

## 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 (Supplemental Application; December 1, 2014 – November 30, 2015)*

This supplemental application describes a continuing effort to develop and apply new generations of *ab initio* electronic structure methods and computer codes based on the coupled-cluster (CC) wave function ansatz, which can provide an accurate description of molecular processes and properties relevant to combustion, catalysis, and photochemistry. The specific focus of the proposed one-year extension of the present 18-month award is the development and benchmarking of the previously unexplored generations of the equation-of-motion (EOM) CC theories that will enable precise and yet relatively inexpensive determination of electronic excitations in open-shell species and excited-state potential energy surfaces (PESs) along bond breaking coordinates. The proposed EOMCC approaches will satisfy the requirements of high accuracy, ease of use, and much lower computational costs compared to other *ab initio* methodologies that aim at similar precision, so that we will be able to study complex molecular problems that emerge in catalysis and photochemistry of inorganic chromophores examined in the context of solar energy conversion schemes, in addition to radical and polyradical species involved in combustion, at unprecedented theory levels. These objectives will be accomplished by concentrating on the following three methodologies: (i) extension of the so-called  $CC(P;Q)$  hierarchy, which combines the previously developed active-space CC approaches with the moment energy corrections, similar to the completely re-normalized (CR) CC methods, to excited electronic states within the EOMCC framework, (ii) further work on the recently developed doubly electron-attached (DEA) and doubly ionized (DIP) EOMCC formalisms with the active-space treatments of high-order excitations aimed at the additional reduction of the computer costs involved, and (iii) extension of the active-space variants of the electron-attached (EA) and ionized (IP) EOMCC methodologies and their DEA and 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. The EOMCC-based  $CC(P;Q)$  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 PESs along bond breaking coordinates. 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, particularly biradicals, triradicals, and inorganic chromophores investigated in the context of solar energy conversion schemes. Work on parallel numerical derivatives enabling, so far, fast geometry optimizations at any level of the CC/EOMCC theory, will continue as well by extending it to transition-state searches and harmonic vibrational analyses in ground and excited states. All of the above methodological and algorithmic advances will be accompanied by several benchmark calculations, including ground- and excited-state PESs of small molecules and (poly)radicals, and recently developed databases for electronic excitations, where comparisons can be made with either the exact, full configuration interaction (CI), or other high-level CC/EOMCC and multi-reference CI/CC data, and molecular applications involving the determination of PESs for radical reactions, photoelectron spectra of gold nano-particles, and photochemistry of inorganic complexes examined in the context of solar energy conversion schemes.