Molecular Dynamics Lectures

Telluride School on Theoretical Chemistry 2013

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The molecular dynamics component of the summer school will focus on three long standing problems within the dynamics community: **transition state theory and beyond**, **condensed phase proton transfer**, and **conical intersections in reaction dynamics**. Two lectures will be devoted to each of the three topics. The lectures will emphasize the theoretical representations and algorithms for treating these problems.

The topic of conical intersections in reaction dynamics will serve to highlight techniques for solving the nuclear Schrödinger equation and the differences between adiabatic and diabatic representations. I will begin by introducing methodologies for treating time-independent variational calculations that include the use of the discrete variable representation and the Lanczos method. Time-dependent dynamics on single potential energy surfaces will be considered using Chebychev and split-operator methods. Approximate methods like Time-Dependent Self-Consistent-Field methods (TDSCF) will be described as well as more exact algorithms

My talks on Transition state theory (TST) will describe TST from a dynamical perspective. I will describe W. H. Miller's work on using correlation functions in quantum extensions of TST. Extensions to TST in the condensed phase will be described, highlighting the role of solvent friction. The direct calculation of k(E) and k(T) in the gas phase will be described and compared to approximate theories. The talk will include a presentation of ring polymer dynamics developed by Manolopoulos [JCP **121** 3368, (2004)].

The last set of talks examines theoretical techniques for solving for proton transfer rates. In the condensed phase I will focus on the work of Hynes (formalism) and then describe the Hammes-Shiffer/Tully surface hopping model . This approach will be compared to the ring-polymer dynamics of Manolopoulos . I will describe our work on double proton transfer in the gas phase drawing analogies to condensed phase work. The last part of the talk introduces mixed quantum/classical methods and well as perturbative treatments and their application to transition state dynamics of the simplest of all proton transfer reactions $H+H_2 \rightarrow H_2+H$.

David Tannor's book, *An Introduction to Quantum Mechanics: A Time Dependent Perspective,* includes a significant amount of the material I will cover. Chapter 6: Correlation Functions and Molecular Spectra and Chapter 8: Linear Algebra and Quantum Mechanics contain good background material. Chapter 11 has an excellent description of numerical methods for solving the time-dependent Schrödinger Equation. Chapter 9 treats TDSCF. Chapter 12 describes chemical reactions and transition state theory. Another option for a text which is much less expensive is *Quantum Mechanics in Chemistry* by George Schatz and Mark Ratner. Chapter 8 Theories of Reaction Rates and Chapter 9: A Time-Dependent Approach to Spectroscopy; Electronic Vibrational, and Rotational Spectra provide background material for my lectures.