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Connected quadruple excitations in the coupled

cluster theory

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Abstract

The role of the connected quadruple excitations in the coupled cluster (CC) theory is discussed. The full inclusion of the T_4 (Q) operator in addition to singles (S), doubles (D) and triples (T) defines the CCSDTQ method which offers a very accurate computational tool applicable to small molecular systems. The efficient organization of the CC equations results in the quasilinear formulation of the CCSDTQ scheme. A wider range of applications can be ensured with the approximate variants of the CCSDTQ approach. Due to possible factorization of the lowest order quadruple contribution to the energy the noniterative scheme has been formulated which requires n^7 scaling. Performance of the CCSDTQ method has been discussed on the basis of the results obtained for several small molecules in confrontation with the reference full configuration interaction data.

1 Introduction

The coupled cluster (CC) method [1-30] has been recognized as an important tool in the treatment of electronic correlation. Since its introduction into quantum chemistry by Cížek and Paldus [1–3] many successful variants have been formulated beginning with the CCD (CC Doubles) scheme developed simultaneously by Bartlett's [11, 12] and Pople's [13] groups. This was the first general purpose CC program. The next extention was to the CCSD (CC Singles, Doubles) model developed by Purvis and Bartlett [14]. Unlike the CCD the CCSD scheme provides exact results for a two-electron correlation problem. The main advantage of the CCSD method is much greater flexibility with respect to the orbital choice since the $exp(T_1)$ effects orbital rotations and is important in the treatment of properties other than the energy. An inclusion of connected triples into the CC wave function has been done through several steps beginning with the T_3 operator at the lowest order which created the CCSDT-1 scheme [17], followed by the other approximate variants, generally denoted as CCSDT-n [18]. The full inclusion of the T_3 operator created the method denoted as CCSDT [19]. The inclusion of the T_3 operator into the CC wave function proved to be critical for creating a method for accurate correlated calculations. The weak point of the CCSDT and CCSDT-n schemes is the high cost of the calculations. It turnes out, however, that this difficulty can be circumvented by creating a method including the T_3 operator in a noniterative manner. This was first done by Urban, et al. [22]. In fact, the generalization of that derivation for the non-HF case, provides the (T) method [9], pursueded by

Raghavachari, et al. [23]. The CCSD(T) [23] noniterative scheme is currently one of the most popular *ab initio* methods. Improvements over it have been made as ACCSD(T) [31,32].

A first try to go beyond the CCSDT scheme was connected with an attempt to establish a new computational scheme based on the expectation value CC (XCC) theory. The advantage of that scheme relies on the fact that the so called factorizable quadruples arise in a very natural way within the XCC approach [33]. Introduction of these terms into the standard CC theory created the method with the acronim CCSDTQ-1 [24]. The CCSDTQ-1 is a method correct through the fifth order of many body perturbation theory (MBPT) and accounts for the largest portion of the electronic correlation beyond the CCSDT.

Since the number of terms contributing to the amplitude equations grows very fast for higher cluster operators there was a need for a proper organization or computation of the CC equations to avoid unnecessary duplication of terms. This was already done in a more or less systematic way by the authors of the most advanced computer programs [19] but doing it completely allows writing the CC equation in a quasilinear manner where no term contains more than a single T which substantially simplifies deriving and coding the CC equations, particularly for higher cluster operators [34]. This made it possible to conveniently construct a compact form of the CC equations with full inclusion of the T_4 operator which led to implementing the CCSDTQ method [25]. A step more was taken with the partial [26] and full [27] inclusion of the T_5 operator. Currently new techniques for the automatic

construction and implementation of the CC equations have been developed. One is the tensor contraction engine (TCE) by Hirata which relies on computer generated FORTRAN codes [35]. A second is the string-based algorithms developed by Kallay and coworkers [28]. They offer new possibilities for efficient coding of the complex CC models [29].

At the CCSDTQ level one can also consider noniterative schemes built on top of the CCSDT and CCSD methods. The former can be considered as a noniterative version of the CCSDTQ-1 method, denoted as CCSDT(Q). Introducing noniterative T_4 together with the noniterative T_3 contribution leads to the method denoted as CCSD(TQ). At the quadruple level — as mentioned above — there is a possibility to factorize the T_4 contribution which introduces negligible error to noniterative contributions. The methods obtained by replacement of the standard noniterative T_4 contributions with the factorized ones carry the acronims $CCSDT(Q_f)$ and $CCSD(TQ_f)$ [36], respectively, for the method based on the CCSDT and CCSD iterative solutions. This factorized approaches can be applied to relatively large basis sets, e.g. for the N_2 molecule [37] and C_2 molecule [38] the largest basis set for which quadruple corrections were evaluated includes 182 basis functions.

In the next section we are going to present more details concerning full and approximate models that engage connected quadruple excitations.

2 Theory

In the coupled-cluster theory the wave function is defined through the exponential Ansatz

$$\Psi = e^T |\Phi_o\rangle \tag{1}$$

where T is the cluster operator expressed as a sum of the operators responsible for single, double, ..., N-tuple excitations:

$$T = T_1 + T_2 + \dots + T_N \tag{2}$$

where N is a number of electrons in the system. The operator T_k is generally defined as:

$$T_k = (k!)^{-2} \sum t^{ab\dots}_{ij\dots} a^{\dagger} b^{\dagger} \dots ji$$
(3)

The usual label convention is assumed with letters: $a, b, \dots (i, j, \dots)$ representing the particle (hole) indices, and the r, s, \dots - the general indices.

The CC equations are obtained by inserting the wave function Ψ into the Schrödinger equation

$$H_N e^T |\Phi_o\rangle = E_{CC} e^T |\Phi_o\rangle \tag{4}$$

$$e^{-T}H_N e^T |\Phi_o\rangle = (H_N e^T)_c |\Phi_o\rangle = E_{CC} |\Phi_o\rangle$$
(5)

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where the normal ordered Hamiltonian H_N is defined as

$$H_{N} = H - \langle \Phi_{o} | H | \Phi_{o} \rangle$$

$$= \sum_{r} e_{r} \{ r^{\dagger}r \} + \sum_{rs} f_{s}^{r} \{ r^{\dagger}s \} + \frac{1}{4} \sum_{rstu} v_{tu}^{rs} \{ r^{\dagger}s^{\dagger}ut \}$$

$$= H_{N}^{o} + F_{N} + W_{N}$$
(6)

where e_r are one-particle eigenenergies and F_N and W_N are one- and two-body operators (see Fig. 1a); $v_{tu}^{rs} = \langle rs | | tu \rangle$ is a two-electron integral; E_{CC} is the coupledcluster correlation energy and the subscript c recognizes that in the commutator expansion of $e^{-T}H_Ne^T$ only connected terms survive; $|\Phi_o\rangle$ is the reference determinant. The working equations for the cluster amplitudes are obtained by projecting Eq. (5) onto appropriate configuration subspaces.

There are two main characteristics of the given coupled cluster model: the accuracy and the cost of calculations. The accuracy can be *a priori* estimated by relating the CC model to the order of MBPT through which it is correct. Correctness of the CC model through the *m*th order of MBPT tells us that when analyzing term-by-term all contributions generated during the CC iterations, all MBPT terms up to *m*th order can be identified. The formal relation between parameter k indicating the rank of the CC model and the parameter m indicating the order of the MBPT theory is simple and can be expressed as

$$m = Int(\frac{3k}{2}) \tag{7}$$

where the integer function m = Int(x) (also known as entier(x) or floor(x)) gives the largest integer not greater than x. This tells us that the CCSD model of rank

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equal 2 is correct through the third order of MBPT (m = 3). The CCSDT scheme (k = 3) is correct through the fourth order of MBPT (m = 4), for the CCSDTQ k = 4 we have m = 6, and so forth.

The estimation of the cost of the calculations for the given model is usually done by determining a scaling parameter s which indicates the increase of the cost of calculations with the size of the system. Sometimes the scaling parameter is referred to as a rank of computational procedure. E.g. the scaling n^s with s=6tells us that when we go from monomer to dimer, i.e., both the number of occupied and virtual levels is doubled then the cost of the calculation increases 64 times (2^6) . Usually the solution for the CC equations requires evaluation of many terms with various scaling and we assume that the most costly term determines the rate of the whole scheme. We have to be aware that for small systems the rate determining step can account for a smaller portion of the total computer time and only for large basis sets does it dominate. On the other hand the scaling parameter is determined by the maximum number of nested loops in the computer code or, equivalently, by the total number of lines (internal and external) within the irreducible diagrammatic term. Thus for the full CC models the scaling is simply related to the rank of the CC model with the formula s = 2k + 2. It means that by going to higher levels (increasing the rank of the cluster operator by 1) the rank of the computational procedure increases by 2.

Full CCSDTQ model 2.1

For the CCSDTQ scheme the cluster expansion is terminated at the quadruple excitations:

$$T = T_1 + T_2 + T_3 + T_4 \tag{8}$$

and we obtain four sets of equations for single, double, triple and quadruple excitation amplitudes, respectively,

$$\langle \Phi_i^a | (H_N e^T)_c | \Phi_o \rangle = 0 \tag{9}$$

$$\langle \Phi_i^a | (H_N e^T)_c | \Phi_o \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | (H_N e^T)_c | \Phi_o \rangle = 0$$

$$\langle \Phi_{ijk}^{abc} | (H_N e^T)_c | \Phi_o \rangle = 0$$

$$\langle \Phi_{ijkl}^{abcd} | (H_N e^T)_c | \Phi_o \rangle = 0$$

$$(12)$$

$$\langle \Phi_{ijk}^{abc} | (H_N e^T)_c | \Phi_o \rangle = 0 \tag{11}$$

$$\langle \Phi_{ijkl}^{abcd} | (H_N e^T)_c | \Phi_o \rangle = 0 \tag{12}$$

which in expanded form look like:

$$\langle \Psi_{ij} | (H_N(1+T_1+T_2+T_3+T_4+T_1/2+T_1T_2+T_1T_3+T_2/2+T_1T_3+T_2/2+T_1T_3+T_1T_3+T_2/2+T_1T_3+T_1T_3+T_1T_3+T_1T_3+T_1T_3+T_1T_3+T_1T_4+T_2^2/2+T_2T_3+T_1T_2/2+T_1T_2+T_1T_2+$$

The terms appearing in the above equation are obtained by the expansion of the exponential and by keeping these terms which only contribute to the relevant

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equation. The standard procedure, adopted in the derivation of the working equations for the amplitudes, is to apply the Wick's theorem to the second-quantized expressions which is usually done with the diagrammatic technique. The crucial problem in the derivation of the computationally effective formula is a treatment of the nonlinear terms. The main advantage of the CC approach over the corresponding configuration interaction (CI) scheme relies on the factorization of the nonlinear terms. We will give an example (using diagrammatic language) explaining benefits offerred by the factorization procedure.

We select one nonlinear term occurring in the T_2 equation, see Eq. (14), written as $\langle \Phi_{ij}^{ab} | (W_N T_1 T_2)_c | \Phi_o \rangle$. There are several diagrammatic terms corresponding to this expression and one of them is shown below:

$$i \qquad i \qquad b \qquad = i \qquad a \qquad b \qquad b \qquad n^7$$

It is easy to see that the rank of the computational procedure connected with this diagram is 7 (four external and three internal lines), i.e., the cost of calculations scales as n^7 . In order to make evaluation of this diagram more efficient we divide it into two pieces:



As a first step we compute an intermediate diagram which scales as n^4

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$$\frac{j}{k} = \int_{k_1}^{j} d n^4$$

and then using this intermediate we evaluate the term occurring in the T_2 equation (scaling n^5):

$$i \qquad i \qquad j \qquad b \qquad = i \qquad b \qquad n^{5}$$

We see that the one-step calculation with scaling n^7 is replaced with two steps scaling as n^4 and n^5 which is a substantial saving in computer time. This procedure is applied to all nonlinear terms.

The second strategy used to simplify the CC equation relies on collecting the identical contributions and computing them in one step. This can be illustrated with the following example. Grouping together the terms we may write

$$H_N T_3 + H_N T_1 T_3 = (H_N + H_N T_1) T_3 = I_3^2 T_3$$
(17)

which means that we first evaluate the quantity in parentheses (the fast step), let us denote it as I_3^2 , and then we take its product with T_3 (the slow step). Thus as a result we have the scheme which requires one T_3 contraction instead of two. This procedure can be generalized to eliminate from the CC equations all nonlinear terms

to obtain the CCSDTQ equations as

$$\langle \Phi_i^a | (I_o^1 + I_1'^1 T_1 + I_2^1 T_2 + I_2'^2 T_1 + I_3'^2 T_2 + I_4^2 T_3)_c | \Phi_o \rangle = 0$$
(18)

$$\langle \Phi_{ij}^{ab} | (I_o^2 + I_1^1 T_2 + I_2^1 T_3 + I_1'^2 T_1 + I_2''^2 T_2 + I_3^2 T_3 + I_4^2 T_4)_c | \Phi_o \rangle = 0$$
(19)

$$\langle \Phi_{ijk}^{abc} | (I_1^1 T_3 + I_2^1 T_4 + I_1''^2 T_2 + I_2^2 T_3 + I_3^2 T_4)_c | \Phi_o \rangle = 0$$
⁽²⁰⁾

$$\langle \Phi_{ijkl}^{abcd} | (I_1^1 T_4 + I_1^2 T_3 + I_2^2 T_4 + I_1'^3 T_2 + I_2'^3 T_3)_c | \Phi_o \rangle = 0$$
(21)

We see that in each term only a single cluster operator occurs since all others are 'hidden' in the properly defined intermediates, I_k^m , where m and k indicate that this is an m-body intermediate with k-annihilation lines (i.e., lines below the vertex or second-quantized annihilation operators). The intermediates which are needed to write the quasilinear form of the CCSDTQ equations from Fig. 2 are presented in Fig. 1c. with the terms occuring in the \bar{H}_N expansion:

$$\bar{H}_N = e^{-T} H_N e^T = (H_N e^T)_c$$
 (22)

which is a very important and useful quantity since we can use it in the equationof-motion CC (EOM-CC), Fock space CC (FS-CC), Λ equations, etc. [9, 10].

Due to the two-body nature of the electronic interaction we have the relation that $k \leq 3$. Formally we can consider k=4, but in this case the intermediate I_4^2 is reduced to the two-electron integral. Similarly as in the case of the CC equation (i.e. when k = 0) we may consider the complete form of the \bar{H}_N element or its full form within the given CC model. The \bar{H}_N elements which represent a complete set of diagrammatic contributions are indicated by a wiggly line. In Ref. [39] we present the general formulas for the number of diagrams contributing to the \bar{H}_N elements and the number of diagrammatic terms occurring for the complete form of the I_k^m element.

We should mention also that there exists a very simple formula to evaluate the rank of the computational procedure for each term in quasilinear form. Namely, for the general term $I_k^m T_l$ the rank of the computational procedure (scaling parameter) is equal to $n^{2(m+l)-k}$.

2.2 Approximate CCSDTQ models

Iterative variants

The approximate variants of the CC method are obtained by neglecting some terms in the CC equations, usually those which are difficult in coding and more costly in computations. The simplest approximate CCSDTQ scheme is that which retains in Eq. (16) only two terms, i.e., those which give the lowest-order contribution. Thus the T_4 equation of the full CCSDTQ model, Eq. (16), is replaced with the following expression:

$$\langle \Phi_{ijkl}^{abcd} | (H_N(T_3 + T_2^2/2))_c | \Phi_o \rangle = 0$$
 (23)

In addition in the T_3 equation, Eq. (15), we neglect the terms in which the T_4 operators occur, i.e., T_4 and T_1T_4 . As we see in Table 1 the CCSDTQ-1 method scales as n^9 and the rate determining step is a construction of the T_4 operator. The T_4 operator built according to Eq. (23) includes — in the first iteration — the third order contributions:

$$T_4^{(3)} = R_4 (W_N (T_2^{(1)2}/2 + T_3^{(2)}))_c$$
(24)

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which substituted into the T_2 equation in the next iteration gives

$$T_2^{(4)}(Q) = R_2(W_N T_4^{(3)}) \tag{25}$$

The R_n operator is defined as

$$R_n(X) = (n!)^{-2} \sum \frac{\langle \Phi_{ij...}^{ab...} | X | \Phi_o \rangle}{e_i + e_j + \dots - e_b - e_a} \{ a^{\dagger} b^{\dagger} \dots ji \}$$
(26)

to ensure the presence of the required denominator and the proper projection subspace for the sequence of operators represented by X.

The final step is the contribution to the energy:

$$E_Q^{(5)} = \langle \Phi_o | W_N T_2^{(4)}(Q) | \Phi_o \rangle = \langle \Phi_o | W_N R_2(W_N T_4^{(3)}) | \Phi_o \rangle$$
(27)

Since this was the only fifth-order contribution left out by the CCSDT model hence the CCSDTQ-1 is a method correct through fifth order of MBPT.

It is easy to show that the lowest-order quadruple contribution to the energy is factorizable. The last expression in Eq. (27) can be expressed diagrammatically as



In the above figure the denominators are denoted by the solid horizontal lines and we can see that the factorization allows replacing the 'long' T_4 denominator

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with the 'short' T_2 denominators. Owing to this we can rewrite the energy formula, Eq. (27), as

$$E_Q^{(5)} = \frac{1}{2} \langle \Phi_o | T_2^{(1)\dagger} T_2^{(1)\dagger} (W_N (T_2^{(1)2}/2 + T_3^{(2)}))_c | \Phi_o \rangle$$
(28)

We see that we can get the fifth-order quadruple contribution to the energy without constructing the T_4 operator. In fact this formula holds also for the converged T_2 and T_3 and is valid as long as two "daggered" operators in Eq. (28) or two top interaction lines in the figure above are identical.

We may try, however, to build such a scheme in which the contribution to the T_2 equation, see Eq. (25), is obtained via factorized expression (CCSDTQ_f-1 approximation):

$$T_2^{CCSDTQ_f-1} = T_2(CCSDT) + \frac{1}{2}R_2(T_2^{(1)\dagger}[W_N(T_2^2/2 + T_3)]_c)$$
(29)

Noniterative variants

The correctness of the CC model through the fifth order of MBPT can be ensured also by the noniterative inclusion of the quadruple contribution. The noniterative variants proved to be very successful when approximating the contribution due to the T_3 operator leading to the CCSD(T) and CCSD[T] approximations.

At the quadruple level we may construct the noniterative T_4 contribution following the derivation of the CCSD[T] approach. Thus in analogy to the construction of the lowest order T_3 term

$$T_3 = R_3(W_N T_2) (30)$$

where T_2 is defined for the amplitudes converged at the CCSD level, we obtain the lowest order contribution to the T_4 operator

$$T_4 = R_4 (W_N (T_2^2/2 + T_3))_c \tag{31}$$

where the T_2 and T_3 operators are determined at the CCSDT level. Next step in the CCSD[T] development is to get the T_2 operator on the basis of the noniterative T_3

$$T_2(T) = R_2(W_N T_3) (32)$$

and then the contribution to the energy

$$E_{[T]} = \langle \Phi_o | T_2^{\dagger}(-H_N^o) T_2(T) | \Phi_o \rangle$$
(33)

Analogous steps for the T_4 operator lead to

$$T_2(Q) = R_2(W_N T_4) (34)$$

and

$$E_Q^5 = \langle \Phi_o | T_2^{\dagger}(-H_N^o) T_2(Q) | \Phi_o \rangle \tag{35}$$

Thus the final formula for E_Q is

$$E_Q^5 = \langle \Phi_o | T_2^{\dagger} W_N T_4 | \Phi_o \rangle = \langle \Phi_o | T_2^{\dagger} W_N R_4 (W_N (T_2^2/2 + T_3))_c | \Phi_o \rangle |$$
(36)

The formula above cannot be factorized due to the fact that the operators contracted with the T_4 are not the same $(T_2^{\dagger} \text{ and } W_N)$ hence the T_4 operator must be constructed which imposes high scaling, i.e. n^9 . The only way to avoid such an unfavourable scaling is to depart from strict rigor and force the factorization

$$E_Q^5 \cong E_{Qf}^5 = \langle \Phi_o | T_2^{\dagger} T_2^{(1)\dagger} (W_N (T_2^2/2 + T_3))_c | \Phi_o \rangle$$
(37)

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Moreover a diagrammatic summary of various expressions for Λ based $CCSD(TQ_f)$ approaches is shown in Fig. 3. For comparison purposes we also present there the $CCSD(TQ_f)$ model. These Λ based variants are especially useful when we are interested in creating PEC (potential energy curves). See Ref. [31,40] for more details. The T_4 contribution obtained with $\Lambda CCSD(TQ_f)$ is defined as:

$$E_{\Lambda}(T_4) = \frac{1}{2} \langle \Phi_o | \Lambda_2 T_2^{(1)\dagger} (W_N (T_2^2/2 + T_3))_c | \Phi_o \rangle$$
(38)

whereas the $\Lambda^2 CCSD(TQ_f)$ gives the T_4 contribution with the following formula:

$$E_{\Lambda^2}(T_4) = \frac{1}{2} \langle \Phi_o | \Lambda_2^2 (W_N(T_2^2/2 + T_3))_c | \Phi_o \rangle$$
(39)

The Λ_n is defined in a similar way to the T_n operator:

$$\Lambda_n = (n!)^{-2} \sum \lambda_{ab...}^{ij...} \{ i^{\dagger} j^{\dagger} ... ba \}$$

$$\tag{40}$$

except it is not connected [9, 10].

Performance

CCSDTQ vs. other CC models

The quality of the new computational method is usually tested in two ways: either relating the results to the data provided by a reference theoretical method of high accuracy or confronting the results with experiment. To take advantage of the second option large basis sets are required which in the case of high accuracy correlated methods is hardly feasible. The reference theoretical scheme for correlated methods is the full configuration interaction (FCI) approach. In Tables 2 - 4 we

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compare the CCSDTQ correlation corrections to the energy with other correlated methods relating them to the FCI values. All calculations use RHF based CC theory. In Table 2 we list the results for H_2O and HF molecules for three different geometries. We observe that the CC scheme converges very fast with the rank of cluster operator. At the CCSD the errors relative to FCI ranges from the 3 to 21 mE_h , at the CCSDT this is reduced to the range $0.3 - 2.5 mE_h$ and for the CCSDTQ scheme the largest error is 0.14 mE_h . With full inclusion of pentuple excitations the CC error is below 0.01 mE_h. The same applies to the results presented in Table 3 for SiH_2 and CH_2 molecules: the CC errors are reduced from tens of a mE_h for the SD level to hundredths of a mE_h for the SDTQ model. We want to point out good performance of the CCSDTQ scheme also for molecules with stretched bonds. In this case due to increased multiconfigurational character of the reference function we have quite a large portion of nondynamical correlation which is more difficult to account for with the single reference approach. However, also in that case, the CCSDTQ scheme works quite well. A similar situation is observed for the N_2 and C_2 molecules, see Table 4. Here the deviation from FCI is larger already at the CCSD level, for the N_2 molecule it amounts to over 13 mE_h but goes down to 1.6 mE_h for the CCSDT and to ca 0.2 for the CCSDTQ. The C_2 is an example of a difficult molecule with multiconfigurational reference state character also at its equilibrium geometry. Here the T_4 operator reduces the error from ca 30 mE_h for the CCSD to 0.6 mE_h for CCSDTQ which is a significant improvement.

In summary we think it is fair to say that when going from connected singles

and doubles to connected triples and quadruples we reduce the error by nearly two orders of magnitude.

CCSDTQ vs. CISDTQ

In Table 2 we may compare the performance of the CI and CC methods. It is a well known fact that the inclusion of triple excitations into the CI scheme has a very small effect on the performance as CISDT gives larger error than CCSD. A significant improvement is observed upon inclusion of quadruples and CISDTQ achieves a performance at the level of CCSDT. Of course, an advantage of the CI approach over CC is that the latter is not variational, e.g. for stretched geometries the CC often overshoots, see the CCSDT value for the H_2O molecule at $R = 2R_e$. Nevertheless we may state that CCSDTQ outperforms the CISDTQ by nearly an order of magnitude.

CCSDTQ vs. MBPT

In the theory section we discussed the relation between the CC and MBPT approaches. In Tables 2 and 3 we list the deviations from the exact (FCI) values for various orders of MBPT. It is a well established observation that even orders of perturbation theory are more stable and reliable than the odd ones. We observe this also here: the MBPT(2) values are comparable with the CISD but much inferior to the CCSD. The accuracy achieved at the MBPT(4) level is comparable with the CCSD whereas at the MBPT(6) we achieve the quality of the CCSDT approach. The CCSDTQ is about an order more accurate than the sixth order MBPT.

Equilibrium geometry

In Table 5 we compare the performance of selected CC models in the evaluation of the equilibrium bond length for the N_2 molecule. Since we relate the theoretical values to the experimental one, a sufficiently large basis set should be used to eliminate the deficiencies in the basis set as a possible source of error. The calculations were done for larger sequence of correlation consistent basis sets out of which we quote in Table 5 only three: the smallest one cc-pVDZ, cc-pV5Z and the largest one cc-pCV6Z. For the cc-pVDZ basis set the calculations were done with all listed CC variants whereas for the larger basis sets the simpler variants were used. Nevertheless for the method involving factorized quadruples we could run the calculations up to the cc-pV5Z basis set obtaining very stable correction due to (Q_f) . We considered this fact as a justification to extrapolate the (Q_f) and CCSDTQ correction to the largest basis set for which the quadruple calculations were no longer feasible. We observe a perfect agreement with experiment with the error within 0.0001 - 0.0002 Å. Similar observations are valid for the C_2 molecule, see Ref. [38].

Harmonic frequencies

In Table 5 we also list computed harmonic frequencies for the N_2 molecule. We applied the same strategy as in the case of the eqilibrium geometry. We see again that quadruples improve the theoretical value by 15 to 20 cm^{-1} . Note that in the triple bond case, the connected pentuple has a nonnegligible effect on the harmonic frequency (ca 4 cm^{-1}).

Potential energy curves

In Fig. 4 we present the potential energy curves for the H_2O molecule. The exact (reference) curve is obtained with the FCI method. There are seven variants of the CC method considered and three of them involve the T_4 operator. The best performance is observed for the CCSDTQ scheme (although the final point on the CCSDTQ curve could not be obtained due to convergence problem). Almost equally good behavior as for the CCSDTQ is observed for the Λ -based CCSD(TQ_f). This is a promising result indicating that the connected quadruples even at an approximate level can offer a remedy for the notorious failure of the CC methods in a proper description of the potential energy curves.

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Figure caption

Figure 1. Diagrammatic form of the one- and two-electon integrals, cluster operators and \bar{H} elements.

Figure 2. Diagrammatic form of the quasilinear form of the CCSDTQ equations in antisymmetrized formulation $(D_{ij...}^{ab...}$ denotes an appropriate denominator).

Figure 3. Diagrammatic form of the various non-iterative variants with factorized quadruples. In the definition of the energy expressions $V_4 = \frac{1}{24^2} \Sigma(e_i + ... - e_d) \times t_{ijkl}^{abcd} a^{\dagger} ... i.$

Figure 4.(Color online) Potential energy curves for the H₂O molecule with various CC methods (reference FCI [52]; R_e =1.84345 a.u. [52]).







Fig. 2. + + + + $D_i^a \searrow$ + D_{ij}^{ab} D_{ijk}^{abc} + D_{ijkl}^{abcd} + +

Fig. 3.





Table 1. Rank of the computational procedure for MBPT and CC schemes

generating methods correct through a given order in MBPT energy.

Order in	Rank of MBPT	Rate deter-	Rank of CC	Rate deter-	
MBPT energy	procedure	mining step	procedure	mining step	Method
3	n^6	$T_2 \rightarrow T_2$	n^6	$T_2 \rightarrow T_2$	CCSD
				$T_2 \rightarrow T_3$	
4	n^7	$T_2 \rightarrow T_3$	n^7	$T_3 \rightarrow T_2$	CCSDT-1
5	n^8	$T_3 \rightarrow T_3$	n^9	$(T_3, T_2^2) \rightarrow T_4$	CCSDTQ-1
6	n^9	$(T_3, T_2^2) \rightarrow T_4$	n^{10}	$T_4 \rightarrow T_4$	CCSDTQ
				$T_4 \rightarrow T_5$	
7	n^{10}	$T_4 \rightarrow T_4$	n^{11}	$T_2T_3 \rightarrow T_5$	CCSDTQP-1
			Q.	$T_2^3 \to T_5$	
		$T_4 \rightarrow T_5$		$T_5 \rightarrow T_6$	
8	n^{11}	$T_2T_3 \rightarrow T_5$	n^{13}	$T_2T_4 \rightarrow T_6$	CCSDTQPH-1
		$T_2^3 \to T_5$		$(T_3^2, T_2^4) \rightarrow T_6$	
9	n^{12}	$T_5 \rightarrow T_5$	n^{14}	$T_6 \rightarrow T_6$	CCSDTQPH

and CC methods relative to FCI^{a} values for HF and H_2O molecules in DZP basis set (frozen core).							
Method		HF			H ₂ O		
	\mathbf{R}_{e}	$1.5 \mathrm{R}_e$	$2.0 \mathrm{R}_e$	\mathbf{R}_{e}	$1.5 \mathrm{R}_e$	$2.0 \mathrm{R}_e$	
$\mathrm{CISD}^{b,c)}$	9.38	14.9	27.6	12.9	30.4	75.6	
$\operatorname{CISDT}^{b,c)}$	7.01	11.1	19.2	10.6	23.5	60.3	
$\mathrm{CISDTQ}^{b,c)}$	0.28	0.49	0.92	0.40	1.55	6.29	
$MBPT(2)^{d}$	7.80	10.6	24.0	13.0	23.3	53.7	
$MBPT(3)^{d}$	5.44	11.9	27.0	7.22	26.4	74.6	
$MBPT(4)^{d}$	-0.26	0.77	4.84	0.92	5.76	14.9	
$MBPT(5)^{d}$	0.81	2.29	8.10	0.70	4.98	17.0	
$MBPT(6)^{d}$	-0.23	-0.41	-1.13	0.08	1.82	4.06	
$\mathrm{CCSD}^{e)}$	3.01	5.10	10.2	4.12	10.2	21.4	
$\mathrm{CCSDT}^{e)}$	0.27	0.65	1.13	0.53	1.78	-2.47	
$\mathrm{CCSDTQ}^{e)}$	0.02	0.04	0.06	0.02	0.14	-0.02	
$\mathrm{CCSDTQP}^{f)}$	0.00	0.00	0.00	0.00	0.03	0.03	

Table 2. Correlation corrections (in mE_h) with various CI, MBPT, and CC methods relative to FCI^{a} values for HF and H_2O

^{a)} Ref. [42] for HF; Ref. [43] for H_2O .

^{b)} Ref. [44].

- $^{c)}$ Ref. [28].
- ^{d)} Ref. [41].
- ^{e)} Ref. [25].

 $^{f)}$ Ref. [27].



Table 3. Correlation correction (in mE_h) with various MBPT and CC
methods relative to $\mathrm{FCI}^{a)}$ values for SiH_2 and CH_2 molecules

in DZP basis set. The 3s combination of the 3d functions

is included for CH₂ but deleted for SiH₂.

Method	SiH_2		CH	H_2		
C	\mathbf{R}_{e}	$1.5 \mathrm{R}_e$	$2.0 \mathrm{R}_e$	R_e	$1.5 \mathrm{R}_e$	
$MBPT(2)^{b}$	29.423	48.582	94.839	31.056		
$MBPT(3)^{b}$	9.701	23.353	52.986	10.590		
$MBPT(4)^{b}$	3.658	11.033	21.489	4.980		
$\mathrm{MBPT}(5)^{b}$	1.617	5.456	8.112	2.949		
$\mathrm{CCSD}^{c)}$	2.843	6.685	14.869	3.544	6.961	
$\mathrm{CCSDT}^{c)}$	0.100	0.058	-3.689	0.206	0.310	
$\mathrm{CCSDTQ}^{c)}$	0.002	-0.015	-0.346	0.007	0.026	
$\mathrm{CCSDTQP}^{c)}$	0.001	0.001	0.001	0.000	0.000	
^{a)} Ref. [45] for SiH ₂ ; Ref. [46] for CH_2 .						
b D C $[4\pi]$						

^{b)} Ref. [47].

 $^{c)}$ Ref. [27].

Molecular Physics

Table 4. Correlation correction (in mE_h) with various CC methods relative to FCI^a)

values for N₂ (R=2.068 au) in cc-pVDZ basis set and for C₂ (R=2.348 au)

in cc-pVDZ basis set augmented by diffuse functions with exponents:

s(0.0469), p(0.04041). The 1s orbitals were frozen.

Molecule	$\mathrm{CCSD}^{b)}$	$\mathrm{CCSDT}^{b)}$	$\mathrm{CCSDTQ}^{b)}$	$\mathrm{CCSDTQP}^{c)}$
C_2	29.597	3.273	0.622	0.103
N_2	13.465	1.626	0.192	0.016
^{a)} Ref. [48]				
^{b)} Ref. [31].				
$^{c)}$ Ref. [9].				

Table 5. Computed and extrapolated equilibrium geometry and harmonic

frequencies with coupled cluster methods for the N_2 molecule.

Basis	No. of			CC			_
set	basis func.	SD(T)	SDT	$SDT(Q_f)$	SDTQ	$SDTQ(P_f)$	Exp.
			R_e [Å]				
cc-pVDZ	28	$1.1189^{a)}$	$1.1185^{a)}$	1.1200^{a}	$1.1198^{a)}$	$1.1201^{b)}$	
cc-pV5Z	182	$1.0994^{a)}$	$1.0987^{a)}$	$1.0999^{a)}$	$1.0997^{a,c)}$	$1.1000^{c,d)}$	
cc-pCV6Z	460	1.0970^{e}	$1.0964^{a,c)}$	$1.0976^{a,c)}$	$1.0978^{a,c)}$	$1.0975^{c,d)}$	1.0977^{f}
				ω [C	em^{-1}]		
cc-pVDZ	28	$2339^{a)}$	2347^{a}	$2325^{a)}$	$2328^{a)}$	2324^{b}	
cc-pV5Z	182	$2360^{a)}$	2370^{a}	$2351^{a)}$	$2354^{a,c)}$	$2350^{c,d)}$	
cc-pCV6Z	460	$2371^{e)}$	$2381^{a,c)}$	$2362^{a,c)}$	$\boldsymbol{2365}^{a,c)}$	${f 2361}^{c,d)}$	2358.6^{f}
^{a)} Ref. [37]				0,			
^{b)} Ref. [49]							
^{c)} Estimate	ed value.						
$^{d)}$ Ref. [9].							
^{e)} Ref. [50]							
f) Ref. [51]							