

Unitary Coupled-Cluster Based Excited-State Theories

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Coupled-cluster (CC) theory is tremendously successful in molecular calculations, although the non-Hermitian nature of CC theory poses difficult unsolved problems, including incorrect crossing conditions for same-symmetry conical intersections and complex energies when combined with complex-valued Hamiltonians. This presentation is focused on work on a unitary version of coupled-cluster (UCC) theory aiming to develop robust non-perturbative size-extensive Hermitian excited-state methods. We present the development of a third-order CC scheme (UCC3) and a quadratic UCC singles and doubles (qUCCSD) scheme. The qUCCSD scheme is demonstrated to improve the accuracy over the previous work based on perturbation theory including UCC3. We also discuss the inclusion of higher-order commutators to improve the accuracy of the qUCCSD scheme.