Problem Set 3
CHM 305, Fall 2023

Distributed: Thursday, September 28, 2023
Due: Thursday, October 5, 2023 @ 5 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. Please see the Submitting Assignments in Canvas page for detailed instructions on how best to do this.

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

Suppose that the wavefunction for a system can be written as

$$\phi(x) = \frac{\sqrt{2}}{4}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x) + \frac{2+\sqrt{2}i}{4}\psi_3(x) \tag{1}$$

and that $\psi_1(x)$, $\psi_2(x)$, and $\psi_3(x)$ are normalized eigenfunctions of the operator $\hat{A}$ with eigenvalues a_1, a_2, and a_3, respectively.

(a) Confirm that $\phi(x)$ is normalized.

(b) What are the possible measurement values that you could observe when applying $\hat{A}$ to this system?

(c) What is the probability of measuring each of these values?

(d) What is the expectation value of this measurement?

2 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:

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

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

(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.

Extra credit will be awarded if you can show that the oscillation amplitude is given by

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

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

(b) 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?

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

4 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:

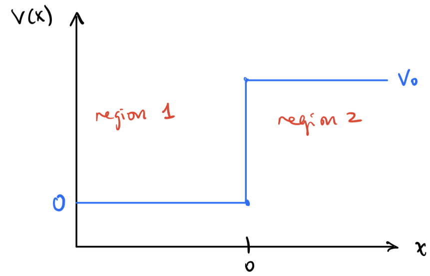
$$\int x \sin(\alpha x) dx = \frac{\sin(\alpha x)}{\alpha^2} - \frac{x \cos(\alpha x)}{\alpha}$$
$$\int x^2 \sin(\alpha x) dx = \frac{2x \sin(\alpha x)}{\alpha^2} - \frac{\alpha^2 x^2 - 2}{\alpha^3} \cos(\alpha x)$$

(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?

5 The Finite Step Potential

In this problem, we will consider what happens when a quantum particle hits a finite potential barrier. We will determine the probabilities that the particle is reflected versus transmitted. Consider a particle moving towards a finite step in the potential, as we discussed in class in Lecture 7:



$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases}$$

where V_0 is a constant. As we discussed in class, if we have a particle approaching the step from the left with energy $E > V_0$, then the solutions to the Schrödinger equation in the two regions are:

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad \text{for } x < 0$$

$$\psi_2(x) = Ce^{ik_2x} \qquad \text{for } x > 0$$

where

$$k_1 = \left[\frac{2mE}{\hbar^2}\right]^{1/2} \qquad \text{and} \qquad k_2 = \left[\frac{2m(E - V_0)}{\hbar^2}\right]^{1/2}$$

Here e^{ikx} terms represent a particle traveling to the right and e^{-ikx} terms represent a particle traveling to the left. The coefficients A, B, and C encode the probabilities that a particle is traveling in a certain direction in a given region. For example, $|A|^2$ represents the probability that the particle is in Region 1, traveling towards the right with momentum $+\hbar k_1$.

If we consider N particles exploring this landscape, then we can interpret the quantity $|A|^2N$ to be the number of particles with momentum $\hbar k_1$ in Region 1. The number of these particles that pass a given point per unit time is given by $v|A|^2N$, where the velocity v is given by $\hbar k_1/m$ in Region 1 and $\hbar k_2/m$ in Region 1.

(a) $\psi(x)$ and $\frac{d\psi}{dx}$ must be continuous at $x = 0$. In other words,

$$\psi_1(0) = \psi_2(0)$$

$$\left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0}$$

Use these boundary conditions to derive the following system of equations:

$$A + B = C$$

$$k_1(A - B) = k_2C$$

(b) Now, let's define the reflection coefficient r

$$r \equiv \frac{\hbar k_1 |B|^2 N/m}{\hbar k_1 |A|^2 N/m} = \frac{|B|^2}{|A|^2}$$

which represents the probability that a particle striking the step from the left will be reflected back into Region 1. Use the system of equations from part (a) to show that:

$$r = \left(\frac{k_1 - k_2}{k_1 + k_2} \right)^2$$

(c) Similarly, let's define the transmission coefficient t

$$t \equiv \frac{\hbar k_2 |C|^2 N/m}{\hbar k_1 |A|^2 N/m} = \frac{k_2 |C|^2}{k_1 |A|^2}$$

which represents the probability that a particle striking the step from the left will be transmitted into Region 2. Use the system of equations from part (a) to show that:

$$t = \frac{4 k_1 k_2}{(k_1 + k_2)^2}$$

(d) Use the expressions from parts (b) and (c) to show that $r + t = 1$. Why should we expect this to be the case?

(e) Show that $r \to 0$ and $t \to 1$ as $V_0 \to 0$. Why should we expect this to be the case?