Syllabus for Chemistry 151 - Spectroscopy

Þorsteinn Aðalsteinsson

Fall 2010

1 General Information

Instructor: Dr. Þorsteinn Aðalsteinsson

Office: Daly Science Rm 101

Phone: 554-5389

e-mail: tadalsteinsson@scu.edu

Lecture times: Mondays, Wednesdays and Fridays 9:15 – 10:20 PM

Room: DS 106

Office hours: 13:30 – 17:00 Tuesdays & 14:00 – 16:00 Wednesday (actually Chem 11 office hours)

2 Course overview

Chem 151 is one of three lecture courses in physical chemistry. In this course the basic theory underlying spectroscopy. In this context the course discusses absorption, vibration and rotation spectroscopy as spectroscopic examples and focuses on fully explaining how the mechanism and probabilities for energy absorption are described in rigorous theoretical environment. The same theoretical framework is also the underpinning theory that has derived the current understanding of electronic structure of atoms and molecules. This is briefly introduced in the course.

This is unfortunately the only spectroscopy course offered in the chemistry department. The course is therefore limited to somewhat tedious mathematical framework that needs to be learned before more current computational methods can be understood. Models d'art that are explored in the course are the harmonic oscillator bond model and the hydrogen atomic orbital model. The former is not sufficiently accurate model to describe the chemical bond dynamics in detail, although it captures the principal features of bond theory. The latter is the only model that can be solved without learning numerical approximation methods, which are not covered here.

2.1 More detail?

The main goal of this course is to teach you to understand what a wavefunction is and how to use it...

This is not quite as easy as it may seem at first. In order to get to this goal we will be learning the mathematical language that surrounds these wave functions. Unfortunately, the lemmas and theorems that describe wave mechanics is in general a tad bit outside of what most chemists are comfortable with, this part may become a bit dense mathematically.[1] Then, we'll be diving into actually using these operators

[1] I hope you can continue to view mathematics here as a means to an end, a tool, rather than something that some, who had no friends, lived all alone and isolated all their lives invented in their darkest and most desperate hours...

and their eigenfunctions to get the eigenvalues, overlap integrals and who knows, we may even dabble with finding solutions to the time dependent Hamiltonian!!![2]

The book that I have chosen for the course author approaches this dense topic with an unusual care and tact,[3] and some of the treatment in the book can be considered (gasp) entertaining.

Chapters 1 through 5 of the book treat the linguistics problem we're faced with. This is where most science fiction authors give up, since knowing this much seems to befuddle the *pubicum vulgaris*[4] sufficiently. Chapters 6 through 12 introduce the first two idealized problems, but do so specifically in the context of spectroscopy. The next FIVE chapters deal in more detail with spectroscopy, especially the spectroscopy of two particle systems. Chapter 18 and 19 talk about the hydrogen atom, without actually deriving the algebraic formula. After all, the elegantly derived hydrogen atom method applies only for the hydrogen atom, and is only partially applicable to He^+, so what's the use spending a full quarter agonizing over raising and lowering operators, permutation operators and the element switch operators.[5] The last two chapters are more advanced topics. I hope to be able to cover one of these topics in the last week of class.

3 Prerequisites for this course:

The course assumes a fair background in mathematics and some experience in using spectroscopic techniques is favored. Student that have taken organic chemistry have developed some important insight into how both molecular and atomic orbitals are used to describe reactivity. This experience is a valuable motivation to learn the mathematical framework that these concepts are based on.

4 Workload in the course

Since I am hoping to cover most of the book in this course, we will be moving a briskly out of the gate. This requires you to actually read the book.[6] In addition I will be assigning problems from the text to help you re-enforce the reaing. I will not be covering every topic in detail, that would take too long.

Much of the work in the course is based around solving homework problems. This can be quite time consuming and sometimes very complex. This is, however, an *extremely* valuable tool to learn the more abstract methods used in this theoretical field. Students are encouraged to study in groups, but it is VERY IMPORTANT that this collaboration does not turn into term-copy sessions. In stead students should try to collaborate to a point where they can solve the problems, or similar ones independently as collaborative work is not acceptable on exams. Physical chemistry, especially spectroscopy, is infamous for the homework, but alas, no other better way for learning the material has been invented.

5 Course material

5.1 Textbooks:

REQUIRED: "Physical chemistry - Quantum Mechanics" by Horia Metiu, Taylor & Francis, NY

RECOMMENDED: "Applied Mathematics for Physical Chemistry" by James Barrante, Prentice Hall, NJ

ALTERNATIVE TEXT: "Physical Chemistry - A Molecular Approach" by D. A. McQuarrie and J. D. Simon, University Science Books, Sausalito, CA

[2] MWHAHAHA!!!
[3] compared to other bricks on the same topic written by the some friendless genii
[4] Lat. average Joe
[5] If your friends know these, it's time to switch friends.
[6] The book isn't such a bad reading, there are many more tedious books out there.

5.2 Other material

ANGEL Website: The website will contain any handouts given in the class. The website also contains the powerpoint slides from last year. This year I will not be using these slides, since I feel I move too fast through the material if I present from slides. The problem sets will also be posted as they are handed out, and the solutions will be posted after the problem sets are due. Finally the equation sheet and review material will be posted on the website for your perusal.

6 My expectations from you

- I expect you to attend lectures, if you can't attend lecture you can e-mail me a notification in advance.
- I expect you to read the book and be ready to discuss the material in class. Since much of the material may be new to you, I don't know how much opportunity there bill be to venture into Socratic discussions. At the beginning at least I am more likely to hold on to the lecture format.
- I expect you to contact me during office hours if you are having difficulties with the material or homework.
- I expect you to work on homework problems to the best of your abilities *without directly collaborating, or copying from your fellow students* that understand the material better. I understand that some problems may be quite challenging, and in such cases, feel free to seek help from me or your fellow students. However, the final work has to be yours and not a collaborative effort.
- I suspect that you will actually enjoy the course. Spectroscopy and quantum mechanics is a topic that is fun once you get over the math-barrier. It is a subject that has a steep learning curve at the beginning, but once you have the basics you can expand quickly.[7] It is not a subject that little knowledge gets you in the door, but then there seems to be endless complexity ahead and you'll never actually master it.[8]

7 Class, department and university policies

7.1 This course can be used as a pathway course in the new core curriculum:

This course is associated with the "Paradigm Shifts and the Nature of Human Knowing" pathway. If you declare a pathway in this area you may use a representative piece of work from this course in the Pathway Portfolio you will complete during your senior year. It is recommended that you keep electronic copies of your work.

7.1.1 What is this pathway?

Many disciplines have experienced drastic changes in thought at some time or another, when people pushed beyond the limits of the disciplineÕs traditional approaches, assumptions, and understandings. Such paradigm shifts away from previously accepted ways of thinking can provide rich opportunities to explore how we learn, how we understand, and how we think. Understanding the many, sometimes wildly different ways knowledge is constructed and evidence interpreted in different disciplines allows students to reflect more insightfully on their own educations. This pathway includes courses that address ways of thinking

[7] This has certain similarity to learning German, but perhaps I'm tainted by the unequal German names used for equations and theorems. It is also something so German about the choice to select almost exclusively Greek letters to represent functions.

[8] This is what it is like for a foreigner learning English

within a discipline that are departures from the accepted norms and courses that include the usual ways of knowing and understanding in a discipline.

7.2 Disability accommodations:

To request academic accommodations for a disability, students must contact Disability Resources located in The Drahmann Center in Benson, Room 214, (408) 554-4111; TTY (408) 554-5445. Students must provide documentation of a disability to Disability Resources prior to receiving accommodations. It may take a week or two to set up an accommodation so do it ASAP.

7.3 Academic integrity clause:

Academic integrity should be at the top of your educational standard here at SCU. Academic dishonesty includes

- Looking at another student's test during an exam, or allowing another student to copy your work
- Using unauthorized materials during an exam. This includes:
  - Using cell phones and programmable calculators during exams, even if they are not very useful.
  - Using a recording device in order to copy or forward the exam.
  - Using crib sheets, or other unauthorized written material.
- Your grade should be based on your original work during the course. Taking *or giving* aid in a graded work may result in course failure. Included in this is:
  - Copying homework problems from your fellow students or in one way or other obtaining it from outside sources, such as the internet. I donÕt consider asking your fellow students for assistance on a homework problem inappropriate, but your answer must be your own at all cost.
  - Obtaining solutions to problems from last years online material
  - Seeking help from an external source to obtain copies or extensive solutions to problem sets, e.g. via e-mail or internet websites.
- Selling or making copies of copyrighted material violates academic guidelines and may result in dismissal. This includes computer programs, textbooks, handouts or online material prepared by the instructor for the class.

8 Evaluation of coursework:

In the course, seven homework problems, one midterm exam and a final exam will be evaluated to assign a final grade for the course. A breakdown of point value given for each of these components is given in Table 1

Past experience has shown that score above the 80% of total point values given is likely to result in a grade of B or above. Score above 90% will most likely be awarded an A^- or A grade. The actual letter grade for the course will be assigned using the total score as a guide, but it remains a subjective decision of the instructor based on general evaluation of the class as a whole.

Table 1: Tentative distribution of points for the quarter

Exercise	# assigned	Points each	Total points
Homework	≈7	350/7	350
Midterms	1	250	250
Final Exam	1	400	400

8.1 Assignments and grading policy

8.1.1 Homework

The problem sets are optional. The point value that would otherwise be awarded to ungraded homework problems will be added to the point weight of the final exam. This policy is in place due to the extended time spent on homework problems in the class. This time commitment may infringe on valuable assignments in other classes. With this policy, you will be able to focus your attention elsewhere at no cost in class ranking.

- Problem sets will be handed out on Friday and are due on Friday the following week. Answer keys to the problems will be posted online on Thursdays and graded assignments should be returned you on the following Wednesday.
- The problems are a combination of written exercises, evaluation of data and mathematical assignments. The bulk of these problems are taken from the textbook, with a few test-problems from other textbooks.
- If a homework appears copied (within a reasonable error) both the original and the copy will be returned ungraded.
- Late homework will not be graded.
- The homework sets will vary in length and difficulty. Each answer will be graded on a 5 point basis for short answers and 10 point basis for longer answers. The final point percentage will be used to award the appropriate value out of 50 points.
- A mockup midterm exam of the approximate format, length and difficulty will be handed out in the week before the midterm exam. No homework will be collected the week before the final exam.

8.1.2 Midterm

The midterm exam is optional. If you opt not to take the midterm, the point value that would otherwise be awarded to the midterm exam will be added to the point weight of the final exam.

The midterm exam will be held on Friday of the sixth week of classes. At that point I hope to have completed Chapter 12.

8.1.3 Final Exam

The final exam is not optional. The exam is currently scheduled for Monday December 8th at 1:30-3:30pm. The final exam will weight more on advanced topics covered in the second half of the course. I will also give you a mockup exam prior to the final exam. This is done to give you a heads-up on what kind of questions I expect you to be able to answer and thereby hopefully reduce your anxiety for the exam. This mockup exam will not be due, nor graded.

9 Course topics

Following is a rough guide of topics covered. A table of approximate dates and classes follows. Ultimately I would like to be able to spend the majority of the class on spectroscopy, and go quickly over the first part of the course. Given that this is the first time I teach this book series, I may very well end up spending too much time in the beginning and end up having to skip one or more segments at the end. We will deal with this situation when it arises. The first midterm is thought to be as a test of the basic principles and the simplified spectroscopy. I placed it here after we cover chapter 11. This is currently approximately in the sixth week of the quarter, but if we are either ahead of schedule or behind, the exam will be shifted accordingly.

9.1 The language of quantum mechanics and spectroscopy

This covers chapters 1 through 5. I will rely on you reading most of the chapters, but I will broadly discuss the topics in class. A thorough understanding of the concepts here is key to further grasping the material. Considering this it would be tempting to spend more time on this, but the concept shown here will re-surface later in the course.

1. Operators
   (a) Using operators
   (b) The common operators in quantum mechanics
2. Eigenfunctions
   (a) Finding the eigenvalue problem
   (b) What is an eigenfunction?
   (c) Nice eigenfunctions
   (d) Being nice to eigenfunctions
   (e) Physical meaning of eigenfunctions
3. Eigenvalues
   (a) Well defined eigenvalues
   (b) Measuring eigenvalues
   (c) Meaning of eigenvalues
   (d) Probability and eigenvalues

9.2 The basics of spectroscopy

This is roughly chapters 6 through 12 in the book. I hope to be able to slow down the coverage of the material here. Some find this material very interesting, since some of odd things surface from the quantum mechanical treatment. This is historically very important material, since the predictions arising here proved that quantum mechanics was able to explain observation, where classical mechanics failed miserably. This is what made quantum mechanics popular in the geek-mainstream literature.

1. Physical meaning of eigenfunctions (again)
   (a) Probability density
   (b) Tunneling

2. Particle in a box
    (a) Setup and limits
    (b) Solving the equation
    (c) The observations of PIB
3. Light adsorption in the classical sense
    (a) Einstein's adsorption theory (if time allows)
    (b) The observations
    (c) Interaction of light and matter
4. Light adsorption in the quantum mechanical sense
    (a) Adsorption probability
    (b) The transition dipole moment
5. Adsorption from PIB and the harmonic oscillator (HO)
    (a) Observations of PIB-like systems
    (b) Observations of HO-like systems
    (c) Selection rules

9.3 More advanced spectroscopy; Two particle systems

OK, so here is the part where chemists need to pay attention. Here is where we start really branching out from the pure physics of quantum mechanics and start getting more relevant bits for chemistry. This is also, unfortunately, where things get a bit convoluted and nasty a bit more nasty. This segment covers chapter 13 through 17, with the good-ol H-atom discussed in chapter 18. I am more likely to brush by the H-atom discussion, since this subject is "cute but useless". Some claim that the H-atom solution is one of the most beautiful piece of algebra one will ever see, which is probably true. Unfortunately if you go above and beyond 1 electron + 1 proton, you're ... sunk. Nevertheless, inspecting the wavefunction and typing them into Mathematica is a fun exercise. A final topic in this segment is on electron spin and how to ensure that every electron is unique (hence the Pauli principle).

1. Setting up the Hamiltonian and the Schrödinger equation
    (a) The angular momentum operator
    (b) Commutation relations
2. Setting up the Schrödinger equation
    (a) Spherical coordinates
    (b) Separation of variables
    (c) Knowing the solutions
3. The solutions to the two particle systems
    (a) The HO approximation
    (b) The rigid rotor approximation

(c) Rovibrations
(d) Spectroscopy of diatomic molecules

4. The Hydrogen atom
    (a) The solution to the Schrödinger equation
    (b) The spectrocopy of H
5. Spin of electrons
    (a) The Zeeman effect
    (b) The Pauli principle; finally, you'll be able to explain it!!

9.4 The last Huzzah!

Either one of the topics may be covered, time allowing. If we have spent time on the H-atom, it may be of interest to slug through the computational methods. These methods are extremely useful in theoretical chemistry today, and anyone going into any type of physical chemistry as a profession is likely to have one or more dedicated course on the matter. For the rest of y'all the use of such coverage is to have more of a chance to understand theoretical chemistry seminars. Alternatively we can venture into NMR spectroscopy, which is where most of the odd and curious features predicted in quantum mechanics shows up. This coverage will also be more of a curiosity level discussion, since a full understanding of NMR spectroscopy takes a bit more practice than what we are able to do.

9.4.1 Computational methods

1. The Born-Oppenheimer approximation
2. Orbital product rule approximation
3. Wavefunction ansisymmetry
4. Minimal basis set in antisymmetrized wavefunctions (a.k.a. MO-LCAO method)
5. Overlap matrices
6. The variational principle for minimization

9.4.2 NMR spectroscopy

1. One spin in magnetic field
2. The chemical shift
3. Spin-spin coupling, peak splitting
4. Two interacting nuclei
5. Setting up the Hamiltonian matrix
6. Perturbation theory
7. Evaluating the spin Hamiltonian matrix

10 General learning objectives:

The course in quantum mechanics and spectroscopy is an introductory course to both a very complex, very powerful yet very elegant field of theoretical chemistry. As an entry point, the course adds numerous concepts and mathematical tools into your repertoire. These tools can then be expanded and further developed into

GOAL 1: Learn the basic mathematical tools and concepts that are used in quantum mechanical descriptions of concepts relevant to chemists:

(a) Understand what an operator is and related terms used to investigate general operator properties, such as operator commutation, operator multiplication and addition.

(b) Learn the basic operators used in chemical quantum mechanics, including the position operator, momentum operator, the angular momentum operator(s) and the energy operators.

(c) Learn to apply these operators to basic functions and to interpret the outcome of these operations.

(d) Learn the basic properties of basic wave functions and how the function is related to average and probabilistic nature of mater.

(e) Learn to extract average properties using operators and wave functions.

(f) Learn to read common notation used in quantum mechanics to describe integrals, matrix elements, operators and eigenvalues.

GOAL 2: Become familiar with the concepts of wave functions

(a) Gain an insight into the physical interpretation of the wave functions and the connection to probability density.

(b) Understand the concept of tunneling, function nodes and other anomalies that the wave functions can give.

(c) Know where to find and how to assemble the wave functions that are solutions to the particle in a box, harmonic oscillator and the hydrogen atom.

GOAL 3: Learn how chemically interesting problems are set up to be solved using quantum mechanics.

(a) Become familiar with what is meant by the eigenvalue problem and what the potential solution to this problem will give.

(b) Know in some detail how three basic problems are set up: The Particle in a Box, The Harmonic Oscillator and The Rigid Rotor.

(c) Know how to use the solutions for the energy eigenstates and the wave functions for these problems

(d) Know how real systems differ from these much simplified problems

GOAL 4: Learn how absorption and transitions between different energy levels is treated in quantum mechanics. This is the basic understanding of all electron and photon absorption experiments used for chemical analysis.

(a) Become familiar with the different components that need to be considered for absorption to occur, namely, dipole momentum transfer, dipole moment of polarized light and the overlap integral.

(b) Know what forbidden and allowed transitions are, and how these probabilities are found

GOAL 5: Be familiar with the solutions and interpretation of the hydrogen atom

(a) Be familiar with how the eigenvalue problem for the hydrogen atom is set up

(b) Be familiar with the solutions to the eigenvalue problem

GOAL 6: Be somewhat familiar with the H_2 molecule

(a) Know what is meant by the Born-Oppehneimer approximation

(b) Know how the hydrogen atom model becomes insoluble when many particles interact

(c) Know some of the common approaches to solve this problem, namely MO-LCAO method, Gaussian orbital approximation, Hartree-Fock approximation and other perturbation theories.