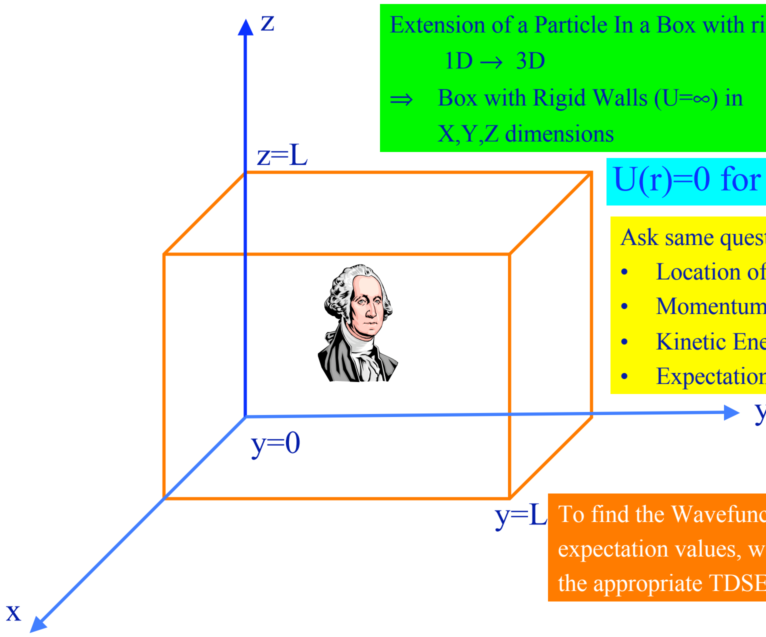
# Physics 2D Lecture Slides
# Lecture 27: March 2nd 2005


Vivek Sharma
UCSD Physics


## Quantum Mechanics In 3D: Particle in 3D Box




Extension of a Particle In a Box with rigid walls

1D → 3D

⇒ Box with Rigid Walls (U=∞) in X,Y,Z dimensions

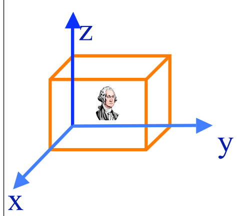
U(r)=0 for (0<x,y,z,<L)

Ask same questions:

- Location of particle in 3d Box
- Momentum
- Kinetic Energy, Total Energy
- Expectation values in 3D

To find the Wavefunction and various expectation values, we must first set up the appropriate TDSE & TISE

## The Schrodinger Equation in 3 Dimensions: Cartesian Coordinates




Time Dependent Schrodinger Eqn:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z,t)+U(x,y,z)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t} \quad \text{.....In 3D}$$

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

$$So\ -\frac{\hbar^2}{2m}\nabla^2=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\right)=[K]$$

$$= \quad [K_x] \quad + \quad [K_x] \quad + \quad [K_x]$$

$so\ [H]\Psi(x,t)=[E]\Psi(x,t)$ is still the Energy Conservation Eq

Stationary states are those for which all probabilities are constant in time and are given by the solution of the TDSE in seperable form:

$$\Psi(x,y,z,t)=\Psi(\vec{r},t)=\psi(\vec{r})e^{-i\omega t}$$

This statement is simply an extension of what we derived in case of 1D time-independent potential

## Particle in 3D Rigid Box : Separation of Orthogonal Spatial (x,y,z) Variables

*TISE* in 3D: $-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z)+U(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$

x,y,z independent of each other , write $\psi(x,y,z)=\psi_1(x)\psi_2(y)\psi_3(z)$

and substitute in the master TISE, after dividing thruout by $\psi=\psi_1(x)\psi_2(y)\psi_3(z)$

and noting that U(r)=0 for (0<x,y,z,<L) $\Rightarrow$

$$\left(-\frac{\hbar^2}{2m}\frac{1}{\psi_1(x)}\frac{\partial^2\psi_1(x)}{\partial x^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{1}{\psi_2(y)}\frac{\partial^2\psi_2(y)}{\partial y^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{1}{\psi_3(z)}\frac{\partial^2\psi_3(z)}{\partial z^2}\right)=E=Const$$

This can only be true if each term is constant for all x,y,z $\Rightarrow$

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1(x)}{\partial x^2}=E_1\psi_1(x)};\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi_2(y)}{\partial y^2}=E_2\psi_2(y)};\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi_3(z)}{\partial z^2}=E_3\psi_3(z)}$$

With $\boxed{E_1+E_2+E_3=E=\text{Constant}}$ (Total Energy of 3D system)

Each term looks like particle in 1D box (just a different dimension)

So wavefunctions must be like $\boxed{\psi_1(x)\propto\sin k_1x}$ , $\boxed{\psi_2(y)\propto\sin k_2y}$ , $\boxed{\psi_3(z)\propto\sin k_3z}$

## Particle in 3D Rigid Box : Separation of Orthogonal Variables

Wavefunctions are like $\psi_1(x) \propto \sin k_1 x$, $\psi_2(y) \propto \sin k_2 y$, $\psi_3(z) \propto \sin k_3 z$

Continuity Conditions for $\psi_i$ and its first spatial derivatives $\Rightarrow$ $n_i \pi = k_i L$

Leads to usual Quantization of Linear Momentum $\vec{p} = \hbar \vec{k}$.....in 3D

$$p_x = \left(\frac{\pi\hbar}{L}\right) n_1 \; ; \; p_y = \left(\frac{\pi\hbar}{L}\right) n_2 \; ; \; p_z = \left(\frac{\pi\hbar}{L}\right) n_3 \quad (n_1, n_2, n_3 = 1, 2, 3, ..\infty)$$

Note: by usual Uncertainty Principle argument neither of $n_1, n_2, n_3 = 0!$ (*why*?)

Particle Energy $E = K + U = K + 0 = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$

Energy is again quantized and brought to you by integers $n_1, n_2, n_3$ (independent) and $\psi(\vec{r}) = A \sin k_1 x \sin k_2 y \sin k_3 z$ (A = Overall Normalization Constant)

$$\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-i\frac{E}{\hbar}t} = A\, [\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$$

## Particle in 3D Box :Wave function Normalization Condition

$$\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-i\frac{E}{\hbar}t} = A\, [\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$$

$$\Psi^*(\vec{r},t) = \psi^*(\vec{r})\, e^{i\frac{E}{\hbar}t} = A\, [\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{i\frac{E}{\hbar}t}$$

$$\Psi^*(\vec{r},t)\Psi(\vec{r},t) = A^2\, [\sin^2 k_1 x \sin^2 k_2 y \sin^2 k_3 z]$$

Normalization Condition : $1 = \iiint_{x,y,z} P(r)\, dx\, dy dz \Rightarrow$

$$1 = A^2 \int_{x=0}^{L} \sin^2 k_1 x\, dx \int_{y=0}^{L} \sin^2 k_2 y\, dy \int_{z=0}^{L} \sin^2 k_3 z\, dz = A^2 \left(\sqrt{\frac{L}{2}}\right)\left(\sqrt{\frac{L}{2}}\right)\left(\sqrt{\frac{L}{2}}\right)$$

$$\Rightarrow A = \left[\frac{2}{L}\right]^{\frac{3}{2}} \text{ and } \Psi(\vec{r},t) = \left[\frac{2}{L}\right]^{\frac{3}{2}} [\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$$

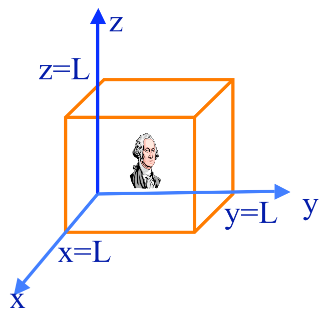
## Particle in 3D Box : Energy Spectrum & Degeneracy

$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2+n_2^2+n_3^2); \quad n_i = 1,2,3...\infty, n_i \neq 0$$

Ground State Energy $E_{111} = \frac{3\pi^2\hbar^2}{2mL^2}$

Next level $\Rightarrow$ 3 Excited states $E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}$

Different configurations of $\psi(r)=\psi(x,y,z)$ have same energy $\Rightarrow$ degeneracy



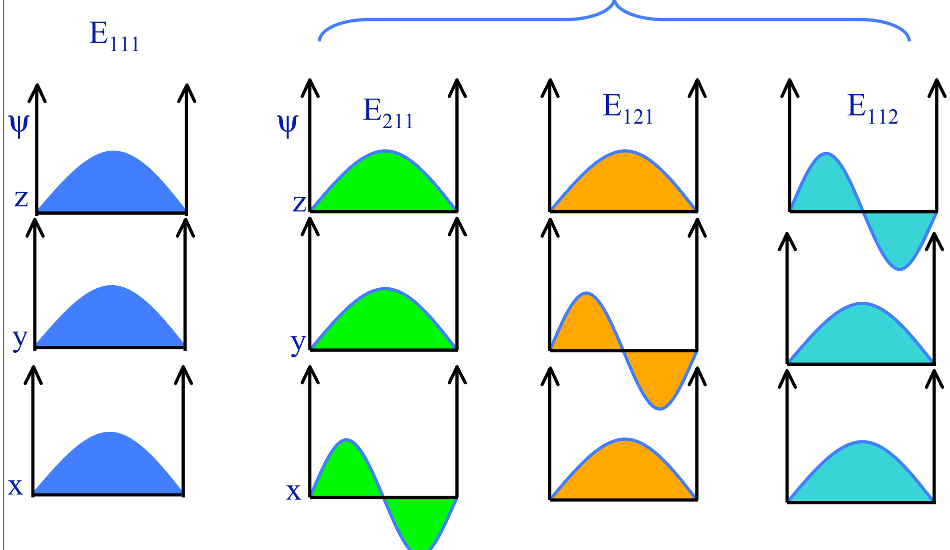

| | $n^2$ | Degeneracy |
|---|---|---|
| $4E_0$ | 12 | None |
| $\frac{11}{3}E_0$ | 11 | 3 |
| $3E_0$ | 9 | 3 |
| $2E_0$ | 6 | 3 |
| $E_0$ | 3 | None |

Degenerate States

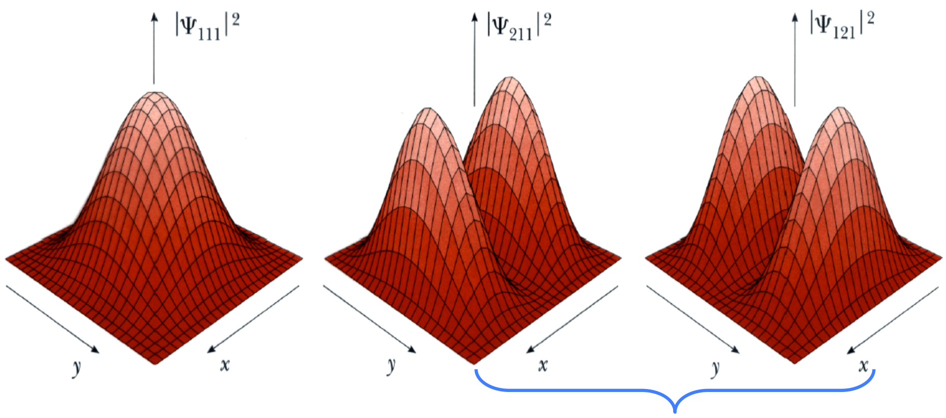
$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}$

Ground State

$E_{111}$



## Probability Density Functions for Particle in 3D Box

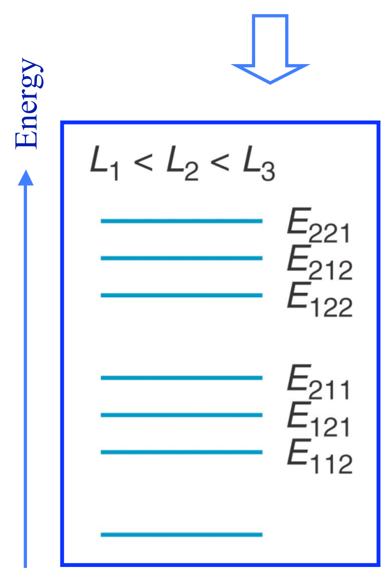



Same Energy → Degenerate States
Cant tell by measuring energy if particle is in 211, 121, 112 quantum State

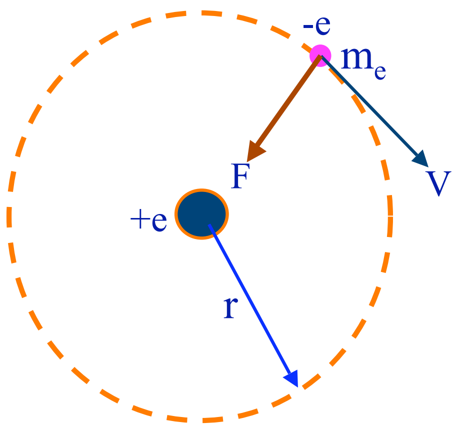
## Source of Degeneracy: How to "Lift" Degeneracy

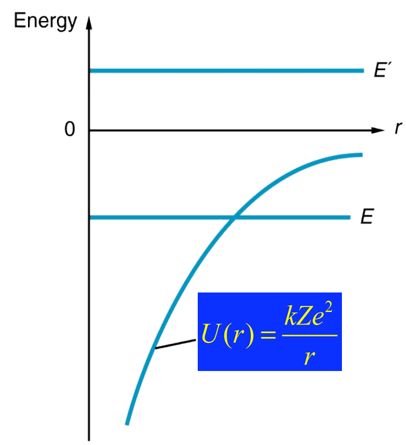
- Degeneracy came from the threefold symmetry of a CUBICAL Box ($L_x = L_y = L_z = L$)
- To Lift (remove) degeneracy → change each dimension such that CUBICAL box → Rectangular Box
  - ($L_x \neq L_y \neq L_z$)
  - Then

$$E = \left(\frac{n_1^2\pi^2}{2mL_x^2}\right) + \left(\frac{n_2^2\pi^2}{2mL_y^2}\right) + \left(\frac{n_3^2\pi^2}{2mL_z^2}\right)$$

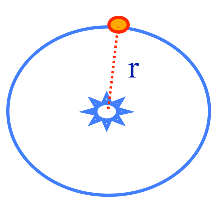


## The Coulomb Attractive Potential That Binds the electron and Nucleus (charge +Ze) into a Hydrogenic atom




## The Hydrogen Atom In Its Full Quantum Mechanical Glory




$U(r) \propto \frac{1}{r} = \frac{1}{\sqrt{x^2+y^2+z^2}}$ $\Rightarrow$ More complicated form of U than box

By example of particle in 3D box, need to use seperation of variables(x,y,z) to derive 3 independent differential. eqns.

This approach will get very ugly since we have a "conjoined triplet"

To simplify the situation, use appropriate variables

Independent Cartesian (x,y,z) $\rightarrow$ Inde. Spherical Polar (r,$\theta$,$\phi$)

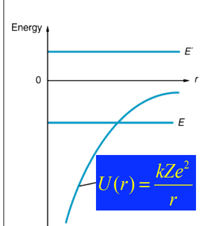
Instead of writing Laplacian $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, write

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi}$$

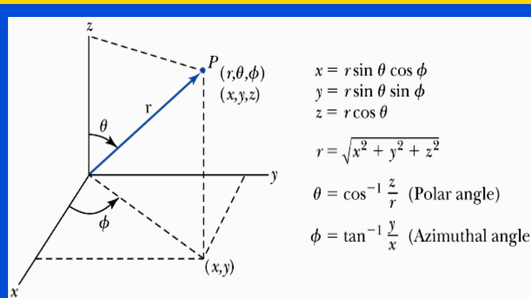
TISE for $\psi(x,y,z)=\psi(r,\theta,\phi)$ becomes

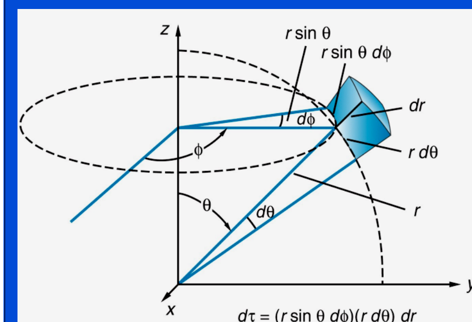
$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial^2\phi} + \frac{2m}{\hbar^2}(E-U(r))\psi(r,\theta,\phi) = 0$$

!!!! fun!!!



## Spherical Polar Coordinate System




Volume Element dV

$$dV = (r\sin\theta d\phi)(rd\theta)(dr)$$
$$= \mathrm{r}^2 \sin\theta dr d\theta d\phi$$

## Don't Panic: Its simpler than you think !

$$\frac{1}{\mathrm{r}^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial^2\phi}+\frac{2\mathrm{m}}{\hbar^2}(\mathrm{E-U(r)})\psi(\mathrm{r},\theta,\phi)=0$$

Try to free up last term from all except $\phi$

This requires multiplying thruout by $\boxed{r^2\sin^2\theta}$ $\Rightarrow$

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial^2\psi}{\partial^2\phi}+\frac{2\mathrm{m}r^2\sin^2\theta}{\hbar^2}(\mathrm{E}+\frac{\mathrm{ke}^2}{\mathrm{r}})\psi=0$$

For Seperation of Variables, Write $\psi(\mathrm{r},\theta,\phi)=\mathrm{R(r)}.\Theta(\theta).\Phi(\phi)$

Plug it into the TISE above & divide thruout by $\psi(\mathrm{r},\theta,\phi)=\mathrm{R(r)}.\Theta(\theta).\Phi(\phi)$

Note that : $\boxed{\begin{array}{l}\frac{\partial\Psi(r,\theta,\phi)}{\partial \mathrm{r}}=\Theta(\theta).\Phi(\phi)\ \frac{\partial\mathrm{R(r)}}{\partial\mathrm{r}}\\ \frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Phi(\phi)\ \frac{\partial\Theta(\theta)}{\partial\theta}\\ \frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Theta(\theta)\ \frac{\partial\Phi(\phi)}{\partial\phi}\end{array}}$ $\Rightarrow$ when substituted in TISE

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}+\frac{2\mathrm{m}r^2\sin^2\theta}{\hbar^2}(\mathrm{E}+\frac{\mathrm{ke}^2}{\mathrm{r}})=0$$

Rearrange by taking the $\phi$ term on RHS

$$\boxed{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2\mathrm{m}r^2\sin^2\theta}{\hbar^2}(\mathrm{E}+\frac{\mathrm{ke}^2}{\mathrm{r}})=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}}$$

LHS is fn. of r,$\theta$ & RHS is fn of $\phi$ only , for equality to be true for all r,$\theta$,$\phi$

$\Rightarrow$ $\boxed{\text{LHS= constant = RHS = } \mathrm{m}_l^2}$

Now go break up LHS to seperate the r & $\theta$ terms.....

$$\text{LHS:}\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}(E+\frac{ke^2}{r})=m_l^2$$

Divide Thruout by $\sin^2\theta$ and arrange all terms with r away from $\theta \Rightarrow$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}(E+\frac{ke^2}{r})=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

Same argument : LHS is fn of r, RHS is fn of $\theta$, for them to be equal for all r,$\theta$

$\Rightarrow$ $\boxed{\text{LHS = const = RHS} = l(l+1)}$ What do we have after shuffling!

$$\frac{d^2\Phi}{d\phi^2}+m_l^2\Phi=0..................(1)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]\Theta(\theta)=0.....(2)$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2mr^2}{\hbar^2}(E+\frac{ke^2}{r})-\frac{l(l+1)}{r^2}\right]R(r)=0....(3)$$

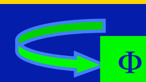
These 3 "simple" diff. eqn describe the physics of the Hydrogen atom.

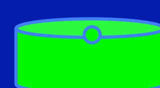
All we need to do now is guess the solutions of the diff. equations

Each of them, clearly, has a different functional form

# Solutions of The S. Eq for Hydrogen Atom

The Azimuthal Diff. Equation : $\boxed{\frac{d^2\Phi}{d\phi^2}+m_l^2\Phi=0}$



Solution : $\Phi(\phi) = A\, e^{im_l\phi}$ but need to check "Good Wavefunction Condition"

Wave Function must be Single Valued for all $\phi \Rightarrow \Phi(\phi)=\Phi(\phi+2\pi)$

$\Rightarrow \Phi(\phi) = A\, e^{im_l\phi} = A\, e^{im_l(\phi+2\pi)} \Rightarrow m_l = 0,\pm1,\pm2,\pm3....$(Magnetic Quantum #)

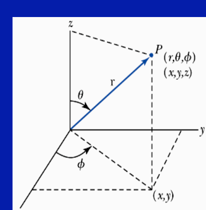
The Polar Diff. Eq: $\boxed{\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]\Theta(\theta)=0}$

Solutions : go by the name of "Associated Legendre Functions"

only exist when the integers $l$ and $m_l$ are related as follows

$m_l = 0,\pm1,\pm2,\pm3....\pm l$ ; $l$ = positive number

$l$ : Orbital Quantum Number




For $l=0, m_l$=0 $\Rightarrow \boxed{\Theta(\theta)=\frac{1}{\sqrt{2}}}$ ;

For $l=1, m_l$=0, $\pm1$ $\Rightarrow$ Three Possibilities for the Orbital part of wavefunction

$\boxed{[l=1, m_l=0] \Rightarrow \Theta(\theta)=\frac{\sqrt{6}}{2}\cos\theta}$ $\boxed{[l=1, m_l=\pm1] \Rightarrow \Theta(\theta)=\frac{\sqrt{3}}{2}\sin\theta}$

$[l=2, m_l=0] \Rightarrow \Theta(\theta)=\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$....*and* so on and so forth (see book)

# Solutions of The S. Eq for Hydrogen Atom

The Radial Diff. Eqn: $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2mr^2}{\hbar^2}(\text{E}+\frac{\text{ke}^2}{\text{r}})-\frac{l(l+1)}{r^2}\right]R(r)=0$

*Solutions* : Associated Laguerre Functions R(r), Solutions exist only if:

1. E>0 or has negtive values given by $\text{E}=-\frac{\text{ke}^2}{2\text{a}_0}\left(\frac{1}{n^2}\right); a_0=\frac{\hbar^2}{mke^2}$ = Bohr Radius

2. And when n = integer such that $\boxed{l=0,1,2,3,4,,,(n-1)}$

n = principal Quantum # or the "big daddy" qunatum #

To Summarize : The hydrogen atom is brought to you by the letters

$$\begin{array}{|l|}\text{n} = 1,2,3,4,5,....\infty \\ l=0,1,2,3,,4....(n-1) \\ \text{m}_l = 0,\pm1,\pm2,\pm3,...\pm l\end{array}$$

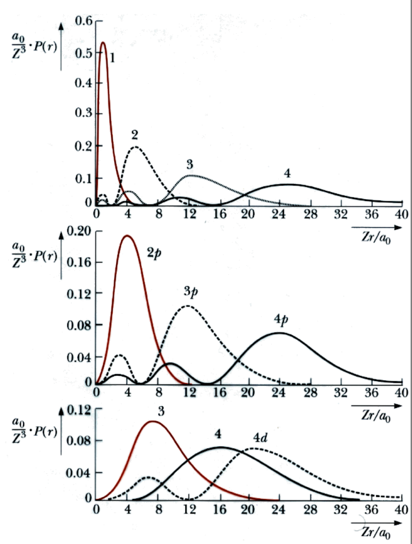
Quantum # appear only in Trapped systems

The Spatial Wave Function of the Hydrogen Atom

$$\Psi(r,\theta,\phi)=R_{nl}(r)\ .\ \Theta_{lm_l}(\theta)\ \ .\ \Phi_{\text{m}_l}(\phi)=R_{nl}\text{Y}_l^{m_l}\ \text{(Spherical Harmonics)}$$

# Radial Wave Functions & Radial Prob Distributions

| n | $l$ | $m_l$ | R(r)= |
|---|---|---|---|
| 1 | 0 | 0 | $\frac{2}{\text{a}_0^{3/2}}\text{e}^{-\text{r/a}}$ |
| 2 | 0 | 0 | $\frac{1}{2\sqrt{2}\text{a}_0^{3/2}}(2-\frac{\text{r}}{\text{a}_0})e^{-\frac{\text{r}}{2\text{a}_0}}$ |
| 3 | 0 | 0 | $\frac{2}{81\sqrt{3}\text{a}_0^{3/2}}(27-18\frac{\text{r}}{\text{a}_0}+2\frac{r^2}{a_0^2})e^{-\frac{r}{3a_0}}$ |




n=1 → K shell
n=2 → L Shell
n=3 → M shell
n=4 → N Shell
……

*l=0→ s(harp) sub shell*
*l=1→ p(rincipal) sub shell*
*l=2→ d(iffuse) sub shell*
*l=3→ f(undamental) ss*
*l=4→ g sub shell*
……..

## Symbolic Notation of Atomic States in Hydrogen

| $l \rightarrow$ / $n \downarrow$ | $s\ (l=0)$ | $p\ (l=1)$ | $d\ (l=2)$ | $f\ (l=3)$ | $g\ (l=4)$ | ..... |
|---|---|---|---|---|---|---|
| 1 | $1s$ | | | | | |
| 2 | $2s$ | $2p$ | | | | |
| 3 | $3s$ | $3p$ | $3d$ | | | |
| 4 | $4s$ | $4p$ | $4d$ | $4f$ | | |
| 5 | $5s$ | $5p$ | $5d$ | $5f$ | $5g$ | |

Note that:

- n =1 non-degenerate system
- n1>1 are all degenerate in l and $m_l$.

  All states have same energy

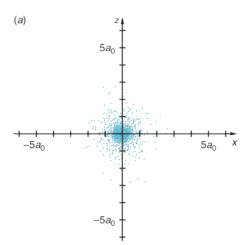
  But different spatial configuration

$$E = -\frac{ke^2}{2a_0}\left(\frac{1}{n^2}\right)$$

## Facts About Ground State of H Atom

$$n=1,\ l=0,\ m_l=0 \Rightarrow R(r)=\frac{2}{a_0^{3/2}}\,e^{-r/a};\quad \Theta(\theta)=\frac{1}{\sqrt{2\pi}};\quad \Phi(\phi)=\frac{1}{\sqrt{2}}$$

$$\Psi_{100}(r,\theta,\phi)=\frac{1}{a_0\sqrt{\pi}}e^{-r/a}$$ ......look at it carefully




1. Spherically symmetric $\Rightarrow$ no $\theta,\phi$ dependence (structure)

2. Probability Per Unit Volume : $|\Psi_{100}(r,\theta,\phi)|^2 = \frac{1}{\pi a_0^3}e^{-\frac{2r}{a}}$

Likelihood of finding the electron is same at all $\theta,\phi$ and depends only on the radial seperation (r) between electron & the nucleus.

3 Energy of Ground State $= -\frac{ke^2}{2a_0} = -13.6eV$

Overall The Ground state wavefunction of the hydrogen atom is quite *boring*

Not much chemistry or Biology could develop if there was only the ground state of the Hydrogen Atom!

We need structure, we need variety, we need some curves!