Multireference Brillouin-Wigner Coupled Clusters Method with a Perturbative Triples Correction

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It is well known in quantum chemistry, that the study of systems with quasi-degenerate orbitals requires a multireference treatment. One of the available approaches is the multireference Brillouin-Wigner coupled clusters (MR BWCC) method [1-3]. As found previously, in order to describe the dynamical correlation quantitatively, it is necessary to include contributions from connected triple excitations into the cluster operator. This approach lead to MR BWCCSDT and MR BWCCSDTα methods, which were shown to yield significantly more accurate vibrational frequencies for the oxygen molecule [4].

Although being rigorous, the iterative inclusion of connected triples is computationally very demanding. The noniterative approach, which would reduce the scaling of the method to only n^7 in a single step, is thus a necessary prerequisite for studying larger and chemically more interesting systems. Recently, the MR BWCCSD(T), which is a multi-reference generalization of the standard CCSD(T) method, was developed. The inclusion of connected triples is performed via corrections to matrix elements of the effective Hamiltonian in an analogous way as in the MR CCSD(T) approach by Balková and Bartlett [5].

For comparison of performance with the iterative methods, MR BWCCSD(T) calculations of the low-lying electronic states of the oxygen molecule have been performed. In order to demonstrate the applicability of the method to larger systems, we studied the energetics of the Bergmann reaction and the automerization barrier in cyclobutadiene.

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