

CHEMISTRY 542 - SPRING 2024

Professor Nancy Makri

Course Outline

1. Fundamentals of time-dependent quantum mechanics

The time-dependent Schrödinger equation.
Time-independent Hamiltonians and stationary states.
Evolution of non-stationary states. Basis set expansions.
Discrete variable representations.
Time-evolution operator and unitarity.
Evolution operator for time-independent Hamiltonians.
The Heisenberg representation. Heisenberg's equation of motion.
The interaction representation.
The propagator.

2. The Born-Oppenheimer approximation

Separation of electronic and nuclear degrees of freedom.
Born-Oppenheimer potential energy surfaces.
Electronic and ro-vibrational states.
Overview of nonadiabatic effects, charge transfer, diabatic states.

3. Quadratic Hamiltonians

The normal mode transformation.
Free particle propagator.
Propagator and time evolution in harmonic potentials.
Classical trajectories. The motion of Gaussian wavepackets.
Anharmonicity and quantum interference.

4. Time-dependence of model systems

Tunneling in molecular systems.
Two-level systems. Site and eigenstate representations.
Tight binding Hamiltonians.
Gaussian wavepackets.

5. Time-dependent external fields

The interaction representation.
Common origins of time-dependent fields.
Time-dependent perturbation theory.
1st and 2nd order transition amplitudes.
Transitions to a continuum. Fermi's golden rule.
Collision-induced molecular transitions.

6. Interaction of radiation with matter

Classical treatment of the radiation field.

Stimulated absorption and emission. One- and multi-photon processes.

The sudden approximation. The Franck-Condon principle.

Quantized radiation field. Spontaneous emission.

7. Temperature and the density matrix

Statistical ensembles.

The Monte Carlo method.

The density operator. Pure and mixed ensembles. Entropy.

The density matrix and its time evolution.

The Boltzmann operator. The Bloch equation.

8. Correlation functions and spectroscopy

The Fourier transform.

Time correlation functions and spectral information.

Electronic spectroscopy.

Vibrational spectroscopy.