Quantum Mechanics

The Schrödinger equation

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

Erwin Schrödinger

The Nobel Prize in Physics 1933
"for the discovery of new productive forms of atomic theory"

The Schrödinger Equation in One Dimension—Time-Independent Form

The Schrödinger equation cannot be derived (??), just as Newton's laws cannot. However, we know that it must describe a traveling wave, and that energy must be conserved.

Therefore, the wave function will take the form:

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

where

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{p}{\hbar}.$$

Since energy is conserved, we know:

$$\frac{\hbar^2 k^2}{2m} + U = E.$$

This suggests a form for the Schrödinger equation, which experiment shows to be correct:

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

Later: QM

$$p \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$$

The Schrödinger Equation normalisation

Since the solution to the Schrödinger equation is supposed to represent a single particle, the total probability of finding that particle anywhere in space should equal 1:

$$\int_{\text{all space}} |\psi|^2 \, dV \;=\; \int |\psi|^2 \, dx \;=\; 1.$$

When this is true, the wave function is normalized.

Time-Dependent Schrödinger Equation

A more general form of the Schrödinger equation includes time dependence (still in one space dimension):

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

Derivation requires more rigorous methods of QM.

Ψ(x,t) is the wave function dependent on space-time coordinates.

The time-independent Schrödinger equation can be derived from it, using the method of "separation of variables".

Note that this is a non-relativistic wave equation:
A Lorentz-covariant formalism gives the Dirac equation

"Separation of variables" - method

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

Assume the potential to be time-independent *U(x)* , and the trial solution

$$\Psi(x,t) = \psi(x)f(t)$$ **then** $$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi f + U\psi f = i\hbar\frac{d}{dt}\psi f$$

Move space coordinates to left and time to right; divide by Ψ

$$\frac{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + U\psi}{\psi} = \frac{i\hbar\frac{d}{dt}f}{f}$$

Left and right side must be independent, equal to a constant, say λ

$$i\hbar\frac{d}{dt}f = \lambda f$$

Solution: $$f(t) = e^{-i\lambda t/\hbar}$$

Oscillating function of time, with frequency $$\omega = \frac{\lambda}{\hbar}$$

Associated with energy: $$E = \hbar\omega = \lambda$$

Hence: $$f(t) = e^{-iEt/\hbar}$$

Stationairy states in QM

For a QM problem with a time-independent potential *U(x)*

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

The solutions are stationairy states:

$$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^*(x)e^{iEt/\hbar}\psi(x)e^{-iEt/\hbar} = |\psi(x)|^2$$

The probalistic aspects do not vary with time !

Stationairy states may have a time-dependent phase

Free Particles; Plane Waves and Wave Packets

Free particle: no force, so $U = 0$. The Schrödinger equation becomes the equation for a simple harmonic oscillator:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \longrightarrow \frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

Independent solutions $\psi(x) = \cos kx$ $\psi(x) = \sin kx$

Also: $\psi(x) = e^{ikx}$ $\psi(x) = e^{-ikx}$

Superposition principle of quantum mechanics:
Any linear combination of solutions is also a solution

Free Particles;
Plane Waves and Wave Packets

Hence solutions:

$$\psi = A \sin kx + B \cos kx,$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}}.$$

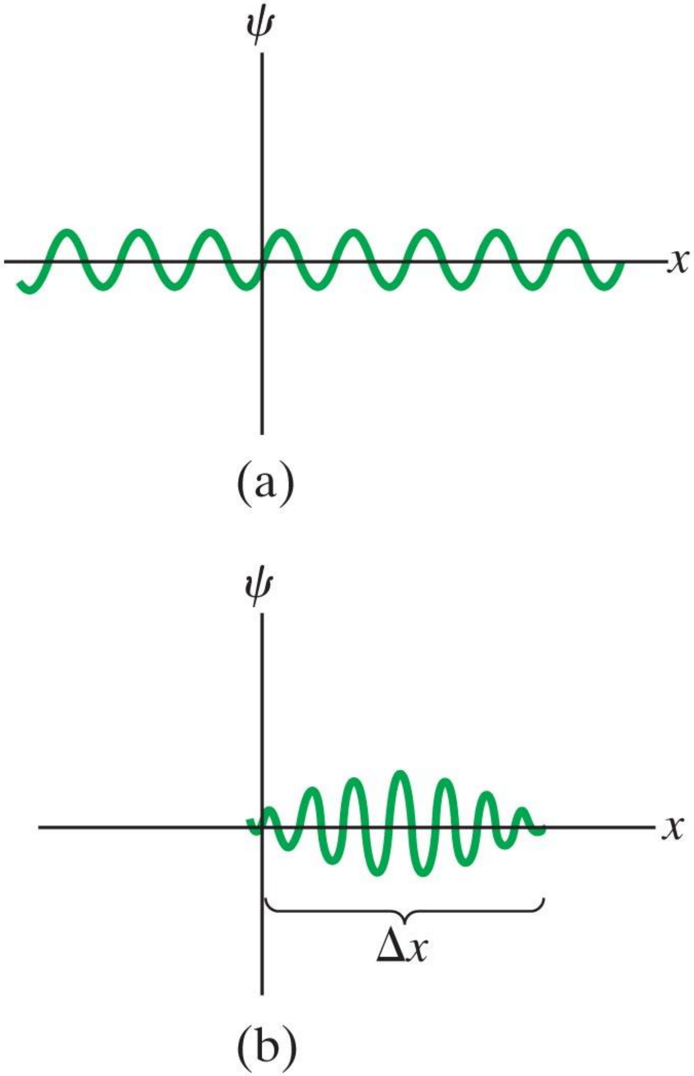
Since $U = 0$, Energy is only kinetic

$$k = \frac{p}{\hbar} = \frac{h}{\lambda \hbar} = \frac{2\pi}{\lambda}.$$

Free Particles;
Plane Waves and Wave Packets

The solution for a free particle is a plane wave, as shown in part (a) of the figure; more realistic is a wave packet, as shown in part (b). The wave packet has both a range of momenta and a finite uncertainty in width.
(normalization problem)

How to describe a wave packet ?



(Famous) Particle in an Infinitely Deep Square Well Potential (a Rigid Box)

Solution for the region between the walls

$$\psi = A \sin kx + B \cos kx,$$

Require that $\psi = 0$ at $x = 0$ and $x = l$

$$\psi(0) = 0 \quad \textbf{and} \quad \psi(l) = 0$$

$$\downarrow$$

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

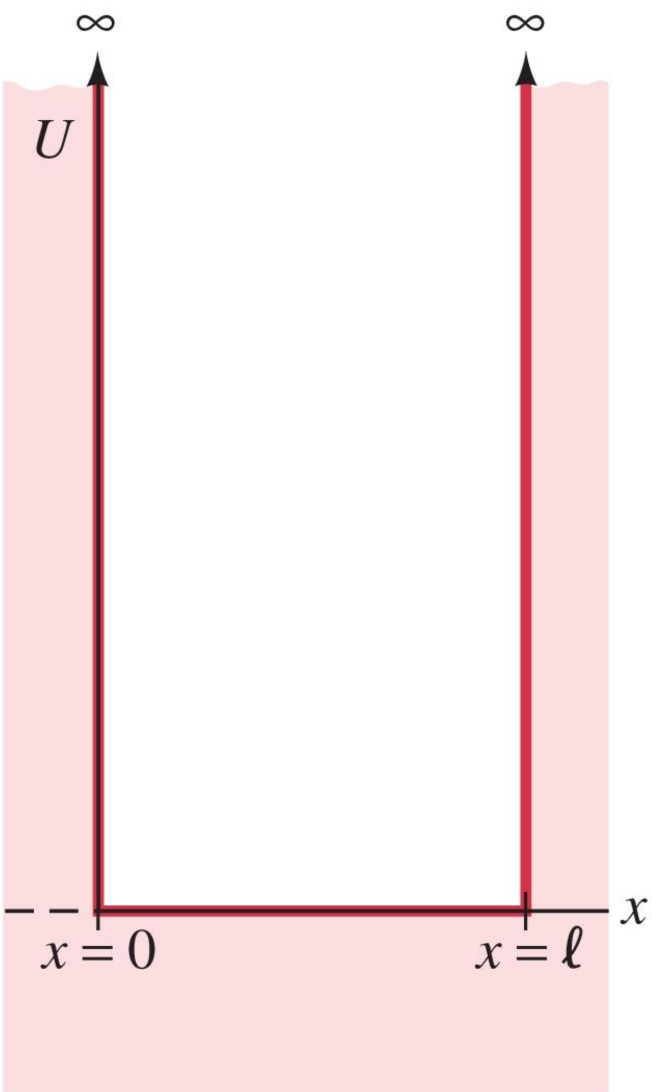
$$\psi(l) = A \sin kl = 0$$

$$\downarrow$$

$$kl = n\pi \quad \textbf{with} \quad n = 1,2,3,\cdots$$

Hence:

$$\psi_n = A \sin\left(\frac{n\pi}{l} x\right)$$



(Famous) Particle in an Infinitely Deep Square Well Potential (a Rigid Box)

Solution:

$$\psi_n = A\sin\left(\frac{n\pi}{l}x\right)$$

Calculate A from normalisation:

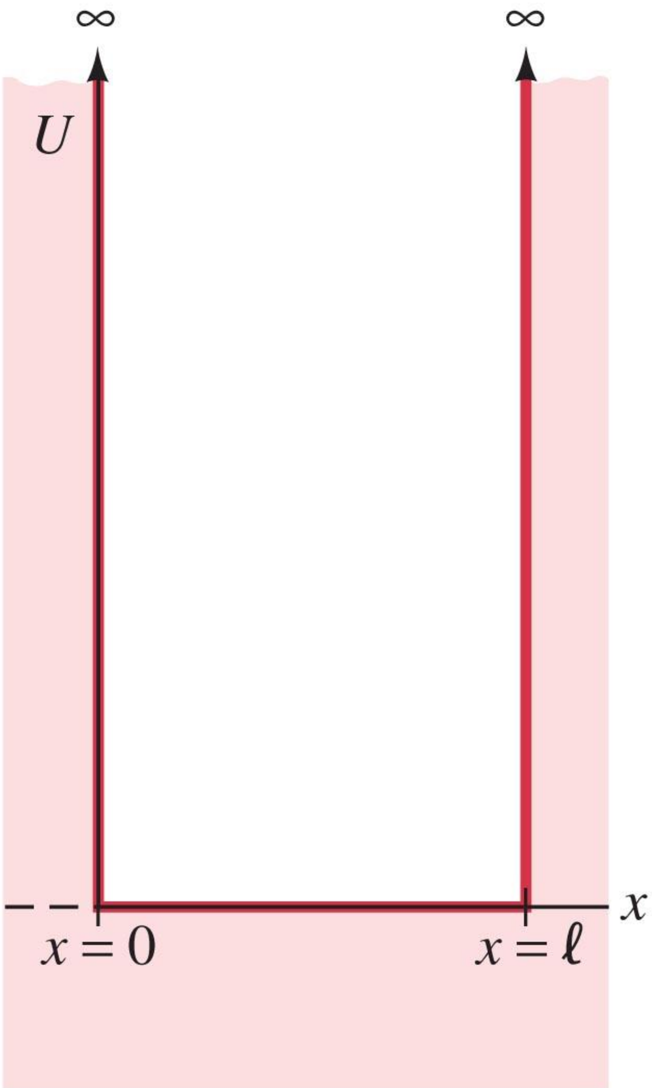
$$\int_0^l A^2 \sin^2\left(\frac{n\pi}{l}x\right)dx = 1 \longrightarrow A = \sqrt{\frac{2}{l}}$$

From:

$$k = \sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{l}$$

$$E = n^2 \frac{h^2}{8m\ell^2}, \qquad n = 1, 2, 3, \cdots$$

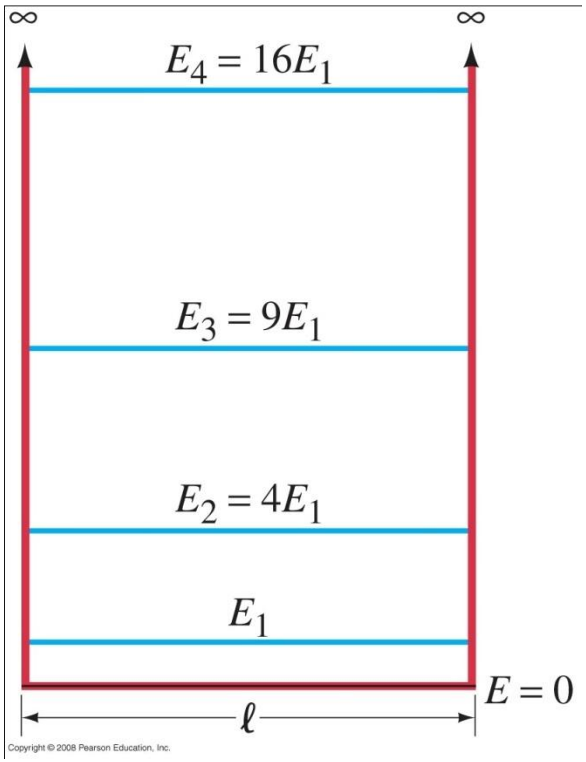
Result: Eigen functions and Eigenvalues

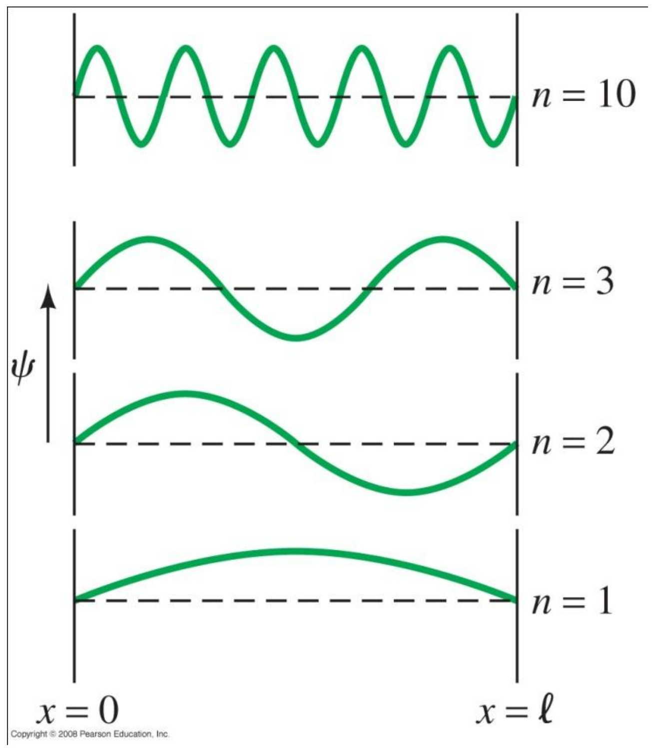


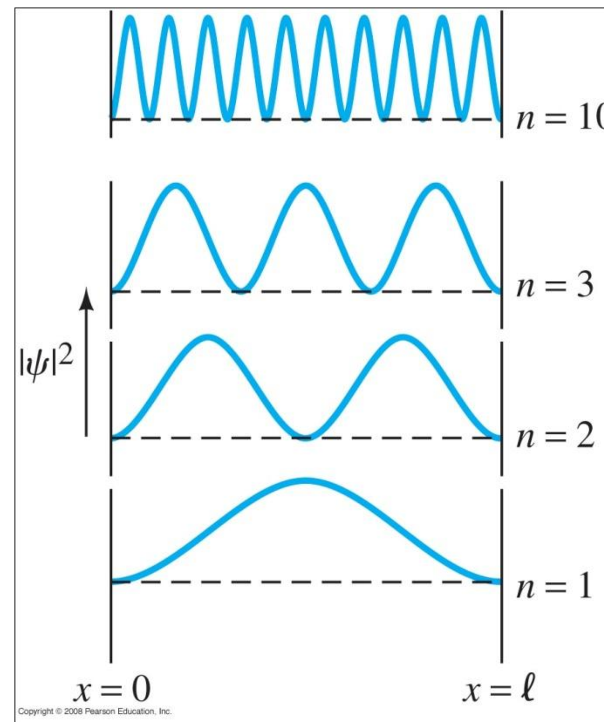
Particle in an Infinitely Deep Square Well Potential (a Rigid Box)

plots of solutions with quantum number *n*

(calculate normalisation constant)







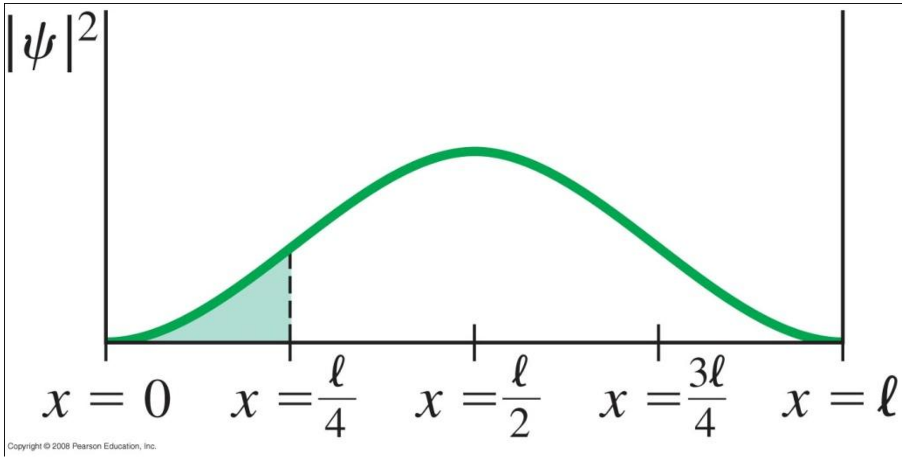
Zero-point energy = nonclassical

$$\left|\Psi\left(\vec{r},t\right)\right|^2$$

Particle in an Infinitely Deep Square Well Potential (a Rigid Box)

Probability of e^- in ¼ of box.

Determine the probability of finding an electron in the left quarter of a rigid box—i.e., between one wall at $x = 0$ and position $x = \ell/4$. Assume the electron is in the ground state.



$$\int_0^{\ell/4} |\Psi|^2 dx = \frac{2}{\ell} \int_0^{\ell/4} \sin^2\left(\frac{\pi}{\ell} x\right) dx$$

Particle in an Infinitely Deep Square Well Potential (a Rigid Box)

Most likely and average positions.

Two quantities that we often want to know are the most likely position of the particle and the average position of the particle. Consider the electron in the box of width = 1.00 x 10^{-10} m in the first excited state n = 2.

(a) What is its most likely position?

ℓ

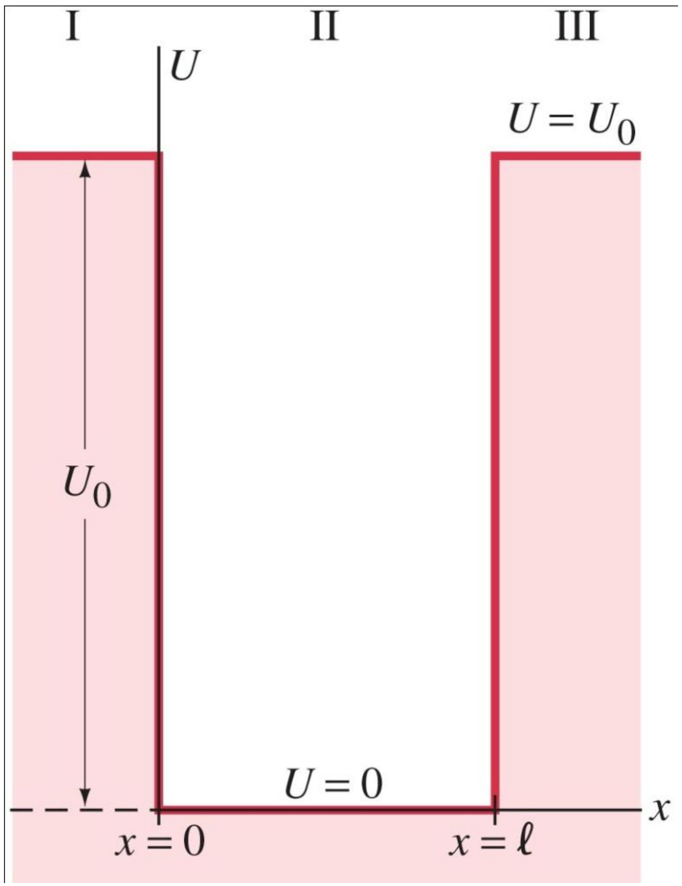
(b) What is its average position?

$$P(x) = \int_0^{\ell} |\Psi(x)|^2 dx$$

$$\bar{x} = \int_0^{\ell} x|\Psi(x)|^2 dx$$

Finite Potential Well

A finite potential well has a potential of zero between $x = 0$ and $x = \ell$, but outside that range the potential is a constant U_0.



The potential outside the well is no longer zero; it falls off exponentially.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U_0\psi = E\psi$$

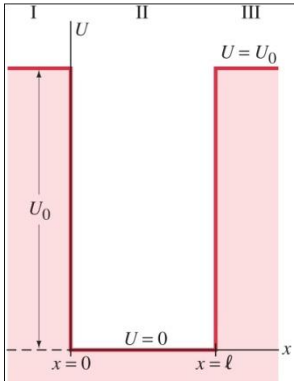
Solve in regions I, II, and III
and use for boundary conditions
Continuity:

$$\psi_I(0) = \psi_{II}(0) \qquad \psi_{II}(\ell) = \psi_{III}(\ell)$$

$$\frac{d\psi_I}{dx}(0) = \frac{d\psi_{II}}{dx}(0) \qquad \frac{d\psi_{II}}{dx}(\ell) = \frac{d\psi_{III}}{dx}(\ell)$$

Bound states: $E < E_0$
Continuum states: $E > E_0$

Finite Potential Well



If $E < U_0$ in the "forbidden regions"

$$\frac{d^2\psi}{dx^2} - \left[\frac{2m(U_0 - E)}{\hbar^2}\right]\psi = 0$$ **with** $$G^2 = \frac{2m(U_0 - E)}{\hbar^2}$$

General solution: $$\psi_{I,III} = Ce^{Gx} + De^{-Gx}$$

Region I $x < 0$ hence $D = 0$ and similarly for *C*

(why? unphysical)

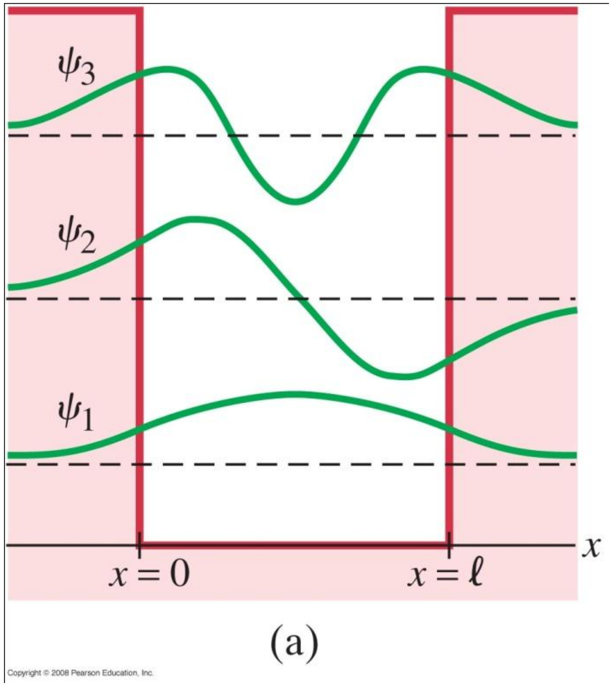
$\psi_I = Ce^{Gx}$ should match $\psi_{II} = A\sin kx + B\cos kx$

Finite value at $x = 0$ exponentially decaying into the finite walls

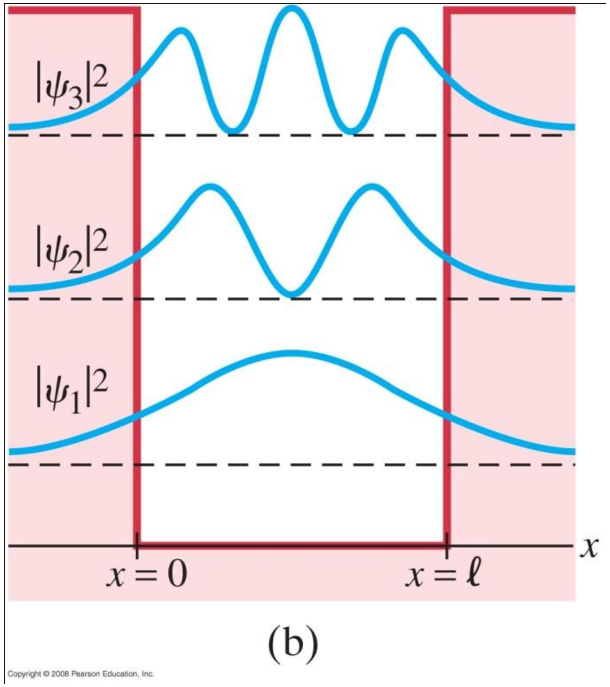
Finite Potential Well

These graphs show the wave functions and probability distributions for the first three energy states.

Nonclassical effects



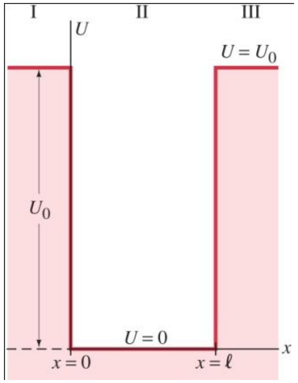
(a)



(b)

Partile can exist in the forbidden region

Finite Potential Well



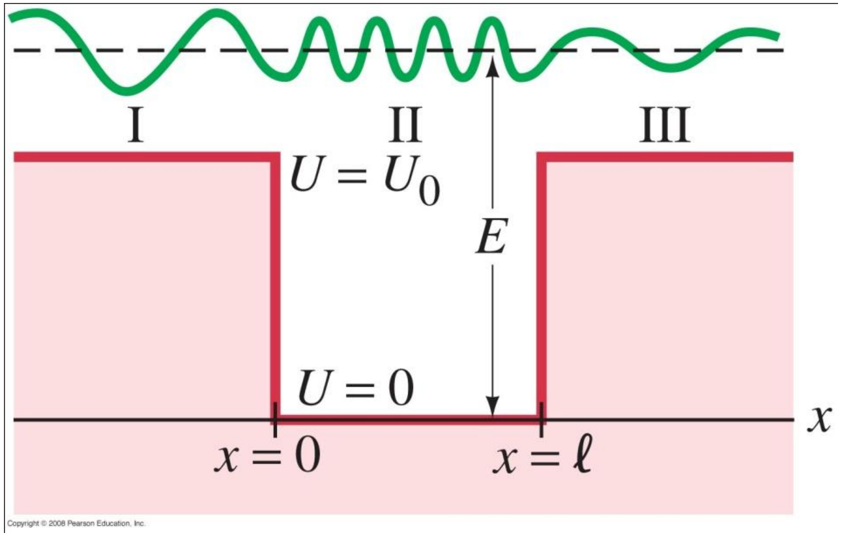
If $E > U_0$ free particle condition

$$\frac{d^2\psi}{dx^2} + \left[\frac{2m(E - U_0)}{\hbar^2}\right]\psi = 0$$

In regions I and III

$$\frac{d^2\psi}{dx^2} + \left[\frac{2mE}{\hbar^2}\right]\psi = 0$$

In region II



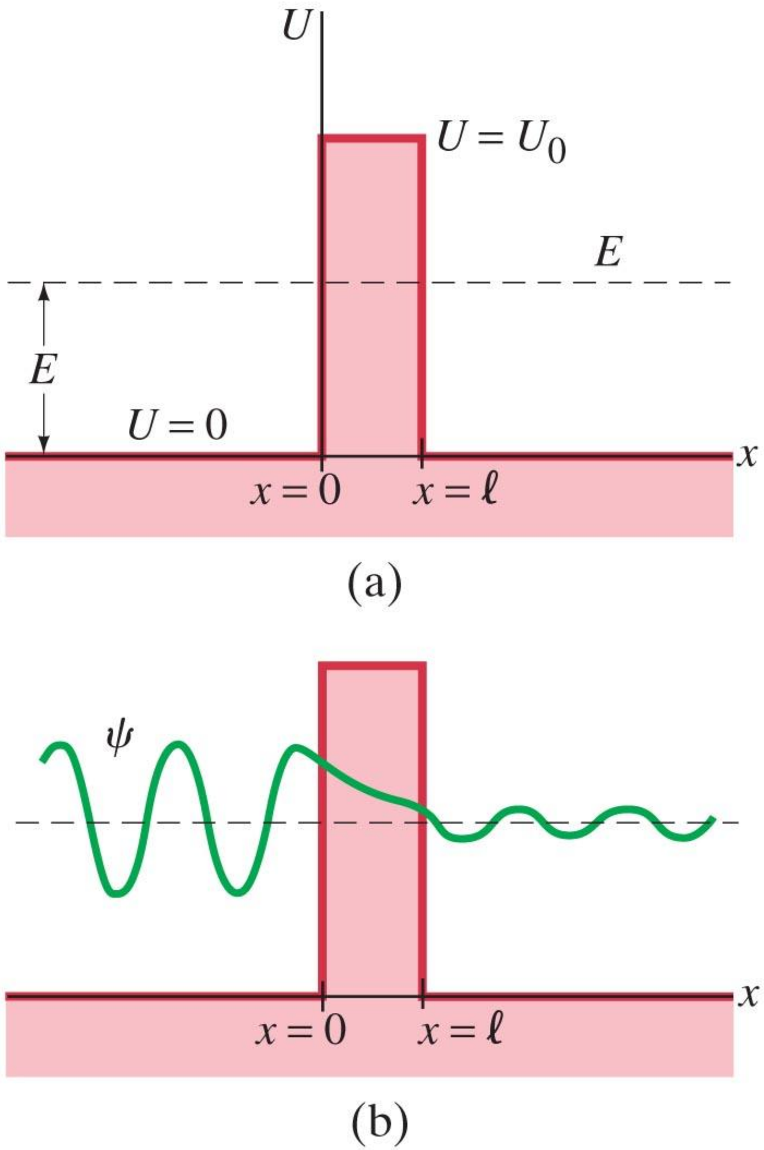
In both cases oscillating free partcile wave function:

I,III: $$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E - U_0)}}$$

II: $$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

$$E = \frac{1}{2}mv^2 + U_0 = \frac{p^2}{2m} + U_0$$

Tunneling Through a Barrier



In region $x < 0$ **oscillating wave**

$$\frac{d^2\psi}{dx^2} + \left[\frac{2mE}{\hbar^2}\right]\psi = 0 \qquad \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

Also in region $x > \ell$

Wave with same wavelength $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$

In the barrier:

$$\frac{d^2\psi}{dx^2} - \left[\frac{2m(U_0 - E)}{\hbar^2}\right]\psi = 0 \qquad \psi_b = Ce^{Gx} + De^{-Gx}$$

Approximation: assume that the decaying function is dominant $\psi_b = De^{-Gx}$

Transmission:

$$T = \frac{|\psi(x=\ell)|^2}{|\psi(x=0)|^2} = \frac{\left(De^{-G\ell}\right)^2}{D^2} = e^{-2G\ell}$$

Tunneling Through a Barrier

The probability that a particle tunnels through a barrier can be expressed as a transmission coefficient, T, and a reflection coefficient, R (where $T + R = 1$). If T is small,

$$T \approx e^{-2G\ell},$$

where

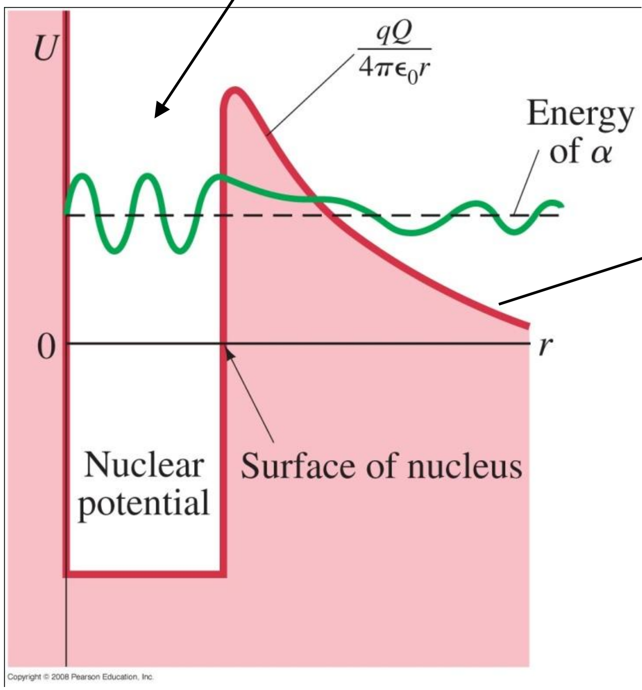
$$G = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}.$$

The smaller E is with respect to U_0, the smaller the probability that the particle will tunnel through the barrier.

Tunneling Through a Barrier

Alpha decay is a tunneling process; this is why alpha decay lifetimes are so variable.

Region of binding by the "strong force"

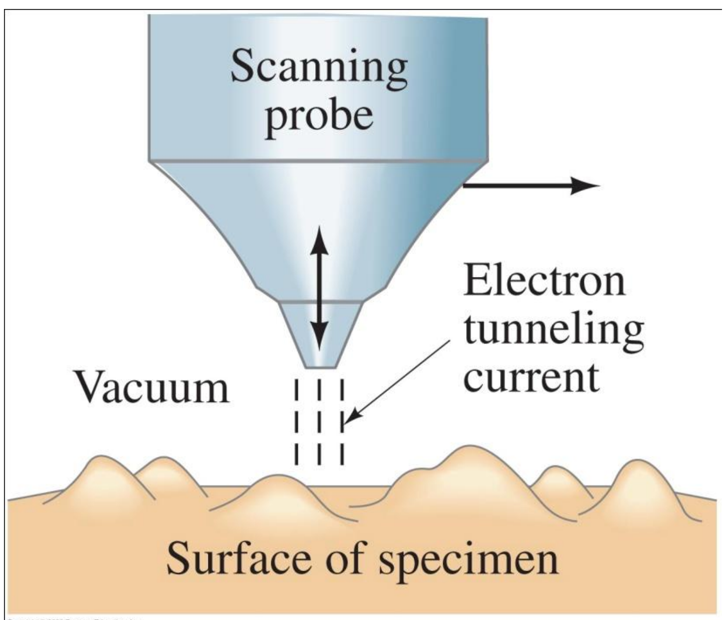


Region of repulsion between positive charges

Note:
Exponential dependence

Tunneling Through a Barrier

Scanning tunneling microscopes image the surface of a material by moving so as to keep the tunneling current constant. In doing so, they map an image of the surface.



Nobel 1986

Gerd Binnig

HeinrichRohrer

"for their design of the scanning tunneling microscope"