

Analysis of coupled cluster methods. II. What is the best way to account for triple excitations in coupled cluster theory?

Zhi He and Dieter Cremer

Theoretical Chemistry, University of Göteborg, Kemigården 3, S-41296 Göteborg, Sweden

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Summary. Various coupled cluster (CC) and quadratic CI (QCI) methods are compared in terms of sixth, seventh, eighth, and infinite order Møller–Plesset (MP_n , $n = 6, 7, 8, \infty$) perturbation theory. By partitioning the MP_n correlation energy into contributions resulting from combinations of single (S), double (D), triple (T), quadruple (Q), pentuple (P), hextuple (H), etc. excitations, it has been determined how many and which of these contributions are covered by CCSD, QCISD, CCSD(T), QCISD(T), CCSD(TQ), QCISD(TQ), and CCSDT. The analysis shows that QCISD is inferior to CCSD because of three reasons: a) With regard to the total number of energy contributions QCI rapidly falls behind CC for large n . b) Part of the contributions resulting from T, P, and higher odd excitations are delayed by one order of perturbation theory. c) Another part of the T, P, etc. contributions is missing altogether. The consequence of reason a) is that QCISD(T) covers less infinite order effects than CCSD does, and QCISD(TQ) less than CCSD(T), which means that the higher investment on the QCI side (QCISD(T): $O(M^7)$, CCSD: $O(M^6)$, QCISD(TQ): $O(M^8)$, CCSD(T): $O(M^7)$, M : number of basis functions) does not compensate for its basic deficiencies. Another deficiency of QCISD(T) is that it does not include a sufficiently large number of TT coupling terms to prevent an exaggeration of T effects in those cases where T correlation effects are important. The best T method in terms of costs and efficiency should be CCSD(T).

Key words: Coupled cluster methods – Perturbation analysis

1 Introduction

Coupled cluster (CC) theory [1–3] provides one of the most powerful ways to account for electron correlation. First, CC theory leads to a well-defined hierarchy of methods which become the more accurate the more excitations are included, for example double excitations (D) in CCD [4], single (S) and D excitations in CCSD [5], S, D, and triple (T) excitations in CCSDT [6], etc. Secondly, all CC methods are size-extensive (size-consistent) [7]. Finally, CC methods cover because of the exponential ansatz finite order effects of those excitations included in the approach.

Compared to these advantages, it is of minor consequence that CC methods are not variational. In practice, one is interested in relative rather than absolute energies and, accordingly, it only matters whether calculated energies are size-extensive. More serious is the fact that CC methods are rather expensive. CCSD scales with $N_{iter}M^6$ and CCSDT with $N_{iter}M^8$, where N_{iter} denotes the number of iteration steps to calculate CC amplitudes and M gives the number of basis functions. With the computer hardware nowadays available it is possible to do routine calculations as long as the method used scales with M^6 or M^7 . However, any method that requires $O(M^8)$ or even $O(M^9)$ can only be applied in selective cases for rather small molecules. These limitations have led to some kind of a dilemma in CC theory since it is very well-known that T excitations have to be included for the correct description of many molecules [8]. To solve this dilemma one of the major goals in CC theory is to find ways for a more economic assessment of T effects.

During the last years essentially three different approximations have been suggested to account for correlation effects resulting from T excitations.

(1) The CCSDT problem is facilitated by simplifying T amplitudes (and sometimes also D amplitudes) of the CCSDT wave function. This leads to the CCSDT- n methods ($n = 1, 2, 3$) suggested by Bartlett and co-workers [9], which scale with $N_{iter}M^7$.

(2) The T effects are calculated in one step by a perturbational approximation using, for example, the amplitudes of a CCSD wave function. This leads to CCSD(T) [10] and related methods [11], which all scale with M^7 .

(3) Yet another research is to use an approximation to the CC ansatz itself and, then, to use either approximation 1 or 2. A method suggested along these lines is the quadratic CI approach by Pople and co-workers [12]. QCISD(T), for example, scales also with M^7 but uses about 20% less computer time than CCSD(T).

Nowadays, one can choose between more than a dozen different methods that handle T excitations according to one of the three approximations. From the available calculational results it is difficult, probably impossible to say which of these methods is the best in terms of computational requirements and obtained accuracy. Many additional calculations will be needed to answer this question, where, of course, in the end the majority of these test calculations will turn out to be superfluous. Since this is not satisfactory, a more theoretical approach is needed to predict which of the suggested T methods should be preferentially used on the basis of the two criteria discussed above.

In a recent publication (henceforth, called paper I), we have begun a comparative investigation of various CC methods described in the literature [13]. Our work was triggered by the fact that the assessment of T correlation effects by QCISD(T) was unsatisfactory and, therefore, many additional calculations became necessary [14, 15]. The basis of our comparison was the expansion of various CC methods in terms of perturbation theory. For this purpose, we worked out the formulas for 6th order Møller–Plesset (MP6) perturbation theory and determined algebraically which terms of MP_n ($n = 2, 3, 4, 5, 6$) were covered by a given method. In addition, we extended this analysis to higher orders of MP_n by graphical means to analyze infinite order effects. One important result of this work was the observation that CCSD covered contrary to QCISD a considerable number of higher order T effects. QCISD(T) compensates

for this deficiency of QCISD, but the question remains whether this compensation is sufficient.

In this work, we present the second part of our MP_n analysis of CC and approximated CC methods concentrating on the question, in which way T correlation effects are best accounted for. We will do this by first expanding CCSD in terms of MP_n perturbation theory, thereby briefly reviewing the results of the first part of this work (Sect. 2). Then, we will present a detailed analysis of CCSD and QCISD concentrating on the differences between these methods (Sect. 3). In the last section, we will investigate whether a noniterative improvement of QCISD and CCSD by T and TQ correlation effects leads to a reduction of the differences between QCI and CC. In this way, we will be able to answer the question posed in the title of this work.

2 Expansion of CCSD to sixth-order perturbation theory

In CC theory, the Schrödinger equation is written as:

$$\bar{H}|\Psi\rangle = \bar{H}e^T|\Phi_0\rangle = E_{corr}e^T|\Phi_0\rangle \quad (1)$$

where Ψ denotes the true wavefunction and Φ_0 is a reference wavefunction, for example the Hartree–Fock (HF) wavefunction. \bar{H} denotes the “normal product” form of the Hamiltonian, which is split into a zero-order operator \hat{H}_0 and a perturbation operator \hat{V} according to standard Møller–Plesset (MP) perturbation theory [16].

$$\bar{H} = \hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle = \hat{H} - E(HF) \quad (2)$$

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \quad (3)$$

$$\hat{H}_0 = \sum_p \hat{F}_p = \sum_p (\hat{h}_p + \hat{g}_p) \quad (4)$$

$$\hat{V} = \sum_{p,q} r_{pq}^{-1} - \sum_p \hat{g}_p \quad (5)$$

with λ being a perturbation parameter and \hat{F} , \hat{h} , and \hat{g} having the usual meaning of Fock, core hamiltonian, and HF electron interaction operator.

In second quantization language, these operators can be expressed in the following way:

$$\begin{aligned} \hat{H}_0 &= \sum_{r,s} \hat{b}_r^+ \hat{b}_s \langle r|\hat{F}|s\rangle \\ &= \sum_i \langle i|\hat{F}|i\rangle + \sum_{r,s} \{\hat{b}_r^+ \hat{b}_s\} \langle r|\hat{F}|s\rangle, \end{aligned} \quad (6)$$

$$\begin{aligned} \bar{H}_0 &= \hat{H}_0 - \sum_i \langle i|\hat{F}|i\rangle \\ &= \sum_{r,s} \{\hat{b}_r^+ \hat{b}_s\} \langle r|\hat{F}|s\rangle, \end{aligned} \quad (7)$$

$$\begin{aligned} \hat{V} &= \frac{1}{4} \sum_{r,s,t,u} \hat{b}_r^+ \hat{b}_s^+ \hat{b}_t \hat{b}_u \langle rs||tu\rangle \\ &= \frac{1}{4} \sum_{r,s,t,u} \{\hat{b}_r^+ \hat{b}_s^+ \hat{b}_t \hat{b}_u\} \langle rs||tu\rangle + \frac{1}{2} \sum_{ij} \langle ij||ij\rangle, \end{aligned} \quad (8)$$

$$\begin{aligned}\bar{V} &= \hat{V} - \frac{1}{2} \sum_{ij} \langle ij || ij \rangle \\ &= \frac{1}{4} \sum_{r,s,t,u} \{ \hat{b}_r^+ \hat{b}_s^+ \hat{b}_t \hat{b}_u \} \langle rs || tu \rangle.\end{aligned}\quad (9)$$

In Eqs. (6) to (9), \hat{b}^+ and \hat{b} denote creation and annihilation operators. The $\{ \}$ sign indicates a normal-order product relative to the starting HF determinant $|\Phi_0\rangle$. Here and in the following, we use subscripts i, j, k, l to denote occupied spin orbitals, a, b, c, d to denote virtual spin orbitals, and r, s, t, u to denote general spin orbitals. Equations (7) and (9) lead to:

$$\bar{H} = \bar{H}_0 + \lambda \bar{V} = \sum_{r,s} \{ \hat{b}_r^+ \hat{b}_s \} \langle r | \hat{F} | s \rangle + \frac{1}{4} \lambda \sum_{r,s,t,u} \{ \hat{b}_r^+ \hat{b}_s^+ \hat{b}_t \hat{b}_u \} \langle rs || tu \rangle. \quad (10)$$

The cluster operator \hat{T} is given by:

$$\hat{T} = \sum_n \hat{T}_n \quad (11a)$$

$$\hat{T}_n = \frac{1}{(n!)^2} \sum a_{ijk\dots}^{abc\dots} \hat{b}_a^+ \hat{b}_i \hat{b}_b^+ \hat{b}_j \hat{b}_c^+ \hat{b}_k \dots, \quad (11b)$$

with $a_{ijk\dots}^{abc\dots}$ denoting cluster amplitudes. Multiplying both sides of Eq. (1) by e^{-T} , yields:

$$\begin{aligned}(\bar{H} e^{\hat{T}})_c |\Phi_0\rangle &= (\bar{H} + [\bar{H}, \hat{T}] + \frac{1}{2} [[\bar{H}, \hat{T}], \hat{T}] + \dots) |\Phi_0\rangle \\ &= E_{corr} |\Phi_0\rangle\end{aligned}\quad (12)$$

by virtue of the fact that:

$$e^{-\hat{T}} \bar{H} e^{\hat{T}} = (\bar{H} e^{\hat{T}})_c \quad (13)$$

where subscript c indicates limitation to connected diagrams. Now it is easy to obtain usual CC projection equations:

$$\langle \Phi_0 | (\bar{H} e^{\hat{T}})_c |\Phi_0\rangle = E_{corr} \quad (14a)$$

$$\langle \Phi_{ij\dots}^{ab\dots} | (\bar{H} e^{\hat{T}})_c |\Phi_0\rangle = 0 \quad (14b)$$

with $\langle \Phi_{ij\dots}^{ab\dots} |$ being a set of singly, doubly, ... excited determinants.

For simplification we restrict our discussion to the CCSD approach, i.e. $\hat{T} = \hat{T}_1 + \hat{T}_2$:

$$\langle \Phi_0 | [\bar{H} \exp(\hat{T}_1 + \hat{T}_2)]_c |\Phi_0\rangle = E_{corr}^{CCSD} \quad (15a)$$

$$\langle \Phi_i^a | [\bar{H} \exp(\hat{T}_1 + \hat{T}_2)]_c |\Phi_0\rangle = 0 \quad (15b)$$

$$\langle \Phi_{ij}^{ab} | [\bar{H} \exp(\hat{T}_1 + \hat{T}_2)]_c |\Phi_0\rangle = 0 \quad (15c)$$

The energy E_{corr}^{CCSD} and the cluster operators \hat{T}_1, \hat{T}_2 in Eqs. (15) can be expanded in terms of the perturbation parameter λ :

$$E_{corr}^{CCSD} = \lambda^2 E_{corr}^{CCSD}(2) + \lambda^3 E_{corr}^{CCSD}(3) + \lambda^4 E_{corr}^{CCSD}(4) + \dots \quad (16)$$

$$\hat{T}_1 = \lambda^2 \hat{T}_1^{(2)} + \lambda^3 \hat{T}_1^{(3)} + \lambda^4 \hat{T}_1^{(4)} + \dots \quad (17a)$$

$$\hat{T}_2 = \lambda \hat{T}_2^{(1)} + \lambda^2 \hat{T}_2^{(2)} + \lambda^3 \hat{T}_2^{(3)} + \lambda^4 \hat{T}_2^{(4)} + \dots \quad (17b)$$

where the fact has been used that the HF reference energy is correct up to second order and $\hat{T}_1^{(1)} = 0$ because of the Brillouin theorem. By inserting Eqs. (16) and

(17) into the CCSD equations (15), we can immediately expand E_{corr}^{CCSD} up to sixth-order:

$$E_{corr}^{CCSD}(m) = \langle \Phi_0 | \bar{V} \hat{T}_2^{(m-1)} | \Phi_0 \rangle_c \quad (m = 2, 3, 4) \quad (18)$$

$$E_{corr}^{CCSD}(5) = \langle \Phi_0 | \bar{V} (\hat{T}_2^{(4)} + \hat{T}_1^{(2)} \hat{T}_1^{(2)}/2) | \Phi_0 \rangle_c \quad (19)$$

$$E_{corr}^{CCSD}(6) = \langle \Phi_0 | \bar{V} (\hat{T}_2^{(5)} + \hat{T}_1^{(2)} \hat{T}_1^{(3)}) | \Phi_0 \rangle_c \quad (20)$$

where, in the Hartree–Fock case, the operators $\hat{T}_i^{(n)}$ ($i = 1, 2$) are of the following form:

$$\langle \Phi_{ij}^{ab} | [\bar{H}_0 \hat{T}_2^{(1)} + \bar{V}]_c | \Phi_0 \rangle = 0 \quad (21)$$

$$\langle \Phi_i^a | [\bar{H}_0 \hat{T}_1^{(2)} + \bar{V} \hat{T}_2^{(1)}]_c | \Phi_0 \rangle = 0 \quad (22a)$$

$$\langle \Phi_{ij}^{ab} | [\bar{H}_0 \hat{T}_2^{(2)} + \bar{V} \hat{T}_2^{(1)}]_c | \Phi_0 \rangle = 0 \quad (22b)$$

$$\langle \Phi_i^a | [\bar{H}_0 \hat{T}_1^{(3)} + \bar{V} (\hat{T}_1^{(2)} + \hat{T}_2^{(2)})]_c | \Phi_0 \rangle = 0 \quad (23a)$$

$$\langle \Phi_{ij}^{ab} | [\bar{H}_0 \hat{T}_2^{(3)} + \bar{V} (\hat{T}_1^{(2)} + \hat{T}_2^{(2)} + \hat{T}_2^{(1)} \hat{T}_2^{(1)}/2)]_c | \Phi_0 \rangle = 0 \quad (23b)$$

$$\langle \Phi_i^a | [\bar{H}_0 \hat{T}_1^{(4)} + \bar{V} (\hat{T}_1^{(3)} + \hat{T}_2^{(3)} + \hat{T}_1^{(2)} \hat{T}_2^{(1)})]_c | \Phi_0 \rangle = 0 \quad (24a)$$

$$\langle \Phi_{ij}^{ab} | [\bar{H}_0 \hat{T}_2^{(4)} + \bar{V} (\hat{T}_1^{(3)} + \hat{T}_2^{(3)} + \hat{T}_1^{(2)} \hat{T}_2^{(1)} + \hat{T}_2^{(1)} \hat{T}_2^{(2)})]_c | \Phi_0 \rangle = 0 \quad (24b)$$

$$\begin{aligned} \langle \Phi_{ij}^{ab} | [\bar{H}_0 \hat{T}_2^{(5)} + \bar{V} (\hat{T}_1^{(4)} + \hat{T}_2^{(4)} + \hat{T}_1^{(2)} \hat{T}_2^{(2)} + \hat{T}_1^{(3)} \hat{T}_2^{(1)} \\ + \hat{T}_2^{(1)} \hat{T}_2^{(3)} + \hat{T}_2^{(2)} \hat{T}_2^{(2)}/2 + \hat{T}_1^{(2)} \hat{T}_1^{(2)}/2)]_c | \Phi_0 \rangle = 0 \end{aligned} \quad (25)$$

Using Eqs. (21) to (25), amplitudes $a_u^{(n)}$ can be derived:

$$a_d^{(1)} = (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} | \Phi_0 \rangle \quad (26)$$

$$a_s^{(2)} = (E_0 - E_s)^{-1} \sum_d^D \langle \Phi_s | \bar{V} | \Phi_d \rangle a_d^{(1)} \quad (27a)$$

$$a_d^{(2)} = (E_0 - E_d)^{-1} \sum_{d_1}^D \langle \Phi_d | \bar{V} | \Phi_{d_1} \rangle a_{d_1}^{(1)} \quad (27b)$$

$$a_s^{(3)} = (E_0 - E_s)^{-1} \sum_u^{S,D} \langle \Phi_s | \bar{V} | \Phi_u \rangle a_u^{(2)} \quad (28)$$

$$a_d^{(3)} = (E_0 - E_d)^{-1} \left[\sum_u^{S,D} \langle \Phi_d | \bar{V} | \Phi_u \rangle a_u^{(2)} + \sum_{d_1 d_2}^D (\langle \Phi_d | \bar{V} | \frac{1}{2} \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 \rangle a_{d_1}^{(1)} a_{d_2}^{(1)})_c \right] \quad (29)$$

$$a_s^{(4)} = (E_0 - E_s)^{-1} \left[\sum_u^{S,D} \langle \Phi_s | \bar{V} | \Phi_u \rangle a_u^{(3)} + \sum_{s_1}^S \sum_d^D (\langle \Phi_s | \bar{V} | \hat{t}_{s_1} \hat{t}_d \Phi_0 \rangle a_{s_1}^{(2)} a_d^{(1)})_c \right] \quad (30)$$

$$\begin{aligned} a_d^{(4)} = (E_0 - E_d)^{-1} \left[\sum_u^{S,D} \langle \Phi_d | \bar{V} | \Phi_u \rangle a_u^{(3)} + \sum_s^S \sum_{d_1}^D (\langle \Phi_d | \bar{V} | \hat{t}_s \hat{t}_{d_1} \Phi_0 \rangle a_s^{(2)} a_{d_1}^{(1)})_c \right. \\ \left. + \sum_{d_1 d_2}^D (\langle \Phi_d | \bar{V} | \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 \rangle a_{d_1}^{(1)} a_{d_2}^{(1)})_c \right] \quad (31) \end{aligned}$$

$$\begin{aligned}
a_d^{(5)} = & (E_0 - E_d)^{-1} \left\{ \sum_u^{S,D} \langle \Phi_d | \bar{V} | \Phi_u \rangle a_u^{(4)} + \sum_s^S \sum_{d_1}^D [\langle \Phi_d | \bar{V} | \hat{t}_s \hat{t}_{d_1} \Phi_0 \rangle (a_s^{(2)} a_{d_1}^{(2)} + a_s^{(3)} a_{d_1}^{(1)})]_c \right. \\
& + \sum_{d_1 d_2}^D [\langle \Phi_d | \bar{V} | \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 \rangle (a_{d_1}^{(1)} a_{d_2}^{(3)} + \frac{1}{2} a_{d_1}^{(2)} a_{d_2}^{(2)})]_c \\
& \left. + \sum_{s_1 s_2}^S (\langle \Phi_d | \bar{V} | \frac{1}{2} \hat{t}_{s_1} \hat{t}_{s_2} \Phi_0 \rangle a_{s_1}^{(2)} a_{s_2}^{(2)})_c \right\} \quad (32)
\end{aligned}$$

In these equations $a_s^{(n)}$, $a_d^{(n)}$, etc. denote singles, doubles, etc. amplitudes at n th order. Operators \hat{t} are excitation operators.

It is obvious that in second- or third-order the energy $E_{corr}^{CCSD}(m)$ given by Eq. (18) ($m = 2$ or 3) leads to the MP2 or MP3 energy by means of Eq. (21) or (22b). Moreover, in fourth-order $E_{corr}^{CCSD}(4)$ (Eq. (18)), which requires the third-order D amplitudes $\hat{T}_2^{(3)}$ determined from Eq. (23b), may conveniently be partitioned as shown in Eq. (33):

$$E_{corr}^{CCSD}(4) = E_S^{(4)} + E_D^{(4)} + E_Q^{(4)} \quad (33)$$

Here, the three parts arise from contributions due to $S(\hat{T}_1^{(2)})$, $D(\hat{T}_2^{(2)})$ and Q excitations ($\frac{1}{2} \hat{T}_2^{(1)} \hat{T}_2^{(1)}$).

Analogously, $E_{corr}^{CCSD}(5)$ is obtained by inserting the expressions for $\hat{T}_2^{(4)}$ and $\hat{T}_1^{(2)}$ (Eqs. (24b) and (22a)) into Eq. (19). By means of the factorization theorem [17], the energy $E_{corr}^{CCSD}(5)$ can be readily split into [18]:

$$\begin{aligned}
E_{corr}^{CCSD}(5) = & E_{SS}^{(5)} + E_{SD}^{(5)} + E_{DS}^{(5)} + E_{DD}^{(5)} + E_{DQ}^{(5)} + E_{QD}^{(5)} + E_{QQ}^{(5)}(I) \\
& + E_{TS}^{(5)} + E_{TQ}^{(5)}(I). \quad (34)
\end{aligned}$$

where (I) denotes those terms that are only partially contained.

It is easy to see that the first two terms of Eq. (34) result from the contribution of $T_1^{(3)}$ (Eq. (23a)) to the expression of $T_2^{(4)}$ (Eq. (24b)), while $E_{DS}^{(5)}$, $E_{DD}^{(5)}$ and $E_{DQ}^{(5)}$ stem from $T_2^{(3)}$ (Eq. (23b)). The next two terms in Eq. (34), i.e. $E_{QD}^{(5)}$ and $E_{QQ}^{(5)}(I)$ are due to the $\hat{T}_2^{(1)} \hat{T}_2^{(2)}$ part of $\hat{T}_2^{(4)}$. This becomes obvious by inserting the corresponding amplitudes and using the factorization theorem as shown in Eqs. (35) to (37):

$$\begin{aligned}
E_{corr}^Q(5) = & \sum_d^D \langle \Phi_0 | \bar{V} | \hat{T}_2^{(4)} \Phi_0 \rangle_c \\
= & \sum_d^D \langle \Phi_0 | \bar{V} | \hat{t}_d^{(4)} \Phi_0 \rangle_c a_d^{(4)} \quad (35)
\end{aligned}$$

$$\begin{aligned}
E_{corr}^Q(5) = & \sum_d^D \langle \Phi_0 | \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} | \hat{T}_2^{(1)} \hat{T}_2^{(2)} \Phi_0 \rangle_c \\
= & \sum_{dd_1 d_2}^D \langle \Phi_0 | \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} | \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 \rangle_c a_{d_1}^{(1)} a_{d_2}^{(2)} \quad (36)
\end{aligned}$$

$$\begin{aligned}
a_{d_1}^{(1)} a_{d_2}^{(2)} = & (E_0 - E_{d_1})^{-1} \langle \Phi_{d_1} | \bar{V} | \Phi_0 \rangle (E_0 - E_{d_2})^{-1} \\
& \times \sum_{d_3}^D \langle \Phi_{d_2} | \bar{V} | \Phi_{d_3} \rangle (E_0 - E_{d_3})^{-1} \langle \Phi_{d_3} | \bar{V} | \Phi_0 \rangle
\end{aligned}$$

$$\begin{aligned}
&= (E_0 - E_{d_1} + E_0 - E_{d_2})^{-1} \left[\langle \Phi_{d_1} | \bar{V} | \Phi_0 \rangle (E_0 - E_{d_2})^{-1} \right. \\
&\quad \times \sum_{d_3}^D \langle \Phi_{d_2} | \bar{V} | \Phi_{d_3} \rangle (E_0 - E_{d_3})^{-1} \langle \Phi_{d_3} | V | \Phi_0 \rangle \\
&\quad \left. + \sum_{d_3}^D \langle \Phi_{d_2} | \bar{V} | \Phi_{d_3} \rangle (E_0 - E_{d_3})^{-1} \langle \Phi_{d_3} | V | \Phi_0 \rangle (E_0 - E_{d_1})^{-1} \langle \Phi_{d_1} | V | \Phi_0 \rangle \right] \\
&\hspace{20em} (37a)
\end{aligned}$$

$$\begin{aligned}
&= (E_0 - E_{d_1} + E_0 - E_{d_2})^{-1} \left[\langle \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 | \bar{V} | \hat{t}_{d_2} \Phi_0 \rangle (E_0 - E_{d_2})^{-1} \right. \\
&\quad \times \sum_{d_3}^D \langle \Phi_{d_2} | \bar{V} | \Phi_{d_3} \rangle (E_0 - E_{d_3})^{-1} \langle \Phi_{d_3} | V | \Phi_0 \rangle \\
&\quad \left. + \sum_{d_3}^D \langle \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 | \bar{V} | \hat{t}_{d_3} \hat{t}_{d_1} \Phi_0 \rangle a_{d_1}^{(1)} a_{d_3}^{(1)} \right] \\
&\hspace{20em} (37b)
\end{aligned}$$

From Eq. (37b) it becomes immediately obvious that $E_{corr}^Q(5)$ covers the QD and the QQ contribution of MP5 where the latter term is only partially contained since summations in Eq. (37) run only over d_1 , d_2 , and d_3 rather than d_1 , d_2 , d_3 , and d_4 . In a similar way, one can show that $\hat{T}_1^{(2)} \hat{T}_1^{(1)}$ in Eq. (24b) and $\hat{T}_1^{(2)} \hat{T}_1^{(2)}/2$ in Eq. (19) lead to the two remaining terms of Eq. (34), $E_{TS}^{(5)}$ and $E_{TQ}^{(5)}(I)$.

In order to derive a similar formula for $E_{corr}^{CCSD}(6)$ (Eq. (20)) as for $E_{corr}^{CCSD}(5)$ (Eq. (19)) the operators $T_2^{(5)}$ and $T_1^{(2)} T_1^{(3)}$ have to be expressed with the aid of Eqs. (25), (22a), and (23a), respectively. A procedure similar to the one described above leads to the final form of $E_{corr}^{CCSD}(6)$:

$$\begin{aligned}
E_{corr}^{CCSD}(6) &= E_{SSS}^{(6)} + 2E_{SSD}^{(6)} + E_{SDS}^{(6)} + 2E_{DD}^{(6)} + 2E_{SDQ}^{(6)} + E_{STS}^{(6)} \\
&\quad + E_{STQ}^{(6)}(I) + E_{QTS}^{(6)}(I) + E_{DSD}^{(6)} + E_{DDD}^{(6)} + 2E_{DDQ}^{(6)} \\
&\quad + E_{DQD}^{(6)} + E_{DQ}^{(6)}(I) + E_{QQD}^{(6)}(I) + E_{DTS}^{(6)} + E_{DTQ}^{(6)}(I) \\
&\quad + E_{QTQ}^{(6)}(I) + E_{QQQ}^{(6)}(I) + E_{QDQ}^{(6)} + E_{QH}^{(6)}(I) + E_{TSD}^{(6)} \\
&\quad + E_{TQD}^{(6)}(I) + E_{TQ}^{(6)}(I) + E_{TSS}^{(6)} + E_{TTS}^{(6)}(I) + E_{TTQ}^{(6)}(I) \quad (38)
\end{aligned}$$

Equation (38) gives those 6th order MP energy contributions that are fully or partially covered by CCSD. We will use this expression and similar expressions for other CC and QCI methods to compare in the following T correlation effects included by the different methods.

3 Comparison of CCSD and QCISD

It is convenient to write the CCSD projection equations using the cluster operator $T'_2 = T_2 + \frac{1}{2}T_1^2$:

$$\langle \Phi_0 | H | \hat{T}'_2 \Phi_0 \rangle = E_{corr} \quad (39)$$

$$\langle \Phi_i^a | \bar{H} | (\hat{T}_1 + \hat{T}'_2 + \hat{T}_1 \hat{T}'_2 - \frac{1}{3} \hat{T}_1^3) \Phi_0 \rangle_c = 0 \quad (40)$$

$$\langle \Phi_{ij}^{ab} | \bar{H} | (\mathbf{1} + \hat{T}_1 + \hat{T}'_2 + \frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{T}'_2 - \frac{1}{3} \hat{T}_1^3 - \frac{1}{12} \hat{T}_1^4) \Phi_0 \rangle_c = 0 \quad (41)$$

The cluster operators in bold print are also contained in the corresponding QCISD equations [12, 19] while the operators in normal print do not appear in the QCISD projection equations. Obviously, the difference between QCISD and CCSD results from the omission of $T_1 T_2'$ and $-\frac{1}{12} T_1^4$ in the doubles equation and the omission of $-\frac{1}{3} T_1^3$ in both the singles and the doubles equations. Since T_1^3 and T_1^4 contribute in eight and higher order MP perturbation theory (see Table 2 of paper I, Ref. 13), the effect of the missing $T_1 T_2'$ operators in the doubles equation of QCISD plays the dominant role in the difference between the two methods [19]. That part of the energy difference $E_{corr}^{CCSD} - E_{corr}^{QCISD}$, that stems from $T_1 T_2'$ in Eq. (41), can be expanded up to seventh-order in the following way:

$$\sum_{n=2}^7 (E_{corr}^{CCSD}(n) - E_{corr}^{QCISD}(n)) = E_{TS}^{(5)} + E_{TQ}^{(5)}(I) + E_{TSS}^{(6)} + E_{TSD}^{(6)} + E_{DTS}^{(6)} + E_{DTQ}^{(6)}(I) + E_{TTS}^{(6)}(I) + E_{TTQ}^{(6)}(I) + E_{TQD}^{(6)}(I) + E_{TQQ}^{(6)}(I) + \sum E_{ABCD}^{(7)} \quad (42)$$

where $\sum E_{ABCD}^{(7)}$ denotes a sum of 41 terms, which can be derived and illustrated by using graphical methods as we will explain in the following.

In Fig. 1, the various energy contributions at n th order perturbation theory are displayed in form of a diagram [13]. For each order n , energy partitioning is indicated by the term $E_{ABC\dots}^{(n)}$ given on the left side of the diagram where A, B, C, etc. denote the possible excitations and ABC... the coupling between the excitations which can occur at that particular order. At 4th order there is no coupling ($E_A^{(4)}$), at 5th order only simple AB coupling ($E_{AB}^{(5)}$), at 6th order ABC coupling ($E_{ABC}^{(6)}$), etc. A particular energy term $E_{ABC\dots}^{(n)}$ is given by the solid line that starts at A (= S, D, T, Q) in the $E^{(n)}$ row and connects B, C, etc. at $n-1$, $n-2$, etc. until $n=4$ is reached. Hence, each energy term is given by a path of

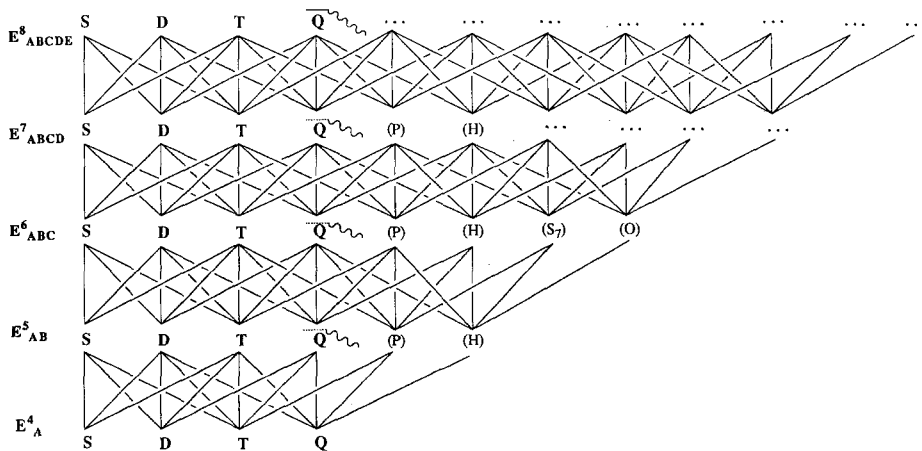


Fig. 1. Graphical representation of energy contributions $E_{ABC\dots}^{(n)}$ at n th order MP perturbation theory ($n = 4, 5, 6, 7, 8$). A particular energy contribution $E_{ABC\dots}^{(n)}$ is given by the solid line that starts at A = S, D, T or Q in the $E^{(n)}$ row and connects B, C, etc. at row $n-1$, $n-2$, etc. until $n=4$ is reached. Note that at the n th order level also those excitations are included that arise from energy terms at higher order levels ($m > n$). They are given in parentheses after a separator (downward directed wiggles) to the right of the S, D, T, Q excitations

solid lines. The paths can extend to the right of the Q column thus coupling pentuple (P), hextuple (H), etc. excitations to T and Q excitations, but coupling has to be done according to Slater rules for matrix elements with the condition that the path returns to the S, D, T, Q set at $n = 4$. At a given level n , excitations (P, H, etc.) that are encountered at higher orders are also included, but they are put into parenthesis and separated by a separator (downward directed wiggles) from S, D, T, Q.

For $E_{AB}^{(5)}$, there are 14 paths corresponding to the 14 energy terms at MP5. Some of them such as $E_{SD}^{(5)}$ and $E_{DS}^{(5)}$ are identical due to symmetry thus reducing the number of unique paths (energy terms) to 9. There are 55 $E_{ABC}^{(6)}$ paths and 221 $E_{ABCD}^{(7)}$ paths, which reduce to 36 and 141, respectively, because of symmetry. It is easy to see that the number of paths increases exponentially, but nevertheless the diagram of Fig. 1 helps to identify all terms at a given order n .

Utilizing a similar graphical representations as the one shown in Fig. 1, the expansion of CC and QCI methods in terms of orders of perturbation theory can easily be visualized. In Fig. 2, the corresponding diagram is shown for CCSD and QCISD. Energy terms that are fully contained in both CCSD and QCISD are denoted by solid bold lines (compare with the bold-face operators in Eqs. (39)–(41)) and those, that are partially contained in both methods, are denoted by hashed lines. Normal solid (dotted) lines indicate that the particular term is fully (partially) contained in CCSD but not in QCISD. The CCSD/QCISD diagram differs from the MP n diagram of Fig. 1 because many terms are only partially contained and/or come in with some delay at a higher order n . To handle these terms and to make the difference between CCSD and QCISD clear,

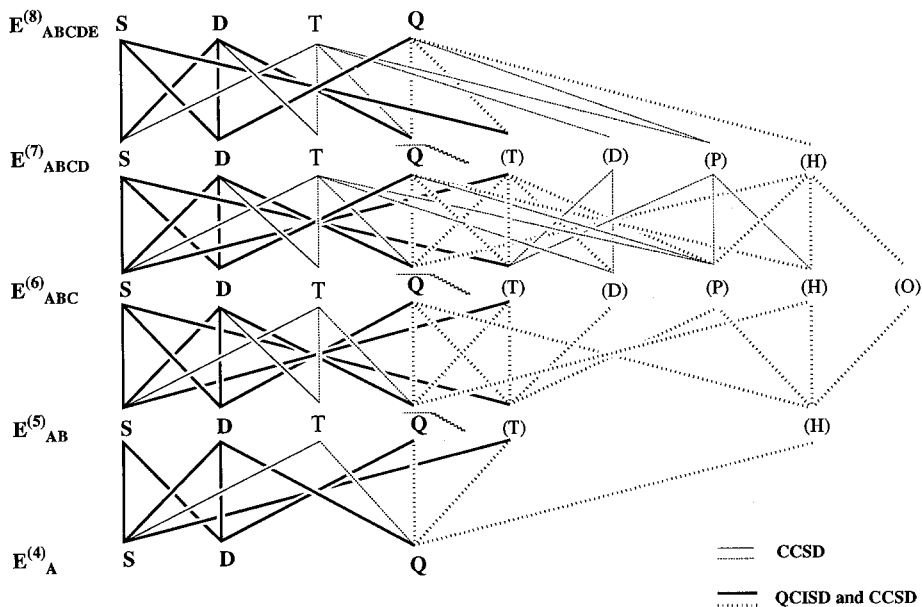


Fig. 2. Graphical analysis of energy contributions at n th order MP perturbation theory ($n = 4, 5, 6, 7, 8$) covered by the CCSD and QCISD correlation energy. See explanations given for Fig. 1. Note that **bold solid** (**hashed**) lines denote energy terms that are fully (partially) contained in both the CCSD and the QCISD correlation energy. Those energy terms, that are only covered by the CCSD energy, are denoted by *normal solid* or *dashed* lines depending on whether they are fully or partially contained. For further explanations see text

excitations have to be given from left to right in a different order than in the MP_n case. Also, some excitations have to reappear to the right of $A = Q$ to clearly distinguish between fully and partially contained energy terms (see, e.g. the TD... terms in Fig. 2). Throughout this and the following diagrams (Figs. 3 and 4) the nature of a particular term (fully or partially) is given by the nature of the path lines. If all lines of the path are solid then the term is fully contained, but if only one connection line within the path is dotted or hashed, then the term is partially contained. The same convention is used when indicating whether a given term is covered by both CC and QCI or just by CC.

Figure 2 shows that both CCSD and QCISD are correct at any order n in the truncated configuration space that is made up from S and D excitations, i.e. within this space all infinite order effects are covered. In addition, the two methods also cover infinite order effects in the truncated SDQ space with the AQQ... and QQ... energy terms being included only partially. This, of course, is trivial since it just reflects the fact that both \hat{T}_1 , \hat{T}'_2 and T''_2 are contained in both the CCSD and QCISD projection equations and, accordingly, all infinite order effects resulting from S, D, and disconnected D excitations have to be found in the graphic representation of Fig. 2. For example, Fig. 2 indicates that both CCSD and QCISD contain all infinite order effects, at least partially, in the SDQH, SDQHO, or any SDQHO...X space where X corresponds to even excitations being generated by $T''_2{}^m$ ($m = 1, 2$). In short QCISD and CCSD are equivalent with regard to infinite order effects in any SDQ...X(even) configuration space.

The main difference between CCSD and QCISD results from the T excitations. CCSD covers (either fully or partially) a considerable number of infinite order T terms that result from the cluster operators $\hat{T}_1\hat{T}'_2$ in the doubles projection equations (Eq. 41). These T contributions build up a TT...T column in the CCSD diagram starting at 5th order and coupling to S, D, and Q. For example, at 5th order CCSD contains the TS term fully and the TQ term partially while these contributions are missing in QCISD. However, closer inspection of Fig. 2 reveals that the QCISD diagram also contains these terms, but they come in at 6th order in form of STS, STQ, QTS and QTQ. The same is true with contributions of the type TT..., TTT..., etc., which come in at sixth, seventh, etc. order at CCSD, but are delayed by just one order at the QCISD level. This is indicated in the diagram of Fig. 2 by the TT...T column to the right of the Q column.

In Fig. 3, the difference between CCSD and QCISD is given in more detail focusing on the contributions that result from the $\hat{T}_1\hat{T}'_2$ operators in the doubles projection equations. The diagrams in Fig. 3 have been derived by expanding $\hat{T}_1\hat{T}'_2$ according to Eqs. (21) and (25). Figure 3a, 3b, 3c, and 3d show, which energy terms are included into the CCSD or QCISD correlation energy at $n = 5, 6, 7$, and 8 because of $\hat{T}_1\hat{T}'_2$. Primarily, these operators lead to (disconnected) T excitations, which then can couple to S, D, T, Q, P excitations. Figure 3 shows that the number of terms resulting from $\hat{T}_1\hat{T}'_2$ increases exponentially (compare with Fig. 3d) and, therefore, the difference between CCSD and QCISD should rapidly increase. However $\hat{T}_1\hat{T}'_2$ is contained in the singles projection equation of QCISD (compare with Eq. (40)), which means that the very same energy terms come into QCISD at order $n + 1$ via coupling with S excitations. Alternatively, these terms can be introduced by $\hat{T}'_2{}^2$ in form of QTS..., QTQ..., etc.

One could argue that despite the differences between CCSD and QCISD at order n , both methods should become equivalent because they should cover the

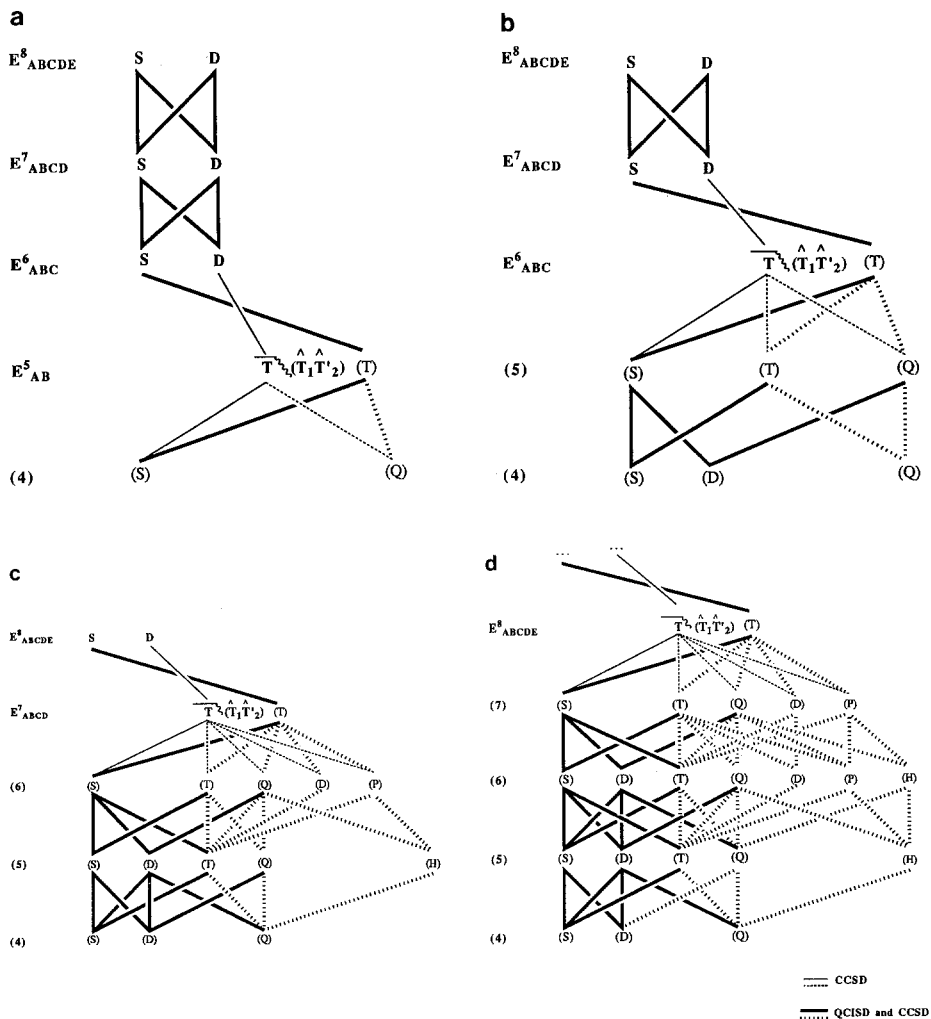


Fig. 3. Graphical analysis of energy contributions at n th order MP perturbation theory ($n = 4, 5, 6, 7, 8$) generated by the cluster operators $\hat{T}_1 \hat{T}_2'$. Note that *bold solid* (*hashed*) lines denote energy terms that are fully (partially) contained in both the CCSD and the QCISD correlation energy. Those energy terms that are only covered by CCSD are denoted by *normal solid* or *dashed lines* depending on whether they are fully or partially contained. (a) Expansion of $\hat{T}_1 \hat{T}_2'$ at $n = 5$. (b) Expansion of $\hat{T}_1 \hat{T}_2'$ at $n = 6$. (c) Expansion of $\hat{T}_1 \hat{T}_2'$ at $n = 7$. (d) Expansion of $\hat{T}_1 \hat{T}_2'$ at $n = 8$

same correlation effects at infinite order. Figure 3 reveals that this is not true. Apart from the fact that the T containing contributions of QCISD are delayed by one order of perturbation theory, QCISD lacks all energy contributions of the type $\dots DT \dots$ that arise from $\hat{T}_1 \hat{T}_2'$ in the CCSD doubles equation (Fig. 3). For example, at sixth order (Fig. 3a) the CCSD terms DTS and DTQ are missing in QCISD and, similarly, all $DT \dots$ terms at $n = 7, 8$, etc. Also, all energy terms that contain the DT part are missing in QCISD. This is the reason why the difference between CCSD and QCISD increases rapidly despite the fact that the basic T terms enter QCISD in form of $ST \dots$ and $QT \dots$ contributions. The neglect of

Table 1. Number of energy contributions covered by CC and QCI methods at n th ($n = 5, 6, 7, 8$) order perturbation theory^a

Method	5	6	7	8
QCISD	7(1)	22(7)	66(31)	221(136)
CCSD	9(2)	30(12)	107(61)	394(276)
QCISD(T)	11(1)	35(7)	110(35)	368(168)
CCSD(T)	12(2)	40(12)	141(65)	513(307)
QCISD(TQ)	14	45(7)	149(40)	502(208)
CCSD(TQ)	14	46(9)	164(57)	597(309)
CCSDT	13(1)	50(9)	195(62)	792(369) ^b
MP n	14	55	221	915

^a For each method, the entry $k(l)$ gives the number k of all terms covered not considering symmetry. Of the k terms l are covered only partially. Note that the k values of MP n denote the maximum number of energy terms at order n .

^b This $k(l)$ entry has been misprinted in paper I [13]

$\hat{T}_1 \hat{T}'_2$ in the QCISD doubles equation has two effects: a) Part of the T contributions is missing; b) another part is delayed by one order of perturbation theory.

Pentuple effects in form of P..., PP... etc. terms are covered by CCSD at $n = 7, n = 8$, etc. while QCISD covers them at the corresponding $n + 1$ order with the exception of terms such as DT..., QP..., etc. which result from \hat{T}'_2 , $\hat{T}'_1 \hat{T}'_2$, $\hat{T}'_1 \hat{T}'_3$, and $\hat{T}'_1 \hat{T}'_4$ (see Fig. 2). Of course, the delayed introduction of the P terms at the QCISD level has also to do with $\hat{T}_1 \hat{T}'_2$ as is reflected by Figs. 3c and 3d. Similar observations can be made for higher odd number excitations such as S(7), N(9), etc. In short,

QCISD is limping behind CCSD by just one order of perturbation theory with regard to the majority of correlation effects resulting from odd excitations (T, P, S(7), etc.), since it has to introduce these terms via a coupling with S and Q excitations. However, it cannot cover any of the DT..., DTP..., etc. terms that directly result from $\hat{T}_1 \hat{T}'_2$ in the CCSD doubles equations.

At higher orders also other energy contributions that are due to T_1^2, T_1^3 , etc. are missing in QCISD. The actual difference between the number of energy terms covered (either fully or partially) by CCSD or QCISD is given in Table 1 where for reasons of simplicity symmetry is not considered. These numbers reveal, for example, that for $n = 8$ QCISD contains (fully or partially) only 24% of the 915 MP n contributions, while CCSD still contains 43% of these terms. In other words, QCISD and CCSD are only similar for small n while for large n QCISD rapidly falls behind CCSD. This discrepancy between QCISD and CCSD will show up the more clearly the slower the perturbation series converges.

4 Comparison of CCSD(T), QCISD(T), CCSD(TQ), and QCISD(TQ)

When T correlation effects are included into CCSD and QCISD in a perturbative way, then CCSD(T) and QCISD(T) are obtained [10, 12]:

$$\Delta E_T(\text{CCSD}) = \sum_u^S \sum_d^D \sum_t^T a_u^{\text{CCSD}} V_{ut} (E_0 - E_t)^{-1} V_{td} a_d^{\text{CCSD}} \quad (43)$$

$$\begin{aligned} \Delta E_T(QCISD) = & \sum_u^S \sum_d^D \sum_t^T a_u^{QCISD} V_{ut}(E_0 - E_t)^{-1} V_{td} a_d^{QCISD} \\ & + \sum_s^S \sum_d^D \sum_t^T a_d^{QCISD} V_{dt}(E_0 - E_t)^{-1} V_{ts} a_s^{QCISD} \end{aligned} \quad (44)$$

with V_{ut} , etc. denoting matrix elements $\langle \Phi_u | \hat{V} | \Phi_t \rangle$, etc.

$$E(CCSD(T)) = E(CSSD) + \Delta E_T(CCSD) \quad (45)$$

$$E(QCISD(T)) = E(QCISD) + \Delta E_T(QCISD) \quad (46)$$

We have analyzed these two methods in a similar way as described for CCSD in the previous section. First, we have set the amplitudes of Eqs. (43) and (44), a_d^{CCSD} and a_d^{QCISD} equal to $a_d^{(1)}$ and a_s^{QCISD} equal to $a_s^{(2)}$ according to Eqs. (26) and (27). Expansion of the CCSD(T) and QCISD(T) correlation energy up to eighth order leads to the terms shown in Fig. 4a. In the next step, we have set the amplitudes to $a_d^{(2)}$ ($a_d^{(3)}$, $a_d^{(4)}$) and $a_s^{(3)}$ ($a_s^{(4)}$, $a_s^{(5)}$), respectively, thus obtaining the terms shown in Fig. 4b (4c, 4d). Hence, the diagrams in Fig. 4 start at different orders n , namely Fig. 4a at $n = 4$, 4b at $n = 5$, 4c at $n = 6$, and 4d at $n = 7$, which is indicated in the Figure by dropping $E_{ABC\dots}^{(n)}$ at lower orders. In each case bold solid or hashed lines indicate that a term is (fully or partially) contained in both CCSD(T) and QCISD(T). Terms that are covered by just one of these methods are denoted as described in Fig. 4.

The number of terms due to a perturbational inclusion of T effects increases exponentially with the order n . Most of these terms are contained at both the CC and QCI level, which means that they represent energy contributions that actually would be first covered by CCSDT. To this class of terms also belong some partial energy contributions that turn up at the CCSD(T) but not at QCISD(T) level for $n \geq 7$. Apart from the newly added ‘‘CCSDT’’ terms, there are some CCSD terms that come in at the QCISD(T) level (e.g., TS at $n = 5$ (Fig. 4a), DTS, TSS, and TSD at $n = 6$ (Fig. 4b), etc.) because they are missing at the QCISD level. These terms are responsible for the fact that there are more corrections added at the QCISD(T) level than at the CCSD(T) level ($4 > 3$ for $n = 5$, $13 > 10$ for $n = 6$, $44 > 34$ for $n = 7$, $147 > 119$ for $n = 8$, see Table 1). Accordingly, the discrepancy between QCI and CC is reduced to some extent at the QCISD(T)-CCSD(T) level. This, however, is not that dramatic that it overcomes the basic deficiencies of QCI.

In Table 1 and Fig. 5 total numbers of energy contributions contained in QCI and CC methods at various orders n of perturbation theory are given as a function of the order n . These numbers reveal that even though QCISD(T) should be better than CCSD, QCISD(T) does not cover more infinite order effects than CCSD does. On the contrary, for $n > 7$ there are more terms covered by CCSD than QCISD(T). Of course, that does not necessarily imply that CCSD is a better method than QCISD(T). But it reveals that a perturbative inclusion of T effects does not lead to a compensation of the basic deficiencies of QCI. Figure 5 clearly shows that there is still a relatively big gap between CCSD(T) and QCISD(T).

In Table 1 and Fig. 5, relevant data for QCISD(TQ) [20] and CCSD(TQ) [20, 21] are also included. Clearly, CCSD(TQ) covers considerably more energy terms than CCSD(T) and, therefore, it should be a better method. At sixth order, CCSD(TQ) is still close to CCSDT, but at higher n it falls back behind CCSDT. For example, at $n = 8$, CCSD(TQ) covers 75% of the CCSDT

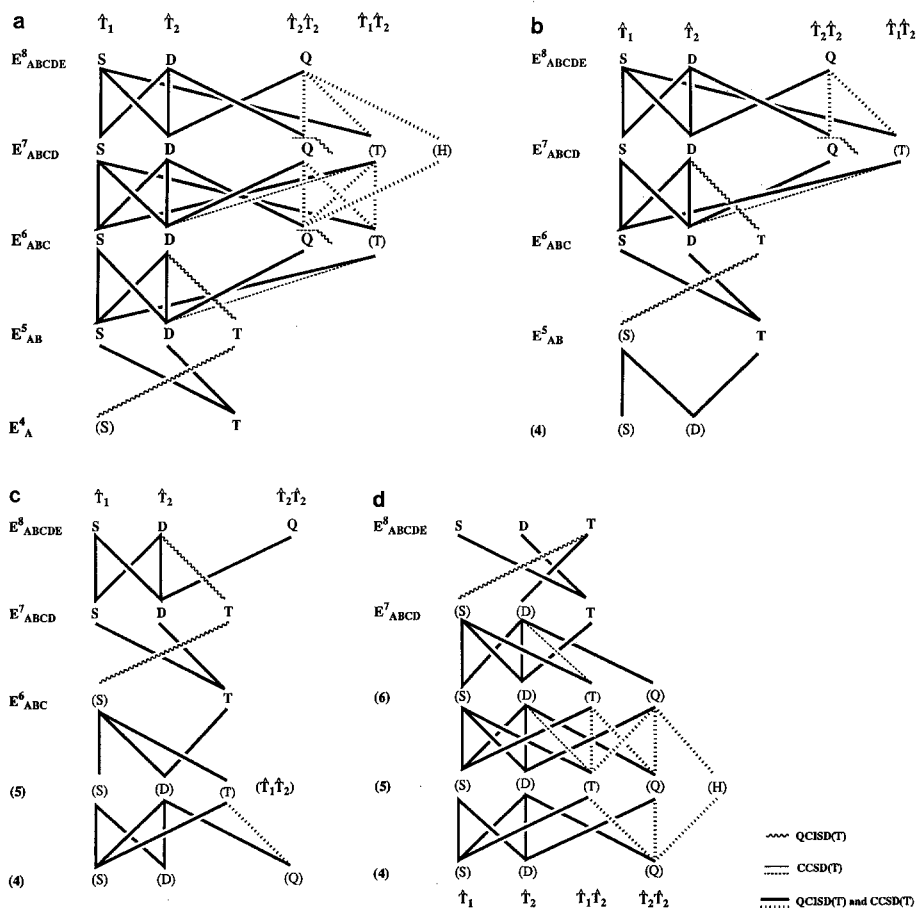


Fig. 4. Graphical analysis of energy contributions at n th order MP perturbation theory ($n = 4, 5, 6, 7, 8$) that are added to CCSD and QCISD at the CCSD(T) and QCISD(T) level, respectively. For an explanation of **4a–d**, see text. Note that *bold solid (hashed) lines* denote energy terms that are fully (partially) contained in both the CCSD(T) and the QCISD(T) correlation energy. Those energy terms that are only covered by the CCSD(T) are denoted by *normal solid or dashed lines* depending on whether they are fully contained. Energy terms that are only covered by QCISD(T) (all fully contained) are given by *wiggled lines*

terms and 65% of all MP8 terms. One should expect a similar behaviour of QCISD(TQ) but this method is actually closer to CCSD(T) than CCSD(TQ) when considering the total number of energy contributions covered. As a matter of fact, QCISD(TQ) even falls behind CCSD(T) at $n = 8$ containing only 502 (CCSD(T): 513, Table 1) of the 755 MP8 energy contributions.

As mentioned above the total number of energy contributions covered by a particular method does not necessarily indicate its performance in molecular calculations. Some energy contributions may be more important than others and as long as one does not know this in detail it is difficult to make any predictions. If higher orders become important because of a slowly convergent perturbation expansion, it probably will not matter any longer whether particular terms are included or not. All terms will lead to rather small contributions to the correlation

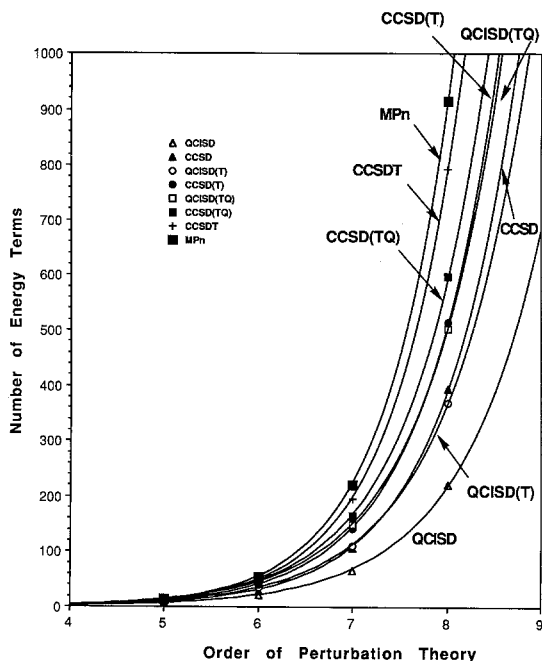


Fig. 5. Number of energy contributions $E_{ABC...}^{(n)}$ covered by QCISD, CCSD, QCISD(T), CCSD(T), QCISD(TQ), CCSD(TQ), CCSDT, and MPn given as a function of the order n . Numbers are given without considering symmetry

energy and, therefore, a satisfactory description of correlation effects will only be obtained if a high percentage of all types of excitations is covered by a particular method. Hence, in these cases it is both justified and useful to compare total numbers of energy contributions contained by the various methods.

For small n , however, particular energy contributions can be much larger than others and, then, a statistical analysis of energy terms does not necessarily lead to a conclusive comparison of CC and QCI methods. In this work, we are particularly interested in the correlation effects resulting from T excitations and we want to answer the question which of the four methods discussed above is best suited to handle T correlation effects. Since it is hardly possible to make reliable predictions on the magnitude of the various T terms, we will answer this question by analyzing the number and type of T terms covered by the CC and QCI methods.

In Table 2, numbers N of T energy contributions are given for the methods discussed in this work. Also given is a detailed analysis that shows how many of these energy terms result from one, two or more T excitations and whether the T excitations directly couple. In Fig. 6, this analysis is given in form of a column graph for $n = 6$. From Table 2 and Fig. 6 the following observations can be made.

1. CCSD contains 33% of all T terms (12 out of 36 terms), but QCISD only 11% (4 out of 36). QCISD(T) contains 47, CCSD(T) 61, QCISD(TQ) 75, CCSD(TQ) 78, and CCSDT 86% of all T terms (Fig. 6a).

2. Among the T terms there are 11 that describe direct or indirect TT coupling. None of the TT coupling terms is contained in either QCISD or QCISD(T). CCSD and CCSD(T), however, cover 2 of these terms at least partially. QCISD(TQ) and CCSD(TQ) contain similar numbers of TT coupling terms (4 and 5, respectively).

Table 2. Number of triple contributions covered by various methods at n th order perturbation theory^a

	QCISD	CCSD	QCISD(T)	CCSD(T)	QCISD(TQ)	CCSD(TQ)	CCSDI	MP n
$n = 5$								
Total		2(1)	4	5(1)	7	7	6	7
$N(T)$		2(1)	4	5(1)	6	6	5	6
$N(TT)$					1	1	1	1
$n = 6$								
Total	4(3)	12(8)	17(3)	22(8)	27(5)	28(7)	31(4)	36
$N(T)$	4(3)	10(6)	17(3)	20(6)	23(5)	23(5)	22(4)	25
$N(TT)$		2(2)		2(2)	4	5(2)	5	6
$N(T \dots T)$							3	4
$N(TTT)$								1
$n = 7$								
Total	20(16)	60(45)	64(20)	94(49)	103(32)	117(48)	142(40)	168
$N(T)$	16(12)	40(26)	56(14)	70(28)	78(22)	81(25)	82(27)	94
$N(TT)$	4(4)	10(10)	4(4)	10(10)	17(4)	20(10)	22(5)	25
$N(T \dots T)$		8(7)	4(2)	12(9)	8(6)	14(11)	26(7)	34
$N(TTT)$		2(2)		2(2)		2(2)	5	6
$N(TT \dots T)$							6(1)	8
$N(TTTT)$							1	1
$n = 8$								
Total	100(85)	267(219)	245(115)	386(250)	379(173)	470(262)	632(266)	755
$N(T)$	64(50)	145(103)	181(62)	234(115)	251(96)	270(113)	300(143)	342
$N(TT)$	16(16)	40(40)	16(16)	40(40)	56(18)	70(42)	82(30)	94
$N(T \dots T)$	16(15)	54(48)	40(29)	80(63)	56(45)	92(72)	150(64)	191
$N(TTT)$	4(4)	10(10)	4(4)	10(10)	4(4)	10(10)	22(5)	25
$N(TT \dots T)$		16(16)	4(4)	20(20)	12(10)	26(23)	52(18)	68
$N(T \dots T \dots T)$							11(4)	16
$N(TTTT)$		2(2)		2(2)		2(2)	5	6
$N(TTT \dots T)$							9(2)	12
$N(TTTT \dots T)$								1
$N(TTTT \dots TT)$								1
$N(TTTT \dots TTT)$								1

^a For each method, the entry $k(l)$ gives the number k of fully and partially covered terms covered not considering symmetry. Of the k terms are l terms that are covered only partially. $N(T)$, $N(TT)$, etc. denote the number of energy with one, two, etc. T excitations. Note that the k values of MP n denote the maximum number of energy terms at order n .

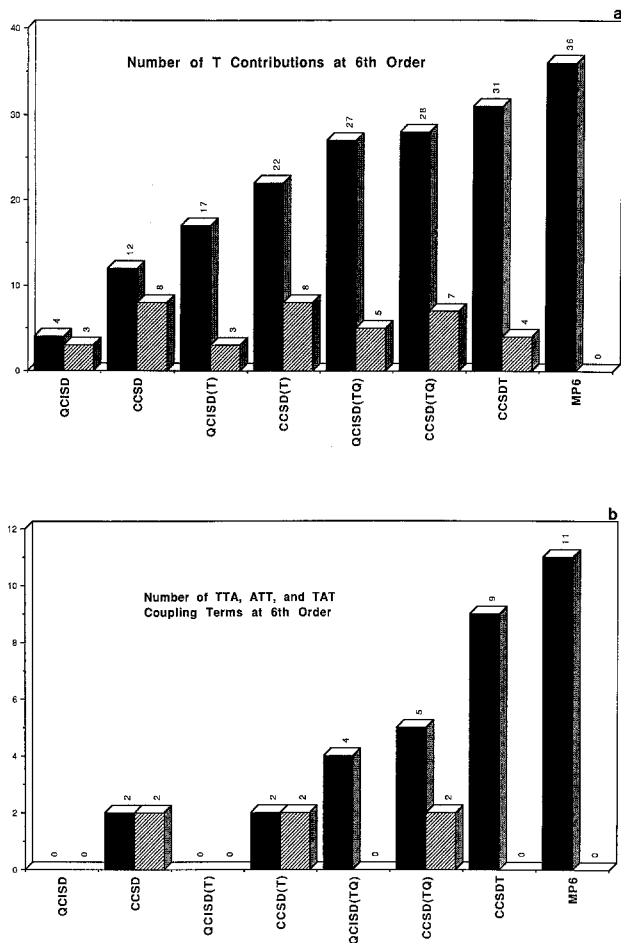


Fig. 6. Schematic representation of (a) the total number of T terms at MP6 and (b) the number of TTA, ATT, and TAT coupling terms at MP6 covered by various CC and QCI methods. Black columns represent the sum of fully and partially covered energy contributions, shadowed columns represent partial covered energy terms

3. CCSDT covers twice as many TT terms as QCISD(TQ) and CCSD(TQ) do, in particular it is the only method that contains the TTT term at sixth order.

Similar observations can be made for $n = 7$ and $n = 8$, which suggests the following conclusions.

1. QCISD does not provide any reasonable account of T correlation effects.
2. QCISD(T) brings in T effects, but it will lead to an exaggeration of T effects since it does contain too few TT coupling terms at $n = 5, 6, 7,$ and 8 .
3. CCSD covers only one third of the T contributions, but does this in a balanced way thus avoiding exaggeration of T effects. A quantitative assessment of both T and TT coupling effects should be first obtained at the CCSD(T) level.
4. QCISD(TQ) and CCSD(TQ) should lead to a comparative and equally good description of T correlation effects. However, the best account of these effects should be provided by CCSDT.

If one considers the fact that both QCISD(TQ), CCSD(TQ), and CCSDT are M^8 methods, then one has to conclude that CCSD(T) is probably the best

method presently available to describe T correlation effects. We have to check in a following paper whether this is also correct when comparing CCSD(T) with CCSDT- n methods [22].

5 Conclusion

As long as little or no calculational results are available that allow reliable predictions on sign, magnitude and general importance of a specific higher order term in energy calculations, an analysis as that carried out in the present work provides the only source of information about the possible performance of a CC method. Of course, a high number of energy contributions covered by a particular method does not necessarily guarantee superior performance in molecular calculations since some terms may be more important than others. Also, the observation that a method contains more partial terms than another does not necessarily imply that the former must be better than the latter since the term partial does not specify which part of the full term is covered. Having this in mind the following conclusions can be drawn from the analysis of CCSD, QCISD, CCSD(T), QCISD(T), CCSD(TQ), QCISD(TQ), and CCSDT in terms of sixth, seventh, and eighth order perturbation theory.

(1) CCSD and QCISD are equivalent in the truncated space of S , D , Q , H , ... X excitations, where X is any even excitation generated by the cluster operator, \hat{T}_2^m . Since these excitations describe orbital relaxation and electron pair correlation effects, which are the most important correlation effects for relatively small closed-shell molecule with just single bonds, it is reasonable to assume that both CCSD and QCISD are appropriate methods to be used in these cases. Actually, QCISD may be the method of choice since it is somewhat simpler to carry out than CCSD.

(2) For molecules that require higher order effects (e.g. in the case of a slowly converging perturbation series due to multi reference character of the model wavefunction or in the case of molecules with distinct T effects), CCSD should perform significantly better than QCISD because of three reasons. (a) QCISD covers a much smaller number of energy contributions than CCSD at higher orders of perturbation theory. (b) Part of the T, P, S(7)...Y contributions (Y is any odd order excitation) generated by the cluster operator $\hat{T}_1\hat{T}'_2$ are delayed at the QCI level by one order of perturbation theory since they have to be introduced by S excitation coupling. (c) Another part of the T, P, S(7)...Y contributions covered by CCSD is not contained in QCISD (see Figs. 2 and 3).

(3) A noniterative improvement of QCISD by T excitations is more important for QCISD than for CCSD. However, QCISD(T) will most probably exaggerate T effects since it does not contain any of the TT coupling terms. As for the total number of energy contributions QCISD(T) falls back behind CCSD at higher orders of perturbation theory.

(4) CCSD(T) should lead to a much better description of T effects than QCISD(T) since it contains more T contributions including important TT coupling terms. Among the CC and QCI methods that include T effects in some way, CCSD(T) is probably the method with the best cost-performance ratio.

(5) The difference between QCI and CC is considerably decreased at the CCSD(TQ) and QCISD(TQ) level of theory if one considers in particular T correlation effects. However, if one considers the total number of energy contributions covered for larger n , then QCISD(TQ) will be even inferior to CCSD(T).

(6) In molecular investigations that require the inclusion of T effects, the various CC and QCI methods should lead to improved results in the following order:

MP4(SDTQ) < QCISD(T) < CCSD(T) < QCISD(TQ), CCSD(TQ) < CCSDT.

In the same order, T effects are covered more and more completely.

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