Quantum Chemistry
Exercises 2C

1. The Schrödinger equation for a particle of mass *m* constrained to move on a circle of radius *a* is

$$-\frac{\hbar^2}{2I}\frac{d^2\psi(\theta)}{d\theta} = E\psi(\theta) \qquad 0 \le \theta \le 2\pi \qquad \text{where } I = ma^2$$

This problem is sometimes called the *particle-on-a-ring* and represents the rotation of a linear molecule in a plane.

Find the solutions to this equation (that is, find the eigenfunctions and eigenvalues), including the normalization constant for the wave function.

Hint: Use the fact that the wave function must be continuous to determine the appropriate boundary conditions needed to solve the problem.

2. Recall the particle on a ring problem from above. The angular momentum operator for a particle on a ring is

$$\hat{L} = -i\hbar\frac{d}{d\theta}$$

a. Assume that the system is in an eigenfunction corresponding to $n = 3$. What is the angular momentum of the particle with this wave function?

b. The problem of the particle-on-a-ring is different from the particle-in-a-box in that the quantum numbers *n* can take on both positive and negative values. Physically, how would you interpret the difference between a particle on a ring described by wavefunctions with $n = +3$ and $n = -3$?

3. Consider the situation in which a particle on a ring can be described by the wave function

$$\Psi(\theta,t) = \frac{\sqrt{3}}{3}\frac{1}{\sqrt{2\pi}}e^{i3\theta}e^{-\frac{iE_3}{\hbar}t} + \frac{\sqrt{3}}{3}\frac{1}{\sqrt{2\pi}}e^{i6\theta}e^{-\frac{iE_6}{\hbar}t} + \frac{\sqrt{3}}{3}\frac{1}{\sqrt{2\pi}}e^{-i6\theta}e^{-\frac{iE_6}{\hbar}t}$$

where the E_n are the energies of the stationary states for a particle on a ring.

a. Is the probability of finding the particle at a particular angle θ independent of time if the state is described by the wave function $\Psi(\theta,t)$ given above?

b. If you were to measure the energy of a particle in this state $\Psi(\theta,t)$, what value or range of values could you obtain? If your answer includes a range of values, what is the probability for obtaining each value in that range?

c. Calculate $\langle E \rangle$, the expectation value of the energy that you would obtain if you were to make repeated measurements on a number of identical systems. (Hint: You can do this without explicitly evaluating any integrals)

d. Let's say you make a measurement of the energy and get $\frac{9\hbar^2}{2I}$ (call this measurement #1). You then make a subsequent measurement (#2) of the energy of the same system you measured the first time. What value or range of values could you obtain in measurement #2?

e. Would your answer to part c) be any different if in between your two measurements of the energy (#1 and #2) you measured the particle's angular momentum? Why or why not? What possible values could you get for the angular momentum? Recall that the angular momentum operator for the particle on a ring is

$$\hat{L} = -i\hbar \frac{d}{d\theta}$$

f. Let's say that after making a measurement of the energy and getting $\frac{9\hbar^2}{2I}$ you measure the angular position and get θ_0 for a result. If your then remeasure the position 10 seconds later, will you get the same result? Why or why not?

g. After making these two measurements of the position (as stated in 3f.), you then measure the energy. What value or range of values could you get?

4. Evaluate the commutator $\left[\hat{A},\hat{B}\right]$ where $\hat{A}$ and $\hat{B}$ are given below.

a. $\hat{A} = \frac{d^2}{dx^2}$ $\qquad$ $\hat{B} = x$

b. $\hat{A} = \frac{d}{dx} - x$ $\qquad$ $\hat{B} = \frac{d}{dx} + x$

5. Answer the following questions TRUE or FALSE and briefly describe the reasoning behind your answer. Be sure to read each question ***carefully***.

a. The wave function for a quantum mechanical system must be an eigenfunction of the Hamiltonian operator.

b. Every physical observable in classical mechanics can be represented by a Hermitian operator in quantum mechanics.

c. If the wave function for a system is not an eigenfunction of the operator $\hat{A}$, then a measurement of the observable corresponding to $\hat{A}$ might give a value that is not one of the eigenvalues of $\hat{A}$.

d. The wave function for a quantum mechanical system is always equal to a function of time multiplied by a function of the coordinates.

e. After making a measurement of the observable corresponding to $\hat{A}$ and getting the result a_n, the wave function becomes one of the eigenfunctions of $\hat{A}$, but you cannot be certain which one.

f. One can sometimes measure two physical observables with infinite relative precision.