

An efficient way to include connected quadruple contributions into the coupled cluster method

Stanisław A. Kucharski^{a)} and Rodney J. Bartlett

Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611

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The general inclusion of the T_4 operator into the coupled cluster equations requires an n^{10} computational procedure, and even n^9 in the lowest order, as in the CCSDTQ-1 (coupled cluster singles, doubles, triples and lowest-order quadruples) method. That level of n -dependence makes it difficult to apply the method to larger systems. In this paper we circumvent this difficulty by a *factorization* approximation that requires only an n^7 procedure, but that provides results nearly identical to those obtained with the CCSDTQ-1 method. This observation offers a practical and accurate method to go beyond the CCSDT (coupled cluster singles, doubles and triples) approach. We also consider noniterative CCSDT(Q_f) (coupled cluster singles, doubles, triples and noniterative quadruples) and CCSD(TQ_f) (coupled cluster singles and doubles with noniterative triples and quadruples) methods. © 1998 American Institute of Physics. [S0021-9606(98)01722-X]

INTRODUCTION

The coupled-cluster method (CC)¹⁻¹⁴ is frequently the method of choice in quantum chemical studies of atoms and molecules. Since its birth,^{1,2} it has undergone a dramatic development and now offers a variety of possibilities beginning with CCD,^{4,5} CCSD,⁶ CCSDT⁷⁻⁹ and CCSDTQ¹⁰ approaches and less expensive iterative analogs like CCSDT-1,¹¹ CCSDTQ-1,¹² and noniterative analogs like CCSD[T]¹³ and CCSD(T),¹⁴ which are routinely used to study moderately sized chemical systems. Of these, the CCSDTQ method,¹⁰ which fully includes the connected four-particle cluster T_4 , provides the highest accuracy correlation corrections apart from the full CI (FCI) scheme. In the present paper, we explore the inclusion of T_4 to propose unusually efficient iterative and noniterative methods for the generation of benchmark high-accuracy results.

It is now well established that the full inclusion of singles, doubles, and triples into the CC method (i.e., CCSDT⁷⁻⁹) creates a very dependable computational scheme. For the majority of cases, the results are in satisfactory agreement with experiment or with FCI calculations. Compared to the FCI reference, near the equilibrium geometry, the CC method provides deviations of the order of only tenths of a mh for molecules the size of HF, H₂O, SiH₂, etc. However, for more pathological cases such as stretched bonds, we arrive at differences of a few mh. Such systems are known to have multiconfigurational character, and some, like the O₃ and C₂ molecules, even at equilibrium, belong to this category. (See Ref. 15 for a recent illustration of the failure of CCSDT for O₃'s force field.) In such situations, we want a method to be able to neutralize the multiconfigurational character of the reference, and a partial remedy for this is an inclusion of the T_4 cluster. We have shown elsewhere¹²

that the simplest approximation to the CCSDTQ method, i.e., CCSDTQ-1 which considers only the initial (third-order) contribution of the T_4 operator, already reduces the equilibrium error of the CCSDT method to hundredths of a mhartree and at the same time, significantly lowers the FCI energy discrepancies for stretched geometries. In the same paper, we presented some suggestions for a noniterative inclusion of the T_4 contributions. The price we pay for this improvement, however, is the higher cost for calculations involving the T_4 cluster. The slowest step in the CCSDT model is the T_3 into T_3 contribution which scales with the size of the basis set as n^8 , whereas the T_4 equation scales as n^9 . This fact also prompts investigating alternative estimates of T_4 , such as extracting part of its effect from a UHF^{16,17} or MCSCF¹⁸ wavefunction.

The possibility of computing the fifth-order quadruple energy correction with a low n^7 scaling is now known¹⁹ and has been used in functionals based upon an expectation value expression.²⁰ However, this model does not perform well at stretched geometries, which are exactly the situations of most interest. In this article we emphasize an attractive, promising possibility of including the connected quadruple excitation operators into the CC wavefunction with a low scaling without any practical loss in the accuracy of the obtained results. We present a large number of examples supporting our observation.

In the spirit of the CCSD[T] or the CCSD(T) models, we also formulate the possibility of including T_4 in a noniterative manner that leads us to a very accurate method [denoted here as CCSDT(Q_f)] that, in turn, permits the inclusion of the connected quadruple contributions in a fraction of the time required for the full CCSDT calculations. Further, we explore combining noniterative T and Q contributions into a new CCSD(TQ_f) method.

^{a)}Permanent address: Silesian University, Institute of Chemistry, Szkolna 9, Katowice, Poland.

CCSDTQ-1 AND CCSDTQ_f-1

The initial inclusion of the T_4 operator into the CCSDT scheme requires a modification of the T_2 equation and the introduction of the T_4 equation to generate the T_4 amplitudes. That is

$$T_2(\text{CCSDTQ}-1) = T_2(\text{CCSDT}) + R_2(W_N T_4), \quad (1)$$

$$T_4(\text{CCSDTQ}-1) = R_4[W_N(T_2^2/2 + T_3)]_c, \quad (2)$$

where the R_n resolvent operator is defined as²¹

$$R_n(X) = (n!)^{-2} \sum \frac{\langle \Phi_{ij\dots}^{ab\dots} | X | 0 \rangle}{e_i + e_j + \dots - e_b - e_a} a^\dagger b^\dagger \dots ji. \quad (3)$$

The resolvent ensures the presence of the required denominator (D_n) for the T_n amplitudes. $T_2(\text{CCSDT})$ represents the full set of diagrams included in the T_2 equation within the CCSDT model; W_N is the two-electron part of the normal-ordered Hamiltonian, $H_N = H_N^0 + W_N = \sum_r \epsilon_r \{ r^\dagger r \} + \frac{1}{4} \sum_{rstu} \langle rs || tu \rangle \{ r^\dagger s^\dagger ut \}$. The subscript c in Eq. (2) indicates that only the connected terms should be considered. Here we limit ourselves to canonical Hartree-Fock references for simplicity.

The contribution to the energy generated by the T_4 operator via the T_2 equation can be expressed as

$$\Delta E(T_4) = \langle 0 | W_N R_2(W_N T_4) | 0 \rangle \quad (4)$$

$$= \langle 0 | T_2^{(1)\dagger} W_N T_4 | 0 \rangle, \quad (5)$$

where $T_2^{(1)\dagger}$ indicates the pure first-order (in W_N) contribution to T_2^\dagger . Introducing the D_4 denominator and taking advantage of the factorization theorem, we may replace the last expression with

$$\Delta E(T_4) = \frac{1}{2} \langle 0 | T_2^{(1)\dagger 2} D_4 T_4 | 0 \rangle, \quad (6)$$

where

$$D_n T_n = (n!)^{-2} \sum (e_i + e_j + \dots - e_b - e_a) \times t_{ij\dots}^{ab\dots} a^\dagger b^\dagger \dots ji. \quad (7)$$

Hence, when we include the T_4 operator into the energy expression, it is possible to rigorously eliminate the T_4 denominator. However, inserting T_4 into the T_2 equation (and into the T_3 one in the general case) destroys the equivalence expressed in Eq. (6) causing the full T_4 operator to be required. We want to emphasize that relations, Eqs. (4)–(6), hold for the general case; however, the elimination of the denominator would gain us a reduced computational procedure only when the internal structure of T_4 permits this, i.e., it does not contain $T_4 \rightarrow T_4$ contributions. In the case of the lowest order T_4 , i.e., $T_4^{(3)}$, we may write

$$E_Q^{(5)} = \frac{1}{2} \langle 0 | T_2^{(1)\dagger 2} D_4 T_4^{(3)} | 0 \rangle \quad (8)$$

and the elimination of the denominator reduces the evaluation of $E_Q^{(5)}$ from $\sim n^9$ to $\sim n^7$.

The essential idea of this paper is the following: Let us *force* the factorization of the T_4 operator in the T_2 amplitude equation. Equation (1) then assumes the form

$$T_2(\text{CCSDTQ}_f-1) = T_2(\text{CCSDT}) + \frac{1}{2} R_2(T_2^{(1)\dagger} D_4 T_4). \quad (9)$$

Now in the CCSDTQ_f-1 method, we can replace $D_4 T_4$ and instead give the equations

$$T_1(\text{CCSDTQ}_f-1) = T_1(\text{CCSDT}),$$

$$T_2(\text{CCSDTQ}_f-1) = T_2(\text{CCSDT}) + \frac{1}{2} R_2\{T_2^{(1)\dagger} [W_N(T_2^2/2 + T_3)]_c\}, \quad (10)$$

$$T_3(\text{CCSDTQ}_f-1) = T_3(\text{CCSDT}),$$

and do not even require the T_4 equation. Thus, only the T_2 equation is modified by adding several new diagrams in Eq. (10). This provides an iterative $n_o^5 n_v^5 \sim n^7$ scheme that should be close to CCSDTQ-1 in accuracy.

CCSDT(Q) AND CCSDT(Q_f)

In analogy to the methods that include the lowest order triple excitation contribution in a noniterative way, we may incorporate in the same manner the lowest order T_4 component. Thus the contribution denoted in Ref. 13 as T(CCSD) that defines CCSD[T]=CCSD+T(CCSD) has the form

$$E_T^{[4]} = \langle 0 | T_2^\dagger W_N T_3^{[2]} | 0 \rangle = \langle 0 | T_3^{[2]\dagger} D_3 T_3^{[2]} | 0 \rangle, \quad (11)$$

$$T_3^{[2]} = R_3(W_N T_2), \quad (12)$$

where T_2 is a solution of the CCSD equations. (Here the $[n]$ indicates order where the converged T_2 from CCSD is considered first order. Then $E_T^{[4]}$ is fourth order in this sense.) The above contribution is the principal (fourth order) one of two components included in addition to CCSD in the CCSD(T) method. The second single-excitation component arises from $T_1 = R_1(W_N T_3)$, leading to a fifth-order energy contribution for SCF (fourth order in non-SCF) cases¹⁴

$$E_{ST}^{[5]} = \langle 0 | T_1^\dagger W_N T_3^{[2]} | 0 \rangle, \quad (13)$$

where the T_1 is the converged T_1 from CCSD.

For the lowest-order quadruple contribution, we have expressions analogous to Eqs. (11) and (12),

$$E_Q^{[5]} = \langle 0 | T_2^\dagger W_N T_4^{[3]} | 0 \rangle, \quad (14)$$

$$T_4^{[3]} = R_4[W_N(T_2^2/2 + T_3)]_c, \quad (15)$$

where T_2 and T_3 are solutions to the CCSDT equations. In analogy to the triples approximations, we will call the approach—including the contribution given by Eq. (14)—a CCSDT(Q) model. Adding the additional triple term $T_3 = R_3(W_N T_4)$ is not recommended because it is not in CCSDTQ-1, as it contributes in the next order and it would require an n^9 procedure.

At this stage of the derivation, we observe that in both approaches we need to construct the higher rank clusters— T_3 for Eq. (11) and T_4 for Eq. (14), which implies using n^7 and n^9 procedures, respectively. For the triples in fourth order, there is no rigorous way to factorize the contribution given by Eq. (11) (it could be forced by averaging denominators or possibly using a Laplace transform technique²²), so we actually use an n^7 step in the CCSD(T) method.

TABLE I. The correlation energies relative to FCI^a values with approximate inclusion of connected quadruple excitations. Basis as shown. (mhartree).

		CC CCSDT	CC SDTQ-1 n^9	CC SDTQ _f -1 $n^7(T_4)$	Δ Q-1-Q _f -1	CC SDT(Q) n^9	CC SDT(Q _f) $n^7(T_4)$	Δ (Q)-(Q _f)
BH(DZP)	R_e	0.068	0.040	0.043	-0.003	0.039	0.042	-0.003
	$1.5R_e$	0.026	0.042	0.044	-0.002	0.044	0.047	-0.003
	$2.0R_e$	-0.091	-0.066	-0.066	0.000	0.107	0.105	0.002
HF(DZP)	R_e	0.266	0.062	0.060	0.002	0.063	0.061	0.002
	$1.5R_e$	0.646	0.110	0.114	-0.004	0.104	0.110	0.004
	$2.0R_e$	1.125	0.352	0.368	-0.016	0.274	0.305	-0.031
H ₂ O(DZ)	R_e	0.434	-0.003	-0.004	-0.001	0.004	0.003	0.001
	$1.5R_e$	1.473	-0.089	-0.052	0.037	-0.126	-0.078	-0.048
	$2.0R_e$	-2.211	-1.858	-1.756	-0.102	-1.450	-1.209	-0.241
H ₂ O(DZP)	R_e	0.531	0.047	0.046	0.001	0.049	0.048	0.001
	$1.5R_e$	1.784	-0.023	0.023	-0.046	-0.087	-0.027	-0.060
	$2.0R_e$	-2.472	-1.581	-1.496	-0.085	-0.993	-0.747	-0.246
SiH ₂ (DZP)	R_e	0.100	0.081	0.082	-0.001	0.080	0.081	0.001
	$1.5R_e$	0.058	0.233	0.234	-0.001	0.266	0.268	-0.002
	$2.0R_e$	-3.689	-0.289	-0.354	-0.065	1.748	1.638	0.110
N ₂ (pVDZ)	R_e	1.626	0.262	0.276	-0.014	0.350	0.275	0.075
C ₂ (pVDZ+)	R_e	3.273	1.008	1.097	-0.089	0.698	0.948	-0.250

^aThe FCI values taken from: Ref. 12 for BH; Ref. 24 for HF; Ref. 25 for H₂O DZ; Ref. 26 for H₂O DZP; Ref. 27 for SiH₂; Ref. 28 for N₂ and C₂.

For the fifth-order quadruples, the expression Eq. (14) is not exactly factorizable either, since we have

$$\langle 0 | T_2^\dagger W_N T_4^{[3]} | 0 \rangle \neq \langle 0 | (D_2 T_2^\dagger) T_2^{(1)\dagger} T_4^{[3]} | 0 \rangle. \quad (16)$$

However, in analogy to the previous case we may insist upon the factorization, which will give

$$E_{Q_f}^{[5]} = \frac{1}{2} \langle 0 | T_2^\dagger T_2^{(1)\dagger} [W_N (T_2^2/2 + T_3)]_c | 0 \rangle. \quad (17)$$

Unlike CCSD[T] and CCSD(T), for CCSDT(Q) no $\langle 0 | T_2^\dagger W_N T_4 | 0 \rangle$ term can arise, so there is no distinction between CCSDT[Q] and CCSDT(Q). Note that since the factorized approximations consist solely of connected diagrams, all results are rigorously size extensive.

CCSD(TQ_f)

An obvious way to keep a method computationally n^7 but to introduce both the initial, dominant effect of triples and connected quadruples is to combine the standard (T) with the (Q_f) correction. This ignores the fact that the former is the full fourth-order correction to CCSD [plus a part of the fifth order, Eq. (13), while $E_{Q_f}^{[5]}$ is one of the remaining three fifth-order terms (see Ref. 23 for a discussion)]. The fifth-order triple excitation term $E_{TT}^{[5]} = \langle 0 | T_3^{[2]\dagger} W_N T_3^{[2]} | 0 \rangle$ first introduced in CCSDT is n^8 and would not be considered along with the term $E_{TQ}^{[5]} = \langle 0 | T_3^{[2]\dagger} [W_N (T_2^2/2)]_c | 0 \rangle$. The Hermitian conjugate of the latter, $E_{QT}^{[5]c} = \langle 0 | (T_2^{2\dagger}/2 W_N)_c T_3^{[2]} | 0 \rangle$ (the c superscripts indicates that this is an internally connected component of the $E_{QT}^{[5]}$), corresponds to a component of the $E_{Q_f}^{[5]}$ contribution, Eq. (17).

NUMERICAL RESULTS

The results of the test calculations are collected in four tables. Tables I and II show the correlation energy contributions obtained from different theoretical approaches relative

to the FCI values. We also consider geometries and harmonic frequencies collected in Tables III and IV, respectively.

Correlation corrections to the energy

The quality of the results for energies obtained with CCSDTQ-1 and CCSDT(Q) methods has already been addressed.¹² Here we add three more molecules—SiH₂ at three geometries and the C₂ and N₂ molecules—and focus on the reliability of the factorized (Q_f) approaches. For all

TABLE II. The correlation energies relative to FCI^a values with approximate inclusion of connected triple and quadruple excitations (mhartree).

		CCSD(T)	CCSD(TQ _f)	ΔQ_f
BH(DZP)	R_e	0.414	0.382	-0.032
	$1.5R_e$	0.552	0.561	0.009
	$2.0R_e$	0.409	0.585	0.176
HF(DZP)	R_e	0.397	0.242	-0.155
	$1.5R_e$	0.887	0.481	-0.406
	$2.0R_e$	0.256	-0.112	-0.368
H ₂ O(DZ)	R_e	0.574	0.166	-0.408
	$1.5R_e$	1.464	0.094	-1.370
	$2.0R_e$	-7.700	-5.914	1.786
H ₂ O(DZP)	R_e	0.717	0.276	-0.441
	$1.5R_e$	1.998	0.473	-1.525
	$2.0R_e$	-4.634	-4.204	0.430
SiH ₂ (DZP)	R_e	0.668	0.641	-0.027
	$1.5R_e$	1.412	1.576	0.164
	$2.0R_e$	-1.884	1.589	3.473
N ₂ (pVDZ)	R_e	1.709	0.751	-0.948
C ₂ (pVDZ+)	R_e	1.863	1.389	-0.474
m.abs.err.		1.620	1.143	

^aSee footnote to Table I.

TABLE III. Equilibrium bond lengths for the first row diatomics with aug-cc-pVDZ basis set and approximate inclusion of the T_4 cluster [Å].

	CCSD $n_o^2 n_v^4$	CCSD(T) $n_o^3 n_v^4$	CCSDT $n_o^3 n_v^5$	CCSD(TQ) _f $n_o^2 n_v^5$	CCSDT(Q) $n_o^4 n_v^5$	CCSDT(Q) _f $n_o^2 n_v^5(T_4)$	Exp.
C ₂	1.26731	1.27203	1.27214	1.27098	1.27325	1.27338	1.2422 ^a
BF	1.30597	1.31004	1.31054	1.30921	1.30975	1.30975	1.2626 ^a
CO	1.14052	1.14727	1.14739	1.14537	1.14698	1.14696	1.1283 ^a
N ₂	1.11427	1.12085	1.12034	1.12172	1.12198	1.12194	1.0977 ^a
NO ⁺	1.07406	1.08191	1.08168	1.08190	1.08276	1.08272	1.064 ^b
CN ⁻	1.19432	1.20160	1.20121	1.20183	1.20213	1.20210	1.177 ^c

^aFrom Ref. 29.^bFrom Ref. 30.^cFrom Ref. 31.

hydrides at the equilibrium geometry, the errors stay below 0.1 mhartree, no matter which computational scheme involving T_4 is considered. For N₂, which has the largest correlation energy of over 600 mhartree, it is approximately 0.27 mhartree for the iterative methods. The C₂ molecule is exceptionally difficult to treat by a single reference method, but even in this case we are off by only about 1 mhartree which is much better than the result generated by the CCSDT method. A similar behavior is observed at stretched geometries for hydrides, where the deviations from the exact results are larger but still much smaller than in the CCSDT case. The important observation is that the iterative T_4 contribution nearly always moves the results in the right direction, independently of whether CCSDT over- or undershoots. The only exceptions are BH and SiH₂ at 1.5 R_e where the CCSDT values are accidentally close to FCI.

The second question pertains to the performance of the noniterative inclusion of the quadruple contribution. For equilibrium geometries, the results are practically the same as for the iterative approach. For example, when comparing the CCSDTQ_f-1 and CCSDT(Q)_f, for most molecules the difference is 1 μ hartree and only for two of them is it larger: H₂O DZ-7 μ hartree and C₂-60 μ hartree. This indicates that the noniterative T_4 offers a better behaved scheme than the noniterative triples. For stretched geometries, we observe reasonably close values, the exceptions being H₂O and SiH₂ at 2 R_e . For the former, the noniterative contributions differ by 0.547 and 0.749 mh for DZ and DZP basis sets, respectively. For SiH₂ a positive T_4 correction of 3.335 mhartree of CCSDTQ_f-1 reduces the large CCSDT error of -3.689

mhartree; the noniterative T_4 correction of 5.237 overcorrects it by 1.638 mhartree.

The most important result of this work is the amazing coincidence of the values of the iterative quadruple contributions according to the standard expression [Eqs. (1), (2)], in the CCSDTQ-1 column in Table I, compared to those using the factorized expression, Eq. (10) (see column CCSDTQ_f-1 in the same table). The next column contains the differences between the two and we see that they are negligibly small. For the BH and HF molecule, they fall around 1–4 μ hartree, except for HF at 2R where it is equal to 16 μ hartree. A similar situation occurs in the case of the H₂O and SiH₂ molecules. For equilibrium the two methods give values differing by 1 μ hartree, and the differences only go up to several tens of a μ hartree for stretched geometries. This observation, in fact, enables us to use the factorized form of the T_4 equation without any practical loss in the accuracy of the results. A very similar situation pertains to the noniterative approach where the differences are collected in the last column of Table I. In most cases they stay equally small. Only for the case of the stretched bonds of H₂O does the difference go up to 0.24–0.25 mhartree, which is still quite small compared to the overall T_4 correction for stretched geometries.

To give an additional illustration of the performance of the Q_f energy correction, we carried out an analogous series of calculations with the CCSD(TQ)_f methods. The resulting energy values (relative to FCI) are collected in Table II. An important observation is that the T_4 correction nearly always improves the results, that is, it brings the values closer to FCI. The only exceptions from this are the same two cases as

TABLE IV. Harmonic frequencies [in cm⁻¹] for the first row diatomics with aug-cc-pVDZ basis set and approximate inclusion of the T_4 cluster.

	CCSD $n_o^2 n_v^4$	CCSD(T) $n_o^3 n_v^4$	CCSDT $n_o^3 n_v^5$	CCSD(TQ) _f $n_o^2 n_v^5$	CCSDT(Q) $n_o^4 n_v^5$	CCSDT(Q) _f $n_o^2 n_v^5(T_4)$	Exp. ^a
C ₂	1850.5	1813.7	1816.0	1832.4	1807.1	1808.3	1855.63 ^a
BF	1258.8	1241.9	1239.1	1246.5	1243.9	1243.8	1390.8 ^a
CO	2171.7	2104.6	2103.6	2119.8	2112.4	2112.7	2170.21 ^a
N ₂	2392.4	2318.9	2327.1	2307.8	2303.9	2304.5	2358.6 ^a
NO ⁺	2437.9	2337.0	2341.9	2343.9	2328.4	2329.1	2376.7 ^b
CN ⁻	2079.2	2016.3	2021.0	2010.60	2012.2	2012.6	2035 ^c

^{a,b,c}See footnote to Table III.

for the CCSDT approach—BH and SiH₂ at the intermediate geometry plus BH at stretched geometry. This tells us that the Q_f energy contribution behaves very stably and independently of the method used to generate the T_2 and T_3 amplitudes and in connection with CCSD(T) approach, may offer an interesting route to account for the connected quadruple effects for larger systems.

Equilibrium geometry

To study the behavior of the T_4 correction in the case of certain molecular properties, we present in Table III the equilibrium geometries for first-row diatomics computed with the inclusion of connected quadruples in an aug-cc-pVDZ basis set. Since the quality of the basis set is not good enough to relate the theoretical results to the experimental ones, we will not discuss the results in this aspect, although for reference we give the experimental data in the last column.

The main points here are the importance of the quadruple contribution in the equilibrium geometry evaluation and the performance of the factorized vs nonfactorized scheme. The effect of triple substitutions is similar for all the systems considered and increases the equilibrium bond length by 0.005 to 0.007 Å, the largest effect being observed for the NO-0.00762 Å. An inclusion of the connected quadruples adds about 0.001–0.002 Å to the CCSDT values for all but the BF and CO molecules. In the latter molecules, the quadruples work in the opposite direction: the bonds get slightly shorter. The largest effect due to quadruples occurs for N₂: 0.00164 Å.

Using the factorized formula gives practically the same bond lengths as the rigorous one: The differences amount in most cases to small differences in the fifth decimal place, i.e., 0.00002 to 0.00004 Å; for C₂ it is somewhat larger: 0.00013 Å.

In addition to the data presented in Table III, we also made calculations for the cc-pVDZ basis sets. We do not quote these results here, since their behavior with respect to the problems discussed here is very similar. We did, however, obtain iterative CCSDTQ-1 and CCSDTQ_f-1 values and the differences are nearly identical to those observed for noniterative schemes: they stay below 0.00004 Å except for the C₂ molecule where it is 0.00008 Å. We could also make a comparison between iterative and noniterative formulations: The differences stay below 0.0001 Å except for the C₂ where we get 0.00023 Å. The general conclusion is that all four of the methods for the inclusion of connected quadruples into the coupled cluster scheme that we explore here give very similar results with respect to equilibrium geometries for these simple cases.

We observe in general a similar effect for the connected quadruple correction on the equilibrium geometry when computed on top of the CCSD(T) method (cf. columns 3 and 5 of Table III). The main difference is a shortening of the C-C bond due to T_4 and also its negligibly small effect on the bond length of the NO⁺ molecule.

Harmonic frequencies

As we see from Table IV, the addition of full connected triples to the CCSD method introduces significant changes

into the computed harmonic frequencies moving them to lower values. The magnitude of the effect varies from about 20 cm⁻¹ for BF and 33 for C₂ to about 100 for NO⁺. The remaining three molecules lower their frequencies by approximately 55–65 wavenumbers.

The effect of quadruples is obviously much smaller but non-negligible. The largest one occurs for the N₂ molecule, lowering the frequency by 23 cm⁻¹. For NO⁺ it amounts to 14 and for CN⁻, CO, and C₂ to 9 cm⁻¹. The smallest effect is observed for BF—5 cm⁻¹. For two molecules, BF and CO, the quadruples increase the frequency, which is consistent with the decrease in the equilibrium bond length. Thus, for these two molecules, an inclusion of quadruples strengthens the bond, while for the remaining ones, the opposite is true.

Going from the standard nonfactorized formula to the factorized one (cf. columns 6 and 7 of Table IV), we observe changes of about 0.5 cm⁻¹ (for C₂ it goes up to 1.2 cm⁻¹), which fully justifies using our fast approximation and algorithm for calculation of the T_4 effect. Similarly, as in the case of the equilibrium geometries, we have carried out iterative inclusion of T_4 for the cc-pVDZ basis set. The results—not quoted here—allowed us to assess the effect of the iterative procedure. It is negligible, amounting to 0.5 cm⁻¹ for all molecules considered but NO⁺, where it is equal to 1.1 cm⁻¹. The changes in the frequencies obtained with all T_4 methods considered here for both basis sets are so small that to account for them, we would have to quote the values up to the first decimal place. This gives us the freedom of selecting the computationally most efficient approach and that would obviously be the CCSDT(Q_f) approach.

Comparing columns 3 and 5 of Table IV, we may see the effect of the T_4 contribution for the frequencies obtained with the CCSD(T) method. In most cases the changes are parallel to those obtained at the full CCSDT level, two exceptions are observed, however, for C₂ and NO⁺ where the T_4 contribution is positive for the CCSD(T) approach and negative for the CCSDT scheme.

CONCLUSIONS

When aiming at the very accurate evaluation of the energy of a molecule and its properties, we have to frequently include the effect of connected quadruple excitations. The effect is larger for multiple bonds and also when two or more single bonds are being stretched simultaneously. Both situations are handled comparatively well at the CCSDTQ level,¹⁰ but not at CCSDT. Hence, such “double”-bond effects require the inclusion of the connected quadruples, T_4 . However, the complete inclusion of the T_4 operator into the CC scheme, an n^{10} procedure, is usually computationally prohibitive. With this communication, we have shown a way to circumvent this difficulty. Using the example of several small systems, we have shown that when including the lowest-order connected quadruples in an iterative way (i.e., according to the CCSDTQ-1 scheme), we may use the factorized formula which uses an n^7 instead of an n^9 computational procedure, yet practically with the same qual-

ity results. This opens the way to routine calculations that include the T_4 operator. The same observation allows us to replace the expression for the noniterative inclusion of the T_4 operator on top of the CCSDT method—derived in the standard way (i.e., in an identical manner as the T_3 noniterative contribution)—with the factorized expression which lowers the rank of the computational procedure for T_4 from n^9 to n^7 . This is a crucial observation when one intends to include the T_4 operator in large-scale correlation calculations.

We have also shown that CCSDT(Q_f) offers a dependable method to include the effect of the connected quadruples for equilibrium geometries and harmonic frequencies, in addition to energies.

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