Chem 3322 homework #5, due March 1, 2024

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?

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?

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.

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.

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.

<u>Problem 5</u> – 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).

<u>Problem 6</u> – 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)

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

and

(b)

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

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