

## Research program and accomplishments.

The research interests of my group at the University of Arizona include considerations of static and dynamic properties and structures of small molecules and clusters, as well as of extended molecular systems relevant to biology and to the chemistry of materials. The broadening of our research interests to more applied areas has served to intensify rather than diminish our efforts in fundamental theoretical studies. Still, the major focus of the research activity of my group remains the development and implementation of new *ab initio* methods of quantum mechanics (QM) for more accurate atomic and molecular calculations performed with and without assuming the Born-Oppenheimer approximation. We are also involved in developing QM methods for describing dynamics of molecular charge/energy transfer processes. In choosing this research path, I have been motivated by the realization that the breadth, accuracy and complexity of the experimental data have been increasing rapidly and they are beginning to reveal deviations that suggest that the accuracy of even the most precise existing calculations is no longer adequate. In advancing our interest in developing new theoretical tools, we have built a broad network of theoretical and experimental collaborations reaching far beyond the traditional boundaries of chemistry. These collaborations have allowed verification of new ideas, models, and molecular designs through theoretical analyses and calculations combined with experimental testing.

The following are among my research accomplishments in the area of quantum and computational chemistry that I consider the most important:

- The first implementation of the explicitly correlated Gaussian basis in the variational-perturbational calculations employing the second-order Hylleraas functional of the correlation energy of molecular systems. This work was completed during my PhD studies under supervision of Prof. Andrzej Sadlej at the Institute of Physical Chemistry, the Polish Academy of Sciences.
- The first implementation of numerical orbitals in multi-configurational self-consistent-field (MCSCF) calculations of diatomic systems. This work was completed during my postdoctoral studies in the group of Prof. Ed McCullough Jr. at the Department of Chemistry, Utah State University.
- The development of an algorithm for the calculation of the analytical gradient of the energy with respect to the nuclear coordinates for the single-reference coupled cluster method. The approach involves the use of the so-called "λ"-method which has been not only employed in the CC geometry optimization aided by the analytical energy gradient but also in the calculation of other properties.
- The implementation of numerical orbitals in the framework of CCSD calculations for diatomic systems.<sup>1</sup>
- Development of a method for generating a compact set of optimized virtual orbitals (also called

first-order correlation orbitals) by the minimization of the second-order Hylleraas functional (the OVOS method). The orbitals are for the use in coupled cluster (CC) calculations of closed- and open-shell molecular systems with the number of electrons exceeding the limits for the conventional CC calculations where the full virtual orbital space is employed. This and the above two projects were performed during my postdoctoral studies with Prof. Rodney Bartlett at the Quantum Theory Project, University of Florida (the UHF and CASSCF extension of the OVOS method was developed at University of Arizona).

The projects described below have been performed under my supervision at the Department of Chemistry and Biochemistry, University of Arizona. Most of the project are still active topics of my research.

- Development of a new state-selective multi-reference coupled cluster method (SSMRCC) based on a single-reference approach for studying bond dissociation processes and processes involving structural transformations of electronically excited molecules (the approach is also known under acronyms CCSDt and CCSDtq). The method represents the first implementation of the complete-active-space approach within the CC method. The more recent version of the method is called CASCCSD and involves partial (or full) spin adaptation of the multi-reference CC wave function. The method has been employed in calculations of potential energy surfaces of molecules in ground and excited electronic states. At present it is one of the most accurate MRCC methods (if not the most accurate) for such calculations.
- The first implementation of the coupled cluster method with single, double, triple, and quadruple excitations (CCSDTQ).
- Development of theory for quantum-mechanical calculations of molecules without assuming the non-Born-Oppenheimer (non-BO) approximation. An array of methods for very accurate non-BO variational calculations of ground and excited states of small molecular systems with arbitrary numbers of electrons and nuclei using various types of all-particle explicitly correlated Gaussian functions have been developed.<sup>2-5</sup> The non-BO calculations involve extensive variational optimizations of the non-linear parameters of the Gaussians using algorithms utilizing the analytical energy gradient determined with respect to those parameters. The methods include algorithms for calculating leading relativistic and quantum-electrodynamics (QED) corrections. This approach has been used to perform very accurate non-BO calculations of ground and excited states of some diatomic and triatomic molecular systems with up to six electrons. For the first time molecules with more than two electrons have been calculated with an approach that does not assume the BO approximation (the largest being the BH molecule). The accuracy of the results produced in our calculations is unmatched by any calculations performed by others and, in some cases, it even exceeds the accuracy of the most accurate experimental measurements. The non-BO molecular approach has been also extended to study molecular systems in

the presence of electric and magnetic fields with strengths unattainable in the laboratory but present in some regions of interstellar space. The approach has also been applied to study the behavior of molecules in confinement formed by molecular cages (e.g. clathrates).

- Development of variational methods for very accurate calculations of ground and excited states of small atoms using all-electron explicitly correlated Gaussians.  $S$ ,  $P$ ,  $D$ , and  $F$  states have been considered. The approach explicitly includes the finite mass of the nucleus (non-BO approach) and the optimization of the non-linear parameters of the Gaussians is carried out with the aid of the energy gradient determined with respect to these parameters. The development also includes algorithms for calculating the leading relativistic and QED corrections, as well as fine and hyperfine interactions, oscillator strengths, and state lifetimes. Our calculations performed for four-,<sup>6</sup> five-,<sup>11</sup> and six-electron atomic systems are the most accurate in the literature. The largest system calculated was the nitrogen atom.
- Development of methods for very accurate variational Born-Oppenheimer calculations of potential energy surfaces (PES) of small molecules and clusters (e.g. hydrogen clusters) using explicitly correlated all-electron Gaussian functions with floating centers. Algorithms for calculating molecules with all  $\sigma$  electrons and with  $\sigma$  and  $\pi$  electrons have been developed. The calculations involve the use of the analytical energy gradient and include relativistic and QED corrections. Our recent calculations on  $\text{H}_3^+$ ,<sup>10</sup>  $\text{H}_4^+$ ,  $\text{H}_4$ ,  $\text{H}_5^+$ , etc. performed with this method are the most accurate ever performed for these systems.
- Development of computational methods for modeling the dynamics of the charge and energy transport in large inhomogeneous molecular systems (DNA, proteins, etc.). Charge transfer in these types of molecules can be viewed as a concerted motion of local vibrational excitations and localized wave packets describing temporary states of excess electrons/holes (the exciton-polaron and charge-hopping models). Various models for electricity-conducting molecular wires have been considered. The molecular conduction phenomenon is related to charge and vibrational energy redistribution and transfer in biological systems. The study of the electrical conductivity of molecular wires based on biologically-inspired inhomogeneous molecules is also related to potential application of these systems as interconnects in molecular nano-electronics.

Collaborations have always been at the core of our work and numerous projects have evolved as a direct result of interfacing our quantum mechanical calculations with experimental studies performed by our collaborators. Some of the collaborative works have resulted in discovery and characterization of new chemical species (e.g. dipole-bound anions of nucleic acid bases), new reaction mechanisms and new configurational forms of molecules and clusters (e.g. some rare tautomers of small amino acids and water complexes of nucleic acid bases). These collaborations have also been an important source of inspiration for us to develop new, more accurate computational methods for particular applications. Our most fruitful theoretical-experimental

collaborations have concerned the following topics:

- Rovibrational spectroscopy of small diatomic ions.<sup>7</sup>
- Rovibrational spectroscopy of  $\text{H}_3^+$ ,<sup>10</sup> its isotopologues, and other triatomic systems with up to four electrons.
- Vibrational spectroscopy of gas-phase and matrix-isolated biological systems such as nucleic acid bases and their clusters, amino acids, small peptides and their derivatives, etc.
- Photochemistry of nucleic acid bases and their complexes.
- Covalent and dipole-bound electron attachment to molecules and clusters.<sup>8,9</sup>
- Chemistry of functionalized graphenes, fullerenes, and carbon nanotubes.

I have published over 648 papers. My h-index is currently 58. As of 1/12/2021 my papers have been cited 14,501 times (11,475 times excluding self citations) and 19 papers have been cited 100 times each. Below I list some selected publications from my laboratory (only those published in **Phys. Rev. Lett.**; for a complete list of my publication see the Publication List).

## References

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