Lecture 12 — Finite Potential Well & Quantum Tunneling

Reading: Engel 4th ed., Chapter 4 (Sections 4.5–4.7)

Learning Objectives

- Contrast the finite and infinite potential wells qualitatively and quantitatively
- Explain the physical meaning of wavefunction penetration into classically forbidden regions
- Derive and apply the transmission coefficient for rectangular barriers
- Describe quantum tunneling and its role in chemistry (proton transfer, STM, nuclear fusion)
- Recognize when tunneling is significant vs. negligible

1. The Finite Potential Well

The Potential

$$V(x) = \begin{cases} 0 & |x| \leq L/2 \\ V_0 & |x| > L/2 \end{cases}$$

where V_0 is finite (not infinite).

Qualitative Differences from the Infinite Well

Feature	Infinite well	Finite well
Wavefunction at walls	Exactly zero	Nonzero (penetrates into barriers)
Number of bound states	Infinite	Finite (depends on V_0 and L)
Energies	$E_n = n^2 h^2/(8ma^2)$	Lower than infinite well values
"Effective" box size	Exactly L	Greater than L (particle "leaks" out)

Inside the Well ($|x| < L/2$, $E < V_0$):

$$\psi(x) = A\cos(kx) + B\sin(kx), \quad k = \frac{\sqrt{2mE}}{\hbar}$$

Outside the Well ($|x| > L/2$):

$$\psi(x) = Ce^{-\kappa x} + De^{\kappa x}, \quad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

Physical requirement: $\psi \to 0$ as $|x| \to \infty$ (normalizability).

Key Result: Wavefunction Penetration

The wavefunction decays exponentially in the classically forbidden region with a **penetration depth**:

$$\boxed{\delta = \frac{1}{\kappa} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}}$$

- Lighter particles penetrate farther (smaller m)
- Particles with energy close to V_0 penetrate farther
- The probability of finding the particle in the forbidden region is nonzero but small

Matching Conditions

At $x = \pm L/2$, we require:

1. ψ is continuous
2. $d\psi/dx$ is continuous

These matching conditions lead to transcendental equations that determine the allowed energies. They must be solved graphically or numerically — no closed-form solution exists.

Bound State Count

The number of bound states in a 1-D finite well of depth V_0 and width L:

$$N \approx 1 + \text{floor}\left(\frac{L\sqrt{2mV_0}}{\pi\hbar}\right)$$

There is **always at least one** bound state in a 1-D finite well (not true in 3-D!).

2. Quantum Tunneling

The Rectangular Barrier

$$V(x) = \begin{cases} V_0 & 0 \le x \le a \\ 0 & \text{otherwise} \end{cases}$$

A particle with energy $E < V_0$ approaches from the left. Classically, it would be completely reflected. Quantum mechanically, there is a nonzero probability of transmission.

The Transmission Coefficient

For $E < V_0$:

$$\boxed{T \approx e^{-2\kappa a}}$$

where $\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$ and a is the barrier width.

More precisely:

$$T = \frac{1}{1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)}}$$

For thick barriers ($\kappa a \gg 1$), the exponential approximation is excellent.

What Controls Tunneling?

$$T \propto e^{-2a\sqrt{2m(V_0 - E)}/\hbar}$$

Tunneling probability increases when:

- **Barrier is narrow** (small a)
- **Barrier is low** ($V_0 - E$ small)
- **Particle is light** (small m)

> [!NOTE] **Concept Check 12.2** If you double the width of a tunneling barrier ($a \rightarrow 2a$), while keeping the height V_0 and the particle's energy E constant, how does the transmission coefficient T change? (Assume the barrier is "thick" so the exponential approximation holds.)

System	m	Tunneling?
Electron through 1 nm oxide	m_e	Significant
Proton through H-bond barrier	m_p	Measurable
Deuteron (same barrier)	$2m_p$	Reduced by $e^{-\sqrt{2}}$
Carbon atom	$12m_p$	Negligible

3. Chemical Applications of Tunneling

Scanning Tunneling Microscope (STM)

Electrons tunnel from a sharp metal tip across a vacuum gap (~1 nm) to a surface. The tunneling current depends exponentially on the tip-surface distance:

$$I \propto e^{-2\kappa d}$$

This extreme distance sensitivity (factor of ~10 per 0.1 nm) enables **atomic-resolution** imaging. Gerd Binnig and Heinrich Rohrer won the 1986 Nobel Prize for the STM.

Proton Tunneling in Chemistry

- **Proton transfer reactions**: Tunneling contributes significantly to reaction rates, especially at low temperatures
- **Kinetic isotope effect**: Replacing H with D reduces tunneling → measurable rate decrease. The ratio $k_H/k_D > 1$ is a signature of tunneling
- **DNA mutations**: Some theories suggest proton tunneling between base pairs could cause rare tautomeric forms

Nuclear Fusion

In the Sun's core, protons tunnel through Coulomb barriers to fuse — classical energies are far too low. Without tunneling, stars would not shine.

Alpha Decay

George Gamow (1928) first explained radioactive alpha decay as tunneling of an alpha particle through the nuclear potential barrier.

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4. The WKB Approximation (Brief)

For barriers of arbitrary shape $V(x)$, the transmission coefficient can be approximated as:

$$T \approx \exp\left(-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m[V(x) - E]}\, dx\right)$$

where x_1 and x_2 are the classical turning points. This **WKB (Wentzel-Kramers-Brillouin)** approximation is widely used in chemistry for reaction rate calculations.

Key Equations Summary

Equation	Expression
Penetration depth	$\delta = \hbar / \sqrt{2m(V_0 - E)}$
Transmission coefficient	$T \approx e^{-2\kappa a}$
Decay constant	$\kappa = \sqrt{2m(V_0 - E)}/\hbar$
WKB approximation	$T \approx \exp\left(-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V - E)}\, dx\right)$

Recent Literature Spotlight

"Recent Developments in Symmetry-Adapted Perturbation Theory" *K. Patkowski*, WIREs Computational Molecular Science, **2020**, 10, e1452. DOI

This comprehensive review describes how quantum mechanical tunneling and finite-barrier effects are handled in symmetry-adapted perturbation theory (SAPT), the premier method for computing intermolecular interaction energies from first principles. The decomposition into electrostatics, induction, dispersion, and exchange — each arising

from different quantum mechanical operators acting on finite-barrier wavefunctions —
demonstrates the power of perturbation theory for chemical problems.

Practice Problems

1. **Finite well.** An electron is in a finite well of depth $V_0 = 10$ eV and width $L = 0.50$ nm.
   (a) Calculate the penetration depth δ for the ground state energy $E \approx 0.6$ eV. (b) How
   does δ change if the particle is a proton instead?

2. **Tunneling probability.** An electron with $E = 5.0$ eV encounters a rectangular barrier
   of height $V_0 = 10.0$ eV and width $a = 0.50$ nm. Calculate the transmission coefficient.
   Repeat for $a = 1.0$ nm and $a = 2.0$ nm.

3. **Isotope effect.** A proton and a deuteron each encounter the same barrier ($V_0 - E =$
   0.4 eV, $a = 0.05$ nm). Calculate the ratio T_H/T_D. This is related to the kinetic isotope
   effect in chemistry.

Next week: Particle-in-a-Box Applications; Operators & Entanglement