Important take home messages from first class

- Quantum Particle behaves *completely differently* than the classical particle
- Quantum entities are *neither wave* nor *particle*!!
- There is an *inherent uncertainty* associated with the quantum world
- Newtonian mechanics does not hold anymore for microscopic world, we *need a new mathematical formalism*
- The new Mathematical formalism is based on certain sets of *postulates or axioms*
- *Experimental results can reproduced* from the *new mathematical formalism*
- *Still we can not visualize* how the event took place at the quantum level!!

Postulates of Quantum Mechanics

The state of a system is *completely specified* by some function y(r,t). Square of "wavefunction" →probability density

To every observable in classical mechanics, there corresponds a linear operator in quantum mechanics

In measurement of observable associated with operator ***A***, *only values that will be observed* are the *eigenvalues of A*

The *average value* of the observable corresponding to ***A*** is

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi \, dv$$

Ψ(x,y,z,t) of a system evolves:

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

Time-Dependent Schrödinger Equation

Hamiltonian (Energy) Operator

$$\Rightarrow \widehat{H} = -\frac{\hbar^2}{2m}\widehat{\nabla}_x^2 + \widehat{V}(x,t) \quad where, \widehat{\nabla}_x^2 = \frac{\partial^2}{\partial x^2} \; in\ 1D$$

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

Very often, V(x,t) = V(x) → solutions to TDSE has the form

$$\Psi(x,t) = \psi(x).f(t)$$

Special Solution where space part and time part can be separated out!

Separation of variables to solve linear 2nd order differential equations

$$TIME-\ DEPENDENT\ PART\ of\ solution$$

$$-\frac{\hbar}{i}\frac{1}{f(t)}\frac{df(t)}{dt}=E \quad \Rightarrow \quad \frac{df(t)}{f(t)}=-\left(\frac{iE}{\hbar}\right)dt$$

$$f(t)\sim e^{-iEt/\hbar}$$

Rearranging $time-INDEPENDENT\ (SPACE)\ part$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+V(x)=E$$

$$Time-Independent\ Schrodinger\ Equation:$$

$$\widehat{H}\psi(x)=E\psi(x) \qquad where\ \ \widehat{H}\equiv-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)=\widehat{T}+\widehat{V}$$

$$|\Psi|^2=|f\psi|^2=(f\psi)^*(f\psi)$$

$$=\left(e^{iEt/\hbar}\psi^*\right)\left(e^{-iEt/\hbar}\psi\right)$$

$$=e^0.\psi^*\psi=|\psi|^2$$

$$\neq F(t)$$

Does not mean that the system is at rest (recap Bohr's stationary state), but energies and the probability do not change with time.

Stationary states (i.e. a solution): Ψ^2 and Energy→ Const. in time

MANY solutions to TISE possible → different Ψ with different energies

Applications

Free Wavicle (No external potential)

$$\textit{Time – Independent Schrodinger Equation:}$$

$$\widehat{H}\psi(x) = E\psi(x) \Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + \overset{0}{V(x)}\psi(x) = E\psi(x)$$

$$2^{nd}\ \textit{Order Linear DE:}\quad \textit{Trial Solution:}\ \psi(x) = A\sin kx + B\cos kx$$

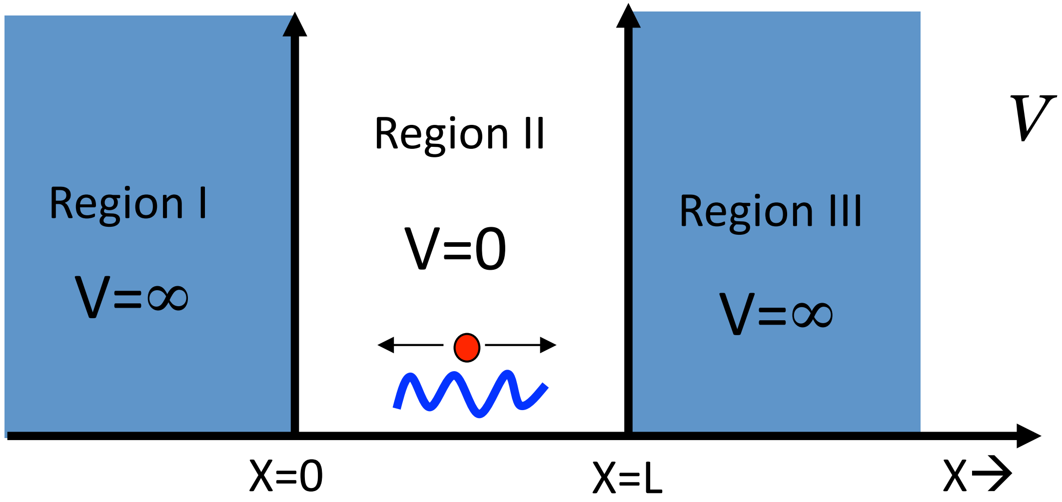
$$\frac{d^2}{dx^2}\psi(x) = -k^2(A\sin kx + B\cos kx) = -k^2\psi(x) \qquad k^2 = \frac{2mE}{\hbar^2}$$

$$E = \frac{k^2\hbar^2}{2m};\ \textit{No restriction on } k;\ \psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

A free wavicle can have any energy

All energies allowed; No energy quantization!

Wavicle in 1-D Potential Well



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

Boundary Conditions
$\Psi(0)=0$ and $\Psi(L)=0$

$\Rightarrow$ Similar to Free Particle, $\boxed{\textit{but now boundary conditions present}}$

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

$$At\ x = 0,\ \psi(0) = 0 \Rightarrow B = 0 \Rightarrow \psi(x) = A\sin kx$$

$$At\ x = L,\ \psi(L) = 0 \Rightarrow A\sin kL = 0 \Rightarrow either\ A = 0\ or\ \sin kL = 0$$

$$kL = n\pi \quad \text{for } n = 1,2,3,4,\ldots$$

$$E_n = \frac{k^2\hbar^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \qquad or \quad E_n = n^2\beta, \quad \text{n=1,2,3,4,...}$$

Energy is no longer continuous: discrete or quantized!!!

Wavicle in Box (WIB) Energies are Quantized: Certain Levels Allowed

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}} \quad or \quad \boxed{E_n = n^2 \beta}, \quad \text{n=1,2,3,4,...}$$

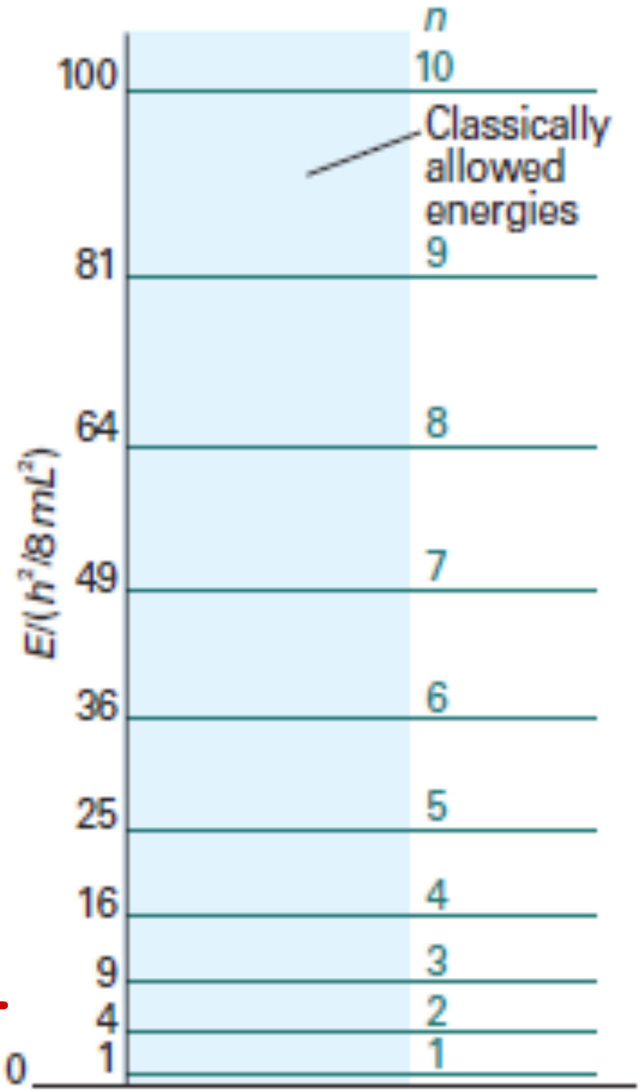
Spectroscopy of WIB in 1 *D*: $n_i \rightarrow n_f$

$\Delta E = h\nu$

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

Larger *the box, smaller the energy gap*;

Larger *wavelength of light absorbed*



m→∞ energy levels merge
L→ ∞, energy levels merge

Zero Point Energy Concept!

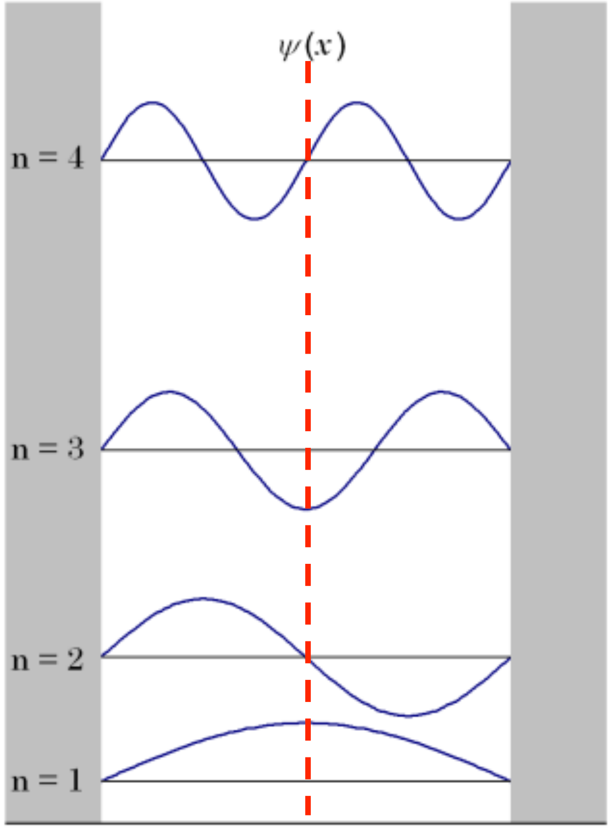
WIB Wave Functions and Probability

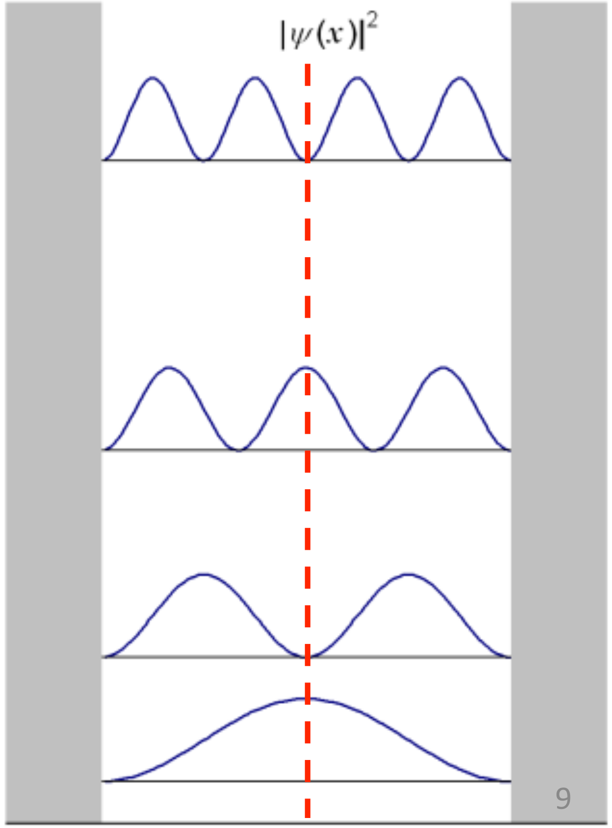
$$Wavefunction: \quad \psi(x) = A\sin kx = A\sin\frac{n\pi}{L}x$$

$$Normalization: \quad \int_0^L \psi^*(x)\psi(x)dx = 1 \quad \Rightarrow \quad \boxed{\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}}$$

No. of Nodes
(Ψ changes sign)
= n-1; increases
With increasing
Energy of states

Ψ is Symmetric
(even function) or
Anti-symmetric f(n)
(odd function)





WIB Wave Functions and Probability

$$Wavefunction: \quad \psi(x) = A\sin kx = A$$

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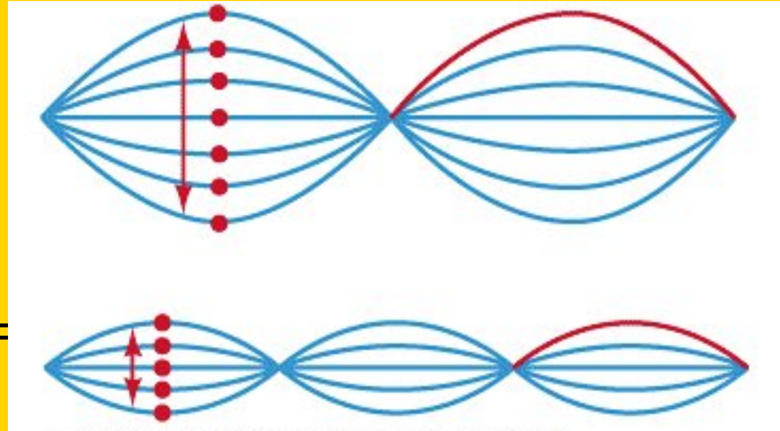

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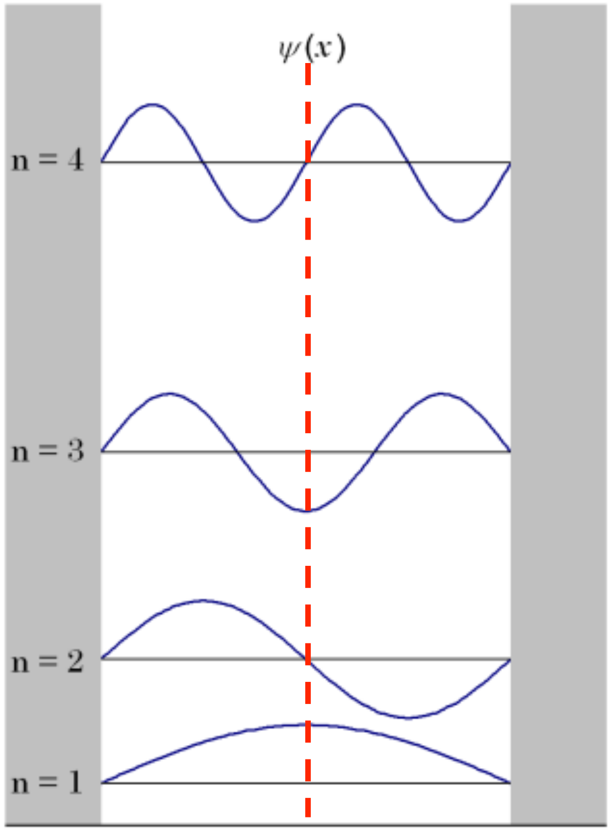
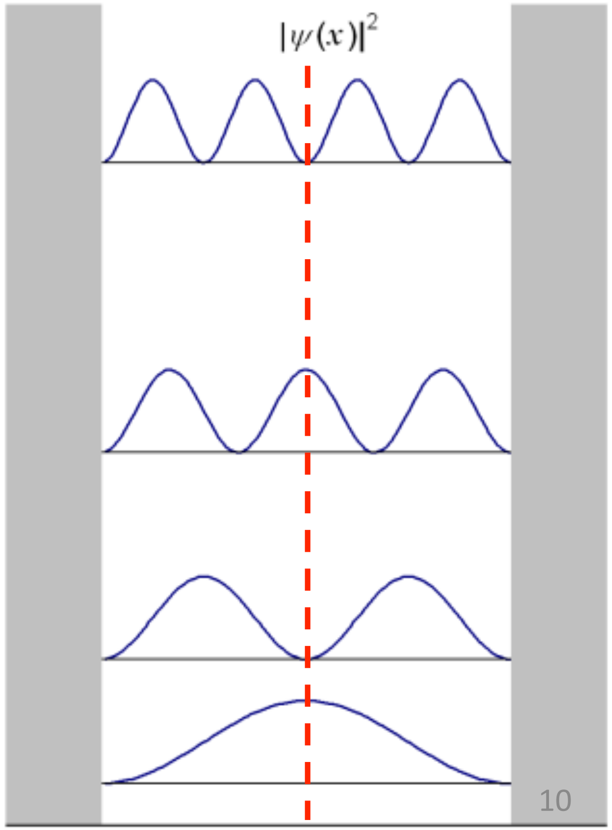




3. Eigenvalues and Average Values

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

Many Eigenstates for the same QM operator.
Every time an energy measurement between any two specified states will lead to the same (eigen) value of observed photon energy

Eigenfunctions of any QM (Hermitian) operator are "<u>Orthogonal</u>"

$$\int_{-\infty}^{+\infty} \psi_m^*(x)\psi_n(x)dx = \begin{cases} \langle \psi_m | \psi_n \rangle = 0 & \text{for } m \neq n \\ \langle \psi_m | \psi_n \rangle = 1 & \text{for } m = n \end{cases}$$

$$\langle a \rangle = \int_{all\ space} \Psi_n^* \hat{A} \Psi_n dv = \langle \Psi_n | \hat{A} | \Psi_n \rangle$$

Expectation Values and Probability

$$\langle x \rangle = \int \psi^* \cdot x \cdot \psi \cdot dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot x \cdot \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot dx$$

$$= \frac{2}{L} \int_0^L x \cdot \sin^2 \frac{n\pi}{L} x \cdot dx$$

$$= \ldots solve \ldots depends\, on?$$

Probability of finding the wavicle in a given small interval (x_1,x_2)

$$P(x_1, x_2) = \int_{x_1}^{x_2} \Psi^* \Psi dx = \frac{2}{L} \int_{x_1}^{x_2} Sin^2 \left(\frac{n\pi x}{L} \right) = \ldots (solve)$$

$$P(x_1, x_2) \approx \frac{2}{L} Sin^2 \left(\frac{n\pi x}{L} \right) . \Delta x \quad \text{if } \Delta x = (x_2 - x_1) \text{ is small}$$

Expectation Values and Probability

$$\langle p_x \rangle = \int \psi^* \cdot \left(-i\hbar \frac{\partial}{\partial x} \right) \cdot \psi \cdot dx$$

$$= -\boxed{i}\hbar \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot \frac{\partial}{\partial x} \cdot \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot dx$$

$$= \frac{-2\boxed{i}\hbar n\pi}{L^2} \int_0^L \sin \frac{n\pi}{L} x \cdot \cos \frac{n\pi}{L} x \cdot dx$$

$$= \ldots solve \ldots and\ the\ answer\ is?$$

Probability of finding the wavicle in a given small interval (x_1,x_2)

$$P(x_1, x_2) = \int_{x_1}^{x_2} \Psi^* \Psi dx = \frac{2}{L} \int_{x_1}^{x_2} Sin^2 \left(\frac{n\pi x}{L} \right) = \ldots (solve)$$

$$P(x_1, x_2) \approx \frac{2}{L} Sin^2 \left(\frac{n\pi x}{L} \right) . \Delta x \quad \text{if } \Delta x = (x_2 - x_1) \text{ is small}$$

The essence of Quantum Mechanics

- **Particles** and **waves** are *not separate and distinct entities*

- **Can not precisely determine** classical observables (*position, velocity etc.*) for a submicroscopic particle/system; $\Psi(x,t)$ can provide *all possible* (*spatio-temporal*) information.

- Only **average values** and **probabilities** can be obtained for classical variables, now in the new form of "**operators**".

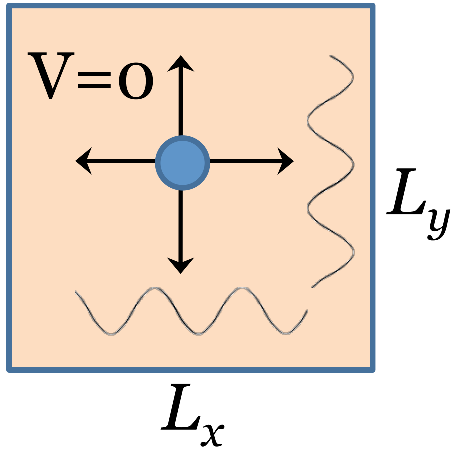
- **Discretization** of energy (or angular momentum) arise spontaneously due to ***restrictions on wavefunction*** (or by imposing *boundary conditions)*

- QM does not violate Classical mechanics for large mass

Predictions of QM agree extremely well with experiments – that's why QM is still out there!

Wavicle in a 2-D Potential well

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



Hamiltonian $\quad \widehat{H}=\widehat{H}_x+\widehat{H}_y=-\dfrac{\hbar}{2m}\dfrac{\partial^2}{\partial x^2}-\dfrac{\hbar}{2m}\dfrac{\partial^2}{\partial y^2}$

$$\psi(x,y)=\psi(x)\cdot\psi(y)=\sqrt{\frac{2}{L_x}}\sin\frac{n_x\pi}{L_x}x\cdot\sqrt{\frac{2}{L_y}}\sin\frac{n_y\pi}{L_y}y$$

Square Box
$\Rightarrow L_x=L_y=L$

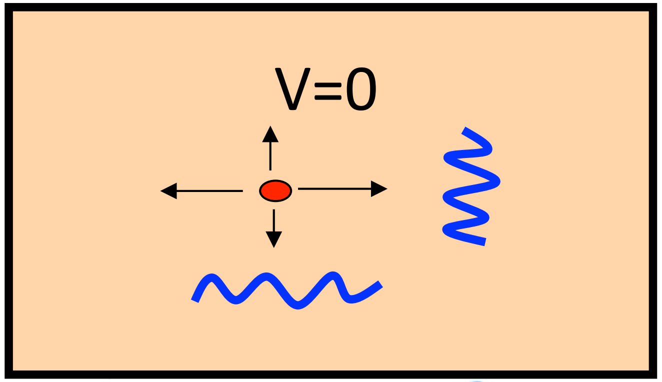
$$\widehat{H}\Psi=\left[\widehat{H}_x+\widehat{H}_y\right]\Psi_x\Psi_y=\left(E_{n_x}+E_{n_y}\right)\Psi_x\Psi_y=E_{n_x,n_y}\Psi$$

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

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

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

Wavicle in a 2-D Well: Energies



$$E_{n_x,n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right),$$

$$n_x, n_y = 1, 2, 3, 4, \ldots.$$

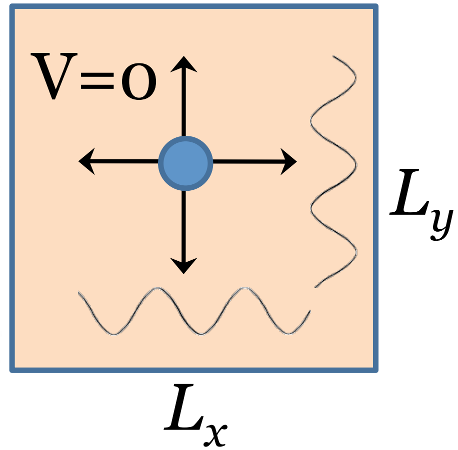
$$E_{n_1,n_2} = (n_1^2 + n_2^2)\frac{h^2}{8mL^2}$$

onsider the cases $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$:

$$\psi_{1,2} = \frac{2}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right) \qquad E_{1,2} = \frac{5h^2}{8mL^2}$$

$$\psi_{2,1} = \frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right) \qquad E_{2,1} = \frac{5h^2}{8mL^2}$$

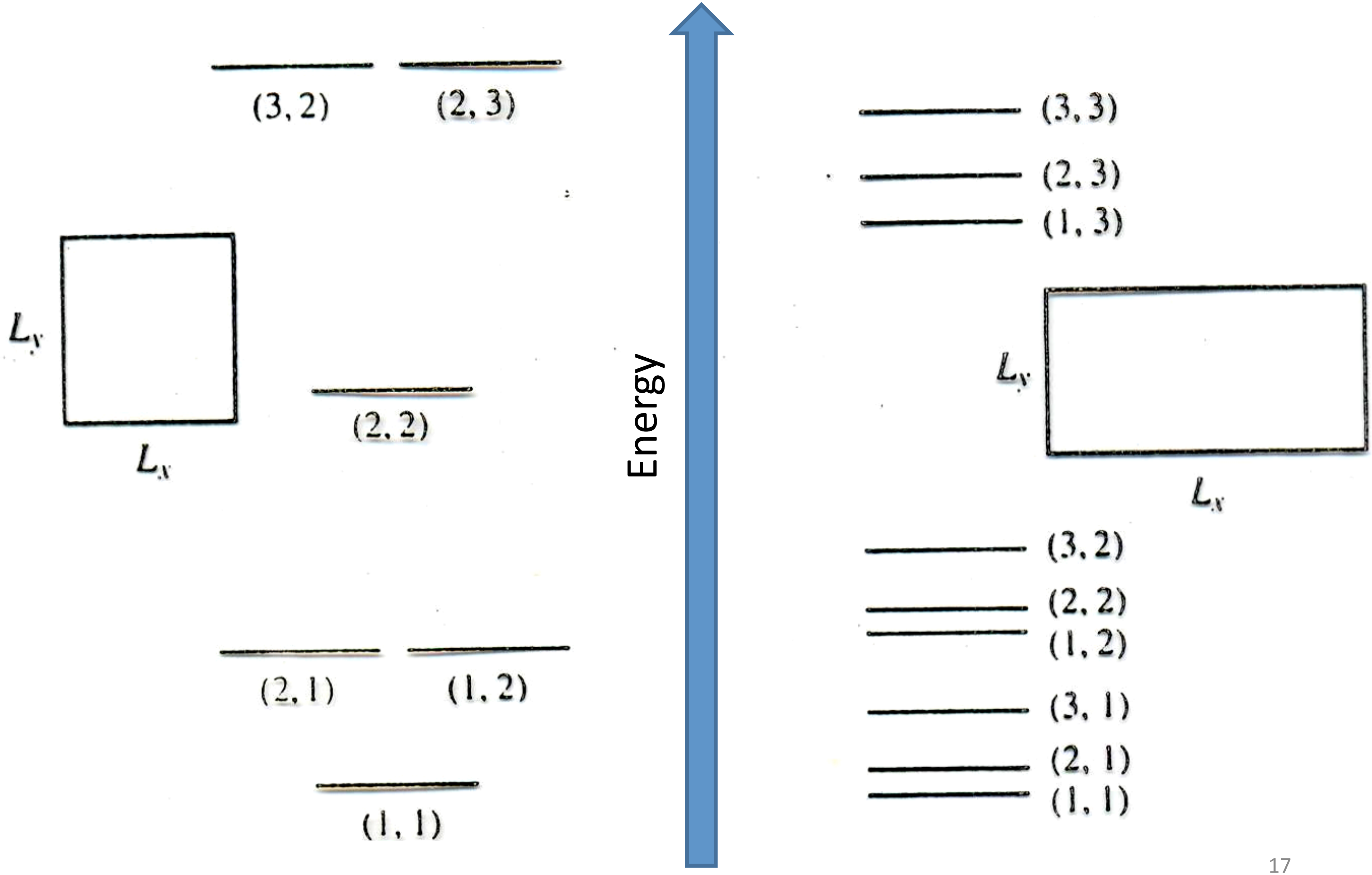
Different wavefunctions correspond to the same energy



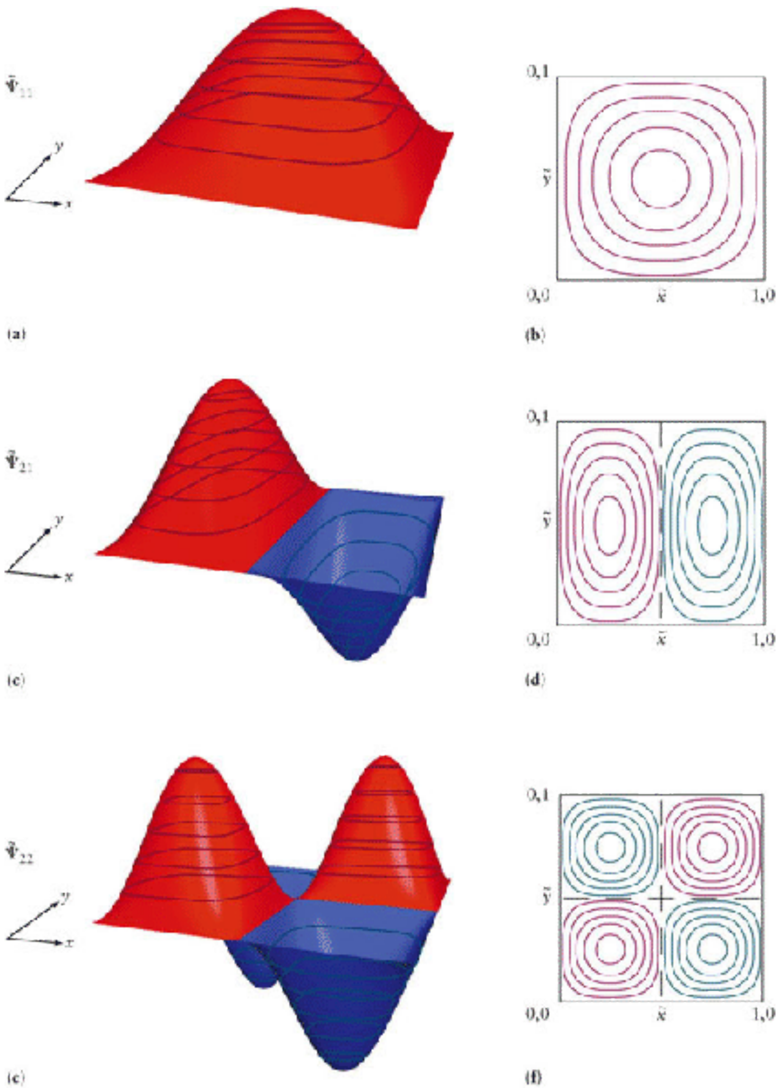
Square Box
$\Rightarrow L_x = L_y = L$

2D Well: 2 Quantum Numbers are required to describe system

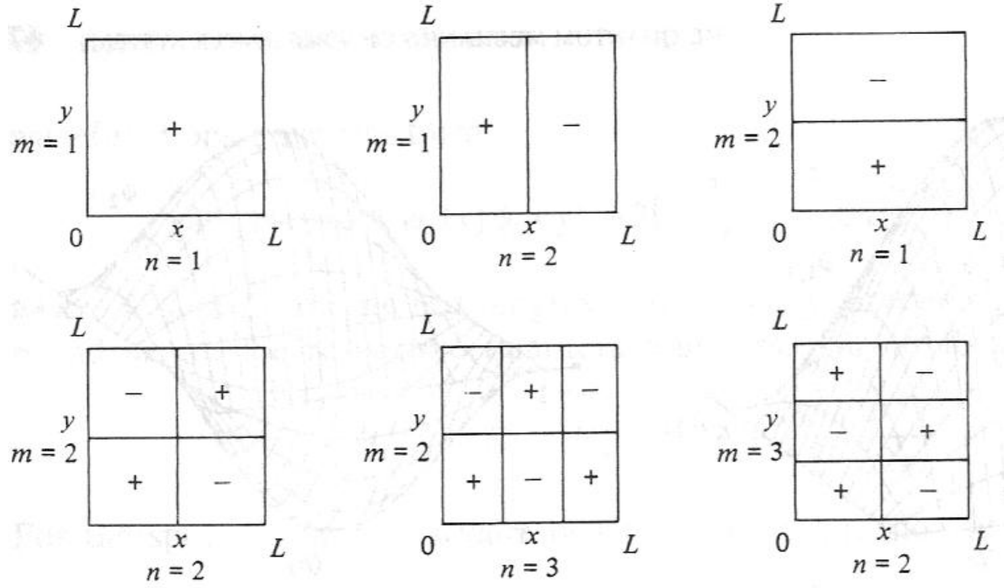
Degeneracy is manifestation of symmetry



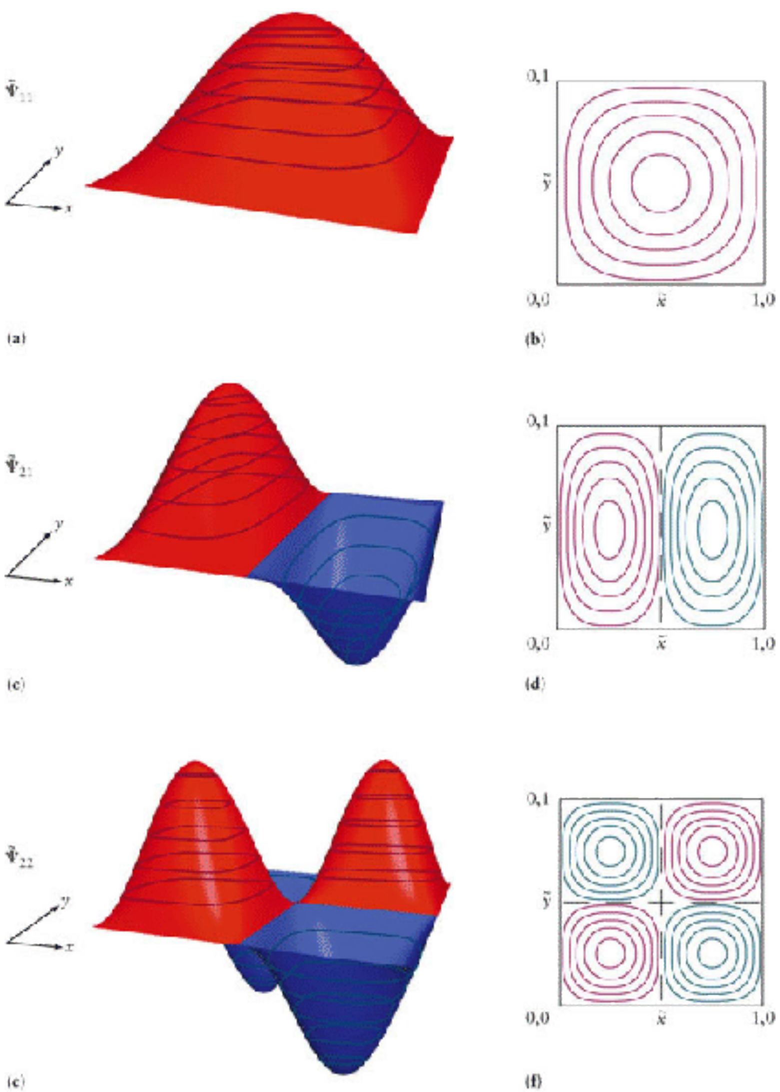
2-D Potential Well - Wavefunctions

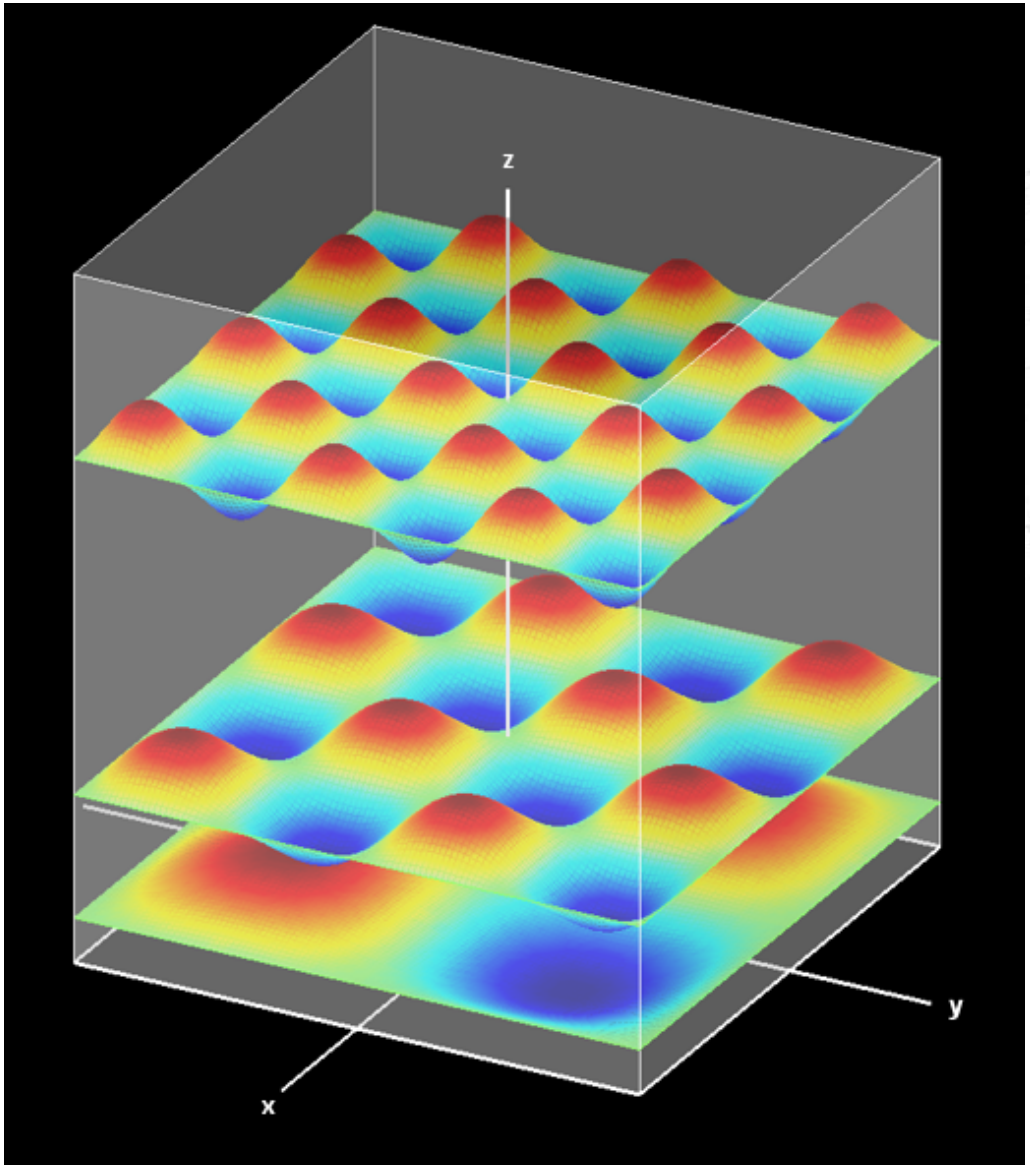


Number of nodes = n_i-1



2-D Potential Well - Wavefunctions





What Quantum Numbers in x and y do this wavefunction correspond to?

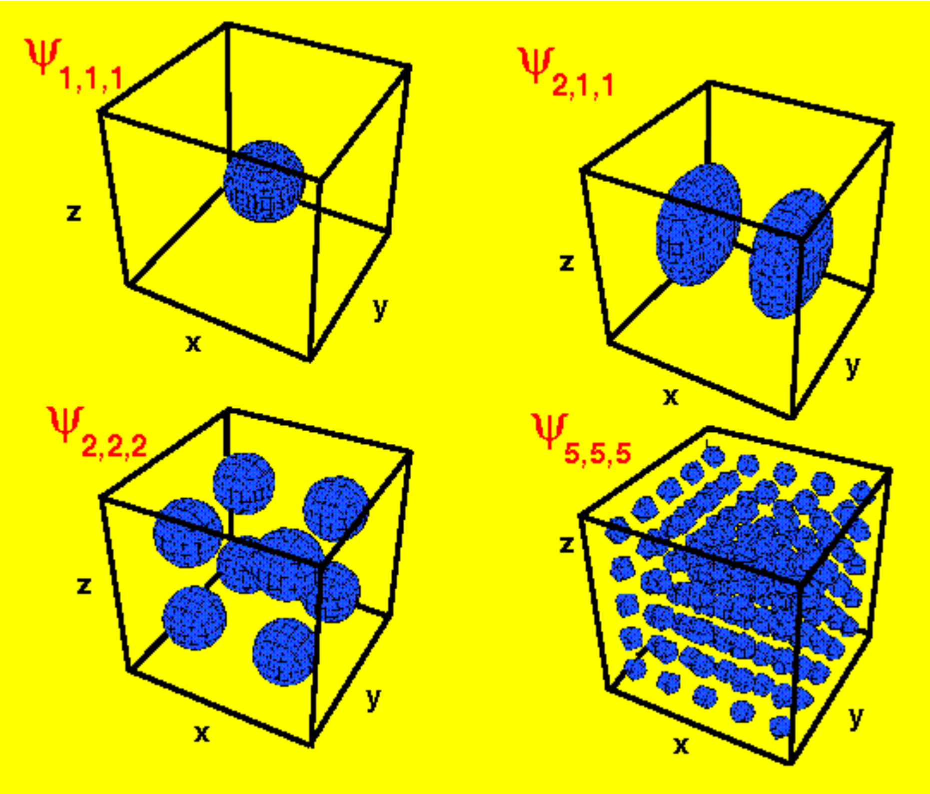
Wavicle in a 3D-Box: Wavefunctions

$$\psi_{n_x n_y n_z}(x,y,z) = \left(\frac{8}{abc}\right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad n_x = 1,2,3,\ldots \quad n_y = 1,2,3,\ldots \quad n_z = 1,2,3,\ldots$$

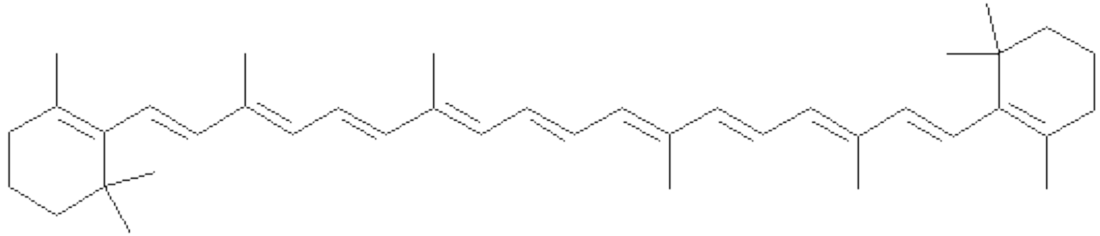
Cubic Box: Wavefunctions

3-D Box: 3 Quantum Numbers

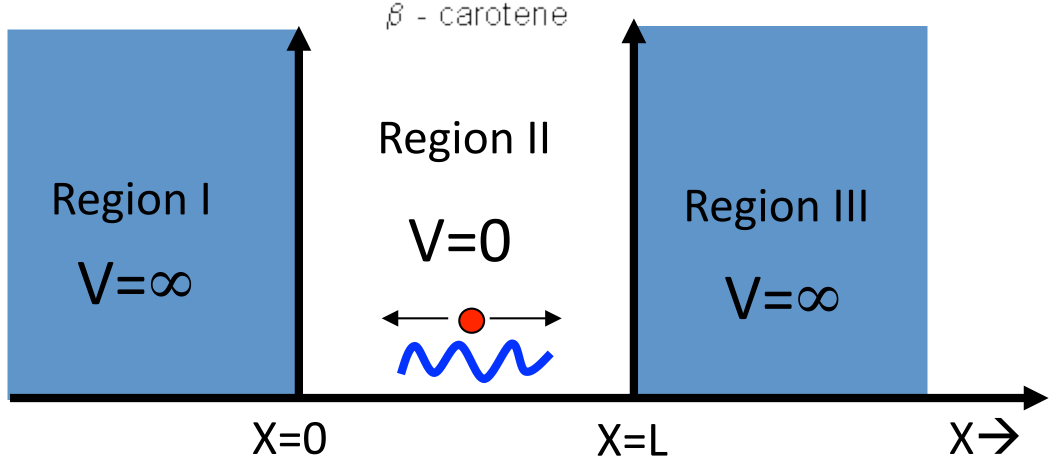


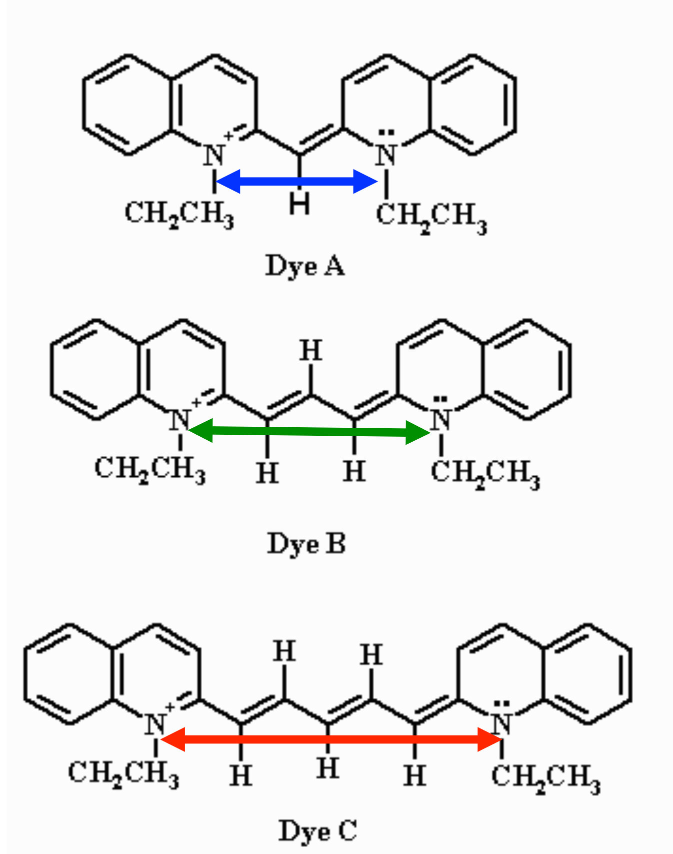
Importance in Chemistry/Spectroscopy

- Electronic spectra of conjugated molecules (loose p-electrons): 1D-PIB



β - carotene





Spectroscopy of PIB in 1 D: $n_i \to n_f$

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

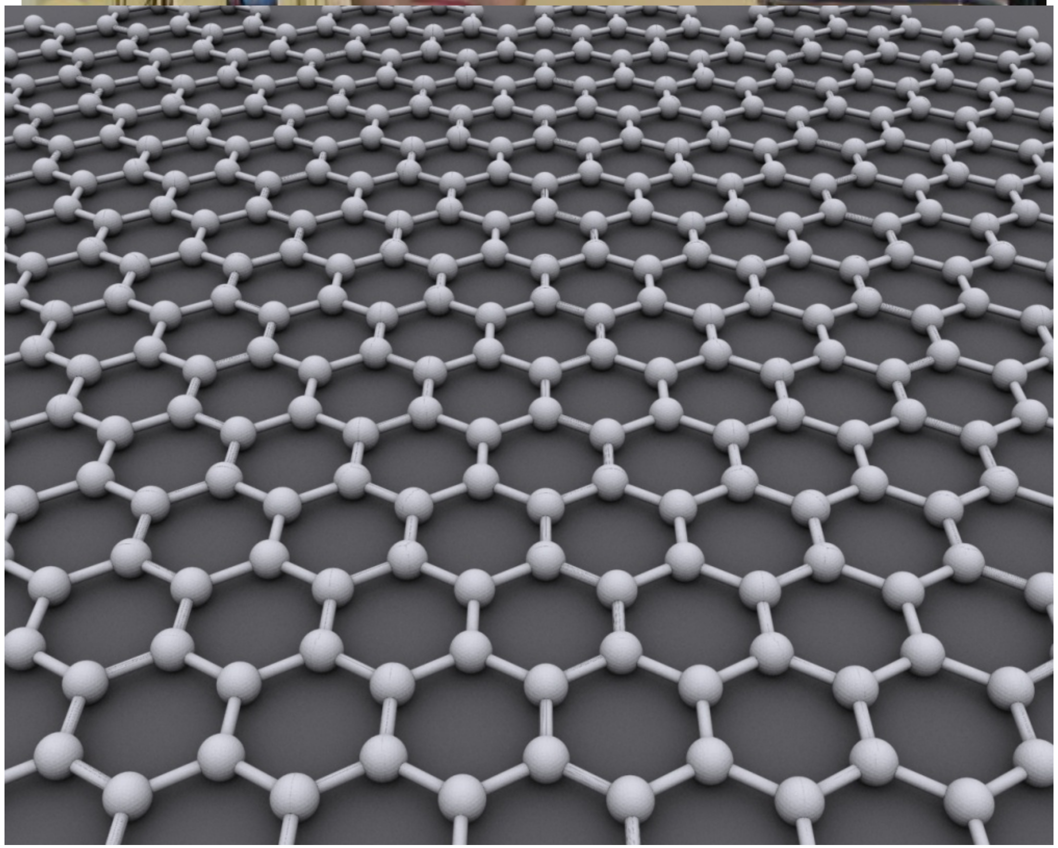
Longer the box, smaller the energy of $h\nu$

Increasing length of the box (i.e. the conjugation length) reduces the energy gaps and hence lower energy photons are absorbed or emitted

Graphene: Electrons in 2D Box
(Nobel Prize 2010 Konstantin Novoselov)

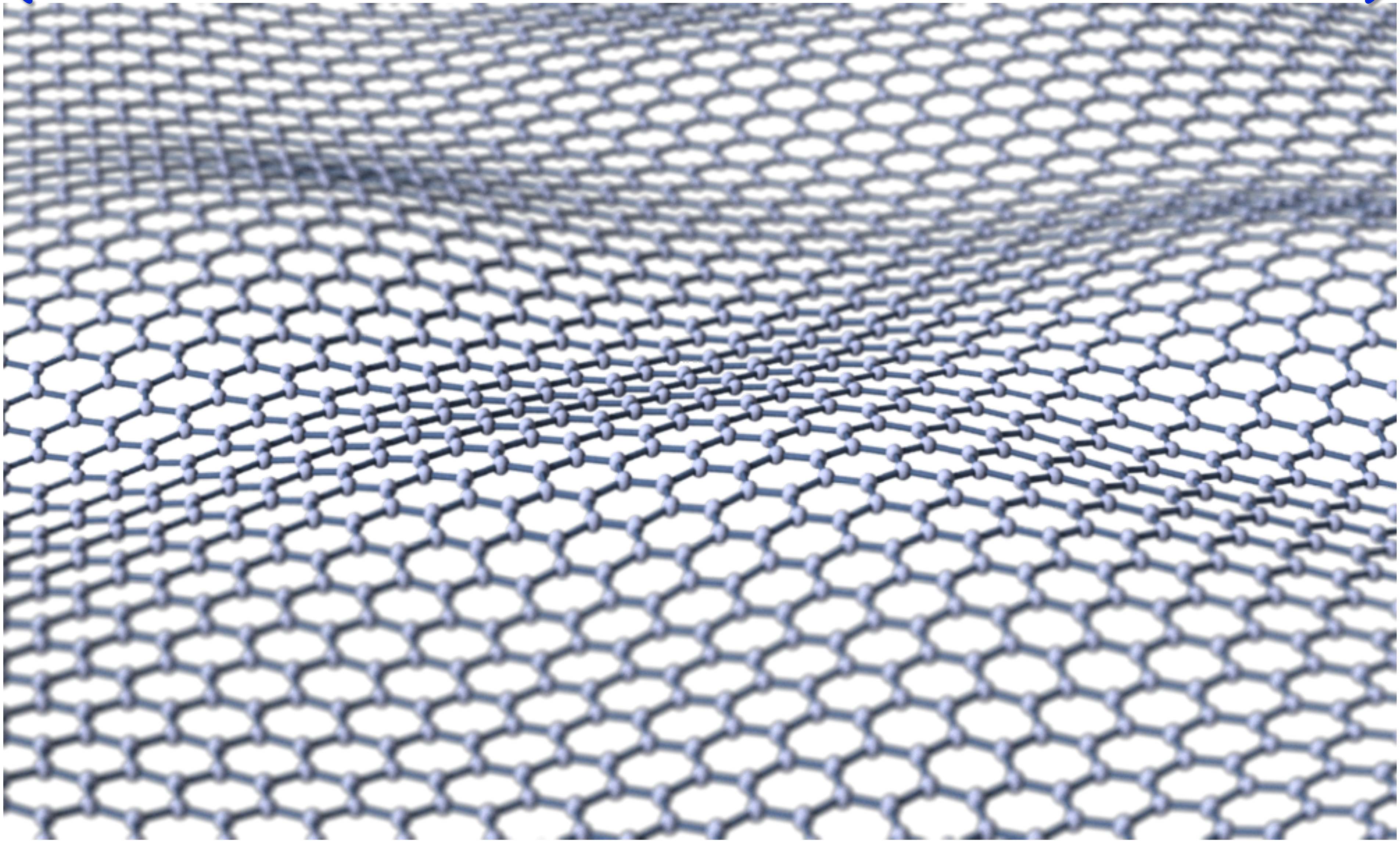
Spectroscopy indicates electrons are confined in 2D

Graphene: Electrons in 2D Box
(Nobel Prize 2010 Konstantin Novoselov)



Spectroscopy indicates electrons are confined in 2D

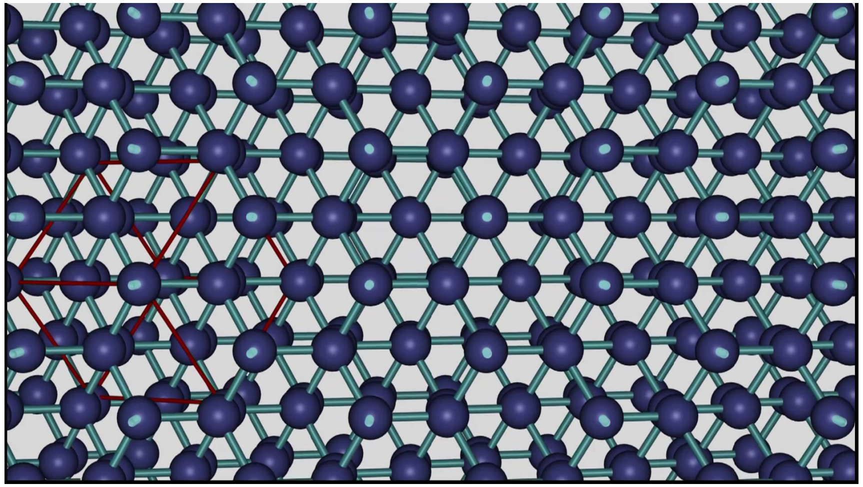
Graphene: Electrons in 2D Box (Nobel Prize 2010 Konstantin Novoselov)

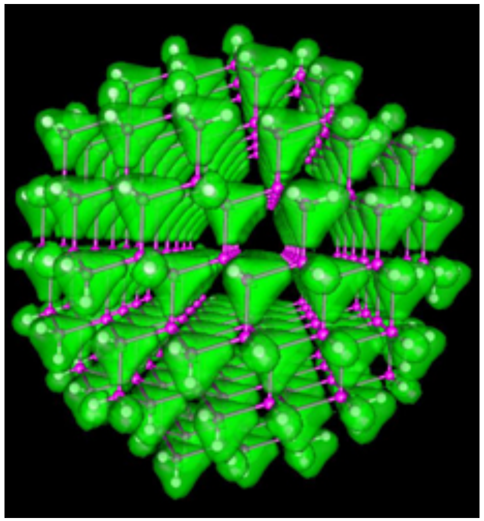


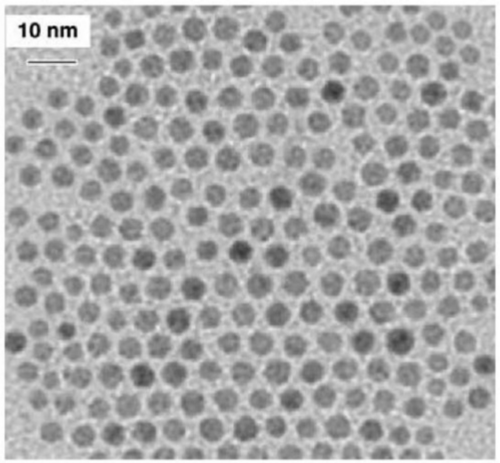
Spectroscopy indicates electrons are confined in 2D

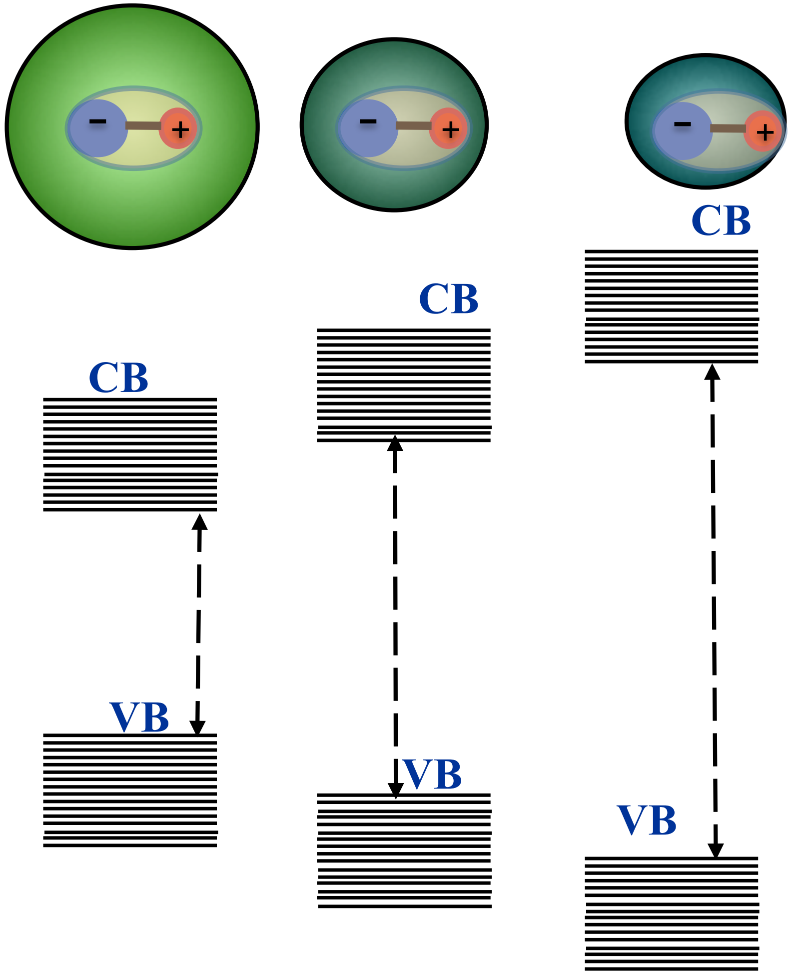
Nanoscience: Quantum Confinement

Quantum Dots – Quasi-Wavicle (excitons) in a Box!



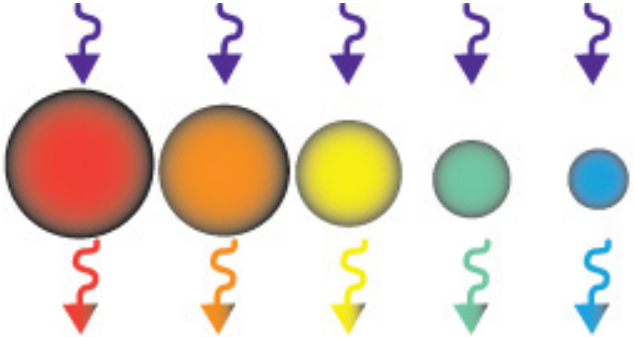


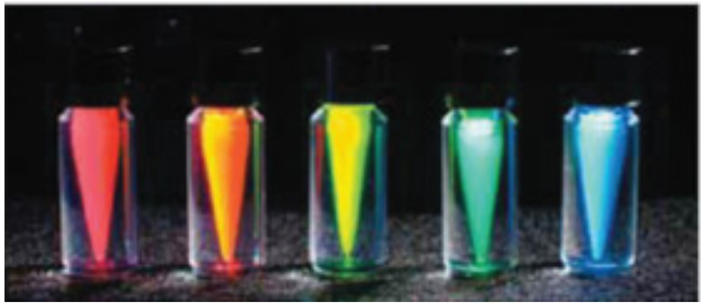




Band gap changes due to confinement, and so will the color of emitted light

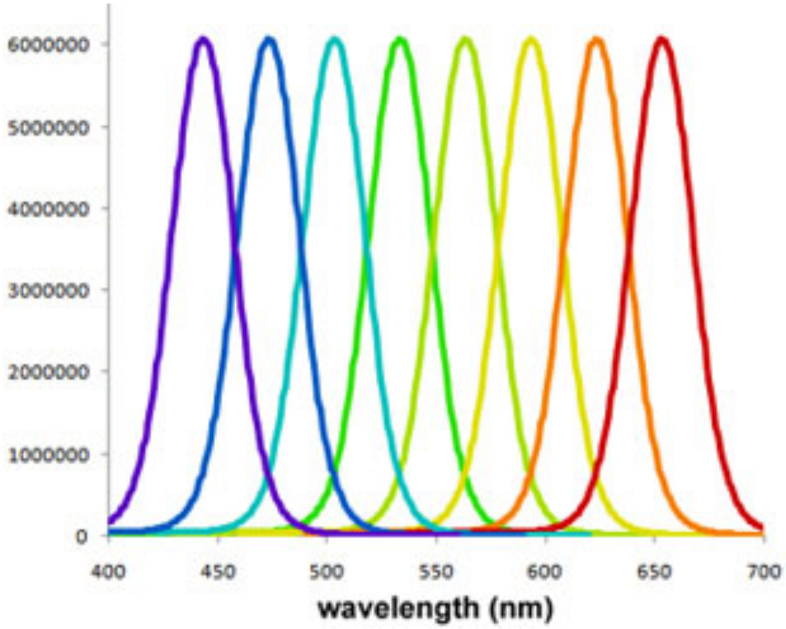
Luminescent Semiconductor Nanocrystals

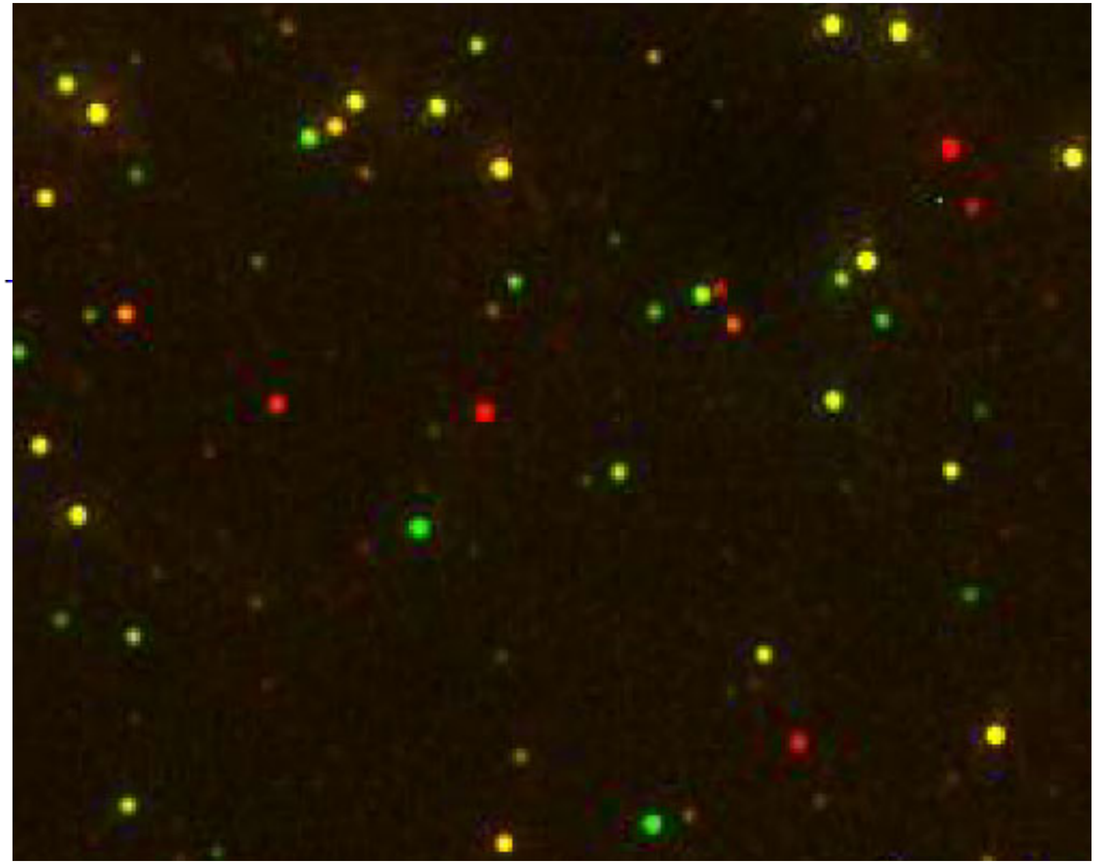




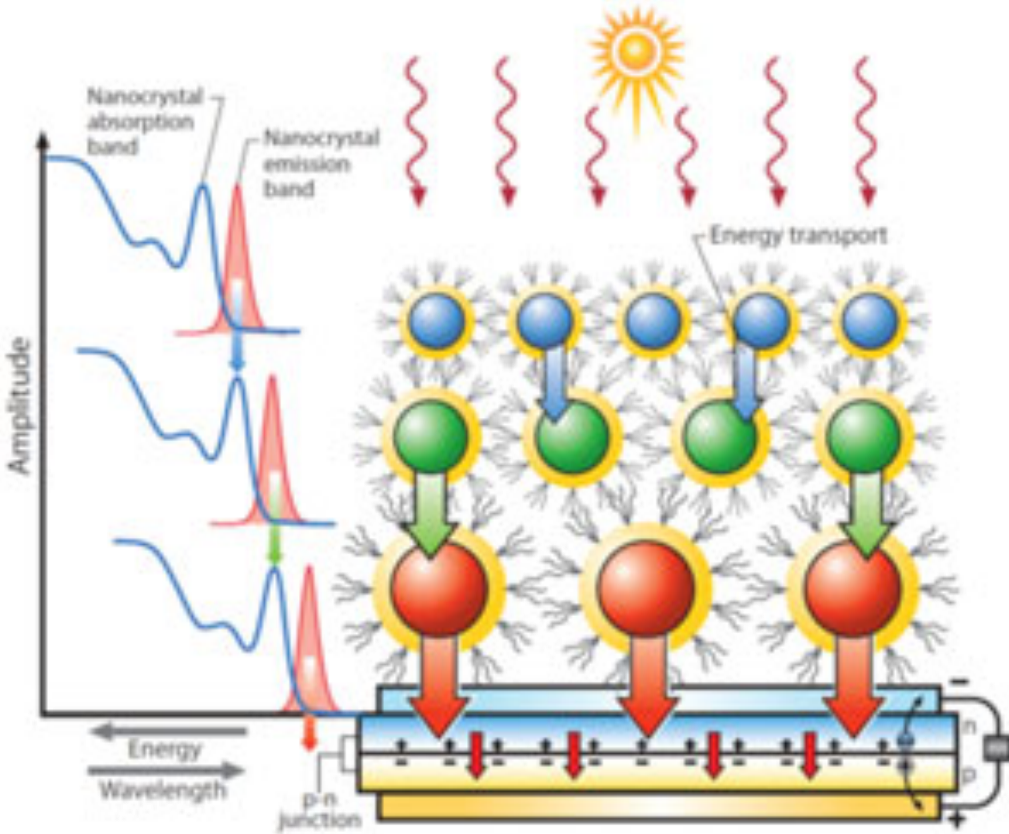
Quantum Dots ARE VERY VERY BRIGHT

Have tremendous applications
in chemistry, biology, and materials science
for photoemission imaging purpose,
as well as light harvesting/energy science

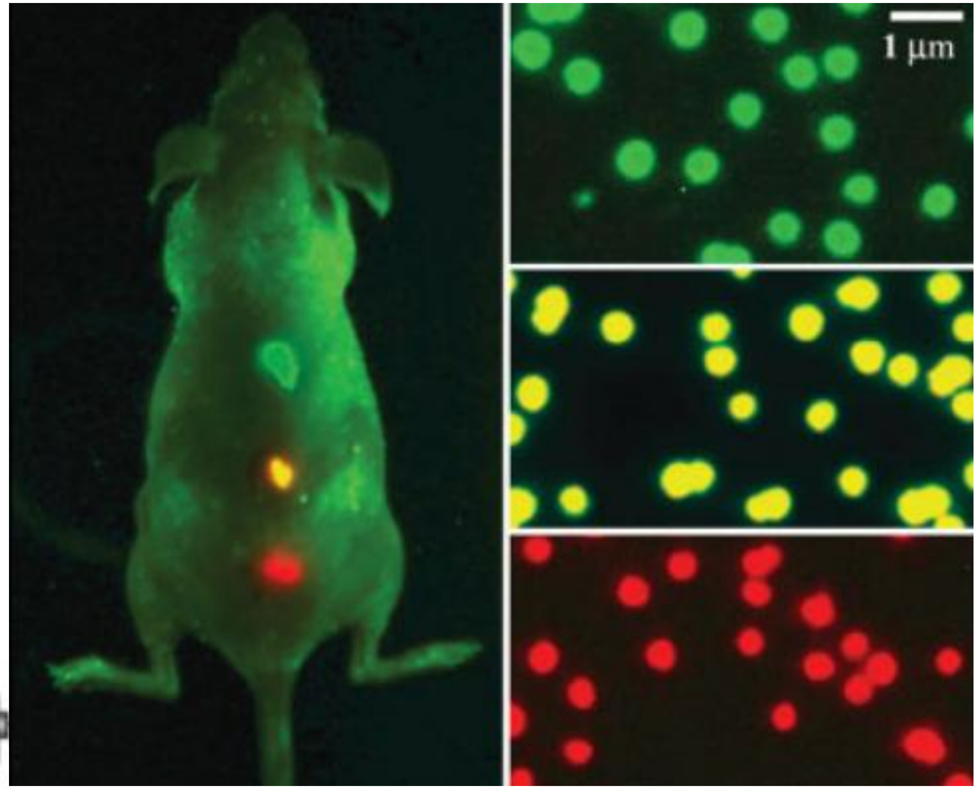




Applications of Quantum-Dots -Rods and -Wells range from medicine to materials science to solar light harvesting

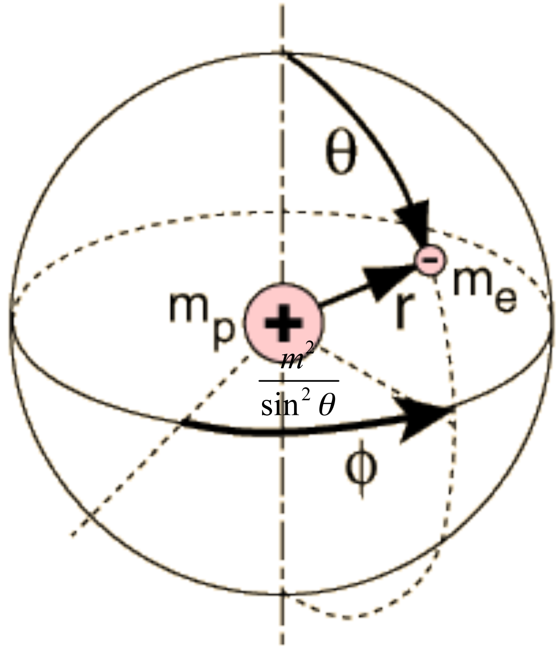


Quantum-Dot based Solar Cells



Quantum-Dot based in-vivo imaging for tumor/cancer

The Hydrogen Atom



A **Completely Solvable** problem!!

(kind of rare, in QM!)

What we learnt from solving PIB?

Formulate a correct Hamiltonian (energy) Operator H

Solve $H\Psi=E\Psi$ (2^{nd} order PDE) by separation of variable and intelligent trial/guess solutions

Impose boundary conditions for eigenfunctions (restriction) and obtain Quantum Numbers

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

Energies of states Corresponding to Quantum Numbers

Probability and Average Values

Quantum Numbers that specify the "state" of the system

H-Atom: Constructing H=T+V

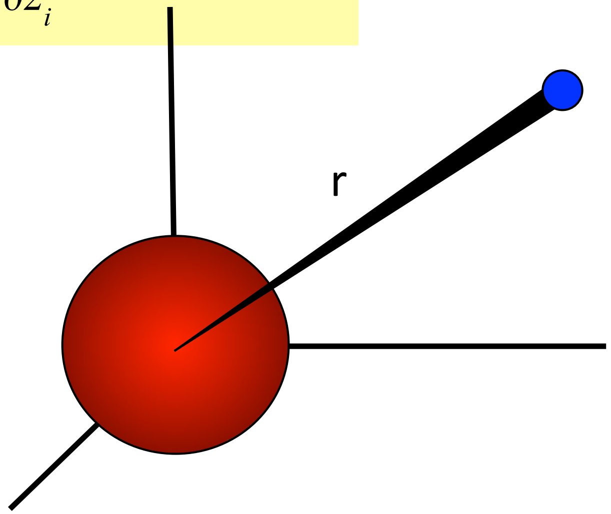
$$\hat{H} = KE + PE = \frac{\hat{P}^2(x,y,z)}{2m} + \hat{V}(x,y,z,t) = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) + V(x,y,z,t)$$

$$\because \hat{P} = -i\hbar\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right) \; and \; V(x,y,z,t) = Potential\ energy$$

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i}\nabla_i^2 + \hat{V},\ where\ \nabla_i^2(Laplacian) = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2};\ i \rightarrow particles$$

Hydrogenic Atoms: 2-Particle System

1 electron moving around a
(massive) central nucleus (+ve)



$$\hat{H} = -\frac{\hbar^2}{2m_{Nucleus}}\nabla^2_{Nucleus} - \frac{\hbar^2}{2m_{Electron}}\nabla^2_{Electron} + \hat{V}_{Electron-Nucleus}$$