Chem 3322 homework #4 solutions

Problem 1 – particle in a box

Consider a particle in a one-dimensional box of length L in its lowest energy (ground) stationary state. Calculate the probability that the particle is

a) in the left half of the box

Solution:

For the lowest energy state, we have

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \tag{1}$$

The probability density of this state is thus

$$\frac{2}{L} \sin^2 \frac{\pi x}{L} \tag{2}$$

You need to integrate this expression. Normally this integral is found in textbooks as

$$\int \sin^2 x \, dx = \frac{1}{2}x - \frac{1}{4} \sin 2x \tag{3}$$

Changing variables from x to $u = \pi x/L$, we have

$$\int_a^b \frac{2}{L} \sin^2 \frac{\pi x}{L} dx = \frac{2}{\pi} \int_{\pi a/L}^{\pi b/L} \sin^2 u \, du \tag{4}$$

For $a = 0$ and $b = L/2$ we get a probability of $1/2$. This makes sense because of symmetry – see Fig 1.

b) in the middle third of the box.

Solution:

put $a = L/3$ and $b = 2L/3$ to get

$$\frac{1}{3} + \frac{\sqrt{3}}{2\pi} \approx 0.609 \tag{5}$$

This makes sense, because we know from the shape of the wavefunction in Fig. 1 that the answer must be more than 1/3.

c) Draw a picture of the wavefunction and associated probability for each of parts a) and b) and justify that your answers make sense in terms of these pictures.

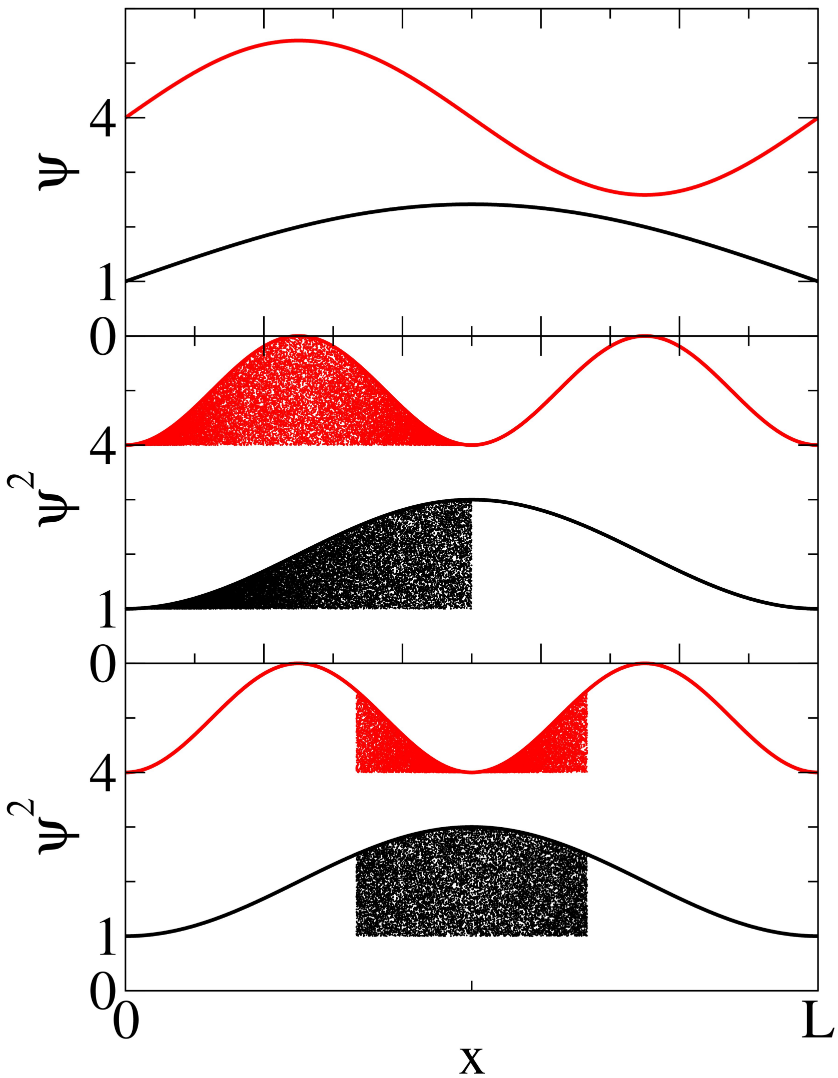

FIG. 1: answers to part c of problem 1 and 2

Problem 2 – **particle in a box**

Consider a particle in a one-dimensional box of length L in its first excited stationary state. Calculate the probability that the particle is

a) in the left half of the box

Solution:

This time we can change variables from x to $u = 2\pi x/L$, giving

$$\int_a^b \frac{2}{L}\sin^2\frac{2\pi x}{L}dx = \frac{1}{\pi}\int_{2\pi a/L}^{2\pi b/L}\sin^2 u\, du \tag{6}$$

Putting $a = 0$ and $b = L/2$ we get a probability of $1/2$. This makes sense because of symmetry (see Fig 1.

b) in the middle third of the box.

Solution:

Putting $a = L/3$ and $b = 2L/3$ gives

$$\frac{1}{3} - \frac{\sqrt{3}}{4\pi} \approx 0.1955 \tag{7}$$

This makes sense, because we know from the shape of the wavefunction in Fig. 1 that the answer must be less than 1/3 due to the node at $x = L/2$.

c) Draw a picture of the wavefunction and associated probability for each of parts a) and b) and justify that your answers make sense in terms of these pictures.

<u>Problem 3</u> – particle in a 1d box

Do problem 3-6 from your textbook (page 97)

Solution:

Following the book, we have the hexatriene length as $3 \times 135 + 2 \times 154 + 2 \times 77 = 867$ pm. With 6 π electrons the HOMO to LUMO transition is $n = 3$ to $n = 4$. This corresponds to the first electronic transition of

$$\frac{\Delta E}{hc} = \frac{(6.626 \times 10^{-34}\text{Js})^2(4^2 - 3^2)}{8(9.109 \times 10^{-31}\text{kg})(867 \times 10^{-12}\text{m})^2(6.626 \times 10^{-34}\text{Js})(3.00 \times 10^8\text{m s}^{-1})} \tag{8}$$

$$= 2.8 \times 10^6\ \text{m}^{-1} = 2.8 \times 10^4\ \text{cm}^{-1} \tag{9}$$

<u>Problem 4</u> – particle in a box

a) Calculate the energy levels of the π-network in octatetraene, C_8H_{10}, using the particle in the box model. To calculate the box length, assume that the molecule is linear and use the values of 135 pm and 154 pm for C=C and C-C bonds, respectively. Note: you should add 77 pm to both ends of the box length to be consistent with problem 3-6 from your textbook.

b) What is the wavelength of light required to induce a transition from the ground state to the first excited state? (Hint: make sure you use the aufbau principle to obtain the ground state electron configuration)

Solution:

There are eight π-electrons in this problem. Since we are modeling these eight electrons as "particles in a box", the ground state is where two of the electrons are in the $n = 1$

orbital, two are in the $n = 2$ level, two are in the $n = 3$ level, and two are in the $n = 4$ level. The first excited state is the next lowest energy arrangement of these eight electrons, which can be decided using the formula for the orbital energies. The first excited state is where one of the $n = 4$ ground state electrons is promoted to the $n = 5$ level. Therefore, the energy different from the ground state to the excited state is to simply move one electron from $n = 4$ to $n = 5$. This energy is given by the particle in a box expression for $E_5 - E_4$. Now, this energy must be supplied by a photon, and for photons we have $c = \lambda\nu$ and $E = h\nu$, so that

$$\lambda = \frac{8mL^2c}{h(5^2 - 4^2)} = \frac{(8)(9.11 \times 10^{-31}\text{kg})(1.156 \times 10^{-9}\text{m})^2(3.0 \times 10^8\text{ms}^{-1})}{(6.626 \times 10^{-34}\text{Js})(25 - 16)} \tag{10}$$

where the box length is 1.156×10^{-9}m. This works out to 490 nm.