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Multireference Coupled-Cluster Theory: The Internally Contracted Route

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ABSTRACT

Transferring the success of the coupled-cluster expansion for single-determinant references to multireference cases remains a challenge. The main dilemma is a proper merge of the exponential ansatz, required for extensivity of the correlation energy, with a linear ansatz, required for an unbiased treatment of near-degenerate state interactions. We argue that the state interaction aspect is important and that therefore the Bloch equations are the necessary starting point for all true multireference coupled-cluster theories. Considering the aspect of spin-adaptation and orbital invariance, we arrive at internally contracted expansions, which indeed have a number of appealing formal properties, but also incur a tremendous increase in the complexity of the resulting working equations. The most striking property of internally contracted expansions is probably that a simple transformation of the reference space turns the multistate equations into state-specific equations without introducing further approximations. We discuss the present shortcomings and perspectives of the internally contracted multireference coupled-cluster theory and discuss issues like the completeness of the equations, alternative expansions using normal ordering, and perspectives for large active spaces and large molecules.

1 | Introduction

Coupled-cluster theory is at the heart of highly accurate quantum chemistry with predictive power [1–4]. Nowadays, a variety of coupled-cluster methods is available to a broad community in computational chemistry that allow for accurately solving the electronic Schrödinger equation. One of the remaining challenges, however, is extending the scope of coupled-cluster theory to systems with a complex open-shell electronic structure, generally addressed as "multireference cases" [5–7]. As the name suggests, these cases require more than a single-reference determinant to provide a viable zeroth-order description of the system and range from homolytic bond-breaking and diradicals to highly complex polynuclear transition-metal clusters. A generalization of coupled-cluster theory to multireference cases has been on the agenda ever since coupled-cluster theory was introduced into quantum chemistry [8, 9], but a general-purpose implementation has remained elusive up to date. In this perspective, we will give our view on what a multireference coupled-cluster (MRCC) theory should accomplish and argue why it should be derived within a multistate framework. The starting point is the Bloch equations. We give a number of arguments in favor of the approach that is now known as internally contracted multireference coupled-cluster (icMRCC) theory and discuss its present shortcomings, as well as perspectives for alternative formulations and related approaches.

2 | Bullet Points for a Multireference Coupled-Cluster Theory

Our view on the aims of a MRCC theory is the following:

- The computed energy must scale correctly with system size, reaching the correct theoretical thermodynamic limits (extensivity of the energy). In particular, the theory should be consistent for all possible ways of partitioning the system into noninteracting subsystems (size-consistency).
- It must be able to treat near-degeneracies in an unbiased way. There should not be any bias toward one special configuration, and ideally, the theory should cover near-degeneracy situations where state interactions play a role.
- As open-shell systems will be a typical application scenario, the theory should be strictly spin-adapted, delivering proper $\hat{S}^2$ and $\hat{S}_z$ eigenstates.
- Moreover, a close relation to the single-reference theory is desirable, ideally in a way that allows combining results from a multireference computation with those of a single-reference computation for a closed-shell subsystem.

In particular, the first two bullet points induce two conflicting approaches to constructing approximate wavefunctions, namely linear versus nonlinear wavefunction ansätze. The fundamental insight behind single-reference coupled-cluster theory is that a proper scaling of the energy requires a product-separable wavefunction [10]. This ultimately leads to the well-known exponential ansatz for the coupled-cluster wavefunction

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle \tag{1}$$

with cluster operators $\hat{T}$ acting on a reference determinant $|\Phi_0\rangle$. The wavefunction is separable as long as it can be split into proper closed-shell (or strictly high-spin coupled open-shell) fragments. Furthermore, important correlation contributions from higher excitations (relative to the reference determinant) are incorporated by products of the cluster operator, most prominently that of quadruple excitations from the $\frac{1}{2}\hat{T}_2^2$ term [10]. Here and in the following, we adopt the standard notation of coupled-cluster theory where, for instance, $\hat{T}_2$ indicates a double excitation operator.

On the other hand, the description of state interactions requires a linear ansatz. Indeed, the basic building blocks of quantum mechanics are linear, observables are connected to linear (and Hermitian) operators, and the superposition principle clearly exploits the linear nature of the underlying Hilbert space. The physics of two interacting states at an intersection and the entire topology of the latter around conical intersections are covered by a linear ansatz

$$|\Psi_+\rangle = \cos(\theta/2)\,|\Psi_1\rangle + \sin(\theta/2)\,|\Psi_2\rangle \tag{2}$$

$$|\Psi_-\rangle = -\sin(\theta/2)\,|\Psi_1\rangle + \cos(\theta/2)\,|\Psi_2\rangle \tag{3}$$

where θ is the mixing angle. This behavior is incompatible with the single-reference ansatz (Equation 1), which leads to artifacts in such situations [11], and clearly calls for a linear ansatz with all relevant states being treated equally. Another problem with Equation (1) is that it strictly only allows for a single *determinant*. Even for cases that are in principle well described by a single *configuration*, but with a more sophisticated spin coupling than a closed-shell or high-spin open-shell case, this is not enough as we need a *linear* combination of at least two determinants to cover this wavefunction symmetry.

These opposing requirements have to be accommodated in a MRCC theory. At the same time, single-reference coupled-cluster theory has reached an extremely advanced state. Highly accurate computations using dedicated protocols are now possible, exploiting the systematic coupled-cluster hierarchies [3, 4]. Many properties can be accessed by gradient and response theory [2] and the scaling wall can be overcome by local approximations [12, 13]. In view of that, there is also demand that an extension of coupled-cluster theory to multireference cases should maintain the single-reference case as its limit. As indicated in our bullet list above, this ideally means that if a system is separated into noninteracting subunits, and if some of the subunits are closed-shell cases, their energy contribution with the MRCC theory should equal that of the single-reference theory for these fragments.

3 | The Multistate Perspective

One obvious approach to addressing both the linearity of interacting states and nonlinearity required for separability and extensivity of the energy is using a formalism put forward by Claude Bloch [14]. In fact, this ansatz was employed in all pioneering work on MRCC [15, 16]. The starting point is a target space, spanned by functions $\{|\Psi_m\rangle\}$, and the diagonalization of the Hamiltonian in this subspace is required to yield the exact states. A projection operator $\hat{P}$ is defined that projects the exact states of the full basis onto a model space with a computationally manageable basis representation

$$|\psi_m\rangle = \hat{P}\,|\Psi_m\rangle \tag{4}$$

where intermediate normalization is assumed: $\langle\psi_m|\Psi_m\rangle = 1$. The essential idea is that the state mixing and the final energies can be computed in this reduced basis representation. The formalism also includes an operator, which accomplishes the mapping from the reduced to the full space:

$$|\Psi_m\rangle = \hat{\Omega}\,|\psi_m\rangle \tag{5}$$

This operator is called the wave operator and must fulfill the Bloch equations [14],

$$\hat{H}\hat{\Omega} = \hat{\Omega}\hat{H}\hat{\Omega} \tag{6}$$

which in this form is exact, that is, equivalent to the Schrödinger equation. The central object is the effective Hamiltonian

$$\hat{H}^{\mathrm{eff}} = \hat{P}\hat{H}\hat{\Omega}\hat{P} \tag{7}$$

which can be diagonalized in the model space representation while giving the exact eigenvalues of the considered states, in particular taking care of state interactions. Approximate theories based on this formalism differ in their ansatz for $\hat{\Omega}$ and the way of solving the equations.

In the realm of coupled-cluster theory, we will consider three choices:

- The approach of Jeziorski and Monkhorst [16] (JM).
- A modification of this approach, which we would like to call generalized Jeziorski–Monkhorst (GJM) ansatz [17].
- An approach involving a universal cluster (UC) operator, initially proposed by Mukherjee and coworkers [15].

The JM approach reads [16]

$$\hat{\Omega}_{\mathrm{JM}} = \sum_{\mu} e^{\hat{T}(\mu)} \left| \Phi_\mu \right\rangle \left\langle \Phi_\mu \right| \tag{8}$$

where the model space is expanded by determinants $|\,\Phi_\mu\,\rangle$ and the wave operator employs the exponential of a cluster operator $\hat{T}(\mu)$ for each determinant individually. Note that $|\,\Phi_\mu\,\rangle$ here explicitly denotes determinants, as the design of $\hat{T}(\mu)$ requires a clear-cut definition of occupied and unoccupied spin orbitals. In addition, a "complete" model space is assumed, that is, the determinants $|\,\Phi_\mu\,\rangle$ exhaust all occupation possibilities of the active orbitals. In that case, the cluster operators $T(\mu)$ can be restricted to those that always involve one orbital outside the active orbital space [16].

The GJM approach uses a very similar wave operator,

$$\hat{\Omega}_{\mathrm{GJM}} = \sum_{m} e^{\hat{T}(m)} |\psi_m\rangle\langle\overline{\psi}_m| \tag{9}$$

which, however, spans the zeroth-order space in terms of multideterminantal functions $|\,\psi_m\,\rangle$. In the simplest case these are configuration state functions (CSFs, to enable proper spin-adaptation), but we will mainly consider general multideterminantal expansions. For the time being, we will again require a complete model space and the $|\,\psi_m\,\rangle$ are therefore general complete active space configuration interaction (CASCI) expansions

$$|\,\psi_m\,\rangle = \sum_{\mu} |\,\Phi_\mu\,\rangle c_\mu^{(m)} \tag{10}$$

with the only requirement that the $\{|\,\psi_m\,\rangle\}$ are linearly independent. The biorthogonal complement states are denoted as $|\,\overline{\psi}_m\,\rangle$ and fulfill $\langle\overline{\psi}_m|\,\psi_n\rangle = \delta_{mn}$. The cluster operator generates internally contracted states [18–21], as illustrated for the reference $|\,\psi_m\,\rangle$

$$e^{\hat{T}(m)}\,|\,\psi_m\,\rangle = e^{\hat{T}(m)} \sum_{\mu} |\,\Phi_\mu\,\rangle c_\mu^{(m)} \tag{11}$$

More details on the choice of $\hat{T}(m)$ will be discussed below, for the present discussion, it suffices to require that it creates states orthogonal to the CASCI space, analogous to the requirement for ansatz Equation (8).

Inserted into the Bloch equations (Equation 6), the two approaches lead to a very similar set of equations [16, 17]. We just give the result for the generalized case:

$$\left\langle \psi_\rho^Q \right| e^{-\hat{T}(m)} \hat{H} e^{\hat{T}(m)} \left| \psi_m \right\rangle = \sum_{n \neq m} \left\langle \psi_\rho^Q \right| e^{-\hat{T}(m)} e^{\hat{T}(n)} \left| \psi_n \right\rangle H_{nm}^{\mathrm{eff}} \tag{12}$$

where $\langle\,\psi_\rho^Q\,|$ denotes a projection to states that are orthogonal to the model space and the effective Hamiltonian is

$$H_{nm}^{\mathrm{eff}} = \left\langle \overline{\psi}_n \right| e^{-\hat{T}(m)} \hat{H} e^{\hat{T}(m)} \left| \psi_m \right\rangle \tag{13}$$

For the last equation, we used that $\langle\,\overline{\psi}_n\,|\,\hat{T}(m) = 0$ and inserted $e^{-\hat{T}(m)}$ to emphasize the connectedness of the expression. Diagonalization of the effective Hamiltonian yields the expansion coefficient $C_m^{(N)}$ from which the full expression for the state can be written as:

$$|\,\Psi_N\,\rangle = \sum_{m} e^{\hat{T}(m)}\,|\,\psi_m\,\rangle\, C_m^{(N)} \tag{14}$$

Note that the cluster operators depend on the initial choice of the model state basis (indicated by the dependence on the index m), therefore the diagonalization of H^{eff} does not have the same effect as choosing the expansion coefficients for the model space functions (Equation 10). This means that also the overall result depends on the choice of the model state basis [17]. This is most evident through the orbital variance of the original Jeziorski–Monkhorst ansatz: The determinantal basis $\{|\,\Phi_\mu\,\rangle\}$ invariably changes as the orbitals of the active space are unitarily rotated, which cannot be compensated by the coefficients $C_m^{(N)}$ in Equation (14) [22]. Typically, better results are obtained for localized orbitals [23]. The generalized Jeziorski–Monkhorst ansatz, on the other hand, can be made orbital invariant, as the expansion coefficients of the reference state $c_\mu^{(m)}$ in Equation (10) can counteract any unitary active space orbital rotation [17]. Still, the result depends on the choice of the model space basis, which leads to the question whether there is a unique choice for an optimal basis. Indeed, we can consider the states that diagonalize the *effective* Hamiltonian, that is, we search for model space states that fulfill (cmp. Ref. [17]).

$$\left\langle \Phi_\mu \right| \left(e^{-\hat{T}(m)} \hat{H} e^{\hat{T}(m)} - E_m^{\mathrm{opt}} \right) \left| \psi_m^{\mathrm{opt}} \right\rangle = 0 \tag{15}$$

The central observation is now that for any state m that fulfills this equation, the multistate equations (Equation 12) reduce to

$$\left\langle \psi_\rho^Q \right| e^{-\hat{T}(m)} \hat{H} e^{\hat{T}(m)} \left| \psi_m^{\mathrm{opt}} \right\rangle = 0 \tag{16}$$

as fulfilling Equation (15) removes all coupling terms [17]. Solving Equations (15) and (16) together defines a state-specific approach that has been introduced as internally contracted multireference coupled-cluster (icMRCC) theory [20, 21]. The above considerations show that the icMRCC theory, originally introduced as a state-specific theory, is fully compatible with a multistate picture! This is illustrated by the fact that the MS-icMRCC theory based on CASCI states and the icMRCC theory based on an optimized reference lead to very similar results (Figure 1). The only price to pay is a more strong nonlinearity in the equations, which can lead to problems at closely avoided crossings; for details see Ref. [17].

A third form of the wave operator employs a UC operator, as initially proposed by Mukherjee and coworkers [15]:

$$\hat{\Omega}_{\mathrm{UC}} = e^{\hat{T}} \sum_{m} |\,\psi_m\,\rangle\,\langle\,\overline{\psi}_m\,| \tag{17}$$

which we write here in a form for generalized CASCI states in the model space expansion (the original proposal was an expansion in terms of determinants or CSFs) [15]. Inserted into the Bloch equations, this leads to

$$\left\langle \psi_\rho^Q \right| e^{-\hat{T}} \hat{H} e^{\hat{T}} \left| \psi_m \right\rangle = 0 \quad \forall \ m \tag{18}$$

while the effective Hamiltonian becomes

$$H_{nm}^{\text{eff,U}} = \left\langle \overline{\psi}_n \right| e^{-\hat{T}} \hat{H} e^{\hat{T}} \left| \psi_m \right\rangle \tag{19}$$

In order to simultaneously fulfill all of the equations in Equation (18) with a single cluster operator, high excitation ranks have to be included [16]. Consideration of a number of additional precautions has ultimately developed this theory into what is now known as Fock space coupled-cluster theory [24]. As the main target of this theory is in most cases the treatment of ionized or excited states (starting from an appropriate single-reference state), we only cover this branch parenthetically here. Equation (18) may also be turned into state-specific theory by choosing $|\psi_m\rangle$ such that it becomes an eigenstate of the effective Hamiltonian, which again leads to icMRCC theory as derived above.

Based on the special Jeziorski–Monkhorst ansatz (Equation 8), a number of state-specific variants have also been suggested [25–28]. These avoid the numerical problems often encountered in solving the multistate equations by modifying them and putting focus on the lowest state in order to ensure a large enough energy gap to higher-lying states. In particular, a sufficient number of equations for all involved cluster amplitudes must be provided (sufficiency conditions) [25] and ensuring spin-adapted solutions requires additional precautions [29].

Extensivity and size-consistency have been studied and established for the JM ansatz [16] and the state-specific variants derived from it [25]. Size-consistency, of course, always hinges on the proper choice of the reference space, which has to support the dissociation into the respective fragments. Extensivity and size-consistency of the icMRCC energy also depend on the proper choice of the linearly independent projection manifold [21, 30, 31]. For MS-icMRCC theory based on the general GJM ansatz, the conditions for extensivity of the energy have not yet been studied in detail.

4 | Issues and Potential Lines for Further Research

The observations in the previous section suggest that from a formal point of view, icMRCC theory is very attractive, being the only MRCC variant covering all the bullet points listed in the beginning of this perspective. In particular, the direct access to spin-adapted solutions appears to be an important property of this theory [32]. Practical implementations of icMRCC theory, however, come with some burden. The complexity of the explicit expressions is dramatically increased relative to single-reference coupled-cluster theory, even in comparison to high-order cluster expansions. Therefore, the only way to approach this target is the use of automatic derivation tools [20, 21]. Our own efforts have resulted in an advanced pilot implementation [33] with an efficiency that at least allowed for demonstrations on realistic few-atom systems with considerably large basis sets, such as global potential energy surfaces and accurate kinetics [34] or benchmarks for astrochemical reactions [35] and small transition-metal compounds [36, 37]. Recently, a more efficient implementation was reported [38] (restricted to the simple CAS(2,2) case, however), which allows (based on finite-difference gradients) the determination of equilibrium structures or vibrational frequencies of small diradicals like *m*-benzyne [38]. Another implementation was recently reported by Lechner et al. [39]. As shown in Table 1, current implementations of icMRCC are still computationally much more demanding than their single-reference counterparts. Apart from these implementational challenges, we want

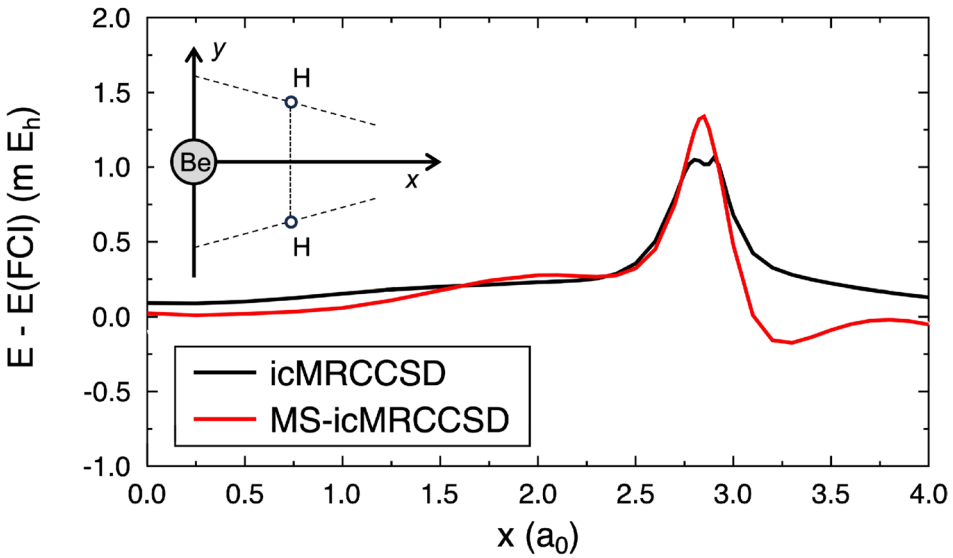

FIGURE 1 | Illustration of multistate and state-specific icMRCCSD methods for the insertion of beryllium into dihydrogen, reaction coordinate *x* as indicated in the inset. The MS-icMRCCSD method uses the GJM ansatz, Equation (9), with a CASCI model space, the icMRCCSD method uses an explicitly optimized (relaxed) reference state. Both computations are based on a CAS(2,2) reference and a DZ basis, depicted are deviations from full CI. Adapted from Ref. [17] with permission of AIP Publishing.

TABLE 1 | Timings (in seconds) of icMRCCSD implementations for the singlet state of *m*-benzyne and a CAS(2,2) reference function, in comparison to timings for an efficient single-reference CCSD implementation.[a]

Method	Basis set[b]	t_{over}/s[c]	t_{iter}/s[d]	n_{iter}[e]
icMRCCSD old[f]	cc-pVDZ	56	42	20
	cc-pVTZ	1282	441	21
icMRCCSD new[g]	cc-pVDZ	0.7	10	21
	cc-pVTZ	3	68	20
	cc-pVQZ	30	593	20
	cc-pV5Z	238	3872	20
CCSD[h]	cc-pVDZ	0.2	0.2	14
	cc-pVTZ	1	1.7	16
	cc-pVQZ	22	17	12
	cc-pV5Z	190	142	16

[a]C_{2v} point group symmetry was exploited. All runs used a single core of an Intel Xeon 6252 Gold (Cascade Lake) @ 2.1 GHz.
[b]Number of basic functions is: 104 (cc-pVDZ), 236 (cc-pVTZ), 450 (cc-pVQZ), 766 (cc-pV5Z).
[c]Time used before start of iterations, mainly for partial (old code: full) integral transformation.
[d]Average time for each iteration.
[e]Number of iterations used to reach an energy that is converged to at least $10^{-6}E_h$.
[f]Old implementation in the GeCCo code. Overhead also contains integral sort and term generation.
[g]New implementation from Ref. [38].
[h]Standard closed-shell CCSD implementation of Molpro from Ref. [40].
Source: Values from Ref. [38].

to highlight here a few issues that we consider to be the most important ones for further progress in this field.

4.1 | Completeness of Equations

The over-completeness of the amplitudes is a particular issue for state-specific MRCC. It is most obvious for state-specific theories based on Equation (8). Each reference determinant that has a nonvanishing contribution to the target state is endowed with a coupled-cluster expansion that potentially converges to the full configuration interaction limit. At a given truncation level, the projection spaces overlap and a simple projection of the ansatz Equation (8) does not lead to a sufficient number of equations, and additional sufficiency conditions are required [25, 41].

Although less obvious, the internally contracted MRCC expansion is also over-complete. To discuss this, we write the cluster operator as $\hat{T} = \sum_\rho t_\rho \hat{\tau}_\rho$ with amplitudes t_ρ and excitation operators $\hat{\tau}_\rho$. For setting up the projection space in the amplitude (Equations 16), we need the linear excitation manifold $\hat{\tau}_\rho \mid \psi_0 \rangle$, which in fact is non-orthogonal and not entirely linearly independent. An orthogonal and linearly independent basis can be obtained by Löwdin orthogonalization and has been established for long time in internally contracted multireference configuration interaction and perturbation theory [42–44]. The procedure requires the computation and diagonalization of reduced density matrices in the active space. However, the manifold of excitation *operators* $\hat{\tau}_\rho$ is not linearly dependent at all. This means that there are less projection states than amplitudes t_ρ. So far, the standard solution has been to confine the cluster operator to those excitations that have a corresponding projected equation [20, 21]. A number of precautions have to be taken to minimize artifacts due to this choice [21, 30, 31]. A possible alternative is the use of many-body equations, which set to zero the off-diagonal elements of the similarity transformed operator $\left(e^{-\hat{T}}\hat{H}e^{\hat{T}}\right)_\rho = 0$, as considered by Nooijen and coworkers [45, 46].

In order to introduce state-specificity, these equation must be formulated within the generalized normal ordering (GNO) formalism [47]. This idea is particularly at the heart of Evangelista's driven similarity renormalization group (DSRG) approach [48].

4.2 | Expansion Types

One issue with the internally contracted ansatz is the non-commutativity of the cluster operators. This leads to contractions between cluster operators in the exponential $\exp\left(\hat{T}\right)$. These may be avoided by introducing the normal ordered exponential [49]

$$\left\{e^{\hat{T}}\right\} = 1 + \hat{T} + \frac{1}{2}\left\{\hat{T}^2\right\} + \ldots \tag{20}$$

where the curly brackets indicate a normally ordered product, effectively forbidding any contractions of $\hat{T}$ in the expansion. This ansatz is inter alia used by Mukherjee and coworkers [50, 51] and Tew and coworkers [52]. The complication lies in the fact that the inverse of Equation (20) is not straightforward and earlier work has tried to avoid it by reformulating the equations [50]. A recursive definition was already discussed by Nooijen [53], who showed that

$$\left\{e^{\hat{T}}\right\}^{-1}\hat{H}\left\{e^{\hat{T}}\right\} =: \hat{G} = \left(\hat{H}\left\{e^{\hat{T}}\right\}\right)_c - \left(\left\{e^{\hat{T}} - 1\right\}\hat{G}\right)_c \tag{21}$$

from which a series expansion can be derived. Recently, Mukherjee and coworkers [51] put forward an alternative formulation (although not explicitly labeled as inverse of the normally ordered exponential in their work):

$$\hat{G} = \left(\left\{e^{\hat{\Theta}}\right\}\left(\hat{H}\left\{e^{\hat{T}}\right\}\right)_c\right)_c \tag{22}$$

where

$$\hat{\Theta} = -\hat{T} + \left(\hat{T}\hat{T}\right)_c - \left(\hat{T}\hat{T}\hat{T}\right)_c + \ldots = \sum_{n=1}^{\infty}(-1)^n\left(\hat{T}^n\right)_c \tag{23}$$

In both formulations, the series can be truncated at a given order, for instance at quadratic terms. From the equations above, however, it becomes clear that the contractions between cluster operators in the amplitude equations enter "through the back door."

4.3 | Scaling With Active Space Size

One issue that plagues multiconfigurational theories is the factorial scaling of complete active spaces. This has prompted the development of systematic approximations that include only selected configurations (like general active spaces [54], or selected CI theories [55, 56]) or tensor decompositions like DMRG [57]. This, however, violates the assumption of a complete model space,

on which the choice of the cluster operator in the previous section was based. Therefore, the cluster operator manifold has to be extended with purely active excitations. Within coupled-cluster theory, this induces two problems: First, the exponential of these operators does not truncate by any kind of exhaustion of the excitation space and second, they potentially violate the intermediate normalization condition. The first problem is not fundamental, as commutator approximations are anyway used in many MRCC implementations and quadratic approximations often work very well [20]. The second problem may be solved based on insights by Li and Paldus [58, 59], who in the realm of generalized model spaces discussed "constraining conditions." In our understanding, these may be boiled down to requiring $\left\langle \Phi_\mu \right| e^{\hat{T}} \left| \Phi_\nu \right\rangle = \delta_{\mu\nu}$. As an example, if two reference determinants are related by a purely active excitation, say $\hat{a}_{tv}^{uw} \left| \Phi_1 \right\rangle = \left| \Phi_2 \right\rangle$, then the sum of this amplitude and all equivalent disconnected clusters must vanish [58, 59]: $t_{uw}^{tv} + t_u^t t_w^v - t_u^v t_w^t = 0$. This ensures that the effective Hamiltonian can still be rewritten as in Equation (13) and therefore retains the connectedness of the energy expression.

A related issue is the occurrence of high-order reduced density matrices (RDMs). For icMRCCSD and truncation of the residual to double commutators, up to five-body RDMs can occur [21]. Approximations by lower-order cumulants may be considered which, however, lead to numerical instabilities [60]. In their work on canonical transformation theory, which can be considered a unitary variant of the icMRCC ansatz, Yanai and Chan [61] proposed an approximation within the GNO formalism in which at each commutator level, the resulting operator is truncated to one- and two-body contributions. In a recent work, Margócsy and Szabados [62] used a generalized valence bond reference and the GNO formalism, and they advocated a related truncation scheme of the equations to avoid high-rank intermediates.

4.4 | Scaling With System Size

A further issue is the generally high scaling of correlated theories with respect to the overall system size. For a given size of active space, icMRCCSD shows the same N^6 scaling as CCSD, which clearly limits applications, not to speak of higher-order cluster corrections. In addition, multireference theories come at present with a considerably higher prefactor. The prefactor can be damped by resorting to approximations like perturbative approaches [63], linearized approaches [64], or hybrids thereof [65, 66]. For single-reference theories, pair-natural orbital based local correlation methods have lead to a fundamental extension of the applicability [12, 13]. Extensions of this approach to the multireference regime have already been reported, for instance for perturbation theory [67], a coupled-electron pair and perturbation theory hybrid approach [65], and a two-determinant version of a state-specific MRCCSD variant [68]. A further interesting development is the exploitation of massive parallel computing environments by stochastic methods [69].

4.5 | Convergence to the Complete Basis Set Limit

Just as their single-reference counterparts, MRCC methods require the use of large basis sets in order to produce results close to the complete basis set (CBS) limit. However, using large basis sets can be a problem for the already computationally expensive methods and is often not feasible. Instead, the issue can be tackled with alternative methods, such as the introduction of geminal functions into the basis set, leading to explicitly correlated MRCC methods [70–73].

5 | Conclusions

There has been considerable progress in understanding how to approach multireference problems in coupled-cluster theory. In particular, we argued in this perspective that there is a straightforward route from the Bloch equations for a set of quasidegenerate states to state-specific internally contracted multireference coupled-cluster (icMRCC) theory. This theory comes with a number of desirable properties, like being size-consistent, treating all reference configurations on the same footing, being fully spin-adapted, and showing orbital invariance. At the same time, the theory faces a number of problems in its technical implementation, and it has not yet found its place in the standard toolbox of quantum chemistry. We have listed a number of potential research lines for which promising preliminary work exists, and we look forward to further common progress in the community to reach the aim of a consolidated approach to an accurate benchmark method for multireference cases.

Author Contributions

Robert G. Adam: writing – original draft (supporting), writing – review and editing (equal). **Alexander Waigum:** writing – original draft (supporting), writing – review and editing (equal). **Andreas Köhn:** conceptualization (lead), methodology (lead), writing – original draft (lead), writing – review and editing (equal).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Related WIREs Articles

State-specific multireference coupled-cluster theory

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