PROJECT SUMMARY
New Single- and Multi-Reference Coupled-Cluster Methods for High Accuracy Calculations of Ground and Excited States

This proposal presents an effort to develop new generations of *ab initio* electronic structure methods and general-purpose computer codes, which can provide a highly accurate description of chemical bond breaking, reactive pathways, electronic excitations in molecules, and molecular properties and spectra. The new coupled-cluster (CC) methods described in this proposal will enable precise modeling of chemical reactions that occur in combustion, catalysis, photochemistry, and photobiology using state-of-the-art computer platforms. Although this proposal focuses on electronic structure methods, the proposed CC approaches can be applied, with equal success, to other many-fermion systems, including nuclei.

The main focus of this proposal is on balancing high accuracy of the results, expected from predictive *ab initio* methods, with ease of use and relatively low computer cost of the proposed approaches, so that the applications are not limited to small, few electron systems and small basis sets. The new approaches, developed in this research program, including the *renormalized coupled-cluster methods* and other approximations employing the *method of moments of coupled-cluster equations,* as well as the *state-selective multi-reference coupled-cluster (MRCC) methods* or *active-space coupled-cluster approaches* and new classes of *genuine multi-reference coupled-cluster methods*, are capable of describing molecular potential energy surfaces and excited electronic states at the fraction of the effort associated with the traditional multi-reference configuration interaction (MRCI) calculations. These new methods can be applied to dynamical and spectroscopic problems that require an accurate mapping of molecular potential energy surfaces that cannot be handled by the standard "black-box" electronic structure approaches. The specific developments in the renewal period include extensions of the renormalized and active-space CC approaches to non-singlet states and excited-state potential energy surfaces along bond breaking coordinates, accurate "black-box" methods for multiple bond breaking, new classes of genuine MRCC methods and noniterative energy corrections for these that considerably reduce the intruder-state problem and the difficulties with using large reference spaces, and response CC codes for molecular properties other than the energy and analytic energy derivatives. The new methods and computer codes, which will be developed in the renewal period, will enable highly accurate calculations for a large number of important problems, including chemical reactions proceeding on non-singlet and excited-state potential energy surfaces, multipole moments, oscillator strengths, geometry optimizations, transition state searches, and electron densities of ground and excited-state molecular systems.

Broader impact. The proposed new methods will find applicability to a wide range of problems in combustion, catalysis, materials science, and photochemistry, particularly when accurate information about potential energy surfaces and excited states is needed. The proposed methods and computer codes will continue to be shared with the entire community by incorporating them in GAMESS, which is a highly scalable and popular electronic structure package distributed at no cost by Professor Mark S. Gordon. By incorporating our CC codes in GAMESS, we will continue to provide powerful research tools that have not been available before. We will continue to collaborate with Professor Mark S. Gordon and coworkers at Ames Laboratory and Iowa State University on developing the GAMESS system. Our new methods will also provide an opportunity to test new programming techniques, including Tensor Contraction Engine, which enables automated parallel implementation of many-body methods.

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 successful collaboration with Professor Mark S. Gordon and coworkers on developing GAMESS and with several other SciDAC participants, and the high caliber of the PI's past and present collaborators, combined with the PI's ability to attract senior researchers to work with the group, create an excellent research and educational environment for its members.