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, 2015 – November 30, 2018)***

This proposal describes a continuing effort to develop, disseminate, and apply new generations of *ab initio* electronic structure approaches and computer codes exploiting the CC wave function ansatz, which enable precise modeling of molecular processes and properties relevant to combustion, catalysis, light harvesting, 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 of the recently developed CC(*P*;*Q*) hierarchy, which allows one to combine the active-space CC and equation-of-motion (EOM) CC approaches with the moment energy expansions used in the completely renormalized CC/EOMCC computations, to excited potential energy surfaces along bond breaking coordinates, (ii) development of novel classes of single-reference CC methods for strongly correlated electronic systems by combining the approximate coupled-pair (ACP) theories with the active-space and moment correction ideas to handle higher-order dynamical correlation effects, (iii) extension of the active-space variants of the electron-attached (EA) and ionized (IP) EOMCC methodologies and their recently developed doubly electron attached (DEA) and doubly ionized (DIP) analogs, which enable precise determination of ground and excited states of open-shell species that differ by one or two electrons from the related closed-shell systems, to the triply electron attached (TEA) and triply ionized (TIP) cases, and (iv) implementation of highly parallel, linear scaling, local correlation CC and ACP codes exploiting the previously developed cluster-in-molecule (CIM) ideas and their multi-level extensions allowing one to mix different electronic structure theory levels in a single computation, which can take full advantage of modern massively parallel, multi-node computer platforms, where each node has multiple cores. The excited-state CC(*P*;*Q*) hierarchy will lead to practical and easy to use methods that can provide relative and – what is particularly important – total energies of excited electronic states to within fractions of a millihartree relative to the numerically exact solutions, even in complex multi-reference situations encountered in the examination of many-electron transitions and excited-state potential energy surfaces along bond breaking coordinates. The proposed mergers of the ACP theories with the active-space and moment correction ideas will enable routine studies of complex bond dissociation patterns and strongly correlated systems beyond the applicability of traditional single- and multi-reference electronic structure approaches. The active-space variants of the DEA/DIP and TEA/TIP EOMCC approaches will enable precise, relatively inexpensive, and rigorously spin-adapted calculations of ground and excited states of open-shell species with two (DEA/DIP) and three (TEA/TIP) electrons outside the closed-shell cores, especially biradicals, triradicals, and inorganic chromophores investigated in the context of solar energy conversion schemes. The proposed next generation of parallel CIM codes will enable routine CC-level computations for systems with hundreds or, when combined with electronic embedding, fragmentation, and QM/MM ideas, thousands of atoms, including reactions in condensed phases and at surfaces. Among the proposed applications are radical-molecule and radical-radical reactions relevant to combustion, properties of aluminum hydride clusters relevant to hydrogen storage, photoelectron spectra of gold, silver, and other transition metal nano-particles, oxidation processes catalyzed by the gold and gold/palladium nano-particles, and photochemistry of inorganic complexes examined in the context of solar energy conversion schemes.

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.