Converging High-Level Coupled-Cluster Energetics with the CC(*P*;*Q*) Methodology: CIPSI-Driven and Adaptive Approaches

Piotr Piecuch
Department of Chemistry and Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, USA

One of the biggest challenges in the coupled-cluster (CC) theory and its equation-of-motion (EOM) and linear-response extensions to excited states has been designing efficient ways of incorporating higher–than–two-body components of the cluster and EOM excitation operators capable of producing accurate energetics equivalent to high-level CC/EOMCC calculations, such as CCSDT, CCSDTQ, and EOMCCSDT, at small fractions of the computational costs, even when electronic quasi-degeneracies become larger and higher–than–two-body components of the cluster and excitation operators become nonperturbative. This challenge can be addressed by adopting moment expansions defining the CC(*P*;*Q*) formalism, which can be viewed as a generalization of the previously developed completely renormalized CC and EOMCC approaches to unconventional truncations in the cluster and EOM excitation operators [1]. For the CC(*P*;*Q*) formalism to be effective, an efficient method must be developed to identify the leading higher–than–doubly excited determinants for inclusion in the subspace of the many-electron Hilbert space used in the iterative steps of the CC(*P*;*Q*) algorithm. This can be done with the help of active orbitals, resulting in the CC(t;3), CC(t,q;3), CC(t,q;3,4), etc. hierarchy [1,2], Quantum Monte Carlo (QMC) wave function propagations employing the configuration interaction (CI) QMC and CCMC approaches, resulting in the semi-stochastic CC(*P*;*Q*) theories [3], sequences of Hamiltonian diagonalizations originating from the selected CI schemes, such as CIPSI, resulting in the CIPSI-driven CC(*P*;*Q*) algorithm [4], and the adaptive, self-improving, CC(*P*;*Q*) framework, which frees us from the user-defined active orbitals and non-CC (CIQMC, CIPSI) or stochastic (CIQMC, CCMC) concepts by taking advantage of the intrinsic mathematical structure of the CC(*P*;*Q*) moment expansions in defining the underlying excitation manifolds [2,5]. In this lecture, we will discuss our recent progress in the CC(*P*;*Q*) methodology, especially in the CIPSI-driven and adaptive CC(*P*;*Q*) algorithms and their extensions to excited states. The usefulness of the CIPSI-driven and adaptive CC(*P*;*Q*) methodologies will be illustrated by chemical bond dissociations and reaction pathways, singlet–triplet gaps in biradicals, and excited states including one- as well as many-electron transitions. Information about the CC(*P*;*Q*) methods in GAMESS and our open-source CCpy package available at https://github.com/piecuch-group/ccpy will be provided as well.

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