

# Sixth-order energy corrections with converged coupled cluster singles and doubles amplitudes

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A concise analysis of sixth-order perturbation theory and coupled cluster theory is presented, and several computational schemes correct through sixth order are constructed based upon an underlying coupled cluster singles and doubles calculation. The sixth-order corrections with respect to the coupled cluster singles and doubles wave function are identified and appropriate contributions are added to the energy using an  $n^9$  algorithm. Depending upon the type of the initial functional, several computational approaches can be developed. All of the methods considered have been tested for several small molecules and the results compared to the exact values. An average error of 0.3 mhartree is achieved compared to 0.1 mhartree for CCSDTQ (coupled cluster singles, doubles, triples, and quadruples). © 1998 American Institute of Physics. [S0021-9606(98)00411-5]

## I. INTRODUCTION

Significant progress has been made in recent years in the implementation of coupled cluster (CC)<sup>1-7</sup> and many-body perturbation theory (MBPT).<sup>8-12</sup> The full inclusion of the  $T_3$  cluster (i.e., coupled cluster single, doubles, and triples—CCSDT) is now available for routine calculations for closed- and open-shell systems.<sup>13,14</sup> In addition, the full inclusion of the  $T_4$  cluster in coupled cluster singles, doubles, triples, and quadruples (CCSDTQ) provides a powerful tool for generating high-accuracy benchmark values for the correlation energy of small molecules.<sup>15</sup> This is a method which is correct through MBPT(6) and it is the most accurate single-reference method currently available apart from full configuration interaction (CI). Since the implemented CC realizations are based on the iterative solution of the CC equations, it is always possible to extract the MBPT corrections to a particular order by moderate modification of the CC programs. In fact, our prior CC work provided the evaluation of the fifth-order, MBPT(5), and sixth-order, MBPT(6), corrections.<sup>10,11</sup>

Large numbers of diagrams in fifth- and sixth-order MBPT (840 and 28 300, respectively) force a departure from a traditional diagram-by-diagram approach. Here we use a diagrammatic formalism only in the context of the classification and verification of the developed algorithm. The diagrammatic technique substantially facilitates various analyses—in particular, those lying on the border between CC and MBPT approaches. Even in the case of a pure perturbation approach, we exploit the CC technique in constructing the order-by-order expansion of the cluster operators and then in constructing the energy diagrams. For example,  $T_2^{(3)}$  represents 39 diagrams and we could either treat them as 39 independent  $T_2^{(3)}$  amplitudes (for each diagram we have an independent set of amplitudes) or sum

them together and treat them as a single set of amplitudes. It is obvious that there is a synergism between the development of the coupled cluster methods and MBPT approaches.

There is, however, an important difference between whether we pursue the given order perturbation corrections strictly within the coupled cluster iterative scheme or whether we treat some of them in an independent manner. This difference justifies the philosophy of noniterative approaches. This derives from the fact that certain contributions require a lower rank computational procedure when treated from the perturbation viewpoint than when they are evaluated within the standard iterative structure. Such an example has already been considered in Ref. 16 where we observed that the simplest CC method correct through fifth order, CCSDTQ-1, requires an  $n^9$  procedure, while the respective fifth-order MBPT diagrams require at most an  $n^8$  scheme. This is due to the fact that the fifth-order connected quadruple contributions,  $E_{QQ}^{(5)}$ , are factorizable and the factorization can be applied only when we consider the respective energy diagrams, hence the rate-determining step is the  $T_3 \rightarrow T_3$  contributions. Within the standard CC iterative scheme (e.g., at the CCSDTQ-1 level), this factorization cannot be achieved and the construction of the  $T_4$  operator, done with an  $n^9$  procedure, is the rate-determining step for the method. Similarly, at the sixth-order level, MBPT requires an  $n^9$  procedure, necessary for the construction of the  $T_4$  operator, where we access the nonfactorizable sixth-order quadruple contribution via the well-known  $2n$  rule of perturbation theory. Computation of the same sixth-order energy contribution within the strict CC scheme would require a  $T_4 \rightarrow T_4$  step which is an  $n^{10}$  procedure.

This observation can be generalized to higher orders as presented in Table I. Here in column 1 we indicate the order of perturbation theory in the energy, while column 2 presents the required rank of the computational procedure when the relevant contribution is evaluated by means of the MBPT method with the rate-determining step specified in the next

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TABLE I. Rank of the computational procedure for MBPT and CC schemes generating methods correct through a given order in the MBPT energy.

Order in MBPT energy	Rank of MBPT procedure	Rate determining step	Rank of CC procedure	Rate determining step
3	$n^6$	$T_2 \rightarrow T_2$	$n^6$	$T_2 \rightarrow T_2$
4	$n^7$	$T_3$	$n^7$	$T_3$
5	$n^8$	$T_3 \rightarrow T_3$	$n^9$	$T_4$
6	$n^9$	$T_4$	$n^{10}$	$T_4 \rightarrow T_4$
7	$n^{10}$	$T_4 \rightarrow T_4$	$n^{11}$	$T_5$
8	$n^{11}$	$T_5$	$n^{13}$	$T_6$
9	$n^{12}$	$T_5 \rightarrow T_5$	$n^{14}$	$T_6 \rightarrow T_6$
10	$n^{13}$	$T_6$	$n^{15}$	$T_7$
11	$n^{14}$	$T_6 \rightarrow T_6$	$n^{17}$	$T_8$
12	$n^{15}$	$T_7$	$n^{18}$	$T_8 \rightarrow T_8$
13	$n^{16}$	$T_7 \rightarrow T_7$	$n^{19}$	$T_9$

column. Similarly, the next two columns give the rank of the computational procedure and the rate-determining step for the standard iterative CC approach. We see that to obtain a method correct through eighth order in the energy, the MBPT approach requires an  $n^{11}$  procedure and the step responsible for this is the generation of the  $T_5$  amplitudes (lowest order), while the level of MBPT accuracy achieved within the CC framework requires an  $n^{13}$  procedure and the rate-determining step is a construction of the (lowest order)  $T_6$  operator. The last row of Table I indicates that to achieve a method correct through 13th order in energy, the highest cluster operator created within the MBPT scheme would be  $T_7$  while the CC method would require a  $T_9$  operator for the same purpose. This means that the connected  $T_8$  contribution creates factorizable contributions both at the MBPT(11), MBPT(12) and MBPT(13) levels and, similarly, the  $T_9$  cluster gives factorizable contributions at the MBPT(13) level. Note, all the above refer to rigorously computed values. Forcing approximate factorization can be used to further drastically reduce the computational scaling.<sup>17</sup>

Table I offers an indication of the optimum computational scheme for calculating the MBPT energy at the given order. Namely, we should use the power of the CC approach to construct the cluster operators  $T_1$  to  $T_k$ , where  $T_k$  is the operator listed in the third column. The contributions originating from the cluster operators,  $T_{k+1}$  to  $T_l$ , where  $T_l$  is an operator listed in the last column, should be evaluated in an MBPT-like manner. In this way, we can best exploit the efficiency of the CC scheme for lower cluster operators and then take advantage of the factorizable nature of the higher cluster contributions.

The above considerations can be viewed as a justification for so-called non-iterative coupled cluster approaches.<sup>6</sup> The principle in the development of such schemes lies in the fact that we solve lower rank coupled cluster equations (e.g., CCSD), and we evaluate the contributions originating from the higher cluster only once, for converged lower rank cluster amplitudes. From the computational viewpoint, there are two main advantages to such an approach: First, the difficult contribution is computed only once, rather than in each CC iteration; second, the contribution in question is evaluated at the MBPT rather than CC rate—that is, the values of the rank of the computational procedure given in column 2 of

Table I apply rather than those given in column 4. The only exception from the latter occurs at the fourth-order level where the inclusion of the  $T_3$  contributions, CCSD + T(CCSD) or CCSD(T), is obtained with the same computational procedure both within MBPT and CC, because both are noniterative approaches to the CCSDT-1 method.<sup>4,18</sup> See Ref. 18 and references therein for a summary of such methods through fourth and fifth order.

For all higher order approaches, the rank of the computational procedure for the noniterative schemes is lower than that for the standard CC approach.

The aim of the present paper is to develop a noniterative approach correct through sixth-order for the coupled cluster solution obtained at the CCSD level. As sixth order represents a stable approximation characteristic of even-orders of perturbation theory,<sup>11</sup> it is likely that such methods will significantly outperform those for fifth order.<sup>18</sup> It follows from Table I that for this purpose we need to construct the  $T_4$  operator, hence the rank of the procedure cannot, rigorously, be lower than  $n^9$ . In addition we also need  $T_3 \rightarrow T_3$  required already at the fifth-order level, which is an  $n^8$  scheme. In the following section, we outline the basic definitions and give a brief summary of the quantities occurring at the fifth-order level presented in Ref. 18.

## II. CC FUNCTIONALS AND EQUATIONS

As in the previous paper,<sup>18</sup> to define sixth-order corrections for CC theory there are several energy expressions which can be used for the wave function defined by an exponential Ansatz

$$\Psi = e^T |\Phi_0\rangle, \quad (1)$$

$T = T_1 + T_2 + T_3 + \dots + T_n$ , with the usual definition of the  $T_n$  cluster. Here we limit ourselves to  $n=4$ , that is, up to connected quadruple excitation cluster operators. The Hamiltonian and notation are the same as in the previous paper.

First, from the CC type energy expression in which only  $T_1$  and  $T_2$  clusters contribute

$$E = \langle 0 | H_N (T_2 + T_1 + \frac{1}{2} T_1^2) | 0 \rangle \quad (2)$$

we can derive the sixth-order energy contributions. The  $T_1$  and  $T_2$  amplitudes are obtained by solving the CC equations for a given model and subsequently are substituted into Eq. (2) to give the CC energy.

The second possibility would be to start with the CC functional<sup>4</sup> introduced in connection with the evaluation of the density matrices and analytical derivatives of the coupled cluster wave function,

$$E = \langle 0 | (1 + \Lambda) e^{-T} H_N e^T | 0 \rangle \quad (3)$$

$$= \langle 0 | (1 + \Lambda) \bar{H} | 0 \rangle \quad (4)$$

$$= \langle 0 | (1 + \Lambda) (H_N e^T)_c | 0 \rangle, \quad (5)$$

where  $\Lambda = \Lambda_1 + \Lambda_2 + \dots + \Lambda_n$  is a de-excitation operator determined from the set of  $\Lambda$  equations,  $P[(1 + \Lambda)\bar{H} - \Delta E \Lambda]Q = 0$ , similar in structure to the CC equations,<sup>4</sup>  $Q\bar{H}P = 0$ , where  $P = |0\rangle\langle 0|$  and  $Q = 1 - P = Q_1 + Q_2 + Q_3 + \dots$ , where the subscript indicates catego-

ries of excitation. The stationarity condition of Eq. (3) with respect to  $\Lambda$  generates the usual CC equations, while stationarity of  $T$  gives  $\Lambda$  equations. The index  $c$  restricts the expansion to connected diagrams only.

The third type of functional would be that corresponding to the expectation value of the energy taken with respect to the CC wave function which is called the XCC functional<sup>19</sup>

$$E_{\text{XCC}} = \langle 0 | e^{T^\dagger} H_N e^T | 0 \rangle_L. \quad (6)$$

The index  $L$  ensures that only linked diagrams are to be considered.

The philosophy of our approach relies on the iterative solution of relatively simple CC equations, followed by the noniterative evaluation of more sophisticated terms obtained from use of the above approaches.

The CC equations can be obtained by taking variations with respect to  $\Lambda$  in the functional (5). To this end we may rewrite Eq. (5) in the more expanded form

$$\begin{aligned} E = & \langle 0 | (1 + \Lambda_1 + \Lambda_2) (H_N e^{T_1 + T_2})_c | 0 \rangle + \langle 0 | (\Lambda_1 + \Lambda_2) \\ & \times (H_N e^{T_3 + T_4})_c | 0 \rangle + \langle 0 | (\Lambda_3 + \Lambda_4) (H_N e^T)_c | 0 \rangle \\ & + \langle 0 | (\Lambda_2 (W_N T_1 T_3))_c | 0 \rangle. \end{aligned} \quad (7)$$

In the standard approach, we would obtain the equations for  $T_1, T_2, T_3$ , and  $T_4$  amplitudes by taking variations with respect to  $\Lambda_1, \Lambda_2, \Lambda_3$ , and  $\Lambda_4$  amplitudes, respectively.

Neglecting  $T_3$  and  $T_4$  clusters and taking variations with respect to  $\Lambda_1$  and  $\Lambda_2$ , we obtain the CCSD equation

$$T_1 = R_1(W_N e^{T_1 + T_2})_c \stackrel{\text{def}}{=} T_1(\text{CCSD}), \quad (8)$$

$$T_2 = R_2(W_N e^{T_1 + T_2})_c \stackrel{\text{def}}{=} T_2(\text{CCSD}), \quad (9)$$

where the symbol  $T_n(\text{CCSD})$  represents all diagrammatic terms present in the  $T_n$  equation within the CCSD model<sup>2</sup>, as discussed in Ref. 18, and  $R_n$  is a resolvent operator ensuring the appropriate excitation subspace and the required denominator is defined<sup>20</sup> as

$$R_n(X) = (n!)^{-2} \sum \frac{\langle \Phi_{ij\dots}^{ab\dots} | X | 0 \rangle}{e_i + e_j + \dots - e_a - e_b} \{a^\dagger b^\dagger \dots ji\}. \quad (10)$$

By solving the CCSD equations, the first term in Eq. (7) becomes the CCSD energy

$$\begin{aligned} E_{\text{CCSD}} = & \langle 0 | (1 + \Lambda_1 + \Lambda_2) (H_N e^{T_1 + T_2})_c | 0 \rangle \\ = & \langle 0 | (H_N e^{T_1 + T_2})_c | 0 \rangle. \end{aligned} \quad (11)$$

The last equality follows from the fact that we have the CCSD equations, Eqs. (8 and 9), solved.

The second term in Eq. (7) gives the contribution to the energy coming from  $T_3$  and  $T_4$  clusters via  $\Lambda_1$ , Eq. (12), or  $\Lambda_2$ , Eq. (13), amplitudes,

$$E_{\Lambda_1} = \langle 0 | \Lambda_1 W_N T_3 | 0 \rangle, \quad (12)$$

$$E_{\Lambda_2} = \langle 0 | \Lambda_2 W_N (T_3 + T_4) | 0 \rangle. \quad (13)$$

We need not consider the third term in Eq. (7) as discussed in Ref. 18.

We now vary the functional in Eq. (7) with respect to  $\Lambda_3$  and  $\Lambda_4$  amplitudes to arrive at the equations for the  $T_3$  and  $T_4$  amplitudes. However, we include into these equations only those terms which contribute up to sixth order in the MBPT energy based upon a canonical Hartree–Fock reference. For such a case,  $T_1$  first appears in second order, and  $F_N$  vanishes. Bearing this in mind, we obtain the following equations:

$$T_3 = R_3[W_N(T_2 + T_3 + \frac{1}{2}T_2^2 + T_4 + T_1T_2 + T_2T_3)]_c, \quad (14)$$

$$T_4 = R_4[W_N(T_3 + \frac{1}{2}T_2^2 + T_4 + T_2T_3 + \frac{1}{6}T_2^3)]_c. \quad (15)$$

Let us now construct the lowest-order contributions for the amplitudes— $T_1, T_2, T_3$ , and  $T_4$ . We treat orders in our usual more general sense (see Refs. 18 and 19), by replacing the  $T_2^{(1)}$  and  $T_1^{(2)}$  with the converged  $T_1$  and  $T_2$  amplitudes, which are considered to be second and first order, respectively. Thus we have

$$T_3^{[2]} = R_3(W_N T_2). \quad (16)$$

Note that we use a square bracket instead of a parenthesis to distinguish the generalized order from the usual understanding of order in MBPT.

Similarly the third-order  $T_3$  amplitude is obtained by the inclusion of the second and third term in Eq. (14):

$$T_3^{[3]} = R_3[W_N T_3^{[2]} + \frac{1}{2}(W_N T_2^2)_c]. \quad (17)$$

Analogously the third-order  $T_4$  amplitude can be expressed as

$$T_4^{[3]} = R_4[W_N T_3^{[2]} + \frac{1}{2}(W_N T_2^2)_c]. \quad (18)$$

We may also construct the third order (in the generalized sense)  $T_2$  and  $T_1$  amplitudes as originating from the  $T_3^{[2]}$  operator

$$T_2^{[3]} = R_2(W_N T_3^{[2]}), \quad (19)$$

$$T_1^{[3]} = R_1(W_N T_3^{[2]}). \quad (20)$$

### III. $\Lambda$ FUNCTIONAL

For the expression based on the  $\Lambda$  functional, we have to define the analogous quantity to those discussed in the previous section for the  $\Lambda$  operator. Thus the second-order  $\Lambda_3$  can be expressed as

$$\Lambda_3^{[2]\dagger} = R_3(W_N \Lambda_2^\dagger). \quad (21)$$

In analogy to Eqs. (19 and 20), we introduce third-order  $\Lambda_2$  and third-order  $\Lambda_1$ :

$$\Lambda_2^{[3]\dagger} = R_2(W_N \Lambda_3^{[2]\dagger}) \quad (22)$$

$$\Lambda_1^{[3]\dagger} = R_1(W_N \Lambda_3^{[2]\dagger}). \quad (23)$$

Although the  $\Lambda$  operator, Eqs. (21)–(23), may contain some disconnected pieces<sup>21</sup>, the energy contributions will be linked since  $\Lambda$  is always combined with a respective connected  $T$  operator.

Taking the third-order  $T_3$  amplitude, Eq. (17), and inserting it into Eq. (12), we obtain the sixth-order single-triple contribution,

$$E_{ST}^{[6]} = \langle 0 | \Lambda_1 W_N T_3^{[3]} | 0 \rangle. \quad (24)$$

We observe that Eq. (12) generates also another sixth-order contribution,

$$E_{TST}^{[6]} = \langle 0 | \Lambda_1^{[3]} W_N T_3^{[2]} | 0 \rangle, \quad (25)$$

from Eq. (23) and Eq. (16).

The remaining sixth-order contributions are generated by Eq. (13). We see that they can arise in three ways: (1) by including the third-order  $T_2$  amplitude, Eq. (19), and the second-order  $T_3$  amplitude, Eq. (16); (2) by including the fourth-order  $T_3$  amplitudes,  $T_3^{[4]}$ ; and (3) by including the fourth-order  $T_4$  amplitudes,  $T_4^{[4]}$ .

The first possibility provides us with a contribution

$$E_{TD}^{[6]} = \langle 0 | \Lambda_2^{[3]} W_N T_3^{[2]} | 0 \rangle. \quad (26)$$

The second group comes from the fourth-order  $T_3$  amplitude obtained from Eq. (14):

$$T_3^{[4]} = R_3 [W_N (T_3^{[3]} + T_4^{[3]} + T_1 T_2 + T_2 T_3^{[2]})]_c. \quad (27)$$

After inserting this into Eq. (13), we obtain the following sixth-order contributions:

$$E_{TT}^{[6]} = \langle 0 | \Lambda_3^{[2]} W_N T_3^{[3]} | 0 \rangle, \quad (28)$$

$$E_{TQ}^{[6]} = \langle 0 | \Lambda_3^{[2]} W_N T_4^{[3]} | 0 \rangle, \quad (29)$$

$$E_{TT_d}^{[6]} = \langle 0 | \Lambda_3^{[2]} (W_N T_1 T_2)_c | 0 \rangle, \quad (30)$$

$$E_{TP}^{[6]} = \langle 0 | \Lambda_3^{[2]} (W_N T_2 T_3^{[2]})_c | 0 \rangle, \quad (31)$$

where we took advantage of Eq. (21);  $\Lambda_3^{[2]}$  incorporates the  $R_3$  denominator from Eq. (27). The subscript notation pertains to the nature of the excitations. Since all the energy contributions Eqs. (28)–(31) are based on the fourth-order triple excitation cluster,  $T_3^{[4]}$ , hence the first index in the subscript to E is T—indicating triples. The second index refers to the internal structure of  $T_3^{[4]}$ : T for connected third-order triple excitation operator,  $T_3^{[3]}$ , the first term in the r.h.s. of Eq. (27); Q for connected quadruple excitation operator,  $T_4^{[3]}$ , the second term in Eq. (27);  $T_d$  for the disconnected triple contribution to  $T_3$ , i.e.,  $T_1 T_2$ , the third term in Eq. (27) and, finally, P for the disconnected pentuples, i.e.,  $T_2 T_3$  operator—the last term in Eq. (27). To be consistent in the notation we should use  $P_d$  instead of P, however, since all the pentuples contributing to the sixth-order energy are disconnected (the connected  $T_5$  operator contributes in seventh order) to make the expression more compact we will use throughout the P index, keeping in mind that this refers to the disconnected  $T_2 T_3$  pentuple excitations. We may note that the component in Eq. (28), corresponding to the first term on the right-hand-side of Eq. (27), has been obtained by performing two iterations of Eq. (14), to obtain  $T_3^{[2]}$  and the next one to create  $T_3^{[3]}$ .

Now we follow the same procedure with respect to the  $T_4$  amplitude, that is, we create the fourth-order  $T_4$  amplitude,  $T_4^{[4]}$ , by including appropriate terms in Eq. (15). We obtain in this way

$$T_4^{[4]} = R_4 [W_N (T_3^{[3]} + T_4^{[3]} + T_2 T_3^{[2]} + T_2^3/6)]_c. \quad (32)$$

Introducing the last quantity into Eq. (13), we obtain the following components of the sixth-order correction:

$$E_{QT}^{[6]} = \langle 0 | \Lambda_2 W_N R_4 (W_N T_3^{[3]}) | 0 \rangle, \quad (33)$$

$$E_{QQ}^{[6]} = \langle 0 | \Lambda_2 W_N R_4 (W_N T_4^{[3]}) | 0 \rangle, \quad (34)$$

$$E_{QP}^{[6]} = \langle 0 | \Lambda_2 W_N R_4 (W_N T_2 T_3^{[2]})_c | 0 \rangle, \quad (35)$$

$$E_{QH}^{[6]} = \frac{1}{6} \langle 0 | \Lambda_2 W_N R_4 (W_N T_2^3)_c | 0 \rangle. \quad (36)$$

Note that here the  $R_4$  denominator is included explicitly rather than being hidden as  $R_3$  was in  $\Lambda_3^{[2]}$  in Eqs. (28)–(31). The notation is analogous to that used in Eqs. (28)–(31); the subscript H refers to the disconnected sextuple excitations represented by  $T_2^3/6$  and similarly as in case of pentuples to keep the formula compact we use H instead of  $H_d$ .

#### IV. DISCONNECTED TRIPLE AND QUADRUPLE CONTRIBUTIONS IN THE SIXTH-ORDER ENERGY

In the standard coupled cluster approach, we do not separately consider any contributions to the energy that would arise from disconnected wave function contributions. They would show up naturally in the course of the CC iterative procedure. For example, second- and third-order disconnected quadruples in the wave function,  $T_2^{(1)2}/2$  and  $T_2^{(1)} T_2^{(2)}$ , contribute through the  $E_{\text{CCSD}}$  energy. The same refers to the disconnected third-order triples,  $T_2^{(1)} T_1^{(2)}$ . However, at the fourth-order level, we have some terms arising from disconnected wave function contributions that are not included into the CCSD energy, and that also do not enter through the  $T_3$  and  $T_4$  pieces since the latter are, by definition, connected. The contributions in question are  $T_2 T_1^{[3]}$ ,  $T_2 T_2^{[3]}$  and also the contributions singled out already in Eq. (7), i.e.,  $T_1 T_3^{[2]}$ . Formally we may say that the first two terms do not arise from the CCSD procedure since the latter—according to the perturbation scheme introduced in Sec. III—produces only first-order  $T_2$  and second-order  $T_1$ .

In a more general CCSDTQ method, all involved equations (e.g.,  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$ ) would be iterated simultaneously. For instance,  $T_2$  contributions can be obtained from the lowest  $T_3$  amplitude and then substituted into the  $T_2^2/2$  term of the  $T_2$  equation, which will produce the above-mentioned contribution to the sixth-order energy coming from  $T_2 T_2^{(3)}$ . In the present case, the  $T_2$  (CCSD) equation is solved before the  $T_3$  amplitudes are generated, and there is no chance to insert the latter back into the  $T_2$  part of the CCSD equations, so such forms have to be handled separately. We may now regroup the above contributions to obtain the following formula for the total non-iterative correction coming from

$$E_{TQ}^{[6]ds} = E_{T_dP}^{[6]} + E_{Q_dP}^{[6]} + E_{T_1T_3}^{[6]}, \quad (37)$$

where the right-hand-side quantities are defined as

$$E_{T_dP}^{[6]} = \langle 0 | \Lambda_3^{[2]} T_2 W_N T_3^{[2]} | 0 \rangle, \quad (38)$$

$$E_{Q_dP}^{[6]} = \langle 0 | \Lambda_2 [W_N T_2 R_2 (W_N T_3^{[2]})]_c | 0 \rangle, \quad (39)$$

$$E_{T_1T_3}^{[6]} = \langle 0 | \Lambda_2 W_N T_1 T_3^{[2]} | 0 \rangle, \quad (40)$$

where the  $T_dP$  and  $Q_dP$  subscripts indicate that the energy contributions arise from the disconnected fourth-order triples and quadruples which, in turn, are obtained from the third-order (disconnected) pentuples. Note that the disconnected terms allow moving  $T_2$  to the left of the  $W_N$  interaction as shown. We may note also that the contribution given by Eq. (31) arises also from pentuples but via fourth-order connected triples, i.e.,  $T_3^{[4]}$  operator.

Finally, the last piece which could contribute to the sixth-order energy would be that that arises from the disconnected  $T_1^2/2$  wave function part entering directly into the energy expression, that is,

$$E_d^{[6]} = \langle 0 | W_N T_1 T_1^{[3]} | 0 \rangle. \quad (41)$$

However, we do not include this term, since closer examination (e.g., decomposition into components of different time-ordering) shows that it will be included in the diagrams given by Eqs. (25), (38), and (40).

Now we may write the total sixth-order contribution computed on top of the CCSD method as

$$E^{[6]} = E_{ST}^{[6]} + E_{TST}^{[6]} + E_{TDT}^{[6]} + E_{TT}^{[6]} + E_{TQ}^{[6]} + E_{Ttd}^{[6]} + E_{TP}^{[6]} \\ + E_{QT}^{[6]} + E_{QQ}^{[6]} + E_{QP}^{[6]} + E_{QH}^{[6]} + E_{TdP}^{[6]} + E_{QdP}^{[6]} + E_{T_1T_3}^{[6]}, \quad (42)$$

and the particular components are given by Eqs. (24), (25), (26), (28), (29), (30), (31), (33), (34), (35), (36), (38), (39), and (40), respectively.

## V. COMPUTATIONAL STRATEGY IN THE CALCULATION OF THE SIXTH-ORDER CORRECTIONS

So far we have disregarded the problem of the computational requirements, or the rank of the computational procedure for the particular sixth-order contribution. We want to indicate that at the sixth-order level, the slowest step involves evaluation of the connected quadruple component. At the fifth order—as mentioned in Ref. 18—the latter component is fully factorizable, which substantially reduces the rank of the computational procedure. Here we encounter a nonfactorizable quadruple component that has to be evaluated at higher cost. Moreover, we observe that the  $E_{QQ}^{[6]}$  component given by Eq. (34) requires an  $n^{10}$  step, which is unacceptable computationally. To avoid this, we exploit the identity introduced in Ref. 22 concerning the sixth-order  $T_4$  into  $T_4$  and  $T_4$  into  $T_3$  contributions, which can be expressed as

$$E_{Qnf}^{[6]} = E_{TQ}^{[6]} + E_{QQ}^{[6]} = \langle 0 | T_4^{\dagger(3)} (-H_N^o) T_4^{(3)} | 0 \rangle \\ + \langle 0 | T_2^{\dagger(2)} T_2^{\dagger(1)} (-H_N^o) T_4^{(3)} | 0 \rangle \\ - \langle 0 | T_2^{\dagger(2)} W_N T_4^{(3)} | 0 \rangle. \quad (43)$$

The full sixth-order contribution arising from  $T_4^{(3)}$  can then be expressed as

$$E^{(6)}(T_4^{(3)}) = \langle 0 | T_2^{\dagger(2)} W_N T_4^{(3)} | 0 \rangle + \langle 0 | T_3^{\dagger(2)} W_N T_4^{(3)} | 0 \rangle \\ + \langle 0 | T_2^{\dagger(1)} W_N R_4 (W_N T_4^{(3)}) | 0 \rangle \quad (44)$$

$$= \langle 0 | (T_4^{\dagger(3)} + T_2^{\dagger(2)} T_2^{\dagger(1)}) (-H_N^o) T_4^{(3)} | 0 \rangle, \quad (45)$$

which is an  $n^8$  procedure (apart from the generation of  $T_4^{(3)}$ ). Note that throughout the last paragraph we have been referring to the order in the usual sense.

On the basis of the analysis we made for the pure sixth-order contributions, we may arrive at the following formula for the nonfactorizable quadruples that can be computed from the CCSD solution:

$$E_{Qnf}^{[6]} = \langle 0 | (T_4^{\dagger[3]} + \frac{1}{2} T_2^{\dagger(1)} T_2^{\dagger(2)}) (-H_N^o) T_4^{[3]} | 0 \rangle. \quad (46)$$

The next computational simplification arises upon grouping together certain terms. Namely, we may compute in one step the sum of the fifth- and sixth-order quadruple contribution. First we may obtain the respective  $T_4$  quantity:

$$T_4^{[3+4]} = R_4 [W_N (T_3^{[2]} + T_3^{[3]} + T_2^2/2 + T_2 T_3^{[2]} + T_2^3/6)]_c. \quad (47)$$

After introducing the proper factorization of all terms in the last expression, the above quantity requires one  $n^9$  step. Hence we may group together the contributions obtained in Eqs. (33), (35), (36) as well as the fifth-order quadruple component  $E_Q^{[5]}$ , see Eq. (68) in Ref. 18 to have

$$E_Q^{[5+6]} = E_Q^{[5]} + E_{QT}^{[6]} + E_{QP}^{[6]} + E_{QH}^{[6]} = \langle 0 | \Lambda_2 W_N T_4^{[3+4]} | 0 \rangle. \quad (48)$$

We have tested numerically the use of the slightly modified expression for the above contribution

$$E_{Qf}^{[5+6]} = \frac{1}{2} \langle 0 | \Lambda_2 T_2^{\dagger(1)} D_4 T_4^{[3+4]} | 0 \rangle, \quad (49)$$

where  $T_2^{(1)} = R_2(W_N)$  and  $D_n T_n = (n!)^{-2} \sum (e_i + e_j + \dots - e_b - e_a) t_{ij}^{ab} \dots a^\dagger b^\dagger \dots ji$ . Unlike the analysis up to this point, this factorized formula is not entirely rigorous, but it is practically equivalent and gives differences of the order of microhartrees for the equilibrium geometry and tens of microhartrees for expanded bonds. Since the latter expression is factorizable it can be evaluated with an  $n^6$ – $n^8$  procedure. However, in these first calculations, we do not take advantage of this possibility, because the more complicated formulas make the coding difficult.

In practice, the  $T_4^{[3]}$  amplitudes [used for the evaluation of nonfactorizable quadruple contributions, Eq. (46)] ought to be computed independently from those of  $T_4^{[3+4]}$ , as given in Eq. (47), so we need two  $n^9$  steps: one for each set of  $T_4$  amplitudes. We may further simplify the algorithm to

use the  $T_4^{[3+4]}$  amplitudes also for the nonfactorizable part, Eq. (46), which makes it possible to get all sixth-order quadruples with one  $n^9$  step. In this way, we still have correct sixth-order contributions, but in addition, we include some higher terms which do not necessarily improve the results due to possible misbalances. Both possibilities have been considered in actual calculations.

## VI. XCC FUNCTIONAL

In this approach, we construct the sixth-order XCC functional in the manner described in Refs. 4 and 19 by starting with expression (6) and considering all amplitudes in their lowest orders. We arrive after expansion at the following functional:

$$\begin{aligned}
 E_{\text{XCC}}^{[6]} = & \frac{1}{2} \langle 0 | T_2^{\dagger 2} H_N^o T_1 T_3 | 0 \rangle + \text{h.c.} + \langle 0 | T_1^{\dagger} T_2^{\dagger} H_N^o T_1 T_2 | 0 \rangle + \langle 0 | T_4^{\dagger} H_N^o T_4 | 0 \rangle + \langle 0 | T_2^{\dagger} T_3^{\dagger} H_N^o T_2 T_3 | 0 \rangle \\
 & + \frac{1}{36} \langle 0 | T_2^{\dagger 3} H_N^o T_2^3 | 0 \rangle + \frac{1}{2} \langle 0 | T_2^{\dagger} W_N T_1^2 | 0 \rangle + \text{h.c.} + \langle 0 | T_1^{\dagger} T_3^{\dagger} W_N T_2 | 0 \rangle + \text{h.c.} + \langle 0 | T_1^{\dagger} W_N T_1 T_2 | 0 \rangle \\
 & + \text{h.c.} + \langle 0 | T_3^{\dagger} W_N T_1 T_2 | 0 \rangle + \text{h.c.} + \langle 0 | T_3^{\dagger} W_N T_2 T_3 | 0 \rangle + \text{h.c.} \\
 & + \langle 0 | T_3^{\dagger} W_N T_4 | 0 \rangle + \text{h.c.} + \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_1 T_2 | 0 \rangle + \text{h.c.} \\
 & + \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_2 T_3 | 0 \rangle + \text{h.c.} + \frac{1}{2} \langle 0 | T_4^{\dagger} W_N T_2^2 | 0 \rangle + \text{h.c.} + \frac{1}{12} \langle 0 | T_2^{\dagger 2} W_N T_2^3 | 0 \rangle + \text{h.c.}, \quad (50)
 \end{aligned}$$

where h.c. indicates the Hermitian conjugate taken with respect to its immediate predecessor and only linked terms are considered.

The general scheme in reducing the above functional is to take advantage of the lower rank XCC equations and eliminate redundant terms.<sup>19</sup> After introducing this we obtain the final XCC functional through sixth order of the form

$$E_{\text{XCC}}^{[6]} = \Delta E(\text{CCSD}) + \Delta E_T^{[4]}(\text{XCC}) + \Delta E_{TQ}^{[5]}(\text{XCC}) + \Delta E_{TQ}^{[6]}(\text{XCC}), \quad (51)$$

where in  $\Delta E(\text{CCSD})$  we have included all terms occurring in the XCC(6) functional that would generate the components of the CCSD equations. The next three terms represent those contributions to the fourth-, fifth-, and sixth-order XCC functional that are not included by the CCSD equations

$$\Delta E_T^{[4]}(\text{XCC}) = \langle 0 | T_3^{\dagger} H_N^o T_3 | 0 \rangle + \langle 0 | T_3^{\dagger} W_N T_2 | 0 \rangle + \langle 0 | T_2^{\dagger} W_N T_3 | 0 \rangle, \quad (52)$$

$$\begin{aligned}
 \Delta E_{TQ}^{[5]}(\text{XCC}) = & \langle 0 | T_1^{\dagger} W_N T_3 | 0 \rangle + \langle 0 | T_3^{\dagger} W_N T_3 | 0 \rangle + \frac{1}{2} \langle 0 | T_3^{\dagger} W_N T_2^2 | 0 \rangle + \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_3 | 0 \rangle \\
 & + \frac{1}{4} \langle 0 | T_2^{\dagger 2} (W_N T_2^2)_c | 0 \rangle, \quad (53)
 \end{aligned}$$

$$\begin{aligned}
 \Delta E_{TQ}^{[6]}(\text{XCC}) = & \langle 0 | T_2^{\dagger} W_N T_1 T_3 | 0 \rangle + \langle 0 | T_3^{\dagger} (W_N T_1 T_2)_c | 0 \rangle + \langle 0 | T_3^{\dagger} (W_N T_2 T_3)_c | 0 \rangle + \langle 0 | T_3^{\dagger} W_N T_4 | 0 \rangle \\
 & + \frac{1}{2} \langle 0 | T_2^{\dagger 2} (W_N T_2 T_3)_c | 0 \rangle + \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_4 | 0 \rangle + \frac{1}{12} \langle 0 | T_2^{\dagger 2} (W_N T_2^3)_c | 0 \rangle + \langle 0 | T_4^{\dagger} H_N^o T_4 | 0 \rangle \\
 & + \langle 0 | T_4^{\dagger} W_N T_3 | 0 \rangle + \frac{1}{2} \langle 0 | T_4^{\dagger} (W_N T_2^2)_c | 0 \rangle. \quad (54)
 \end{aligned}$$

By making the functional in Eqs. (51)–(54) stationary with respect to the  $T_3^{\dagger}$  operator, we arrive exactly at Eq. (14); similarly, by taking variations with respect to the  $T_4^{\dagger}$  operator, we obtain the first two terms in relation (15). Now substituting the  $T_3$  and  $T_4$  quantities back into the functional (51) causes most of the terms to disappear to yield the following expression for the energy:

$$\begin{aligned}
 \Delta E_{TQ}^{[6]}(\text{XCC}) = & \langle 0 | T_2^{\dagger} W_N T_3 | 0 \rangle + \langle 0 | T_1^{\dagger} W_N T_3 | 0 \rangle + \frac{1}{4} \langle 0 | T_2^{\dagger 2} (W_N T_2^2)_c | 0 \rangle + \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_3 | 0 \rangle + \langle 0 | T_2^{\dagger} W_N T_1 T_3 | 0 \rangle \\
 & + \frac{1}{2} \langle 0 | T_2^{\dagger 2} (W_N T_2 T_3)_c | 0 \rangle + \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_4 | 0 \rangle + \frac{1}{12} \langle 0 | T_2^{\dagger 2} (W_N T_2^3)_c | 0 \rangle. \quad (55)
 \end{aligned}$$

The components in Eqs. (52)–(54) represent all terms that through sixth order remain beyond the CCSD scheme with the exception of two terms that will be discussed later. In most cases, the sixth-order contributions obtained from the expression, Eq. (55), are identical with those obtained in the previous sections. Thus after introducing the second-order  $T_3$ , Eq. (16), and third-order  $T_2$ , Eq. (19), into the first term of the functional (55), we may obtain the sixth-order contributions  $E_{TD}^{[6]X}$ , see Eq. (26). Similarly, introducing the fourth-order  $T_3^{[4]}$  amplitude as given by Eq. (27) into the

same term, we obtain contributions  $E_{TT}^{[6]X}$ ,  $E_{TQ}^{[6]X}$ ,  $E_{TT_d}^{[6]X}$ , and  $E_{TP}^{[6]X}$ , which are exactly those given by Eqs. (28)–(31), with  $\Lambda_2$  being replaced with  $T_2^{\dagger}$ . Considering the second term of the last functional, we obtain two sixth-order contributions in the same manner as in Sec. III; that is, by combining the second-order  $T_1$  amplitude with third-order  $T_3$  and the third-order  $T_1$  amplitude with the second-order  $T_3$  ones, we obtain components  $E_{ST}^{[6]X}$  and  $E_{TS}^{[6]X}$  given by Eqs. (24) and (25), respectively. So far, all the sixth-order contributions derived from the  $\Lambda$ -based functional are identical to those obtained

in the present section apart from the  $\Lambda$  being replaced with  $T^\dagger$ . Now going to the remaining terms of Eq. (55), we encounter some slightly different forms. First of all, we observe that the next term,  $\frac{1}{4}\langle 0|T_2^{\dagger 2}(W_N T_2^2)_c|0\rangle$ , does not produce any contribution to the sixth order. The next five terms give the following sixth-order component (indicated by a superscript X to distinguish them from the analogous contribution obtained from the  $\Lambda$  functional)

$$E_{QT}^{[6]X} = \frac{1}{2}\langle 0|T_2^{\dagger 2}W_N T_3^{[3]}|0\rangle, \quad (56)$$

$$E_{QQ}^{[6]X} = \frac{1}{2}\langle 0|T_2^{\dagger 2}W_N T_4^{[3]}|0\rangle, \quad (57)$$

$$E_{QP}^{[6]X} = \frac{1}{2}\langle 0|T_2^{\dagger 2}(W_N T_2 T_3^{[2]})_c|0\rangle, \quad (58)$$

$$E_{QH}^{[6]X} = \frac{1}{12}\langle 0|T_2^{\dagger 2}(W_N T_2^3)_c|0\rangle, \quad (59)$$

$$E_{T_1 T_3}^{[6]X} = \langle 0|T_2^\dagger W_N T_1 T_3^{[2]}|0\rangle. \quad (60)$$

We may compare the above components of the sixth-order corrections with the corresponding quantities obtained from the  $\Lambda$  functional. We observe that the last term is identical to that given in Eq. (43), whereas the other four as given by Eqs. (56)–(59) are very close to those in Eqs. (33)–(36). The main difference lies in the fact that here we never employ the  $T_4^{[4]}$  quantity, so we never have to worry about  $T_4$  into  $T_4$  contributions being the bottleneck, which we were able to overcome only by adopting a special computational strategy in Sec. V. It may be easily recognized that both sets of sixth-order components give identical contributions as far as the pure sixth-order values are concerned. That means that replacing all the infinite-order amplitudes with finite-order quantities we may write

$$E_{QT}^{(6)} = E_{QT}^{(6)X} \quad (61)$$

or

$$\langle 0|T_2^{\dagger(1)}W_N(R_4 W_N T_3^{(3)})|0\rangle = \frac{1}{2}\langle 0|T_2^{\dagger(1)2}W_N T_3^{(3)}|0\rangle. \quad (62)$$

The equality of the two expressions originates from the well-known factorization theorem that enables replacing the ‘‘long’’  $T_4$  denominator introduced by the  $R_4$  operator with ‘‘short’’  $T_2$  denominators.

To complete the derivation of the sixth-order XCC type corrections, we need to account for the other two contributions that in the present formalism, should be generated by the XCC(4) and XCC(5) equations. Namely, on carrying out the reduction of the initial functional, Eq. (50), to the final form, Eqs. (51)–(54), we assumed that XCC(5)  $T_1$  and XCC(4)  $T_2$  equations have the standard form

$$T_1(\text{XCC}) = R_1(W_N T_2 + W_N T_1 + W_N T_3) \quad (63)$$

$$T_2(\text{XCC}) = R_2(W_N + W_N T_2 + W_N T_1 + \frac{1}{2}W_N T_2^2 + W_N T_3). \quad (64)$$

We see that both contain the term  $W_N T_3$ , which is not present in the CCSD equations—those we actually solve. That means we have to include the sixth-order contributions that would be generated by the iterative solutions to those equations and there are two such terms

$$E_{T_1}^{[6]}(\text{XCC}(5)) = \langle 0|T_3^{\dagger[2]}W_N(D_1 T_1^{[3]})|0\rangle, \quad (65)$$

$$E_{T_2}^{[6]}(\text{XCC}(4)) = \langle 0|T_2^\dagger W_N R_4(T_2(D_2 T_2^{[3]}))|0\rangle. \quad (66)$$

We immediately recognize that the above contributions are identical to those in Eqs. (38) and (39), respectively.

In the same way as before, we may group together some terms to facilitate the computations. We may add together terms in Eqs. (56), (58), and (59) as well as the  $E_{Q}^{[5]X}$  (see Ref. 18) to obtain

$$\begin{aligned} E_{Qf}^{[5+6]X} &= E_Q^{[5]X} + E_{QT}^{[6]X} + E_{QP}^{[6]X} + E_{QH}^{[6]X} \\ &= \frac{1}{2}\langle 0|T_2^{\dagger 2}((W_N T_2^2/2)_c + W_N T_3^{[3]} + (W_N T_2 T_3^{[2]})_c \\ &\quad + (W_N T_2^3/6)_c)|0\rangle. \end{aligned} \quad (67)$$

Similarly, we may replace the contributions  $E_{TQ}^{[6]X}$  and  $E_{QQ}^{[6]X}$  with

$$E_{Qnf}^{[6]X} = \langle 0|T_4^{\dagger[3]}(-H_N^o)T_4^{[3]}|0\rangle \quad (68)$$

obtaining the corresponding 10 terms as before. Out of them, eight are identical and two have different form.

## VII. SUMMARY OF THE SIXTH-ORDER CONTRIBUTIONS

To summarize the theoretical considerations, we present in Table II how each of the sixth-order contributions is generated by the current method. First we have to divide the sixth-order corrections into classes, which we can do on the basis of the general sixth-order perturbation terms

$$\begin{aligned} E^{(6)} &= \sum_{klm} \langle 0|W_N Q_2 D_2^{-1} W_N Q_k D_k^{-1} W_N Q_l D_l^{-1} \\ &\quad \times W_N Q_m D_m^{-1} W_N Q_2 D_2^{-1} W_N|0\rangle_L, \end{aligned} \quad (69)$$

where  $Q_n D_n^{-1}$  indicates appropriate  $n$  excitations and denominators. Subject to linked diagrams and unrestricted summation over orbital labels, all renormalization terms are cancelled. Alternatively we can simply disregard the renormalization terms in our classification. Using the CI designation, the indices  $k, m$  may assume values 1, 2, 3, and 4, corresponding to single, double, triple and quadruple excitations, respectively; whereas the index  $l$  may, in addition, be equal to 5 and 6, corresponding to pentuple and hextuple excitations. We keep in mind that the adjacent indices cannot differ by more than 2. We may then classify all sixth-order terms on the basis of the values of the indices  $k, l, m$ . In Table II, we use letters S, D, T, Q, P, and H with obvious meanings. For example, the term denoted in Table II as QPQ would correspond to the following expression:

$$\begin{aligned} E_{QPQ}^{(6)} &= \langle 0|W_N Q_2 D_2^{-1} W_N Q_4 D_4^{-1} W_N Q_5 D_5^{-1} \\ &\quad \times W_N Q_4 D_4^{-1} W_N Q_2 D_2^{-1} W_N|0\rangle_L. \end{aligned} \quad (70)$$

(As all of those quantities are represented diagrammatically the configuration classification is really a diagrammatic one meaning that EPV parts of the diagrams are incorporated in the numerical value of the quantity like  $E_{QPQ}^{(6)}$ ).

TABLE II. Generation of the classes of the sixth-order contributions by the CCSD and non-iterative terms.

Sixth-order term	Included by	Sixth-order term	Included by	Sixth-order term	Included by	Sixth-order term	Included by
SSS	CCSD	DSS	CCSD	TSS	CCSD	QDS	CCSD
SSD	CCSD	DSD	CCSD	TSD	CCSD	QDD	CCSD
SST	$E_{ST}^{[5]}$	DST	$E_{ST}^{[5]}$	TST	$E_{TST}^{[6]}$	QDT	$E_T^{[4]}$
SDS	CCSD	DDS	CCSD	TDS	$E_T^{[4]}$	QTS	CCSD, $E_{T_1T_3}^{[6]}$
SDD	CCSD	DDD	CCSD	TDD	$E_T^{[4]}$	QTD	$E_Q^{[5]}$
SDT	$E_T^{[4]}$	DDT	$E_T^{[4]}$	TDT	$E_{TDT}^{[6]}$	QTT	$E_{QT}^{[6]}$
SDQ	CCSD	DDQ	CCSD	TDQ	$E_T^{[4]}$	QTQ	CCSD, $E_{QT}^{[6]}$ , $E_{T_1T_3}^{[6]}$
STS	CCSD	DTS	CCSD	TTS	CCSD, $E_{TTd}^{[6]}$	QQD	CCSD, $E_Q^{[5]}$
STD	$E_{ST}^{[5]}$	DTD	$E_T^{[4]}$	TTD	$E_T^{[5]}$	QQT	$E_{QQ}^{[6]}$
STT	$E_{ST}^{[6]}$	DTT	$E_T^{[5]}$	TTT	$E_{TT}^{[6]}$	QQQ	CCSD, $E_Q^{[5]}$ , $E_{QQ}^{[6]}$
STQ	CCSD, $E_{ST}^{[6]}$	DTQ	CCSD, $E_T^{[5]}$	TTQ	CCSD, $E_{TT}^{[6]}$ , $E_{TTd}^{[6]}$	QPT	$E_{QP}^{[6]}$ , $E_{T_1T_3}^{[6]}$ , $E_{QdP}^{[6]}$
		DQD	CCSD	TQD	CCSD, $E_T^{[5]}$	QPQ	$E_{QP}^{[6]}$ , $E_{T_1T_3}^{[6]}$ , $E_{QdP}^{[6]}$
		DQT	$E_Q^{[5]}$	TQT	$E_{TQ}^{[6]}$	QHQ	CCSD, $E_{QH}^{[6]}$
		DQQ	CCSD, $E_Q^{[5]}$	TQQ	CCSD, $E_T^{[5]}$ , $E_{TQ}^{[6]}$		
				TPT	$E_{TP}^{[6]}$ , $E_{TdP}^{[6]}$		
				TPQ	$E_{TP}^{[6]}$ , $E_{TdP}^{[6]}$		

In columns 1, 3, 5, and 7, we list all sixth-order terms, and in the adjacent columns, we specify the expression which generates the latter. In many cases, we have more than one expression, which means that within a given class we may still distinguish certain subclasses. As an example let us analyze the class QPQ that is generated by the disconnected pentuples (i.e.,  $T_2T_3$  contribution). From Table II we see that the diagrams belonging to this class are generated by the three different sixth-order contributions:  $E_{QP}^{[6]}$ ,  $E_{T_1T_3}^{[6]}$  and  $E_{QdP}^{[6]}$ , which can be expressed as  $\langle 0|T_2^\dagger W_N R_4(W_N T_2 T_3^{[2]})_c|0\rangle$ ,  $\langle 0|T_2^\dagger W_N R_4(T_2 W_N T_3^{[2]})|0\rangle$ , and  $\langle 0|T_2^\dagger W_N R_4(T_3^{[2]} W_N T_2)|0\rangle$ , respectively. The permutation of the  $T_i$  and  $W_N$  operators is possible only when the two operators are not connected. Thus, we see that these three expressions correspond to the situations where: the  $W_N$  operator is connected both to  $T_2$  and  $T_3$  operators, is connected only to the  $T_3$  operator, and only to the  $T_2$  operator.

Out of 55 classes of sixth-order diagrams, 16 are generated entirely by the CCSD method and 10 partially. The fourth-order noniterative contribution  $E_T^{[4]}$  is responsible for seven classes. Similarly, the three fifth-order contributions introduced in Ref. 18 are responsible for 11 classes: 3, 4, and 4 for the components  $E_{ST}^{[5]}$ ,  $E_T^{[5]}$  and  $E_Q^{[5]}$ , respectively. So the remaining 19 classes are generated partially or entirely by the sixth-order contributions. The fact that each of the classes of the sixth-order diagrams can be placed among the terms derived for our sixth-order energy formula shows that all the desired terms are included in our computational scheme.

In the next section we will briefly discuss the results.

### VIII. TEST RESULTS

To test the performance of the non-iterative approaches developed in previous sections, we selected the same five molecules from Ref. 18 for which the FCI results are known:

BH, HF,  $H_2O$ ,  $N_2$ , and  $C_2$ . For the first three molecules, the reference data are also available for the stretched bonds at  $1.5 R_e$  and  $2 R_e$  ( $R_e$ , equilibrium bond length). The results of the calculations are collected in Table III where we show the deviations of the correlation energies calculated in the present work from the FCI data. In actual calculations, we have tested three different approaches denoted in Table III as  $\Lambda$ ,  $T(\Lambda)$ , and  $T$ , and within each of them, two computational schemes used to evaluate the nonfactorizable quadruples. In the columns with a  $\Lambda$  header, we have listed the results obtained from the expression given in Eq. (42) including the simplifications included in Eqs. (46)–(49). The columns headed by the  $T(\Lambda)$  contain results obtained with the same formulas as in the preceding column but in all expressions, the  $\Lambda$  amplitudes have been replaced by  $T^\dagger$  amplitudes. Finally, the last two columns correspond to the XCC-based sixth-order corrections developed in Sec. VI (the header  $T$ ). For each of the approaches, we computed the nonfactorizable quadruple contribution on the basis of the total  $T_4$  amplitudes,  $T_4^{[3+4]}$  given in Eq. (47) (this corresponds to one  $n^9$  step) or on the basis of independently computed third order  $T_4$  amplitudes,  $T_4^{[3]}$  (this corresponds to two  $n^9$  steps), since to obtain the latter quantity, we need to run an additional  $n^9$  cycle (see the last paragraph of Sec. V).

The principal difference in the quality of the obtained results is connected with the character of the reference function. In the cases where the reference function is of single-configurational character, as in the case of equilibrium geometries of the hydrides, all the computational schemes give similar results. They start to differ when going to distorted geometries or to the  $C_2$  molecule where nondynamic correlation can be important. It follows from the data collected in Table III that the most consistent results are given by the  $\Lambda$  approach: they rarely overshoot—slightly in the case of the HF molecule at  $R_e$  and  $1.5 R_e$ —and give consequently too

TABLE III. The correlation energies relative to the FCI values for the CCSD based non-iterative methods correct through sixth order [mhartree].

		$\Lambda$		$T(\Lambda)$		T	
		one $n^9$ step	two $n^9$ steps	one $n^9$ step	two $n^9$ steps	one $n^9$ step	two $n^9$ steps
BH <sup>a</sup> (DZP)	$R_e$	0.123	0.129	0.016	0.022	0.010	0.016
	$1.5R_e$	0.126	0.148	-0.031	-0.009	-0.002	0.020
	$2.0 R_e$	0.029	0.115	-0.590	-0.504	-0.385	-0.299
HF <sup>a</sup> (DZP)	$R_e$	-0.094	-0.112	-0.034	-0.052	-0.033	-0.051
	$1.5 R_e$	-0.025	-0.061	-0.087	-0.123	-0.087	-0.123
	$2.0 R_e$	0.989	0.909	-0.133	-0.213	-0.089	-0.169
H <sub>2</sub> O <sup>a</sup> (DZP)	$R_e$	0.071	0.049	0.038	0.015	0.030	0.007
	$1.5R_e$	0.853	0.759	0.518	0.411	0.194	0.100
	$2.0 R_e$	2.607	2.253	-0.625	-0.979	1.571	1.217
N <sub>2</sub> <sup>b</sup> (pVDZ)	$R_e$	0.635	0.514	0.294	0.173	0.252	0.131
C <sub>2</sub> <sup>b</sup> (pVDZ+)	$R_e$	1.040	0.036	-1.727	-2.731	-0.546	-1.550
m. abs. err.		0.599	0.462	0.372	0.476	0.291	0.335
max. deviat.		2.607	2.253	1.727	2.731	1.571	1.550

<sup>a</sup>The basis sets, geometries and FCI values were taken from Refs. 22, 23, 24 for BH, HF and H<sub>2</sub>O molecules, respectively.

<sup>b</sup>The basis sets, geometries and FCI values were taken from Ref. 25.

positive values for the quasi-degenerate situation (cf. the C<sub>2</sub> values and those for HF and H<sub>2</sub>O at  $2R_e$ ). Replacing  $\Lambda$  with  $T^\dagger$ , to which it is equivalent through linear terms,<sup>21</sup> dramatically changes the results for the distorted geometries as in all cases we go to more negative values, although the results for hydrides are closer to the exact ones. For the C<sub>2</sub> molecule, it goes below the exact value by 1.7 and 2.7 mhartree depending on the scheme. The results obtained with the XCC-based formulas tend to overshoot for the BH and C<sub>2</sub> systems. In these cases they are similar to the  $T(\Lambda)$  approach but the surprising exception is H<sub>2</sub>O at  $2R_e$  for which the XCC-based values stay above the exact answer by more than one mhartree.

If we judge by the mean absolute error rather than stability, the most satisfactory data seem to come out from the XCC approaches: 0.291 and 0.335 mhartree for the mean absolute error compared to 0.372 and 0.476 mhartree for that of the  $T(\Lambda)$  scheme. However, this conclusion could be mis-

leading since the behavior of the method, when evaluating on an average basis, is to some extent obscured by the extreme cases. Here such an example is provided by the C<sub>2</sub> molecule: Taking average errors for all but the C<sub>2</sub> system would work in favor of the  $T(\Lambda)$  approach. Obviously, we do need to consider other properties, other molecules, and larger basis sets to adequately assess performance.

In Table IV we compare the results obtained with the current methods to those generated with the noniterative methods correct through fourth and fifth order and with those obtained with standard CC approaches correct through the fourth, fifth and sixth order (i.e., CCSDT, CCSDTQ-1 and CCSDTQ, respectively). We observe that going from the noniterative method correct through fourth order to those correct through fifth and sixth, we reduce the average error from 0.887 to 0.827 and 0.372 mhartree in case of the  $\Lambda$ -based approaches, or from 1.387 through 0.694 to 0.291 mhartree for the XCC-based methods. The gain in the accu-

TABLE IV. The correlation energies relative to the FCI<sup>a</sup> values for the standard CC methods and the CCSD based non-iterative approaches correct through fourth, fifth and sixth order.

		CC4SD[T]		CC5SD[TQ]		CC6SD[TQ]		CC4	CC5	CC6
		$\Lambda$	T	$\Lambda$	T	$T(\Lambda)$	T	SDT	SDTQ-1	SDTQ
BH(DZP)	$R_e$	0.482	0.387	0.168	0.046	0.016	0.010	0.068	0.040	0.001
	$1.5R_e$	0.580	0.387	0.195	0.047	-0.031	-0.002	0.026	0.042	0.000
	$2.0 R_e$	0.629	-0.425	0.010	-0.588	-0.590	-0.385	-0.091	0.066	0.001
HF(DZP)	$R_e$	0.140	0.098	0.186	0.330	-0.034	-0.033	0.266	0.061	0.018
	$1.5 R_e$	0.404	0.148	0.407	0.564	-0.087	-0.087	0.646	0.110	0.041
	$2.0 R_e$	0.255	-1.913	0.652	-0.184	-0.133	-0.089	1.125	0.351	0.062
H <sub>2</sub> ODZP)	$R_e$	0.633	0.561	0.200	0.189	0.038	0.030	0.531	0.047	0.023
	$1.5R_e$	1.998	1.379	0.676	0.128	0.518	0.194	1.784	-0.027	0.139
	$2.0 R_e$	-1.504	-6.711	-0.405	-1.989	-0.625	1.571	-2.472	-1.581	-0.015
N <sub>2</sub> (pVDZ)	$R_e$	1.569	1.050	1.233	0.956	0.294	0.252	1.626	0.262	0.192
C <sub>2</sub> (pVDZ+)	$R_e$	1.563	-2.202	4.968	2.620	-1.727	-0.546	2.273	1.008	0.622
m. abs. err.		0.887	1.387	0.827	0.694	0.372	0.291	0.992	0.327	0.101
max. deviat.		1.998	6.711	4.968	2.620	1.727	1.571	2.472	1.581	0.622

<sup>a</sup>See footnote to Table III.

racy of the analogous series of the standard CC iterative approaches is larger—the respective values are 0.992, 0.327, and 0.101 mhartree. Comparing the noniterative approaches with their iterative counterparts, we find that the  $\Lambda$ -based CC4SD[T] is reasonably close to the CCSDT results: the analogous approach correct through fifth order (CC5SD[TQ]) gives better results than CCSDT except for the notorious  $C_2$  case. Here it is significantly worse being off by nearly 5 mhartree compared to 2.3 mhartree for CCSDT.

The current sixth-order results should be compared with the CCSDTQ-1 and CCSDTQ methods: in fact we see that the average error of the present method is comparable to that of the CCSDTQ-1 one. Comparing each of the molecules, however, we see that there are substantial differences between the two approaches, in particular for the hydrides at distorted geometries and for  $C_2$ .

Because of the poor convergence of perturbation theory, there is little reason to pursue non-iterative corrections to CCSD or CCSDT beyond sixth order. Furthermore, sixth order is a natural stopping point since, unlike odd orders, even orders offer comparatively stable approximations. The dramatic improvement of MBPT(6) over MBPT(5) is well known.<sup>11</sup> However, there are quite significant improvements in sixth-order corrected CCSD compared to fourth order approximations like CCSD(T) or the fifth-order counterparts. There is good reason to have such corrections available. The fact that we solve the CC equations at the SD level makes the iterative part of the method very fast. The noniterative contributions are obviously slower, but since they are computed only once it does not unduly affect the efficiency of the method. In addition, all the connected quadruple contributions are computed with lower  $n$ -dependence than the analogous terms within the iterative CC scheme. The bivariational-based methods that would actually employ  $\Lambda$ , as opposed to the  $T(\Lambda)$  ones where  $\Lambda$  is replaced by  $T^\dagger$ , are slightly more expensive than the  $T$ -based methods as both  $\Lambda_1$ ,  $\Lambda_2$  and  $T_1$ , and  $T_2$  are required, but they seem to offer desirable stability (see Table II) in fourth and fifth order showing some potential improvement compared to the ubiquitous CCSD(T) method.<sup>18</sup> To test the performance of the several methods more thoroughly, one needs to go to larger basis sets and a wider variety of properties to compare the computed quantities to experiment.

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