NON-ITERATIVE FIFTH-ORDER TRIPLE AND QUADRUPLE EXCITATION ENERGY CORRECTIONS IN CORRELATED METHODS

Rodney J. BARTLETT, J.D. WATTS, S.A. KUCHARSKI [1] and J. NOGA [2]

Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, FL 32611-2085, USA

Received 26 October 1989; in final form 20 November 1989

In critical cases, single-reference correlated methods like coupled-cluster theory or its quadratic CI approximations fail because of the importance of additional highly excited excitations that cannot usually be included, like connected triple and quadruple excitations. Here we present the first, non-iterative method to evaluate the full set of fifth-order corrections to CCSD and QCISD and assess their accuracy compared to full CI for the very sensitive Be_2 curve and other cases.

1. Introduction

Today it is well known that coupled-cluster (CC) theory provides highly accurate results for molecular energies and properties (see ref. [1] for a recent review). For routine applications CC methods have frequently been limited to double ($\mathrm{CCD}=\exp(T_2)\,|0\rangle$ [2]), and single and double $\mathrm{CCSD}=\exp(T_1+T_2)\,|0\rangle$ excitations [3], since these are efficient (they scale with the number of basis functions as $N_{\mathrm{it}}n^6$ where N_{it} is the number of iterations with n the number of basis functions). Both methods include the principal (disconnected) part of the quadruple excitations ($\frac{1}{2}T_2^2$) while CCSD also adds disconnected triples like T_1T_2, etc. Although the CCSD results are far better than the corresponding single reference CISD methods because of the elimination of size-inextensive terms and the additional higher levels of excitation introduced, they will still fail when the reference function is too poor an approximation to the particular electronic state of interest. This failure occurs when multiple bonds are broken, for example, because several configurations might be necessary to provide the correct zero-order description. Whereas a single electron pair bond breaking only requires double excitations to get correct separation, double bonds require quadruple, and triple bonds, hextuple excitations, which often recommend multi-reference methods [4]. Nevertheless, the unambiguous application of a single reference method has merit for many problems. To obtain sufficiently accurate answers, however, generally requires consideration of *connected* triple (T_3) and for difficult cases, *connected* quadruple (i.e. T_4) cluster operators. The former has been included previously in CCSDT-1 [5], which unlike CCSD is correct through fourth-order in the energy. Additional fifth- and higher-order terms are introduced in CCSDT-2 [6] and in the full CCSDT [7] method. Whereas CCSDT-1,2 are $N_{\mathrm{it}}n^7$ methods and do not require storage of the T_3 amplitudes, the full CCSDT method requires storage of T_3 plus an $N_{\mathrm{it}}n^8$ step in its evaluation. However, for difficult cases, the improvement of CCSDT compared to CCSDT-1,2 can be significant [7–9].

Repeating an n^7 step N_{it} times makes such methods much more expensive computationally than a non-iterative n^7 step that may be added onto CCSD. Such a method, CCSD+T(CCSD), correct through fourth order, has been proposed [10], along with others that added non-iterative singles and triples to CCD [11]. For energies, CCSD+T(CCSD) is usually close to the CCSDT-1 results, but closer inspection for difficult cases such as for some diatomic potential curves, where CCSD results are equally good [12], or the frequencies of

[1] Permanent address: Silesian University, Chemistry Department, Szkolna 9, 40-006 Katowice, Poland.

[2] Permanent address: Slovak Academy of Sciences, Institute of Inorganic Chemistry, 84236 Bratislava, Czechoslovakia.

0009-2614/90/$ 03.50 © Elsevier Science Publishers B.V. (North-Holland)

O_3, where it fails [13], emphasizes the necessity of including some higher-order correlation corrections, primarily those that occur in fifth order [14].

For a CC method to be correct through fifth order in the energy, however, consideration of T_4 is also required. Two iterative CC methods that are correct through fifth order have been presented: the CCSDTQ-1 method [15] and the alternative expectation value ansatz, XCC(5) approach [16,17]. The considerable improvement of the former over CCSDT has been demonstrated [15]. However, the iterative inclusion of T_4 in CCSDTQ-1 requires an $N_{\rm it}n^9$ step, which is one power of n worse than CCSDT. Hence, T_4 can also benefit from a non-iterative inclusion of these effects. In this regard, XCC(5) introduces a new factorization that does not occur in standard CC theory. This makes it possible to evaluate the fifth-order T_4 correction with only a *single* n^7 procedure [14,15]. In the following the theory is derived and results presented for the first full non-iterative inclusion of *all* terms that contribute in the fifth-order energy with only one term, the T_3 to T_3 contribution, which scales as n^8, scaling worse than n^7. Such a method, CCSD+TQ*(CCSD), or the alternative n^7 method we present, can be easily added to a converged CCSD result to obtain a measure of the higher-order correlation corrections, should be close to the full CI limit, as shown here for some examples, including the difficult Be_2 curve. Hence it might well offer a single-reference method of high and routine applicability. To illustrate, for a 100 basis function example, the non-iterative method presented here is about $\approx 10^3$ times less expensive than CCSDTQ-1, and about $\approx 10^5$ compared to a full CCSDTQ or CISDTQ result.

2. Theory

In operator form, we can write the CCSDTQ equations for an SCF reference as

$$D_2T_2 = W_N + W_NT_2 + W_NT_1 + W_NT_3 + W_NT_2^2/2 + W_NT_4 + W_NT_1T_2$$
$$+ (W_NT_1T_3 + W_NT_1^2/2 + W_NT_1^2T_2/2 + W_NT_1^3/3! + W_NT_1^4/4!)\,, \tag{1a}$$

$$D_1T_1 = W_NT_2 + W_NT_1 + W_NT_3 + (W_NT_1T_2 + W_NT_1^2/2 + W_NT_1^3/3!)\,, \tag{1b}$$

$$D_3T_3 = W_NT_2 + W_NT_3 + W_NT_2^2/2 + (W_NT_4 + W_NT_1T_2 + W_NT_3T_2 + W_NT_1T_3 + W_NT_1T_4$$
$$+ W_NT_2^2T_1/2 + W_NT_1^2T_2/2 + W_NT_1^2T_3/2 + W_NT_1^3T_2/3!)\,, \tag{1c}$$

$$D_4T_4 = W_NT_3 + W_NT_2^2/2 + (W_NT_4 + W_NT_2^3/3! + W_NT_1^2T_4/2 + W_NT_2T_3 + W_NT_1T_3 + W_NT_2T_4$$
$$+ W_NT_1T_2T_3 + W_NT_2^2T_1/2 + W_NT_2^2T_1^2/4 + W_NT_1T_4 + W_NT_1^2T_3/2 + W_NT_1^3T_3/3!)\,. \tag{1d}$$

These equations operate on the right on the Fermi vacuum $|0\rangle$, and are to be projected from the left by the appropriate category of n-fold excitation space, $Q_n = |\boldsymbol{h}_n\rangle\langle\boldsymbol{h}_n|$, where $\boldsymbol{h}_n$ are the n-fold excited determinants, to determine T_n and the appropriate denominator D_n. For $\boldsymbol{h}_3$, e.g. $Q_3D_3T_3 = (\epsilon_i+\epsilon_j+\epsilon_k-\epsilon_a-\epsilon_b-\epsilon_c)t_{ijk}^{abc}$. The resolution of the identity is $1 = |0\rangle\langle 0| + \sum_n Q_n$. In all cases, the restriction to connected terms is understood except when it is necessary to make it explicit. The inability to obtain connected terms for W_NT_2, $W_NT_1^2T_2/2$ or $W_NT_1^4/4!$ eliminates such contributions to D_4T_4, e.g.

The operator H_N is the usual normal-ordered two-electron operator

$$H_N = \sum_{p,q} f_{pq} N[p^\dagger q] + \tfrac{1}{4}\sum_{p,q,r,s}\langle pq\|rs\rangle N[p^\dagger q^\dagger sr] = \sum_p \epsilon_p N[p^\dagger p] + W_N = H_N^{(0)} + W_N \tag{2}$$

in the canonical SCF case. The orders in the correlation energy, W_N, in which the various terms first appear are determined by noting that T_2 is first order, T_1 and T_3 second order, and T_4 third order. The correlation energy expression is

$$\Delta E = \langle 0|W_NT_2|0\rangle + \langle 0|W_NT_1^2/2|0\rangle\,. \tag{3}$$

Hence, all terms included in parentheses in eq. (1) only contribute beyond fifth order to ΔE. For T_2 such terms are higher than fourth order in W_N, while for T_1, T_3 and T_4 nothing higher than third-order contributions can contribute within fifth order in ΔE.

In CCSD the wavefunction is defined as $\exp(T_1+T_2)|0\rangle$, hence all contributions composed exclusively of T_2 and T_1 in eqs. (1a) and (1b) are retained regardless of order. In the QCISD approximation to CCSD [18], all the T_1 and T_2 terms in eqs. (1a) and (1b) which are not in parentheses are included, except for the $W_N T_1 T_2$ term in eq. (1a), contributing in fifth order while the sixth-order $W_N T_1 T_2$ term in eq. (1b) is retained. QCISD also neglects the second term (also fifth order) in eq. (3).

The first correction to CCSD results from triple excitations. The only fourth-order energy contribution comes from the Q_3 projection of the second-order term in eq. (1c),

$$Q_3 D_3 T_3 = Q_3 W_N T_2 \,. \tag{4}$$

Taking T_2 from a converged CCSD calculation, $T_2=\bar{T}_2$, within the spirit of the CC method we can evaluate the energy correction as

$$Q_3 D_3 T_3^{[2]} = Q_3 W_N \bar{T}_2 \,, \tag{5a}$$

where $T_3^{[2]}$ indicates that this T_3 contribution involves second-order and higher terms. $T_3^{(2)}$ would indicate the pure second-order contribution, with $\Delta E_T^{(4)}$ the pure fourth-order MBPT triples correction. Then

$$Q_2 D_2 T_{2T}^{[4]} = Q_2 W_N T_3^{[2]} = Q_2 W_N Q_3 W_N \bar{T}_2/D_3 \tag{5b}$$

and

$$\Delta E_{Ta}^{[4]} = \langle 0| W_N T_{2T}^{[4]} |0\rangle \,. \tag{6}$$

This then defines the energy,

$$\Delta E = \Delta E_{CCSD} + \Delta E_{Ta}^{[4]} \,. \tag{7}$$

Replacing $\Delta E_{Ta}^{[4]}$ by $\Delta E_T^{(4)}$ would also be correct through fourth order but would not benefit from the infinite-order effects in $\bar{T}_2$.

Alternatively, we could also consider the expectation value expression for the energy,

$$\Delta E = \langle 0| [\exp T^{\dagger} H_N \exp T]_C |0\rangle \,, \tag{8}$$

where the denominator is eliminated by virtue of restricting ΔE to just connected terms. This expression is only exactly true for an untruncated T operator. Hence, for $T=T_1+T_2$,

$$\langle 0| [\exp(\bar{T}_1^{\dagger}+\bar{T}_2^{\dagger})\, H_N \exp(\bar{T}_1+\bar{T}_2)]_C |0\rangle$$

$$= \Delta E_{CCSD} + \langle 0| \bar{T}_2^{\dagger 2}/2 (W_N \bar{T}_2^2/2)_C |0\rangle + \langle 0| \bar{T}_1^{\dagger} \bar{T}_2^{\dagger} (W_N T_2)_C |0\rangle + \text{higher-order terms} \,. \tag{9}$$

The extra fifth-order terms in eq. (9) will be discussed later. We should note, however, that the Hermitian conjugate of the third term in eq. (9) does not occur because it contributes to ΔE_{CCSD}. Adding the connected triple excitation term, we have the increment to eq. (9),

$$\Delta E_T = (\langle 0| [\exp T_3^{\dagger} H_N \exp(\bar{T}_1+\bar{T}_2)]_C |0\rangle + \text{h.c.}) + \langle 0| (\exp T_3^{\dagger} H_N \exp T_3)_C |0\rangle - \Delta E_{CCSD} \,. \tag{10}$$

Restricting to just triple excitation terms that are initially fourth order in eq. (10),

$$\Delta E_T^{[4]} = \langle 0| T_3^{[2]\dagger} f_N T_3^{[2]} |0\rangle + (\langle 0| T_3^{[2]\dagger} W_N \bar{T}_2 |0\rangle + \text{h.c.})$$

with h.c. indicating the Hermitian conjugate of the other term(s) in the same parentheses. Recognizing that $Q_3 f_N T_3^{[2]} = -Q_3 D_n T_3^{[2]} = -Q_3 W_N \bar{T}_2$,

$$\Delta E_{Tb}^{[4]} = \langle 0| T_3^{[2]\dagger} D_3 T_3^{[2]} |0\rangle \,. \tag{11}$$

Using this quadratic measure of the converged triple excitations gives what we have called CCSD+T(CCSD) [10],

$$\Delta E = \Delta E_{\mathrm{CCSD}} + \Delta E^{[4]}_{\mathrm{T}b} . \tag{12}$$

The difference in eq. (7) and eq. (12) is that the higher-order correlation corrections contained in $\bar{T}_2$ are introduced twice in the latter. All such fifth- and higher-order terms introduced are valid (non-redundant) correlation corrections. For correlation energies, the errors in $\Delta E^{[4]}_{\mathrm{T}b}$ are generally in the correct direction, so CCSD+T(CCSD) will frequently give excellent agreement with full CI energies (see table 1), although in some difficult cases the shape of the energy surface may not be as reliable or even better than that for CCSD [12,13].

To introduce non-iterative fifth-order corrections we need to consider all terms not in parentheses in eq. (1) that depend upon T_3 or T_4. Since eq. (5a) provides us with the approximation $T^{[2]}_3$ that results in an energy correct to fourth order, we can define the terms that will first contribute in fifth order as

$$Q_3 D_3 T^{[3]}_3 = Q_2 W_{\mathrm{N}} (\bar{T}^2_2/2 + T^{[2]}_3) , \tag{13a}$$

$$Q_4 D_4 T^{[3]}_4 = Q_4 W_{\mathrm{N}} (\bar{T}^2_2/2 + T^{[2]}_3) . \tag{13b}$$

The $T^{[2]}_3$ to $T^{[3]}_3$ term in eq. (13a) is n^8, while eq. (13b) would be n^9 without further simplification. Then by determining the contributions of eq. (13) to T_2 and T_1, we have

$$Q_3 D_3 T^{[4]}_{2\mathrm{T}} = Q_3 W_{\mathrm{N}} T^{[3]}_3 , \tag{14a}$$

$$Q_2 D_2 T^{[4]}_{2\mathrm{Q}} = Q_2 W_{\mathrm{N}} t^{[3]}_4 , \tag{14b}$$

$$Q_2 D_2 T^{[4]}_{2\mathrm{ST}} = Q_2 W_{\mathrm{N}} T^{[3]}_{1\mathrm{T}} , \tag{14c}$$

$$Q_1 D_1 T^{[3]}_{1\mathrm{T}} = Q_1 W_{\mathrm{N}} T^{[2]}_3 , \tag{14d}$$

$$Q_1 D_1 T^{[2]}_{1\mathrm{D}} = Q_1 W_{\mathrm{N}} \bar{T}_2 . \tag{14e}$$

Defining $T^{[4]}_2 = T^{[4]}_{2\mathrm{T}} + T^{[4]}_{2\mathrm{Q}} + T^{[4]}_{2\mathrm{ST}}$, within the standard projected scheme using eq. (3), we have the energy contributions,

$$\Delta E^{[5]} = \langle 0 | W_{\mathrm{N}} T^{[4]}_2 | 0 \rangle + \langle 0 | W_{\mathrm{N}} T^{[2]^2}_1 /2 | 0 \rangle = \Delta E^{[5]}_{\mathrm{T}a} + \Delta E^{[5]}_{\mathrm{Q}a} + \Delta E^{[5]}_{\mathrm{ST}a} + \Delta E^{[5]}_{\mathrm{SD}} . \tag{15}$$

The direct T_1 contribution to the energy contributes for the first time in fifth-order subject to an SCF reference, so that is absorbed into $\Delta E^{[5]}_{\mathrm{SD}}$ along with the other fifth-order terms included in CCSD. In the form of eq. (13b), the $T^{[4]}_{2\mathrm{Q}}$ term would require an n^9 algorithm, although as shown elsewhere this term called $Q^{(1)}$ [15]

Table 1
Non-iterative contributions of triple and quadruple excitations to the coupled-cluster energy (hartree) [a]

		$E_{\mathrm{SCF}}+\Delta E_{\mathrm{CCSD}}$	$\Delta E^{[4]}_{\mathrm{T}}$	$\Delta E^{[5]}_{\mathrm{ST}}$	$\Delta E^{[5]}_{\mathrm{TD}}$	$\Delta E^{[5]}_{\mathrm{TT}}$	$\Delta E^{[5]}_{\mathrm{Q}} = \mathrm{Q}^*$	Q[T(CCSD)] [b]
BH	R_e	−25.225834	−0.001406	+0.000026	+0.000041	−0.000359	−0.000050	−0.000032
	$1.5R_e$	−25.173332	−0.002257	+0.000165	+0.000038	−0.000565	+0.000022	+0.000009
	$2.0R_e$	−25.122298	−0.005477	+0.000835	−0.000028	−0.001328	+0.000359	+0.000176
HF	R_e	−100.247963	−0.002908	+0.000299	+0.000222	−0.000134	−0.000155	−0.000155
	$1.5R_e$	−100.155296	−0.004951	+0.000738	+0.000316	−0.000244	−0.000392	−0.000406
	$2.0R_e$	−100.070927	−0.012093	+0.002169	+0.000655	−0.000825	−0.000270	−0.000368
H_2O	R_e	−76.252502	−0.003560	+0.000155	+0.000254	−0.000344	−0.000438	−0.000442
	$1.5R_e$	−76.061247	−0.008780	+0.000620	+0.000754	−0.001118	−0.001506	−0.001527
	$2.0R_e$	−75.930865	−0.028115	+0.002077	+0.004362	−0.004499	+0.002812	+0.000433

[a] All basis sets are DZP as defined in ref. [21].
[b] The alternative Q[T(CCSD)] approximation is given by $\frac{1}{2}\langle 0 | T^{(1)\dagger}_2 \bar{T}_2 (W_{\mathrm{N}} \bar{T}^2_2/2 + T_3)_{\mathrm{C}} | 0 \rangle$, ref. [15].

can be reduced to an n^7 evaluation by the factorization theorem. To introduce more infinite-order effects one can again appeal to the alternative energy expressions, eqs. (8) and (9).

From eq. (10), the fifth-order contributions from T_3 are

$$\Delta E^{[5]}_{\mathrm{T}b} = (\langle 0|T_3^{[3]\dagger} f_N T_3^{[2]}|0\rangle + \langle 0|T_3^{[3]\dagger} W_N \bar{T}_2|0\rangle + \mathrm{h.c.}) + (\langle 0|T_3^{[2]\dagger} f_N \bar{T}_1 \bar{T}_2|0\rangle + \mathrm{h.c.})$$
$$+ (\langle 0|T_3^{[2]\dagger} W_N \bar{T}_2^2/2|0\rangle + \mathrm{h.c.}) + \langle 0|T_3^{[2]\dagger} W_N T_3^{[2]}|0\rangle + (\langle 0|\bar{T}_1^\dagger W_N T_3^{[2]}|0\rangle + \mathrm{h.c.}) . \tag{16}$$

Through *fifth order*, the first parenthesis vanishes by virtue of eq. (5a) that says that through *second-order* $Q_3(f_N T_3^{[2]} + W_N \bar{T}_2) = 0 + \delta(3)$ making any non-vanishing corrections to this term sixth and higher order.

To begin to simplify the remaining terms in eq. (16) we employ the concept of *internally disconnected* terms [16]. This recognizes that some quantities in eq. (16), even though connected en toto, may be written in terms of a connected and a disconnected part,

$$\langle 0|[T_3^{[2]\dagger} W_N \bar{T}^2/2]_C|0\rangle = \langle 0|[T_3^{[2]\dagger}(W_N \bar{T}^2/2)]_C|0\rangle + \langle 0|[T_3^{[2]\dagger}(W_N \bar{T}^2/2)_D]_C|0\rangle \tag{17a}$$

and

$$\langle 0|[T_3^{[2]\dagger} f_N \bar{T}_1 \bar{T}_2]_C|0\rangle = \langle 0|[T_3^{[2]\dagger} \bar{T}_2 (f_N \bar{T}_1)_C]_C|0\rangle + \langle 0|[T_3^{[2]\dagger} \bar{T}_1 (f_N \bar{T}_2)_C]_C|0\rangle . \tag{17b}$$

Similarly, the h.c. of the last quantity in eq. (16) is

$$\langle 0|[T_3^{[2]\dagger} W_N \bar{T}_1]_C|0\rangle = \langle 0|[T_3^{[2]\dagger}(W_N \bar{T}_1)_D]_C|0\rangle = \langle 0|[T_3^{[2]\dagger} \bar{T}_1 W_N]_C|0\rangle . \tag{17c}$$

We are separating these terms asymmetrically, as may be noted by recognizing that the conjugate of the term in eq. (17a) must have the two right-hand operators connected. The alternative of symmetrizing these quantities that distinguishes the unitary (UCC) method from the expectation value (XCC) method [16] will be considered elsewhere. The purpose of the separation into connected and disconnected parts is that it is possible to eliminate all fifth-order internally disconnected terms up to sixth order. That is from eqs. (17b) and (17c)

$$\langle 0|[T_3^{[2]\dagger} \bar{T}_1 W_N]_C|0\rangle + \langle 0|[T_3^{[2]\dagger} \bar{T}_1 (f_N \bar{T}_2)_C]_C|0\rangle = 0 + \delta(6) , \tag{18}$$

since $Q_2(f_N \bar{T}_2 + W_N) = 0 + \delta(2)$; and recognizing that the resolution of the identity may be inserted with only the double excitation part Q_2 surviving. Similarly, from eqs. (17a) and (17b)

$$\langle 0|[T_3^{[2]\dagger} \bar{T}_2 (W_N \bar{T}_2)_C]_C|0\rangle + \langle 0|[T_3^{[2]\dagger} \bar{T}_2 (f_N \bar{T}_1)_C]_C|0\rangle = 0 + \delta(6) .$$

The $\langle 0|\bar{T}_1^\dagger \bar{T}_2^\dagger (W_N T_2)_C|0\rangle$ term in eq. (9) is cancelled by the h.c. of eq. (17b). The remaining terms derived from T_3 in eq. (16) plus the remaining internally connected term from eq. (17a) may be written as

$$\Delta E^{[5]}_{\mathrm{T}b} = \langle 0|T_3^{[2]\dagger} D_3 T_3^{[3]}|0\rangle + \langle 0|\bar{T}_2^{\dagger 2}/2 W_N T_3^{[2]}|0\rangle + \langle 0|\bar{T}_1^\dagger D_1 T_{1\mathrm{T}}^{[3]}|0\rangle , \tag{19a}$$

$$= \Delta E^{[5]}_{\mathrm{TT}} + \Delta E^{[5]}_{\mathrm{TD}} + \Delta E^{[5]}_{\mathrm{QT}} + \Delta E^{[5]}_{\mathrm{ST}} . \tag{19b}$$

The first two terms in eq. (19b) follow simply from eq. (13a), while the third is the h.c. in the third parentheses of eqs. (16). The last term derives from the simplified form of the remaining conjugate in the last parentheses of eq. (16), using eq. (14d).

The connected quadruple contributions in fifth order potentially have two parts: the extra term in eq. (9) and that derived directly from T_4,

$$(\langle 0|\bar{T}_2^\dagger W_N T_4^{[3]}|0\rangle + \mathrm{h.c.}) + (\langle 0|\bar{T}_2^\dagger/2 f_N T_4^{[3]}|0\rangle + \mathrm{h.c.}) . \tag{20}$$

But from the fact that $\bar{T}_2^\dagger Q_2(W_N + T_2^\dagger f_N) = 0 + \delta(3)$, we see that eq. (20) can only contribute in sixth and higher order. Hence, through fifth order, we only need to consider the fifth-order term of eq. (9),

$$\Delta E^{[5]}_{\mathrm{QQ}} = \langle 0|[\bar{T}_2^{\dagger 2}/2(W_N \bar{T}_2^2/2)_C]_C|0\rangle , \tag{21}$$

which together with the second term on the right-hand side of eq. (19a), i.e. $\Delta E^{[5]}_{\mathrm{QT}}$, gives

$$\Delta E_{\mathrm{Q}}^{[5]} = \Delta E_{\mathrm{QQ}}^{[5]} + \Delta E_{\mathrm{QT}}^{[5]} . \tag{22}$$

Closer inspection demonstrates [16] that though formally independent of T_4, these two terms are the factorized form of the fifth-order T_4 corrections.

Computationally the first term in eq. (22) is n^6 while the second is n^7. Consequently, by taking the initial n^7 approximation to T^3, i.e. $T_3^{[2]}$ from eq. (5a), all fifth-order non-iterative correction terms are determined by an n^7 non-iterative procedure except for the part of $\langle 0|\bar{T}_3^{[2]} D_3 \bar{T}_3^{[3]}|0\rangle$ that comes from $T_3^{[2]}$ in eq. (13a) (i.e. the $\Delta E_{\mathrm{TT}}^{[5]}$ part), which requires a single n^8 step. Using converged T_3 amplitudes from CCSDT, we call the quantity in eq. (22), Q*(CCSDT) to distinguish it from Q and $Q^{(1)}$ discussed elsewhere [15]. Limiting ourselves to a fourth-order approximation to the T_3 amplitudes, $T_3^{[2]}$, $\Delta E_{\mathrm{Q}}^{[5]} = \mathrm{Q^*[T(CCSD)]}$. Putting all of these terms together we have the CCSD+TQ*(CCSD) method, whose energy is

$$\Delta E = \Delta E_{\mathrm{CCSD}} + \Delta E_{\mathrm{TT}}^{[5]} + \Delta E_{\mathrm{TD}}^{[5]} + \Delta E_{\mathrm{QT}}^{[5]} + \Delta E_{\mathrm{ST}}^{[5]} . \tag{23}$$

We previously [15] considered a slightly modified form of the T_4 correction, defined as $Q = \frac{1}{2}\langle 0|T_2^{(1)\dagger}\bar{T}_2(W_{\mathrm{N}}\bar{T}_2^2/2 + \bar{T}_3)_{\mathrm{C}}|0\rangle$ which differs from Q* by having one $T_2^\dagger$ limited to first order rather than infinite order. The origin of the approximation lies in the XCC(5) method [16].

Of the four distinct terms contributing in fifth order, two will normally be negative away from quasi-degenerate situations, the $\Delta E_{\mathrm{Q}}^{[5]}$ and $\Delta E_{\mathrm{TT}}^{[5]}$ contributions, while $\Delta E_{\mathrm{ST}}^{[5]}$ and $\Delta E_{\mathrm{TD}}^{[5]}$ will usually be positive. Hence, we can propose a model involving only one of these terms as CCSD+T*(CCSD) which will be $\Delta E_{\mathrm{CCSD}} + \Delta E_{\mathrm{T}}^{[4]} + \Delta E_{\mathrm{TD}}^{[5]}$. The numerical justification for this approximation is the degree of cancellation of the remaining three terms, or better, the cancellation of all higher correlation corrections as judged by comparison with full CI. From a theoretical viewpoint, this term derives from converged T_2 amplitudes in CCSD and requires only a single n^7 step in its evaluation, which is easy when the two terms $W_{\mathrm{N}}(\bar{T}_2 + \bar{T}_2^2/2)$ are properly evaluated in terms of the intermediates discussed elsewhere [19]. Similarly, we could choose only the $\Delta E_{\mathrm{ST}}^{[5]}$ term, which defines $\Delta E_{\mathrm{CCSD}} + \Delta E_{\mathrm{T}}^{[4]} + \Delta E_{\mathrm{ST}}^{[5]}$ or what has been called CCSD(T) [20]. From the CC viewpoint this involves T_3 instead of just T_2 and T_1, since $W_{\mathrm{N}}T_3$ provides a connected contribution to D_1T_1, but since $W_{\mathrm{N}}T_1$ is not a connected contribution to D_3T_3, it does not appear directly in the CC equations.

3. Numerical results

In table 1 the individual contributions for the fifth-order corrections are shown for the BH, HF and H_2O molecules at R_e, $1.5R_e$ and $2.0R_e$ in the DZP basis defined elsewhere [21]. An RHF reference is used in each case. $\Delta E_{\mathrm{TT}}^{[5]}$ is negative in all cases, while $\Delta E_{\mathrm{Q}}^{[5]}$ is usually negative except when highly degenerate cases are encountered like $2.0R_e$ for H_2O. The fourth-order triples correction $\Delta E_{\mathrm{T}}^{[4]} = \mathrm{T(CCSD)}$ is always at least an order of magnitude larger than $\Delta E^{[5]}$. Of the other terms, $\Delta E_{\mathrm{ST}}^{[5]}$ and $\Delta E_{\mathrm{TD}}^{[5]}$ are usually positive. Depending upon the system, either can be larger positive correction, however, and no single correction dominates. For example, in the most difficult case of H_2O at $2.0R_e$ all the terms in eq. (23) exceed 2 mhartree in magnitude. The alternative quadruple formula Q[T(CCSD)] has a smaller value.

Comparisons with full CI are shown in table 2, along with CCSDT [7] ad CCSDTQ-1 [15]. Whereas CCSDT already reduces the mean absolute error to the order of 1 mhartree for R_e and $1.5R_e$, CCSDTQ-1 improves upon this result by an order of magnitude, and about a factor of 2 at $2.0R_e$. Limiting the infinite-order sums to CCSD, with T_3 and T_4 effects evaluated as described in the text, i.e. CCSD+TQ*(CCSD), loses some of the accuracy of CCSDTQ-1 but still offers an improvement over CCSDT. It is also somewhat better than the alternative CCSD+TQ(CCSD) for these few examples. The dramatic improvement of any of the partial infinite-order methods over MBPT(5) is notable.

Since the fourth-order CCSD+T(CCSD) can be too low, selecting just one positive non-iterative fifth-order correction to augment it to damp the overestimation of the correlation energy, we choose to add the $\Delta E_{\mathrm{TD}}^{[5]}$

Table 2
Differences of correlation energies for various methods compared to full CI [a] (mhartree)

		CCSD +T(CCSD)	CCSDT	CCSDTQ-1	CCSD +TQ*(CCSD)	QCISD TQ*(QCISD)	CCSD +TQ(CCSD)	QCISD +TQ(QCISD)	CCSD +T*(CCSD)	CCSD(T)	MBPT(5) [b]
BH	R_e	0.375	0.056	0.028	0.033	0.028	0.051	0.046	0.416	0.401	2.514
	$1.5R_e$	0.387	0.026	0.042	0.005	−0.093	0.034	−0.107	0.425	0.552	3.604
	$2.0R_e$	−0.442	−0.108	−0.049	−0.604	−0.864	−0.787	−1.051	−0.470	0.393	6.055
HF	R_e	0.098	0.266	0.061	0.330	0.166	0.330	0.166	0.320	0.397	0.811
	$1.5R_e$	0.146	0.646	0.110	0.564	0.343	0.550	0.330	0.462	0.884	2.294
	$2.0R_e$	−1.912	1.125	0.351	−0.183	0.870	−0.281	0.798	−1.251	−0.257	8.103
H_2O	R_e	0.562	0.531	0.047	0.189	0.086	0.185	0.083	0.816	0.717	0.700
	$1.5R_e$	1.378	1.784	−0.023	0.128	−0.134	0.107	−0.142	2.132	1.998	4.983
	$2.0R_e$	−6.711	−2.472	−1.581	−1.959	−1.080	−4.338	−2.436	−2.351	4.634	16.97
mean absolute error											
	R_e	0.345	0.284	0.045	0.184	0.093	0.189	0.098	0.517	0.505	1.342
	$1.5R_e$	0.637	0.819	0.058	0.232	0.190	0.230	0.193	1.006	1.145	3.627
	$2.0R_e$	3.022	1.235	0.660	0.915	0.938	1.802	1.428	1.357	1.761	10.38

[a] Full CI results are taken from ref. [21]. [b] MBPT(5) results are taken from ref. [23].

Table 3
Quadruple excitation contributions as a function of different choices for T_3 amplitudes (mhartree)

		Q*(CCSDT)	Q(CCSDT)	Q(CCSDT-2)	Q*[T(CCSD)]	Q[T(CCSD)]	Q*[T(QCISD)]	Q[T(QCISD)]
BH	R_e	0.046	−0.027	−0.038	−0.050	−0.032	−0.050	−0.031
	$1.5R_e$	0.039	0.020	0.001	0.022	0.009	+0.025	+0.011
	$2.0R_e$	0.389	0.192	0.168	0.359	0.176	+0.370	+0.183
HF	R_e	−0.201	−0.205	−0.202	−0.155	−0.155	−0.155	−0.155
	$1.5R_e$	−0.518	−0.535	−0.497	−0.392	−0.406	−0.398	−0.411
	$2.0R_e$	−0.757	−0.834	−0.508	−0.270	−0.368	−0.365	−0.438
H_2O	R_e	−0.483	−0.483	−0.501	−0.438	−0.442	−0.411	−0.444
	$1.5R_e$	−1.841	−1.811	−1.847	−1.506	−1.527	−1.585	−1.593
	$2.0R_e$	7.185	1.725	0.844	2.812	0.433	+0.365	−0.990

term to define the n^7 CCSD+T*(CCSD) model. This is the same term that when evaluated iteratively gives the CCSDT-2 method [6]. CCSDT-2 was previously shown to be able to correctly describe the vibrational frequencies of O_3 [22] when lower-order methods like CCSD+T(CCSD) and CCSDT-1 could not [13]. The considerable improvement compared to the fourth-order CCSD+T(CCSD) is apparent. Although less accurate than CCSD+TQ*(CCSD), for these examples the error is on the order of 1 mhartree. The other choice of using the $\Delta E_{TS}^{[5]}$ term as in CCSD(T) has been considered by others [20]. At least for these examples, the mean energy errors would appear to be greater, but the errors tend to lie on the positive side of the full CI helps to avoid the characteristic turnover of a potential curve.

We also show results based upon QCISD instead of CCSD. The difference in obtaining TQ*(QCISD) is that QCISD ignores the $T_1^2/2$ term in eq. (3) and the $W_N T_1 T_2$ contributions to eq. (1a). Through fifth-order, these contributions are the same as $\Delta E_{ST}^{[5]}$, so this term is added twice to obtain the proper fifth-order estimate. Also, since QCISD is a truncation of CCSD, it neglects some energy contributions that are normally positive, giving lower energies than CCSD.

Since the connected quadruple correction can change depending upon the choice for the T_3 amplitudes, and the particular choice for the Q approximations, we illustrate that behavior in table 3. At R_e and $1.5R_e$ the measures are quite similar despite the different choices for T_3. Once large amounts of quasi-degeneracy apply as in H_2O at $2.0R_e$, the differences can be large. For example, using converged T_2 and T_3 amplitudes from CCSDT adds over 4 mhartree to the Q* estimate for $2.0R_e$ H_2O. Of course, such estimates of Q lose the clear fifth-order breakdown of T_3 and T_4.

A final result that is unusually informative is the Be_2 potential curve where only four electrons are correlated. In the 7s3p1d basis used [24], only CCSDT has accounted for a curve whose shape is in good agreement with full CI [8,25]. Lower approximations correct to fourth-order like CCSD+T(CCSD), QCISD(T), and CCSDT-1 give the results shown in fig. 1. However, CCSD+TQ*(CCSD) does an excellent job as shown in fig. 2. Here, the most important effect is the $\Delta E_{TT}^{[5]}$ term, but $\Delta E_{Q}^{[5]}$ is still significant. When the bond length is stretched to 100 a_0, so that the system corresponds to two separated Be atoms, TQ*(CCSD)=0, as it should, since the CCSD method is size extensive and exact for a two-electron system.

Other systems we have considered like the N_2 and F_2 potential curves offer very different kinds of correlation

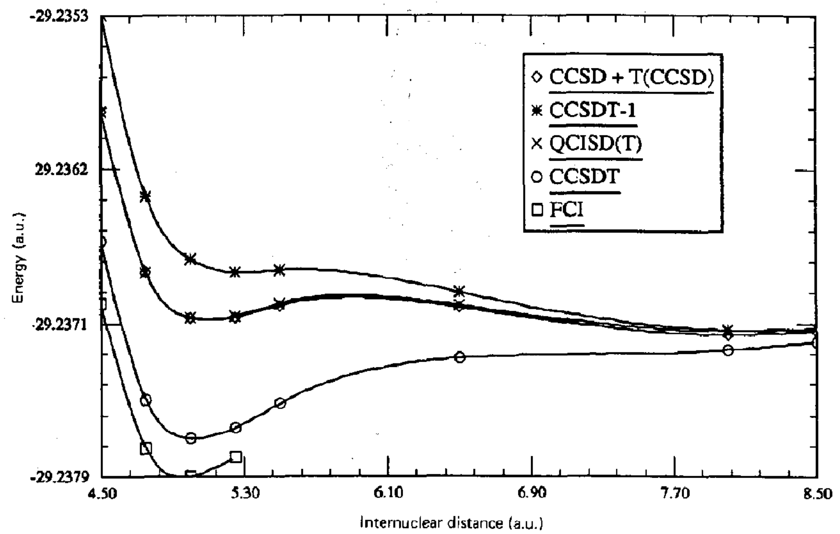

Fig. 1. Potential energy curves for the ground state of the Be_2 molecule calculated at the CCSD+T(CCSD), CCSDT-1, QCISD(T), CCSDT, and FCI levels of theory. The CCSD+T(CCSD), CCSDT-1, and CCSDT data are from ref. [8], and the FCI data are from ref. [25]. Note that on this scale the CCSD+T(CCSD) and QCISD(T) curves are almost exactly superimposable.

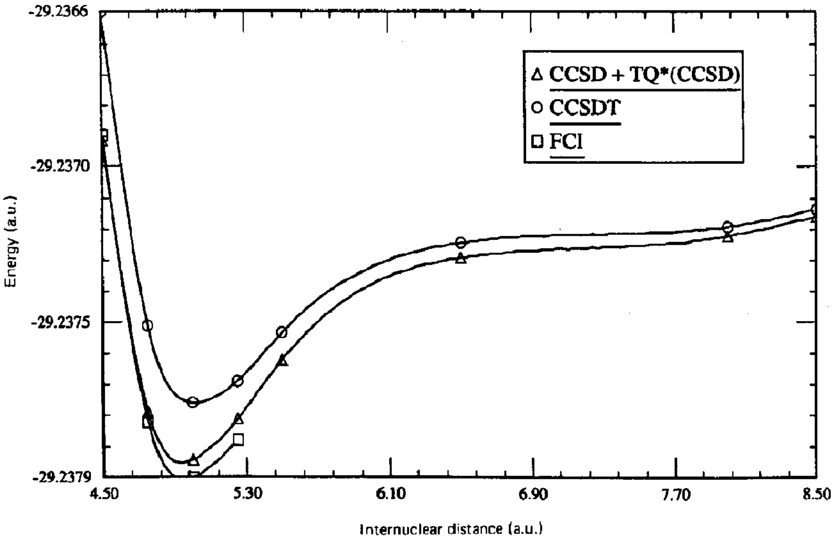

Fig. 2. A comparison between the potential energy curves of the Be_2 molecule calculated at the CCSD+TQ*(CCSD), CCSDT, and FCI levels. The CCSDT and FCI data are from ref. [8] and ref. [25] respectively.

corrections than the simple systems studied here. These will be presented elsewhere to further substantiate the reliability of single reference non-iterative corrections for higher-order correlation corrections.

Acknowledgement

This work has been supported by the US Air Force Office of Scientific Research under Grant No. AFOSR-88-0041. We acknowledge helpful conversations with L. Meissner and J. Paldus.

References

[1] R.J. Bartlett, J. Phys. Chem. 93 (1989) 1697.
[2] R.J. Bartlett and G.D. Purvis III, Intern. J. Quantum Chem. 14 (1978) 561; Physica Scripta 21 (1980) 255.
[3] G.D. Purvis III and R.J. Bartlett, J. Chem. Phys. 76 (1982) 1910.
[4] W.D. Laidig and R.J. Bartlett, Chem. Phys. Letters 104 (1984) 424;
L. Meissner, K. Jankowski and J. Wasilewski, Intern. J. Quantum Chem. 34 (1988) 535.
[5] Y.S. Lee, S.A. Kucharski and R.J. Bartlett, J. Chem. Phys. 81 (1984) 5906.
[6] J. Noga, R.J. Bartlett and M. Urban, Chem. Phys. Letters 134 (1987) 126.
[7] J. Noga and R.J. Bartlett, J. Chem. Phys. 86 (1987) 7041; 89 (1988) 3401 (E).
[8] C. Sosa, J. Noga and R.J. Bartlett, J. Chem. Phys. 88 (1988) 5974.
[9] G.E. Scuseria and H.F. Schaefer III, Chem. Phys. Letters 152 (1988) 383.
[10] M. Urban, J. Noga, S.J. Cole and R.J. Bartlett, J. Chem. Phys. 83 (1985) 4041.
[11] K. Raghavachari, J. Chem. Phys. 82 (1985) 4607.
[12] L. Adamowicz, R.J. Bartlett, J.S. Kwiatkowski and W.B. Person, Theoret. Chim. Acta 73 (1988) 135.
[13] J.F. Stanton, W.N. Libscomb, D.H. Magers and R.J. Bartlett, J. Chem. Phys. 90 (1989) 3241.
[14] S.A. Kucharski and R.J. Bartlett, Advan. Quantum Chem. 18 (1986) 281.
[15] S.A. Kucharski and R.J. Bartlett, Chem. Phys. Letters 158 (1989) 550.

[16] R.J. Bartlett and J. Noga, Chem. Phys. Letters 150 (1988) 29;
R.J. Bartlett, S.A. Kucharski and J. Noga, Chem. Phys. Letters 155 (1989) 133;
R.J. Bartlett, S.A. Kucharski, J. Noga, J.D. Watts and G.W. Trucks, in: Lecture notes in chemistry, Vol. 52, ed. U. Kaldor (Springer, Berlin, 1989) p. 125.
[17] J. Noga, S.A. Kucharski and R.J. Bartlett, J. Chem. Phys. 90 (1989) 3399.
[18] J.A. Pople, M. Head-Gordon and K. Raghavachari, J. Chem. Phys. 87 (1987) 5968.
[19] R.J. Bartlett and S.A. Kucharski, Computer Phys. Rept., to be published.
[20] K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, Chem. Phys. Letters 157 (1989) 479.
[21] C.W. Bauschlicher Jr. and P.R. Taylor, J. Chem. Phys. 85 (1985) 2779, 6510; 86 (1987) 1420.
[22] D.H. Magers, W.N. Lipscomb, R.J. Bartlett and J.F. Stanton, J. Chem. Phys. 91 (1989) 1945.
[23] S.A. Kucharski, J. Noga and R.J. Bartlett, J. Chem. Phys. 90 (1989) 7282.
[24] C.E. Dykstra, H.F. Schaefer III and W. Meyer, J. Chem. Phys. 12 (1976) 5140.
[25] R.J. Harrison and N.C. Handy, Chem. Phys. Letters 98 (1983) 97.