CHEMISTRY 550: ADVANCED QUANTUM DYNAMICS

Spring Semester 2022
Instructor: Nancy Makri

Lectures: Tuesdays & Thursdays. 9:30-10:50 online

COURSE OUTLINE

The lectures will cover 80-90% of the following topics. The precise selection will depend on available time and students' interests.

1. Fundamentals
The time-dependent Schrödinger equation.
Time evolution of eigenstates.
Time evolution via basis set expansion.
The time evolution operator. The propagator.
Introduction to two-level systems.
The Heisenberg representation.

2. Some widely used tools
The time-independent self-consistent field (SCF) approximation.
Time-dependent self-consistent field theory.
Discrete variable representations (DVR).

3. The Monte Carlo method in chemistry and physics
Introduction to stochastic sampling.
The Monte Carlo method.
The Metropolis algorithm.

4. Introduction to classical and quantum nonlinear dynamics
Lagrangian and Hamiltonian formulations.
Molecular dynamics (MD) tools.
Canonical transformations. Action-angle variables.
Integrable systems, invariant tori and constants of motion.
Non-integrable systems and chaotic motion. The KAM theorem.
Surfaces of section. The Henon-Heiles model. The stadium model.

5. The Born-Oppenheimer approximation
The adiabatic approximation for a slowly varying Hamiltonian.
The Born-Oppenheimer separation.
Adiabatic and diabatic representations. Nonadiabatic transitions.
The Landau-Zener model.
Quantum-classical approximations.

6. Semiclassical theory
Time-independent WKB theory in one dimension.
Multidimensional generalization. Invariant tori and EBK quantization.
Quantum mechanical spectra: the transition from Poisson to Wigner statistics.

Quantum eigenstates of classically chaotic systems. Periodic orbits, wavefunctions and scars.
Time-dependent WKB theory. Interference, caustics, phase shifts.
Coherent states and the motion of Gaussian wavepackets.
Semiclassical initial value representations.
The Wigner density. Quasiclassical methods.

7. Finite temperature. Dynamics in the presence of a heat bath

The Boltzmann operator.
The reduced density matrix.
The system-bath Hamiltonian.
Classical description: the generalized Langevin equation (GLE). Constant temperature molecular dynamics.
Friction kernel and spectral density.
Dissipative tunneling. The spin-boson model.

8. Path integral formulation of quantum dynamics

Path integral representation of the propagator.
Short time approximations, the sum over paths, interpretation.
The split operator method for low-dimensional systems.
The stationary phase approximation and the semiclassical limit of the path integral.
Examples: linear potential, harmonic oscillator.
Systems with many degrees of freedom.
Derivation of the time-dependent Schrödinger equation from the path integral.
Gaussian influence functional and nonlocal kernels.
Quantum statistical mechanics: the imaginary time path integral.
Path integral representation of quantum partition functions; the classical isomorphism.
The path integral Monte Carlo (PIMC) method for equilibrium properties.
Numerical path integral methods for real time dynamics in dissipative environments.