

V25.0109: General Chemistry I (Honors)

Problem set #4 Due 10/9

Practice problems from Appendix B (page 744): 1, 2, 3
Practice problems from Chapter 3: 22, 23

Graded problems

1. Prove that the particle-in-a-box wave functions

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

satisfy the orthogonal relation

$$\int_0^L \psi_n^*(x) \psi_m(x) dx = 0$$

when $n \neq m$.

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

- a. Show by explicitly performing the integration 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

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

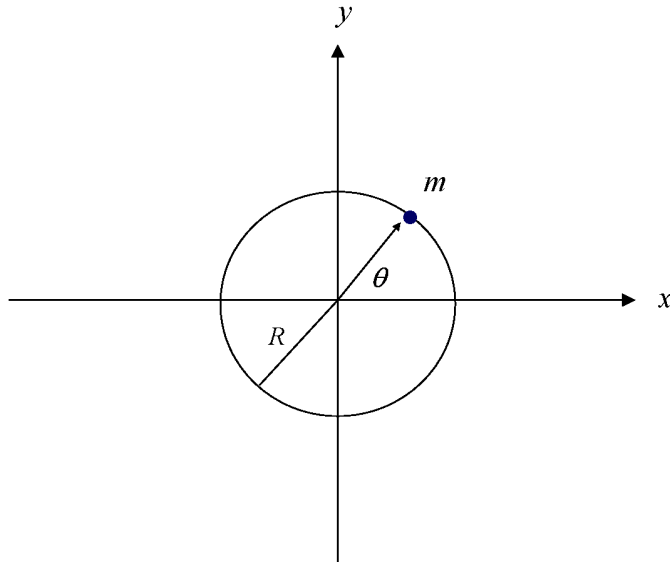
where, again, \hat{H} is the Hamiltonian in part a. Calculate E_g and show that it is close to but greater than E_1 . This exercise illustrates a more general result that no matter what choice is made for $\psi_g(x)$, unless $\psi_g(x) = \psi_1(x)$, E_g will *always* be larger than E_1 .

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?

3. 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 $x = 0$ if the particle is in its first excited state?
- c. Next, consider a particle of mass m moving in a circle of fixed radius R . Let θ 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 θ is the only coordinate needed to describe the particle's position, the wave functions are functions of θ , 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 $\psi(\theta) = A \exp(ia\theta)$.

4. 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

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

- Show that $\Psi(x)$ is properly normalized
- Calculate the probability that a measurement of the particle's position will yield a value between $x = L/2$ and $x = 3L/4$.
- A measurement of the particle's energy must yield one of the allowed values E_n . The average energy $\langle E \rangle$ over many such measurements can be calculated using

$$\langle E \rangle = \int_0^L \Psi^*(x) \hat{H} \Psi(x) dx$$

Calculate the average energy for the given wave function. Rationalize your answer based on the fact that any individual measurement must yield one of the E_n .

Hint: You can do this calculation without doing any actual integrals by simply using the fact that $\hat{H}\psi_n(x) = E_n\psi_n(x)$. The answer you get should make perfect sense.

5. 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?