CHEM 352. Physical Chemistry II

TR 900-1015, Bil 335

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REQUIRED TEXT:	Physical Chemistry: A Molecular Approach, D. McQuarrie & J. Simon	
PREREQUISITE:	**CHEM 351** (which required Calculus III and PHYS 170-272 as prerequisites)	
RECOMMENDATIONS:	Minimum grades of "C" or better in 351, Calculus III **and** PHYS 170-272.	
GRADING:	In-Class Exams (2 exams, 25% each)	50%
	Final Exam, Thursday, May 14, 2020, 9:45-11:45 a.m.	40%
	Problem Sets (Homework)	10%
		100%

TENTATIVE SCHEDULE OF TOPICS:

STRUCTURE, PART I – INTRODUCTION, FOUNDATIONS, & THE 1-DIMENSIONAL SYSTEMS

This section will begin with lectures on the historical background of quantum mechanics. We will then study the Schrodinger equation and the one-dimensional "particle-in-the-box". Interwoven with the mathematical aspects of this material will be the postulates and general principles of quantum mechanics. To conclude this section, we will discuss the details of the harmonic oscillator.

A. Historical Background **(Weeks 1-2)**

*Reading: Chapter 1 (all sections)

- Blackbody radiation (ultraviolet catastrophe, Planck's hypothesis) and the photoelectric effect.
- Bohr's model of the atom to explain line spectra in H atom.
- Heisenberg Uncertainty Principle. DeBroglie's wave-particle duality.

B. The Schrodinger Equation and Simple Applications and

C. Postulates & General Principles of Quantum Mechanics **(Weeks 2-5)**

Reading: Chapters 3 (all sections except 3.9) & 4

- Operators and operator algebra. Commutation. Eigenfunctions & eigenvalues. Wave equations & the time-independent Schrodinger equation.
- QM postulates, including Hermitian operators, expectation values, orthogonality & orthonormality, and the significance of the commutator.
- Particle in the box.
  - Wavefunctions. Born Interpretation & normalization for particle in the box. Probability. Orthogonality.
  - Energies and energy level diagram
  - Expectation values.
  - Butadiene example

D. The Harmonic Oscillator **(Weeks 5-7)**

Reading: Chapter 5 (sections 5.1-5.7)

- Classical picture.
- Schrodinger Equation, general expressions for the wavefunctions. Hermite polynomials. Tunneling.
- Energies of the harmonic oscillator.
- Morse potential for real molecules. Vibrational spectroscopy.

III. STRUCTURE, PART II – 3-DIMENSIONAL SYSTEMS, APPROXIMATE METHODS, & ATOMS

This section will begin with the simpler three-dimensional systems, including the multi-dimensional particle-in-a-box and the rigid rotor. We will then discuss the atomic structure of the hydrogen atom. For the heavier atoms, we will briefly cover approximate methods and will utilize various means of describing polyelectronic atoms.

A. Three-Dimensional Systems with Exact Solutions

1. Particle in a Box in 2 and 3 Dimensions (Week 8)

Reading: Section 3.9

2. Rigid Rotor (Week 8-10)

Reading: MathChapter D (spherical coordinates), Chapters 5 (sections 5.8 & 5.9) & 6 (sections 6.2-6.3)

- Review of Cartesian and spherical coordinate space. Laplacian.
- "Particle on a ring" (or 2D rotational motion). Hamiltonian. wavefunction.
- Rigid rotor (or "particle on a sphere").
    - Separation of variables to RR wavefunctions.
    - Energies. Angular momentum.
    - Rotational spectroscopy. Rotational-vibrational spectroscopy.

3. Hydrogen Atom (Weeks 11-12)

Reading: Chapter 6 (sections 1, 4-6)

- Radial equation and radial probabilities. Orbitals (overall wavefunctions). Most probable distance and <r>.
- Energies.

B. Approximate Methods and Polyelectronic Atoms (Weeks 13-14)

Reading: Chapters 6 (section 6.7), 7 (all sections), 8 (all sections)

- Approximate methods. Time-independent perturbation theory. Variational method.
- Polyelectronic atoms.
    - Stern-Gerlach and spin eigenfunctions.
    - Ground-state wavefunction for He.
    - Permutation operator and antisymmetric wavefunctions.
    - Total angular momentum (J) and L-S coupling. Term symbols. Atomic selection rules, energy diagram, jj coupling.

III. STRUCTURE, PART III – MOLECULAR STRUCTURE (Weeks 15-16)

There are complexities associated with all of the polyelectronic atoms, so methods of approximation are discussed, particularly with respect to the He atom. We will discuss the coupling of angular momenta, i.e., term symbols to describe the atom. The semester ends with the basics of molecular structure, including a review of molecular orbital theory for diatomic molecules.

Reading: Chapters 9 (Sec. 1-13) & 11 (Sec. 1-3)

- Born-Oppenheimer approximation.
- MO theory
- Energies, wavefunctions, bond order, dia- and paramagnetism).

**Tentative reading assignments for each topic are noted. Additional sections from the textbook may be added, and/or you may be advised to focus on some (but not all) of the sections in a given chapter. Additional reading (from other sources) may also be suggested.*

Policies on Exams:

1. **The exams cover material from the lectures, reading assignments, and homework problems.** More details about the exam content will be given in class.
2. **There will be two exams during the semester, in addition to the Final Exam. Exam dates will be announced in class**, roughly 1-2 weeks in advance.
3. **Regarding absence from an exam,**
   - If you know ahead of time that you will not be here for an exam, please let me know as soon as possible, so we can arrange for you to take the exam early.
   - If a family, medical, or other personal emergency arises on the day of the exam, please let me know as soon as reasonably possible. If it is possible for you to take a makeup exam, you will be asked to do so ASAP. If you are absent for an extended duration, I'll discuss other options. Regardless of the length of your absence, it is expected that ONLY TRUE EMERGENCIES will be accepted for excused absences and/or makeup exams. Also be aware that you will be asked to provide some kind of documentation, such as a physician's note for a medical emergency.
4. All exams are **closed-book**.
5. **For each exam, you will be allowed one index card (4" by 6") to be used as a "formula sheet".** You can write whatever you want on it, and it should be prepared well in advance of the exam. It will not be collected or graded – it is solely for your use and benefit.
6. **For each exam, you will need a <u>calculator</u>.** Calculators may not be shared during the exam period. You must use an electronic object designed specifically and solely for calculation (i.e., not the cell phone app). Use of all other electronic devices - such as cell phones, music players, netbooks, laptops, and cameras - is explicitly prohibited during an exam.
7. **We'll use the entire class period for each exam.** Please be ready to start at 9:00 a.m. No time extensions will be given to latecomers, except in unusual and exceptional circumstances.

Problem Sets:

1. **Successful completion of the problem sets <u>and</u> thorough review of the problems with the posted answer key are essential for building a strong skill set and a reasonable working knowledge of quantum chemistry and spectroscopy.** As such, few students earn a good (or even passing) grade in CHEM 352 without doing the problems.
2. **The problem set is due at the start of class (<u>9:00 a.m. sharp</u>) on the due date.** Due dates will be announced in class. You should expect a problem set every 1-2 weeks.
3. **Late homework will be accepted for grading until 5 p.m. on the day after the due date, and a penalty will be assessed.** For example, Problem Set 5999 is due on a Tuesday at 9 a.m. If you miss the due date/time, you can submit PS 5999 for grading on Tuesday from 9:01-10:30 a.m. (10% penalty), Tuesday 10:31 a.m.-5 p.m. (20% penalty), or Tuesday 5:01 p.m. through Wednesday 5 p.m. (50% penalty). Homework sets are not accepted after 5 p.m. on the next business day, regardless of your reason or excuse.
4. **All Problem Sets should be submitted to me (Professor Kumashiro).** Please do not give them to your TAs.
5. You should expect 8-10 problem sets over the semester. **The "homework grade" is the average of the PS scores.**
6. **Solutions to the homework will be posted shortly after the deadline at our Laulima site**. For obvious reasons, problem sets will not be accepted after the solutions are posted.

General Class Policies:

1. **Success usually comes with regular attendance <u>and</u> timely completion of reading and problem assignments.** If you do not do the work (which includes attending all lectures, reading the book, and doing the homework problems), it is extremely likely that your lack of effort will be reflected in a very poor grade.
2. **Your attendance is expected.** Bear in mind that you are responsible for all information transmitted during class, whether quantum chemistry or a general class announcement.
   - **Reasonable excuses for missing a lecture** include a medical or family emergency, severe and/or contagious illness (such as the flu!), or some other extreme and unfortunate incident (such as a traffic accident). Some "good things" can also take you out of class, such as attending a conference or other academic excursion.
   - **Poor excuses for missing class** include oversleeping, traffic/parking (if it happens more than once), working an outside job, a hangover, & your 10:30 class (studying for exam, finishing a problem set, etc.).
   - **If you choose to skip class frequently for any of the "poor" excuses, then you should consider yourself warned** – I expect that you will **<u>not</u>** waste my time (or my grader's time!) by seeing me in my office with your questions.
3. **Generally speaking, I am happy to help you with your questions outside of our regular class time.** Please, however, let me be very clear on my expectations.
   - **Please prepare your questions in advance of an appointment with me.** Bring specific questions about specific homework problems, tell me where the lecture is confusing, etc.
   - With short questions, I can usually help right after the lecture is finished. For more help, I can often meet right after our class is done. Or, you can talk to me about setting aside some time on another afternoon for your questions. I find that a more flexible arrangement works best with small classes such as this one.
   - **I generally and strongly discourage appointments and last-minute questions on the day of *and the day before* an exam.** This general outlook is completely consistent with the idea that you should never fall behind in this class.
4. **This class starts at 9:00 a.m. It ends at 10:15 a.m.**
   - **Be prompt and stay for the entire class.** If you need to leave early or arrive late, I'd appreciate the courtesy of letting me know ahead of time (if possible) or afterwards (if an emergency arises).
   - If you arrive late, please use the back door to minimize the disruption to the class and do NOT interrupt my lecture by handing in your homework in front of everyone. If you must leave early, you should exercise every reasonable option to make a quiet exit.
5. **The best, easiest, and most efficient way to communicate with me is face-to-face.**
   - If you have a question/concern about the grading of an exam or homework problem, please let me know after class or send me an email to set up a time to meet (to discuss in person). <u>*Generally speaking, email is not an acceptable way to discuss grades (for you and for me).*</u>
   - A common misconception is the idea that I am a customer service agent and thusly responsible for answering a student's email or returning a call ASAP. If I do not respond to your email or voice mail, then you should follow-up in person.
   - If you must call or send email, please use common sense and courtesy.