Application of Quadratic CI with Singles, Doubles, and Triples (QCISDT): An Attractive Alternative to CCSDT

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ABSTRACT

The size-extensive quadratic CI method with single (S), double (D), and triple (T) excitations, QCISDT, is compared with QCISD, QCISD(T), CCSDT-n, and CCSDT. It is shown that QCISDT results are more accurate than are either QCISD or QCISD(T) results. In particular, QCISDT turns out to be more stable than are QCISD and QCISD(T) in cases with considerable multireference character. QCISDT and CCSDT results are of similar accuracy with slight advantages for the former method. Since QCISDT is much easier to implement on a computer than is CCSDT, it is an attractive alternative to CCSDT. © 1996 John Wiley & Sons, Inc.

Introduction

Triple (T) excitation effects are known to be quite important in correlation energy calculations. Today, a number of approximate methods is available to cover T correlation effects. The most frequently used single-determinant methods are fourth-order many-body perturbation theory, MBPT(4) [1], which covers single (S), double (D), T, and quadruple (Q) excitations; configuration interaction with S, D, and T excitations (CISDT) [2]; perturbational extensions of coupled cluster (CC) or quadratic CI (QCI) SD methods such as CCSD(T) [3] or QCISD(T) [4]; and, finally, CCSDT [5] and CCSDT-related approximations such as CCSDT-n (n =

1, 2, 3, 4) [6]. Of these methods, MBPT(4) is least costly because it requires just $O(M^7)$ operations, where M is the number of basis functions. QCISD(T) and CCSD(T) are also $O(M^7)$ methods, but they imply an iterative solution of the CCSD [7] and QCISD projection equations [4], which involves $N_{iter}O(M^6)$ operations. Both CISDT and CCSDT are iterative $O(M^8)$ methods and, therefore, they are (apart from full CI) the most expensive methods presently in use.

As for the accuracy of these methods, it is well known that MBPT(4) is the least accurate while CCSDT is the most accurate, i.e., the accuracy of calculated energies increases with the computational work involved. A deficiency of the perturbation theory-based T methods is that they often overestimate the importance of T correlation effects

[8–10] which has to do with the fact that π coupling terms that come in at fifth order and guarantee a balanced description of T effects are not covered by MBPT(4), CCSD(T), and QCISD(T) [11]. QCISD(T), although it covers infinite-order effects, contains just a few TTA or TAT (A = S, D, T, Q) coupling terms at sixth-order perturbation theory, MBPT(6) [9], which makes it superior to MBPT(4), but still not secure against an unbalanced description of T correlation effects. [9, 10, 12, 13] A significant improvement of QCISD(T), however, would be achieved if T excitations could be included at the CC level rather that just at the perturbation theory level. This would lead to QCISDT [14, 15], which together with CCSDT, should provide the best treatment of T correlation effects, but which should also offer some advantages with regard to CCSDT.

We recently extended the QCISD method of Pople, et al. [4] to a hierarchy of size-extensive QCI methods and published formulas for size-extensive QCISDT [14, 15],* which we implemented into the COLOGNE ab initio package [17]. In this work, we report on the first applications of QCISDT and present a systematic analysis of QCISDT correlation energies considering the following questions:

1. Does QCISDT, which can be considered as a simplified CCSDT method, lead to the same accuracy of results as does CCSDT. In particular, are T correlation effects handled in a balanced way?

2. Does QCISDT offer any advantages with regard to CCSDT?

3. How does QCISDT compare with QCISD and QCISD(T)?

To answer these questions, we proceed in the following way: In the next section, we summarize the theory of QCISDT and compare it with CCSDT and other T methods using perturbation theory. In the third section, we present various applications of QCISDT and discuss them in comparison with the results of other approximate methods. In the last section, we show that QCISDT is more accurate than is either QCISD or QCISD(T) and that it is an attractive alternative to CCSDT.

*Pople, Head-Gordon, and Raghavachari [4a] suggested a QCISDT method that is not size-extensive and, therefore, does not fulfill the basic requirement of a QCI method. See [14, 16].

Theory

The CISDT wave function is given by

$$|\Phi_{\text{CISDT}}\rangle = \left(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3\right)|\Phi_0\rangle, \quad (1)$$

where the reference function $|\Phi_0\rangle$ is set equal to the Hartree–Fock (HF) wave function for reasons of simplicity and the CI excitation operators take the form

$$\hat{C}_n = \frac{1}{(n!)^2} \sum_{ij\ldots} \sum_{ab\ldots} c_{ij\ldots}^{ab\ldots} \, \hat{b}_a^+ \hat{b}_i \hat{b}_b^+ + \hat{b}_{j\ldots}, \quad (2)$$

with $c_{ij\ldots}^{ab\ldots}$, $\hat{b}^+$, and $\hat{b}$ having the usual meaning of CI expansion coefficients, creation, and annihilation operators. Here and in the following, we use subscripts $i, j, \ldots (a, b, \ldots)$ for occupied (virtual) spin orbitals, while subscripts $p, q, \ldots$ denote general orbitals. S, D, and p-fold excited determinants are obtained from the HF wave function according to Eqs. (3), (4), and (5):

$$\hat{C}_1 |\Phi_0\rangle = \sum_{i,a} c_i^a |\Phi_i^a\rangle \quad (3)$$

$$\hat{C}_2 |\Phi_0\rangle = \frac{1}{4} \sum_{ij,ab} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \quad (4)$$

$$\hat{C}_p |\Phi_0\rangle = \frac{1}{(p!)^2} \sum_p c_p |\Phi_p\rangle. \quad (5)$$

With these definitions, the CISDT projection equations are given by

$$\langle\Phi_0| \bar{H}\hat{C}_2 |\Phi_0\rangle = E_{corr}^{\text{CISDT}} \quad (6)$$

$$\langle\Phi_i^a| \bar{H}\left(\hat{C}_1 + \hat{C}_2 + \hat{C}_3\right)|\Phi_0\rangle = c_i^a E_{corr}^{\text{CISDT}} \quad (7)$$

$$\langle\Phi_{ij}^{ab}| \bar{H}\left(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3\right)|\Phi_0\rangle = c_{ij}^{ab} E_{corr}^{\text{CISDT}} \quad (8)$$

$$\langle\Phi_{ijk}^{abc}| \bar{H}\left(\hat{C}_1 + \hat{C}_2 + \hat{C}_3\right)|\Phi_0\rangle = c_{ijk}^{abc} E_{corr}^{\text{CISDT}}, \quad (9)$$

where $E_{corr}^{\text{CISDT}} = E(\text{CISDT}) - E(\text{HF})$ denotes the CISDT correlation energy, and $\bar{H}$, the normal-order Hamiltonian defined by

$$\bar{H} = \bar{H} - E(HF) = \bar{H}_0 + \bar{V} \quad (10)$$

$$\bar{H} = \sum_{rs} \left\{\hat{b}_r^+ \hat{b}_s\right\}\langle r| \hat{F} |s\rangle$$

$$+ \frac{1}{4} \sum_{rstu} \left\{\hat{b}_r^+ \hat{b}_s^+ \hat{b}_t \hat{b}_u\right\}\langle rs||tu\rangle. \quad (11)$$

CISDT is not size-extensive because of disconnected terms that appear in Eqs. (7), (8), and (9). We showed in a recent article [14] that size-extensivity is obtained by adding or subtracting terms that lead to a cancellation of disconnected terms and, thereby, of physically unreasonable energy contributions. Changes comprise the following steps:

1. The CI excitation operators $\hat{C}_p$ are replaced by CC cluster operators $\hat{T}_p$:

$$\hat{T}_n = \frac{1}{(n!)^2} \sum_{ijk\ldots} \sum_{abc\ldots}$$
$$\times a_{ijk\ldots}^{abc\ldots} \hat{b}_a^+ \hat{b}_i \hat{b}_b^+ \hat{b}_j \hat{b}_c^+ \hat{b}_k \ldots , \quad (12)$$

where coefficients $a_{ijk\ldots}^{abc\ldots}$ denote cluster amplitudes.

2. In the S and D projection Eqs. (7) and (8), the terms $\hat{T}_1 \hat{T}_2$ and $\frac{1}{2}\hat{T}_2^2$, respectively, are added on the left side to eliminate all disconnected terms on the right side of these equations.

3. In the T Eq. (9), there appear two disconnected terms $\langle \Phi_{ijk}^{abc}| \bar{H}\hat{C}_1 |\Phi_0 \rangle (= \langle ab| ij \rangle c_k^c)$ and $c_{ijk}^{abc} E_{corr}^{CISDT}$. Introducing $-\bar{H}\hat{T}_1$ and parts of the term $\bar{H}\hat{T}_2\hat{T}_3$, namely, $(\bar{H}\hat{T}_2\hat{T}_3)_C$, as well as $(\hat{T}_3(\bar{H}\hat{T}_2)_C)_{dis}$, on the left side of Eq. (9) leads to cancellation of all disconnected terms in the T equations.

With (1), (2), and (3), size-extensive QCISDT results:

$$\langle \Phi_0| \bar{H}\hat{T}_2 |\Phi_0 \rangle = E_{corr}^{QCISDT} \quad (13)$$

$$\langle \Phi_i^a| \bar{H}\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2\right) |\Phi_0 \rangle$$
$$= a_i^a E_{corr}^{QCISDT} \quad (14)$$

$$\langle \Phi_{ij}^{ab}| \bar{H}\left(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_2^2\right) |\Phi_0 \rangle$$
$$= a_{ij}^{ab} E_{corr}^{QCISDT} \quad (15)$$

or, alternatively,

$$\langle \Phi_i^a| \bar{H}\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2\right) |\Phi_0 \rangle_C = 0$$
$$(14a)$$

$$\langle \Phi_{ij}^{ab}| \bar{H}\left(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_2^2\right) |\Phi_0 \rangle_C = 0$$
$$(15a)$$

$$\langle \Phi_{ijk}^{abc}| \bar{H}\left(\hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3\right) |\Phi_0 \rangle_C = 0 \quad (16)$$

The matrix elements of the QCISDT projection equations have been expressed in terms of two-electron integrals in order to obtain a form that can be implemented on a computer [15]:

$$E_{corr}^{QCISDT} = \frac{1}{4} \sum_{ij, ab} \langle ij| |ab \rangle a_{ij}^{ab} \quad (17)$$

$$(\epsilon_i - \epsilon_a)a_i^a = u_i^a + v_i^a$$
$$+ \sum_{l<m} \sum_{d<e} \langle lm| |de \rangle a_{ilm}^{ade} \quad (18)$$

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)a_{ij}^{ab}$$
$$= u_{ij}^{ab} + v_{ij}^{ab} + \sum_{i,d<e} \left(\langle bl| |de \rangle a_{ijl}^{ade}\right.$$
$$+ \langle al| |de \rangle a_{ijl}^{dbe}\right) + \sum_{l<m,d} \left(\langle lm| |dj \rangle a_{ilm}^{abd}\right.$$
$$+ \langle lm| |di \rangle a_{ljm}^{abd}\right) \quad (19)$$

$$(\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)a_{ijk}^{abc}$$
$$= -\sum_p (-1)^P P(i/jk | a/bc)$$
$$\times \left[\sum_d X_1(i, d, b, c)a_{jk}^{ad}\right.$$
$$+ \sum_l X_2(j, k, l, a)a_{il}^{bc}\right]$$
$$+ \sum_p (-1)^P P(a/bc)$$
$$\times \left[\frac{1}{2} \sum_{ef} X_3(b, c, e, f)a_{ijk}^{aef}\right.$$
$$+ \sum_f Y_1(f, a)a_{ijk}^{fbc}\right]$$
$$+ \sum_p (-1)^P P(i/jk)$$
$$\times \left[\frac{1}{2} \sum_{mn} X_4(m, n, j, k)a_{imn}^{abc}\right.$$
$$+ \sum_n Y_2(n, i)a_{njk}^{abc}\right]$$
$$- \sum_p (-1)^P P(i/jk | a/bc)$$
$$\times \sum_{mc} X_5(m, a, i, e)a_{jkm}^{bcc}, \quad (20)$$

where u_i^a, v_i^a, u_{ij}^{ab}, and v_{ij}^{ab} and the intermediate arrays X_n, Y_m have been defined elsewhere [15]. The permutation symbol $\sum_p (-1)^P P(i/jk|a/bc)$ re-

quires summation of the identity permutation and permutations that interchange orbital label i and j,k or a and b,c without permuting $j \leftrightarrow k$ or $b \leftrightarrow c$.

It is interesting to compare the QCISDT projection Eqs. (13)–(16) with the corresponding CCSDT Eqs. (21)–(24):

$$\langle \Phi_0 | \, \bar{H}\left(\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2\right) | \Phi_0 \rangle = E_{corr}^{CCSDT} \qquad (21)$$

$$\langle \Phi_i^a | \, \bar{H}\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2 \right.$$

$$\left. + \frac{1}{2}\,\hat{T}_1^2 + \frac{1}{3!}\,\hat{T}_1^3\right) | \Phi_0 \rangle_C = 0 \qquad (22)$$

$$\langle \Phi_{ij}^{ab} | \, \bar{H}\left(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \right.$$

$$+ \frac{1}{2}\,\hat{T}_2^2 + \frac{1}{2}\,\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3$$

$$\left. + \frac{1}{2}\,\hat{T}_1^2\hat{T}_2 + \frac{1}{3!}\,\hat{T}_1^3 + \frac{1}{4!}\,\hat{T}_1^4\right) | \Phi_0 \rangle_C$$

$$= 0 \qquad (23)$$

$$\langle \Phi_{ijk}^{abc} | \, \bar{H}\left(\hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3 \right.$$

$$+ \frac{1}{2}\,\hat{T}_2^2 + \hat{T}_2\hat{T}_3 + \frac{1}{2}\,\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\,\hat{T}_1^2\hat{T}_3$$

$$\left. + \frac{1}{2}\,\hat{T}_1\hat{T}_2^2 + \frac{1}{3!}\,\hat{T}_1^3\hat{T}_2\right) | \Phi_0 \rangle_C = 0, \qquad (24)$$

in which cluster operators also contained in QCISDT are given in bold-faced print. In QCISDT, all cubic and quartic terms are deleted from the CCSDT projection equations, which is reasonable because these terms only contribute to the correlation energy in higher orders of perturbation theory [14, 15]. As for the quadratic CCSDT terms, only that term is retained in each QCISDT projection equation that involves the D excitation operator $\hat{T}_2$. Clearly, pair correlation effects described by $\hat{T}_2$ are the most important correlation effects and, therefore, the coupling of $\hat{T}_2$ (pair correlation effects) with the S excitations operator $\hat{T}_1$ (orbital relaxation effects) is the most important coupling effect in the S projection equations. Similarly, the coupling of pair correlations with other pair correlations is the most important coupling effect in the D projection equations. As for the T projection equations, one could say that $\frac{1}{2}\hat{T}_2^2$ (Q correlation effects) describes more important correlation effects than does the coupling term $\hat{T}_2\hat{T}_3$. However, Q effects are par-

tially covered in the D equations and, therefore, the inclusion of $\hat{T}_2\hat{T}_3$ in the T equations of QCISDT is more important to guarantee a balanced description of T correlation effects.

The relationship between QCISDT and CCSDT becomes more transparent when comparing QCISDT and CCSDT correlation energies in terms of fourth, fifth, sixth, and infinite-order perturbation theory as described in articles I [9], II [10], and III [18] of this series. From such analysis, one gets the energy contributions $E_{ABC...}^{(n)}$ resulting at nth-order MBPT from a coupling of excitations A, B, C, etc. (corresponding to S, D, T, Q, etc). In Figure 1, the various energy contributions covered by QCISDT and CCSDT at fourth and fifth order are listed and compared with the energy contributions covered by QCISDT(T), CCSD(T), and CCSDT-n. A similar comparison is given in Figure 2 for sixth-order perturbation theory. In Figure 3, QCISDT is analyzed diagrammatically so that infinite-order effects can be assessed. Some of the energy contributions are not fully covered by QCISDT, which is indicated by parentheses in Figures 1 and 2 or dashed lines in the diagram of Figure 3.

All eight methods compared in Figures 1 and 2 are correct up to fourth order but lack one or more energy terms already at fifth order. For example, QCISD(T) neither covers the TT term at fifth order nor any of the 11 TTA or TAT coupling terms at sixth order (Fig. 2). This is the reason why QCISD(T) often exaggerates T effects in those cases where they become important [10, 13]. CCSD(T) is not as bad as is QCISD(T) with regard to the correct description of T effects since it covers at least two of the TTA coupling terms at sixth order. But QCISDT and CCSDT should be clearly superior to QCISD(T) or CCSD(T) since they both cover the TT term at fifth order and six (9) TTA or TAT terms (including the TTT term) at sixth order, which should guarantee a balanced treatment of T effects.

QCISDT does not include TS, TSA, TQ, and TQA contributions at fifth and sixth order of perturbation theory. Hence, CCSDT and also CCSDT-4, which both contain TS.. and TQ.. energy contributions, should be superior in those cases where orbital relaxation effects or pair–pair correlation effects significantly couple to T effects. Clearly, this will happen in molecules with strong T correlation effects, e.g., molecules with multiple bonds, which, in addition, possess multireference character and/or pair–pair correlation effects as in conjugated systems. Accordingly, one can expect a reduced accuracy of QCISDT when describing the

Analysis in Terms of MBPT(4)

	QCISD(T)	CCSD(T)	CCSDT-1	CCSDT-2	CCSDT-3	CCSDT-4	CCSDT	QCISDT
S	yes	yes	yes	yes	yes	yes	yes	yes
D	yes	yes	yes	yes	yes	yes	yes	yes
T	yes	yes	yes	yes	yes	yes	yes	yes
Q	yes	yes	yes	yes	yes	yes	yes	yes

Analysis in Terms of MBPT(5)

	QCISD(T)	CCSD(T)	CCSDT-1	CCSDT-2	CCSDT-3	CCSDT-4	CCSDT	QCISDT
SS	yes	yes	yes	yes	yes	yes	yes	yes
DD	yes	yes	yes	yes	yes	yes	yes	yes
TT						yes	yes	yes
QQ	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)
SD,DS	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,y	y,y
ST,TS	y,y	y,y	y,y	y,y	y,y	y,y	y,y	y,-
DT,TD	y,y	y,y	y,y	y,y	y,y	y,y	y,y	y,y
TQ,QT		y,-	(y),-	y,-	y,-	y,-	y,-	

FIGURE 1. Analysis of energy contributions at fourth- and fifth-order many-body perturbation theory covered by QCISD(T), CCSD(T), CCSDT-n (n = 1, 2, 3, 4), CCSDT, and QCISDT correlation energies. Yes or y denotes that the particular term(s) shown at the left side of the diagram is (are) fully contained in the correlation energy, while (yes) or (y) indicates that the term(s) is (are) only partially covered.

dissociation of a triple bond, conjugation in a multiple bond system, or, in general, when the system to be calculated possesses significant multireference character.

In Figure 3, all energy terms covered by QCISDT at nth-order perturbation theory (n = 4, 5, 6, 7, 8) are displayed in form of a diagram [9]. For each order n, the correlation energy is partitioned into terms $E_{ABC...}^{(n)}$ which are represented by paths leading from the nth-order level down to the fourth-order level. Such a path can only start at A = S, D, T, or Q and end at X = S, D, T, or Q. Between levels n and 4, it can extend to the right of the Q column, thus coupling pentuple (P), hextuple (H), etc., excitations to T and Q excitations, but coupling has to be done according to Slater rules for matrix elements always with the condition that the path returns to the S, D, T, Q set at n = 4. For $E_{AB}^{(5)}$, there are 14 paths corresponding to the 14

energy terms at MBPT(5). Some of them such as $E_{SD}^{(5)}$ and $E_{DS}^{(5)}$ are identical due to symmetry, thus reducing the number of unique paths (energy terms) to 9. There are 55 $E_{ABC}^{(6)}$ paths and 221 $E_{ABCD}^{(7)}$ paths, which reduce to 36 and 141, respectively, because of symmetry.

The number of paths and energy contributions increase exponentially, but a diagram such as the one shown in Figure 3 helps to identify all terms at a given order n and to describe infinite-order effects. An approximate method (e.g., QCISDT) does not contain all energy paths and some of the paths are only partially covered. In Figure 3, solid lines indicate that the particular energy term is fully contained in QCISDT. If only one part of the path representing a given energy contribution is dashed, then the term is only partially covered. If it happens that for an approximate method a particular term is delayed and comes in at a higher order n,

Analysis in Terms of MBPT(6)

	QCISD(T)	CCSD(T)	CCSDT-1	CCSDT-2	CCSDT-3	CCSDT-4	CCSDT	QCISDT
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
DQD	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
DQQ,QQD	(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
QQQ	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)
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	yes	yes
DTQ,QTD		(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,y	y,-
SDT,TDS	y,y	y,y	y,y	y,y	y,y	y,y	y,y	y,y
STT,TTS		-,(y)	-,(y)	-,(y)	-,y	y,y	y,y	y,-
DST,TSD	y,y	y,y	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	y,y	y,y
DQT,TQD		-,(y)	-,(y)	-,y	-,y	-,y	-,y	
DTT,TTD						y,y	y,y	y,y
TDQ,QDT	y,y	y,y	y,y	y,y	y,y	y,y	y,y	y,y
TQQ,QQT		(y),-	(y),-	(y),-	(y),-	(y),-	(y),-	
TTQ,QTT		(y),-	(y),-	(y),-	(y),-	y,-	y,-	
TST			yes	yes	yes	yes	yes	
TDT			yes	yes	yes	yes	yes	yes
TQT								
TTT						yes	yes	yes
QPQ			(yes)	(yes)	(yes)	(yes)	(yes)	(yes)
QHQ	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)	(yes)
TPQ,QPT			(y),(y)	(y),(y)	(y),(y)	(y),(y)	(y),(y)	(y),(y)
TPT			(yes)	(yes)	(yes)	(yes)	yes	(yes)

FIGURE 2. Analysis of energy contributions at sixth-order many-body perturbation theory covered by QCISD(T), CCSD(T), CCSDT-n ($n = 1, 2, 3, 4$), CCSDT, and QCISDT correlation energies. Yes or y denotes that the particular term(s) shown at the left side of the diagram is (are) fully contained in the correlation energy, while (yes) or (y) indicates that the term(s) is (are) only partially covered.
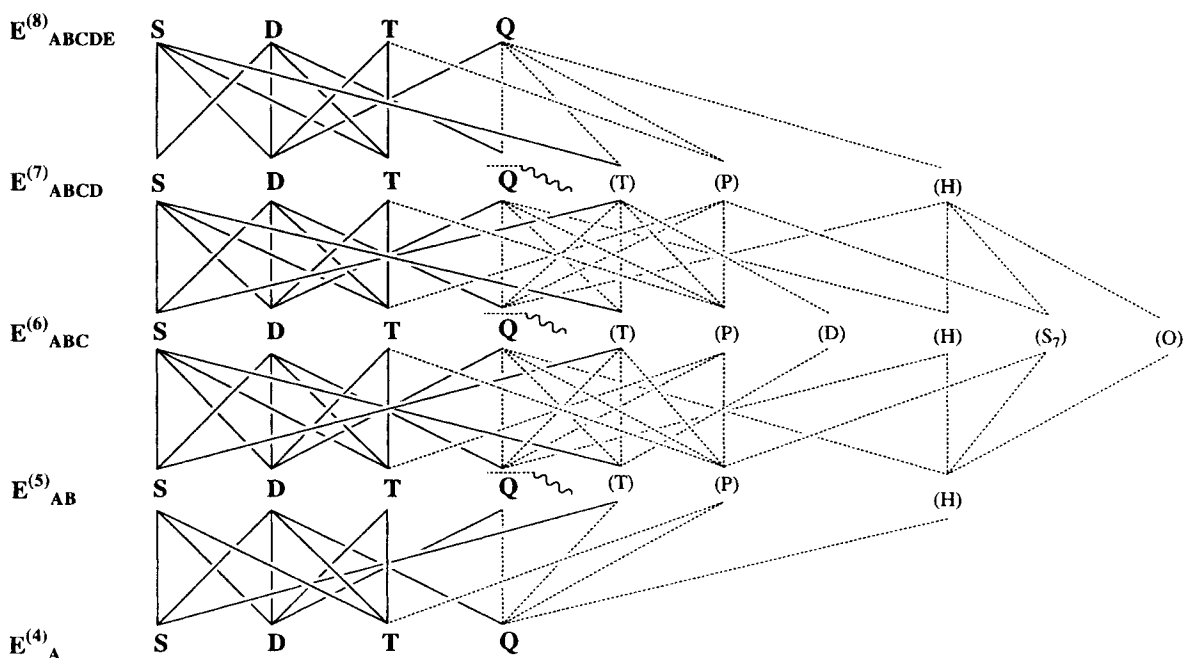
FIGURE 3. Graphical representation of energy contributions $E_{ABC}^{(n)}$ at nth-order many-body perturbation theory (n = 4, 5, 6, 7, 8) covered by QCISDT. A particular energy contribution $E_{ABC}^{(n)}$ is given by the solid line that starts at A = S, D, T, or Q in the $E^{(n)}$ row and connects B, C, etc., at row $n - 1$, $n - 2$, etc., until $n = 4$ is reached. Dashed lines denote partially covered energy contributions. 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 (downward directed wiggles) to the right of the S, D, T, Q excitations.

then this can only be described by reentering a lower excitation to the right of the Q column (e.g., T and D in Fig. 3).

QCISDT covers 11 out of 14 MBPT(5) terms (78%), 41 out of 55 MBPT(6) terms (75%), 143 out of 221 MBPT(7) terms (65%), and 537 out of 915 MBPT(8) terms (59%) fully or partially, i.e., at higher orders, it clearly falls back with regard to CCSDT, which e.g., at eighth order, still covers 87% of all terms [9]. It is also interesting to note that, beginning with ...QQ excitation effects, all higher excitation effects are only partially covered by QCISDT. On the other hand, QCISDT contains, with the exception of the ..TS terms, all infinite-order terms in the truncated configuration space that is made up from S, D, and T excitations (Fig. 3). Actually, the ..TS terms are not totally missing, but they are delayed by one order of perturbation theory, which means that these effects are underestimated by QCISDT.

We have previously shown the QCISD and, thereby, also QCISDT, covers all infinite-order effects, at least partially, in any truncated SDQHO...X(even) configuration space (O = eight fold

excitations), which is important for the coupling between pair correlation effects and orbital relaxations. However, Figure 3 reveals that coupling between T and Q excitations, P and H excitations, S_7 and O excitations, etc. (S_7 = seven-fold excitations), etc., is severely underestimated by QCISDT, which probably causes problems the more electrons correlate.

The major differences between CCSDT and QCISDT are due to the absence of the $\hat{T}_1\hat{T}_2$ term in the D Eq. (15) and the $\frac{1}{2}\hat{T}_2^2$ term in the T Eq. (16) of QCISDT. These terms contribute to the CCSDT energy in the following way:

$$\Delta E_{corr}^{CCSDT}\left(\hat{T}_1\hat{T}_2 \text{ in } D \text{ } Eq.\right)$$
$$= E_{TS}^{(5)} + E_{TQ}^{(5)}(I) + E_{DTS}^{(6)}$$
$$+ E_{DTQ}^{(6)}(I) + E_{TSS}^{(6)} + E_{TTS}^{(6)}(I)$$
$$+ E_{TSD}^{(6)} + E_{TTQ}^{(6)}(I) + E_{TQD}^{(6)}(I)$$
$$+ E_{TQQ}^{(6)}(I) + E_{TST}^{(6)} + E_{TPT}^{(6)}(I)$$
$$+ E_{TPQ}^{(6)}(I) + O(E^{(7)}) \tag{25}$$

$$\Delta E_{corr}^{CCSDT}\left(\tfrac{1}{2}\hat{T}_2^2 \ in \ T \ Eq.\right)$$

$$= E_{TQ}^{(5)}(II) + E_{TQD}^{(6)}(II) + E_{DTQ}^{(6)}(II)$$

$$+ E_{STQ}^{(6)}(II) + E_{TTQ}^{(6)}(II) + O(E^{(7)}). \quad (26)$$

It is possible to improve QCISDT by adding terms that make the method correct up to fifth order:

$$E_{corr}^{QCISDT}(5) = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \bar{V}\tfrac{1}{2}\hat{T}_1^2 | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{T}_2^\dagger \left(\bar{V}\hat{T}_1\hat{T}_2\right)_C | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{T}_3^\dagger \left(\hat{V}\tfrac{1}{2}\hat{T}_2^2\right)_C | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \tfrac{1}{2}\left(\hat{T}_2^\dagger\right)^2 \left[\bar{V}\left(\hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2\right)\right]_C | \Phi_0 \rangle. \quad (27)$$

The additional terms of Eq. (27), which represent the TS, TQ, QT, and part of the QQ contribution at fifth order, can be evaluated using S, D, and T amplitudes from the QCISDT calculation. The cost of the additional calculational step is proportional to M^7 and, accordingly, it is not significant compared to the M^8 dependence of each QCISDT iteration step.

A similar improvement to obtain a QCISDT correlation energy correct up to sixth order would require the use of Eq. (28):

$$E_{corr}^{QCISDT}(6) = E_{corr}^{QCISDT}(5) + \langle \Phi_0 | \tfrac{1}{2}\left(\hat{T}_2^\dagger\right)^2$$

$$\times \left[\bar{V}\left(\hat{T}_2\hat{T}_3 + \frac{1}{3!}\hat{T}_2^3\right)\right]_C | \Phi_0 \rangle$$

$$+ \sum_q^Q \langle \Phi_0 | \left[\left(\hat{T}_3^\dagger + \tfrac{1}{2}\left(\hat{T}_2^\dagger\right)^2\right)\bar{V}\right]_C$$

$$\times | \Phi_q \rangle (E_0 - E_q)^{-1}$$

$$\times \langle \Phi_q | \left[\bar{V}\left(\hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2\right)\right]_C | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{T}_2^\dagger \left[\bar{V}\left(\tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_3\right)\right]_C | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{T}_3^\dagger \left(\bar{V}\hat{T}_1\hat{T}_2\right)_C | \Phi_0 \rangle; \quad (28)$$

however, this would involve a computational step proportional to M^9, which would be too expensive compared to the QCISDT iterations.

Since some of TS and TQ energy contributions are positive, QCISDT correlation energies will always be more negative than the corresponding CCSDT energies. Apart from the cases described

above, it is difficult to predict whether the lack of these terms means, in general, that QCISDT energies become less accurate than CCSDT energies. An answer to this question can only be given by comparing calculated energies, which is done in the section Numerical Results and Discussion.

Computational Methods

The QCISDT projection equations [Eqs. (18), (19), and (20)] are solved iteratively to get the QCISDT correlation energy E_{corr}^{QCISDT} [Eq. (17)]. We programmed these equations and inserted the corresponding computer code into the ab initio package COLOGNE [17]. In addition, we wrote a CCSDT program in order to be able to directly compare QCISDT and CCSDT results using the same program routines for an iterative solution of the projection equations. We found that a relatively safe way of obtaining a correctly functioning CCSDT program is provided by programming the CCSDT-n methods [6] from $n = 1$ to $n = 4$ and checking calculated CCSDT-n correlation energies at each level with energies published in the literature [6]. In any case, the programming task for getting a functioning CCSDT routine is much more demanding than for getting a functioning QCISDT routine. Therefore, QCISDT offers the possibility of getting a T method with much lower programming efforts than needed for CCSDT.

In the QCISDT calculations, the most time-consuming step is the evaluation of the third term in Eq. (20), which involves asymptotically $n_{occ}^3 n_{virt}^5$ operations. The computational effort per iteration cycle is for QCISDT similar to that for CCSDT, which becomes obvious when replacing in Eq. (25) QCISDT intermediate arrays by the corresponding CCSDT intermediate arrays [15]. QCISDT has some advantages with regard to the number of $O(M^6)$ steps, but the amount of computer time needed for these operations is only a fraction of the total QCISDT or CCSDT time. This is confirmed by a computer-timing comparison between QCISDT and CCSDT which shows that per iteration step 5–10% of the CCSDT time is saved by QCISDT.

However, considerable time savings up to 60% result from the fact that QCISDT converges much faster than does CCSDT, particularly in those cases where the wave function possesses considerable multireference character. These time savings can be explained if one considers the expansion of

QCISDT and CCSDT in terms of perturbation theory. Because of its simpler structure, QCISDT covers considerably less energy terms at a higher order of perturbation theory than does CCSDT (see above). Although most of these terms represent rather small energy contributions, their large number leads to significant additions to the correlation energy at higher orders.

Since during the CC iterations higher and higher perturbation contributions are added to the correlation energy, the method that is more complete (covers more higher-order terms) will need more iteration steps to reach convergence. It seems that the number of iteration steps reflects in a way the number of correlation effects covered by a given CC method. Therefore, it is reasonable that QCISDT converges faster than does CCSDT, in particular, in those cases where due to multireference character correlation effects of higher order play an important role.

Numerical Results and Discussion

In Table I, QCISDT correlation energies calculated for some atoms and simple molecules are compared with the corresponding full CI (FCI) [19] and

CCSDT energies [20] obtained with the same basis set at the same geometry. Although CCSDT correlation energies had been published already earlier [20], they were recalculated in this work in order to obtain timing and other information needed for the comparison with QCISDT. In Table II, QCISDT, CCSDT, and FCI energies are compared for AH_n molecules both in their equilibrium geometry and in various geometries with symmetrically stretched AH bonds ("stretched geometries"). Calculation of the latter represents a critical test on the performance of QCISDT because wave functions of molecules with stretched geometries possess considerable multireference character. To make an assessment of the performance of either QCISDT or CCSDT in the case of strong multireference character, we used the $\mathscr{T}_1$ criterion of Lee and co-workers [21] and calculated the Euclidean norm of the vector t_1 of S excitation amplitudes:

$$\mathscr{T}_1 = \frac{\|t_1\|}{N^{1/2}}, \tag{29}$$

where N denotes the number of electrons correlated in the CC or QCI treatment.

The S excitations describe orbital relaxation effects, which should be the larger the more multi-

TABLE I
Comparison of CCSDT, QCISDT, and FCI correlation energies.[a]

System	Basis	SCF	CCSDT	$\mathscr{T}_1$	QCISDT	$\mathscr{T}_1$	FCI
1, Ne, ^1S	$4s2p1d$	-128.522354	-0.180175	0.0050	-0.180657	0.0048	-0.180108
2	$6s4p1d$	-128.543823	-0.223950	0.0096	-0.224559	0.0096	-0.224065
3	$5s3p2d$	-128.524013	-0.244788	0.0057	-0.245302	0.0056	-0.244864
4, F, ^2P	$4s3p1d$	-99.398964	-0.147713	0.0107	-0.148130	0.0108	-0.147656
5	$4s3p2d$	-99.399543	-0.167044	0.0105	-0.167525	0.0106	-0.166940
6	$5s4p2d$	-99.399983	-0.194909	0.0102	-0.195372	0.0103	-0.194894
7, F$^-$, ^1S	$4s3p1d$	-99.442848	-0.210164	0.0315	-0.213031	0.0343	-0.210493
8	$4s3p2d$	-99.442848	-0.234509	0.0302	-0.237229	0.0313	-0.234828
9	$5s4p2d$	-99.443696	-0.262721	0.0295	-0.265627	0.0306	-0.262994
10, NH_3, $^1A_1$	$(9s5p/4s)$ $[4s2p/2s]$	-56.165930	-0.126333	0.0083	-0.12658	0.0083	-0.126681
11, CH_2, $^3B_1$	$(9s5p1d/4s1p)$ $[4s2p1d/2s1p]$	-38.933045	-0.113198	0.0130	-0.113322	0.0131	-0.113215
12, CH_2, $^1A_1$	$(9s5p1d/4s1p)$ $[4s2p/2s1p]$	-38.886297	-0.140679	0.0137	-0.140910	0.0139	-0.140886
13, C_2H_2, $^1\Sigma_g$	$(9s5p1d/4s1p)$ $[4s2p1d/2s1p]$	-76.831819	-0.280941	0.0166	-0.282743	0.0167	
14, CO, $^1\Sigma_g$	$(9s5p1d)$ $[4s2p1d]$	-112.760093	-0.304008	0.0249	-0.307292	0.0254	

[a] Energies in Hartrees. $\mathscr{T}_1$ defined in Eq. (25); see [21]. Basis sets, geometries, and FCI energies from [19].

TABLE II

Comparison of CCSDT, QCISDT, and FCI correlation energies for AH_n molecules with stretched geometries.[a]

System	Basis	Geometry	SCF	CCSDT	$\mathscr{S}_1$	QCISDT	$\mathscr{S}_1$	FCI
15, FH, $^1\Sigma_g$	$(9s5p1d/4s1p)$	$1.0\ R_e$	-100.047087	-0.203617	0.0082	-0.204150	0.0081	-0.203882
16	$[4s2p1d/2s1p]$	$1.5\ R_e$	-99.933229	-0.226519	0.0252	-0.227616	0.0252	-0.227165
17		$2.0\ R_e$	-99.817572	-0.262408	0.0721	-0.264498	0.0702	-0.263536
18		$3.0\ R_e$	-99.686306	-0.355505	0.1924	-0.356484	0.1746	
19, H_2O, $^1A_1$	$(4s1p/9s5p1d)$	$1.0\ R_e$	-76.040541	-0.215550	0.0095	-0.216053	0.0095	-0.216082
20	$[2s1p/4s2p1d]$	$1.5\ R_e$	-75.800494	-0.269126	0.0343	-0.270890	0.0349	-0.270911
21		$2.0\ R_e$	-75.582285	-0.372435	0.0765	-0.376140	0.0731	-0.369983
22, NH_2, $^2B_1$	$(9s5p1d/4s1p)$	$1.0\ R_e$	-55.577182	-0.165220	0.0103	-0.165484	0.0103	-0.165438
23	$[4s2p1d/2s1p]$	$1.5\ R_e$	-55.424272	-0.179711	0.1694	-0.180886	0.1702	-0.180937
24		$2.0\ R_e$	-55.393626	-0.109622	0.1168	-0.110437	0.1188	-0.111898
25, NH_2, $^2A_1$	$(9s5p1d/4s1p)$	$1.0\ R_e$	-55.526381	-0.162157	0.0077	-0.162404	0.0077	-0.162381
26	$[4s2p1d/2s1p]$	$1.5\ R_e$	-55.325079	-0.191729	0.0368	-0.192594	0.0369	-0.192535
27		$2.0\ R_e$	-55.260731	Not converged		-0.154599	0.1521	-0.154402
28, CH_3, $^2A_2''$	$(9s5p1d/4s1p)$	$1.0\ R_e$	-39.570629	-0.150450	0.0097	-0.150637	0.0098	-0.150583
29	$[4s2p1d/2s1p]$	$1.5\ R_e$	-39.298446	-0.183730	0.0929	-0.184555	0.0938	-0.184407
30		$2.0\ R_e$	-39.188279	-0.112681	0.4728	-0.122579	0.5159	-0.114853
31, BH, $^1\Sigma_g$	$(9s5p1d/4s1p)$	$1.0\ R_e$	-25.125260	-0.102298	0.0168	-0.102385	0.0169	-0.102355
32	$[4s2p1d/2s1p]$	$1.5\ R_e$	-25.062213	-0.113736	0.0273	-0.114065	0.0275	-0.113763
33		$2.0\ R_e$	-24.988201	-0.139243	0.0673	-0.140500	0.0691	-0.139132
34, SiH_2, $^3B_1$	$(12s8p1d/4s1p)$	$1.0\ R_e$	-290.009980	-0.094600	0.0212	-0.094750	0.0216	-0.094571
35	$[6s4p1d/2s1p]$	$1.5\ R_e$	-289.880549	-0.109749	0.1285	-0.110894	0.1347	-0.109939
36		$2.0\ R_e$	-289.837287	-0.087286	0.1825	-0.088235	0.1999	-0.088107

[a] Energies in Hartrees. $\mathscr{S}_1$ defined by Eq. (25); see [21]. Basis sets, geometries, and FCI energies from [19].

reference character a wave function possesses. Of course, such a criterion may be considered as being not very reliable since the s amplitudes can also become large because of serious deficiencies of the basis set used. In addition, multireference effects will also be reflected to some extent by D or T amplitudes and, therefore, a criterion based just on s amplitudes may be criticized. However, the $\mathscr{S}_1$ criterion may gain its usefulness from the fact that the s contributions are indirect, through interactions with D and T terms, and, in this way, they reflect the importance of D and T terms in the wave function. This explains why the $\mathscr{S}_1$ criterion has given useful information on the nature of calculated wave functions in many cases [21].

All energies obtained at the QCISDT level of theory are lower than the corresponding CCSDT energies obtained with the same basis set at the same geometry. Differences vary from just 0.1 mHartree in the case of CH_2, $^3B_1$ (calculation #11) to 10 mHartrees for the stretched geometry $(2R_e)$ of CH_3, $^2A_2''$ (#30). Without the latter case, QCISDT correlation energies are, on the average, 1 mHartree more negative than the corresponding CCSDT energies. In general, they are closer for equilibrium

geometries while energy differences increase for nonequilibrium geometries, i.e., for systems with considerable multireference character. Obviously, positive TS and TQ energy terms that are missing in QCISDT are responsible for $E(\text{QCISDT}) \leq E(\text{CCSDT})$. For example, the fifth-order contribution $E(\text{TS})$ is ≥ 0, amounting to several mHartrees in some cases.

While only some of the CCSDT energies are lower than the corresponding FCI energies, this holds for almost all QCISDT energies. This is not surprising in view of the fact that both CCSDT and QCISDT are nonvariation methods. Despite the nonvariational character of projected CC and QCI, Pople and co-workers investigated whether QCISD and QCISD(T) energies come close to FCI results [4]. Such a test is also carried out in Table III, where energy differences $E(\text{approx}) - E(\text{FCI})$ for QCISDT, CCSDT, and a number of other approximate methods are summarized. For example, for MBPT(4), the mean absolute deviation of calculated correlation energies from the corresponding FCI values is 12 mHartrees while it drops down to 6 mHartrees in the case of QCISD and just 2 mHartrees in the case of QCISD(T). Pople and co-workers interpreted this decrease as

TABLE III

Analysis of differences $E(\text{approx}) - E(\text{FCI})$.[a]

# System	Geometry	MBPT(4)	QCISD	QCISD(T)	QCISDT	CCSDT	$E(\text{QCISDT})$	$E(\text{FCI})$
1 Ne ^1S		−0.873	+1.708	−0.155	−0.549	−0.066	−128.703011	−128.702462
2		+2.562	+2.511	−0.040	−0.493	+0.119	−128.768382	−128.767889
3		−0.563			−0.438	+0.076	−128.769315	−128.768877
4 F ^2P		+1.830	+1.463	−0.011	−0.475	−0.058	−99.547095	−99.546620
5		+0.268	+2.250	−0.033	−0.585	−0.104	−99.567068	−99.566483
6		+0.529	+3.097	+0.047	−0.478	−0.015	−99.595355	−99.594877
7 F$^-$ ^1S		−4.748	+2.232	+0.112	−2.538	+0.329	−99.655879	−99.653341
8		−5.044	+3.533	+0.085	−2.410	+0.319	−99.680077	−99.677676
9		−5.398	+5.935	−0.367	−2.633	+0.273	−99.709323	−99.706690
10 NH$_3$ $^1A_1$		+1.921			+0.099	+0.348	−56.292512	−56.292611
11 CH$_2$ $^3B_1$		+1.880	+2.054	+0.343	−0.107	+0.017	−39.046367	−39.046260
12 $^1A_1$		+4.979	+3.522	+0.867	−0.024	+0.207	−39.027207	−39.027183
15 FH $^1\Sigma_g$	1.0 R_e	−1.263	+2.567	+0.242	−0.268	+0.266	−100.251237	−100.250969
16	1.5 R_e	+0.769	+4.136	+0.664	−0.452	+0.645	−100.160845	−100.160393
17	2.0 R_e	+4.841	+8.395	+1.383	−0.962	+1.125	−100.082070	−100.081108
19 H$_2$O $^1A_1$	1.0 R_e	+0.917	+3.879	+0.617	+0.030	+0.533	−76.256594	−76.256624
20	1.5 R_e	+5.764	+9.365	+1.814	+0.021	+1.785	−76.071384	−76.071405
21 #	2.0 R_e	+14.860	+21.381	−1.261	−6.156	−2.451	−75.958425	−75.952269
22 NH$_2$ $^2B_1$	1.0 R_e	+1.900	+3.134	+0.510	−0.046	+0.216	−55.742666	−55.742620
23	1.5 R_e	+39.230	+9.985	+3.609	+0.051	+1.226	−55.605158	−55.605209
24	2.0 R_e	+18.790	+11.034	+7.393	+1.461	+2.277	−55.504063	−55.505524
25 $^2A_1$	1.0 R_e	+1.615	+2.908	+0.492	−0.023	+0.223	−55.688785	−55.688762
26	1.5 R_e	+7.779	+7.276	+1.966	−0.059	+0.811	−55.517673	−55.517614
27	2.0 R_e	+41.297	+19.926	+9.951	−0.197	—	−55.415330	−55.415133
28 CH$_3$ $^2A_2''$	1.0 R_e	+1.463			−0.054	+0.133	−39.721266	−39.721212
29	1.5 R_e	+20.859			−0.148	+0.677	−39.483001	−39.482853
30 #	2.0 R_e	+127.841			−7.726	+2.172	−39.310858	−39.303132
31 BH $^1\Sigma_g$	1.0 R_e	+5.048			−0.030	+0.057	−25.227645	−25.227615
32	1.5 R_e	+7.231			−0.302	+0.027	−25.176278	−25.175976
33	2.0 R_e	+13.328			−1.369	−0.111	−25.128702	−25.127333
34 SiH$_2$ $^3B_1$	1.0 R_e	+2.555			−0.222	−0.029	−290.104773	−290.104551
35	1.5 R_e	+22.848			−0.955	+0.181	−289.991443	−289.990488
36	2.0 R_e	+25.582			−0.128	+0.824	−289.925522	−289.925394
Mean abs. dev[b]		12.011	6.013	1.453	0.954	0.553		
Mean abs. dev#[b]		8.183	5.281	1.364	0.568	0.436		

[a] Absolute energies in Hartrees; energy differences in mHartrees. Nos. correspond to the entries in Tables I and II. MBPT(4), QCISD, etc., denote the differences $E(\text{MBPT}(4)) - E(\text{FCI})$, $E(\text{QCISD}) - E(\text{FCI})$, etc.

[b] Mean absolute deviation for 33 calculations and mean deviation when excluding two calculations indicated by #.

reflecting (a) the superiority of CC methods over MBPT methods and (b) the importance of T excitations. For QCISDT and CCSDT, the mean absolute deviation is further reduced to 0.9 and 0.6 mHartree, respectively. If calculations 21 and 30 (H$_2$O, 2R$_v$; CH$_3$, 2R$_e$, Table III), which have the largest deviations from FCI values, are excluded from the comparison, mean absolute deviations are 0.6 and 0.5 mHartree, respectively, for QCISDT and CCSDT. These values suggest that QCISDT and CCSDT lead to comparably good approximations of

FCI values and that improvements are based in both cases on the inclusion of T effects at the CC level of theory [14, 15] rather than at the MBPT level as in the case of QCISDT(T) [4].

Calculated $\mathscr{T}_1$ diagnostics reveal the expected trends indicating, e.g., increased multireference character for systems with low-lying excited states (#7, 8, 9, F$^-$), open-shell molecules (#11, 12, CH$_2$), molecules with multiple bonds (#13, C$_2$H$_2$) or dative bonds (#14, CO), etc. (see Table I). Also, the stretching of bonds leads to an increase of the $\mathscr{T}_1$

diagnostics, thus indicating increased multireference character (Table II). Lee and co-workers [21] showed that $\mathcal{T}_1$ is always larger for QCISD or QCISD(T) than for CCSD or CCSD(T) and that it increases too strongly for the QCI methods with increasing nondynamical correlation. This suggests that QCISD and QCISD(T) are less stable than are the corresponding CC methods with regard to strong multireference character of the wave function.

The $\mathcal{T}_1$ values of Tables I and II suggest that orbital relaxation effects are similarly treated by QCISDT and CCSDT, but that, in most cases, $\mathcal{T}_1$(QCISDT) is slightly larger than or equal to $\mathcal{T}_1$(CCSDT). Obviously, the inclusion of T excitations improves the stability of QCI with regard to multireference effects. Large $\mathcal{T}_1$ values that may indicate instability of the method are found for stretched geometries (Table II); however, in these cases, they are found for both CCSDT and QCISDT. There is actually only one problem, namely, the stretched geometry of CH_3 (#30 Table II), for which QCISDT leads to a significantly higher $\mathcal{T}_1$ value than the value obtained with CCSDT. In this calculation, three H atoms are kept at a distance of about 2.2 Å from the C atom, which means that both T correlation effects and orbital relaxation will be strong, probably leading to sizable TS energy contributions, which are not covered by QCISDT. This seems to be the reason for the relatively large QCISDT correlation energy overshooting the corresponding FCI value by 8 mHartrees and the CCSDT value underestimating FCI by 2 mHartrees (see above). However, both $\mathcal{T}_1$(CCSDT) = 0.473 and $\mathcal{T}_1$(QCISDT) = 0.516 indicate that for a problem such as 30 neither CCSDT nor QCISDT guarantee a good energy value.

We conclude that QCISDT leads to correlation energies close to CCSDT and FCI values, that the method is much better than either QCISD or QCISD(T), and that it possesses a similar stability to CCSDT with regard to multireference character. Accordingly, QCISDT can replace CCSDT in applications without lowering the accuracy of calculated energies. This is also confirmed by the calculated relative energies.

ELECTRON AFFINITY OF FLUORINE

The CCSDT energies of F and F^- given in Table I lead to electron affinity values of 2.894, 3.014, and 3.035 eV, respectively, which are quite close to the corresponding FCI values (2.904, 3.016, 3.043 eV, Table I), but underestimate the experimental value (3.399 eV [22]) by 0.4 eV. At the QCISDT level, the

values for the electron affinity are 2.960, 3.075, and 3.101 eV, which means a slight improvement of 0.06 eV for all basis sets considered (Table I). Inspection of the correlation energies listed in Table I shows that the improvement is caused by a better description of the F^- ion.

SINGLET–TRIPLET ENERGY DIFFERENCE OF CH_2

The FCI/[4s2p1d/2s1p] value of the energy difference between CH_2, $^3B_1$, and CH_2, $^1A_1$ is 11.97 kcal/mol [19b] (Table I). The corresponding MBPT(4) value is 13.91 kcal/mol. Both QCISD and CCSD reduce the MBPT(4) difference by 1 kcal/mol to 12.89 kcal/mol, while QCISD(T) and CCSD(T) lead to 12.30 kcal/mol [4, 20b]. The best agreement with the FCI singlet–triplet splitting is achieved by QCISDT (12.02 kcal/mol) and CCSDT (12.09 kcal/mol) with the QCI value being slightly but not significantly better than the CC value.

ENERGY OF THE $^2A_1$ EXCITED STATE OF THE AMINO RADICAL

The FCI/[4s2p/2s1p] value of the energy difference between NH_2, $^2B_1$ and NH_2, $^2A_1$ is 33.8 kcal/mol [19e] (Table II). At all QCI and the CCSDT level of theory, this energy difference is reproduced within 0.1 kcal/mol or better. Even the corresponding MBPT(4) differs from the FCI value by just 0.2 kcal/mol. However, this changes for the stretched geometries. If the energy difference between the $^2B_1$ and $^2A_1$ states is evaluated at 1.5 R_e, only QCISDT can reproduce FCI values within 0.1 kcal/mol. For the series CCSDT, QCISD(T), QCISD, MBPT(4), deviations from FCI relative energies increase from -0.26, -1.03, -1.70, to -19.74 kcal/mol. At $2R_e$, the QCISD error (-1.04 kcal/mol) cannot be compared with the corresponding CCSDT error, because the latter method does not converge for the $^2A_1$ state (Table II). However, errors are clearly larger for QCISD(T), QCISD, and MBPT(4) (1.60, 5.58, and 14.12 kcal/mol, Table III), indicating erratic deviations in the case of MBPT(4), QCISD, and even QCISD(T).

DISSOCIATION ENERGIES D_e FOR MOLECULES WITH TRIPLE BONDS

In Table IV, dissociation energies D_e for the triple bond in acetylene, molecular nitrogen, and carbon monoxide are given for various levels of

TABLE IV
Dissociation energies D_e of HCCH, N_2, and CO.[a]

Method	Basis	C, ^3P	N, ^4S	O, ^3P	CH, $^2\Pi$	HCCH	N_2	CO
QCISD	6-31G(d)	−37.75318	−54.47357	−74.89769	−38.36589	−77.09247	−109.26198	−113.03560
						226.3	197.6	241.4
QCISD(T)	6-31G(d)	−37.75415	−54.47421	−74.89849	−38.36762	−77.10304	−109.27359	−113.04478
						230.8	204.1	246.5
CCSDT	6-31G(d)	−37.75648	−54.47624	−74.89859	−38.36804	−77.10299	−109.27323	−113.04459
						230.2	201.3	244.4
QCISDT	6-31G(d)	−37.75651	−54.47627	−74.89872	−38.36819	−77.10515	−109.27568	−113.04802
						231.4	202.8	246.5
CCSDT	PVTZ[b]	−37.78999	−54.52519	−74.98523	−38.42430	−77.21835	−109.39959	−113.18059
						231.9		219.1254.4
Exp.[c]					234.4	228.4	259.2	

[a] Absolute energies in Hartrees; D_e values in kcal / mol.
[b] Polarized valence TZ correlation consistent basis: [4s3p2d1f / 3s2p1d] [24].
[c] Experimental D_e values derived from experimental heats of formation considering vibrational corrections as described in [23].

theory and compared with experimental data [23]. As indicated by CCSDT/[4s3p2d1f] values (basis from [24]), accurate D_e values can only be expected for rather large basis sets including several sets of d, f, and g polarization functions. Since it was the goal of this work to compare QCISDT and CCSDT energies rather than obtaining the most accurate dissociation energies, we carried out the comparison with a much more modest basis set, namely, Pople's 6-31G(d) basis [25].

QCISDT dissociation energies are 5 kcal/mol better than the corresponding QCISD energies, which clearly demonstrates the importance of T excitations for the description of multiple bonds. But QCISDT values are also 1–1.5 kcal/mol better than CCSDT energies, which seems to result from the fact that CCSDT includes TS and TQ energy contributions while QCISDT does not. The TS term is positive at fifth order and rather small for an atom while it becomes larger for a molecule with a triple bond. Neglect of the TS term leads to a decrease of the D_e value. Noteworthy is that QCISD(T) dissociation energies are as large or even larger than QCISDT values. This has to do with the fact that QCISD(T), which includes T excitations only via perturbation theory, does not cover the important TT coupling effects. Since the latter prevent the T effects from being overestimated, QCISD(T) predicts T correlations effects, which are more important for the molecule than for the atom, much too large, thus artificially increasing calculated dissociation energies.

The data in Table IV show that an accurate determination of D_e is more difficult for N_2 and

CO than for HCCH. This is not surprising in view of the fact that a balanced treatment of N (spherical charge distribution) and N_2 (cylindrical charge distribution with large anisotropies at the atoms) at the same time is very difficult, while for CH and HCCH (both with cylindrical charge distributions), a certain cancellation of errors can be expected. To get a reasonable description of N and N_2, large basis sets and additional nodal planes introduced by f- and g-polarization functions are necessary.

THE POTENTIAL ENERGY CURVE OF Be_2

The potential energy curve of Be_2 was investigated by Sosa and co-workers at the CCSDT and the various CCSDT-n levels of theory in order to test whether CC theory can reproduce FCI results [26]. The test was carried out with a (7s3p1d) basis set and frozen core. At this level of theory, the FCI dissociation energy D_e is just 0.7 kcal/mol [27], although the experimental D_e value is about 2 kcal/mol [28]. Harrison and Handy showed that the inclusion of f-type polarization functions into a basis increases the FCI value of D_e to 1.86 kcal/mol, i.e., that an accurate account of D_e is a basis set problem while the location of the energy minimum can already be done at the FCI/(7s3p1d) level of theory [27]. Accordingly, approximate methods can be tested whether they reproduce the small energy well for the potential energy curve of Be_2 and how their D_e values compare with the FCI value of 0.7 kcal/mol. In Table V, QCISDT energies are given together with the corresponding CCSDT-4, CCSDT, and FCI energies for a number of Be,Be

TABLE V

Comparison of total energies calculated for Be$_2$ with a (7s3p1d) basis set.[a]

R	CCSDT-4	CCSDT	QCISDT	FCI
4.50	−29.237113	−29.236596	−29.236876	−29.236940
4.75	−29.237920	−29.237476	−29.237663	−29.237747
5.00	−29.238069	−29.237692	−29.237803	−29.237903
5.25	−29.237944	−29.237630	−29.237689	−29.237797
5.50	−29.237764	−29.237496	−29.237524	
6.50	−29.237376	−29.237244	−29.237253	
8.00	−29.237240	−29.237198	−29.237207	
8.50	−29.237178	−29.237150	−29.237156	
2 Be	−29.236800	−29.236787	−29.236801	

[a] Energies in Hartrees; distance R in bohrs. CCSDT, CCSDT-4, and FCI energies have been taken from [26].

distances R along the potential energy curve. In Figure 4, calculated potential energy curves are given for the four methods considered.

Sosa and coworkers showed that the appearance of a minimum at 5 bohr depends on the inclusion of $V\hat{T}_3$ into the T projection equations which is first done at the CCSDT-4 level of theory [26]. Thus, the multireference character of Be$_2$ can only be regained by T excitation effects included into the T equations. QCISDT contains $V\hat{T}_3$ but also the important nonlinear term $V\hat{T}_2\hat{T}_3$, which is missing in CCSDT-4. Therefore, it should perform better than CCSDT-4.

For all methods considered, the energy minimum of the van der Waals complex Be$_2$ is at 5 bohr. The best approximation to the FCI energy at the minimum is given by QCISDT, which leads to an energy just 0.1 mHartree above the FCI value. The CCSDT energy deviates by 0.2 mHartree while the CCSDT-4 value overshoots the FCI energy by almost the same amount. In the region between 4.5 and 5.25 bohr, QCISDT values are closer to FCI energies than either CCSDT or CCSDT-4 energies. Beyond 6 bohr, CCSDT and QCISDT energies approach each other within 0.01 mHartree while CCSDT-4 values deviate considerably. The dissociation energy D_e of the van der Waals complex Be$_2$ is 0.80 (CCSDT-4), 0.57 (CCSDT) [26], and 0.63 kcal/mol (QCISDT), respectively, compared to an FCI value of 0.7 kcal/mol [27]. Hence, QCISDT leads to slightly better D_e values than CCSDT does.

Advantages of QCISDT

The discussion has shown so far the following advantages of QCISDT:

1. QCISDT is superior to both QCISD and QCISD(T) with regard to the reproduction of FCI energies. In addition, it leads to better relative energies than either QCISD or QCISD(T).

2. Compared to QCISD and QCISD(T), QCISDT is more stable in calculations of systems with multireference character.

3. QCISDT reproduces CCSDT absolute energies for the examples discussed within 1 mHartree. Its relative energies are slightly better than CCSDT energies. In some cases, even absolute QCISDT correlation energies compare better than CCSDT energies with the corresponding FCI data. However, the better agreement of QCISDT energies with FCI energies is simply due to a fortuitous cancellation of errors, which results from the omission of positive terms such as the TS contribution at fifth order.

4. Compared to CCSDT, the implementation of QCISDT on a computer is relatively easy, and, therefore, attractive for those who do not want to set up the matrix elements for a CCSDT program.

Apart from those advantages, QCISDT converges somewhat faster in cases with stretched bond geometries. Stretching of bonds increases multireference character, orbital relaxation, and T correlation effects. One can expect that this also leads to an increased coupling among S, D, and T amplitudes. The correlation energy directly depends only on the D amplitudes, but the latter depend on both the S and T amplitudes. The simpler this coupling is expressed by nonlinear terms $\hat{T}_n\hat{T}_m$ the quicker the D amplitudes adjust to orbital relaxation and T correlation effects. Accordingly, a method such as
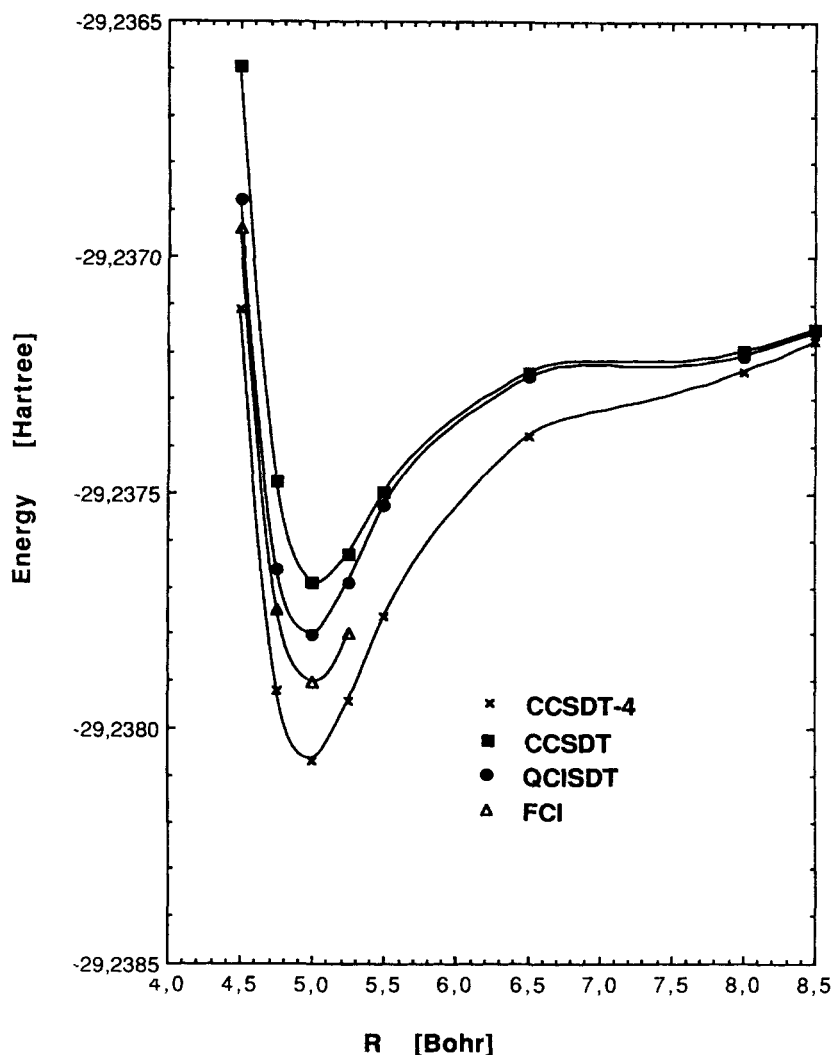
FIGURE 4. Calculated potential energy curves for the ground state of Be_2, $^1\Sigma_g^+$.

QCISDT with just three quadratic coupling terms $(\hat{T}_1\hat{T}_2, \hat{T}_2\hat{T}_2, \hat{T}_2\hat{T}_3)$ should converge faster than a method such as CCSDT, which possesses a complicated coupling structure. Differences in convergence behavior will show more for stretched geometries (relatively large multireference character) than for equilibrium geometries (relatively small multireference character). We conclude that QCISDT is an attractive alternative to CCSDT because of the reasons mentioned above.

ACKNOWLEDGMENTS

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