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Externally and internally corrected coupled cluster approaches: an overview

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Abstract The single-reference (SR) coupled-cluster (CC) approaches proved to be remarkably efficient in handling the dynamic correlation and continue to be widely exploited in quantum chemical computations of the molecular electronic structure. Yet, in the presence of quasi-degeneracy, e.g., when handling molecules away from their equilibrium geometry or when dealing with strongly correlated systems, a proper account of a non-dynamic correlation becomes essential and calls, in general, for a multi-reference (MR) type methodology. However, in view of the ambiguity, complexity, and computational demands of such MR approaches it is tempting to design SR CC type methods that are capable of accommodating both kinds of correlation effects. One avenue how to achieve this goal is to employ the complementarity of perturbative (i.e., CC) and variational (i.e., UHF, VB, CI, CAS SCF, etc.) type approaches and exploit the latter to remedy the CC methods—primarily CCSD or CCSD(T)—for the lack of the static or non-dynamic correlation effects. This leads to the so-called *externally corrected* (ec) ecCCSD or ecCCSD(T) approaches, which amend the standard CCSD or CCSD(T) methods by accounting for higher-than-pair clusters, extracted from various external sources. The same goal that leads simultaneously to more efficient SR CC algorithms may also be achieved by an effective implicit account of higher-order clusters via the so-called *internally corrected* methods (e.g., ACP-D45, ACCD, ACPQ, etc). While both types of these approaches were formulated and exploited long time ago, they recently enjoyed a certain renaissance. The objective of this work is to review, classify, and interrelate these efforts and highlight the advances made in this direction.

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1 Introduction

The coupled cluster (CC) approaches [1–4] (for recent reviews, see, e.g., [5–13], for a historical perspective, see [14,15]) represent one of the most successful and efficient ways of handling the correlation effects in calculations of the atomic and molecular electronic structure. This is particularly true for closed-shell, non-degenerate ground states, in which case the single-reference (SR) CC methods are being successfully used, even though much progress has also been made in handling of quasi-degenerate and open-shell systems, including excited states, by relying on multi-reference (MR) CC approaches (see, e.g., Ref. [16,17]). Nonetheless, the exploitation of CC Ansätze for quasi-degenerate or highly-degenerate states, such as found in metallic-like extended systems and in molecular systems away from their equilibrium geometry, i.e., when breaking chemical bonds or generating potential energy curves (PECs) or surfaces (PESs), is far from being settled. For this reason there has been recently a renewed interest in what we refer to as the externally and internally corrected CC approaches that were first explored more than three decades ago. These methods eventually developed into a number of practical schemes that enable an efficient handling of quasi-degeneracy in bond-breaking situations and in strongly correlated systems. It is the goal of this paper to systematize and classify these methods, as well as to elucidate their relationship with recent new developments.

The CC methods are based on Hubbard's *connected cluster theorem* [18] of the many-body perturbation theory (MBPT). This theorem asserts that the exact wave function $|\Psi\rangle$ of an N-electron system can be expressed in the exponential form in terms of i-body *connected* cluster components T_i acting on an independent particle model (IPM) wave function $|\Phi_0\rangle$ (usually represented by a single-determinant Hartree–Fock wave function), i.e.,

$$|\Psi\rangle = e^T |\Phi_0\rangle \quad \text{with} \quad T = \sum_{i=1}^{N} T_i, \tag{1}$$

where we employed the intermediate normalization $\langle\Phi_0|\Psi\rangle = 1$. The efficiency of this approach stems from the fact that higher than two-body contributions can be largely accounted for via the products of the lower-order components that arise thanks to the exponential Ansatz. This is particularly the case for the four-body clusters that may be often efficiently represented via the products of pair clusters, which is sometimes symbolically represented by the inequality $T_4 \ll \frac{1}{2}T_2^2$.

Next, due to the fact that the electronic Hamiltonian involves at most two-body interactions, the exact correlation energy $\Delta E = E - \langle H \rangle$ relative to some IPM reference $|\Phi_0\rangle$ with energy $\langle H \rangle \equiv \langle\Phi_0|H|\Phi_0\rangle$, as given by the time-independent Schrödinger equation

$$H_N|\Psi\rangle = \Delta E|\Psi\rangle \quad H_N = H - \langle H \rangle, \tag{2}$$

where H_N designates the normal product form of the Hamiltonian (cf., e.g., [1,2,4, 19]), is fully determined by the one- and two-body cluster components T_1 and T_2, respectively, namely

$$\Delta E = \langle \Phi_0 | H_N e^T | \Phi_0 \rangle = \left\langle \Phi_0 \left| H_N \left(T_1 + T_2 + \frac{1}{2} T_1^2 \right) \right| \Phi_0 \right\rangle, \tag{3}$$

or by T_2 only if we employ the maximum overlap or Brueckner molecular orbitals (BMOs), in which case T_1 vanishes. Nonetheless, the higher-order cluster components $T_i, i > 2$, contribute thanks to their interaction with T_1 and T_2, as implied by the chain of CC equations that results when we project Schrödinger equation (2), with $|\Psi\rangle$ given by the cluster Ansatz of Eq. (1), onto the i-times excited configuration states $|\Phi_k^{(i)}\rangle$, $\langle \Phi_k^{(i)} | \Phi_l^{(j)} \rangle = \delta_{ij} \delta_{kl}, (i, j = 1, 2, \ldots, N; k, l$ ranging), i.e.,

$$\langle \Phi_k^{(i)} | H_N e^T | \Phi_0 \rangle_C = 0 \quad i = 1, 2, \ldots, N, \tag{4}$$

where the subscript C implies a restriction to only the *connected* components.

Needless to say that we assume here a standard *ab initio* or a semi-empirical approach, in which one employs a finite-dimensional subspace of a general N-electron space spanned by a chosen set of atomic orbitals. The explicit CC equations then take the form of a system of nonlinear algebraic equations, i.e.,

$$a_k + \sum_i b_{ki} t_i + \sum_{i \leq j} c_{kij} t_i t_j + \cdots = 0, \tag{5}$$

where t_i are relevant cluster amplitudes and the coefficients a_k, b_{ki}, c_{kij}, etc. are most easily found using diagrammatic techniques of the second quantization formalism (see, e.g., [1–11]). In our developments we found it beneficial to rely on the orthogonally spin adapted (OSA) form of the CCD or CCSD equations [20]. In this case the important, pair-interaction, nonlinear terms are given by the five Goldstone–Hugenholtz-type diagrams (cf. Fig. 3 of [20]), unless we employ the unitary group approach (UGA) [21,22] CC formalism [23,24].

The basic workhorse which provides the required T_1 and T_2 cluster amplitudes is the CCSD method that results by setting $T_i = 0$ for $i > 2$ in the CC chain (4). This decouples the CCSD equations involving the T_1 and the T_2 clusters from the rest of the chain. The use of BMOs reduces then CCSD to CCD, which involves only pair-clusters T_2. A small, but often important T_3 component is usually accounted for perturbatively via the CCSD(T) method [25–29], which is often referred to as the "gold standard" of quantum chemistry, since it provides very accurate and reliable results. Unfortunately, this is no longer the case when handling strongly correlated or quasi-degenerate systems when CCSD(T), and often even CCSD itself, break down.

The simplest well-known example of such strongly-correlated systems is the π-electron model of cyclic polyenes $C_N H_N$ having a non-degenerate ground state ($N = 4\nu + 2$), as described by semi-empirical Hubbard or Pariser–Parr–Pople (PPP)

Hamiltonians, modeling liner metallic-like systems with Born-von Kármán boundary conditions (see, e.g., [30–33] and references therein). Indeed, with the increasing size of these polyenes the importance of quadruples, hexuples, etc, also increases to a degree that the CCD method completely breaks down [33], as do even higher-order versions, such as the CCSDTQ method [34]. In fact, some of the connected quadruples no longer possess the corresponding disconnected quads, and similarly for hexuples and higher order clusters, the number of which increases with the excitation order [35], indicating a very complex structure of the pertinent wave function (as also implied by the Bethe Ansatz; see, e.g., [36]). Indeed, as stated by Thouless [37]: "the wave function of a many-body system is so complicated that any approximation to it will be almost orthogonal to it". We note here that in the case of cyclic polyenes the CCD method is equivalent to CCSD, since the MOs are given by the symmetry as Bloch orbitals and thus represent BMOs. In the following, for the sake of simplicity, we will often assume that $T_1 = 0$. Moreover, in the case of the Hubbard Hamiltonian, the geometry is irrelevant, since only the on-site Coulomb integrals are involved.

Another useful system enabling one to continuously vary the degree of quasi-degeneracy via a single geometry parameter, and which can be exploited at the *ab initio* level, turned out to be the so-called H4 and P4 models involving four hydrogen atoms in either isosceles trapezoidal (H4) or rectangular (P4) configurations [38]. These models have been exploited in well over 200 studies [39] that explore the ability of various approaches to handle the quasi-degeneracy effects. They were later extended to the H8 model [40] and the very challenging S4 model [41]. Further, the same kind of difficulties when using the standard CC approaches arise in bond-breaking situations, being particularly severe in the triple-bond breaking and simultaneous multiple-bond breaking (for early work, see, e.g., [42]).

One way of accounting for the above mentioned deficiencies of the standard SR-CC approaches is via the so-called *externally corrected* (ec) CC methods [43–45]. The principal idea here is based on the fact that the electronic Hamiltonian involves at most two-body potentials, so that not only the energy is fully determined by the one- and two-body clusters, but also the bi-excited configurations can directly interact with at most quadruply-excited ones. We know that the CCD or CCSD equations arise by neglecting the three- and four-body clusters (i.e., by setting $T_3 = T_4 = 0$), which decouples them from the rest of the CC chain. Thus, if we could extract a suitable approximation $T_3^{(0)} \approx T_3$ and $T_4^{(0)} \approx T_4$ of, respectively, the T_3 and T_4 clusters from some independent source and account for them in the CCD equations, i.e.,

$$\left\langle \Phi_k^{(i)} \left| H_N \left(T_2 + \frac{1}{2}T_2^2 + T_3^{(0)} + T_4^{(0)} \right) \right| \Phi_0 \right\rangle_C = 0, \tag{6}$$

we would achieve a more meaningful decoupling of the CC chain (4) than that provided by the standard CCD. We refer to such methods as the *externally corrected* CCD or, including singles, CCSD and designate them as ecCCD and ecCCSD, respectively. In fact, if we would choose the exact T_3 and T_4 clusters, extracted, for example, from the exact full configuration interaction (FCI) wave function, then the ecCCSD equations (6) would yield the exact FCI energy.

Now, this idea opens up a question how to find a suitable external source of approximate $T_3^{(0)}$ and $T_4^{(0)}$ clusters that would be easy to generate and that would provide a good approximation to the exact ones. Before we dwell into this problem let us mention that, historically, such attempts led to a realization that the role of the T_4 clusters can be accounted for by a cancelation of certain terms in standard CCD or CCSD equations, namely those represented by the diagrams that are not separable over the internal hole lines [38,46]. We shall refer to such approaches as the *internally corrected* (ic) CC methods and address them in Sect. 3.2.2.

2 CC formalism ancillaries

Prior to dealing with the ecCC and icCC approaches we wish to point out a few relevant items concerning the role played by the molecular orbitals (MOs) or spin-orbitals (MSOs) in the CC formalism and in its spin adaptation, as well as to comment on distinct ways which can be employed to truncate the full chain of CC equations.

The basic general form of CC equations employs MSOs $|A\rangle \equiv |a\rangle|\sigma\rangle$, given by a simple product of a MO $|a\rangle$ and a pure spin-up or spin-down functions $|\sigma\rangle$, $\sigma = \alpha, \beta$. The advantage of such an approach is its generality, enabling to treat, in principle, both closed- and open-shell systems. In the latter case one often employs the unrestricted Hartree–Fock (UHF) reference and the corresponding MSOs. This may also be beneficial when breaking chemical bonds. Of course, the use of the UHF MSOs generally results in a spin-contamination of the states considered. However, when handling closed-shell singlet ground states, such a spin-nonadapted approach is computationally uneconomical, since it unnecessarily increases the dimension of the problem. For these very reasons one strives, whenever possible, for a spin-adapted formalism.

Considering closed-shell, singlet, ground states, the simplest way to spin-adapt the CC equations is to rely on the Goldstone version of the relevant diagrams and to associate a factor of two with each closed-loop of oriented lines [1,2,4]. This implies, however, that one implicitly employs non-orthogonal configuration states $|\Phi_k^{(i)}\rangle$. This is of little importance in actual applications when considering at most doubly-excited configurations, i.e., when $k \leq 2$. Yet, already when including triples, this unnecessarily increases the number of amplitudes considered (for details see [4]). Nonetheless, even when we are primarily interested in CCD or CCSD, the use of the OSA formalism [20] is beneficial, providing sparser matrices for cluster coupling coefficients and enabling us to cast the CC formalism into the SCEP (self-consistent electron pair) form, as shown by Chiles and Dykstra [46]. The OSA formalism is also useful for gaining a better insight into the approximate coupled pair (ACP) type approximations, as we shall see below.

In order to generate the OSA CC formalism, we have basically two options: We can employ either the *particle-hole particle-hole* (*ph–ph*) or the *particle–particle hole–hole* (*pp-hh*) coupling, the latter being preferable for several reasons [20] (cf. also [47–51]). It not only leads to a simpler formalism, but it also possesses simple transformation properties for the relevant configuration states and corresponding cluster amplitudes [20] (for the case of triples, see [52]). We shall see later that the OSA CC formalism is also beneficial when formulating icCCD, particularly the so-called

ACPQ (ACP with quadruples) approach [53] (see also [33]). Indeed, most of our work dealing with the icCCD approaches relied on the OSA version of CCD (or CCSD).

We next address the options for a truncation of the CC chain of equations (4), $i = 1, 2, \ldots, N$, focussing on CCD or CCSD methods that provide the essential T_2, or T_1 and T_2, clusters that are required to determine the desired energy, Eq. (3). As already mentioned, the standard way is to simply truncate by the excitation order, i.e., to ignore the higher-order cluster components and the corresponding higher-excited configurations. Thus, for CCSD, we set $T_3 = T_4 = 0$ and consider equations projected onto the singly- and doubly-excited configurations, $|\Phi_k^{(1)}\rangle$ and $|\Phi_k^{(2)}\rangle$, respectively, thus achieving a decoupling from the rest of the CC chain, Eq. (4). Similarly for CCSDT we set $T_4 = T_5 = 0$, for CCSDTQ $T_5 = T_6 = 0$, etc., since $|\Phi_k^{(i)}\rangle$ configurations can interact at most with $|\Phi_k^{(i+1)}\rangle$ and $|\Phi_k^{(i+2)}\rangle$ configurations. The advantage of this type of truncation is its simplicity and a straightforward nature. Yet, it leads to a formalism that comprises a number of high-order terms in the resulting non-linear algebraic equations that involve few-body clusters, in particular the amplitudes constituting T_1. Indeed, already at the CCSD level we require quartic terms associated with the $\frac{1}{4!}T_1^4$ component. Although the number of one-body clusters is relatively small and they can be completely eliminated by relying on BMOs, they may play a non-negligible role when employing non-HF MOs. Of course, the number of such non-linear terms increases when proceeding beyond the CCSD level, in which case it will involve even higher-order clusters than T_1.

Another option for a truncation of the CC chain of equations is to avoid terms that play a negligible role, such as those involving one-body clusters just mentioned or, generally, even those involving T_i clusters, such as $T_j T_{(i-j+k)}$ with $k = 0, 1, 2$ and $j = 1, 2, \ldots$. We can roughly assess the importance of individual terms by considering the lowest order of the perturbation theory (PT), based on the IPM zero-order wave function, in which such terms will contribute for the first time and eliminate those that contribute to the wave function beyond the prescribed cut off (cf., e.g., Table II of [54]). We note that such an approach was successfully used in the first *ab initio* application of the CC method which explored the role of triexcited clusters [4]. It may also be beneficial to exclude some terms in the standard CC equations, as in the icCC approaches, as will be apparent later on (cf. Sect. 3.2.2).

Yet another interesting approach, initiated by Bartlett and Musiał [55,56], is to consider only those terms in the CC equations that provide an exact result for an n-electron system. This leads to the so-called nCC hierarchy of CC equations, which will be addressed in Sect. 3.2.2.1. An alternative way to simplify standard approaches that proceed beyond the CCSD level is to delineate a subset of MOs bordering the Fermi level as the so-called active MOs and to consider only a subset of higher-than-pair cluster amplitudes that involve these active MOs. This leads to various CCSDt or even CCSDtq [57,58] or, e.g., CAS(4,4)CCSD [59] approaches.

3 Classification of approximate CCSD approaches

We shall classify the CCSD approaches according to whether they correct the resulting CCSD energy *a posteriori*, based on the PT, such as CCSD(T) [28], or whether they

first correct the CCSD equations and evaluate the energy using *a priori* corrected cluster amplitudes. We refer to the former ones as the *energy correcting* methods and to the latter ones as the *amplitude correcting* approaches. Those correcting the energy perturbatively can do so also during the iterative process, as in the CCSDT-*n* approaches [26,27].

The amplitude correcting approaches can then do so either externally (ecCCSD), relying on externally generated higher-order cluster amplitudes (e.g., [43]), or internally (icCCSD) by deleting specific cluster components in standard CCSD equations, as in the ACP-D45, ACCSD, ACPQ, etc. methods (e.g., [38]). The latter can then be based either on hypothetical UHF-implied higher-than-pair clusters [53] or on the terms that give a vanishing contribution for *n*-electron systems when considering, e.g., *n*CC methods [55,56], in particular 2CC, or be guided by the exclusion principle violating (EPV) terms and CEPA ideas (see below). We shall see that, remarkably, different approaches may lead to essentially the same method.

3.1 Energy-corrected approaches

Although we focus in this work on amplitude corrected CC methods, we briefly consider the energy-based corrections (for a comparison of the energy and amplitude corrected approaches see [60–62]). The simplest way to approach this topic is to start with the following energy-type functional [60]

$$\mathcal{E} \equiv \mathcal{E}(\chi, \Psi) = \frac{\langle \chi | H | \Psi \rangle}{\langle \chi | \Psi \rangle}, \tag{7}$$

which yields the exact energy E

$$E \equiv \mathcal{E}_{\text{exact}} = \frac{\langle \chi | H | \Psi_{\text{exact}} \rangle}{\langle \chi | \Psi_{\text{exact}} \rangle} = \frac{\langle \chi_{\text{exact}} | H | \Psi \rangle}{\langle \chi_{\text{exact}} | \Psi \rangle}, \tag{8}$$

when either the bra or the ket state represent the exact wave function. Of course, $|\chi_{\text{exact}}\rangle \equiv |\Psi_{\text{exact}}\rangle$.

Using now the CC Ansatz (1) for $|\Psi\rangle$ in (7) we can write

$$\mathcal{E}(\chi, \text{CC}) = \frac{\langle \chi | H | e^T \Phi_0 \rangle}{\langle \chi | e^T \Phi_0 \rangle} = D^{-1} \langle \chi | H | e^T \Phi_0 \rangle, \tag{9}$$

where we designated the norm by D, $D \equiv \langle \chi | e^T \Phi_0 \rangle$. Considering, next, the numerator of Eq. (9) and using the resolution of the identity, we find that

$$\begin{aligned}
\langle \chi | H | e^T \Phi_0 \rangle &= \sum_k \langle \chi | e^T | \Phi_k \rangle \langle \Phi_k | e^{-T} H e^T | \Phi_0 \rangle \\
&= \langle \chi | e^T | \Phi_0 \rangle \langle \Phi_0 | \overline{H} | \Phi_0 \rangle + \sum_{i \geq 1, \Phi_k^{(i)} \notin \Omega_i} \sum_k \langle \chi | e^T | \Phi_k^{(i)} \rangle \langle \Phi_k^{(i)} | \overline{H} | \Phi_0 \rangle,
\end{aligned} \tag{10}$$

where $\overline{H}$ designates the similarity transformed Hamiltonian, i.e., $\overline{H} = e^{-T} H e^{T} = (H e^{T})_{\mathcal{C}}$, with $\mathcal{C}$ indicating again the connected component and Ω_i represents the set of configurations spanning the i-times excited configuration space that are considered at a given level of the CC approach. Clearly, the terms $\langle \Phi_k^{(i)} | \overline{H} | \Phi_0 \rangle$ with $\Phi_k^{(i)} \in \Omega_i$ vanish in view of the validity of CC equations (6).

In the case of CCSD we can thus write

$$\mathcal{E}(\chi, \text{CCSD}) = E_{\text{CCSD}} + D^{-1} \sum_{i > 2} \sum_k \langle \chi | e^T | \Phi_k^{(i)} \rangle \langle \Phi_k^{(i)} | \overline{H} | \Phi_0 \rangle$$
$$\equiv E_{\text{CCSD}} + \Delta \mathcal{E}(\chi, \text{CCSD}), \tag{11}$$

where $i > (2)$ implies that the sum extends over higher than doubly-excited configurations $|\Phi_k^{(i)}\rangle$ and $T = T_1 + T_2$ in both D and $\overline{H}$, which in turn implies that $\langle \chi | e^T | \Phi_k^{(i)} \rangle$ vanishes unless $|\chi\rangle$ involves higher-than-doubly-excited configuration states. Thus, as long as $|\chi\rangle$ belongs to the space spanned by singly- and doubly-excited configurations (or in the general CCSDTQ$\cdots$ case to the space spanned by the relevant excited state manifold Ω), we always obtain the standard CCSD (or CCSDTQ$\cdots$) energy. However, when $|\chi\rangle$ contains higher-than-doubly-excited configurations [or, in general, $|\chi\rangle \notin \text{Span}(\Omega)$], the energy given by Eq. (11) equals the standard CCSD energy E_{CCSD}, plus the correction $\Delta \mathcal{E}(\chi, \text{CCSD})$, represented as a linear combination of moments $\langle \Phi_k^{(i)} | \overline{H} | \Phi_0 \rangle$. For this reason this approach is sometimes referred to as the *method of moments* (MM) CC (see also [63]), as well as the *energy-corrected* or the *energy-based* CC approach.

The last factor in Eq. (10) or in the expression for $\Delta \mathcal{E}(\chi, \text{CCSD})$, as implied by Eq. (11), (namely a projection onto the i-fold excited configuration $|\Phi_k^{(i)}\rangle$ of the similarity transformed Hamiltonian acting on reference $|\Phi_0\rangle$), is referred to as an i-body (or ith order or i-tuple) moment (or, simply a moment), and is designated as $M_k^{(i)}$. Clearly, the zero order moment $M_0^{(0)}$ (when $|\Phi_k^{(i)}\rangle \equiv |\Phi_0\rangle$) gives the standard CC (or CCSD) energy, while the CCSD equations require the vanishing of the first and second order momenta, i.e., $M_k^{(1)} = M_k^{(2)} = 0$. The state $|\chi\rangle$ must thus involve at least triply-excited configurations lest the $\Delta \mathcal{E}(\chi, \text{CCSD})$ correction vanish. This correction may thus be decomposed into the triple, quadruple, etc., components. The highest nonvanishing moment in the CCSD case is then $M_k^{(6)}$ [62].

Kowalski and Piecuch introduced several versions of the MM-CC approaches [64,65], including the renormalized (R-) and the completely renormalized (CR-) CCSD(T) and CCSD(TQ) methods. Later on, Piecuch and Włoch [66,67] reformulated these methods in terms of the left eigenstates of the similarity transformed Hamiltonian of CC theory [68,69], thus developing the so-called CR-CC(2,3) method [or, generally, the CR-CC(m_A, m_B) methods] that provide a noniterative correction to the CC energy due to the higher-than-m_A-tuply excited clusters and the excitation level m_B. These approximations not only encompass and provide an insight into the previously formulated noniterative CC methods, such as CCSD(T) but, moreover, are size extensive and very accurate. In particular, the CR-CC(2,3) method corrects for the triples and mimics well the full CCSDT approach, even in the bond-breaking situations where CCSD(T) fails (see [70] for examples and extensive references to an earlier work).

In order to account for quadruples one would need CR-CC(2,4) approach, which is computationally much more demanding (cf., e.g., [71]).

Finally, we must mention here the so-called CCSDT-n methods [26,72–75] and their various "a" and "b" variants (see also [10]), whose iterative versions could also be counted among the amplitude-correcting methods. However, their CCSD[T] or CC4SD[T] [26] and the ubiquitous CCSD(T) [28] versions simply add a non-iterative triple correction to the CCSD energy and may thus be regarded as the energy-correcting methods.

3.2 Amplitude-corrected approaches

Unlike the energy-corrected approaches, the amplitude-corrected methods do not seek *a posteriori* energy correction to the CCSD energy, but instead account for higher-than-pair cluster amplitudes that were neglected when decoupling CCSD equations from the rest of the CC chain, namely the T_3 and T_4 clusters. This can be done either explicitly by finding a suitable approximation of the three- and four-body cluster amplitudes and using them to correct the CCSD equations, which leads to the *externally-corrected* (ec) CCSD methods (ecCCSD), or by accounting for such clusters implicitly by considering only a subset of diagrams that are associated with the disconnected $\frac{1}{2}T_2^2$ clusters. These latter approaches rely on possible, approximate, implicit cancelations of disconnected and connected quadruples or on a mutual cancelation of certain cluster components when only a small, finite number of electrons is involved. To such schemes we shall refer to as the *internally-corrected* (ic) methods. They will be addressed in Sect. 3.2.2, where we also provide an insight into such approaches that is based on the information provided, generally, by broken-symmetry IPM solutions, specifically those of the UHF-type. In both the ecCCSD and the icCCSD approaches we shall pay attention to recent advances that fall into these categories and outline their relationship with earlier developments.

3.2.1 Externally-corrected approaches

As already intimated above, the basic idea of the externally corrected approaches, specifically of the ecCCSD method, stems from the fact that (i) the energy is completely determined by the one- and two-body clusters T_1 and T_2, Eq. (3) and, (ii) the CCSD equations—representing the smallest subset of CC equations in the full CC chain (4) that determine these one- and two-body clusters—involve at most four-body clusters T_4, i.e.,

$$\left\langle \Phi_k^{(1)} | H_N e^{T_1+T_2} + H_N T_3 | \Phi_0 \right\rangle_C = 0$$
$$\left\langle \Phi_k^{(2)} | H_N e^{T_1+T_2} + H_N (T_3 + T_4 + T_1 T_3) | \Phi_0 \right\rangle_C = 0. \tag{12}$$

To decouple these equations from the rest of the CC chain one sets $T_3 = T_4 = 0$. Clearly, having a reasonable estimate of the T_3 and T_4 clusters, we should be able to achieve a physically more meaningful decoupling of the CCSD equations from the rest

of the CC chain by approximately accounting for the neglected three- and four-body cluster amplitudes.

Designating, thus, the approximate triples and quadruples by $T_3^{(0)}$ and $T_4^{(0)}$, respectively, we can employ the Ansatz

$$T = T_1 + T_2 + T_3^{(0)} + T_4^{(0)}, \tag{13}$$

leading to the ecCCSD equations

$$\langle \Phi_k^{(1)} | H_N e^{T_1+T_2} + H_N T_3^{(0)} | \Phi_0 \rangle_C = 0$$
$$\langle \Phi_k^{(2)} | H_N e^{T_1+T_2} + H_N \big(T_3^{(0)} + T_4^{(0)} + T_1 T_3^{(0)} \big) | \Phi_0 \rangle_C = 0. \tag{14}$$

Obviously, should we have available the exact three- and four-body amplitudes, such as those provided by the cluster analysis of the exact FCI wave function, the ecCCSD equations (14) would yield the exact FCI energy.

This immediately entails the problem of finding a suitable, independent, external source of such higher-than-pair clusters. The obvious criteria for such a source are that it: (i) be universally and easily accessible without significantly encumbering the computational effort, (ii) be size-consistent as far as possible, (iii) account for the non-dynamic or static correlations that are missing in standard SR-CC approaches and, finally, (iv) be open to a systematic improvement.

Once the approximate $T_3^{(0)}$ and $T_4^{(0)}$ cluster amplitudes are available, we simply evaluate the pertinent $\langle \Phi_k^{(i)} | V_N T_3^{(0)} | \Phi_0 \rangle_C$, $i = 1, 2$ and $\langle \Phi_k^{(2)} | V_N T_4^{(0)} | \Phi_0 \rangle_C$ terms, once and for all, and use them to correct the absolute term a_k in CCSD equations (5). The $T_1 T_3^{(0)}$ term can then be handled in several ways: (i) it can be made to vanish using BMOs or by relying on the CCD approximation, (ii) it can be recalculated in each iteration using the current values of singles when solving iteratively CCSD equations or, simply, (iii) it can be handled like the other $T_3^{(0)}$ and $T_4^{(0)}$ terms using approximate values for $T_1 \approx T_1^{(0)}$ that are, in general, automatically obtained in the cluster analysis of the external source wave function. Since the contribution of this term is usually very small, the latter option has been employed in most of our applications.

We next discuss various options for possible sources of higher-than-pair cluster amplitudes, proceeding in the order of their historical exploitation and, at the same time, shall point out recent exploitations and extensions wherever applicable.

3.2.1.1 UHF-based CCSD′ and CCSDQ′ methods

Our initially contemplated source for approximate higher-than-pair clusters was the UHF wave function of the different-orbitals-for-different-spins (DODS) type or, rather, its projected version onto the singlet state (PUHF). The motivation for this choice was the fact that the UHF wave function provides the exact result in the fully correlated limit of the cyclic polyene model, in which we were interested at the time [33] (cf. also [76–92]). Moreover, the UHF wave functions are easily accessible, even though for standard closed-shell molecular species they are available only if the restricted HF (RHF) solution is triplet (or non-singlet) unstable [93] (cf. also [94–96]). This, generally, happens either in strongly correlated systems, like cyclic polyenes, or in

standard molecular species for geometries away from the equilibrium one, e.g., when exploring the entire PECs or PESs. Of course, in the latter case, this implies a singular behavior at the triplet instability onset. Moreover, these wave functions cannot provide three-body clusters [33,53,97]. We thus set $T_3 = T_3^{(0)} = 0$, as in the standard CCSD method, and consider only $T_4^{(0)}$, namely the term

$$\langle \Phi_k^{(2)} | V_N T_4 | \Phi_0 \rangle_{\mathcal{C}} =: \Lambda_k^{(4)}(T). \tag{15}$$

For this purpose we first express the IPM, broken-spin symmetry, UHF wave function $|\Phi_{BS}\rangle$ in an exponential form via the single-excitation operator R_1 (that has the same form as T_1; see Thouless' theorem, e.g., [95,98]) and project it onto the singlets with P_0, i.e.,

$$P_0 |\Phi_{BS}\rangle = P_0 \exp(R_1)|\Phi_0\rangle = \exp(K)|\Phi_0\rangle, \tag{16}$$

where

$$K = K_2 + K_4 + \cdots, \tag{17}$$

since the terms involving odd powers of R_1 are projected out by P_0. The relevant $k_j^{(i)}$ amplitudes defining the K_i operators may then be extracted from the UHF wave function (see, e.g., [97]).

Considering, next, the term associated with quadruples, i.e.,

$$P_0 \left(\frac{1}{4!} R_1^4 \right) |\Phi_0\rangle = \left(\frac{1}{2} K_2^2 + K_4 \right) |\Phi_0\rangle =: C_4'|\Phi_0\rangle, \tag{18}$$

where C_4' designates an approximation to the corresponding FCI quadruple component, we can write for the correction term $\Lambda_k^{(4)}(T)$, Eq. (15), that

$$
\begin{aligned}
\Lambda_k^{(4)}(K) &:= \left\langle \Phi_k^{(2)} \middle| V_N K_4 \middle| \Phi_0 \right\rangle_{\mathcal{C}} \\
&= \left\langle \Phi_k^{(2)} \middle| V_N \left(C_4' - \frac{1}{2} K_2^2 \right) \middle| \Phi_0 \right\rangle_{\mathcal{C}} =: \Lambda_4^{(4)} - \Lambda_{2,2}^{(4)} \\
&= \left(\Lambda_4^{(4)} - \Lambda_{2,2}^{(4)} \right)_l + \left(\Lambda_4^{(4)} - \Lambda_{2,2}^{(4)} \right)_u \\
&= \widetilde{a}_k - \sum_{i \leq j} c_{kij} k_i k_j..
\end{aligned}
\tag{19}
$$

Here we approximated T_4 by K_4, $K_4 = T_4^{(0)} \approx T_4$, and used (18) in the second equation. The resulting terms $\Lambda_4^{(4)} \equiv \langle \Phi_k^{(2)} | V_N C_4' | \Phi_0 \rangle_{\mathcal{C}}$ and $\Lambda_{2,2}^{(4)} \equiv \langle \Phi_k^{(2)} | V_N \frac{1}{2} K_2^2 | \Phi_0 \rangle_{\mathcal{C}}$ are then split into their linked (l) and unlinked (u) parts. The unlinked part can be shown to give a vanishing contribution (see [53,97]), while the linked $\Lambda_4^{(4)}$ term contributes to the absolute term a_k and the $\Lambda_{2,2}^{(4)}$ term has a bilinear form in terms of the k_i amplitudes (for actual evaluation of these quantities in terms of the R_1 amplitudes, see [53,97]).

Thus, the CCSD$'$ equations take the form

$$a_k + \widetilde{a}_k + \sum_i b_{ki} t_i + \sum_{i \le j} c_{kij}(t_i t_j - k_i k_j) = 0, \tag{20}$$

where, for the sake of simplicity we suppressed higher than bilinear terms involving $t_k^{(1)}$ amplitudes.

Let us note, finally, that the UHF-based CCSD$'$ formalism enables an insight into the icCCSD approaches that were carried out independently earlier, in particular the ACP-D45 method [38], as will be seen in Sect. 3.2.2, while the actual implementation of the UHF-based CCSD$'$ method was carried out only later on [97].

Very recently, this method, as well as its perturbatively corrected versions for triples (see also [99]), was successfully applied to the H8 model [40] by Tobola [100]. Of course, this could be done only for geometries where the RHF solution is triplet unstable.

3.2.1.2 VB based ecCCSD method

An excellent potential source of the required higher-order cluster components is represented by the valence-bond (VB) wave functions, since they provide an ideal description of the bond-breaking processes, while requiring only a few covalent (and, if necessary, ionic) structures [101]. We employed VB wave functions as an external source at the semiempirical PPP-level in the first exploration of the ecCCSD approaches [43–45]. The generation of the VB wave functions, their cluster analysis, and the ecCCSD formalism were done within the unitary group approach (UGA) [23,24]. When compared with the FCI energies, the CCSD-VB method provided excellent results for cyclic and linear polyenes in the whole range of the coupling constant [44]. The same very good results were obtained when considering bond-breaking or bond-formation processes, involving both closed- and open-shell type subsystems (cyclobutadiene ring opening and dissociation into the ethylenic fragments, as well as benzene dissociation along the Diels–Alder mode into the closed shell fragments and also into the open-shell radicaloid C_3 fragments) [45]. Unfortunately, VB wave functions are not readily available at the *ab initio* level, not to mention computational difficulties due to the non-orthogonality of the atomic orbitals that are required in the general case.

3.2.1.3 CAS SCF based ecCCSD methods

In order to account for quasi-degeneracy that is associated with bond-breaking processes within the MO formalism, we have to involve relevant configuration states characterizing the dissociation process. Further, not all the triples and quadruples are of equal importance. The most important ones will naturally arise within a properly chosen active space. For those reasons we have turned our attention to the CAS SCF and CAS CI wave functions [102–104] as a possible external source for triples and quadruples, while relying on the UGA CC formalism [23,24]. Within the standard CC formalism, the CAS SCF corrected CCSD was first proposed by Stolarczyk [105], but no actual implementation has been carried out.

Most recently, an important advance has been made by Xu and Li [106], who base their approach on CCSDt and involve T_4 as well as T_5 clusters as externals, using the Ansatz

$$T = T_1 + T_2 + t_3 + T_4^{(0)} + T_5^{(0)}, \tag{21}$$

where t_3 represents active triples of the type t_{Ijk}^{Abc} with I and A representing active occupied and virtual orbitals, respectively. The fixed clusters $T_4^{(0)}$ and $T_5^{(0)}$ (designated by the authors as S_4 and S_5) are then obtained from the CAS SCF wave function and their contribution to CCSDt equations evaluated once and for all. It seems that the $T_1 T_4^{(0)} \equiv T_1 S_4$ term in triples equation is evaluated in every iteration and that the quadruple and quintuple clusters are generated by cluster analysis of the FCI wave function within the active space. It also seems that only active triples are accounted for.

The results for a symmetric dissociation of water, spectroscopic constants of several diatomics, the cyclobutadiene automerization barrier, and $Cl + O_3 \rightarrow ClO + O_2$ reaction are very good (the cyclobutadiene barrier also agrees well with the RMR-CCSD result [107]) when compared with the experiment or the exact results (FCI or DMRG) and are considerably better than the CCSDt or even the CCSDT results. The authors propose to extend the ecCC idea to CCSDtq-CASSCF and exploit DMRG (Density Matrix Renormalization Group) and FCIQMC (Quantum Monte Carlo FCI) as the external sources.

Our own experience with CAS SCF or CAS FCI indicated the need for relatively large active spaces when breaking multiple bonds, requiring in turn substantial computational effort, which turned us to an exploitation of multi-reference CISD (MR-CISD) wave functions [108–110] as an external source (see also [6,111]).

3.2.1.4 RMR-CCSD method

The RMR-CCSD method employs the subsets $T_3^{(0)}$ and $T_4^{(0)}$ of the three- and the four-body amplitudes, respectively, provided by a small size MR-CISD method. The choice of MR-CISD has been primarily motivated by the complementarity of the CC and CI approaches in their ability to account for the dynamic and the non-dynamic (or static) correlation effects. Moreover, a suitable modest size MR-CISD takes into account configurations that guarantee proper dissociation products. Indeed, such an MR-CISD, employing only a small reference space spanned by active MOs, provides us with a small subset of triples and quadruples relative to the reference $|\Phi_0\rangle$ which are primarily responsible for a correct description of the dissociation channel of interest. The great majority of core-virtual quadruples that are primarily responsible for a dynamic correlation are then accounted for via the CCSD exponential cluster Ansatz.

Needless to say that the subsets of triples and quadruples constituting $T_3^{(0)}$ and $T_4^{(0)}$ also explicitly account for higher than quadruples, as implied by the fact that the exact triples and quadruples would restore the FCI result. Numerous practical applications showed that a low-dimensional MR-CISD, relying on an appropriate active space, provides the most important connected triples and quadruples, while the CC Ansatz takes care of the remaining higher-than-pair clusters. Another advantage of the RMR-CCSD approach is a possibility of an extension to open-shells [112] and to MR-CC

approaches [113–115] of the state-universal (SU) type [116] (see also [11]), which are briefly described below.

In summary, the RMR-CCSD method involves the following three steps: (i) A selection of a suitable reference space and a computation of the corresponding MR-CISD wave function, (ii) the cluster analysis of the MR-CISD wave function of step (i), renormalized relative to $|\Phi_0\rangle$, yielding a subset of three- and four-body cluster amplitudes constituting the $T_3^{(0)}$ and $T_4^{(0)}$ operators, and, finally, (iii) an evaluation of the correcting terms $\langle\Phi_k^{(i)}|V_N T_3^{(0)}|\Phi_0\rangle_C$, $i = 1, 2$ and $\langle\Phi_k^{(2)}|V_N(T_1^{(0)}T_3^{(0)} + T_4^{(0)})|\Phi_0\rangle_C$, adding them to the absolute term a_k of (5), and solving the standard form of CCSD equations.

To enable applications to larger species we have also developed a truncated version of RMR-CCSD [117,118], as well as an analogue to the standard CCSD(T) method perturbatively accounting for the secondary triples (i.e., those that are not included in $T_3^{(0)}$), designated by the acronym RMR-CCSD(T) [119]. These approaches enabled us to handle rather large systems, e.g., nickel carbonyls [120] and transition metal ions with methylene [118]. The RMR-CCSD and RMR-CCSD(T) methods were also employed in handling of the singlet-triplet splitting in biradicals [121,122], reaction barrier heights [123,124], symmetry-breaking in radicals [125,126], in computation of PECs including a dissociation of a triple-bond in N_2 [110,127], and in generation of the harmonic force field of ozon [128] (see also other methodological developments in [129–132]).

3.2.1.5 GMS-SU-CC and (M,N)-CCSD methods

Although we focuss in this work on SR-CC approaches, we now briefly outline a generalization of the RMR-CCSD method to MR-CC approaches of the state-universal (SU) and state-selective (SS) types, leading to the ecSU-CCSD or ecSS-CCSD methods. These developments rely on an extension of the ecCCSD idea to what is referred to as a *general model space* (GMS) and enable us to handle not only the lowest state of a given symmetry species, but also the higher-lying states of the same symmetry [113–115]. Here must be recalled that the standard version of the MR-SU-CC formalism [116] requires a *complete model space* (CMS) in order to warrant the size-extensivity. This is computationally demanding and impractical, since in most instances we are only interested in low-lying excited states that are associated with single and double excitations from the ground state, rather than with all the possible excitations associated with a given number of electrons and active orbitals. Such low-lying excited states form, in general, an *incomplete model space* (IMS), in which case the CMS formalism cannot be applied lest the size-extensivity of the SU-CC equations be violated and the exact result in the limit when all clusters are accounted for be achieved. For this reason we introduced the GMS-based SU-CC theory which is rigorous even in the IMS case (we use the term GMS rather than IMS to emphasize a complete generality, since GMS can be spanned by an arbitrary set of configurations, independently of CMS).

The crucial ingredient in this development [113] is the concept of the so-called *connectivity* or *constraint conditions* (*C-conditions* for short) that must be imposed on cluster amplitudes that are associated with the internal excitations (i.e., those acting within the model space, transforming one reference into another one). The

C-conditions require that the corresponding connected n-body cluster amplitude be canceled by the sum of all possible disconnected n-body terms (see [113]). In an actual computer implementation of this approach, the C-conditions must be respected in every iteration.

The GMS-approach that exploits the C-conditions is primarily useful in the SU-CCSD method which can simultaneously describe N excited states when using an N-dimensional reference or model space [133] (also labeled as NR-RMR-CCSD or NR-SU-CCSD).

The size-extensivity of GMS-SU-CC approaches was tested in [134] and their general performance in [135–137]. However, it can also be beneficial in the Brillouin–Wigner version of the CC method (BW-CC) [138] and, especially, in the *state-selective* or *state specific* (SS) MR-SS-CC approaches that focus on one state at a time. An often used SS-CC version of the MR-SU-CC method was developed by Mukherjee et al. [139,140], and is usually designated by the acronym MkCCSD. Like other MR-SU-CC methods, its original formulation relies on a CMS and its exploitation has been almost exclusively focused on ground states (or, generally, the lowest state of a given symmetry species), even though, in principle, it can access excited states as well. A comparison of the performance of the NR-SU-CCSD or NR-SU-CCSD(T) methods with MkCCSD for the ground state indicates the usefulness of the C-conditions when relying on the IMS or GMS [141]. It is, of course, particularly interesting to examine the performance of these methods for the excited states, including excited state PECs [137, 142]. When we compared NR-SU-CCSD with MkCCSD for a number of excited states of ethylene [143], we found that in all cases the MkCCSD method yielded practically the same result as did the GMS-SU-CCSD method, as long as the convergence could be achieved, which, unfortunately, was not the case in many instances [143]. Note that the SS-CC methods compute every state separately, while the SU-CC approaches yield all the states represented by the model space in a single calculation.

The development of the algorithm for the cluster analysis of general MR-CI wave functions that is based on the SU-CC Ansatz [144] and the formulation of the SU-CC method employing GMS [113] enabled us to formulate the GMS-based SU-CC theory which can be regarded as a multistate version of the RMR-CCSD method. Here again we could employ, in principle, any external sourse of higher-order cluster amplitudes. Yet, for a number of reasons we use modest size MR-CISD wave functions for that purpose. In general, we thus employ the SU-CCSD theory that is based on an M-dimensional GMS and extract a subset of higher-than-pair cluster amplitudes from an N-reference MR-CISD wave function. We refer to the resulting approach as the N-reference, M-state CCSD method and use the acronym (N, M)-CCSD [114]. Note that $(N, 1)$-CCSD is identical with the RMR-CCSD or NR-RMR-CCSD approaches and $(0, M)$-CCSD is the same as the standard M-reference SU-CCSD. The size-extensivity of this approach was tested in [134] and the correction for triples was developed in [145,146]. The initial testing using the LiH molecule [147] was then extended to a number of systems exploring both the ground and the excited states [133,148], including the PECs for an asymmetric dissociation of water [149].

Table 1 Correlation of various diagram designations

This work	Ref. [33,38,53][a]	Ref. [20][b]	Ref. [169][c]	Ref. [171][d]	Ref. [168][e]
D1	1	(i_κ)	D	A	D[c]
D2	2	(ii_κ)	D	A'	D[ex]
D3	3	(iii_κ)	C	C	C
D4	4	(iv_κ)	A	D	A
D5	5	(v)	B	B	B

[a] Ref. [33], Fig. 10(c); Ref. [38], Fig. 1; Ref. [53], Fig. 4
[b] Ref. [20], Fig. 3(c)
[c] Ref. [169], Fig. 1
[d] Ref. [171], Fig. 1
[e] Ref. [168], Fig. 1

3.2.2 Internally-corrected approaches

In order to better understand the role played by the terms describing pair interactions that are associated with the disconnected quadruples $\frac{1}{2}T_2^2$ of the CCD or CCSD formalism—especially in quasi-degenerate situations—and possibly design computationally more efficient approximate schemes for handling of these non-linear terms (see, e.g., [55]), we employed several minimum basis set H_4 models, in which we could continuously vary the degree of degeneracy via a single geometry parameter, from a non-degenerate to a completely degenerate regime. We were also motivated by an approximate handling of pair interactions by the CEPA (coupled electron pair approximation) schemes [150–153] and especially by the role played by factorizable EPV diagrams, particularly those that are separable over the hole lines (see, e.g., [54,55,154]; see also [155,156]).

The simplest way to appreciate the role of the EPV terms is to realize that both CISD and CCSD will yield the exact result for two-electron systems, unlike L-CCSD. Indeed, all the terms resulting from the $\frac{1}{2}T_2^2$ diagrams of CCD or CCSD represent in this case factorizable EPV terms that are required to compensate for the fact that we use unrestricted summations over the hole and/or particle labels, which in turn greatly facilitate computations [54,154] (see also Appendix F of [19]).

We found that, indeed, the EPV diagrams play a special role, particularly when the quasi-degeneracy sets in. This led to a formulation of the so called ACP-D45 (approximate coupled pair) approximation [38] using only the diagrams that separate over the one or the two hole lines (labeled as diagrams 4 and 5; see below). This method provided an excellent approximation to the exact FCI energies even in a highly degenerate regime, thus significantly improving the standard CCSD results. This approximation was also exploited at the *ab initio* level to handle the quasi-degeneracy in the ground state of the Be atom [157,158].

Here we must comment on the diagram labeling that will be used throughout this section. We rely on the Goldstone–Hugenholtz-type representation, which enables an easy spin-adaptation using the OSA formalism [20]. We then number the five relevant Goldstone–Hugenholtz diagrams representing the pair-interaction term $\frac{1}{2}T_2^2$ as Di, with $i = 1, 2, \ldots, 5$. These diagrams are shown in Fig. 3(c) of [20] [where they are

labeled by Roman numerals (i) through (v)] or in Fig. 10(c) of [33], in Fig. 1 of [38], and in Fig. 4 of [53]. When we retain only the diagrams Di and Dj, for example, i.e., $Di + Dj$, we shall write simply Dij, and similarly, in general, the symbol $Dijk\ldots$ will imply

$Di + Dj + Dk + \cdots$, i.e., $Dijk\cdots \equiv Di + Dj + Dk + \cdots$. The relationship with notations used by other authors is shown in Table 1.

We found that ignoring the first three diagrams D123 which do not separate over the hole lines (for more details, see below) not only considerably simplifies the CCSD formalism, but in fact greatly improves it in the degenerate regime. On the other hand, the ACP-D123 approximation, in which only the first three diagrams are accounted for, yields similar results as does the linear CCSD (L-CCSD) approximation (which is also equivalent to CEPA-0) that retains only linear terms (i.e., the terms $\frac{1}{2}T_2^2$ are ignored), until reaching a singularity of L-CCSD, in which case ACP-D123 no longer converges [38]. We hasten to add here that very similar results were obtained at almost the same time by Chiles and Dykstra [46,159–161], who designated the method by the acronym ACCD (approximate CCD). We must also point out an exploitation of the ACP-type approaches by Jeziorski et. al. in their basis-set free approaches based on explicitly correlated geminals for He, Be, H_2, and LiH [162,163] and Ne [164]. These authors refer to their variant of the ACP or ACCD approaches as the *factorized coupled pair* (FCP) approximation (cf. also [165]).

As already mentioned, the ACCD or the ACP-D45 approximation works extremely well in highly degenerate situations, such as arising in metallic-like systems, exemplified by the cyclic polyene model, in which case the standard CCD [33,83] or even CCSDT or CCSDTQ [34] completely break down. Nonetheless, there seems to be a wrong sign for the T_4 contribution in the CCSDT treatment of some H_4 models [166] when also T_3 are accounted for. This was likely the reason that while the H_4 models (especially the so-called H4 model [38]) became extremely popular for testing of various approaches handling quasi-degeneracy, being employed in hundreds of papers [39], the ACCD or ACP-D45 approximation (and later ACPQ [53]) were seldom used till the recent renewed interest, as will be seen in the following sections.

A better understanding of modus operandi of the ACCD approach was later provided by exploiting the UHF wave function as an external source, which also led to the formulation of the ACPQ approximation [33,53] (see also Sect. 3.2.1.1), which provides yet better results for cyclic polyenes and the exact result in the fully correlated limit ($\beta = 0$). Assuming, thus, that the UHF or PUHF approximate amplitudes k_i, Eq. (20), are exact, so that $k_i = t_i$, the last term in (20) will vanish, yielding

$$a_k + \widetilde{a}_k + \sum_i b_{ki} t_i = 0, \tag{22}$$

where $\widetilde{a}_k = (\Lambda_4^{(4)})_l \equiv \langle \Phi_k^{(2)} | V_N C_4' | \Phi_0 \rangle_C$ can be shown to be given by the D45 diagrams (or, in fact, also by $\frac{1}{2}$(D34) + D5 or even by D14 or D1+$\frac{1}{2}$(D34), as implied by Fig. 14 of [53] (see also [90]).

Let us next consider more recent CC approaches of the icCCSD type and relate them with an earlier work. Since the authors of these developments use different labeling of

the relevant five diagrams for $\frac{1}{2}T_2^2$, we provide a correlation between these respective notations in Table 1. To avoid a possible confusion, we shall use the notation in terms of Di, $i = 1, 2, \ldots, 5$, symbols given in the first column of Table 1.

3.2.2.1 nCC methods

In their search for computationally more efficient CC algorithms, Bartlett and Musiał [55,56] came up with an interesting idea to formulate what they refer to as the *n*CC hierarchy of CC approximations. This new paradigm simply requires the *n*CC approximation to be exact for an *n*-electron system and involves only the minimum necessary number of relevant diagrams. Thus, 2CC will be exact for 2-electron systems and will involve only a subset of CCSD diagrams, 3CC will be exact for 3-electron systems and involve only a subset of CCSDT diagrams, etc. In fact, 2CC will also be exact for all products of 2-electron units, 3CC for product of 3-electron units, etc., thanks to the size-extensivity of the CC formalism.

The idea likely arose from the fact that while CISD and CCSD are both exact for 2-electron systems, not all the terms in the relevant formalism need be retained, as already noted (see, e.g., [54,154–156]). In fact, it turns out that 2CC is identical with the ACP-D45 [38] or ACCD [46] methods (when extended by singles or when using Brueckner orbitals), thus offering a new viewpoint on these approaches.

To proceed to a general *n*CC case, the authors classify the relevant diagrams as the hole–hole conjoint (HCJ) diagrams and the non-HCJ (NHCJ) diagrams. This classification is in fact related with the concept of the so-called non-factorizable EPV diagrams (see, e.g., [54,154]). In the 2CC case, the HCJ diagrams are precisely those that are separable over the one or the two internal hole lines, namely the diagrams D4 and D5, while the NHCJ ones are given by the diagrams D1, D2, and D3 (note that Fig. 1 of [55] employs the Goldstone representation of Hugenholtz diagrams; see, e.g., [6,167]).

For the general *n*CC case, the authors formulate the rules which eliminate the irrelevant NHCJ diagrams. For the nonlinear terms, this leads to an algorithm that lowers the power in the dependence on the number of virtual orbitals n_p by one, yielding a computationally more efficient codes. Unfortunately, this is not the case for the linear term, so that already 3CC will have to store $n_h^3 n_p^3$ T_3 amplitudes.

It is thus clearly the 2CC method that brings useful benefits relative to CCSD. It is not only exact for 2-electron systems, but also for all products of 2-electron units. Further, it facilitates an evaluation of non-linear terms, reducing the effort to $\sim n_h^4 n_p^2$ from $\sim n_h^3 n_p^3$. On the whole, the authors state that [55]: "The numerical results of *n*CC are close to those for the full CC variant, and in some cases are closer to the full CI reference result. As 2CC is exact for separated electron pairs, it is the natural zeroth-order approximation for the correlation problem in molecules with other effects introduced as these units start to interact". Yet, on the basis of their earlier work [166], the authors are noncommittal regarding a possible compensation of the T_4 clusters through the neglect of NHCJ terms, particularly in quasi-degenerate regimes.

In a very recent paper [168] Bartlett et al. focus their attention on the problem of triple-bond breaking. In this work they separate the Hugenholtz diagram for D12 into its direct (D1) and exchange (D2) parts, thus considering the five Goldstone–Hugenholtz diagrams (see Table 1) that are characterizing the OSA formalism, yet

employ the spin-orbital formalism. This is important in view of a special role played by the exchange term D2 in bond breaking process (see also Sect. 3.2.2.3).

3.2.2.2 Parametrized CC theory pCCSD

In view of a disparate role played by individual diagrams of the CCSD method, Huntington and Nooijen [169] searched for an optimal mix of contributions from the four Hugenholtz diagrams constituting the $\frac{1}{2}T_2^2$ interaction term (see Table 1 for their diagram labeling), being inspired by CEPA approaches [150–153]. For this purpose they employed a test set of 19 molecules involving first row atoms and focused on their equilibrium bond-lengths and bond angles, using a cc-pVTZ basis set and the CCSD(T) results as a reference.

In order to minimize the number of variational parameters to be optimized they employed the fact that in two-electron systems the D123 diagrams do not contribute, i.e., D123 = 0, in which case also $\frac{1}{2}$D4 + D5 = 0. Their Ansatz can thus be obtained by adding these terms that vanish in the two-electron case weighted with variational parameters to the full set of CCSD $\frac{1}{2}T_2^2$ diagrams D12345, namely

$$
\begin{aligned}
&\text{D12345} + \kappa \text{D123} + \lambda \left(\frac{1}{2}\text{D4} + \text{D5} \right) \\
&= (1 + \kappa)\text{D123} + \frac{1}{2}\text{D4} + (1 + \lambda) \left(\frac{1}{2}\text{D4} + \text{D5} \right) \\
&= \frac{1}{2}(1 + \alpha)\text{D4} + \alpha \text{D5} + \beta \text{D123},
\end{aligned}
\tag{23}
$$

where in the last equation we introduced new variation parameters $\alpha = 1 + \lambda$ and $\beta = 1 + \kappa$ (i.e., in the author's notation $\frac{1}{2}(1+\alpha)\text{A} + \alpha \text{B} + \beta(\text{C}+\text{D})$; Eq. (8) of [169]). Designating, thus, the resulting procedure by an acronym pCCSD(α, β), the standard CCSD corresponds to pCCSD(1,1), while pCCSD(1,0) gives the 2CC = ACCD = ACP-D45 methods (again up to, possibly, the one-body clusters).

For the equilibrium bond lengths and bond angles of their first-row test set of molecules the authors found—relying on the absolute and standard deviations from the CCSD(T) reference—that the optimal results are provided by the pCCSD(−1,1) scheme, while pCCSD(1,0) (i.e., 2CC or ACCSD) yields results that are almost the same as those provided by standard CCSD. This could have been, however, expected since in the absence of quasi-degeneracy the ACP-D45, ACPQ or 2CC approximations are known to yield almost the same result as the standard CCSD method. It is in the quasi-degenerate or degenerate situations, which were not investigated, that ACP-D45 or ACPQ prove to be beneficial, as pointed out above (see, e.g., [33,34,38], etc.).

As the next step, the authors investigated reaction energies and barrier heights for a set of 36 reactions introducing an additional parameter γ weighing the $T_1 T_2$ diagrams, whose contribution again vanishes in the two-electron case [170]. The resulting pCCSD(α, β, γ) scheme gives again the exact result in the two-electron case for any choice of the parameters α, β, γ. Using local pair natural orbitals (LPNOs) they found that the variants pCCSD(−1,1,1), pCCSD(−1,1,−1), pCCSD(−1.5,1,1), and pCCSD(−1.5,1,−1) yield more or less equivalent best results for the reaction energies and barrier heights. The authors warn that "the pCCSD approaches may have their

limitation, in particular as the T-amplitudes grow in magnitude, these methods lose reliability" [170].

On the whole, as already noted in the original pCCSD(α, β) paper [169], "the choice of optimal parameters in pCCSD is empirical, and we consider it not very likely that one can find a first principles theoretical justification for the $(-1,1)$ values for the parameters recommended here or to find a theoretical argument why the approach includes (rather than mimics) triple excitation effects".

3.2.2.3 Distinguishable cluster (DC) approximations

Quite a different line of approach, more akin to the early work leading initially to the ACCD or ACP-D45 approximations [38,46,159–161], and later to the ACPQ [33,53], nCC [55,56], and pCCSD(α, β) [169,170] approaches, was followed by Kats and Manby [171–173]. In contrast to pCCSD, however, they distinguish direct and exchange terms that are associated with the first Hugenholtz diagram involving particle-hole interactions (i.e., Fig. 5(a) of [53]), namely the diagrams D1 and D2 (A and A′ in their notation, cf. Table 1), and remove the exchange diagram D2 hypothesizing "that the approximate description of physically irrelevant exchange processes could be the source of the poor behaviour of CCSD for dissociation".

Relying then again on the fact that 2D2 + D3 = 0 = D4 + 2D5 holds for two-electron systems, and adding $a(2D2 + D3) + b(D4 + 2D5) = 0$ to D12345, they get

$$
\begin{aligned}
\text{D12345} &+ a(2\text{D2} + \text{D3}) + b(\text{D4} + 2\text{D5}) \\
&= \text{D1} + (1 + 2a)\text{D2} + (1 + a)\text{D3} + (1 + b)\text{D4} + (1 + 2b)\text{D5} \\
&= \text{D1} + \frac{1}{2}(\text{D3} + \text{D4}),
\end{aligned}
\tag{24}
$$

where they set $a = b = -\frac{1}{2}$ in the last equation. This approach is referred to by the authors as the distinguishable cluster (DC) approximation and is labeled by the acronym DCD, or BDCD when BMOs are used.

The resulting DCD approach is reminiscent of the ACP-D14 approximation that was shown earlier to provide an excellent description for cyclic polyenes in the whole range of the coupling constant (cf. Table 1 of [90]; see also [91]). In fact, in the case of a relatively large cyclic polyene $C_{22}H_{22}$, both ACP-D45 and ACP-D14 results differ only marginally in the whole range of the coupling constant, ranging from the fully correlated to a weakly correlated limit, the largest difference amounting to about half an meV (see Table 2). Indeed, in the case of the PPP or Hubbard model of cyclic polyenes (or, in fact, in any case when a minimum basis set (MBS) is employed and Coulson's pairing theorem holds), we find that the hole–hole diagram D4 provides the same contribution as the particle–particle diagram D3 thanks to the presence of the particle-hole symmetry of MBS MOs, so that in such cases we have that ACP-D14 ≡ ACP-D1$\frac{1}{2}$(34). Although this was not realized at the time, the PUHF-based interpretation of these approximations involves the same diagrams as ACP-D45 (this can be realized by separating the UHF-based diagrams in the first and second rows of Fig. 14 of [53] into those corresponding to the direct and the exchange terms and neglecting those associated with an unlinked contribution or involving an odd number of closed loops), indicating thus their "equivalence". As shown by Kats and Manby

Table 2 Correlation energy per electron $\Delta E/N$ for the Hubbard Hamiltonian model of cyclic polyene $C_{22}H_{22}$ in the whole range of the coupling constant given by the reciprocal value of the resonance (hopping) integral β, ranging from the fully correlated ($\beta = 0$) to a weakly correlated ($\beta = -5$ eV) limit, as obtained withe the ACP-D45 $\equiv$ D45 and ACP-D41 $\equiv$ D14 methods

$-\beta$ (eV)	FCI[a] (eV)	ΔD45[a] (eV)	ΔD14[b] (eV)	$\Delta\Delta$ (meV)
5.0	0.0855	0.0003	0.0003	0.0
2.5	0.1758	0.0040	0.0039	0.1
2.0	0.2242	0.0088	0.0087	0.1
1.5	0.3074	0.0203	0.0201	0.2
1.0	0.4601	0.0401	0.0396	0.5
0.5	0.2651	0.0423	0.0419	0.4
0.0	1.2500	0.0000	0.0000	0.0

The exact FCI energies were obtained by solving Lieb–Wu equations [174] and we define the energy differences as follows: ΔD45 = FCI− D45 and ΔD14 = FCI− D14. Note that for the Hubabrd Hamiltonian ACP-D45 $\equiv$ ACPQ
[a] Ref. [33]
[b] Ref. [90]

[171], this approximation indeed produces very good results (see also [172,173]). Their examples for the dissociation of the H_{50} chain and the $4 \times 4 \times 4$ cube of H atoms are especially impressive and indicate a potential usefulness of this approximation for highly degenerate metallic-like systems.

Most recently Kats derived the DCD equations by exploiting an effective screened Coulomb interaction and a *p-h* symmetrized Fock matrix [175]. The screening was achieved by modifying one-electron densities by relying on the so-called direct-ring CCD (drCCD) or, an equivalent, dRPA (direct random phase approximation), see, e.g., [176]. Also, a perturbative triple correction to DCSD that employs screened Coulomb integrals, DCSD(T), was shown to be superior to the "naive" CCSD(T) that relies on a standard (T) correction, although still lacking when employed in quasi-degenerate situations when non-dynamic or static correlation effects are essential [175].

As our earlier work and recent developments leading to the *n*CC (in particular 2CC) and to the DCD or BDCD approximations indicate, it is important to separate the direct and the exchange *ph–ph* terms and to remove the exchange term D2 (see also [168]).

This was not done in the pCCSD approaches [169,170], where both diagrams D1 and D2 are lumped together. Their separation, however, would not very likely change the pCCSD results that focussed on systems in their equilibrium geometry, as already pointed out above.

4 Conclusions

We attempted to provide an overview of the existing externally and internally corrected CCD or CCSD approaches, elucidating their relationship by relying on common foundations. Depending on an external source, the ecCCSD methods may slightly violate the exact size-extensivity, yet all actual applications clearly indicate that these devi-

ations are, generally, insignificant, since these methods still rely on the exponential CC Ansatz for the wave function (cf., e.g., [177]) and, with a proper choice of the reference space are size-consistent (i.e., describing a correct dissociation channel). Indeed, it is to be pondered whether an undue insistence on the exact size-extensivity rather than an overall accuracy and reliability is to be preferred, particularly in view of an unsatisfactory performance of exactly size-extensive methods like CCSD(T), or even CCSD itself, in quasi-degenerate situations.

Clearly, any reasonable approximation of the three- and the four-body amplitudes provides a physically more meaningful decoupling of the full CC chain of equations than setting $T_3 = T_4 = 0$ yielding standard CCSD, particularly in view of the fact that by employing the FCI amplitudes, the ecCCSD will return the exact FCI energy. Of course, the icCCSD approaches are always exactly size-extensive irrespective of the choice of the subset of the CCSD diagrams that is selected. All these approaches retain the other desirable properties of CC methods, namely the invariance to a separate unitary transformation in the occupied and virtual MO or MSO spaces, the ease of application and extension to open-shells and to MR CC approaches relying on either the standard or the UGA formalism, and provide an efficient account of the dynamic correlation effects.

The ecCCSD methods that are based on either a single or a multiple reference, specifically the RMR-CCSD, GMS-SU-CCSD, (M, N)-CCSD and the new CCSDt-CASSCF methods, enabled numerous practical applications yielding reliable PESs or PECs and the related spectroscopic data, excitation energies, reaction barriers, binding energies in transition metal complexes, and force fields, including diradicaloid species, etc. The GMS-SU-MRCC version enabled a simultaneous generation of vertical excitation energies for the excited states of the same symmetry species and, in contrast to the SS-CC method, namely the so-called MkCCSD, is not plagued by convergency problems. A wider exploitation of these approaches would be certainly beneficial in many applications.

After a considerable hiatus, the icCCD or icCCSD methods are gaining a new attention, bringing novel viewpoints, understanding, and prospects of computationally more efficient and, simultaneously, more desirable exploitations. These methods, namely ACC(S)D, ACP-D45, ACPQ, 2CC or BDCD, etc., usually yield more meaningful results than standard CCSD, particularly in the presence of quasi-degeneracy, while being computationally more effective. Although these approaches account in one way or another for missing quadruples, especially in highly degenerate situations, the absence of triples may be an impediment in some situations. The use of OSA MOs is certainly to be preferred, since it minimizes the dimension of the resulting system of algebraic equations and offers a possibility to employ the ACPQ approximation. In our opinion, these methods offer the greatest promise when applied to highly degenerate situations, thus enabling to simulate extended systems.

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