**Multireference Coupled Cluster Theory**

**Introduction**

Coupled-cluster theory,\(^1\)-\(^8\) which treats the dynamical electron correlation problem in terms of an infinite-order exponential ansatz of interacting clusters of electrons, has emerged over the last two decades as the most powerful and practical approach for achieving highly accurate quantum chemical predictions. The CCSD(T) method,\(^9\)-\(^12\) an extension of the standard coupled-cluster singles and doubles model\(^13\) that employs a balanced perturbative correction term for connected triple excitations, has proved to be remarkably successful in myriad chemical applications.\(^14\) Indeed, many consider CCSD(T) to be the current “gold standard” of \textit{ab initio} quantum chemistry.

The problem is that single-reference methods such as CCSD(T) can fail dramatically during homolytic bond cleavage or when electronic near-degeneracies arise in general.\(^15\),\(^16\)

For multireference systems various remedies have been advanced that remain within the single-reference coupled cluster framework, including the reduced multireference (RMRCC) method,\(^16\)-\(^28\) active-space coupled-cluster approaches,\(^29\)-\(^48\) tailored CCSD,\(^49\),\(^50\) orbital-optimized coupled-cluster schemes,\(^51\)-\(^53\) spin-flip methods,\(^54\)-\(^59\) higher-order, non-iterative corrections derived from the similarity-transformed Hamiltonian,\(^60\)-\(^63\) and a broad class of method-of-moments (MM) and renormalized coupled-cluster methods.\(^56\),\(^64\)-\(^81\) However, the development of \textit{genuine} multireference coupled-cluster (MRCC) methods\(^82\)-\(^137\) has lagged far behind the success of single-reference approaches, despite important recent advances.\(^87\)-\(^134\) Very few chemical problems have been tackled with these powerful techniques of largely unrealized potential. Our group is now at the forefront of the development and large-scale implementation of refined and efficient MRCC methods.\(^136\),\(^137\)

Succinct overviews providing direction into the extensive literature of MRCC methods can be found in papers published by Li and Paldus,\(^120\) by Pittner,\(^99\) and by us,\(^136\),\(^137\) as well as chapters in a recent compilation of reviews on the first forty years of computational chemistry.\(^8\) Briefly, MRCC methods may be classified in three broad categories: Fock-space or valence-universal (VU) theories, Hilbert-space or state-universal (SU) approaches, and state-specific (SS) methods. Fock-space methods are designed for computing differential properties of states with variable numbers of electrons, providing ionization potentials and electron affinities within a single computation. Hilbert-space methods simultaneously converge wave functions for entire sets of electronic states with the same number of electrons, yielding an excitation energy spectrum within a single computation; in essence, these methods are multireference, multirooting schemes suitable for mapping a manifold of potential energy surfaces. The application of Hilbert-space methods has been plagued by intruder state problems, occurring when a determinant outside the model (reference) space closely approaches the energy of a state inside this space at some point on a potential energy surface. Intruder states may not only spoil the convergence of multireference, multirooting procedures but may even lead to unphysical features on computed potential energy surfaces. Such difficulties, coupled with the need for multireference, state-specific coupled cluster theories (SS MRCC) for treating one electronic state at a time, have spawned new formal developments.\(^89\)-\(^93\),\(^95\),\(^96\),\(^99\),\(^101\),\(^103\),\(^104\),\(^106\)-\(^108\),\(^110\),\(^112\),\(^113\),\(^132\),\(^133\),\(^135\),\(^137\)

The usual formulation of MRCC methods entails a partitioning of the electronic structure problem into a pre-selected, internal model (reference) space \(M\) spanned by the Slater determinants \(\{ \Phi_x \}\) and its external complement \(M\) spanned by \(\{ \Phi_x \}\). Often \(M\) is taken as the active space from a prior CASSCF computation involving some set of valence molecular orbitals. The final wave function \(|\Psi_x\rangle\) for state \(x\), expressed in intermediate normalization, may be projected onto the \(M\) and \(M\) spaces via operators \(\hat{P}_M\) and \(\hat{Q}_M\), respectively, and the wave operator \(\hat{\Omega}_x\) is sought which yields \(\Psi_x\) from its reference component \(\Psi_{x,M}^w\):

\[
|\Psi_x\rangle = (\hat{P} + \hat{Q}_M) |\Psi_{x,M}^w\rangle = |\Psi_{x,M}^w\rangle + \hat{\Omega}_x |\Psi_{x,M}^w\rangle = \hat{\Omega}_x |\Psi_{x,M}^w\rangle \quad .
\]

Our benchmark and general implementation studies\(^136\),\(^137\) have found that the best state-specific MRCC wave functions are obtained from a formalism originally proposed by Mukherjee and co-workers.\(^106\)-\(^108\) We have very recently programmed the first production-level code\(^137\) for this approach and have designated this theory as Mk-MRCC. The Mk-MRCC ansatz for the wave operator is the Jeziorski-Monkhorst (JM) form\(^138\)

\[
\hat{\Omega}_x = \sum_{\mu=0}^\infty e^{\mu \hat{T}_{x,M}^w} |\Phi_0\rangle \langle \Phi_0| \quad ,
\]

in which a coupled-cluster excitation operator \(\hat{T}_{x,M}^w\) appears for each reference determinant in the model space. Combining Eqs. (1) and (2) gives
\[ |\Psi_a\rangle = \hat{\Omega}_a |\Psi_a^m\rangle = \sum_{\mu} e^{i\epsilon^\mu} |\Phi_\mu\rangle c_\mu^a, \]  
(3)
where the coefficients \( c_\mu^a = \langle \Phi_\mu | \Psi_a^m \rangle \). From the Schrödinger equation, one thus has
\[ \sum_\mu \hat{H} e^{i\epsilon^\mu} |\Phi_\mu\rangle c_\mu^a = E_a \sum_\mu e^{i\epsilon^\mu} |\Phi_\mu\rangle c_\mu^a. \]  
(4)

Left-projection of Eq. (4) onto the model space \( \mathcal{M} \) gives the energies \( E_a \) and configuration interaction coefficients \( c_\mu^a \) as eigenvalues and eigenvectors of the effective Hamiltonian matrix
\[ H_\mathcal{M} = \langle \Phi_\mu | \hat{H} \hat{e}^{i\epsilon} | \Phi_\nu \rangle; \quad \sum_\mu H_\mathcal{M} c_\mu^a = E_a c_\nu^a. \]  
(5a,5b)

Let us now write a useful reduction of the identity operator as
\[ 1 = e^{i\rho} e^{-i\rho} = e^{i\rho} (\hat{P} + \hat{Q}) e^{-i\rho} = \sum_\nu e^{i\rho} |\Phi_\nu\rangle \langle \Phi_\nu | e^{i\rho} + e^{i\rho} \hat{Q} e^{i\rho} \equiv \hat{P} + \hat{Q}, \]  
(6)
and then project it onto the left side of Eq. (4), providing
\[ \sum_\mu e^{i\epsilon} |\Phi_\nu\rangle \langle \Phi_\nu | \hat{H} e^{i\epsilon} | \Phi_\mu\rangle c_\mu^a + \sum_\nu e^{i\epsilon} \hat{Q} \hat{H}_\mu |\Phi_\mu\rangle c_\nu^a = E_a \sum_\nu e^{i\epsilon} |\Phi_\nu\rangle c_\mu^a. \]  
(7)

The notation of Eq. (7) involves the familiar similarity-transformed Hamiltonian
\[ \hat{H}_\mu = e^{i\epsilon} \hat{H} e^{i\epsilon}. \]  
(8)

A key feature of the Mk-MRCC method\textsuperscript{106,107} is an interchange of the dummy indices \( \mu \) and \( \nu \) on the left side of Eq. (7). With subsequent factorization (and definition of an operator \( \hat{R}_\mu^\nu \))
\[ \sum_\mu e^{i\epsilon} \left[ \sum_\nu c_\nu^a \langle \Phi_\mu | \hat{H}_\nu | \Phi_\nu \rangle e^{-i\epsilon} e^{i\epsilon} + c_\mu^a \hat{Q} \hat{H}_\mu - E_a c_\nu^a \right] |\Phi_\mu\rangle \equiv \sum_\mu e^{i\epsilon} \hat{R}_\mu^\nu |\Phi_\mu\rangle = 0. \]  
(9)

In state-specific (SS) multireference coupled cluster methods built on the JM wave operator of Eq. (2), additional sufficiency conditions must be applied, because the number of equations that can be derived by introducing the ansatz into the Schrödinger equation is less than the number of \( t \)-amplitudes contained in the \( \hat{T}_\mu^\nu \) operators. In particular, a redundancy exists among the \( t \)-amplitudes related to any determinant that can be generated from multiple references within the chosen excitation level cutoff. Various theories impose different sufficiency conditions, with far-reaching consequences on the mathematical properties of the method.

In Mk-MRCC theory, the sufficiency conditions are that Eq. (9) is satisfied by setting \( \hat{R}_\mu^\nu |\Phi_\mu\rangle = 0 \) for each reference \( \mu \). Upon projection onto the external complement space \( \mathcal{M} \), the resulting amplitude equations are
\[ \langle \Phi_\mu^{ab} \rangle |\hat{H}_\nu | \Phi_\nu \rangle c_\nu^a + \sum_{\nu,\mu} \langle \Phi_\mu^{ab} \rangle e^{-i\epsilon} e^{i\epsilon} |\Phi_\nu \rangle \langle \Phi_\nu | \hat{H}_\mu | \Phi_\mu \rangle c_\mu^a = 0, \]  
(10)

where \( \Phi_\mu^{ab} \) denotes a determinant obtained from \( \Phi_\mu \) by excitation from occupied spin-orbitals \( i, j, \ldots \) to virtual spin-orbitals \( a, b, \ldots \). Equation (10) provides sufficient and nonredundant conditions for all cluster amplitudes of the multiple references \( \Phi_\mu \).

The Brillouin-Wigner (BW) coupled cluster method of Hubač and collaborators\textsuperscript{89-104} is another state-specific MR-CC theory. In this approach the Schrödinger equation is satisfied implicitly by requiring the JM wave operator to obey the condition
\[ \hat{\Omega}_a = \hat{T} + \hat{B}_S \hat{V} \hat{\Omega}_a, \]  
(11)
where \( \hat{B}_S = (\hat{H}_a - \hat{H}_{\mathcal{M}})^{-1} \hat{Q} \) is the BW resolvent and the Hamiltonian is partitioned as \( \hat{H} = \hat{H}_a + \hat{V}. \) The BW-MRCC sufficiency conditions are equivalent to satisfying Eq. (4) by equating the individual \( \mu \) terms. Projection onto determinants (\( \Phi_\mu \)) of the \( \mathcal{M} \) space then yields the equations for the cluster amplitudes within the \( \hat{T}_\mu^\nu \) operators,
\[ E_a \langle \Phi_\mu | \hat{H} e^{i\epsilon} | \Phi_\mu \rangle = \langle \Phi_\nu | \hat{H} e^{i\epsilon} | \Phi_\nu \rangle. \]  
(12)
The critical difference in the single-root Mk-MRCC theory\textsuperscript{106-108} and the alternative BW-MRCC approach\textsuperscript{89-104} is that the MR-BWCC scheme involves only indirect coupling of \( \hat{T}_\mu^\nu \) and \( \hat{T}_\alpha^\nu \) amplitudes (via \( E_a \)), but at the expense of \textit{not} being fully size extensive, whereas the Mk-MRCC scheme has more complicated direct coupling of \( T_\mu^\nu \) and \( T_\alpha^\nu \) amplitudes, while retaining rigorous size extensivity.
Synopsis

Our research on MRCC theory has very recently achieved breakthroughs toward realizing the potential of these powerful methods and making them widely applicable. In particular, we have developed and implemented Mk-MRCCSD theory, which has all of these desirable properties: (1) it is built on a wave operator formalism, in which the energy is obtained as a root of an effective Hamiltonian; (2) it is a state-specific, Hilbert space method that retains all of the flexibility of the wave function for optimizing the description of a single, target electronic state; (3) it exhibits rigorous size extensivity (correct scaling with the number of electrons) and size consistency (additively separable energy upon dissociation into fragments); (4) it is resistant to intruder state problems, occurring when a determinant outside the reference space closely approaches the energy of a state inside this space at some point on a potential energy surface; (5) it poses no difficulties in converging the MRCC amplitude equations in most cases; and (6) it is a mathematically tractable theory that can be applied to large chemical systems.

In our first paper, high-order excitations \( n > 2 \) were studied within three competing multireference coupled cluster theories for the first time. For the classic H4, P4, BeH2, and H8 model problems, multireference coupled cluster wave functions, with complete excitations ranging from doubles to hexuples, were computed with a new arbitrary-order string-based code that we devised. Comparison was then made to corresponding single-reference coupled cluster and full configuration interaction (FCI) results. The error curves (with respect to FCI) demonstrated that for ground electronic states our Mk-MRCC theory is clearly superior to previous state-universal coupled cluster methods at all levels of truncation of the cluster operator. One qualitative measure of the performance of MRCC methods is the degree to which the error curves remain flat throughout the single and multireference regions of the geometric configuration space. For our model problems, Mk-MRCCSDT met this criterion exceedingly well. Another measure of performance is the absolute error with respect to FCI at the geometric points of maximum multireference character. Here Mk-MRCC theory proved to be as accurate at these points as conventional coupled-cluster methods in single-reference systems. In summary, our Mk-MRCC approach proved to be the clear method of choice among existing MRCC formalisms. The code we have developed is general and currently found in the freely distributed PSI3 program.

In our second paper, simple closed-form expressions were derived for the “same vacuum” renormalization terms that arise in state-specific multireference coupled cluster theories. Explicit equations were provided for these coupling terms through the triple excitation level of MRCC theory, and a general expression was included for arbitrary-order excitations. This discovery was a breakthrough, because the coupling terms in Mk-MRCC theory were previously thought to be intractable for general programming. With this advance we developed the first production-level code (PSIMRCC) for state-specific and rigorously size-extensive Mk-MRCCSD computations. Our code is also capable of computing wave functions for other MRCC variants. Using correlation-consistent basis sets (cc-pVXZ, \( X = D, T, Q \)), Mk-MRCCSD was then tested on two classic multireference problems: (1) the dissociation potential curve of molecular fluorine, and (2) the structure and vibrational frequencies of ozone. Particularly accurate results for \( F_2 \) were obtained by applying the Mk-MRCCSD method at the complete basis set (CBS) limit with localized molecular orbitals; specifically, the dissociation energy, equilibrium bond distance, and harmonic vibrational frequency were predicted to within 0.2 kcal mol\(^{-1}\), 0.0015 Å, and 2 cm\(^{-1}\), respectively. Finally, to demonstrate the efficacy of multireference Mk-MRCCSD theory for larger systems, we computed the singlet-triplet splittings in ortho-, meta-, and para-benzene, coming within 1.5 kcal mol\(^{-1}\) of experiment in all cases.

The implementation of our powerful multireference coupled cluster methods in efficient production level codes will allow us to investigate diverse chemical environments that cannot be described in zeroth order by a single electronic configuration, including potential energy surfaces for homolytic bond cleavage, species with strong diradical character, processes involving avoided crossings and nonconservation of orbital symmetry, pure angular momentum states of linear molecules, Renner-Teller vibronic manifolds, and various electronic symmetry breaking phenomena. We are confident that many new and longstanding chemical problems will be solved by our MRCC methods in the coming months.

References


