6b (and eq 3.1.2b for the CCSD pair energies).

Table 2. DEC-CC (MP2, CCSD, and CCSD(T)) Total Errors (δCC, a.u.) and Recoveries (ΔCC, %) with Respect to the Conventional Correlation Energies in Table 1 for Different Values of the FOT (a.u.)

FOT	10^{-3}	10^{-4}	10^{-5}	10^{-3}	10^{-4}	10^{-5}
		System 1a			System 1b	
δMP2	1.75×10^{-2}	3.11×10^{-3}	2.10×10^{-4}	4.37×10^{-2}	5.72×10^{-3}	5.58×10^{-4}
δCCSD	9.98×10^{-3}	-5.47×10^{-4}	-4.58×10^{-4}	3.57×10^{-2}	4.84×10^{-3}	2.87×10^{-4}
δCCSD(T)	1.70×10^{-2}	2.42×10^{-3}	-8.99×10^{-5}	4.70×10^{-2}	7.11×10^{-3}	6.61×10^{-4}
δ(T)	7.06×10^{-3}	2.97×10^{-3}	3.68×10^{-4}	1.13×10^{-2}	2.27×10^{-3}	3.74×10^{-4}
δ[4]	7.49×10^{-3}	3.12×10^{-3}	4.05×10^{-4}	1.20×10^{-2}	2.39×10^{-3}	4.00×10^{-4}
δ[5]	-4.23×10^{-4}	-1.54×10^{-4}	-3.71×10^{-5}	-7.04×10^{-4}	-1.18×10^{-4}	-2.55×10^{-5}
ΔMP2	99.46	99.90	99.99	98.96	99.86	99.99
ΔCCSD	99.70	100.02	100.01	99.18	99.89	99.99
ΔCCSD(T)	99.50	99.93	100.00	98.94	99.84	99.99
Δ(T)	93.29	97.18	99.65	86.29	97.24	99.54
Δ[4]	93.09	97.12	99.63	86.08	97.23	99.54
Δ[5]	86.51	95.10	98.82	81.53	96.91	99.33
		System 2a			System 2b	
δMP2	4.68×10^{-2}	4.54×10^{-3}	5.50×10^{-4}	4.63×10^{-2}	6.05×10^{-3}	6.69×10^{-4}
δCCSD	2.77×10^{-2}	6.93×10^{-4}	-1.37×10^{-5}	1.76×10^{-2}	3.40×10^{-3}	3.79×10^{-4}
δCCSD(T)	3.78×10^{-2}	2.59×10^{-3}	3.49×10^{-4}	2.90×10^{-2}	5.11×10^{-3}	6.29×10^{-4}
δ(T)	1.01×10^{-2}	1.89×10^{-3}	3.63×10^{-4}	1.15×10^{-2}	1.71×10^{-3}	2.49×10^{-4}
δ[4]	1.04×10^{-2}	1.96×10^{-3}	3.66×10^{-4}	1.20×10^{-2}	1.77×10^{-3}	2.55×10^{-4}
δ[5]	-3.17×10^{-4}	-6.63×10^{-5}	-2.87×10^{-6}	-4.74×10^{-4}	-6.03×10^{-5}	-5.14×10^{-6}
ΔMP2	98.16	99.82	99.98	98.25	99.77	99.97
ΔCCSD	98.96	99.97	100.00	99.38	99.88	99.99
ΔCCSD(T)	98.64	99.91	99.99	99.01	99.83	99.98
Δ(T)	90.81	98.28	99.67	87.15	98.09	99.72
Δ[4]	90.81	98.27	99.68	87.06	98.09	99.72
Δ[5]	90.89	98.10	99.92	84.33	98.01	99.83
		System 3a			System 3b	
δMP2	2.29×10^{-2}	3.64×10^{-3}	2.11×10^{-4}	3.61×10^{-2}	5.36×10^{-3}	3.99×10^{-4}
δCCSD	2.42×10^{-4}	-9.54×10^{-4}	-8.81×10^{-4}	9.33×10^{-3}	1.16×10^{-3}	-6.03×10^{-4}
δCCSD(T)	1.02×10^{-2}	1.10×10^{-3}	-5.35×10^{-4}	2.06×10^{-2}	3.06×10^{-3}	-2.81×10^{-4}
δ(T)	9.92×10^{-3}	2.05×10^{-3}	3.46×10^{-4}	1.13×10^{-2}	1.89×10^{-3}	3.22×10^{-4}
δ[4]	1.09×10^{-2}	2.26×10^{-3}	4.15×10^{-4}	1.26×10^{-2}	2.20×10^{-3}	3.90×10^{-4}
δ[5]	-9.87×10^{-4}	-2.08×10^{-4}	-6.98×10^{-5}	-1.26×10^{-3}	-3.12×10^{-4}	-6.76×10^{-5}
ΔMP2	99.10	99.86	99.99	98.64	99.80	99.98
ΔCCSD	99.99	100.04	100.03	99.66	99.96	100.02
ΔCCSD(T)	99.62	99.96	100.02	99.27	99.89	100.01
Δ(T)	91.50	98.24	99.70	87.96	97.99	99.66
Δ[4]	91.13	98.16	99.66	87.56	97.82	99.61
Δ[5]	84.03	96.64	98.87	82.24	95.59	99.05
		System 4a			System 4b	
δMP2	4.64×10^{-2}	4.17×10^{-3}	5.32×10^{-4}	5.77×10^{-2}	6.65×10^{-3}	9.21×10^{-4}
δCCSD	1.43×10^{-2}	-1.80×10^{-3}	2.02×10^{-5}	2.56×10^{-2}	6.17×10^{-4}	-1.32×10^{-4}
δCCSD(T)	2.96×10^{-2}	1.17×10^{-3}	4.84×10^{-4}	4.03×10^{-2}	3.63×10^{-3}	5.26×10^{-4}
δ(T)	1.53×10^{-2}	2.97×10^{-3}	4.64×10^{-4}	1.47×10^{-2}	3.01×10^{-3}	6.58×10^{-4}
δ[4]	1.54×10^{-2}	3.04×10^{-3}	4.82×10^{-4}	1.51×10^{-2}	3.12×10^{-3}	6.89×10^{-4}
δ[5]	-1.69×10^{-4}	-6.51×10^{-5}	-1.86×10^{-5}	-4.11×10^{-4}	-1.10×10^{-4}	-3.06×10^{-5}
ΔMP2	97.58	99.78	99.97	97.25	99.68	99.96
ΔCCSD	99.28	100.09	100.00	98.86	99.97	100.01
ΔCCSD(T)	98.59	99.94	99.98	98.27	99.84	99.98
Δ(T)	85.08	97.10	99.55	84.49	96.82	99.31
Δ[4]	85.24	97.10	99.54	84.43	96.79	99.29
Δ[5]	92.58	97.14	99.18	81.96	95.20	98.66

In Figure 2, we observe how the CCSD as well as the fourth- and fifth-order (T) contributions all decay rapidly with interatomic pair distance for system 1b. As expected, the fourth-order contributions are roughly an order of magnitude
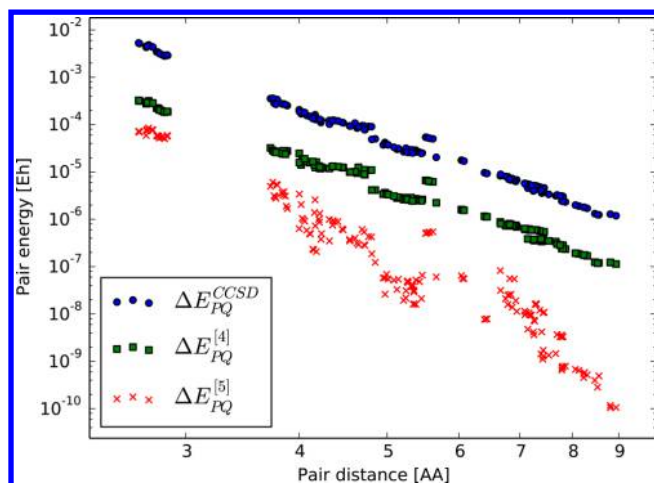
Figure 2. CCSD (ΔE_{PQ}^{CCSD}, blue circles) as well as fourth- and fifth-order (T) ($\Delta E_{PQ}^{[4]}/\Delta E_{PQ}^{[5]}$, green squares and red crosses, respectively) contributions to the CCSD(T) pair interaction energy as a function of the interatomic pair distance for system 1b.

lower than the CCSD energies, while the fifth-order contributions are roughly 2 orders of magnitude lower in energy. In line with the discussion in section 3.2, the dominant fourth-order contributions to the (T) correction decay at the same formal rate as the total CCSD energy and the fourth-order contributions are hence found to remain below the corresponding CCSD energies for all pair interaction energies in Figure 2. By carrying out similar analyses for systems 2b, 3b, and 4b in Figure 3, this is found to be a general trend, although more dense plots are inevitably obtained for these systems due to their characteristics (i.e., heterogeneity). Thus, Figures 2 and 3 collectively show how the pairs which may be screened away in a DEC-CCSD calculation—because their energy contributions are negligible in comparison with the intrinsic DEC error—may also be omitted from a DEC-CCSD(T) calculation without compromising the overall accuracy of the calculation. In fact, since the (T) contribution to the total pair interaction energy is much smaller on average than the corresponding CCSD contribution, one could even consider more elaborate schemes where individual pairs are preordered according to their estimated energy contribution (or interatomic distance) and partitioned into three different levels; at the first level (the smallest energy contributions), the pair interaction energies are neglected altogether, while, at the two following levels, they are evaluated at the CCSD and CCSD(T) levels of theory,

respectively. The practical details of such schemes will be described elsewhere.

5. SUMMARY AND CONCLUSION

We have proposed a reformulation of the (T) triples correction to the CCSD energy in terms of local HF orbitals such that its structural form aligns with our recently developed linear-scaling DEC-CC framework. As a result of the coupling to the DEC scheme, the precision of the total DEC-CCSD(T) correlation energy with respect to that obtained from a conventional calculation may be tuned via a single energy-based input parameter. In the DEC-CCSD(T) model, a number of triples intermediates are initially determined from individual CCSD(T) calculations within local atomic fragment and pair fragment orbital spaces, and the (T) energy correction next evaluated in terms of atomic fragment and pair interaction energies from a formula that structurally resembles that for the DEC-CCSD correlation energy.

The reformulated expression for the (T) triples energy correction, which forms the basis for the DEC-CCSD(T) model, is found to exhibit a formal computational cost that is twice that of the standard expression. However, in contrast to the formulation of the correction used in standard implementations, which is restricted to the nonlocal canonical HF basis, the alternative expression of the present work may be evaluated in any basis of optimized HF orbitals. As a consequence, the (T) correction can be evaluated in a basis of localized orbitals, making it possible to take advantage of the locality of the triples amplitudes and obtain a reduced overall computational scaling.

We have discussed how coupled cluster triples effects—in a basis of localized HF orbitals—may be accurately treated within small subsets of the total orbital space for the full molecular system. In summary, we have found that the same fragment orbital spaces may be used in the calculation of the CCSD correlation energy and the (T) correction, which we have substantiated through the numerical results of a series of proof of concept calculations. From the dominant distance decay of the (T) pair interaction energies, which fall off at the same formal rate as the underlying CCSD counterparts, we have furthermore found that these may be neglected beyond a certain interatomic distance (as for the DEC-CCSD model). This ultimately leads to a linear-scaling algorithm for the evaluation of the (T) correction and, in return, the total CCSD(T) correlation energy. Additionally, since the CCSD(T) atomic fragment and pair interaction energies may be evaluated
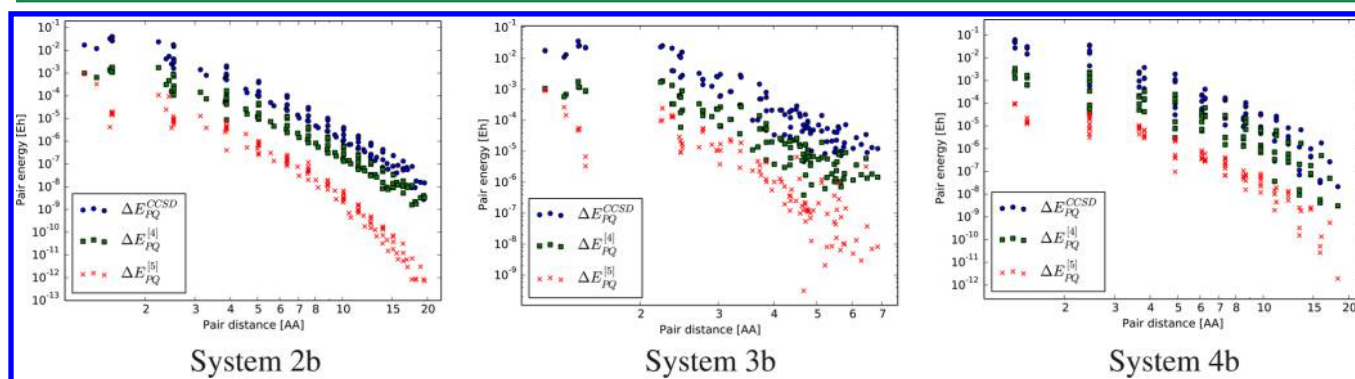
Figure 3. CCSD (ΔE_{PQ}^{CCSD}, blue circles) as well as fourth- and fifth-order (T) ($\Delta E_{PQ}^{[4]}/\Delta E_{PQ}^{[5]}$, green squares and red crosses, respectively) contributions to the CCSD(T) pair interaction energy as a function of the interatomic pair distance for systems 2b, 3b, and 4b.

independently, the algorithm for the DEC-CCSD(T) model becomes massively parallel.

As a final outlook, we note how the general structure of the (T) energy correction within the DEC scheme will also be applicable to the energy corrections of alternative noniterative CC triples models, such as, e.g., the asymmetric CCSD(T) model (the ΛCCSD(T) model)[34−36] and the so-called [T] variants of the CCSD(T) model (the CCSD[T] model[37]) and the ΛCCSD(T) model (the ΛCCSD[T] model[38]). Additionally, the perturbative energy corrections of the recently proposed CCSD(T−n) models[38−40] may also be formulated such that they align with the structure of the (T) energy correction within the DEC scheme. Although all of these alternative models come at a higher computational cost than the CCSD(T) model, applying the DEC strategy will warrant that the models may also be evaluated using formally linear-scaling algorithms.

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Notes
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