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 (July 1, 2025 – June 30, 2026)***

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 high accuracy, ease of use, and lower computational costs compared to other quantum chemistry techniques that aim at similar precision, so that one can study larger and complex molecular problems, in addition to smaller systems, in a predictive and systematically improvable manner, supporting experiments or in the absence of experimental information.

The first part of the proposed new effort will focus on the powerful quantum-mechanical many-body methodology known as CC(P;Q), which is designed to target higher levels of the CC and equation-of-motion CC (EOMCC) theories, such as CCSDT, CCSDTQ, EOMCCSDT, *etc.*, at tiny fractions of the computational costs, even in challenging multireference situations characterized by large and nonperturbative higher–than–two-body cluster and EOM excitation amplitudes, where conventional perturbative approximations of the CCSD(T), CC3, CCSD(TQ), EOMCCSD(T), and similar types fail or struggle. This will enable the PI's group to **(i)** further advance and conclude their foundational work on the adaptive and selected-configuration-interaction-driven CC(P;Q) approaches, especially their extensions to excited electronic states, and **(ii)** test and apply new types of the approximate coupled-pair (ACP) methods combining the ACP and CC(P;Q) ideas, designed to handle strongly correlated systems characterized by the entanglement of larger numbers of electrons, for which conventional single- and multireference CC hierarchies fail or become inapplicable. The second part of the proposed effort, which may stretch beyond the proposed performance period, will focus on the double ionization potential (DIP) and double electron-attachment (DEA) EOMCC approaches with full and active-space treatments of 4-hole–2-particle (4h-2p) and 4-particle–2-hole (4p-2h) excitations and three-body clusters and the similarly high-level IP-EOMCC and EA-EOMCC methods with up to 3h-2p and 3p-2h excitations and singly, doubly, and triply excited clusters in the underlying CC computations for single ionization and electron attachment, alongside the CC(P;Q)-inspired noniterative corrections to the lower-order IP- and EA-EOMCC methods to capture the missing electron correlation effects in radical species in a robust manner. Among the proposed applications, which will also continue beyond the proposed project performance period, are singlet–triplet gaps in biradical species and polyacenes, electronic excitation spectra of radicals, and reactivity of small organic molecules enabled by strong-field ionizing laser pulses.

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 in ground and excited states and molecular electronic spectra 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 open-source software on GitHub. The proposed projects will provide excellent training experiences in the forefront physical sciences for members of the PI's group.