PROJECT SUMMARY

This proposal represents 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 practical methods and efficient computer codes, which provide an accurate description of bond breaking, reaction pathways involving radical and biradical species, including complex systems with hundreds of non-hydrogen atoms, electronic excitations in molecules, and molecular properties and spectra. Among the proposed applications are the reaction and photo-dissociation mechanisms relevant to combustion, particularly the reactions involving nitrogen oxides and hydrocarbon radicals, the relative energetics and properties of gold clusters, relevant to catalysis, the reaction pathways involved in the catalytic oxygen generation, relevant to solar energy conversion, and the proton-transfer processes involving dithiophosphinic acids and water clusters, of significance for nuclear waste management.

The proposed new generations of the local correlation CC approaches will result in a rich suite of methods and computer codes for closed- and open-shell systems with thousands of electrons, including chemical reactions of large molecular species, reactions in solvents, and molecular processes at surfaces. Among the key advances will be the development of multi-level approaches that combine the high-level CC methods, such as the completely renormalized and active-space approaches to treat the reactive part of a large molecular system, with the lower-order schemes to handle the chemically inactive regions. The extensions of the local correlation single- and multi-level CC methods to large open-shell systems and properties other than energy will be pursued as well. The proposed single- and multi-level local correlation methods are characterized by the coarse- and fine-grain levels of code parallelization, which ideally matches the present road-map for the development of computer platforms that consist of multi-core nodes. The possibility of exploiting the GPU technology in high-level CC calculations will be explored as well. The proposed multi-level local correlation methods will enhance the existing hybrid schemes of the QM/MM type by enlarging the quantum region that one can handle today with the high-level approaches of the CC type to hundreds of non-hydrogen atoms. The development of the size extensive left-eigenstate completely renormalized CC and equation-of-motion (EOM) CC approaches, and their locally renormalized analogs will continue, with a focus on higher-order schemes and properties other than energy. The previously developed active-space CC and EOMCC approaches, including the electron-attached and ionized methods that enable precise calculations of ground and excited states of radical species, will be extended to doubly attached and doubly ionized schemes. New classes of multi-reference CC methods that reduce the intruder problem and that address the difficulties with employing larger reference spaces will be pursued by focusing on a more symmetric treatment of the excitation manifolds corresponding to different reference determinants, non-iterative energy corrections, and practical ways of reducing computer costs through perturbative treatment of the inactive core-virtual excitations.

Broader impact. The proposed approaches address important challenges of modern electronic structure theory, which are the development of practical and systematically improvable computational schemes that can provide a balanced and accurate description of closed- and open-shell systems, and the rapidly changing electron correlation effects along reaction coordinates and in electronic excitations, and the development of algorithms that can reduce prohibitive costs of traditional high-accuracy *ab initio* calculations by attacking the scaling laws that define the dependence of the computational costs on the system size. The proposed methods will find use in a wide range of chemical applications, particularly those where accurate information about reaction pathways in the gas and condensed phases, and electronic excitations in molecules is needed, 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 peer-reviewed publications, talks, and conference presentations.

Human resource development. The proposed projects will provide an excellent educational/training experience for members of the PI's group. The PI has worked with 11 postdocs and 9 PhD students, including 9 who are professors and 2 who are senior researchers in federally funded research laboratories, and 5 research undergraduates. Among former members of the PI's group are one African-American who presently is a professor, and 4 women, including 2 who are professors and one who is a senior researcher.