Quantum Mechanics I

PHY 3103

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The Postulates of Quantum Mechanics

The Postulates of QM

Postulate 1. The state of a quantum-mechanical system is completely specified by a wavefunction Ψ that depends on the coordinates and time. The square of this function $\Psi^*\Psi$ gives the probability density for finding the system with a specified set of coordinate values.

The wavefunction must be single-valued, finite and continuous.	$\int \Psi^*\Psi \, d\tau = 1$

The Postulates of QM

Postulate 2. Every observable in quantum mechanics is represented by a linear, hermitian operator.

A linear operator is one which satisfies the identity $\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\hat{A}\psi_1 + c_2\hat{A}\psi_2$

Postulate 3. In any measurement of an observable A, associated with an operator $\hat{A}$, the only possible results are the eigenvalues a_n, which satisfy an eigenvalue equation

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

The Postulates of QM

Postulate 4. For a system in a state described by a normalized wave function Ψ, the average or expectation value of the observable corresponding to A is given by

$$\langle A \rangle = \int \Psi^* \hat{A} \, \Psi \, d\tau$$

Postulate 5. The wavefunction of a system evolves in time in accordance with the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \, \Psi$$

Time-dependent Schrödinger wave equation

$$i\hbar \frac{\partial \Psi(x,\, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,\, t)}{\partial x^2} + V\Psi(x,\, t)$$

Time-independent Schrödinger wave equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$
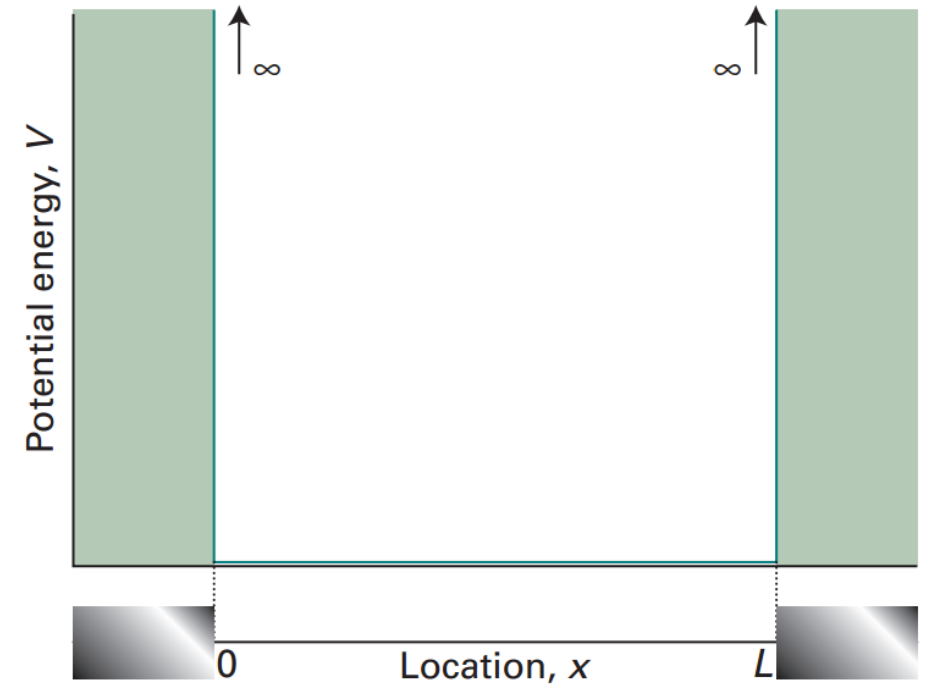
Infinite Square-Well Potential
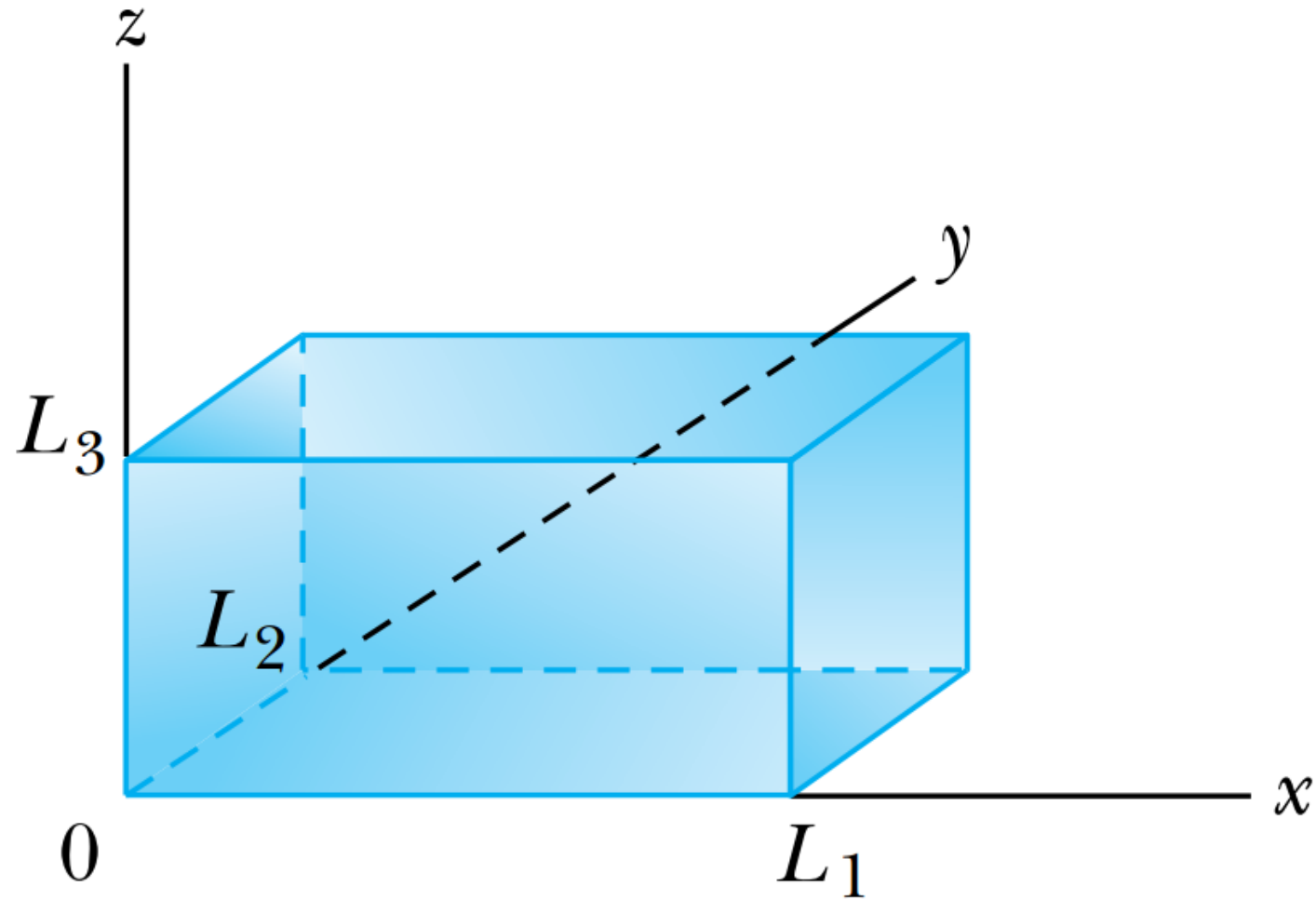
Infinite-Potential Well

Particle in a box

Infinite Square-Well Potential

$$V(x) = \begin{cases} \infty & x \le 0, \; x \ge L \\ 0 & 0 < x < L \end{cases}$$

Particle in a Box

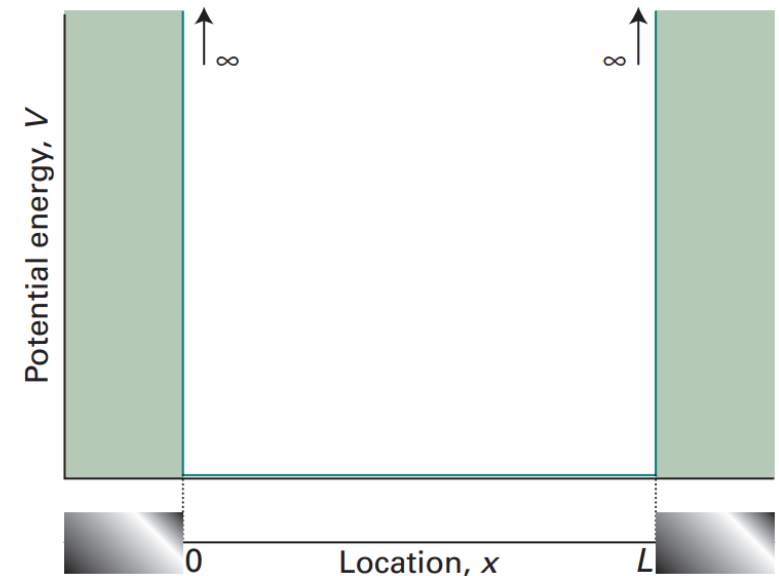# Infinite Square-Well Potential

One dimensional time-independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

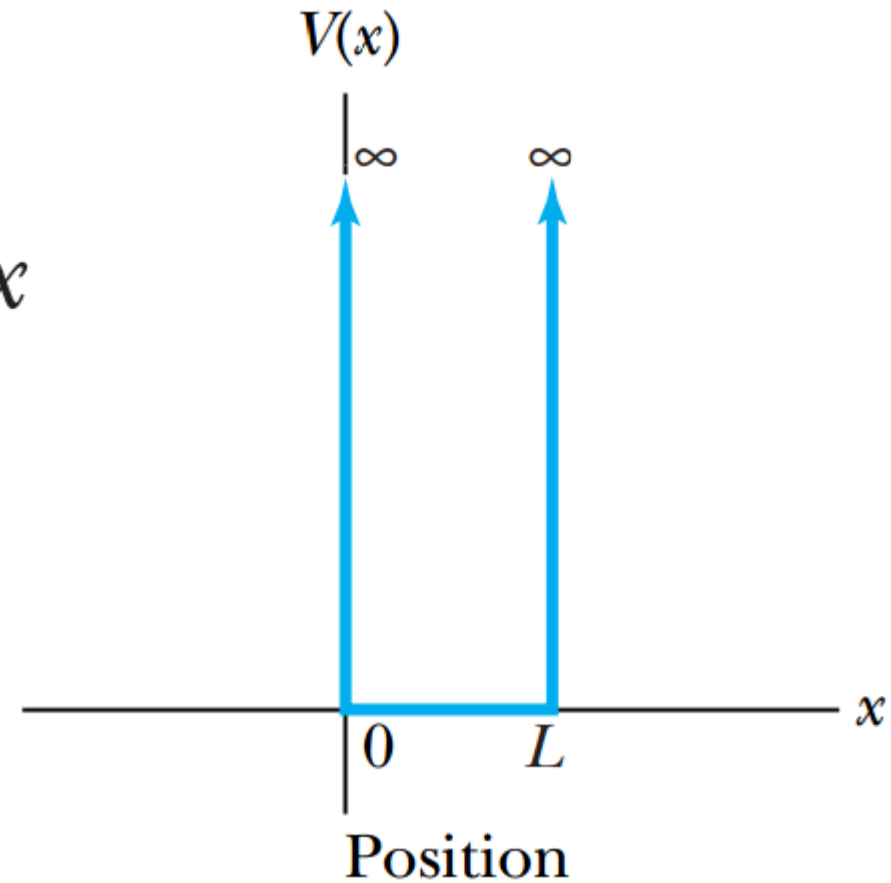$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)}$$

Infinite Square-Well Potential

A suitable solution is

$$\psi(x) = A \sin kx + B \cos kx$$

$$\psi(x = 0) = 0 \qquad\qquad B = 0$$

$$\psi(x = L) = 0 \qquad\qquad kL = n\pi$$

Infinite Square-Well Potential

The wave function is

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \quad (n = 1, 2, 3, \ldots)$$

The normalized wave function is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (n = 1, 2, 3, \ldots)$$
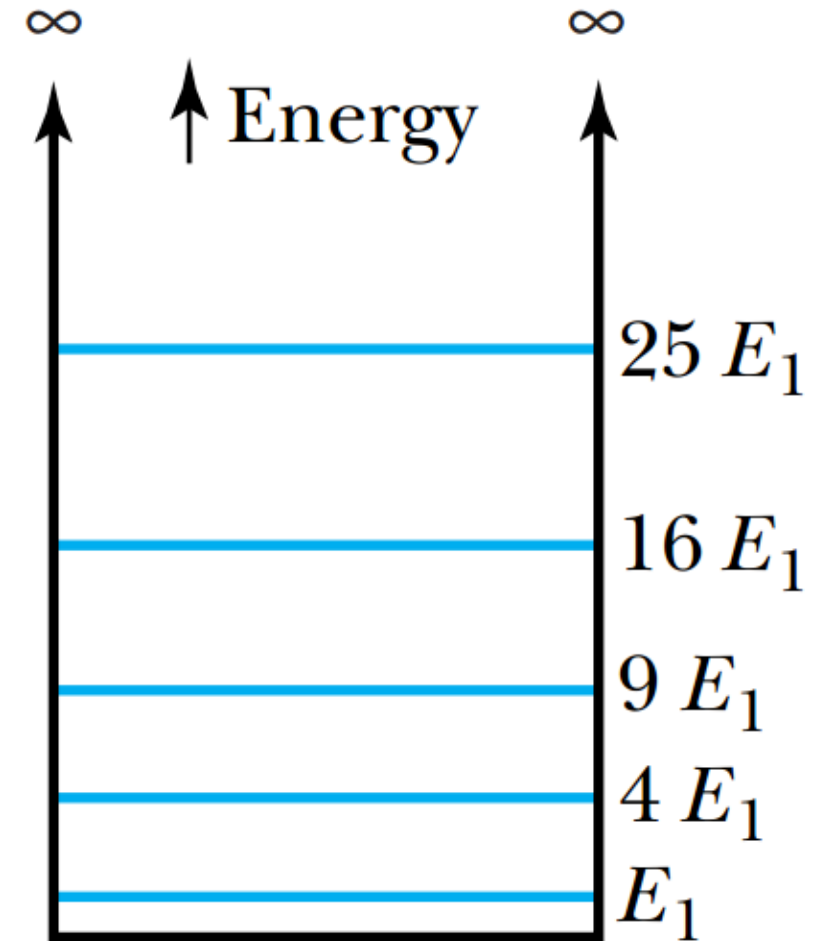
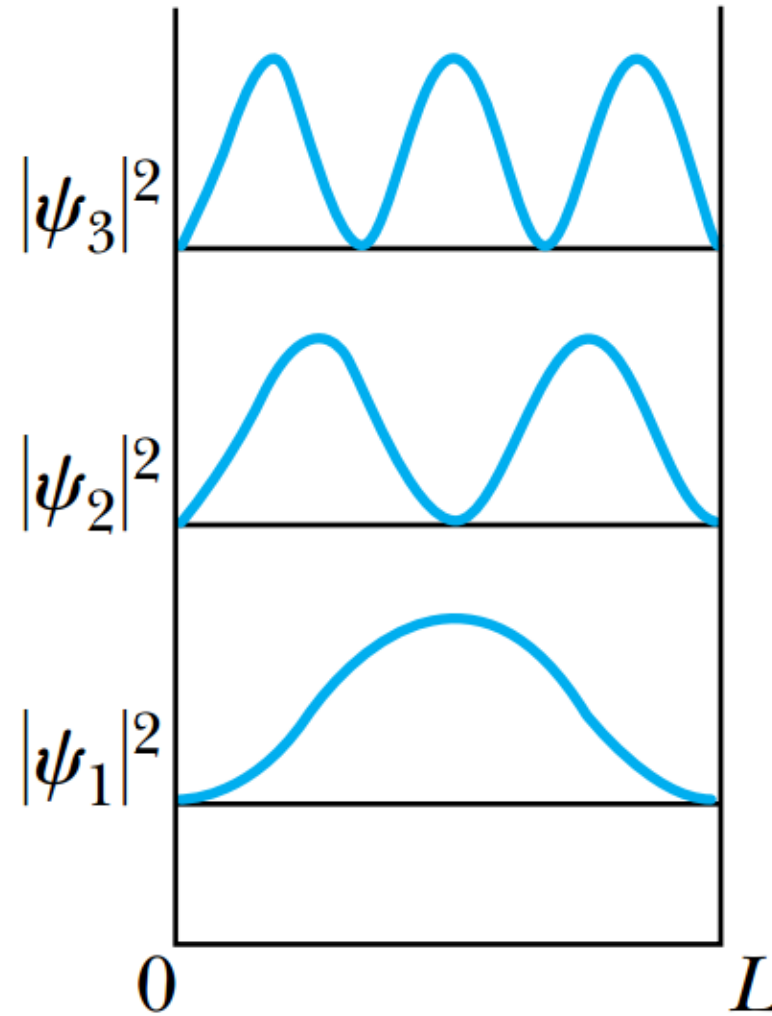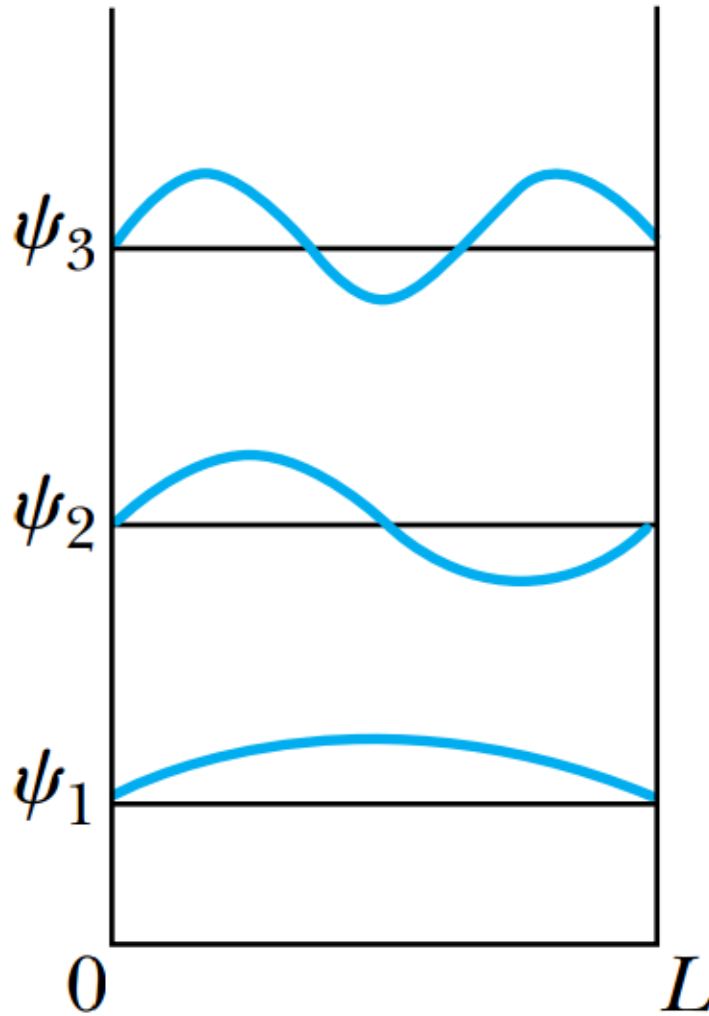# Infinite Square-Well Potential

$$k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$$

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \ldots)$$

Quantized energy levels

Infinite Square-Well Potential

Infinite Square-Well Potential

The normalized wave function is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (n = 1, 2, 3, \ldots)$$

Quantized energy levels

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \ldots)$$

The expectation value of the position

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\psi|^2 \, dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} \, dx$$

$$= \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8(n\pi/L)^2} \right]_0^L$$

$$= \frac{2}{L} \left(\frac{L^2}{4} \right) = \frac{L}{2}$$

The expectation value of the position

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi \, dx = \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \psi \, dx$$

$$= \frac{\hbar}{i} \frac{2}{L} \frac{n\pi}{L} \int_0^L \sin \frac{n\pi x}{L} \cos \frac{n\pi x}{L} \, dx$$

$$= \frac{\hbar}{iL} \left[\sin^2 \frac{n\pi x}{L} \right]_0^L = 0$$

The expectation value of the momentum

$$E = p^2/2m.$$

$$p_n = \pm \sqrt{2mE_n} = \pm \frac{n\pi\hbar}{L}$$

$$p_{av} = \frac{(+n\pi\hbar/L) + (-n\pi\hbar/L)}{2} = 0$$

$$\hat{p}\psi_n = p_n\psi_n$$

The expectation value of the momentum

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{1}{2i} e^{i\theta} - \frac{1}{2i} e^{-i\theta}$$

Momentum eigenfunctions for trapped particle

$$\psi_n^+ = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{in\pi x/L}$$

$$\psi_n^- = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{-in\pi x/L}$$

The expectation value of the momentum

$$\hat{p}\psi_n^+ = p_n^+ \psi_n^+$$

$$p_n^+ = +\frac{n\pi\hbar}{L}$$

Similarly the wave function ψ_n^- leads to
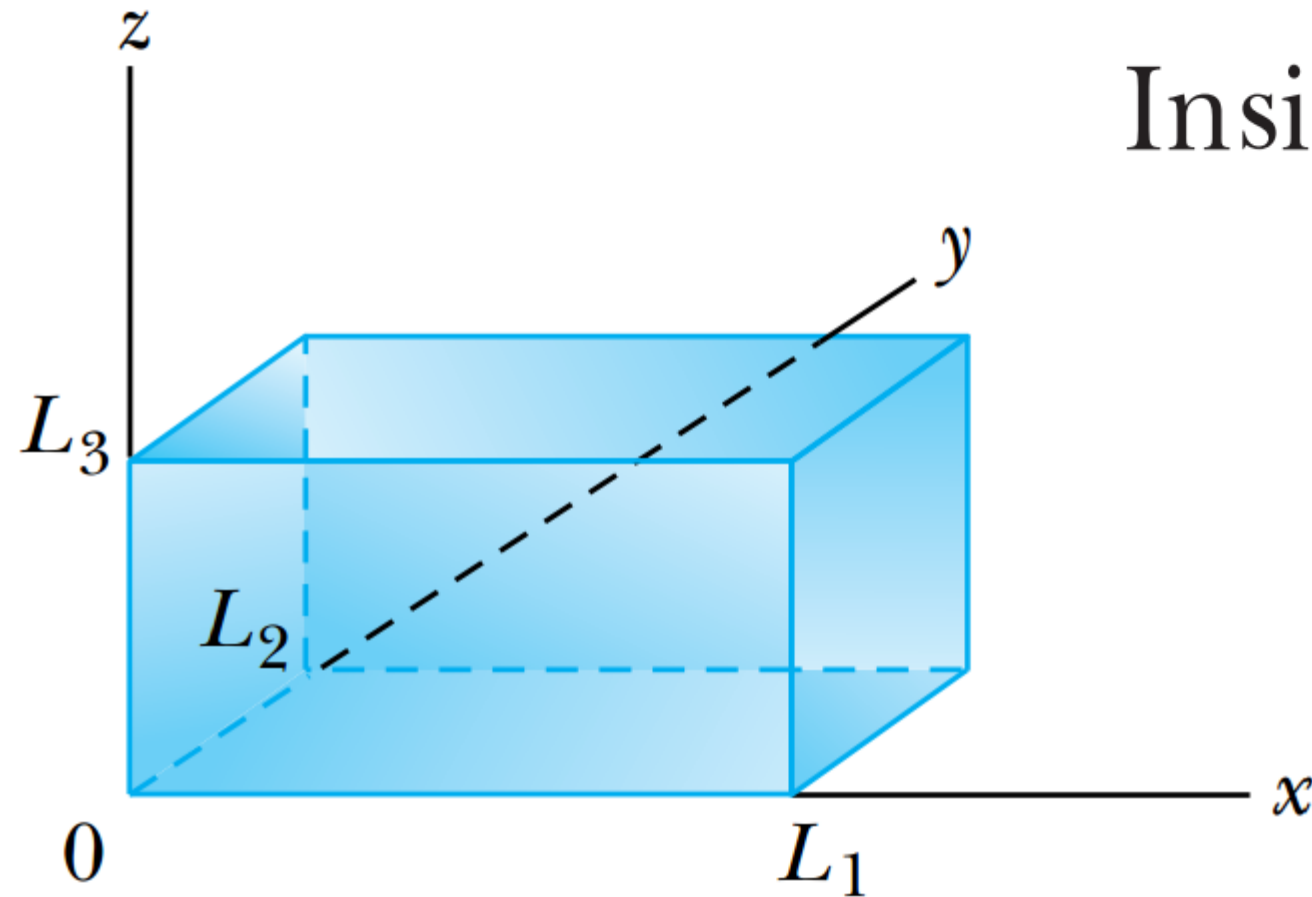
$$p_n^- = -\frac{n\pi\hbar}{L}$$

Determine the expectation values for x, x^2, p, and p^2 of a particle in an infinite square well for the first excited state.

The first excited state corresponds to $n = 2$.

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$$

Three-Dimensional Infinite-Potential Well

Inside the box $V = 0$

Three-Dimensional Infinite-Potential Well

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + V\psi = E\psi$$

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

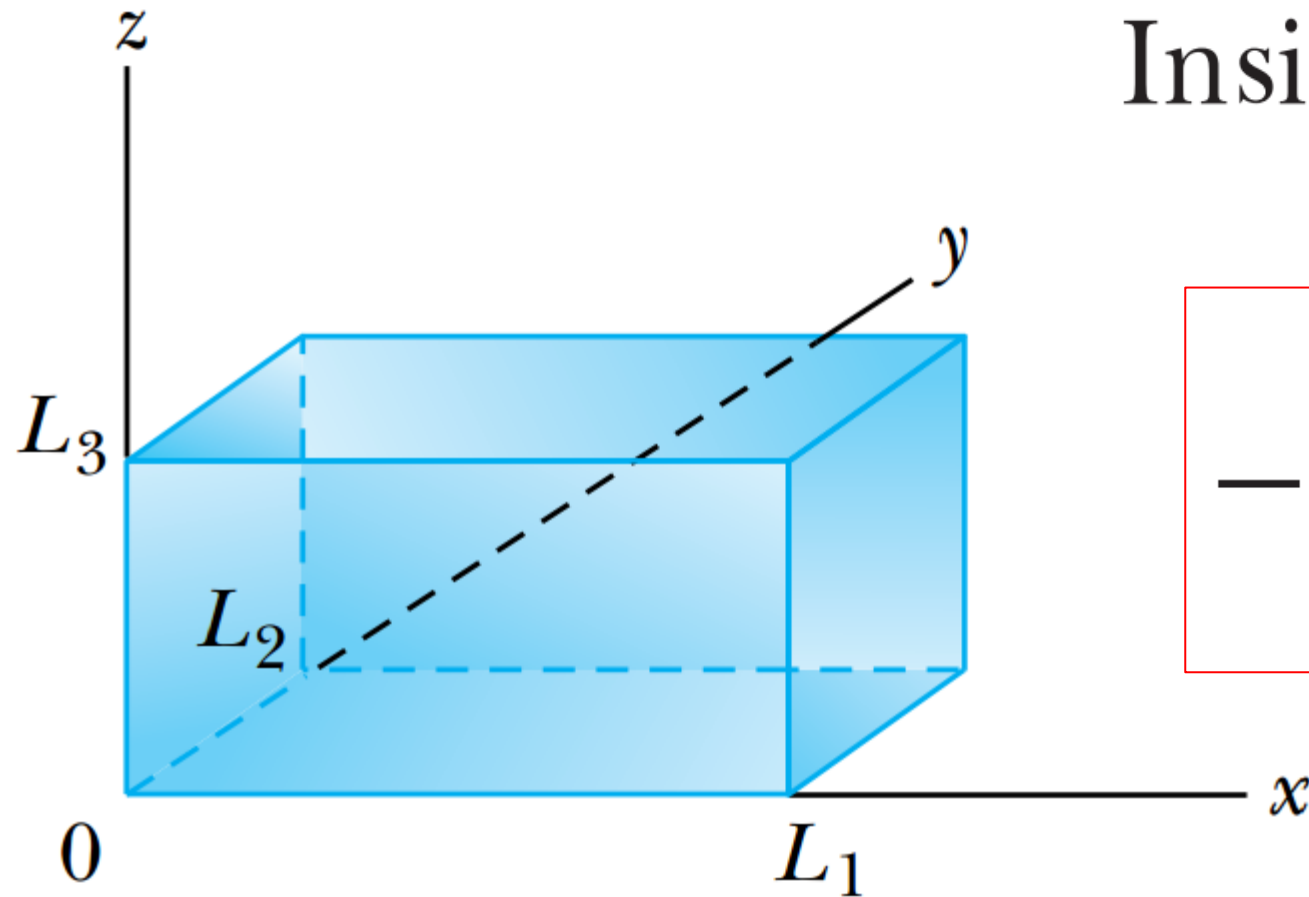$$\hat{p}_y \psi = -i\hbar\frac{\partial \psi}{\partial y}$$

$$\hat{p}_z \psi = -i\hbar\frac{\partial \psi}{\partial z}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

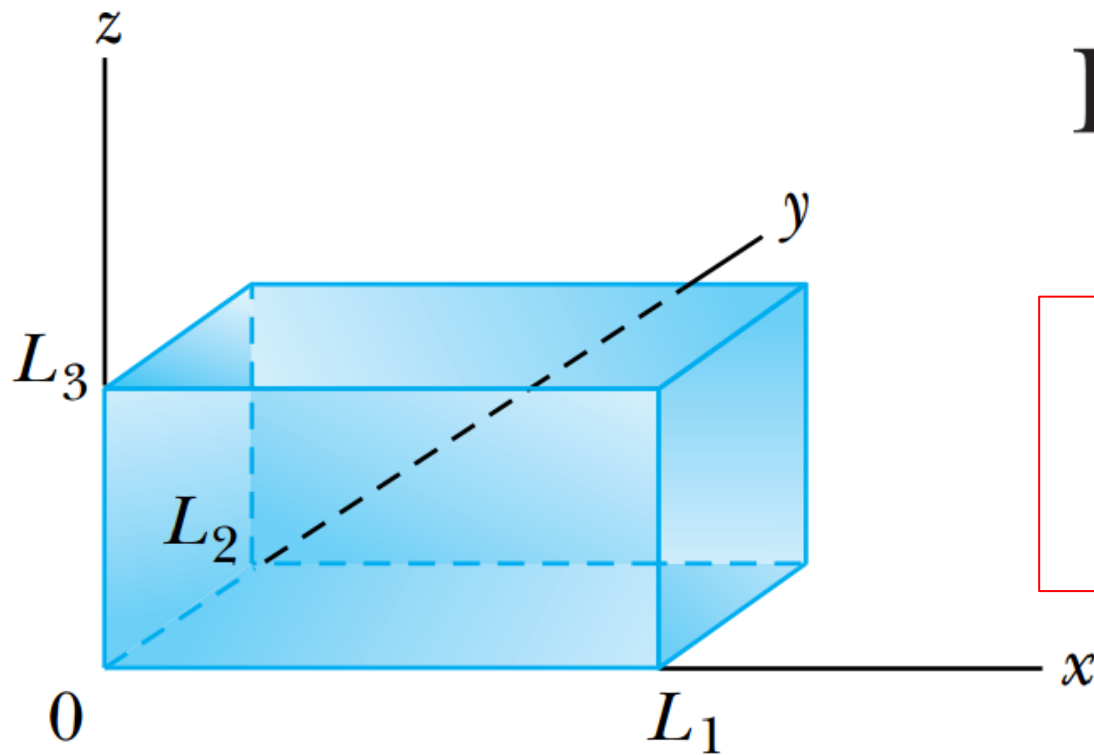$$-\frac{\hbar^2}{2m}\nabla^2 \psi + V\psi = E\psi$$

Three-Dimensional Infinite-Potential Well

Inside the box $V = 0$

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

Three-Dimensional Infinite-Potential Well

Inside the box $V = 0$

$$k_1 = \frac{n_1\pi}{L_1} \qquad k_2 = \frac{n_2\pi}{L_2} \qquad k_3 = \frac{n_3\pi}{L_3}$$

$$\psi(x, y, z) = A \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$$

Three-Dimensional Infinite-Potential Well

$$\frac{\partial \psi}{\partial x} = \frac{\partial}{\partial x}\left[A \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)\right]$$

$$= k_1 A \cos(k_1 x)\sin(k_2 y)\sin(k_3 z)$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x}\left[k_1 A \cos(k_1 x)\sin(k_2 y)\sin(k_3 z)\right]$$

$$= -(k_1)^2 A \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$$

$$= -k_1^2 \psi$$

Three-Dimensional Infinite-Potential Well

$$\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)\psi = E\psi$$

Three-Dimensional Infinite-Potential Well

$$E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)$$

$$E = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)$$

The allowed energy values depend on the values of the three quantum numbers n_1, n_2, and n_3.

For the *cubical* box, with $L_1 = L_2 = L_3 = L$.

$$E = \frac{\pi^2 \hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$$

$$n_1 = n_2 = n_3 = 1$$

$$\psi_{gs} = A \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

Three-Dimensional Infinite-Potential Well

What is the energy of the first excited state?

$$E = \frac{\pi^2 \hbar^2}{2 m L^2}(n_1^2 + n_2^2 + n_3^2)$$

What is the energy of the first excited state? Higher values of the quantum numbers n_i correspond to higher energies; therefore, it is logical to try something like $n_1 = 2$, $n_2 = 1$, and $n_3 = 1$. But we could just as well assign quantum numbers $n_1 = 1$, $n_2 = 2$, $n_3 = 1$ to the first excited state, or $n_1 = 1$, $n_2 = 1$, $n_3 = 2$. In each of these cases the total energy is

$$E_{1st} = \frac{\pi^2 \hbar^2}{2mL^2}(2^2 + 1^2 + 1^2) = \frac{3\pi^2 \hbar^2}{mL^2}$$

Three-Dimensional Infinite-Potential Well

n_1	n_2	n_3	E
1	1	1	E_{gs}
2	1	1	$2E_{\text{gs}}$
1	2	1	$2E_{\text{gs}}$
1	1	2	$2E_{\text{gs}}$
2	2	1	$3E_{\text{gs}}$
2	2	2	$4E_{\text{gs}}$

$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

$$\boxed{E_{\text{gs}} = \frac{3\pi^2 \hbar^2}{2mL^2}}$$

Degenerate State

In physics we say that a given state is degenerate when there is more than one wave function for a given energy.

In our case all three possible wave functions for the first excited state have the same energy. The degeneracy in this case is a result of the symmetry of the cube.

If the box had sides of three different lengths, we say the degeneracy is removed, because the three quantum numbers in different orders (211, 121, 112) would result in three different energies.

Correspondence principle

The behavior of systems described by the theory of quantum mechanics reproduces classical physics in the limit of large quantum numbers.

Complementarity principle

Certain pairs of complementary properties which cannot all be observed or measured simultaneously.

- Position and momentum
- Energy and duration