Toward Exact Quantum Chemistry by a Combination of Stochastic Wave Function Sampling and Deterministic Coupled-Cluster Computations

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One of the main goals of electronic structure theory is to precisely describe increasingly complex polyatomic systems. It is widely accepted that size extensive methods based on the coupled-cluster (CC) theory and their extensions to excited states via the equation-of-motion (EOM) formalism are excellent candidates for addressing this goal. Indeed, when applied to molecular properties and chemical reaction pathways, the CC hierarchy, including CCSD, CCSDT, CCSDTQ, etc., rapidly converges to the limit of the exact, full configuration interaction (FCI), diagonalization of the Hamiltonian, allowing one to capture the relevant many-electron correlation effects in a conceptually straightforward manner through particle-hole excitations from a single Slater determinant. One of the key challenges has been how to incorporate higher–than–two-body components of the cluster operator, needed to achieve a quantitative description, without running into prohibitive computational costs of CCSDT, CCSDTQ, and similar schemes, while eliminating failures of the more practical perturbative approximations of the CCSD(T) type in multi-reference situations, such as chemical bond breaking. In this talk, we examine a radically new way of obtaining accurate energetics equivalent to high-level CC calculations, even when electronic quasi-degeneracies become significant, at the small fraction of the computational cost, while preserving the black-box character of single-reference computations. The key idea is a merger of the deterministic formalism, abbreviated as CC(P;Q) [1,2], with the stochastic CI [3,4] and CC [5] Quantum Monte Carlo (QMC) approaches [6]. We also demonstrate that one can take the merger of the stochastic and deterministic ideas to the ultimate level and use it to enable precise extrapolations of the exact, FCI, energetics based on the early stages of FCIQMC propagations [7]. The advantages of the new methodologies will be illustrated by molecular examples, where the goal is to recover the nearly exact, CCSDT and CCSDTQ, and exact, FCI, energetics in situations involving chemical bond dissociations and reaction pathways. Extensions of this work to excited electronic states by a combination of stochastic CIQMC and deterministic EOMCC computations [8] and converging FCI energetics in strongly correlated systems, such as those involved in modeling metal–insulator transitions [9], will be mentioned as well.

References

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