

Local Coupled-Cluster Methods for Chemical Reaction Pathways Involving Large Molecular Systems and their Multi-Level Generalizations

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Coupled-cluster (CC) theory has become the *de facto* standard for high-accuracy molecular calculations, but as all electronic structure approaches that aim at the accurate description of many-electron correlation effects, it faces a number of challenges. Among them are the prohibitive costs of CC calculations for larger molecular systems. To address this challenge, we have recently extended a number of CC methods, including the size-extensive, left-eigenstate, completely renormalized CC method with singles, doubles, and non-iterative connected triples, abbreviated as CR-CC(2,3), which is known to provide an accurate description of chemical reaction profiles involving single bond breaking and biradicals, to larger systems with hundreds of atoms through the use of the local correlation, cluster-in-molecule (CIM) ansatz. The resulting CIM-CR-CC(2,3) and other CIM-CC methods are characterized by (i) the linear scaling of the CPU time with the system size when the same level of theory is applied to all CIM subsystems, (ii) the use of orthonormal orbitals in subsystem calculations, (iii) the natural coarse-grain parallelism, which can be further enhanced by the additional fine-grain parallelism of each subsystem calculation, (iv) the high computational efficiency, enabling calculations for large molecular systems at high levels of CC theory, (v) the purely non-iterative character of the local triples and other perturbative corrections to correlation energy, and (vi) the applicability to the covalently and weakly bound molecular systems. In addition, one can use the flexibility of the CIM local correlation ansatz to mix different CC or CC and non-CC methods within a single calculation, enabling the rigorous formulation of multi-level local correlation theories that combine the high-level CC methods, such as CR-CC(2,3), to treat, for example, the reactive part of a large molecular system with the lower-order *ab initio* (e.g., MP2) scheme(s) to handle the chemically inactive regions without splitting it into *ad hoc* fragments and saturating dangling bonds. The performance of the CIM-CR-CC(2,3) approach in applications involving chemical reaction profiles is illustrated by examining the bond dissociation curves in normal alkanes and alkyl radicals, the diffusion of atomic oxygen on the silicon surface, the proton transfer in the aggregates of dithiophosphinic acids with the water molecules, and the Co-C bond dissociation in methylcobalamin.