

# Accurate Electronic Energies by Stochastic Wave Function Sampling and Deterministic Coupled-Cluster and Equation-of-Motion Coupled-Cluster Computations

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One of the main goals of quantum chemistry is an accurate description of ground- and excited-state energetics of increasingly complex polyatomic systems, especially when non-equilibrium structures and systems with stronger correlations are examined. Size extensive methods based on the coupled-cluster (CC) theory and their extensions to excited states via the equation-of-motion (EOM) framework have become *de facto* standards for addressing this goal. In the vast majority of chemistry problems, the CC hierarchy, including CCSD, CCSDT, CCSDTQ, etc., and its EOM counterpart provide the fastest convergence toward the exact, full configuration interaction (FCI), limit, allowing one to capture the leading many-electron correlation effects in a systematic manner by employing particle-hole excitations from a single reference determinant. Unfortunately, computational costs associated with the incorporation of higher-than-two-body components of the relevant cluster and excitation operators, which are required to achieve a fully quantitative description, are often prohibitive. This has created the need for new ideas in this area that do not suffer from failures of perturbative CC methods of the CCSD(T) type in multi-reference situations, while preserving the simplicity of a single-reference formalism. In response to this need, we have proposed a novel, computationally cost-effective strategy for obtaining accurate molecular electronic energetics, equivalent to those obtained with high-level CC methods, such as CCSDT and CCSDTQ, or the exact, FCI, approach, even when wave function quasi-degeneracies become significant, by merging the deterministic CC framework, especially CC( $P;Q$ ) [1,2], with the stochastic CI [3,4] and CC [5] Quantum Monte Carlo (QMC) approaches [6]. In this presentation, we discuss our recent progress in this area, including (i) extension of the original work [6] to excited states by using CIQMC propagations to identify higher-than-doubly excited wave function components in deterministic EOMCC computations [7] and (ii) direct recovery of the FCI energetics via cluster analysis of FCIQMC wave functions combined with CCSD-like calculations, in which singly and doubly excited clusters, needed to determine the energy, are iterated in the presence of their three- and four-body counterparts extracted from FCIQMC [8]. Our work toward converging FCI energetics in strongly correlated systems, such as those involved in modeling metal-insulator transitions [9], by combining short FCIQMC runs with inexpensive deterministic CC computations will be discussed as well.

## References

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