



Size-extensive quadratic CI methods including quadruple excitations: QCISDTQ and QCISDTQ(6) – On the importance of four-electron correlation effects

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Abstract

Size-extensive Quadratic CI with single (S), double (D), triple (T), and quadruple (Q) excitations (QCISDTQ) and its non-iterative extension to a method correct at sixth-order perturbation theory, QCISDTQ(6), are developed and applied to electronic systems, for which full CI (FCI) results are available. It is shown that QCISDTQ results are more accurate than either QCISDT or CCSDT. In particular, QCISDTQ(6) correlation energies differ from FCI correlation energies on the average by just 0.04 mhartree. The improvement is caused preferentially by the balanced addition of connected and disconnected four-electron correlation effects, which confirms observations that four-electron correlation effects are important for a balanced description of electron correlation. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Among the electron correlation effects that are included into correlated ab initio methods to improve the results of Hartree–Fock (HF) theory, two- (pair) and three-electron correlation effects are the most important (for a recent review, see Ref. [1]). It is generally assumed that four-electron correlation effects are not important and, accordingly, can be neglected. In recent work by Cremer and He [2,3], it was shown that this assumption seems to be correct for atoms and molecules with well-separated (localized) electron pairs (class-A systems: saturated hydrocarbons, boranes, derivatives of Li, Be, etc. [2]). Using sixth-order many-body perturbation theory

with the Møller–Plesset (MP) perturbation operator (MBPT-6 \equiv MP6) [1,2], which considers correlation contributions from single (S), double (D), triple (T), quadruple (Q), pentuple (P), and hextuple (H) excitations, these authors could show that all connected Q contributions that describe the correlated movement of four electrons at the same time are negligible. However, in the case of electronic systems with strong clustering of electrons in a confined region of atomic or molecular space (class-B systems: electronegative atoms, molecules with multiple bonds, hypervalent or nonclassical bonding, etc. [2]), Q contributions became significant. As a simple example, correlation contributions at MP6 calculated with an cc-pVTZ basis set [4] for the F^- anion are shown in Fig. 1.

While at fifth-order MBPT (MBPT-5 \equiv MP5) the Q contributions DQ, TQ, and QQ are all disconnected describing the independent, but simultaneous

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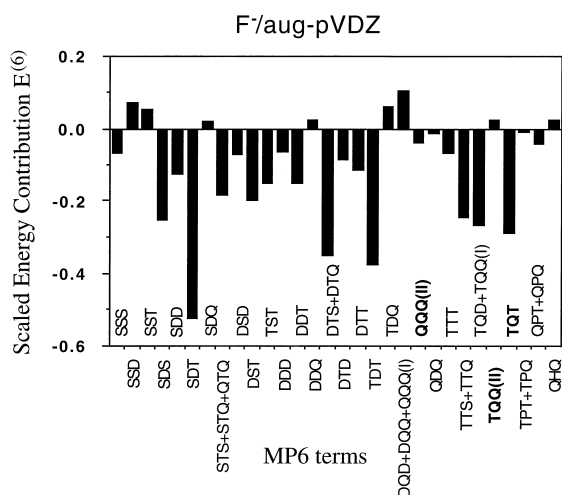


Fig. 1. MP6 spectrum for the F^- anion calculated with a pVTZ basis set. The square root of the sum of squared correlation energy contributions $E_{ABC}^{(6)}$ was used as scaling factor to establish a basis for the comparison with other MP6 results. The MP6 terms are given in the way they are calculated. Terms in bold (QQQ(II), TQQ(II), and TQT) give the correlation contributions arising from connected Q excitations that correspond to four-electron correlation effects.

pair correlations of two electron pairs, at MP6 there are three important contributions (QQQ(II), TQQ(II), TQT), which involve connected four-electron correlation effects (QQQ(I), TQQ(I), DQQ, DQQ, TTQ, TQD cover the corresponding disconnected four-electron contributions) [2,3]. Fig. 1, which gives the relative magnitude of MP6 correlation contributions and which is typical of the MP6 results for a class-B system, reveals that the connected Q correlation contributions are predominantly negative (stabilizing) and amount to $\sim 10\%$ of the total correlation contribution at MP6, which if neglected would lead to ~ 0.3 kcal/mol error per electron pair in energy comparisons involving both class-A and -B systems.

Clearly, with the number of electrons clustering in a confined area of atomic or molecular space, four-electron correlation effects are no longer negligible and it is desirable to have some theory to estimate their contributions. This is of particular importance in configuration interaction (CI) theory where the Q contributions represent the most important contribution to correct CI for its size-extensivity error (for a recent review, see Ref. [5]).

MP6 theory is probably the easiest way to get a description of four-electron correlation effects [2].

However, MP results for class-B systems are known to oscillate with the order of perturbation applied [2,7]. At lower orders this is known to result from an exaggeration of pair correlation effects but also three-electron correlation effects can be exaggerated so that one cannot exclude a similar exaggeration for connected Q contributions. Alternatively, one could carry out CI calculations with S, D, T, Q excitations (CISDTQ) where the possibility exists to reduce the calculational work by deleting many of the (A, T) and (A, Q) off-diagonal elements of the CI matrix ($A = S, D, T, Q$) as was recently demonstrated by Sychrovský and Čársky [6]. In this way rather accurate energies are obtained, which do not suffer any longer so much from the size-extensivity error of CI theory [5].

However, the best account of correlation effects is provided by Coupled Cluster (CC) theory since CC theory is size-extensive and includes, contrary to MBPT and CI, infinite order effects [8]. CCSD, CCSD(T), and CCSDT are well-established in the repertoire of correlation corrected ab initio methods [8]. Even CCSDTQ [9–11] was developed and exploratory calculations for few small molecules were reported. The price for the high accuracy of the CCSDTQ approach is its enormous calculational cost which scale with $N_{\text{iter}} M^{10}$ (M : number of basis functions; M^8 to calculate the Q matrix elements; M^2 to calculate CC amplitudes a) where N_{iter} gives the number of CC iterations needed for getting self-consistent CC amplitudes. Any time, Q excitations are fully included in a self-consistent way, the M^{10} working-load cannot be avoided and, therefore, one has to focus on reducing the number of M^{10} terms or keeping the number of iterations to a minimum.

Pople and co-workers [12] developed quadratic CI theory with S and D (QCISD) and a perturbative inclusion of T excitations (QCISD(T)) as a size-extensive improvement of CI theory and, accordingly, as an approximation to CCSD and CCSD(T). Due to some error cancellation and (some minor) reduction of calculational cost [13], QCISD and QCISD(T) are frequently used as substitutes for the more correct CC methods. The non-perturbative inclusion of T excitations into QCI theory as suggested by Pople and co-workers turned out to be no longer size-extensive [14] and, therefore, Cremer and He [15] developed a connected QCI theory in which the

original QCI concept is systematically extended to size-extensive QCISDT, QCISDTQ, etc., no longer considering this theory as an improvement of the corresponding CI methods, but simply using QCI as a simple approximation to the more correct CC method.

QCISDT was implemented by He and co-workers [16,17] and it was found that QCISDT energies favorably approach the corresponding CCSDT values offering at the same time two important advantages: (i) QCISDT is easier to program since it contains less cluster terms; and (ii) calculation of the QCI amplitudes, although a $O(M^8)$ procedure, is cheaper than a CCSDT calculation because of the smaller number of cluster terms and a somewhat faster convergence of the cluster amplitudes.

Because of the positive experience with QCISDT, we extend in this work QCI theory to the QCISDTQ level where three goals should be accomplished: (a) a faster converging and easier to program alternative to CCSDTQ should be established; (b) available MP6, QCISDT and CCSDT results should be checked with a CC method containing Q excitations; and (c) the importance of connected four-electron correlation effects established with the help of MP6 calculations should be verified with a Q-containing method that also includes infinite order effects.

In the following, we will present QCISDTQ by first developing the basic theory (Section 2). Then, we will extend QCISDTQ to a new method that is correct at sixth order perturbation theory (Section 3). Finally, in Section 4, we will present results of benchmark calculations that make it possible to test the usefulness of QCISDTQ and to discuss the importance of four-electron correlation effects.

2. Quadratic CI theory with S, D, T, and Q (QCISDTQ)

The QCI methods can be described as CC methods, for which only the cluster operators \hat{T}_n :

$$\hat{T}_1 = \sum_i \sum_a a_i^a \hat{b}_a^+ \hat{b}_i, \quad (1)$$

$$\hat{T}_2 = \frac{1}{4} \sum_{ij} \sum_{ab} a_{ij}^{ab} \hat{b}_a^+ \hat{b}_i \hat{b}_b^+ \hat{b}_j, \quad (2)$$

or, in general,

$$\hat{T}_n = \frac{1}{(n!)^2} \sum a^{abc\dots}{}_{ijk\dots} \hat{b}_a^+ \hat{b}_i \hat{b}_b^+ \hat{b}_j \hat{b}_c^+ \hat{b}_k \dots \quad (3)$$

(\hat{b}^+ and \hat{b} : creation and annihilation operators; indices i, j, k, l denote occupied spin orbitals, indices a, b, c, d virtual spin orbitals) and the products $\hat{T}_2 \hat{T}_n$ are considered thus drastically simplifying the CC projection equations [15]. This simplification is based on the fact that pair correlation effects are the most important effects and that higher-order correlation effects introduced by cluster operator \hat{T}_n have to be considered with regard to their coupling to electron pair correlation [1,15]. The projection equations for the hierarchy of size-extensive QCI methods (truncated at level n) are given in Eqs. (4) and (7) in their connected (C) form [15]:

$$\Delta E_{\text{QCI}} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle, \quad (4)$$

$$\langle \Phi_s | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_{\text{C}} = 0, \quad (5)$$

$$\langle \Phi_d | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle_{\text{C}} = 0, \quad (6)$$

$$\langle \Phi_p | \bar{H} \left(\sum_{i=p-1}^{\min[p+2,n]} \hat{T}_i \right) + \hat{T}_2 \hat{T}_p | \Phi_0 \rangle_{\text{C}} = 0$$

$$(n \geq p \geq 3), \quad (7)$$

where \bar{H} denotes the normal-order Hamiltonian,

$$\bar{H} = \hat{H} - E(\text{HF}) = \bar{H}_0 + \bar{V} = \sum_{rs} \{ \hat{b}_r^+ \hat{b}_s \} \langle r | \hat{F} | s \rangle$$

$$+ \frac{1}{4} \sum_{rstu} \{ \hat{b}_r^+ \hat{b}_s^+ \hat{b}_t \hat{b}_u \} \langle rs || ut \rangle, \quad (8)$$

$|\Phi_0\rangle$ the HF reference wavefunction, and s, d, and p are S, D, and general excitation indices. ΔE_{QCI} corresponds to the QCI correlation energy

$$\Delta E_{\text{QCI}} = E(\text{QCI}) - E(\text{HF}). \quad (9)$$

The corresponding QCISDTQ projection equations are obtained by truncating the expansion for the

operator \hat{T} at $n=4$, i.e. to S, D, T, and Q excitations:

$$\Delta E_{\text{QCISDTQ}} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle, \quad (10)$$

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_C = 0, \quad (11)$$

$$\langle \Phi_{ij}^{ab} | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle_C = 0, \quad (12)$$

$$\langle \Phi_{ijk}^{abc} | \bar{H} (\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_2 \hat{T}_3) | \Phi_0 \rangle_C = 0, \quad (13)$$

$$\langle \Phi_{ijkl}^{abcd} | \bar{H} (\hat{T}_3 + \hat{T}_4 + \hat{T}_2 \hat{T}_4) | \Phi_0 \rangle_C = 0. \quad (14)$$

Eqs. (10) and (14) have to be transformed into two-electron integral Eqs. (15) and (19) to obtain QCISDTQ in a form that can be programmed for a computer.

$$\Delta E_{\text{QCISDTQ}} = \frac{1}{4} \sum_{ij, ab} \langle ij || ab \rangle a_{ij}^{ab}, \quad (15)$$

$$(\epsilon_i - \epsilon_a) a_i^a = u_i^a + v_i^a + \sum_{l < m} \sum_{d < e} \langle lm || de \rangle a_{ilm}^{ade}, \quad (16)$$

$$\begin{aligned} & (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) a_{ij}^{ab} \\ &= \sum_P (-1)^P P(a/b) \left[\sum_{l, d < e} \langle bl || de \rangle a_{ijl}^{ade} \right] \\ &+ \sum_P (-1)^P P(i/j) \left[\sum_{l < m, d} \langle lm || dj \rangle a_{ilm}^{abd} \right] \\ &+ \langle ab || ij \rangle + u_{ij}^{ab} + v_{ij}^{ab} + \frac{1}{4} \sum_{cd, kl} \langle kl || cd \rangle a_{ijkl}^{abcd}, \end{aligned} \quad (17)$$

$$\begin{aligned} & (\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c) a_{ijk}^{abc} \\ &= - \sum_P (-1)^P P(i/jk|a/bc) \left[\sum_d X_1(i, d, b, c) a_{jk}^{ad} \right. \\ &+ \sum_l X_2(j, k, l, a) a_{il}^{bc} \left. \right] + \sum_P (-1)^P P(a/bc) \\ &\times \left[\frac{1}{2} \sum_{ef} X_3(b, c, e, f) a_{ijk}^{aef} + \sum_f Y_1(f, a) a_{ijk}^{fbc} \right] \\ &+ \sum_P (-1)^P P(a/bc) \left[\frac{1}{2} \sum_{lde} \langle al || de \rangle a_{ijkl}^{dbce} \right] \end{aligned}$$

$$\begin{aligned} & + \sum_P (-1)^P P(i/jk) \left[\frac{1}{2} \sum_{mn} X_4(m, n, j, k) a_{imn}^{abc} \right. \\ &+ \sum_n Y_2(n, i) a_{njk}^{abc} \left. \right] - \sum_P (-1)^P P(i/jk) \\ &\times \left[\frac{1}{2} \sum_{lmd} \langle lm || id \rangle a_{ljk}^{abcd} \right] \\ &- \sum_P (-1)^P P(i/jk|a/bc) \\ &\times \sum_{me} X_5(m, a, i, e) a_{jkm}^{bce}, \quad (18) \\ & (\epsilon_i + \epsilon_j + \epsilon_k + \epsilon_l - \epsilon_a - \epsilon_b - \epsilon_c - \epsilon_d) a_{ijkl}^{abcd} \\ &= \sum_P (-1)^P P(i/jkl|ab/cd) \\ &\times \left[\sum_e \langle ab || ie \rangle a_{jkl}^{ecd} \right] \\ &+ \sum_P (-1)^P P(ij/kl|a/bcd) \\ &\times \left[\sum_m \langle ma || ij \rangle a_{mkl}^{bcd} \right] \\ &+ \sum_P (-1)^P P(i/jkl|a/bcd) \\ &\times \left[\sum_{me} X_5(m, a, i, e) a_{mjkl}^{ebcd} \right] \\ &+ \sum_P (-1)^P P(ab/cd) \\ &\times \left[\frac{1}{2} \sum_{ef} X_3(a, b, e, f) a_{ijkl}^{efcd} \right] \\ &+ \sum_P (-1)^P P(ij/kl) \\ &\times \left[\frac{1}{2} \sum_{mn} X_4(m, n, i, j) a_{mnkl}^{abcd} \right] \\ &+ \sum_P (-1)^P P(ij/kl|a/bcd) \\ &\times \left[\sum_e Z_1(k, l, b, c, d, e) a_{ij}^{ae} \right] \\ &+ \sum_P (-1)^P P(i/jkl|ab/cd) \end{aligned}$$

$$\begin{aligned}
 & \times \left[\sum_n Z_2(j,k,l,c,d,n) a_{in}^{ab} \right] \\
 & + \sum_P (-1)^P P(a/bcd) \\
 & \times \left[\sum_f Y_1(f,a) a_{ijkl}^{abcd} \right] \\
 & + \sum_P (-1)^P P(i/jkl) \\
 & \times \left[\sum_f Y_2(n,i) a_{ijkl}^{abcd} \right]. \tag{19}
 \end{aligned}$$

The intermediate arrays u_i^a , v_i^a , u_{ij}^{ab} , v_{ij}^{ab} , X_i , Y_i and Z_i appearing in these equations are given in Appendix A.

3. QCISDTQ theory correct at sixth-order MBPT: QCISDTQ(6)

The performance of a particular CC method can be predicted by analyzing which MBPT contributions are covered at a given order [18,19]. The results of such an analysis are given for QCISDT and QCISDTQ as well as the corresponding CC methods at fifth and sixth order in Fig. 2.

According to this analysis, both QCISDT (CCSDT) and QCISDTQ are not correct at fifth order. QCISDTQ corrects QCISDT at fifth order just by the QT term ($E_{QT}^{(5)}$), which actually represents a disconnected Q contribution that is added in the first iteration of the Q projection (Eq. (14)) when all \hat{T}_4 amplitudes are still zero. According to Fig. 2, the

(a)

$E_{AB}^{(5)}$	QCISDT	CCSDT	QCISDTQ	QCISDTQ(6)
SS	yes	yes	yes	yes
DD	yes	yes	yes	yes
TT	yes	yes	yes	yes
QQ	(yes)	(yes)	(yes)	yes
SD,DS	y,y	y,y	y,y	y,y
DQ,QD	y,y	y,y	y,y	y,y
ST,TS	y,-	y,y	y,y	y,y
DT,TD	y,y	y,y	y,y	y,y
TQ,QT		y,-	y,-	y,y

(b)

$E_{ABC}^{(6)}$	QCISDT	CCSDT	QCISDTQ	QCISDTQ(6)
SSS	yes	yes	yes	yes
SSD,DSS	y,y	y,y	y,y	y,y
SDS	yes	yes	yes	yes
SDD,DDS	y,y	y,y	y,y	y,y
SDQ,QDS	y,y	y,y	y,y	y,y
DSD	yes	yes	yes	yes
DDD	yes	yes	yes	yes
DQD	yes	yes	yes	yes
DDQ,QDD	y,y	y,y	y,y	y,y
DQQ,QQD	(y),(y)	(y),(y)	(y),(y)	y,y
QDQ	yes	yes	yes	yes
QQQ	(yes)	(yes)	(yes)	yes
STS	yes	yes	yes	yes
STD,DTS	y,-	y,y	y,-	y,y
STQ,QTS	(y),(y)	y,y	(y),(y)	y,y
DTD	yes	yes	yes	yes
DTQ,QTD		y,-	y,-	y,y
QTQ	(yes)	(yes)	(yes)	yes
SST,TSS	y,-	y,y	y,-	y,y
SdT,TDS	y,y	y,y	y,y	y,y
STT,ITS	y,-	y,y	y,-	y,y
DST,ISD	y,-	y,y	y,-	y,y
DDT,TDD	y,y	y,y	y,y	y,y
DQT,TQD		y,-	y,-	y,y
DTT,ITD	y,y	y,y	y,y	y,y
TDQ,QDT	y,y	y,y	y,y	y,y
TQQ,QQT		(y),-	y,-	y,y
TTQ,QTT		y,-	y,-	y,y
TST		yes		yes
TDT	yes	yes	yes	yes
TQT			yes	yes
TTT	yes	yes	yes	yes
QPQ	(yes)	(yes)	(yes)	yes
QHQ	(yes)	(yes)	(yes)	yes
TPQ,QPT	(y),(y)	(y),(y)	(y),(y)	y,y
TPT	(yes)	yes	(yes)	yes

Fig. 2. Analysis of energy contributions at: (a) fifth-order and (b) sixth-order many-body perturbation theory covered by QCISDT, CCSDT, QCISDTQ, and QCISDTQ(6) correlation energies. Yes or y denote that the particular term(s) shown at the left-hand side of the diagram is (are) fully contained in the correlation energy while (yes) or (y) indicate that the term(s) is (are) only partially covered.

relationship between QCISDT and QCISDTQ is given by Eq. (20):

$$\begin{aligned} \Delta E_{\text{QCISDTQ}} = & \Delta E_{\text{QCISDT}} + \lambda^5 E_{\text{QT}}^{(5)} + \lambda^6 [E_{\text{QTD}}^{(6)} + E_{\text{QTT}}^{(6)} \\ & + E_{\text{QQT}}^{(6)} + E_{\text{TQT}}^{(6)} + E_{\text{DQT}}^{(6)}] + O(\lambda^7). \end{aligned} \quad (20)$$

One can predict that the improvements in going from QCISDT to QCISDTQ are dominated by the QT term, which is known to have normally relatively large positive values (see also Fig. 3) [2]. Hence, absolute QCISDTQ correlation energies could be smaller than the corresponding QCISDT correlation energies. Also, it is certainly not useful to compare MP6 results for four-electron correlations with a method that is not correct at both fifth and sixth order. Therefore, we added to the QCISDTQ method additional terms in a non-iterative manner that make the method correct up to sixth order thus yielding QCISDTQ(6).

$$\Delta E_{\text{QCISDTQ}(6)} = \Delta E_{\text{QCISDTQ}} + \sum_u^9 \Delta E_u(6), \quad (21)$$

with

$$\begin{aligned} \Delta E_1(6) = & \langle \Phi_0 | \hat{T}_2^\dagger \bar{V} \hat{T}_1 \hat{T}_2 | \Phi_0 \rangle_{\text{C}} = \lambda^5 (E_{\text{TS}}^{(5)} + E_{\text{TQ}}^{(5)}(\text{I})) \\ & + \lambda^6 [E_{\text{DTS}}^{(6)} + E_{\text{DTQ}}^{(6)}(\text{I}) + E_{\text{TTS}}^{(6)}(\text{I}) \\ & + E_{\text{TTQ}}^{(6)}(\text{I})_a + E_{\text{TQD}}^{(6)}(\text{I}) + E_{\text{TQQ}}^{(6)}(\text{I})_a \\ & + E_{\text{TSS}}^{(6)} + E_{\text{TSD}}^{(6)} + E_{\text{TPT}}^{(6)}(\text{I}) + E_{\text{TPQ}}^{(6)}(\text{I}) \\ & + E_{\text{TST}}^{(6)}] + O(\lambda^7), \end{aligned} \quad (22)$$

$$\begin{aligned} \Delta E_2(6) = & \langle \Phi_0 | \hat{T}_3^\dagger (\bar{V} \hat{T}_2) | \Phi_0 \rangle_{\text{C}} = \lambda^5 (E_{\text{TQ}}^{(5)}(\text{II})) \\ & + \lambda^6 [E_{\text{DTQ}}^{(6)}(\text{II}) + E_{\text{TQD}}^{(6)}(\text{II}) + E_{\text{TQQ}}^{(6)}(\text{I})_b \\ & + E_{\text{TTQ}}^{(6)}(\text{II})] + O(\lambda^7), \end{aligned} \quad (23)$$

$$\begin{aligned} \Delta E_3(6) = & \langle \Phi_0 | \frac{1}{2} (\hat{T}_2^\dagger)^2 (\bar{V} \hat{T}_2) | \Phi_0 \rangle_{\text{C}} = \lambda^5 (E_{\text{QQ}}^{(5)}(\text{II})) \\ & + \lambda^6 [E_{\text{DQQ}}^{(6)}(\text{II}) + E_{\text{QQQ}}^{(6)}(\text{II})_a + E_{\text{QQD}}^{(6)}(\text{II}) \\ & + E_{\text{QQQ}}^{(6)}(\text{I})_a] + O(\lambda^7), \end{aligned} \quad (24)$$

$$\begin{aligned} \Delta E_4(6) = & \langle \Phi_0 | \hat{T}_2^\dagger \hat{T}_1^\dagger (\bar{V} \hat{T}_2) | \Phi_0 \rangle_{\text{C}} = \lambda^6 [E_{\text{STQ}}^{(6)}(\text{II}) \\ & + E_{\text{QTD}}^{(6)}(\text{II})_a] + O(\lambda^7), \end{aligned} \quad (25)$$

$$\begin{aligned} \Delta E_5(6) = & \sum_q^Q \langle \Phi_0 | (\hat{T}_3^\dagger + \frac{1}{2} (\hat{T}_2^\dagger)^2 \bar{V}) | \Phi_q \rangle \\ & \times (E_0 - E_q)^{-1} \langle \Phi_q | (\bar{V} \hat{T}_2) | \Phi_0 \rangle_{\text{C}} \\ = & \lambda^6 [E_{\text{TQQ}}^{(6)}(\text{II}) + E_{\text{QQQ}}^{(6)}(\text{II})_b] + O(\lambda^7), \end{aligned} \quad (26)$$

$$\begin{aligned} \Delta E_6(6) = & \langle \Phi_0 | \hat{T}_3^\dagger (\bar{V} \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_{\text{C}} = \lambda^6 [E_{\text{TTS}}^{(6)}(\text{II}) \\ & + E_{\text{TTQ}}^{(6)}(\text{I})_b] + O(\lambda^7), \end{aligned} \quad (27)$$

$$\begin{aligned} \Delta E_7(6) = & \sum_t^T \langle \Phi_0 | (\frac{1}{2} (\hat{T}_2^\dagger)^2 \bar{V}) | \Phi_t \rangle \\ & \times (E_0 - E_t)^{-1} \langle \Phi_t | (\bar{V} \hat{T}_2) | \Phi_0 \rangle_{\text{C}} \\ = & \lambda^6 E_{\text{QTD}}^{(6)}(\text{II})_b + O(\lambda^7), \end{aligned} \quad (28)$$

$$\begin{aligned} \Delta E_8(6) = & \langle \Phi_0 | \frac{1}{2} (\hat{T}_2^\dagger)^2 \left[\bar{V} \left(\hat{T}_2 \hat{T}_3 + \frac{1}{3!} \hat{T}_2^3 \right) \right] | \Phi_0 \rangle_{\text{C}} \\ = & \lambda^6 [E_{\text{HQ}}^{(6)}(\text{II}) + E_{\text{QPT}}^{(6)}(\text{II}) + E_{\text{QPQ}}^{(6)}(\text{II})] \\ & + O(\lambda^7), \end{aligned} \quad (29)$$

$$\begin{aligned} \Delta E_9(6) = & \langle \Phi_0 | \hat{T}_2^\dagger (\bar{V} \hat{T}_1 \hat{T}_3) | \Phi_0 \rangle_{\text{C}} = \lambda^6 [E_{\text{QPT}}^{(6)}(\text{I})_b \\ & + E_{\text{QPQ}}^{(6)}(\text{I})_b + E_{\text{QTS}}^{(6)}(\text{I})_b + E_{\text{QTQ}}^{(6)}(\text{I})_b] \\ & + O(\lambda^7). \end{aligned} \quad (30)$$

The computational cost for these additional energy terms scale just with $O(M^7)$, which is negligible in view of the $O(M^{10})$ dependence of QCISDTQ. QCISDTQ(6) should be considerably better than QCISDTQ since it covers all terms up to MP6:

$$\begin{aligned} \Delta E_{\text{QCISDTQ}(6)} = & \Delta E_{\text{QCISDTQ}} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} \\ & + \lambda^4 E^{(4)} + \lambda^5 E^{(5)} + \lambda^6 E^{(6)} + O(\lambda^7). \end{aligned} \quad (31)$$

QCISDTQ was programmed within the ab initio package COLOGNE 99 [20] by adding to an existing QCISDT program [15] the Q equation. QCISDTQ was debugged by checking in the first iteration the QT term obtained from the Q equations with the corresponding result from an MP5 calculation. In a similar test, the TQT term obtained in the second iteration was compared with the TQT term from an

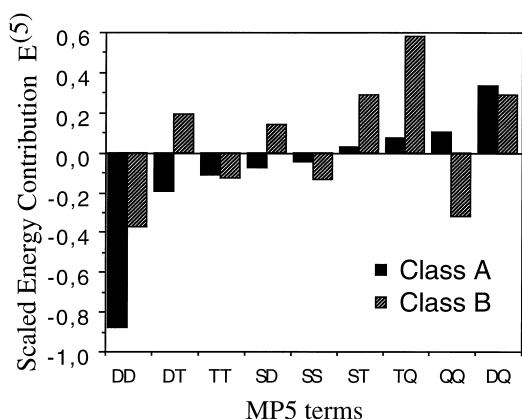


Fig. 3. Average MP5 spectra for 10 class-A and 14 class-B electronic systems [26].

MP6 calculation [2]. Differences between the QCISDTQ terms and the corresponding MP energies were smaller than 10^{-8} which was considered to be a sufficient indication that QCISDTQ results are correct.

The QCISDTQ projection equations are solved in an iterative procedure (steps (1)–(4)):

- (1) initialize a_i^a , a_{ij}^{ab} amplitudes while setting $a_{ijk}^{abc} = 0$, $a_{ijkl}^{abcd} = 0$;
- (2) calculate new a_i^a , a_{ij}^{ab} , a_{ijk}^{abc} and a_{ijkl}^{abcd} amplitudes according to Eqs. (16) and (19);
- (3) check the convergence of a_i^a and a_{ij}^{ab} amplitudes; if they are converged, go to step (4), otherwise back to step (2);
- (4) calculate the energy $\Delta E_{\text{QCISDTQ}}$ and the additional terms $\Delta E_u(6)$.

QCISDTQ converges in about the same number of iterations as QCISDT does. According to theory, the computational cost of QCISDTQ should be larger than those of QCISDT by a factor of M^2 . However, in reality the increase in computer time is just 30% of the expected cost increase.

4. Results and discussion

In this Letter, we present QCISDTQ and QCISDTQ(6) correlation energies for atoms and molecules, for which full CI (FCI) energies are available ([21]; for Ne, see Ref. [22]; for NH_2 , see Ref. [23]; for BH, CH_2 , see Ref. [24]; for H_2O , FH, see Ref. [25]). In the previous study on QCISDT, basis sets and ge-

ometries used in the FCI calculations are described in detail and, therefore, these details are not repeated here [16]. In Table 1, results are compared with QCISD, QCISDT, CCSD, CCSD(T), CCSDT, and FCI energies where for reasons of simplification deviations from FCI correlation energies are listed. Also, an error analysis in terms of mean and standard deviation of calculated QCI and CC energies from the corresponding FCI results is given in Table 1. While this first comparison is limited to ground and some excited states in their equilibrium geometry, in Table 2, similar data are collected for electronic systems with considerable multi-reference character such as C_2 or BH, H_2O , FH, and C_2 with symmetrically stretched AH bonds (“stretched geometries”). Calculations of the latter represent critical tests on the performance of QCISDTQ and QCISDTQ(6) since single determinant theories are known to fail for systems with considerable multireference character.

All energies obtained at the QCISDTQ level of theory are less negative than the corresponding QCISDT energies obtained with the same basis set at the same geometry. By this, the agreement with FCI correlation energies is significantly improved relative to that found for QCISDT [16,17], which is documented by the calculated mean (from 0.35 to 0.25), mean absolute (from -0.31 to 0.01), and standard deviation (from 0.87 to 0.48 mhartree, see Table 1). For QCISD and CCSD, the corresponding values for the mean absolute deviation are ~ 3 mhartree, for CCSD(T) and CCSDT 0.49 and 0.30 mhartree, respectively.

In Fig. 3, the MP5 correlation energy contributions for the same set of electronic systems are shown in form of an *energy spectrum* [2] for both class-A and -B electronic systems. Obviously, the TQ energy term represents always a positive correction to other negative fifth-order (or lower) order energy contributions, which in the case of class-B systems is actually the dominant term at MP5. Hence, the inclusion of the TQ term at QCISDTQ represents the most important correction relative to QCISDT and is responsible for the better agreement with FCI results. Similar observations can be made for the stretched geometries although deviations in these cases are larger by a factor 3–10 because of the strong multi-reference character of these systems.

Table 1

Comparison of QCISDTQ energies with FCI and other CC energies for atoms and molecules in their equilibrium geometry ^a

Molecule	Basis	FCI	$E(\text{approx.}) - E(\text{FCI})$							
			CCSD	CCSD(T)	CCSDT	MP6	QCISD	QCISDT	QCISDTQ	QCISDTQ(6)
F ⁻	cc-pVDZ	-99.558917	1.071	0.464	0.446	0.044	1.057	0.398	0.452	-0.002
	aug-cc-pVDZ	-99.669369	6.679	0.735	0.397	-8.662	4.177	-2.719	-1.675	0.330
	cc-pVTZ(-f)	-99.675158	5.109	0.208	0.232	-0.194	4.734	-0.607	0.002	0.007
Ne	4s2p1d	-128.702462	2.142	-0.001	-0.066	-0.227	1.708	-0.549	-0.202	0.052
	6s4p1d	-128.767889	2.875	0.114	0.119	-0.368	2.511	-0.493	-0.183	0.000
	cc-pVDZ	-128.679025	1.233	0.189	0.160	-0.027	1.097	-0.008	0.139	0.020
	aug-cc-pVDZ	-128.709476	2.972	0.181	0.061	-0.550	2.343	-0.634	-0.294	0.060
	cc-pVTZ(-f)	-128.777048	3.756	0.066	0.059	-0.176	3.459	-0.523	-0.155	0.002
BH	DZP	-25.227627	1.792	0.412	0.068	1.305	1.760	-0.019	0.014	0.021
	cc-pVDZ	-25.215126	1.834	0.479	0.067	1.328	1.815	-0.020	0.025	-0.004
	aug-cc-pVDZ	-25.218227	1.986	0.474	0.027	1.263	1.973	-0.061	-0.020	-0.059
CH ₂ (³ B ₁)	DZP	-39.046260	2.090	0.359	0.017	0.363	2.054	-0.107	-0.037	-0.049
CH ₂ (¹ A ₁)	DZP	-39.027183	3.544	0.873	0.207	1.977	3.522	-0.024	0.113	0.014
NH ₂ (² B ₁)	DZP	-55.742620	3.212	0.548	0.216	0.336	3.134	-0.046	0.121	-0.025
NH ₂ (² A ₁)	DZP	-55.688762	2.993	0.534	0.223	1.263	2.908	-0.023	0.139	-0.016
H ₂ O	DZ	-76.157866	1.790	0.574	0.434	0.087	1.482	0.072	0.297	0.036
	DZP	-76.256624	4.123	0.718	0.531	0.077	3.880	0.030	0.348	0.015
	cc-pVDZ	-76.241650	3.666	0.634	0.472	0.016	3.527	0.090	0.335	0.000
	cc-pVDZ(+)	-76.258208	4.421	0.684	0.494	-0.204	3.995	-0.274	0.108	0.016
FH	DZP	-100.250969	3.006	0.397	0.266	-0.229	2.567	-0.268	0.079	0.056
	cc-pVDZ	-100.228640	2.414	0.493	0.404	-0.008	2.232	0.117	0.291	0.012
	aug-cc-pVDZ	-100.264113	4.667	0.528	0.329	-0.972	3.861	-0.727	-0.263	0.070
N ₂	cc-pVDZ	-109.276527	13.465	1.708	1.626	-0.321	12.510	-0.736	0.683	0.064
Mean abs. deviation			3.351	0.492	0.298	0.862	2.993	0.349	0.253	0.040
Mean deviation			3.515	0.494	0.295	-0.169	3.144	-0.310	0.014	0.027
Standard derivation			2.496	0.329	0.328	2.189	2.243	0.870	0.483	0.073

^a Absolute energies in hartree, deviations in mhartree. FCI energies are taken from Refs. [21–25] where details on basis sets and geometries are published.

Contrary to CCSDT correlation energies, QCISDT correlation energies are typically below FCI energies since they are lacking the important QT term. Since QCISDTQ energies contain the QT term, their value is mostly above or in some cases slightly below the FCI value. QCISDTQ(6) covers in addition MP5 and MP6 terms (see Eqs. (22) and (30)), which can be either positive or negative, but in total correct the QCISDTQ energies in such a way that the mean absolute deviation from FCI values decreases by a factor 6 to 0.04 mhartree and the standard deviation by a factor of almost 7 to 0.07 mhartree. With a few exceptions, QCISDTQ(6) correlation energies approach FCI values from above. For basis sets without diffuse functions the reproduction of FCI results is clearly better than for basis sets including diffuse functions. Cremer and co-workers showed recently

that the addition of diffuse functions to a basis set not fully saturated with s,p functions leads to an exaggeration of higher order correlation effects, which diminishes the accuracy of a given MBPT or CC method [7].

It is interesting to note that QCISDTQ(6) performs poorly in the cases of FH and H₂O with bond lengths of $2R_e$ (Table 2). In these cases orbital relaxation and state mixing are most important and an inclusion of correction terms with frozen amplitudes seems to drastically overcorrect QCISDTQ results.

Analysis of MP5 and MP6 contributions that are added because of the Q projection equation at QCISDTQ reveals that the former are predominantly positive thus correcting the too negative QCISDT values back to a level relatively high over FCI correlation

Table 2

Comparison of QCISDTQ energies with FCI and other CC energies for electronic systems with multi-reference character ^a

Molecule	Geom.	Basis	FCI	$E(\text{approx.}) - E(\text{FCI})$							
				CCSD	CCSD(T)	CCSDT	MP6	QCISD	QCISDT	QCISDTQ	QCISDTQ(6)
C ₂	1.0 R _e	cc-pVDZ	-75.721843	22.713	-4.853	-3.497	-9.264	17.970	-14.351	-10.146	-4.423
BH	1.5 R _e	DZP	-25.175976	2.642	0.550	0.026	1.448	2.343	-0.305	-0.226	0.124
BH	2.0 R _e	DZP	-25.127350	5.048	0.406	-0.091	2.203	3.856	-1.355	-1.165	1.174
FH	1.5 R _e	DZP	-100.160395	5.099	0.887	0.645	-0.407	4.136	-0.452	0.174	0.307
FH	2.0 R _e	DZP	-100.081107	10.178	0.255	1.125	-1.132	8.392	-0.962	0.370	2.966
H ₂ O	1.5 R _e	DZ	-76.014521	5.590	1.465	1.473	1.910	4.740	-0.109	0.865	0.331
H ₂ O	2.0 R _e	DZ	-75.905246	9.365	-7.675	-2.211	3.970	9.589	-7.991	-4.461	11.776
H ₂ O	1.5 R _e	DZP	-76.071405	10.159	1.999	1.784	1.816	9.366	0.021	1.097	0.220
H ₂ O	2.0 R _e	DZP	-75.952269	21.410	-4.630	-2.472	4.057	21.386	-6.153	-3.224	8.670
Mean abs. deviation				10.245	2.524	1.480	2.912	9.086	3.522	2.414	3.332
Mean deviation				10.245	-1.288	-0.358	0.511	9.086	-3.517	-1.857	2.349
Standard derivation				5.584	8.205	7.314	9.302	5.460	11.198	9.599	8.506

^aAbsolute energies in hartree, deviations in mhartree. FCI energies are taken from Refs. [21–25] where details on basis sets and geometries are published.

energies. However, the connected Q contributions, in particular the relatively large negative TQT contribution is responsible for a closer approach to the FCI values. The additional improvement obtained at the QCISDTQ(6) level is a result of a complicated interplay of positive and negative contributions, in which a relatively large DTS + DTQ contribution plays an important role.

We conclude that QCISDTQ(6) leads to correlation energies close to CCSDTQ and FCI values, that the method is much better than either MP6, QCISD(T), CCSD(T), QCISDT or CCSDT and that it is the cheapest of all Q methods covering infinite order correlation effects introduced by the \hat{T}_4 operator. Apart from this, QCISDTQ results can be used as a reasonable guess for the more accurate CCSDTQ results. Finally, QCISDTQ calculations confirm the importance of connected four-electron correlation effects, which are needed to approach FCI correlation energies.

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Appendix A.

The intermediate arrays used in the QCISDTQ program are defined in Eq. (A.1) to Eq. (A.13).

$$u_i^a = - \sum_{ld} \langle la||id \rangle a_i^d - \frac{1}{2} \sum_{lde} \langle la||de \rangle a_{li}^{de} - \frac{1}{2} \sum_{lmd} \langle lm||id \rangle a_{lm}^{ad}, \quad (\text{A.1})$$

$$u_{ij}^{ab} = \sum_d (\langle ab||dj \rangle a_i^d - \langle ab||di \rangle a_j^d) + \sum_l (\langle la||ij \rangle a_l^b - \langle lb||ij \rangle a_l^a) + \frac{1}{2} \sum_{de} \langle ab||de \rangle a_{ij}^{de} + \frac{1}{2} \sum_{lm} \langle lm||ij \rangle a_{lm}^{ab} - \sum_{ld} \sum_p (-1)^p P(ij/ab) \langle lb||jd \rangle a_{li}^{ad}, \quad (\text{A.2})$$

$$v_i^a = \frac{1}{2} \sum_{lm} \sum_{de} \langle lm||de \rangle (a_i^d a_{lm}^{ea} + a_l^a a_{im}^{ed} + 2 a_l^d a_{im}^{ae}), \quad (\text{A.3})$$

$$v_{ij}^{ab} = \frac{1}{4} \sum_{lm} \sum_{de} \langle lm || de \rangle \left[a_{ij}^{de} a_{lm}^{ab} - 2 \left(a_{ij}^{ad} a_{lm}^{be} + a_{ij}^{be} a_{lm}^{ad} + a_{il}^{ab} a_{jm}^{de} + a_{il}^{de} a_{jm}^{ab} \right) + 4 \left(a_{il}^{ad} a_{jm}^{be} + a_{il}^{be} a_{jm}^{ad} \right) \right], \quad (\text{A.4})$$

$$X_1(i, d, b, c) = \langle id || bc \rangle + \frac{1}{2} \sum_{mne} \langle mn || ed \rangle a_{imn}^{ebc}, \quad (\text{A.5})$$

$$X_2(j, k, l, a) = \langle jk || la \rangle + \frac{1}{2} \sum_{mef} \langle ml || ef \rangle a_{mjk}^{aef}, \quad (\text{A.6})$$

$$X_3(b, c, e, f) = \langle bc || ef \rangle + \frac{1}{2} \sum_{mn} \langle mn || ef \rangle a_{mn}^{bc}, \quad (\text{A.7})$$

$$X_4(m, n, j, k) = \langle mn || jk \rangle + \frac{1}{2} \sum_{ef} \langle mn || ef \rangle a_{jk}^{ef}, \quad (\text{A.8})$$

$$X_5(m, a, i, e) = \langle ma || ie \rangle - \sum_{nf} \langle mn || ef \rangle a_{in}^{af}, \quad (\text{A.9})$$

$$Y_1(f, a) = \frac{1}{2} \sum_{mne} \langle mn || ef \rangle a_{mn}^{ae}, \quad (\text{A.10})$$

$$Y_2(n, i) = \frac{1}{2} \sum_{mef} \langle mn || ef \rangle a_{im}^{ef}, \quad (\text{A.11})$$

$$Z_1(k, l, b, c, d, e) = \frac{1}{2} \sum_{m, n, f} \langle mn || ef \rangle a_{mnkl}^{fbcd}, \quad (\text{A.12})$$

$$Z_2(j, k, l, c, d, n) = -\frac{1}{2} \sum_{m, e, f} \langle mn || ef \rangle a_{mjk}^{efcd}. \quad (\text{A.13})$$

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