

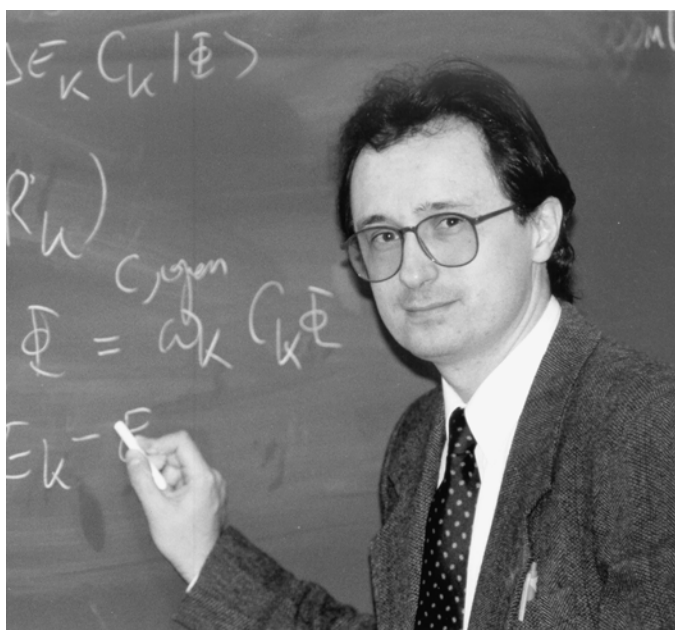
Quantum Chemistry, Reaction Dynamics, and Intermolecular Forces

My research focuses on (i) *ab initio* quantum theory of molecular electronic structure, (ii) molecular properties and spectroscopy, (iii) reaction dynamics, and (iv) theory of intermolecular forces. The aim is to design and apply quantum-mechanical methods that enable precise determination of potential energy surfaces and property functions for both existing and hypothetical molecular systems in their ground and excited states as well as calculations of intermolecular potentials and spectra for van der Waals complexes.

Quantum theory of molecular electronic structure. The key to understanding molecular electronic structure and dynamic behavior of molecules is an accurate assessment of electron correlation effects. Our group focuses on new quantum-chemical methods that include correlation, particularly on the coupled-cluster theory and its multi-reference and response generalizations that allow us to study electronically excited states, bond breaking, electron-transfer processes, molecular properties in vibrationally and electronically excited states, and transition probability coefficients for various types of spectroscopy. Our primary interest is in high-accuracy methods that allow us to be predictive, so that we can provide ongoing experiments with new insights and study reaction intermediates and hypothetical species in the absence of experiment.

Molecular properties and spectroscopy. We use our linear-response coupled-cluster methods along with other *ab initio* approaches, such as multi-reference configuration interaction method, to calculate molecular electric multipole moments and (hyper)polarizabilities and the effect of nuclear motion on these properties. We use first-principles theories to obtain rovibrational and electronic spectra of molecules, including systems of astrophysical interest and van der Waals complexes that are precursors of photoinduced charge-transfer reactions.

Reaction dynamics. We study the photoinduced charge-transfer (“harpooning”) reactions between alkali and alkaline earth metal atoms and halides using state-of-the-art *ab initio* and dynamical methods. These electronically non-adiabatic reactions are studied experimentally by the leading research groups,



including Professor Polanyi’s group at the University of Toronto. Collaboration with Professor Polanyi’s group gives us an opportunity to test our theoretical models and, at the same time, to contribute to a rapidly growing field of “transition state spectroscopy.” We also study the kinetics of elementary reactions pertinent to atmospheric chemistry and the dynamics of photoinduced reactions that proceed on a single electronic potential. Again, we rely on *ab initio* potential energy surfaces and properties. We combine *ab initio* and dynamical approaches to characterize quasibound states of van der Waals molecules that are precursors of the photoinduced chemical reactions.

Theory of intermolecular forces. Intermolecular potentials are a necessary ingredient for the determination of the structure, stability, and dynamics of weakly bound clusters and condensed phases. Our group focuses on pairwise non-additive interactions which are important when three or more atoms or molecules interact. Interactions in dimers are studied as well. We use state-of-the-art quantum chemistry to generate the necessary information about interacting species.

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REPRESENTATIVE PUBLICATIONS

In Search of the Relationship between Multiple Solutions Characterizing Coupled-Cluster Theories, P. Piecuch and K. Kowalski, *Computational Chemistry: Reviews of Current Trends*, ed. J. Leszczynski (World Scientific, Singapore, 2000), Vol. 5, p. 1.

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Bound and Quasi-Bound States of the Na...FH van der Waals Molecule, V. Špirko, P. Piecuch, and O. Bludsky, *J. Chem. Phys.*, 112, 189 (2000).

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Infrared Absorption Line Strengths of the Na...FH van der Waals Molecule, M. S. Topaler, P. Piecuch, and D. G. Truhlar, *J. Chem. Phys.*, 110, 5634 (1999).