

# Lecture 8 — Postulates I–III: State Functions, Operators & Measurement

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**Reading:** Engel 4th ed., Chapter 3 (Sections 3.1–3.3)

## Learning Objectives

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- State and interpret Postulates I–III of quantum mechanics
  - Identify valid quantum-mechanical state functions
  - Construct quantum-mechanical operators from classical expressions
  - Verify that an operator is Hermitian
  - Solve eigenvalue equations — using the particle in a box as a primary example
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## Postulate I — The State Function

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The state of a quantum-mechanical system is completely specified by a function  $\Psi(\mathbf{r}, t)$  — the wavefunction — that depends on the coordinates of the particle(s) and on time. All observable properties can be extracted from  $\Psi$ .

## Key Implications

- $\Psi$  contains all information about the system
- $|\Psi|^2$  gives the probability density (Born interpretation, Lecture 7)
- $\Psi$  must satisfy the requirements from Lecture 7: single-valued, continuous, normalizable

## PIB Example: The State Function in Action

The PIB wavefunctions  $\psi_n(x) = \sqrt{2/a} \sin(n\pi x/a)$  are valid state functions:

- They satisfy the Schrödinger equation inside the box
- They meet all wavefunction constraints (Lecture 7)

- From  $\psi_n$  alone, we can extract everything: energies, probabilities, expectation values

The particle can also exist in a **superposition** of these states:

$$\Psi(x) = c_1\psi_1(x) + c_2\psi_2(x) + \dots$$

This is also a valid state function, and Postulate I tells us it contains all the information about the system.

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## Postulate II — Observables and Operators

**For every observable (measurable quantity) in classical mechanics, there is a corresponding linear, Hermitian operator in quantum mechanics. The operator is obtained by replacing classical variables with their quantum-mechanical counterparts.**

### The Replacement Rules

$$x \rightarrow \hat{x} = x \quad (\text{multiplication})$$

$$p_x \rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

Any classical quantity expressed as  $A(x, p)$  becomes  $\hat{A}(\hat{x}, \hat{p})$ .

### Table of Important Operators

Observable	Classical	Operator $\hat{A}$
Position	$x$	$x$
Momentum	$p_x$	$-i\hbar \frac{\partial}{\partial x}$
Kinetic energy	$\frac{p_x^2}{2m}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$V(x)$
Total energy	$H = T + V$	$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$
Angular momentum ( $z$ )	$L_z = xp_y - yp_x$	$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$

### PIB Example: Building the Hamiltonian

For the PIB ( $V = 0$  inside,  $V = \infty$  outside):

$$\hat{H}_{\text{PIB}} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (0 < x < a)$$

Acting on  $\psi_n$ :

$$\hat{H}\psi_n = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left[ \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \right] = \frac{n^2\pi^2\hbar^2}{2ma^2} \psi_n = E_n \psi_n$$

The PIB wavefunctions are **eigenfunctions** of  $\hat{H}$  with **eigenvalues**  $E_n$  — we built the operator from the classical recipe, and the known energies emerge automatically.

## Linearity

An operator  $\hat{A}$  is **linear** if:

$$\hat{A}(c_1 f + c_2 g) = c_1 \hat{A}f + c_2 \hat{A}g$$

All quantum-mechanical operators are linear.

[!NOTE] **Concept Check 8.1** Classically, kinetic energy is expressed as  $T = p^2/(2m)$ . Using the operator for momentum  $\hat{p} = -i\hbar \frac{d}{dx}$ , show that the quantum kinetic energy operator is indeed  $\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ . Then verify that  $\psi_2 = \sqrt{2/a} \sin(2\pi x/a)$  is an eigenfunction by applying  $\hat{T}$  to it.

## Hermitian Operators

An operator  $\hat{A}$  is **Hermitian** (self-adjoint) if:

$$\int \psi_1^* \hat{A} \psi_2 dx = \int (\hat{A}\psi_1)^* \psi_2 dx$$

or equivalently in Dirac notation:  $\langle \psi_1 | \hat{A} | \psi_2 \rangle = \langle \hat{A}\psi_1 | \psi_2 \rangle$ .

**Why Hermitian?** Because Hermitian operators guarantee:

1. **Real eigenvalues** — measurement outcomes must be real numbers
2. **Orthogonal eigenfunctions** — eigenfunctions belonging to different eigenvalues are orthogonal

### Proof: Eigenvalues are Real

If  $\hat{A}\psi = a\psi$ :

$$\int \psi^* \hat{A}\psi dx = a \int |\psi|^2 dx = a$$

$$\int (\hat{A}\psi)^*\psi dx = a^* \int |\psi|^2 dx = a^*$$

Hermiticity requires these to be equal, so  $a = a^*$ , meaning  $a$  is real. ■

### PIB Verification: Orthogonality

For the PIB,  $\hat{H}$  is Hermitian, so its eigenfunctions must be orthogonal. Indeed:

$$\int_0^a \psi_m^*(x)\psi_n(x) dx = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx = \delta_{mn}$$

The  $n = 1$  and  $n = 2$  states are orthogonal — physically, they represent completely distinguishable states with different energies.

## Postulate III — Measurement

**When a measurement of observable  $A$  is made on a system in state  $\Psi$ , the only possible results are the eigenvalues  $\{a_n\}$  of the corresponding operator  $\hat{A}$ .**

$$\hat{A}\psi_n = a_n\psi_n$$

### Implications

- Measurement *always* yields one of the eigenvalues — never anything in between
- If the system is in an eigenstate  $\psi_n$ , measurement gives  $a_n$  with certainty
- If the system is in a superposition, the result is probabilistic (Postulate IV, next lecture)

### PIB Example: What Can You Measure?

If you measure the **energy** of a particle in a box, the only possible results are:

$$E_n = \frac{n^2 h^2}{8ma^2}, \quad n = 1, 2, 3, \dots$$

You can *never* measure an energy between  $E_1$  and  $E_2$ . Even if the particle is in a superposition  $\Psi = c_1\psi_1 + c_2\psi_2$ , you will measure either  $E_1$  or  $E_2$  — never  $(E_1 + E_2)/2$ .

[!NOTE] **Concept Check 8.2** A particle in a box is in the state  $\Psi = \frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{2}}\psi_3$ . (a) If you measure the energy, what values can you get? (b) Can you ever measure  $E_2$ ? Why or why not? (c) Is the average energy  $(E_1 + E_3)/2$ ?

## Eigenvalue Equations — Worked Example

### Is a PIB wavefunction an eigenfunction of momentum?

Apply  $\hat{p} = -i\hbar \frac{d}{dx}$  to  $\psi_1 = \sqrt{2/a} \sin(\pi x/a)$ :

$$\hat{p}\psi_1 = -i\hbar \sqrt{\frac{2}{a}} \cdot \frac{\pi}{a} \cos\left(\frac{\pi x}{a}\right)$$

This is proportional to  $\cos(\pi x/a)$ , not  $\sin(\pi x/a)$ . Therefore  $\psi_1$  is **not** an eigenfunction of  $\hat{p}$ .

Physical interpretation: a PIB state has definite energy but *not* definite momentum — the particle bounces back and forth, with equal probability of moving left or right.

## Discrete vs. Continuous Spectra

	Discrete	Continuous
Example	Particle in a box	Free particle
Eigenvalues	$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$	$E = \frac{\hbar^2 k^2}{2m}$ (any $k$ )
Normalization	$\int  \psi_n ^2 dx = 1$	$\int \psi_k^* \psi_{k'} dx = \delta(k - k')$

## Key Equations Summary

Equation	Expression
Postulate I	$\Psi(\mathbf{r}, t)$ fully specifies the state
Postulate II	Observables $\rightarrow$ linear Hermitian operators
Postulate III	Measurements yield eigenvalues only
PIB eigenvalue eq.	$\hat{H}\psi_n = E_n\psi_n$
Hermiticity condition	$\int \psi_1^* \hat{A} \psi_2 dx = \int (\hat{A}\psi_1)^* \psi_2 dx$
Orthogonality	$\int \psi_m^* \psi_n dx = \delta_{mn}$

## Recent Literature Spotlight

"Catalytic Hydrogenation Dominated by Concerted Hydrogen Tunneling at Room Temperature" *B. Wüstenberg, T. N. Ponath, G. T. Vries, P. Chen, et al.*, JACS, **2024**, 146, 32263–32268. [DOI](#)

This study provides compelling evidence that quantum mechanical hydrogen tunneling can dominate a chemical reaction pathway at room temperature. Using kinetic isotope effects and Arrhenius analysis, the authors show that a catalytic hydrogenation proceeds primarily through a concerted tunneling mechanism — an operator eigenvalue problem made real in an enzyme active site.

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## Practice Problems

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- 1. Hermiticity.** Show that  $\hat{p} = -i\hbar \frac{d}{dx}$  is Hermitian. (Hint: use integration by parts and assume wavefunctions vanish at  $\pm\infty$ .)
  - 2. PIB eigenvalue check.** Apply  $\hat{H}$  to the PIB wavefunction  $\psi_3(x) = \sqrt{2/a} \sin(3\pi x/a)$  and verify that the eigenvalue is  $E_3 = 9\hbar^2/(8ma^2)$ .
  - 3. Operator construction.** Construct the quantum-mechanical operator for the angular momentum component  $L_z = xp_y - yp_x$ . Verify that it is equivalent to  $-i\hbar \frac{\partial}{\partial \phi}$  in cylindrical coordinates.
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Next lecture: Postulates IV–VI — Expansion, Expectation Values & Time Evolution