

# V25.0109: General Chemistry I (Honors)

## Problem set #4 Due 10/3

Practice problems from Appendix B (page 744): 1, 2, 3

Practice problems from Chapter 3: 22, 23

### Graded problems

1. Consider a particle of mass  $m$  in a one-dimensional box with walls at  $x = 0$  and  $x = L$ .

- a. Show that if the particle's wave function is  $\psi_n(x) = \sqrt{2/L} \sin(n\pi x/L)$ , its energy  $E_n$  is given by the formula

$$E_n = \int_0^L \psi_n(x) \hat{H} \psi_n(x) dx$$

where  $\hat{H}$  is the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

- b. Now suppose the particle is in the  $n = 1$  state, and suppose we do not know that the wave function is  $\psi_1(x) = \sqrt{2/L} \sin(\pi x/L)$ . Rather, suppose we make an educated "guess" of the wave function of the form

$$\psi_g(x) = x(L - x)$$

Show that  $\psi_g(x)$  satisfies the boundary conditions of the particle in a box.

- c. Plot  $\psi_g(x)$  and  $\psi_1(x)$  on the same graph for the case  $L = 1$ . How closely does  $\psi_g(x)$  match  $\psi_1(x)$ ?
- d. The "guess" wave function  $\psi_g(x)$  can be used to calculate a corresponding estimate of the energy  $E_1$  using the formula

$$E_g = \frac{\int_0^L \psi_g(x) \hat{H} \psi_g(x) dx}{\int_0^L \psi_g^2(x) dx}$$

where, again,  $\hat{H}$  is the Hamiltonian in part a. Calculate  $E_g$  and show that it is close to but greater than  $E_1$ . This exercise illustrates a more general result that no matter what choice is made for  $\psi_g(x)$ , unless  $\psi_g(x) = \psi_1(x)$ ,  $E_g$  will *always* be larger than  $E_1$ .

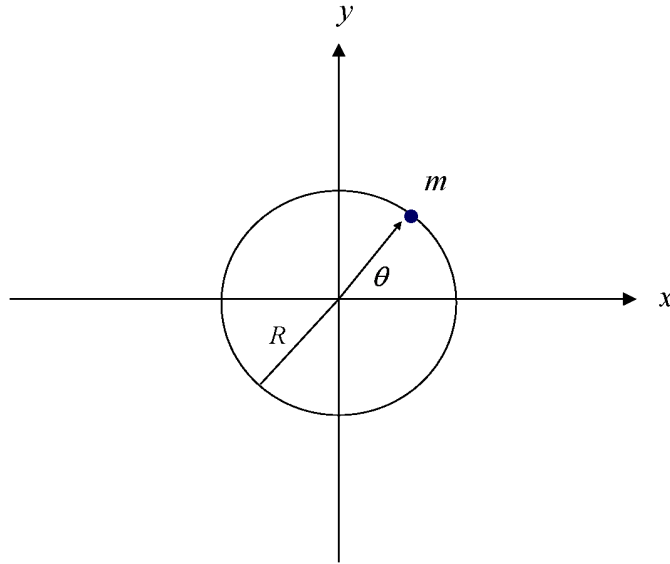
- e. Try plotting the function

$$\psi_g(x) = \sqrt{\frac{30}{L^5}} x(L - x)$$

on the same graph as  $\psi_1(x)$ . Does this help explain why  $E_g$  and  $E_1$  are so close?

2. a. Consider a particle of mass  $m$  in a one-dimensional box with walls at  $x = -L/2$  and  $x = L/2$ . What are the allowed energies  $E_n$  and corresponding wave functions  $\psi_n(x)$ ? Note that you do not need to solve any differential equations. You already know that the solutions are sin and/or cos. Explain any similarities or differences between the energies and wave functions for this box and the box with walls at  $x = 0$  and  $x = L$ .

- b. For the particle in part a, what is the probability that a measurement of the particle's location will yield a value between  $x = -L/4$  and  $x = 0$ ?
- c. Next, consider a particle of mass  $m$  moving in a circle of fixed radius  $R$ . Let  $\theta$  be the angle made by the particle's position vector and the positive  $x$ -axis as shown in the figure:



The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\theta^2}$$

Find the allowed energies and wave functions. Note that since the variable  $\theta$  is the only coordinate needed to describe the particle's position, the wave functions are functions of  $\theta$ , i.e.  $\psi_n(\theta)$ . Moreover, because the particle moves on a ring, there is no actual "boundary". The only condition that the wave functions need to satisfy is

$$\psi_n(0) = \psi_n(2\pi)$$

**Hint:** Try starting with solutions that are not sin and cos but rather  $\psi(\theta) = A \exp(ia\theta)$ .

3. A particle of mass  $m$  is in a box of length  $L$  that extends from  $x = 0$  to  $x = L$ . The particle's wave function is prepared such that

$$\Psi(x) = \sqrt{\frac{1}{3}}\psi_2(x) + \sqrt{\frac{2}{3}}\psi_3(x)$$

- a. Show that  $\Psi(x)$  is properly normalized
- b. Calculate the probability that a measurement of the particle's position will yield a value between  $x = L/2$  and  $x = 3L/4$ .
4. Consider a particle of mass  $m$  in a one-dimensional box with walls at  $x = 0$  and  $x = L$  in a state with  $n = 2$ . The wave function is

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$$

Note that at  $x = L/2$ ,  $\psi_2(L/2) = 0$ , which means that the probability of finding the particle in a small region about  $x = L/2$  is zero. Nevertheless, there is equal probability to find the particle in the left half of the box ( $0 \leq x \leq L/2$ ) as in the right half of the box ( $L/2 \leq x \leq L$ ). How is this possible if the particle has no way of passing through the point  $x = L/2$ ? Is this an unresolvable paradox in quantum mechanics?