**5.61 Fall 2013**
**Problem Set #3**

**1.** **A**. McQuarrie, page 120, #3-3.
**B.** McQuarrie, page 120, #3-4.
**C.** McQuarrie, page 182, #4-11.

**2**. McQuarrie, pages 121-122, #3-11.

**3.** **A**. McQuarrie, page 123, #3-17.
**B.** McQuarrie, page 123, #3-18.
**C.** McQuarrie, page 127, #3-36.

**4**. Solve for the energy levels of the particle confined to a ring as a crude model for the electronic structure of benzene. The two dimensional Schrödinger Equation, in polar coordinates, is

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}+U(r,\phi)\right]\psi = E\psi.$$

For this problem, $U(r,\phi) = \infty$ for $r \neq a$, but when $r = a$, $U(a,\phi) = 0$.

**A**. This implies that $\psi(r,\phi) = 0$ for $r \neq a$. Why?

**B**. If $\psi(r,\phi) = 0$ for $r \neq a$, then $\frac{\partial\psi}{\partial r} = 0$. What is the simplified form of the Schrödinger Equation that applies when the particle is confined to the ring?

**C**. Apply the boundary condition that $\psi(a,\phi) = \psi(a,\phi + 2\pi)$ to obtain the $E_n$ energy levels.

**D**. The C–C bond length in benzene is 1.397 Å. Thus a circle which goes through all 6 carbon atoms has a radius $r = 1.397$ Å. Use this to estimate the $n = 2 \leftarrow n = 1$ transition for "benzene" treated as a particle on a ring. The longest wavelength allowed electronic transition for real benzene is at 2626 Å. Explain why the agreement is not perfect.

**5**. This problem illustrates tunneling. It requires either iterative or graphical solution (see McQuarrie problems 4-49 and 4-54 for inspiration). This is one of my favorite guided "magical mystery tours". Consider the potential energy function

| | | |
|---|---|---|
| $V(x) = \infty$ | $\lvert x\rvert \geq a/2$ | Regions I ($x < 0$) and V ($x > 0$) |
| $V(x) = 0$ | $a/10 \leq \lvert x\rvert < a/2$ | Regions II ($x < 0$) and IV ($x > 0$) |
| $V(x) = \frac{32h^2}{8ma^2}$ | $\lvert x\rvert < a/10$ | Region III $-a/10 < x < a/10$ |

**A.** Draw $V(x)$ and label the regions.

---

**Some Background**

Two boundary conditions are $\psi(\pm a/2) = 0$. The potential, $V(x)$, has left-right symmetry about $x = 0$. Thus all eigenfunctions of $\hat{H}$ must be either symmetric or antisymmetric, thus

$$\psi_n(x < 0) = (-1)^{n+1}\, \psi_n(x > 0) \text{ for } n = 1, 2, \ldots.$$

So all you will eventually need to do is find either $\psi(x < 0)$ or $\psi(x > 0)$ and join them at $x = 0$ so that *both* $\psi(x)$ and $\frac{d\psi}{dx}$ are continuous at $x = 0$. The best way to begin the construction of $\psi_n$ is to write $\psi_{n,\text{trial}}$ in Regions II and IV as

$$\psi_{n,\text{trial IV}}(x > 0) = A\cos\,[k(x - a/2) + \pi/2]$$
$$\psi_{n,\text{trial II}}(x < 0) = A\cos\,[k(-x - a/2) + \pi/2],$$

These trial functions satisfy the $x = a/2$ and $x = -a/2$ boundary conditions for all values of $k$.

Note that the arguments of the cosines are set up so that $\psi_{n,\text{trial II}}$ initially *increases* from 0 as x becomes larger than $-a/2$ and $\psi_{n,\text{trial iv}}$ initially *increases* from 0 as $x$ becomes smaller than $+a/2$. Thus $\psi_{n,\text{trial II}}$ and $\psi_{n,\text{trial IV}}$ are mirror images of each other and $\psi_{n,\text{trial}}$ is necessarily continuous at $x = 0$.

---

**B**. What is $k$, expressed in terms of $E$, $\hbar$, and $m$?

**C**. The barrier causes each of the energy levels to be shifted to higher energy than the corresponding levels of the simple $V(x) = 0$, $\lvert x\rvert \leq a/2$ box

$$E_n^{\text{barrier}} - E_n^{\text{normal}} > 0.$$

Before doing any calculations, answer this qualitative question: Do you expect the level shifts of the even-$n$ levels (anti-symmetric, node at $x = 0$)

to be systematically larger or smaller than those for the odd-$n$ levels (symmetric, anti-node at $x = 0$)? Why?

Choose either path 1 or path 2

**Path 1: D**. The wavefunctions in Region III have the form

$$\psi_n^{\text{III}} = Be^{\kappa x} + Ce^{-\kappa x} \qquad \left(\kappa = \left[\frac{32\pi^2}{a^2} - \frac{2mE}{\hbar^2}\right]^{1/2}\right)$$

for $E < \frac{32h^2}{8ma^2}$ and

$$\psi_n^{\text{III}} = De^{ikx} + Ee^{-ikx} \qquad \left(k = \left[\frac{2mE}{\hbar^2} - \frac{32\pi^2}{a^2}\right]^{1/2}\right)$$

for $E > \frac{32h^2}{8ma^2}$.

You can solve for (B,C) or (D,E) at the region II, III boundary ($x < 0$) by enforcing continuity of $\psi$ and $\frac{d\psi}{dx}$ at $x = -a/10$. The same solution is valid at the region III, IV boundary ($x > 0$). Show that $\psi_{\text{left}}^{\text{III}}$ propagated in from the II, III boundary is equal at $x = 0$ to $\psi_{\text{right}}^{\text{III}}$ propagated in from the III, IV boundary. Note that, at the value of $E$ you have chosen, $\frac{d\psi}{dx}$ is probably discontinuous at $x = 0$.

**E**. To find each of the $E_n^{\text{barrier}}$ eigenenergies, you need to increase the trial value of $E_n^{\text{barrier}}$ relative to $E_n^{\text{normal}}$ until $\frac{d\psi}{dx}$ is continuous at $x = 0$. A graphical method, where you plot $\frac{d\psi_{\text{left}}^{\text{III}}}{dx} - \frac{d\psi_{\text{right}}^{\text{III}}}{dx}$ at x = 0 vs. $E_n^{\text{trial}}$, will permit you to find the eigenenergies. Find $E_n^{\text{barrier}}$ for n = 1, 2, 3, 4, 5, and 6, and plot them next to $E_n^{\text{normal}} = n^2 \frac{h^2}{8ma^2}$.

[There will be two classes of eigenfunctions for the barrier-box. The odd-$n$ functions will have $\left.\frac{d\psi_n}{dx}\right|_{x=0} = 0$ at $x = 0$ and the even-$n$ functions will have $\psi_n(x) = 0$ at $x = 0$. You can find the eigen-energies, $E_n^{\text{barrier}}$, by either adjusting $E$ until $\frac{d\psi}{dx}$ is continuous at $x = 0$ or, for odd-$n$, $\left.\frac{d\psi_n}{dx}\right|_{x=0} = 0$, and for even-$n$, $\psi(0) = 0$.]

**Path 2**:

**D.** The wavefunctions in Region III have the form

$$\psi_n^{III} = Be^{\kappa x} + Ce^{-\kappa x} \qquad \left( \kappa = \left[ \frac{32\pi^2}{a^2} - \frac{2mE}{\hbar^2} \right]^{1/2} \right)$$

for $E < \frac{32h^2}{8ma^2}$ and

$$\psi_n^{III} = De^{ikx} + Ee^{-ikx} \qquad \left( k = \left[ \frac{2mE}{\hbar^2} - \frac{32\pi^2}{a^2} \right]^{1/2} \right)$$

for $E > \frac{32h^2}{8ma^2}$.

Find the general form of the wavefunction in regions I and II as well. Use symmetry arguments to simplify these expressions. Note that you have to use different symmetry arguments for the odd-symmetry and even-symmetrry eigenfunctions.

**E.** Use the fact that the wavefunction and its first derivative are continuous at the boundaries between regions to determine the values of the coefficients and therefore the energy eigenvalues for the even-symmetry and odd-symmetry cases that you described in part D. Do this for energy eigenvalues for n=1,2,3,4,5,6, and then plot them against the standard infinite well case where the energy eigenvalues are $E_n = \frac{h^2 n^2}{8ma^2}$.

**Both Paths do F and G**

**F**. Discuss the energy level pattern. Make whatever generalizations you can about the effect of a central barrier on the pattern of energy levels. Suggest (without full calculation) what would happen to this pattern if the barrier were made twice as high or twice as wide. Which effect is stronger, making the barrier higher or wider?

**G**. Plot $\psi_1 + \psi_2$ and $\psi_1 - \psi_2$ and comment on the left, right localization of the resultant non-eigenstate probability amplitude distributions.

# 5.61 Physical Chemistry

Fall 2013