5.61 Fall 2017
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 127, #3-36.

4. **A**. McQuarrie, page 122, #3-12. Answer this problem qualitatively by drawing a cartoon for $n = 2$ and $n = 3$ states.
B. Is there a simple mathematical/physical reason why the probabilities are not 1/4 for all four regions: $0 \leq x \leq a/4$, $a/4 \leq x \leq a/2$, $a/2 \leq x \leq 3a/4$, and $3a/4 \leq x \leq a$?
[**HINT**: where are the nodes in $\psi_n(x)$?]

5. 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 "periodic" 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 $n = 2 \leftarrow n = 1$ electronic transition for "benzene" treated as an electron on a ring. The longest wavelength allowed electronic transition for real benzene is at 2626 Å. Explain why the agreement is not perfect.

6. <u>1-Dimensional Infinite Wells with Steps</u>

Consider the potential

$$\begin{aligned} &V(x) = \infty && x < 0, x > a \\ &V(x) = 0 && 0 \le x \le a/2 \\ &V(x) = V_0 = \frac{h^2}{8ma^2}(2)^2 && a/2 < x \le a \end{aligned}$$

A. Sketch V(x) vs. x.

B. What are the boundary conditions for $\psi(x)$ at $x = 0$ and $x = a$?

C. What requirements must be satisfied at $x = a/2$?

D. Solve for the $\boldsymbol{n} = \mathbf{2}$ (one node) and $\boldsymbol{n} = \mathbf{3}$ (two nodes) $\psi_n(x)$ eigenfunctions of $\widehat{H}$ and E_n energy levels.

Hints: (i) For $0 \le x \le a/2$, $\psi_{\mathrm{I}}(x) = \mathrm{A} \sin k_{\mathrm{I}} x$

$k_{\mathrm{I}} = \left[2mE/\hbar^2\right]^{1/2}$

(ii) For a/2 < x ≤ a, $\psi_{\mathrm{II}}(x) = \mathrm{B} \sin k_{\mathrm{II}}(a - x)$

$k_{\mathrm{II}} = \left[2m(E - V_0)/\hbar^2\right]^{1/2}$

(iii) $\psi_{\mathrm{I}}(a/2) = \mathrm{A} \sin(k_{\mathrm{I}}\, a/2)$

$\psi_{\mathrm{II}}(a/2) = \mathrm{B} \sin(k_{\mathrm{II}}\, a/2)$

$$\left.\frac{d\psi_{\mathrm{I}}}{dx}\right|_{x=a/2} = Ak_{\mathrm{I}} \cos\left(k_{\mathrm{I}}\, a/2\right)$$

$$\left.\frac{d\psi_{\mathrm{II}}}{dx}\right|_{x=a/2} = -Bk_{\mathrm{II}} \cos(k_{\mathrm{II}}\, a/2)$$

E. Compare your values of E_2 and E_3 to what you obtain from the de Broglie quantization condition

$$(n/2) = \frac{a/2}{\lambda_{n,\mathrm{I}}} + \frac{a/2}{\lambda_{n,\mathrm{II}}}$$

$$\lambda = h/p = 2\pi/k = h\left[2m\left(E - V(x)\right)\right]^{-1/2}$$

F. For the $\boldsymbol{n} = \mathbf{2}$ and $\boldsymbol{n} = \mathbf{3}$ energy levels, what are the probabilities, P_2 and P_3, of finding the particle in the $0 \le x \le a/2$ region?

G. (*optional*) Will the **n = 2** and **3** energy levels of the $V_1(x)$ and $V_2(x)$ potentials (defined below) be identical, as suggested by part **E**? Why?

$$V_1(x): \quad V_1(x) = \infty \quad x < 0, x > a$$
$$V_1(x) = 0 \quad 0 \le x \le a/2$$
$$V_1(x) = V_0 \quad a/2 < x \le a$$

versus

$$V_2(x): \quad V_2(x) = \infty \quad x < 0, x > a$$
$$V_2(x) = 0 \quad 0 \le x \le a/4, 3a/4 \le x \le a$$
$$V_2(x) = V_0 \quad a/4 < x < 3a/4$$

H. Solve for the $n = 1$ $\psi_1(x)$ and E_1 for V_1.

HINTS: For $a/2 < x \le a, \quad \psi_{\text{II}}(x) = Be^{\kappa_{\text{II}}(a-x)} + Ce^{-\kappa_{\text{II}}(a-x)}$

$$\kappa_{\text{II}} = \left[2m\left(V_0 - E\right)/\hbar^2\right]^{1/2}$$

I. (*optional*) Is E_1 for V_1 larger or smaller than E_1 for V_2? Why? A cartoon will be helpful.