Approaching Exact Quantum Chemistry by 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 exponential wave function ansatz of coupled-cluster (CC) theory and their extensions to excited states via the equation-of-motion (EOM) formalism are excellent candidates for addressing this goal. The Sanibel Symposium, which celebrates its 60th anniversary this year, and members of the Quantum Theory Project (QTP) at the University of Florida, who organize the Sanibel Symposia, have played a key role in bringing the CC and EOMCC methodologies to the forefront of molecular sciences, so the first part of this talk will reflect on the role of the QTP and Sanibel Symposia in the history of CC approaches. We will then proceed to a discussion of a radically new way of obtaining accurate energetics equivalent to high-level CC calculations, such as CCSDT or CCSDTQ, at a small fraction of the computational cost, even when multi-reference correlation effects become significant, resulting from the merger of a 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 will also demonstrate that one can take the merger of stochastic and deterministic ideas to the ultimate level and use it to extract the exact, full CI (FCI), energetics out of the early stages of FCIQMC propagations with the help of relatively inexpensive polynomial steps similar to CCSD calculations, eliminating exponential complexity of conventional FCI Hamiltonian diagonalizations altogether [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 and many-electron systems beyond the reach of FCI. Extensions 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], where the traditional CCSD, CCSDT, CCSDTQ, etc. hierarchy breaks down, will be discussed as well.

References:

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