CHEM 6472:
Quantum Chemistry and Molecular Spectroscopy

Problem Set IV

Due Thursday, October 10

1. **Particle in a box as a model of linear polyenes:** A polyene is a conjugated hydrocarbon with alternating single and double carbon-carbon bonds. The conjugation of such a molecule means that it is easy for electrons to travel from one end of the molecule to the other. Hence, the pi electrons in a polyene can be modeled (very roughly) as particles in a one-dimensional box.

   Let n denote the number of double bonds in the polyene. Each double bond gives one doubly occupied pi orbital (one alpha and one beta pi electron). Since the behavior of alpha electrons will be identical to that of beta electrons, let us ignore spin for this problem and just work with the alpha electrons, so that one double bond gives one (alpha) pi electron.

   The length of the "box" is the length of the polyene, which is proportional to the number of double bonds n. You will need to use this proportionality.

   Given the above, work out the frequency of light required to promote an electron from the highest occupied level to the lowest unoccupied level of the box. Show that this frequency is inversely proportional to n. If a certain polyene absorbs green light, would it take a longer or shorter chain to make it absorb red light?

2. Consider the particle in a box problem. Assume the particle is in a box with infinite walls at 0 and L. The energy eigenfunctions are

$$\Psi_n(x) = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right). \tag{1}$$

   Let the particle be in an initial state

$$\Psi(0) = \sqrt{\frac{2}{3L}} sin\left(\frac{4\pi x}{L}\right) + 2\sqrt{\frac{1}{3L}} sin\left(\frac{5\pi x}{L}\right). \tag{2}$$

   (a) What is $\Psi(x,t)$ at later times t?

   (b) What is the average value of the energy at $t = 0$? Does this change at later times?

   (c) What is the average value of momentum as a function of time?

   (d) What is the probability of measuring an energy equal to $\pi^2\hbar^2/2mL^2$ at $t = 0$?