Problem Set 4
CHM 305, Fall 2021

Distributed: Tuesday, September 28, 2021
Due: Tuesday, October 5, 2021 @ 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 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:

\[
\Phi(x, 0) = \begin{cases} 
Ax(a-x) & 0 \leq x \leq a \\
0 & \text{elsewhere}
\end{cases}
\]

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:

\[
c_n = \begin{cases} 
0 & n \text{ even} \\
\frac{8\sqrt{15}}{(n\pi)^3} & n \text{ odd}
\end{cases}
\]
**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 \( \Phi(x, t) \).

\section{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? **Hint:** Consider the commutator of the corresponding quantum operators.

\section{Particle-in-a-Box Uncertainties}

(a) Calculate \( \langle x \rangle \), \( \langle x^2 \rangle \), \( \langle p \rangle \), and \( \langle p^2 \rangle \) for the \( n \)th 1D particle-in-a-box eigenfunction (e.g. \( \psi_n(x) \) from Problem 1).

*Note:* You may already have evaluated some of these quantities in a previous problem set. 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. Another useful integral may be:

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

(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 comes closest to the uncertainty limit?

4 Quantum Harmonic Oscillator Wavefunctions

The first few eigenfunctions of the quantum harmonic oscillator are

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

recalling that we defined $\alpha \equiv \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$ for compactness.

(a) Sketch $\psi_0(x)$, $\psi_1(x)$, and $\psi_2(x)$.

(b) In class, we verified that the ground state wavefunction $\psi_0(x)$ satisfied the Schrödinger equation. Verify that $\psi_1(x)$ satisfies the Schrödinger equation as well.

(c) Recall that eigenfunctions of the same Hamiltonian should be mutually orthogonal. Show that $\psi_0(x)$ is orthogonal to both $\psi_1(x)$ and $\psi_2(x)$ by explicit integration. Hint: Consider the useful properties of even and odd integrands:

$$\int_{-\infty}^{\infty} f(x)dx = 0 \quad \text{for } f(x) \text{ odd}$$

$$\int_{-\infty}^{\infty} f(x)dx = 2 \int_{0}^{\infty} f(x)dx \quad \text{for } f(x) \text{ even}$$

The following Gaussian integrals may also come in handy, where $n$ represents a positive integer:

$$\int_{0}^{\infty} e^{-\alpha x^2}dx = \left(\frac{\pi}{4\alpha}\right)^{1/2}$$

$$\int_{0}^{\infty} x^{2n} e^{-\alpha x^2}dx = \frac{1 \cdot 3 \cdot 5 \cdot \cdots (2n - 1)}{2^{n+1}\alpha^n} \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$\int_{0}^{\infty} x^{2n+1} e^{-\alpha x^2}dx = \frac{n!}{2\alpha^{n+1}}$$

Note: Use Eqn. (2) for even powers of $x$, and Eqn. (3) for odd powers of $x$. 