

New coupled-cluster methods for the ground and excited states: Locally renormalized and active-space coupled-cluster approaches.

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Abstract

Parallel development of novel theoretical approaches and efficient computer codes is pivotal for further progress in quantum chemistry. Two recently developed and implemented theories: the locally renormalized CC methods and active CC approaches may significantly broaden the applicability range of the CC methodology. Locally renormalized CC methods (LR-CC) [K. Kowalski, P. Piecuch, *J. Chem. Phys.* **122**, 074107 (2005); K. Kowalski, *J. Chem. Phys.* **123**, xxx (2005)] eliminate the dramatic failures of the standard CCSD(T) and CCSD(TQ) methods at larger internuclear separations and, in contrast to the completely renormalized (CR) CCSD(T) and CCSD(TQ) approaches, become rigorously size extensive if the orbitals are localized on noninteracting fragments. Additionally, the approximate inclusion of local denominators, the so-called *all-holes- J_n* coupling, assures characteristic N^7 scaling of ensuing class of LR-CCSD(T) approaches. An alternative approach that accounts for the highly-excited clusters is offered by the active-space CC and Equation-of-motion (EOMCC) formalisms that use only a limited subset of triply and/or quadruply excited cluster amplitudes (CCSDt/EOMCCSDt and/or CCSDtq/EOMCCSDtq approaches) that are selected based on the active orbitals relevant to a given chemical problem. It is also well documented that the CCSDt/EOMCCSDt approaches are capable of providing CCSDT/EOMCCSDT quality of results for the fraction of costs associated with the full inclusion of triply excited clusters. Excellent performance of the LR-CCSD(T) and CCSDt/EOMCCSDt methods is illustrated on several challenging examples including ground-state calculations for transition metal oxides and excited states of metal clusters. It is also shown that the TCE implementation of the CC methods can greatly benefit from using the CPU subgroups and from restructuring several classes of diagrams.