

January 16, 2009

TO: Prospective Chemistry 554 Students
FROM: Peter Gaspar
SUBJECT: Course Syllabus for Chemistry 554, Spring 2009

Chemistry 554, Spring 2009

The topic of this course is the background and practice of chemical structure theory and its applications to determining the structures and energies of molecules and to the elucidation of the mechanisms of chemical reactions. It will assume exposure to quantum mechanics at the level of an undergraduate physical chemistry course, and a nodding acquaintance with molecular orbitals and their utilization in organic chemistry at the level of the Anslyn and Dougherty text employed in Chemistry 5511.

The aim of the lectures will be to provide some understanding of what it means to solve the time-independent Schrödinger equation, and the approximations employed in obtaining these solutions for systems of chemical interest. Different levels of approximation will be discussed, from Hückel theory, through semi-empirical SCF theory, to *ab initio* SCF molecular orbital calculations with correlation corrections. Density functional calculations as alternatives to established CI and perturbation theory corrections for electronic correlation will be covered, as will non-quantum mechanical models for the estimation of molecular structures and their (relative) energies such as molecular mechanics. The various modes of interpretation of electronic structures will include Bader's "Atoms in Molecules" approach.

The availability of user-friendly program packages to actually do calculations will be exploited, including assignments and projects employing the "Spartan" package which facilitates molecular mechanics calculations, MO calculations at various levels of approximation, and density functional calculations. The "Gaussian" suite of programs is also available within the Department, and some discussion of its capabilities will be included if time permits..

The text for Chemistry 556 is Christopher J. Cramer, "Essentials of Computational Chemistry - Theories and Models, second edition" John Wiley and Sons, Chichester, 2004. Handouts from various sources will also be provided.

The basis for the final grade for Chemistry 554 will include: 1. A written midterm exam in the middle of the semester covering the conceptual background for electronic structure and molecular mechanics calculations (20% of total grade). 2. Participation in class discussion will be rewarded by up to 5% of the total grade for the semester.

After some practice illustrating the operation of the "Spartan" molecular modeling software and its capabilities for answering questions about the structure and properties of molecules, including the mechanisms of their reactions, students will be asked to write a brief (< 5 pp.) proposal for a computational chemistry research project which they will then carry out. The proposal will be read, edited, and graded by the professor, and revision may be requested. The grade on the proposal will contribute 20% to the total semester grade.

Since the homework requirements of Chemistry 554 will be small, students should be able to focus on their computational chemistry projects throughout much of the semester,

The semester grade for Chemistry 554 will be based in part (20%) on the graded reports on the computational chemistry "laboratory exercises" that will be a "warm-up" for the research project, a written "term paper," (25% of total grade) and a brief oral report (10% of total grade) on the results and their interpretation that you will obtain from a computational chemistry research project for which you will be asked to write a proposal. The reports on the computational chemistry project will be due at the end of the semester.

"Hands-on" exercises with the Spartan package will be introduced early. The contents of *A Laboratory Book of Computational Organic Chemistry*, one of the required texts, will be discussed. This will review the capabilities of computational organic chemistry and allow students to pick those exercises that are of greatest interest to them. Purchase of a "Tutorial and User's Guide" for the Spartan software package will also be encouraged.

Week Topic

1 Fundamental ideas of electronic structure theory - Cramer chapters 1 and 4, and handouts

(lectures 1, 2 & 3, January 12, 14 & 16)

- The wave equation and its relationship to wave-particle duality and the non-commutation of position and momentum in a microscopic world.
- Separation of variables and solutions of the wave equation.
 - * Spatial and time coordinates
 - * Motion of nuclei and electrons - the Born-Oppenheimer approximation.
 - * The orbital approximation and the LCAO MO
- The H_2^+ ion
- From n-electron wave equation to n (identical) one-electron wave equation.
 - * Non-interacting electrons: the Hückel molecular orbital theory wave equation.

2 Working with the wave equation - Cramer chapter 4, handouts

(lectures 4, 5, 6, 7, 8 & 9, January 21, 23, 26, 28, 20, February 2)

- How to "solve" wave equations - the Variation Principle
- The Hückel theory secular equations and secular determinant.
 - * The π -MO energies and AO coefficients for ethylene.
 - * The matrix eigenvalue problem.

3 · Chemical information from MO energies and AO coefficients

- * Examples from Hückel theory, and the need to include electronic repulsion.
 - Pi-electron density, bond order
 - Delocalization energy
 - ESR spectra as clear example of limitations of Hückel theory

- Perturbation theory.

4 "Menu" of the capabilities of a modern MO package like Spartan and a tour of the Spartan tutorial; molecular mechanics - Spartan Tutorial and User's Guide

(edition to be announced), Hehre, Shusterman & Huang "A Laboratory Book of Computational Organic Chemistry," Cramer, chapter 2

(lectures 10, 11 & 12, February 4, 6 & 9)

- Overview of the Spartan Tutorial and "A Laboratory Book of Computational

Organic

Chemistry

Week Topic

- How to familiarize yourself with Spartan
 - The hierarchy of MO calculations and how we shall approach them
 - A few words about molecular mechanics
- 5** **Brief comments on selected exercises from the workbook by Hehre, Shusterman and Huang and *ab initio* calculations with the Spartan package** - "A Laboratory Book of Computational Organic Chemistry," the Spartan Tutorial (lecture 13 & 14, February 11 & 13)
- Molecular geometries
 - Isodesmic reactions
 - Solvent effects
 - Charges on atoms in molecules
 - Conformations and conformational effects
 - *Pi*-interactions involving *sigma*-electrons
 - Chemical reactivity and selectivity in conformationally mobile systems
 - Graphical models and graphical modeling - electrostatic potentials
 - Visualizing molecular orbitals
 - Reactive intermediates and the Hammond postulate
 - MO descriptions of substituent effects
 - Weakly bonded and not-so-weakly bonded molecules
 - Isotope effects
 - Finding transition states
 - Thermodynamic *vs* kinetic control via MO calculations
 - *Ab initio* calculations with the Spartan package.
- 6** **Inclusion of electron-electron repulsion in the Hamiltonian** - Cramer chapter 4, and handouts (lectures 15, 16, 17, 18 & 19, February 18, 20, 23, 25 & 27)
- Hierarchy of MO calculations
 - Indistinguishability of electrons, spin, antisymmetrization, Slater determinants.
 - The Hartree-Fock equations - how does one obtain a one-electron wave equation including electron-electron repulsion?
 - The exchange integral demystified
 - Basis functions and basis sets
- 7** • A descriptive view of *ab initio* calculations - LCAO MO's and energies by iterative "solution" of the Hartree-Fock equations.
• Cost *vs* benefit of *ab initio* calculations and the need for correlation energy corrections
- 8** **Beyond self-consistent field molecular orbital theory** - Cramer chapters 7 & 8 (lectures 20, 21, 22, 23 & 24, March 2, 4, 6 & 16)
- Correlation corrections, configuration interaction, perturbation theory, and density functional calculations.
 - Beyond Spartan - multiconfiguration SCF calculations.
- Large and very large systems handled by much faster but less accurate calculations; simulation of molecular assemblies** - Cramer, chapters 5 & 2 (lectures 25, 26, 27, 28 & 29, March 18, 20, 23, 25 & 27)
- Week Topic**

- 9
- Semi-empirical SCF MO calculations and the parametrization of terms in the Fock operator - advantages and disadvantages
 - Types of semiempirical calculations - what are their differences and how does one choose among them?
 - Semiempirical calculations with the Spartan package.
 - Comparison of results from semiempirical, *ab initio*, and density functional calculations
 - Molecular mechanics calculations - a semi-classical ball-and-sticks model
- 10 **Finding and verifying transition structures; models for solvent effects** - handouts, and Cramer chapters 11, 12 (lectures 30, 31, 32, 33 & 34, March 30, April 1, 3, 6 & 8)
- Locating transition structures and verifying them through vibrational analysis and intrinsic reaction coordinate calculations
- 11
- Implicit and explicit solvent models
- A brief introduction to the properties of systems with many minima of similar energy** - Cramer chapter 3, and handouts
(lectures 35, 36, 37, 38 & 39, April 10, 13, 15, 17, 20)
- Methods for exploring conformational space
- 12
- Molecular dynamics simulation methods
 - Monte Carlo simulation methods
 - Protein structure prediction, sequence analysis, and protein folding
- 13 **Reports on computational chemistry semester projects**
(Lectures 40 & 41, April 22, 24)

End of the semester