

Chem 3322 homework #5 solutions

Problem 1 – tunneling

We found that, for a finite depth particle-in-a-box, the wavefunction amplitude decays in the barrier (classically forbidden region) according to $\psi(x) = A \exp[-\sqrt{2m(V_0 - E)/\hbar^2} x]$. This result will be used to calculate the sensitivity of the scanning tunneling microscope. Assume that the tunneling current through a barrier of width a is proportional to $I = |A|^2 \exp[-2\sqrt{2m(V_0 - E)/\hbar^2} a]$.

a) If $(V_0 - E)$ is 4.50 eV, how much larger would the current be for a barrier width of 0.20 nm than for 0.30 nm?

Solution:

We will compare by using a ratio.

$$\frac{I(a = 2 \times 10^{-10} \text{m})}{I(a = 3 \times 10^{-10} \text{m})} = \exp \left[-2\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} (2 \times 10^{-10} \text{m} - 3 \times 10^{-10} \text{m}) \right] \quad (1)$$

Putting in the numbers and converting units so that we get a dimensionless exponent results in an answer of 8.78. Therefore even a small distance change results in a substantial change in the tunneling current.

b) Somebody claims that a proton tunneling microscope would be equally effective. For a 0.20 nm barrier width, by what factor is the tunneling current changed if protons are used instead of electrons?

Solution:

Again, we can set it up as a ratio:

$$\frac{I(\text{proton})}{I(\text{electron})} = \frac{\exp \left[-2\sqrt{\frac{2m_{\text{proton}}(V_0 - E)}{\hbar^2}} a \right]}{\exp \left[-2\sqrt{\frac{2m_{\text{electron}}(V_0 - E)}{\hbar^2}} a \right]} = \exp \left[-2\sqrt{\frac{2(V_0 - E)}{\hbar^2}} (\sqrt{m_{\text{proton}}} - \sqrt{m_{\text{electron}}}) a \right] \quad (2)$$

Putting in the numbers and converting units gives an answer of 1.2×10^{-79} . Therefore a proton tunneling microscope does not look promising.

Problem 2 – particle in a 3d box

Solve the particle in a 3d box problem in your own words. You may use section 3-9 of the textbook and the 3d box section in my lecture notes as a guide. As part of your solution, you should obtain the stationary state wavefunctions and energy levels. For a cubic box, there are degeneracies as shown in Fig. 3.6 of the textbook. Please attempt to draw the $(2,1,1)$, $(1,2,1)$, and $(1,1,2)$ probability densities for the case of a cubic box. The goal of your drawing is to convince me that these 3 orbitals are different from one another (unlike the $n = 1$ and $n = -1$ cases for the particle in a 1d box). One way to do this is to sketch the nodal planes.

Solution:

See the sketch. Since the nodal planes (shaded in the sketch) are in different directions, the probability densities corresponding to these three wavefunctions are distinct, which is why these represent different physical states (orbitals).

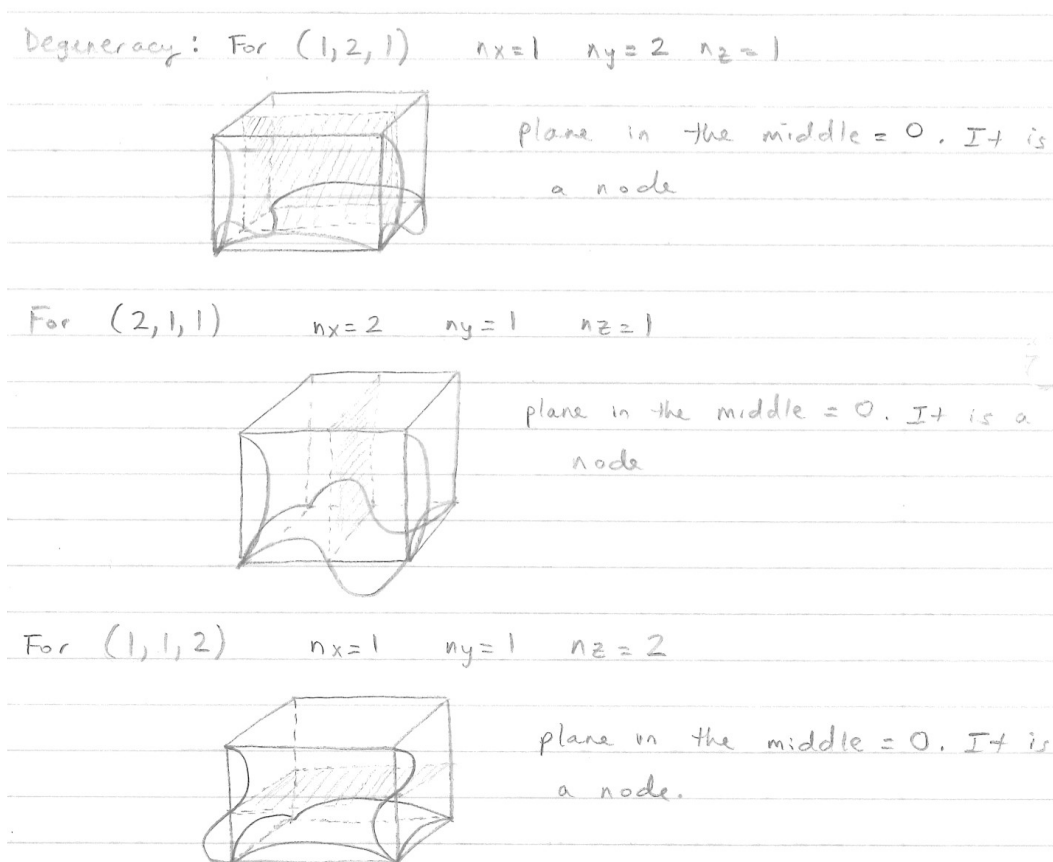


FIG. 1: sketch of the $(2,1,1)$, $(1,2,1)$, and $(1,1,2)$ orbitals

Problem 3 – particle in a 2d box

Do problem 3-27 from your textbook (page 99). Note that there is an error in the book: there are 26 π electrons in this molecule, not 18.

Solution:

First we need to figure out the energy level diagram. The energy is proportional to $(n_x^2 + n_y^2)$. The first few levels (in order of increasing energy) are

n_x	n_y	$n_x^2 + n_y^2$
1	1	2
2	1	5
1	2	5
2	2	8
1	3	10
3	1	10
3	2	13
2	3	13
1	4	17
4	1	17
3	3	18
4	2	20
2	4	20
4	3	25
3	4	25

The pattern of degeneracies is hard to predict; you just have to work them out. With 26 π electrons the HOMO to LUMO gap corresponds to $n_x^2 + n_y^2 = 20$ to $n_x^2 + n_y^2 = 25$. In terms of wavenumbers, this is

$$\frac{(6.626 \times 10^{-34} \text{Js})(25 - 20)}{(8)(9.11 \times 10^{-31} \text{kg})(1.0 \times 10^{-9} \text{m})^2(3.0 \times 10^{10} \text{cm s}^{-1})} = 15000 \text{cm}^{-1} \quad (3)$$

Problem 4 – particle in a 2d box

Consider a particle in a two-dimensional box of side lengths a and b , where $b = 2a$. Write down (in order of energy) the quantum numbers corresponding to the first 5 energy levels of this system. Note any degeneracies.

Solution:

The energy of the stationary states, as a function of the two quantum numbers n_x and n_y , is proportional to $n_x^2 + n_y^2/4$, or $4n_x^2 + n_y^2$. The first 5 energy levels are proportional to, using the first relation,

n_x	n_y	$E \propto n_x^2 + n_y^2/4$	
1	1	1.25	1st
1	2	2.00	2nd
1	3	3.25	3rd
2	1	4.25	4th
1	4	5.00	5th
2	2	5.00	5th

Therefore the 5th level is doubly degenerate and the first 4 levels are non-degenerate (also called singly degenerate)

Problem 5 – particle on a ring

The π electrons in benzene can be approximated as particles on a ring. Calculate the diameter of this “electron ring” if it is assumed that a transition occurring at 250.0 nm corresponds to an electron going from the highest occupied orbital (HOMO) to the lowest unoccupied orbital (LUMO). Compare this diameter to the diameter of a benzene molecule, if you approximate the carbon hexagon with a circle (you will have to look up the carbon-carbon bond length in benzene).

Solution:

The transition is from $n = 1$ to $n = 2$ because the $n = 0$ level is singly degenerate (non-degenerate) and the $n = 1$ level is doubly degenerate, so that the six π electrons fill the $n = 0$ and $n = 1$ levels, giving the HOMO to LUMO transition as $n = 1$ to $n = 2$. Then, using $E = h\nu$ and $c = \lambda\nu$, the photon of wavelength 250 nm gives an energy to the molecule of $E = 7.95 \times 10^{-19}$ J. The energy promotes the $n = 1$ to $n = 2$ transition,

$$E = \frac{2^2\hbar^2}{2mR^2} - \frac{1^2\hbar^2}{2mR^2} \quad (4)$$

Using the mass of an electron, since this is what is undergoing the transition, we get $R = 1.52 \text{ \AA}$.

The carbon-carbon bond length in benzene is 1.39 \AA . Assuming that the circumference of the π -electron “ring” in benzene is six times this distance, we get a radius of 1.33 \AA . Therefore our estimate is too high.

Problem 6 – particle in a box correspondence principle

Show that the probability associated with the state ψ_n for a particle in a one-dimensional box of length a obeys the following relationships:

(a)

$$\text{Prob}(0 \leq x \leq a/4) = \text{Prob}(3a/4 \leq x \leq a) = \begin{cases} \frac{1}{4} & \text{if } n \text{ is even} \\ \frac{1}{4} - \frac{(-1)^{n/2-1/2}}{2n\pi} & \text{if } n \text{ is odd} \end{cases} \quad (5)$$

and

(b)

$$\text{Prob}(a/4 \leq x \leq a/2) = \text{Prob}(a/2 \leq x \leq 3a/4) = \begin{cases} \frac{1}{4} & \text{if } n \text{ is even} \\ \frac{1}{4} + \frac{(-1)^{n/2-1/2}}{2n\pi} & \text{if } n \text{ is odd} \end{cases} \quad (6)$$

Explain the motivation behind this question by paraphrasing page 85/86 of McQuarrie/Simon.

Solution:

We can develop a general formula as follows:

$$\text{Prob}(a \leq x \leq b) = \int_a^b \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) dx \quad (7)$$

$$= \frac{2}{L} \left[\frac{x}{2} - \frac{\sin(2n\pi x/L)}{4(n\pi/L)} \right]_{x=a}^{x=b} \quad (8)$$

$$= \frac{b-a}{L} - \frac{1}{2n\pi} [\sin(2n\pi b/L) - \sin(2n\pi a/L)] \quad (9)$$

Now, in this question we have $b - a = L/4$. The answers to (a) and (b) then follow by considering whether the sin function is 0, 1, or -1 at the values of a and b given in each part (which depends on n).

Motivation:

These probabilities oscillate as they converge to the uniform distribution limit (of $1/4$), which is the classical probability density. This is an instance of the correspondence principle.