Midterm Preparation Guide for Computational Chemistry 126 / 226
Kahn, Fall 2011

The Chem 126/226 midterm on November 17th will cover the following topics

1) **Optimization Methods (Jensen:12,16)**
    a. Basic math: functions, derivatives, Hessian matrix
    b. Mathematical conditions for minima and maxima
    c. Examples of situation in which optimization is important
    d. Classification of optimization methods
    e. Steepest Descent: the principles and the algorithm
    f. Newton-Rhapson: the principle and algorithms, its limitations
    g. Hessian update schemes, BFGS: the principle and advantages
    h. Know which optimizer is best suited for a given task
2) **Molecular Mechanics of Isolated Molecules (Jensen 2; Cramer 2)**
    a. The concept of the force field: energy as a sum of many classical terms
    b. Description of bond stretching: quadratic, cubic, quartic terms
    c. Description of bond dissociation: Kratzer and Morse potentials
    d. Description of bond bending: quadratic function
    e. Description of torsional modes: cosine series
    f. Description of Coulombic interaction via multipole expansion
    g. Description of Coulombic interactions via the distributed point charges
    h. Description of van der Waals interactions: the Lennard-Jones potential
    i. Physical meaning of Lennard-Jones parameters sigma and epsilon.
    j. Comparison and applicability of common force fields: MM3, AMBER, OPLS-AA.
    k. Common applications of molecular mechanics: minimization and conformational analysis
    l. Limitations of molecular mechanics
3) **Molecular Simulations of Liquids (Cramer 3)**
    a. Differences between isolated molecules and condensed media
    b. The Boltzamnn distribution
    c. Monte Carlo: principles and applications
    d. Calculation of probability distributions from Monte Carlo simulations
    e. Monte Carlo conformational search
    f. Molecular simulations: applications and advantages over minimization
4) **Principles of quantum mechanics (Jensen 1.8; Cramer 4.2)**
    a. Description of matter in the quantum theory
    b. Features of quantum mechanics: discreet energy states, uncertainty
    c. Features of satisfactory wave functions: differentiability and integrability
    d. Observables as eigenvalues of operator equations
    e. Hamiltonian operator as the quantum mechanical energy operator
    f. Time-dependent Schrödinger equation and its applications
    g. Time-independent Schrödinger equation and its applications
    h. The physical meaning of eigenvalues of the Schrödinger equation
    i. The physical interpretation of eigenfunction of the Schrödinger equation

j. Analytically solvable problems: the non-relativistic hydrogen atom

5) **Approximate solutions to multi-electron problems (Jensen:3.1-3.4; Cramer 4.5)**
   a. Molecular Hamiltonian operator in the general case
   b. Non-relativistic molecular Hamiltonian in zero-external-field case: complete mathematical expression
   c. Born-Oppenheimer approximation: its essence and consequences
   d. Difficulties in solving the electronic Schrödinger equation for fixed nuclei: dynamic electron-electron interaction
   e. Hartree-product wave function; application to He atom
   f. Hartree approximation: one electron in the field of all other electrons
   g. Slater determinant as a mathematical way to count for electron's spin
   h. Variational principle as a guide to obtain molecular energy
   i. Overlap integral, resonance integral
   j. LCAO approach to molecular orbitals
   k. The Hartree–Fock method: principles

6) Semiempirical Quantum Chemistry (Cramer 5; Jensen 3.10-3.14)
   a. Simplifications to the Hartree-Fock method
   b. Characteristics and parameterization of AM1, and PM3 method
   c. Applicability and accuracy of semiempirical methods for description of chemical reaction energetics
   d. Advantages and limitations of semiempirical methods

7) Ab Initio Quantum Chemistry at the Hartree–Fock Level (Cramer 4.5, Jensen 3.2-3.8, 5.1-5.4)
   a. The need for initial guess for solving the Schrödinger equation
   b. Atomic (Slater) orbitals as a natural choice for atomic orbitals
   c. Mathematical difficulties with Slater Orbitals; Gaussian primitives as a computationally convenient solution; multiplication of Gaussians
   d. The cusp-related limitations of Gaussian primitives
   e. Mathematical form of Gaussian primitives: *s*, *p*, and *d* angular momentum
   h. Structure of Gaussian basis sets; tight and diffuse functions
   i. The zeta-nomenclature: single-ζ, double-ζ, triple-ζ basis
   j. The Pople family of basis sets, polarization and diffuse functions
   k. The structure of correlation-consistent basis sets
   l. Exponential extrapolation to estimate the HF limit

8) Approaches to treat electron correlation (Cramer 7, Jensen 4)
   a. Correlation of same-spin electrons in Hartree–Fock theory
   b. What was ignored in the Hartree–Fock theory?
   c. Static and dynamic electron correlation
   d. MCSFC approach to handle static electron correlation
   e. Virtual excitations as a way for electrons to avoid each other
   f. Configuration interaction method for dynamic correlation, full CI
   g. Truncated configuration interaction (CISD): principle and limitations
   h. First-order perturbation theory: He example
   i. Møller–Plesset perturbation theory: applicability, limitations, and cost

j. Couple cluster theory: applicability, limitations, and cost
k. Basis set requirements for correlated calculations
l. Inverse power-series extrapolation of correlation energy
m. Explicitly correlated r_{12} methods: Hylleraas-type treatment of He atom

9) Practical Aspects of Computation

a. Principles of writing good programs
b. Program input and output considerations
d. The concept of the Z-matrix for molecular structure
e. The concept of atom types and its relation to force field parameters
f. The precision vs. cost dilemma in Monte Carlo simulations
g. How to recognize insufficient sampling in a Monte Carlo simulation
h. Performance considerations for quantum chemistry programs
i. Understanding the output of energy calculations and optimizations
j. Choice of appropriate basis sets
k. Choice of minimization algorithms

Required Reading

1) All tutorials, homework assignments, and answer keys for assignments 1-3
2) All literature marked "Required" on the course website