Chemistry 30321 | Fall 2012
Professor J. Daniel Gezelter | Due Fri. 9/21/2012

Problem Set 4
(Postulates, particles in boxes, models for π electron energies in benzene)
Get an early start!

1. Do problem 3-16 in McQuarrie and Simon.
2. Do problem 3-27 in McQuarrie and Simon, but don't trust what the book says about the number of π electrons. Count for yourselves!
3. Determine the energy levels and eigenfunctions for the following problem:

$$V(x) = 0 \quad -\frac{a}{2} \leq x \leq \frac{a}{2}$$

$$V(x) = \infty \quad |x| > \frac{a}{2}$$

   (Hint: There are two ways to do this problem; one easy way and one hard way that replicates a lot of work. You have my permission to be lazy and do it the easy way...)

4. Do problem 4-3 in McQuarrie and Simon.
5. Consider a particle-in-a-box prepared in the "mixed" state:

$$\Psi(x,t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}$$

   $\psi_1(x)$ and $\psi_2(x)$ are the first two normalized eigenfunctions of the Hamiltonian with energies E_1 and E_2. You can further assume that:

$$\int \psi_1^*(x)\psi_2(x)dx = \int \psi_2^*(x)\psi_1(x)dx = 0$$

   (i.e. ψ_1 and ψ_2 are orthogonal).

   (a) Is there a relationship between c_1 and c_2? If so, what is this relationship?
   (b) Derive an experssion for $\langle E(t)\rangle$, the time-dependent expectation value for the energy.
   (c) Derive an experssion for $\langle x(t)\rangle$, the time-dependent expectation value for the position.
   (d) Are $\langle x(t)\rangle$ and $\langle E(t)\rangle$ real or complex quantities? How do you know?

6. Do problem 4-9 in McQuarrie and Simon.

7. Do problem 4-11 in McQuarrie and Simon.

8. Extra Credit: The Schrödinger equation for a particle of mass m constrained to move on a circle of radius a is

$$-\frac{\hbar^2}{2I}\frac{d^2\psi}{d\theta^2} = E\psi(\theta) \quad (1)$$

where $I = ma^2$ is the moment of inertia and θ is the angle that describes the position of the particle around the ring $(0 \leq \theta \leq 2\pi)$.

a) Show that the solutions to this equation are

$$\psi(\theta) = Ae^{in\theta} \quad (2)$$

where $n = \sqrt{2IE}/\hbar$.

b) Explain why the appropriate boundary condition is $\psi(\theta) = \psi(\theta + 2\pi)$ and use this to show that

$$E = \frac{n^2\hbar^2}{2I}, n = 0, \pm 1, \pm 2, \cdots \quad (3)$$

c) Show that the normalization constant A is $1/\sqrt{2\pi}$.

d) Show that two of these eigenfunctions with different values of n are orthogonal, i.e.

$$\int_0^{2\pi} \psi_1^*(\theta)\psi_2(\theta)d\theta = 0 \quad (4)$$

e) How might you use these results for a free-electron model of benzene? Which states and energies of the particle on a ring are relevant?