Recent Progress in Multireference Hilbert-Space Coupled Cluster Methods: Explicit Correlation, Massively Parallel Implementation, and USS Corrections

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The standard coupled cluster (CC) method, like other single reference methods, exhibits a poor performance when quasidegeneracies are encountered, unless high-level excitations are included. One possibility how to solve this problem is a multireference generalization of the CC method (MRCC) based on the Jeziorski-Monkhorst ansatz. This leads to Hilbert-space MRCC methods, which can be state-universal (SU MRCC), or state-specific (Brillouin-Wigner MRCC, Mukherjee's MRCC). The state-universal method suffers from the intruder state problem, while the Brillouin-Wigner method is not rigorously size-extensive, leaving the Mukherjee's MRCC (MkCC) as the most promising one from this class of methods. Although MkCC method still does not satisfy some requirements from a "wish-list" of the properties of an ideal MRCC, it represents a reasonably accurate and practicable method for small model spaces. We have thus pursued the development of explicitly correlated version of this method, at the SD level and recently also with the non-iterative triples, employing the SP ansatz and standard approximation together with the Slater (F12) correlation factor. The results confirm the significantly faster convergence with respect to the basis set limit compared to the "traditional" one.

Application of MRCC methods to realistic chemical systems requires development of parallelized implementations, which can efficiently exploit available supercomputer architectures. We present such implementations of the BWCC and MkCC methods at singles, doubles, and perturbative triples level, which offer excellent scaling up to several thousand cores.

The Universal State-Selective (USS) corrections proposed by K. Kowalski aim to improve MRCC energies towards FCI and can be applied to any type of MRCC theory based on the Jeziorski-Monkhorst Ansatz. For BWCCSD, the main effect of the USS correction is to approximately restore size-extensivity, while for MkCCSD it seems to (at least partially) take into account Hamiltonian matrix elements not present in the original MkCCSD theory due to the separate projection manifolds employed. We have recently implemented the USS correction including non-diagonal terms in the NWChem program and compare the results with the previously published approximate one, which contained only diagonal terms (USSD).