

# Noniterative energy corrections through fifth-order to the coupled cluster singles and doubles method

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Perturbation corrections through fifth order in the many-body perturbation theory energy with respect to a coupled cluster singles and doubles reference have been derived and analyzed. The formulas employ the  $T_1$  and  $T_2$  amplitudes obtained as a solution of the coupled cluster singles and doubles equations. Four different energy functionals have been considered as a starting point in the derivation: the regular coupled cluster energy expression, the coupled cluster functional incorporating  $\Lambda$  amplitudes, the one constructed via an expectation value coupled cluster method, and that obtained on the basis of the extended coupled cluster method. The proposed corrections have been applied to several small molecules to test their performance compared to full configuration interaction. The fourth-order  $\Lambda$ -based formulas improve upon CCSD(T), (coupled cluster singles and doubles with noniterative triples), while the best fifth-order formulas reduce the fourth-order error by about two-thirds. We also introduce a factorized evaluation of connected  $T_4$  in fifth order, which reduces its calculation from an  $n^9$  algorithm to  $n^7$ . This permits  $T_4$  to be included at approximately the same cost as CCSD(T). © 1998 American Institute of Physics. [S0021-9606(98)00311-0]

## I. INTRODUCTION

The coupled cluster<sup>1</sup> singles and doubles method (CCSD)<sup>2-5</sup> is now one of the most routinely used computational schemes for electron correlation. Its high cost-effectiveness and use of molecular symmetry<sup>6</sup> permit its application to quite sizeable chemical systems like porphyrin.<sup>7</sup> On the other hand, the inclusion into the coupled cluster (CC) theory of higher excitation connected clusters like  $T_3$ <sup>8-11</sup> and  $T_4$ ,<sup>12,13</sup> which are required to provide highly accurate values for the correlation energy, are often computationally prohibitive. The alternative to the CC approach—if we insist on considering only size-extensive theories—would be many-body perturbation theory (MBPT),<sup>14-16</sup> now implemented through fifth<sup>17</sup> and sixth order,<sup>18</sup> which allows for the inclusion of higher excitations in a less costly (i.e., noniterative) manner. However, the deficiencies of perturbation approaches are well known, and, in particular, they fail when the reference function becomes quasidegenerate. In such cases an infinite summation technique is absolutely essential.

A compromise between accuracy and effectiveness is potentially offered by hybrid methods that combine iterative techniques for lower-rank clusters with an inclusion of the higher ones in a noniterative manner. The first such approach introduced a noniterative inclusion of the triple excitation clusters on top of the CCSD scheme, generating the T(CCSD) method,<sup>19</sup> which is correct through the fourth-order energy and second-order wave function for Hartree–Fock references. The latter method has been modified to include, also, the fifth-order singles–triples contribution

(fourth-order in the non-Hartree–Fock case) giving the ubiquitous CCSD(T) approach.<sup>20-22</sup> Once it was found that the fifth-order  $T_4$  quadruples were factorizable and could be computed with a low (i.e., an  $n^6-n^7$ ) procedure,<sup>17,18</sup> an efficient inclusion of the fifth-order connected quadruples became possible. This has been done in a noniterative manner on top of the CCSDT method in Ref. 12 and for the CCSD solution.<sup>22</sup> These provided a method correct through fifth order in which the rate-determining step is the fifth-order connected triple–triple contribution, an  $n^8$  computational procedure. The noniterative contributions correct through sixth order with respect to the CCSDT wave function have also been reported<sup>23</sup> and the rate-determining step there is the construction of the  $T_4$  operator, which is an  $n^9$  procedure. More recently, such noniterative CC approximations have been further considered for fourth-order triples,<sup>24,25</sup> the open-shell singlet case,<sup>26</sup> spin-adapted open-shell approaches<sup>27</sup> and for excited states.<sup>28,29</sup>

From the operational point of view, noniterative approaches exploit just the MBPT expression for the contribution of a given (say, fourth, fifth, or sixth) order replacing the lowest order in  $T_1$  and  $T_2$  amplitudes with the converged ones. In some cases there remains some freedom in the choice of  $T_1$  and  $T_2$  amplitudes to be replaced and also in the type of the equation used to obtain converged values.

The aim of the present paper is to systematically construct and test several noniterative approaches correct through fourth and fifth order. Each of them is based upon the solution of the CCSD equations, and some also employ the solution of the so-called  $\Lambda$  equations introduced in the theory of density matrices and analytical derivatives of the

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CC wave function.<sup>30,31</sup> The following paper deals with non-iterative methods correct through sixth order.

## II. CC FUNCTIONALS AND EQUATIONS

There are several energy expressions in which the wave function defined by an exponential Ansatz,

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

can be employed. The T operator is a cluster operator defined as  $T = T_1 + T_2 + T_3 + \dots + T_n$ , with the usual definition of the  $T_n$  cluster:  $T_n = (n!)^{-2} \sum_{ijk\dots} t_{ijk\dots}^{abc\dots} \{a^\dagger b^\dagger \dots ji\}$ , where the normal ordering is assumed. Here we limit ourselves to  $n=4$ , that is, up to connected quadruple excitation cluster operators. We may begin with the CC type energy expression to which only  $T_1$  and  $T_2$  clusters contribute

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

The normal ordered Hamiltonian  $H_N$  is defined as

$$\begin{aligned} H_N &= H - \langle 0 | H | 0 \rangle \\ &= \sum_r \varepsilon_r \{r^\dagger r\} + \sum_{rs} f_{rs} \{r^\dagger s\} \\ &\quad + \frac{1}{4} \sum_{rstu} \langle rs || tu \rangle \{r^\dagger s^\dagger ut\} \\ &= H_N^0 + F_N + W_N, \end{aligned} \quad (3)$$

where  $\varepsilon_r$  are one-particle eigenenergies and  $F_N$  and  $W_N$  are one- and two-body operators with  $F_N$  disappearing for the canonical Hartree–Fock reference state. The  $T_1$  and  $T_2$  amplitudes are obtained by solving the CC equations for a given model and subsequently substituted into Eq. (2) to give the CC energy.

The other possibility would be to start with the CC functional based upon the  $\Lambda$  introduced in Refs. 30 and 31 in connection with the evaluation of the analytical derivatives of the coupled cluster wave function,

$$\begin{aligned} E &= \langle 0 | (1 + \Lambda) e^{-T} H_N e^T | 0 \rangle \\ &= \langle 0 | (1 + \Lambda) \bar{H} | 0 \rangle \\ &= \langle 0 | (1 + \Lambda) (H_N e^T)_c | 0 \rangle, \end{aligned} \quad (4)$$

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>31</sup>  $Q\bar{H}P = 0$ , where  $P = |0\rangle\langle 0|$  and  $Q = 1 - P = Q_1 + Q_2 + Q_3 + \dots$ , with  $Q_n = |\mathbf{h}_n\rangle\langle \mathbf{h}_n|$ , where  $\mathbf{h}_n$  are  $n$ -fold excited determinants. The stationarity condition of Eq. (4) 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  $\Lambda_n$  is defined in a similar manner to the respective  $T_n$  operator, though not entirely connected

$$\Lambda_n = (n!)^{-2} \sum \lambda_{ijk\dots}^{abc\dots} \{i^\dagger j^\dagger \dots ba\}. \quad (5)$$

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>32–34</sup>

$$E_{\text{XCC}} = \langle 0 | e^{T'} H_N e^T | 0 \rangle_L. \quad (6)$$

The index L ensures that only linked diagrams are to be considered. For closed diagrams linked and connected are synonymous.

At the fourth-order level, we have studied one more energy functional—namely, that based on the extended coupled cluster (ECC) approach of Arponen.<sup>35,36</sup> Within this formalism the energy is expressed as

$$E_{\text{ECC}} = \langle 0 | e^{T'} (H_N e^T)_c | 0 \rangle_{DL}, \quad (7)$$

where

- (1) DL (doubly linked) indicates that the  $T'$  operator is connected with H or with at least two T operators and
- (2) T and  $T'$  operators are defined in the same way as T and  $\Lambda$  in Eqs. (1) and (4,5), respectively.

The philosophy of our approach relies on the iterative solution of the relatively simple CCSD equations, followed by the noniterative inclusion of more sophisticated terms. The CC equations can be obtained by taking variations with respect to  $\Lambda$  in the functional (4). To this end we may rewrite Eq. (4) in the more expanded form

$$\begin{aligned} E &= \langle 0 | (1 + \Lambda_1 + \Lambda_2) (H_N e^{T_1 + T_2})_c | 0 \rangle + \langle 0 | (\Lambda_1 + \Lambda_2) \\ &\quad \times (H_N e^{T_3 + T_4})_c | 0 \rangle + \langle 0 | (\Lambda_3 + \Lambda_4) (H_N e^T)_c | 0 \rangle \\ &\quad + \langle 0 | \Lambda_2 (W_N T_1 T_3)_c | 0 \rangle. \end{aligned} \quad (8)$$

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.

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

$$T_1 = R_1 [W_N e^{(T_1 + T_2)}]_c \stackrel{\text{def}}{=} T_1(\text{CCSD}), \quad (9)$$

$$T_2 = R_2 [W_N e^{(T_1 + T_2)}]_c \stackrel{\text{def}}{=} T_2(\text{CCSD}), \quad (10)$$

where the subscript c indicates that only connected terms are considered.

We introduce here the resolvent operator  $R_n$  (Ref. 37) ensuring the appropriate excitation subspace and the required denominator, which in general can be defined as

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

By solving the CCSD equations, the first term in Eq. (8) 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. (9 and 10), solved.

The second term in Eq. (8) gives the contribution to the energy coming from  $T_3$  and  $T_4$  clusters via  $\Lambda_1$ , Eq. (12), or  $\Lambda_2$ , amplitudes, Eq. (13),

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

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

The third term in Eq. (8) determines the equations for the  $T_3$  and  $T_4$  amplitudes in general, or for any desired order of perturbation theory. Insertion of the associated amplitudes back into this term would cause the contribution to the energy to vanish through the desired order, which means that in the generation of the energy contributions we may disregard this term.

By varying the functional in Eq. (8) with respect to  $\Lambda_3$  and  $\Lambda_4$  amplitudes, we 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 fifth order in the MBPT energy based upon both a Hartree–Fock and non-Hartree–Fock reference. Bearing this in mind, we obtain the following equations:

$$T_3 = R_3 [W_N (T_2 + T_3 + \frac{1}{2} T_2^2 + T_1 T_2)]_c, \quad (14)$$

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

### III. ORDERS OF PERTURBATION THEORY WITH RESPECT TO THE CCSD REFERENCE

In order to simplify our discussion, we will generalize the concept of perturbation order. Here we are assuming the CCSD function to act as the reference, and with respect to that we define the perturbation corrections. Hence we assume that the  $T_2$  amplitude—as obtained from the CCSD equation—is always of first order and the inclusion into it of any of the terms present in the CCSD equations does not increase its order. That is,

$$T_2^{[1]} = T_2(\text{CCSD}) = T_2, \quad (16)$$

$$T_2^{[2]} = 0, \quad (17)$$

$$T_2^{[3]} = R_2 (W_N T_3^{[2]}), \quad (18)$$

and so forth. Note that we use the square brackets instead of parentheses to make a distinction to our generalized orders from the usual orders of perturbation theory subject to the Moeller–Plesset splitting.

Similarly, we have the following expression for the  $T_1$  corrections:

$$T_1^{[1]} = 0, \quad (19)$$

$$T_1^{[2]} = T_1(\text{CCSD}) = T_1, \quad (20)$$

$$T_1^{[3]} = R_1 (W_N T_3^{[2]}). \quad (21)$$

For the non-Hartree–Fock reference, the  $T_1$  corrections have a similar structure to those for the  $T_2$  amplitudes

$$T_1^{[1]} = T_1(\text{CCSD}) = T_1, \quad (22)$$

$$T_1^{[2]} = 0. \quad (23)$$

The expression for the perturbation corrections for  $T_3$  and  $T_4$  amplitudes is obtained on the basis of Eqs. (14) and (15), with the usual assumption that  $T_3^{[1]} = T_4^{[1]} = T_4^{[2]} = 0$ . Considering only the first term in Eq. (14), we have

$$T_3^{[2]} = R_3 (W_N T_2). \quad (24)$$

By including the additional two terms, we generate the third-order contribution to  $T_3$

$$T_3^{[3]} = R_3 [W_N T_3^{[2]} + \frac{1}{2} (W_N T_2^2)_c]. \quad (25)$$

We observe that the other contribution to  $T_3^{[3]}$  coming from the second-order  $T_2$  amplitude disappears due to Eq. (17). In the same way, we obtain the expression for the third-order  $T_4$  amplitude

$$T_4^{[3]} = R_4 [W_N T_3^{[2]} + \frac{1}{2} (W_N T_2^2)_c]. \quad (26)$$

A construction of the higher-order terms follows in the same manner, but we have to bear in mind that beginning with the third order, the  $T_2$  amplitude should also be taken into account since  $T_2^{[3]}$  is nonzero.

In an analogous manner, we define orders in the  $\Lambda$  quantity. Similarly as in the  $T_2$  case,  $\Lambda_2$ , as obtained from the  $\Lambda$  equation solved within the CCSD framework, is a first-order quantity

$$\Lambda_2^{[1]} = \Lambda_2(\text{CCSD}) = \Lambda_2, \quad (27)$$

$$\Lambda_2^{[2]} = 0. \quad (28)$$

Similarly,

$$\Lambda_1^{[1]} = 0, \quad (29)$$

$$\Lambda_1^{[2]} = \Lambda_1(\text{CCSD}) = \Lambda_1. \quad (30)$$

Analogously as in the case of Eqs. (22 and 23) for the non-Hartree–Fock reference we have

$$\Lambda_1^{[1]} = \Lambda_1(\text{CCSD}) = \Lambda_1, \quad (31)$$

$$\Lambda_1^{[2]} = 0. \quad (32)$$

The above definitions are sufficient through the fifth-order contributions.

### IV. FOURTH-ORDER CORRECTIONS

The classification of the various approaches we consider may be visualized in Fig. 1, where we have presented in fourth-order diagrams all six approaches considered: three for the Hartree–Fock case and three for the non-Hartree–Fock situation. We observe that they differ only in the form of the top interaction in each diagram. Below we give algebraic expressions for each of the functionals.

#### A. Standard CC energy expression

##### 1. Hartree–Fock reference

By introducing the third-order  $T_2$  amplitude, Eq. (18), into the CC energy expression, Eq. (2), we obtain the fourth-order correction on top of the CCSD energy

$$E_T^{[4]}(\text{CC}) = \langle 0 | W_N T_2^{[3]} | 0 \rangle, \quad (33)$$

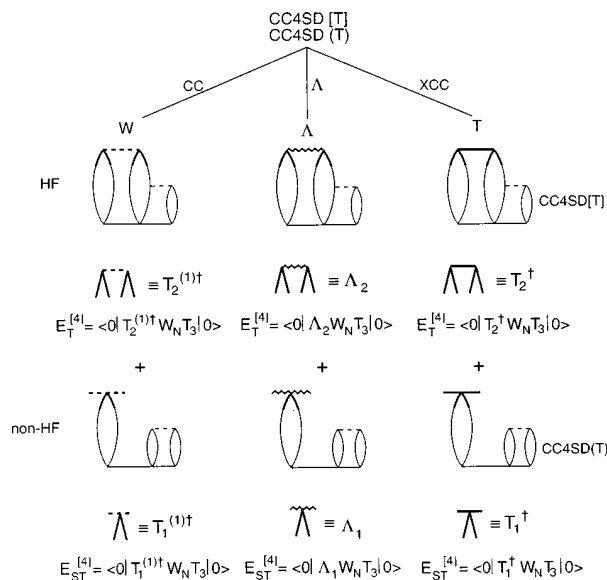


FIG. 1. Diagrammatic summary of alternative expressions for noniterative fourth-order corrections to CCSD. CCSD(T)=CC4SD(T) corresponds to the XCC route.

which combined with the CCSD energy creates a method correct through fourth order in the energy and second order in the wave function.

## 2. Non-Hartree–Fock reference

Here we have additional fourth-order noniterative contributions obtained by substitution of the third order  $T_1$  amplitude given by Eq. (21) into the CC energy expression, Eq. (2)

$$E_{ST}^{[4]}(\text{CC}) = \langle 0 | F_N T_1^{[3]} | 0 \rangle. \quad (34)$$

Thus the noniterative contribution for the non-Hartree–Fock reference is composed of two terms given by Eqs. (33) and (34).

## B. $\Lambda$ functional

### 1. Hartree–Fock reference

By using Eq. (24) in Eq. (13) and assuming  $T_4^{[2]}=0$ , we obtain the fourth-order triple excitation contribution to the energy,  $E_T^{[4]}(\Lambda)$ ,

$$E_T^{[4]}(\Lambda) = \langle 0 | \Lambda_2 W_N T_3^{[2]} | 0 \rangle. \quad (35)$$

Obviously,  $\Lambda_2^{(1)} = T_2^{(1)}$ , hence the latter equation gives the correct fourth-order corrections, with different higher-order terms.

### 2. Non-Hartree–Fock reference

The corrections for the non-Hartree–Fock reference arise in a similar manner as those for the standard CC energy expression (see Sec. IV A); that is, one additional term appears corresponding to that in Eq. (34). We employ now Eq. (12) since  $\Lambda_1$  is a first order quantity, see Eq. (31), which gives

$$E_{ST}^{[4]}(\Lambda) = \langle 0 | \Lambda_1 W_N T_3^{[2]} | 0 \rangle. \quad (36)$$

The total fourth-order correction is obtained by combining the contribution given in the last equation with that of Eq. (35). This is exactly CCSD(T) through fourth order (in the non-HF case),<sup>21</sup> since  $\Lambda_{1,2}^{(1)} = T_{1,2}^{(1)}$ . The current approximations differ by the higher-order contributions that distinguish  $\Lambda$  from  $T^\dagger$ . Note, that even in the HF case, this term is nonvanishing. It simply changes the meaning of the order series for HF, as  $T_1$  is usually considered to be second order, then.

## C. XCC functional

### 1. Hartree–Fock reference

The third type of energy expression is based on the XCC approach, Eq. (6). In Refs. 32 and 33 the respective fourth-order functional was derived that we will express as

$$E_{\text{XCC}}^{[4]} = E_{\text{XCC}}^{[4]}(\text{CCSD}) + \Delta E_T^{[4]}(\text{XCC}), \quad (37)$$

where  $E_{\text{XCC}}^{[4]}(\text{CCSD})$  represents all terms in  $E_{\text{XCC}}^{[4]}$  which are already included within the CCSD framework and  $\Delta E_T^{[4]}(\text{XCC})$  is given by

$$\begin{aligned} \Delta E_T^{[4]}(\text{XCC}) = & \langle 0 | T_3^\dagger H_N^o T_3 | 0 \rangle + \langle 0 | T_3^\dagger W_N T_2 | 0 \rangle \\ & + \langle 0 | T_2^\dagger W_N T_3 | 0 \rangle. \end{aligned} \quad (38)$$

Taking variations with respect to  $T_3^\dagger$ , we obtain Eq. (24). Substituting back the  $T_3$  into the last equation, we obtain the contribution to the energy

$$E_T(\text{XCC}) = \langle 0 | T_2^\dagger W_N T_3 | 0 \rangle, \quad (39)$$

$$E_T^{[4]}(\text{XCC}) = \langle 0 | T_2^\dagger W_N T_3^{[2]} | 0 \rangle = \langle 0 | T_3^{[2]\dagger} (-H_N^o) T_3^{[2]} | 0 \rangle. \quad (40)$$

In the second equality we took advantage of Eq. (24). The above contribution, when added to the CCSD energy, creates another method correct through fourth order, denoted, according to our nomenclature, as CC4SD[T]<sup>22</sup> or CCSD + T(CCSD).<sup>19</sup> The SD means infinite order in singles ( $T_1$ ) and doubles ( $T_2$ ), while the 4 indicates fourth order in triples ( $T_3$ ) and also correctness through fourth order. When limited to a HF reference, we use a square bracket [T].

### 2. Non-Hartree–Fock reference

In the case of the non-Hartree–Fock reference, the fourth-order XCC functional has several additional terms. However, all of them except for one are included within the CCSD framework. We may write then

$$\begin{aligned} E_{\text{XCC}}^{[4]} = & E_{\text{XCC}}^{[4]}(\text{CCSD}) + \langle 0 | T_3^\dagger H_N^o T_3 | 0 \rangle + \langle 0 | T_3^\dagger W_N T_2 | 0 \rangle \\ & + \langle 0 | T_2^\dagger W_N T_3 | 0 \rangle + \langle 0 | T_1^\dagger W_N T_3 | 0 \rangle \\ = & \langle 0 | T_2^\dagger W_N T_3^{[2]} | 0 \rangle + \langle 0 | T_1^\dagger W_N T_3^{[2]} | 0 \rangle, \end{aligned} \quad (41)$$

and the last component represents a new term compared to the Hartree–Fock case. Employing the  $T_3^{[2]}$  given by Eq. (24), we obtain the new contribution equal to the latter component, that is,

$$E_{ST}^{[4]}(\text{XCC}) = \langle 0 | T_1^\dagger W_N T_3^{[2]} | 0 \rangle. \quad (42)$$

For Hartree–Fock cases, this corresponds to CCSD(T) or CC4SD(T), and counts  $T_1$  as first order making Eq. (42) fourth order. In true non-Hartree–Fock cases, where

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

		CC4SD[T]				CC4SD(T)				CC4	CC4	
		CCSD	CC	$\Lambda$	XCC <sup>b</sup>	CC	$\Lambda$	XCC <sup>c</sup>	ECC	ECC <sub>a</sub> <sup>d</sup>	SDT-1	SDT
BH(DZP) <sup>a</sup>	$R_e$	1.793	0.889	0.482	0.387	0.903	0.498	0.414	0.414	0.420	0.460	0.068
	$1.5R_e$	2.644	1.197	0.580	0.387	1.271	0.673	0.552	0.593	0.611	0.608	0.026
	$2.0R_e$	5.052	2.110	0.629	-0.425	2.455	0.956	0.409	0.455	0.256	0.740	-0.091
HF(DZP) <sup>a</sup>	$R_e$	3.006	0.061	0.140	0.098	0.360	0.251	0.397	0.566	0.556	0.169	0.266
	$1.5R_e$	5.099	0.425	0.404	0.148	1.069	0.728	0.887	1.236	1.166	0.489	0.646
	$2.0R_e$	10.181	1.044	0.255	-1.913	2.745	1.103	0.256	0.946	-0.328	0.221	1.125
H <sub>2</sub> O(DZP) <sup>a</sup>	$R_e$	4.122	0.631	0.633	0.562	0.766	0.722	0.717	0.822	0.819	0.596	0.531
	$1.5R_e$	10.158	2.401	1.998	1.379	2.861	2.497	1.998	2.504	2.514	1.991	1.784
	$2.0R_e$	21.404	1.420	-1.504	-6.711	2.905	0.138	-4.634	-2.355	-2.672	-2.646	-2.472
SiH <sub>2</sub> (DZP) <sup>a</sup>	$R_e$	2.843	1.201	0.724	0.604	1.234	0.768	0.668	0.431	0.413	0.688	0.100
	$1.5R_e$	6.685	2.935	1.546	0.898	3.175	1.757	1.422	0.628	0.562	1.468	0.058
	$2.0R_e$	14.869	3.676	0.257	-5.371	5.606	0.730	-1.884	-2.321	-2.580	-0.781	-3.689
mean abs. err.		7.321	1.499	0.763	1.574	2.112	0.902	1.186	1.106	1.075	0.905	0.905

<sup>a</sup>The basis sets, geometries and FCI values were taken from Refs. 23,42,43,44 for BH, HF, H<sub>2</sub>O and SiH<sub>2</sub> molecules, respectively.

<sup>b</sup>This is the CCSD+T(CCSD) method.

<sup>c</sup>This is the CCSD(T) method.

<sup>d</sup>ECC<sub>a</sub> results are obtained including  $\Delta E_a^{[4]}$ (ECC) contribution, see Eq. (47).

$V_N = F_{OV} + W_N$ , where  $F_{OV}$  indicates the occupied–virtual part of  $F_N$ , we also use (T). This recognizes that  $T_1$  contributes in first order since  $T_1^{(1)} = F_{OV}$ , and two other terms are necessary.<sup>21</sup> In the generalized case, CC4SD(T) = CCSD(T) is invariant with respect to occupied–occupied or virtual–virtual orbital transformations just like the standard CCSD method.<sup>21</sup>

## D. ECC functional

### 1. Hartree–Fock reference

The fourth-order ECC functional may be expressed in the same way as that defined for the XCC approach

$$E_{\text{ECC}}^{[4]} = E_{\text{ECC}}^{[4]}(\text{CCSD}) + \Delta E_T^{[4]}(\text{ECC}), \quad (43)$$

where  $E_{\text{ECC}}^{[4]}(\text{CCSD})$  represents all terms in  $E_{\text{ECC}}^{[4]}$  which are already included within the CCSD framework and  $\Delta E_T^{[4]}(\text{ECC})$  is given by

$$\begin{aligned} \Delta E_T^{[4]}(\text{ECC}) = & \langle 0 | T'_3 H_N^o T_3 | 0 \rangle + \langle 0 | T'_3 W_N T_2 | 0 \rangle \\ & + \langle 0 | T'_2 W_N T_3 | 0 \rangle. \end{aligned} \quad (44)$$

Since the current approach is based on the CCSD amplitudes, we have to approximate  $T'$  by  $T^\dagger$  and the fourth-order corrections for the Hartree–Fock reference are exactly the same as those obtained for the XCC formulation.

### 2. Non-Hartree–Fock reference

Contrary to the previous formulations, the fourth-order ECC functional has several additional terms

$$\begin{aligned} \Delta E_{n\text{HF}}^{[4]}(\text{ECC}) = & \frac{1}{2} \langle 0 | T_1'^2 W_N | 0 \rangle + \frac{1}{2} \langle 0 | T_1'^2 W_N T_1 | 0 \rangle \\ & + \frac{1}{2} \langle 0 | (T_1' T_2' W_N)_c T_2 | 0 \rangle \\ & + \langle 0 | (T_1' T_2' W_N)_c T_2 | 0 \rangle. \end{aligned} \quad (45)$$

Within the ECC scheme (after differentiating with respect to  $T_1'$  and  $T_2'$ ), we include their contribution into  $T_1$  and  $T_2$  amplitudes to generate, in the next step, contributions to the

energy.<sup>38</sup> We separate them into two parts:  $E_a^{[4]}(\text{ECC})$ , which includes the fifth-order terms counted with respect to the Hartree–Fock reference, and  $E_b^{[4]}(\text{ECC})$  involving higher order terms. Thus we have

$$\Delta E_{n\text{HF}}^{[4]}(\text{ECC}) = E_a^{[4]}(\text{ECC}) + E_b^{[4]}(\text{ECC}), \quad (46)$$

$$\begin{aligned} E_a^{[4]}(\text{ECC}) = & \frac{1}{2} \langle 0 | T_1' T_1'^{(1)} W_N | 0 \rangle \\ & + \langle 0 | (T_1' T_2'^{(1)} W_N)_c T_2 | 0 \rangle \end{aligned} \quad (47)$$

$$\begin{aligned} E_b^{[4]}(\text{ECC}) = & \frac{1}{2} \langle 0 | T_1' T_1'^{(1)} W_N T_1 | 0 \rangle \\ & + \frac{1}{2} \langle 0 | (T_1' T_1'^{(1)} W_N)_c T_2 | 0 \rangle. \end{aligned} \quad (48)$$

In actual calculations carried out in the present work, we use the Hartree–Fock reference and replace  $T_1'^{(1)}$  with  $T_1^{\dagger(2)}$  and  $T_1'$  with  $T_1^\dagger$ . In Table I we present results referring to the inclusion of the term a, see Eq. (47) or both a and b terms, Eq. (46).

## V. FIFTH-ORDER CORRECTIONS

### A. Standard CC energy expression

#### 1. Hartree–Fock reference

In order to generate the fifth-order energy corrections from Eq. (2), we have to construct the fourth-order  $T_2$  amplitude according to the formula

$$T_2^{[4]} = R_2(W_N T_1^{[3]} + W_N T_2^{[3]} + W_N T_3^{[3]} + W_N T_4^{[3]}). \quad (49)$$

The third-order cluster operators appearing on the right-hand side of the last equation are defined in Eqs. (21), (18), (25), and (26). In this manner we obtain the four contributions to the energy

$$E_{ST}^{[5]}(\text{CC}) = \langle 0 | W_N R_2(W_N T_1^{[3]}) | 0 \rangle, \quad (50)$$

$$E_{DT}^{[5]}(\text{CC}) = \langle 0 | W_N R_2(W_N T_2^{[3]}) | 0 \rangle, \quad (51)$$

$$E_T^{[5]}(\text{CC}) = \langle 0 | W_N R_2(W_N T_3^{[3]}) | 0 \rangle, \quad (52)$$

$$E_Q^{[5]}(\text{CC}) = \langle 0 | W_N R_2 (W_N T_4^{[3]}) | 0 \rangle, \quad (53)$$

$$= \frac{1}{2} \langle 0 | T_2^{\dagger(1)2} (D_4 T_4^{[3]}) | 0 \rangle, \quad (54)$$

$$= \frac{1}{2} (\langle 0 | T_2^{\dagger(1)2} (W_N T_3^{[2]}) | 0 \rangle + \frac{1}{4} \langle 0 | T_2^{\dagger(1)2} (W_N T_2^2)_c | 0 \rangle). \quad (55)$$

The quantity  $D_n T_n$  refers to the  $T_n$  operator with the appropriate denominator removed, i.e.,

$$D_n T_n = (n!)^{-2} \sum (e_i + e_j + \dots - e_b - e_a) \times t_{ij}^{ab} \dots a^\dagger b^\dagger \dots j_i. \quad (56)$$

We observe that three of the above contributions correspond to the fifth-order corrections discussed in Ref. 22. Namely, the  $E_{ST}^{[5]}(\text{CC})$  is closely related to the  $\Delta E_{ST}^{[5]}$ , the  $E_T^{[5]}(\text{CC})$  corresponds to the sum of  $\Delta E_{TT}^{[5]} + \Delta E_{TD}^{[5]}$  and the quadruple contribution  $E_Q^{[5]}(\text{CC})$  may be related to the  $\Delta E_Q^{[5]}$  of Ref. 22. The contribution  $E_{DT}^{[5]}(\text{CC})$  is an additional term which arises due to the standard (as opposed to XCC<sup>22</sup>) formulation of the fifth-order correction to ensure the correctness of the energy through fifth order. We see also that the fifth-order quadruple correction, Eq. (53), in the present scheme is factorizable and can be computed with an  $n^6$  to  $n^7$  procedure. This is demonstrated in Eqs. (54 and 55), where, due to the factorization theorem,<sup>39</sup> the long  $D_4$  denominator can be eliminated. In the last equality, Eq. (55), we have taken advantage of the relation, Eq. (26), and we see that we can compute the energy contribution directly without generation of  $T_4$  amplitudes. This leaves the Eq. (52) which requires the evaluation of  $T_3$  into  $T_3$  via Eq. (25) as a rate determining step in the current approach.

## 2. Non-Hartree–Fock reference

The derivation of the fifth-order corrections to the CCSD energy for the non-Hartree–Fock reference is in all but one case identical to that of the sixth-order corrections for the HF reference.<sup>40</sup> The new contributions arise in two ways: either by the fourth-order  $T_1$  amplitude, which by substitution into Eq. (2) gives the fifth-order energy contribution, or by creating a new contribution to the fourth-order  $T_2$  amplitude in addition to those presented in Eq. (49). The first option gives

$$T_1^{[4]} = R_1(W_N T_3^{[3]}) + R_1(W_N R_3(W_N T_1 T_2)_c), \quad (57)$$

while the second possibility generates the following contributions to  $T_2^{[4]}$ :

$$T_2^{[4]} = T_2^{[4]}(\text{HF}) + R_2(W_N R_3(W_N T_1 T_2)_c) + R_2(W_N T_1 T_3^{[2]}), \quad (58)$$

where  $T_2^{[4]}(\text{HF})$  represents the contributions to  $T_2$  given by Eq. (49).

Thus we have altogether four new contributions for the non-Hartree–Fock case which could be generally expressed as

$$E_{ST(T+Q)}^{[5]}(\text{CC}) = \langle 0 | F_N R_1 (W_N T_3^{[3]}) | 0 \rangle \quad (59)$$

$$E_{ST_d}^{[5]}(\text{CC}) = \langle 0 | F_N R_1 (W_N R_3 (W_N T_1 T_2)_c) | 0 \rangle \quad (60)$$

$$E_{TT_d}^{[5]}(\text{CC}) = \langle 0 | W_N R_2 (W_N R_3 (W_N T_1 T_2)_c) | 0 \rangle \quad (61)$$

$$E_{T_1 T_3}^{[5]}(\text{CC}) = \langle 0 | W_N R_2 (W_N T_1 T_3^{[2]}) | 0 \rangle. \quad (62)$$

The  $T_d$  subscript refers to the disconnected triples, i.e.,  $T_1 T_2$  as opposed to  $T$ —referring to the  $T_3^{[2]}$  cluster. Thus  $E_{ST_d}^{[5]}(\text{CC})$  would represent the singles-disconnected triples contribution, and  $E_{TT_d}^{[5]}(\text{CC})$ —connected–disconnected triples–triples contribution. We see that the  $E_{ST_d}^{[5]}$  component, Eq. (60), for the Hartree–Fock reference either disappears or, when replacing  $F_N$  with  $T_1^{(2)}$ , represents a seventh-order contribution. The remaining terms are of sixth order. The total fifth-order contribution is obtained by adding quantities listed in Eqs. (59)–(62) to those given by Eqs. (50)–(53).

## B. A functional

### 1. Hartree–Fock reference

The fifth-order corrections in the present formulation are obtained on the basis of Eqs. (12) and (13) upon substitution of the respective amplitudes in their appropriate orders. Thus in Eq. (12), we need the lowest order  $\Lambda_1$  and  $T_3$  amplitudes, see Eqs. (30) and (24), respectively,

$$E_{ST}^{[5]}(\Lambda) = \langle 0 | \Lambda_1 W_N T_3^{[2]} | 0 \rangle. \quad (63)$$

Again  $\Lambda_1^{(2)} = T_1^{\dagger(2)}$ ; hence correctness through fifth order is ensured.

Similarly, by employing third-order  $T_3$  amplitudes, Eq. (25), in the Eq. (13) we obtain

$$E_T^{[5]}(\Lambda) = \langle 0 | \Lambda_2 W_N T_3^{[3]} | 0 \rangle \quad (64)$$

or, separating the  $E_T^{[5]}(\Lambda)$  into contributions coming from  $T_3^{[2]}$  and  $T_2^2/2$ , see Eq. (25),

$$E_T^{[5]}(\Lambda) = E_{TT}^{[5]}(\Lambda) + E_{TQ}^{[5]}(\Lambda), \quad (65)$$

$$E_{TT}^{[5]}(\Lambda) = \langle 0 | \Lambda_2 W_N R_3 (W_N T_3^{[2]}) | 0 \rangle, \quad (66)$$

$$E_{TQ}^{[5]}(\Lambda) = \frac{1}{2} \langle 0 | \Lambda_2 W_N R_3 (W_N T_2^2)_c | 0 \rangle. \quad (67)$$

Subsequently, by using third-order  $T_4$  amplitudes, Eq. (26) we obtain

$$E_Q^{[5]}(\Lambda) = \langle 0 | \Lambda_2 W_N T_4^{[3]} | 0 \rangle. \quad (68)$$

Note that  $E_{TT}^{[5]}(\Lambda)$  and  $E_{TQ}^{[5]}(\Lambda)$  are just  $\Delta E_{TT}^{[5]}$  and  $\Delta E_{TQ}^{[5]}$  in Ref. 22, respectively, with  $T_2^\dagger$  being replaced with  $\Lambda_2$ , whereas  $E_Q^{[5]}(\Lambda)$  is closely related to the  $\Delta E_Q^{[5]}$  of Ref. 22. The basic difference is that in the current formulation the fifth-order  $E_Q^{[5]}(\Lambda)$  contribution requires the determination of the  $T_4$  amplitudes, which means that an  $n^9$  computational procedure must be employed. In the pure fifth-order calculations, avoiding such a step is of crucial importance, hence the formula used in Ref. 17 provides a much more efficient computational scheme. In the sixth-order calculations, the knowledge of the  $T_4$  amplitude is required, so once they are computed it is straightforward to exploit them also in the fifth-order calculations.

There is, however, a very good approximation which circumvents this difficulty by replacing the *nonfactorizable*  $E_Q^{[5]}(\Lambda)$  component with the *factorizable one* giving an  $n^7$

procedure.<sup>41</sup> Lets denote it as  $E_{Q_f}^{[5]}(\Lambda)$ , according to the following relationship analogous to that exploited in Eqs. (54 and 55)

$$E_{Q_f}^{[5]}(\Lambda) \cong \frac{1}{2} \langle 0 | \Lambda_2 W_N T_4^{[3]} | 0 \rangle + \langle 0 | (D_2 \Lambda_2) T_2^{\dagger(1)} T_4^{[3]} | 0 \rangle \quad (69)$$

$$= \frac{1}{2} \langle 0 | \Lambda_2 T_2^{\dagger(1)} (D_4 T_4^{[3]}) | 0 \rangle \quad (70)$$

$$= \frac{1}{2} \langle 0 | \Lambda_2 T_2^{\dagger(1)} (W_N T_3^{[2]}) | 0 \rangle + \frac{1}{2} \langle 0 | \Lambda_2 T_2^{\dagger(1)} (W_N T_2^2)_c | 0 \rangle. \quad (71)$$

where  $D_2 \Lambda_2$  is defined analogously as  $D_4 T_4$ ; see Eq. (56). Similarly as in the previous section we can evaluate  $E_{Q_f}^{[5]}(\Lambda)$  without the  $T_4$  step. In this case, however, this is not rigorous, since  $E_{Q_f}^{[5]}(\Lambda)$  is only approximately equal to  $E_Q^{[5]}(\Lambda)$ , Eq. (68), and the performance of such an approximation is discussed in connection with Table VI. Note this approximation is size-extensive, as only linked diagrams are involved.

## 2. Non-Hartree–Fock reference

Since the basic equations for the contributions considered in this section are Eqs. (12 and 13), we look at the origin of the new fifth-order components slightly differently than in the previous section. Namely, we have one new contribution  $E_{ST(T+Q)}^{[5]}(\Lambda)$ , obtained by the introduction of the familiar  $T_3^{[3]}$  operator, Eq. (25), into the energy expression, Eq. (12):

$$E_{ST(T+Q)}^{[5]}(\Lambda) = \langle 0 | \Lambda_1 (W_N T_3^{[3]}) | 0 \rangle. \quad (72)$$

Next, we have an additional contribution to  $T_3^{[3]}$  obtained as

$$T_{3d}^{[3]} = R_3 (W_N T_1 T_2)_c \quad (73)$$

and by inserting the last quantity into Eqs. (12) and (13), we obtain two new terms:

$$E_{STT_d}^{[5]}(\Lambda) = \langle 0 | \Lambda_1 (W_N R_3 (W_N T_1 T_2)_c) | 0 \rangle, \quad (74)$$

$$E_{TT_d}^{[5]}(\Lambda) = \langle 0 | \Lambda_2 (W_N R_3 (W_N T_1 T_2)_c) | 0 \rangle. \quad (75)$$

Finally, the last component of the fifth-order non-Hartree–Fock correction comes from the last term of Eq. (8)

$$E_{T_1 T_3}^{[5]}(\Lambda) = \langle 0 | \Lambda_2 (W_N T_1 T_3^{[2]}) | 0 \rangle. \quad (76)$$

The *d* (disconnected) subscript in Eq. (73) indicates that the  $T_3$  operator is constructed from the disconnected  $T_1 T_2$  quantity. We need to stress here that all quantities of the type  $T_n^{[lm]}$  are—by definition—connected, since they are cluster operators. Hence, the indices like one in the Eq. (73), point to the internal structure of the cluster operator not to its overall connectedness which is always assumed. For example, the cluster operator  $T_{3d}^{[3]}(T) \equiv T_{3d}^{[3]}$ , Eq. (73), differs from the cluster operator  $T_3^{[3]}(T)$  defined as

$$T_3^{[3]}(T) = R_3 (W_N T_3^{[2]}) \quad (77)$$

since the former is based on the second-order (in the non-HF sense) disconnected triples, i.e.,  $T_1 T_2$ , while the latter—on the connected ones, i.e.,  $T_3^{[2]}$ .

## C. XCC functional

### 1. Hartree–Fock reference

The fifth-order correction derived from the XCC functional has been analyzed and computed in Ref. 22. The new terms with respect to those given in Eq. (38) are, after carrying out necessary cancellations,

$$\begin{aligned} \Delta E_{TQ}^{[5]}(\text{XCC}) &= \langle 0 | T_1^\dagger W_N T_3 | 0 \rangle + \langle 0 | T_3^\dagger W_N T_3 | 0 \rangle \\ &+ \frac{1}{2} \langle 0 | T_3^\dagger (W_N T_2^2)_c | 0 \rangle + \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_3 | 0 \rangle \\ &+ \frac{1}{4} \langle 0 | T_2^{\dagger 2} (W_N T_2^2)_c | 0 \rangle. \end{aligned} \quad (78)$$

Now taking variations with respect to  $T_3^\dagger$  both in  $\Delta E_T^{[4]}$ , Eq. (38) and in Eq. (78), we obtain expressions for the  $T_3$  amplitudes as given by Eq. (25). Introducing this back into Eq. (78) and disregarding higher order terms, we obtain the following contributions identical to those given in Ref. 22:

$$E_{ST}^{[5]}(\text{XCC}) = \langle 0 | T_1^\dagger W_N T_3^{[2]} | 0 \rangle, \quad (79)$$

$$E_{TT}^{[5]}(\text{XCC}) = \langle 0 | T_2^\dagger W_N R_3 (W_N T_3^{[2]}) | 0 \rangle, \quad (80)$$

$$E_{TQ}^{[5]}(\text{XCC}) = \frac{1}{2} \langle 0 | T_2^\dagger W_N R_3 (W_N T_2^2)_c | 0 \rangle, \quad (81)$$

$$\begin{aligned} E_Q^{[5]}(\text{XCC}) &= \frac{1}{2} \langle 0 | T_2^{\dagger 2} W_N T_3^{[2]} | 0 \rangle \\ &+ \frac{1}{4} \langle 0 | T_2^{\dagger 2} (W_N T_2^2)_c | 0 \rangle. \end{aligned} \quad (82)$$

As has been mentioned, they are very close to those obtained in previous subsections except for the quadruple component which is now of the form given by Eq. (82). In analogy to the expression (55), the latter contribution is fully factorizable and can be computed with a low-rank computational procedure [i.e.,  $n^7$ , see Eqs. (55) and (71)].

### 2. Non-Hartree–Fock reference

The first source of new terms in this case is that the fifth-order XCC functional now has certain additional terms

$$\begin{aligned} \Delta E_{TQ}^{[5]}(\text{XCC}_{n\text{HF}}) &= \langle 0 | T_1^\dagger W_N T_1 T_3 | 0 \rangle \\ &+ \langle 0 | T_3^\dagger (W_N T_1 T_2)_c | 0 \rangle. \end{aligned} \quad (83)$$

By taking variations with respect to  $T_3^\dagger$ , we obtain a new term contributing to  $T_3^{[3]}$  in addition to those given in Eq. (25)

$$T_{3d}^{[3]} = R_3 (W_N T_1 T_2)_c. \quad (84)$$

Now by inserting the  $T_3^{[3]}$  component as given by Eq. (25) and that given by the last equation into the first term of the r.h.s. of Eq. (78) we obtain

$$E_{ST(T+Q)}^{[5]}(\text{XCC}) = \langle 0 | T_1^\dagger W_N T_3^{[3]} | 0 \rangle, \quad (85)$$

$$E_{STT_d}^{[5]}(\text{XCC}) = \langle 0 | T_1^\dagger W_N R_3 (W_N T_1 T_2)_c | 0 \rangle. \quad (86)$$

Similarly, by inserting new  $T_3$  contribution, Eq. (84), into Eq. (39) we obtain

$$E_{TT_d}^{[5]}(\text{XCC}) = \langle 0 | T_2^\dagger W_N R_3 (W_N T_1 T_2)_c | 0 \rangle. \quad (87)$$

where the subscript *d* indicates internally disconnected structure of  $T_3^{[3]}$ , see the discussion following Eq. (76). And fi-

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

		CC5SD[TQ]			CC5SD(TQ)			CC5	CC6
		CC	$\Lambda$	XCC <sup>†</sup>	CC	$\Lambda$	XCC	SDTQ-1	SDTQ
BH(DZP) <sup>a</sup>	$R_e$	0.404	0.168	0.046	0.404	0.168	0.049	0.040	0.001
	1.5 $R_e$	0.488	0.196	0.047	0.486	0.190	0.057	0.042	0.000
	2.0 $R_e$	0.737	0.010	-0.588	0.818	0.112	-0.378	0.066	0.001
HF(DZP) <sup>a</sup>	$R_e$	0.421	0.186	0.330	0.329	0.125	0.242	0.061	0.018
	1.5 $R_e$	0.994	0.407	0.564	0.806	0.302	0.368	0.110	0.041
	2.0 $R_e$	2.252	0.652	-0.184	2.110	1.004	-0.319	0.351	0.062
H <sub>2</sub> O(DZP) <sup>2</sup>	$R_e$	0.260	0.200	0.189	0.238	0.186	0.166	0.047	0.023
	1.5 $R_e$	1.188	0.676	0.128	1.244	0.719	0.148	-0.027	0.139
	2.0 $R_e$	3.621	-0.405	-1.989	4.064	-0.093	-1.806	-1.581	-0.015
SiH <sub>2</sub> (DZP) <sup>a</sup>	$R_e$	0.505	0.301	0.163	0.495	0.289	0.153	0.081	0.002
	1.5 $R_e$	1.476	0.778	0.420	1.397	0.664	0.314	0.233	-0.015
	2.0 $R_e$	2.543	0.321	2.070	1.578	-0.560	-0.627	-0.289	-0.17 <sup>b</sup>
mean abs. error		1.241	0.358	0.560	1.164	0.368	0.386	0.244	0.040

<sup>a</sup>See footnote a to Table I.<sup>b</sup>Convergence to two decimal places was obtained.

nally, the last term is obtained by introducing the lowest order  $T_3$  into the first term of the functional (83)

$$E_{T_1 T_3}^{[5]}(XCC) = \langle 0 | T_2^\dagger W_N T_1 T_3^{[2]} | 0 \rangle. \quad (88)$$

As we see from the Eqs. (85)–(88), they have a structure identical to those obtained for the  $\Lambda$  functional, that is Eqs. (72)–(76), with the obvious modification that the  $\Lambda$  operator is replaced by  $T^\dagger$  and, of course,  $\Lambda$  and  $T^\dagger$  are equivalent through linear terms.<sup>31</sup>

## VI. TEST RESULTS

The main results of the calculations presented in this paper are collected in Tables I, II, and III. They show deviations from the exact results (i.e., those obtained with the FCI method) for all the molecules considered—BH, HF, H<sub>2</sub>O, and SiH<sub>2</sub>—at three different geometries: equilibrium  $R_e$ , 1.5  $R_e$  and  $2R_e$  as well as for N<sub>2</sub> and C<sub>2</sub> at their equilibrium geometries. The basis for all the hydrides is a standard DZP set; for the other two molecules, we use cc-pVDZ and an aug-cc-pVDZ basis for N and C atoms, respectively, the diffuse  $d$  function on the carbon atom being removed. All the details concerning the geometry and the basis sets can be found in the papers reporting the FCI results (see Refs. 42–45 for the above-listed molecules, respectively). Table

IV shows the net fourth- and fifth-order contributions while Table V shows the values of the individual components both at the fourth- and fifth-order level. Table VI demonstrates the validity of the approximations when replacing the quadruple contributions within the  $\Lambda$  formulation with the factorizable expression.

The noniterative methods specified in Table I are denoted with acronyms CC4SD[T] or CC4SD(T), which indicates the method correct through the fourth-order in energy, iterative inclusion of singles and doubles and noniterative incorporation of the fourth-order triples counted either with respect to the Hartree–Fock reference [T] or the non-HF one (T). The latter give different results even in the HF case, since the non-HF development forces the inclusion of the initial form derived from  $T_1$  even when it is technically second order. This, of course, is also the distinction between CCSD(T) and CCSD+T(CCSD). The column headers CC,  $\Lambda$ , XCC, ECC indicate the type of the functional employed to generate the required correction (see Secs. IV and V). In Table II we have analogous situations considering this time methods correct through fifth order and including in a non-iterative manner both fifth-order triples and fifth-order quadruples taken with respect to the HF reference—CC5SD[TQ]—or to the non-HF one—CC5SD(TQ).

The most natural way to include a  $T_3$  contribution in a

TABLE III. The correlation energies relative to the FCI<sup>a</sup> values for the CCSD based non-iterative methods correct through fourth and fifth orders [mhartree].

	CCSD	CC	$\Lambda$	XCC	CC	$\Lambda$	XCC	CC4SDT-1	CC4SDT
		CC4SD[T]			CC4SD(T)				
N <sub>2</sub> (pVDZ)	13.465	0.608	1.569	1.050	1.235	1.998	1.709	1.216	1.626
C <sub>2</sub> (pVDZ)	29.597	-0.766	1.563	-2.202	2.395	4.360	1.863	0.691	3.273
		CC5SD[TQ]			CC5SD(TQ)			CC5SDTQ-1	CC6SDTQ
N <sub>2</sub> (pVDZ)		1.365	1.233	0.956	1.244	1.174	0.870	0.262	0.192
C <sub>2</sub> (pVDZ)		10.178	4.968	2.620	9.849	5.014	2.540	1.008	0.622

<sup>a</sup>The basis sets, geometries and FCI values were taken from Ref. 45.

TABLE IV. Total fourth- and fifth-order non-iterative contributions to the correlation energy [mhartree].

		CCSD	Method	$\Delta E_{\text{HF}}^{[4]}$	$\Delta E_{n\text{HF}}^{[4]}$	$\Delta E_{\text{HF}}^{[5]}$	$\Delta E_{n\text{HF}}^{[5]}$	$\Delta E_{\text{HF}}^{[4+5]}$	$\Delta E_{n\text{HF}}^{[4+5]}$
BH	$R_e$		CC	-0.904	-0.891	-0.485	-0.499	-1.389	-1.390
		-100.574	$\Lambda$	-1.311	-1.296	-0.314	-0.329	-1.625	-1.625
			XCC	-1.406	-1.379	-0.342	-0.365	-1.748	-1.744
	$1.5 R_e$		CC	-1.447	-1.373	-0.709	-0.786	-2.156	-2.159
		-111.119	$\Lambda$	-2.064	-1.972	-0.385	-0.482	-2.449	-2.455
			XCC	-2.257	-2.092	-0.340	-0.496	-2.597	-2.588
	$2.0 R_e$		CC	-2.942	-2.597	-1.373	-1.637	-4.315	-4.234
		-134.097	$\Lambda$	-4.422	-4.096	-0.620	-0.845	-5.042	-4.941
			XCC	-5.477	-4.642	-0.163	-0.788	-5.640	-5.430
HF	$R_e$		CC	-2.945	-2.647	0.361	-0.030	-2.585	-2.677
		-200.876	$\Lambda$	-2.866	-2.755	0.046	-0.126	-2.820	-2.881
			XCC	-2.908	-2.610	0.231	-0.154	-2.677	-2.764
	$1.5 R_e$		CC	-4.674	-4.030	0.569	-0.263	-4.106	-4.293
		-222.066	$\Lambda$	-4.695	-4.371	0.003	-0.426	-4.692	-4.797
			XCC	-4.951	-4.213	0.417	-0.519	-4.534	-4.731
	$2.0 R_e$		CC	-9.136	-7.435	1.208	-0.636	-7.928	-8.071
		-253.356	$\Lambda$	-9.925	-9.077	0.396	-0.099	-9.529	-9.176
			XCC	-12.093	-9.924	1.728	-0.576	-10.365	-10.499
H <sub>2</sub> O	$R_e$		CC	-3.491	-3.355	-0.371	-0.528	-3.862	-3.884
		-211.960	$\Lambda$	-3.489	-3.399	-0.433	-0.536	-3.922	-3.935
			XCC	-3.560	-3.405	-0.373	-0.551	-3.933	-3.956
	$1.5 R_e$		CC	-7.758	-7.297	-1.213	-1.617	-8.971	-8.914
		-260.752	$\Lambda$	-8.160	-7.662	-1.322	-1.779	-9.482	-9.442
			XCC	-8.780	-8.160	-1.251	-1.851	-10.031	-10.011
	$2.0 R_e$		CC	-19.985	-18.500	2.201	1.160	-17.783	-17.340
		-348.579	$\Lambda$	-22.908	-21.266	1.099	-0.231	-21.809	-21.497
			XCC	-28.115	-26.038	4.722	2.828	-23.393	-23.210

noniterative manner would be to evaluate the  $T_3$  equation on top of the CCSD solution and then to compute the energy according to the standard CC expression. The results of this approach are listed in Table I in the CC column. Comparing these values and those obtained with the CCSD method (see previous column), one might say that the approach works quite well reducing the average error nearly five times. However, the error in the vicinity of the equilibrium stays around 1 mhartree. The XCC values (those obtained by closing the  $T_3$  amplitude with the  $T_2^\dagger$  operator) are of better quality for the equilibrium geometry; however, they fail for the distorted geometries. The errors introduced at the stretched bonds ( $2R_e$ ) (cf. -6.711 and -5.371 for H<sub>2</sub>O and SiH<sub>2</sub>, respectively) are large enough to make the average error go beyond that based on the standard CC expression.

A more correct behavior is provided by the new approach we introduce here based on the  $\Lambda$  functional (see Sec. IV B). In the vicinity of the equilibrium, it behaves like the XCC approach staying close to the exact values and also gives satisfactory results for distorted geometries. It overshoots only for the notorious H<sub>2</sub>O  $2R_e$  case, but being off by -1.504 mhartree is much better than the -6.711 value of the XCC-based approach. The average error is quite small (0.763 mhartree) and is about half of those for the other two models.

The results collected in the next five columns include in addition  $T_1$  contributions combined with the  $T_3$  one: For the first three columns this is simply the term  $E_{ST}^{[5]}$  (see Sec. IV). Because this term is always positive, in most cases the re-

sults will be moved farther from the exact values since the positive quantity is added to the values which are already too high compared to the exact result, however, a certain stability might be added. We observe that for the CC formulation, the average energy error is larger by nearly 50%. However, the only model which really benefits by inclusion of this term is the XCC one—the commonly used acronym is CCSD(T). We see that for the equilibrium and  $1.5 R_e$  values, CCSD(T) gives worse results than CC4SD[T]; however, for the distorted geometry, it gains ca. 2 mhartree for HF and H<sub>2</sub>O and almost 3.5 mhartree for SiH<sub>2</sub>, attesting to its greater stability. This is enough to reduce the average error from 1.574 to 1.186. The  $\Lambda$  formulation also benefits by inclusion of the  $E_{ST}^{[5]}$  component in reducing the error for the H<sub>2</sub>O molecule from -1.504 to +0.138 mhartree. Although the average error is slightly larger, the overall behavior of the CC4SD(T) method based on the  $\Lambda$  functional is more stable, staying in all cases above the exact value. The average error for the methods based on the  $\Lambda$  functional is comparable with that for the iterative CC methods correct through fourth order, that is for CCSDT-1 and CCSDT, shown in the last two columns of Table I: 0.763 and 0.902 for the CCSD[T] <sub>$\Lambda$</sub>  and CCSD(T) <sub>$\Lambda$</sub> , respectively, compared to the 0.905 mhartree for CCSDT-1 and CCSDT methods (they incidentally coincide). Overall, the CCSD(T) <sub>$\Lambda$</sub>  method would appear to be the best fourth-order approximation both in average error, in maximum error, and in its bounding properties.

The ECC results listed in the next two columns are very similar in behavior to the XCC values [the CCSD(T)

TABLE V. Individual contributions to the fourth- and fifth order non-iterative corrections [mhartree].

	Method	$E_T^{[4]}$	$E_{ST}^{[5]}$	$E_{dT}^{[5]}$	$E_{TQ}^{[5]}$	$E_{TT}^{[5]}$	$E_Q^{[5]}$	$E_{ST(T+Q)}^{[5]}$	$E_{STTd}^{[5]}$	$E_{TTd}^{[5]}$	$E_{T_1T_3}^{[5]}$		
BH	$R_e$	CC	-0.9040	0.0134	-0.2863	0.0287	-0.2227	-0.0182	0.0037	-0.0007	-0.0019	-0.0012	
		$\Lambda$	-1.3109	0.0151		0.0386	-0.3346	-0.0332	0.0041	-0.0012	-0.0013	-0.0014	
		XCC	-1.4057	0.0263		0.0411	-0.3588	-0.0503	0.0072	-0.0016	-0.0013	-0.0012	
	$1.5 R_e$	CC	-1.4468	0.0741	-0.4655	0.0299	-0.3523	0.0046	0.0210	-0.0030	-0.0137	-0.0070	
		$\Lambda$	-2.0637	0.0921		0.0363	-0.5186	0.0055	0.0264	-0.0046	-0.0197	-0.0075	
		XCC	-2.2573	0.1650		0.0378	-0.5655	0.0223	0.0464	-0.0066	-0.0212	-0.0093	
	$2.0 R_e$	CC	-2.9417	0.3450	-1.1120	0.0010	-0.6952	0.0877	0.0930	-0.0182	0.0277	-0.0214	
		$\Lambda$	-4.4224	0.3268		-0.0099	-1.0810	0.1444	0.0854	-0.0064	0.0455	-0.0224	
		XCC	-5.4773	0.8349		-0.0284	-1.3279	0.3585	0.2212	-0.0378	0.0682	-0.0415	
	HF	$R_e$	CC	-2.9454	0.2989	0.1013	0.2332	-0.1181	-0.1546	-0.0352	-0.0071	0.0213	-0.0711
			$\Lambda$	-2.8658	0.1106		0.2198	-0.1319	-0.1817	-0.0109	-0.0021	0.0203	-0.0680
			XCC	-2.9081	0.2986		0.2221	-0.1343	-0.1549	-0.0345	-0.0070	0.0204	-0.0661
$1.5 R_e$		CC	-4.6743	0.6440	0.1674	0.3334	-0.1562	-0.4199	-0.0880	-0.0530	0.1278	-0.1744	
		$\Lambda$	-4.6954	0.3243		0.3061	-0.2298	-0.3973	-0.0334	-0.0296	0.1271	-0.1695	
		XCC	-4.9508	0.7382		0.3157	-0.2439	-0.3927	-0.0973	-0.0663	0.1352	-0.1694	
$2.0 R_e$		CC	-9.1362	1.7013	-0.2439	0.6032	-0.3810	-0.4719	-0.2583	-0.6216	1.1937	-0.4559	
		$\Lambda$	-9.9248	0.8473		0.5596	-0.6797	-0.3311	-0.0935	-0.3419	1.2245	-0.4367	
		XCC	-12.0926	2.1688		0.6549	-0.8255	-0.2702	-0.3177	-0.8657	1.5474	-0.4988	
H <sub>2</sub> O		$R_e$	CC	-3.4909	0.1354	-0.0059	0.2603	-0.3151	-0.4457	-0.0093	-0.0043	0.0089	-0.0172
			$\Lambda$	-3.4887	0.0896		0.2498	-0.3371	-0.4354	-0.0030	-0.0026	0.0087	-0.0169
			XCC	-3.5601	0.1552		0.2539	-0.3443	-0.4376	-0.0097	-0.0050	0.0087	-0.0170
	$1.5 R_e$	CC	-7.7577	0.4602	0.0019	0.7311	-0.8289	-1.5775	-0.0218	-0.0491	0.1173	0.0097	
		$\Lambda$	-8.1602	0.4986		0.6978	-1.0452	-1.4734	-0.0210	-0.0624	0.1281	-0.0021	
		XCC	-8.7798	0.6195		0.7535	-1.1179	-1.5061	-0.0289	-0.0862	0.1377	-0.0030	
	$2.0 R_e$	CC	-19.9845	1.4850	-0.2301	3.7763	-2.2995	-0.5306	-0.3360	-0.5599	1.1398	0.1996	
		$\Lambda$	-22.9084	1.6423		3.2527	-4.0411	0.2455	-0.3503	-0.5042	1.2122	-0.0458	
		XCC	-28.1149	2.0769		4.3615	-4.4989	2.7821	-0.4704	-0.9230	1.5610	0.0153	

method], although they involve more  $T_1$  containing terms, see Eqs. (46)–(48). The basic difference lies in the fact that the error for the stretched geometry of H<sub>2</sub>O is reduced by half. It goes down from -4.634 for CCSD(T) to -2.355 mhartree for the ECC one. On the other hand, for the HF molecule, the ECC values are worse (too positive) by several tens of mhartree, which gives an overall average error comparable for both approaches. The ECC<sub>a</sub> results obtained by inclusion of two non-Hartree–Fock terms instead of four, see Eq. (47), are not much different, which means that the two terms are small. There is, however, a distinct tendency to go to more negative energies for stretched geometries for the ECC<sub>a</sub> variant. One should keep in mind that an additional aspect of the ECC approaches is that the non-Hartree–Fock terms are all factorizable—that is, they do not require the  $T_3$  denominator.

In Table III we report results of the calculations for the N<sub>2</sub> and C<sub>2</sub> molecules. At the fourth-order level we observe that the smallest deviations from the exact results occur for the approach based on the standard CC energy expression (see CC column), which stay below 1 mhartree. The  $\Lambda$  approach gives reasonable agreement with FCI and CCSD[T], is quite good for N<sub>2</sub>, but is worse for C<sub>2</sub>; in the latter case, it goes beyond FCI by ca. 2.2 mhartree. Adding the  $E_{ST}^{[5]}$  term moves all the results up, which for C<sub>2</sub> yields better agreement with FCI data reducing the error from -2.2 to ca. +1.9. We may note the fortuitously good result provided by the CCSDT-1 model compared to the full CCSDT method, in particular for the C<sub>2</sub> case. As has been observed before for

some situations,<sup>22</sup> fifth-order corrections are hardly improvements over fourth order for N<sub>2</sub>, and are worse for C<sub>2</sub>.

Judging by the average error at the fifth-order level (see Table II), we observe a significant improvement of the results for the  $\Lambda$  and XCC approaches. For these two methods the error is reduced from 0.763 to 0.358 and from 1.574 to 0.560 mhartree, respectively, while for the CC-type functional it decreases from 1.499 to 1.164 mhartree.

There are certain regular patterns in the behavior of the fifth-order corrections. For the majority of cases the fifth-order values are negative, see also Table IV, and reduce the positive errors introduced by the fourth-order methods. There are two exceptions from this general behavior. The first one is the HF molecule for which the fifth-order contribution is always positive. This implies that its inclusion will

TABLE VI. Comparison of the  $E_Q^{[5]}$  contribution for the  $\Lambda$  functional obtained by factorizable and non-factorizable formulation [mhartree].

		$E_{Q_f}^{[5]}$	$E_{Q_{nf}}^{[5]}$
BH	$R_e$	-0.030	-0.033
	$1.5 R_e$	0.008	0.005
	$2.0 R_e$	0.147	0.144
HF	$R_e$	-0.155	-0.182
	$1.5 R_e$	-0.398	-0.397
	$2.0 R_e$	-0.350	-0.331
H <sub>2</sub> O	$R_e$	-0.438	-0.435
	$1.5 R_e$	-1.451	-1.473
	$2.0 R_e$	0.290	0.245

move the results away from the FCI value. This really happens except for the XCC based approach for  $2R_e$  where the fourth-order error is negative and the fifth-order correction reduces the error from  $-1.913$  to  $-0.184$  mhartree. However, for the  $\Lambda$  based approach the fifth-order corrections for the HF molecule are rather small (0.046, 0.003 and 0.396) and their impact on the overall performance of the method is limited. The second exception are the positive fifth-order corrections for most cases of stretched geometries ( $2R_e$ ). Here their positive values are crucial in reducing large negative errors introduced at the fourth-order level. For example, the fifth-order corrections for the XCC based approach are 7.441 and 4.722 mhartree for  $\text{SiH}_2$  and  $\text{H}_2\text{O}$  at  $2R_e$ , respectively. They reduce the fourth-order errors from  $-5.371$  to 2.070 and  $-6.711$  to  $-1.989$  mhartree, respectively.

We may also conclude from Table II that the most stable approach is that based on the  $\Lambda$  functional. The maximum deviation is by far the smallest for all considered methods, 0.778 mhartree (for  $\text{SiH}_2$  at intermediate geometry), in addition it overshoots only in one case: the  $\text{H}_2\text{O}$  at  $2R_e$ . The XCC based approach gives smaller errors at the equilibrium and intermediate geometries, however, it is very sensitive with respect to the increasing multiconfigurational character of the reference function, introducing in such cases large negative errors.

For the non-Hartree-Fock based methods the average errors are similar as for the Hartree-Fock case: 1.164, 0.368, and 0.386 mhartree for CC,  $\Lambda$  and XCC formulations, respectively. The largest improvement occurs for the XCC due to the significant reduction of the error for the  $\text{SiH}_2$  molecule at stretched geometry: 2.070 to  $-0.627$  mhartree.

In Table V, we have listed the values of the individual components of the fifth-order corrections both for the Hartree-Fock and non-Hartree-Fock derived formulas. We may observe certain general rules as far as the sign and the magnitude of the given component are concerned. We have already mentioned that the  $E_{ST}^{[5]}$  contribution retains its positive value for all examples and methods with increasing magnitude for distorted geometries. The same pattern is observed also in the case of the  $E_{TQ}^{[5]}$  piece, although its magnitude is generally larger. The largest fifth-order contribution is due to the  $E_{TT}^{[5]}$  component, its value being always negative. Out of the non-Hartree-Fock fifth-order contributions, listed in the last four columns of Table V, the largest is  $E_{TT_d}^{[5]}$  which for stretched geometries exceeds one mhartree, and is positive in nearly all cases. The  $E_{STT_d}^{[5]}$  part, which for the Hartree-Fock reference is seventh order, also brings in non-negligible contributions and achieves a value of several tenths of a mhartree. This is the only piece that is consistently negative for all examples considered. The remaining two components  $E_{ST(T+Q)}^{[5]}$  and  $E_{T_1T_3}^{[5]}$  are in most cases negative with magnitudes rarely exceeding 0.1 mhartree.

The general pattern found in most of the examples studied is that the components calculated on the basis of the  $\Lambda$  functional assume intermediate values between those based on the XCC and CC formulations. The HF molecule is in several cases an exception to this. For example, for the components  $E_{ST}^{[5]}$ ,  $E_{TQ}^{[5]}$ , in the latter cases, the  $\Lambda$  value is the

smallest and this is important in reducing the total error of the method.

In connection with the noniterative corrections based on the  $\Lambda$  functional, there is one other point. In Sec. VB we pointed out that, in principle, this formulation requires a construction of the  $T_4$  operator, see Eq. (68). To avoid such a step, we can use an approximate expression given in Eq. (71). In Table VI, we collected the  $E_Q^{[5]}$  contributions obtained according to Eq. (71) [see the  $E_{Q_f}^{[5]}$  column and that for the rigorous formulation, Eq. (68), column  $E_{Q_{nf}}^{[5]}$ ]. For the BH molecule the error introduced is 3  $\mu$ hartree, for HF it goes up to 20  $\mu$ hartree, and, in the worst case, for  $\text{H}_2\text{O}$  at  $2R_e$  it reaches 45  $\mu$ hartree. As the introduced approximation works very well, we can practically use the factorizable expression for connected fifth-order quadruples for each of the discussed functionals with little loss in accuracy. This factorized approach is discussed in depth elsewhere.<sup>41</sup>

In conclusion we emphasize two aspects of the present work. First, we wanted to consider alternative origins for higher-order cluster contributions and to assess how the noniterative corrections to the CCSD energy work for the three different initial functionals. This, in our opinion, covers most of the prospects for the search for reliable and fast noniterative methods based upon CC/MBPT theory. We conclude that the best results should be expected by combining  $T$  and  $\Lambda$  amplitudes. This is recommended by the CC functional, and an analog for the excited states, EOM-CCSD( $\bar{T}$ ) has been considered.<sup>28</sup> However, the actual determination of the bivariational  $\Lambda$ , rather than simply using the  $T^\dagger$  operators that are already available as is done in the CCSD(T) and its XCC fifth-order analogues, does add some computational complexity.

The second aspect refers to the investigation of the possibility of adding some new terms to both fourth- and fifth-order corrections. These new terms (1) should be easy to code and (2) should retain the same rank of the computational procedure as the original method. The criterion we have chosen for the selection of such terms is the correctness of the energy through a given order based upon non-Hartree-Fock count of order. This results in the inclusion of one term at the fourth-order level,  $E_{ST}^{[5]}$ , giving CCSD(T).<sup>21</sup> In addition we have investigated two additional formulations. To obtain a method correct through fifth order in this case we need to add four additional terms. Although they are small in magnitude, their inclusion into the total correlation energy stabilizes the method and seems to be important, particularly for distorted geometries.

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<sup>1</sup>J. Čížek J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **14**, 15 (1969); J. Paldus J. Čížek, and I. Shavitt, Phys. Rev. A **5**, 50 (1974).

<sup>2</sup>G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

<sup>3</sup>R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989); in *Modern Theoretical*

- Chemistry*, Part 2, edited by D. Yarkony (World Scientific, Singapore, 1995), pp. 1047–1131.
- <sup>4</sup>G. E. Scuseria, A. C. Scheiner, T. J. Lee, J. E. Rice, and H. F. Schaefer, *J. Chem. Phys.* **86**, 288 (1987).
- <sup>5</sup>T. J. Lee and J. E. Rice, *Chem. Phys. Lett.* **150**, 406 (1988).
- <sup>6</sup>J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, *J. Chem. Phys.* **94**, 4334 (1991); J. Gauss, J. F. Stanton, and R. J. Bartlett, *J. Chem. Phys.* **95**, 2623 (1991).
- <sup>7</sup>M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **106**, 6449 (1997).
- <sup>8</sup>Y. S. Lee, S. A. Kucharski, and R. J. Bartlett, *J. Chem. Phys.* **81**, 5906 (1984).
- <sup>9</sup>J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987); *ibid.* **89**, 3401 (1988).
- <sup>10</sup>G. Scuseria and H. F. Schaefer, III, *Chem. Phys. Lett.* **152**, 382 (1988).
- <sup>11</sup>J. D. Watts and R. J. Bartlett, *J. Chem. Phys.* **93**, 6104 (1989).
- <sup>12</sup>S. A. Kucharski and R. J. Bartlett, *Chem. Phys. Lett.* **158**, 550 (1989); S. A. Kucharski and R. J. Bartlett, *Theor. Chim. Acta* **80**, 387 (1991).
- <sup>13</sup>S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **97**, 4282 (1992).
- <sup>14</sup>H. P. Kelly, *Adv. Chem. Phys.* **14**, 129 (1969).
- <sup>15</sup>R. J. Bartlett and D. M. Silver, *Chem. Phys. Lett.* **29**, 199 (1974); *Phys. Rev. A* **10**, 1927 (1974); *J. Chem. Phys.* **62**, 3258 (1975); R. J. Bartlett and G. D. Purvis III, *Int. J. Quantum Chem.* **14**, 561 (1978).
- <sup>16</sup>R. Krishnan, M. J. Frish, and J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980).
- <sup>17</sup>S. A. Kucharski and R. J. Bartlett, *Adv. Quantum Chem.* **18**, 281 (1986); S. A. Kucharski, J. Noga, and R. J. Bartlett, *J. Chem. Phys.* **90**, 7282 (1989).
- <sup>18</sup>S. A. Kucharski and R. J. Bartlett, *Chem. Phys. Lett.* **237**, 264 (1995).
- <sup>19</sup>M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1986); J. Noga, R. J. Bartlett, and M. Urban, *Chem. Phys. Lett.* **134**, 126 (1987).
- <sup>20</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- <sup>21</sup>J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
- <sup>22</sup>R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990).
- <sup>23</sup>S. A. Kucharski and R. J. Bartlett, *Chem. Phys. Lett.* **206**, 574 (1993).
- <sup>24</sup>M. J. Deegan and P. Knowles, *Chem. Phys. Lett.* **227**, 321 (1994).
- <sup>25</sup>H. Koch, O. Christiansen, P. Jørgensen, A. M. Sanchez de Mores, and T. Helgaker, *J. Chem. Phys.* **106**, 1808 (1997).
- <sup>26</sup>A. Balkova and R. J. Bartlett, *J. Chem. Phys.* **101**, 8972 (1994).
- <sup>27</sup>P. Piecuch and J. Paldus, *Theor. Chim. Acta* **78**, 65 (1990); P. Piecuch, R. Tobola, and J. Paldus, *Int. J. Quantum Chem.* **55**, 133 (1995).
- <sup>28</sup>J. D. Watts and R. J. Bartlett, *Chem. Phys. Lett.* **258**, 581 (1996).
- <sup>29</sup>O. Christiansen, H. Koch, and P. Jørgensen, *J. Chem. Phys.* **105**, 1451 (1996).
- <sup>30</sup>R. J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, edited by P. Jørgensen and J. Simons (Reidel, Dordrecht, The Netherlands, 1986), p. 35.
- <sup>31</sup>E. A. Salter, G. W. Trucks, and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989).
- <sup>32</sup>R. J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29 (1988).
- <sup>33</sup>R. J. Bartlett, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **155**, 133 (1989); J. Noga, S. A. Kucharski, and R. J. Bartlett, *J. Chem. Phys.* **90**, 3399 (1989).
- <sup>34</sup>P. Szalay, M. Nooijen, and R. J. Bartlett, *J. Chem. Phys.* **103**, 281 (1995).
- <sup>35</sup>J. S. Arponen, *Ann. Phys.* **151**, 311 (1983).
- <sup>36</sup>J. S. Arponen, R. F. Bishop, and E. Pajanne, *Phys. Rev. A* **36**, 2519 (1987).
- <sup>37</sup>B. Jeziorski and H. J. Monkhorst, *Phys. Rev. A* **24**, 1668 (1981).
- <sup>38</sup>S. A. Kucharski, M. Kolaski and R. J. Bartlett (in preparation).
- <sup>39</sup>L. M. Frantz and R. L. Mills, *Nucl. Phys.* **15**, 16 (1960).
- <sup>40</sup>S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **108**, 5255 (1998), following paper.
- <sup>41</sup>S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* (in press).
- <sup>42</sup>C. W. Bauschlicher, Jr. and P. R. Taylor, *J. Chem. Phys.* **86**, 1420 (1987).
- <sup>43</sup>C. W. Bauschlicher, Jr. and P. R. Taylor, *J. Chem. Phys.* **85**, 2779 (1986).
- <sup>44</sup>C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **86**, 1420 (1987).
- <sup>45</sup>O. Christiansen, H. Koch, P. Jørgensen, and J. Olsen, *Chem. Phys. Lett.* **256**, 185 (1996).