CHEMISTRY 550: ADVANCED QUANTUM DYNAMICS

Spring Semester 2014
Instructors: Nancy Makri and Sharon Hammes-Schiffer

Lectures: Tuesdays and Thursdays 2:00-3:20 p.m. in 163 Noyes Lab

Course Outline

1. **Basic background (NM)**
   - The time-dependent Schrödinger equation.
   - Stationary and non-stationary states.
   - Time evolution operator and propagator.
   - Example: Two-level systems and tunneling.
   - The density matrix. Pure and mixed states.
   - Time evolution of the density matrix. The quantum Liouville equation.
   - Entropy and the canonical ensemble. The Boltzmann operator. The Bloch equation.

2. **Molecular dynamics (SHS)**
   - Molecular mechanical force fields.
   - Algorithms for molecular dynamics.
   - Boundary conditions, temperature, periodic boundary conditions, analysis of data.
   - Nuclear quantum effects in MD. Grid-based methods, path integral-based methods. The CMD and RPMD approximations.
   - Variational transition state theory with semiclassical tunneling contributions.

3. **Nonadiabatic dynamics (SHS)**
   - The Born-Oppenheimer approximation. Ehrenfest’s theorem.
   - Surface hopping, multiple spawning and QM/MM methods.
   - Non-Born-Oppenheimer methods in electronic structure.

4. **Classical dynamics and semiclassical approximations (NM)**
   - Lagrangian and Hamiltonian formulations.
   - Integrable systems, invariant tori and constants of motion.
   - Non-integrable systems. The KAM theorem. Surfaces of section.
   - Time-independent WKB theory in one dimension.
   - Coherent states and the motion of Gaussian wavepackets.

5. **Path integral formulation of quantum dynamics (NM)**
   - Path integral representation of the propagator.
   - Short time approximations, the sum over paths.
   - The split operator method.
   - The stationary phase approximation and the semiclassical limit of the path integral.
   - Derivation of the time-dependent Schrödinger equation from the path integral.
   - Gaussian influence functional and nonlocal kernels.
5. Quantum statistical mechanics and applications of the path integral (NM)
   Imaginary time path integral formulation of quantum statistical mechanics.
   The quantum-classical isomorphism. Applications to low-temperature fluids.
   Dissipative processes. Reduced density matrices.

6. Electron and proton transfer (SHS)
   Electron transfer. Marcus theory. Inverted region, the golden rule and beyond.
   Proton transfer. Basic concepts, Bell correction, Hynes theory, vibrationally adiabatic and nonadiabatic
   processes.
   Proton-coupled electron transfer.

7. Quantum mechanical simulation methods for condensed-phase processes (NM)
   Introduction to Monte Carlo methods. The Metropolis algorithm.
   Numerical path integral methods for equilibrium properties. Path integral Monte Carlo.
   Numerical path integral methods for real time dynamics in dissipative environments. The sign problem.
   Iterative path integral methods.