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Comparison of CCSDT-*n* methods with coupled-cluster theory with single and double excitations and coupled-cluster theory with single, double, and triple excitations in terms of many-body perturbation theory – what is the most effective triple-excitation method?

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Abstract. CCSDT-*n* methods ($n = 1, \ldots, 4$) are analyzed in terms of many-body perturbation theory and compared with CCSD, CCSD(T), and CCSDT. Correlation terms, which are introduced at each CCSDT-*n* level are identified and discussed with regard to their importance for the total energy. CCSDT-1a represents the strongest improvement of CCSD since it covers 75% of the T terms added at the CCSDT level. At CCSDT-2 and CCSDT-3, only partial energy terms are added where the positive ..TQ.. coupling terms at CCSDT-2 are more important than the slightly negative ..TTS terms at CCSDT-3. CCSDT-4 leads to new ..TT.. coupling effects, which lower the energy. Calculated CCSDT-*n*/correlation-consistent polarized-valence triple-zeta spectra reveal that the energy changes caused by CCSDT-2, CCSDT-3, CCSDT-4, and CCSDT largely cancel each other out; however, because of a dependence of these contributions on electron clustering the importance of these effects for the correct description of certain chemical reactions must be considered. It is shown that CCSDT-1 (as well as all other CCSDT-*n*) calculations lead to atomization energies as accurate as G2 values, where this result reflects the importance of including at least some of the T effects.

Key words: Coupled-cluster methods – CCSDT – CCSDT-*n* – Many-body perturbation theory analysis – Atomization energies

1 Introduction

Coupled cluster (CC) theory [1–6] with single (S), double (D), and triple (T) excitations (CCSDT) [4] belongs to the most accurate single-determinant methods presently used in quantum chemistry. CCSDT is size-extensive, contains because of the exponential ansatz (the wave operator takes the form $\exp\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_3\right)$ with $\hat{T}_n$ denoting the S, D, and T cluster operators) infinite-order effects and, as an iterative T method, it can even lead to reasonable results in the case of electronic systems with multireference character. The fact that CCSDT as a projection CC method is nonvariational and, therefore, can lead to energies that are lower than the corresponding full configuration interaction (FCI) energies obtained with the same basis set is of no serious disadvantage. For most chemical problems, relative rather than absolute energies have to be considered and, then, the property of size-extensivity is more important than the variational character of the method. However, it is problematic that CCSDT is an $O(M^8)$ method (M: number of basis functions) or, in terms of n_{occ} occupied and n_{virt} virtual orbitals, an $\mathrm{n}_{\mathrm{occ}}^3\mathrm{n}_{\mathrm{virt}}^5$ method that with the computational resources available today can only be applied to relatively small molecules [7, 8].

Therefore, approximate CCSDT methods were invented using different strategies [9–18]. The first attempts in this direction were made by Paldus, Cizek, and Shavitt on the basis of their coupled-pair many-electron theory (CPMET; equivalent to CCD) by extending the CPMET cluster operator by the S and T cluster operators in a linear fashion, $\exp\left(\hat{T}_2\right) + \hat{T}_1 + \hat{T}_3$, thus yielding E-CPMET [9]. In this way, higher-order disconnected terms are neglected; however, in the projections onto the S, D, and T subspaces the form of the CC wave function is maintained. A similar approach was suggested by Kvasnicka [10]; however, because of its high computational cost E-CPMET was only applied to very small molecules in the 1970s. Later, Urban et al. [11] suggested using the T contribution at fourth order as a correction to the CCSD energy [denoted as CCSD + T(4)] or alternatively to calculate the fourth-order T correction with the help of the converged $\hat{T}_2$(CSSD) amplitudes, thus yielding CCSD + T(CCSD) [11]. Since CCSD + T(CCSD) has a tendency to exaggerate T correlations effects, Raghavachari et al. [12] introduced CCSD(T), after a similar extension of the approximate CC method quadratic CI with S and D excitations (QCISD) to

QCISD(T) [13], which adds beside the fourth-order T term also fifth-order terms ST and DT + TD to avoid an overestimation of T correlation effects.

Parallel to the development of noniterative methods for the introduction of T excitations at the CCSD level, Bartlett and coworkers [11, 14–18] suggested a class of iterative T methods, which (in contrast to the E-CPMET method [9]) simplified the complete CCSDT approach by using different cluster expansions in the projections onto the S, D, and T subspaces with the aim of reducing computational cost as much as possible. These are the CCSDT-*n* ($n =$ 1a, 1b, 2, 3, 4) approximations, which according to Urban and et al. [3] can be characterized as shown in Scheme 1.

CCSDT-1 includes into the CCSD projection equations [19] the primary effects of connected T excitations iteratively, CCSDT-2 adds to CCSDT-1 some fifth- (and higher-) order effects, CCSDT-3 leads to additional sixth- (and higher-) order effects, CCSDT-4 includes for the first time TT coupling effects, while CCSDT-5 = CCSDT complements all effects of connected T excitations. Hence, the CCSDT-*n* methods represent a smooth transition from CCSD to CCSDT. Since CCSDT-1,2,3 are $O(M^7)$ methods while CCSDT-4 similar to CCSDT is an $O(M^8)$ method, one might ask whether any of the CCSDT-*n* methods offer an optimal treatment of T effects in terms of cost-efficiency considerations.

In some selected cases insight was gained into the performance of all CCSDT-*n* methods, while extended testing was only performed at the CCSDT-1 level of theory [8, 11, 14–18, 20–24]. However, even with regard to CCSDT-1, results close to FCI as well as examples of complete failure were reported. At present, there is no general understanding as to which of the CCDT-*n* methods is the best in terms of computational requirements and accuracy obtained for a given problem. Many additional investigations are needed to find out about the usefulness of CCSDT-*n* methods. Since such a trial and error approach to test the applicability of a given method, although widely used, is not satisfactory, He and Cremer developed a more systematic procedure for the comparison of CC methods [25, 26]. In two previous articles (henceforth, called articles 1 [25] and 2 [26]), CC methods were expanded in terms of many-body perturbation theory (MBPT) contributions for increasing orders, *n*. For this purpose, formulas for sixth-order MBP, MBPT(6), [27–29] were worked out and it was determined algebraically which terms of MBPT(*n*) ($n = 2, \ldots, 6$) are covered by a given method. In addition, the analysis was extended to higher orders of MBPT ($m < 9$) using a graphical approach that helps to analyze infinite-order effects [25, 26]. In this way, CCSD, QCISD, CCSD(T), QCISD(T), CCSD(TQ), QCISD(TQ), and CCSDT were analyzed.

In this work, we present a similar analysis of CCSDT-*n* methods from $n = 0$ (CCSD) to $n = 5$ (CCSDT). We will focus on the following questions.

1. Which correlation effects are covered by each of the six CCSDT-*n* methods?
2. How do the CCSDT-*n* methods compare with methods that include T excitations in a noniterative way?
3. What is the best CCSDT-*n* method in terms of accuracy and costs?

We will compare the results of the theoretical analysis with results of CCSDT-n calculations carried out in this work. In particular, we will investigate CCSDT-*n* atomization energies of molecules difficult to describe with correlation-corrected ab initio methods not containing T excitations.

2 Analysis of CCSDT-*n* in terms of MBPT

The CCSD equations [19] are given in Eqs (1), (2), and (3)

$$\left\langle \Phi_0 \middle| \bar{H}\left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right)\Phi_0 \middle| \right\rangle = E_{\text{corr}}^{\text{CCSD}} \ , \tag{1}$$

$$\left\langle \Phi_i^a \middle| \bar{H}\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3\right)\Phi_0 \middle| \right\rangle_C = 0 \ , \tag{2}$$

$$\begin{aligned} &\left\langle \Phi_{ij}^{ab} \middle| \bar{H}\Phi_0 \left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 \right.\right. \\ &\left.\left. + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{4!}\hat{T}_1^4\right) \middle| \Phi_0 \right\rangle_C = 0 \ , \end{aligned} \tag{3}$$

where the reference wave function $|\Phi_0\rangle$ is assumed to be the Hartree–Fock (HF) wavefunction and $\bar{H}$ denotes the normal product form of the Hamiltonian, namely

$$\begin{aligned} \bar{H} &= \bar{H}_0 + \bar{V} \\ &= \sum_{rs} \left\{\hat{b}_r^+ \hat{b}_s\right\} \langle r|F|s\rangle + \sum_{rstu} \left\{\hat{b}_r^+ \hat{b}_s^+ \hat{b}_t \hat{b}_u\right\} \langle rs||tu\rangle \end{aligned} \tag{4}$$

Symbols $\hat{b}^+$ and $\hat{b}$ denote creation and annihilation operators, respectively, and the symbol {} indicates a normal-order form. In this article, we adhere to the usual convention that subscripts *i*, *j*, *k*, *l* are used for occupied spin orbitals; *a*, *b*, *c*, *d* for virtual orbitals; and *r*, *s*, *t*, *u* for

Scheme 1. Cluster expansion used in the projection onto the single (*S*), double (*D*), and triple (*T*) subspaces [3]

Method	S	D	T
CCSD	$\exp(\hat{T}_1 + \hat{T}_2)$	$\exp(\hat{T}_1 + \hat{T}_2)$	Not included
CCSDT-1a	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2) + \hat{T}_3$	$1 + \hat{T}_2$
CCSDT-1b	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$1 + \hat{T}_2$
CCSDT-2	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_2)$
CCSDT-3	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2)$
CCSDT-4	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2) + \hat{T}_3$
CCSDT	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$	$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)$

general spin orbitals. In Eqs (1), (2), (3), and (4), $\hat{T}_1$, $\hat{T}_2$, and $\hat{T}_3$ are cluster operators generating singly, doubly, and triply excited determinants $|\Phi_{\mathrm{i}}^{\mathrm{a}}>$, $|\Phi_{\mathrm{ij}}^{\mathrm{ab}}>$ and $|\Phi_{\mathrm{ijk}}^{\mathrm{abc}}>$.

Noga and Bartlett [7] analyzed the CCSDT-*n* methods by transferring the CCSDT amplitude equations into an operator form based on the expansion of the effective CC Hamiltonian in orders of perturbation theory. They clarified at what level in the CCSDT-*n* hierarchy a given cluster operator term is introduced and at which order of perturbation theory this term starts to contribute. The present analysis is also based on an extension of cluster amplitudes in orders of MBPT as is described in more detail in articles 1 and 2 [25, 26]. In article 1 it is also shown in terms of MBPT orders how a given cluster operator in the S and D equations of CCSD contributes to the correlation energy (Ref. [25], Table II) or alternatively how the various MBPT terms are generated order by order by the CCSD equations (Ref. [25], Table III). The repeated substitution of the CC amplitudes during the MBPT analysis can also be connected to the iterative solution of the CC equations, thus demonstrating which MBPT terms are introduced at a given iteration step [25, 26]. In this work we follow the procedure outlined in articles 1 and 2.

2.1 Comparison of CCSDT-1 with CCSD

The CCSDT-1a equations [8, 9] are given by Eqs. (5), (6), (7), and (8).

$$\left\langle \Phi_0 \middle| \bar{H}\left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right)\Phi_0 \middle| \right\rangle = E_{\mathrm{corr}}^{\mathrm{CCSD-1a}} \tag{5}$$

$$\left\langle \Phi_i^a \middle| \bar{H}\left(\hat{T}_1 + \hat{T}_2 + \hat{\mathbf{T}}_3 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3\right) \middle| \Phi_0 \right\rangle_{\mathrm{C}} = 0 \tag{6}$$

$$\left\langle \Phi_{ij}^{ab} \middle| \bar{H}\left(1 + \hat{T}_1 + \hat{T}_2 + \mathbf{T}_3 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{4!}\hat{T}_1^4\right) \middle| \Phi_0 \right\rangle_{\mathrm{C}} = 0 \tag{7}$$

$$\left\langle \Phi_{ijk}^{abc} \middle| \bar{H}_0\hat{\mathbf{T}}_3 + \bar{V}\hat{\mathbf{T}}_2 \middle| \Phi_0 \right\rangle = 0 \tag{8}$$

The cluster operators in normal print are already contained in the CCSD equations [15], while the operators in bold print appear for the first time in the CCSDT-1a equations. For CCSDT-1b the term $\hat{T}_1\hat{T}_3$ has to be added to the D excitation equation (Eq. 7) [11].

By introducing a perturbation parameter, λ, into Eq. (4), the CCSDT-1a Eqs. (5), (6), (7), and (8) can be rewritten in the form of Eqs. (9), (10), (11), (12)

$$E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}} = \lambda\left\langle \Phi_0 \middle| \bar{V}\left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) \middle| \Phi_0 \right\rangle , \tag{9}$$

$$a_i^a = \lambda\left(E_0 - E_i^a\right)^{-1} \times \left\langle \Phi_i^a \middle| \bar{V}\left(\hat{T}_1 + \hat{T}_2 + \hat{\mathbf{T}}_3 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3\right) \middle| \Phi_0 \right\rangle_{\mathrm{C}} , \tag{10}$$

$$a_{ij}^{ab} = \lambda\left(E_0 - E_{ij}^{ab}\right)^{-1} \times \left\langle \Phi_{ij}^{ab} \middle| \bar{V}\left(1 + \hat{T}_1 + \hat{T}_2 + \mathbf{T}_3 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{4!}\hat{T}_1^4\right) \middle| \Phi_0 \right\rangle_{\mathrm{C}} , \tag{11}$$

$$a_{ijk}^{abc} = \lambda\left(E_0 - E_{ijk}^{abc}\right)^{-1}\left\langle \Phi_{ijk}^{abc} \middle| \bar{V}\hat{\mathbf{T}}_2 \middle| \Phi_0 \right\rangle , \tag{12}$$

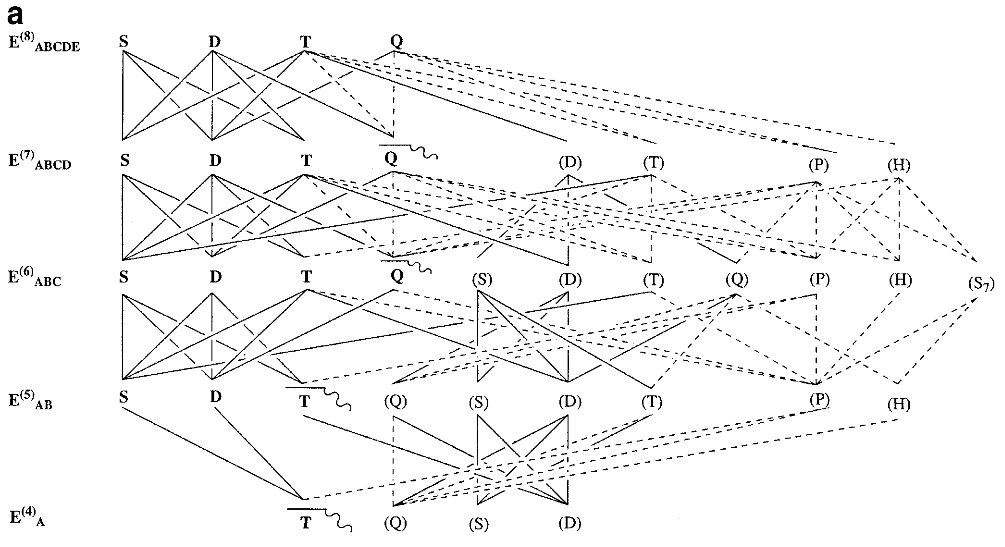

Fig. 1a, b. Graphical analysis of energy contributions at *MBPT(n)* ($n = 4,\ldots,8$) covered by the energy difference $\Delta = E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}} - E_{\mathrm{corr}}^{\mathrm{CCSD}}$. **a** Inclusion of new terms introduced by CCSDT-1a. Note that a particular energy contribution $E_{\mathrm{ABC}\ldots}^{(n)}$ in Δ is given by the *solid* or *dashed lines* that start at A = S, D, T, or Q in the $E^{(n)}$ row and connect B, C, etc. at row $n-1$, $n-2$, etc. until $n = 4$ is reached. In addition, *solid* (*dashed*) lines denote energy terms that are fully (partially) contained in Δ. **b** Inclusion of terms originally partially covered by CCSD, but fully contained in CCSDT-1a. For further explanations, see text

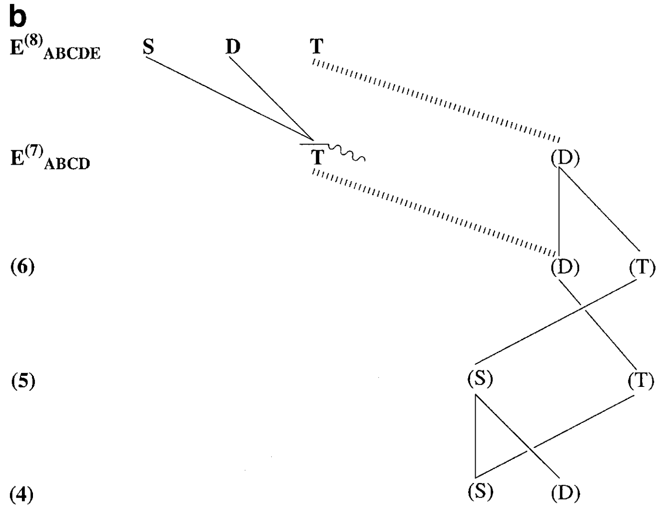

Fig. 1 Contd.

where $(E_0 - E_i^a)^{-1}$, $(E_0 - \mathrm{E}_{ij}^{ab})^{-1}$, and $(E_0 - E_{ijk}^{abc})^{-1}$ are the S, D, and T excitation energies. As was described elsewhere, [21, 22] one can use Eqs. (9), (10), (11), and (12) to expand $E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}}$ in different orders of perturbation theory. For example, at second order, one obtains

$$E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}}(2) = \left\langle \Phi_0 | \bar{V} | \hat{T}_2^{(1)} \Phi_0 \right\rangle \tag{13}$$

and

$$a_i^{a(2)} = \left(E_0 - E_i^a\right)^{-1} \left\langle \Phi_i^a \middle| \bar{V} \hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle \ , \tag{14}$$

$$a_{ij}^{ab(2)} = \left(E_0 - E_{ij}^{ab}\right)^{-1} \left\langle \Phi_{ij}^{ab} \middle| \bar{V} \hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle \ , \tag{15}$$

$$a_{ijk}^{abc(2)} = \left(E_0 - E_{ijk}^{abc}\right)^{-1} \left\langle \Phi_{ijk}^{abc} \middle| \bar{V} \hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle \ , \tag{16}$$

with

$$\hat{T}_2^{(1)} = \sum_{ij,ab} a_{ij}^{ab(1)} b_a^+ b_i b_b^+ b_j \ , \tag{17}$$

$$a_{ij}^{ab(1)} = \left(E_0 - E_{ij}^{ab}\right)^{-1} \left\langle \Phi_{ij}^{ab} | \bar{V} | \Phi_0 \right\rangle \ . \tag{18}$$

Since the difference between CCSDT-1a and CCSD results from the additional $\hat{T}_3$ terms in the CCSDT-1a equations, one has to concentrate on those energy terms in $E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}}$ that result from $\hat{T}_3$. These are given in Eq. (19):

$$\begin{aligned} E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}} - E_{\mathrm{corr}}^{\mathrm{CCSD}} &= E_{\mathrm{T}}^{(4)} + E_{\mathrm{ST}}^{(5)} + 2E_{\mathrm{DT}}^{(5)} \\ &+ \sum_{\mathrm{A}}^{\mathrm{SDQ}} \left(\sum_{\mathrm{B}}^{\mathrm{SD}} E_{\mathrm{ABT}}^{(6)} + E_{\mathrm{TDA}}^{(6)} \right) + \sum_{\mathrm{B}}^{\mathrm{SD}} \left(E_{\mathrm{TBT}}^{(6)} + E_{\mathrm{BTD}}^{(6)} \right) \\ &+ \sum_{\mathrm{AB}}^{\mathrm{TQ}} E_{\mathrm{ATB}}^{(6)}(\mathrm{I}) + E_{\mathrm{QTS}}^{(6)}(\mathrm{II}) + O\left(E_{\mathrm{ABCD}}^{7}\right) \ , \end{aligned} \tag{19}$$

where $E_{\mathrm{A}}^{(4)}$ denotes the MBPT(4) energy contributions, $E_{\mathrm{A}}^{(5)}$ the MBPT(5) energy contributions, etc. for A, B, ... = S, D, T, Q. Symbols I and II denote that the corresponding energy terms are only partially contained. For example, the term $E_{\mathrm{QTS}}^{(6)} = E_{\mathrm{QTS}}^{(6)}(\mathrm{I}) + E_{\mathrm{QTS}}^{(6)}(\mathrm{II})$ is partially contained in $E_{\mathrm{corr}}^{\mathrm{CCSD}}$ but fully in $E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}}$, which means that in the energy difference $E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}} - E_{\mathrm{corr}}^{\mathrm{CCSD}}$ of Eq. (19) $E_{\mathrm{QTS}}^{(6)} - E_{\mathrm{QTS}}^{(6)}(\mathrm{I}) = E_{\mathrm{QTS}}^{(6)}(\mathrm{II})$ appears.

The difference $E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}} - E_{\mathrm{corr}}^{\mathrm{CCSD}}$ is shown up to eighth order in form of a graphical representation in Fig. 1. Figure 1a gives the new energy contributions added at the CCSDT-1a level, while Figure 1b depicts just those energy terms that are already partially contained in CCSD, but fully covered by CCSDT-1a. Figure 1 as well as all other figures included in this article are based on a graphical method that was developed to analyze CC methods [21, 22]. In each of these diagrams, a particular energy contribution, $E_{\mathrm{ABC}\ldots}^{(n)}$, is given by a solid line that starts at A = S, D, T, or Q in the $E^{(n)}$ row and connects B, C, etc. at row $n-1$, $n-2$, etc. until $n = 4$ is reached. Coupling between A and B, B and C, etc., strictly follows Slater rules, which means that at the $n-1$ level for A = T pentuple excitations are possible for B, for A = Q pentuple and hextuple excitations for B, etc. provided the path leads back to S, D, T, Q at $n = 4$. Therefore, at each order, n, higher than Q excitations are included (in parentheses after a downward directed wiggle as a separator) that could be contained in $E^{(m)}{}_{\mathrm{ABC}\ldots}$ with $m > n$. Further details are included in the graphical representations, such as Fig. 1, by using solid, dashed, and hashed lines for the connections between A, B, C, etc. of $E^{(n)}{}_{\mathrm{ABC}\ldots}$. In this way we distinguish between fully (all connection lines are solid) and partially contained energy terms [at least one connection line is dashed (I) or hashed (II)].

Figure 1a reveals that CCSDT-1a in contrast to CCSD covers (either fully or partially) a considerable number of infinite-order T terms that result from the cluster operator $\hat{T}_3$ in the S, D, and T equations (Eqs. 6–8). At nth order with $n = 6$, 7, and 8, the number of newly added terms is 15 (3), 69 (31), and 318 (195), where the numbers in parentheses give the partially added terms. Most of these terms are of the type, $E_{\ldots\mathrm{T}\ldots}^{(n)}$ as is clearly reflected by Eq. (19) and Fig. 1. Consequently, CCSDT-1a is correct in fourth order, while CCSD is not.

By introducing the term $\hat{T}_1\hat{T}_3$ into the D equation (Eq. 7) the exponential ansatz with regard to the projection onto the D subspace is completed (see Scheme 1) and the CCSDT-1b method is obtained [11].

$$\begin{aligned} \Big\langle \Phi_{ij}^{ab} \Big| \bar{H} \Big(1 &+ \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 \\ &+ \hat{\mathbf{T}}_1\hat{\mathbf{T}}_3 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{4!}\hat{T}_1^4 \Big) \Big| \Phi_0 \Big\rangle_{\mathrm{C}} = 0 \end{aligned} \tag{20}$$

Analysis of Eq. (20) along the lines described previously leads to the energy difference $E_{\mathrm{corr}}^{\mathrm{CCSDT-1b}} - E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}}$ (compare also with Fig. 2):

$$\begin{aligned} &E_{\mathrm{corr}}^{\mathrm{CCSDT-1b}} - E_{\mathrm{corr}}^{\mathrm{CCSDT-1a}} \\ &\quad = E_{\mathrm{QTS}}^{(6)}(\mathrm{II}) + \sum_{\mathrm{A}}^{\mathrm{SDT}} E_{\mathrm{QTSA}}^{(7)}(\mathrm{II}) + O\left(E^{(8)}\right) \ . \end{aligned} \tag{21}$$

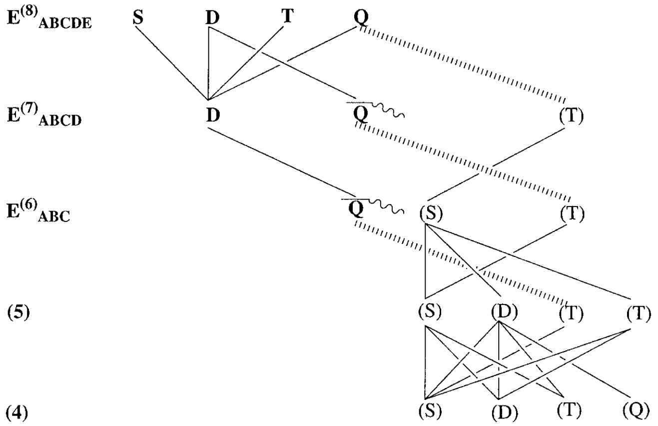

Fig. 2. Graphical analysis of energy contributions at MBPT(n) ($n = 4,\ldots,8$) in the energy difference $E_{\text{corr}}^{\text{CCSDT-1b}} - E_{\text{corr}}^{\text{CCSDT-1a}}$

Obviously, the addition of $\hat{T}_1\hat{T}_3$ does not have any effect for the energy at fourth and fifth order although $\hat{T}_1\hat{T}_3$ represents a fourth-order wave function term and, by this, is of lower wave function order than some of the other cluster terms already included into CCSDT-1a. At sixth, seventh, and eighth order, some energy terms of the type $E^{(n)}_{\ldots\text{QTS}\ldots}$, which are partially contained at the CCSDT-1a level, are complemented. Since no new energy terms enter at the CCSDT-1b level, CCSDT-1a and CCSDT-1b are so close that they should lead to almost identical results.

In view of the success of methods that include T effects in a perturbative way at the CC level [12], it is interesting to compare CCSDT-1 with CCSD(T). The energy of CCSD(T) is given by Eq. (22) [12]

$$E_{\text{corr}}^{\text{CCSD(T)}} = E_{\text{corr}}^{\text{CCSD}} + \Delta E_{\text{T}}(\text{CCSD}) \ , \tag{22}$$

where

$$\Delta E_{\text{T}}(\text{CCSD}) = \sum_{u}^{\text{SD}}\sum_{d}^{\text{D}}\sum_{t}^{\text{T}} a_u^{\text{CCSD}} \langle\Phi_u|V|\Phi_t\rangle (E_0 - E_t)^{-1} \times \langle\Phi_t|V|\Phi_d\rangle a_d^{\text{CCSD}} \ . \tag{23}$$

According to the analysis given in article 2 [26], CCSD(T) is identical to CCSDT-1a up to fifth order. At sixth, seventh, and eighth order, it fully or partially contains 87% (40 out of 46 energy terms), 80% (141 out of 176), and 72% (513 out of 712) of the CCSDT-1 terms (see Table 1 and Ref. [26]). Hence, CCSDT-1 covers more T terms than CCSD(T), but the differences are not so severe. In view of the fact that CCSD(T) is considerably cheaper than CCSDT-1, cost-efficiency considerations should clearly favor CCSD(T).

2.2 Comparison of CCSDT-2 with CCSDT-1

The CCSDT-2 method is given by Eqs. (5), (6), (20), and (24):

$$\left\langle \Phi_{ijk}^{abc} \middle| \bar{H}_0\hat{T}_3 + \bar{V}\left(\hat{T}_2 + \frac{1}{2}\hat{T}_2^2\right) \middle| \Phi_0 \right\rangle_{\text{C}} = 0 \ , \tag{24}$$

where the CCSDT-2 amplitudes a_{ijk}^{abc} can be expanded in terms of λ according to Eq. (25):

$$a_{ijk}^{abc} = \lambda\left(E_0 - E_{ijk}^{abc}\right)^{-1} \left\langle \Phi_{ijk}^{abc} \middle| \bar{V}\left(\hat{T}_2 + \frac{1}{2}\hat{T}_2^2\right) \middle| \Phi_0 \right\rangle_{\text{C}} \ . \tag{25}$$

The differences between CCSDT-2 and CCSDT-1b result from adding $\hat{T}_2^2$ to the T excitation (Eq. 24), thus converting the cluster expansion from $\hat{T}_2$ to $\exp\left(\hat{T}_2\right)$ (see Scheme 1). Analysis of the contributions due to $\hat{T}_2^2$ leads to the energy difference $E_{\text{corr}}^{\text{CCSDT-2}} - E_{\text{corr}}^{\text{CCSDT-1b}}$ given by Eq. (26) and Fig. 3.

$$E_{\text{corr}}^{\text{CCSDT-2}} - E_{\text{corr}}^{\text{CCSDT-1b}} = E_{\text{TQ}}^{(5)}(\text{II}) + E_{\text{TQD}}^{(6)}(\text{II}) + \sum_{\text{A}}^{\text{SD}} E_{\text{ATQ}}^{(6)}(\text{II}) + O\left(E^{(7)}\right) \tag{26}$$

The analysis reveals that the inclusion of $\hat{T}_2^2$ in Eq. (24) does not lead to any new energy contributions, but adds parts of the TQ coupling terms, which are missing at the CCSDT-1b level. At fifth, sixth, seventh, and eighth order, 1, 3, 15, and 62 energy contributions, respectively, of the type $E^{(\text{n})}_{\ldots\text{TQ}\ldots}$ are completed by CCSDT-2. Most of these terms should be positive (the TQ term at fifth order is a typical correction term [28, 39]), thus correcting a possible exaggeration of electron correlation effects at the CCSDT-1 level of theory.

2.3 Comparison of CCSDT-3 with CCSDT-2

By including cluster operators $\hat{T}_1\hat{T}_2$, $\frac{1}{2}\hat{T}_1^2\hat{T}_2$, $\frac{1}{2}\hat{T}_1\hat{T}_2^2$, and $\frac{1}{3!}\hat{T}_1^3\hat{T}_2$ into the CCSDT-2 Eq. (24), the cluster expansion takes the form $\exp\left(\hat{T}_1 + \hat{T}_2\right)$ (Scheme 1) and the CCSDT-3 equations for T excitations are obtained:

$$\left\langle \Phi_{ijk}^{abc} \middle| \bar{H}_0\hat{T}_3 + \bar{V}\left(\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{3!}\hat{T}_1^3\hat{T}_2\right) \middle| \Phi_0 \right\rangle_{\text{C}} = 0 \ , \tag{27}$$

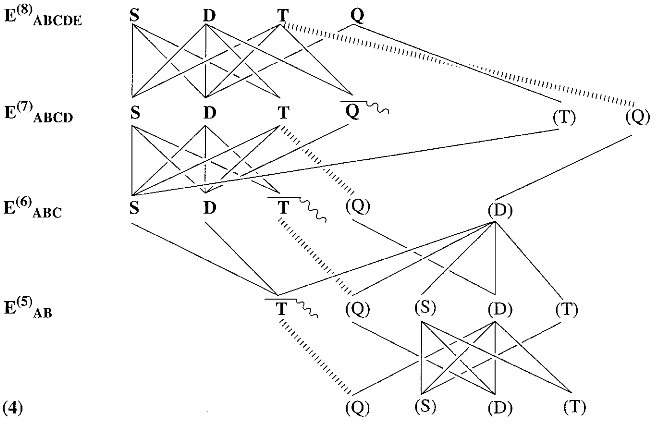

Fig. 3. Graphical analysis of energy contributions at MBPT(n) ($n = 4,\ldots,8$) in the energy difference $E_{\text{corr}}^{\text{CCSDT-2}} - E_{\text{corr}}^{\text{CCSDT-1b}}$

where

$$a_{ijk}^{abc} = \lambda\left(E_0 - E_{ijk}^{abc}\right)^{-1}\left\langle \Phi_{ijk}^{abc}\middle|\bar{V}\left(\hat{T}_2+\frac{1}{2}\hat{T}_2^2 +\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{2}\hat{T}_1\hat{T}_2^2+\frac{1}{3!}\hat{T}_1^3\hat{T}_2\right)\middle|\Phi_0\right\rangle_C . \quad (28)$$

Since $\hat{T}_1^2\hat{T}_2$, $\hat{T}_1\hat{T}_2^2$, and $\hat{T}_1^3\hat{T}_2$ contribute to the correlation energy in seventh and higher order of perturbation theory, the addition of $\hat{T}_1\hat{T}_2$ predominantly determines the difference between CCSDT-3 and CCSDT-2. That part of $E_{\text{corr}}^{\text{CCSDT}-3} - E_{\text{corr}}^{\text{CCSDT}-2}$ which results from $\hat{T}_1\hat{T}_2$ in Eq. (27), is given by Eq. (29):

$$E_{\text{corr}}^{\text{CCSDT}-3} - E_{\text{corr}}^{\text{CCSDT}-2} = E_{\text{TTS}}^{(6)}(\text{II}) + \sum_{\text{A}}^{\text{SDT}} E_{\text{TTSA}}^{(7)}(\text{II}) + \sum_{\text{B}}^{\text{SD}} E_{\text{BTTS}}^{(7)}(\text{II}) + O\left(E^{(8)}\right) . \quad (29)$$

Equation (29) shows that $\hat{T}_1\hat{T}_2$ in Eq. (28) introduces at $n = 6$ and higher-order partial contributions of the type $E_{\ldots\text{TTS}\ldots}^{(n)}$, which are missing at the CCSDT-2 level. Figure 4, which gives $E_{\text{corr}}^{\text{CCSDT}-3} - E_{\text{corr}}^{\text{CCSDT}-2}$ up to eighth order, confirms that at the CCSDT-3 level just the $E_{\ldots\text{TTS}\ldots}^{(n)}$ terms are complemented without adding any other new energy contributions. Since these terms describe important TT coupling effects that help to avoid an exaggeration of T effects in correlation calculations [25, 26], these changes can be important for electron systems with strong electron clustering (high-order correlation effects [28]); however, in other cases their importance may be small because the TTS effects enter MBPT one order later (Eq. 29) than the TQ effects introduced at CCSDT-2 (Eq. 26).

2.4 Comparison of CCSDT-4 with CCSDT-3

The CCSDT-4 method is obtained by introducing the $\hat{T}_3$ cluster operator into the T equations of CCSDT-3 in a linear fashion (Eq. 27, Scheme 1).

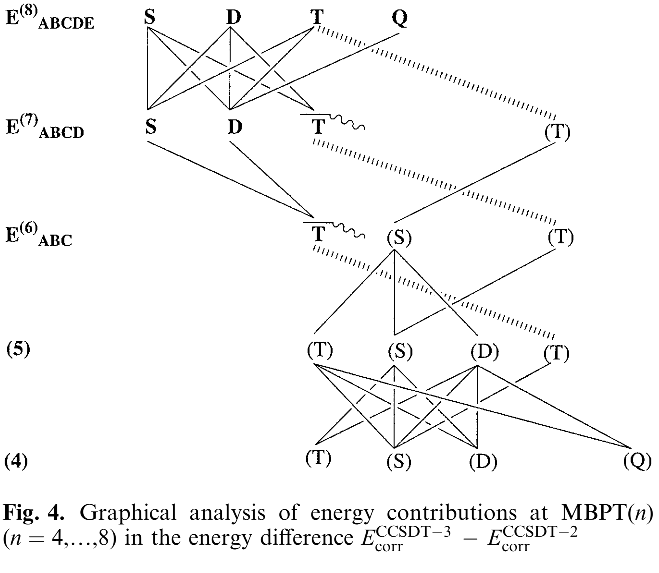

Fig. 4. Graphical analysis of energy contributions at MBPT(n) ($n = 4,\ldots,8$) in the energy difference $E_{\text{corr}}^{\text{CCSDT}-3} - E_{\text{corr}}^{\text{CCSDT}-2}$

$$\left\langle \Phi_{ijk}^{abc}\middle|\bar{H}\left(\hat{T}_2+\hat{T}_3+\frac{1}{2}\hat{T}_2^2+\hat{T}_1\hat{T}_2 +\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{2}\hat{T}_1\hat{T}_2^2+\frac{1}{3!}\hat{T}_1^3\hat{T}_2\right)\middle|\Phi_0\right\rangle_C = 0 \quad (30)$$

According to the analysis carried out in this work, this leads to differences in the correlation energies between CCSDT-3 and CCSDT-4 at fifth and higher orders:

$$E_{\text{corr}}^{\text{CCSDT}-4} - E_{\text{corr}}^{\text{CCSDT}-3} = E_{\text{TT}}^{(5)} + \sum_{\text{A}}^{\text{SDT}} E_{\text{ATT}}^{(6)} + E_{\text{TTD}}^{(6)} + E_{\text{TTQ}}^{(6)}(\text{II}) + O\left(E^{(7)}\right) . \quad (31)$$

Hence, at the CCSDT-4 level important new TT and TTT coupling terms appear, which are introduced by $\hat{T}_3$ in Eq. (30). Figure 5a, in which a more detailed analysis of the difference $E_{\text{corr}}^{\text{CCSDT}-4} - E_{\text{corr}}^{\text{CCSDT}-3}$ is given, indicates that 4, 19(2), and 81(16) TT terms are added at sixth, seventh, and eighth order. Beside the newly added TT coupling terms, other TT terms, which are already partially contained in CCSDT-3, are also completed at CCSDT-4 (one for $n = 6$, five for $n = 7$ and 25 for $n = 8$, cf. Fig. 5b).

2.5 Comparison of CCSDT with CCSDT-4

The correct T equation of CCSDT is obtained by adding $\hat{T}_2\hat{T}_3$ and $\hat{T}_1\hat{T}_3$ to Eq. (30), thus getting the complete exponential ansatz (Scheme 1):

$$\left\langle \Phi_{ijk}^{abc}\middle|\bar{H}\left(\hat{T}_2+\hat{T}_3+\frac{1}{2}\hat{T}_2^2+\hat{T}_1\hat{T}_2+\hat{T}_1\hat{T}_3+\hat{T}_2\hat{T}_3 +\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{2}\hat{T}_1\hat{T}_2^2+\frac{1}{3!}\hat{T}_1^3\hat{T}_2+\frac{1}{2}\hat{T}_1^2\hat{T}_3\right)\middle|\Phi_0\right\rangle_C = 0 . \quad (32)$$

The energy difference between CCSDT and CCSDT-4 is described by Eq. (33) and Fig. 6.

$$E_{\text{corr}}^{\text{CCSDT}} - E_{\text{corr}}^{\text{CCSDT}-4} = E_{\text{TPT}}^{(6)}(\text{II}) + E_{\text{TQTS}}^{(7)}(\text{II}) \sum_{\text{A}}^{\text{SDT}} E_{\text{ATPT}}^{(7)}(\text{II}) + O\left(E^{(8)}\right) \quad (33)$$

Obviously, CCSDT-4 and CCSDT are closely related since they differ in just the second part (II) of some …TPT and some ..TQTS.. energy contributions. At eighth order, 16 E(II) parts of this nature come in at the CCSDT level, which is not much in view of the fact that there is a total of 915 (583 unique) energy contributions at this order. Therefore, CCSDT-4 and CCSDT are approximately equivalent in cases where TPT and TQTS contributions are not important, which otherwise should lead to a positive correction because of the fact that the TPT contribution is larger zero at sixth order MBPT [28, 39].

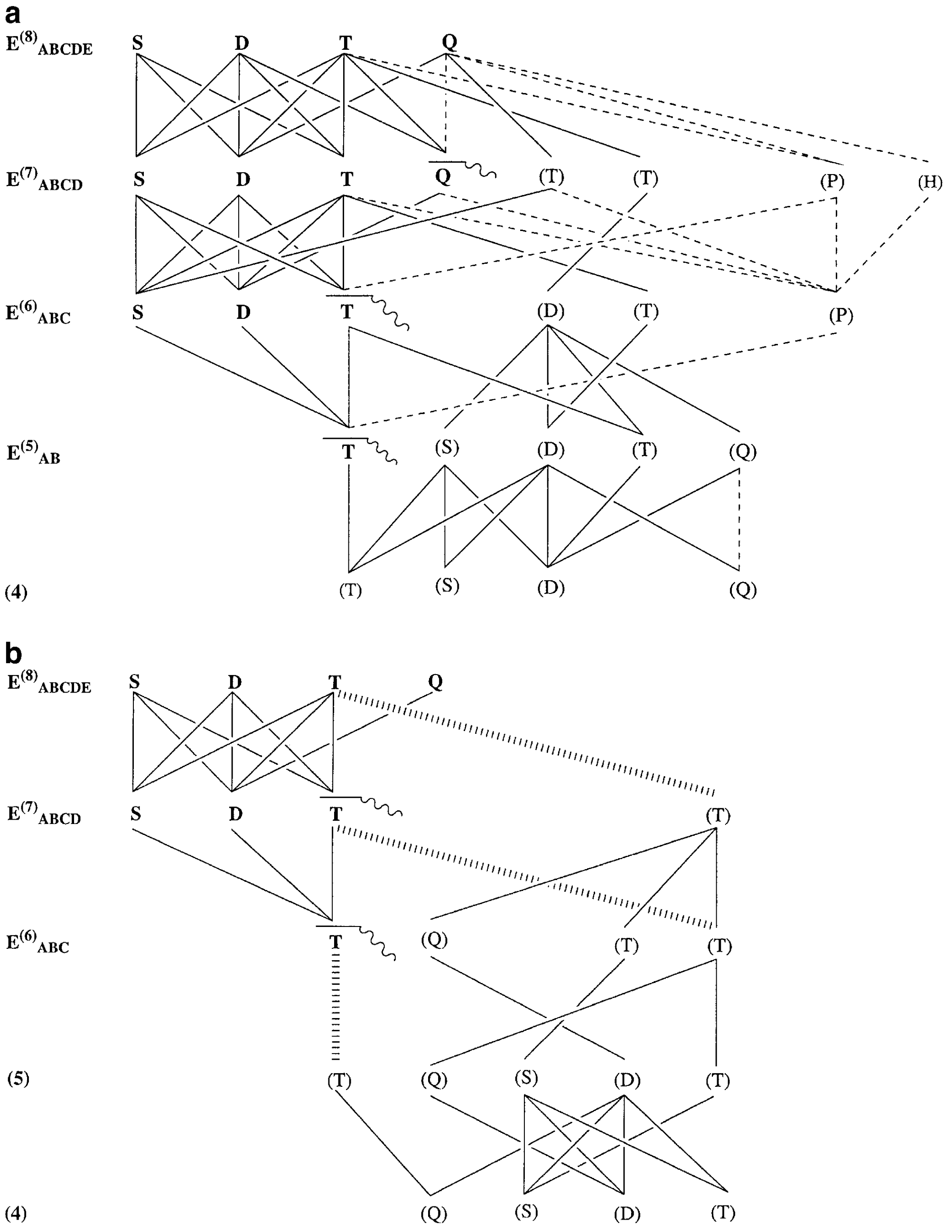

Fig. 5a, b. Graphical analysis of energy contributions at MBPT(n) ($n = 4,\ldots,8$) in the energy difference $E_{\mathrm{corr}}^{\mathrm{CCSDT-4}} - E_{\mathrm{corr}}^{\mathrm{CCSDT-3}}$. **a** Inclusion of contributions that are not covered by CCSDT-3, but that are contained in CCSDT-4. **b** Inclusion of terms partially included in CCSDT-3 and fully in CCSDT-4

By utilizing the diagrams shown in Figs. 1–6 together with the corresponding diagram for CCSD [25], a graphical analysis of energy contributions covered by CCSDT can be given (Fig. 7). The contents of Figs. 1–7, Tables 1 and 2, as well as the discussion given earlier are summarized in Table 3. All the methods in Table 3 are iterative, where the reference method CCSD is the least costly since the number of operations necessarily increases with just the sixth power of the number, M, of basis functions used. CCSDT is the most expensive method because of its $O(M^8)$ dependence. In view of the computational resources available nowadays, $O(M^6)$ and $O(M^7)$ calculations can be routinely done for small and medium-sized molecules, while $O(M^8)$ methods such as CCSDT can only be applied to relatively small molecules.

In Sect. 3, the actual performance of CCSDT-n methods is discussed on the basis of a series of calculations for some typical molecules difficult to describe with uncorrelated methods.

3 Application of CCSDT-*n* methods

For a set of small molecules with two or three atoms, atomization energies were calculated using unrestricted HF–CCSDT-n theory in connection with Dunning's correlation-consistent polarized-valence double-zeta (cc-pVDZ) and correlation-consistent polarized-valence triple-zeta (cc-pVTZ) basis sets [30], which correspond to (10s5p2d1f/5s2p1d) [4s3p2d1f/3s2p1d] and (9s4p1d/4s1p) [3s2p1d/2s1p] contractions. All the calculations were carried at experimental geometries [31–37] using the ab initio program package COLOGNE99 [38]. Calculated CCSDT-*n* energies obtained with the cc-pVTZ basis are listed in Table 4 for the molecules investigated, while the corresponding atomic energies needed to calculate atomization energies are listed in Table 5.

Changes in the CCSDT-*n* energy caused by increasing *n* were analyzed by first scaling and then averaging calculated energy differences $\Delta E(\text{CCSDT-}n) = E(\text{CCSDT-}n) - E(\text{CCSDT} - n')$ ($n > n'$; $n = 0$: CCSD reference) over all molecules considered. The scaling factor for the individual correlation contributions at a given CCSDT-*n* level was determined using Eq. (34):

$$f = \left(\sum_{n}^{4} [\Delta E(\text{CCSDT} - n)]^2\right)^{-1/2} . \tag{34}$$

A scaled correlation energy contribution ε(CCSDT-*n*) was defined as

$$\varepsilon(\text{CCSDT} - n) = \frac{\Delta E(\text{CCSDT} - n)}{f} , \tag{35}$$

where the ε(CCSDT-*n*) fulfill normalization Eq. (36):

$$[\varepsilon(\text{CCSDT} - 1)]^2 + [\varepsilon(\text{CCSDT} - 2)]^2 + \ldots = 1 . \tag{36}$$

For each molecule, trends in the individual CCSDT-*n* contributions can be described by the scaled energy terms in a comparative way. Accordingly, one can present the scaled energy terms ε(CCSDT-*n*) in the form of bar diagrams, for which we coin the term CCSDT-*n* spectrum with reference to the term MP*n* spectrum recently introduced [28].

The CCSDT-*n* spectrum of the molecules listed in Table 4 is obtained by averaging the scaled energy terms over all molecules investigated according to Eq. (37):

$$\bar{\varepsilon}(\text{CCSDT} - n) = \frac{1}{N} \sum_{i}^{N} \varepsilon(\text{CCSDT} - n)(i) , \tag{37}$$

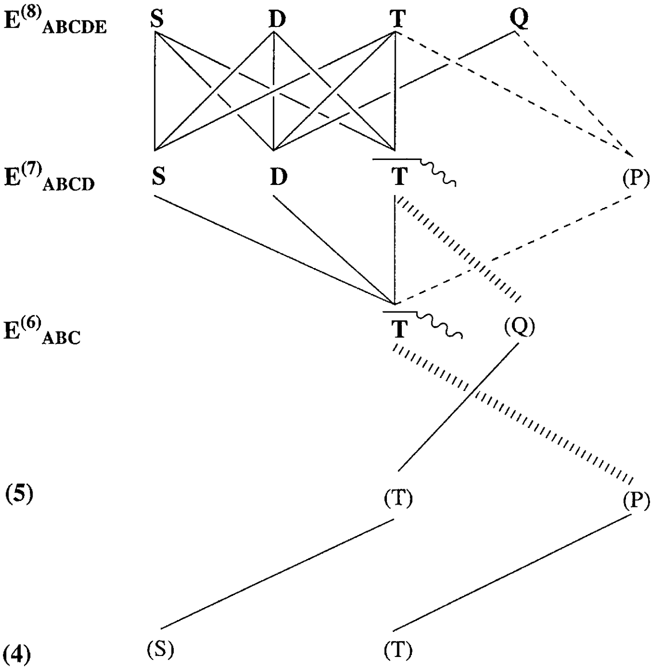

Fig. 6. Graphical analysis of energy contributions at MBPT(*n*) ($n = 4,\ldots,8$) in the energy difference $E_{\text{corr}}^{\text{CCSDT}} - E_{\text{corr}}^{\text{CCSDT-4}}$

Table 1. The total number of energy contributions covered by CCSDT-*n* at different orders of perturbation theory. For each method, the entry *k*(*l*) gives the number, *k*, of all terms covered not considering symmetry. Of the *k* terms *l* terms are covered only partially

Methods	5	6	7	8
CCSD	9(2)	30(12)	107(61)	394(276)
CCSDT-1a	12(2)	46(16)	176(91)	712(466)
CCSDT-1b	12(2)	46(15)	176(87)	712(450)
CCSDT-2	12(1)	46(12)	176(74)	712(404)
CCSDT-3	12(1)	46(11)	176(69)	712(381)
CCSDT-4	13(1)	50(10)	195(66)	792(372)
CCSDT	13(1)	50(9)	195(62)	792(356)

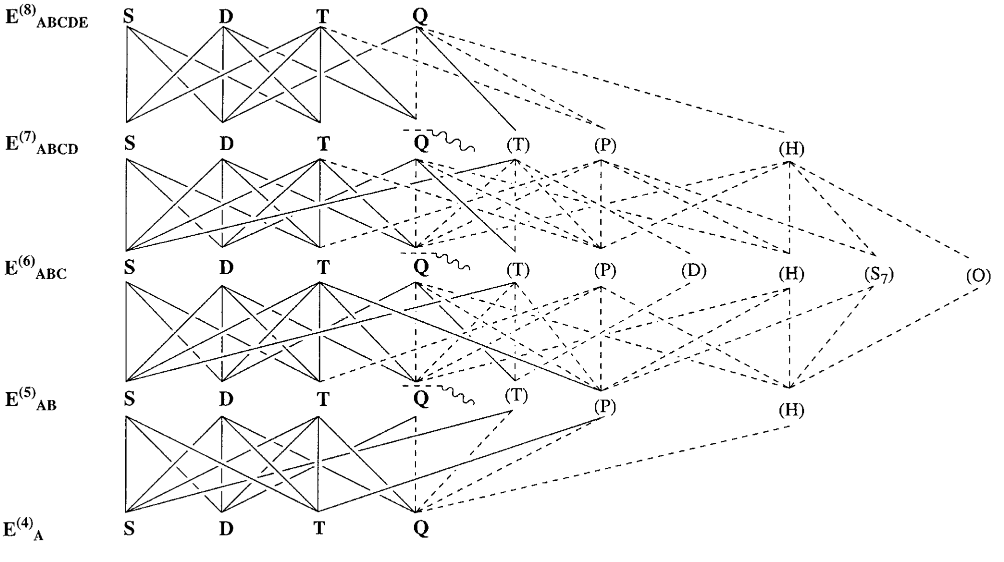

Fig. 7. Graphical analysis of energy contributions at MBPT(*n*) ($n = 4,\ldots,8$) covered by the CCSDT correlation energy. Note that in Fig. 5 of Ref. [21] some terms are missing at seventh and eighth order because in Ref. [21] the MBPT analysis of the CCSDT energy at sixth order was used to investigate higher- and infinite-order effects in CCSDT

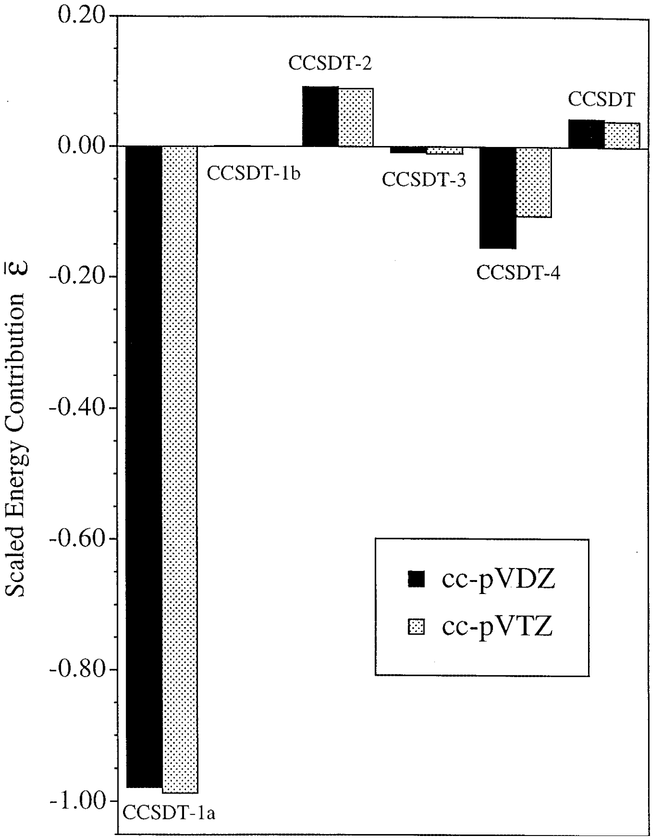

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Fig. 8. General CCSDT-*n* spectrum shown in the form of a bar diagram and based on the CCSDT-*n*/correlation-consistent polarized-valence double-zeta (*cc-pVDZ*) and CCSDT-*n*/correlation-consistent polarized-valence triple-zeta (*cc-pVTZ*) energies listed in Table 4

where $N = 13$ is the total number of molecules i listed in Table 4. The CCSDT-*n* spectra obtained in this work are shown in Figs. 8 (averaged spectrum) and 9 (individual molecules both for the cc-pVDZ and the cc-pVTZ basis sets).

The CCSDT-*n*/cc-pVTZ spectrum of Fig. 8 confirms what was found in the MBPT(*n*) analysis: CCSDT-1a leads to the largest energy-lowering, so the calculated energies are similar or even lower than CCSDT energies (Table 4). On average, CCSDT-1a correlation energies correspond to 101.7% of the T correlation energy of CCSDT (cc-pVTZ; cc-pVDZ: 97.9%), while the

Table 3. Summary of the analysis of CCSDT-*n* methods. M is the number of basis functions. If the percentage of terms covered does not change for $n \rightarrow n + 1$, the T terms added are just partial terms

Method	Terms added	T terms covered	Cost
CCSD	Reference	0%	$O(M^6)$
CCSDT-1a	...T...	75%	$O(M^7)$
CCSDT-1b	..QTS..(I)	75%	$O(M^7)$
CCSDT-2	..TQ..(II)	75%	$O(M^7)$
CCSDT-3	..TTS..(II)	75%	$O(M^7)$
CCSDT-4	..TT..	100%	$O(M^8)$
CCSDT	..TPT(II), ..TQTS(II)	100%	$O(M^8)$

Table 2. Number of triple contributions covered by CCSDT-*n* at different orders of many-body perturbation theory. For each method, the entry $k(l)$ gives the number, k, of fully and partially covered terms not considering symmetry. Of the k terms there are l terms that are covered only partially. N(T), N(TT), etc. denote the number of energy terms with one, two, etc. T excitations

Order	CCSD	CCSDT-1b	CCSDT-2	CCSxDT-3	CCSDT-4	CCSDT
Fifth						
Total	2(1)	5(1)	5	5	6	6
N(T)	2(1)	5(1)	5	5	5	5
N(TT)				1	1	
Sixth						
Total	12(8)	27(10)	27(7)	27(6)	31(5)	31(4)
N(T)	10(6)	22(7)	22(4)	22(4)	22(4)	22(4)
N(TT)	2(2)	2(2)	2(2)	2(1)	5	5
N(T..T)		3(1)	3(1)	3(1)	3(1)	3
N(TTT)					1	1
Seventh						
Total	60(45)	123(63)	123(52)	123(47)	142(44)	142(40)
N(T)	40(26)	82(35)	82(27)	82(27)	82(27)	82(27)
N(TT)	10(10)	11(11)	11(11)	11(7)	22(5)	22(5)
N(T..T)	8(7)	26(13)	26(10)	26(10)	26(10)	26(7)
N(TTT)	2(2)	2(2)	2(2)	2(2)	5	5
N(TT..T)		2(2)	2(2)	2(1)	6(2)	6(1)
N(TTTT)					1	1
Eighth						
Total	267(219)	552(360)	552(314)	552(291)	632(282)	632(266)
N(T)	145(103)	300(171)	300(143)	300(143)	300(143)	300(143)
N(TT)	40(40)	47(47)	47(47)	47(33)	82(30)	82(30)
N(T..T)	54(48)	150(91)	150(73)	150(73)	150(73)	150(64)
N(TTT)	10(10)	11(11)	11(11)	11(11)	22(5)	22(5)
N(TT..T)	16(16)	29(29)	29(29)	29(20)	52(21)	52(18)
N(T..T..T)		11(7)	11(7)	11(7)	11(7)	11(4)
N(TTTT)	2(2)	2(2)	2(2)	2(2)	5	5
N(TTT..T) (or TT..TT)		2(2)	2(2)	2(2)	9(3)	9(2)
N(TTTTT)					1	1

Table 4. CCSDT-*n* energies calculated for some molecules in their ground state. All energies in hartree. $\bar{\varepsilon}$(CCSDT-*n*) values are calculated according to Eq. (37). Experimental geometries from Refs. [27] [CO($^1\sum^+$): 1.128 Å; F$_2$($^1\sum^+{}_g$): 1.412 Å; FH($^1\sum^+$): 0.917 Å; N$_2$($^1\sum^+{}_g$): 1.098 Å; O$_2$($^3\sum^-{}_g$); 1.207 Å; NO($^2\Pi_r$): 1.151 Å], [28] [CH$_2$(^{1}A$_1$): 1.113 Å; 100.5°; CN($^2\sum^+$): 1.172 Å], [29] [CH$_2$(^{3}B$_1$): 1.075 Å; 133.9°], [30] [HCN($^1\sum$): CH: 1.066 Å; CN: 1.153 Å], [31] [HNC($^1\sum$): NH: 0.994; CN: 1.169 Å], [32] [HNO(^{1}A′): NO: 1.212, NH: 1.063 Å; HNO: 108.6°], and [33] [HOF(^{1}A′): OH: 0.966; OF: 1.435 Å; HOF: 97.6°]

Molecule	CCSD	CCSD(T)	CCSDT-1a	CCSDT-1b	CCSDT-2	CCSDT-3	CCSDT-4	CCSDT
1. cc-pVDZ calculations								
$CH_2(^1A_1)$	−39.01939	−39.02229	−39.02232	−39.02232	−39.02215	−39.02215	−39.02314	−39.02300
$CH_2(^3B_1)$	−39.03953	−39.04124	−39.04125	−39.04125	−39.04117	−39.04118	−39.04167	−39.04162
$CN(^2\sum^+)$	−92.48943	−92.48909	−92.48943	−92.48946	−92.48780	−92.48916	−92.49317	−92.49162
$HCN(^1\sum)$	−93.17643	−93.18828	−93.18878	−93.18879	−93.18747	−93.18748	−93.18897	−93.18849
$HNC(^1\sum)$	−93.15175	−93.16313	−93.16403	−93.16403	−93.16265	−93.16270	−93.16416	−93.16362
$CO(^1\sum^+)$	−113.04373	−113.05439	−113.05573	−113.05572	−113.05434	−113.05438	−113.05535	−113.05484
$N_2(^1\sum_g^+)$	−109.26339	−109.27525	−109.27576	−109.27576	−109.27443	−109.27442	−109.27578	−109.27533
$NO(^2\Pi_r)$	−129.59894	−129.59794	−129.59894	−129.59886	−129.59758	−129.59771	−129.59910	−129.59855
$HNO(^1A')$	−130.15926	−130.17129	−130.17186	−130.17184	−130.17055	−130.17053	−130.17213	−130.17160
$O_2(^3\sum_g^-)$	−149.97602	−149.98572	−149.98613	−149.98612	−149.98510	−149.98511	−149.98624	−149.98591
$FH(^1\sum^+)$	−100.22623	−100.22815	−100.22823	−100.22824	−100.22810	−100.22810	−100.22827	−100.22824
$HOF(^1A')$	−175.14306	−175.15195	−175.15225	−175.15219	−175.15143	−175.15138	−175.15255	−175.15224
$F_2(^1\sum_g^+)$	−199.09758	−199.09748	−199.09758	−199.09755	−199.09686	−199.09679	−199.09808	−199.09775
$\bar{\varepsilon}$(CCSDT-*n*)			−0.97852	0.00114	0.09113	−0.00849	−0.15455	0.04274
Mean absolute deviation, μ			0.01410	0.00184	0.01948	0.01431	0.06298	0.01072
Standard deviation, σ			0.0181	0.0260	0.0237	0.0267	0.0795	0.0219
2. cc-pVTZ calculations								
$CH_2(^1A_1)$	−39.05653	−39.06135	−39.06144	−39.06144	−39.06118	−39.06120	−39.06238	−39.06215
$CH_2(^3B_1)$	−39.07446	−39.07784	−39.07788	−39.07788	−39.07773	−39.07775	−39.07843	−39.07833
$CN(^2\sum^+)$	−92.54722	−92.56571	−92.56628	−92.56631	−92.56403	−92.56580	−92.57011	−92.56806
$HCN(^1\sum)$	−93.25725	−93.27512	−93.27603	−93.27605	−93.27418	−93.27424	−93.27567	−93.27496
$HNC(^1\sum)$	−93.23409	−93.25133	−93.25254	−93.25255	−93.25065	−93.25075	−93.25225	−93.25149
$CO(^1\sum^+)$	−113.13855	−113.15546	−113.15708	−113.15709	−113.15511	−113.15523	−113.15631	−113.15559
$N_2(^1\sum_g^+)$	−109.35536	−109.37384	−109.37477	−109.37479	−109.37284	−109.37289	−109.37423	−109.37356
$NO(^2\Pi_r)$	−129.69838	−129.71682	−129.71822	−129.71815	−129.71614	−129.71638	−129.71794	−129.71713
$HNO(^1A')$	−130.27845	−130.29840	−130.29943	−130.29942	−130.29737	−130.29742	−130.29916	−130.29836
$O_2(^3\sum_g^-)$	−150.11121	−150.12900	−150.12989	−150.12989	−150.12808	−150.12817	−150.12952	−150.12896
$FH(^1\sum^+)$	−100.33199	−100.33836	−100.33863	−100.33864	−100.33811	−100.33812	−100.33849	−100.33839
$HOF(^1A')$	−175.31630	−175.33428	−175.33504	−175.33499	−175.33334	−175.33336	−175.33488	−175.33430
$F_2(^1\sum_g^+)$	−199.27812	−199.29610	−199.29660	−199.29658	−199.29504	−199.29504	−199.29667	−199.29610
$\bar{\varepsilon}$(CCSDT-*n*)			−0.98692	0.00021	0.08898	−0.01042	−0.10632	0.03946
Mean absolute deviation, μ			*0.00788*	*0.00109*	*0.01651*	*0.01217*	*0.05117*	*0.01043*
Standard deviation, σ			*0.0102*	*0.0014*	*0.0202*	*0.0229*	*0.0606*	*0.0198*

Table 5. CCSDT-*n*/cc-pVTZ energies for some atoms in their ground state. All energies in hartree

Atom	CCSD	CCSD(T)	CCSDT-1a	CCSDT-1b	CCSDT-2	CCSDT-3	CCSDT-4	CCSDT
$H(^1S)$	−0.49981	−0.49981	−0.49981	−0.49981	−0.49981	−0.49981	−0.49981	−0.49981
$C(^3P)$	−37.77873	−37.78076	−37.78073	−37.78073	−37.78071	−37.78071	−37.78129	−37.78123
$N(^4S)$	−54.51471	−54.51471	−54.51471	−54.51471	−54.51465	−54.51465	−54.51508	−54.51503
$O(^3P)$	−74.97105	−74.97396	−74.97400	−74.97400	−74.97387	−74.97387	−74.97431	−74.97425
$F(^2P)$	−99.61677	−99.62036	−99.62045	−99.62045	−99.62023	−99.62023	−99.62059	−99.62054

corresponding value for CCSD(T) is 97.0% (cc-pVTZ; cc-pVDZ: 93.5%). CCSDT-1b does not change CCSDT-1a energies significantly; however, CCSDT-2 leads to an increase rather than a decrease of energies. This is a result of adding ..TQ.. terms because the TQ term at MBPT(5) and TQA terms at MBPT(6) represent positive correction terms (coupling between three- and four-electron correlation) [39] similarly as the Q term at MBPT(4) does (for a discussion see Ref. [40]). CCSDT-3 leads to a negligible energy change because just some terms contained partially at CCSDT-2 are complemented (Table 2). At CCSDT-4, a number of ..TT.. coupling terms representing new electron correlation effects are added, which leads to a substantial lowering of the energy (Fig. 8). Finally, at CCSDT-5 = CCSDT additional correction terms containing TQ and TP coupling effects (Table 3) are considered, so the energy increases slightly (Fig. 8). Changes at CCSDT-2 to

CCSDT largely cancel each other out, thus explaining the similarity of CCSDT-1a and CCSDT energies, which might be considered as an argument for approximating CCSDT by CCSDT-1a rather than any more complete CCSDT-*n* method.

For CCSDT-*n* calculations, a valence triple-zeta polarized (VTZP) basis such as the cc-pVTZ basis set fulfills the minimum requirements of a basis to be used for the calculation of three-electron correlation effects; however, often valence double-zeta polarized (VDZP) basis sets are used because of computational limitations hindering application of a VTZP basis. In Fig. 8, the CCSDT-*n*/cc-pVDZ spectrum is compared with the corresponding cc-pVTZ spectrum. There are two major differences, which indicate the drawbacks of employing a smaller basis set not flexible enough to describe higher-order electron correlation effects. First, T effects are underestimated at the CCSDT-1a level when using the cc-pVDZ basis set. Second, TT correlation effects are exaggerated at CCSDT-4 and this seems to be related to the underestimation of T effects at CCSDT-1a. We note that the TT effects at CCSDT-4 also cover the positive correction terms TTQ and TTS (Eq. 31), which reduce the negative TT effects depending on the importance of three-electron correlation. If the latter is large, the corrections are also large and lead to a reduction in the TT contributions at CCSDT-4. Since a small basis set such as the VDZP basis set underestimates the importance of three-electron correlation effects [40], it also leads to an exaggeration of the TT effects at CCSDT-4.

The individual CCSDT-*n* spectra are shown in Fig. 9 for both the cc-pVDZ and the cc-pVTZ basis set used. The CCSDT-*n*/cc-pVDZ spectrum of Fig. 9a suggests that all the molecules investigated are similarly described at the various CCSDT-*n* levels of theory and that, therefore, there seems to be little reason to invest in these methods. However, it is well known that VDZP basis sets are not

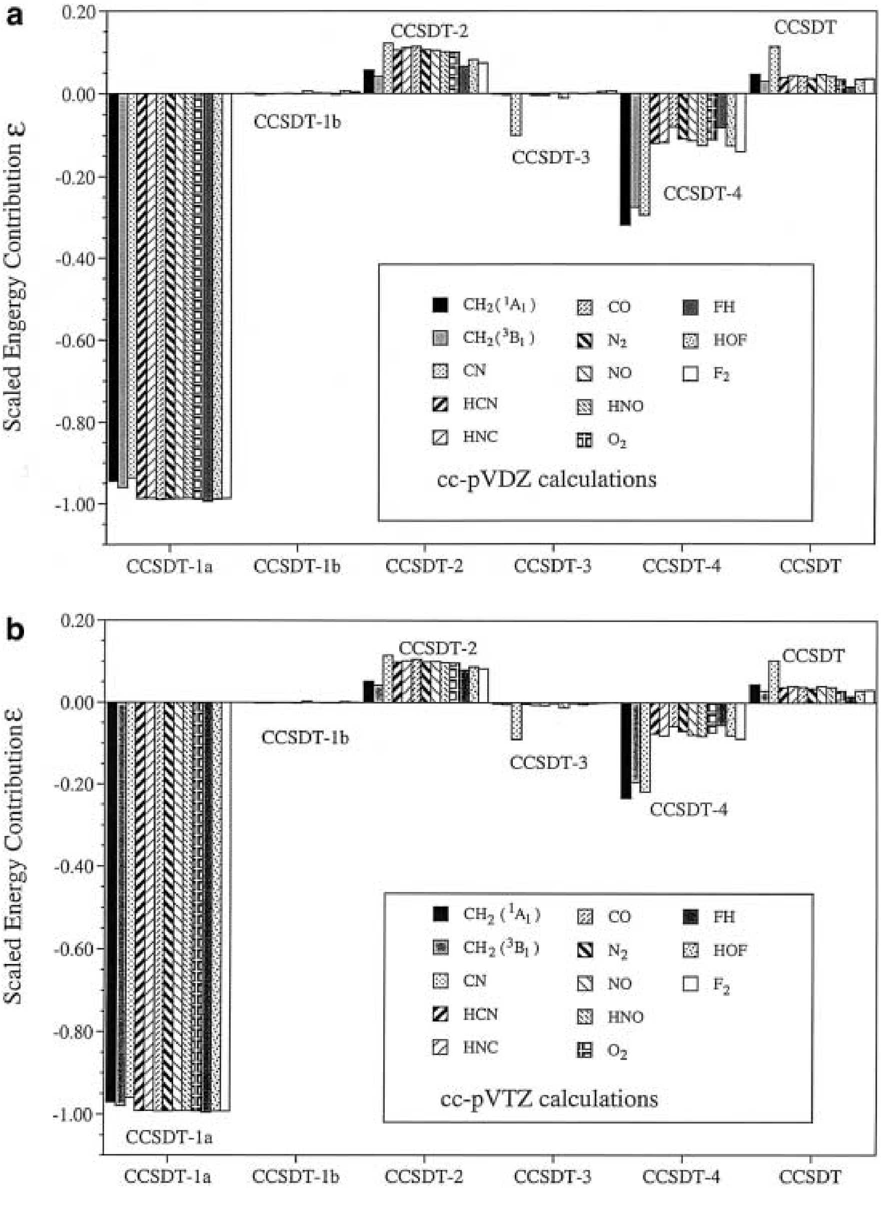

Fig. 9a, b. Individual CCSDT-*n* spectra shown in the form of a bar diagram for the molecules listed in Table 4. **a** cc-pVDZ calculations and **b** cc-pVTZ calculations suitable for use in highly correlated methods. This is also confirmed by the CCSDT-*n*/cc-pVTZ spectra of Fig. 9b, which reveal much more variation in calculated energy changes upon increasing the CCSDT-*n* level. Since variations are still significant at CCSDT-4 and even at CCSDT, there seems to be the necessity to apply even CCSDT to get reliable results. However, neither the S-T splitting of CH_2 (CCSDT-1a: 10.4; CCSDT: 10.2 kcal/mol; experimental value: 9.2 kcal/mol), the isomerisation energy for HCN → HNC (14.9; 14.7 kcal/mol; experimental: 14.8 kcal/mol [41]) nor the atomization energies listed in Table 6 (maximum changes of 1.2 kcal/mol) confirm that there is the necessity to apply CCSDT to get reliable relative energies, which, of course, does not exclude the fact that CCSDT may be needed for the description of other problems in chemistry.

The explanation for the constants of relative energies, in particular atomization energies at all levels of CCSDT-*n* theory, is found when comparing the CCSDT-*n* spectra of molecules (Fig. 9) and atoms (Fig. 10). T contributions at CCSDT-*n* vary in a characteristic way with respect to the electronegativity of the atom considered. Absolute CCSDT-1a and CCSDT-2 contributions increase with the electronegativity of the atom, while CCSDT-2 and CCSDT contributions decrease; similar trends can be found for the molecules of Fig. 9. The electronegativity of an atom determines the contraction of negative charge toward the nucleus and by this the degree of electron clustering in the valence shell. The larger the electronegativity the more electrons around the nucleus cluster and the more important three-electron correlation effects become for an effective separation of electrons in a confined space. Hence, the T effects covered by CCSDT-1a increase in magnitude from C to F. Also, positive correction terms for electron correlation either concerning an exaggeration of pair or three-electron correlation increase, thus being responsible for the relatively large ..TQ.. terms at CCSDT-2 or the relatively small ..TT.. terms at CCSDT-4.

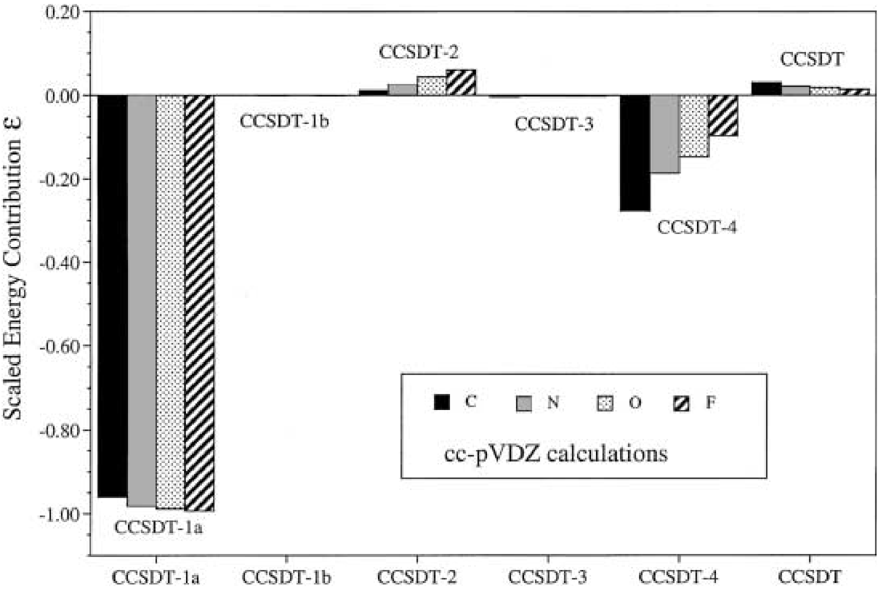

Fig. 10. Individual CCSDT-*n* spectra shown in the form of a bar diagram for the atoms listed in Table 5

Table 6. CCSDT-*n*/cc-pVTZ atomization energies for some molecules in their ground state. All energies in kilocalorie per mole

Molecule	CCSD	CCSD(T)	CCSDT-1a	CCSDT-1b	CCSDT-2	CCSDT-3	CCSDT-4	CCSDT
$CH_2(^1A_1)$	176.4	176.3	176.4	176.4	176.2	176.3	176.6	176.5
$CH_2(^3B_1)$	185.8	186.7	186.7	186.7	186.6	186.6	186.7	186.7
$CN(^2\Sigma^+)$	170.0	169.6	170.0	170.0	168.6	169.7	171.8	170.6
$HCN(^1\Sigma)$	292.6	301.1	301.7	301.7	300.6	300.6	300.9	300.5
$HNC(^1\Sigma)$	287.0	286.2	287.0	287.0	285.8	285.9	286.2	285.8
$CO(^1\Sigma^+)$	244.0	251.5	252.5	252.5	251.4	251.4	251.5	251.1
$N_2(^1\Sigma_g^+)$	207.4	216.1	216.7	216.7	215.6	215.6	215.9	215.6
$NO(^2\Pi_r)$	134.9	143.2	144.0	144.0	142.9	143.0	143.4	143.0
$HNO(^1A')$	185.2	194.5	195.1	195.1	193.9	194.0	194.5	194.1
$O_2(^3\Sigma_g^-)$	106.1	113.6	114.1	114.1	113.2	113.2	113.5	113.2
$FH(^1\Sigma^+)$	135.2	136.9	137.0	137.0	136.9	136.9	136.9	136.8
$HOF(^1A')$	143.5	150.7	151.1	151.1	150.3	150.3	150.7	150.4
$F_2(^1\Sigma_g^+)$	28.0	34.8	35.0	34.9	34.3	34.2	34.8	34.5
Mean absolute deviation	14.4	7.8	7.3	7.3	8.2	8.1	7.6	8.0

Table 7. Comparison of CCSDT-*n*/cc-pVTZ atomization energies with G2 and experimental results. All energies in kilocalorie per mole. QCISD(T)/6-311G(d,p), ΔBasis(G2), ΔCorr(G2) energy differences were taken from G2 calculations [42], where ΔBasis(G2) and ΔCorr(G2) are the estimated increments for the atomization energies that have to be included into the G2 atomization energy because of basis set extension to a 6-311 + G(2df,p) basis set and because of higher-order electron correlation effects. For CCSDT higher-order correlation effects are based on increments of −7.4 mhartree for an electron pair and −0.28 mhartree for a single electron. G(CCSDT) corresponds to a CCSDT-based G2 value. Δ(G2) and Δ[G(CCSDT)] are the deviations from experimental atomization enthalpies (see Ref. [32]) corrected to energies (without zero-point-energy correction), where in the case of G[CCSDT] experimental values were complemented by G2 results (numbers in *parentheses*)

Molecule	QCISD(T)/ 6-311G(d,p)	ΔBasis(G2)	ΔCorr(G2)	CCSDT/ cc-pVTZ	ΔCorr (CCSDT)	G2	G (CCSDT)	Δ(G2)	Δ [G(CCSDT)]	Expt.
$CH_2(^1A_1)$	168.4	7.9	5.8	176.5	8.7	182.1	185.0	1.4	2.9	180.7
$CH_2(^3B_1)$	181.0	5.1	2.9	186.7	4.3	189.0	190.9	−1.0	1.9	190.0
$CN(^2\Sigma^+)$	160.6	12.1	5.8	170.6	8.7	178.6	179.1	−2.8	−2.3	181.3
$HCN(^1\Sigma)$	290.5	13.8	8.7	300.5	13.0	313.0	313.2	2.4	2.6	310.6
$HNC(^1\Sigma)$	275.1	14.3	8.7	285.8	13.0	298.1	298.5		0.4	(298.1)
$CO(^1\Sigma^+)$	246.5	8.8	5.8	251.1	8.7	261.1	259.6	1.8	0.3	259.3
$N_2(^1\Sigma_g^+)$	205.4	13.2	8.7	215.6	13.0	227.4	228.3	−1.1	−0.2	228.5
$NO(^2\Pi_r)$	135.2	12.4	5.8	143.0	8.7	153.4	151.5	0.6	−1.3	152.8
$HNO(^1A')$	183.0	15.2	8.7	194.1	13.0	206.9	206.8		−0.1	(206.9)
$O_2(^3\Sigma_g^-)$	105.9	9.3	2.9	113.2	4.3	118.1	117.4	−2.1	−2.8	120.3
$FH(^1\Sigma^+)$	130.4	8.5	2.9	136.8	4.3	141.9	141.0	2.4	1.6	139.5
$HOF(^1A')$	138.9	13.8	5.8	150.4	8.7	158.4	158.9		0.4	(158.4)
$F_2(^1\Sigma_g^+)$	26.8	8.5	2.9	34.5	4.3	38.2	38.7	−0.1	0.5	38.2
Mean absolute deviation	16.7			8.0				1.6	1.3	

Table 8. $\langle \hat{S}^2 \rangle$ values for some radicals and biradicals calculated at the unrestricted Hartree–Fock (*UHF*) and UHF-CCSD levels of theory. For explanation of terms, see text. cc-pVDZ calculations

Molecule	$\langle \hat{S}^2 \rangle_{UHF}$	$\langle \hat{S}^2 \rangle^{I}_{CCSD}$	$\langle S^2 \rangle^{I+III}_{CCSD}$	$\langle S^2 \rangle^{total}_{CCSD}$
$CH_2(^3B_1)$	2.0158	2.0007	2.0000	2.0003
$CN(^2\Sigma^+)$	1.1505	0.7872	0.7481	0.7532
$NO(^2\Pi_r)$	0.7957	0.7534	0.7500	0.7505
$O_2(^3\Sigma_g^-)$	2.0330	2.0007	2.0000	2.0005

Mean absolute deviations of calculated CCSDT-*n* atomization energies from the corresponding experimental values (obtained from experimental heats of formation [32] corrected to energies with the help of either calculated or measured vibrational frequencies) or atomization energies from G2 calculations [42] show such a small variation (7.3–8 kcal/mol, Table 6) that CCSDT-1a calculations turn out to be sufficient. Actually, atomization energies calculated with the less costly CCSD(T) method agree even better with CCSDT values although both differ from experimental or G2 values by 8 kcal/mol.

Table 7 provides data which show that actually the starting point of the G2 calculations given by QCISD(T)/6-311G(d,p) leads to a mean absolute deviation twice as large as that calculated at the CCSDT level. The success of G2 in reproducing experimental values [42] is accomplished by estimating basis set and higher-order electron correlation corrections as large as 24 kcal/mol in a systematic way. Since the cc-pVTZ basis set actually used in this work is of comparable size as the basis modeled in G2 with the help of correction increments, we can refrain from such an incremental procedure. As for higher-order electron correlation effects, a pair correction of −7.4 mhartree and a single electron correction of −0.28 mhartree (G2: −5 and −0.19 mhartree [42]) lead to the G2-type but CCSDT-based [abbreviated as G(CCSDT)] atomization energies of Table 7, which agree slightly better with experiment than G2 values.[1]

Noteworthy are the relatively large errors in the calculated atomization energies for the *CN* radical (Table 7), which are parallel to the large variations in the CCSDT-*n* correlation energies calculated for this dublet radical (Figure 9, see, e.g., CCSDT-3 contributions). As indicated by the calculated $\langle \hat{S}^2 \rangle$ values listed in Table 8, the UHF-CCSD description of the *CN* radical suffers from considerable spin contamination. Actually, UHF-CCSD and UHF-CCSDT are free from any S + 1 contamination so that spin contamination at these levels of theory is a result of S + 2 and higher contaminants [44]. The degree of spin contamination can be assessed by calculating the energy-related part of $\langle \hat{S}^2 \rangle_{CCSD}$ denoted in Table 8 as $\langle \hat{S}^2 \rangle^{I+III}_{CCSD}$ (note that $\langle \hat{S}^2 \rangle_{CCSD}$ itself is misleading in this respect [44]). In the case of the *CN* radical, $\langle \hat{S}^2 \rangle^{I+III}_{CCSD}$ (= 0.7481) deviates significantly from the ideal value of 0.75 confirming spin-contamination by S + 2 and higher contaminants at the UHF-CCSD and the UHF-CCSDT-*n* levels of theory.

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[1] The higher-order correlation corrections must be (in absolute terms) larger for CCSDT than for QCISD(T) because the latter method does not contain important (positive) coupling corrections in the energy and, therefore, QCISD(T) energies become more negative, for example, than CCSD(T) energies. Also, the G2-extrapolation procedure of basis set effects turns out to exaggerate energy-lowering relative to energies actually calculated with the basis set modeled

4 Conclusions

The following conclusions can be drawn from this work.

1. CCSDT-1 is the most important step on the way from CCSD to CCSDT. About 75% of the extra energy contributions contained in CCSDT are brought in at this level, of which up to 30% are just partial contributions. The major advantage of CCSDT-1 is that it covers much better than CCSD triple excitation effects; however, since CCSDT-1 contains only a few additional TT coupling terms at higher orders (Table 2) there exists the danger that the method exaggerates T effects.
2. CCSDT-2 and CCSDT-3 contain the same number of energy contributions as CCSDT-1 does; however, some of these contributions are fully contained in CCSDT-2,3, while they are only partially contained in CCSDT-1. With regard to TQ and TT coupling CCSDT-2,3 should be somewhat better than CCSDT-1, but apart from this CCSDT-2,3 are not methods that represent a major step in the direction of CCSDT.
3. At the CCSDT-4 level, CCSDT quality is reached with regard to the total number of energy contributions. Despite the fact that some of these energy contributions are just partially contained in CCSDT-4, one can expect that this method already provides a balanced description of T effects, thus avoiding their exaggeration.
4. Since CCSDT-4 is as expensive as CCSDT, it is difficult to see any reason to perform CCSDT-4 rather than CCSDT calculations. Therefore, our analysis suggests that the most interesting CCSDT-*n* method is CCSDT-1 since it already contains a considerable amount of T effects while still being an $O(M^7)$ method.
5. CCSD(T) should provide a better cost-performance ratio than CCSDT-1. Up to fifth order CCSD(T) is identical with CCSDT-1a and at higher orders it fully and partially contains 87% ($n = 6$), 80% ($n = 7$), and 72% ($n = 8$) of the CCSDT-1 terms. Since it includes fewer T terms but the same number of TT coupling terms as CCSDT-1 [26], it will probably avoid exaggeration of T effects better than CCSDT-1.
6. There is no reliable procedure of predicting the CCSDT energy from calculated CCSDT-*n* energies because of the alternating signs of the correlation contributions added at the various levels. One could overcome this problem if a general CCSDT-*n* spectrum existed for each basis set used; however, the CCSDT-*n* spectra calculated in this work indicate that there is considerable variation in the spectra obtained for individual molecules.
7. The CCSDT-*n* methods provide an excellent basis for investigating the stepwise inclusion of connected T excitations in CC theory. CCSD methods with the most important T effects, either CCSDT-1 or CCSD(T), provide a reliable procedure for predicting atomization energies with the help of an incremental G2-type approach as was already exploited by some other authors [43]. For practical applications, use of CCSD(T) or the complete set of T excitations at CCSDT is preferable.

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