What is the best multireference coupled-cluster method?

Thomas-C. Jagau[1]
Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Germany

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1 Introduction

Among the most interesting problems in state-of-the-art theoretical chemistry ranks the question: How can electronic states with multireference character be efficiently treated with chemical accuracy? Multireference problems include bond-breaking processes, biradicalic species, as well as many transition-metal compounds. Their thorough understanding is of great interest for different branches of chemistry and related applied sciences. At the theoretical level, all multireference problems share the common feature of quasi-degenerate states so that strong static electron correlation is present. A single Slater determinant built from orbitals obtained within Hartree-Fock (HF) theory [1] is therefore not a valid zeroth-order *ansatz* for the electronic wavefunction and a linear combination of several determinants, whose occupation vector differs in some active orbitals, has to be used instead to obtain a qualitatively correct description resulting in the MCSCF (multi-configurational self-consistent field) wavefunction.[2] Unfortunately, the inclusion of dynamical electron correlation into the wavefunction is required as well in most cases to obtain chemically accurate results.

For systems qualitatively described by HF theory, single-reference coupled-cluster (SRCC) theory [3] has proven to be a powerful approach for the inclusion of dynamical electron correlation. But since the generalization of SRCC theory to the multireference case is neither obvious nor unique, a variety of multireference coupled-cluster (MRCC) *ansätze* is possible and has been proposed.[4-10] Even though considerable effort has been devoted to this field during the last thirty years, none of the available MRCC *ansätze* has evolved yet into a computational tool as successful and widely applicable as the SRCC *ansatz*.

In the following, we will give an overview of the problems that appear when the SRCC *ansatz* is generalized to the multireference case and discuss different MRCC methods that have been developed.

2 Discussion

SRCC theory is nowadays a powerful computational tool to explore energetics as well as molecular properties in a routine manner. Its main advantage over configuration-interaction (CI) methods consists in the fact that energies obtained by SRCC theory are rigorously size-extensive, which means that the correlation energy scales linearly with the system size in the limit of a large system.[11] In contrast to CI methods that use a linear wavefunction expansion, the coupled-cluster approach employs an exponential expansion of the wavefunction

$$|\Psi\rangle = e^{\hat{T}} |\Phi\rangle \tag{1}$$

with the cluster operator defined as $\hat{T} = \sum_q t_q \hat{\tau}_q$ and t_q and $\hat{\tau}_q$ denoting cluster amplitudes and excitation operators, respectively. $|\Phi\rangle$ is a single-determinant reference state, often the HF wavefunction. The exponential *ansatz* guarantees size-extensivity of the method regardless of a truncation of the cluster operator to a certain excitation level, which is the reason for the great success of approximated schemes like CC singles and doubles (CCSD) or CC singles, doubles and triples (CCSDT).

To treat quasi-degenerate states, several approaches that introduce only slight modifications into the SRCC *ansatz* have been proposed. Among these rank for example the active space CC method [12] and the reduced MRCC method [13] that include several higher excitations into the cluster operator. Another reasonable access to the treatment of quasi-degenerate states is provided by approximately size-extensive MRCI-based methods like the multireference averaged quadratic coupled-cluster (MR-AQCC) method [14] and the multireference averaged coupled-pair functional (MR-ACPF) method.[15] In particular, the latter methods have shown to provide reasonably accurate descriptions for several multireference cases. However, in this paper, we will focus on genuine MRCC approaches based on a multi-determinantial zeroth-order wavefunction.

Before we discuss the existing ansätze let us summarize in brief some general features that a convincing MRCC *ansatz* should fulfill from the theoretical perspective. To begin with, the *ansatz* ought to lead to a wavefunction that represents a valid parametrization of the full CI wavefunction if no truncations are applied. The *ansatz* is furthermore expected to conserve the appealing properties of the SRCC *ansatz* (1). This includes the possibility to apply truncations to the cluster operator without losing size-extensivity. From the technical point of view, a potentially successful MRCC method should be implementable as an algorithm as robust and stable as it is possible for SRCC. The computational cost should not exceed those of comparable MRCI-based methods to secure competitiveness. Since a large number of determinants is often required for a valid zeroth-order description, a factorial scaling of the computational cost with the number of active orbitals is prohibitive.

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[1] Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 11, 55128 Mainz

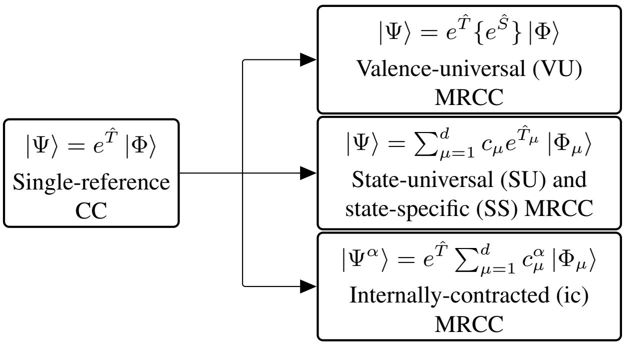

Figure 1: Wavefunction *ansätze* in MRCC theory

From a high-altitude perspective all available MRCC methods can be divided into three classes, whose generic ansätze for the wavefunction are shown in Figure 1. Early attempts to formulate a general MRCC approach led to two different branches of multiroot methods that treat more than one electronic state within the same calculation. Valence-universal (VU) MRCC methods,[4] also called Fock-space CC methods, simultaneously calculate several states having different numbers of valence electrons and are closely related to the equation-of-motion (EOM) CC methods.[16] Different sectors of the Fock-space are reached via the action of the operator $\{e^{\hat{S}}\}$ on a closed-shell reference $|\Phi\rangle$.

In contrast, state-universal (SU) MRCC methods [5] cover a manifold of electronic states with a constant number of valence electrons within the same calculation. The SU *ansatz* for the wavefunction, originally introduced by Jeziorski and Monkhorst (JM), employs a linear combination of determinants $|\Phi_\mu\rangle$ as reference that form the model space $\mathcal{M}$. $\hat{T}_\mu$ and c_μ represent the reference-specific cluster operators and weighting coefficients, respectively. In SU MRCC theory the energies for all considered states and the corresponding weighting coefficients c_μ are obtained by diagonalizing an effective Hamiltonian matrix constructed by projecting the Schrödinger equation onto the model space

$$\sum_{\mu} \langle\Phi_\nu|\,\hat{H}e^{\hat{T}_\mu}\,|\Phi_\mu\rangle\, c_\mu = E c_\nu\ . \tag{2}$$

The amplitude equations are defined via projection onto the set of excited determinants. The JM *ansatz* has also been employed to formulate state-specific (SS) MRCC theories that always treat only one state α within a calculation. In this case, additional sufficiency conditions have to be invoked to uniquely define the amplitudes as the JM *ansatz* leads to an underdetermined SS MRCC wavefunction. This problem relates to the fact that a certain excited determinant may be reached from more than one reference. Proposed SS MRCC approaches include the Brillouin-Wigner (BW) MRCC *ansatz*,[6] the Mk-MRCC *ansatz* [7] introduced by Mukherjee et al. and the MRexpT *ansatz* by Hanrath.[8] Equation (2) is also valid for SS MRCC approaches with the restriction that only one root of the effective Hamiltonian is physically meaningful.

Yet another MRCC approach is given by internally-contracted (ic) methods.[9,10] The ic-MRCC wavefunction is based on a reference-independent cluster operator that acts on a zeroth-order MCSCF wavefunction. Equations for determining the energy and cluster amplitudes are obtained similarly to equation (2) by projection of the Schrödinger equation on the reference space and its complement but possess a significantly more complicated structure compared to this case. While state-universal and state-specific formulations of ic-MRCC theory are principally possible, we will only discuss the state-specific variant.

After having presented some important MRCC ansätze the naturally arising question is how these ansätze perform and which advantages and disadvantages they carry. Figure 2 summarizes a couple of relevant criteria. Regarding VU and SU MRCC approaches it turns out that they carry two problems that severely limit their applicabilty, although the SU *ansatz* looks like a rather simple generalization of the SRCC *ansatz*. The first problem is obvious: In many cases, one is interested in a single root and the necessity to calculate more than one root is just a drawback that increases the computational cost. The other problem is more subtle and consists in so-called intruder states [17] that are not included in $\mathcal{M}$, but come energetically close to it at some regions of the potential energy surface. As intruder states often spoil the iterative solution of the CC equations by causing divergence problems, the choice of the model space plays a crucial role in SU MRCC calculations.

These deficiencies may serve as a strong motivation to pursue SS MRCC approaches, which avoid the intrinsic disadvantages of SU and VU methods by always treating one single state α at a time. For SS MRCC methods based on the JM *ansatz*, the already mentioned need to introduce sufficiency conditions causes further complications. The conceptionally most simple scheme is probably the Brillouin-Wigner (BW) MRCC *ansatz*, where independent amplitude equations coupled only via the effective Hamiltonian matrix are obtained for each reference. However, this *ansatz* does not preserve size-extensivity, thereby losing the main advantage of CC theory. The SS MRCC *ansatz* introduced by Mukherjee et. al. (Mk-MRCC) in contrast employs more sophisticated sufficiency conditions, which lead to explicit coupling between the amplitudes for different references and ensure rigorous size-extensivity. While the Mk-MRCC method has proven to deliver reasonably accurate results for some model applications,[18,19] it still suffers from severe limitations. One drawback, introduced via the sufficiency conditions, consists in the fact that the projected Schrödinger equation is fulfilled only in the intersection of the references' excitation manifolds but not in their union. This has been termed a violation of the "proper residual condition" [20] and motivates the MRexpT *ansatz*, which circumvents this problem by fixing the number of excited determinants to that of cluster amplitudes and thus solving the redundancy problem. While MRexpT has been shown to fulfill the proper residual condition, it does not preserve size-extensivity in general. A further, particular delicate issue is revealed by looking at orbital rotations. In theory, the energy is expected to be invariant under separate rotations of occupied, active, and virtual orbitals, but this property is violated by all methods relying on the JM *ansatz*.[21]

	VU-MRCC	SU-MRCC	BW-MRCC	Mk-MRCC	MR-expT	icSS-MRCC
intruder state free	yes	yes	no	no	no	no
size-extensivity	yes	yes	no	yes	no	yes
orbital invariance	??	no	no	no	no	yes
proper residual	yes	yes	no	no	yes	??
easy to implement	yes	yes	yes	yes	no	no

Figure 2: Comparison of several MRCC ansätze

Since this gives rise to a certain arbitrariness of energies and molecular properties, it is considered a serious problem of JM-based methods. However, it cannot be ruled out that the JM *ansatz* may be employed to formulate a fully orbital-invariant MRCC method. A further problematic feature common to all MRCC methods based on the JM *ansatz* is the linear scaling of the computational cost with the number of reference determinants. This property renders the application of model spaces with more than six or eight electrons close to impossible.

In MRCI theory, an efficient way to reduce the computational cost is provided by the use of internally-contracted wavefunctions.[22] In analogy to that, it has been also tried to set up an internally-contracted (ic) MRCC wavefunction. While this *ansatz* possesses two distinct advantages over the JM *ansatz*, namely that the number of amplitudes becomes nearly independent of the number of reference determinants and that the cluster operator can be chosen such that full orbital invariance is ensured, it leads to significant complications, too. Due to a more involved structure of the cluster operator $\hat{T}$, the Baker-Campbell-Hausdorff expansion that is in general employed to derive explicit expressions for the cluster amplitudes does not truncate as it does in the case of SRCC and JM-based MRCC wavefunctions, which significantly impedes the implementation of ic-MRCC. Several concepts including automated implementation techniques have been proposed to deal with this issue,[10,23] but a convincing realization of the theory in a production-level code has not yet been presented.

3 Conclusion

In this paper, we have given an overview into MRCC theory. We presented several MRCC approaches currently under consideration and showed that they all violate certain criteria that a convincing MRCC approach is expected to fulfill. Although remarkable progress in the field of MRCC theory has been achieved during the last years and some MRCC methods show reasonably well performance for model applications, it still remains an open question if it is possible to set up a MRCC method satisfying all theoretical criteria discussed. Furthermore, it is unclear if either one of the three presented wavefunction *ansätze* is suited for the formulation of such a method or if a novel *ansatz* is needed. But even if such an optimal MRCC method exists in theory, it needs to deliver significantly better results than SRCC, MR-AQCC and MR-ACPF methods to prevail against the latter. This is not a small hurdle given the often surprisingly good performance of MR-AQCC and MR-ACPF and the well-known ability of SRCC methods to correct for quasi-degeneracy effects by inclusion of higher excitations into the cluster operator. Despite these challenges, we are convinced that the use of genuine MRCC methods represents the best approach to treat quasi-degeneracy effects at a level of high accuracy and that the formulation of a perfect MRCC *ansatz* is possible.

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