

**Look at the other part:**

Time-Independent Schrödinger equation (TISE)

$$\left[ -\frac{\hbar^2}{2m} \vec{V}^2 + \hat{V}(\vec{r}) \right] \Psi(\vec{r}) = E\Psi(\vec{r})$$

**TISE is an eigenvalue problem**

- Eigenvalue equations are of the type

$$\hat{A}\Psi_n = a_n \Psi_n$$

- $\hat{A}$  is an operator and  $a_n$  is a number.
- A solution  $\Psi_n$  of such an equation is called an eigenfunction corresponding to the eigenvalue  $a_n$  of the operator A.
- Operator A acting on certain function(the eigenfunction) will give back their function multiplied by constants  $a_n$ .

The total wavefunction :

$$\Psi(\vec{r}, t) = \Psi(\vec{r}) e^{-i\frac{Et}{\hbar}}$$

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r})$$

(TISE)

Probability density :

$$\begin{aligned} \rho(\vec{r}, t) &= \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) \\ &= \Psi^*(\vec{r}) \Psi(\vec{r}) e^{-i\frac{(E-E^*)t}{\hbar}} \end{aligned}$$

$$\int \rho(\vec{r}, t) dV = 1$$

$$\frac{\partial}{\partial t} \int \rho(\vec{r}, t) dV = 0$$

$$\Rightarrow -i \frac{(E - E^*)}{\hbar} e^{-i\frac{(E-E^*)t}{\hbar}} \int \Psi^*(\vec{r}) \Psi(\vec{r}) dV = 0$$

The integral  $\int \Psi^*(\vec{r}) \Psi(\vec{r}) dV = 1$ 

Valid for all time.

 $E = E^* \Rightarrow E$  is real

$$E = E^* \Rightarrow E \text{ is real}$$

So, what happens to the probability density?

$$\rho(\vec{r}, t) = \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) = \Psi^*(\vec{r}) \Psi(\vec{r}) e^{-i\frac{(E-E^*)t}{\hbar}}$$

$$\rho(\vec{r}, t) = \rho(\vec{r}) = \Psi^*(\vec{r}) \Psi(\vec{r}) = |\Psi(\vec{r})|^2$$

**As E is real, the probability density is independent of time**  
**& then  $\Psi(\vec{r}, t) = \Psi(\vec{r}) e^{-i\frac{Et}{\hbar}}$  is called stationary state**

There is always a set of solutions for Equation  $\hat{H}\psi(x) = E\psi(x)$

thus

$$\Psi_n(x, t) = \psi_n(x) \exp(-iE_n t / \hbar)$$

The probability density is

$$\begin{aligned} \Psi_n^*(x, t) \Psi_n(x, t) dx &= \psi_n^*(x) \exp(iE_n t / \hbar) \psi_n(x) \exp(-iE_n t / \hbar) dx \\ &= \psi_n^*(x) \psi_n(x) \end{aligned}$$

The average is

$$\langle \hat{H} \rangle = \frac{\int_{-\infty}^{\infty} \psi_n^*(x) \hat{H} \psi_n(x) dx}{\int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx}$$

- Because the probability density and the average are independent of time, the  $\psi_n(x)$  are known as stationary-state wave functions.
- The stationary energy states of an atom or molecule are obtained by solving the Schrödinger equation in 1-, 2- and 3-dimensions.

## Dirac Brackets

In Dirac notation, integrals are written as:

$$\int \psi^* \hat{Q} \psi d\tau = \langle \psi^* | \hat{Q} | \psi \rangle$$

$$\int \psi^* \psi d\tau = \langle \psi^* | \psi \rangle$$

$|\psi\rangle$  is called the **ket**, and denotes the state described by the function  $\psi$ .

$\langle \psi^* |$  is called the **bra**, and denotes the complex conjugate of the function  $\psi^*$ .

## Theorems of Quantum Mechanics

### ❖ The eigenvalues of Hermitian operators are real (Can we prove it?)

Suppose  $\hat{Q}$  is a **Hermitian operator** with a square-integrable eigenfunction  $\psi(x)$ :

$$\hat{Q}\psi = \alpha\psi$$

Expressing each side as a real and an imaginary part, keeping in mind that the real parts must be equal to each other and likewise the imaginary parts, gives:

$$\hat{Q}^* \psi^* = \alpha^* \psi^*$$

Multiplying  $\psi^*$  from the left of the Equation  $\hat{Q}\psi = \alpha\psi$  followed by integration gives

$$\langle \psi^* | \hat{Q} | \psi \rangle = \alpha \langle \psi^* | \psi \rangle$$

Also, multiplying  $\psi$  from the left of the Equation  $\hat{Q}^* \psi^* = \alpha^* \psi^*$  followed by integration gives:

$$\langle \psi | \hat{Q}^* | \psi^* \rangle = \alpha^* \langle \psi | \psi^* \rangle$$

Since the operator is Hermitian, the left-hand sides of the above two Equations are equal, and thus their right-hand sides are equal, and their difference is zero:

$$(\alpha - \alpha^*) \langle \psi | \psi^* \rangle = 0$$

Remember that Hermitian operator obey the following condition

$$\int_{-\infty}^{\infty} \psi_i^* \hat{Q} \psi_j d\tau = \int_{-\infty}^{\infty} \psi_i \hat{Q}^* \psi_j^* d\tau$$

Since  $\psi$  is square-integrable, the integral  $\langle \psi | \psi^* \rangle \neq 0$   
 & thus  $(\alpha - \alpha^*) = 0 \rightarrow$  which requires that  $\alpha$  be real.

### ❖ Orthogonality Theorem

Eigenfunctions corresponding to different eigenvalues for the same Hermitian operator are orthogonal.

Let  $\psi_i$  and  $\psi_j$  represent two eigenfunctions corresponding to two different eigenvalues,  $\alpha_i$  and  $\alpha_j$ , respectively, for the same Hermitian operator  $\hat{Q}$ :

$$\begin{aligned}
 \hat{Q}\psi_i &= \alpha_i\psi_i && \text{Multiplying } \psi_j^* \text{ from the left} \\
 \hat{Q}^*\psi_j^* &= \alpha_j\psi_j^* && \text{followed by integration} \\
 \langle \psi_j^* | \hat{Q} | \psi_i \rangle &= \alpha_i \langle \psi_j^* | \psi_i \rangle && \text{Multiplying } \psi_i \text{ from the left} \\
 \langle \psi_i | \hat{Q}^* | \psi_j^* \rangle &= \alpha_j \langle \psi_i | \psi_j^* \rangle && \text{followed by integration} \\
 \end{aligned}$$

**Note: the LHSs are equal due to the property of Hermitian operator**

So, the difference of their RHSs gives:

So, the difference of their RHSs gives:

$$(\alpha_i - \alpha_j) \langle \psi_j^* | \psi_i \rangle = 0$$

The integral in the Equation above vanishes when  $\alpha_i \neq \alpha_j \rightarrow$

$$\langle \psi_j^* | \psi_i \rangle = 0 \quad \Rightarrow \text{Hence, they are orthogonal}$$

Please refer to the following:

$$\begin{aligned}
 \int_{-\infty}^{\infty} \psi_i^* \psi_j d\tau &= \delta_{ij} \text{ (Kronecker delta)} \\
 \delta_{ij} &= \begin{cases} 0 & \text{when } i \neq j \text{ (orthogonal)} \\ 1 & \text{when } i = j \text{ (normal)} \end{cases}
 \end{aligned}$$

❖ Commuting operators have simultaneous eigenfunctions

Let  $\hat{A}$  and  $\hat{B}$  represent two different operators and  $f$  represents an arbitrary square-integrable function.

The operators are said to commute when

$$[\hat{A}, \hat{B}]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f$$

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f = 0 \quad \Rightarrow \hat{A}\hat{B} - \hat{B}\hat{A} = \hat{0}$$

$\hat{0}$  is known as the null operator if  $\hat{0}f = 0$ .

The difference of the product of operators is called the commutator.

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

$[\hat{A}, \hat{B}] = 0 \rightarrow$  The operators commute  $\rightarrow$  the corresponding observables can be measured simultaneously with arbitrary precision

$[\hat{A}, \hat{B}] \neq 0 \rightarrow$  Operators do not commute  
Operators are incompatible,  
 $\rightarrow$  leads to the Heisenberg's uncertainty principle.

Let  $\psi_i$  be the eigenfunctions for  $\hat{B}$  so that:  $\hat{B}\psi_i = b_i\psi_i$

where all the  $b_i$  are different, meaning that the eigenfunctions are nondegenerate.

When  $[\hat{A}, \hat{B}] = \hat{0}$ :  $\hat{B}(\hat{A}\psi_i) = \hat{A}\hat{B}\psi_i = \hat{A}b_i\psi_i = b_i(\hat{A}\psi_i)$



The bracket is meant to stress that the function obtained by operating on  $\psi_i$  with  $\hat{A}$  is an eigenfunction of  $\hat{B}$  with eigenvalue  $b_i$

However, the function can only be a constant multiplied by  $\psi_i$  itself and therefore for nondegenerate  $\psi_i$ :  $\hat{A}\psi_i = c\psi_i$

Commuting operators have simultaneous eigenfunctions, meaning that a set of eigenfunctions can be found for one of the operators that is also an eigenfunction set for the other operator.

## Commutators and Uncertainty

There are important consequences for the existence of simultaneous eigenfunctions for various operators, and this is embodied in the uncertainty principle.

Consider a particle moving towards positive  $x$ .

Let the wave function  $\psi(x)$  of the particle be  $N e^{ikx}$  with  $N$  being the normalisation factor. Where can we find the particle?

To answer this question, calculate the probability density:

$$|\psi|^2 = (N e^{-ikx}) \times (N e^{ikx}) = N^2 (e^{-ikx})(e^{ikx}) = N^2$$

- ✓ Since the probability density is independent of  $x$ , there is an equal probability of finding the particle anywhere on the  $x$ -axis.
- ✓ In other words, the **position of the particle can not be predicted**.
- ✓ Put it in a different way: **knowing the linear momentum precisely makes it impossible to know anything about the position.**

Find  $\langle \hat{x} \hat{p}_x - \hat{p}_x \hat{x} \rangle$

**DO YOU REMEMBER THIS?**

$$\begin{aligned} \langle \hat{x} \hat{p}_x - \hat{p}_x \hat{x} \rangle &= \int_{-\infty}^{+\infty} \Psi^*(\vec{r}, t) (\hat{x} \hat{p}_x - \hat{p}_x \hat{x}) \Psi(\vec{r}, t) dx \\ &= -i\hbar \int_{-\infty}^{+\infty} \Psi^*(\vec{r}, t) \left[ \frac{x \partial \Psi}{\partial x} - \frac{\partial(x\Psi)}{\partial x} \right] dx \\ &= -i\hbar \int_{-\infty}^{+\infty} \Psi^*(\vec{r}, t) \left[ \frac{x \partial}{\partial x} - \psi - x \frac{\partial(\Psi)}{\partial x} \right] dx \\ &= i\hbar \int_{-\infty}^{+\infty} \Psi^* \Psi dx \\ &= i\hbar \end{aligned}$$

$$[\hat{x}, \hat{p}_x] = i\hbar$$

Position and momentum are thus complementary observables

Time and energy are also complementary

$$[\hat{E}, \hat{t}] = ?$$

$$[\hat{t}, \hat{E}] = ?$$

$$[\hat{E}, \hat{t}]\psi(t) = (\hat{E}\hat{t} - \hat{t}\hat{E})\psi(t)$$

$$\hat{E}\hat{t}\psi(t) = i\hbar \frac{\partial}{\partial t} (t\psi(t)) = i\hbar(\psi(t) + t \frac{\partial\psi}{\partial t})$$

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

$$[\hat{E}, \hat{t}]\psi(t) = (\hat{E}\hat{t} - \hat{t}\hat{E})\psi(t) = i\hbar(\psi(t) + t \frac{\partial\psi}{\partial t}) - i\hbar(t \frac{\partial\psi}{\partial t}) = i\hbar\psi(t)$$

$$[\hat{E}, \hat{t}] = i\hbar$$

→ A non-zero constant

→ implies that the operators do not commute

→ The corresponding observables (energy and time) cannot be known with precision at the same time.

**This is the basis for Heisenberg's uncertainty principle!!**

### Heisenberg's uncertainty principle

The principle says it is impossible to specify simultaneously, with precision, both the momentum and the position of a particle.

$$\Delta x \Delta p \geq \frac{1}{2} \hbar$$

The standard deviation in these quantities, **position and momentum**, corresponding to the **operators**, represents the uncertainty in the observed values of the physical quantities:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

standard deviation  
in position

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

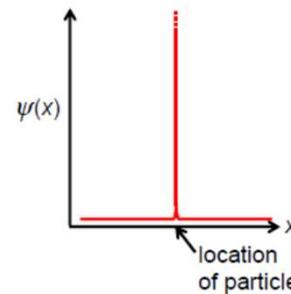
standard deviation  
in momentum

Note that for any operator  $\hat{A}$ , the standard deviation  $\Delta A$  of the measurement from the mean value is

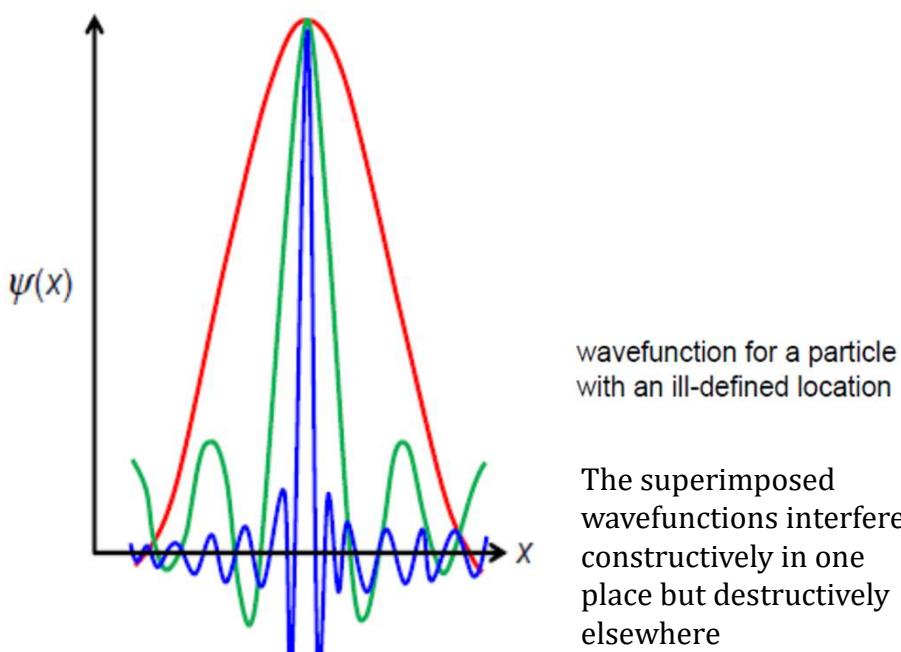
$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

where  $\langle A^2 \rangle = \int \psi^* \hat{A}^2 \psi d\tau$        $\langle A \rangle^2 = \left( \int \psi^* \hat{A} \psi d\tau \right)^2$

If a particle is at a definite location, its wave function is large there and zero everywhere else. Such a wavefunction can be created by superimposing a large number of functions. Such a sharply localised wavefunction is known as a *wavepacket*.



wave function for a particle  
at a well-defined location



wavefunction for a particle  
with an ill-defined location

The superimposed  
wavefunctions interfere  
constructively in one  
place but destructively  
elsewhere

## Applications of Quantum Mechanics

### Particle in a Box - 1D

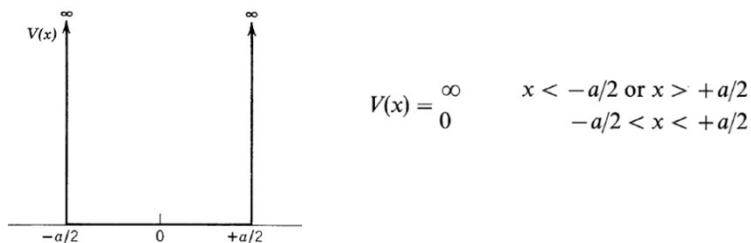
*It tells us how boundary conditions and normalization determine wave functions*

#### **THE INFINITE SQUARE WELL POTENTIAL**

A particle trapped in a box with infinitely hard walls.

Let us now tackle the problem in a more formal way.

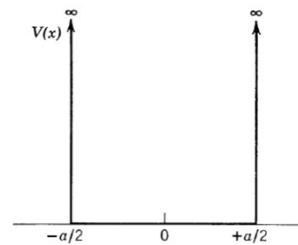
This will give us the wave function  $\psi_n$  that corresponds to each energy level.

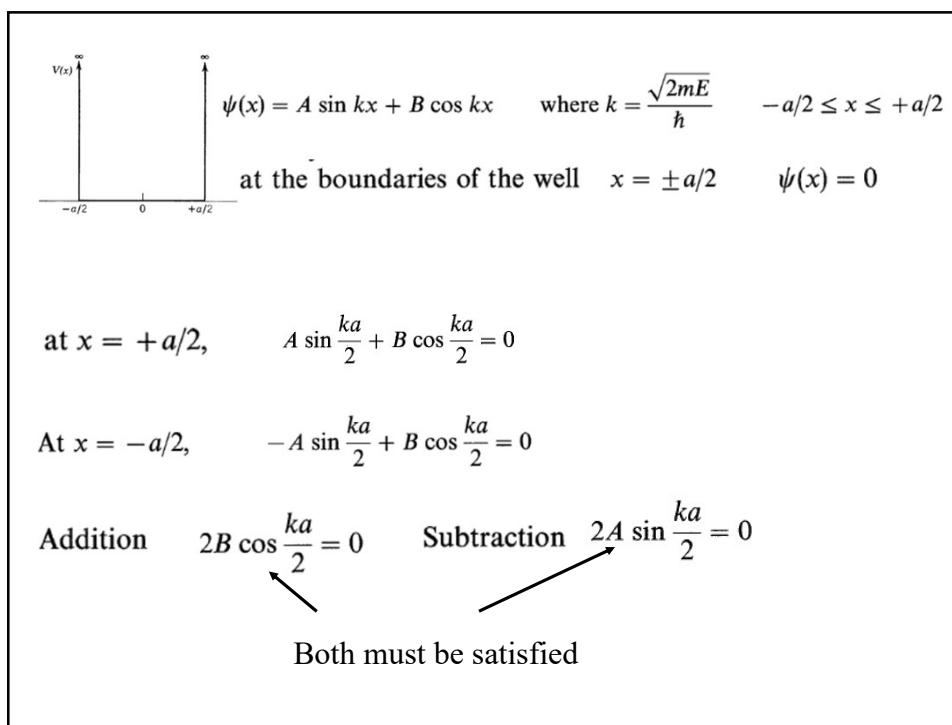
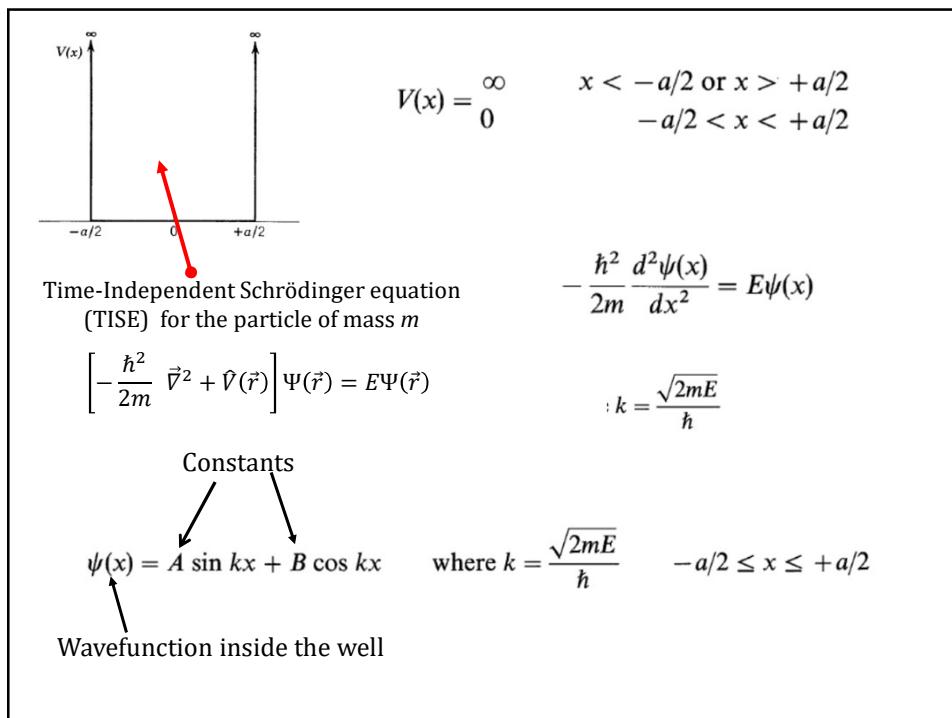


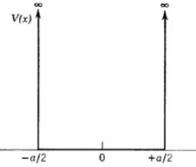
We specify the particle's motion

- It is restricted to traveling along the  $x$ -axis between  $x = -a/2$  and  $x = +a/2$  by infinitely hard walls.
- A particle does not lose energy when it collides with such walls, so that its total energy stays constant.
- The potential energy  $V$  of the particle is  $\infty$  on both sides of the box
- while  $V$  is a constant — say 0 for convenience, inside
- Since the particle cannot have an infinite amount of energy, it cannot exist outside the box.
- Its wave function  $\psi$  is 0 for  $x \leq -a/2$  and  $x \geq +a/2$ .

Our task is to find what  $\psi$  is within the box, between  $x = +a/2$  and  $x = +a/2$







$$\psi(x) = A \sin kx + B \cos kx \quad \text{where } k = \frac{\sqrt{2mE}}{\hbar} \quad -a/2 \leq x \leq +a/2$$

at the boundaries of the well  $x = \pm a/2$   $\psi(x) = 0$

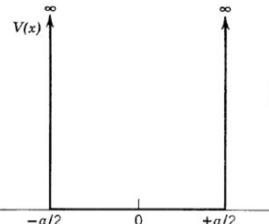
$$2B \cos \frac{ka}{2} = 0$$

$$2A \sin \frac{ka}{2} = 0$$

Both must be satisfied

There is no value of the parameter  $k$  for which both  $\cos(ka/2)$  and  $\sin(ka/2)$  are simultaneously zero. And we certainly do not want to satisfy the two equations by setting both  $A$  and  $B$  equal to zero, for then  $\psi(x) = 0$  everywhere

$$\psi(x) = A \sin kx + B \cos kx \quad \text{where } k = \frac{\sqrt{2mE}}{\hbar} \quad -a/2 \leq x \leq +a/2$$



Boundary condition at  $x = \pm a/2$   $\psi(x) = 0$

$$2B \cos \frac{ka}{2} = 0 \quad 2A \sin \frac{ka}{2} = 0 \quad \text{Both solutions must be satisfied}$$

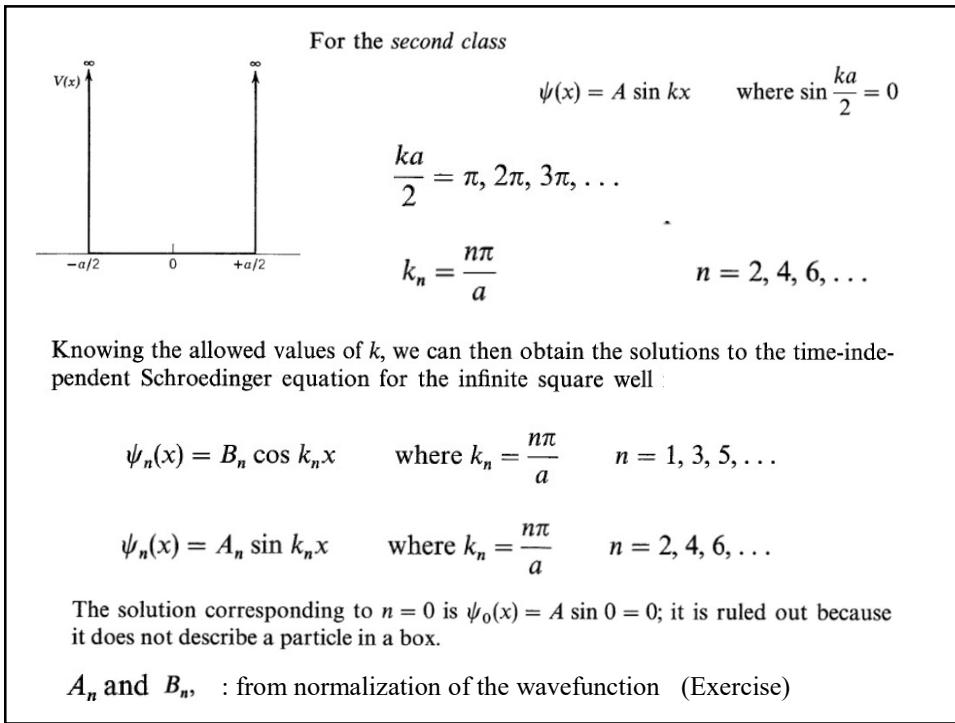
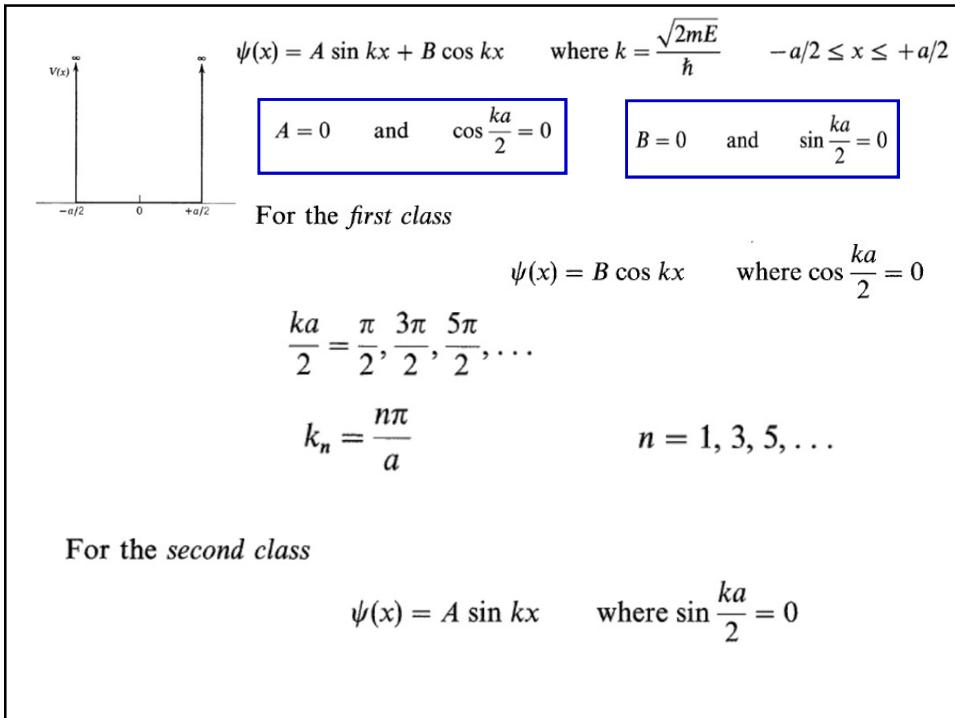
$$A = 0 \quad \text{and} \quad \cos \frac{ka}{2} = 0$$

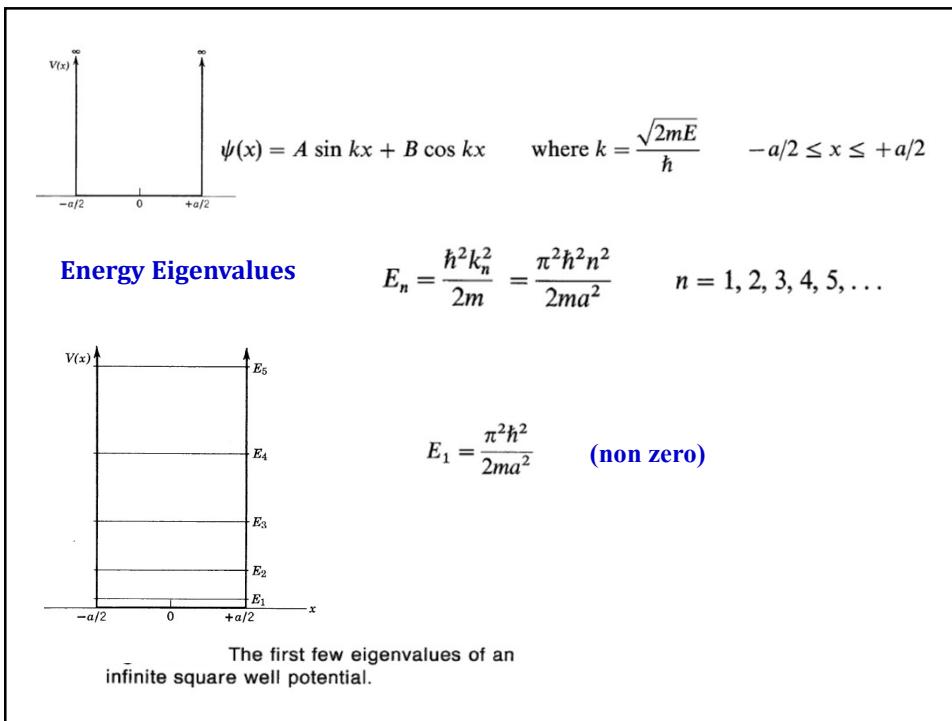
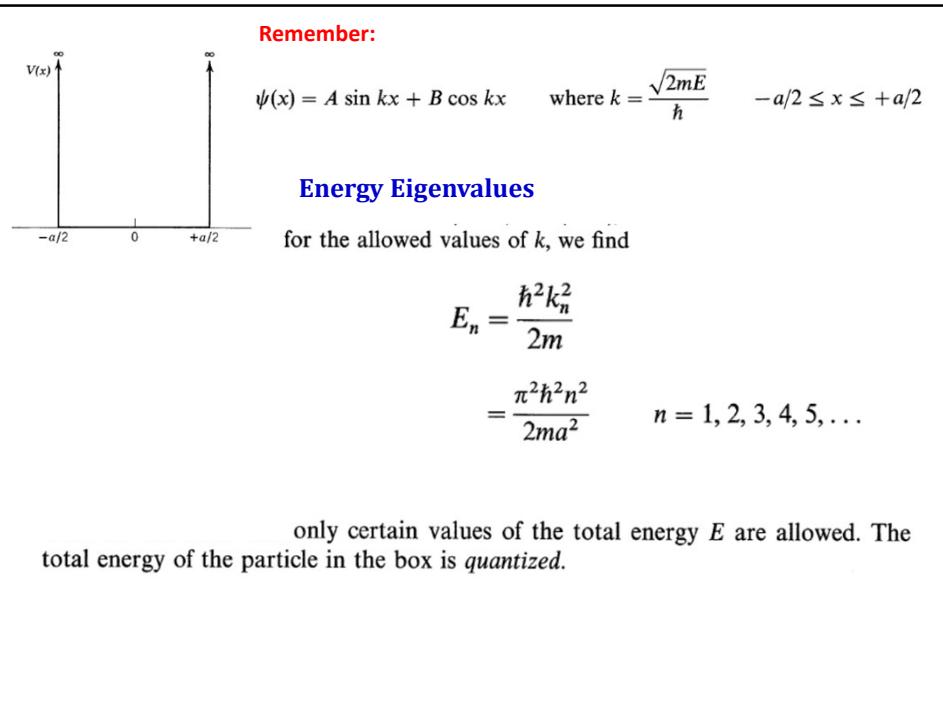
$$B = 0 \quad \text{and} \quad \sin \frac{ka}{2} = 0$$

Thus there are two classes of solutions.

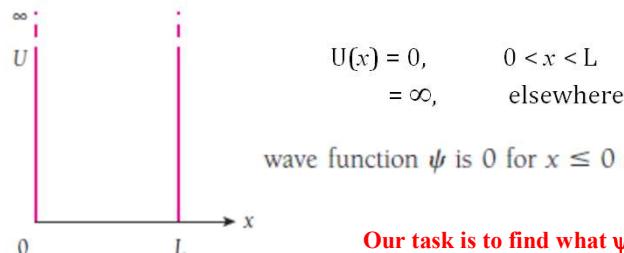
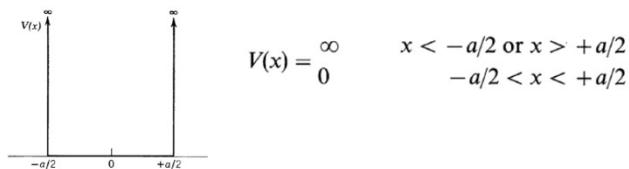
For the *first class*

$$\psi(x) = B \cos kx \quad \text{where } \cos \frac{ka}{2} = 0$$





**THE INFINITE SQUARE WELL POTENTIAL** (Particle in a box)



Our task is to find what  $\psi$  is within the box,  
between  $x = 0$  and  $x = L$



wave function  $\psi$  is 0 for  $x \leq 0$  and  $x \geq L$ .

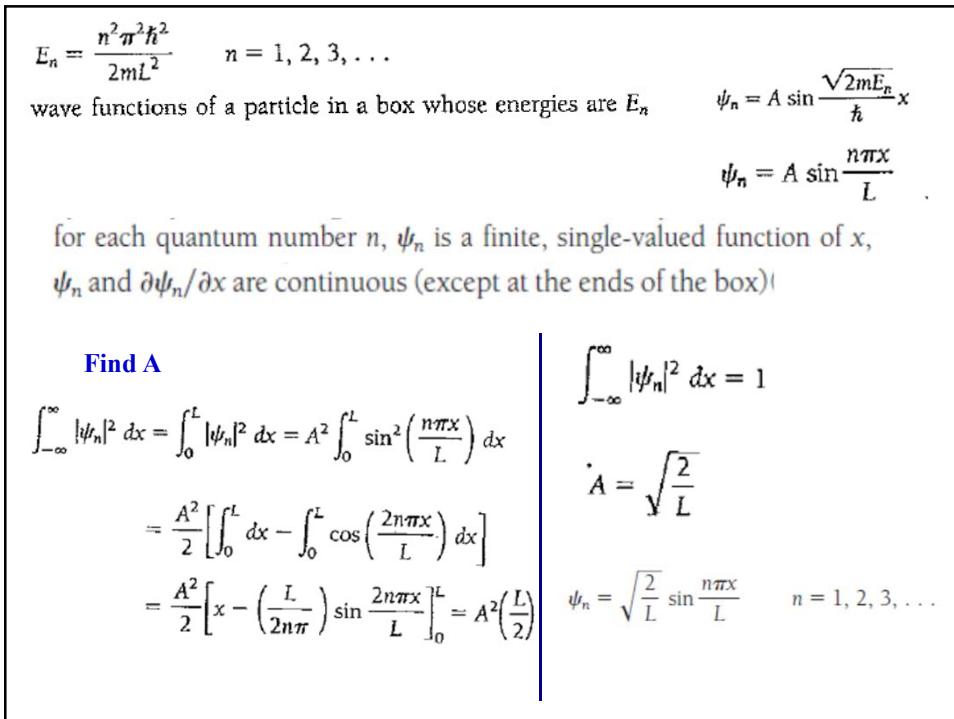
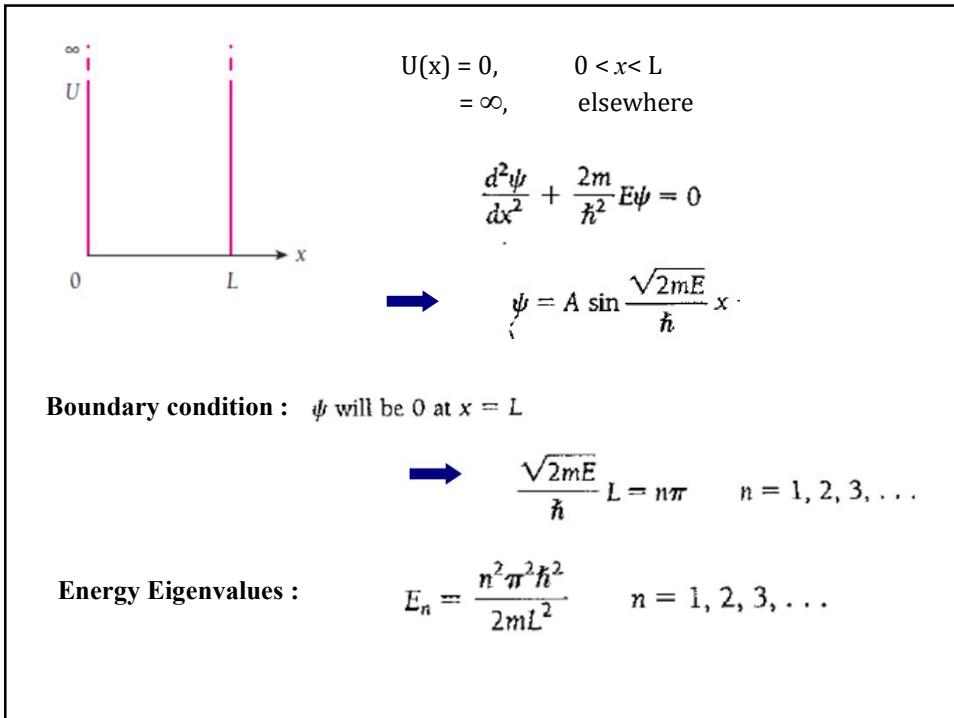
Time Independent Schrödinger Equation  
(for particle in the box)

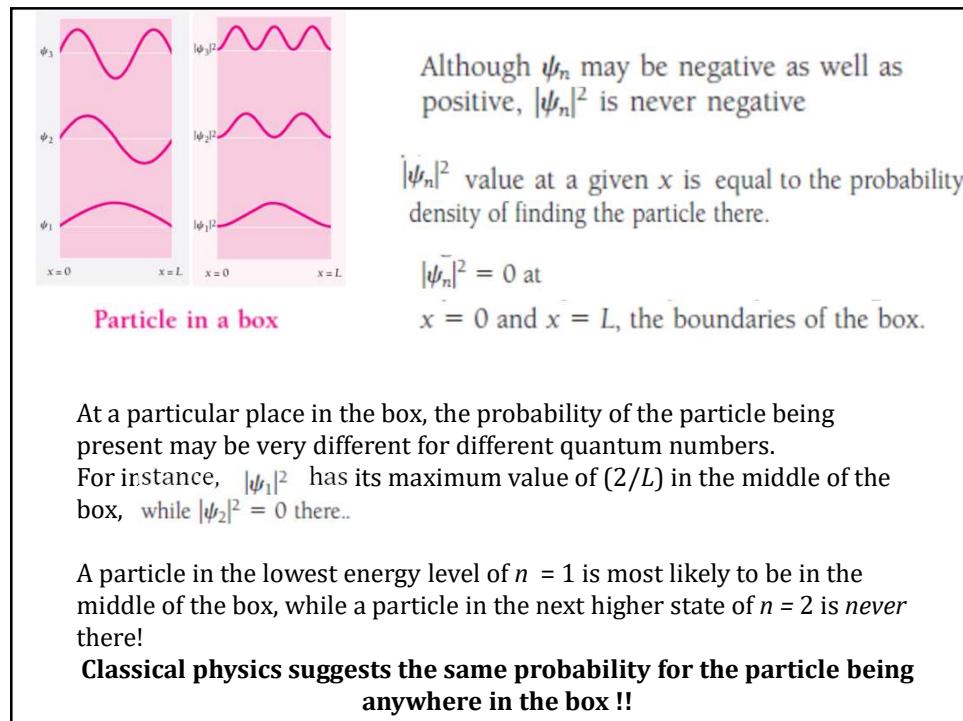
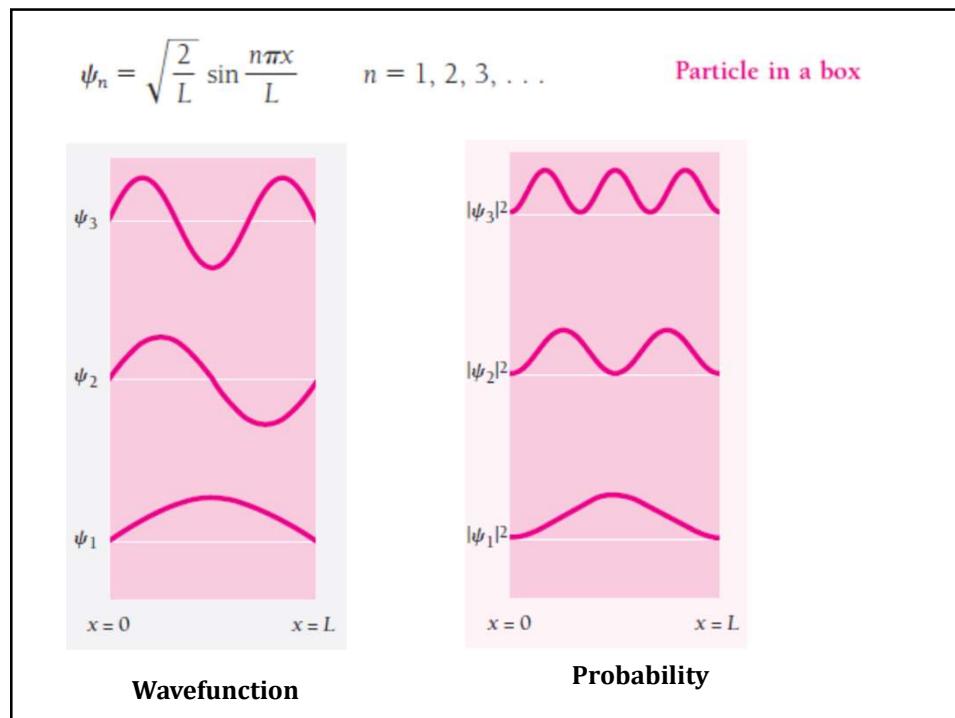
$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0$$

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

Boundary condition :  $\psi = 0$  for  $x = 0$   $\rightarrow$   $B = 0$

$$\psi = A \sin \frac{\sqrt{2mE}}{\hbar} x$$





### Example 5.4

Find the probability that a particle trapped in a box  $L$  wide can be found between  $0.45L$  and  $0.55L$  for the ground and first excited states.

#### Solution

This part of the box is one-tenth of the box's width and is centered on the middle of the box.

Classically, one would expect the particle to be in this region 10% of the time. Quantum mechanics gives quite different predictions that depend on the quantum number of the particle's state.

The probability of finding the particle between  $x_1$  and  $x_2$  when it is in the  $n^{\text{th}}$  state is

$$\begin{aligned} P_{x_1, x_2} &= \int_{x_1}^{x_2} |\psi_n|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx \\ &= \left[ \frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2} \end{aligned}$$

Here  $x_1 = 0.45L$  and  $x_2 = 0.55L$ .

For the ground state, which corresponds to  $n = 1$ ,

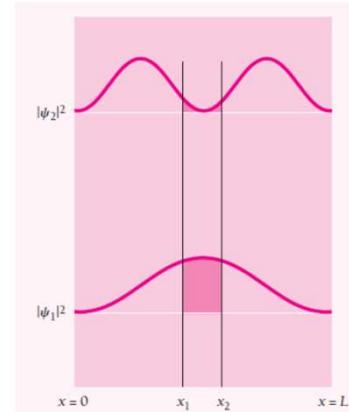
$$P_{x_1, x_2} = 0.198 = 19.8 \text{ percent}$$

This is about twice the classical probability.

For the first excited state, which corresponds to  $n = 2$ ,

$$P_{x_1, x_2} = 0.0065 = 0.65 \text{ percent}$$

This low figure is consistent with the probability density of  $|\psi_n|^2 = 0$  at  $x = 0.5L$ .



For more fun of Quantum Mechanics  
Google for [Schrödinger's cat] ➔ A thought experiment