Analysis of Coupled Cluster and Quadratic Configuration Interaction Theory in Terms of Sixth-Order Perturbation Theory

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Abstract

The energy at sixth-order Møller-Plesset (MP6) perturbation theory is given and dissected into 36 size-consistent energy contributions resulting from single (S), double (D), triple (T), quadruple (Q), pentuple (P), and hextuple (H) excitations. It is shown that MP6 is an $O(N^9)$ method, but less costly approximations to MP6 are possible. MP6 is used to analyze and compare coupled cluster (CC) and quadratic configuration interaction (QCI) methods, namely CCD, CCSD, CCSD(T), CCSD(TQ), CCSDT, CCSDT(Q), CCSDT(QQ), QCISD, QCISD(T), and QCISD(TQ). For larger molecules and molecules with distinct T contributions, CCSD is significantly better than QCISD because CCSD covers a relatively large number of T contributions and in particular T,T coupling effects at sixth order. Differences between the two methods become larger at higher orders of perturbation theory. If T and Q excitations are included in QCISD and CCSD in a noniterative way—thus leading to QCISD(T), CCSD(T), QCISD(TQ), and CCSD(TQ)—then differences between QCI and CC decrease. Hence, if a given molecular problem depends on the inclusion of T effects, improved calculational results will be obtained in the following order: MP4(SDTQ) < QCISD(T) < CCSD(T) < QCISD(TQ), CCSD(TQ) < CCSDT. None of the methods investigated is correct in sixth order. Only if CCSDT is extended to CCSDT(QPH), which is also an $O(N^9)$ method, are all MP6 energy contributions then covered.

Introduction

Nowadays electron correlation methods are routinely applied for many chemical problems with generally available computer packages. Most work has been done in the framework of many-body perturbation theory (MBPT) using the Møller-Plesset (MP) perturbation operator [1]. MP perturbation theory offers a hierarchy of well defined methods that allow one to calculate correlation corrections in single, noniterative steps with increasing accuracy the higher the order of perturbation theory applied. Today computer programs are available to calculate second-order (MP2) [2], third-order (MP3) [3], fourth-order (MP4) [4,5], and fifth-order (MP5) [6,7] correlation corrections to the energy. At MP2 and MP3, double (D) excitations are included; at MP4 and MP5, single (S), D, triple (T), and quadruple (Q) excitations are included. MP methods yield large parts of dynamical correlation corrections; they are economical to use; and they are size-consistent [3,8] or, even more gen-

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erally, size-extensive [22]. Furthermore, with MP2, MP3, and MP4 methods, molecular geometries, vibrational frequencies, and many response properties can be calculated using available gradient techniques [9–13].

Because of the advantages of MP methods and their many successful applications, there is a wide-spread belief among the average user of MP correlation methods that MP4 calculations, in particular if the T excitations are included [MP4(SDTQ)], provide sufficiently accurate results in those cases in which electron correlation corrections are required. This hope is certainly not justified, as has been pointed out many times [14,15]. If high accuracy is needed, MP methods fail even in those cases in which the single-determinant description is adequate [15]. Of course, they have to lead to erroneous results when the problem in question can only be handled by a multireference approach [14].

The insufficient accuracy of lower-order MP methods can be easily explained in the following way. Even-order methods always introduce a new correlation effect into the MP approach. For example, MP2 brings in D excitations, while MP4 in addition brings in S, T, and Q excitations, and MP6 in addition pentuple (P) and hextuple (H) excitations, and so on. Accordingly, the MP correlation energy is substantially increased at even-order levels. However, at odd-order MP levels the excitations previously introduced are coupled. For example, at MP3 the D excitations interact, at MP5, the S, T, and Q excitations couple, etc. Hence, the increase in correlation found at the even-order level as a result of the new excitations is significantly reduced at the following odd-order level. In other words, at one level a newly introduced correlation effect is described in a somewhat exaggerated way while at the next level it is probably underestimated because of strong direct coupling. As a consequence, many calculated MP properties oscillate between two boundaries that are often given by the HF (=MP1) and the MP2 result. This has been observed for (among others) relative energies, charge distributions, dipole moments, quadrupole moments, electric field gradients, geometries, vibrational frequencies, and infrared intensities [15,16].

The question is how fast oscillations in MP results damp out and converge to a limiting value. All the available results show that this is not the case at MP4 [15,16]. MP5 will reduce MP4 results in the direction of MP3 results, but probably without coming close to the limit value. Most likely, MP6 will change results again in the direction of MP4, and so on. This is indicated in Figure 1, where the ozone dipole moment has been taken as an example. Because of this there is a need for more accurate correlation corrected methods. These could be higher-order MP methods, as, for example, MP6, MP7, or MP8. We will investigate in the next section this possibility and look at the feasibility of high-order MP calculations.

Alternatively, one could take a different approach for calculating correlation corrections. Most promising are the coupled cluster (CC) methods [17,18]. The CC approach also leads to a well-defined hierarchy of methods, which become more accurate as more excitations are included (D, SD, SDT, etc). Due to the exponential representation of the wave function, CC contains infinite-order effects, which make CC results more accurate than either MP or configuration interaction (CI) methods
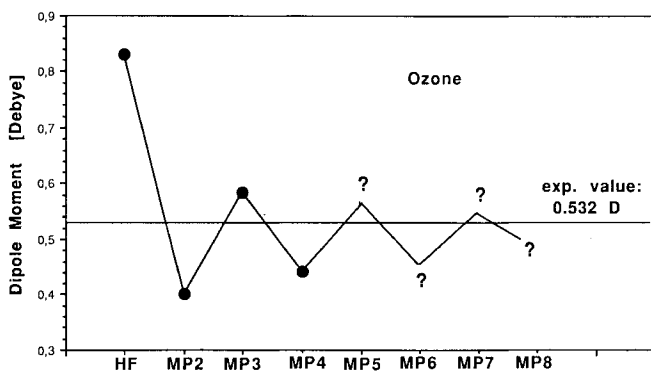
Figure 1. Dependence of the value of the ozone dipole moment on the order of perturbation theory. Calculations up to MP4 are done with the 6-31G(d) basis set. Predictions for higher order MPn results are indicated.

being based on the same excitations. Furthermore, CC methods are size-consistent (size-extensive). Since for CCD [19], CCSD [20], and CCSDT [21] routine calculations can be done nowadays, the CC approach is and will continue to be applied more and more to problems of chemical interest [8,22].

Recently, Pople et al. [23] have introduced the quadratic CI (QCI) method. The QCI equations are obtained by either simplifying the corresponding CC equations or by extending the CI equations in such a way that CI becomes size-consistent (size-extensive). Pople et al. [23,24] have chosen to take the latter view. QCISD is size-consistent (size-extensive), contains infinite-order effects, and treats correlation for a two-electron system correctly. The same properties apply to QCISD(T), where (T) indicates that the triple excitations are handled in a noniterative way using converged QCISD amplitudes [23].

There has been considerable dispute on how QCI compares with CC methods computationally [24–27]. Considerable work has been put in a comparison of the two approaches. In principle, such a comparison could be done (a) on formal grounds [23–25], (b) on the basis of computational requirements [26], (c) on the basis of the accuracy of calculated results, or (d) in form of an analysis in terms of perturbation theory [7,28].

We will consider here only the last aspect; the others have been dealt with in previous work. For example, Paldus et al. [25] have stressed that from a formal point of view QCISD is a simplified CC approach that is closely related to the CPMET(C) method of Paldus, Čížek, and Shavitt [18] as well as the CCSD-1 method of Purvis and Bartlett [20]. The QCI approach does not lead to a hierarchy of well defined methods as CC does. As a matter of fact, higher QCI methods such as QCISDT are no longer size-consistent (size-extensive) [25]. Scuseria and Schaefer [26] have found that the computational needs are similar if QCISD and CCSD are programmed carefully. Using the T_1 criterion [29], Lee et al. [27] have stressed that QCI might be less stable in the case of molecular systems that require a multireference treatment.

We will base our investigation of CC and QCI methods on a perturbational analysis [30]. Such an analysis has been carried out before up to fifth order by Kucharski and Bartlett [6] and by Raghavachari and co-workers [7,28]. Here, we will extend this analysis to sixth-order MP (MP6) perturbation theory. For this purpose, we will derive formulas for the determination of the MP6 energy. Also, we will discuss some properties of MP6. Then we will present a comparison of CC and QCI methods in terms of MP6. In particular, we will investigate CCD, CCSD, QCISD, CCSD(T) [28], QCISD(T), CCSD(TQ), QCISD(TQ) [7], CCSDT, and some possible noniterative extensions of CCSDT by Q and higher excitations. Results of the sixth-order perturbation analysis are helpful to look at infinite-order effects covered by the different CC and QCI methods. By doing so we want to answer the following questions.

1. How do CC and QCI methods compare at sixth order?
2. Which is the simplest CC or QCI method that is correct to sixth order?
3. How do CC and QCI methods compare at infinite order?
4. Is there a possibility to predict which method is best suited for a given computational problem in quantum chemistry?

MP6 Perturbation Theory

In standard MP perturbation theory [1], the Hamiltonian is split into a zero-order operator $\hat{H}_0$ and a perturbation operator $\hat{V}$

$$\hat{H} = \hat{H}_0 + \hat{V},\tag{1}$$

where $\hat{H}_0$ and $\hat{V}$ are given by

$$\hat{H}_0 = \sum_p \hat{F}_p = \sum_p (\hat{h}_p + \hat{g}_p),\tag{2}$$

$$\hat{V} = \sum_{p<q} \hat{r}_{pq}^{-1} - \sum_p \hat{g}_p.\tag{3}$$

If Φ_0 is the Hartree-Fock (HF) ground-state wave function and Ψ the true ground-state wave function, then the wave operator $\hat{\Omega}$ is defined by [31,32]

$$|\Psi\rangle = \hat{\Omega}|\Phi_0\rangle,\tag{4}$$

which means that the action of the wave operator on Φ_0 produces the exact wave function. The wave operator can be expressed in terms of powers of the perturbation operator for each order n if all $\hat{\Omega}^{(m)}$ with $m < n$ are known.

$$\hat{\Omega}^{(n)} = \hat{G}_0 \left[\hat{V}\hat{\Omega}^{(n-1)} - \sum_{m=1}^{n-1} E^{(m)}\hat{\Omega}^{(n-m)} \right]\tag{5}$$

where the reduced resolvant is given by

$$\hat{G}_0 = \sum_{k=0} \frac{|\Phi_k\rangle\langle\Phi_k|}{E_0 - E_k}.\tag{6}$$

With $\hat{\Omega}^{(n)}$ the MPn energy $E^{(n)}$ can be written as

$$E^{(n)} = \langle \Phi_0 | \hat{V} \hat{\Omega}^{(n-1)} | \Phi_0 \rangle , \tag{7}$$

where $\hat{V}\hat{\Omega}^{(n-1)}$ is the reaction operator of order $n - 1$. Using Eq. (5), it is straightforward to write down MPn energies $E^{(n)}$ for n up to 6. The number of terms in each order is given by

$$\frac{(2n - 2)!}{n!(n - 1)!} . \tag{8}$$

Thus the number of terms rapidly increases with the order of perturbation:

$$
\begin{array}{llllllll}
n & 1 & 2 & 3 & 4 & 5 & 6 & \cdots \\
\# & 1 & 1 & 2 & 5 & 14 & 42 & \cdots
\end{array} \tag{9}
$$

At sixth order, the MP energy is given by the principal term and 41 terms that make up the renormalization part.

$$E(\text{MP6}) = \langle \Phi_0 | \hat{V} \hat{G}_0 \hat{V} \hat{G}_0 \hat{V} \hat{G}_0 \hat{V} \hat{G}_0 \hat{V} | \Phi_0 \rangle + \text{renormalization terms} . \tag{10}$$

Considering the possible excitations that can occur at MP6, the 42 terms can be condensed to four terms that contain different sums over S, D, T, Q, P, and H excitations:

$$E(\text{MP6}) = A + B + C + D , \tag{11}$$

$$
\begin{aligned}
A = \sum_{d_1,d_2}^{D} \sum_{t_1,t_2}^{SDTQ} \sum_{p}^{SDTQPH} & V_{0d_1}(E_0 - E_{d_1})^{-1} \bar{V}_{d_1 t_1}(E_0 - E_{t_1})^{-1} \bar{V}_{t_1 p} \\
& \times (E_0 - E_p)^{-1} \bar{V}_{p t_2}(E_0 - E_{t_2})^{-1} \bar{V}_{t_2 d_2}(E_0 - E_{d_2})^{-1} V_{0d_2}
\end{aligned} \tag{12}
$$

$$
\begin{aligned}
B = -\sum_{d_1,d_2,d_3}^{D} \sum_{t}^{SDTQ} & V_{0d_1}(E_0 - E_{d_1})^{-1} \bar{V}_{d_1 t}(E_0 - E_t)^{-1} \bar{V}_{t d_2}(E_0 - E_{d_2})^{-1} V_{d_2 0} \\
& \times [(E_0 - E_{d_1})^{-1} + (E_0 - E_{d_2})^{-1} + (E_0 - E_t)^{-1} \\
& \quad + (E_0 - E_{d_3})^{-1}] V_{0d_3}(E_0 - E_{d_3})^{-1} V_{d_3 0}
\end{aligned} \tag{13}
$$

$$
\begin{aligned}
C = -\sum_{d_1,d_2}^{D} \sum_{d_3,d_4}^{D} & V_{0d_1}(E_0 - E_{d_1})^{-1} \bar{V}_{d_1 d_2}(E_0 - E_{d_2})^{-1} V_{d_2 0} \\
& \times [(E_0 - E_{d_1})^{-1} + (E_0 - E_{d_2})^{-1}] V_{0d_3}(E_0 - E_{d_3})^{-1} \bar{V}_{d_3 d_4}(E_0 - E_{d_4})^{-1} V_{d_4 0}
\end{aligned} \tag{14}
$$

$$
\begin{aligned}
D = \sum_{d_1,d_2,d_3}^{D} & V_{0d_1}(E_0 - E_{d_1})^{-1} V_{d_1 0}(E_0 - E_{d_1})^{-1} V_{0d_2}(E_0 - E_{d_2})^{-1} \\
& \times V_{d_2 0}[(E_0 - E_{d_1})^{-1} + (E_0 - E_{d_2})^{-1}] V_{0d_3}(E_0 - E_{d_3})^{-1} V_{d_3 0}
\end{aligned} \tag{15}
$$

with

$$V_{0s} = \langle \Phi_0 | \hat{V} | \Phi_s \rangle \qquad (s = d, d_1, d_2 \cdots)$$

and

$$\bar{V}_{s_1 s_2} = V_{s_1 s_2} - \delta_{s_1 s_2} \langle \Phi_0 | \hat{V} | \Phi_0 \rangle .$$

A contains the principal term plus 15 renormalization terms, and B, C, and D contain 16, 8, and 2 renormalization terms, respectively. For reasons of simplicity, we will consider the sum of B, C, and D as the renormalization part [5].

It has been shown for MP4 [4,5] and MP5 [6,7] that it is advantageous to dissect the MP perturbation theory into contributions from specific excitations; for example,

$$E(\text{MP4}) = E^4(\text{S}) + E^4(\text{D}) + E^4(\text{T}) + E^4(\text{Q}) \tag{16}$$

$$E(\text{MP5}) = E^5(\text{SS}) + 2E^5(\text{SD}) + 2E^5(\text{ST}) + E^5(\text{DD}) + 2E^5(\text{DT})$$
$$+ 2E^5(\text{DQ}) + E^5(\text{TT}) + 2E^5(\text{TQ}) + E^5(\text{QQ}) , \tag{17}$$

where the fact that $E^5(\text{SD}) = E^5(\text{DS})$, etc., is considered by a factor of 2.

In Eqs. (16) and (17) the renormalization terms E_R have also been dissected into contributions from specific excitations and then summed into the appropriate partial energies. For example, E_R^4 leads to a contribution to $E^4(\text{Q})$ and E_R^5 to $E^5(\text{DQ})$, $E^5(\text{QD})$, and $E^5(\text{QQ})$. By taking correct account of these contributions, all terms that are not proportional to the number of electrons cancel. Accordingly, each partial energy in Eqs. (16) or (17) is size-consistent (size-extensive) [3,8,22]. This, of course, is the essence of the linked diagram theorem, i.e., correct cancellation of the renormalization terms according to the linked diagram theorem can be used to check whether the formulas derived are correct.

To get for the MP6 energy a similar dissection into partial energies, which are all size-consistent (size-extensive), one must first write down the renormalization part in the appropriate form. For this purpose, we start from Eq. (18),

$$E_R^6 = B + C + D , \tag{18}$$

in which the terms B, C, and D can be rewritten in the following form:

$$B = -E(\text{MP4}) \sum_d^{\text{D}} |a_d^1|^2 - E(\text{MP2}) \sum_t^{\text{SDTQ}} |a_t^2|^2$$
$$-2E(\text{MP2}) \sum_d^{\text{D}} \sum_t^{\text{SDTQ}} a_d^1 (E_0 - E_d)^{-1} \bar{V}_{dt} a_t^2 , \tag{19}$$

$$C = -2E(\text{MP3}) \sum_d^{\text{D}} a_d^1 a_d^2 , \tag{20}$$

$$D = E(\text{MP2}) \sum_d^{\text{D}} [E(\text{MP2})(E_0 + E_d)^{-1} |a_d^1|^2 + |a_d^1|^4] , \tag{21}$$

with

$$a_d^1 = (E_0 - E_d)^{-1} V_{d0} \,,$$

$$a_t^2 = (E_0 - E_t)^{-1} \sum_d^D \bar{V}_{td} a_d^1, \qquad (t = \text{S, D, T, } \cdots) \,.$$

Further expansion of Eqs. (19), (20), and (21) leads to the final form of the re-normalization term,

$$\begin{aligned}
E_R^6 = -[\,&2E_R^6(\text{SDQ}) + 2E_R^6(\text{DDQ}) + 2E_R^6(\text{TDQ}) + E_R^6(\text{QDQ}) \\
&+ 2E_R^6(\text{STQ}) + 2E_R^6(\text{DQQ}) + 2E_R^6(\text{TPQ}) + E_R^6(\text{QHQ}) \\
&+ E_R^6(\text{QTQ}) + E_R^6(\text{QQQ}) + E_R^6(\text{QPQ}) + E_R^6(\text{STS}) \\
&+ E_R^6(\text{QDQ}) + E_R^6(\text{TPT})\,]\,.
\end{aligned} \qquad (22)$$

Performing a similar dissection for the MP6 energy and summing the various contributions of the renormalization term given in Eq. (22) into the appropriate terms of the MP6 energy, one obtains the sixth-order perturbation energy in its final form,

$$\begin{aligned}
E(\text{MP6}) = \ &E^6(\text{SSS}) + 2E^6(\text{SSD}) + 2E^6(\text{SST}) + E^6(\text{SDS}) + 2E^6(\text{SDD}) \\
&+ 2E^6(\text{SDT}) + 2E^6(\text{SDQ}) + E^6(\text{STS}) + 2E^6(\text{STD}) \\
&+ 2E^6(\text{STT}) + 2E^6(\text{STQ}) + E^6(\text{DSD}) + 2E^6(\text{DST}) \\
&+ E^6(\text{DDD}) + 2E^6(\text{DDT}) + 2E^6(\text{DDQ}) + E^6(\text{DTD}) \\
&+ 2E^6(\text{DTT}) + 2E^6(\text{DTQ}) + E^6(\text{DQD}) + 2E^6(\text{DQT}) \\
&+ 2E^6(\text{DQQ}) + E^6(\text{TST}) + E^6(\text{TDT}) + 2E^6(\text{TDQ}) \\
&+ E^6(\text{TTT}) + 2E^6(\text{TTQ}) + E^6(\text{TQT}) + 2E^6(\text{TQQ}) \\
&+ E^6(\text{TPT}) + 2E^6(\text{TPQ}) + E^6(\text{QDQ}) + E^6(\text{QTQ}) \\
&+ E^6(\text{QQQ}) + E^6(\text{QPQ}) + E^6(\text{QHQ})\,.
\end{aligned} \qquad (23)$$

A pictorial way of deriving this equation from the fifth-order perturbation energy is given in Scheme I. The MP6 energy can be characterized in the following way. It contains 55 contributions, which can be reduced to 36 because of symmetry. Each of the partial energy terms given in Eq. (23) is size-consistent (size-extensive). Therefore it is possible to group the various contributions as indicated in Scheme I by dashed lines. There are 12 different terms that contain just S, D, or Q excitations. They constitute what may be called the SDQ space at sixth order. The T excitations can interact with all other but the H excitations. By interaction with S, D, and Q excitations they yield 20 terms including the TTT part. This may be called the T space. Finally, there are four terms that arise from P and H excitations that first appear at sixth-order perturbation theory. They form the PH space.

In previous work, it has been shown that MP4 calculations require $O(N^7)$ and MP5 calculations $O(N^8)$ operations where N defines the size of the basis set [6,7]. A detailed analysis of Eq. (23) shows that MP6 calculations lead to $O(N^9)$. The

	S	D	Q	T	P	H
SS	SSS	SDS		STS		
SD, DS	SSD, DSS	SDD, DDS		STD, DTS		
(sq, qs)		SDQ, QDS		STQ, QTS		
DD	DSD	DDD	DQD	DTD		
DQ, QD		DDQ, QDD	DQQ, QQD	DTQ, QTD		
QQ		QDQ	QQQ	QTQ	QPQ	QHQ
ST, TS	SST, TSS	SDT, TDS		STT, TTS		
DT, TD	DST, TSD	DDT, TDD	DQT, TQD	DTT, TTD		
TT	TST	TDT	TQT	TTT	TPT	
TQ, QT		TDQ, QDT	TQQ, QQT	TTQ, QTT	TPQ, QPT	

Scheme I.   Dissection of the MP6 correlation energy into partial energies that result from specific excitations. In the first column the 14 MP5 energy terms are given, which lead to the 55 MP6 terms by correct combinations with S, D, T, Q, P, and H excitations. Note that a combination (sq, qs) not present at MP5 has to be included in the first column to take account of the coupling with D and T excitations. Dashed lines indicate the grouping of the MP6 terms discussed in the text.

most expensive terms that appear at MP6 are given in Table I. For small basis sets, it will probably be possible to carry out MP6 calculations. After computer programs for calculating MP5 energies have successfully been implemented [6,7], it is only a question of time when the same will be done for MP6. This could be done by first considering approximations to MP6 such as MP6(SDQ).

TABLE I.   MP6 energy contributions that require high calculational costs.

Energy contribution	Costs[a]
$E^6(\text{TTT})$	$O(N^8)$
$E^6(\text{TPT}) + E^6(\text{TPQ})(I)$	$\leq O(N^8)$
$E^6(\text{QPT}) + E^6(\text{QPQ})(I)$	$\leq O(N^9)$
$E^6(\text{TQT})$	$O(N^9)$
$E^6(\text{TTQ})$	$\leq O(N^8)$
$E^6(\text{QQT})$	$O(N^9)$
$E^6(\text{QTQ})$	$O(N^7)$
$E^6(\text{QQQ})$	$\leq O(N^9)$
$E^6(\text{QHQ})$	$\leq O(N^8)$

[a] In some cases only an upper bound to the costs are given since two-electron integral formulas have not been worked out.

It is clear that at present any method that requires $O(N^8)$ steps or even more is too costly to be used for larger molecules. But even for small molecules it is the question how far one can go beyond MP5. For example, is MP7 or MP8 possible? The number of terms arising from combinations of the various excitations increases dramatically at these orders as can be seen from Scheme II. At MP7, a coupling between the SDTQPH excitations becomes possible and, therefore, one encounters 221 terms, which by symmetry reduce to 141 terms. At MP8, septuple [S(7)] and

E^5_{AB} (9, 14)

5	S	D	T	Q
S	1	1	1	
D	1	1	1	1
T	1	1	1	1
Q		1	1	1
P			1	1
H				1
S(7)				
O(8)				

E^6_{ABC} (36, 55)

6	S	D	T	Q
S	3	3	3	2
D	3	4	4	3
T	3	4	5	4
Q	2	3	4	5
P			3	4
H			2	3
S(7)			1	2
O(8)				1

E^7_{ABCD} (141, 221)

7	S	D	T	Q
S	9	11	12	9
D	11	14	16	14
T	12	16	19	18
Q	9	14	18	19
P			15	18
H			10	15
S(7)			6	10
O(8)			3	6
N(9)			1	3
D(10)				1
U(11)				
U(12)				

E^8_{ABCDE} (583, 915)

8	S	D	T	Q
S	32	41	47	41
D	41	55	65	60
T	47	65	80	78
Q	41	60	78	84
P			68	80
H			52	68
S(7)			35	52
O(8)			20	35
N(9)			10	20
D(10)			4	10
U(11)			1	4
U(12)				1

Scheme II. Number of contributions resulting from specific excitations at the MPn level ($n = 5, 6, 7$, and 8). In the heading of each diagram the type and the number of energy contributions at MPn is shown. Numbers in parentheses give total number of energy terms after and before symmetry reduction. In the upper half of each diagram the number of all S.S, S..D, D..S, etc., terms that contribute to the MPn correlation energy is depicted. The lower half of the diagram is used to calculate the number of energy contributions at MPm with $m > n$.

octuple [O(8)] excitations are introduced as new contributions thus increasing the number of unique contributions to 573.

Considering that the computational work increases by one power of N at each order of perturbation theory, one has to face $O(N^{10})$ and $O(N^{11})$ operations at MP7 and MP8, respectively. Hence, it seems to be impossible at the moment to go beyond MP6. Progress in this direction can only be expected if the speed of present computers is improved significantly. Also, the derivation of the appropriate two-electron integral formulas at MP7 or MP8 will require computer software that helps to automate this process to a high extent.

Analysis of the CCSD and QCISD Equations

The CCSD equations [20,23,25] are given in Eqs. (24), (25), and (26).

$$\langle \Phi_0 | \hat{H} | (\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2)\Phi_0 \rangle = E_{corr} \tag{24}$$

$$\langle \Phi_i^a | \bar{H} | (\hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \tfrac{1}{6}\hat{T}_1^3)\Phi_0 \rangle = a_i^a E_{corr} \tag{25}$$

$$\langle \Phi_{ij}^{ab} | \bar{H} | (\mathbf{1} + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \tfrac{1}{6}\hat{T}_1^3 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{24}\hat{T}_1^4)\Phi_0 \rangle$$
$$= a_{ij}^{ab} E_{corr}, \tag{26}$$

where $\bar{H} = \hat{H} - E_0$, Φ_0, and E_0 are the HF ground-state wave function and energy, E_{corr} is the correlation energy, and $\hat{T}_p$ denotes cluster operators

$$\hat{T}_1 = \sum_{ia} a_i^a \hat{t}_i^a \tag{27}$$

$$\hat{T}_2 = \tfrac{1}{4} \sum_{ij,ab} a_{ij}^{ab} \hat{t}_{ij}^{ab}, \tag{28}$$

which generate p-times excited configurations such as Φ_i^a ($p = 1$), Φ_{ij}^{ab} ($p = 2$), etc., multiplied by the corresponding cluster amplitudes a_i^a and a_{ij}^{ab}. The operator $\hat{t}_i^a$ and $\hat{t}_{ij}^{ab}$ represent elementary substitution operators. The cluster operators given in boldface in Eqs. (24), (25), and (26) appear in both the CCSD and the QCISD projection equations. In other words, the QCISD equations are obtained from Eqs. (24), (25), and (26) just by dropping the cluster operators not given in bold print [23–26].

To compare the CCSD and QCISD equations, in Table II we give, for each term of the three CCSD equations (24) through (26), the lowest order of perturbation theory at which the cluster operators will make the first contribution to the correlation energy E_{corr}. Actually, such an analysis has already been given by Paldus et al. [25] in their careful comparison of CC and QCI methods. Here, we extend their analysis by explicitly identifying the corresponding contributions to E_{corr} in terms of the partial energies given in Eqs. (16), (17), and (23) (see also Scheme I).

As has been pointed out before, CCSD and QCISD are equivalent up to fourth

TABLE II. Analysis of the CCSD and QCISD equations in terms of perturbation theory.

Equation[a]	Cluster operator[b]	First contribution at MPn[c]	
		Order n	Energy
$\langle\Phi_0|\hat{H}|$	$\hat{T}_2$	2	E^2
	$(\frac{1}{2})\hat{T}_1^2$	5	$E^5(\text{TS}) + E^5(\text{TQ})(I)$
$\langle\Phi_i^a|\bar{H}|$	$\hat{T}_1$	5	$E^5(\text{SS})$
	$\hat{T}_2$	4	$E^4(\text{S})$
	$(\frac{1}{2})\hat{T}_1^2$	7	$E^7(\text{SDTS}) + E^7(\text{SDTQ})(I)$
	$\hat{T}_1\hat{T}_2$	6	$E^6(\text{STS}) + E^6(\text{STQ})(I)$
	$(\frac{1}{6})T_1^3$	9	$E^9(\text{STQDTS}) + E^9(\text{STQDTQ})(I)$ $+ E^9(\text{STQPTS})(I) + E^9(\text{STQPTQ})(I)$ $+ E^9(\text{STQPHQ})(I)$
$\langle\Phi_{ij}^{ab}|\bar{H}|$	1	2	E^2
	$\hat{T}_1$	4	$E^4(\text{S})$
	$\hat{T}_2$	3	E^3
	$(\frac{1}{2})\hat{T}_1^2$	6	$E^6(\text{DTS}) + E^6(\text{DTQ})(I)$
	$\hat{T}_1\hat{T}_2$	5	$E^5(\text{TS}) + E^5(\text{TQ})(I)$
	$(\frac{1}{6})\hat{T}_1^3$	8	$E^8(\text{TQDTS}) + E^8(\text{TQDTQ})(I)$ $+ E^8(\text{TQPTS})(I) + E^8(\text{TQPTQ})(I)$ $+ E^8(\text{TQPHQ})(I)$
	$(\frac{1}{2})\hat{T}_2^2$	4	$E^4(\text{Q})$
	$(\frac{1}{2})\hat{T}_1^2\hat{T}_2$	7	$E^7(\text{QDTS}) + E^7(\text{QDTQ})(I)$ $+ E^7(\text{QPHQ})(I) + E^7(\text{QPTS})(I)$ $+ E^7(\text{QPTQ})(I)$
	$(\frac{1}{24})\hat{T}_1^4$	10	

[a] Compare with Eqs. (24) to (26).

[b] Boldface operators appear in both the CCSD and the QCISD equations. The corresponding energy contributions are covered by both CCSD and QCISD. Operators and energies in normal print are only present in CCSD.

[c] The lowest order of perturbation theory, at which first energy contributions come in, is given.

order [7,28]. At the QCI level, this is achieved by including in the doubles projection formula (26) disconnected quadruply excited clusters $\frac{1}{2}\hat{T}_2^2$ rather than the disconnected triply excited clusters $\hat{T}_1\hat{T}_2$. This leads to some inconsistency, because $\hat{T}_1\hat{T}_2$ is included in the singles projection formula (25). However, Table II reveals that this choice is justified. The cluster operator $\frac{1}{2}\hat{T}_2^2$ already contributes at fourth order, yielding the important $E^4(\text{Q})$ contribution to E_{corr}, while $\hat{T}_1\hat{T}_2$ first contributes at fifth order in the doubles equation.

Differences between QCISD and CCSD first appear at fifth order because of the neglect of $\hat{T}_1\hat{T}_2$ in Eq. (26) and $\frac{1}{2}\hat{T}_1^2$ in Eq. (24) [25]. These terms are responsible for $E^5(\text{TS})$ and (partially) for $E^5(\text{TQ})$, which arise from disconnected triple excitations. Calculations have shown that in most cases these energy contributions are

positive thus leading to an increase of the CCSD correlation energy [33]. As a consequence, QCISD energies are more negative than CCSD energies, which of course does not mean that QCISD is better than CCSD, as neither of these methods is variational.

Differences between QCISD and CCSD at sixth, seventh, eighth, and ninth order are also given in Table II in terms of the corresponding partial energies included or not included in E_{corr}. In this article we are particularly interested in the differences at sixth order and at infinite order. But before discussing them in detail, it is useful to complete the analysis given in Table II by explicitly identifying for each partial energy up to fifth order the cluster operators in Eqs. (24) through (26) that lead

TABLE III.   Analysis of the CCSD and QCISD equations up to fifth-order perturbation theory.

Order	Energy contribution	Equation[a]	Operator that generates $E^M(A\ldots)$ in nth order[b]
2	E^2	$\langle\Phi_0\|H\|$	$\hat{T}_2$
		$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	**1**
3	E^3	$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_2$
4	$E^4(\text{S})$	$\langle\Phi_i^a\|\bar{H}\|$	$\hat{T}_2$
		$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_1$
	$E^4(\text{D})$	$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_2$
	$E^4(\text{T})$	Not contained	
	$E^4(\text{Q})$	$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$(\frac{1}{2})\hat{T}_2^2$
5	$E^5(\text{SS})$	$\langle\Phi_i^a\|\bar{H}\|$	$\hat{T}_1$
	$E^5(\text{DD})$	$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_2$
	$E^5(\text{TT})$	Not contained	
	$E^5(\text{SD})$	$\langle\Phi_i^a\|\bar{H}\|$	$\hat{T}_2$
		$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_1$
	$E^5(\text{DS})$	$\langle\Phi_i^a\|\bar{H}\|$	$\hat{T}_1$
		$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_2$
	$E^5(\text{DQ}) + E^5(\text{QQ})(I)$	$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_2$
		$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$(\frac{1}{2})\hat{T}_2^2$
	$E^5(\text{QD})$	$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_2$
		$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$(\frac{1}{2})\hat{T}_2^2$
	$E^5(\text{ST})$	Not contained	
	$E^5(\text{TS}) + E^5(\text{TQ})(I)$	$\langle\Phi_{ij}^{ab}\|\bar{H}\|$	$\hat{T}_1\hat{T}_2$
	$E^5(\text{DT})$	Not contained	
	$E^5(\text{TD})$	Not contained	
	$E^5(\text{QT})$	Not contained	

[a] Compare with Eqs. (24) to (26).
[b] Boldface operators appear in both the CCSD and the QCISD equations.

to the term in question. This analysis is given in Table III, which, when inspected, again reveals that in the doubles equation it is better to include $\frac{1}{2}\hat{T}_2^2$ rather than $\hat{T}_1\hat{T}_2$. The former leads to important contributions not only at MP4 but also at MP5, where DQ (=QD) and QQ effects are brought in.

Analysis of CC and QCI Methods in Terms of MP6

An analysis of CC or QCI methods in terms of perturbation theory up to fifth order has been carried out by several authors [6,7,28]. The results of their analysis are summarized in Scheme III. Scheme III reveals that CCSD is not correct at fourth order because it is lacking the T effects. One way of extending CCSD to make it correct at fourth order is realized in CCSD(T) [28]. The same is true for QCISD(T), which is the first QCISD method correct in fourth order [23,28]. To make CC and QCI correct to fifth order one has to include Q excitations. There are several ways to do this as has been pointed out by Kucharski and Bartlett [34]. Actually, the CCSD + TQ*(CCSD) method suggested by Bartlett et al. [35] was the first CCSD-based method correct in fifth order, but we will discuss this method elsewhere [36]. Here, we consider two other methods correct at fifth order, namely CCSD(TQ) and QCISD(TQ) [7] (see Scheme III).

For a comparison of these methods at the MP6 level, CC and QCI correlation energies E_{corr} have to be expanded up to sixth order. We begin by first expanding the CCD energy. For this purpose, we use the projection equations of CCD [19].

	CCD	QCISD	CCSD	QCISD(T)	CCSD(T)		CCSDT	QCISD(TQ)	CCSD(TQ)	CCSDT(QQ)
E(MP2)	yes	yes	yes	yes	yes	D	yes	yes	yes	yes
E(MP3)	yes	yes	yes	yes	yes	D	yes	yes	yes	yes
E(MP4)		yes	yes	yes	yes	S	yes	yes	yes	yes
	yes	yes	yes	yes	yes	D	yes	yes	yes	yes
	yes	yes	yes	yes	yes	Q	yes	yes	yes	yes
				yes	yes	T	yes	yes	yes	yes
E(MP5)		yes	yes	yes	yes	SS	yes	yes	yes	yes
	yes	yes	yes	yes	yes	DD	yes	yes	yes	yes
	(yes)	(yes)	(yes)	(yes)	(yes)	QQ	(yes)	yes	yes	yes
						TT	yes	yes	yes	yes
		y, y	y, y	y, y	y, y	SD, DS	y, y	y, y	y, y	y, y
	y, y	y, y	y, y	y, y	y, y	DQ, QD	y, y	y, y	y, y	y, y
			-, y	y, y	y, y	ST, TS	y, y	y, y	y, y	y, y
				y, y	y, y	DT, TD	y, y	y, y	y, y	y, y
			(y), -		(y), -	TQ, QT	y, -	y, y	y, y	y, y

Scheme III. Energy contributions to various CC and QCI methods up to fifth-order perturbation theory. The energy terms are characterized by the appropriate excitations given in the center between the two diagrams. A yes or y denotes that the term in question is fully contained, (yes) or (y) that the term is partially contained [40].

$$\langle \Phi_0 | \hat{H} | \hat{T}_2 \Phi_0 \rangle = E_{\text{corr}}^{(\text{CCD})} \tag{29}$$

$$\langle \Phi_d | \bar{H} | (1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2) \Phi_0 \rangle = a_d(\text{CCD}) E_{\text{corr}}^{(\text{CCD})} , \tag{30}$$

with Φ_d and a_d denoting D excited configurations Φ_{ij}^{ab} and the corresponding amplitudes a_{ij}^{ab}, respectively. Using the Hamiltonian in the form of Eq. (1), correlation energy $E_{\text{corr}}^{(\text{CCD})}$ and amplitudes a_d are obtained by Eqs. (31) and (32).

$$E_{\text{corr}}^{(\text{CCD})} = \lambda \langle \Phi_0 | \hat{V} | \hat{T}_2 \Phi_0 \rangle$$

$$= \lambda \sum_d^{\text{D}} \langle \Phi_0 | \hat{V} | \Phi_d \rangle a_d \tag{31}$$

$$a_d(\text{CCD}) = \lambda (E_0 - E_d)^{-1} [\langle \Phi_d | \bar{\hat{V}} | (1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2) \Phi_0 \rangle$$
$$- \langle \Phi_0 | \hat{V} | \hat{T}_2 \Phi_0 \rangle a_d(\text{CCD})] . \tag{32}$$

Substituting Eq. (32) into Eq. (31) leads to the expansion of $E_{\text{corr}}^{(\text{CCD})}$ up to second order

$$E_{\text{corr}}^{(\text{CCD})} = \lambda^2 E(\text{MP2}) + \lambda^2 \sum_d^{\text{D}} \sum_{d_1}^{\text{D}} V_{0d}(E_0 - E_d)^{-1}$$

$$\times [\hat{V}_{dd_1} a_{d_1} + \tfrac{1}{2} \sum_{d_2}^{\text{D}} \langle \Phi_d | \hat{V} | \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 \rangle a_{d_1} a_{d_2} - V_{0d_1} a_{d_1} a_d] . \tag{33}$$

By repeated substitution of the D amplitudes in Eq. (33) the correlation energy is expanded to third, fourth, fifth, and finally to sixth order,

$$E_{\text{corr}}^{(\text{CCD})} = \lambda^2 E(\text{MP2}) + \lambda^3 E(\text{MP3}) + \lambda^4 [E^4(\text{D}) + E^4(\text{Q})]$$
$$+ \lambda^5 [E^5(\text{DD}) + 2E^5(\text{DQ}) + E^5(\text{QQ})(I)]$$
$$+ \lambda^6 [E^6(\text{DDD}) + 2E^6(\text{DDQ}) + E^6(\text{DQD})$$
$$+ E^6(\text{QDQ}) + E^6(\text{DQQ})(I) + E^6(\text{QQD})(I)$$
$$+ E^6(\text{QQQ})(I) + E^6(\text{QHQ})(I)] + O(\lambda^7), \tag{34}$$

where $E^5(\text{QQ})(I)$, $E^6(\text{DQQ})(I)$, $E^6(\text{QQD})(I)$, $E^6(\text{QQQ})(I)$, and $E^6(\text{QHQ})(I)$, are only partially contained at CCD as indicated by (I). It has to be noted that some of the terms cannot directly be compared with the corresponding MP5 and MP6 terms. They have to be divided up by means of the factorization theorem [37].

$$(xy)^{-1} = (x + y)^{-1}(x^{-1} + y^{-1}) \tag{35}$$

in order to become comparable with the MP components of the energy.

The repeated substitution of the CC amplitudes corresponds to the iterative solution of the CCD equations. In the kth iteration, the amplitude $a_d^{(k)}(\text{CCD})$ is given by

$$a_d^{(k)}(\text{CCD}) = \lambda(E_0 - E_d)^{-1}V_{d0} + \lambda(E_0 - E_d)^{-1}$$

$$\times \left[\sum_{d_1}^{D} \bar{V}_{dd_1}a_{d_1}^{(k-1)} + \sum_{d_1 d_2}^{D} \left\langle \Phi_d | \hat{V} | \tfrac{1}{2}\hat{t}_{d_1}\hat{t}_{d_2}\Phi_0 \right\rangle \right.$$

$$\left. \times a_{d_1}^{(k-1)}a_{d_2}^{(k-1)} - \sum_{d_1}^{D} V_{0d_1}a_{d_1}^{(k-1)}a_d^{(k-1)} \right]. \qquad (36)$$

Accordingly, $a_d^{(1)}$ is expanded to first order

$$a_d^{(1)} = \lambda(E_0 - E_d)^{-1}V_{d0} = \lambda C_{1,d}^{(1)} \qquad (37)$$

and $a_d^0 = 0$. The energy $E_{\text{corr}}^{(1)}$ is given in the first iteration step by

$$E_{\text{corr}}^{(1)} = \lambda \sum_{d}^{D} \left\langle \Phi_0 | \hat{V} | \Phi_d \right\rangle a_d^{(1)} = \lambda^2 E(\text{MP2}). \qquad (38)$$

In the second iteration step ($k = 2$) one gets

$$a_d^{(2)} = \lambda C_{1,d}^{(2)} + \lambda^2 C_{2,d}^{(2)} + \lambda^3 C_{3,d}^{(2)} \qquad (39)$$

with the coefficients $C_{i,d}^{(2)}$ given by

$$C_{1,d}^{(2)} = C_{1,d}^{(1)} \qquad (40a)$$

$$C_{2,d}^{(2)} = (E_0 - E_d)^{-1} \sum_{d_1}^{D} \bar{V}_{dd_1}C_{1,d_1}^{(1)} \qquad (40b)$$

$$C_{3,d}^{(2)} = (E_0 - E_d)^{-1} \left[\sum_{d_1 d_2}^{D} \left\langle \Phi_d | \hat{V} | \tfrac{1}{2}\hat{t}_{d_1}\hat{t}_{d_2}\phi_0 \right\rangle C_{1,d_1}^{(1)}C_{1,d_2}^{(1)} \right.$$

$$\left. - \sum_{d_1}^{D} V_{0d_1}C_{1,d_1}^{(1)}C_{1,d}^{(1)} \right]. \qquad (40c)$$

Hence, E_{corr} is expanded up to fourth order

$$E_{\text{corr}}^{(2)} = \lambda^2 E(\text{MP2}) + \lambda^3 E(\text{MP3}) + \lambda^4(E^4(\text{D}) + E^4(\text{Q})). \qquad (41)$$

In the third iteration step ($k = 3$), the amplitudes $a_d^{(3)}$ are expanded up to seventh order

$$a_d^{(3)} = \sum_{n=1}^{7} \lambda^n C_{n,d}^{(3)} \qquad (42)$$

with

$$C_{1,d}^{(3)} = C_{1,d}^{(1)} \tag{43a}$$

$$C_{n,d}^{(3)} = (E_0 - E_d)^{-1} \sum_{d_1}^{D} \bar{V}_{dd_1} C_{n-1,d_1}^{(2)} \qquad (n = 2, 3, 4) \tag{43b}$$

$$C_{m,d}^{(3)} = (E_0 - E_d)^{-1}$$

$$\times \sum_{i=m-4}^{3} \left[\sum_{d_1,d_2}^{D} \langle \Phi_d | \hat{V} | \tfrac{1}{2} \hat{t}_{d_1} \hat{t}_{d_2} \Phi_0 \rangle C_{i,d_1}^{(2)} C_{m-1-i,d_2}^{(2)} - \sum_{d_1}^{D} V_{0d_1} C_{i,d_1}^{(2)} C_{m-1-i,d}^{(2)} \right]$$

$$(m = 5, 6, 7) . \tag{43c}$$

Hence, for $k = 3$ the correlation energy $E_{\text{corr}}^{(\text{CCD})}$ is expanded up to eighth order

$$
\begin{aligned}
E_{\text{corr}}^{(3)} = {} & \lambda^2 E(\text{MP2}) + \lambda^3 E(\text{MP3}) + \lambda^4 (E^4(\text{D}) + E^4(\text{Q})) \\
& + \lambda^5 (E^5(\text{DD}) + 2E^5(\text{DQ}) + E^5(\text{QQ})(I)) \\
& + \lambda^6 (E^6(\text{DDD}) + 2E^6(\text{DDQ}) + E^6(\text{DQD}) + E^6(\text{QDQ}) + E^6(\text{DQQ})(I) \\
& \quad + E^6(\text{QQD})(I) + E^6(\text{QQQ})(I) + E^6(\text{QHQ})(I)) \\
& + \lambda^7 \left[\sum_{abcd}^{\text{DQ}} E^7(abcd)(J) + E^7(\text{DQHQ})(I) + E^7(\text{QHQD})(I) \right. \\
& \left. \qquad + E^7(\text{QQHQ})(I) + E^7(\text{QHQQ})(I) + E^7(\text{QHHQ})(I) \right] \\
& + \lambda^8 \left[\sum_{abcde}^{\text{DQ}} E^8(abcde)(J) + E^8(\text{DDQHQ})(I) + E^8(\text{DQHHQ})(I) \right. \\
& \qquad + E^8(\text{DQHQQ})(I) + E^8(\text{DQQHQ})(I) + E^8(\text{QHQHQ})(I) \\
& \qquad + E^8(\text{QHHHQ})(I) + E^8(\text{QHHQQ})(I) + E^8(\text{QHHQD})(I) \\
& \qquad + E^8(\text{QHQQQ})(I) + E^8(\text{QHQQD})(I) + E^8(\text{QHQDQ})(I) \\
& \qquad + E^8(\text{QHQDD})(I) + E^8(\text{QQHHQ})(I) + E^8(\text{QQHQQ})(I) \\
& \qquad + E^8(\text{QDQHQ})(I) + E^8(\text{QQHQD})(I) + E^8(\text{QQQHQ})(I) \\
& \left. \qquad + E^8(\text{QDQHQ})(I) + E^8(\text{QHOHQ})(I) \right] , \tag{44}
\end{aligned}
$$

with a, b, c, d, and e running over all possible combinations of D and Q excitations. The (J) indicates that some of the later terms are contained only partially.

At the kth iteration step, the CCD amplitude and energy contain perturbation contributions up to the order 2^k and $2^k - 1$, respectively. In the way the CCD iterations proceed, the CCD correlation energy is expanded to higher and higher orders. Since 2^k increases much faster than k, fast convergence of the CCD correlation energy is guaranteed.

Similar expansions as described for CCD can be carried out for the QCISD, CCSD, and CCSDT correlation energy and the corresponding S, D, and T amplitudes. The expansions for the various methods differ in so far as the expansion coefficients are different and different orders of perturbation theory are reached at a given iteration step. Common to all methods is that the highest order n of the energy contribution $E^n(ABC..)$ to E_{corr} increases rapidly with the number of iteration steps k and that E_{corr} converges faster than the S, D, and T amplitudes.

Formulas for the expansion of the CCSD correlation energy E_{corr} up to sixth-order perturbation theory have been worked out [36]. From these formulas, the corresponding expansions for the QCISD correlation energy as well as the other CC- and QCI-based correlation energies considered here can easily be derived. Results of the perturbation analysis for CCD, CCSD, QCISD, CCSD(T), QCISD(T), CCSD(TQ), QCISD(TQ), and CCSDT are summarized in Scheme IV, which complements Scheme III. In Scheme IV, the sixth-order analysis is given in three steps (Scheme IVa, IVb, IVc) according to the dissection of the SDTQPH space discussed above.

Inspection of Schemes III and IV leads to the following conclusions:

(1) CC and QCI methods that contain the same type of excitations are equivalent up to fourth-order perturbation theory, i.e., they contain the same energy contributions arising from S, D, T, or Q excitations.

(2) CC and QCI differ at fifth order. CCSD has in addition to the terms contained at QCISD a TS and partially a TQ contribution. CCSD(T) differs from QCISD(T) by just the partial TQ term because QCISD(T) contains the TS term.

(3) CCSDT should be substantially better than both CCSD(T) and QCISD(T) because at fifth order it only lacks the QT term (QQ is partially contained). Contrary to CCSD(T) and QCISD(T), it contains a TT coupling term, which prevents the method from overestimating T effects.

(4) CCSD(TQ) and QCISD(TQ) are methods exact at fifth order [7]. These methods seem to be better than CCSDT, but this is only true if the analysis is terminated at MP5 (see below).

(5) At sixth order, QCI and CC methods are equivalent in the SDQ space, i.e., with regard to those energy terms that contain just S, D, and Q effects. None of the methods investigated is fully correct in the SDQ space because the DQQ, QQD, and QQQ contributions are covered just partially.

(6) Differences between QCI and CC arise solely from T effects at MP6. Table IV gives an analysis of sixth-order T contributions contained in the various QCI and CC methods.

From points (1)–(6) it becomes clear that QCI and CC methods should yield similar results in all those cases, in which T effects do not play an important role. However, if T effects become important, then CC should be superior to QCI. Table IV reveals that CCSD covers (at least partially) one-third of the T contributions at sixth order while QCISD contains just 4 out of the 33 T terms in the SDTQ space.

If T excitations are handled in a noniterative way at the CCSD(T) and QCISD(T) level of theory, then the differences between the two methods are somewhat reduced. However, there remains a major difference arising from T,T coupling terms (see

a) SDQ space

12 (17)

	CCD	QCISD	CCSD	QCISD(T)	CCSD(T)		QCISD(TQ)	CCSD(TQ)	CCSDT	CCSDT(QQ)
SSS		yes	yes	yes	yes		yes	yes	yes	yes
SSD, DSS		y, y	y, y	y, y	y, y		y, y	y, y	y, y	y, y
SDS		yes	yes	yes	yes		yes	yes	yes	yes
SDD, DDS		y, y	y, y	y, y	y, y		y, y	y, y	y, y	y, y
SDQ, QDS		y, y	y, y	y, y	y, y		y, y	y, y	y, y	y, y
DSD		yes	yes	yes	yes		yes	yes	yes	yes
DDD	yes	yes	yes	yes	yes		yes	yes	yes	yes
DQD	yes	yes	yes	yes	yes		yes	yes	yes	yes
DDQ, QDD	y, y	y, y	y, y	y, y	y, y		y, y	y, y	y, y	y, y
DQQ, QQD	(y), (y)	(y), (y)	(y), (y)	(y), (y)	(y), (y)		y, y	y, y	(y), (y)	y, y
QDQ	yes	yes	yes	yes	yes		yes	yes	yes	yes
QQQ	(yes)	(yes)	(yes)	(yes)	(yes)		(yes)	(yes)	(yes)	(yes)

b) T space

20 (33)

	CCD	QCISD	CCSD	QCISD(T)	CCSD(T)		QCISD(TQ)	CCSD(TQ)	CCSDT	CCSDT(QQ)
STS		yes	yes	yes	yes		yes	yes	yes	yes
STD, DTS		-, y	y, y	y, y	y, y		y, y	y, y	y, y	y, y
STQ, QTS		(y), (y)	(y), (y)	(y), (y)	(y), (y)		(y), (y)	(y), (y)	y, y	y, y
DTD				yes	yes		yes	yes	yes	yes
DTQ, QTD			(y), -		(y), -		y, y	y, y	y, -	y, y
QTQ		(yes)	(yes)	(yes)	(yes)		(yes)	(yes)	(yes)	(yes)
SST, TSS		-, y	y, y		y, y		y, y	y, y	y, y	y, y
SDT, TDS			y, y		y, y		y, y	y, y	y, y	y, y
STT, TTS			-, (y)		-, (y)		y, y	y, (y)	y, y	y, y
DST, TSD			-, y		y, y		y, y	y, y	y, y	y, y
DDT, TDD			y, y		y, y		y, y	y, y	y, y	y, y
DQT, TQD			-, (y)		-, (y)		y, y	y, y	-, y	y, y
DTT, TTD							y, y	y, y	y, y	y, y
TDQ, QDT				y, y	y, y		y, y	y, y	y, y	y, y
TQQ, QQT			(y), -		(y), -		(y), (y)	(y), (y)	(y), -	(y), (y)
TTQ, QTT			(y), -		(y), -			(y), -	y, -	y, y
TST									yes	yes
TDT									yes	yes
TQT										yes
TTT									yes	yes

c) PH space

4 (5)

	CCD	QCISD	CCSD	QCISD(T)	CCSD(T)		QCISD(TQ)	CCSD(TQ)	CCSDT	CCSDT(QQ)
QPQ									(yes)	(yes)
QHQ	(yes)	(yes)	(yes)	(yes)	(yes)		(yes)	(yes)	(yes)	(yes)
TPQ, QPT									(y), (y)	(y), (y)
TPT									yes	yes

Scheme IV. Energy contributions to various CC and QCI methods at sixth-order perturbation theory. The energy terms are characterized by the appropriate excitations given in the center between the two diagrams. A yes or y denotes that the term in question is fully contained, (yes) or (y) that the term is partially contained. (a) SDQ space, (b) T space [41], and (c) PH space.

TABLE IV.   Sixth-order triple contributions at QCI and CC.

Method	T-contributions[a]		T, T coupling terms[b]		
	Number	%	TAT	TTA	TTT
QCISD	4 (3)	12 (9)	—	—	—
CCSD	12 (8)	36 (24)	—	(2)	—
QCISD(T)	17 (3)	51 (9)	—	—	—
CCSD(T)	22 (8)	66 (24)	—	(2)	—
QCISD(TQ)	27 (5)	82 (15)	—	4	—
CCSD(TQ)	28 (7)	85 (21)	—	5 (2)	—
CCSDT	28 (2)	85 (6)	3	5	1
CCSDT(QQ)	33 (3)	100 (10)	4	6	1
Total	33	100	4	6	1

[a] The total number of triple contributions arising from a coupling with S, D, Q excitations is given where symmetric terms such as *ABC* and *CBA* are counted separately. In parentheses, the number of those T contributions is given, which are only contained partially. These numbers are also given in percents with regard to the total number of T contributions in SDQ space.

[b] The number of terms with indirect (TST, TDT, TQT, TPT) or direct T, T coupling (TTS, STT, TTD, DTT, TTQ, QTT, and TTT) are given. Those terms, which are only partially, are given in parentheses.

Table IV and Scheme IV). While both CCSD and CCSD(T) contain (at least partially) two terms that account for T,T coupling, the corresponding QCI methods do not. This means that T effects are exaggerated at the QCI, in particular at the QCISD(T) level of theory.

Noniterative inclusion of Q excitations leading to CCSD(TQ) and QCISD(TQ) [7] decreases the difference between CC and QCI even more. Both methods contain the greater part of all T contributions, differing mainly in the TTQ term. Furthermore, both methods account in a similar way for T,T coupling effects (see Table IV and Scheme IV). Hence, at sixth order the two methods can be considered to be equivalent [38].

CCSDT is the first of the CC and QCI methods that also contains the TTT contribution at sixth order. Furthermore, it covers 28 of the 33 T contributions in SDTQ space. Apart from this it accounts for effects arising from P excitations (QPQ, TPQ, QPT, and TPT, see Scheme IV). Therefore, CCSDT is clearly better at sixth order than any of the other methods discussed so far.

The perturbation analysis carried out up to sixth order provides a basis for a distinction between the different methods. If molecules are to be investigated for which T effects are important, more accurate descriptions can be expected in the following order

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

In the same direction, the exaggeration of T effects is reduced. In other words, MP4 results should be handled with care since they are definitely exaggerating T
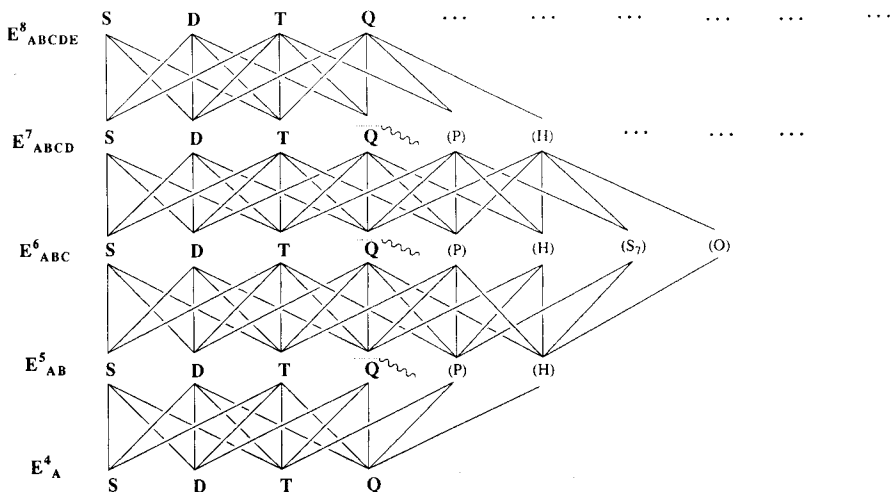
Energy Contributions at MPn

Figure 2. Graphical representation of all energy contributions at nth-order MP perturbation theory (n = 4, 5, 6, 7, and 8). A particular energy contribution $E^n_{ABC..}$ 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 nth-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 to the right of the scheme.

effects in the correlation energy. This, of course, is well known [15,16,42]. However, less known is the fact that QCISD(T) also exaggerates to some extent T effects since coupling between T excitations is not covered by QCISD(T) at fifth- or sixth-order perturbation theory.

From the analysis given in Scheme IV, it becomes also clear that CCSDT is not correct at sixth order. It is the question whether a noniterative improvement of CCSDT, for example by Q excitations [39] according to

$$\Delta E_Q(\text{CCSDT}) = \sum_{uv}^{DT} \sum_q^{Q} \sum_t^{T} a_u V_{uq}(E_0 - E_q)^{-1} V_{qt}(E_0 - E_t)^{-1} \bar{V}_{tv} a_v \qquad (45)$$

leads to a new method that is correct in sixth order. Therefore, we have extended our analysis to CCSDT(Q). CCSDT(Q) contains at fifth order the QT term fully, but it is still lacking part of the QQ term. This, however, can be explicitly included in the same way as done for CCSD + TQ*(CCSD) [35] or CCSD(TQ) [7]. Hence, CCSDT(QQ) would be fully correct in fifth order [39]. In sixth order, CCSDT(Q) contains all 36 energy contributions but some of them are included only partially. This is true both with regard to the SDQ, the T, and the PH space. CCSDT(QQ) contains some more terms at sixth order (e.g., DQQ and QQD fully), but it is also not fully correct at sixth order (see Schemes IVa,b,c).
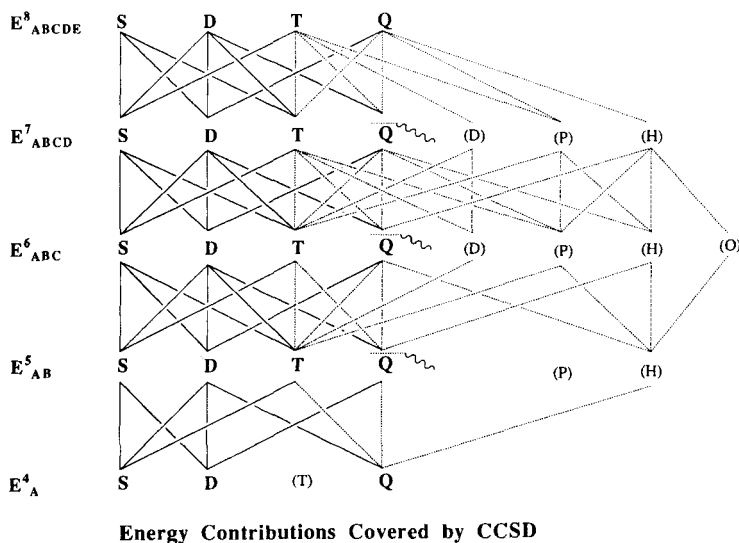
E^8_{ABCDE} S   D   T   Q

E^7_{ABCD} S   D   T   Q   (D)   (P)   (H)

E^6_{ABC} S   D   T   Q   (D)   (P)   (H)   (O)

E^5_{AB} S   D   T   Q   (P)   (H)

E^4_A S   D   (T)   Q

Energy Contributions Covered by CCSD

Figure 3. Graphical analysis of energy contributions at nth-order MP perturbation theory (n = 4, 5, 6, 7, and 8) covered by the CCSD correlation energy. See explanations given for Figure 2. Note that solid (dashed) lines denote energy terms fully (partially) contained in the CCSD correlation energy.

To get a method that is correct in sixth order, one has to include P and H excitations, thus leading to CCSDT(QPH). With the P excitations, all but the QHQ term are obtained fully. Hence, CCSDT(QP) is not fully correct at sixth order and, therefore, one has to go to CCSDT(QPH). Of course, CCSDT(QPH) will be as expensive as MP6 since it will require iterative N^8 steps and in addition a N^9 dependence.

Analysis of Infinite-Order Effects at the CC and QCI Level of Theory

A perturbation analysis at higher orders than n = 6 becomes too difficult and, therefore, it is advisable to investigate higher-order and infinite-order effects in a different way. In Figure 2, the various energy contributions at nth-order perturbation theory are displayed in a graphical way. At each order (given by the rows in the diagram), the term $E^n(ABC...)$ with A, B, C, etc. referring to S, D, T, etc., excitations denotes which interactions have to be considered. However, at the nth-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 to the right of the scheme.

A particular energy contribution $E^n(ABC..)$ is given by the solid line that starts at A in the E^n row and connects B, C, etc., at $n - 1$, $n - 2$, etc. until $n = 4$ is reached. For $E^5(AB)$, there are 14 paths starting from S, D, T, or Q, that correspond to the 14 possible energy contributions to the MP5 energy. Similarly, there are 55
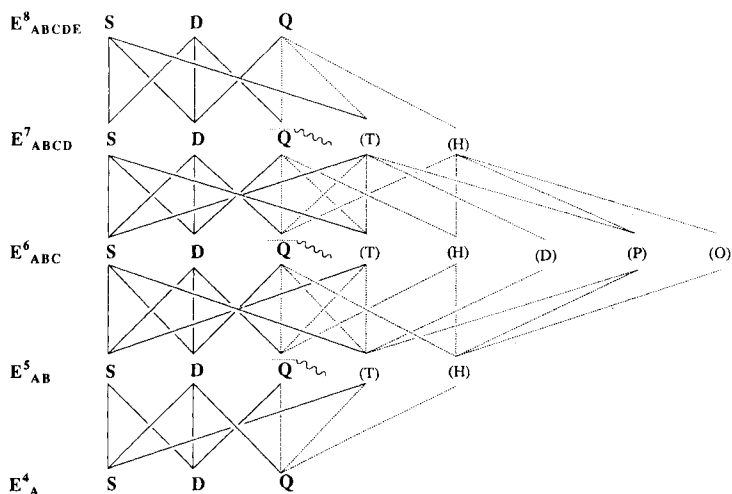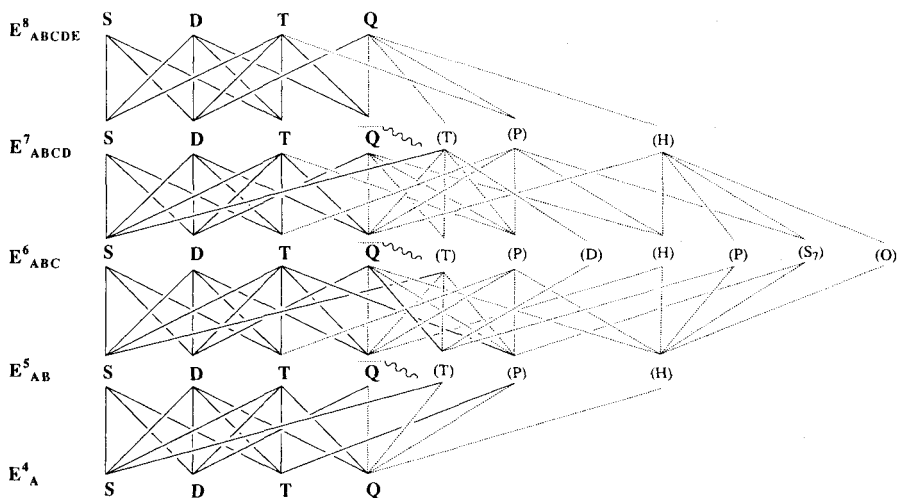
Energy Contributions Covered by QCISD

Figure 4.   Graphical analysis of energy contributions at nth-order MP perturbation theory
(n = 4, 5, 6, 7, and 8) covered by the QCISD correlation energy. See explanations given
for Figure 2. Note that solid (dashed) lines denote energy terms fully (partially) contained
in the QCISD correlation energy.

different E^6(ABC) paths and 221 different E^7(ABCD) paths that start at S, D, T, or
Q for n = 6 and n = 7. Of these, some paths are equivalent due to symmetry leading
to a total of 36 (n = 6) and 141 (n = 7) unique energy contributions as shown in
Scheme II. Hence, the extension of Figure 2 to higher n leads to an easy dissection
of MPn energies.

Using similar graphical representations as the one shown in Figure 2, the expan-
sion of CC and QCI methods in terms of orders of perturbation theory can easily be
visualized. In Figures 3, 4, and 5, the corresponding diagrams for QCISD, CCSD, and
CCSDT are shown. In these diagrams, terms that are fully contained at a particular
order of perturbation theory are given by solid lines, and those, which are only
partially contained, are given by dashed lines.

Figures 3 and 4 indicate that both CCSD and QCISD are correct at any order of
perturbation theory 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 the
same way, CCSDT is correct at all orders within the truncated configuration space
of S, D, and T excitations (see Fig. 5). This, of course, is trivial since it just reflects
the nature of the coupled cluster ansatz [17,18]. More important is that for both
CCSD and QCISD, infinite-order effects are also covered in the SDQ space with just
the A...QQ terms being partial. Hence, it is a general observation that CC and QCI
methods are equivalent with regard to infinite-order effects in the SDQ configuration

Energy Contributions Covered by CCSDT

Figure 5. Graphical analysis of energy contributions at nth-order MP perturbation theory (n = 4, 5, 6, 7, and 8) covered by the CCSDT correlation energy. See explanations given for Figure 2. Note that solid (dashed) lines denote energy terms fully (partially) contained in the CCSDT correlation energy.

space. Since disconnected H excitations are introduced at MP6 by coupling with the Q excitations, it is also true that CC and QCI are equivalent with regard to infinite-order effects in the SDQH space or in general any SDQHO(8)..X space where X excitations are generated from cluster operators $\hat{T}_2^m$.

The major difference between QCISD and CCSD is in the SDTQ space (compare with Figs. 3 and 4). While in CCSD a considerable number of contributions including T effects is contained up to infinite order either partially or even fully, QCISD covers only some of the E^n(A..T...B) contributions. However, there are no terms E^n(T...S), E^n(T...D), E^n(T...T), or E^n(T...Q), that are (fully or partially) contained in CCSD. For CCSD T effects first come in at fifth order, while for QCISD they are first introduced at sixth order. As a consequence, one obtains with CCSD T,T or T,T,T coupling terms always one order of perturbation theory earlier (n = 6, n = 7) than with QCISD (n = 7, n = 8). Further differences with regard to higher excitations such P, S(7), etc., arise from coupling with T excitations. For example, TP...A terms appear in CCSD already at MP7 while for QCISD they are introduced at MP8.

The differences between CCSD and QCISD in the SDTQ configuration space are summarized in Tables V and VI, where the number of energy terms arising from the various excitations are given up to eighth order of perturbation theory. There are 2(1), 6(4), 26(20), and 97(82) terms E^n(T... A) (including TP terms) that are (partially) covered by CCSD at nth-order perturbation theory with n = 5, 6, 7, and 8. However, none of these energy contributions is included at the QCISD level. The

TABLE V.   Energy contributions resulting from specific excitations covered by QCISD, CCSD, and CCSDT at MPn with n = 5, 6, 7, and 8.[a]

Order		QCISD			CCSD			CCSDT			
		S	D	Q	S	D	Q	S	D	T	Q
5	S	1	1	—	1	1	—	1	1	1	—
	D	1	1	1	1	1	1	1	1	1	1
	T	—	—	—	1	—	1 (1)	1	1	1	1
	Q	—	1	1 (1)	—	1	1 (1)	—	1	—	1 (1)
6	S	3	2	2 (1)	3	2	2 (1)	3	3	3	2
	D	2	3	2 (1)	3	3	3 (2)	3	4	3	3 (1)
	T	—	—	—	2 (1)	2 (1)	2 (2)	3	4	4	4 (2)
	Q	2 (1)	2 (1)	4 (3)	2 (1)	2 (1)	4 (3)	2	2 (1)	2 (1)	5 (4)
7	S	7 (1)	7 (1)	6 (4)	8 (1)	7 (1)	7 (5)	9	11	10	9 (3)
	D	7 (1)	7 (1)	8 (5)	10 (2)	9 (2)	11 (8)	11	13 (1)	12 (1)	14 (7)
	T	—	—	—	9 (6)	6 (4)	11 (10)	12 (1)	15 (3)	14 (3)	18 (11)
	Q	6 (4)	8 (5)	10 (9)	8 (5)	8 (5)	13 (12)	8 (5)	11 (7)	9 (6)	17 (15)
8	S	23 (8)	20 (6)	25 (19)	27 (9)	22 (7)	29 (23)	32 (1)	39 (4)	36 (4)	42 (21)
	D	20 (6)	22 (7)	24 (18)	35 (14)	30 (12)	42 (35)	40 (6)	50 (11)	45 (10)	58 (36)
	T	—	—	—	31 (24)	26 (20)	40 (38)	46 (12)	59 (19)	54 (18)	75 (55)
	Q	25 (19)	24 (18)	38 (35)	33 (25)	29 (22)	50 (47)	37 (26)	45 (33)	42 (31)	75 (68)

[a] The entry $k(l)$ indicates that l of the k energy terms are only partially included.

number of terms covered by QCISD (see Table VI) decreases rapidly from about 50% to 24% at MP8, while at the same time the percentage of those terms that are covered only partially strongly increases from 14% to about 60%. Similar trends can be observed for CCSD (Table VI). However, at MP8, CCSD covers still 40% of the energy contributions. Obviously, as the difference between the two methods becomes the larger, the larger the order of perturbation theory is. This can be visualized by inspection of Figure 6, where the numbers given in Table VI are plotted against the order n. We conclude that CCSD and QCISD differ strongly with regard to infinite-order effects.

Figures 4 and 5 and Table V confirm the superiority of CCSDT with regard to both CCSD and QCISD. TT and partially QQ coupling terms are covered by CCSDT at all orders starting at n = 5. Therefore, CCSDT represents a significant improvement with regard to CCSD, CCSD(T), and QCISD(T). Furthermore, Figure 6 and Table VI reveal that CCSDT is the only method that comes close to a complete method covering all infinite-order effects. Of course, some of the terms given in Figure 6 are only partially contained (see Fig. 5 and Tables V and VI), but this number increases much more slowly than for CCSD and QCISD.

The analysis given here for QCISD, CCSD, and CCSDT can be extended to methods with noniterative improvements by higher excitations [36]. Results of such an analysis confirm that the differences between QCI and CC decrease when apart from

TABLE VI. Number of energy contributions covered by QCISD, CCSD, and CCSDT at MPn with n = 5, 6, 7, and 8.[a]

Order	Total	QCISD	CCSD	CCSDT
5	14	7 (1)	9 (2)	13 (1)
		50 (14)	64 (22)	93 (8)
6	55	22 (7)	30 (12)	50 (9)
		40 (32)	54 (40)	91 (18)
7	221	66 (31)	107 (61)	193 (63)
		30 (47)	48 (57)	87 (33)
8	915	221 (136)	394 (276)	774 (355)
		24 (62)	43 (70)	85 (46)

[a] Total gives the total number of energy contributions at MPn (not considering symmetry) (compare with Scheme II). For each method the first entry $k(l)$ gives the number k of energy terms contained at MPn of which l are only partially contained. The second entry $p(q)$ gives k in percent with regard to the total number and, in addition, specifies by q how many percent of the k energy terms are partially covered.

T also Q corrections are included [36]. However, both CCSD(TQ) and QCISD(TQ) are inferior to CCSDT, even though they seem to be better at MP5 (see Scheme III).

While it is straightforward to analyze infinite-order effects of CC and QCI methods in this way, the question remains whether energy contributions at higher orders are large enough to decrease the correlation energy significantly. This will not be the case if the molecule considered is small. However, with increasing size of the molecule, higher-order effects will become more and more important. Also, the large number of energy contributions at higher orders will lead to a substantial addition to the correlation energy.

Conclusion

It has been shown that the MP6 energy can be expressed in terms of 36 partial contributions arising from S, D, T, Q, P, and H excitations. Each of these partial contributions is size-consistent (size-extensive). An analysis of CC and QCI methods in terms of MP6 leads to the following conclusions.

(1) If one assumes that S, D, Q, and H, etc., excitations describe essentially orbital relaxation and electron pair correlation effects, then all these effects are similarly described by CC and QCI methods. For a relatively small closed-shell molecule with just single bonds one may encounter only these correlation effects. In this case, QCISD is the method of choice, because it is somewhat simpler to carry out than CCSD.

(2) For larger molecules and for molecules with distinct T effects, CCSD should perform significantly better than QCISD, because it covers (contrary to QCISD) a
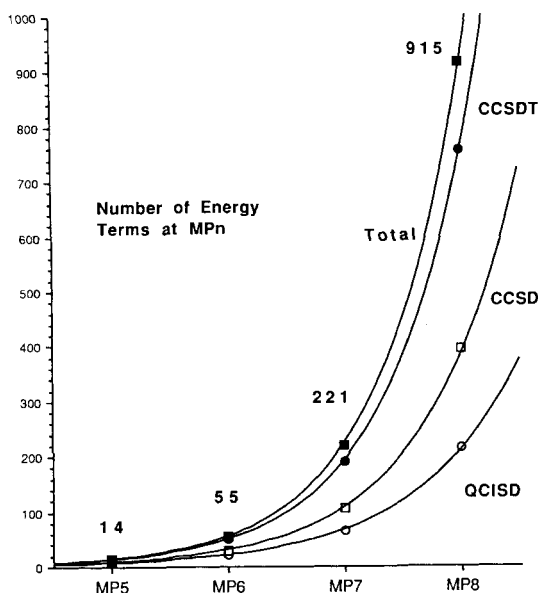
Figure 6.   Number of energy contributions E^n(ABC..) covered by QCISD, CCSD, and CCSDT at MPn. Numbers are given without considering symmetry.

considerable number of higher-order T effects including important T,T coupling effects.

(3) A noniterative improvement of QCISD by T excitations is more important for QCISD than CCSD. Nevertheless, CCSD(T) should still perform much better than QCISD(T), because the latter method does not contain important T,T coupling terms. As a consequence, QCISD(T) exaggerates T effects, which has to be considered in calculations of molecules.

(4) The difference between QCI and CC is considerably decreased at the CCSD(TQ) and QCISD(TQ) level of theory. Both methods should perform similarly in calculations.

(5) CCSDT is clearly better than CCSD(TQ) and QCISD(TQ) at higher orders of perturbation theory, even though this seems to be not the case at MP5 (Scheme III). Furthermore, CCSDT is the only method among those investigated that comes reasonably close to covering all important infinite order effects (see Fig. 6).

(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, the overestimation of T effects is reduced.

(7) To make CCSDT correct at sixth order it has to be extended to CCSDT(QPH), which is an iterative $O(N^8)$ method with a $O(N^9)$ dependence.

Acknowledgments

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[39] Various ways of including Q excitations at the CCSDT level have been first suggested in Ref. 34. See also Ref. 36.

[40] Note that CCSD(TQ) and QCISD(TQ) but not CCSDT contain the DDQ and QQD terms since in the former methods one explicitly corrects for the QQ term at fifth order, which as a consequence leads to DQQ and QQD at sixth order.

[41] Note that the TTS term is only partially covered by CCSD(TQ). This is a direct consequence of setting x (Ref. 7) equal to 2 for QCISD(TQ) but to 1 for CCSD(TQ).

[42] J. A. Pople, M. Head-Gordon, and K. Raghavachari, Int. J. Quantum Chem. Symp. **22**, 377 (1988).