# Multireference Mukherjee's Coupled Cluster method with triexcitations in the linked formulation: Efficient implementation and applications

Kiran Bhaskaran-Nair, Ondřej Demel, and Jiří Pittner
*J. Heyrovský Institute of Physical Chemistry, v.v.i.,*
*Academy of Sciences of the Czech Republic.*

The standard coupled cluster method does not perform well in many situations of great chemical interest, for example during bond breaking, double bond twisting, for diradicals, and reaction intermediates; therefore a multireference generalization of coupled cluster theory is highly desirable. The state-universal Hilbert space MRCC methods conveniently yield energies of several states in one calculation, but often suffer from intruder state problems, leading to severe convergence difficulties. For this reason, the state-specific methods, where only one eigenvalue of the effective Hamiltonian has a physical meaning, have become more popular in the last years [1].

The multireference Brillouin-Wigner coupled cluster method (BWCC) [2, 3] belongs to the group of state specific Hilbert space methods. The method does not suffer from intruder states, has very simple amplitude equations coupled only through the exact energy, however, due to the presence of unlinked terms, it is no longer size–extensive. This disadvantage is not present in state-specific MRCC method proposed by Mukherjee et al. [4, 5] and later developed by Evangelista [6] which still eliminates the intruder state problem [4].

We have formulated and implemented the multireference Mukherjee's coupled cluster method with non iterative triples (MR MkCCSD(T)) [7] and iterative triexcitations (MR MkCCSDT) employing the linked formulation in the ACES II package. The assessment of the new method has been performed on the first three electronic states of the oxygen molecule, and on studies of singlet-triplet gap in methylene and twisted ethylene, where a comparison with other multireference coupled cluster treatments and with experimental data is available. The results obtained for these systems employing model spaces with 2-8 reference determinants are encouraging. Since its computational cost is high, the MR MkCCSDT method seems to be a promising candidate only for benchmark treatment of systems where the static correlation plays an important role, while the MR MkCCSD(T) variant can be used for application calculations [8].

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