Final Preparation Guide for Computational Chemistry 126 / 226

Kahn, Fall 2011

The Chem 126/226 Final will be held on Friday, Dec 8 at 8 – 11 AM in Buchanan 1934. The following topics will be covered in addition to topics that were covered in the Midterm.

1) Electron Correlation: Density Functional Theory

a. Density Functional Theory: principles
b. Hohenberg–Kohn existence theorem
c. Hohenberg–Kohn variational theorem
d. Representation of molecular energy in DFT
e. Exchange-correlation functionals: B3LYP
f. Advantages and limitations of DFT

2) Molecular Structure Optimization: Concepts

a. The concept of the potential energy surface (PES)
b. Mathematical definition of a minimum on a one-dimensional PES
c. Mathematical definition of a maximum on a one-dimensional PES
d. Mathematical definition of a minimum on a multi-dimensional PES
e. Mathematical definition of a saddle point on a multi-dimensional PES
f. Optimization of minima: advantages and disadvantages of calculating second derivatives. Use of CalcAll, CalcFC, and ReadFC options in Gaussian
g. Optimization of transition states: Identity reactions and symmetry
h. Optimization of transition state structures: From a single guess structure
i. Optimization of transition state structures: QST2 and QST3 methods
j. Optimization of transition state structures: Scanning the PES
k. Verification of transition states

3) Molecular Structure Optimization: Ab initio Methods

a. Know which methods and basis sets are giving reasonable structures for
   (i) van der Waals complexes (e.g. neon dimer)
   (ii) dipolar complexes (e.g. water dimer)
   (iii) stable closed-shell molecules (e.g. water monomer, CO, F_2)
   (iv) transition states (e.g. in S_N2 reactions)
b. Advantages of using molecular symmetry during optimization
c. Capabilities and limitations of the HF method
d. Capabilities and limitations of the MP2 method

4) Vibrational Spectroscopy and Thermodynamics

a. Separation of molecular wave function to electronic and nuclear wave functions
b. Schrödinger equation for one dimensional harmonic oscillator
c. Vibrational wave functions for the one-dimensional harmonic oscillator
d. Vibrational energy levels for one-dimensional harmonic oscillator

e. Relationship between force constant and harmonic frequencies
f. Reduced mass and the Wilson G-matrix
g. Analytical and numerical calculation of second derivatives
h. How to calculate harmonic vibrational frequencies in water: general approach
i. Accuracy of HF frequencies; scaling
j. Accuracy of frequencies at correlated ab initio levels
k. Thermochemistry with composite models (idea behind G2 and W1 methods)
l. Limitations of the harmonic approximation
m. Zero-point vibrational energy: how to calculate from frequencies
n. Gas phase thermodynamics: the principles
o. Translational contributions to enthalpy and entropy
p. Rotational contributions to enthalpy and entropy depend on the shape
q. Vibrational contributions to enthalpy and entropy depend on vibrational frequencies.
r. How to compare results from calculations with experimental equilibrium constants.
s. How to compare results from calculations with experimental rate constants
t. Kinetic isotope effect: origin and computational prediction
u. Understanding the output of frequency calculations

5) Basic physical and organic chemistry

a. The concept of atomic orbitals
b. Exo- and endothermic reactions, fast and slow reactions
c. S_N1 and S_N2 reactions; the Menchutkin reaction
d. The concept of potential energy surface for description of reactions
e. Arrhenius and Eyring equations for calculating rate constants

Required reading. You should be familiar with the tutorials/assignments posted on the website. You should know the material in the "Required reading category".