PROJECT SUMMARY

PI: ***Piotr Piecuch (Michigan State University)***
Title: ***High-Level Coupled-Cluster Energetics by Monte Carlo Sampling and Moment Expansions***

Overview
One of the goals of quantum chemistry is to precisely describe increasingly complex polyatomic systems and molecular potential energy surfaces. It is generally accepted that size extensive methods based on the exponential wave function ansatz of coupled-cluster (CC) theory and their extensions to excited states are excellent candidates for addressing this goal. This is because in great many applications relevant to chemical reactivity, spectroscopy, and photochemistry, the CC methods with a full treatment of higher-than-doubly excited clusters, including CCSDT, CCSDTQ, etc., rapidly converge to the limit of the exact, full configuration interaction (CI) diagonalization of the Hamiltonian, allowing one to capture the relevant dynamical and non-dynamical correlation effects in a conceptually straightforward manner through particle-hole excitations from a single Slater determinant. Over the years, one of the key challenges has been how to incorporate higher–than–two-body components of the cluster and excitation operators, needed to achieve a quantitative description, without running into prohibitive computational costs of the CCSDT, CCSDTQ, and similar schemes, while eliminating failures of the more practical approximations of the CCSD(T) type in situations involving significant bond rearrangements, biradicals, and excited states dominated by two-electron transitions. The present project promises to revolutionize this area by developing a radically new way of obtaining accurate energetics equivalent to high-level CC calculations of the CCSDT, CCSDTQ, and similar types, even when electronic quasi-degeneracies and higher–than–pair excitations become significant, at the small fraction of the computational cost and preserving the black-box character (minimum input information) of conventional single-reference computations. The key idea is a merger of the deterministic methodology, abbreviated as CC(*P*;*Q*), which enables one to correct energies obtained with conventional as well as unconventional truncations in the cluster and excitation operators for any category of many-electron correlation effects of interest, with the stochastic CI and CC Monte Carlo approaches. The proposed methodological advances will be shared with the community via open-source mechanisms, including interfacing the resulting codes with the widely used GAMESS package. They will be accompanied by benchmark calculations, including potential energy surfaces involving smaller molecular species, where comparisons can be made with the exact, full CI, and nearly exact CCSDT, CCSDTQ, and similar data, and applications involving aerobic oxidation reactions catalyzed by colloidal gold nanoparticles under ambient conditions at low temperatures.

Intellectual Merit
The proposed approaches will address one of the key challenges in modern electronic structure theory, namely, the development of practical and systematically improvable *ab initio* computational schemes aimed at an accurate description of molecular energetics. The proposed methods and computer codes will find use in a wide variety of molecular applications, including those beyond the scope of this proposal, from the gas-phase chemistry, catalysis, and reactions at surfaces to materials science. The availability of the proposed codes via open-source mechanisms will enhance the development of new electronic structure methods by other groups, in addition to more routine applications, advancing the field of computational chemistry.

Broader Impacts
Methods and computer codes developed in this program will be shared at no cost with the community by interfacing them with the popular GAMESS package, which is used by thousands of practicing chemists, biochemists, molecular physicists, and chemical engineers around the world in academia, research laboratories, and industry, and in training students and postdocs. Findings resulting from the proposed activities will be used in teaching courses and communicated through publications in peer-reviewed journals and books, seminars, and conference presentations. The proposed projects will provide excellent training experiences in the forefront physical sciences for members of the PI's group.