CHM 305 Problem Set 3

Distributed: Tuesday, September 29, 2026
Due: Monday, October 5, 2026 @ 11:59 PM ET

Problem Set Submission: Please submit assignment by uploading your files to Canvas. You may upload scanned handwritten work or digital documents as .pdf files.

Collaboration: Students are encouraged to interact with one another and to collaborate in learning and understanding the course material and homework problems. However, each student's assignments are expected to be their own work, reflecting their own understanding of the course material.

1 Expectation Values of the 1D PIB

Earlier in this class, we learned that the 1D particle-in-a-box wavefunctions take the form

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

where the particle is confined along the x axis between 0 and a, with $n = 1, 2, \cdots$

(a) Calculate the average position of the particle using

$$\langle x \rangle = \int_0^a \psi_n^*(x) \cdot x \cdot \psi_n(x)\, dx$$

and show that it is equal to $a/2$ for **all values of** n. Is this result physically reasonable? An integral that might be useful to you is:

$$\int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

(b) For the same particle in a 1D box of length a, show that average momentum $\langle p \rangle = 0$ **for all states**. Is this result physically reasonable? Use the fact that the momentum operator is defined as $\hat{p} = -i\hbar\frac{\partial}{\partial x}$. You may want to make use of the trigonometric identity:

$$\sin(\alpha x)\cos(\alpha x) = \frac{1}{2}\sin(2\alpha x)$$

2 Time-dependence of a 1D PIB Superposition State

Consider the time-dependent superposition of the first two PIB eigenstates, which has already been normalized:

$$\Phi(x,t) = \sqrt{\frac{1}{a}} \sin\left(\frac{\pi x}{a}\right) e^{-iE_1 t/\hbar} + \sqrt{\frac{1}{a}} \sin\left(\frac{2\pi x}{a}\right) e^{-iE_2 t/\hbar}$$

where $E_n = \frac{\hbar^2}{2m}(\frac{n\pi}{a})^2$.

(a) Evaluate the average position of the particle

$$\langle x \rangle = \int_0^a \Phi^*(x,t) \cdot x \cdot \Phi(x,t)\, dx$$

and show that it can be expressed as

$$\langle x \rangle = \frac{a}{2} + c \cdot \cos(\omega_{12} t)$$

where c and ω_{12} are constants. This result suggests that the expected position of a particle in this superposition state oscillates about the center of the box. Determine an expression for the oscillation frequency ω_{12}. The integral from Problem 2(a) may come in handy again.

(b) Show that the oscillation amplitude from part (a) is given by

$$c = -\frac{16a}{9\pi^2}$$

You may make use of any trigonometric identities or integrals that you see fit.

(c) If you measure the energy of the particle in this superposition state, what values might you find, and what is the probability of measuring each of them?

(d) Find the expectation value of the Hamiltonian operator, $\hat{H}$, when applied to $\Phi(x,t)$.

3 Basis Set Expansions of Wavefunctions

At time $t = 0$, a 1D particle-in-a-box trapped in the region $x = [0, a]$ has the initial wavefunction:

$$\Phi(x,0) = \begin{cases} Ax(a-x) & 0 \le x \le a \\ 0 & \text{elsewhere} \end{cases}$$

for some constant A.

(a) Sketch $\Phi(x,0)$ inside the box (e.g. in the region $x = [0, a]$).

(b) Determine A by normalizing $\Phi(x,0)$.

(c) Find the basis set expansion of $\Phi(x,0)$ in terms of the 1D particle-in-a-box eigenfunctions $\psi_n(x)$. In other words, find the coefficients c_n such that:

$$\Phi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

where

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

In particular, you will show that:

$$c_n = \begin{cases} 0 & n \text{ even} \\ \dfrac{8\sqrt{15}}{(n\pi)^3} & n \text{ odd} \end{cases}$$

Hint: Recall that we learned in Lecture 5 that the coefficients of a basis set expansion of an arbitrary wavefunction are given by the overlap integral of that arbitrary wavefunction with the n^{th} eigenfunction. So you should evaluate:

$$c_n = \int_0^a \psi_n^*(x)\Phi(x,0)dx$$

You may want to make use of the following trigonometric identities:

$$\int x\sin(\alpha x)dx = \frac{\sin(\alpha x)}{\alpha^2} - \frac{x\cos(\alpha x)}{\alpha}$$

$$\int x^2\sin(\alpha x)dx = \frac{2x\sin(\alpha x)}{\alpha^2} - \frac{\alpha^2x^2-2}{\alpha^3}\cos(\alpha x)$$

(d) Using your basis set expansion of $\Phi(x,0)$ from part (c) and what we have learned about the time-dependence of eigenfunctions of the Hamiltonian, write down a complete expression for $\Phi(x,t)$.

(e) What is the probability that a measurement of the energy will yield the value $\pi^2\hbar^2/2ma^2$ at time t?

4 Commutators and Uncertainty Relations

(a) Evaluate the commutator $\left[\frac{d}{dx}, \frac{1}{x}\right]$ by applying the operators to an arbitrary function $f(x)$.

(b) Can the position and kinetic energy of an electron along the x axis be measured simultaneously to arbitrary precision? Why or why not? Consider the commutator of the corresponding quantum operators.

(c) Prove the following commutator identity:

$$\left[\hat{A} + \hat{B}, \hat{C}\right] = \left[\hat{A}, \hat{C}\right] + \left[\hat{B}, \hat{C}\right]$$

(d) Prove the following commutator identity:

$$\left[\hat{A}\hat{B}, \hat{C}\right] = \hat{A}\left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{C}\right]\hat{B}$$

(e) Prove that two non-commuting operators $\hat{A}$ and $\hat{B}$ cannot have a complete set of common eigenfunctions. *Hint:* Show that if $\hat{A}$ and $\hat{B}$ have a complete set of common eigenfunctions, then $\left[\hat{A}, \hat{B}\right]\psi = 0$ for any wavefunction ψ.

5 Particle-in-a-Box Uncertainties

(a) Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, and $\langle p^2 \rangle$ tor the n^{th} 1D particle-in-a-box eigenfunction.

Note: You may already have evaluated some of these quantities in a previous problem. No need to redo any calculations, just write down any result derived previously and reference where it came from.

You may use any trigonometric integrals or identities given in this problem set or on any previous problem set. You can also reference the list of integrals and identities posted on Canvas. Another useful integral may be:

$$\int x^2 \sin^2(\alpha x) dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha x) - \frac{x \cos(2\alpha x)}{4\alpha^2}$$

(b) Using your results from part (a), calculate $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ and $\sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$.

(c) Check that the uncertainty principle is satisfied for each $\psi_n(x)$. In other words, check whether $\sigma_x \sigma_p \geq \hbar/2$ for each n.

(d) Which eigenfunction of the PIB comes closest to the uncertainty limit?