Lecture 6 — Free Particle & Particle in a 1-D Infinite Box

Reading: Engel 4th ed., Chapter 4 (Sections 4.1–4.2)

Learning Objectives

- Solve the TISE for a free particle and discuss the continuous energy spectrum
- Solve the TISE for a particle in a 1-D infinite square well by applying boundary conditions
- Sketch the wavefunctions and probability densities for the lowest energy levels
- Explain quantization as a consequence of boundary conditions
- Calculate energies, wavelengths, and transition frequencies for confined particles

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1. The Free Particle ($V = 0$ everywhere)

The TISE becomes:

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

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k = \frac{\sqrt{2mE}}{\hbar}$$

General solution:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

- Ae^{ikx}: traveling wave moving in $+x$ direction with momentum $p = +\hbar k$
- Be^{-ikx}: traveling wave moving in $-x$ direction with momentum $p = -\hbar k$

Energy: $E = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$ — any non-negative value is allowed (continuous spectrum).

Key point: No boundary conditions → no quantization. The free particle has a continuous energy spectrum.

> [!NOTE] **Concept Check 6.1** A free particle is described by the state $\psi(x) = Ae^{ikx}$. If you measure the momentum of this particle, what result(s) can you obtain? What is the uncertainty in its position (Δx)?

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2. Particle in a 1-D Infinite Square Well (Particle in a Box)

The Potential

$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & x < 0 \text{ or } x > a \end{cases}$$

The particle is confined to the region $[0, a]$ by infinitely high walls.

Boundary Conditions

Since $V = \infty$ outside the box, $\psi = 0$ for $x \le 0$ and $x \ge a$.

Continuity of ψ requires:

$$\psi(0) = 0, \qquad \psi(a) = 0$$

Solution Inside the Box

The TISE inside ($V = 0$):

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad k = \frac{\sqrt{2mE}}{\hbar}$$

General solution: $\psi(x) = Ce^{ikx} + De^{-ikx}$

From Exponential to Trigonometric Form: For a confined particle, it is often more convenient to express the wavefunction in terms of trigonometric functions. Using Euler's formula, $e^{\pm ikx} = \cos(kx) \pm i\sin(kx)$, we can rewrite the general solution:

$$\psi(x) = C(\cos(kx) + i\sin(kx)) + D(\cos(kx) - i\sin(kx)) \; \psi(x) = (C + D)\cos(kx) + i(C - D)\sin(kx)$$

By defining new constants $A = i(C - D)$ and $B = C + D$, we obtain: $\psi(x) = A\sin(kx) + B\cos(kx)$

This form makes applying the boundary conditions at $x = 0$ much simpler.

Apply $\psi(0) = 0$:

$A\sin(0) + B\cos(0) = B = 0$

So $\psi(x) = A\sin(kx)$.

Apply $\psi(a) = 0$:

$A\sin(ka) = 0$

Since $A \neq 0$ (otherwise $\psi = 0$ everywhere), we need $\sin(ka) = 0$:

$ka = n\pi, \quad n = 1, 2, 3, \ldots$

(We exclude $n = 0$ because it gives $\psi = 0$, and negative n values give the same functions.)

> [!NOTE] **Concept Check 6.2** Why must we exclude $n = 0$ as a valid quantum number for the particle in a box? (Hint: Consider both the normalization condition and the uncertainty principle.)

Quantized Energies

$k_n = \frac{n\pi}{a} \implies E_n = \frac{\hbar^2 k_n^2}{2m}$

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2}, \quad n = 1, 2, 3, \ldots}$$

Key Features of the Energy Spectrum

1. **Quantization:** Only discrete energies are allowed — a direct result of confinement + boundary conditions
2. **Zero-point energy:** $E_1 = \frac{h^2}{8ma^2} \neq 0$ — consistent with the uncertainty principle
3. **Quadratic spacing:** $E_n \propto n^2$ — energy levels get farther apart as n increases
4. **Size dependence:** $E_n \propto 1/a^2$ — smaller box → larger energy gaps
5. **Mass dependence:** $E_n \propto 1/m$ — lighter particles → larger energy gaps

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)}$$

Derivation of the Normalization Constant (A): To ensure the total probability of finding the particle in the box is 1, we must satisfy the normalization condition: $\int_0^a |\psi_n(x)|^2 dx = 1$

Substitute $\psi_n(x) = A\sin(\frac{n\pi x}{a})$: $A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$

Using the trigonometric identity $\sin^2\theta = \frac{1-\cos(2\theta)}{2}$: $A^2 \int_0^a \frac{1-\cos(\frac{2n\pi x}{a})}{2} dx = 1$
$\frac{A^2}{2}\left[\int_0^a dx - \int_0^a \cos\left(\frac{2n\pi x}{a}\right) dx\right] = 1$

The second integral is zero over a full period (or n periods): $\frac{A^2}{2}\left[x - \frac{a}{2n\pi}\sin\left(\frac{2n\pi x}{a}\right)\right]_0^a = 1$
$\frac{A^2}{2}[a-0] = 1 \implies \frac{A^2 a}{2} = 1$ $\boxed{A = \sqrt{\frac{2}{a}}}$

Orthogonality

$\int_0^a \psi_m^*(x)\,\psi_n(x)\,dx = \delta_{mn} = \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$

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3. Properties of the Solutions

Wavefunctions $\psi_n(x)$

- ψ_n has $n-1$ **nodes** (zeros inside the box)
- More nodes → higher kinetic energy (more oscillatory → steeper curvature)
- Each ψ_n has definite **parity** about the center $x = a/2$:
  - n odd: symmetric (even parity about center)
  - n even: antisymmetric (odd parity about center)

Probability Density $|\psi_n(x)|^2$

- **Ground state ($n = 1$):** Maximum probability at center, zero at walls
- **Higher states:** n equal probability maxima, $n-1$ nodes
- In the classical limit ($n \to \infty$), the probability becomes uniform — the **correspondence principle**

Classical Limit

For large n, the closely-spaced oscillations of $|\psi_n|^2$ average to a uniform distribution (particle equally likely everywhere), matching the classical prediction. The energy spacing becomes negligible compared to the total energy: $\Delta E/E \approx 2/n \to 0$.

> [!NOTE] **Concept Check 6.3** For the $n = 3$ state of a particle in a box, (a) how many nodes does the wavefunction have? (b) At what positions x are you most likely to find the particle? (c) At what positions is the probability of finding the particle exactly zero?

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4. Worked Example

Problem: An electron is confined to a 1-D box of length $a = 1.0$ nm. Calculate E_1, E_2, and the wavelength of light needed for the $1 \rightarrow 2$ transition.

Solution:

$E_n = \frac{n^2 h^2}{8 m_e a^2} = \frac{n^2 (6.626 \times 10^{-34})^2}{8(9.109 \times 10^{-31})(1.0 \times 10^{-9})^2}$

$E_1 = 6.02 \times 10^{-20} \text{ J} = 0.376 \text{ eV}$

$E_2 = 4 \times E_1 = 2.41 \times 10^{-19} \text{ J} = 1.504 \text{ eV}$

$\Delta E = E_2 - E_1 = 3E_1 = 1.81 \times 10^{-19} \text{ J}$

$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34})(3.0 \times 10^8)}{1.81 \times 10^{-19}} = 1100 \text{ nm (near-IR)}$

Key Equations Summary

Equation	Expression
Free particle energy	$E = \hbar^2 k^2 / (2m)$, continuous
PIB energies	$E_n = n^2 h^2 / (8ma^2)$
PIB wavefunctions	$\psi_n = \sqrt{2/a} \sin(n\pi x / a)$
Number of nodes	$n - 1$
Transition energy	$\Delta E = (n_f^2 - n_i^2) h^2 / (8ma^2)$

Recent Literature Spotlight

"Highly Efficient and Stable InP/ZnSe/ZnS Quantum Dot Light-Emitting Diodes" *Y.-H. Won, O. Cho, T. Kim, D.-Y. Chung, T. Kim, et al.*, Nature, **2019**, 575, 634–638. DOI

Quantum dots are real-world "particles in a box" — semiconductor nanocrystals whose optical properties are governed by quantum confinement. This paper reports InP quantum dot LEDs reaching 21.4% external quantum efficiency using environmentally friendly cadmium-free materials. The emission wavelength is tuned by simply changing the dot size, exactly as the particle-in-a-box model predicts: smaller confinement → larger energy gap → shorter wavelength emission. This work was recognized as part of the 2023 Nobel Prize in Chemistry for quantum dot research.

Practice Problems

1. **Energy levels.** Calculate the first three energy levels of a proton confined to a box of width $a = 10$ fm (10^{-14} m, roughly the size of a nucleus). Express your answers in MeV.

2. **Nodes and probability.** For $n = 3$ in the particle in a box, (a) identify the positions of the nodes, (b) find the position(s) of maximum probability density.

3. **Correspondence principle.** Calculate the fractional energy spacing $(E_{n+1} - E_n)/E_n$ for $n = 1$, $n = 10$, and $n = 1000$. At what level does the system behave essentially classically?

Next lecture: Probability Interpretation & Normalization — Using the Particle in a Box