Approaching Exact Quantum Chemistry by Stochastic Wave Function Sampling and Deterministic Coupled-Cluster Computations

Piotr Piecuch
Department of Chemistry and Department of Physics & Astronomy, Michigan State University, East Lansing, Michigan 48824, United States

It is well established that the exponential wave function ansatz of coupled-cluster (CC) theory and its extensions to excited, open-shell, and multireference states are among the most efficient ways of incorporating many-electron correlation effects in molecular applications. In this talk, I will discuss novel ways of obtaining accurate energetics equivalent to high-level CC calculations, such as CCSDT, CCSDTQ, and EOMCCSDT, at small fractions of the computational costs, even when multireference correlation effects become significant, which result from the merger of the deterministic CC(*P*;*Q*) formalism [1] with the stochastic configuration interaction (CI) [2] and CC [3] Quantum Monte Carlo (QMC) propagations in the many-electron Hilbert space [4,5]. I will also demonstrate that one can take the merger of the 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 the relatively inexpensive polynomial steps similar to those of CCSD, eliminating exponential complexity of conventional FCI Hamiltonian diagonalizations altogether [6–8]. The advantages of the new methodologies will be illustrated by chemical bond dissociations and reaction pathways [4,6], singlet–triplet gaps and excited electronic states [5,9], many-electron systems beyond the reach of FCI [7], and strongly correlated systems that emerge in modeling metal–insulator transitions [8], where the traditional CCSD, CCSDT, CCSDTQ, etc. hierarchy breaks down.

References

[1] J. Shen and P. Piecuch, *Chem. Phys.* **401**, 180 (2012); J. Shen and P. Piecuch, *J. Chem. Phys.* **136**, 144104 (2012); N. P. Bauman, J. Shen, and P. Piecuch, *Mol. Phys*. **115**, 2860 (2017).
[2] G. H. Booth, A. J. W. Thom, and A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009); D. Cleland, G. H. Booth, and A. Alavi, *J. Chem. Phys.* **132**, 041103 (2010).
[3] A. J. W. Thom, *Phys. Rev. Lett.* **105**, 263004 (2010).
[4] J. E. Deustua, J. Shen, and P. Piecuch, *Phys. Rev. Lett.* **119**, 223003 (2017); J. E. Deustua, J. Shen, and P. Piecuch, *J. Chem. Phys.* **154**, 124103 (2021).
[5] J. E. Deustua, S. H. Yuwono, J. Shen, and P. Piecuch, *J. Chem. Phys.* **150**, 111101 (2019); S. H. Yuwono, A. Chakraborty, J. E. Deustua, J. Shen, and P. Piecuch, *Mol. Phys.* **118**, e1817592 (2020).
[6] J. E. Deustua, I. Magoulas, J. Shen, and P. Piecuch, *J. Chem. Phys.* **149**, 151101 (2018).
[7] J. J. Eriksen *et al.*, *J. Phys. Chem. Lett.* **11**, 8922 (2020).
[8] I. Magoulas, J. E. Deustua, J. Shen, and P. Piecuch, in preparation.
[9] A. Chakraborty, S. H. Yuwono, J. E. Deustua, J. Shen, and P. Piecuch, *J. Chem. Phys.*, in press (2022); arXiv: 2205.10707.