Midterm Examination will be held on Wednesday, 13 February

- **Covering:**
  - Lectures 1-13
  - All Problems in Homework Assignments 1-4
- **Bring**
  - Calculator (any type, but lap top computers are not allowed)
  - Pencil/Pen
  - Straight Edge (for drawing graphs)
  - Blue/Green Book
  - 1 page of notes (double-sided, see below)
- **Format:**
  - Closed Book.
  - Open Notes.
    - One page permitted, 8.5 inches by 11 inches, double-sided,
    - You may write, Xerox, scan, etc. anything on the two sides of this page that you wish.
    - If you put a lot of effort into preparing these notes, keep track of them. You can use them at the final exam.
- **Grading:** Grading of the examination will be based on the standards stated in the Chemistry 453 course syllabus. Please review the standards section of the syllabus. Important points to keep in mind:
  - Partial credit is USUALLY given in units of 3-5 points.
  - Obtaining the correct numerical answer is counted in partial credit grading. An answer that is within 10% of the correct answer will be fully credited.
  - Calculations must include physical units and a proper dimensional analysis must be included in the calculation.
  - Students are expected to understand how to use their calculators properly. Students will NOT be forgiven for mistakes resulting from calculator errors.
  - When you are asked to explain an answer or are asked to define a term, carefully worded complete sentences are required.
  - If you are given the option to choose from a list of problems (e.g. answer three of the following five questions) you will NOT be credited for answering more than the requested number. For example, if you are allowed to select three problems out of five for answering…and you answer all five… the grader will NOT credit you for the highest three scoring problems out of five. The first three problems presented on the blue book will be graded.
Subjects to study …

- Understand concept of black body radiation and be able to explain how the quantum hypothesis of Planck explains the spectrum of a black body radiator.
- Heat capacity of Einstein’s solid.
- How the energy level spacing for a particular motion (translational, rotational, vibrational) versus the size of kT influences the form of the heat capacity for that motion.
- Bohr Atom: know the expression for the energy and energy changes ΔE when an electron changes its orbit (I recommend you write the Rydberg constant for hydrogen in your notes).
- Expression for the deBroglie wavelength of a particle.
- Heisenberg Uncertainty Principle: Be able to state it in terms of uncertainties in momentum/position and be able to illustrate it with pictures of particle wave.
- Define a wave function and explain its use in classical and quantum mechanics.
- Understand the relationship between a wave function and the probability of a particle being in a physical state…
- General form for the time-independent Schroedinger wave equation in 1 and 3 dimensions.
- Know Schroedinger’s equation for a particle in 1D, 2D and 3D boxes.
- Know wave functions and energies for a particle in a 1D, 2D and 3D box.
- Calculate the average displacement, average displacement squared, average momentum and average momentum squared for particle in a box.
- Calculate probability of particle being found in a region of a 1D box.
- Know Schroedinger’s equation for a harmonic oscillator.
- Understand the classical and quantum harmonic oscillator…their similarities and differences.
- Know the expression for the energies of a quantum harmonic oscillator.
- How to calculate the frequency of an oscillator from the force constant and reduced mass.
- Know how to calculate the reduced mass, average displacement, average displacement squared, average kinetic/potential energy for a harmonic oscillator.
- Know how to write the wave function of a oscillator in a given energy state in terms of Hermite polynomials. It would not hurt to list the hermite polynomials for n=0-4 in your notes.
- Be able to draw the wave functions and the probabilites for n=0-4 for a harmonic oscillator.
- Schroedinger’s equation for a rigid rotor.
- The energies for a rigid rotor and it would not hurt to put the J=0,1,2 wave functions into your notes.
- Schroedinger’s equation for the hydrogen atom in spherical coordinates.
• Know what three quantities that are quantized in the hydrogen atom, explain what the quantum numbers are, and how they vary
• Know the expression for the energy of an electron in hydrogen
• Be able to sketch the radial wave functions and probabilities for n=1, 2, 3.
• Know the two ways to express orbital size
• How to calculate the probability of finding an electron in a r range or angular range
• Be able to sketch the angular wave functions for l=1 (p orbitals), Know their dependences on theta and phi.
• LCAO and Variational Principles

**Examination Study Guidelines:** Here is a general outline of the type of examination that will be presented to you on 6 Feb. Sample questions and answers are presented.

**Section 1 (usually about 24 points total)** Define or explain and discuss maybe four out of six terms or phrases provided. Note: The “up-side” of this problem: lots of points for virtually no calculations. The down-side: a real danger that you will get bogged down writing lengthy answers to simple questions. Also, if you write poorly you may lose points just because the grader does not understand your reasoning (or perhaps cannot read your handwriting). *Watch the clock. You should be done with this in less than 10 minutes.*

Example 1.1: State Heisenberg’s Uncertainty Principle. Fundamental assumptions in classical mechanics include the ability to describe to arbitrarily high accuracy any number of dynamical variables such as particle position, particle momentum, energy, etc. Explain how the uncertainty principle affects these assumptions.

**Answer:** A basic postulate of classical mechanics is that is principle any number of variables (coordinates, momenta) can be measured simultaneously to arbitrarily high accuracy. The uncertainty principle states that there is a limit to the accuracy with which coordinates and momenta can be simultaneously measured. The accuracies are limited by the statement \[ \Delta x \cdot \Delta p \geq \frac{\hbar}{2\pi} \]

Example 1.2. Rank the importance of the following motions to the molar heat capacity of an ideal diatomic molecule at room temperature:

- Translational molecular motions
- Electronic motions
- Bond vibrations
- Molecular rotations

Give a simple explanation for your ranking based on quantization effects.

**Answer:** Translation>Rotation>Vibration> Electronic. At room temperature kT is on the order of 4x10^-21 J. Translational and rotational motions both have energy level spacings much, much less than kT at room temperature. Vibrational and electronic motions both have energy level spacing much greater than kT at room temperature. In the latter case the heat energy will not be adsorbed by the system.
and therefore vibrations and electronic motions cannot be thermally excited at room temperature.

**Section 2 (36 points)** Short calculations. In these problems you are usually asked to calculate one quantity or read and interpret a graph. A single equation is usually involved. Answer three problems out of four. I will give six problems and you have to answer 4. **Allow 5 minutes or so for each problem.**

**Example 2.1** What is the probability of locating a particle of mass m between $x=L/4$ and $x=L/2$ in a one dimensional box of length L? Assume the particle is in the $n=1$ energy state. Hint: The indefinite integral $\int \sin^2 \left( \frac{n\pi x}{L} \right) \, dx = \frac{x}{2} - \frac{L}{4n\pi} \sin \left( \frac{2n\pi x}{L} \right)$ is useful in working this problem.

**Solution:**

$$
\int_{L/4}^{3L/4} \psi^2(x) \, dx = \frac{2}{L} \int_0^{3L/4} \sin^2 \left( \frac{\pi x}{L} \right) \, dx = \frac{2}{L} \left[ \frac{x}{2} - \frac{L}{4\pi} \sin \left( \frac{2\pi x}{L} \right) \right]_0^{3L/4}
$$

$$
= \frac{2}{L} \left( \frac{3L}{4} - \frac{L}{4} \right) - \frac{2}{L} \frac{L}{4\pi} \left[ \sin \left( \frac{3\pi}{2} \right) - \sin \left( \frac{\pi}{2} \right) \right] = \frac{1}{2} + \frac{1}{\pi} = 0.81
$$

**Section 4: (40 points)** I usually require you to work out 1 problem from out of 2 choices. Here is a problem that I have used in the past...complete with solutions...Chose wisely. Forty percent of the exam points are in these problems. You should allow 20 minutes for working this problem. There is partial credit grading for this section.

All additional homework problems are good models for multi-step problems. Here is another. Study them carefully.

**Example:** The HCl molecule has a force constant of 516 N/m and a bond length of $1.3 \times 10^{-10}$ m. The atomic weights of hydrogen and chlorine are 1 gm/mole and 35.5 gm/mole, respectively.

a) Calculate the reduced mass and moment of inertia of HCl.

**Solution:**

$$
\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{1}{N_A} \times \frac{M_H M_{Cl}}{M_H + M_{Cl}} = \frac{1}{6.023 \times 10^{23} / \text{mole}} \times \frac{35.5 \text{ gm/mole}}{36.5} = 1.62 \times 10^{-24} \text{ gm}
$$

$$
I = \mu R^2 = \left( 1.62 \times 10^{-27} \text{ kg} \right) \left( 1.3 \times 10^{-10} \text{ m} \right)^2 = 2.74 \times 10^{-47} \text{ kg} \cdot \text{m}^2
$$

b) Calculate the force constant and the bond vibration frequency for HCl
Solution: The force constant is already given as $\kappa = 516 \text{ N/m}$. Then

$$\nu = \frac{1}{2\pi} \left( \frac{\kappa}{\mu} \right)^{1/2} = \frac{1}{2\pi} \left( \frac{516 \text{ N/m}}{1.62 \times 10^{-27} \text{ kg}} \right)^{1/2} = 5.64 \times 10^{13} \text{s}^{-1}$$

(c) Assume HCl behaves as a rigid rotor and a harmonic oscillator. Assume molecular rotation and bond vibration are independent. Calculate the energy change $\Delta E$ when HCl makes a transition from a vibrational state $n=0$ and rotational state $J=2$ to a vibrational state $n=1$ and rotational state $J=1$.

Solution:

$$\Delta E = h\nu + \frac{\hbar^2}{2I} \left[ J''(J''+1) - J'(J'+1) \right]$$

$$= \left( 6.62 \times 10^{-34} \text{ J} \cdot \text{s} \right) \left( 5.64 \times 10^{13} \text{s}^{-1} \right) + \left( \frac{6.62 \times 10^{-34} \text{ J} \cdot \text{s}}{2.74 \times 10^{-47} \text{ kg} \cdot \text{m}^2} \right)^2 \left( 2 - 6 \right)$$

$$= 3.73 \times 10^{-20} J - 8.11 \times 10^{-22} J = (3.73 - 0.08) \times 10^{-20} J = 3.65 \times 10^{-20} J$$

(d) Calculate the frequency of radiation that is resonant with this transition.

Solution: $\nu = \frac{\Delta E}{\hbar} = \frac{3.65 \times 10^{-20} J}{6.62 \times 10^{-34} \text{ J} \cdot \text{s}} = 5.51 \times 10^{13} \text{s}^{-1}$