

Molecular Structure and Dynamics – Chem 548

0. Overview: the molecular Hamiltonian
 - a. Translational, rotational, vibrational and electronic structure
 - b. Tools: coordinate transformations, Raleigh-Schrödinger and Van Vleck perturbation theories
1. Symmetry and group theory
 - a. Unitary operators and matrices
 - b. Symmetry operators and generators
 - c. Symmetry groups and matrix representations
 - d. Irreducible representations, group tables
 - e. Products of symmetries and symmetry classification
 - f. Projection operators and traces
 - g. Case study: methanol point and CNPI groups and spectra
2. Rotations and angular momentum
 - a. Euler angles
 - b. Space and body-fixed axes, Eckart conditions
 - c. Angular momentum and frequency
 - d. Rigid rotors: symmetric and asymmetric energy levels
 - e. Advanced properties of quantum angular momentum operators
 - f. Basic angular momentum coupling theory: 3-J symbols
 - g. Application: spectra of open shell molecules and NMR J-couplings
3. The Born-Oppenheimer approximation
 - a. Virial theorem and mass scaling
 - b. Review: the Born-Oppenheimer approximation and its range of validity
 - c. Application: Jahn-Teller effect
 - d. Avoided crossings (Landau-Zener) and conical intersections
 - e. Geometric phase
4. Quantitative Electronic structure theory
 - a. Hartree-Fock wavefunctions
 - b. Hartree-Fock energy
 - c. Minimal basis sets: H_2 , NH and Walsh diagrams for triatomics
 - d. Breakdown of the Hartree-Fock equations
 - e. SCF theory and Roothahn equations
 - f. Practical basis sets: Dunning and n-kl (e.g. 6-31) basis sets
 - g. Configuration interaction
 - h. Møller-Plesset (MP2) perturbation theory
 - i. Generalized valence bond theory
 - j. Density functional theory: Kohn-Sham theorem and functional types
5. The molecular rotation-vibration Hamiltonian
 - a. Body-fixed axes and Eckart conditions
 - b. Advanced normal coordinates: F and G matrix method
 - c. The full rovibrational Hamiltonian
 - d. Quantum Hamiltonian and full rovibronic Hamiltonian
6. Reaction rate models
 - a. Dissociative potentials, minima and saddle points
 - b. Ground and excited state photochemistry

- c. RRKM theory (microcanonical rate theory)
 - d. Canonical rate theory
 - e. Approximation to b and c: Transition state theory
7. The Marcus theory of electron transfer
- a. Electronic curve crossings and redox reactions
 - b. Derivation using central limit theorem for the bath
 - c. Inverted region
8. Electronic and vibrational relaxation
- a. IVR: Golden Rule, tier and state space models
 - b. Spin-orbit coupling and vibronic relaxation

There will be 8 homework sets, one for each segment. Since people have different interest areas, you will be able to 'deselect' two of these problem sets without grade penalty. I still recommend you come to lecture for 'deselected' segments because the material sequentially builds on previous sections, and it helps to at least know the gist of each section.

Instead of a midterm or a final exam, you will have to write a 10 page referenced paper on a subject related to one of the 8 sections. This paper must be a focused and rigorous treatment of a very specific topic of interest to you, including basic derivations. It is not allowed to be a vague overview article, but must demonstrate instead mathematical command of your chosen subject. An abstract, outline, literature section, etc. will be due at various times throughout the semester before the final paper is due.