PROJECT SUMMARY

Applicant: ***Michigan State University***

PI: ***Piotr Piecuch***

Title: ***New Single- and Multi-Reference Coupled-Cluster Methods for High Accuracy Calculations of Ground and Excited States (December 1, 2021 – June 30, 2025)***

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 simulations of molecular processes and properties relevant to energy science, including, but not limited to, combustion, catalysis, photochemistry, and harnessing light to drive and control chemical reactivity. 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 fashion, supporting ongoing experiments or in the absence of experimental information. The proposed new effort concentrates on **(i)** a novel form of the CC(P;Q) theory and its extension to the electronically excited and open-shell states via the equation-of-motion (EOM) CC formalism, including states that display a substantial multireference character, in which the previously exploited stochastic configuration interaction (CI) Quantum Monte Carlo (QMC) propagations, used to identify the dominant higher–than–doubly excited determinants for the inclusion in the initial CC/EOMCC steps, are replaced by the selected CI approach abbreviated as CIPSI; **(ii)** a novel externally corrected CC (ec-CC) approach using the triply (T_3) and quadruply (T_4) excited clusters extracted from the selected CI (CIPSI) runs and correcting the resulting energies for the missing T_3 and T_4 correlations not captured by CIPSI with the help of moment expansions similar to those defining the bi-orthogonal CR-CC and CC(P;Q) theories, along with the utilization of the CIPSI-driven ec-CC framework in formulating a new type of multireference CC technique, in which the relatively inexpensive CIPSI diagonalizations provide the desired multiconfigurational reference states; and **(iii)** development of a new type of the adaptive, self-correcting, "black-box" CC(P;Q) methodology, which will allow one to converge the high-level CC/EOMCC (CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, etc.) energetics in single- as well as multireference situations at the small fraction of the computational costs and without having to rely on non-CC concepts. We will also continue our work toward the development of semi-stochastic CC(P;Q) theories, especially their extensions to excited and open-shell sates, the cluster-analysis-driven FCIQMC framework aimed at recovering the exact, full CI, energetics, and extending the single and double electron-attachment and ionization EOMCC methodologies to the triple electron-attachment and triple ionization 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. Last, but not least, we will enrich the previously developed linear scaling, local correlation CC codes 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. Among the proposed applications are radical-radical reactions relevant to combustion, singlet-triplet gaps and electronic excitation spectra of polyacenes, electronic structure of chains, rings, and three-dimensional lattices of hydrogen atoms that can be used to model metal-insulator transitions, and computational studies of super photoreagents.

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 wide variety of molecular applications and will continue to be shared at no cost with the community via the GAMESS package and GitHub. The proposed projects will provide excellent training experiences in the forefront physical sciences for members of the PI's group.