PROJECT SUMMARY

Applicant: ***Michigan State University***

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Title: ***New Single- and Multi-Reference Coupled-Cluster Methods for High Accuracy Calculations of Ground and Excited States (December 1, 2018 – November 30, 2021)***

This proposal describes a continuing effort to develop, disseminate, and apply new generations of *ab initio* electronic structure approaches and computer codes exploiting the coupled-cluster (CC) wave function ansatz, which enable precise modeling of molecular processes and properties relevant to energy science, especially combustion, catalysis, energy storage, and photochemistry. The emphasis is on methods that offer high accuracy, ease of use, and lower computational costs compared to other approaches that aim at similar precision, so that one can study complex molecular problems with dozens or hundreds of atoms, in addition to smaller systems, in a predictive and systematically improvable manner, supporting ongoing experiments or in the absence of experimental information. The proposed new effort concentrates on **(i)** extension the CC(*P*;*Q*) methodology merged with the stochastic configuration interaction (CI) and CC Quantum Monte Carlo (QMC) approaches to excited electronic states, and exploration of the analogous ideas that combine the CC(*P*;*Q*) framework with the adaptive CI algorithms, **(ii)** development of novel classes of single-reference CC methods for strongly correlated systems by combining the approximate coupled-pair (ACP) theories with the active-space, stochastic CIQMC and CCMC, and adaptive CI methodologies to capture the connected three-body clusters, and **(iii)** acceleration of convergence of the stochastic full CI (FCI) QMC approach and the adaptive CI techniques by cluster analyses of the corresponding wave functions. We will enrich the previously developed linear scaling, local correlation CC codes in the GAMESS package, exploiting the cluster-in-molecule framework, and their multi-level extensions allowing one to mix different levels of electronic structure theory in a single computation, which can take advantage of modern, massively parallel computer platforms, by the active-space CC and CC(*P*;*Q*) options. We will also complete our work on extending the singly and doubly electron-attached and ionized equation-of-motion CC methodologies to the triply electron-attached and triply ionized cases, which can be useful in studies of triradicals and inorganic chromophores, of interest in solar energy conversion schemes, which emerge out of d^3 electronic configurations. The proposed extension of the CC(*P*;*Q*) framework merged with the stochastic CIQMC and CCMC and adaptive CI algorithms to excited states will lead to practical black-box methods that can provide highly accurate excited-state energetics to within fractions of a millihartree relative to numerically exact solutions, even in complex multi-reference situations characterizing many-electron transitions and excited-state potential energy surfaces along bond breaking coordinates. The proposed fusion of the ACP theories with the active-space, stochastic CIQMC/CCMC, and adaptive CI methodologies to capture the connected three-body clusters will enable accurate studies of complex bond dissociation patterns and strongly correlated systems beyond the applicability of traditional single- and multi-reference electronic structure approaches. The acceleration of the stochastic FCIQMC and adaptive CI techniques by cluster analyses of the corresponding wave functions will facilitate converging the exact, FCI-level, energetics. Among the proposed applications are radical-radical reactions relevant to combustion, singlet-triplet gaps and electronic excitation spectra of polyacenes and other organic molecules, and electronic structure of chains, rings, and three-dimensional lattices of hydrogen atoms, focusing on their dissociative behavior and metal-insulator transitions.

Broader impacts. The proposed approaches address important challenges of modern electronic structure theory, including the development of practical and systematically improvable computational schemes aimed at an accurate description of chemical reaction pathways and molecular electronic excitations in the gas and condensed phases. The proposed methods will find use in a variety of molecular applications and continue to be shared at no cost with the community via the GAMESS package. The proposed projects will provide excellent training experiences in the forefront physical sciences for members of the PI group.