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On the convergence of perturbative coupled cluster triples expansions: Error cancellations in the CCSD(T) model and the importance of amplitude relaxation

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Recently, we proposed a novel Lagrangian-based perturbation series—the CCSD(T- n) series—which systematically corrects the coupled cluster singles and doubles (CCSD) energy in orders of the Møller-Plesset fluctuation potential for effects due to triple excitations. In the present study, we report numerical results for the CCSD(T- n) series up through fourth order which show the predicted convergence trend throughout the series towards the energy of its target, the coupled cluster singles, doubles, and triples (CCSDT) model. Since effects due to the relaxation of the CCSD singles and doubles amplitudes enter the CCSD(T- n) series at fourth order (the CCSD(T-4) model), we are able to separate these effects from the total energy correction and thereby emphasize their crucial importance. Furthermore, we illustrate how the Λ CCSD[T]/(T) and CCSD[T]/(T) models, which in slightly different manners augment the CCSD energy by the [T] and (T) corrections rationalized from many-body perturbation theory, may be viewed as approximations to the second-order CCSD(T-2) model. From numerical comparisons with the CCSD(T- n) models, we show that the extraordinary performance of the Λ CCSD[T]/(T) and CCSD[T]/(T) models relies on fortuitous, yet rather consistent, cancellations of errors. As a side product of our investigations, we are led to reconsider the asymmetric Λ CCSD[T] model due to both its rigorous theoretical foundation and its performance, which is shown to be similar to that of the CCSD(T) model for systems at equilibrium geometry and superior to it for distorted systems. In both the calculations at equilibrium and distorted geometries, however, the Λ CCSD[T] and CCSD(T) models are shown to be outperformed by the fourth-order CCSD(T-4) model. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4904754>]

I. INTRODUCTION

Within the field of high precision wave function-based electronic structure calculations, coupled cluster (CC) theory is preminent due to its hierarchy of size-extensive models of increasing accuracy, often representing the only obvious choice for a variety of chemical scenarios. In particular, the coupled cluster singles and doubles (CCSD) model¹ is the regular workhorse. However, in order to achieve relative energies of chemical accuracy (~ 1 kcal/mol), the CCSD energy has to be augmented by correction terms built from higher-level excitations. To a lowest approximation, corrections for effects due to connected triple excitations have to be considered.²

To date, a multitude of such non-iterative triples correction models have been devised, see, e.g., the introduction to Ref. 3 for a recent overview. Among these, the CCSD(T) model,⁴ which also exists in an asymmetric form as the Λ CCSD(T) model,^{5,6} is the most prominent. Common for both of these models is that they introduce the effect of triple excitations by accounting for some of the lowest-order triples energy contributions to the many-body perturbation theory (MBPT) series.⁷

More specifically, the CCSD(T) and Λ CCSD(T) models are rationalized from the sum of the lowest-order (fourth-order) triples contribution to the MBPT series and a single out of a variety of triples candidate contributions at fifth order. By retaining only the leading fourth-order contribution to the energy correction, both the CCSD(T) and the Λ CCSD(T) model may be approximated, giving rise to the CCSD[T]⁸ and Λ CCSD[T] models, respectively.

The Λ CCSD[T]/(T) and CCSD[T]/(T) models are all said to have been rationalized rather than constructed from MBPT triples contributions, since the perturbation quantities entering the original expressions are replaced by their CCSD counterparts in the models. As a result of these substitutions, higher-order effects due to the relaxation of the singles and doubles amplitudes towards their CCSD values are introduced into the final energy corrections of the models. However, whereas the right- and left-hand MBPT amplitudes entering the triples contributions are replaced by corresponding right- and left-hand (Λ) CC state parameters in the Λ CCSD[T]/(T) models, the asymmetry of these parameters in CC theory is not respected in the CCSD[T]/(T) models. We note that while the CCSD[T], CCSD(T), and Λ CCSD(T) models have all been extensively studied,^{9,10} the Λ CCSD[T] model has gone by remarkably unnoticed in the literature.

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By limiting non-iterative triples models to account for a selection of the lowest-order MBPT triples contributions only, they will not be designed to describe the effects that the triple excitations have on the underlying CCSD singles and doubles amplitudes, under the assumption that such effects are of less importance. Thus, although the parameters entering the MBPT-like energy corrections of the Λ CCSD[T]/(T) and CCSD[T]/(T) models have been replaced by the singles and doubles amplitudes of the preceding CCSD calculation, their relaxation due to the presence of triple excitations is not accounted for in any of the models. Furthermore, as all such correction models rationalized from MBPT are built upon a Hartree-Fock (HF) reference state, they will inevitably give corrections in orders of the perturbation to the HF energy, and hence not the energy which they are in fact designed to correct, i.e., the CCSD energy. To address this inconsistency, alternative models have been proposed that are built upon the CCSD state. In a recent paper,³ we used a coupled cluster singles, doubles, and triples¹¹ (CCSDT) energy Lagrangian and a Møller-Plesset partitioning of the Hamiltonian to derive a new class of perturbative triples models, denoted the CCSD(T- n) series, in which the corrections are aimed at the CCSD energy. In Ref. 3 and a consecutive paper,¹² we showed how the energy corrections of the second-order, CCSD(T-2), and third-order, CCSD(T-3), models of the CCSD(T- n) series closely resemble the corresponding corrections of the lowest-order models of the so-called CC(2)PT(n) series by Hirata and co-workers.^{13,14} In Ref. 12, we even demonstrated how the second- and third-order models of the CC(2)PT(n) series become identical to the CCSD(T-2) and CCSD(T-3) models, respectively, if they are truncated at the level of triple excitations. Like the models of the CCSD(T- n) series, the CC(2)PT(n) models are designed to correct the CCSD energy, but derived from the equation-of-motion CC (EOM-CC) ansatz rather than a CCSDT energy Lagrangian. However, in spite of their commonalities at lower orders, the CCSD(T- n) and CC(2)PT(n) series eventually start to differ at fourth order, as the energy corrections of the CC(2)PT(n) series become non-size extensive at this order in the perturbation, contrary to those of the CCSD(T- n) series that remain size extensive at any given order. This is so because fourth order is the lowest order at which changes to the CCSD singles and doubles amplitudes due to triple excitations—the so-called relaxation of the CCSD amplitudes—contribute to the energy correction. In fact, it is the improper treatment of these relaxation effects to the CCSD singles and doubles amplitudes that leads to fourth- and higher-order corrections in the CC(2)PT(n) series that are not size extensive.

In the present study, we report the first numerical results obtained with the second-, third-, and fourth-order models of the CCSD(T- n) series. As we will demonstrate, the Λ CCSD [T]/(T) and CCSD[T]/(T) models may be adequately viewed as approximations to the second-order CCSD(T-2) model. For this reason, we will present the CCSD(T- n) results alongside corresponding results obtained with the Λ CCSD[T]/(T) and CCSD[T]/(T) models in order to (i) generally compare the performance of all seven triples models in recovering the CCSDT correlation energy and (ii) interpret the results of the four latter HF-based models in terms of the CCSD(T-2)

results. Furthermore, by comparing the results obtained with the various models, we will be able to single out those contributions to the correlation energy that originate from a relaxation of the CCSD singles and doubles amplitudes. Finally, we will test how the individual models respond to (i) an increase in the size of the one-electron basis, (ii) the frozen-core approximation, and (iii) static correlation resulting from a distortion of the equilibrium geometry.

The study is thus outlined as follows. In Sec. II, we summarize the two different flavours of Lagrangian-based perturbation theory used herein—based on either a HF or a CCSD reference state—paving the way for discussions and comparisons of the different triples models under investigation. In Sec. III, the energy corrections of the three lowest-order models of the CCSD(T- n) series are discussed, while the Λ CCSD[T]/(T) and CCSD[T]/(T) models are briefly revisited in Sec. IV. In Sec. V, we perform a theoretical comparison of all seven models followed by details on the implementation of the CCSD(T- n) models in the `CFOUR` program¹⁵ in Sec. VI and computational details in Sec. VII. In Sec. VIII, we look at the general performance of the various models by performing calculations on a test set of small-sized molecules at their equilibrium geometries; the recovery of the full CCSDT correlation energy is the topic of Sec. VIII A, amplitude relaxation effects in the CCSD(T- n) series are separated out and analyzed in Sec. VIII B, Sec. VIII C investigates the error cancellation occurring in the Λ CCSD[T]/(T) and CCSD[T]/(T) models, and basis set convergence and the handling of core correlation are the topics of Sec. VIII D. In Sec. IX, we examine how all of the seven models under investigation respond to bond stretching in two simple cases (the HF and H₂O molecules). Some conclusive remarks are finally given in Sec. X.

II. COUPLED CLUSTER PERTURBATION THEORY USING LAGRANGIAN TECHNIQUES

In coupled cluster theory, we adapt an exponential ansatz for the wave function

$$|\text{CC}\rangle = \exp(\hat{T})|\text{HF}\rangle. \quad (2.1)$$

The cluster operator in Eq. (2.1) is expressed as $\hat{T} = \sum_i^N \hat{T}_i$, where $\hat{T}_i = \sum_{\mu_i} t_{\mu_i} \hat{\tau}_{\mu_i}$, N is the number of electrons, and $|\text{HF}\rangle$ is the Hartree-Fock state. Here, $\hat{\tau}_{\mu_i}$ refers to an excitation operator for the excited determinant $|\mu_i\rangle = \hat{\tau}_{\mu_i}|\text{HF}\rangle$, and t_{μ_i} is the cluster amplitude describing the excitation. Generally, we will reserve the greek indices, $\{\mu_i, \nu_j, \eta_k, \dots\}$, for specific excitations within manifolds at excitation levels i, j, k, \dots , and we will assume real spin orbitals.

The CC energy is given as

$$\begin{aligned} E_{\text{CC}} &= \langle \text{HF} | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \text{HF} \rangle \\ &= \langle \text{HF} | \hat{H} \exp(\hat{T}) | \text{HF} \rangle, \end{aligned} \quad (2.2)$$

where the cluster amplitudes satisfy the cluster amplitude equations

$$\langle \mu_i | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \text{HF} \rangle = 0. \quad (2.3)$$

The Hamiltonian in Eqs. (2.2) and (2.3) may be partitioned as in regular Møller-Plesset perturbation theory²

$$\hat{H} = \hat{f} + \hat{\Phi}, \quad (2.4)$$

where, assuming a canonical HF basis, the Fock operator, \hat{f} , is given as $\hat{f} = \sum_P \epsilon_P a_P^\dagger a_P$ and ϵ_P is the orbital energy of spin orbital P . In Eq. (2.4), $\hat{\Phi}$ denotes the Møller-Plesset fluctuation potential, $\hat{\Phi} = \hat{g} - \hat{V}_{\text{HF}}$, where \hat{g} is the two-electron repulsion operator and $\hat{V}_{\text{HF}} = \sum_{PQ} V_{PQ} a_P^\dagger a_Q$ is the Fock potential with elements $V_{PQ} = \sum_I g_{PQII}^a$ (the index I runs over the full set of occupied spin orbitals and indices P, Q are unrestricted). In the Fock potential, $g_{PQRS}^a = g_{PQRS} - g_{PSRQ}$ is an antisymmetrized two-electron integral written in ordinary Mulliken notation,² and we note that the electron-independent contribution to the energy from the nuclei, h_{nuc} , has been omitted from the Hamiltonian in Eq. (2.4).

The CC energy in Eq. (2.2) is not variational with respect to variations in the cluster amplitudes. To obtain an energy expression that is variational, we introduce the CC energy Lagrangian, in which the amplitude equations are added to the energy as a constraint via a term that contains undetermined Lagrange multipliers, $\{\tilde{t}_{\nu_j}\}$ ^{2,16}

$$\begin{aligned} L(\mathbf{t}, \tilde{\mathbf{t}}) &= \langle \text{HF} | \hat{H} \hat{T} | \text{HF} \rangle + \sum_j \langle \tilde{t}_j | \hat{H} \hat{T} | \text{HF} \rangle \\ &= \langle \Lambda | \hat{H} \hat{T} | \text{HF} \rangle. \end{aligned} \quad (2.5)$$

In Eq. (2.5), we have introduced the similarity-transformed Hamiltonian

$$\hat{H}^{\hat{T}} = \exp(-\hat{T}) \hat{H} \exp(\hat{T}) \quad (2.6)$$

as well as a shorthand notation for the multiplier state $\langle \tilde{t}_j |$

$$\langle \tilde{t}_j | = \sum_{\nu_j} \tilde{t}_{\nu_j} \langle \nu_j |. \quad (2.7)$$

Furthermore, we have introduced the linearly parametrized left-hand $\langle \Lambda |$ CC state

$$\langle \Lambda | = \langle \text{HF} | + \sum_j \langle \tilde{t}_j |, \quad (2.8)$$

the parameters of which we will refer to as Lagrange multipliers, or multipliers for short, while we will reserve the amplitude label for the parameters of the exponentially parametrized right-hand CC state in Eq. (2.1). The variational conditions on the Lagrangian in Eq. (2.5) give equations for determining both the cluster amplitudes and multipliers

$$\partial L / \partial \tilde{t}_{\mu_i} = 0, \quad (2.9a)$$

$$\partial L / \partial t_{\mu_i} = 0. \quad (2.9b)$$

If we introduce the Møller-Plesset partitioning of the Hamiltonian (Eq. (2.4)) in the expression for the Lagrangian in Eq. (2.5) as well as in the amplitude and multiplier equations of Eq. (2.9), perturbative energy corrections may be determined in orders of the fluctuation potential by applying Wigner's $2n+1$ rule for the amplitudes and the $2n+2$ rule for the multipliers.^{17,18} Depending on the state of reference, corrections may be determined to either the HF energy or the energy of any truncated CC model.

By truncating the Lagrangian in Eq. (2.5) at the CCSDT level, we have recently shown how corrections to the CCSD energy can be determined that formally converge towards the

CCSDT target limit.^{3,12} These energy corrections, forming a perturbation series denoted the CCSD(T- n) series, are derived by parametrizing the CCSDT energy Lagrangian around the CCSD energy as the reference point. Explicit expressions for the CCSD(T- n) energy corrections are given in Sec. III A.

Alternatively, the CCSD energy may be augmented by correction terms rationalized from the leading-order (fourth- and fifth-order) triples contributions to the MBPT series²

$$E_{\text{T}}^{[4]} = \langle \tilde{t}_2^{[1]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle, \quad (2.10a)$$

$$\begin{aligned} E_{\text{T}}^{[5]} &= \langle \tilde{t}_1^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle + \langle \tilde{t}_2^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle \\ &\quad + \langle \tilde{t}_3^{[2]} | [\hat{\Phi}, \hat{T}_2^{[2]}] | \text{HF} \rangle + \langle \tilde{t}_3^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle \\ &\quad + \frac{1}{2} \langle \tilde{t}_3^{[2]} | [[\hat{\Phi}, \hat{T}_2^{[1]}], \hat{T}_2^{[1]}] | \text{HF} \rangle. \end{aligned} \quad (2.10b)$$

In Eq. (2.10), the operator $\hat{T}_i^{[p]}$ for excitation level i is defined as

$$\hat{T}_i^{[p]} = \sum_{\mu_i} t_{\mu_i}^{[p]} \hat{\tau}_{\mu_i}, \quad p = 1, 2, \dots, \quad (2.11)$$

where $t_{\mu_i}^{[p]}$ is the amplitude of order p in the fluctuation potential (with respect to the HF state) for the excitation μ_i . The first-order doubles amplitudes and multipliers are given as

$$\begin{aligned} \epsilon_{\mu_2} t_{\mu_2}^{[1]} &= -\langle \mu_2 | \hat{\Phi} | \text{HF} \rangle = -\langle \text{HF} | [\hat{\Phi}, \hat{\tau}_{\mu_2}] | \text{HF} \rangle \\ &= \epsilon_{\mu_2} \tilde{t}_{\mu_2}^{[1]}, \end{aligned} \quad (2.12)$$

while the second-order singles, doubles, and triples amplitudes and multipliers are given as

$$\begin{aligned} \epsilon_{\mu_i} t_{\mu_i}^{[2]} &= -\langle \mu_i | [\hat{\Phi}, \hat{T}_2^{[1]}] | \text{HF} \rangle = -\langle \tilde{t}_2^{[1]} | [\hat{\Phi}, \hat{\tau}_{\mu_i}] | \text{HF} \rangle \\ &= \epsilon_{\mu_i} \tilde{t}_{\mu_i}^{[2]}, \quad i = 1, 2, 3. \end{aligned} \quad (2.13)$$

In Eqs. (2.12) and (2.13), ϵ_{μ_i} denotes the difference in orbital energies between the virtual and occupied spin orbitals involved in excitation μ_i .

As mentioned in Sec. I, prominent examples of models devised in this manner include the CCSD(T), CCSD[T], and ACCSD(T) models, and in Sec. IV, we will also consider the ACCSD[T] model, which is the asymmetric analogue of the CCSD[T] model. Furthermore, the lowest-order MBPT triples contributions may be used for interpreting the lowest-order CCSD(T- n) models (Sec. III B), and one may examine how, for instance, the CCSD(T) and ACCSD(T) models differ from one another by looking at their constituent contributions from an MBPT perspective (Sec. V). At this point, it suffices to state that the main differences between deriving the MBPT series from the Lagrangian in Eq. (2.5) as opposed to the CCSD(T- n) series are that no truncations are made to the cluster operator and orders are counted in the fluctuation potential with respect to the HF energy, not the CCSD energy.

III. CCSD STATE-BASED NON-ITERATIVE TRIPLES MODELS

In this section, we briefly revisit the lowest-order models of the CCSD(T- n) series. In Sec. III A, we give explicit expressions for the energy corrections of the models, while these are

interpreted in terms of the triples contributions to the MBPT series in Sec. III B.

A. The CCSD(T-*n*) series

In the CCSD(T-*n*) series,^{3,12} the energy of the zeroth- and first-order models is equal to the CCSD energy, i.e., CCSD(T-0) = CCSD(T-1) = E_{CCSD} . In the CCSD(T-*n*) series, we will use ordinary parentheses for counting orders with respect to the CCSD reference state, thereby distinguishing the notation from when we are counting orders in the MBPT series, in which the order designation is with respect to the HF reference state and where we will use a square bracket notation (cf. Eq. (2.10)). The second-, third-, and fourth-order corrections to the CCSD energy resulting from the CCSD(T-2), CCSD(T-3), and CCSD(T-4) models are given as

$$E_{T-2}^{(2)} = \langle {}^* \hat{t}_1 | [\hat{\Phi}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle + \langle {}^* \hat{t}_2 | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle, \quad (3.1a)$$

$$E_{T-3}^{(3)} = \langle \delta \hat{t}_3^{(1)} | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle, \quad (3.1b)$$

$$E_{T-4}^{(4)} = \langle {}^* \hat{t}_2 | [[\hat{\Phi}, \delta \hat{T}_3^{(1)}], \delta \hat{T}_1^{(2)}] | \text{HF} \rangle + \langle \delta \hat{t}_3^{(1)} | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(2)}] | \text{HF} \rangle + \langle \delta \hat{t}_3^{(1)} | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_1^{(2)} + \delta \hat{T}_2^{(2)}] | \text{HF} \rangle, \quad (3.1c)$$

where the asterisk notation indicates that the corresponding amplitudes and multipliers are those obtained from a CCSD calculation. In Eq. (3.1), the operator $\delta \hat{T}_i^{(p)}$ is defined in analogy with Eq. (2.11), and the singles, doubles, and triples right-hand state amplitudes entering the cluster operators are given as

$$\delta t_{\mu_3}^{(1)} = -\epsilon_{\mu_3}^{-1} \langle \mu_3 | \hat{\Phi}^{*\hat{T}} | \text{HF} \rangle, \quad (3.2a)$$

$$\delta t_{\mu_1}^{(2)} = -\epsilon_{\mu_1}^{-1} \langle \mu_1 | [\hat{\Phi}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle, \quad (3.2b)$$

$$\delta t_{\mu_2}^{(2)} = -\epsilon_{\mu_2}^{-1} \langle \mu_2 | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle, \quad (3.2c)$$

$$\delta t_{\mu_3}^{(2)} = -\epsilon_{\mu_3}^{-1} \langle \mu_3 | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle. \quad (3.2d)$$

The first-order triples left-hand state parameters (multipliers) in Eq. (3.1) are given as

$$\delta \bar{t}_{v_3}^{(1)} = -\epsilon_{v_3}^{-1} (\langle {}^* \hat{t}_1 | [\hat{\Phi}, \hat{t}_{v_3}] | \text{HF} \rangle + \langle {}^* \hat{t}_2 | [\hat{\Phi}^{*\hat{T}}, \hat{t}_{v_3}] | \text{HF} \rangle), \quad (3.3)$$

and the operator $\hat{\Phi}^{*\hat{T}}$ in Eqs. (3.1)–(3.3) is the CCSD similarity-transformed fluctuation potential

$$\hat{\Phi}^{*\hat{T}} = \exp(-({}^* \hat{T}_1 + {}^* \hat{T}_2)) \hat{\Phi} \exp({}^* \hat{T}_1 + {}^* \hat{T}_2). \quad (3.4)$$

We note how all of the corrections of the CCSD(T-*n*) series in Eq. (3.1) are expressed in terms of either the HF bra state, $\langle \text{HF} |$, or a multiplier state. Furthermore, we note that the energy and amplitude/multiplier corrections are all expressed in terms of the CCSD similarity-transformed fluctuation potential of Eq. (3.4).

B. Fourth- and fifth-order MBPT energy contributions in the CCSD(T-*n*) series

We will now identify which fourth- and fifth-order MBPT energy contributions of Eq. (2.10) are contained in the corrections of Eq. (3.1). As the CCSD singles and doubles amplitudes

may be expanded in MBPT as

$${}^* t_{\mu_1} = \bar{t}_{\mu_1}^{[2]} + \mathcal{O}(3), \quad (3.5a)$$

$${}^* t_{\mu_2} = \bar{t}_{\mu_2}^{[1]} + \bar{t}_{\mu_2}^{[2]} + \mathcal{O}(3), \quad (3.5b)$$

we can express the CCSD doubles operator entering the $\delta t_{\mu_3}^{(1)}$ amplitudes in Eq. (3.2a) as

$${}^* \hat{T}_2 = \hat{T}_2^{[1]} + \hat{T}_2^{[2]} + \mathcal{O}(3) \quad (3.6)$$

and, in return, express the CCSD(T-2) energy correction as

$$\begin{aligned} E_{T-2}^{(2)} &= \langle {}^* \hat{t}_1 | [\hat{\Phi}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle + \langle {}^* \hat{t}_2 | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle \\ &= \langle \bar{t}_1^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle + \langle \bar{t}_1^{[1]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle \\ &\quad + \langle \bar{t}_2^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle + \langle \bar{t}_3^{[2]} | [\hat{\Phi}, \hat{T}_2^{[2]}] | \text{HF} \rangle \\ &\quad + \frac{1}{2} \langle \bar{t}_3^{[2]} | [[\hat{\Phi}, \hat{T}_2^{[1]}], \hat{T}_2^{[1]}] | \text{HF} \rangle + \mathcal{O}(6). \end{aligned} \quad (3.7)$$

In Eq. (3.7), we have neglected explicit terms of sixth and higher order in MBPT. For the third-order energy correction, we insert—in addition to the $\delta t_{\mu_3}^{(1)}$ amplitudes—also the $\delta \bar{t}_{\mu_3}^{(1)}$ multipliers of Eq. (3.3) and arrive at

$$\begin{aligned} E_{T-3}^{(3)} &= \langle \delta \bar{t}_3^{(1)} | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(1)}] | \text{HF} \rangle \\ &= \langle \bar{t}_3^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle + \mathcal{O}(6). \end{aligned} \quad (3.8)$$

Comparing the $E_{T-2}^{(2)}$ and $E_{T-3}^{(3)}$ corrections with the MBPT triples contributions in Eq. (2.10), we recognize that $E_{T-2}^{(2)}$ contains all fourth- and fifth-order triples contributions, except for that contained in $E_{T-3}^{(3)}$. In addition, the presence of the similarity-transformed fluctuation potential in the expression for the triples amplitudes (Eq. (3.2a)) introduces a manifold of higher-order terms (all belonging to the MBPT series) in both the $E_{T-2}^{(2)}$ and $E_{T-3}^{(3)}$ corrections.

No new fifth-order contributions are introduced in the $E_{T-4}^{(4)}$ correction—as all are accounted for by the sum of the $E_{T-2}^{(2)}$ and $E_{T-3}^{(3)}$ corrections—but we note how relaxation effects in the singles and doubles spaces due to the first-order triples amplitudes in Eq. (3.2a) are introduced from terms that involve the second-order singles and doubles amplitudes of Eqs. (3.2b) and (3.2c). This relaxation of the CCSD singles and doubles amplitudes is an effect entirely different from those that are accounted for in the $E_{T-2}^{(2)}$ and $E_{T-3}^{(3)}$ corrections. The $E_{T-4}^{(4)}$ correction thus accounts not only for the direct effect of triple excitations but also for the indirect influence of these excitations on the amplitudes from the underlying CCSD calculation. For this reason, we may construct the energy ($E_{T-4}^{(4)}$ (trip)) of a hypothetical model, denoted CCSD(T-4)-trip, that omits the contribution from the relaxed singles and doubles amplitudes ($E_{T-4}^{(4)}$ (relax))

$$E_{T-4}^{(4)} = E_{T-4}^{(4)}(\text{trip}) + E_{T-4}^{(4)}(\text{relax}), \quad (3.9a)$$

$$E_{T-4}^{(4)}(\text{trip}) = \langle \delta \bar{t}_3^{(1)} | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_3^{(2)}] | \text{HF} \rangle, \quad (3.9b)$$

$$\begin{aligned} E_{T-4}^{(4)}(\text{relax}) &= \langle {}^* \hat{t}_2 | [[\hat{\Phi}, \delta \hat{T}_3^{(1)}], \delta \hat{T}_1^{(2)}] | \text{HF} \rangle \\ &\quad + \langle \delta \bar{t}_3^{(1)} | [\hat{\Phi}^{*\hat{T}}, \delta \hat{T}_1^{(2)} + \delta \hat{T}_2^{(2)}] | \text{HF} \rangle. \end{aligned} \quad (3.9c)$$

The energy difference between results obtained with the CCSD(T-4) and CCSD(T-4)-trip models may thus be ascribed

to the relaxation of the CCSD singles and doubles amplitudes, $E_{T-4}^{(4)}$ (relax).

IV. HF STATE-BASED NON-ITERATIVE TRIPLES MODELS

In this section, we briefly outline how the Λ CCSD(T) and CCSD(T) models as well as the related Λ CCSD[T] and CCSD[T] models are obtained from the MBPT triples contributions of Sec. II. As in Sec. III, we begin in Sec. IV A by giving explicit expressions for the energy corrections of the different models followed in Sec. IV B by an identification of the specific fourth- and fifth-order MBPT triples contributions contained in each of the models.

A. The Λ CCSD[T]/(T) and CCSD[T]/(T) models

In both the Λ CCSD[T] and CCSD[T]⁸ models, the fourth-order MBPT energy contribution from triple excitations in Eq. (2.10a) is explicitly added to the CCSD energy. However, the perturbation quantities entering this term (first-order multipliers as well as first-order amplitudes via the triples amplitudes in Eq. (2.13)) are replaced by their CCSD counterparts in the two models. These replacements improve the description of the correction term, as the CCSD amplitudes and multipliers are determined to infinite order within the singles and doubles spaces (in the absence of triple excitations). In the Λ CCSD[T] model, the perturbation amplitudes and multipliers are substituted by corresponding CCSD amplitudes and multipliers, respectively, resulting in the Λ CCSD[T] triples correction to the CCSD energy

$$\begin{aligned} E^{\Lambda\text{CCSD[T]}} &= {}^*E_{\Lambda[\text{T}]}^{[4]} \\ &= \langle {}^*\hat{t}_2 | [\hat{\Phi}, {}^*\hat{T}_3] | \text{HF} \rangle, \end{aligned} \quad (4.1)$$

where the triple excitation operator, ${}^*\hat{T}_3$, in Eq. (4.1) is constructed from the amplitudes

$${}^*t_{\mu_3} = -\epsilon_{\mu_3}^{-1} \langle \mu_3 | [\hat{\Phi}, {}^*\hat{T}_2] | \text{HF} \rangle. \quad (4.2)$$

In the CCSD[T] model, however, we replace not only the perturbation amplitudes by CCSD amplitudes but also the perturbation multipliers, giving the CCSD[T] energy correction

$$\begin{aligned} E^{\text{CCSD[T]}} &= {}^*E_{[\text{T}]}^{[4]} \\ &= \langle {}^*t_2 | [\hat{\Phi}, {}^*\hat{T}_3] | \text{HF} \rangle. \end{aligned} \quad (4.3)$$

By replacing the multipliers of the Λ CCSD[T] model by amplitudes in the CCSD[T] model, the inherent difference between the parameters of the linearly parametrized left-hand CC state in Eq. (2.8) and those of the exponentially parametrized right-hand CC state in Eq. (2.1) is not respected.

In the Λ CCSD(T)^{5,6} and CCSD(T)⁴ models—based on a somewhat arbitrary selection—not only the fourth-order triples energy correction in Eq. (2.10a) but also the first of the fifth-order triples energy correction terms in Eq. (2.10b) are explicitly added to the CCSD energy

$$\begin{aligned} E^{\Lambda\text{CCSD(T)}} &= {}^*E_{\Lambda(\text{T})}^{[5]} + {}^*E_{\Lambda[\text{T}]}^{[4]} \\ &= \langle {}^*t_1 | [\hat{\Phi}, {}^*\hat{T}_3] | \text{HF} \rangle + \langle {}^*t_2 | [\hat{\Phi}, {}^*\hat{T}_3] | \text{HF} \rangle, \quad (4.4a) \\ E^{\text{CCSD(T)}} &= {}^*E_{(\text{T})}^{[5]} + {}^*E_{[\text{T}]}^{[4]} \\ &= \langle {}^*t_1 | [\hat{\Phi}, {}^*\hat{T}_3] | \text{HF} \rangle + \langle {}^*t_2 | [\hat{\Phi}, {}^*\hat{T}_3] | \text{HF} \rangle. \quad (4.4b) \end{aligned}$$

As in the CCSD[T] model, multipliers (both singles and doubles) are replaced by amplitudes in the CCSD(T) model, and the asymmetry between the left- and right-hand CC states is therefore also neglected in the CCSD(T) model.

While similar in appearance, there exist subtle differences between the Λ CCSD[T]/CCSD[T] and Λ CCSD(T)/CCSD(T) models. In Sec. V, we will discuss these from a theoretical point of view, while they will be quantified from a numerical point of view in Sec. VIII. In Sec. VIII, we will further compare the results obtained with these models to corresponding results obtained with the models of the CCSD(T-*n*) series.

B. MBPT terms in the Λ CCSD(T) and CCSD(T) models

We will now identify which fourth- and fifth-order MBPT energy contributions are considered in the Λ CCSD[T]/(T) and CCSD[T]/(T) energy corrections. As triple excitations first enter the MBPT singles and doubles amplitude and multiplier equations at third order, the CCSD singles and doubles amplitudes and multipliers will be correct (and equal to one another) through second order when a standard CCSD calculation is carried out. Since only amplitudes and multipliers through second order are needed for MBPT energy contributions through fifth order (cf. Eq. (2.10)), it is clear that—through this order—the Λ CCSD(T) and CCSD(T) models will be equivalent. The same then trivially applies for the Λ CCSD[T] and CCSD[T] models, and for this reason we will only look at the CCSD[T] and CCSD(T) energy corrections in detail.

By using Eqs. (3.5) and (3.6), we may express the ${}^*E_{[\text{T}]}^{[4]}$ contribution to the CCSD(T) energy correction in Eq. (4.4b) as

$$\begin{aligned} {}^*E_{[\text{T}]}^{[4]} &= \langle \hat{t}_2^{[1]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle + \langle \hat{t}_2^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle \\ &\quad + \langle \hat{t}_3^{[2]} | [\hat{\Phi}, \hat{T}_2^{[2]}] | \text{HF} \rangle + \mathcal{O}(6). \end{aligned} \quad (4.5)$$

The CCSD[T] and Λ CCSD[T] energy corrections thus contain (and share) one fourth-order MBPT term and two terms of fifth order. Similarly, we may express the ${}^*E_{(\text{T})}^{[5]}$ contribution in Eq. (4.4b) as

$${}^*E_{(\text{T})}^{[5]} = \langle \hat{t}_1^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle + \mathcal{O}(6). \quad (4.6)$$

The CCSD(T) energy correction in Eq. (4.4b) may therefore be expressed as

$$\begin{aligned} E^{\text{CCSD(T)}} &= \langle \hat{t}_1^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle \\ &\quad + \langle \hat{t}_2^{[1]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle + \langle \hat{t}_2^{[2]} | [\hat{\Phi}, \hat{T}_3^{[2]}] | \text{HF} \rangle \\ &\quad + \langle \hat{t}_3^{[2]} | [\hat{\Phi}, \hat{T}_2^{[2]}] | \text{HF} \rangle + \mathcal{O}(6) \end{aligned} \quad (4.7)$$

of which the Λ CCSD(T) energy correction contains the same fourth- and fifth-order terms. In the derivation of Eq. (4.7) in Refs. 2 and 16, the fourth term in Eq. (4.7) is missing.

V. COMPARISON OF THE DIFFERENT NON-ITERATIVE TRIPLES MODELS

Comparing first the CCSD(T- n) models of Sec. III to one another, we may interpret these in the following manner: although the CCSD(T-2) correction in Eq. (3.1a) describes the leading-order triples contributions to the CCSD energy correction, by accounting for projections of triples excitations onto the CCSD singles and doubles spaces, the CCSD(T-3) correction and the triples-only $E_{T-4}^{(4)}$ (trip) part (Eq. (3.9b)) of the CCSD(T-4) energy correction give contributions that arise from relaxed triples effects. The $E_{T-4}^{(4)}$ (relax) part (Eq. (3.9c)) of the CCSD(T-4) energy correction, however, describes contributions to the energy correction that arise from the relaxation of the CCSD singles and doubles amplitudes induced by the triple excitations.

Comparing next the CCSD(T- n) energy corrections in Eq. (3.1) with those of the HF-based models in Sec. IV, we note that the second-order correction, $E_{T-2}^{(2)}$, in Eq. (3.1a) is structurally similar to that of the ACCSD(T) model in Eq. (4.4a), as both corrections may be viewed as containing two distinct terms: one that describes the projection of triple excitations onto the CCSD singles space $\{\{\tilde{t}_1\}\}$ and one that describes the projection onto the CCSD doubles space $\{\{\tilde{t}_2\}\}$. Due to this similarity between the two models, we will, henceforth, refer to the two projection terms as the singles and doubles contributions to the CCSD(T-2) and ACCSD(T) energy corrections, accordingly, in the analyses to follow.

However, whereas the two projections are constructed from $\delta t_{\mu_3}^{(1)}$ triples amplitudes (Eq. (3.2a)) in the CCSD(T-2) model, ${}^*t_{\mu_3}$ amplitudes (Eq. (4.2)) are used in the corresponding ACCSD(T) projections. Additionally, the overall CCSD(T-2) energy correction as well as the involved triples amplitudes are expressed in terms of the CCSD similarity-transformed fluctuation potential in Eq. (3.4), whereas the corresponding ACCSD(T) energy correction and triples amplitudes are described in terms of the bare fluctuation potential. The ACCSD(T) model may thus be viewed as an approximation to the CCSD(T-2) model, obtained by (i) approximating the triples amplitudes in Eq. (3.2a) by the leading term (Eq. (4.2)) and (ii) expressing both contributions to the energy correction in terms of the bare rather than the CCSD similarity-transformed fluctuation potential as in the CCSD(T-2) model. By further retaining only the triples projection against the CCSD doubles space (the doubles contribution to the ACCSD(T) correction), the ACCSD[T] correction in Eq. (4.1) is obtained.

As discussed in Sec. IV A, the CCSD[T]/(T) models are best viewed as those approximations to the ACCSD[T]/(T) models that replace CCSD multipliers by amplitudes, and the models thereby neglect the differences that originate from the different parametrizations of the left- and right-hand CC states. From an inspection of the amplitude and multiplier equations in HF-based perturbation theory, it can be demonstrated how the CCSD amplitudes and multipliers are identical through second order but start to differ at third order. In general, left- and right-hand CC state parameters thus have to be carefully distinguished between when perturbation quantities are replaced by CCSD quantities, as false terms, i.e., terms that do not belong to the MBPT series, will be introduced if this distinction is not

respected. This is indeed the case for the CCSD[T]/(T) models, as leading-order differences from the MBPT series (and the ACCSD(T) model) begin to appear at sixth order in the perturbation. Numerically, we may examine the differences that arise from using right-hand instead of left-hand CC state parameters by comparing results obtained with (i) the ACCSD[T] and CCSD[T] models and (ii) the ACCSD(T) and CCSD(T) models. Finally, we recognize that the CCSD(T) model (like the ACCSD(T) model) too contains a singles and a doubles contribution to the energy correction (cf. Eq. (4.4b)), of which the CCSD[T] model only retains the doubles contribution in Eq. (4.3). The CCSD(T-2) model thus constitutes a theoretical second-order reference against which we may compare the ACCSD[T]/(T) and CCSD[T]/(T) models, as the singles and doubles contributions in these models are approximations to those in the CCSD(T-2) model. In Sec. VIII C, we will use these connections between the different models for interpreting their numerical performance.

VI. DETAILS ON THE IMPLEMENTATION

The CCSD(T- n) models for $n = 2 - 4$ have been implemented within the `CFOUR` quantum chemical program package.¹⁵ In addition, the ACCSD(T) model has been implemented, while the standard CCSD(T) model is available in numerous program packages. As the corresponding [T] analogues of the two models (ACCSD[T] and CCSD[T]) are given by retaining only the doubles contributions to the ACCSD(T) and CCSD(T) energies, cf. Eqs. (4.1) and (4.3), respectively, implementations of these follow implicitly from the ACCSD(T) and CCSD(T) implementations. In general, the implementation of the various models was facilitated by the availability of an existing code for the computation of analytic CCSDT gradients in `CFOUR`,¹⁹ as all necessary contractions between triples amplitudes and the corresponding Lagrange multipliers were readily available and could be reused.

To be more specific, the various models have been implemented in the following manner:

- ACCSD(T): For the ACCSD(T) model, the triples amplitudes in Eq. (4.2) are computed like in the CCSD(T) model. Unlike in the CCSD(T) model, these are subsequently used to compute the corresponding increments to the residuals of the singles and doubles amplitude equations, while their contractions with the CCSD singles and doubles multipliers yield the energy correction.
- CCSD(T-2): For the CCSD(T-2) model, the calculation proceeds as for the ACCSD(T) model, except that the similarity-transformed fluctuation potential is used in all steps instead of the bare potential. As for the ACCSD(T) model, the computational cost scales as M^7 , where M is a measure of the system size, and is thus about twice that of the CCSD(T) model.
- CCSD(T-3): A scheme for the CCSD(T-3) model requires either the first-order triples multipliers in Eq. (3.3) or, alternatively, parts of the second-order triples amplitudes in Eq. (3.2d). In our current implementa-

tion, the second-order triples amplitudes are computed from the first-order triples amplitudes via the triples-triples contraction already available in the CCSDT code of `cFOUR`. The second-order amplitudes are then used for computing the increments to the residuals of the singles and doubles amplitude equations, which via contractions with the CCSD multipliers yield the energy correction. Alternatively, the computation may be structured such that the second-order triples multipliers are determined and then used for obtaining the energy correction. The cost of a CCSD(T-3) calculation is of the order of M^8 , i.e., roughly that of one CCSDT iteration.

- **CCSD(T-4):** The triples-only contribution in Eq. (3.9b) is most simply obtained by computing parts of the third-order triples amplitudes from the second-order triples, again exploiting the triples-triples contraction in the existing CCSDT code, and then determining the resulting energy correction as for the CCSD(T-3) model. The first term of the relaxation contribution in Eq. (3.9c) is obtained by computing the increment to the residual of the doubles amplitude equation from the first-order triples amplitudes with the second-order fluctuation potential ($[\hat{\Phi}, \delta \hat{T}_1^{(2)}]$). Finally, the second term in Eq. (3.9c) is determined by computing from the singles and doubles increments within a CCSD(T-2) calculation the second-order corrections to the singles and doubles amplitudes (Eqs. (3.2b) and (3.2c)) and then determining the resulting third-order triples contributions together with their energy corrections. The cost of a CCSD(T-4) calculation is twice that of a CCSD(T-3) calculation, i.e., a CCSD(T-4) calculation is roughly twice as expensive as one CCSDT iteration.

Our implementations of the various models have been carefully verified by (i) comparing results against reference data obtained from simple in-core implementations (based on an unrestricted HF (UHF) reference state and use of C_1 symmetry only) and (ii) implementing most of the terms in Eqs. (3.1a)–(3.1c) using alternative algorithms (e.g., by using higher-order triples multipliers instead of amplitudes for the computations). The implementations in `cFOUR` exploit Abelian point group symmetries and work for closed-shell restricted HF (RHF) reference states, thereby achieving efficiency through rigorous spin adaptation.²⁰

VII. COMPUTATIONAL DETAILS

We will now perform a statistical performance analysis of the seven non-iterative triples models considered in Secs. III and IV—the ACCSD[T]/(T), CCSD[T]/(T), CCSD(T-2), CCSD(T-3), and CCSD(T-4) models. In doing so, we will carry out calculations on a test set of 17 small closed-shell molecules at their equilibrium geometries, all optimized at the all-electron CCSD(T)/cc-pCVQZ level of theory (listed in Sec. VIII A). This same test set was previously used in Ref. 2 for benchmarking the performance of the CCSD(T) model. As all of the models under investigation may be viewed as correcting the CCSD energy for the effects of triple excitations, and

all of the models have errors with respect to the target CCSDT model that are size extensive, we will use the following size-intensive performance measure:

$$\Delta_i(\%) = \frac{E_{\text{model},i} - E_{\text{CCSD},i}}{E_{\text{CCSDT},i} - E_{\text{CCSD},i}} \quad (7.1)$$

as a measure of the recovery of the CCSDT triples correlation energy (TCE). In Eq. (7.1), the index i references one of the sample molecules of the test set. In all of the calculations in Sec. VIII, we use Dunning’s correlation-consistent core-valence cc-pCVXZ ($X = \text{D, T, Q}$) basis sets²¹ for both all-electron and valence-electron (frozen-core) calculations, while we use the cc-pVTZ basis set for the frozen-core calculations in Sec. IX.

In performing the actual statistical analysis, we will present results in terms of the following standard statistical measures:

$$\bar{\Delta} = \frac{1}{n} \sum_{i=1}^n \Delta_i, \quad (7.2a)$$

$$\Delta_{\text{std}} = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (\Delta_i - \bar{\Delta})^2}. \quad (7.2b)$$

Furthermore, we will use Δ_{max} for denoting the recovery which has the maximum deviation (in percentage points) from the CCSDT reference. Graphically, the mean recovery ($\bar{\Delta}$) in Eq. (7.2a) and the standard deviation (Δ_{std}) in Eq. (7.2b) will be represented in terms of normal distributions

$$\rho(\Delta) = K \exp \left[-\frac{1}{2} \left(\frac{\Delta - \bar{\Delta}}{\Delta_{\text{std}}} \right)^2 \right]. \quad (7.3)$$

In Eq. (7.3), K is a normalization constant.

VIII. CALCULATIONS AT EQUILIBRIUM GEOMETRIES

In this section, we will examine the various models of Secs. III and IV by reporting their recovery of the CCSDT TCE for the molecules across the test set, cf. Eq. (7.1). In Sec. VIII A, we will look at the general performance of the models and inspect their recovery of the CCSDT TCE for the individual sample molecules. In Sec. VIII B, we will separate out the contribution to the CCSD(T-4) energy correction that originates from relaxation effects in the singles and doubles spaces ($E_{\text{T-4}}^{(4)}(\text{relax})$ in Eq. (3.9c)), while we will turn our attention to the HF-based models of Sec. IV in Sec. VIII C and inspect how intricate cancellations of errors occur for these. In Sec. VIII D, we end by examining how each of the seven models under investigation converges with respect to an increase in the one-electron basis set and how the various models respond to the frozen-core approximation.

A. General performance

In Table I, we report calculations of Δ for the individual molecules of the test set using the cc-pCVQZ basis set, while standard statistical measures are presented in Table II. In Table I, the molecules of the test set have been ranked according to the occupation number for the lowest unoccupied natural orbital (Θ) as calculated from the one-particle density

TABLE I. Recovery of the CCSDT TCE in percent (%) for the individual triples models.^a The occupation numbers for the lowest unoccupied natural orbital (Θ) have been calculated from CCSD(T) one-particle density matrices. In all calculations, all electrons have been correlated and the basis set used is cc-pCVQZ.

#	Molecule	(T-2)	(T-3)	(T-4)	[T]	(T)	Λ [T]	Λ (T)	Θ
1	NH ₃	91.1	94.2	99.9	101.5	98.6	98.9	97.1	0.027
2	HF	93.2	94.3	99.9	103.8	100.5	101.9	99.6	0.028
3	H ₂ O	92.0	94.0	99.7	102.6	99.9	100.4	98.4	0.029
4	CO	90.7	89.8	100.2	107.1	99.6	101.6	97.9	0.065
5	HCN	89.7	90.2	99.7	104.7	99.6	99.6	96.8	0.066
6	C ₂ H ₂	90.1	91.4	100.0	104.5	100.4	99.5	96.9	0.068
7	CO ₂	91.4	89.5	101.1	108.1	101.0	102.8	98.9	0.069
8	N ₂	91.6	91.8	100.4	106.7	101.9	102.1	99.0	0.074
9	CH ₂ (¹ A ₁)	80.8	88.7	94.4	89.5	87.4	85.3	84.0	0.076
10	CH ₂ O	90.7	91.6	99.9	105.5	99.8	100.8	97.5	0.077
11	H ₂ O ₂	90.8	92.7	99.6	103.7	100.6	100.2	97.8	0.078
12	C ₂ H ₄	89.2	92.2	99.3	101.7	98.4	97.2	95.2	0.078
13	HOF	90.5	92.3	99.5	104.5	100.2	100.3	97.4	0.092
14	N ₂ H ₂	90.1	91.7	99.4	104.0	100.5	99.4	97.1	0.097
15	HNO	89.8	90.9	99.2	105.2	100.3	100.1	97.1	0.107
16	F ₂	89.9	92.2	99.4	104.1	100.4	99.4	96.5	0.118
17	O ₃	86.9	85.9	100.2	108.6	101.5	100.4	95.5	0.217

^a(T- n) = CCSD(T- n); [T]/(T) = CCSD[T]/(T); Λ [T]/(T) = Λ CCSD[T]/(T).

matrix at the CCSD(T)/cc-pCVQZ level of theory. Recalling that the first-order correction of the CCSD(T- n) series vanishes, we observe from Table II a convergence trend up through the CCSD(T- n) series with the second-order CCSD(T-2) model recovering on average 89.9% of the CCSDT TCE, the third-order CCSD(T-3) model recovering 91.4%, and the fourth-order CCSD(T-4) model recovering 99.5%. While the CCSD(T-4) model generally tends to slightly underestimate the CCSDT TCE, the CCSD(T-2) and CCSD(T-3) models lead to large underestimations of this reference. Inspecting the distributions of the errors around the average CCSDT TCE recoveries, we recognize two immediate and distinct features of the CCSD(T- n) series. First of all, the ordinary staircase convergence of perturbation theory based on the HF state is preserved; while the even-ordered corrections contribute significantly to the TCE, the average third-order correction is much smaller. There are exceptions, however, like for methylene, which we will return to shortly. Second, the errors in the TCE with respect to the CCSDT results tend to group more compactly around the average recovery when moving up the CCSD(T- n) series, as is also clear from the normal distributions in Figure 1.

In Tables I and II and Figure 1, we also report the corresponding Λ CCSD[T], Λ CCSD(T), CCSD[T], and CCSD(T) results. As discussed in Sec. I, all of these models—with the

exception of the Λ CCSD[T] model—have previously been subjected to a fair number of studies. For instance, the CCSD[T] model has been shown to be tainted from a consistent overestimation of triple excitation effects,²² a flaw which is generally replenished in the CCSD(T) model.²³ Furthermore, as noted in a recent series of papers,¹⁰ results obtained with the Λ CCSD(T) model do not generally improve upon CCSD(T) results for molecules at their equilibrium geometry. However, for calculations on more distorted geometries, this balance has in some cases been shown to shift in favour of the Λ CCSD(T) model. We will investigate this further in Sec. IX where comparisons of the performance of these three models will also be made to that of the Λ CCSD[T] model.

Comparing the Λ CCSD[T]/(T) and CCSD[T]/(T) results, we notice that the Λ CCSD[T] and CCSD(T) results are of similar quality, recovering on average 99.4% and 99.5% of the CCSDT TCE, respectively, while the CCSD[T] model makes an overestimation ($\bar{\Delta} = 103.9\%$) and the Λ CCSD(T) model makes an underestimation ($\bar{\Delta} = 96.6\%$). On average, the amount of the CCSDT TCE recovered by the Λ CCSD[T] and CCSD(T) models is seen to be of the same quality as that recovered by the CCSD(T-4) model. However, the consistency of the CCSD(T-4) model is not reproduced by the Λ CCSD[T] and CCSD(T) models, ultimately resulting in larger spreads in the CCSDT TCE recoveries. In fact, Table II and Figure 1

TABLE II. Standard statistical measures (Eq. (7.2)) of the CCSDT TCE recovery in percent (%) for the individual triples models. The results in parentheses are obtained with the methylene molecule omitted from the test set in Table I. In the calculations, all electrons have been correlated and the basis set used is cc-pCVQZ.

Measure	(T-2)	(T-3)	(T-4)	[T]	(T)	Λ [T]	Λ (T)
Δ_{\max}	80.8(86.9)	85.9(85.9)	94.4(101.1)	89.5(108.6)	87.4(101.9)	85.3(102.9)	84.0(95.2)
$\bar{\Delta}$	89.9(90.5)	91.4(91.5)	99.5(99.8)	103.9(104.8)	99.5(100.2)	99.4(100.3)	96.6(97.4)
Δ_{std}	2.7(1.4)	2.1(2.1)	1.4(0.5)	4.2(2.1)	3.2(0.9)	3.9(1.4)	3.5(1.2)

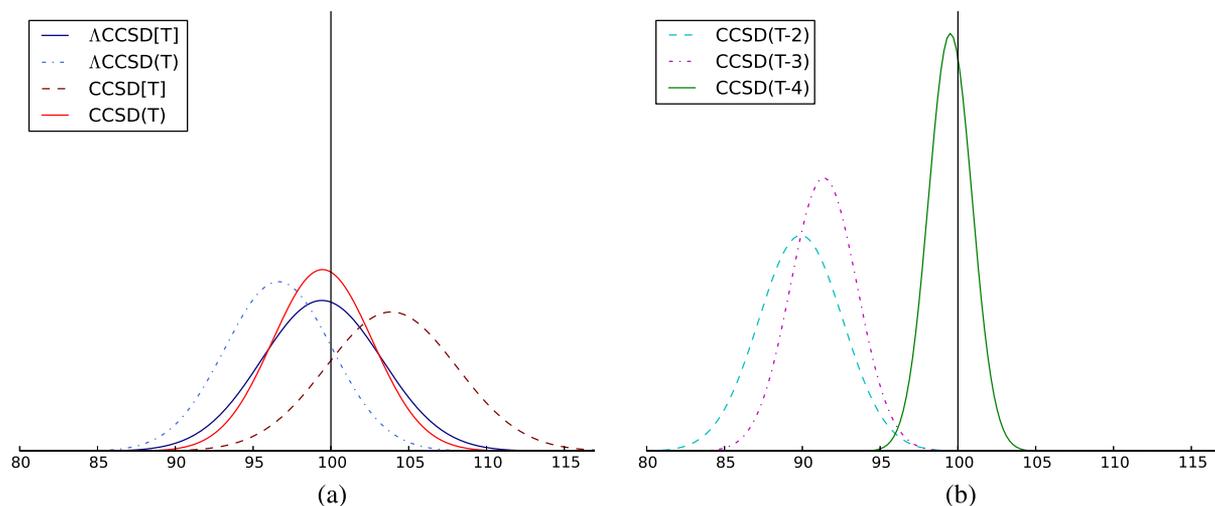


FIG. 1. Normal distributions of the CCSDT TCE recovery in percent (%) for ACCSD[T]/(T) and CCSD[T]/(T) calculations (Figure 1(a)) and CCSD(T-2), CCSD(T-3), and CCSD(T-4) calculations (Figure 1(b)). In the calculations, all electrons have been correlated and the basis set used is cc-pCVQZ.

reveal how all of the HF-based models have error bars that are inferior to those of the CCSD(T- n) models.

As mentioned above, the methylene molecule (in its singlet state of A_1 symmetry) turns out to be a problematic case for all of the triples models under investigation. From Table I, we see how the ACCSD[T] and CCSD(T) models only manage to recover 85.3% and 87.4% of the CCSDT TCE, respectively, while the CCSD(T-3) and CCSD(T-4) models recover 88.7% and 94.4%, respectively. This is not unexpected as the correlation energy for methylene is known to converge excessively slow when moving upwards through the Møller-Plesset hierarchy due to its low-lying doubly excited state.²⁴ For this reason, we will on certain occasions report statistical results obtained by removing the methylene result from the test set. However, excluding this outlier from the test set, we recognize from Table II that the standard deviation in the CCSDT TCE recovery for the CCSD(T-4) model (0.5%) is still smaller than those for the CCSD(T) (0.9%) and ACCSD[T] (1.4%) models.

B. Indirect triples effects

As mentioned previously, the relaxation of the CCSD singles and doubles amplitudes induced by triple excitations is first introduced in the CCSD(T- n) series at fourth order. The current implementation of the CCSD(T-4) model in `cfour` allows for a division of the total fourth-order correction into a triples-only contribution (the energy of the hypothetical CCSD(T-4)-trip model in Eq. (3.9b)) and one that involves relaxed singles and doubles amplitudes (the difference in energy between the CCSD(T-4) and CCSD(T-4)-trip models in Eq. (3.9c)), cf. the discussion in Sec. V. Plotting the distribution of the CCSD(T-4)-trip recovery of the CCSDT TCE alongside the second-, third-, and fourth-order recoveries in Figure 2 complements the conclusions drawn from Figure 1 in two ways; first and foremost, we notice how direct triples corrections to the CCSD energy converge fast when moving up the CCSD(T- n) series, and how the explicit contribution to the TCE from these effects obviously converges to a limit far off the CCSDT TCE. Second, it is clear how it is the singles and

doubles relaxation contribution to the CCSD(T-4) energy that makes the model perform well. Without this contribution, the CCSDT energy is unattainable, a point which we will return to in Sec. VIII C.

These observations are further substantiated by the results in Table III where we report the individual increments (in %) to the CCSD(T-4) TCE ($E_{T-4}^{(4)}$) from the CCSD(T-2) and CCSD(T-3) models ($E_{T-2}^{(2)}$, $E_{T-3}^{(3)}$), the hypothetical CCSD(T-4)-trip model ($E_{T-4}^{(4)}$ (trip)), and the contribution arising from the fourth-order relaxation of the CCSD singles and doubles amplitudes ($E_{T-4}^{(4)}$ (relax)). From Table III, we see how the third-order direct triples effects add to the second-order effects by 1.5% on average, while the final average increment at fourth order amounts to 1.4%. The incremental contribution from the relaxed singles and doubles amplitudes, however, amounts to a full 6.8% on average. Comparing the standard deviations in Table III, we recognize how the individual contributions to the final TCE become more systematic and consistent when moving up through the CCSD(T- n) series, in line with what we expect from a sound perturbation series.

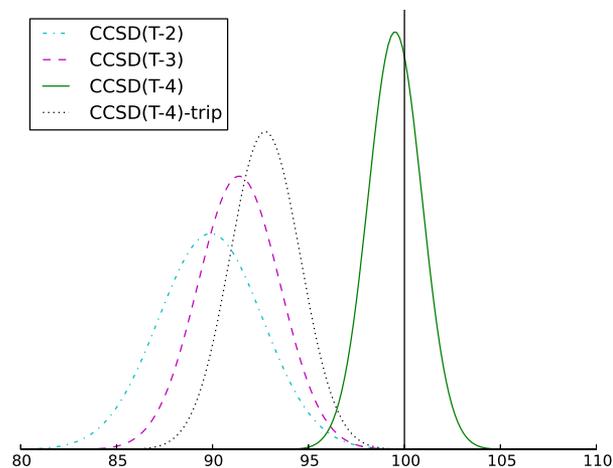


FIG. 2. Normal distributions of the CCSDT TCE recovery in percent (%) for CCSD(T-2), CCSD(T-3), CCSD(T-4)-trip, and CCSD(T-4) all-electron calculations in a cc-pCVQZ basis set.

TABLE III. Individual increments to the TCE from triple excitations ($E_{T-2}^{(2)}$, $E_{T-3}^{(3)}$, and $E_{T-4}^{(4)}$ (trip)) and singles/doubles amplitude relaxation ($E_{T-4}^{(4)}$ (relax)) in percent (%) of the total CCSD(T-4) TCE. The statistical results in parentheses are obtained with the methylene molecule omitted from the test set. In the calculations, all electrons have been correlated and the basis set used is cc-pCVQZ.

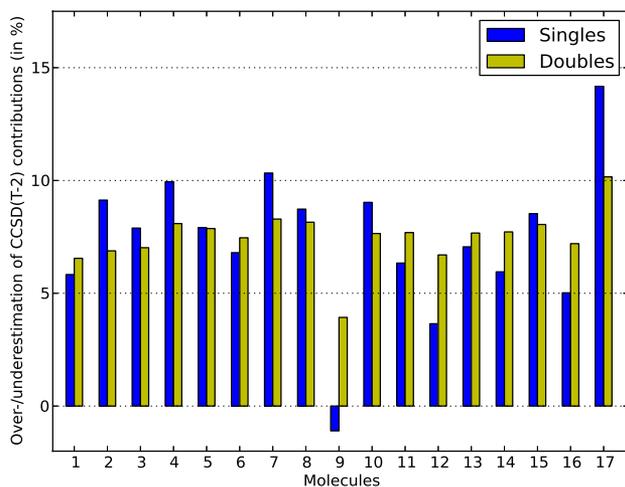
#	Molecule	$E_{T-2}^{(2)}$	$E_{T-3}^{(3)}$	$E_{T-4}^{(4)}$ (trip)	$E_{T-4}^{(4)}$ (relax)
1	NH ₃	91.2	3.1	1.1	4.5
2	HF	93.3	1.1	0.8	4.8
3	H ₂ O	92.3	2.0	0.9	4.8
4	CO	90.5	-0.9	1.8	8.6
5	HCN	90.0	0.5	1.6	7.9
6	C ₂ H ₂	90.1	1.2	1.4	7.2
7	CO ₂	90.4	-1.9	1.7	9.8
8	N ₂	91.2	0.2	1.4	7.2
9	CH ₂ (¹ A ₁)	85.6	8.5	2.3	3.7
10	CH ₂ O	90.7	1.0	1.3	7.0
11	H ₂ O ₂	91.2	2.0	1.1	5.8
12	C ₂ H ₄	89.8	3.0	1.4	5.8
13	HOF	90.9	1.8	1.1	6.2
14	N ₂ H ₂	90.6	1.6	1.3	6.4
15	HNO	90.6	1.0	1.4	7.0
16	F ₂	90.5	2.3	1.0	6.2
17	O ₃	86.7	-1.0	1.8	12.5
	Mean	90.3(90.6)	1.5(1.1)	1.4(1.3)	6.8(7.0)
	Std. dev.	1.8(1.4)	2.3(1.4)	0.4(0.3)	2.1(2.0)

By inspecting the individual entries of Table III, we see that some of the molecules of the test set, like the nitrogen molecule, carbon monoxide, carbon dioxide, and ozone, have fourth-order triples contributions that are similar in size or even larger than the corresponding third-order triples contributions. From Table I, we further see that these molecules are the ones for which the CCSD(T-4) model overestimates the CCSDT target, and we note that fifth-order direct and indirect triples effects are most likely required for these cases in order to achieve the same close agreement with the CCSDT TCE as we observe for the remainder of the test set in Table I. For all

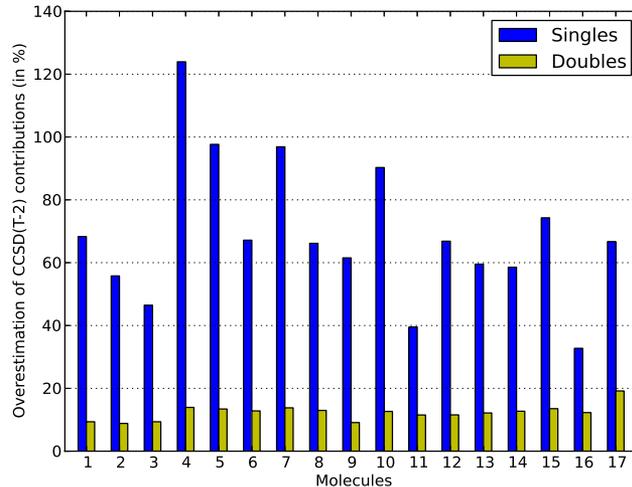
of the members of the test set, however, we expect the fifth-order contributions to the TCE to be minuscule, cf. the mean $E_{T-4}^{(4)}$ (trip) increment and its standard deviation in Table III.

C. Error cancellation

From the numerical results of Secs. VIII A and VIII B, it is clear that the CCSD(T- n) series indeed converges towards the CCSDT limit. Thus, the CCSD(T-2) model gives the second-order triples correction to the CCSD energy and recovers about 90% of the CCSDT TCE on average. As mentioned in Sec. V,



(a)



(b)

FIG. 3. Singles and doubles contributions to the Δ CCSD(T) (Figure 3(a)) and CCSD(T) (Figure 3(b)) triples energy corrections. The results are given with respect to the corresponding CCSD(T-2) results and in all the (all-electron) calculations, a cc-pCVQZ basis has been used. The numbering of the individual molecules of the test set corresponds to that of Table I.

the ACCSD[T]/(T) models may be viewed as approximations to the CCSD(T-2) model, while the CCSD[T]/(T) models are obtained from the ACCSD[T]/(T) models by substituting CCSD multipliers with CCSD amplitudes. As the energy corrections of the CCSD(T-2), ACCSD(T), and CCSD(T) models can all be divided into a singles and a doubles contribution, of which the ACCSD[T] and CCSD[T] models retain only the ACCSD(T) and CCSD(T) doubles contributions, respectively, we will in the following attempt to interpret the results of the HF-based models in terms of the CCSD(T-2) results.

In Figure 3, we present the individual ACCSD(T) (in Figure 3(a)) and CCSD(T) (in Figure 3(b)) singles and doubles contributions to the total energy correction as measured relative to the corresponding CCSD(T-2) contributions. From the figures, we see that both the ACCSD(T) and CCSD(T) models consistently overestimate the two contributions with respect to the CCSD(T-2) model (disregarding the methylene case, which is molecule no. 9 in both figures). While the overestimations are fairly constant for the ACCSD(T) model and roughly equal for the two contributions, only the overestimation of the doubles contribution is systematic for the CCSD(T) model. The overestimation of the singles contribution in the CCSD(T) model—a contribution which is smaller in magnitude and of opposite sign compared to the doubles contribution for all three models—appears rather erratic, both with respect to the CCSD(T-2) model and with respect to the pattern observed for the ACCSD(T) model in Figure 3(a). Furthermore, the overestimation of the CCSD(T-2) singles contribution in the CCSD(T) model is exceedingly larger than that in the ACCSD(T) model, the average values being 69.0% and 7.4%, respectively. However, even though the average overestimation of the CCSD(T-2) doubles contribution is also larger in the CCSD(T) model (12.3%) than in the ACCSD(T) model (7.5%), it turns out to be the combination of the two overestimations and, in particular, the overestimation of the singles contribution which the CCSD(T) model owes its extraordinary performance to.

To substantiate these findings, we have in Figure 4 plotted the individual increments to the total recovery of the CCSDT TCE from the ACCSD(T) and CCSD(T) singles and doubles contributions. Alongside these, we have furthermore plotted the CCSDT TCE recoveries of the CCSD(T-4)-trip and CCSD(T-4) models for comparison. Disregarding again the methylene case, we see from Figure 4 how the overestimation of the singles contribution in the CCSD(T) model systematically counterbalances the overestimation of the doubles contribution (comparing the CCSD(T) and CCSD[T] results), resulting in a vanishing overall error in the recovery of the CCSDT TCE. A similar pattern is not observed for the ACCSD(T) model. However, when the singles contribution is removed from the ACCSD(T) energy correction (resulting in the ACCSD[T] correction), the results improve remarkably. In fact, the statistical results in Table II for the ACCSD[T] model ($\bar{\Delta} = 99.4\%$ and $\Delta_{\text{std}} = 3.9\%$) are practically as good as those for the CCSD(T) model ($\bar{\Delta} = 99.5\%$ and $\Delta_{\text{std}} = 3.2\%$). The addition of a singles contribution—and an overestimation of this contribution with respect to that of the CCSD(T-2) model—thus shifts the final ACCSD(T) TCE results away from the CCSDT reference results, rather than closer to them

as for the CCSD(T) model. Recalling the derivation of the ACCSD[T]/(T) models in Sec. IV A, we may trace back the remarkable performance of the ACCSD[T] model in the following manner. By augmenting the CCSD energy only by the (structurally correct) leading-order MBPT triples contribution in Eq. (2.10a) and replacing the perturbation amplitudes and multipliers entering this by their CCSD counterparts, the ACCSD[T] model becomes the physically least arbitrary of all of the non-iterative CC triples models rationalized from MBPT. This is so, as it is constructed as a strict fourth-order model (alongside the CCSD[T] model) and the difference between left- and right-hand CC state parameters is respected (unlike the CCSD[T] model).

However, the results in Figures 3 and 4 collectively show how the results obtained with all of the HF-based models are as fortuitous as they are extraordinary. Besides the relaxation effects inherently considered in the underlying CCSD model (i.e., in the absence of triple excitations), none of these models take into account any relaxation of the singles and doubles amplitudes beyond the CCSD level. From Table III and Figure 4, we recognize that these singles and doubles relaxation effects contribute between 5% and 10% to the total CCSD(T-4) TCE, and we are thus led to conclude that the performance of any of the HF-based models relies considerably on an error cancellation of direct and indirect triples effects.

D. Basis set convergence and core excitations

Having established the convergence of the CCSD(T-*n*) series towards the CCSDT target limit in the reasonably-sized cc-pCVQZ basis set in Secs. VIII A and VIII B, and examined the commonalities and differences between the HF-based models in Sec. VIII C, the question remains as to how the overall precision of any of the models behaves when the basis set is increased. In Figure 5, the recoveries of the

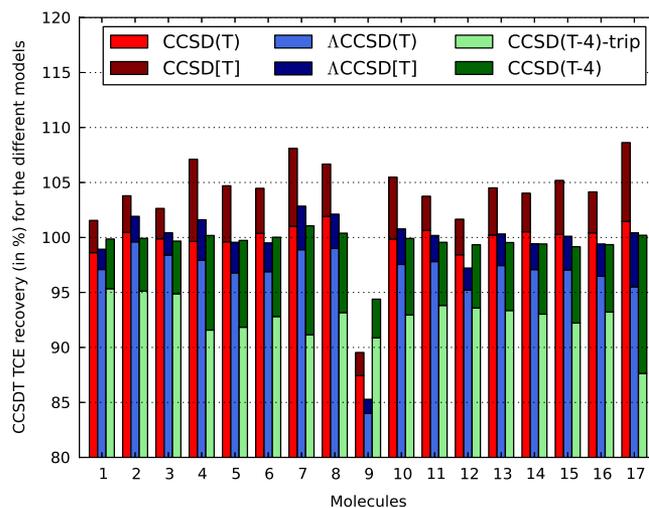


FIG. 4. CCSDT TCE recoveries of the ACCSD[T]/(T), CCSD[T]/(T), CCSD(T-4)-trip, and CCSD(T-4) models. For brevity, the ACCSD(T), CCSD(T), and CCSD(T-4)-trip recoveries have been superimposed on the ACCSD[T], CCSD[T], and CCSD(T-4) recoveries, respectively. In all the calculations, a cc-pCVQZ basis has been used, and the numbering is the same as that in Table I and Figure 3.

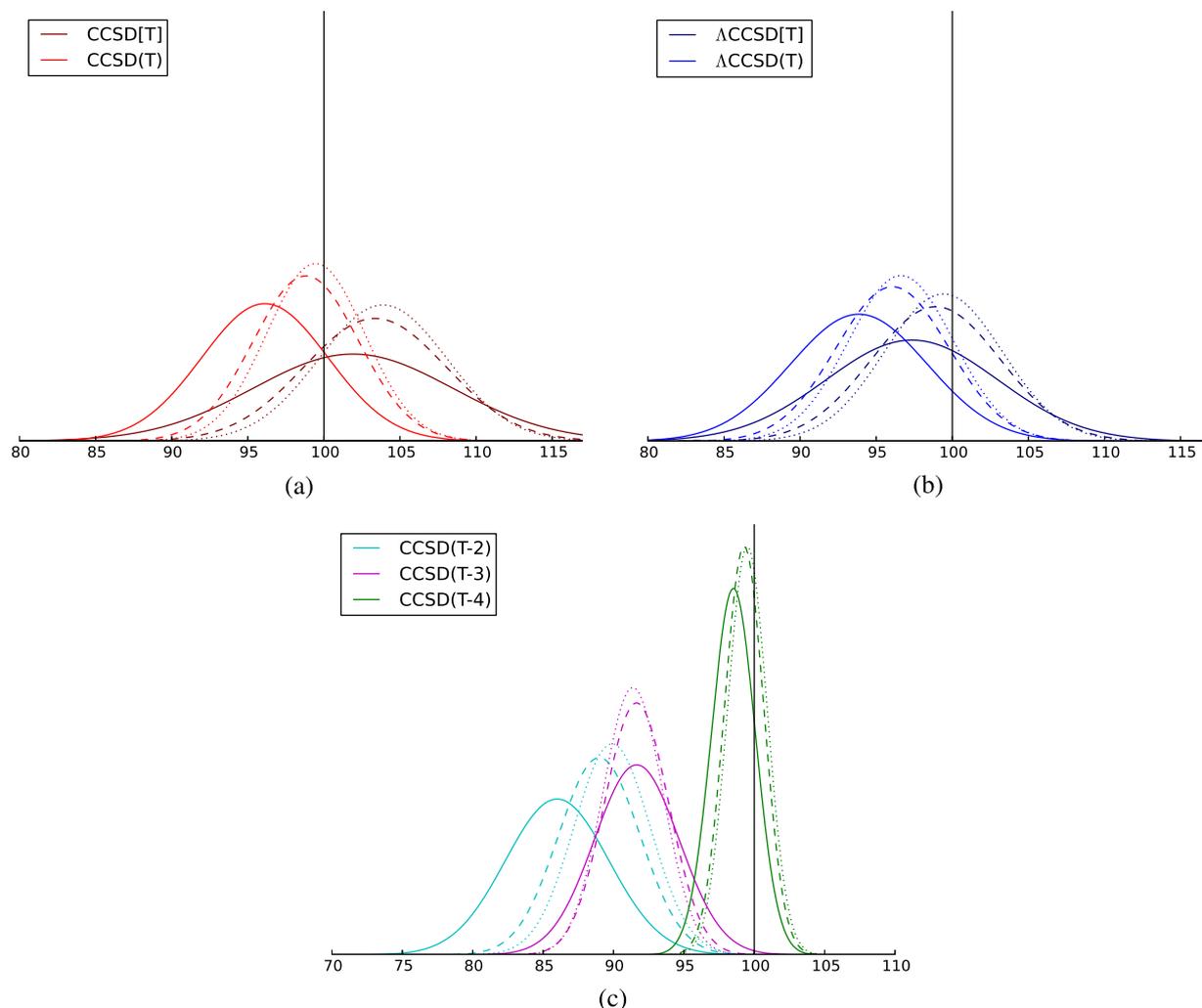


FIG. 5. Normal distributions of the CCSDT TCE recovery in percent (%) for CCSD[T]/(T) and ACCSD[T]/(T) all-electron calculations (Figures 5(a) and 5(b)) and CCSD(T-2), CCSD(T-3), and CCSD(T-4) all-electron calculations (Figure 5(c)) in the basis sets cc-pCVXZ ($X = D, T, Q$). For all the models, the line styles are: full (DZ), dashed (TZ), and dotted (QZ).

CCSDT TCE for all-electron calculations with the cc-pCVXZ ($X = D, T, Q$) basis sets are compared for all the models, with the HF-based models in Figures 5(a) and 5(b) and the models of the CCSD(T- n) series in Figure 5(c).

Examining first the distributions in Figures 5(a) and 5(b), we observe similar convergence patterns for the ACCSD[T] and CCSD[T] models and for the ACCSD(T) and CCSD(T) models. Comparing the ACCSD[T]/CCSD[T] models to the ACCSD(T)/CCSD(T) models reveals how the addition of a singles contribution to the energy corrections in the ACCSD(T) and CCSD(T) models makes the standard deviations smaller in the double-zeta basis set, but less so in the larger basis sets. Looking next at the distributions in Figure 5(c), we immediately observe that the staircase convergence in the CCSD(T- n) series holds not only for the average errors in the recovery of the CCSDT TCE but also for the standard deviations around the mean. While the HF-based models in Figures 5(a) and 5(b) respond remarkably similar to changes in the cardinal basis set number, the variation between the CCSD(T- n) models is more pronounced. In fact, all of the HF-based models are seen to behave much like the CCSD(T-2) model, justifying the comparison made in Figure 3 of Sec. VIII C.

Although Figure 5 states nothing about the convergence of the absolute energies with respect to an increase of the one-electron basis for the different models (these convergence rates are no better than for ordinary iterative CC models, i.e., dreadfully slow), it does make an interesting point about the strength of the CCSD(T- n) models in recovering the full CCSDT TCE, in particular for the CCSD(T-4) model. From the distributions in Figure 5(c), the CCSD(T-4) error in the recovery of the CCSDT TCE is seen to be basically converged at the triple-zeta basis set level. For the best among the HF-based models in Figures 5(a) and 5(b)—the ACCSD[T] and CCSD(T) models—there are still slight improvements in moving from a triple- to a quadruple-zeta basis set. In fact, the performance of the CCSD(T-4) model at the double-zeta level is remarkable in itself and little variation in neither $\bar{\Delta}$ nor Δ_{std} occurs for cardinal basis set numbers $X > D$.

Finally, we look at the contribution to the correlation energy from core orbitals, as neglecting this is one of the most common approximations for high-level CC calculations due to the cost savings it gives rise to. It is therefore important to assess the stability of this approximation for the different triples models across the molecules of the test set. In here, we

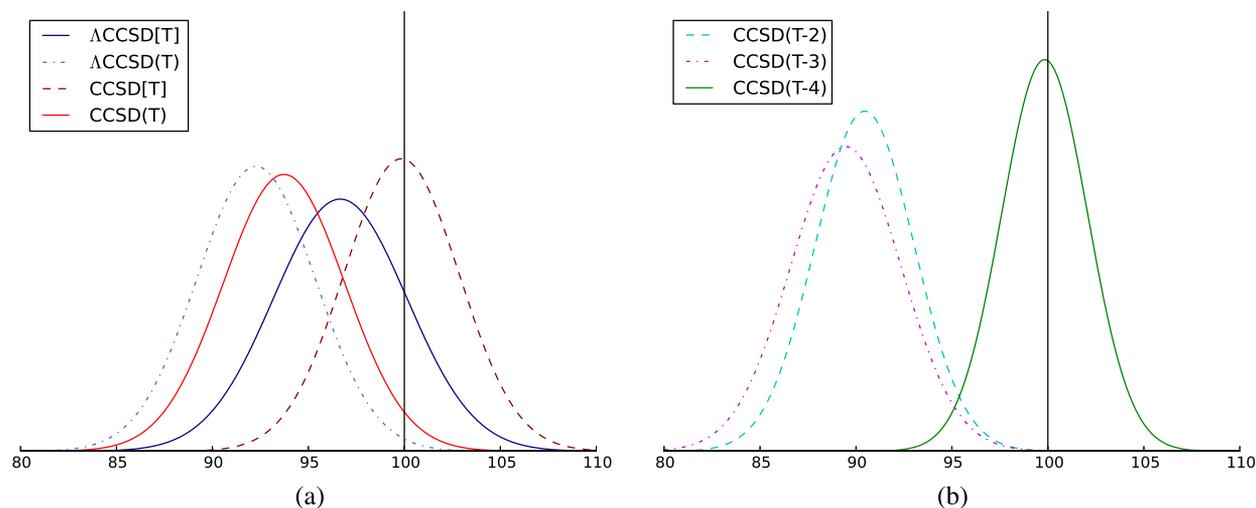


FIG. 6. Normal distributions of the CCSDT core TCE recovery in percent (%) for the ACCSD[T]/(T) and CCSD[T]/(T) models (Figure 6(a)) and the CCSD(T-2), CCSD(T-3), and CCSD(T-4) models (Figure 6(b)). The core contribution recoveries have been obtained by subtracting valence-electron energies from all-electron energies, both calculated in a cc-pCVQZ basis.

address the core contribution recovery by subtracting valence-electron energies from all-electron energies, both calculated in a cc-pCVQZ basis. Using the CCSDT core TCE as the reference, results are shown for the ACCSD[T]/(T) and CCSD[T]/CCSD(T) models in Figure 6(a) and the CCSD(T- n) models in Figure 6(b). From Figure 6(a), we recognize how all of the HF-based models are seen to have more or less the same standard deviation from the CCSDT results, and by comparing Figures 6(a) and 6(b), it is seen how all of these models (as well as the second- and third-order models of the CCSD(T- n) series) give results that are inferior to those of the CCSD(T-4) model.

IX. CALCULATIONS AT DISTORTED GEOMETRIES

As an alternative test, we investigate how the various models perform for molecules at distorted rather than equilibrium geometries. In Figures 7 and 8, we present frozen-core

results obtained with a cc-pVTZ basis set for the hydrogen fluoride and water molecules, respectively, as examples of (symmetric) stretches where one and two bonds are elongated. As stretching bonds introduce multiconfigurational character into the wave function, thereby making the RHF reference state increasingly worse, we plot the CCSDT TCE recoveries alongside the occupation number for the lowest unoccupied natural orbital (Θ) to monitor the amount of static correlation at each bond length. For both the hydrogen fluoride and the water case, the Θ values have been calculated from the one-particle density matrix at the CCSD(T)/cc-pVTZ level of theory.

For the hydrogen fluoride molecule, full configuration interaction (FCI) results (in a 6-31G** basis set) for the potential energy curve are available in the literature up to an elongation of the bond of 120%.²⁵ By calculating an analogous CCSDT curve and comparing the results against the tabulated FCI results of Ref. 25, we are able to assess the performance of the CCSDT model across the range of tested bond lengths. These results are not reported in full here, but in summary

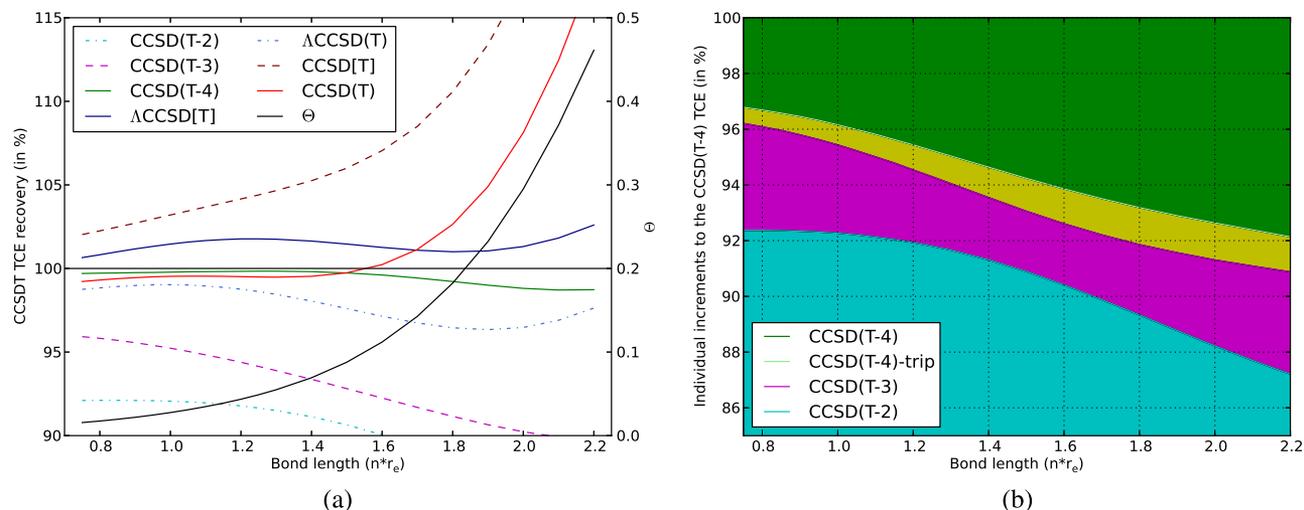


FIG. 7. Recovery of the CCSDT TCE (Figure 7(a)) and individual increments to the CCSD(T-4) TCE (Figure 7(b)) for the hydrogen fluoride molecule at various bond lengths. The results are for frozen-core calculations using a cc-pVTZ basis set and the equilibrium bond length (r_e) is 91.6 pm.

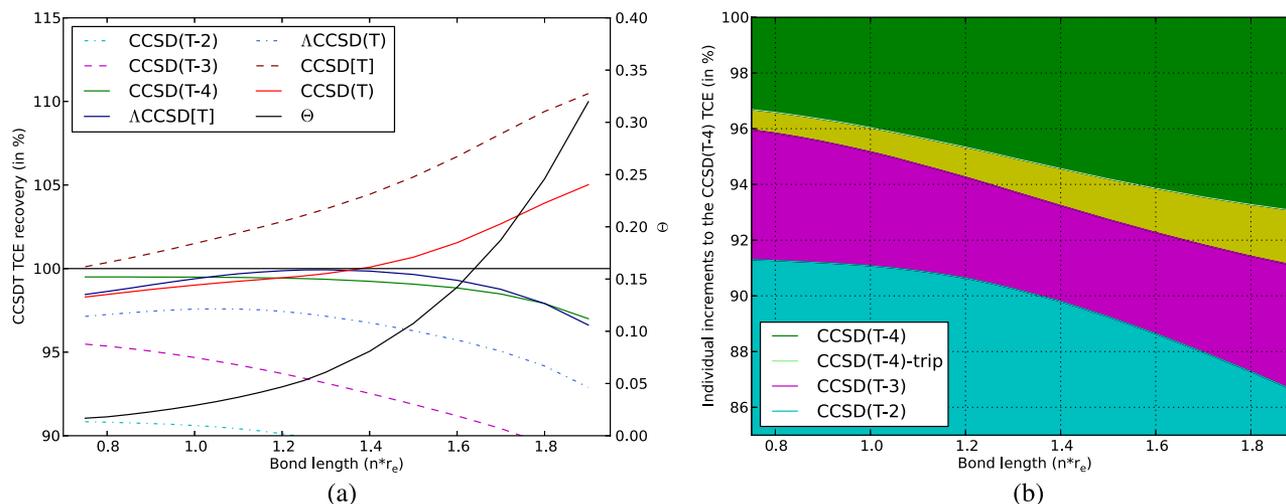


FIG. 8. Recovery of the CCSDT TCE (Figure 8(a)) and individual increments to the CCSD(T-4) TCE (Figure 8(b)) for the water molecule at various bond lengths. The results are for frozen-core calculations using a cc-pVTZ basis set and the equilibrium bond length (r_e) is 95.7 pm.

they show that the CCSDT potential energy curve remains parallel to the FCI curve with marginal errors between 26 and 31 mE_h . In return, this demonstrates the validity of the CCSDT model for the HF stretch over this interval and every model that mimics the CCSDT results will thus be capable of describing hydrogen fluoride correctly for the tested bond lengths.

Inspecting the recovery of the CCSDT TCE in Figure 7(a) for the various models, we notice how the HF- and CCSD-based models behave substantially different in their responses to the stretching of the bond away from its equilibrium length. If we define a conservative confidence interval to be spanned by a maximal error in the CCSDT TCE recovery of $\pm 2\%$, we see that the CCSD[T], CCSD(T-2), and CCSD(T-3) models are never close to this except near the equilibrium bond length, the ACCSD(T) model is within it up until a 40% stretch of the equilibrium bond length, the CCSD(T) model up until a 75% stretch, the ACCSD[T] model until a 110% stretch, whereas the CCSD(T-4) model stays within throughout the tested range of bond lengths. While we do expect all of the models to break down at geometries that become too distorted—due to the non-iterative nature of the models and the increasing multiconfigurational character of the system—it is noteworthy to see how the ACCSD[T] and CCSD(T-4) results stay parallel to the corresponding CCSDT results at all the tested bond lengths, showing no real sign of blowing up even for $\Theta > 0.4$, implying that these two models are capable of dissociating hydrogen fluoride at the same level of accuracy as the CCSDT model up to this point. This is in contrast to the results of all of the other models, which deviate increasingly more from the CCSDT results as the bond is stretched. In particular, we see that the CCSD(T) results start to diverge from the CCSDT results already at a stretch of 50% ($\Theta \sim 0.1$). Although superior to the ACCSD(T) results at the equilibrium geometry, that changes when the CCSD(T) results start to blow up, in line with the conclusions of Ref. 10. However, for the hydrogen fluoride case, both the ACCSD(T) and the CCSD(T) model clearly perform inferior to the ACCSD[T] model.

In Figure 7(b), we examine the CCSD(T-4) TCE in more detail by dividing the total fourth-order correction into

the same increments as were discussed in connection with Table III. While the contribution to the fourth-order energy correction from relaxation effects in the singles and doubles spaces is small at the equilibrium geometry, we recognize from Figure 7(b) how this amount increases steadily as the bond is stretched. In fact, since the increments from the third-order correction and the contribution from direct triples effects to the fourth-order correction (CCSD(T-4)-trip) are approximately constant—at least up to about an 80% elongation of the bond—it is the increasing size of the contribution from singles and doubles relaxation effects that eventually covers for the decreasing triples contribution, making the CCSD(T-4) and CCSDT models perform equally well in the description of the hydrogen fluoride bond stretch.

For water, FCI results (in a cc-pVDZ basis set) also exist in the literature for the same tested range of bond lengths.²⁶ Unlike for the single-bond stretch in hydrogen fluoride, the CCSDT model only remains parallel to the corresponding FCI curve within a limited range of bond lengths (also shown in Figure 5.18 of Ref. 2), after which the model collapses. This CCSDT collapse occurs at about $r(\text{OH}) = 180$ pm, which corresponds to an elongation of the bonds of about 90% away from their equilibrium length. It is therefore only of interest to test the performance of the approximate triples models within this region.

In Figure 8, the recovery of the CCSDT TCE for the various models is reported. By inspecting the results for the symmetric water stretch in Figure 8(a), we see that the findings for the single-bond stretch in hydrogen fluoride are repeated to a large degree. Here, the results for the CCSD(T-2) and CCSD(T-3) models again fall outside the confidence interval, as do the ones for the CCSD[T] and ACCSD(T) models (except near the equilibrium geometry), while the CCSD(T), ACCSD[T], and CCSD(T-4) results stay within up until stretches of about 65%, 75%, and 80%, respectively. The ACCSD(T) results are thus no improvements over the corresponding CCSD(T) results for the symmetric water stretch, while the ACCSD[T] results represent a slight improvement. Comparing the division of the CCSD(T-4) TCE

for hydrogen fluoride in Figure 7(b) with the corresponding one for water in Figure 8(b), we see how the two appear very similar, indicating a general overall behaviour.

X. SUMMARY AND CONCLUSION

In the present study, we have detailed the second-, third-, and fourth-order models of our recently proposed CCSD($T-n$) perturbation series, which corrects the CCSD energy in orders of the Møller-Plesset fluctuation potential for effects due to triple excitations. As the CCSD($T-n$) series is based on the CCSDT energy Lagrangian, the series is guaranteed to converge towards the CCSDT energy, with the corrections of the series starting out at second order. By performing a rigorous theoretical comparison of the CCSD($T-2$), CCSD($T-3$), and CCSD($T-4$) models of the CCSD($T-n$) series, which is based on a CCSD reference state, with the ACCSD[T]/(T) and CCSD[T]/(T) models rationalized from the leading-order triples contributions to the HF-based MBPT series, we have illustrated how the four latter models may be viewed as approximations to the second-order CCSD($T-2$) model. Due to the convergence of the CCSD($T-n$) series towards the CCSDT limit, the CCSD($T-2$) model thus constitutes a theoretical second-order reference against which it is possible to compare the ACCSD[T]/(T) and CCSD[T]/(T) models.

Following the theoretical comparison, numerical results have been reported for the CCSD($T-2$), CCSD($T-3$), and CCSD($T-4$) models which confirm the predicted theoretical convergence trend throughout the series towards the target CCSDT energy. As we are capable of separating out those effects from the total energy correction that originate from a relaxation of the CCSD singles and doubles amplitudes in the presence of triple excitations, we have been able to examine the size and importance of these indirect triples effects in detail. Additionally, the numerical performance of the CCSD($T-n$) models has been compared to that of the ACCSD[T]/(T) and CCSD[T]/(T) models in a statistical analysis of the recovery of the CCSDT triples correlation energy. From the results of this analysis on a test set of 17 small closed-shell molecules at their equilibrium geometry, we have shown how it is the contribution from the relaxation of the CCSD singles and doubles amplitudes that makes the CCSD($T-4$) model perform superior to all of the other tested models. Without this contribution, which amounts to between 5% and 10% of the total contribution to the correlation energy from triple excitations, the CCSDT reference results are unattainable. As a result of this, we have been able to expose how the performance of the ACCSD[T]/(T) and CCSD[T]/(T) models relies on a cancellation of two types of errors: an overestimation of the contribution to the correlation energy from direct triples effects and a missing account of the contribution from relaxed singles and doubles amplitudes.

The basis set convergence and the handling of core correlation have also been examined for the various triples models. Statistical results for these investigations confirm the inferior performance of any of the models to that of the CCSD($T-4$) model, as its recovery of the CCSDT triples correlation energy converges fast with respect to an increase in the cardinal basis set number and it gives the most consistent recovery of the

CCSDT core correlation contribution among all of the tested models. Finally, the performance of the different models has been examined for two examples of bond stretching: the single-bond stretch in hydrogen fluoride and the symmetric O–H stretch in water. For both of these cases, the CCSD($T-4$) model is found to perform parallel to the CCSDT model up until an elongation of the bond(s) to twice the equilibrium length, an impressive performance only challenged by the ACCSD[T] model.

In summary, the CCSD($T-4$) model is found to outperform any of the other models under investigation. In fact, the performance of the model in recovering the CCSDT correlation energy is so impressive that one might consider using it in areas of electronic structure theory where a consistent high accuracy is called for, e.g., in the field of computational thermochemistry. We are currently investigating this. However, our collected results also lead us to reconsider the ACCSD[T] model, due to not only its rigorous theoretical foundation—where it is shown to be the least arbitrary among the models rationalized from MBPT—but also its numerical performance. For systems at their equilibrium geometry, the performance of the ACCSD[T] model is shown to be similar to that of the conventional CCSD(T) model, which in return outperforms both the CCSD[T] and ACCSD(T) models. However, for systems at distorted geometries, the results of the ACCSD[T] model are found to be superior to those of the CCSD(T) model. As a result of these findings, we find it astonishing that the ACCSD[T] model has not previously been subjected to the same types of scrutinizations as, for instance, the ACCSD(T) and CCSD(T) models. While we acknowledge that the renowned CCSD(T) model has additional advantageous features over the ACCSD[T] model, e.g., its minimal number of cost-determining operations, the theoretical rigour of the ACCSD[T] model in addition to its performance capabilities should be arguments for reconsidering its future use in electronic structure calculations.

ACKNOWLEDGMENTS

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¹G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).

²T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory*, 1st ed. (Wiley & Sons, Ltd., West Sussex, England, 2000).

³J. J. Eriksen, K. Kristensen, T. Kjærgaard, P. Jørgensen, and J. Gauss, *J. Chem. Phys.* **140**, 064108 (2014).

⁴K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

⁵S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **108**, 5243 (1998); **108**, 9221 (1998).

- ⁶T. D. Crawford and J. F. Stanton, *Int. J. Quantum Chem.* **70**, 601 (1998).
- ⁷I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics: Many-Body Perturbation Theory and Coupled-Cluster Theory* (Cambridge University Press, Cambridge, UK, 2009).
- ⁸M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985).
- ⁹R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990).
- ¹⁰A. G. Taube and R. J. Bartlett, *J. Chem. Phys.* **128**, 044110 (2008); **128**, 044111 (2008).
- ¹¹J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987); G. E. Scuseria and H. F. Schaefer, *Chem. Phys. Lett.* **152**, 382 (1988).
- ¹²J. J. Eriksen, P. Jørgensen, J. Olsen, and J. Gauss, *J. Chem. Phys.* **140**, 174114 (2014).
- ¹³S. Hirata, M. Nooijen, I. Grabowski, and R. J. Bartlett, *J. Chem. Phys.* **114**, 3919 (2001); S. Hirata, P.-D. Fan, A. A. Auer, M. Nooijen, and P. Piecuch, *ibid.* **121**, 12197 (2004).
- ¹⁴S. R. Gwaltney and M. Head-Gordon, *Chem. Phys. Lett.* **323**, 21 (2000); *J. Chem. Phys.* **115**, 2014 (2001).
- ¹⁵CFOUR, Coupled-Cluster Techniques for Computational Chemistry, a quantum-chemical program package by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowitz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.
- ¹⁶H. Koch, O. Christiansen, P. Jørgensen, A. Sanchez de Merás, and T. Helgaker, *J. Chem. Phys.* **106**, 1808 (1997).
- ¹⁷T. Helgaker and P. Jørgensen, in *Methods in Computational Molecular Physics*, edited by S. Wilson and G. H. F. Diercksen (Plenum, New York, USA, 1992).
- ¹⁸K. Kristensen, P. Jørgensen, A. J. Thorvaldsen, and T. Helgaker, *J. Chem. Phys.* **129**, 214103 (2008).
- ¹⁹J. Gauss and J. Stanton, *J. Chem. Phys.* **116**, 1773 (2002).
- ²⁰D. A. Matthews, J. Gauss, and J. Stanton, *J. Chem. Theory Comput.* **9**, 2567 (2013).
- ²¹T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989); D. E. Woon and T. H. Dunning, Jr., *ibid.* **103**, 4572 (1995).
- ²²J. F. Stanton, W. N. Lipscomb, D. H. Magers, and R. J. Bartlett, *J. Chem. Phys.* **90**, 1077 (1989).
- ²³R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990).
- ²⁴J. Olsen, P. Jørgensen, T. Helgaker, and O. Christiansen, *J. Chem. Phys.* **112**, 9736 (2000).
- ²⁵A. Dutta and C. D. Sherrill, *J. Chem. Phys.* **118**, 1610 (2003).
- ²⁶J. Olsen, P. Jørgensen, H. Koch, A. Balkova, and R. J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).