Chem 332: Problem Set #4

Due in class: Friday, Feb. 15th

(1) Consider a quantum particle of mass m that is completely free to travel in one-dimension, $V(x) = 0$.

(a) Write out the full expression for the time independent Schrödinger equation.

(b) Show that $\psi(x) = Ae^{ikx} + Be^{-ikx}$ is a general solution where $k = \sqrt{\dfrac{2mE}{\hbar^2}}$.

(c) Consider the two cases where A=0 and then where B=0. Determine if these wavefunctions are (separately) eigenfunctions of the momentum operator and, if so, what the eigenvalues are.

(d) Are there any restrictions on the total energy for this particle?

(2) The function $\psi(x) = A\left(\dfrac{x}{L}\right)^2\left[1-\left(\dfrac{x}{L}\right)\right]$ is an acceptable wave function for the particle in a 1-dimensional infinitely deep box of length L.

a) Calculate the normalization constant A.

b) Calculate the average values of x and x^2 for this state, and use these to calculate the standard deviation, $\sigma_x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$. Based on the Heisenberg uncertainty principle, what then is the minimum standard deviation in the momentum σ_p?

(3) For a particle in a 1-dimensional infinite depth box of length L, the first excited state wave function is $\Psi_2(x) = \sqrt{\dfrac{2}{L}}\sin\left(\dfrac{2\pi}{L}x\right)$. What is the probability that the particle will be found in the middle third of the box?

(4) The eigenvalues of the particle in a box system form the basis for describing the translational motion of atoms and molecules. For a single He atom in a 1-dimensional box, calculate the value of the quantum number n of the energy level for which the energy is equal to $\dfrac{3}{2}k_BT$ at 300 K when the box is 1 nm long and also when it is 10^{-2} m long. Under the latter conditions, what is the energy separation between quantum states with n and n+1? What is the de Broglie wavelength?

(5) The energy states for a particle in a 3-dimensional box with lengths L_1, L_2, and L_3 are given by $E\left(n_1,n_2,n_3\right)=\frac{h^2}{8m}\left[\left(\frac{n_1}{L_1}\right)^2+\left(\frac{n_2}{L_2}\right)^2+\left(\frac{n_3}{L_3}\right)^2\right]$.

These energy levels are sometimes used to model the motion of electrons in a central metal atom that is surrounded by six ligands.

a) Show that the lowest energy level is nondegenerate and the 2nd level is triply degenerate if the box is cubical. Label the states by their quantum numbers n_1, n_2, n_3.

b) Consider a box of volume V = $L_1L_2L_3$ with 3 electrons inside (2 in the lowest energy level, 1 in the next). Show that the total energy in this case is equal to $E=\frac{h^2}{8m}\left(\frac{12}{L_1^2}\right)$ if L_1=L_2=L_3.

c) Compared to part (b), a lower total energy results upon rectangular distortion (L_1=L_2≠L_3) at constant volume (V), $E=\frac{h^2}{8m}\left(\frac{6}{L_1^2}+\frac{6}{L_3^2}\right)$, where L_3>L_1 . Show that the ratio of L_3 to L_1 that minimizes the total energy is equal to $\sqrt{2}$. This problem is related to Jahn-Teller distortions in molecules. (Hint: minimize E with respect to L_1 and remember that $L_3=\frac{V}{L_1^2}$ where V is constant.)

(6) Calculate the first 4 energy levels of the π-network in hexatriene, C_6H_8, using the free electron molecular orbital model. To calculate the box length, assume that the molecule is linear and use the values 135 and 154 pm for the C=C and C–C bonds, respectively. Sketch and label an energy level diagram showing the occupied levels and the first unoccupied one. What is the wavelength of light required to induce a transition from the ground state to the first excited state? How does this compare with the experimentally observed value of 240 nm?

Hexatriene: H_2C=CH–CH=CH–CH=CH_2