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REGULAR ARTICLE

Leszek Meissner · So Hirata · Rodney J. Bartlett

Making more extensive use of the coupled-cluster wave function: from the standard energy expression to the energy expectation value

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Abstract The standard coupled-cluster (CC) scheme with single and double excitations in the cluster operator (CCSD) includes only up to quadruple excitations in the equations. The CCSD exponential expansion generates, however, all possible excitations out of the reference function through products of the cluster operators. Clearly, in all standard approximate CC approaches only a part of the CC wave function is used in the equations. If the standard CCSD wave function is inserted into the energy expectation value expression then the complete CCSD wave function contributes to the energy. Such an energy expectation value expression can be presented as a sum of the standard CCSD energy formula plus correction terms. The correction terms provide an information about the quality of the total CC function. Contributions associated with the presence of higher than double excitations in the bra CCSD wave function supplement the CCSD energy obtained within the standard scheme. These contributions can be generated in a sequential way by considering intermediate excitation levels for the bra CCSD wave function in the expectation value expression before reaching the highest excitation level. In this way the importance of particular components differing in the standard and expectation value CCSD energies can be investigated. Some of the contributions can be recognized as close to or identical with the so-called renormalized noniterative corrections to the CC methods. We try to see to what an extent the nonstandard energy expressions, like the energy expectation value or the asymmetric energy formula, can be used to extend the applicability of the CCSD method illustrating our considerations with some numerical examples.

Dedicated to Professor Jean-Paul Malrieu to honor his contribution to quantum chemistry and physics

L. Meissner(✉)
Institute of Physics, Nicholas Copernicus University,
87-100 Toruń, Poland
E-mail: meissner@phys.uni.torun.pl

S. Hirata · L. Meissner · R. J. Bartlett
Quantum Theory Project, University of Florida,
Gainesville, FL 32611, USA

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1 Introduction

The single-reference coupled-cluster (CC) method [1–7] has proved to be very successful in describing nondegenerate states of atoms and molecules. The basic CC approximation with singles and doubles (CCSD) usually provides satisfactory results [8–12]. Having the same number of parameters as the linear configuration interaction (CI) expansion with singles and doubles (CISD), the CCSD method by virtue of employing the exponential ansatz introduces effective approximate description of higher than single and double excitations through products of lower excitation-rank cluster operators. The CCSD equations are obtained by means of the projection technique and the approach is not variational. As a consequence, the CCSD energy does not provide an upper bound to the exact energy like the CISD one. On the other hand the use of the exponential expansion leads to size-extensivity which is nowadays considered a very important property. Size-extensivity means a proper scaling of the energy with the number of particles and is especially important when separation of a system into noninteracting subsystems or extended systems are considered. An extension of the CCSD scheme to include higher than double excitations in the cluster operator is numerically demanding, so different ways of approximate accounting for the effect of triple and quadruple excitations in the cluster operator T have been investigated. Noniterative corrections due to triples (T_3) have emerged as most suitable computational tools in large-scale calculations. While the simplest form of the correction constituting the CCSD + T(CCSD) method (also known as CCSD[T]) [13] gives an approximate but reliable description of contributions from T_3 in nondegenerate cases, the extra term included in the CCSD(T) scheme [14] permits extending its applicability to the cases when some moderate degree of quasi-degeneracy is present.

Along with the development of the standard single-reference CC approaches, possible alternative formulations built upon the exponential ansatz have also been studied. Some of them have arisen from a requirement that the CC methods should be both size-extensive and obtained from a variational principle. These include the normal (NCC) [15], unitary (UCC) [16,17], expectation value (XCC) [18] and extended CC (ECC) methods [15]. Some of the proposed energy functionals assume different parameterization for the bra and ket states which doubles the number of parameters and the number of coupled-cluster amplitude equations [15], some other introduce nonterminating series which can pose serious problems [16–18]. These variational variants of the CC method are usually so much more complicated than the standard one that they have never been really competitive (for a more detailed discussion we refer to Ref. [19]). The interest in variational formulations of the CC method can be easily understood. First, it allows us to take advantage of the generalized Hellmann–Feynman theorem making analytical gradient and property calculations easier. Second, if the variational principle is applied to the symmetric CC energy expectation value functional then one can expect the CC energy not only to give the upper bound but also to smoothly approach from above the exact energy limit with the increasing level of excitations included in T. The improved wave function which includes new parameters must lead to a better energy. This is not what can always be expected in the case of the traditionally formulated CC method when the inclusion of higher excitation-rank T operators can make the energy deviation with respect to the exact full CI (FCI) energy larger, thus the result worse from the energetic point of view. However, since fully variational CC calculations are so much more tedious than the conventional ones then up to very recently [20] even results of benchmark calculations had not been available. This is the reason why Kutzelnigg [21] has proposed a hierarchy of approximate CC methods under the name of improved coupled-cluster (ICC) [21] of which the standard CC method is the first step and which ends with the variational CC scheme. The first method and the last one in this hierarchy are size-extensive while this does not necessarily hold for the steps in between. Kutzelnigg [19] also considers a situation when the cluster amplitudes do not satisfy any stationary conditions. In such a case the energy expectation value, which provides a rigorous upper bound to the exact energy, will give a result being above the variational energy. If the cluster amplitudes are taken from the standard CC calculation then the expectation value expression gives the standard CC energy plus correction terms. According to Kutzelnigg [19] the correction or, more precisely, the leading term in the correction, can be used to see how far the standard CC energy is off from an upper bound and, in this way, to judge its quality.

One of the aspects which can be discussed in this context is the use of CC wave function within particular approaches. Focusing on the case with T restricted to singles and doubles it can be noticed that only a part of the CCSD function that is generated by the exponential expansion is used in the standard CCSD model. Because of a natural termination of the expansion only up to quadruple excitations contribute to the equations. Contrary to that the variational CCSD method involves the complete CCSD wave function in which all possible excitations are included. If the energy expectation value expression is used to determine the energy while the cluster amplitudes are obtained from the standard CCSD scheme then the information about contributions from higher than quadruple excitations is also included in the energy. The CCSD energy expectation value is above the variational one and the difference can show the quality of the standard cluster amplitudes compared to those obtained from the variational principle. On the other hand the difference between the standard CCSD energy and the CCSD expectation value energy can indicate to what an extent the Schrödinger equation with the CCSD wave function is satisfied while projected on higher than doubly excited determinants. Because of the limited number of parameters included in the CCSD wave function the Schrödinger equation is satisfied when the projection space is restricted to singly and doubly excited determinants.

Very recently alternative single-reference CC approaches have also been investigated as a way of extending the applicability of the CC schemes beyond typically single-reference situations. In general, the standard CCSD(T) method is capable of accurate description only of a near-equilibrium region and it usually fails for larger internuclear distances which can be associated with the growing component of nondynamic correlation. Several model calculations employing fully variational CCD approach [20] have shown that, in spite of some improvement over the standard CCD method, the results for stretched bonds cannot be considered satisfactory. The use of the method of moments (leading to an asymmetric energy expectation value-like expression [22]) to correct the CCSD energy [23–27] has provided more promising results. The new versions of the standard CC corrections derived from this expression seem to broaden significantly the range of molecular geometries for which a posteriori corrections can be successfully applied. The so-called renormalized and completely renormalized CC corrections prevent the rapid deterioration of results given by their standard counterparts when quasidegeneracy becomes stronger, thus enabling us to deal more efficiently with the bond-breaking problem. Let us recall here that the expectation-value-type expression was already used while deriving the standard CCSD(T) [14] and CCSD(TQ) [28] corrections but to keep the connected structure of the corrections the relaxation effect of the energy was not taken into account. If this effect is considered in the standard derivations then the renormalized versions can also be obtained, of course, at the cost of giving up size-extensivity of the approach [29]. The use of the CCSD expectation value and the asymmetric energy expression to generate corrections to the CCSD energy have much in common if one assumes that construction of the latter is based exclusively on the CCSD results. Whereas the triple correction cannot be constructed without a perturbative estimate of T_3 and is not present in the CCSD expectation value corrections, the form of quadruple corrections is very much the same in both approaches.

In this paper we try to analyze the problem of correcting the standard CCSD energy. Our considerations are based on employing the energy expectation value as an alternative to the standard CCSD energy expression and are illustrated with some numerical examples involving bond-breaking situations. We try to see to what extent the alternative energy expressions can be useful to extend applicability of the single-reference CC methods. Let us finally mention that the attempts to make the single-reference CC methods capable of describing the states of the multi-reference character are stimulated by problems which can be faced while applying genuine multi-reference CC schemes [10]. It seems, however, that these difficulties can be overcome and a further development of the multi-reference CC approaches is required. Such new formulations of the multi-reference CC methods using pioneering ideas introduced by Malrieu and his co-workers [30] have been recently proposed [31–35].

2 Theory

Single-reference CC methods are built on employing the exponential expansion for the wave function

$$|\Psi\rangle = \exp T|\Phi\rangle, \tag{1}$$

where Φ is usually the Hartree–Fock (HF) determinant and T the second-quantized cluster excitation operator defined with respect to the HF function as a Fermi vacuum. The advantages of this form of the wave function are visible when approximate schemes are considered which are generated by truncating T at some excitation level. The most basic approximation restricts T to single and double excitations:

$$T = T_1 + T_2. \tag{2}$$

In such a case the Schrödinger equation takes the form

$$H_N \exp(T_1 + T_2)|\Phi\rangle = E \exp(T_1 + T_2)|\Phi\rangle, \tag{3}$$

where $H_N = H - \langle\Phi|H|\Phi\rangle$ and E is the electron correlation energy. The exponential expansion generates singly and doubly excited determinants out of the reference function Φ by the direct action of the T operator and all higher excitations are created by products of the cluster operators. The Schrödinger equation (3) cannot be satisfied in the entire space because of the limited number of parameters (cluster amplitudes) in the wave function; however, it can be satisfied in some subspace of the projection space. A natural choice for this subspace is the space spanned by the HF determinant and all singly and doubly excited determinants with respect to it. In such a case the number of unknowns equals the number of equations. In spite of the fact that such a selection of the projection space is most obvious it should be noted that other choices for the projection subspace have also been considered [36]. With the projection space consisting of the HF determinant and all singly and doubly excited determinants the standard CC method with singles and doubles (CCSD) is obtained. The set of CCSD equations reads

$$\begin{aligned}
&E_{\mathrm{CCSD}} = \langle\Phi|H_N(T_2 + \frac{1}{2}T_1^2)|\Phi\rangle,\\
&\langle\Phi_i^a|H_N \mathrm{e}^{T_1+T_2}|\Phi\rangle - \langle\Phi_i^a|T_1|\Phi\rangle E_{\mathrm{CCSD}} = 0,\\
&\langle\Phi_{ij}^{ab}|H_N \mathrm{e}^{T_1+T_2}|\Phi\rangle - \langle\Phi_{ij}^{ab}|T_2 + \frac{1}{2}T_1^2|\Phi\rangle E_{\mathrm{CCSD}} = 0,
\end{aligned} \tag{4}$$

where $i, j, \ldots$ and $a, b, \ldots$ are used to label occupied and unoccupied spin orbitals in Φ, respectively. The $\Phi_{ij\ldots}^{ab\ldots}$ determinant is obtained from the HF one by substituting occupied spin orbitals $i, j, \ldots$ with unoccupied $a, b, \ldots$ ones. It is not so difficult to show the cancellation of disconnected contributions to these equations, so the disconnected terms do not have to be considered in the equations which can be written in terms of connected quantities:

$$\begin{aligned}
&E_{\mathrm{CCSD}} = \langle\Phi|[H_N(T_2 + \frac{1}{2}T_1^2)]_{\mathrm{C}}|\Phi\rangle,\\
&\langle\Phi_i^a|(H_N \mathrm{e}^{T_1+T_2})_{\mathrm{C}}|\Phi\rangle = 0,\\
&\langle\Phi_{ij}^{ab}|(H_N \mathrm{e}^{T_1+T_2})_{\mathrm{C}}|\Phi\rangle = 0,
\end{aligned} \tag{5}$$

where $()_{\mathrm{C}}$ stands for the connected part of the operator. It follows that T is a connected operator and, hence, the CC energy expression is connected as well which is essential for the size-extensivity of the method.

It is easy to notice that with the projection space employed in the standard CCSD approach only a part of the CCSD wave function, Eqs. (1) and (2), can contribute to the equations. The highest excitation level of wave function contributions to the energy is two and it rises to three and four when proceeding to the so-called equations for singles and doubles, respectively. This is because of the at most two-particle character of the Hamiltonian. In this way only a part of the CCSD function, which includes up to quadruple excitations, is represented in the equations and the remaining part does not influence the CCSD result. Alternatively it is possible to start with the CCSD energy expectation value expression

$$E_{\mathrm{CCSD}}^{\mathrm{exp}} = \frac{\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)H_N \exp(T_1 + T_2)|\Phi\rangle}{\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)\exp(T_1 + T_2)|\Phi\rangle}, \tag{6}$$

and make it stationary with respect to $T^\dagger$. This approach makes use of the complete CCSD function. A connected form of $E_{\mathrm{CCSD}}^{\mathrm{exp}}$ [3] is obtained after cancellation of the normalization term in the numerator and the denominator:

$$\begin{aligned}
E_{\mathrm{CCSD}}^{\mathrm{exp}} &= \frac{\langle\Phi|\left(\exp(T_1^\dagger + T_2^\dagger)H_N \exp(T_1 + T_2)\right)_{\mathrm{C}}|\Phi\rangle\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)\exp(T_1 + T_2)|\Phi\rangle}{\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)\exp(T_1 + T_2)|\Phi\rangle}\\
&= \langle\Phi|\left(\exp(T_1^\dagger + T_2^\dagger)H_N \exp(T_1 + T_2)\right)_{\mathrm{C}}|\Phi\rangle.
\end{aligned} \tag{7}$$

The connected form is of little practical use if one wants to calculate $E^{\mathrm{exp}}_{\mathrm{CCSD}}$ exactly since the expansion in powers of T is infinite. The nonterminating expansion arises from the necessity of including the so-called exclusion principle violating (EPV) terms to be able to arrive at the form of the numerator presented in Eq. (7). The cluster amplitude equations can be obtained by variation of the connected form of $E^{\mathrm{exp}}_{\mathrm{CCSD}}$ with respect to $T_1^\dagger$ and $T_2^\dagger$. Whereas variation with respect to $T_1^\dagger$ does not generate disconnected contributions to the equations, variation with respect to $T_2^\dagger$ can produce disconnected terms. It can be seen, however, that the use of the set of equations obtained while varying with respect to $T_1^\dagger$ in the T_2 equations leads to vanishing of the disconnected contributions. Thus, the method is size-extensive since both the cluster amplitude equations and the energy expression are represented by connected terms only. Again, the connected form of the cluster amplitude equations is expressed via infinite expansions in powers of T, so the usefulness of this form in practical applications is limited. The connected expression is, however, important to show that another equivalent form of the variational CCSD equations, which is not explicitly connected, leads to size-extensivity. This form can be obtained by requiring that $E^{\mathrm{exp}}_{\mathrm{CCSD}}$ given by Eq. (6) is stationary with respect to variations of $T^\dagger$:

$$\langle\Phi|X_k^\dagger \exp(T_1^\dagger + T_2^\dagger)(H_N - E^{\mathrm{exp}}_{\mathrm{CCSD}}) \exp(T_1 + T_2)|\Phi\rangle = 0, \quad (k = 1, 2), \tag{8}$$

where X_k is the excitation operator of the excitation-rank k with respect to Φ. Equations (6) and (8), in spite of their complexity, can be solved exactly since we do not have to deal with the nonterminating series. The cancellation of disconnected contributions is purely numerical here. Results of some benchmark calculations based on Eq. (8) have been recently reported [20]. The calculations were done by exploring some of the possibilities given by modified FCI codes.

In general, in the fully variational CC methods not only are the stationary conditions complicated coupled equations but even the evaluation of $E^{\mathrm{exp}}_{\mathrm{CCSD}}$ is also very tedious [37]. Because of that some hierarchies of approximations which start with the standard CCSD scheme in the first step and end with the fully variational CCSD method have been suggested. One of them, the improved coupled-cluster (ICC) method [21], starts from the asymmetric expectation-value-like expression

$$E = \frac{\langle\Phi|(1 + T^\dagger)H_N \exp(T)|\Phi\rangle}{\langle\Phi|(1 + T^\dagger)\exp(T)|\Phi\rangle}, \tag{9}$$

then goes via

$$E = \frac{\langle\Phi|(1 + T^\dagger + \frac{1}{2}T^{\dagger 2})H_N \exp(T)|\Phi\rangle}{\langle\Phi|(1 + T^\dagger + \frac{1}{2}T^{\dagger 2})\exp(T)|\Phi\rangle}, \tag{10}$$

etc., to finally reach the full expectation value expression. The T equations are obtained by varying energy with respect to $T^\dagger$. The first method in this hierarchy can be easily recognized as the normal CCSD method [15]. Another form which has been suggested to see a relation between the expectation value and the traditional CC energy [19] is

$$E_{\mathrm{exCC}} = E_{\mathrm{CC}} + \frac{\langle\Phi|\Lambda \bar{H}_N|\Phi\rangle}{\langle\Phi|\Lambda|\Phi\rangle}, \tag{11}$$

where

$$\Lambda = \exp(T^\dagger)\exp(T), \tag{12}$$

$$\bar{H}_N = \exp(-T)H\exp(T) - \langle\Phi|\exp(-T)H\exp(T)|\Phi\rangle, \tag{13}$$

and T is taken from the standard CC calculation. If T is restricted to singles and doubles and is obtained within the standard CCSD scheme then Eq. (11) gives

$$E_{\mathrm{exCCSD}} = E_{\mathrm{CCSD}} + \sum_{k=3,\ldots,6} \frac{\langle\Phi|\Lambda_k^{12}\bar{H}_N^{12}|\Phi\rangle}{\langle\Phi|\Lambda_0^{12}|\Phi\rangle}, \tag{14}$$

where the superscript 12 indicates that T is restricted to singles and doubles and the Λ_k is used for the k particle component of Λ. The second term on the right hand-side represents a correction which must be added to the standard CCSD energy to arrive at the expectation value energy. It has been suggested that evaluation of the leading term in the correction should be used to obtain an estimate of how far the standard CCSD energy is off an upper bound limit to judge the quality of the CCSD result [19]. However, Eq. (14) is not very convenient for the purpose of systematic study one can make in practice. The reason is that Λ_k is represented by an infinite expansion in powers of T, thus the fact that Λ_k can be restricted to $k = 6$ in the numerator does not introduce a significant simplification. More suitable form can be obtained from

$$\begin{aligned} &E_{\mathrm{exCCSD(k)}} \\ &= \frac{\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)P_k H_N \exp(T_1 + T_2)|\Phi\rangle}{\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)P_k \exp(T_1 + T_2)|\Phi\rangle} \\ &= E_{\mathrm{CCSD}} + \frac{\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)P_k(H_N - E_{\mathrm{CCSD}})\exp(T_1 + T_2)|\Phi\rangle}{\langle\Phi|\exp(T_1^\dagger + T_2^\dagger)P_k \exp(T_1 + T_2)|\Phi\rangle}, \end{aligned} \tag{15}$$

where

$$\begin{aligned} P_k = {} & |\Phi\rangle\langle\Phi| + \sum |\Phi_{i_1}^{a_1}\rangle\langle\Phi_{i_1}^{a_1}| \\ & + \cdots + \sum |\Phi_{i_1,\ldots,i_k}^{a_1,\ldots,a_k}\rangle\langle\Phi_{i_1,\ldots,i_k}^{a_1,\ldots,a_k}|. \end{aligned} \tag{16}$$

It follows that

$$\begin{aligned} E_{\mathrm{CCSD}} &= E_{\mathrm{exCCSD(2)}}, \\ E_{\mathrm{exCCSD}} &= E_{\mathrm{exCCSD(N)}}, \end{aligned} \tag{17}$$

where N is the number of electrons. Here the correction to E_{CCSD} can be expressed in terms of increasing excitation level k admitted by the projection operator P_k and can be computed. The hierarchy of exCCSD(k) schemes may also be employed to discuss some specific features of the asymmetric energy expression in which the CCSD results are exclusively used. Such an approach has been recently proposed and intensively studied [23,22]. The asymmetric energy expression is obtained by projecting the Schrödinger equation on some function χ having a nonzero overlap with the wave function Ψ

$$E = \frac{\langle \chi | H_N | \Psi \rangle}{\langle \chi | \Psi \rangle}. \tag{18}$$

If one of the functions, χ or Ψ, is exact then E is the exact energy regardless of the quality of the other function. The simplest choice for the χ function is the HF determinant Φ. This choice gives the standard energy expression

$$E = \langle \Phi | H_N | \Psi \rangle, \tag{19}$$

where the intermediate normalization for Ψ ($\langle \Phi | \Psi \rangle = 1$) is assumed. Considering more complex projection functions as an alternative to Φ in the energy expression (18) does not make too much sense when Ψ is the exact wave function. It follows that in practice both, χ and Ψ must be approximate. Let us assume that the standard coupled-cluster function is used for Ψ with T truncated at some excitation level i. The cluster amplitudes T are obtained from projecting the Schrödinger equation on determinants of the excitation level up to i. One may say that the Schrödinger equation with such a wave function is satisfied in the projection space spanned by Φ and determinants of excitation level up to i. The situation is analogous to that in the case when Ψ is exact in the sense that as long as χ belongs to the standard CC projection space the asymmetric energy expression gives the standard CC energy and again the use of more complicated form of χ than the HF determinant does not make any sense. In order to obtain other than the standard CC energies, χ must contain a component from the orthogonal complement of the projection space. Let us note that by replacing the standard bra function Φ with such a χ the additional components in the ket CCSD function are also included, so in this way the energy expression benefits from the extension of both the bra and ket functions. Obviously the same concerns the exCCSD(k) scheme. The χ functions can be obtained in different ways. First, they can be provided by some external source [22]. This however, requires performing calculation using a method in which the wave function includes a description of some component from the orthogonal complement of the CC projection space. The resulting energies are difficult to interpret. One may say that, in some sense, they contain a combined effect of the χ and Ψ functions. If one assumes that, in order to keep the computational cost low, the χ function should be obtained by means of some simple and numerically inexpensive method then the question is to what extent the combined effect of two functions poorly describing the system can lead to a high-quality energy using Eq. (18).

The other option which can be considered while making choices for χ is to resign from the external source and base the construction of χ on results contained in the CC wave function Ψ. Assuming the CCSD approximation

$$\begin{aligned} E &= \frac{\langle \chi | H_N \exp(T_1 + T_2) | \Phi \rangle}{\langle \chi | \exp(T_1 + T_2) | \Phi \rangle} \\ &= E_{\mathrm{CCSD}} + \frac{\langle \chi | (H_N - E_{\mathrm{CCSD}}) \exp(T_1 + T_2) | \Phi \rangle}{\langle \chi | \exp(T_1 + T_2) | \Phi \rangle}, \end{aligned} \tag{20}$$

one can see that this is possible because the CCSD expansion produces higher than double excitations. One can select the most important contributions to χ by applying an analysis based on the single-reference perturbation theory. It can be seen that the CCSD expansion produces the lowest order contributions to the even-level excitations, while this is not the case for the odd-level excitations. This is because the lowest order even-level excitations are represented by products of T_2 while for the odd-level excitations the lowest order terms are contained in T_3, $T_2 T_3$, etc. Perturbation theory allows us to build the lowest order estimates of T_3, $T_2 T_3$, etc., so they can be used in the χ function. The simplest choice for the χ function would be

$$|\chi\rangle = [1 + T_1 + \frac{1}{2} T_1^2 + T_2 + R_3(V_N T_2)] | \Phi \rangle, \tag{21}$$

where $R_3(\,)$ projects on triply excited determinants and associates the standard Møller–Plesset energy denominator. If χ of this form [with $(1/2)T_1^2$ neglected] is inserted into Eq. (20) then the so-called completely renormalized CCSD[T] (CR-CCSD[T]) method is obtained [23]. The leading term in the numerator is identical with the CCSD[T] correction so if only this term is included then we have the renormalized CCSD[T] (R-CCSD[T]) correction. Similarly the CR-CCSD(T) and R-CCSD(T) methods can be derived and we refer to Ref. [23] for more detailed description. With corrections for quadruples the situation is simpler since that concerns the even-level excitations and the lowest order quadruple excitations are given by $(1/2)T_2^2$. Because of that the leading term in the quadruple correction arising from Eq. (20) [methods R-CCSD(TQ) and CR-CCSD(TQ)] is identical with that in exCCSD(4), Eq. (15). It is worth noting here that, unlike the CCSD(TQ) correction to the CCSD energy, the CR-CCSD(TQ) correction contains disconnected contributions. Of course, the same concerns the exCCSD(4) scheme.

The use of single-reference perturbative arguments while constructing χ functions within the CR-CCSD(T) and CR-CCSD(TQ) approaches suggests that the applicability of both corrections should be rather restricted to the single-reference situations. In spite of that, the corrections have been successfully tested in the presence of strong quasi-degeneracy. In typically single-reference situations the CR-CC corrections perform slightly worse than their standard counterparts but they behave much better in quasi-degenerate situations. While the standard corrections break down when the degree of quasi-degeneracy is getting high, the R-CC and CR-CC corrections usually do not follow this pattern of behavior and still provide energies quite close to the FCI ones [23,24]. This is mainly because of the presence of the denominator in Eq. (20). This behavior of the R-CC and CR-CC corrections is quite surprising and difficult to explain. As mentioned, formula (18) gives the exact energy if one of the functions, χ or Ψ, is the exact one. In the CR-CC corrections none of them can be considered close to FCI when describing quasi-degenerate states. Their quality depends on the quality of cluster operators which is definitely poor in such a case. Cluster expansions can be successfully applied when the so-called cluster conditions are satisfied. In quasi-degenerate situations neither the cluster conditions are fulfilled nor the perturbative estimate of T_3 can be considered reliable. Thus, the question is whether by using some alternative energy expressions the applicability of CCSD methods can be really extended to quasi-degenerate states when relying exclusively on the CCSD results and on the single-reference perturbative analysis of the cluster amplitudes whose validity can be questioned in such a case. One of the aspects of this problem is the importance of particular contributions to the energy expressions. It should be noted that the cluster amplitudes can be large, so it is hard to say that terms which are not included in the corrections and which are higher in powers of T can be neglected. It seems that their significance increases with the growing degree of quasi-degeneracy, so they should be taken into account.

To study the problem the CCSD expectation-value-like expression, Eq. (15), can be useful especially if applied in cases when contributions corresponding to the even-level excitations in the bra function play a dominant role. Such excitations are normally well represented in the CCSD expansion, so the correction terms appearing in Eq. (15) and the corresponding contributions generated by the CR-CCSD corrections are very close. In the following section results of such model calculations are presented and discussed.

3 Results

Exploring the possibilities given by advanced FCI programs it is relatively easy to successively calculate the correction terms to the CCSD energy generated by increasing value of k in exCCSD(k), Eq. (15), to finally reach the exCCSD energy. Of course, the use of FCI code limits the size of basis sets which can be used so the standard STO-3G basis sets are employed in the calculations. Our calculations are performed for the nitrogen molecule, acetylene and two ionized systems, NO^+ and CN^-, for geometries corresponding to the bond length ranging from 0.9 Å to more than 2 Å. The largest internuclear distance considered in the calculation for a particular system reflects our ability to obtain convergence in the Hartree–Fock calculations. Since general tendencies are quite visible for geometries which are reported we did not put an additional effort to go beyond these distances.

The N_2 molecule is frequently used to test the performance of different kinds of methods in describing potential energy surfaces. Our results for N_2 are shown in Table 1. The reference point for results obtained within approximate schemes is the FCI energy, so energies given by methods other than FCI are reported through their deviation from FCI [in mhartree, ex(k) stands for exCCSD(k)]. The k index in exCCSD(k) method runs from $k = 2$ to $k = 6$ which is the highest excitation level allowed in the N_2 model considered. The $k = 2$ case gives, of course, the CCSD energy. It can be seen from the entries of Table 1 that extensions of the projection from P_2 to P_3 and from P_4 to P_5 do not bring significant changes to the exCCSD(k) energies and that seems to indicate that unlinked triples and pentuples do not play an important role in the CCSD wave function. This is definitely not the case when the even-level excitations, quadruples and sextuples, are considered in the bra function. For the internuclear distance R between 0.9 and 1.4 Å the main contribution to the energy expectation value is associated with inclusion of the quadruples whereas the sextuple contribution is negligible. The energy deviation of exCCSD(4) from CCSD is getting larger while increasing R and that, in accordance with the Kutzelnigg postulate, can be used as a measure of the quality of the standard CCSD approach. The exCCSD(4) scheme can also be used to introduce a correction to the CCSD energy as done in the CR-CC approaches since up to $R = 1.8$ Å it quite effectively reproduces the full exCCSD results. The exCCSD results for this region represent an improvement over the CCSD ones reducing the CCSD deviation from the FCI energy. However, for larger values of R the exCCSD(4) correction is no longer a scheme which includes the leading term (using Kutzelnigg's terminology [19]) because projection on sextuples also gives a significant contribution to the exCCSD energy and, thus, relying on the result given by exCCSD(4) is no longer justified. The quality of the CCSD results deteriorates rapidly and the CCSD function cannot be considered as a reliable source of information for constructing any type of correction. Indeed, the exCCSD energy gap, which can be used as a measure of the quality of the CCSD wave function, increases significantly for $R > 1.7$ Å. Let us recall here that the expectation value expression gives an upper bound to the exact energy, so the rising value of the exCCSD energy with respect to the exact one means the lower quality of the CCSD function. This situation is pictured in Fig. 1. The CCSD method breaks down completely around $R = 1.7$ Å and the exCCSD energies, which are only slightly above the FCI ones for $R \leq 1.7$ Å, are rapidly going up reflecting a sudden deterioration of the quality of the CCSD function. The exCCSD(4) and exCCSD potential energy curves, being very close up to $R = 1.7$ Å, split showing the importance of the additional correction terms generated by exCCSD(6) (equivalent to exCCSD). It is worth noting that the exCCSD(4) energies continue to be very close to the FCI ones making an impression that the method is capable of providing a good approximation to the FCI energies even in cases of complete breakdown of the CCSD scheme. Of course, this can happen when the bra function is arbitrarily truncated at some excitation level and, in this way, contributions which are not negligible are eliminated. The truncation which can be justified for $R < 1.8$ Å is not legitimate for larger R values. This indicates that one should be rather very careful while manipulating with terms which can be potentially of great importance. Values of cluster amplitudes become large in the quasi-degenerate situations, so there is no longer any justification for neglecting terms which are large in powers of T, they become important.

Our results for the HCCH molecule with the H-C bond fixed at 1.08 Å are presented in Table 2. Again the inclusion of the odd-level excitations in the bra function in exCCSD(k) brings very little changes. Up to the C–C bond length of 1.7 Å the leading term in the correction is provided by the projection on quadruples and well reproduces the exCCSD energy.

Table 1 The FCI energies (in a.u.) of the ground state for N_2 obtained with the STO-3G basis set

R (Å)	FCI	CCSD	ex(3)	ex(4)	ex(5)	exCCSD
0.9	-107.293076	1.702	1.711	1.246	1.246	1.243
1.0	−107.549302	2.578	2.598	1.688	1.689	1.681
1.1	−107.654123	3.925	3.966	2.296	2.298	2.276
1.2	−107.677340	5.901	5.974	3.126	3.132	3.078
1.3	−107.659370	8.542	8.659	4.188	4.199	4.076
1.4	−107.623175	11.530	11.697	5.328	5.348	5.087
1.5	−107.581636	13.776	13.980	6.131	6.163	5.634
1.6	−107.542086	12.734	12.936	6.129	6.173	5.184
1.7	−107.508729	3.766	3.889	5.677	5.715	4.504
1.8	−107.483458	−19.532	−19.598	6.024	5.994	8.807
1.9	−107.466114	−59.428	−59.428	6.446	6.258	28.307
2.0	−107.455156	−101.829	−102.445	2.883	2.546	56.967
2.1	−107.448633	−135.738	−136.466	−4.750	−5.139	78.203

Results of other methods are given in mhartree relative to the FCI energies

Table 2 The FCI energies (in a.u.) of the ground state for HCCH obtained with the STO-3G basis set

R (Å)	FCI	CCSD	ex(3)	ex(4)	ex(5)	ex(6)	ex(7)	ex(8)	ex(9)	exCCSD
0.9	−75.612199	0.739	0.742	0.464	0.464	0.457	0.457	0.457	0.457	0.457
1.0	−75.871739	1.091	1.093	0.598	0.598	0.585	0.585	0.585	0.585	0.585
1.1	−75.990613	1.656	1.658	0.816	0.816	0.790	0.790	0.790	0.790	0.790
1.2	−76.025787	2.503	2.505	1.144	1.144	1.098	1.098	1.098	1.098	1.098
1.3	−76.013095	3.661	3.662	1.595	1.595	1.517	1.517	1.516	1.516	1.516
1.4	−75.975029	5.016	5.014	2.134	2.134	2.008	2.008	2.007	2.007	2.007
1.5	−75.925649	6.116	6.106	2.633	2.631	2.448	2.448	2.446	2.446	2.446
1.6	−75.873695	5.844	5.818	2.941	2.935	2.731	2.731	2.728	2.728	2.728
1.7	−75.824461	2.138	2.075	3.331	3.316	3.360	3.359	3.359	3.359	3.359
1.8	−75.780845	−7.630	−7.769	5.131	5.093	6.546	6.544	6.567	6.567	6.567
1.9	−75.744003	−25.318	−25.611	9.673	9.586	16.195	16.188	16.303	16.303	16.303
2.0	−75.713956	−51.038	−51.603	15.652	15.473	35.754	35.737	36.111	36.111	36.113
2.1	−75.690136	−82.441	−83.419	19.374	19.041	64.527	64.491	65.361	65.361	65.365
2.2	−75.671737	−114.575	−116.077	18.138	17.577	94.669	94.606	96.109	96.109	96.116
2.3	−75.657866	−142.871	−144.962	12.441	11.591	117.800	117.706	119.806	119.806	119.816

Results of other methods are given in mhartree relative to the FCI energies

The quality of the CCSD function gets poorer with increasing values of R but the CCSD energy can be to a large extent improved by adding the exCCSD(4) correction. However, for $R > 1.7$ Å the CCSD method breaks down. The CCSD energies significantly overestimate the exact ones and the poor quality of the wave function provided by the CCSD scheme is reflected by the CCSD energy expectation values being higher and higher above FCI energies while increasing R. In spite of that, the exCCSD(4) energy stays close to the FCI one, so the pattern of its behavior, which can be seen in Fig. 2, is similar to that for N_2.

Results for two ionized systems, NO^+ and CN^-, are reported in Tables 3 and 4, and shown in Figs. 3 and 4, respectively. One can observe that changes introduced by projections on triples and pentuples are not so small as they were for N_2 and HCCH; however, again we would like to concentrate on results given by CCSD, exCCSD(4) and exCCSD. As can be seen from Figs. 3 and 4, for a long range of the internuclear distance, energies given by the three methods are very close so they practically form one curve. For larger R values (> 1.6 Å for NO^+ and > 1.8 Å for CN^-) they split to create three well-separated curves. In both cases the CCSD potential energy curves display an artificial hump and this kind of behavior is repeated by the exCCSD(4) and exCCSD curves. After that the CCSD curve is rapidly going down while the exCCSD curve goes up increasing the distance from the FCI one. Surprisingly, while the CCSD and exCCSD energy gap relative to FCI is growing the exCCSD(4) results are again located very close to the exact ones.

Our results show that the CCSD expectation value method can improve the standard CCSD energy when the CCSD method provides sufficiently accurate results and good approximation to the exact wave function. Using a perturbative analysis one can identify the leading correction term in exCCSD(4) giving an estimate of the difference between CCSD and exCCSD energy. In more general approaches one can also rely on perturbative estimates of connected triples as long as the use of perturbation theory arguments is justified. This is definitely not the case when a significant contribution of nondynamic correlation is present. If the standard CCSD method breaks down then the use of the expectation value expression does not help since the description given by the CCSD wave function is not reliable. It can happen, however, that by ignoring the fact that we have quasi-degenerate

Table 3 The FCI energies (in a.u.) of the ground state for NO^+ obtained with the STO-3G basis set

R (Å)	FCI	CCSD	ex(3)	ex(4)	ex(5)	exCCSD
0.9	−127.025789	2.910	3.229	2.590	2.597	2.592
1.0	−127.278458	4.744	5.506	4.226	4.249	4.235
1.1	−127.383797	7.650	9.282	6.890	6.958	6.918
1.2	−127.412255	12.019	15.140	11.005	11.175	11.074
1.3	−127.402780	18.178	23.517	16.925	17.289	17.060
1.4	−127.376476	26.308	34.595	24.880	25.556	25.082
1.5	−127.344738	36.847	49.257	35.821	37.004	36.103
1.6	−127.313767	51.871	75.219	58.110	61.557	59.804
1.7	−127.286554	67.623	115.945	107.855	123.387	118.909
2.0	−127.228486	−101.745	−111.992	19.131	13.664	83.408
2.1	−127.214678	−133.053	−150.103	12.810	2.143	108.170

Results of other methods are given in mhartree relative to the FCI energies

Table 4 The FCI energies (in a.u.) of the ground state for CN^- obtained with the STO-3G basis set

R (Å)	FCI	CCSD	ex(3)	ex(4)	ex(5)	exCCSD
0.9	−90.681351	1.461	1.551	1.245	1.246	1.245
1.0	−90.938300	2.192	2.398	1.833	1.837	1.833
1.1	−91.051308	3.312	3.753	2.753	2.766	2.756
1.2	−91.082902	4.984	5.853	4.166	4.198	4.175
1.3	−91.070334	7.376	8.949	6.245	6.318	6.267
1.4	−91.035673	10.630	13.242	9.140	9.287	9.183
1.5	−90.991778	14.807	18.793	12.917	13.186	12.985
1.6	−90.945986	19.851	25.434	17.514	17.949	17.581
1.7	−90.902419	25.672	32.845	22.830	23.438	22.808
1.8	−90.863334	33.011	41.926	29.751	30.516	29.524
1.9	−90.829775	45.787	60.996	45.583	47.693	46.097
2.0	−90.801830	61.595	93.788	82.361	92.338	88.767
2.3	−90.744386	−86.941	−93.674	15.522	12.022	67.152
2.5	−90.720480	−133.075	−149.094	4.635	−6.371	101.507

Results of other methods are given in mhartree relative to the FCI energies

situation and using a scheme whose validity is restricted to single-reference cases, results incidentally close to the exact ones can be obtained. This makes an impression that by using alternative energy expressions a single-reference CC approach is capable to deal efficiently with a multi-reference situation. In our calculations such an example is given by the exCCSD(4) scheme which, by being somewhere between CCSD and exCCSD, gives energies close to the FCI ones. This is, of course, because of neglecting some important contributions appearing in the exCCSD expression.

There is no doubt that it would be nice to have a single-reference method whose applicability would be extended beyond typically single-reference cases. It is, however, hard to believe that there is a way of a posteriori correcting a method which gives completely wrong results relying only on information coming from these results. It seems more sensible to employ a single-reference scheme in which an additional information about nondynamic correlation coming from some external source is effectively introduced [38–45].

4 Conclusion

In this paper we have tried to see to what extent the applicability of the standard CCSD schemes can be extended. In view of significant problems associated with the use of multi-reference CC methods and many-body perturbation theories, making the single-reference CC approaches more efficient in dealing with quasi-degenerate situations may seem very attractive. We investigate possibilities given by employing the CCSD energy expectation value expression. The scheme has been advocated by Kutzelnigg perhaps not as a way of improving the standard CCSD method but at least as a way of checking the quality of the CCSD results. A hierarchy of the exCCSD(k) schemes similar to that suggested by Kutzelnigg can be used to show the importance of particular components contributing to the CCSD energy expectation value. Our results indicate that when the CCSD description is sufficiently accurate then the information contained in the CCSD wave function can be successfully used for a further improvement of the CCSD energy. However, in multi-reference cases when the CCSD scheme breaks down the information about the wave function provided by CCSD is not reliable and therefore any single-reference estimate used for constructing the correction terms based on the CCSD result either. The terms which can be considered most important in the single-reference cases are usually not the leading ones when the quasi-degeneracy is present since other terms, which can be neglected when the CCSD method performs well, can give quite large contributions in such a situation. These terms usually contain high powers of T and, since the cluster

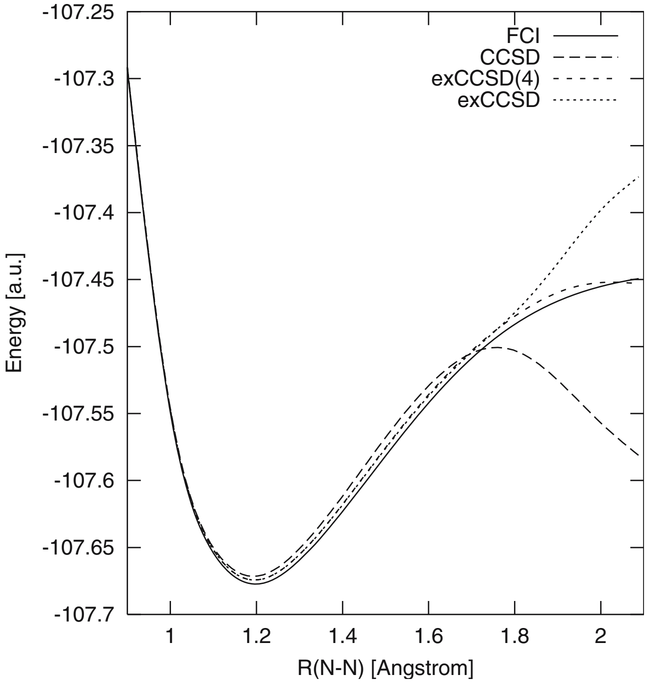

Fig. 1 Comparison of the FCI potential energy curve for STO-3G model of the N_2 molecule with those given by the standard CCSD, exCCSD(4) and exCCSD

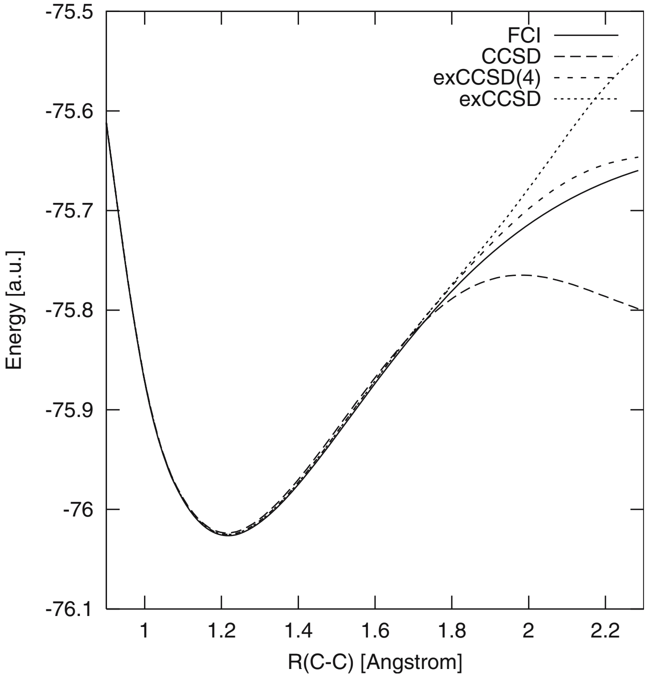

Fig. 2 Comparison of the FCI potential energy curve for STO-3G model of the HCCH molecule with those given by the standard CCSD, exCCSD(4) and exCCSD

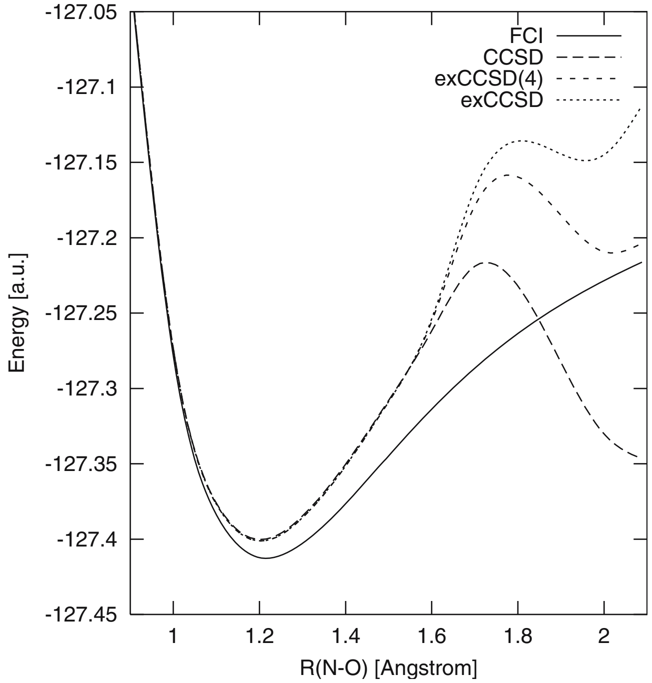

Fig. 3 Comparison of the FCI potential energy curve for STO-3G model of the NO^+ molecule with those given by the standard CCSD, exCCSD(4) and XCCSD

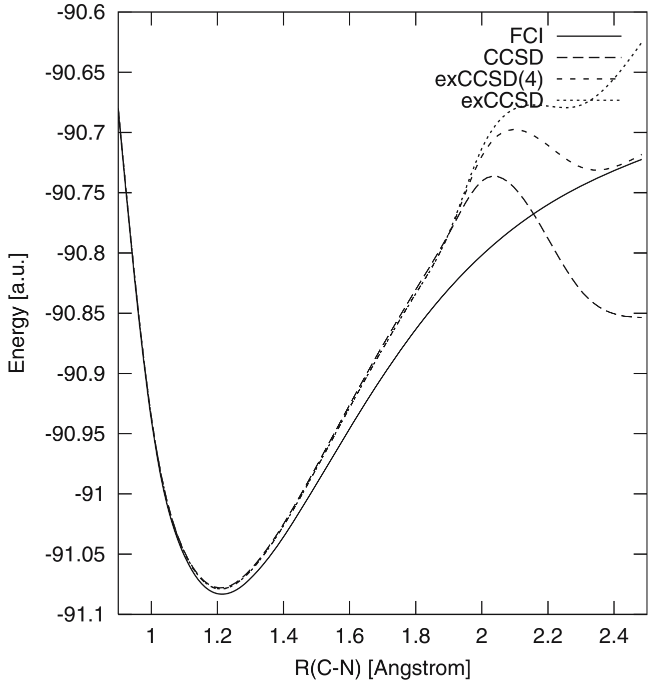

Fig. 4 Comparison of the FCI potential energy curve for STO-3G model of the CN^- molecule with those given by the standard CCSD, exCCSD(4) and XCCSD

amplitudes can be large trying to describe a significant component of nondynamic correlation, they must be taken into consideration. As our calculations show, if these important contributions are neglected by including only low-level excitations in the bra CCSD function then the resulting scheme can incidentally provide energies very close to the FCI ones.

The exCCSD(k) scheme can be considered as a special case of slightly more general approach employing the asymmetric energy expression in which the CCSD results are exclusively used. Since both approaches are essentially based on the same idea, our findings to a large extent also concern the R-CC and CR-CC corrections. It follows from our study that it is rather difficult to expect that in cases of the complete breakdown of the CCSD method the CCSD energy can be effectively a posteriori corrected by using alternative energy expression. More extensive use of the CCSD wave function cannot help when the CCSD description is not reliable. Methods which combine a multi-reference type of scheme and a single-reference CC approach look more promising; however, in our opinion an additional effort should also be put in developing multi-reference CC and MBPT methods. Several such attempts based on the concept of intermediate Hamiltonian introduced by Malrieu and his co-workers [30] have been recently made.

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