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***

This proposal describes a continuing effort to develop, disseminate, and apply new generations of *ab initio* electronic structure methods based on the coupled-cluster (CC) wave function ansatz. The focus is on high-level and yet affordable approaches that enable precise modeling of molecular processes and properties relevant to combustion, catalysis, light harvesting, and photochemistry. The proposed new effort concentrates on (i) the CC(P;Q) hierarchy, which combines the previously developed active-space CC and equation-of-motion (EOM) CC approaches that recover much of the non-dynamical and some dynamical electron correlation effects with the moment energy corrections, similar to those used in the completely renormalized CC/EOMCC methods, to capture the remaining, mostly dynamical, correlations missing in the active-space CC/EOMCC considerations and (ii) the extensions of the active-space electron-attached and ionized EOMCC methods to the multiply electron-attached and multiply ionized formalisms, which are applicable to open-shell species with two or more electrons outside closed-shell cores. The CC(P;Q) hierarchy will lead to practical and easy-to-use methods that can provide relative and – what is particularly worth emphasizing – total ground- and excited-state energies to within fractions of a millihartree relative to the numerically exact solutions, even in complex multi-reference situations encountered in the examination of chemical reaction pathways and many-electron transitions. The active-space variants of the multiply electron-attached and multiply ionized EOMCC approaches will enable precise, inexpensive, and spin-adapted calculations for biradicals, triradicals, and other polyradical species and transition states, and their electronic spectra, without invoking complicated steps of multi-reference theories. The previous effort that has resulted in the linear-scaling, local-correlation, "cluster-in-molecule" (CIM) CC approaches and their (sub)linear-scaling multi-level extensions, which combine the high-level CC methods to treat the reactive part of a large molecular system with the lower-order schemes to handle the chemically inactive regions and which are already applicable to systems with hundreds of correlated electrons, will be continued as well by incorporating the CC(P;Q) approaches into the multi-level CIM framework and by combining the CIM and embedding theories, so that one can examine chemical reaction profiles in condensed phases. Combining the EOMCC methods with the one-electron effective potentials resulting from the frozen-density embedding theory will provide a computationally efficient avenue for an accurate description of solvent effects on molecular electronic spectra. The CIM approaches are characterized by the coarse- and fine-grain levels of code parallelization, which ideally matches modern computer platforms that consist of multiple multi-core nodes. Another idea, which has the same characteristics and which will be pursued, too, is the development of parallel numerical energy derivatives, enabling fast geometry optimizations and vibrational frequency calculations at any level of electronic structure theory. Among the proposed applications are the reaction and photo-dissociation mechanisms relevant to combustion, particularly those that involve the hydrocarbon radicals and biradicals, the structural and optical properties of the neutral and charged gold particles, and the oxidation processes catalyzed by the gold and gold/palladium nano-particles.

Broader impacts. The proposed approaches address important challenges of modern electronic structure theory, including the development of practical and systematically improvable computational schemes, which can provide an accurate description of chemical reaction pathways in the gas and condensed phases, and molecular electronic excitations and the development of algorithms that can reduce prohibitive costs of high-accuracy *ab initio* calculations by utilizing parallel computer architectures, while attacking intrinsic scaling laws that define these costs. The proposed approaches will find use in a wide range of molecular applications and continue to be shared at no cost with the community by incorporating them in the GAMESS package. Findings resulting from the proposed activity will be communicated through publications and conference presentations. The proposed projects will provide excellent training and educational experiences in the forefront physical sciences for members of the PI group.