Chemistry 542
Fall, 2002
Problem Set 4
Due Friday, Sept. 27

Finish reading chapters 2 and 3.

1. A particle in a one-dimensional box of length L has the following wave function:

$$\psi(x) = Cx \sin \frac{n\pi x}{L},$$

where n is any positive integer. Calculate its energy by evaluating the expectation value of the Hamiltonian. Express your answer as a ratio to E_1 (i.e., as a dimensionless quantity).

2. In the previous problem, expand the wave function in a Fourier sine series and determine the probability P_s of finding the particle in any state s, including s=n.

A. Identify the three states that are most likely to be populated and show that they account for nearly 100% of the population.

B. Calculate the expectation value of the energy for n=6, and show that it equals the result in Problem 1. Express your answer as a ratio to E_1 (i.e., as a dimensionless quantity).

C. For extra credit, write a computer program that calculates the sum over P_s and $\langle E \rangle$ for any n, and compare the energy with the result in problem 1.

3. A. Derive an expression for the number of states with energy $\leq E$ and an expression for the density of states for a particle in a two-dimensional box with side L.

B. In the Sept. 13, 2003 issue of *Science*, page 1853, the authors state that the density of states for a particle in a one-dimensional well varies as $E^{-1/2}$. Prove that this is correct.

4. A hydrogen atom initially has a kinetic energy of 1 eV and a potential energy of 4 EV. It then passes into a region of zero potential, so that its kinetic energy increases to 5 eV. In other words, it passes over a step barrier going from high to low potential energy. Calculate the probability that the atom is reflected backwards from the step and the probability that it passes over the step.

Do Levine 2.18, 2.21, 2.22.