

PROJECT SUMMARY

This proposal presents a continuing effort to develop and apply new generations of *ab initio* electronic structure methods based on the coupled-cluster wave function ansatz. The focus is on practical methods and efficient computer codes, which can provide an accurate description of bond breaking, reaction pathways involving radical and biradical species, electronic excitations in molecules, and molecular properties and spectra. The single- and multi-reference coupled-cluster methods described in this proposal will be applied to molecular processes and properties relevant to combustion, catalysis, photochemistry, and photobiology. The coupled-cluster approaches developed in this program can also be applied, with success, to other many-fermion systems, including heavier atomic nuclei.

Among the proposed applications are the computational studies of reaction mechanisms relevant to combustion, particularly the reactions involving hydroxyl radicals and the reactions involving nitrogen oxides, the collisional quenching of the electronically excited species, relevant to monitoring the hydroxyl radicals, the relative energetics of different forms of the (di)copper-dioxygen cores supported by various ligands, relevant to catalysis and activation of molecular oxygen by metalloenzymes, and the fluorescence of DNA, of fundamental importance in photobiology. The proposed size extensive generalizations of the renormalized coupled-cluster approaches and their open-shell extensions represent a new generation of systematically improvable single-reference procedures, which can be applied to multi-reference situations created by radicals and biradicals with a more or less “black-box” effort. The proposed open-shell generalizations of the previously developed active-space coupled-cluster approaches via the electron attached and ionized variants of the equation-of-motion coupled-cluster formalism, and their extensions to higher-order excitations and multiply attached and ionized schemes, will enable routine and accurate calculations of ground- and excited-state potential energy surfaces of radical species. The relatively low costs of the proposed approaches will make them applicable to a wide range of molecular sizes, from a few light atoms to several light and a few transition metal atoms. The proposed local extensions of the size extensive renormalized coupled-cluster approaches and the extensions of these methods based on the fragment molecular orbital approach will make them applicable to larger systems. All of the proposed methods address one of the main challenges of modern electronic structure theory, which is the development of practical computational schemes that can provide a balanced and accurate description of the rapidly changing dynamical and non-dynamical electron correlation effects along reaction coordinates. The development of genuine multi-reference coupled-cluster methods that considerably reduce the intruder-state problem and difficulties with using large reference spaces, and response coupled-cluster codes for properties other than the energy and analytic energy derivatives will continue as well.

Broader impact. In addition to specific applications discussed in the proposal, methods developed in this program will find use in a wide range of chemical problems, particularly those where accurate information about reaction pathways and electronic excitations in molecules is needed. The proposed methods will continue to be shared with the entire community by incorporating them in the GAMESS package. Findings resulting from the proposed activity will be used in teaching courses in computational and physical chemistry and communicated through publications, talks, and conference presentations. The proposed methods will also find use in nuclear structure theory.

Human resource development. The proposed projects will provide a unique educational/training experience for members of the Piecuch group. Since joining Michigan State University eight years ago, the PI has worked with five postdoctoral associates (Drs. R. Burel, J. Edwards, A. Kinal, K. Kowalski, and M. Włoch), two visiting professors (Drs. S.A. Kucharski and V. Špirko), two visiting scholars (Dr. J. Pittner and Mr. T. Kuś), four Ph.D. students who completed their Ph.D. programs (Drs. I.S.O. Pimienta, P.-D. Fan, R.L. Jacobsen, and M.J. McGuire), and two other students who are in various stages of their Ph.D. work (Mr. J.R. Gour, who is an NSF Graduate Research Fellow, Ms. M.D. Lodriguito, and Mr. Jesse J. Lutz). The PI has also worked with several undergraduate research students. A minority person, Dr. J. Edwards, who was awarded the Affirmative Action Postdoctoral Fellowship to work with the PI, is currently an Assistant Professor at the Florida Agricultural and Mechanical University. Among present and former members of the PI’s group, there are four outstanding women (Dr. M. Włoch, Dr. R.C. Jacobsen, Ms. M.D. Lodriguito, and Ms. E. Kratz).