

# Converging High-Level Coupled-Cluster Energetics via Adaptive Selection of Excitation Manifolds Driven by Moment Expansions

**Karthik Gururangan<sup>1</sup> and Piotr Piecuch<sup>1,2</sup>**

<sup>1</sup> *Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA*

<sup>2</sup> *Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA*

It is well established that size extensive approaches based on the exponential wave function ansatz of coupled-cluster (CC) theory and their extensions to open-shell, multiconfigurational, and excited states are among the best ways of describing many-electron correlation effects. This is especially true in applications involving structural and spectroscopic properties of molecular systems, chemical reaction pathways, noncovalent interactions, and photochemistry. In all these and similar cases, the CC hierarchy, including CCSD, CCSDT, CCSDTQ, and so on and its equation-of-motion (EOM) and linear-response extensions rapidly converge to the exact, full configuration interaction limit. Unfortunately, the CCSDT, CCSDTQ, and similar methods, needed to achieve a quantitative description, incur a steep increase in computational costs, rendering their application to larger many-electron systems prohibitively expensive. This challenge can be addressed by turning to the  $CC(P;Q)$  framework [1], which uses suitably defined moment expansions to incorporate the leading higher-than-two-body components of the cluster and excitation operators in a computationally efficient manner, while avoiding failures of the popular perturbative CC approximations, such as CCSD(T), in systems characterized by substantial electronic quasi-degeneracies. Here, we present a novel  $CC(P;Q)$  approach capable of rapidly converging high-level CC energetics of the CCSDT, CCSDTQ, and similar types in a fully automated fashion, even in cases of stronger correlations, which frees us from the use of active orbitals and information provided by the non-CC or stochastic sources exploited in the previous formulations of  $CC(P;Q)$  [1–3]. The key idea is an adaptive selection of the excitation manifolds defining higher-than-two-body components of the cluster and excitation operators driven by the  $CC(P;Q)$  moment expansions. The usefulness of the resulting methodology, called adaptive  $CC(P;Q)$  [4], is illustrated by a few molecular examples, including the significantly stretched  $F_2$  and  $F_2^+$  molecules and the automerization of cyclobutadiene, where the goal is to recover the full CCSDT energetics when the noniterative triples corrections to CCSD fail. Along with demonstrating the rapid convergence toward the parent CCSDT results, we will present the CPU timings to highlight vast reductions in the computational effort relative to CCSDT offered by the adaptive  $CC(P;Q)$  calculations. The extension of the adaptive  $CC(P;Q)$  methodology to excited electronic states is currently being developed, and the results of the calculations aimed at recovering full EOMCCSDT energetics may be presented as well.

## References

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