

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

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

Learning Objectives

- 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
-

Postulate I — The State Function

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 Ψ .

Key Implications

- Ψ contains *all* information about the system
- $|\Psi|^2$ gives the probability density (Born interpretation, Lecture 7)
- Ψ 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 ψ_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.

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 ψ_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 Ψ , 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 ψ_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 ψ_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.

Practice Problems

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.
-

Next lecture: Postulates IV–VI — Expansion, Expectation Values & Time Evolution