Chemistry 6485: Computational Chemistry

Instructor

Meetings:	MWF 9:05-9:55, MS&E 1224
[redacted]	[redacted]
Office Hours:	MW 3-4 or by appointment
Unofficial TA:	Edward Hohenstein, MS&E 4201
Office Hours :	TBA

Description

This introductory course in computational chemistry will discuss molecular mechanics, semiempirical, and particularly *ab initio* approaches. The course will be project-based, and students will be encouraged to pursue projects related to their own research if possible. The course will highlight the computational algorithms used to implement the theoretical methods. This is a graduate-level course but should be accessible to advanced undergraduates. Graduate-level quantum mechanics is not required, but students will need to become familiar with some basic concepts from quantum chemistry such as eigenvectors and eigenvalues, the Schroedinger equation, orbitals, and variational and perturbational methods. This material will be reviewed briefly at appropriate times during the course. Students will learn the basic theory and algorithms behind computational chemistry methods, and they will also learn the advantages and disadvantages of these methods and how to use them to solve problems of interest in chemistry and molecular sciences.

Requirements and Grading Scheme

Problem sets and labs	25%
Midterm	25%
Final	25%
Project	25%

A substantial part of the grade will be determined by a class project in computational chemistry which is to be carried out during the course of the semester. A different project will be selected by

each student in the first few weeks of the semester, with the approval of the instructor. Students are encouraged to select a class project relevant to their own research, if feasible. Auditors are required to take the midterm and final and demonstrate a minimal understanding of the subject, *or* they may turn in a satisfactory class project. Pass/fail students are required to turn in a class project and take both the midterm and the final and receive an overall passing grade.

Topics

Because this is a special topics course, there is some room to adjust the topics to be covered. At the first meeting, a discussion will be held about whether any additional topics are of interest to the class.

- Introduction (1 lecture): Scope of computational chemistry; course topics; review of key concepts from linear algebra
- Molecular Mechanics / Force Field Methods (3 lectures): Introduction to molecular mechanics; comparison of popular force fields; performance of molecular mechanics (slides)
- Molecular dynamics (2 lectures)
- Review of postulates of quantum mechanics (1 lecture)
- The Born-Oppenheimer approximation, potential energy surfaces, local and global minima, transition states, and Hessian indices (1 lecture) (slides)
- Review of the variational method (1 lecture)
- Hartree-Fock molecular orbital theory (4 lectures): Slater determinants, anti-symmetry principle, deriving the Hartree-Fock equations, Hartree-Fock energy expressions for arbitrary spin-orbital configurations, spin integration, restricted and unrestricted references, self-consistent-field (SCF) procedure
- Basis sets (2 lectures): Slater and Gaussian functions, contractions, polarization and diffuse functions, split-valence sets, correlation-consistent sets, core-valence sets, general contractions, EMSL basis set exchange (slides)
- Molecular integrals (1 lecture): types of integrals, Gaussian product theorem, permutational symmetry of integrals
- The Hartree-Fock algorithm (1 lecture)

- Electronic spin (1 lecture): $\hat{S}^2$ operator, degeneracy, evaluating the spin of Slater determinants
- Electron configurations, term symbols, Aufbau principle, diatomic MO diagrams, Walsh's rules (2 lectures)
- Group theory (2 lectures): molecular point groups, computational simplifications
- Molecular properties (1 lecture): dipole moment, polarizability, hyperpolarizability, magnetic moment, NMR shifts, methods for computing properties
- Semiempirical methods (1 lecture)
- Density-functional theory (2 lectures)
- Geometry optimization (1 lecture) (slides)
- Vibrational frequency analysis (2 lectures): symmetry analysis, harmonic vs. fundamental frequencies, zero-point vibrational energies (ZPVE's), Hessian index, distinguishing minima from transition states (slides)
- Intrinsic reaction coordinate (IRC) analysis (1 lecture)
- Transition state theory, statistical mechanics, and thermodynamic properties (2 lectures) (slides)
- Introduction to electron correlation; configuration interaction (2 lectures) (slides)
- Many-body perturbation theory (1 lecture)
- Useful approximations: resolution of the identity (density fitting) and local correlation (1 lecture)
- Coupled-cluster theory (2 lectures)
- Nondynamical correlation and multiconfigurational self-consistent-field (MCSCF) theory (1 lecture) (slides)
- Comparing the performance of electronic structure theories (2 lectures)
- Example applications (1 lecture)

Textbooks

1. F. Jensen, *Introduction to Computational Chemistry*, 2nd Edition, (Wiley, New York, 2007). Good introductory textbook covering a variety of topics.

2. A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory*, 1st ed., revised (Dover, 1989). More mathematical detail for many of the *ab initio* electronic structure methods.

Recommended Supplementary Books

1. D. A. McQuarrie, *Quantum Chemistry* (University Science Books, Mill Valley, CA, 1983). Very readable introductory text for undergraduate-level quantum chemistry.

2. I. N. Levine, *Quantum Chemistry*, 4th ed. (Prentice Hall, Englewood Cliffs, NJ, 1991). Covers some of the topics in this course.

3. F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed. (Wiley, New York, 1990). Classic reference on the subject.

4. E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (Dover, New York, 1980). Classic reference on the subject, in affordable Dover paperback form.