

A new approach to the problem of noniterative corrections within the coupled-cluster framework

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Noniterative corrections to the coupled-cluster (CC) method with singles and doubles (CCSD) due to triple and higher excitations in the cluster operator are investigated. The derivation is based on the standard procedure for evaluating contributions coming from higher excitation rank cluster operators into the CC equations for singles and doubles. The noniterative nature of the approach leads to a direct modification of the CCSD energy through *a posteriori* corrections, however, unlike previous derivations, we take into account the coupling between the energy and cluster amplitudes in the CC equations. The coupling is not present in the fully iterative CC schemes due to the linked diagram theorem which makes the cluster amplitude equations energy independent. We show, however, that if the problem of unlinked contributions is re-examined in the context of noniterative approaches, then their complete cancellation does not occur. This leads to a partial restoration of the energy dependence. The energy dependence then gives the cluster amplitudes more flexibility in adjusting to the energy changes within the noniterative approach which is especially important in quasidegenerate situations when the standard energy corrections become large. The resulting modifications introduce disconnected contributions to the energy so size-extensivity is no longer preserved. This approach provides a new hierarchy of CC corrections in which the standard corrections, like CCSD[T] or CCSD(T), appear as a natural first step in the derivation. Some of the corrections can be easily identified as analogous to those recently proposed by Kowalski and Piecuch in the context of the method of moments of CC equations. We also suggest new approximations. © 2001 American Institute of Physics. [DOI: 10.1063/1.1373434]

I. INTRODUCTION

The single-reference coupled-cluster (CC) method^{1–4} has proven to be very successful in describing nondegenerate states of atoms and molecules for which its basic approximation with singles and doubles (CCSD) provides very good results.^{5–9} To increase the accuracy one can employ noniterative corrections to CCSD which give an estimate of contributions coming from higher excitation rank cluster operators T_n , first from connected triples (T_3).^{10,11} While the fourth-order correction due to triples which is included in the CCSD+T(CCSD) method¹⁰ [also known as CCSD[T] (Ref. 12)] works pretty well for nondegenerate states its performance deteriorates rapidly when even relatively weak quasidegeneracy is present. In such a case perturbative arguments are not sufficient. Taking only the fourth-order contribution and an additional fifth-order term arising from the modification of the CCSD equations projected on singly excited determinants improves the performance of the correction.¹³ While the fifth-order term usually makes the result slightly worse in completely nondegenerate cases it has a significant effect on correcting the unphysical behavior of the fourth-order term when the state becomes quasidegenerate. That may be related to the increasing importance of single excitations (T_1) in the cluster operator since, according to the Thouless theorem,¹⁴ they can be considered re-

sponsible for the orbital rotation. The zeroth-order description based on Hartree–Fock (HF) orbitals becomes inadequate in quasidegenerate cases and the modification of the equation for T_1 , similar to that for doubles (T_2), is required. The two-term correction to the CCSD method constituting the CCSD(T) method is one of the basic CC computational schemes used in routine calculations.^{5–9} Its generalization to non-HF cases has also been presented.¹⁵ Obviously, there are more advanced CC approaches implemented like CCSDT-1, and particularly CCSDT-3 (Refs. 16–18) which use the same idea of modifying the T_1 and T_2 equations with terms in which T_3 is expressed as a simple function of T_2 but, unlike the noniterative approaches, the equations are solved iteratively. Only the storage of the T_1 and T_2 amplitudes is required which is an important advantage of these methods, however, the numerical effort can become significant because of the more complicated structure of the included terms. Finally, the full CCSDT method can be used,¹⁹ and its range of applicability now exceeds benchmark calculations.^{20,21} A more practical approach than CCSDT is the CCSDt method^{22–24} in which only an active orbital subset of the T_3 amplitudes and the corresponding equations is considered, namely those representing a desired level of excitation with respect to some selected reference space rather than to a single reference determinant. That eliminates the rate determining $\sim n^8$ step in CCSDT substan-

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tially, reducing the number of T_3 amplitudes and corresponding CC equations to be considered, making CCSDt and its variants²³ potentially wildly applicable.

The strategy outlined above can be extended to the case when the effect of quadruple excitations (T_4) ought to be included. That provides several computational schemes like those containing noniterative corrections to the CCSD or CCSDT methods, CCSD(TQ), CCSD(TQ_f), CCSDT(Q_f), and CCSDT(Q_f),^{25–27} or those of an iterative nature, CCSDtq (Refs. 22–24) and the full CCSDTQ method.²⁶ For the detailed description of these approaches and discussion of the accuracy they provide, we refer to Refs. 22–27. Clearly, the most appropriate in quasidegenerate cases would be to use the genuine multireference CC schemes^{28,29} (except for the two-determinantal open-shell singlet case³⁰), however, in spite of tremendous progress that has been recently made in developing these approaches they still do not constitute ‘‘blackbox’’ methods. That is mainly because of their formal complexity and the so-called intruder state problem. Some attempts have been also undertaken to simplify the multireference schemes and provide more efficient computational schemes by employing intermediate Hamiltonian techniques³¹ which seem quite promising.^{32–35} Another possibility that has been exploited is to introduce two-step procedures in which the nondynamical correlation effects are assumed to be given by a multi-reference configuration interaction (MR-CI) method and then the description of the dynamical part is corrected via subsequent single-reference CC calculation^{36,37} or by a single-reference coupled-cluster correction.³⁸ A third possibility is to exploit the usual MR-CI framework rather than orbital based CC procedure, but to incorporate approximation for unlinked diagrams in the modified CI framework, like MR-ACPF (Ref. 39) or MR-AQCC.⁴⁰ See also the use of EOM-CC as an indirect approach to some multireference situations.⁴¹

Since the multireference methods so far have not been able to provide us with reliable, inexpensive, and wildly applicable computational schemes it seems that the extension of the applicability of the single-reference CC methods to deal more efficiently with increasing degree of quasidegeneracy is still desirable. There is no doubt that from the point of view of large scale calculations, noniterative corrections should be of primary interest since the CCSD[T] and CCSD(T) methods are usually less costly than other alternatives. Unfortunately, the CCSD[T] method which performs very well at the equilibrium geometry displays unphysical behavior at larger distances significantly overshooting the exact result. The extra term containing T_1 , included in CCSD(T), moderates this behavior, however, even this does not help much when quasidegeneracy is significant in bond breaking. To remedy the situation, recently Kowalski and Piecuch have proposed a new approach to the problem of *a posteriori* corrections to the truncated CC schemes named the method of moments of CC equations (MMCC) (Refs. 42, 43) which originates from the so-called Fundamental Theorem of the β Nested Equations.^{44,45} A variety of the MMCC methods has been introduced which one may divide into two categories, simple corrections (the so-called renormalized

and corrections requiring a relatively substantial numerical effort (completely renormalized).⁴²

In this paper we shall show that corrections of this type can be easily and rigorously derived within the traditional CC framework without the necessity of considering the Fundamental Theorem of the β Nested Equations or any other expression involving the full configuration interaction (FCI) wave function. The basic idea of the derivation is to reconsider the problem of cancellation of unlinked terms in the cluster amplitude equations. While the iterative approaches allow T_1 and T_2 cluster amplitudes to absorb the information about contributions arising from the inclusion of higher excitation rank T operators in a self-consistent manner, and then transfer it to the standard CC energy expression, the noniterative schemes do not have such an ability and the effect is introduced directly via additional terms to the standard CC energy formula. Changes in the energy expression cause the cancellation of unlinked terms in the cluster amplitude equations considered within the scheme to not be as complete which can be seen by reexamining the problem. The resulting energy dependence of the cluster amplitude equations provides more flexibility to the scheme, meaning that initial changes in the CCSD equations leading to modification of the energy (standard CCSD corrections) cause a subsequent modification of the cluster amplitudes, and so on. In the single-reference situations the coupling is very weak since it is realized through very high order terms which are small in such a case. For quasidegenerate states, however, this is not the case and the coupling helps the corrections to behave in more moderate manner and give a more reasonable estimate of the higher excitation rank T contributions.

We shall also discuss some aspects of using an energy expression in which both, the right-hand and left-hand wave functions are parameterized differently which was used by Kowalski and Piecuch in their derivation.^{42,43} We concentrate on limiting cases in which the expression has a simple interpretation emphasizing that in other cases the expression seems to provide a combined effect from both wave functions. Finally, we shall test some simple modifications of the renormalized corrections on the DZ H₂O and DZ HF model systems.

II. MODIFICATION OF THE CCSD EQUATIONS PROJECTED ON SINGLY AND DOUBLY EXCITED DETERMINANTS

A. Coupled-cluster expansion and linked diagram theorem

The CC method is based on employing the exponential expansion for the wave function

$$|\Psi\rangle = \exp T|\Phi\rangle, \quad (1)$$

where Φ is usually the HF determinant and T is the second-quantized cluster excitation operator defined with respect to the HF function as a Fermi vacuum. The advantages of using exponential parameterization are visible when approximate schemes are considered. The approximate CC approaches are

generated by truncating the cluster operator T at some level of excitation. For example, for the CCSD scheme the approximation,

$$T = T_1 + T_2, \quad (2)$$

is imposed. One can note that the exponential expansion (1), in spite of truncation (2), is capable of producing all excited determinants. That can be contrasted with the fact that a similar truncation introduced for the linear expansion as in CI generates only singly and doubly excited determinants. However, the quality of the description of the higher than double excitations depends on fulfilling the so called cluster conditions.

Inserting Eq. (1) into the time-independent Schrödinger equation gives

$$H_N \exp(T)|\Phi\rangle = E \exp(T)|\Phi\rangle, \quad (3)$$

where

$$H_N = H - \langle\Phi|H|\Phi\rangle, \quad (4)$$

is defined to give the correlation energy E calculated with respect to the HF energy $\langle\Phi|H|\Phi\rangle$.

The set of equations for the cluster amplitudes and the energy is obtained by using the projection technique meaning that Eq. (3) is projected on a suitable set of functions spanning the Hilbert space considered within an algebraic approximation. The two most frequently used projection sets are $\{\langle\Phi|, \langle\Phi_i^a|, \langle\Phi_{ij}^{ab}|, \dots\}$ and $\{\langle\Phi|, \langle\Phi_i^a|e^{-T}, \langle\Phi_{ij}^{ab}|e^{-T}, \dots\}$, where Φ_i^a, \dots denotes the excited determinant obtained from Φ by replacing occupied spin-orbitals $i \dots$ by unoccupied spin-orbitals $a \dots$.

In the case of truncated schemes, like that of Eq. (2), one has to select a subset of the complete set of projected CC equations so their number is reduced to the number of the unknowns, i.e., the energy and cluster amplitudes. For the CCSD scheme a subset associated with Φ , and singly and doubly excited determinants is considered to be a natural choice, however, some nonstandard projection subspaces can also be taken into account.⁴⁶ When the second set of the projection functions mentioned above is used then one can immediately obtain the CCSD equations in terms of connected quantities since we have

$$\begin{aligned} \langle\Phi|H_N e^{T_1+T_2}|\Phi\rangle &= E, \\ \langle\Phi_i^a|e^{-(T_1+T_2)}H_N e^{T_1+T_2}|\Phi\rangle &= 0, \\ \langle\Phi_{ij}^{ab}|e^{-(T_1+T_2)}H_N e^{T_1+T_2}|\Phi\rangle &= 0. \end{aligned} \quad (5)$$

The connectivity follows from the Hausdorff formula and the property that commutators of second-quantized operators produce connected terms only. Because of that we have

$$e^{-(T_1+T_2)}H_N e^{T_1+T_2} = (H_N e^{T_1+T_2})_C = \tilde{H}_N^{12}, \quad (6)$$

where $(\)_C$ stands for connected terms and \tilde{H}_N^{12} is introduced to denote the similarity transformed H_N operator with T restricted to T_1 and T_2 .

Obtaining the equivalent form of the CCSD equations while using the first set of projection functions is slightly

more complicated since it requires explicit cancellation of unlinked terms. The projection leads to the following set of equations:

$$\begin{aligned} \langle\Phi|H_N e^{T_1+T_2}|\Phi\rangle &= \langle\Phi|\tilde{V}_N^{12}|\Phi\rangle = E, \\ \langle\Phi_i^a|H_N e^{T_1+T_2}|\Phi\rangle &= \langle\Phi_i^a|T_1|\Phi\rangle E, \\ \langle\Phi_{ij}^{ab}|H_N e^{T_1+T_2}|\Phi\rangle &= \langle\Phi_{ij}^{ab}|T_2 + \frac{1}{2}T_1^2|\Phi\rangle E, \end{aligned} \quad (7)$$

where we assume partitioning of the Hamiltonian H into the zeroth-order part H^0 and the perturbation V and introduce

$$\begin{aligned} H_N^0 &= H^0 - \langle\Phi|H^0|\Phi\rangle, \quad V_N = V - \langle\Phi|V|\Phi\rangle, \\ \tilde{V}_N^{12} &= (V_N e^{T_1+T_2})_C. \end{aligned} \quad (8)$$

To show cancellation of disconnected terms in Eq. (7) it is convenient to operate with diagrammatic techniques. The first line of Eq. (7) can be expressed in more explicit form as

$$E = \langle\Phi|V_N(T_2 + \frac{1}{2}T_1^2)|\Phi\rangle = \langle\Phi|(\tilde{V}_N^{12})_0|\Phi\rangle, \quad (9)$$

which contains connected terms (diagrams). $(\)_n$ is used for the n -particle component of an operator and that is introduced to make our considerations more transparent. The energy expression depends always on T_1 and T_2 only, even for approximations including higher excitations in T . While analyzing the second line of Eq. (7) one can construct connected and disconnected contributions to the equation. This can be schematically written as

$$\langle\Phi_i^a|(\tilde{H}_N^{12})_1 + T_1(\tilde{V}_N^{12})_0|\Phi\rangle - \langle\Phi_i^a|T_1|\Phi\rangle E = 0. \quad (10)$$

The zero-particle part $(\tilde{V}_N^{12})_0$ is identical with the energy expression (9) and, hence, the last two disconnected terms in Eq. (10) are canceled leaving connected contributions in the equation, now reduced to

$$\langle\Phi_i^a|(\tilde{H}_N^{12})_1|\Phi\rangle = 0. \quad (11)$$

Similarly, the third line of Eq. (7) can be written in terms of connected and disconnected components,

$$\begin{aligned} \langle\Phi_{ij}^{ab}|(\tilde{H}_N^{12})_2 + T_1(\tilde{H}_N^{12})_1 + (T_2 + \frac{1}{2}T_1^2)(\tilde{V}_N^{12})_0|\Phi\rangle \\ - \langle\Phi_{ij}^{ab}|T_2 + \frac{1}{2}T_1^2|\Phi\rangle E = 0. \end{aligned} \quad (12)$$

As before, the last two terms are canceled. In addition to that the second term on the left-hand side disappears because of the equation for T_1 , Eq. (11), which is assumed to be satisfied. Again only connected contributions give rise to the equation and we have

$$\langle\Phi_{ij}^{ab}|(\tilde{H}_N^{12})_2|\Phi\rangle = 0. \quad (13)$$

As is well known the equations given by employing either of the projection sets are the same and, consequently, in the CCSD equations one can consider only connected terms or diagrams to evaluate the connected cluster operator [the connected diagram theorem which is a consequence of the linked diagram theorem (LDT)]. This finding can be easily extended to the case when an arbitrary excitation level is assumed for T and the corresponding set of the projected CC equations is taken into account. It is worth noting here that

some attempts have been made to use nonstandard projections within the CC framework. In such a case the CC equations projected on functions of higher excitation rank than that generated by the truncated T can be taken into consideration. Unlike the standard projections this may lead to inequivalent results when using both projection sets. The use of the second set maintains connectivity by virtue of producing the similarity transformed Hamiltonian in Eq. (6) which is always connected, while the use of the first set may lead to quite different situations when irreducible disconnected contributions occur.

The standard CCSD method allows us to satisfy the Schrödinger equation with the exponential expansion for the wave function given by Eqs. (1) and (2) in the projection space spanned by Φ , and singly and doubly excited determinants with respect to it. The limitation is associated with the number of parameters in the T operator. The equations can be simplified by making use of the LDT. The connected structure proves size-extensivity of the method. While looking closer at the CCSD Eqs. (9), (11), and (13) one can immediately see that the highest excitation level that is generated by the cluster expansion in the equations is four in spite of the fact that the cluster expansion, even if it originates from the truncated form of T , Eq. (2), produces all possible excitations while acting on the reference function Φ . This is because of the projection employed and the at most two-particle character of the Hamiltonian.

Alternatively, one can examine the importance of the higher excitations in the CCSD wave function expansion by considering the energy expectation value expression,

$$E_{\text{CCSD}}^{\text{exp}} = \frac{\langle \Phi | e^{T_1^\dagger + T_2^\dagger} H_N e^{T_1 + T_2} | \Phi \rangle}{\langle \Phi | e^{T_1^\dagger + T_2^\dagger} e^{T_1 + T_2} | \Phi \rangle}, \quad (14)$$

to which now the total CCSD wave function contributes. Of course, the expectation value expression gives an upper bound to the exact energy, and it introduces certain higher excitation effects like quadruples from terms including $\frac{1}{2}(T_2^\dagger)^2$.⁴⁷ When the number of the parameters increases by including higher excitation operators in T , so does the ability to satisfy the Schrödinger equation in the larger space. In the limit of having all excitation operators in T the Schrödinger equation can be satisfied in the whole space and the correlation energy expectation value formula is again reduced to the standard CC energy expression (9),

$$E_{\text{FCC}}^{\text{exp}} = \frac{\langle \Phi | e^{T^\dagger} H_N e^T | \Phi \rangle}{\langle \Phi | e^{T^\dagger} e^T | \Phi \rangle} = \langle \Phi | V_N (T_2 + \frac{1}{2} T_1^2) | \Phi \rangle, \quad (15)$$

where FCC stands for the exact (full) CC method. The expectation value expression is always represented by connected terms only as shown by Čížek² and that does not depend on the truncation scheme used for T ,

$$E_{\text{CC}}^{\text{exp}} = \langle \Phi | (e^{T^\dagger} H_N e^T)_C | \Phi \rangle = \langle \Phi | (e^{T^\dagger} e^T (H_N e^T)_C)_C | \Phi \rangle. \quad (16)$$

The expectation value expression is usually considered while deriving noniterative corrections approximating the effect of higher excitations in T on the correlation energy.¹⁰ It has also been considered more generally in the XCC equations.⁴⁸

B. Standard noniterative corrections to the CCSD energy

The extension of the CC method to higher levels than CCSD is numerically demanding, so different ways of approximate accounting for the effect of triple and quadruple excitations in T have been investigated. Most of them rely on a simplified version of the CC equations for T_3 (or T_3 and T_4) from which T_3 (or T_3 and T_4) can be calculated directly as a function of the lower excitation rank T operators. While the complete CCSDT equation projected on triply excited determinants reads

$$\langle \Phi_{ijk}^{abc} | (\tilde{H}_N^{123})_3 | \Phi \rangle = 0, \quad (17)$$

the basic simplified equation contains only the lowest-order terms,¹⁶

$$\langle \Phi_{ijk}^{abc} | (H_N^0 T_3 + V_N T_2) | \Phi \rangle = 0. \quad (18)$$

Unlike the former equation the latter can be easily solved for the cluster amplitudes associated with T_3 since H_N^0 is diagonal,

$$\langle \Phi_{ijk}^{abc} | T_3 | \Phi \rangle = \frac{\langle \Phi_{ijk}^{abc} | V_N T_2 | \Phi \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \quad (19)$$

where ϵ_r is the orbital energy of the r th spin-orbital. Due to the hierarchical structure of the FCC equations in which the energy depends on T_1 and T_2 (9), and the CC equations projected on singles, doubles and so on contain cluster operators up to T_3 , up to T_4 , and so on, respectively, T_3 cannot modify the energy directly but only through equations projected on singles and doubles. The lowest-order term arising from the inclusion of T_3 in the CC equations projected on doubly excited determinants is

$$\langle \Phi_{ij}^{ab} | V_N T_3 | \Phi \rangle = \langle \Phi_{ij}^{ab} | V_N R_3 V_N T_2 | \Phi \rangle, \quad (20)$$

where the approximate form of T_3 , Eq. (19) has been inserted and the reduced resolvent,

$$R_N = \sum_{\substack{a_1 < a_2 < \dots < a_n \\ i_1 < i_2 < \dots < i_n}} \frac{|\Phi_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n}\rangle \langle \Phi_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n}|}{\epsilon_{i_1} + \epsilon_{i_2} + \dots + \epsilon_{i_n} - \epsilon_{a_1} - \epsilon_{a_2} - \dots - \epsilon_{a_n}}, \quad (21)$$

has been introduced. Now one can use the approximate contribution from T_3 (20) in Eq. (13) obtaining

$$\langle \Phi_{ij}^{ab} | (\tilde{H}_N^{12})_2 + V_N R_3 V_N T_2 | \Phi \rangle = 0. \quad (22)$$

Since the extra term is connected size-extensivity is preserved. The modified set of CCSD equations, Eqs. (9), (11), and (22) requires solving for T_1 and T_2 amplitudes so the number of unknown cluster amplitudes and the number of equations are exactly the same as in the CCSD scheme. Only Eq. (22) is more complicated than the CCSD Eq. (13). The method is known as CCSDT-1.¹⁶

The CCSDT-1 method requires an iterative solution of Eqs. (11) and (22) but another computationally simpler scheme emerges when one assumes that the change of T_2 given by CCSDT-1 with respect to CCSD is not pronounced, and leaves Eqs. (11) and (22) with the converged T_1 and T_2 amplitudes from the CCSD calculation. That can be justified

by the relatively high third-order character of the additional term (20). Equation (22) is then not satisfied in the projection space chosen for the CCSD scheme. To make it satisfied a new auxiliary T'_2 operator can be introduced replacing T_2 only in one, $H_N^0 T_2$, term in Eq. (22),

$$\langle \Phi_{ij}^{ab} | H_N^0 T'_2 + (\tilde{V}_N^{12})_2 + V_N R_3 V_N T_2 | \Phi \rangle = 0. \quad (23)$$

While comparing Eq. (23) with Eq. (13) it is easy to see that

$$T'_2 | \Phi \rangle = T_2 | \Phi \rangle + R_2 (V_N R_3 V_N T_2) | \Phi \rangle. \quad (24)$$

The last term gives a noniterative estimate of the change of the T_2 operator caused by the presence of the additional term (20) in Eq. (22). Replacing T_2 with T'_2 in the CC energy expression (9) generates an *a posteriori* correction to the CCSD energy,

$$\begin{aligned} E &= \langle \Phi | V_N (T'_2 + \frac{1}{2} T_1^{\dagger 2}) | \Phi \rangle \\ &= E_{\text{CCSD}} + \langle \Phi | V_N R_2 V_N R_3 V_N T_2 | \Phi \rangle. \end{aligned} \quad (25)$$

To obtain an alternative version of the correction the CC expectation value expression (16) has been used.¹⁰ When the CCSD equations projected on singles and doubles are satisfied then projection on any function from the space spanned by Φ and singly and doubly excited determinants gives the CCSD energy. In particular,

$$E_{\text{CCSD}} = \langle \Phi | (1 + T_1^\dagger + T_2^\dagger + \frac{1}{2} T_1^{\dagger 2}) \tilde{H}_N^{12} | \Phi \rangle. \quad (26)$$

When the CCSD equation (13) is replaced by the CCSDT-1 equation (22) and the corresponding change is made in Eq. (26), then assuming an iterative approach, the CCSDT-1 energy is obtained as

$$\begin{aligned} E_{\text{CCSDT-1}} &= \langle \Phi | (\tilde{V}_N^{12})_0 + T_1^\dagger (\tilde{H}_N^{12})_1 + (T_2^\dagger + \frac{1}{2} T_1^{\dagger 2}) \\ &\quad \times (\tilde{H}_N^{12} + V_N R_3 V_N T_2)_2 | \Phi \rangle. \end{aligned} \quad (27)$$

However, if the idea of a noniterative treatment of approximate triples is followed, then Eq. (22) is not satisfied and then the right-hand side of Eq. (27) gives instead of the CCSDT-1 energy the CCSD energy supplemented with an energy correction. The correction has been proposed by Urban *et al.* and is known as the CCSD+T(CCSD) (Ref. 10) or the CCSD[T] (Ref. 12) method. Inserting T_1 and T_2 cluster amplitudes from the CCSD calculation into Eq. (27) we have

$$E_{\text{CCSD[T]}} = E_{\text{CCSD}} + \langle \Phi | T_2^\dagger V_N R_3 V_N T_2 | \Phi \rangle, \quad (28)$$

where the high-order term associated with $\frac{1}{2} T_1^{\dagger 2}$ has been neglected. It is easy to see that Eq. (25) can be obtained from Eq. (28) by replacing T_2^\dagger with its first-order contribution. Correction (28) gives the lowest-order contribution from connected triples to the energy and is negative because of its symmetric structure and the fact that the denominator in R_3 (21) is negative for a ground state. Hence, the CCSD[T] energy is always lower than the CCSD one and in non-quasidegenerate cases the method performs very well making the result closer to the exact one. However, in a bond breaking situation, where other determinants start to be particularly important, one or several of the T_2 amplitudes become large and so is the correction. That can lead to a significant overshooting of the FCI results. This behavior of

CCSD[T] can be partly alleviated by considering the lowest-order contribution from T_3 in the CC equations projected on singles. In quasidegenerate situations some T_1 amplitudes can also be large because the HF method does not provide a good zeroth-order approximation in such cases. T_1 , which can be considered responsible for the orbital rotation, tries to reduce this effect. The noniterative inclusion of the approximate contribution from T_3 (19) in the CCSD equation projected on singles leads to

$$\langle \Phi_i^a | (\tilde{H}_N^{12})_1 + V_N R_3 V_N T_2 | \Phi \rangle = 0, \quad (29)$$

which within the noniterative framework gives an additional correction term to the energy. This term, supplementing the energy expression (28), leads to the CCSD(T) scheme,

$$E_{\text{CCSD(T)}} = E_{\text{CCSD[T]}} + \langle \Phi | T_1^\dagger V_N R_3 V_N T_2 | \Phi \rangle. \quad (30)$$

The extra term is usually positive, relatively small for non-degenerate geometries and more significant when quasidegeneracy is present.

The CCSD(T) method has been very successful in describing the potential energy surface in the range from non-degenerate to weakly quasidegenerate geometries. The two terms represent in such cases a balanced contribution from T_3 which is not, in fact, completely based on a perturbative analysis since the second term gives only one of the fifth-order contributions. Single-reference perturbative arguments are not valid, however, when the single HF determinant does not provide a reliable zeroth-order approximation. But when the quasidegeneracy becomes stronger the CCSD(T) method breaks down completely.

While the triple corrections are of prime interest, other types of CC corrections can be derived following the same philosophy by introducing the effect of higher excitation rank T operators through modifications of the standard CC equations, first of all those projected on doubles. For example, in the CCSDT(Q) approach⁴⁹ the CC method with singles, doubles and triples is corrected to give the lowest-order contribution from T_4 . In this case the following simplified equation for T_4 is considered,

$$\langle \Phi_{ijkl}^{abcd} | H_N^0 T_4 + (\frac{1}{2} V_N T_2^2 + V_N T_3)_C | \Phi \rangle = 0, \quad (31)$$

which contains the lowest-order terms. The T_4 obtained from the equation gives the following lowest-order contribution to the CC equation projected on doubles:

$$\langle \Phi_{ij}^{ab} | V_N R_4 (\frac{1}{2} V_N T_2^2 + V_N T_3)_C | \Phi \rangle. \quad (32)$$

The noniteratively corrected CCSDT energy constitutes the CCSDT(Q) approach,

$$E_{\text{CCSDT(Q)}} = E_{\text{CCSDT}} + \langle \Phi | T_2^\dagger V_N R_4 (\frac{1}{2} V_N T_2^2 + V_N T_3)_C | \Phi \rangle. \quad (33)$$

In the CCSD(TQ) method⁴⁹ the CCSD cluster amplitudes are used to give an estimate of the combined contribution from T_3 and T_4 . T_3 is not available now in Eq. (32) and, hence, the approximate T_3 amplitudes given by Eq. (19) must be used. Note also that a contribution from T_1^\dagger can occur as it does in CCSD(T). The two component correction to the CCSD(T) energy is then given by

$$E_{\text{CCSD(TQ)}} = E_{\text{CCSD(T)}} + \langle \Phi | T_2^\dagger V_N R_4 \times (\frac{1}{2} V_N T_2^2 + V_N R_3 V_N T_2)_C | \Phi \rangle. \quad (34)$$

Some considerations from the factorization theorem allow us to arrive at some simpler, although not completely equivalent forms of Eq. (34), which leads to the CCSD(TQ_f) scheme,⁴⁹

$$E_{\text{CCSD(TQ}_f)} = E_{\text{CCSD(T)}} + \frac{1}{2} \langle \Phi | V_N R_2 T_2^\dagger \times (\frac{1}{2} V_N T_2^2 + V_N R_3 V_N T_2)_C | \Phi \rangle. \quad (35)$$

By replacing the long denominator in R_4 with the short denominator in R_2 the new form significantly reduces the numerical effort ($\sim n^9$ to $\sim n^6$) necessary to calculate the correction (see Ref. 50 for the detailed equation). A similar change made within the CCSDT(Q) method gives the CCSDT(Q_f) scheme.⁴⁹

C. Problem of cancellation of disconnected terms revisited: Renormalized corrections to the CCSD energy

Construction of the standard corrections to the CCSD energy has been mainly guided by perturbative arguments. Analysis of the CC equations allows us in such a case to select the lowest-order contributions arising from inclusion of higher excitation rank T operators in the T_2 (or T_2 and T_1) equations and express them in terms of the CCSD T_2 (or T_2 and T_1) cluster operators. This strategy proves very successful as long as the single-reference perturbation expansion can be employed as a valid tool in the analysis. This, of course, is not the case when a significant degree of quasidegeneracy is present, so perhaps other criteria for examining the CC equations are necessary to reveal the possibility of constructing corrections that are better able to deal with such a situation.

When the iterative versions of the CCSD equations corrected to include the approximate contributions from triples or quadruples are considered like, for example, CCSDT-1, then the T_1 and T_2 amplitudes determined by the self-consistent procedure absorb contributions given by the extra terms and transfer it to the standard CC energy expression (9). Focusing our attention on the CCSDT-1 scheme it can be seen that the CCSDT-1 Eq. (22) obtained from the CCSD Eq. (13) by supplementing it with the approximate triple contribution (20) is equivalent to the initial CCSD equation (12) with the same triple contribution,

$$\langle \Phi_{ij}^{ab} | (\tilde{H}_N^{12})_2 + V_N R_3 V_N T_2 + T_1 (\tilde{H}_N^{12})_1 + (T_2 + \frac{1}{2} T_1^2) \times [(\tilde{V}_N^{12})_0 - E] | \Phi \rangle = 0, \quad (36)$$

as long as the iterative approach is assumed. This is because of cancellation of disconnected terms which reduces Eq. (36) to its connected form (22). A similar cancellation does not happen, however, when a noniterative scheme is invoked. The analog of Eq. (36) in such a case is

$$\langle \Phi_{ij}^{ab} | H_N^0 T_2' + (\tilde{V}_N^{12})_2 + V_N R_3 V_N T_2 + T_1 (\tilde{H}_N^{12})_1 + (T_2 + \frac{1}{2} T_1^2) \times [(\tilde{V}_N^{12})_0 - E] | \Phi \rangle = 0, \quad (37)$$

with E given by the first relation in Eq. (25) depending on T_2' . $(\tilde{V}_N^{12})_0$, which is constructed from the CCSD amplitudes, T_1 and T_2 , is equal to E_{CCSD} and, obviously, is not identical with E . That leaves irreducible unlinked contributions in the equation which when solved for T_2' give

$$T_2' | \Phi \rangle = T_2 | \Phi \rangle + R_2 [V_N R_3 V_N T_2 - (T_2 + \frac{1}{2} T_1^2) \Delta E] | \Phi \rangle, \quad (38)$$

with

$$\Delta E = E - E_{\text{CCSD}}. \quad (39)$$

Inserting T_2' into the energy expression (25),

$$\Delta E = \langle \Phi | V_N R_2 V_N R_3 V_N T_2 | \Phi \rangle - \langle \Phi | V_N R_2 (T_2 + \frac{1}{2} T_1^2) | \Phi \rangle \Delta E, \quad (40)$$

and solving the equation for ΔE leads to

$$\Delta E = \frac{\langle \Phi | V_N R_2 V_N R_3 V_N T_2 | \Phi \rangle}{1 + \langle \Phi | V_N R_2 (T_2 + \frac{1}{2} T_1^2) | \Phi \rangle}. \quad (41)$$

When the expectation value expression is used instead of introducing the auxiliary operator T_2' , then $\langle \Phi | T_2^\dagger$ replaces its first-order contribution $\langle \Phi | V_N R_2$ in both the numerator and the denominator of Eq. (41),

$$\Delta E = \frac{\langle \Phi | T_2^\dagger V_N R_3 V_N T_2 | \Phi \rangle}{1 + \langle \Phi | T_2^\dagger (T_2 + \frac{1}{2} T_1^2) | \Phi \rangle}. \quad (42)$$

So far only the equation for T_2 has been considered in which the initial modification was made. However, the equation for T_1 which is a part the computational scheme is also affected by the correction in spite of the fact that no direct change in the equation is made. Again this is because the cancellation of unlinked terms is not complete and hence from Eq. (10) one has

$$\langle \Phi_i^a | (\tilde{H}_N^{12})_1 - T_1 \Delta E | \Phi \rangle. \quad (43)$$

In principle, one can also take into account the simplified equation for T_3 (18) for which a similar consideration leads to

$$T_3 | \Phi \rangle = R_3 (V_N T_2 - e^{T_1 + T_2} \Delta E) | \Phi \rangle. \quad (44)$$

Equation (44) used instead of Eq. (19) in the T_2 equation with the lowest order term including T_3 gives

$$\langle \Phi_{ij}^{ab} | (\tilde{H}_N^{12})_2 + V_N R_3 V_N T_2 - (T_2 + \frac{1}{2} T_1^2 + V_N R_3 e^{T_1 + T_2}) \Delta E | \Phi \rangle, \quad (45)$$

which together with including Eq. (43) in the reduced expectation value expression, finally leads to a correction which can be easily identified as the renormalized CCSD[T] (R-CCSD[T]) correction discussed by Kowalski and Piecuch in the context of the method of moments of CC (MMCC) equations,⁴²

$$\Delta E_{R\text{-CCSD[T]}} = \frac{\langle \Phi | T_2^\dagger V_N R_3 V_N T_2 | \Phi \rangle}{\langle \Phi | [1 + T_1^\dagger + T_2^\dagger (1 + V_N R_3)] e^{T_1 + T_2} | \Phi \rangle}. \quad (46)$$

It is easy to see that as a result of the incomplete cancellation of unlinked terms the standard CCSD[T] correction is divided by a term which can be seen as an overlap of the CCSD wave function and a simple function,

$$(1 + T_1 + T_2 + R_3 V_N T_2) |\Phi\rangle, \quad (47)$$

which includes up to triply excited determinants.

When one wants to consider an analog of the CCSD(T) method then the approximate T_3 , Eq. (44), must also be used to modify the equation projected on singles in a way similar to that in the CCSD(T) approach,

$$\langle \Phi_i^a | (\tilde{H}_N^{12})_1 + V_N R_3 (V_N T_2 - e^{T_1 + T_2} \Delta E) - T_1 \Delta E | \Phi \rangle. \quad (48)$$

That gives the renormalized CCSD(T) correction,

$$\Delta E_{\text{CCSD(T)}} = \frac{\langle \Phi | (T_1^\dagger + T_2^\dagger) V_N R_3 V_N T_2 | \Phi \rangle}{\langle \Phi | [1 + (T_1^\dagger + T_2^\dagger)(1 + V_N R_3)] e^{T_1 + T_2} | \Phi \rangle}. \quad (49)$$

Finally, if all possible terms containing the CCSD cluster amplitudes are included in the simplified T_3 equation instead of only the lowest-order ones,

$$T_3 |\Phi\rangle = R_3 (\tilde{V}_N^{12} - \Delta E e^{T_1 + T_2}) |\Phi\rangle, \quad (50)$$

then the so called completely renormalized CCSD[T] (CR-CCSD[T]) (Ref. 42) correction,

$$\Delta E_{\text{CR-CCSD[T]}} = \frac{\langle \Phi | T_2^\dagger V_N R_3 \tilde{V}_N^{12} | \Phi \rangle}{\langle \Phi | [1 + T_1^\dagger + T_2^\dagger (1 + V_N R_3)] e^{T_1 + T_2} | \Phi \rangle}, \quad (51)$$

and the completely renormalized CCSD(T) correction,

$$\Delta E_{\text{CR-CCSD(T)}} = \frac{\langle \Phi | (T_1^\dagger + T_2^\dagger) V_N R_3 \tilde{V}_N^{12} | \Phi \rangle}{\langle \Phi | [1 + (T_1^\dagger + T_2^\dagger)(1 + V_N R_3)] e^{T_1 + T_2} | \Phi \rangle}, \quad (52)$$

are obtained. It is worth noting that the denominators in the renormalized and completely renormalized versions of a particular correction are the same.

Guided by the same principle of taking into account the coupling between the energy and cluster amplitude equations, one can easily derive renormalized versions of the remaining standard CC corrections described in Sec. II B. The most interesting case from the point of view of practical applications is the CCSD(TQ_f) method for which the renormalized version is

$$\begin{aligned} \Delta E_{\text{R-CCSD(TQ}_f)} \\ = \frac{\Delta E_{\text{CCSD(TQ}_f)}}{\langle \Phi | [1 + (T_1^\dagger + T_2^\dagger + \frac{1}{2} T_2^\dagger T_2^{(1)\dagger})(1 + V_N R_3)] e^{T_1 + T_2} | \Phi \rangle}, \end{aligned} \quad (53)$$

where $T_2^{(1)\dagger}$ stands for the first-order contribution to T_2^\dagger .

The most visible feature of the renormalized corrections is their size-inextensivity. The renormalized corrections ΔE_R can be schematically expressed in the form,

$$\Delta E_R = \frac{\Delta E}{1 + S}, \quad (54)$$

where ΔE is used for the standard corrections and S is a part of the denominators containing at least second-order terms from the point of view of the single-reference perturbation expansion. When quasidegeneracy is not present, then $|S| < 1$ and

$$\Delta E_R = \Delta E - S \Delta E + S^2 \Delta E \dots, \quad (55)$$

so all terms that are generated by the denominator in addition to the standard corrections have disconnected character if the so-called exclusion principle violating terms are not taken into account. Since the standard corrections are of the fourth and higher orders and S is at least of the second order the inextensivity error can be considered small in single-reference cases. Moreover, renormalized corrections have the same nice property as the standard ones of vanishing when the CC method being corrected becomes exact. For example, for the CCSD method this is the case for a two-electron system or a system consisting of noninteracting two-electron systems.⁴² This follows from the fact that if ΔE vanishes then ΔE_R disappears as well.

While in the single-reference situations ΔE_R differs very little from ΔE the difference becomes large when the degree of quasidegeneracy increases. The basic component of the standard CCSD corrections, $\Delta E_{\text{CCSD[T]}}$, which is negative, because of the presence of large T_2 amplitudes significantly overshoots the exact energy. However, if this is combined with the growing value of the denominator in the renormalized corrections then the net effect can place the result close to the exact one. To find a balance between both effects more numerical experience is required, nevertheless, the renormalized corrections offer a promising way of extending applicability of the standard corrections to a larger range of molecular geometries.

In this section we have presented a derivation of the renormalized noniterative corrections to the CCSD energy based on recognizing the coupling between the cluster amplitude equations and the energy. Similar corrections have been proposed by Kowalski and Piecuch within the so called method of moments of CC equations (MMCC). The inspiration for them was the Fundamental Theorem of the Formalism of β -Nested Equations which can provide a simple-formula relation between the exact (FCI) energy and the energy obtained within any truncated T CC scheme assuming that the FCI wave function is given. Then, the idea of using a simple estimate of the ground state function from some inexpensive external source has been suggested.⁴² In practice, a very low order of the single-reference perturbation expansion or some rough description based on the knowledge of CCSD cluster amplitudes have been used.^{42,43} In spite of that, the test calculations^{42,43} have shown that the resulting renormalized corrections offer a significant improvement over the standard ones for the geometries distant from the equilibrium.^{42,43} This is rather surprising since in such cases the single-reference trial function does not provide an adequate approximation of the exact wave function. The advantage of the derivation presented here is that it is done entirely within the CC framework and, as a consequence, guessing some arbitrary function as it is necessary within the MMCC equations is avoided. Instead, the ‘‘trial’’

function arises naturally. It is also worth noting that the standard corrections constitute the first initial step in our derivation.

III. THE SCHRÖDINGER EQUATION PROJECTED ON THE CC WAVE FUNCTION

In order to obtain the simple-formula relation discussed by Kowalski and Piecuch^{42,43} it is enough to project the Schrödinger equation in the bra-space,

$$\langle \Psi | H_N = \langle \Psi | E, \quad (56)$$

on the CC wave function,

$$\langle \Psi | H_N e^{T'} | \Phi \rangle = \langle \Psi | e^{T'} | \Phi \rangle E, \quad (57)$$

where E is the energy relative to the HF energy. If calculation of the energy E with respect to some other reference energy is preferable, then that can be easily accomplished by redefining the Hamiltonian in a similar way to how H_N was defined (4). For example, if T is limited to singles and doubles, Eq. (2), and the cluster amplitudes are obtained from the standard CCSD calculation one can calculate the energy with respect to the CCSD correlation energy E_{CCSD} by using the shifted energy Hamiltonian $H_N - E_{\text{CCSD}}$ instead of H_N . In such a case from Eq. (57) we have

$$\Delta E \langle \Psi | e^{T_1 + T_2} | \Phi \rangle = \langle \Psi | (H_N - E_{\text{CCSD}}) e^{T_1 + T_2} | \Phi \rangle, \quad (58)$$

where ΔE is defined by Eq. (39). If Ψ is the FCI wave function, then Eq. (58) gives the exact FCI energy relative to E_{CCSD} . Formula (58) has been used as a starting point in the derivation of the MMCC equations. The purpose was to obtain an explicit and rigorous relationship between the energy obtained in an approximate correlated calculation, like CCSD, and the exact energy. One can see that in the limit of having Ψ as the FCI wave function it does not matter too much whether the Schrödinger equation (56) is projected on the CCSD function or on any other function since Eq. (56) is satisfied in the whole space. At first glance, formula (58) suggests that even in the case of the FCI function disconnected contributions to the energy difference ΔE are generated which is, of course, not true. To see the cancellation of disconnected terms a many-body representation of Ψ can be used. From the well known relation between the FCI coefficients (C) and the FCC amplitudes (T'),

$$T'_1 = C_1,$$

$$T'_2 = C_2 - \frac{1}{2} T_1'^2, \quad (59)$$

...

the FCI wave function can be represented as the FCC one,

$$|\Psi\rangle = e^{T'} |\Phi\rangle. \quad (60)$$

Now the ΔE expression gives

$$\begin{aligned} \Delta E &= \frac{\langle \Phi | e^{T'} (H_N - E_{\text{CCSD}}) e^{T'} | \Phi \rangle}{\langle \Phi | e^{T'} e^{T'} | \Phi \rangle} \\ &= \langle \Phi | (e^{T'} H_N e^{T'})_C | \Phi \rangle - E_{\text{CCSD}}, \end{aligned} \quad (61)$$

where cancellation of disconnected terms can be shown in a way similar to that indicated by Čížek.² Equation (61) also shows that any other kind of exponential expansion, not necessarily the FCC one, leads to a connected structure for ΔE . However, use of the function (60) truncated at some excitation level so only up to n -tuply ($n < \text{number of electrons}$) excited determinants are created from Φ , generates irreducible disconnected terms.

Another limiting case, in which it is clear what ΔE really means, is when Ψ represents a wave function obtained from the truncated CI calculation with singles and doubles (CISD). While the FCI equations are satisfied in the whole space, the Schrödinger equation with the CCSD wave function is satisfied in the projection space spanned by Φ and singly and doubly excited determinants. Here $\Delta E = 0$ and again it does not matter whether the equation is projected onto CISD or any other function restricted up to double excitations. However, since the CISD coefficients and the CCSD amplitudes do not differ very much in single-reference cases, it is possible to find an approximate relation between the CCSD and CISD energy. For the sake of simplicity we neglect single excitations, comparing CID and CCD methods. The CID function reads

$$|\Psi_{\text{CID}}\rangle = (1 + C_2) |\Phi\rangle, \quad (62)$$

and the set of the CID equations,

$$\begin{aligned} E_{\text{CID}} &= \langle \Phi | H_N C_2 | \Phi \rangle, \\ \langle \Phi |_{ij}^{ab} H_N (1 + C_2) | \Phi \rangle &= E_{\text{CID}} \langle \Phi |_{ij}^{ab} C_2 | \Phi \rangle, \end{aligned} \quad (63)$$

where the intermediate normalization is imposed on the CID wave function and C_2 is the double excitation operator associated with the CID coefficients. From Eq. (58) we have

$$\begin{aligned} \Delta E (1 + \langle \Phi | C_2^\dagger T_2 | \Phi \rangle) \\ = \langle \Phi | (1 + C_2^\dagger) (H_N - E_{\text{CCD}}) (1 + T_2 + \frac{1}{2} T_2^2) | \Phi \rangle. \end{aligned} \quad (64)$$

Since the CCD equations are satisfied in the space spanned by Φ and doubly excited determinants, then $\Delta E = 0$,

$$\langle \Phi | (1 + C_2^\dagger) (H_N - E_{\text{CCD}}) (1 + T_2 + \frac{1}{2} T_2^2) | \Phi \rangle = 0. \quad (65)$$

Using Eq. (63), Eq. (65) can be rewritten in the form,

$$\begin{aligned} E_{\text{CID}} + E_{\text{CID}} \langle \Phi | C_2^\dagger T_2 | \Phi \rangle + \frac{1}{2} \langle \Phi | C_2^\dagger V_N T_2^2 | \Phi \rangle \\ - E_{\text{CCD}} (1 + \langle \Phi | C_2^\dagger T_2 | \Phi \rangle) = 0. \end{aligned} \quad (66)$$

The third term can be expressed in terms of connected and disconnected components,

$$\begin{aligned} \frac{1}{2} \langle \Phi | C_2^\dagger V_N T_2^2 | \Phi \rangle &= \frac{1}{2} \langle \Phi | (C_2^\dagger V_N T_2^2)_C | \Phi \rangle \\ &+ E_{\text{CCD}} \langle \Phi | C_2^\dagger T_2 | \Phi \rangle, \end{aligned} \quad (67)$$

and we have

$$E_{\text{CCD}} - E_{\text{CID}} = E_{\text{CID}} \langle \Phi | C_2^\dagger T_2 | \Phi \rangle + \frac{1}{2} \langle \Phi | (C_2^\dagger V_N T_2^2)_C | \Phi \rangle. \quad (68)$$

Since C_2 and T_2 differ in the third order of the perturbation expansion, it is easy to see that replacing T_2 with C_2 in Eq. (68) causes changes of a very high order. So as long as the single-reference perturbative arguments hold, one can consider

$$E_{\text{CCD}} - E_{\text{CID}} \approx E_{\text{CID}} \langle \Phi | C_2^\dagger C_2 | \Phi \rangle + \frac{1}{2} \langle \Phi | (C_2^\dagger V_N C_2^2)_c | \Phi \rangle, \quad (69)$$

as a good approximation of the difference between CCD and CID energies. The first term in Eq. (69) can be recognized as the so called renormalized Davidson correction (RDC).⁵¹⁻⁵⁴ Indeed, if we switch to the normalized to unity CID vector and denote by c_0 the coefficient associated with the reference function Φ , then

$$c_0^2 = \frac{1}{1 + \langle \Phi | C_2^\dagger C_2 | \Phi \rangle}. \quad (70)$$

Using this relation the standard form of the RDC can be obtained,

$$\text{RDC} = E_{\text{CID}} \langle \Phi | C_2^\dagger C_2 | \Phi \rangle = E_{\text{CID}} \frac{1 - c_0^2}{c_0^2}. \quad (71)$$

It should be emphasized that the renormalized Davidson correction itself leads to the linear version of the CCD method^{53,54} rather than to its full version, which shows the importance of the second term in Eq. (69). Some numerical tests show the relation in Eq. (69) can give a quite good approximation of the CCD and CID energy difference.⁵⁵

In other than those limiting cases described above like, for example, with the left-hand wave function Ψ truncated at the triple excitation level and the CCSD left-hand wave function, the ΔE expression seems to give a combined effect coming from both wave function expansions. Nevertheless, guided by the form of the standard CCSD corrections and properly selecting contributions to Ψ and $H_N \exp(T_1 + T_2)$ one can arrive at the renormalized and completely renormalized corrections to CCSD (Refs. 42, 43) which, as shown in the previous section, can be easily obtained within the traditional CC approach.

IV. POSSIBLE MODIFICATIONS OF THE SIMPLE CCSD CORRECTIONS FOR TRIPLES

The completely renormalized corrections, CR-CCSD[T] (51) and CR-CCSD(T) (52), can be seen as most effective because of taking into account all possible terms containing CCSD amplitudes including all nonlinear ones in the T_3 Eq. (50).⁴² The nonlinear terms should moderate the behavior of the linear terms which are exclusively present in the R-CCSD[T] and R-CCSD(T) approaches while the denominators are the same in each category of the corrections. However, the disadvantage of the completely renormalized schemes is that they can be quite numerically demanding making them less practical. Obviously, it would be desirable to improve the performance of the simple corrections through changes which do not increase their numerical complexity. Just to show that such modifications are still possible we would like to present and test two new versions. Throughout our derivation the importance of single excitations has been emphasized several times so the first change we would like to suggest is to include the term arising from the inclusion of $\frac{1}{2}T_1^\dagger$ which has been neglected when constructing the CCSD[T] correction. The modified CCSD[T] correction is now

$$\Delta E_{\text{CCSD[T]\{M\}}} = \langle \Phi | (T_2^\dagger + \frac{1}{2}T_1^\dagger) V_N R_3 V_N T_2 | \Phi \rangle. \quad (72)$$

If the change is incorporated in the CCSD(T) scheme, then

$$\Delta E_{\text{CCSD(T)\{M\}}} = \langle \Phi | (T_1^\dagger + T_2^\dagger + \frac{1}{2}T_1^\dagger) V_N R_3 V_N T_2 | \Phi \rangle. \quad (73)$$

The renormalized versions are

$$\begin{aligned} \Delta E_{\text{R-CCSD[T]\{M\}}} &= \frac{\Delta E_{\text{CCSD[T]\{M\}}}}{\langle \Phi | [1 + T_1^\dagger + (T_2^\dagger + \frac{1}{2}T_1^\dagger)(1 + V_N R_3)] e^{T_1 + T_2} | \Phi \rangle}, \end{aligned} \quad (74)$$

$$\begin{aligned} \Delta E_{\text{R-CCSD(T)\{M\}}} &= \frac{\Delta E_{\text{CCSD(T)\{M\}}}}{\langle \Phi | [1 + (T_1^\dagger + T_2^\dagger + \frac{1}{2}T_1^\dagger)(1 + V_N R_3)] e^{T_1 + T_2} | \Phi \rangle}. \end{aligned} \quad (75)$$

The next modification comes from recognizing the importance of the renormalization term in the CC equations when noniterative corrections for a more effective description of quasidegenerate states are considered. In our derivation of the renormalized corrections the renormalization term plays a critical role. Keeping this in mind we concentrate our attention on the simplified equation for T_3 (18). This is a linear equation in T_3 assuming that T_2 is known. It does not mean, however, that this is a consequence of the linear dependence of the wave function on T_3 . If the wave function depends linearly on T_3 ,

$$|\Psi\rangle = (e^{T_1 + T_2 + T_3})|\Phi\rangle, \quad (76)$$

then the Schrödinger equation projected on triply excited determinants gives

$$\begin{aligned} \langle \Phi_{ijk}^{abc} | H_N (e^{T_1 + T_2 + T_3}) | \Phi \rangle \\ - \langle \Phi_{ijk}^{abc} | T_1 T_2 + \frac{1}{3!} T_1^3 + T_3 | \Phi \rangle E = 0. \end{aligned} \quad (77)$$

Obviously, the linear dependence of Ψ on T_3 generates disconnected terms. If the T_1 and T_2 amplitudes and the energy are taken from the CCSD calculations, then

$$\langle \Phi_{ijk}^{abc} | (\tilde{V}_N^{12})_3 | \Phi \rangle + \langle \Phi_{ijk}^{abc} | (H_N - E_{\text{CCSD}}) T_3 | \Phi \rangle = 0. \quad (78)$$

Now a simplified equation for T_3 can be given by

$$\langle \Phi_{ijk}^{abc} | V_N T_2 | \Phi \rangle + \langle \Phi_{ijk}^{abc} | (H_N^0 - E_{\text{CCSD}}) T_3 | \Phi \rangle = 0, \quad (79)$$

providing an approximate expression for the T_3 amplitudes

$$\langle \Phi_{ijk}^{abc} | T_3 | \Phi \rangle = \frac{\langle \Phi_{ijk}^{abc} | V_N T_2 | \Phi \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c + E_{\text{CCSD}}}. \quad (80)$$

Expression (80) differs from the previous expression for T_3 (19) by having an energy dependent denominator which to a large extent resembles, although it is not identical with, the Brillouin–Wigner {BW} denominator. We use {BW} to indicate replacing the standard denominator in the corrections with that of the Brillouin–Wigner-type, Eq. (80).

The test calculation has been carried out for two molecular systems, H₂O and HF, which have been frequently used to investigate the performance of various single- and multi-

TABLE I. The FCI energies (in a.u.) of the ground state of the DZ H₂O model and energies of CCSD, CCSDT, and CCSD + various noniterative corrections due to triples relative to FCI (in mH). All results, except those corresponding to {M}, {BW}, and {M,BW}, are taken from Ref. 42, and references therein.

	1 R _e	1.5 R _e	2 R _e
FCI	-76.157 866	-76.014 521	-75.905 247
CCSD	1.790	5.590	9.333
CCSDT	0.434	1.473	-2.211
CCSD[T]	0.362	0.751	-11.220
CCSD[T]{M}	0.365	0.808	-10.444
R-CCSD[T]	0.428	1.391	-3.623
R-CCSD[T]{M}	0.431	1.440	-3.183
R-CCSD[T]{BW}	0.471	1.637	-2.169
R-CCSD[T]{M,BW}	0.474	1.681	-1.797
CCSD(T)	0.574	1.465	-7.699
CCSD(T){M}	0.578	1.522	-6.923
R-CCSD(T)	0.631	2.013	-1.376
R-CCSD(T){M}	0.634	2.061	-0.928
R-CCSD(T){BW}	0.667	2.214	-0.266
R-CCSD(T){M,BW}	0.670	2.259	0.112
CR-CCSD[T]	0.560	2.053	1.163
CR-CCSD(T)	0.738	2.534	1.830

reference methods.^{56,17,24,49,37} These molecules have also been selected by Kowalski and Piecuch for their preliminary calculations employing a hierarchy of the renormalized and completely renormalized CCSD corrections.⁴² Using the same double-zeta basis sets,⁵⁷ we supplement their results with results given by our modified corrections {M}, {BW} and their combination {M, BW}. Results for H₂O are collected in Table I. The table shows the FCI results (in Hartree) which are the reference points for all other results as they are given in mHartree relative to the corresponding FCI energies. Three geometries corresponding to simultaneous stretching of both O–H bonds are considered, R=1R_e, R=1.5R_e, and R=2R_e, where R_e is the equilibrium value of O–H bonds. The quality of the CCSD energy deteriorates with the O–H bonds stretching and the T₃ effect starts to be important in the CC calculation. Although the inclusion of T₄ is expected to improve the CC energy, the T₃ contribution is dominant.⁴⁹ For the equilibrium geometry R=1R_e this contribution is quite well reproduced by the standard CCSD[T] or CCSD(T) corrections. That is what is expected since the perturbation expansion should be rapidly convergent and the lowest fourth-order term from connected triples in the CCSD[T] as well as in the CCSD(T) correction provides a good estimate of the T₃ contribution to the energy. Denominators in the R-CCSD[T] and R-CCSD(T) corrections introduce only very small changes of these results. The modification {M} is completely unimportant which is again in accordance with the perturbative arguments. Similarly, the {BW} versions do not defer much from those in which the Rayleigh–Schrödinger (RS) denominators are used showing that the denominators in Eq. (80) are dominated by the orbital energy differences. This is what one can expect in the single-reference case when there is a large gap between occupied and unoccupied orbital energy levels. The completely renormalized corrections are only a little bit larger than the

renormalized ones. The situation does not change dramatically when we proceed to the 1.5R_e geometry. Still both, CCSD[T] and CCSD(T), perform well, however, it can be seen that CCSD[T] tends to slightly overshoot the CCSDT result. The importance of the denominators in R-CCSD[T] and R-CCSD(T) is growing as is the gap between CCSD[T] and CCSD(T), and their renormalized counterparts. Also the completely renormalized versions are not so close to the renormalized ones. Once again modifications {M} and {BW} give very small contributions. In spite of the increasing differences all the corrections represent a significant improvement over the CCSD energy. This is, however, not the case for the 2R_e geometry. The quasidegenerate nature of the ground state wave function causes a complete break down of the CCSD[T] correction. The extra term provided by the CCSD(T) scheme reduces the error with respect to FCI by 30%, which does not make the result more sensible. For CCSD[T]{M} and CCSD(T){M} the overestimation of FCI is further reduced but the real improvement is given by the renormalized corrections. In this case the simple modifications contained in the R-CCSD[T]{M,BW} and R-CCSD(T){M,BW} schemes help to obtain results close to the FCI ones. The completely renormalized corrections, in contrast with the simple standard and renormalized corrections, show the same previous tendency to underestimate the FCI energies (Table II).

For the HF molecule four internuclear distances have been selected⁵⁸ ranging from the equilibrium geometry up to R=5R_e. For all the geometries T₃ plays a crucial role in reducing the CCSD error relative to FCI as can be seen from the CCSDT energies. For the equilibrium geometry the situation is similar to that for H₂O. All corrections improve the CCSD energy which can already be considered very good. For R=2R_e the CCSD result is less satisfactory. The CCSD[T] method gives an energy below the FCI one but that is corrected by the extra term in CCSD(T). Changes introduced by other corrections of the [T] type gradually reduce the initial error of -2.725 mH to -0.360 mH. However, in case of the (T)-type corrections the error systematically increases reaching 1.768 mH which can be still considered as relatively small. It should be noted that both modifications, {M} and {BW}, start playing an important role. This becomes really visible when the internuclear distance R=3R_e is considered. In this case both methods, CCSD[T] and CCSD(T), fail completely in spite of the fact that CCSD(T) improves the CCSD[T] result by almost 14 mH. Surprisingly, also a significant contribution comes from CCSD[T]{M} which cuts down the error by another 8 mH. This is because of the importance of monoexcited configurations at large internuclear separations. The {BW} modification seems also quite effective. In fact the R-CCSD(T){M,BW} scheme belonging to the category of simple corrections overestimates FCI only by 2 mH. That can be compared with the original R-CCSD(T) result for which the error is more than 3 times larger. For R=5R_e the starting point is given by the CCSD[T] result -75.101 mH. Two contributions appearing subsequently in CCSD(T) (~22 mH) and in CCSD(T){M} (~14 mH) reduce this error to -39.315 mH. Finally, the renormalized version

TABLE II. The FCI energies (in a.u.) of the ground state for the DZ HF model and energies of CCSD, CCSDT, and CCSD + various noniterative corrections due to triples relative to FCI (in mH). All results, except those corresponding to {M}, {BW}, and {M,BW}, are taken from Ref. 42, and references therein.

	1 R_e	2 R_e	3 R_e	5 R_e
FCI	-100.160 300	-100.021 733	-99.985 281	-99.983 293
CCSD	1.634	6.047	11.596	12.291
CCSDT	0.173	0.855	0.957	0.431
CCSD[T]	-0.070	-2.725	-38.302	-75.101
CCSD[T]{M}	-0.063	-2.218	-30.663	-61.233
R-CCSD[T]	-0.010	-1.127	-13.526	-23.169
R-CCSD[T]{M}	-0.004	-0.749	-10.712	-19.574
R-CCSD[T]{BW}	0.031	-0.715	-11.030	-18.386
R-CCSD[T]{M,BW}	0.037	-0.360	-8.494	-15.263
CCSD(T)	0.325	0.038	-24.480	-53.183
CCSD(T){M}	0.332	0.545	-16.841	-39.315
R-CCSD(T)	0.371	1.137	-6.535	-14.246
R-CCSD(T){M}	0.377	1.527	-3.388	-10.049
R-CCSD(T){BW}	0.402	1.402	-4.873	-10.934
R-CCSD(T){M,BW}	0.408	1.768	-2.044	-7.308
CR-CCSD[T]	0.163	0.700	2.508	3.820
CR-CCSD(T)	0.500	2.031	2.100	1.650

R-CCSD(T){M,BW} gives -7.308 mH, which in spite of more than a tenfold reduction of the initial error, can hardly be considered as a satisfactory result. That shows the limitation of this approach.

To summarize, let us note that to make the triple corrections more applicable to quasidegenerate cases the main effort has been placed in neutralizing the large effect of the lowest-order term constituting the CCSD[T] correction. The other contributions that can be considered are also substantial in such cases helping to obtain a more balanced description than that given by the standard corrections. Obviously, much more numerical experience is required to attain a simple, yet dependable scheme which would be able to well approximate the CCSDT result in a noniterative fashion for more than typically single-reference cases. Both Λ -based formalism²⁷ and expectation value type,^{47,27} might offer further improvement, although a different strategy might be recommended, if more robust corrections are required. The ultimate problem lies in increasingly large higher-rank cluster amplitudes for general bond breaking.

V. CONCLUSION

The problem of the cancellation of unlinked terms in the coupled-cluster equations within a noniterative approach that attempts to include contributions from higher excitation rank cluster operators has been discussed. The standard concept of considering connected contributions only to the CC equations follows from the linked diagram theorem which has been shown to pertain for the iterative CC schemes. Within the usual way of deriving noniterative CC corrections we have reconsidered the unlinked term cancellation problem showing that the energy corrections leave unlinked terms in the CC equations. It seems that the unlinked terms can give cluster amplitudes more flexibility in adjusting to the energy changes especially when they are unphysically large which is the case when the quasidegeneracy is present.

The form of the new corrections differs from the standard ones by the presence of denominators which can be interpreted as an overlap between two wave functions, one of which has a CC character. Similar modifications of the standard corrections have been recently proposed by Kowalski and Piecuch in the context of method of moments of CC equations which describes relations among approximate CC schemes, like CCSD, and the FCI energy.^{42,43} Our derivation, on the other hand, uses classical CC techniques and does not require any reference to the FCI wave function. We also discuss two limiting cases for the energy expression introduced by Kowalski and Piecuch in which it offers a simple interpretation of the results.

An obvious question which might be asked is the validity of the CC approach which introduces disconnected contributions to the cluster operators and the energy destroying rigorous size-extensivity. In fact we have considered size-extensivity as perhaps the essential feature of the coupled-cluster methods. However, very recently several CC methods, for which maintaining rigorous size-extensivity was not possible or practical, have been introduced^{33,37,38} to expediently overcome some of shortcomings of the fully size-extensive CC schemes. The proposed corrections fall into this category of CC methods.

Finally we suggest and discuss the effect some modifications of the simple corrections have on their performance illustrating this with test calculations for DZ H₂O and DZ HF.

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