Phys 153: Fundamentals of Physics III

Unit #5 – Quantum Mechanics

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Quantum Mechanics

The general framework of quantum mechanics (first described by Paul Dirac and clarified mathematically by Johnny Von Neumann) is beyond the scope of this course. We will stick mostly to wave mechanics, and that basically means solving the Schrödinger equation.

"...in one of the next colloquia [early in 1926], Schrödinger gave a beautifully clear account of how de Broglie associated a wave with a particle and how he [i.e., de Broglie] could obtain the quantization rules...by demanding that an integer number of waves should be fitted along a stationary orbit. When he had finished Debye casually remarked that he thought this way of talking was rather childish... [that to] deal properly with waves, one had to have a **wave equation**."   – Felix Bloch

The Schrödinger Equation...

...for a non-relativistic particle with mass m

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

- i is the complex unit defined such that $i^2 = -1$

- $U(x)$ is a potential energy function describing the interaction of our quantum particle with a much larger system that is essentially fixed.

- $\Psi(x,t)$ is the particle's *wave function*, containing nearly all information about the particle, including its position (or rather, possible positions).

Technically, this is just "a" Schrödinger equation, not "the" Schrödinger equation

Differential Equations

The Schrödinger equation (SE) is a linear partial differential equation with non-constant coefficients. The solutions depend sensitively on the potential energy function.

- If Ψ_1 and Ψ_2 are solutions, then $c_1\Psi_1 + c_2\Psi_2$ is a solution.

- When $U(x)$ is constant, the go-to strategy is to try exponential solutions because they have the nice property that $(e^x)' = e^x$
  - Even if exponential solution doesn't work, a linear combination of them may work.

- To fully solve the SE, we need initial conditions and boundary conditions.

Definite Energy States

In quantum mechanics, **energy** is essentially defined as the real number E such that

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = E\, \Psi(x, t)$$

- This is an **eigenvalue equation** for the **differential operator** $i\hbar \frac{\partial}{\partial t}$

- There is a class of wave functions with definite energy, and they have the general form
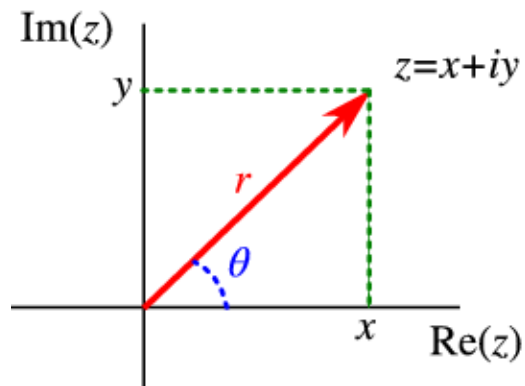
$$\Psi(x, t) = \psi(x) e^{-iEt/\hbar}$$

"Time-independent wave function"

Complex exponential function

Complex Numbers

In standard form, $z = x + iy$ is a complex number

- $i^2 = 1$, $x = \mathrm{Re}[z]$ (real part), $y = \mathrm{Im}[z]$ (imaginary part)

- Think of a complex number like a "2D number" or vector.

Modulus: $|z| = \sqrt{x^2 + y^2}$

Complex conjugation: $z^* = x - iy$

$z\,z^* = z^*\,z = x^2 + y^2 = |z|^2$

Euler's Formula

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \frac{x^5}{5!} + \cdots$$

$$e^{ix} = 1 + ix + \frac{(ix)^2}{2!} + \frac{(ix)^3}{3!} + \frac{(ix)^4}{4!} + \frac{(ix)^5}{5!} + \cdots$$

$$= 1 + ix - \frac{x^2}{2!} - i\frac{x^3}{3!} + \frac{x^4}{4!} + i\frac{x^5}{5!} + \cdots$$

$$= \left(1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots \right) + i\left(x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots \right)$$

$$\underbrace{\phantom{1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots}}_{\cos x} \qquad \underbrace{\phantom{x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots}}_{\sin x}$$

$$i^2 = -1$$
$$i^3 = -i$$
$$i^4 = +1$$
$$i^5 = +i$$

$$\therefore \quad e^{ix} = \cos x + i\sin x$$

Polar Form

Complex numbers can be written in **polar form**

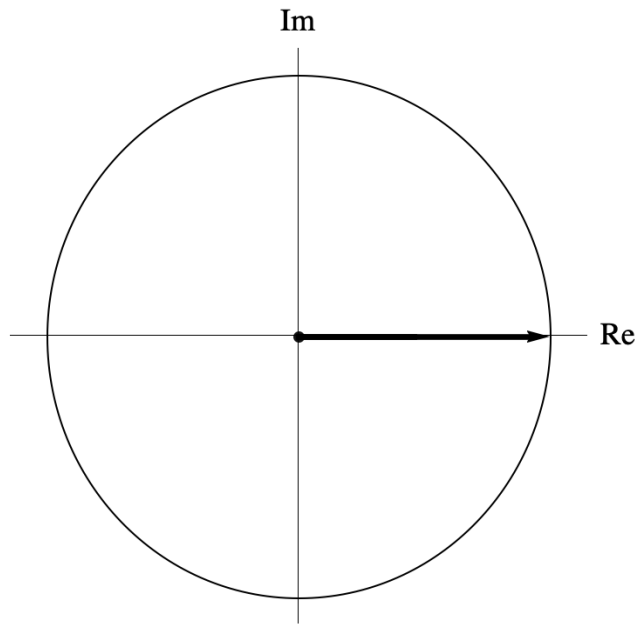$$r = |z| = x^2 + y^2$$

$$x = r \cos \theta$$

$$y = r \sin \theta$$
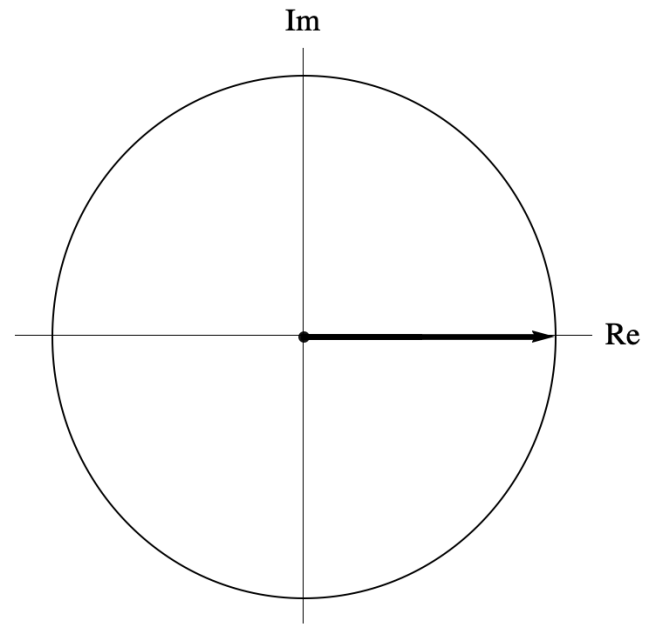
$$z = x + iy = |z|e^{i\theta}$$

Modulus
(magnitude)

Phase
(direction)

The complex exponential is the mathematical underpinning of phasors (if you've seen those before).

$e^{i\omega t}$ rotates CCW

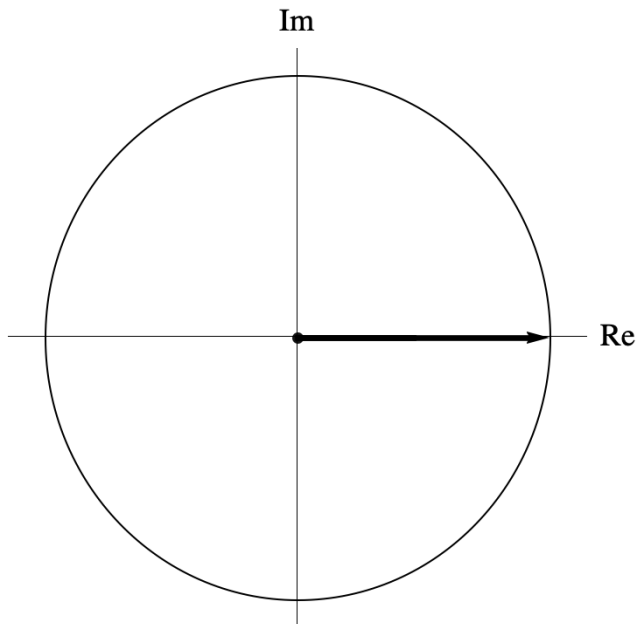$e^{-i\omega t}$ rotates CW

both with angular frequency ω

$\psi(x)$ may be a complex number, $\psi(x) = |\psi(x)|e^{i\delta}$

$$\Psi(x,t) = |\psi(x)| \exp[-i(Et/\hbar - \delta)]$$

For fixed x, a definite energy state is described by a complex number rotating clockwise with frequency

$$\omega = \frac{E}{\hbar}$$

What is a wave function anyways?

The wave function is a "probability amplitude."

The probability of finding a particle at any precise value of x is technically zero, but really, we should be asking **what's the probability to find the particle near x within a very small interval dx?**
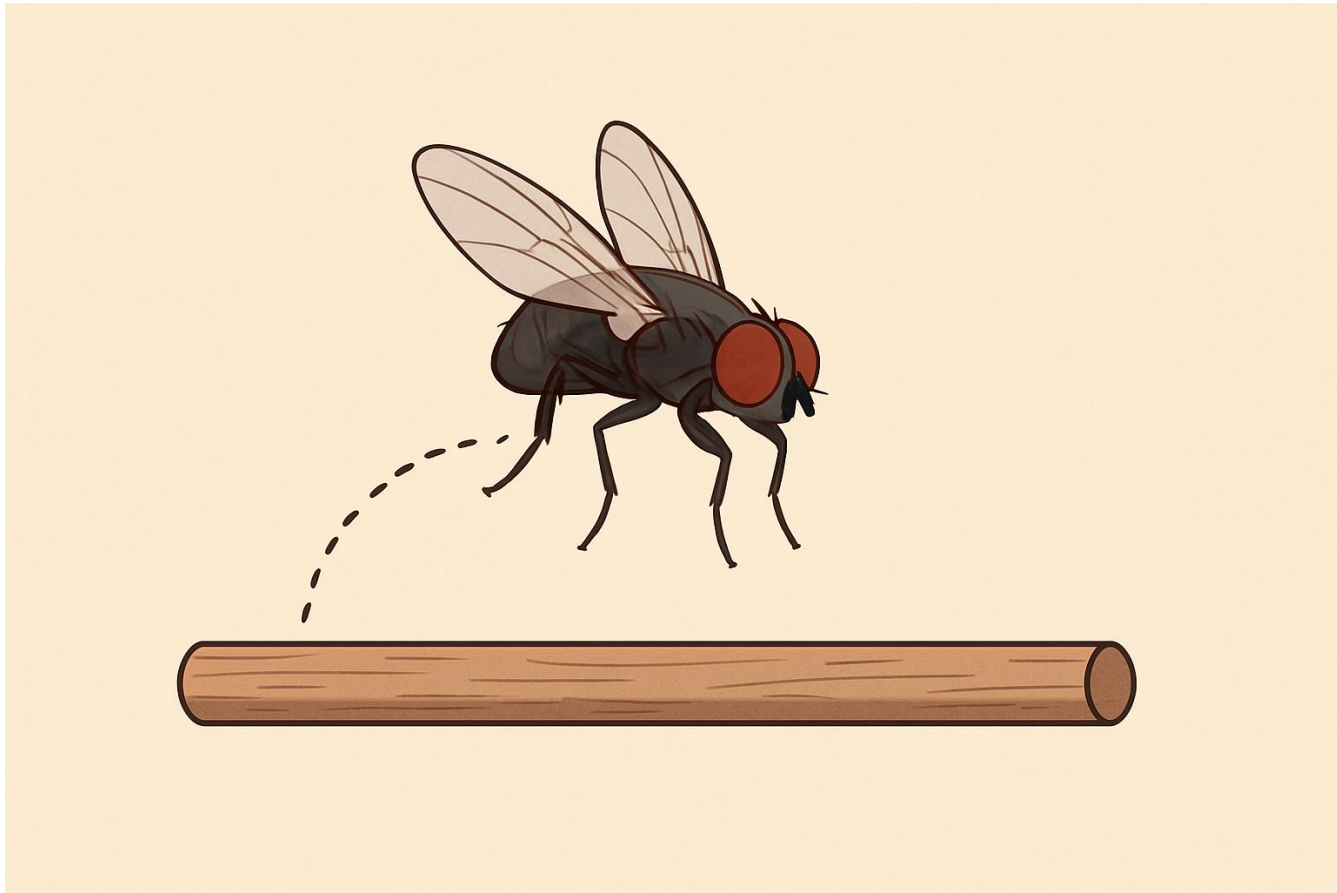
The answer is given by the **Born rule**

$$|\Psi(x,t)|^2 dx$$

Hence, the probability of finding the particle in the range $a < x < b$ is

$$P(a < x < b) = \int_a^b |\Psi(x,t)|^2 \, dx$$

Normalization

The square-modulus of the wave function represents a probability distribution, and it must be **normalized**, i.e. the total probability to find the particle *somewhere* in the range $-\infty < x < \infty$ must be one.

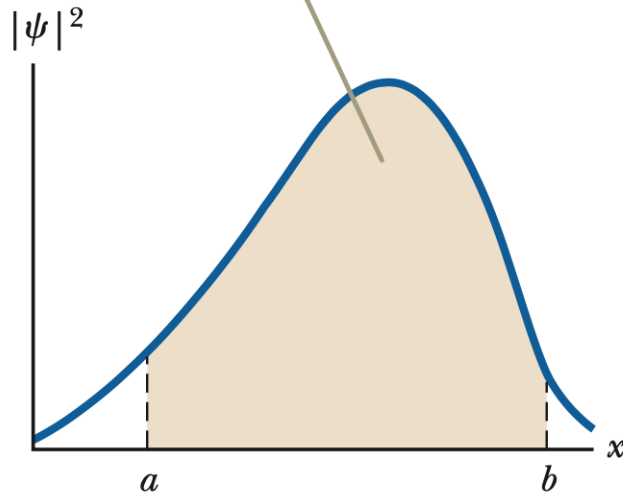$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = 1$$

Normalization constitutes a constraint on the wave function.

Any physically meaningful wave function must solve the Schrödinger equation and satisfy normalization.

$\Psi(x,t)$ must go to zero as $x \to \pm\infty$, otherwise it could not be normalizable.

Statistical Interpretation

The probability of a particle being in the interval $a \leq x \leq b$ is the area under the probability density curve from a to b.

$|\psi|^2$

Average position

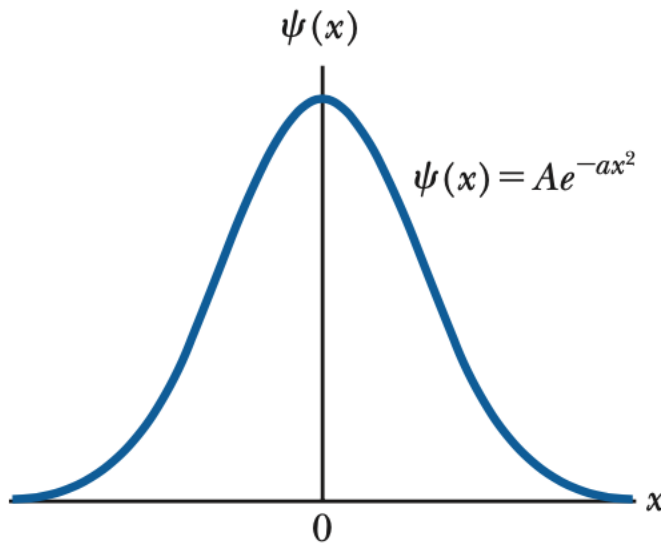$$\langle x \rangle = \int_{-\infty}^{\infty} x \, |\Psi|^2 \, dx$$

Expectation value

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) \, |\Psi|^2 \, dx$$

An expectation value is a weighted average, weighted by the probability

Consider a particle whose wave function is graphed in the figure and is given by $\psi(x) = Ae^{-ax^2}$.

(a) What is the value of A if this wave function is normalized?

(b) What is the average position for this particle?

SE is Normalization Preserving

The Schrödinger equation ensures that a wave function normalized at $t = 0$ will remain normalized for all time!

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} (\Psi^*\Psi) dx$$

$$\frac{\partial}{\partial t} (\Psi^*\Psi) = \Psi \frac{\partial \Psi^*}{\partial t} + \Psi^* \frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^*}{\partial x^2} \right)$$

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = \frac{i\hbar}{2m} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) dx$$
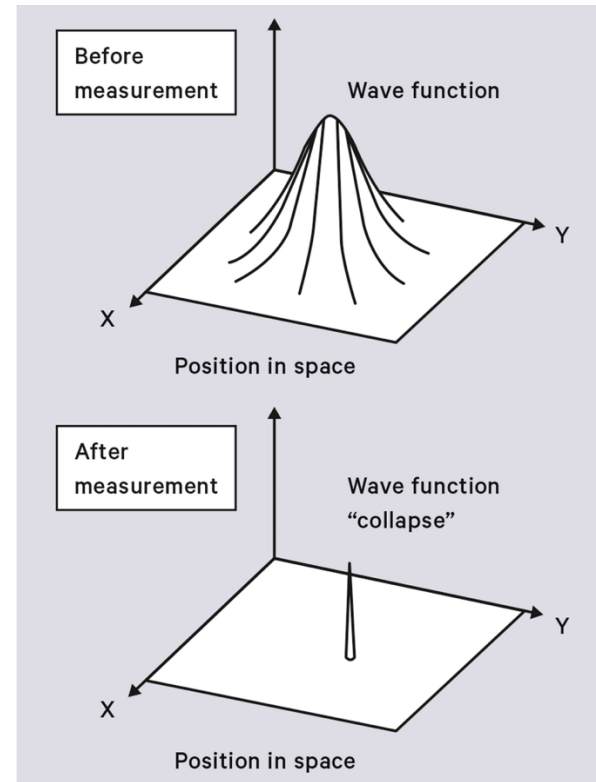
$$= \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \Big|_{-\infty}^{\infty}$$

$$= 0 \qquad (\Psi \to 0 \text{ as } x \to \pm\infty)$$

Wave Function Collapse

A particle is a localized object. When its position is measured, the wave function "collapses."

- No one completely understands this process, and many (myself included) doubt that it's even physical.

- The wave function is merely a tool for calculation—this does not undermine its importance!

"The motion of the particle follows the laws of probability, but the probability itself propagates in accord with causal laws."   – Max Born

Time-Independent SE

Notice for a definite energy state,

$$|\Psi(x,t)|^2 = \psi^*(x)\, e^{+i\omega t}\psi(x)e^{-i\omega t} = |\psi(x)|^2$$

- Probability density is stationary, meaning it doesn't change with time.

- Substitute $\psi(x)e^{-iEt/\hbar}$ into the SE,

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

This is often called the "time-independent Schrödinger equation."

Constant Potential

When $U(x)$ is constant, the time-independent SE is a linear differential equation with constant coefficients.

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

- If $E > U$, the solution is a linear combination of complex exponential functions representing oscillations in x.

- If $E < U$, the solution is a linear combination of real exponential functions; exponential growth/decay in x.

Free Particle

Consider particle with energy $E > 0$ and $U(x) = 0$.

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

- Two basic solutions are $e^{\pm ikx}$ (non-normalizable)
- When $U = 0$, the energy E must be kinetic energy:

$$\hbar k = \sqrt{2mE} = p \qquad\qquad k = \frac{p}{\hbar}$$

- Notice that E can be any real number—no quantization.

Plane Wave Solutions

$$\Psi(x, t) = \underbrace{Ae^{-i(\omega t - kx)}}_{} + \underbrace{Be^{-i(\omega t + kx)}}_{}$$

$+x$ direction $-x$ direction

$$\omega(k) = \frac{E(k)}{\hbar} = \frac{\hbar k^2}{2m} \text{ (a dispersion relation)}$$

- Plane wave solutions are useful for analyzing quantum phenomena
- Complete solution is a linear combination of plane wave solutions that satisfies initial conditions and normalization. This involves the Fourier transform and is beyond the scope of our class.

Real Solutions

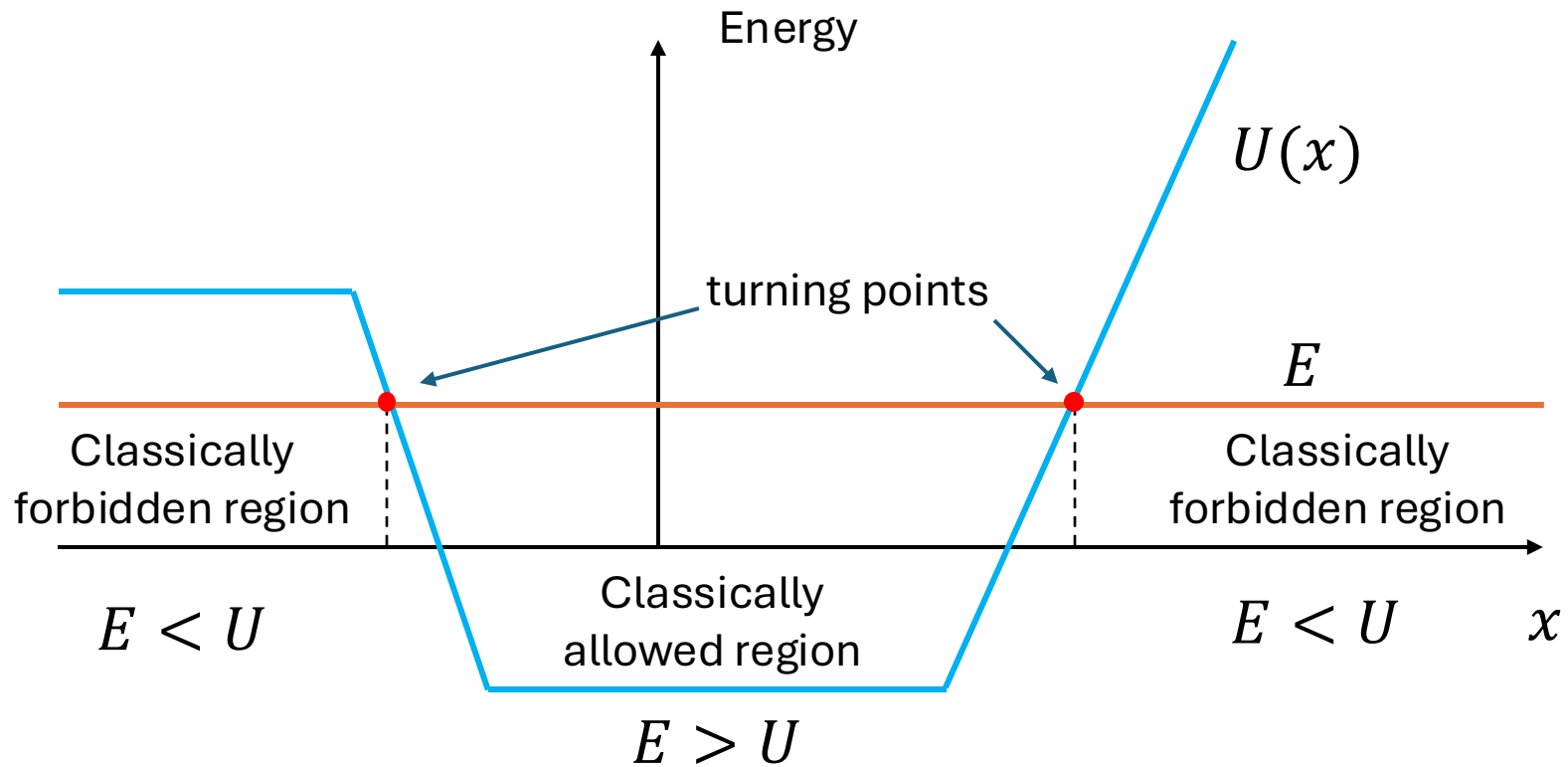In 1D, $\psi(x)$ can always be chosen to be a real function.

$$\Psi(x, t) = \left(A e^{+ikx} + B e^{-ikx}\right) e^{-i\omega t}$$

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

This is also a solution to
the time-independent SE

Energy Diagrams

In classical mechanics, kinetic energy cannot be negative.

Energy

$U(x)$

turning points

E

Classically
forbidden region

Classically
forbidden region

Classically
allowed region
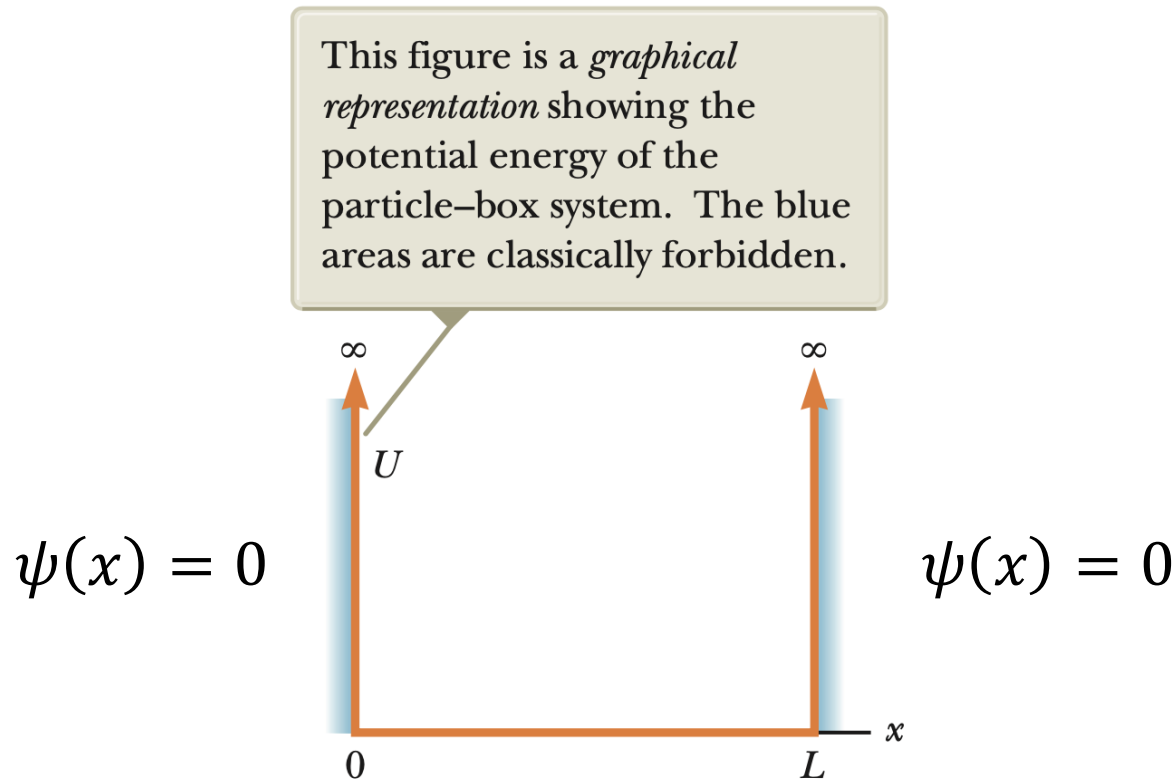
$E < U$

$E > U$

$E < U$

x

Bound Systems

A **bound system** is any system of interacting objects where the nature of the interactions keep their relative separations limited.

Our particle is bound if it is in a classically allowed region enclosed by two classically forbidden regions (or barriers).

- Building blocks of matter are bound quantum systems (atoms, molecules, even nuclei)

- Consequences for macroscopic systems like crystalline solids (conductors, semiconductors)

Infinite Square Well

This figure is a *graphical representation* showing the potential energy of the particle–box system. The blue areas are classically forbidden.

∞

U

∞

$\psi(x) = 0$

$\psi(x) = 0$

x

0

L

For $0 < x < L$,

- Solution to the SE is $\psi(x) = A\cos(kx) + B\sin(kx)$
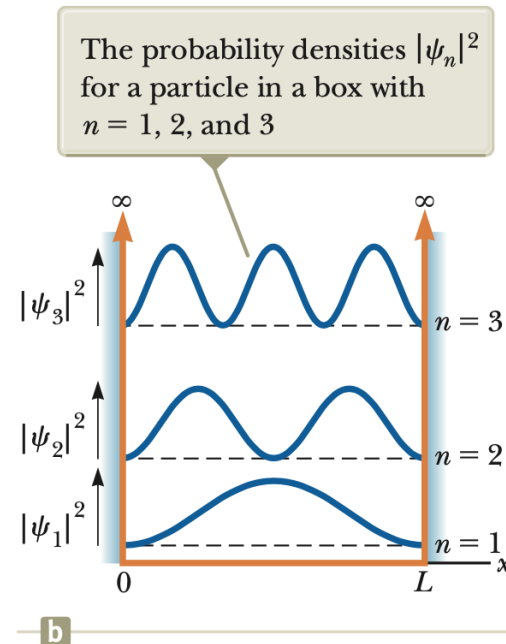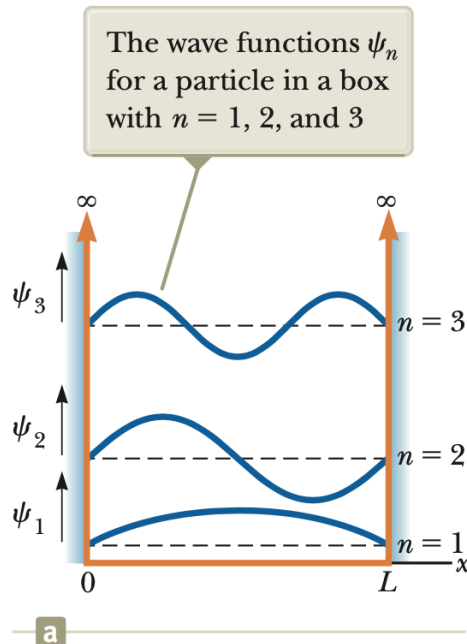- Boundary conditions: $\psi(0) = \psi(L) = 0$

$$\hbar k = \sqrt{2mE}$$

Infinite Square Well

- Solutions are standing waves with quantized energies!
- The integer n starts at 1, $n = 0$ cannot be normalized.

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \qquad E_n = \left(\frac{h^2}{8mL^2}\right)n^2$$

The wave functions ψ_n for a particle in a box with $n = 1, 2,$ and 3

ψ_3 $n = 3$

ψ_2 $n = 2$

ψ_1 $n = 1$ x

0 L

a

The probability densities $|\psi_n|^2$ for a particle in a box with $n = 1, 2,$ and 3

$|\psi_3|^2$ $n = 3$

$|\psi_2|^2$ $n = 2$

$|\psi_1|^2$ $n = 1$ x

0 L

b

Example 2: Particle in a Box

A particle in a box is in its ground state. Calculate the probability that the particle will be found in the region
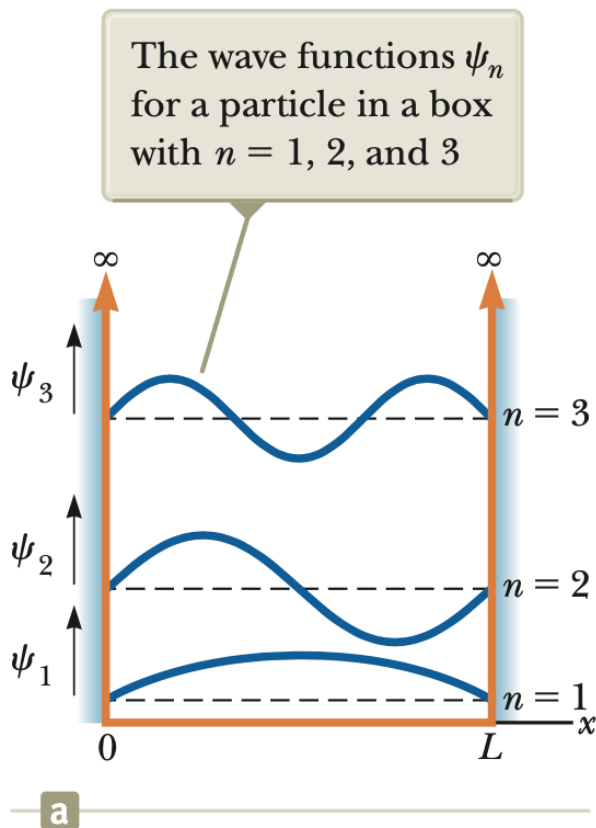
(a) $0 < x < L/2$,

(b) $0 < x < L/3$,

(c) $0 < x < 3L/4$.

(d) Estimate the probability of finding the particle in a *very small region* $\Delta x = 0.01L$ centered on position $x = 3L/8$.

If $U(x)$ is an **even function,** then $\psi(x)$ can always be taken to be either even or odd.

The wave functions ψ_n for a particle in a box with $n = 1, 2,$ and 3

This is why definite-energy solutions to the infinite square well alternate parity with respect to the center of the well.
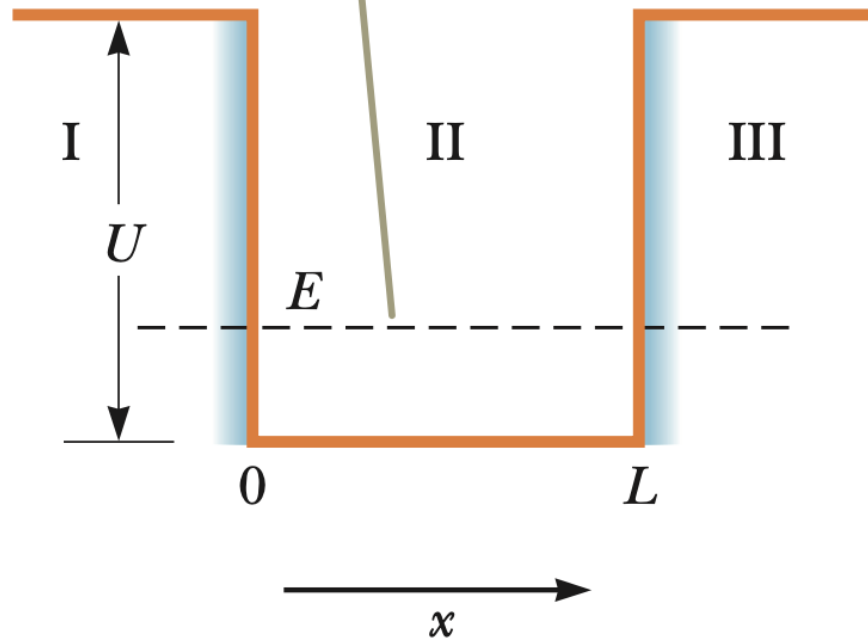
Physical Wave Functions

The wave function must obey the following rules to be *physically acceptable*

1. ψ must be normalizable

2. $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$

3. ψ must be finite and continuous everywhere

4. $\dfrac{d\psi}{dx}$ must be finite and continuous everywhere for finite values of $U(x)$

SE depends on second derivative, which requires the first derivative to be continuous.

Finite Square Well

If the total energy E of the particle–well system is less than U, the particle is trapped in the well.

We already know what solutions look like in region 2.

$$\frac{d^2\psi}{dx^2} = \frac{2m(U-E)}{\hbar^2}\psi = C^2\psi \qquad \text{where } C^2 > 0$$

$$\psi(x) = Ae^{Cx} + Be^{-Cx} \qquad \text{real exponentials}$$

$$\psi_1 = Ae^{Cx} \text{ for } x < 0$$

$$\psi_3 = Be^{-Cx} \text{ for } x > L$$

$$\psi \to 0 \text{ as } x \to \pm\infty$$

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

$$\psi_2(x) = F\sin kx + G\cos kx$$

Must satisfy the boundary conditions

Boundary Conditions

Four boundary conditions and normalization are sufficient to determine the four constants A, B, F, and G and the allowed values of the energy E.

1. $\psi_1(0) = \psi_2(0)$

2. $\psi_2(L) = \psi_3(L)$

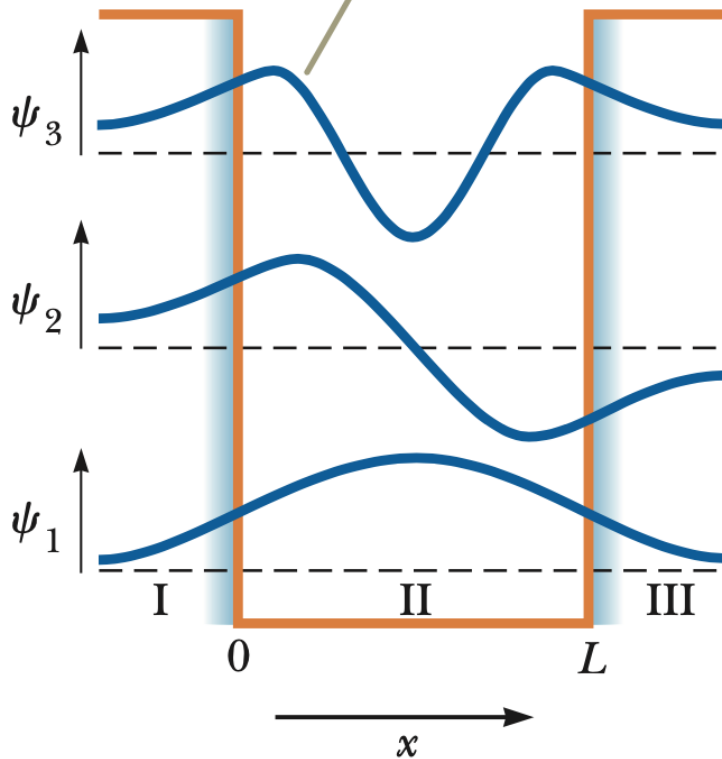3. $\left.\dfrac{d\psi_1}{dx}\right|_0 = \left.\dfrac{d\psi_2}{dx}\right|_0$

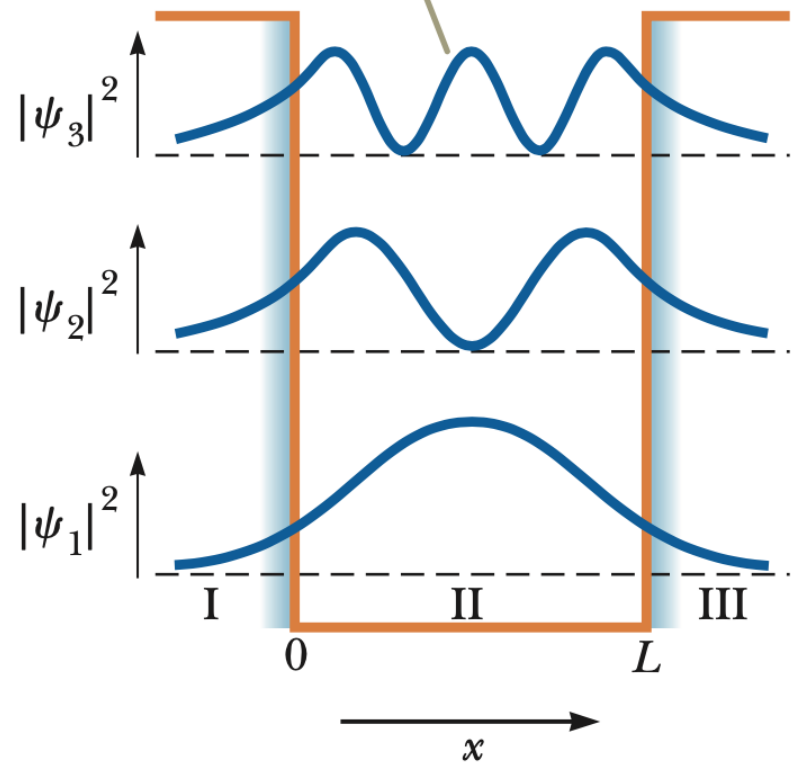4. $\left.\dfrac{d\psi_2}{dx}\right|_L = \left.\dfrac{d\psi_3}{dx}\right|_L$

5. $\int |\psi|^2 dx = 1$

Finite Square Well

The wave functions ψ_n for a particle in a potential well of finite height with $n = 1, 2,$ and 3

The probability densities $|\psi_n|^2$ for a particle in a potential well of finite height with $n = 1, 2,$ and 3
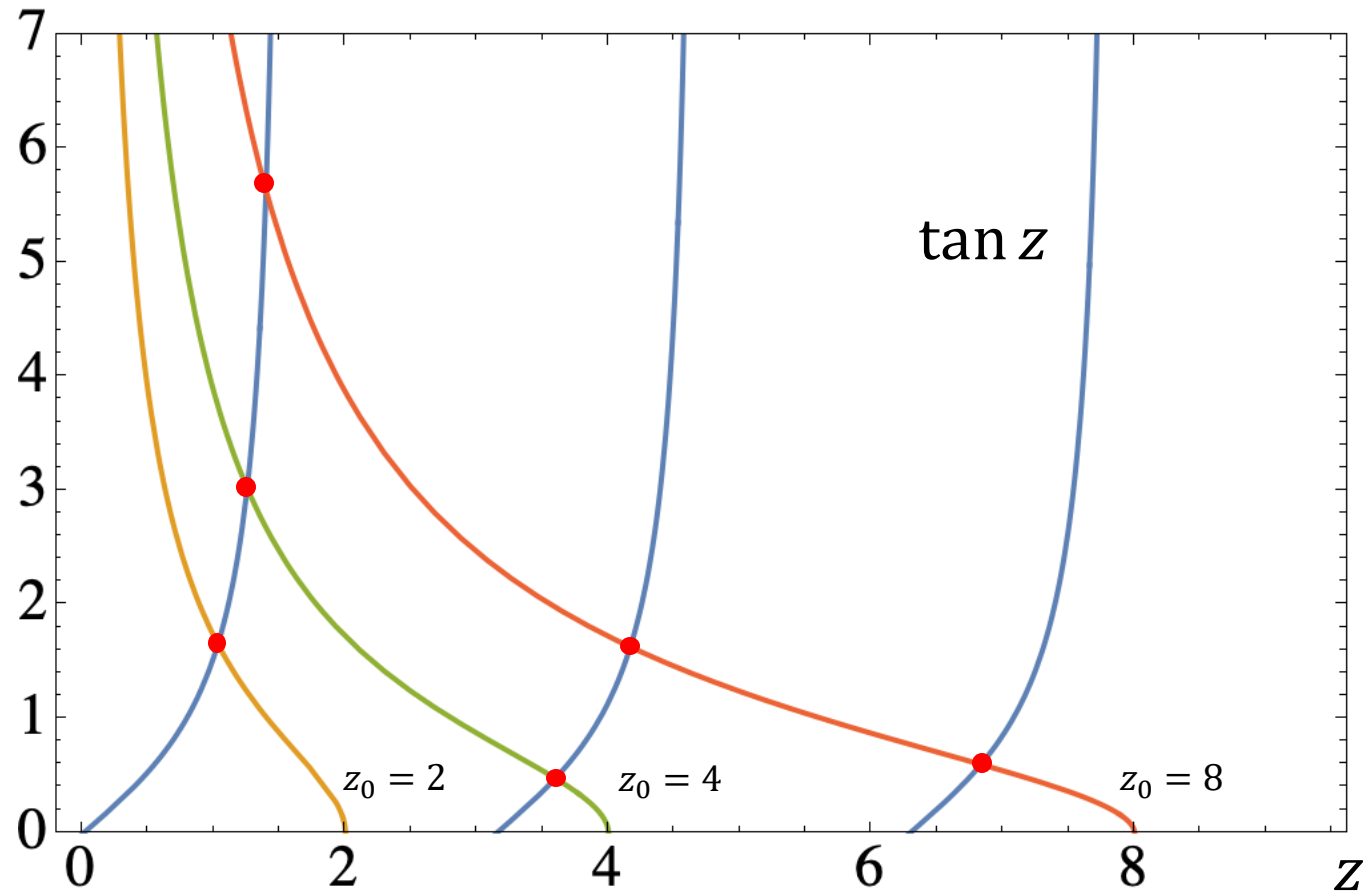
Allowed Energies

The solutions alternate parity.

Even solutions: $\tan z = \sqrt{\dfrac{z_0^2}{z^2} - 1}$

Odd solutions: $\cot z = \sqrt{\dfrac{z_0^2}{z^2} - 1}$
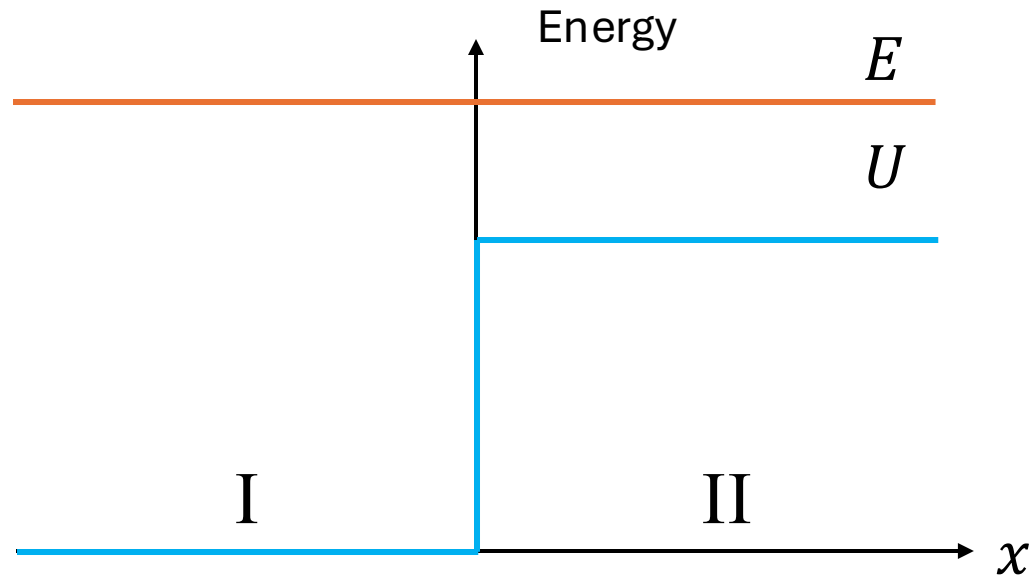
$$z = kL$$

$$z_0^2 = \frac{2mU\,L^2}{\hbar^2}$$

These equations can be solved *numerically* to find the allowed energies for bound states of the finite square well.

Intersections of $\tan z$ with $\sqrt{\frac{z_0^2}{z^2} - 1}$ correspond to solutions

for allowed energies. Note that $\frac{z_0^2}{z^2} = \frac{U}{E}$

Step Potential ($E > U$)

$$\psi_1(x) = Ae^{ik_1 x} + Be^{-ik_1 x}$$

$$\psi_2(x) = Ce^{ik_2 x} + De^{-ik_2 x}$$

Boundary Conditions

- No left-moving wave in region II: $D = 0$

$$\psi_1(0) = \psi_2(0) \qquad \psi_1'(0) = \psi_2'(0)$$

$$A + B = C \qquad ik_1(A - B) = ik_2 C$$

$$B = \frac{k_1 - k_2}{k_1 + k_2} A$$

$$C = \frac{2k_1}{k_1 + k_2} A$$

Step Potential ($E < U$)

$$\psi_1(x) = Ae^{ik_1 x} + Be^{-ik_1 x}$$

$$\psi_2(x) = Ce^{k_2 x} + De^{-k_2 x}$$

Boundary Conditions

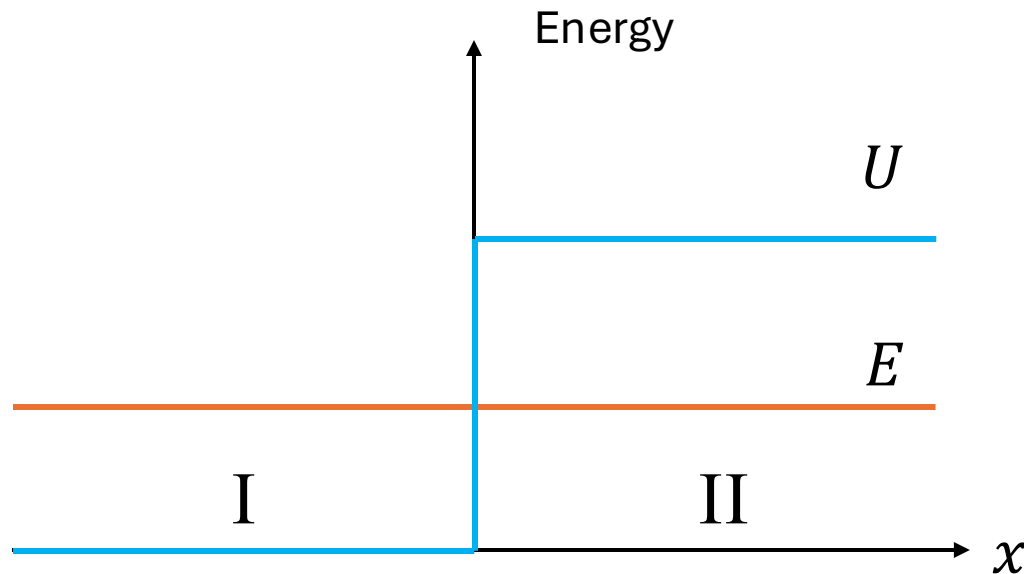- No left-moving wave in region II: $D = 0$

$$\psi_1(0) = \psi_2(0) \qquad \psi_1'(0) = \psi_2'(0)$$

$$A + B = C \qquad ik_1(A - B) = k_2 C$$

$$B = \frac{ik_2 + k_1}{k_1 - ik_2} A$$

$$C = \frac{2k_1}{k_1 - ik_2} A$$

Sketching Wave Functions

$$\frac{\psi''}{\psi} = \frac{2m(U - E)}{\hbar^2}$$

1. In classically allowed regions, ψ oscillates and always curves toward the x axis. Curvature is proportional to U.

2. In classically forbidden regions, ψ curves away from x axis and exhibits exponential growth or decay.

3. In bound systems where $U(x)$ is even about some point, solutions alternate parity about that point.

4. In bound systems, quantum probability distribution matches the *classical probability distribution* as the energy index $n \rightarrow \infty$. Local amplitude is proportional to $U(x)$ in classically allowed regions.

Classical Probability Distribution

For a bound classical system oscillating between two turning points, the probability of finding a particle within a small interval dx near x is given by

$$\rho(x)dx = \frac{dt}{T} = \frac{1}{T}\frac{dx}{v(x)} \qquad T = \int_0^T dt = \int_a^b \frac{dx}{v(x)}$$

Total time it takes to go from one turning point to the other

$$\rho(x) = \frac{1}{v(x)T}$$

You are more likely to find a particle at locations where it's moving slowly.

Example 3: Classical PDF

(a) Use conservation of energy to express $v(x)$ in terms of the total energy E and potential energy $U(x)$.

(b) Find $\rho(x)$ for a simple harmonic oscillator with

$$U(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2$$

(c) Plot $\rho(x)$ and sketch the probability densities for the first few definite energy states of the quantum harmonic oscillator using the rules for sketching wave functions we discussed earlier.

A particle of mass m on a table at $y = 0$ can be described by the potential energy function $U(y) = mgy$ for $y \geq 0$ and $U = \infty$ for $y < 0$.

For some positive value of total energy E, indicate the classically allowed region on a sketch of $U(y)$ versus y. Sketch also the kinetic energy versus y. The Schrödinger equation for this problem is quite difficult to solve.

Sketch "educated guesses" for the shape of the wave function for the ground state and first two excited states.