

Syllabus - CHE 417 / CHE 5417

Theoretical Chemistry

Fall Semester, 2003

Class: Hederman Science Building, Room 307

3 semester hours credit

T 4:00 - 7:00 PM

Professor: David H. Magers, Ph.D.

Office: Hederman Science Building, Room 418-B

Research Lab: Hederman Science Building, Room 418-A

Phone: (601) 925-3851

Lab Phone: 925-3852

e-mail: magers@mc.edu

Instructional Materials:

The required texts are Introduction to Quantum Mechanics in Chemistry by Mark A. Ratner and George C. Schatz and Essentials of Computing in Chemistry: Theories and Models by Christopher J. Cramer. In addition to this text you will need a scientific calculator. Many of the class notes will be distributed.

Prerequisites: CHE 318. In addition to this specific prerequisite, students enrolled in CHE 5417 must have previously completed at least eighteen hours of chemistry.

Disclaimer: Although I expect to conduct the course according to the following, I reserve the right to make modifications if circumstances dictate.

Course Description: A study of theoretical chemistry, chemical physics, theoretical molecular spectroscopy, and solid-state chemistry with emphasis on fundamentals of quantum mechanics, vibrational and rotational spectroscopy, crystallography, and molecular electronic spectra.

Rationale: The expanding role of quantum chemistry makes it highly desirable for students in all areas of chemistry to understand modern methods of electronic structure calculation. In particular, theoretical chemistry is essential for a thorough understanding of bonding theories and spectroscopy. As in all physical chemistry courses at Mississippi College, development of problem solving and critical thinking skills are stressed.

Academic integrity: Mississippi College students are expected to be honest. Please refer to the *2003-2004 Mississippi College Undergraduate Bulletin*, page 56 or to the *2003-2004 Mississippi College Graduate Catalog*, page 13 for a discussion of plagiarism and cheating. Also refer to the *2003-2004 Mississippi College Tomahawk* or to University Policy 2.19.

Methods of Instruction: Class will consist primarily of lectures and working problems. Occasionally, students enrolled in CHE 5417 will be required to present oral reports to the rest of the class.

Attendance: Your attendance at all class meetings is expected. Please refer to the *2003-2004 Mississippi College Undergraduate Bulletin*, pages 53 and 54 or to the *2003-2004 Mississippi College Graduate Catalog*, page 32 for a discussion of the university's attendance policy. Absences are recorded on the grade report that is mailed at the end of the semester. If a regular class meeting is missed, it is the student's responsibility to obtain any assignments or instructions that were given by the instructor. Missing a class is **not** an excuse for not preparing for the next class meeting or not having an assignment ready on time. Don't miss a scheduled test! In the event of an extreme emergency and an excused absence, a make-up test will be given. The test must be made up prior to the graded tests being returned to the class. Make-up tests are usually different from the regular test and may be more difficult. If the student cannot return to class until after the tests have been returned, the grade on the final exam may be substituted for the missing grade.

Required Practices: You are expected to read the appropriate sections of your text and work any problems assigned before coming to class. Periodically throughout the semester special problem sets will be distributed which must be completed for a grade. Some of these problem sets will involve computational problems which will require the use of computational chemistry software located in the chemistry computer labs. The grades from all of the problem sets will be added to quiz grades as discussed below. Students enrolled in CHE 5417 will have additional computational problems assigned. In addition, CHE 5417 students will be required to prepare reports on special topics periodically throughout the semester and present these reports orally to the rest of the class. Finally, as previously mentioned, all students will need a good scientific calculator and be fairly proficient with it.

Grading: Three tests will be given during the semester, each with a value of 100 points. Unannounced pop tests are given periodically, the total number of pop test points and points from homework assignments will be approximately 100. Pop tests that are missed are not made up. The final exam is comprehensive and is worth 150 to 200 points. Your overall grade is determined by dividing your grand total by the total possible points. Occasionally there are opportunities for extra credit points by attending a special seminar or a visiting lecture.

CHE 417: Final letter grades are determined on a 10-point scale. Please refer to the *2003-2004 Mississippi College Undergraduate Bulletin*, pages 47 and 48 for a discussion of the university's grading system and how quality points are assigned.

CHE 5417: In addition to the above, approximately 100 points may be earned from the periodic reports and oral presentations mentioned above. Final letter grades are determined on the following scale:

91-100 % = A	72 - 77 = C+	55 - 64 = D
85 - 90 % = B+	65 - 71 = C	below 55 = F
78 - 84 % = B		

Please refer to the *2003-2004 Mississippi College Graduate Catalog*, pages 35 and 36 for a discussion of the university's graduate grading system and how grade points are assigned.

Course Overview: The course covers material presented in chapters 1-14 of the Ratner and Schatz text and chapters 1-10 of the Cramer text. Chapter 1 of the Ratner and Schatz text presents an introduction to quantum mechanics, some key concepts from classical physics including both particle and wave behavior, and some early history of quantum mechanics. Chapter 2 presents the postulates of quantum theory and introduces some key concepts like operators, eigenfunctions, eigenvalues, orthogonality, and expectation values. Chapter 3 discusses particles in infinite square-well potentials, and chapter 4 discusses rigid-rotor models. Molecular vibrations and time-independent perturbation theory are discussed in chapter 5, while the hydrogen atom is presented in chapter 6. Chapter 7 discusses the helium atom and variational theory, and chapter 8 discusses electron spin and the Pauli Principle. Chapter 9 introduces methods to study many-electron atoms, and chapter 10 presents models for homonuclear diatomic atoms. Chapter 11 discusses *ab initio* and density functional methods, while chapter 12 introduces semiempirical methods. Chapter 13 presents molecular symmetry and group theory, and chapter 14 discusses applications of electronic structure theory.

The Cramer text begins with a discussion in chapter 1 of what exactly is meant by the terms *theory*, *computation*, and *modeling*. Chapters 2 and 3 discuss molecular mechanics. Chapter 4 presents the foundations of molecular orbital theory. Semiempirical methods are discussed in chapter 5, *ab initio* methods in chapters 6 and 7, and density functional theory in chapter 8. The first *ab initio* chapter focuses on Hartree-Fock theory and the second on electron correlation. Finally, spectroscopic properties are discussed in chapter 9, and thermodynamic properties are discussed in chapter 10. In the beginning of the course, the quantum mechanics text will be the primary text, and the computational chemistry text will be used more in the latter half of the course.

Course Outline:

I. Introduction to Theoretical Chemistry and Chemical Physics

II. Mathematical Review

- A. Operator Algebra
- B. Basic matrix algebra
- C. Matrix diagonalization and eigenvalues

III. Review of Quantum Chemistry Basics

- A. Quantum Phenomena
- B. Wave character and wavefunctions
 - 1. De Broglie's relation
 - 2. Normalization
 - 3. Orthogonalization
- C. Quantum mechanical operators and Schrödinger's Equation
- D. Noncommuting operators and the Heisenberg Uncertainty Principle
- E. Particle in an infinite square-well potential
- F. Quantum mechanical harmonic oscillator

IV. Harmonic Motion Revisited

- A. Hamilton's equations of motion
- B. Classical harmonic oscillator
- C. Motion through several degrees of freedom and harmonic vibration of many particles
- D. Classical normal mode analysis

- V. Postulates of Quantum Mechanics
- VI. Hermitian Operators
- VII. Multidimensional Problems and Degeneracy
- VIII. Variation Theory
- IX. Perturbation Theory
- X. Time Dependence and Transitions; Derivatives of Schrödinger's Equation.
- XI. Angular Momentum
 - A. Operators
 - B. The rigid rotor
 - C. Spherical harmonics
 - D. coupling
 - E. Raising and lowering operators
 - F. Atomic term symbols
- XII. Vibrational-Rotational Spectroscopy of Diatomic Molecules
 - A. Basic treatment
 - B. Centrifugal distortion
 - C. Coupling
 - D. Vibrational anharmonicity
 - E. Selection rules
 - F. Infrared spectra
- XIII. Vibrational and Rotational Spectroscopy of Polyatomic Molecules
 - A. Rotational spectroscopy of linear molecules
 - B. Harmonic picture of polyatomic vibrations
 - C. Polyatomic vibrational spectra
 - D. Characteristic frequencies
 - E. Inversion and interconversion
 - F. Rotational states of nonlinear molecules
- XIV. Molecular Electronic Structure
 - A. Born-Oppenheimer approximation
 - B. Potential energy surfaces
 - C. Molecular orbital picture / linear combination of atomic orbitals
 - D. Slater-Condon rules
 - E. Self-consistent field wavefunctions
 - F. Spectroscopic states (spin and symmetry)
 - G. Electron correlation
 - 1. Configuration Interaction
 - 2. Many-body Perturbation Theory
 - H. UV-visible spectra of molecules
- XV. Computational Methods
 - A. Molecular mechanics
 - B. Molecular Orbital Theory
 - 1. Semiempirical methods
 - 2. *Ab Initio* methods
 - a. SCF theory
 - b. post-Hartree-Fock methods
 - 3. Density functional theory

Learning Objectives: (This is not an exhaustive list.)

- 1) Learn to use differential and integral calculus in chemical and physical problems.
- 2) Learn how to compute the n th root of a complex number by using De Moivre's theorem.
- 3) Learn how to compute commutators.
- 4) Learn how to compute probabilities beyond the classical turning points for the quantum-mechanical one-dimensional harmonic oscillator.
- 5) Learn how to use ladder operators to generate eigenfunctions for another operator.
- 6) Learn the axioms of modern quantum theory.
- 7) Learn how to solve the problem of a particle in a three-dimensional infinite square-well potential.
- 8) Learn what the term *degenerate* means in quantum mechanics.
- 9) Learn what the virial theorem says and what it means.
- 10) Learn what the Hellmann-Feynman theorem says and what it means.
- 11) Learn how to generate the Hermite polynomials.
- 12) Learn how to solve the problems of a particle on a ring and a particle on the surface of a sphere.
- 13) Learn what the spherical harmonics are.
- 14) Learn how orbital angular momentum and spin angular momentum differ.
- 15) Learn how to couple angular momentum vectors.
- 16) Learn how to determine atomic term symbols associated with electron configurations.
- 17) Learn what atomic spectroscopic selection rules follow from the atomic term symbols.
- 18) Learn what symmetry elements are used to describe the symmetry in molecules.
- 19) Learn how to classify molecules by their symmetry point group.
- 20) Learn what a matrix representation of a group is.
- 21) Learn how to determine how many irreducible representations a given group has.
- 22) Learn to reduce reducible representations into irreducible representations.
- 23) Learn how to take direct products of matrix representations.
- 24) Learn how to form representations from points in a molecule or from motions of a molecule.
- 25) Learn how symmetry is relevant to problems in quantum mechanics and spectroscopy.
- 26) Learn what the Born-Oppenheimer approximation is.
- 27) Learn how the molecular Hamiltonian may be divided between the electronic and the nuclear Hamiltonians.
- 28) Learn how to calculate the energy levels in conjugated pi systems using simple Hückel theory.
- 29) Learn what SCF theory means and how it works.
- 30) Learn how to apply SCF theory to a problem of chemical interest via a computational chemistry software package.
- 31) Learn how molecular mechanics differ from quantum mechanical applications.
- 32) Learn how semiempirical methods, *ab initio* methods, and density functional theory methods differ.
- 33) Learn Koopman's Theorem.
- 34) Learn what electron correlation is, why it is important, and different ways to calculate it.
- 35) Learn why density functional theory is not an *ab initio* method, but may be as accurate or more accurate than some of them.
- 36) Learn what molecular properties may be computed with computational chemistry packages in addition to the energy.