

# Lecture # 2

Models of Atom  
Rutherford vs  
Bohr

Explains the  
Atomic Spectra  
(Quantum  
Leap)



Uncertainty  
Principle

Wave-Particle  
Duality  
for light or  
electrons

Schrodinger's philosophy  
“New theory is required to explain the  
behavior of electrons”

de-Broglie  
matter waves  
 $\lambda = h/p$

Need a new theory to understand  
(dynamics of) electrons and atoms

- Wavelike equation for describing sub-atomic systems



**"Where did we get that (equation) from? Nowhere.  
It is not possible to derive it from anything you  
know.**

**It came out of the mind of Schrödinger."**

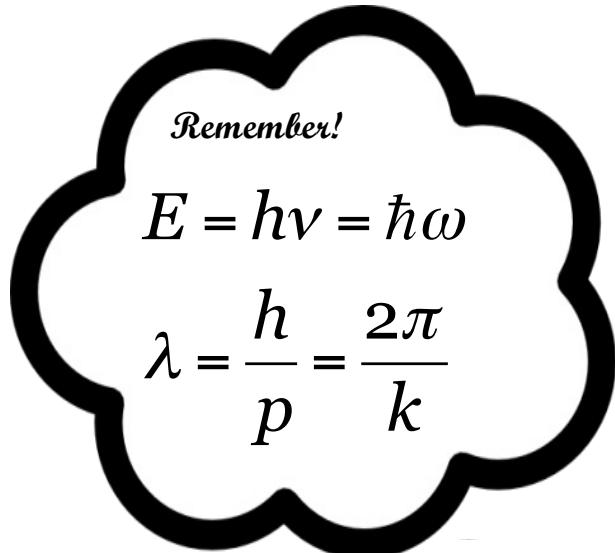
**- Richard Feynman**

# Schrodinger's philosophy

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \Psi(x,t)}{\partial t^2} \quad \text{Classical Wave Equation}$$

$\Psi(x,t)$  = Amplitude

$\Psi(x,t) = Ce^{i\alpha}$  ; Where  $\alpha = 2\pi \left( \frac{x}{\lambda} - vt \right)$  is the phase



$$\alpha = 2\pi \left( \frac{x}{\lambda} - vt \right) = \frac{x \cdot p - E \cdot t}{\hbar}$$

# Schrodinger Equation

In classical mechanics  $\hat{H}$  represents total energy

We can therefore write

$$\hat{H}\psi = W\psi \quad \text{as} \quad \hat{H}\psi = E\psi$$

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \cdot \psi(x)$$

Time-dependent Schrodinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \cdot \Psi(x,t) = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(x) \right] \Psi(x,t)$$

Schrodinger equation is an eigenvalue equation

There can be many solutions  $\psi_n(x)$  each corresponding to different energy  $E_n$

# Laws of Quantum Mechanics

1. The state of a system is *completely specified* by a wave- function  $\Psi(r,t)$ .  
Square of “wavefunction”  $\rightarrow$  probability density
2. To every observable in classical mechanics, there corresponds a linear operator in quantum mechanics
3. In measurement of observable associated with operator  $\mathbf{A}$ , *only values that will be observed* are the (real) *eigenvalues of A, which satisfy the eigenvalue eq.*

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

$\Psi_n$  are the eigenfunctions of the system and  $a_n$  are corresponding eigenvalues

If the system is in state  $\Psi_k$ , a measurement on the system will yield an eigenvalue  $a_k$

# Schrodinger Equation

Time-dependent Schrodinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \cdot \Psi(x,t) = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(x) \right] \Psi(x,t)$$

$$\hat{H} \cdot \Psi(x,y,z,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,y,z,t) ; \quad \hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(x,y,z)$$

Schrodinger equation in 3-dimensions

# Schrodinger Equation

Time-dependent Schrodinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \cdot \Psi(x,t) = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(x) \right] \Psi(x,t)$$

$$\hat{H} \cdot \Psi(x,y,z,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,y,z,t) ; \quad \hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(x,y,z)$$

$$\Psi(x,y,z,t) = \psi(x,y,z) \cdot \phi(t) \Rightarrow \Psi = \psi \cdot \phi$$

$$\hat{H} \cdot \Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

$$\hat{H}(\psi \cdot \phi) = i\hbar \frac{\partial}{\partial t} (\psi \cdot \phi)$$

# Schrodinger Equation

$$\widehat{H}(\psi \cdot \phi) = i\hbar \frac{\partial}{\partial t} (\psi \cdot \phi)$$

$\widehat{H}$  operates only on  $\psi$  and  $\frac{\partial}{\partial t}$  operates only on  $\phi$

$$\phi \cdot \widehat{H}\psi = \psi \left( i\hbar \frac{\partial}{\partial t} \phi \right)$$

Divide by  $\psi \cdot \phi$

$$\frac{\widehat{H}\psi}{\psi} = \frac{1}{\phi} \left( i\hbar \frac{\partial}{\partial t} \phi \right)$$

LHS is a function of co-ordinates and RHS is function of time. If these two have to be equal then both functions must be equal to constant, say W

# Schrodinger Equation

$$\frac{\hat{H}\psi}{\psi} = \frac{1}{\phi} \left( i\hbar \frac{\partial}{\partial t} \phi \right) = W$$

$$\frac{\hat{H} \cdot \psi}{\psi} = W \qquad \qquad \hat{H}\psi = W\psi$$

$$\frac{1}{\phi} \left( i\hbar \frac{\partial}{\partial t} \phi \right) = W \qquad i\hbar \frac{\partial}{\partial t} \phi = W\phi$$

**Separation of variables**

The solution of the differential equation

$$i\hbar \frac{\partial}{\partial t} \phi = W\phi \qquad \text{is} \quad \phi(t) = e^{-iWt/\hbar}$$

# Schrodinger Equation

In classical mechanics  $\hat{H}$  represents total energy

We can therefore write

$$\hat{H}\psi = W\psi \quad \text{as} \quad \hat{H}\psi = E\psi$$

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \cdot \psi(x)$$

Schrodinger equation is an eigenvalue equation

There can be many solutions  $\psi_n(x)$  each corresponding to different energy  $E_n$

# Laws of Quantum Mechanics

4. All the eigenfunctions of Quantum Mechanical operators are “Orthogonal”

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx = \langle \psi_m | \psi_n \rangle = 0 \quad \text{for } m \neq n$$

Imp

# Laws of Quantum Mechanics

5. The average value of the observable corresponding to operator  $\hat{A}$  is

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\nu$$

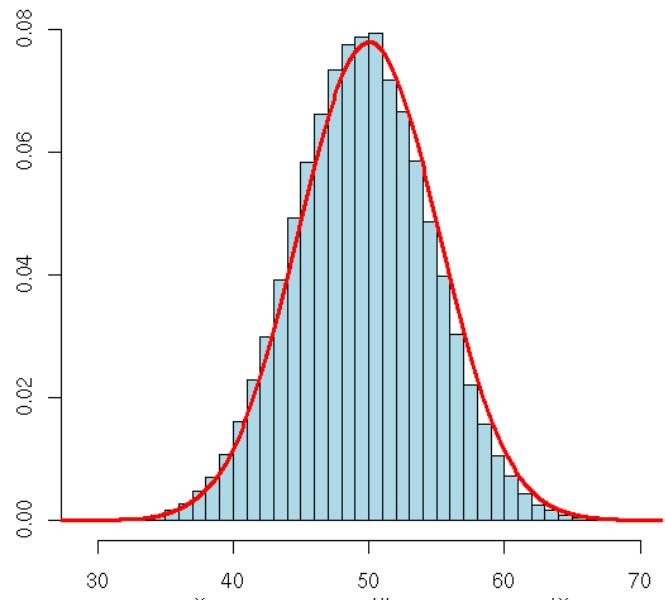
From classical correspondence we can define average values for a distribution function  $P(x)$

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) \cdot dx \text{ and } \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) \cdot dx$$

$\langle a \rangle$  corresponds to the average value of a classical physical quantity or observable , and  $\hat{A}$  represents the corresponding Quantum mechanical operator

$$\langle a \rangle = \int_{-\infty}^{+\infty} \hat{A} \cdot P(x) dx = \int_{-\infty}^{+\infty} \hat{A} \cdot |\Psi|^2 dx \underset{\text{all space}}{\approx} \int \Psi^* \hat{A} \Psi dx = \langle \Psi | \hat{A} | \Psi \rangle$$

### Math-3. Probability Distributions: Expectation (Average/Mean value) and Most-Probable Value



If mp value is asked,  
differentiate  $\psi^2$

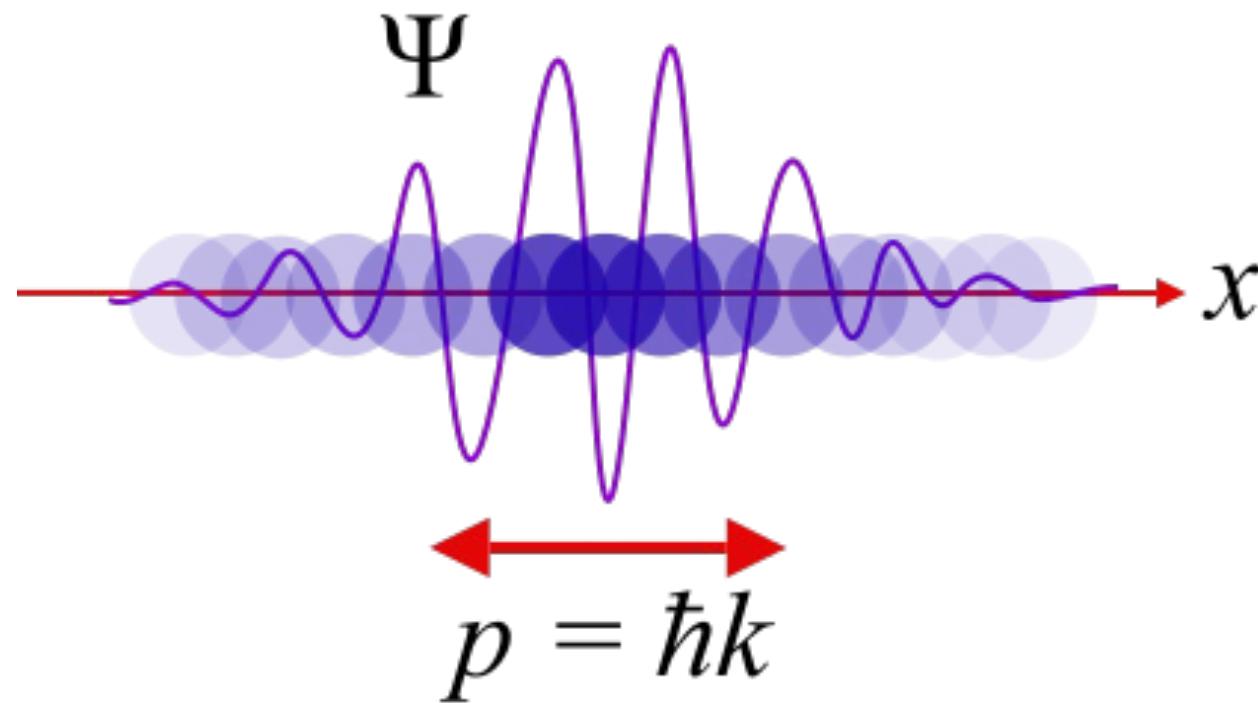
if avg value is asked,  
use integrals in previous  
slides

If  $P(x)$  is the probability distribution

Most Probable (Modal) value at *Maxima*  $\rightarrow \frac{dP(x)}{dx} = 0$

$$\text{Mean: } E(x) = \langle x \rangle = \sum_{j=1}^n x_j P_j(x_j) \text{ and } E(x^2) = \langle x^2 \rangle = \sum_{j=1}^n x_j^2 P_j(x_j)$$

# What can you get from solving the Schrodinger Equation?



**$\Psi$  is a mathematical function; real or complex**

**What is the meaning of  $\Psi(x,t)$ ?**

# Born Interpretation



**Classical wave equation:**

$\Psi(x,t)$  = Amplitude and  $|\Psi(x,t)|^2$  = Intensity

## Quantum mechanical system:

- The state is completely specified by a wavefunction  $\Psi(x,t)$ , which can be complex
- All possible information can be derived from  $\Psi(x,t)$
- Intensity is equivalent to Probability.
- $|\Psi(x,t)|^2 = P(x)$

# Born Interpretation

Note the difference, while finding the mp value , differentiate the probability , not the probability density, that is multiply  $\psi^2$  by  $dxdydz$  first

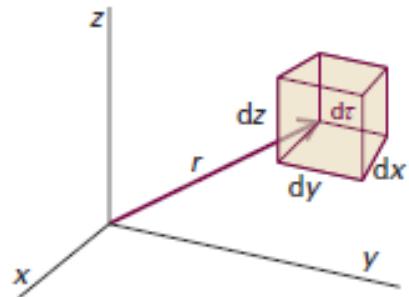


## Probability density

$$P(x) = |\Psi(x,t)|^2 = \Psi^*(x,t) \cdot \Psi(x,t)$$

## Probability

$$P(x_a \leq x \leq x_a + dx) = |\Psi(x,t)|^2 dx = \Psi^*(x_a, t) \cdot \Psi(x_a, t) dx$$



## Probability in 3-dimensions

$$\begin{aligned} P(x_a \leq x \leq x_a + dx, y_a \leq y \leq y_a + dy, z_a \leq z \leq z_a + dz) \\ &= \Psi^*(x_a, y_a, z_a, t') \cdot \Psi(x_a, y_a, z_a, t') dx dy dz \\ &= |\Psi(x_a, y_a, z_a, t')|^2 d\tau \end{aligned}$$

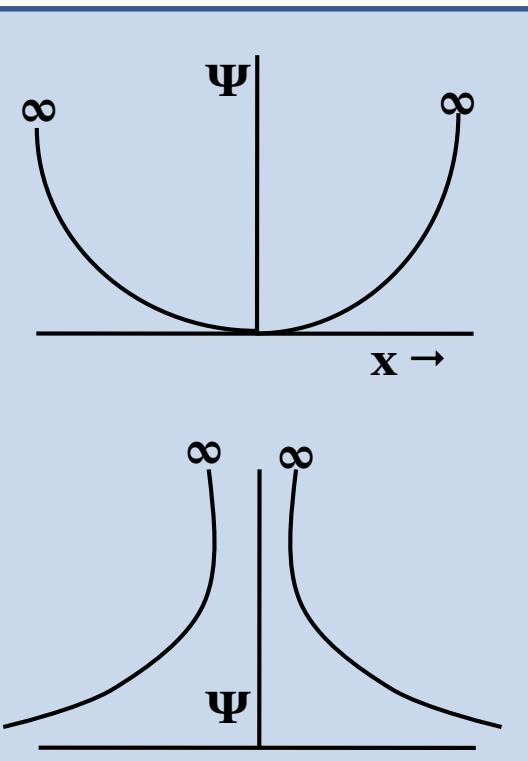
# 6. Normalization of Wavefunction

Pay attention to tut 1 as question related to normalization will be asked in mini quiz

Since  $\Psi^*\Psi d\tau$  is the probability, the total probability of finding the particle somewhere in space has to be unity

$$\iiint_{\text{all space}} \Psi^*(x, y, z) \cdot \Psi(x, y, z) dx dy dz = \int_{\text{all space}} \Psi^* \Psi d\tau = \langle \Psi | \Psi \rangle = 1$$

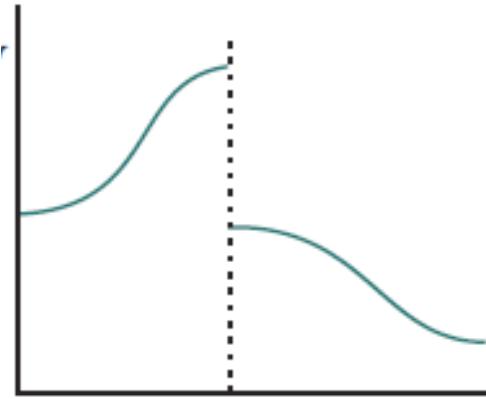
If function diverges, i.e.  $\rightarrow \infty$ :  $\Psi$  can not be normalized, and therefore is NOT an acceptable wave function.



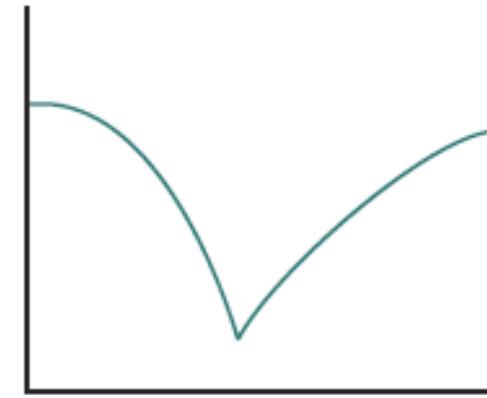
Unacceptable wavefunction

**$\Psi$**  must vanish at  $\pm\infty$ , or more appropriately at the boundaries and  **$\Psi$**  must be finite

# Restrictions on wavefunction



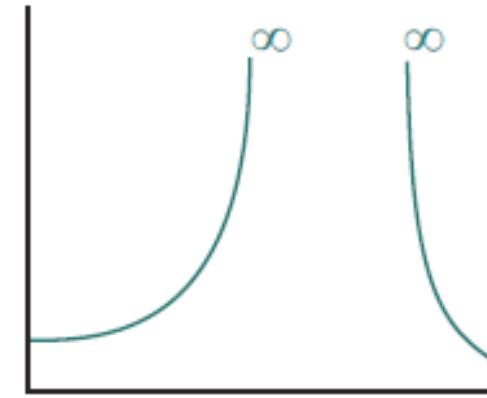
Unacceptable because  
 $\psi$  is not continuous



Unacceptable because  
 $d\psi/dq$  is not continuous



Unacceptable because  
 $\psi$  is not single-valued



Unacceptable because  
 $\psi$  goes to infinity

## Restrictions on wavefunction

$\psi$  must be a solution of the Schrodinger equation

$\psi$  must be normalizable:  $\psi$  must be finite and  $\rightarrow 0$  at boundaries/  $\pm\infty$

$\Psi$  must be a continuous function of x,y,z

$d\Psi/dq$  must be must be continuous in x,y,z

$\Psi$  must be single-valued

$\Psi$  must be quadratically-intergrable

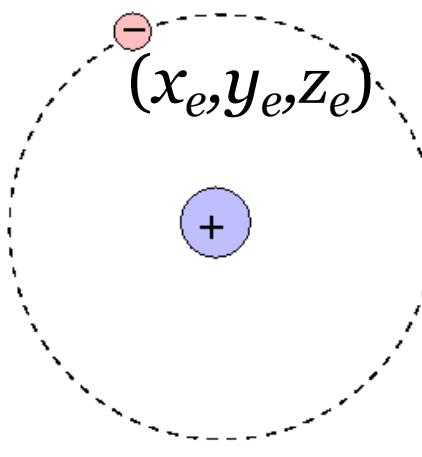
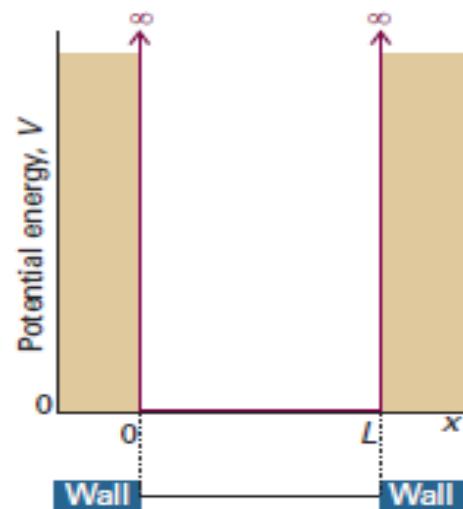
(square of the wavefunction should be integrable)

Boundary conditions: Quantization

# Quantum Mechanics

## Examples of Exactly Solvable Systems

1. Free Particle
2. Particle in a Square-Well Potential
3. Hydrogen Atom



## Free Particle

Time-independent Schrodinger equation

$$\hat{H}\psi = E\psi$$

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \cdot \psi(x)$$

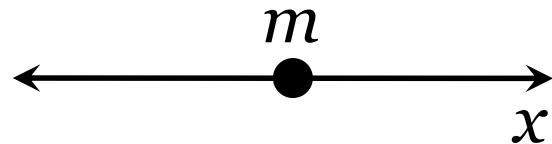
For a free particle  $V(x)=0$

There are no external forces acting

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

## Free Particle

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



Second-order linear differential equation

Let us assume

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

Trial Solution

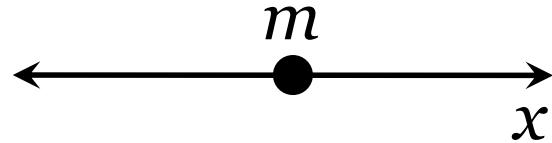
$$\psi(x) = A \sin kx + B \cos kx$$

$$\frac{\partial}{\partial x} \psi(x) = \frac{\partial}{\partial x} (A \sin kx + B \cos kx) = k(A \cos kx - B \sin kx)$$

$$\frac{\partial^2}{\partial x^2} \psi(x) = -k^2 (A \sin kx + B \cos kx) = -k^2 \psi(x)$$

## Free Particle

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



Second-order linear differential equation

Let us assume

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

Trial Solution

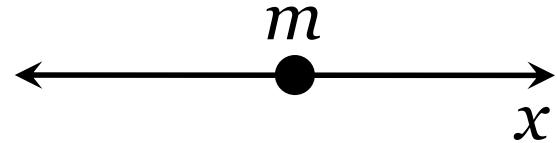
$$\psi(x) = A \sin kx + B \cos kx$$

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$$\frac{\partial^2}{\partial x^2} \psi(x) = -k^2 (A \sin kx + B \cos kx) = -k^2 \psi(x)$$

## Free Particle

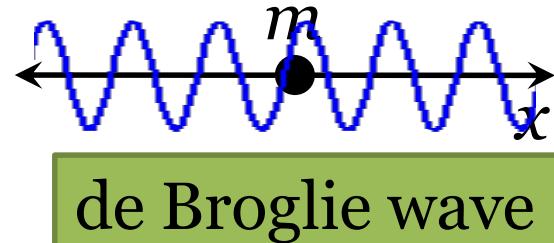
$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E \cdot \psi(x)$$



$$\frac{\hbar^2}{2m} k^2 \psi(x) = E \cdot \psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm \frac{\sqrt{2mE}}{\hbar}$$

## Free Particle

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



$$\frac{\hbar^2}{2m} k^2 \psi(x) = E \cdot \psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm \frac{\sqrt{2mE}}{\hbar}$$

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

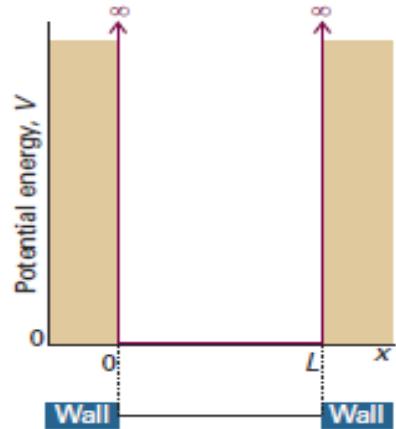
There are no restrictions on  $k$   
 $E$  can have any value  
Energies of free particles are continuous

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

No Quantization

All energies are allowed

# Particle in 1-D Square-Well Potential



$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \leq x \leq L \\ \infty & x > L \end{cases}$$

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

For regions in the space  $x < 0$  and  $x > L \Rightarrow V = \infty$

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

Normalization condition not satisfied  $\Rightarrow$

$$\psi(x < 0) = 0 \quad \text{and} \quad \psi(x > L) = 0$$

## Particle in 1-D Square-Well Potential

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

For regions in the space  $0 \leq x \leq L \Rightarrow V = 0$

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

This equation is similar to free particle Schrodinger  
However, boundary conditions are present

Let us assume

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

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

Trial Solution

Energy

## Particle in 1-D Square-Well Potential

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

Boundary Condition  $x = 0 \Rightarrow \psi(x) = 0$

$$\psi(x) = A \sin kx \quad \because \cos 0 = 1$$

Boundary Condition  $x = L \Rightarrow \psi(L) = 0$

$$\psi(L) = 0 \Rightarrow A \sin kL = 0 \Rightarrow A = 0 \text{ or } \sin kL = 0$$

But the wavefunction  $\psi(x)$  CANNOT be ZERO everywhere

$$\sin kL = 0 \Rightarrow kL = n\pi \quad n=1,2,3,4\dots$$

Wavefunction is  $\psi(x) = A \sin kx$

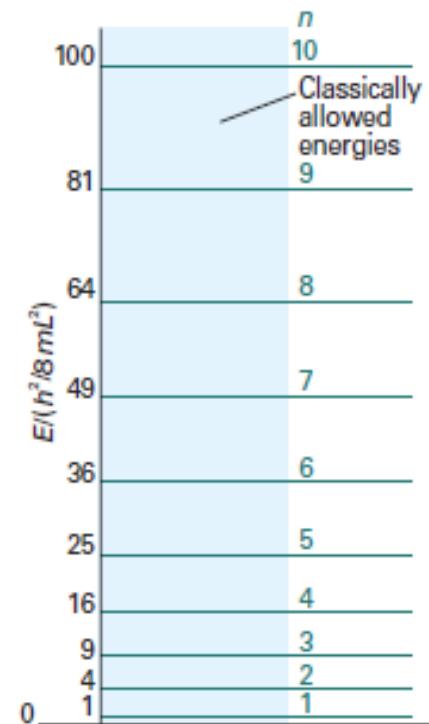
# Particle in 1-D Square-Well Potential

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{and} \quad k = \frac{n\pi}{L}$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad n=1,2,3,4\dots$$

Energy is no longer continuous but has discrete values; Quantization of energy

Energy separation increases with increasing values of  $n$



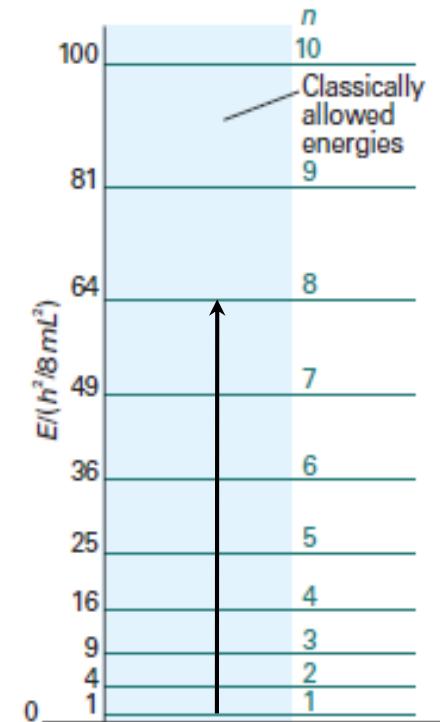
The lowest allowed energy level is for  $n=1$

$E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$  has a non zero value  $\Rightarrow$  Zero Point Energy

## Particle in 1-D Square-Well Potential: Spectroscopy

$$h\nu = \Delta E = E_f - E_i = \frac{n_f^2 h^2}{8mL^2} - \frac{n_i^2 h^2}{8mL^2} = (n_f^2 - n_i^2) \frac{h^2}{8mL^2}$$

Larger the box, smaller the energy of  $h\nu$



# Particle in 1-D Square-Well Potential: Spectroscopy

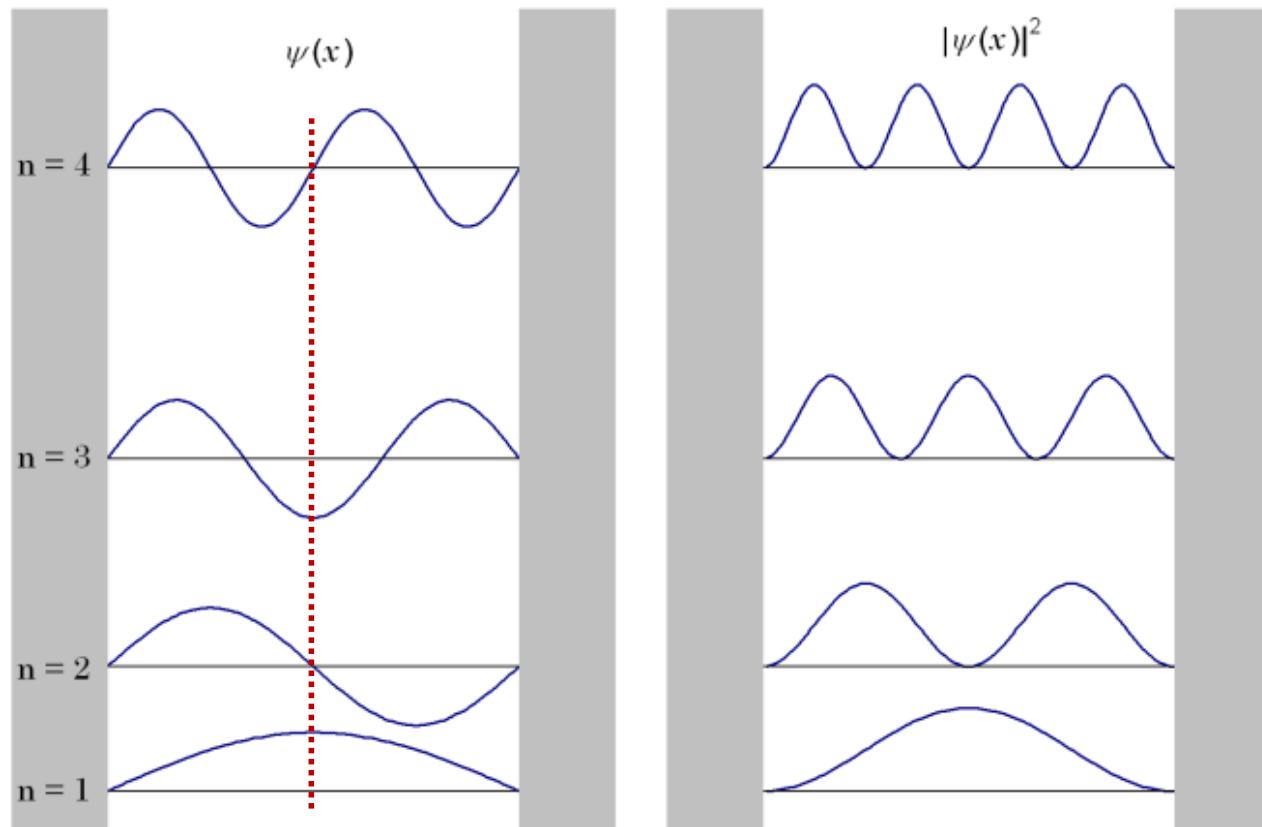
Wavefunction

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

$n=1,3..$  (odd)  
Symmetric  
(even function)

$n=2,4..$  (even)  
Anti-Symmetric  
(odd function)

Number of Nodes  
(zero crossings) =  $n-1$



## Particle in 2-D Square-Well Potential

Hamiltonian

$$\hat{H} = -\frac{\hbar}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar}{2m} \frac{\partial^2}{\partial y^2} = \hat{H}_x + \hat{H}_y$$

$$\hat{H} \cdot \psi(x, y) = E_n \cdot \psi(x, y)$$

Let us assume that

$$\psi(x, y) = \psi(x) \cdot \psi(y)$$

## Particle in 2-D Square-Well Potential

$$\begin{aligned}\hat{H} \cdot \psi(x, y) &= \hat{H} \cdot (\psi(x) \cdot \psi(y)) \\&= [\hat{H}_x + \hat{H}_y] (\psi(x) \cdot \psi(y)) \\&= \psi(y) \cdot \hat{H}_x \cdot \psi(x) + \psi(x) \cdot \hat{H}_y \cdot \psi(y) \\&= \psi(y) \cdot E_x \cdot \psi(x) + \psi(x) \cdot E_y \cdot \psi(y) \\&= E_x \cdot \psi(x) \cdot \psi(y) + E_y \cdot \psi(x) \cdot \psi(y) \\&= (E_x + E_y) \cdot (\psi(x) \cdot \psi(y)) \\&= (E_x + E_y) \cdot (\psi(x, y))\end{aligned}$$

## Particle in 2-D Square-Well Potential

Hamiltonian

$$\hat{H} = -\frac{\hbar}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar}{2m} \frac{\partial^2}{\partial y^2} = \hat{H}_x + \hat{H}_y$$

$$\hat{H} \cdot \psi(x, y) = E_n \cdot \psi(x, y)$$

$$\psi(x, y) = \psi(x) \cdot \psi(y)$$

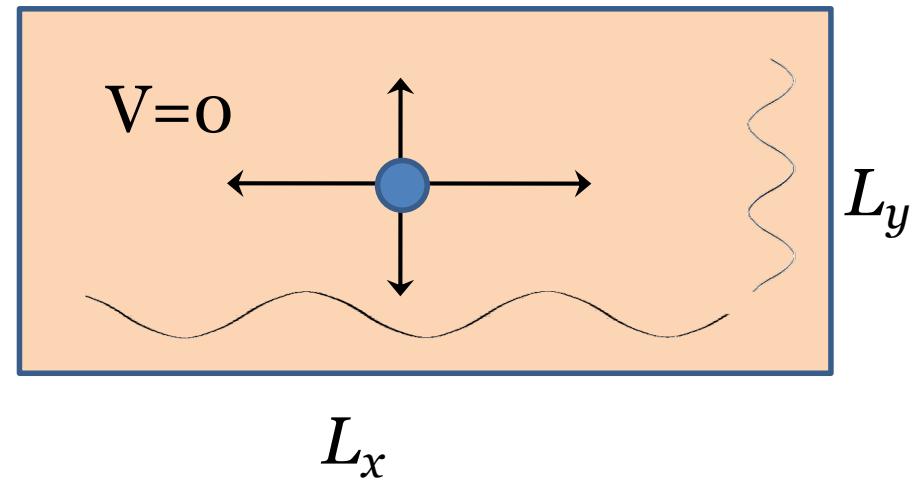
$$E_n = E_{n_x, n_y} = E_{n_x} + E_{n_y}$$

$\psi$  is a product of the eigenfunctions of the parts of  $\hat{H}$

$E$  is sum of the eigenvalues of the parts of  $\hat{H}$

## Particle in 2-D Square-Well Potential

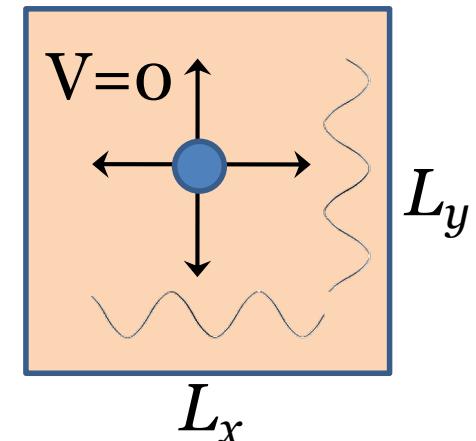
$$\begin{aligned}\psi(x,y) &= \psi(x) \cdot \psi(y) \\ &= \sqrt{\frac{2}{L_x}} \sin \frac{n\pi}{L_x} x \cdot \sqrt{\frac{2}{L_y}} \sin \frac{n\pi}{L_y} y \\ &= \frac{2}{\sqrt{L_x L_y}} \sin \frac{n\pi}{L_x} x \cdot \sin \frac{n\pi}{L_y} y\end{aligned}$$



$$\begin{aligned}E_{n_x, n_y} &= E_{n_x} + E_{n_y} \\ &= \frac{n_x^2 h^2}{8m L_x^2} + \frac{n_y^2 h^2}{8m L_y^2} \\ &= \frac{h^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \quad n_x, n_y = 1, 2, 3, 4, \dots\end{aligned}$$

## Particle in 2-D Square-Well Potential

$$\begin{aligned}\psi(x,y) &= \psi(x) \cdot \psi(y) \\ &= \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} y \\ &= \frac{2}{L} \sin \frac{n\pi}{L} x \cdot \sin \frac{n\pi}{L} y\end{aligned}$$



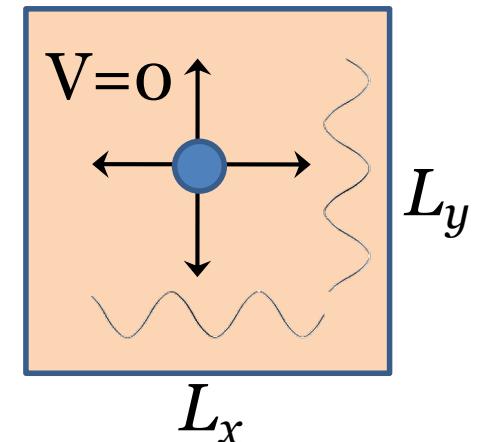
Square Box  
 $\Rightarrow L_x = L_y = L$

$$\begin{aligned}E_{n_x, n_y} &= E_{n_x} + E_{n_y} \\ &= \frac{n_x^2 h^2}{8mL^2} + \frac{n_y^2 h^2}{8mL^2} \\ &= \frac{h^2}{8mL^2} (n_x^2 + n_y^2) \quad n_x, n_y = 1, 2, 3, 4, \dots\end{aligned}$$

## Particle in 2-D Square-Well Potential

$$\psi_{1,2} = \psi_1 \cdot \psi_2 = \frac{2}{L} \sin \frac{\pi}{L} x \cdot \sin \frac{2\pi}{L} y$$

$$E_{1,2} = E_1 + E_2 = \frac{5\hbar^2}{8mL^2}$$



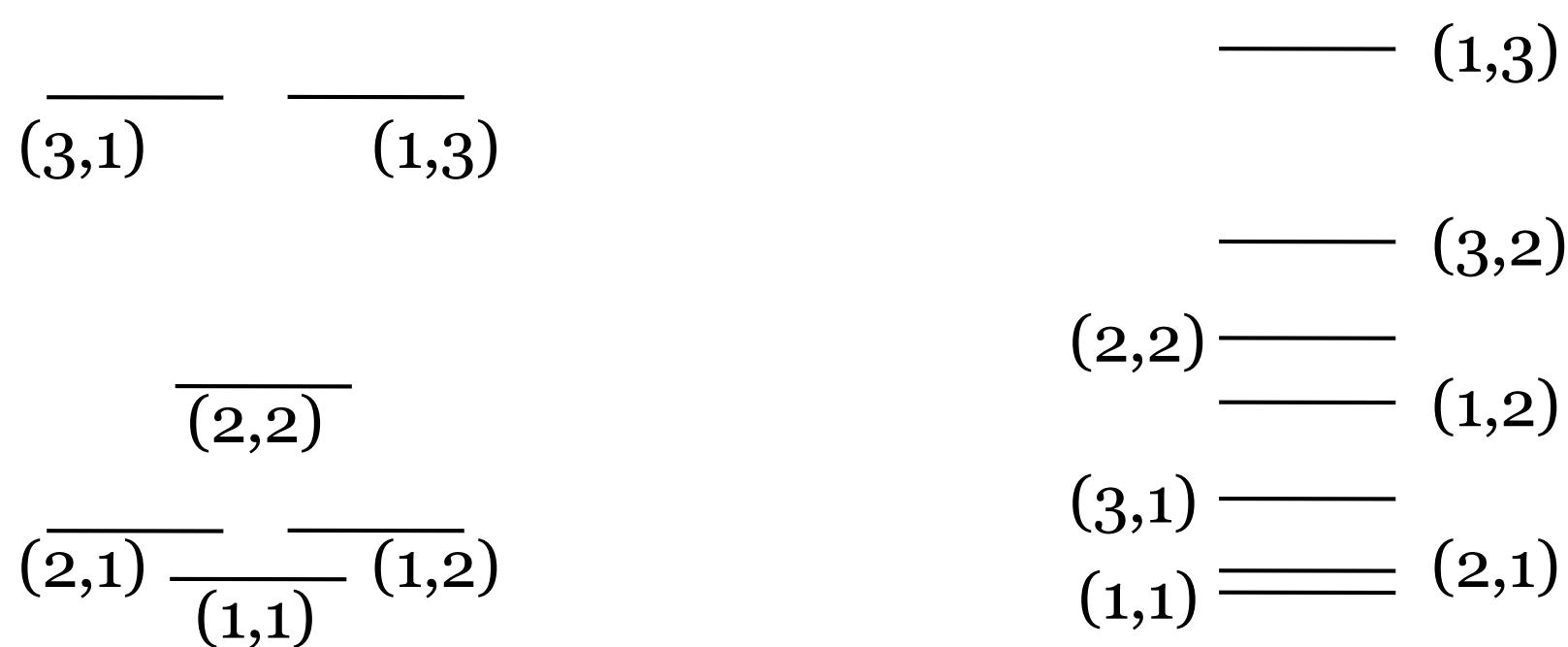
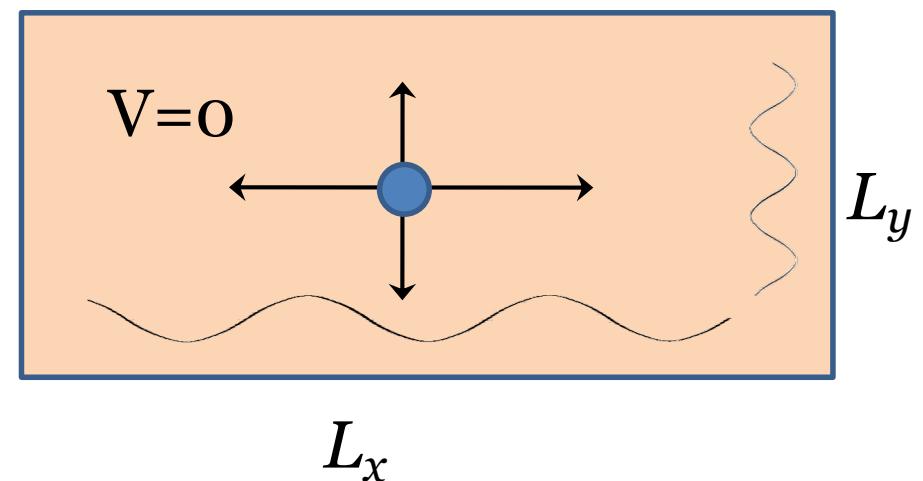
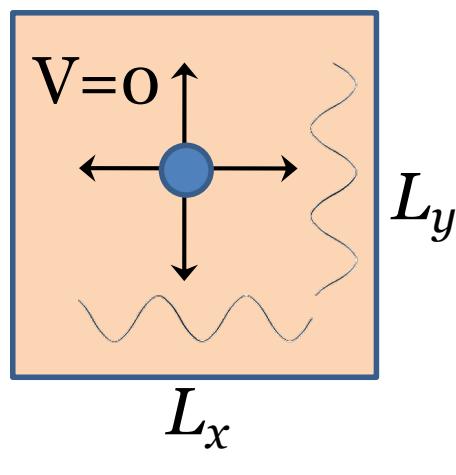
$$\psi_{2,1} = \psi_2 \cdot \psi_1 = \frac{2}{L} \sin \frac{2\pi}{L} x \cdot \sin \frac{\pi}{L} y$$

$$E_{2,1} = E_2 + E_1 = \frac{5\hbar^2}{8mL^2}$$

Square Box  
 $\Rightarrow L_x = L_y = L$

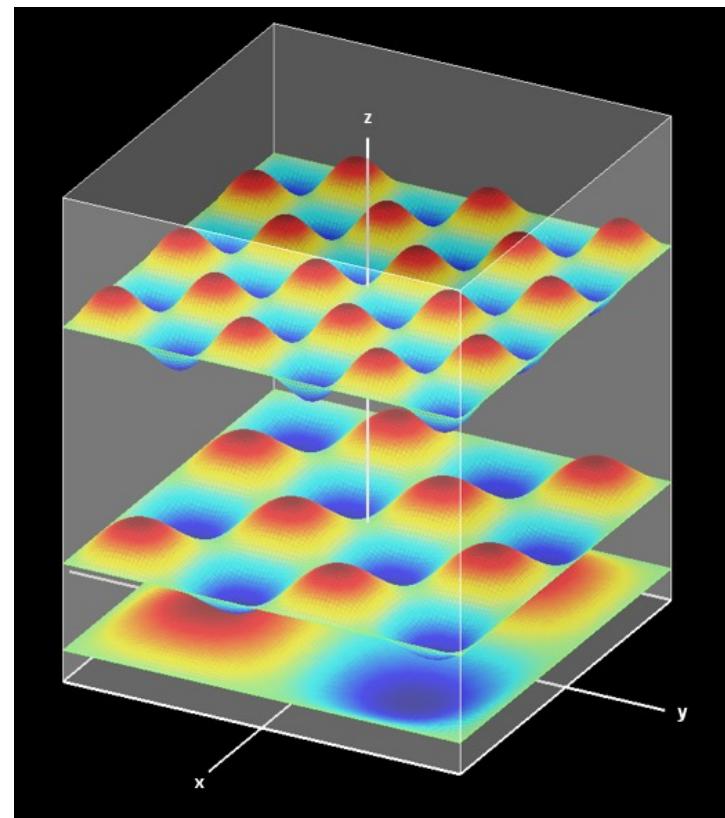
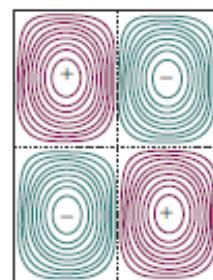
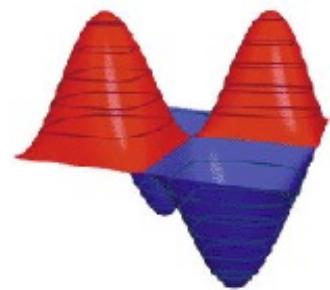
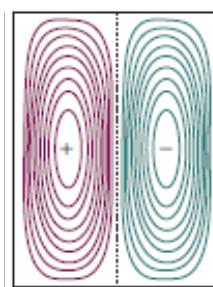
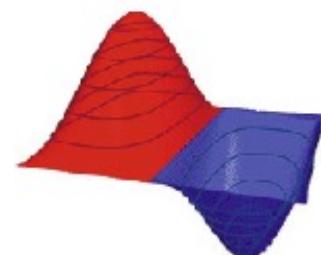
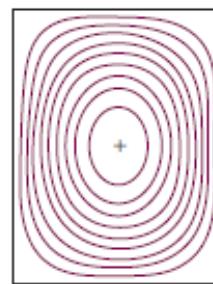
$E_{1,2} = E_{2,1} \Rightarrow \psi_{1,2}$  and  $\psi_{2,1}$  are degenerate wavefunctions

## Particle in 2-D Square-Well Potential – Symmetry



This question can be asked in mini quiz, remember to draw signs in the contour plots

## Particle in a 2-D Well – Wavefunctions



$$\text{Number of nodes} = n_x + n_y - 2$$

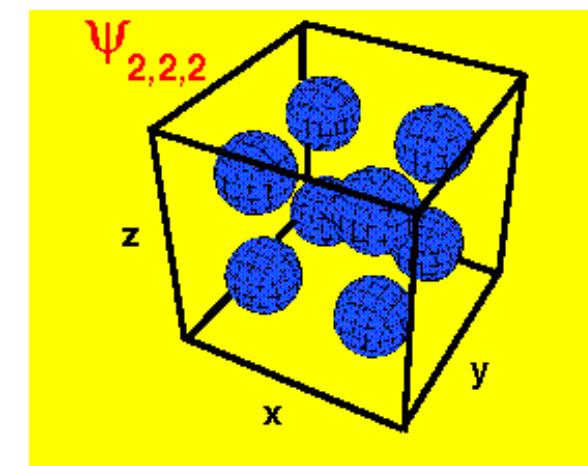
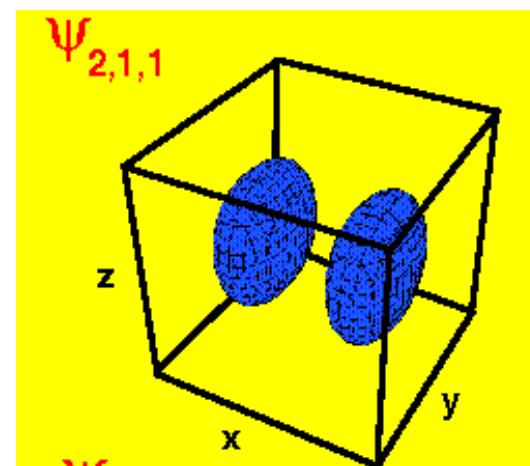
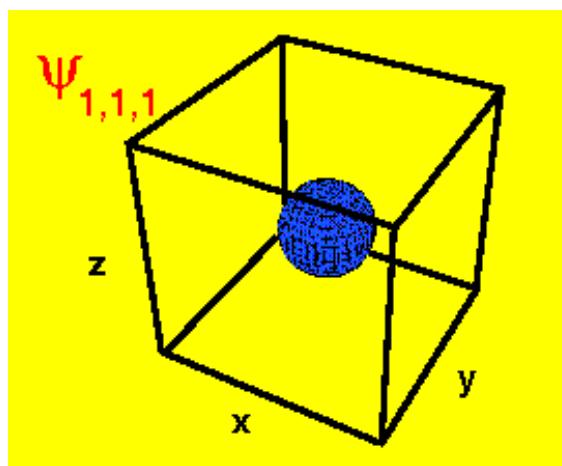
## Particle in a 3D-Box

$$\psi(x,y,z) = \psi(x) \cdot \psi(y) \cdot \psi(z)$$

$$= \sqrt{\frac{2}{L_x}} \sin \frac{n_x \pi}{L_x} x \cdot \sqrt{\frac{2}{L_y}} \sin \frac{n_y \pi}{L_y} y \cdot \sqrt{\frac{2}{L_z}} \sin \frac{n_z \pi}{L_z} z$$

$$E_{n_x, n_y, n_z} = E_{n_x} + E_{n_y} + E_{n_z}$$

$$= \frac{n_x^2 h^2}{8m L_x^2} + \frac{n_y^2 h^2}{8m L_y^2} + \frac{n_z^2 h^2}{8m L_z^2} \quad n_x, n_y, n_z = 1, 2, 3, 4, \dots$$



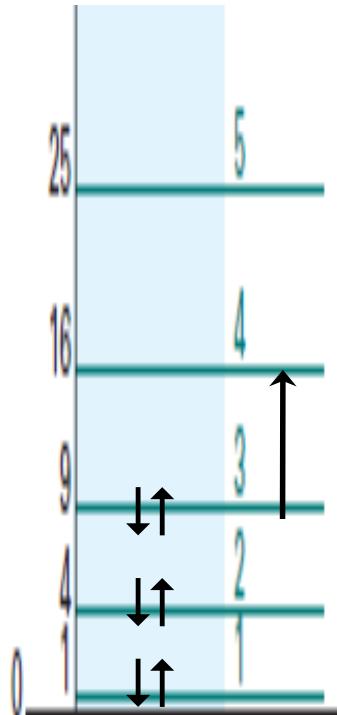
Interesting !!!!

## Particle in a Box – Application in Chemistry

Hexatriene is a linear molecule of length 7.3 Å

It absorbs at 258 nm

Use particle in a box model to explain the results.



Six  $\pi$  electron fill  
lower three levels

$$\Delta E = E_f - E_i = \left( n_f^2 - n_i^2 \right) \frac{h^2}{8mL^2} = \frac{hc}{\lambda}$$

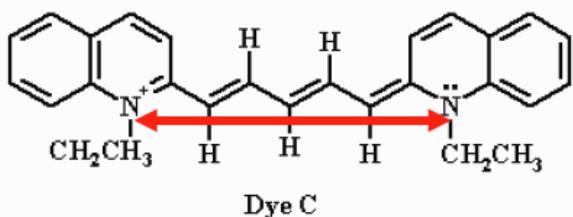
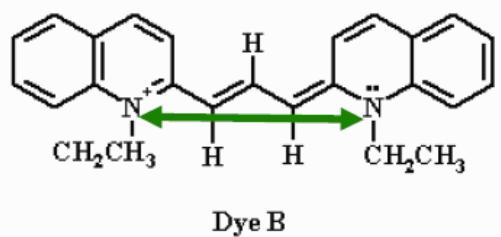
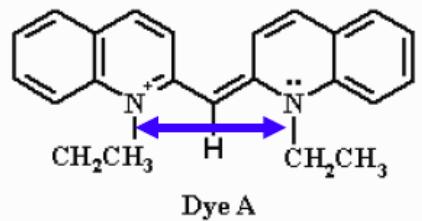
$$\lambda = \frac{8mL^2c}{h} \left( n_f^2 - n_i^2 \right) \approx 251\text{nm}$$

Agrees well with the experimental value of 258 nm

Particle in a box is a good model

# Particle in a Box – Application in Chemistry

## Electronic spectra of conjugated molecules

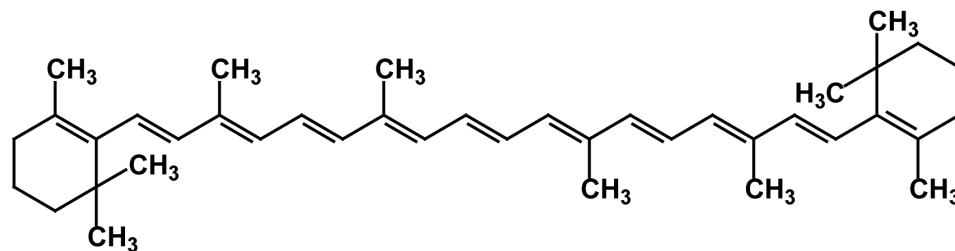


$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2} \Rightarrow \lambda \propto L^2$$

Increase in bridge length increase the emission wavelength.

Predicts correct trend and gets the wavelength almost right.

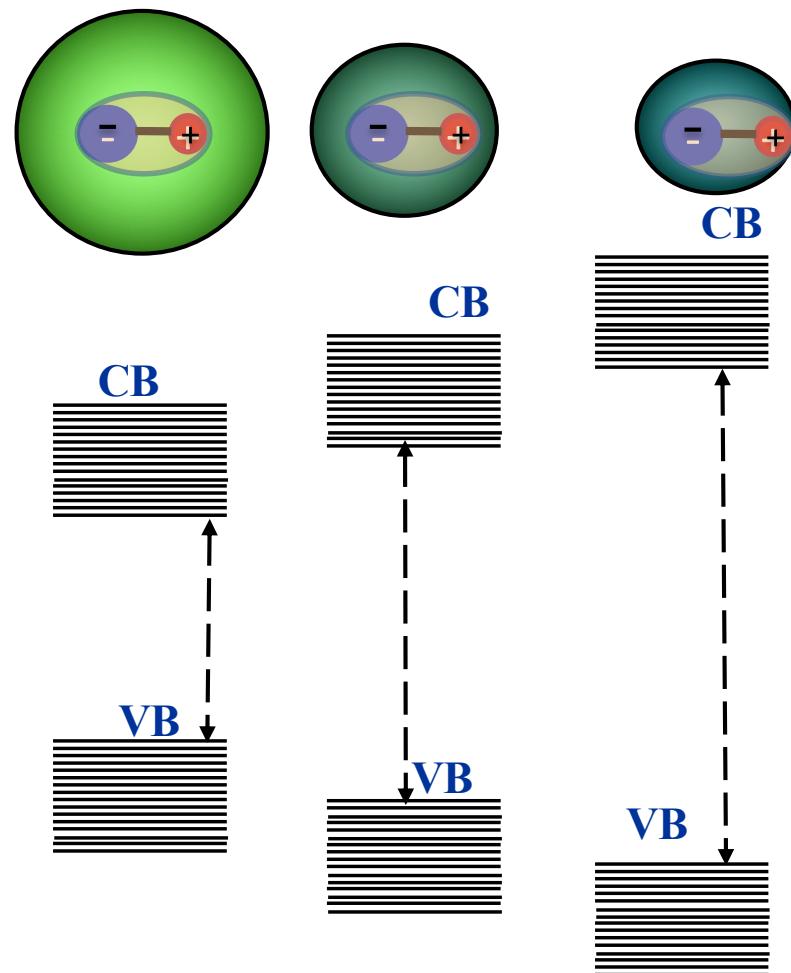
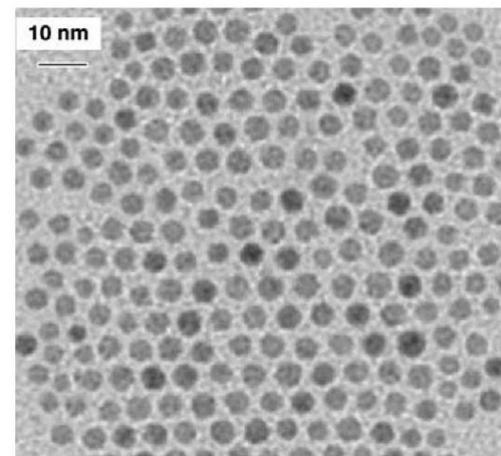
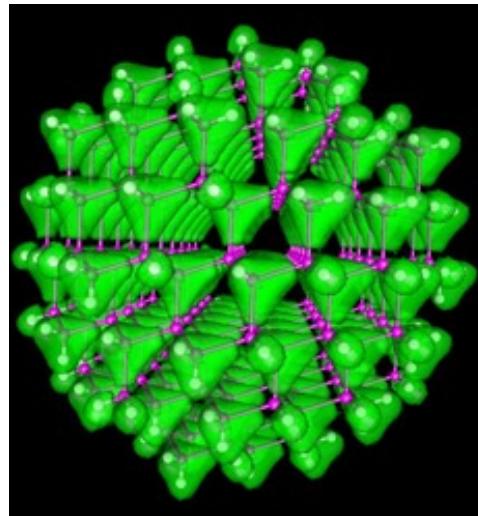
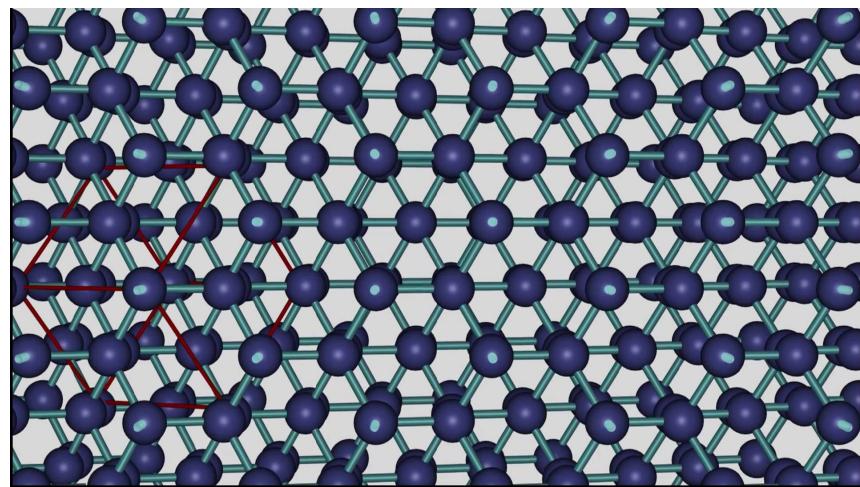
Particle in a box is a good model



B-carotene is orange because of 11 conjugated double bonds

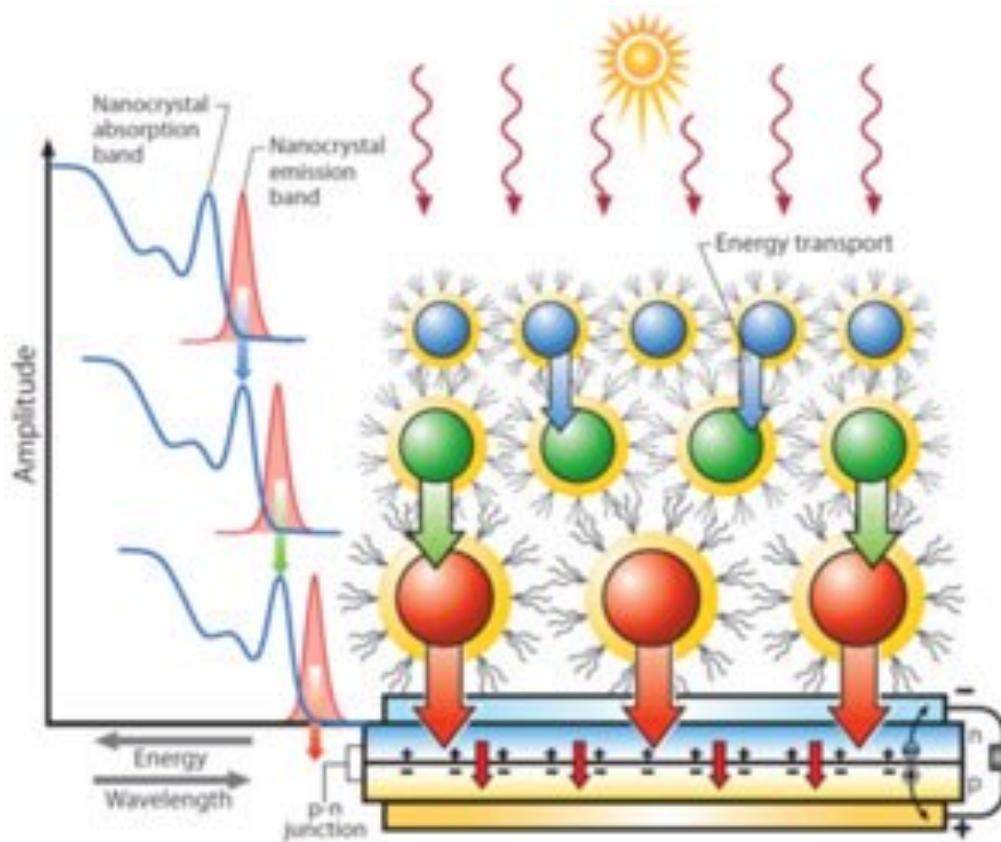
## Particle in a Box – Application in nano-science

Quantum Dots – Quasi-particle (exciton) in a Box!



Band gap changes due to confinement,  
and so will the color of emitted light

## Application of quantum dots



Quantum-Dot based Solar Cells

Quantum-Dot based <sup>51</sup><sub>in-vivo</sub> imaging for tumor/cancer

## What have we learnt?

Formulate a correct Hamiltonian  
(energy) Operator  $H$

Solve TISE  $H\Psi=E\Psi$   
by separation of variables and  
intelligent trial wavefunction

Impose boundary conditions for  
eigenfunctions and obtain  
Quantum numbers

Eigenstates or Wavefunctions:  
Should be “well behaved” -  
Normalization of Wavefunction

Probabilities and Expectation Values