PROJECT SUMMARY

New Coupled-Cluster Methods for Molecular Potential Energy Surfaces

Molecular electronic structure calculations, followed by dynamical studies, have been recognized as a cornerstone for the successful modeling of elementary chemical processes. This includes processes that are of importance to the Department of Energy, such as combustion. In view of the unprecedented advances in computer technology, the role of theory and computing in studies of chemical reactivity will continue to increase. New *ab initio* approaches that can *accurately and efficiently* describe many-electron correlation effects and that can be used to study *entire potential energy surfaces of ground and excited states* will play a critical role in these developments.

To meet the challenge created by new generations of high-performance parallel computers and to advance *ab initio* theory to a new level of accuracy, predictability, and applicability, so that routine calculations for all kinds of molecular systems and all kinds of electronic states become possible in not-too-distant future, the efficiency of the existing computer codes has to be increased and new methods and algorithms have to be developed. The proposed research program promises to bring a significant progress in this area by focusing on the "holy grail" of the *ab initio* electronic structure theory, i.e., the development of "black-box" and affordable methods that can provide a highly accurate description of entire potential energy surfaces of ground and excited states of molecular systems, including bond breaking and reaction intermediates. The proposed *method of moments of coupled-cluster equations* and *renormalized CCSD[T], CCSD(T), CCSD(TQ), and CCSDT(Q) approaches* that remove the pervasive failing of the popular coupled-cluster approximations, such as CCSD(T), when chemical bonds are stretched or broken, while retaining the simplicity and the "black-box" character of the noniterative perturbative coupled-cluster methods, will have a significant impact on the calculations of ground-state potential energy surfaces. The proposed *active-space equation-of-motion coupled-cluster methods* and *extensions of the method of moments of coupled-cluster equations to excited states* will allow us to accurately describe entire excited-state potential energy surfaces at the fraction of the computer effort associated with multireference configuration interaction calculations. The proposed new coupled-cluster methods are the first examples of simple, single-reference, correlated approaches that can be successfully applied to entire potential energy surfaces in spite of using restricted Hartree-Fock orbitals.

The new approaches will be used to provide the in-depth understanding of the dynamics of chemical processes that occur in combustion and atmospheric studies, particularly the reactions involving the OH radical and the reactions involving nitrogen oxides. The proposed calculations include studies of the decay dynamics of the vibrationally activated van der Waals precursor complexes and studies of the collisional quenching of electronically excited radical species.

Broader impact of the proposed activity. The proposed methods and computer programs are general and developed with a clear intent of applying them to all kinds of molecular systems and all kinds of potential energy surfaces. Thus, scientists working in all areas of electronic structure and dynamics, where highly accurate potential energy surfaces are needed, will benefit from our effort. The proposed new methods and computer programs will be shared with the scientific community by incorporating our codes in the popular GAMESS package. We will collaborate with Professor Mark S. Gordon and coworkers at Iowa State University and Ames Laboratory on developing a highly scalable version of GAMESS, which will take advantage of new high-performance parallel computer architectures and have, along with other methods that Professors Mark S. Gordon, James Evans, and Klaus Ruedenberg describe in their proposal, our new coupled-cluster codes. Current version of GAMESS does not have any coupled-cluster option, so that our group will also be responsible for providing codes for the standard coupled-cluster methods. All findings resulting from the proposed activity will be communicated through publications, talks, and conference presentations.

Human resource development. The proposed projects will provide a unique educational experience for members of the Piecuch research group. By developing new methods, which require a variety of skills, ranging from advanced mathematical methods to scientific computing, programming, and working in parallel computer environment, and by performing large-scale calculations, members of the Piecuch group will be trained in an important area of computational chemistry. The long history of the PI's contributions to theoretical and computational chemistry, the proposed collaboration with Professor Mark S. Gordon and coworkers on developing a highly scalable version of GAMESS, the high caliber of the PI's current collaborators (Professor John C. Polanyi, Professor Donald G. Truhlar, and others), combined with the PI's ability to attract senior researchers to work with the group, create an excellent research and educational environment for members of the Piecuch group.