QUANTUM MECHANICS

Ch.5 of Arthur Beiser

WAVE FUNCTION: probability & wave equation, linearity and superposition of wave of wave functions, expectation values SCHRÖDINGER EQUATION: time dependent and time independent SE, eigenvalue & eigenfunctions, boundary conditions on wave function,

APPLICATION OF SE: Particle in a box, Finite potential Well (optional).

- **Wave equation**
- **Time dependent Schrodinger equation**
- **Linearity & superposition**
- **Expectation values**
- **Observables as operators**
- **Stationary states and time evolution of stationary states**
- **Eigenvalues & Eigenfunctions**
- **Boundary conditions on wave function**
- **Application of SE (Particle in a box,)**

Quantum Mechanics/Physics

CENTRAL IDEA

Quantum physics deals with matter with wave properties. The behavior of a particle is described with a wave function, using Schrodinger's equation. The wave function is interpreted using probability because we cannot say exactly where a particle is. We judge where something is using generalized probability but cannot perform a measurement without the collapse of the **wave function**.

Quantum physics:

What happens to physics when we give wave properties to matter

So it's described by something called a wave function

Ψ

"everything" about the system!

that's going to take the place of a position, a momentum and all those things

Instead of that we describe the behaviour of a particle by its wave function

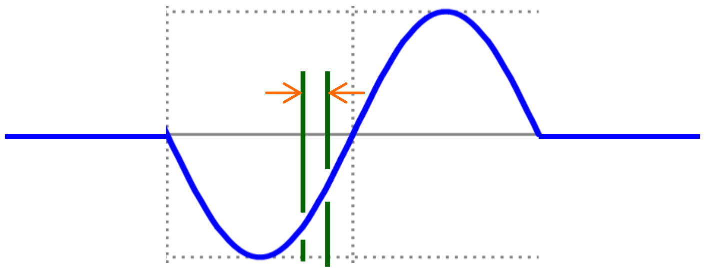
if we leave the particle alone, it behaves like a wave.

So we're just sitting there letting the system do whatever it wants to do and it's described by its wave function.

However, if we perform a measurement, suddenly we get something called the collapse of the wave function. So for example, if we've got a wave function that looks like that, and then we perform a measurement and we say, is the particle between these two green lines?

Is or isn't….not both

PROBABILITY



wave function will give us probabilities. It will say alright. If you did that measurement 100 times, 6 times you're going to find that it was between the green bars and the other 94 times you're going to find that it wasn't.

Since $\Psi(x,t)$, describes a particle, its evolution in time under the action of the wave equation ***describes the future history of the particle***

$\Psi(x,t)$ is determined by $\Psi(x, t = 0)$

Uncertainty built in from the beginning

Wave function is complex $\Psi = A + iB$

$$|\Psi|^2 = \Psi^*\Psi = A^2 - i^2B^2 = A^2 + B^2$$

is a positive real quantity: proportional to the probability density P of finding the body described by ψ

Than integral of $|\psi|^2$ over all space must be finite—the body is *somewhere.*

Particle in certain region of x_1 to x_2

$$\boxed{P_{x_1x_2} = \int_{x_1}^{x_2} |\Psi|^2 \, dx}$$

If $\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 0$ *Particle doesn't exist.*

Normalization

if the particle exists somewhere at all times

$$\boxed{\int_{all\ space} \left|\Psi(\vec{r},t)^2\right| d^3\vec{r} = 1} \quad \text{or} \quad \boxed{\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 1} \quad \text{or} \quad \boxed{\int_{-\infty}^{\infty} P \, dV = 1}$$

In 1D: $\boxed{\int_{-\infty}^{\infty} \left|\Psi(x,t)^2\right| dx = 1}$ - a wavefunction which obeys this condition is said to be normalized

Suppose we have a solution to the Sch. Eq. that is not normalized. The recipe for normalization:

- Calculate the ***normalization integral*** $N = \int_{-\infty}^{\infty} \left|\Psi(x,t)\right|^2 \mathrm{d}x$
- *Re-scale* the wave function as $\Psi'(\vec{r},t) = \frac{1}{\sqrt{N}}\Psi(\vec{r},t)$

This procedure works because any solution of the S.Eq. being multiplied by a constant remains a solution: the S..Eq. is ***linear*** and ***homogeneous***.

Ex.1 Find the value of the normalization constant *A for the wave* function $\psi = Axe^{-x^2/2}$.

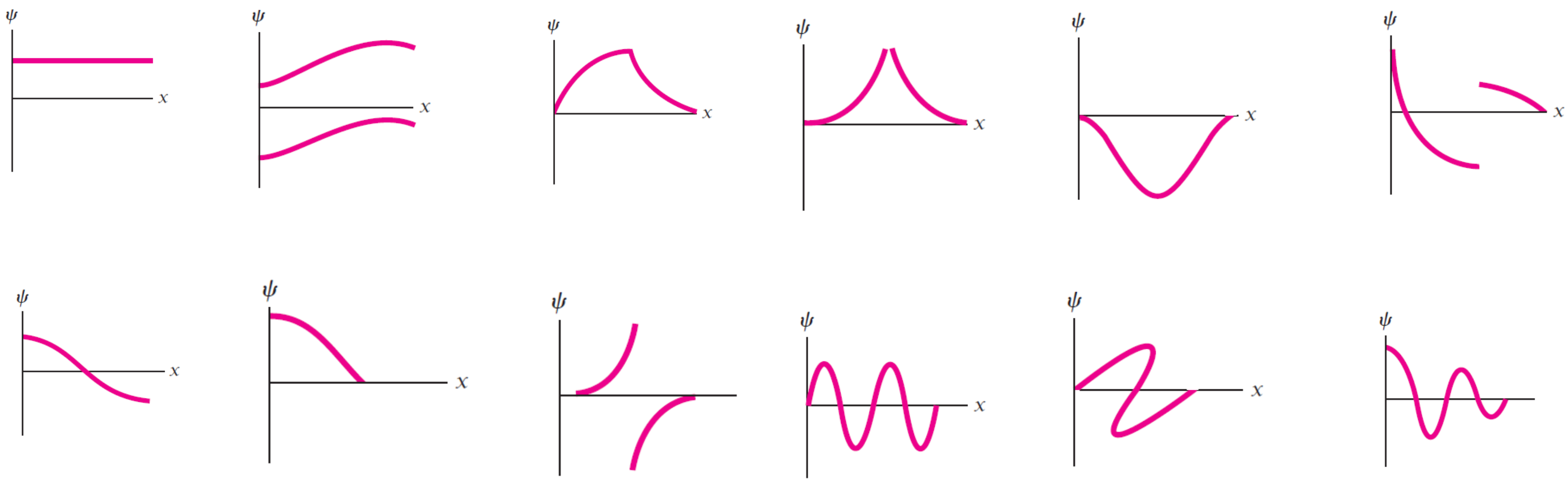
Ex.2: The wave function of a certain particle is $\psi = A\cos^2 x$ *for* $-\pi/2 < x < \pi/2$. *(a) Find the value of A. (b) Find the probability* that the particle be found between $x = 0$ *and* $x = 4$.

The well behaved wave function Ψ must be:

1. be a ***continuous*** and ***single-valued*** function of all *x* and *t* (the probability density must be uniquely defined)

2. have a ***continuous first derivative and single valued*** (the exception - points where the potential is infinite)

3. Have a ***finite normalization integral*** (so we can define a normalized probability)



(a) $A \sec x$ (b) $A \tan x$ (c) Ae^{x^2} (d) Ae^{-x^2}

The wave function satisfies something called Schrodinger's equation which kind of takes the place of conservation of energy

Time dependent Schrödinger Equation

Schrödinger developed the wave equation which can be solved to find the wavefunction by translating the equation for energy of classical physics into the language of waves

We assume that ψ for a particle moving freely in the x direction is specified by

$$\Psi = Ae^{-i\omega(t-x/v)} \quad \text{or} \quad \Psi = Ae^{-2\pi i(\nu t-x/\lambda)}$$

since

$$E = h\nu = 2\pi\hbar\nu$$

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

then

$$\Psi = Ae^{-(i/\hbar)(Et-px)}$$

differentiating ψ once with respect to t,

$$\frac{\partial\Psi}{\partial t} = -\frac{iE}{\hbar}\Psi$$

or

$$E\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}$$

differentiating ψ for twice with respect to *x*,

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\Psi$$

or

$$p^2\Psi = -\hbar^2\frac{\partial^2\Psi}{\partial x^2}$$

Total energy of the particle $$E = \frac{p^2}{2m} + U(x, t)$$

then $$E\Psi = \frac{p^2\Psi}{2m} + U\Psi$$

Substitute the value of $E\psi$ and $p^2\psi$

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

Time-dependent Schrödinger equation in one dimension

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

Time-dependent Schrödinger equation in three dimension

Schrödinger's equation cannot be derived from other basic principles of physics; it is a basic principle in itself.

Properties of Ψ

Wave functions add, not the probabilities

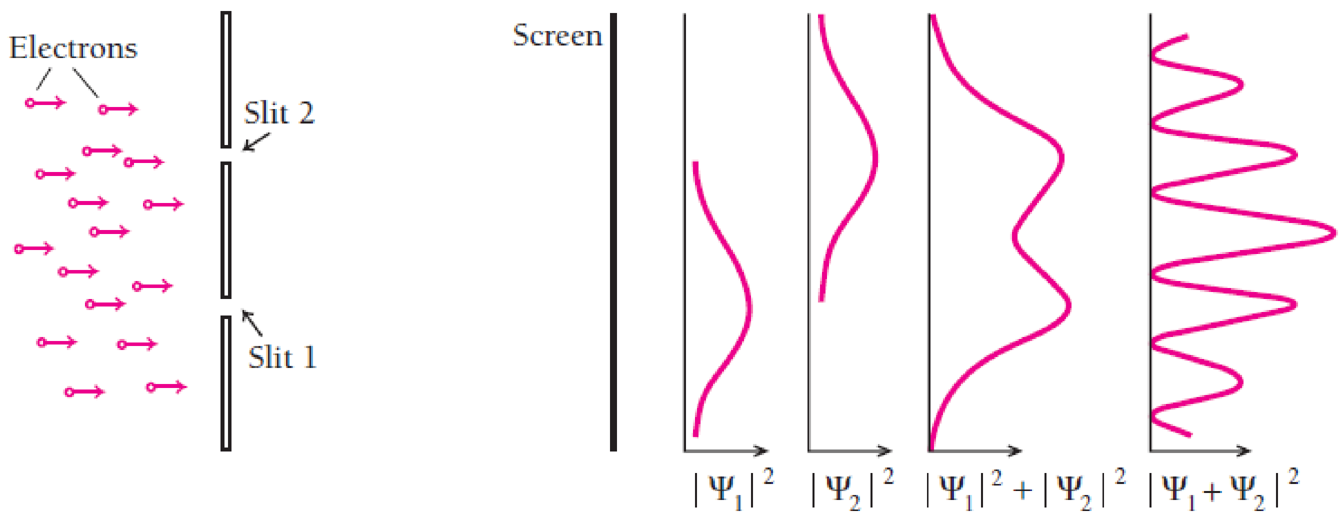
(i) Linearity and superposition

Linearity: An important properties of Schrodinger equation: it is linear in the Ψ, the equation has terms that contain Ψ and its derivatives but no terms independent of Ψ or that involve higher powers of Ψ or its derivatives.

Superposition: If Ψ_1 and Ψ_2 are two solutions,
$\Psi = a_1\Psi_1 + a_2\Psi_2$ is also a solution; Ψ_1 and Ψ_2 obey the superposition principle.

Interference effects can occur for wave functions just as they can for light, sound, etc

Superposition's to the diffraction of an electron beam:



Slit 1 is open: probability density: $P_1 = |\Psi_1|^2 = \Psi_1^* \Psi_1$

Slit 2 is open: probability density: $P_2 = |\Psi_2|^2 = \Psi_2^* \Psi_2$

Both open, probability density at screen:

$$P = |\Psi|^2 = |\Psi_1 + \Psi_2|^2 = (\Psi_1^* + \Psi_2^*)(\Psi_1 + \Psi_2)$$

$$= \Psi_1^* \Psi_1 + \Psi_2^* \Psi_2 + \Psi_1^* \Psi_2 + \Psi_2^* \Psi_1$$

$$= P_1 + P_2 + \underbrace{\Psi_1^* \Psi_2 + \Psi_2^* \Psi_1}$$

Responsible for oscillations of the e^- intensity at screen

(ii) Stationary state

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

Probability is independent of time

for every expectation value is constant in time

$$\langle Q(x, \hat{p})\rangle = \int \psi^* Q(x, \hat{p}) \psi dx$$

EXPECTATION VALUES

How to extract information from a wave function

let us calculate the **expectation value <x>** of the position of a particle confined to the x axis that is described by the wave function $\psi(x, t)$.

What is the average position x of a number of identical particles distributed along the x axis in such a way that there are N_1 particles at x_1, N_2 particles at x_2, and so on?

$$\bar{x} = \frac{N_1x_1 + N_2x_2 + N_3x_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\sum N_i x_i}{\sum N_i}$$

When we are dealing with a single particle, we must replace the number N_i of particles at x_i by the probability P_i that the particle be found in an interval dx at x_i.
This probability is

$$P_i = |\Psi_i|^2 \, dx$$

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

Expectation value for position

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

Expectation value for any quantity

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

OPERATORS

Another way to find expectation values

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

$$\hat{E} = i\hbar\frac{\partial}{\partial t}$$

$$\hat{E} = \hat{KE} + \hat{U}$$

$$\hat{KE} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

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

An **operator** tells us what operation to carry out on the quantity that follows it.

OPERATOR and expectation value

Because *p* and *E* can be replaced by their corresponding operators in an equation, we can use these operators to obtain expectation values for *p* and *E*.

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

$$\langle E \rangle = \int^{\infty} \Psi^* \hat{E} \Psi \, dx = \int^{\infty} \Psi^* \left(i\hbar\frac{\partial}{\partial t}\right) \Psi \, dx = i\hbar \int^{\infty} \Psi^* \frac{\partial \Psi}{\partial t} \, dx$$

Physical Quantity → Operators

- **Any measurement of the observable *a* corresponds to operator $\hat{A}$, the only values that will ever be observed are the *eigenvalues* of $\hat{A}$, which satisfy the *eigenvalue equation***

$$\boxed{\hat{A}\Psi(x,t) = A\,\Psi(x,t)}$$

- **If a system is in a state described by a wave function Ψ (*x*,*t*), then the average/expectation value of the observable *a* (measured once on many identical systems) is given by**

$$\boxed{\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x,t)\,\hat{A}\,\Psi(x,t)\,dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\,\Psi(x,t)\,dx}}$$

These are values of physical quantities that quantum mechanics predicts and which, from experimental point of view, are averages of multiple measurements

SCHRÖDINGER'S EQUATION: STEADY-STATE FORM

In many situations, the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence *U*, vary with the position of the particle only. When this is true, Schrödinger's equation may be simplified by removing all reference to *t*.

$$\text{1D:}\ \frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

$$\text{3D:}\ \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

An important property of Schrödinger's steady-state equation is that, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy *E*.

Thus energy quantization appears in wave mechanics as a natural element of the theory, and energy quantization in the physical world is revealed as a universal phenomenon characteristic of *all* stable systems.

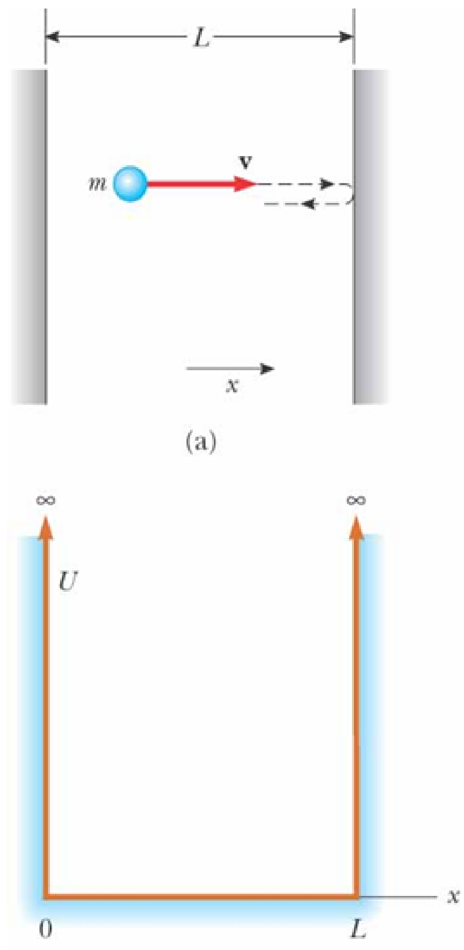
APPLICATION OF SCHRÖDINGER EQUATIONS

- **Particle in a box/Infinite potential well**
- **Finite potential Well**
- **Tunnel Effect**

Particle in a box with "*Infinite Hard walls*"

✷ ***Boundary conditions and normalization determines*** ψ

$$U(x) = \begin{cases} +\infty & x \le 0 \\ 0 & 0 < x < L \\ +\infty & x \ge L \end{cases}$$



Since the walls are impenetrable, there is zero probability of finding the particle outside the box.

Zero probability means:

$\psi(x) = 0$, for $x \le 0$ and $x \ge L$

The wave function must also be 0 at the walls (x = 0 and $x = L$), since the wavefunction must be continuous

Mathematically, $\psi(0) = 0$ and $\psi(L) = 0$

Schrödinger Equation

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial^2 x} + U(x)\psi(x) = E\psi(x)}$$

for Particle in a Box

For $0 < x < L$, where $U(x) = 0$, the Schrödinger equation can be expressed in the form

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

We can re-write it as

$$\frac{\partial^2\psi(x)}{\partial^2 x} = -\frac{2mE}{\hbar^2}\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial^2 x} = -k^2\psi(x)$$

$$k^2 \equiv \frac{2mE}{\hbar^2}$$

$$\boxed{\frac{\partial^2\psi(x)}{\partial^2 x} = -k^2\psi(x)}$$

The most general solution to this differential equation is:

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

A and B are constants which are determined from the properties of the ψ as well as boundary and normalization conditions

1. *Sin(x)* and *Cos(x)* are finite and single-valued functions

2. Boundary Condition: $\psi(0) = \psi(L) = 0$

- $\psi(0) = A\sin(k0) + B\cos(k0) = 0 \Rightarrow B = 0$
  $\Rightarrow \psi(x) = A\sin(kx)$
- $\psi(L) = A\sin(kL) = 0 \Rightarrow \sin(kL) = 0 \Rightarrow kL = n\pi,\ n = \pm1, \pm2\ldots$

$$\boxed{k_n = \frac{\pi}{L} n \qquad n = 1,2,3\ldots}$$

Particle in a Box

Energy Levels:

$$\boxed{E_n = \frac{\hbar^2 k_n^{\ 2}}{2m} = \frac{\hbar^2 (\frac{\pi}{L} n)^2}{2m} = \left(\frac{\pi^2 \hbar^2}{2mL^2}\right) n^2 = \left(\frac{h^2}{8mL^2}\right) n^2}$$

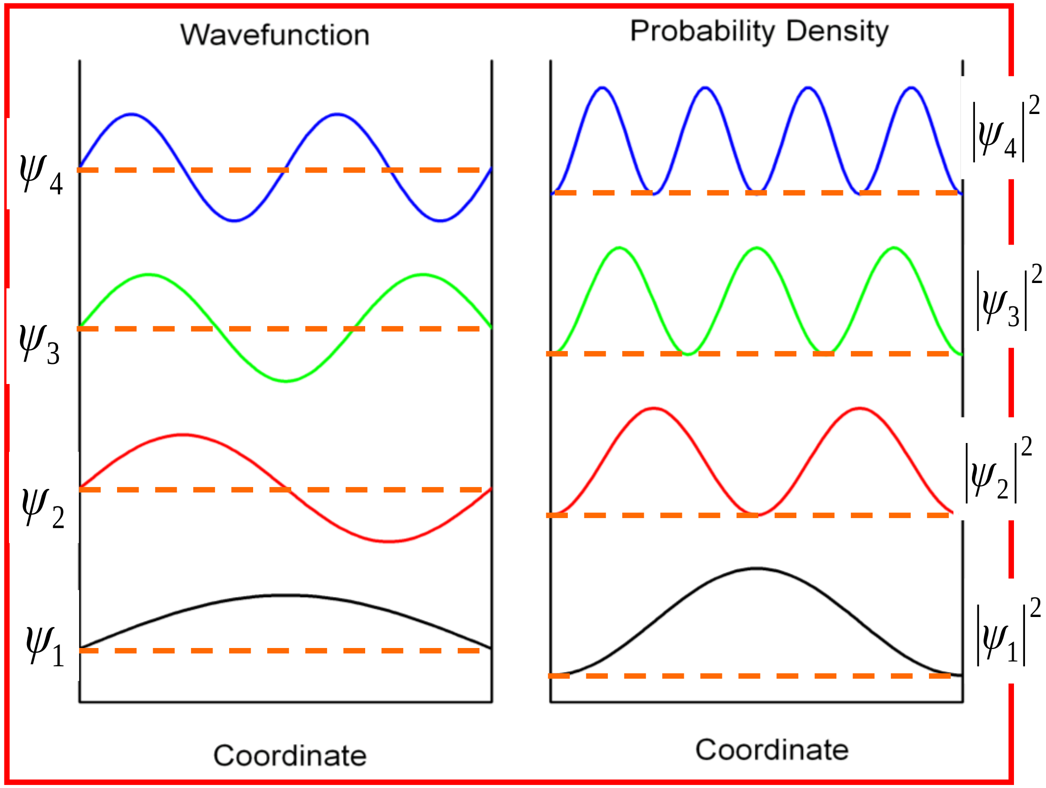
- The allowed wave functions are given by

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

- The normalized wave function:

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

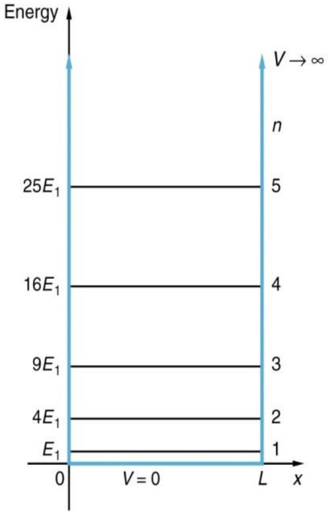
$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$



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

$$E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2 \equiv E_0 n^2,\ with\ E_0 = \frac{\pi^2\hbar^2}{2mL^2}$$

$$ground\ state(n = 1)\ energy,\ E_1 = E_0$$



Ex-1: *e^- in a 10nm wide Well with infinite barriers. Calculate E_0 for L = 10 nm*

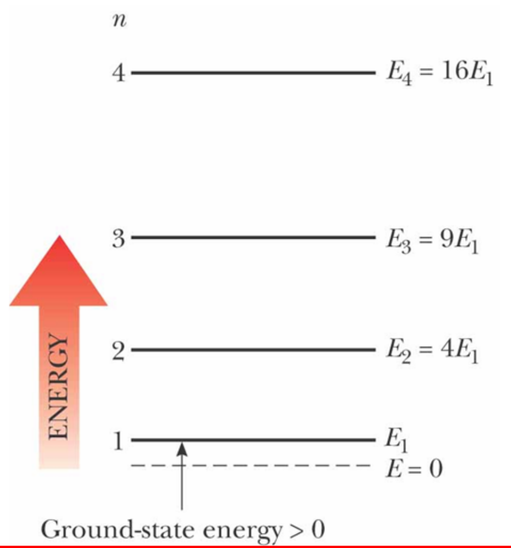
$$\boxed{E_n = E_0 n^2, \text{ where } E_1 = E_0 = \frac{\pi^2 \hbar^2}{2mL^2}}$$

$$E_0 = \frac{3.14^2 (1.05\times10^{-34})^2}{2\times9.1\times10^{-31}\times(10\times10^{-9})^2}$$

$$E_0 \approx 6\times10^{-22}\ \mathrm{J} = 0.00375\ \mathrm{eV} = 3.75\ \mathrm{meV}$$

$$1\ \mathrm{meV} = 10^{-3}\ \mathrm{eV}$$

Ex-2: *Assume that a photon is absorbed, and the electron is transferred from the ground state (n = 1) to the second excited state (n = 3). What was the wavelengths of the photon?*



$$\boxed{E_{ground} \equiv E_1 = E_0 = 0.00375\ \mathrm{eV}}$$

Third excited state is E_3

$$E_3 = E_0 \times 3^2 = 9\times0.00375\,\mathrm{eV} \approx 0.0338\,\mathrm{eV}$$

$$(h\nu) = E_3 - E_1 = 0.0338 - 0.00375 \approx 0.030\,\mathrm{eV}$$

$$\lambda = \frac{1240}{0.03} \approx 41333\,\mathrm{nm} \approx 41\,\mu\mathrm{m}$$

Average Momentum of Particle in a Box (Infinite Potential Well) problem

$$\boxed{\begin{aligned} < p_x > &= \int_0^L \Psi^*(x)\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi^*(x)dx \\ &= \int_0^L [\sqrt{\frac{2}{L}}\sin kx]\frac{\hbar}{i}\frac{\partial\sqrt{\frac{2}{L}}\sin kx}{\partial x}dx \\ &= \frac{2}{L}\frac{\hbar}{i}k\int_0^L \sin(kx)\cos(kx)dx = 0 \end{aligned}}$$

Note: the right hand side is either 0 or imaginary, but momentum cannot be imaginary so it must be zero

But

$$\boxed{< p_x^2 > \neq 0}$$ Why ???

SUMMARY

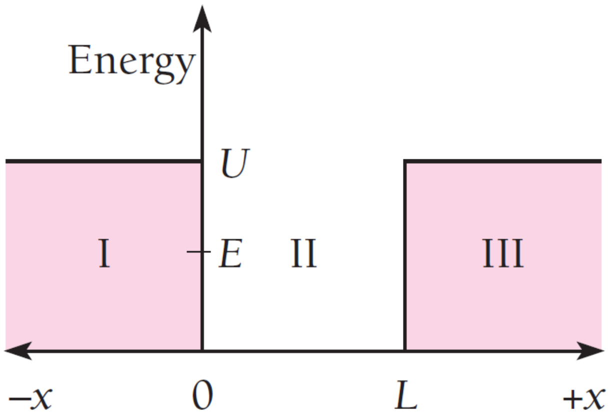
Classical and quantum behaviour of a particle confined in one dimensional Box

Features	Classical behaviors	Quantum behaviors
1. Allowed energy levels	A classical particle have any energy	The particle can have discrete energy values given by $$E_n = \frac{\pi^2\hbar^2}{2mL^2} n^2; n = 1,2,3\ldots$$
2. Minimum energy	The minimum energy of the particle is zero	The minimum energy of the particle is $$E_1 = \frac{\pi^2\hbar^2}{2mL^2}$$
3. Position probability	It has a value at all points within the well	The probability of finding the quantum mechanical particle at position x depends on $\lvert\Psi_n(x)\rvert^2$ and hence has different points and for different states.

Finite Potential Well

Potential energies are never infinite in the real world, and the box with infinitely hard walls of the previous section has no physical counterpart. However, potential wells with barriers of finite height certainly do exist. Let us see what the wave functions and energy levels of a particle in such a well are.

$$U(x) = \begin{cases} U & x \le 0 \\ 0 & 0 < x < L \\ U & x \ge L \end{cases}$$



We also assume that energy of the particle, E, is less than the "height" of the barrier, i.e. $E < U$

In regions I and III Schrödinger's steady-state equation is

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

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \qquad \begin{matrix} x < 0 \\ x > L \end{matrix}$$

The solutions are real exponentials:

$$\psi_{\mathrm{I}} = Ce^{ax} + De^{-ax}$$

$$\psi_{\mathrm{III}} = Fe^{ax} + Ge^{-ax}$$

$$a = \frac{\sqrt{2m(U-E)}}{\hbar}$$

Both ψ_{I} and ψ_{III} must be finite everywhere. Since $e^{-ax} \to \infty$ as $x \to -\infty$ and $e^{ax} \to \infty$ as $x \to \infty$, the coefficients D and F must therefore be 0. Hence we have

$$\psi_{\mathrm{I}} = Ce^{ax}$$

$$\psi_{\mathrm{III}} = Ge^{-ax}$$

These wave functions decrease exponentially inside the barriers at the sides of the well.

Within the well

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

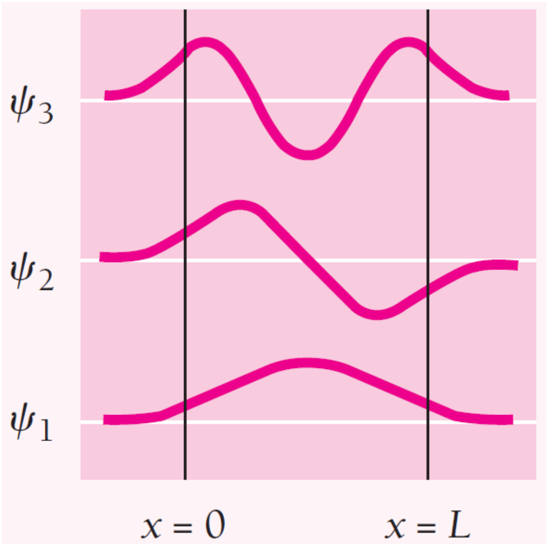
$$\psi_{\mathrm{II}} = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

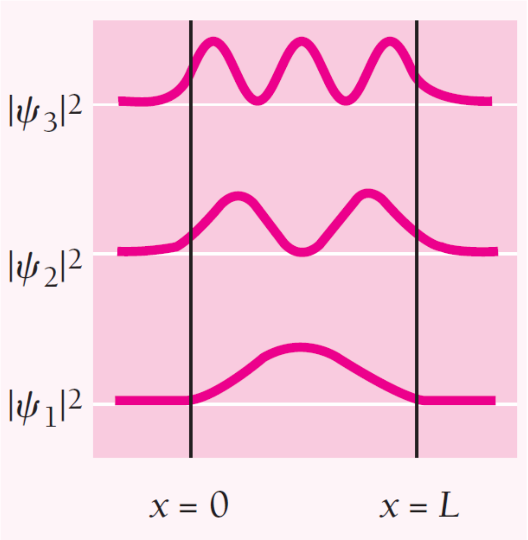
In the case of a well with infinitely high barriers, we found that $B = 0$ in order that $\psi = 0$ *at* $x = 0$ *and* $x = L$. Here, however, $\psi_{II} = C$ *at* $x = 0$ *and* $\psi_{II} = G$ *at* $x = L$, so both the sine and cosine solutions are possible

➢ For either solution, both ψ *and* $d\psi/dx$ must be continuous *at* $x = 0$ *and* $x = L$*: the* wave functions inside and outside each side of the well must not only have the same value where they join but also the same slopes, so they match up perfectly.

➢ When these boundary conditions are taken into account, the result is that exact matching only occurs for certain specific values E_n *of the particle energy*.

Wave function and probability





Because the λ that fit into the well are longer than for an infinite well of the same width, the corresponding particle momenta are lower (we recall that λ = h/p). Hence the energy levels $\boldsymbol{E_n}$ are lower for each n than they are for a particle in an infinite well.

Outside the potential well, classical physics forbids the presence of the particle

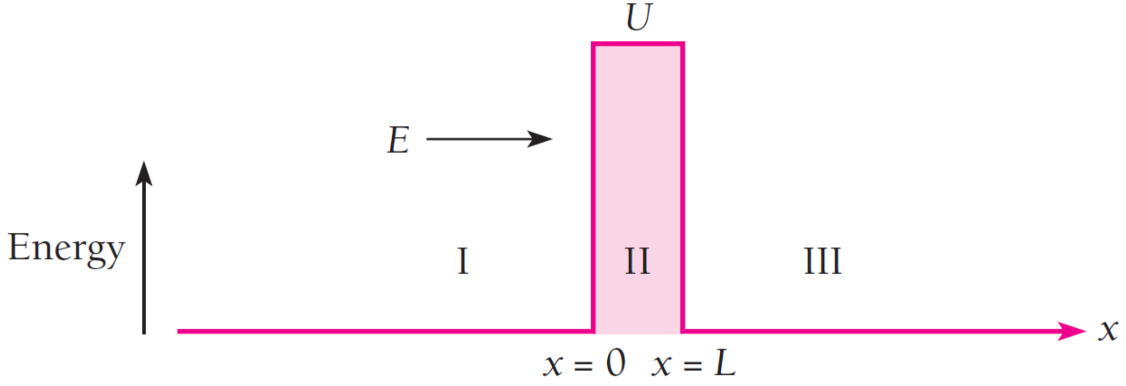
Quantum mechanics shows the wave function decays exponentially to zero

The functions are smooth at the boundaries

Outside the box, the probability of finding the particle decreases exponentially, but it is not zero!

Tunneling

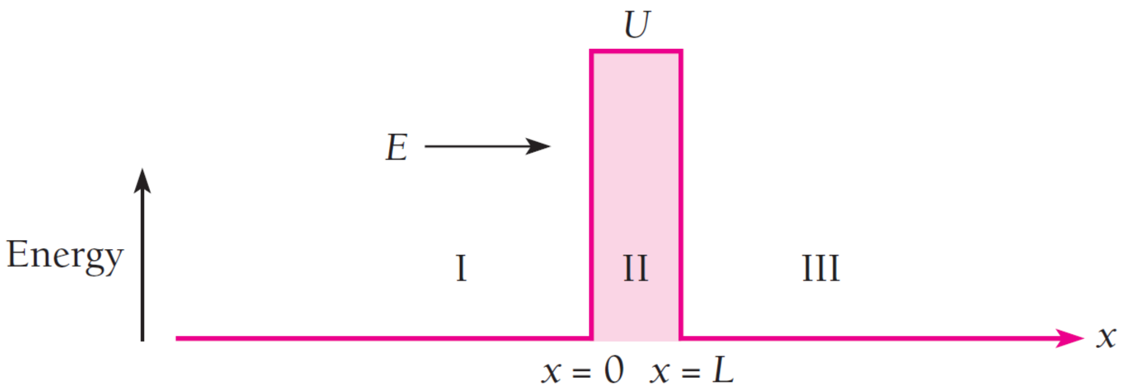
situation of a particle that strikes a potential barrier of height U, again with E < U, but here the barrier has a finite width



The potential energy has a constant value U in the region of width L and zero in all other regions. This a called a **barrier**

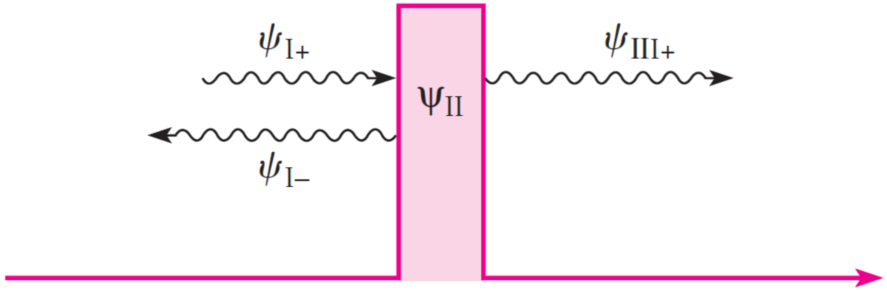
When a particle of energy E < U approaches a potential barrier, according to classical mechanics the particle must be reflected.

In quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted, which means that the particle has a finite chance of penetrating the barrier.



Let us consider a beam of identical particles all of which have the kinetic energy E. The beam is incident from the left on a potential barrier of height U and width L.

On both sides of the barrier $U = 0$, *which means that no forces act on the* particles there.



ψ_{I+} : incoming particles moving to the right

ψ_{I-} : reflected particles moving to the left;

ψ_{III} : transmitted particles moving to the right.

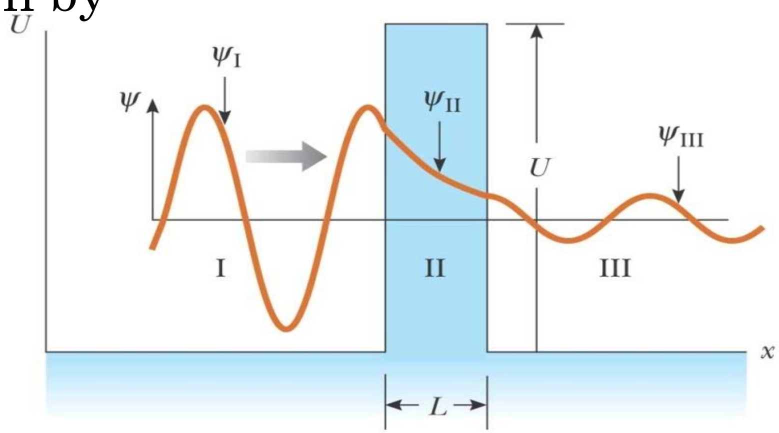
ψ_{II} : particles inside the barrier, some of which end up in region III while the others return to region I.

The transmission probability *T for a particle to pass through the barrier is* equal to the fraction of the incident beam that gets through the barrier.

Approximate value of probability is given by

$$T = e^{-2k_2L} \qquad k_2 = \frac{\sqrt{2m(U - E)}}{\hbar}$$

L: width of the barrier



- According to quantum mechanics, all regions are accessible to the particle
  - The probability of the particle being in a classically forbidden region is low, but not zero
  - Amplitude of the wave is reduced in the barrier
  - A fraction of the beam penetrates the barrier

The examples of **tunnel effect:**

▪ **Alpha** particles emitted by certain radioactive nuclei. An alpha particle whose K.E is only a few MeV is able to escape from a nucleus whose potential wall is perhaps 25 MeV high.

The probability of escape is so small that the alpha particle might have to strike the wall 10^{38} or more times before it emerges, but sooner or later it does get out.

▪ Operation of certain **semiconductor diodes** in which e^- pass through potential barriers even though their K.E < U

Based on principle:

- Scanning Tunnelling Microscope (STM)
- Atomic Force Microscope (AFM)