

CHEM 334 - Quantum Chemistry & Structure of Matter - Spring 2009

INSTRUCTOR: Frank Rioux

1. Office: Ardolf Science Center 241
2. Phone: 363-5385
3. Email: frioux@csbsju.edu

TEXTBOOK: *Quantum Chemistry and Spectroscopy* by Thomas Engel (this text is the second half of *Physical Chemistry* by Engel and Reid)

Office Hours and Teaching Schedule - Spring Semester 2009

Period\Day	1	2	3	4	5	6
I	CHEM 334 ASC 135	Office Hour ASC 241	CHEM 334 ASC 135	Office Hour ASC 241	CHEM 334 ASC 135	Department Meeting
II	Office Hour ASC 241		Office Hour ASC 241		Office Hour ASC 241	Office Hour ASC 241
III						
IV		CHEM 334 Lab ASC 135				
V		CHEM 334 Lab ASC 135				
VI		CHEM 334 Lab ASC 135				

Course Description: This course deals with the fundamental principles of quantum theory and their application to the atomic and molecular systems of interest to chemists. A major goal of CHEM 334 is to illustrate how theory and experiment work together in the development of a viable model for the nano-world of atoms and molecules. In short, quantum chemistry deals with the stability, structure and transformations of matter, and its interaction with electromagnetic radiation. However, while the primary concern of this

course is an operational mastery of fundamental principles, the rich historical and philosophical background of quantum theory will not be neglected.

There are a number of interesting quantum sites on the World Wide Web that can serve as resources for this course. They are listed below. To visit just point and click.

- [Chemistry Resources Home Page](#)
- [A Brief Review of Quantum Chemistry](#)
- [A Periodic Table](#)
- [NIST Chemistry Webbook](#)
- [NIST Physical Reference Data](#)
- [Jack Simons' Theoretical Chemistry Page](#)

Many of the scientific achievements that we study in this course have earned their discoverers the Nobel Prize. There are two web sites that have extensive treatments of the contributions of the Nobel Laureates.

- [The Nobel Prize Internet Archive](#)
- [The Nobel Foundation](#)
- [Nobel Prizes in Chemistry](#)
- [Nobel Prizes in Physics](#)

The following journals frequently publish quantum mechanical articles and also contain daily updates on current advances in science. CSB|SJU has online subscriptions to both journals.

- [Science Magazine](#)
- [Nature Magazine](#)

Lecture: In lecture we will cover the 18 chapters in Engel's text. These are chapters 12 to 29 in *Physical Chemistry* by Engel and Reid, the text many of you have. We will spend between two and three days on each chapter. I have prepared a significant amount of supplementary material for this course which can be found on my homepage: <http://www.users.csbsju.edu/~frioux/workinprogress.html>.

In a mathematically oriented course such as this it is extremely important that you work at it on a daily basis. This means regular attendance in class, asking lots of questions, working recommended problems at the end of the chapter, and faithfully completing the computer and spectroscopy exercises.

Your grade in CHEM 334 will be based on your performance on exams, quizzes and a cumulative final (May 6, 2009, 6:00 – 8:00 pm, ASC 135). There will be three exams and as many as five quizzes during the semester. You will be given a week's notice on exams and at least a day's notice on quizzes.

Laboratory: The laboratory work in this course falls into two major classifications: theoretical computer exercises and analysis of spectroscopic data. The purpose of the computer exercises is to illustrate important theoretical principles and computational techniques. The emphasis in the spectroscopy exercises is on the various ways that theoretical models are used to interpret the interaction of electromagnetic radiation with matter and to extract from the spectra various molecular parameters. Material covered in lab will also appear on exams and quizzes.

Lab will consist of twelve computer/spectroscopy exercises chosen from the following lists.

Computer Exercises

1. Using Mathcad for Routine Problem Solving
2. Applications of Integral and Differential Calculus in Quantum Mechanics
3. Calculations on the One-dimensional Hydrogen Atom in Coordinate and Momentum Space
4. Quantum Mechanical Calculations on the Three-dimensional Hydrogen Atom
5. Numerical Solutions to Schrödinger's Equation
6. Introduction to the Variational Method
7. Quantum Mechanics of Two-electron Atoms or Ions
8. A Simple SCF Calculation for Two Electron Systems
9. Molecular Orbital Calculation on Hydrogen Molecule Ion
10. The Virial Theorem and the Covalent Bond in H_2
11. Numeric and Symbolic Hückel Molecular Orbital Theory Calculations
12. Introduction to Spartan: Molecular Mechanics, Semi-empirical and Ab Initio Quantum Mechanics
13. Molecular Orbital Theory, Hybridization, VSEPR, and Photoelectron Spectroscopy
14. Spartan Special Project

Spectroscopy Exercises

1. Analysis of the Visible Spectra of Cyanine Dyes Using Three Quantum Mechanical Models
2. Analysis of the Pure Rotational Spectra of HCl and CO

3. Analysis of the Vibrational-Rotational Spectra of HCl and CO
4. Determination of the Bond Dissociation Energy of Bromine
5. Analysis of the Visible Spectrum of Iodine
6. Applications of Group Theory to Vibrational and Electronic Spectroscopy
7. NMR - Quantum Mechanical Treatment of Three Proton Systems - Vinyl Acetate and Acrylonitrile

Naturally, you will be expected to be present for all exams, quizzes and laboratory sessions. Only under unusual circumstances will make-up exams, quizzes or labs be permitted.

Miscellaneous: The Calculus I and II prerequisites are very important for CHEM 334 because of its mathematical orientation. If you do not feel that your background in differential and integral calculus is adequate it would be advisable to spend some time reviewing these subjects early in the semester. Our textbook has a useful mathematics supplement in Appendix A that you should review. It deals with complex numbers, integral and differential calculus, spherical coordinates, determinants, vectors, matrices, and partial differentiation.

Computer Hardware and Software: All computer labs and much of the day-to-day calculations will be done on the PCs located in Room 135 of the Ardolf Science Center. Two major software packages will be used in this course: Mathcad and Spartan. Mathcad is a high level programming environment for doing essentially all the mathematics (numerical and analytical) we will encounter in our study of quantum chemistry. We will use it on a daily basis for routine problem solving and also to do the computer labs. The first two computer labs will be devoted to an introduction to Mathcad. Approximately 75% of exam and quiz questions will be answered using Mathcad. Spartan is an advanced software package for doing molecular mechanics, semi-empirical and ab initio quantum mechanics on molecules of intermediate complexity. It has a powerful graphical user interface and is very easy to use. Your previous experience with Spartan in organic chemistry (and perhaps general chemistry) will be helpful.

Chapter 1 - From Classical to Quantum Mechanics

This introductory chapter provides historical background on the failures of classical physics and the need for a new mechanics, appropriate for the nanoworld of atoms and molecules. Among the phenomena that could not be explained classically were: black body radiation, the photoelectric effect, Compton scattering, low temperature heat capacities, atomic line spectra, and atomic and molecular stability. In addition to discussing how these classical failures led to the development of quantum mechanics, this chapter introduces the famous double-slit experiment. Richard Feynman said it has in it “the heart of quantum mechanics” and illuminates its only mystery – the superposition principle.

Recommended problems: 2-9 17 19-23

Chapter 1.5 - Matrix Mechanics and Dirac Notation

As you are aware, there is no Chapter 1.5 in our text. The instructor will provide supplemental material which covers these areas.

There are two great computational traditions in quantum theory: Heisenberg's matrix mechanics and Schrödinger's wave mechanics. They are formally equivalent, but each has particular strengths in certain applications. Schrödinger's wave mechanics might be considered the default for chemists, but the basic concepts of quantum theory are probably most easily introduced via matrix mechanics.

In the early days of quantum theory Dirac introduced an elegant and powerful notation that is useful in setting up quantum mechanical calculations. After using Dirac's notation to set a calculation up, one generally chooses either matrix or wave mechanics to complete the calculation, using that method which is most computationally convenient.

Chapter 2 - The Schrödinger Equation

The Schrödinger equation is the key equation of non-relativistic quantum mechanics. It is a mathematical generalization of de Broglie's wave hypothesis for matter, $\lambda = h/mv$. De Broglie's conjecture that matter has wave-like properties and that its wavelength is inversely proportional to its momentum is the foundation of quantum mechanics. In this chapter we see that the Schrödinger equation can be *derived* by substituting the de Broglie wave equation into the classical equation for a plane wave.

Recommended problems: 1 2 5 9 10-21 24 25 29 30

Chapter 3 - The Quantum Mechanics Postulates

Chapter 6 – Commuting and Noncommuting Operators and the Surprising Consequences of Entanglement

These chapters present the basic postulates and computational procedures of quantum mechanics. Among the key postulates of quantum theory are the assertions that the wave function contains all the physically meaningful information about a system and that there is an operator associated with every observable property. The postulates tell us how to obtain values for observable properties of a system from its wave function. The postulates also tell us that, unlike classical mechanics, in quantum mechanics there are restrictions on our knowledge of observables; that certain observables, such as position and momentum have a conjugate or incompatible relationship. That is if you have precise knowledge of one observable property, you have limited or no knowledge of the conjugate property. The most common conjugate observable pairs are position and momentum, and energy and time.

It is a great strength of this text that it deals with contemporary quantum theory. Thus, in this chapter it introduces the strange and subtle concept of entanglement. In other

chapters it deals with other contemporary concepts such as the importance of the superposition principle, quantum mechanical tunneling, teleportation and the possibility of quantum computers. Surprisingly these important subjects are ignored in most quantum chemistry texts for undergraduates.

Recommended problems for chapter 6: 2 3 15 16 20

Chapter 4 – Using Quantum Mechanics on Simple Systems

Chapter 5 – The Particle in the Box and the Real World

While de Broglie's wave equation can be used directly to solve a number of simple problems, the Schrödinger equation is more general and is the basis of all computational quantum mechanics at the atomic and molecular level. In this chapter we learn how to solve Schrödinger's equation for the celebrated particle in the box (PIB) problem. Once solved the PIB model will be used interpret the pi-electron spectra of conjugated organic molecules, conductivity in metals, and quantum mechanical tunneling. In lab we will explore numerical solutions for Schrödinger's equation for a number of other simple models related to the particle in the box.

Recommended problems for chapter 4: 3-6 8-10 12-21 25

Recommended problems for chapter 5: 3 and 4

Chapter 7 – A Quantum Mechanical Model for the Vibration and Rotation of Molecules

Chapter 8 – The Vibrational and Rotational Spectroscopy of Diatomic Molecules

In chapter 7 Schrödinger's equation is solved for the harmonic oscillator and the rigid rotor, the chemists most rudimentary models for molecular vibration and rotation. Chapter 8 reveals how chemists use these simple models to analyze the microwave and infrared spectra of molecules to extract molecular parameters, such as bond lengths and bond angles.

Recommend problems for chapter 7: 1-10 13 14 17 24 29

Recommend problems for chapter 8: 1-4 6 8 13 14 24

Chapter 9 - The Hydrogen Atom

Schrödinger's equation can be solved exactly for only a small number of problems. Fortunately, the hydrogen atom is among the list of exactly soluble problems. The reason this is important is that the exact solution of the hydrogen atom problem, suitably parameterized, can serve as a starting point in obtaining approximate solutions for more complicated atomic and molecular systems.

When Schrödinger's equation is solved for the hydrogen atom one obtains a set of eigenfunctions (orbitals) and associated eigenvalues (allowed energies) for the electron. This solution is in excellent agreement with the atomic line spectrum for hydrogen. Furthermore, the solutions for this one-electron problem form a basis for interpreting and understanding the chemist's periodic table.

For most problems of interest to a chemist Schrödinger's equation does not have an exact solution. However, approximate methods are available which, under ideal circumstances, provide solutions to an arbitrary degree of accuracy. Two approximate techniques for solving Schrödinger's equation will be emphasized in the next two chapters and used throughout the remainder of the course - the variation method and perturbations theory.

Recommended problems: 1-8 10 11 14 15 19 21 24

Chapter 10 – Many Electron Atoms

Chapter 11 – Examples of Spectroscopy Involving Atoms

The Schrödinger's equation for the helium atom cannot be solved exactly, but the variational method (presented in computer lab 7) yields results in agreement with experiment. Simple variational calculations will be performed on atoms containing two, three, and four electrons. The multitude of electronic states that arise for multi-electron atoms will be analyzed by deriving atomic term symbols and comparing the theoretical results with atomic line spectra. The Hartree-Fock Self-consistent field method will be illustrated with a simple calculations on two-electron atoms and ions.

Recommended problems for chapter 10: 6-12 17 20

Recommended problems for chapter 11: 1-4 8 9 13

Chapter 12 - Chemical Bonding in H_2^+ and H_2

Chapter 13 – Chemical Bonding in Diatomic Molecules

The prototype in explaining atomic structure and stability was the simplest atom, the one-electron hydrogen atom. It is not surprising, therefore, that the one-electron hydrogen molecule ion, H_2^+ , will be exploited to explain molecular stability and the physical nature of the chemical bond. In particular, the contributions of John C. Slater and Klaus Ruedenberg to our understanding of the chemical bond will be studied. It must be stressed that the chemical bond is actually a very challenging concept. There is much disagreement in the research community regarding its quantum mechanical basis. In addition to this simple molecule, the qualitative molecular orbital theory of the homonuclear diatomics from H_2 to F_2 and several heteronuclear diatomics will be studied.

Recommended problems for chapter 12: 2-5

Recommended problems for chapter 13: 5-15 19

Chapter 14 – Molecular Structure and Energy Levels for Polyatomic Molecules

The use of hybrid atomic orbitals in interpreting the structure and bonding in polyatomic molecules is introduced and evaluated. The basic premise of VSEPR (molecular geometry is determined by a reduction in electron–electron repulsion) is challenged. The Huckel molecular orbital approximation is used to model the pi-electrons of conjugated organic molecules. Qualitative molecular orbital theory is used to interpret the photoelectron spectroscopy of polyatomic molecules and to critique the concept of hybridization. Localized (valence bond theory) and delocalized (molecular orbital theory) bonding models are compared and evaluated. Molecular orbital theory is extended to simple solid structures.

Recommended problems: 3 4 15-19

Chapter 15 - Electronic Spectroscopy

Electronic transitions in molecules are the focus of this chapter. However, electronic transitions are accompanied by rotational and vibrational energy changes leading to a sometimes complicated spectroscopic fine structure. A variety of methods will be used to extract molecular parameters from the spectroscopic data.

Recommended questions: 1 8 14 plus additional exercises provided by the instructor

Chapter 16 - Computational Chemistry

John Pople shared the 1998 Nobel Prize in Chemistry for his enormous contributions to the development of the field of computational quantum chemistry. While the basic principles of quantum theory have been known for 80 years it is only recently through the efforts of Pople and others that calculations on large molecules have become feasible. This has enhanced the stature of theory and made it an equal partner with experiment in contemporary chemical research. This chapter provides a concise outline of computational quantum chemistry that will provide the background necessary to appreciate the capabilities of the electronic structure program, Spartan, which we will use in lab.

Warren Hehre is the author of this chapter and the Spartan program we will use. His Ph.D. research advisor was John Pople.

Spartan special project: Each student will choose a problem at the end of this chapter as a Spartan project.

Chapter 17 - Molecular Symmetry

Most molecules don't have any symmetry, but for those that do group theory is a powerful analytic tool. In this chapter we learn how to classify molecules into symmetry groups. Then we will use this information plus the principles of group theory to construct molecular orbitals and to interpret the vibrational and electronic spectra of molecules. The power of group theory will be demonstrated by its application to a detailed study of molecules as simple as water and as large as the relatively new allotropic form of carbon, C₆₀.

Recommended problems: computer exercises provided by instructor.

Chapter 18 - Nuclear Magnetic Resonance Spectroscopy

The quantum mechanical basis of nuclear magnetic resonance will be clarified by the analysis of the nmr spectra of two, three-proton ABC spin systems: acrylonitrile and vinyl acetate (the vinyl protons do not interact appreciably with the methyl protons). The high field and low field nmr spectra of both molecules will be analyzed using a variational calculation on the nuclear spin states. Our analysis of the nmr spectra will illustrate the appropriateness of Heisenberg's matrix mechanics in this application. The complexity of the low-field acrylonitrile spectrum will be interpreted in terms of the superposition principle.

Recommended problems: 2-7 plus computer lab describe above.

Back to Frank Rioux's [homepage](#).