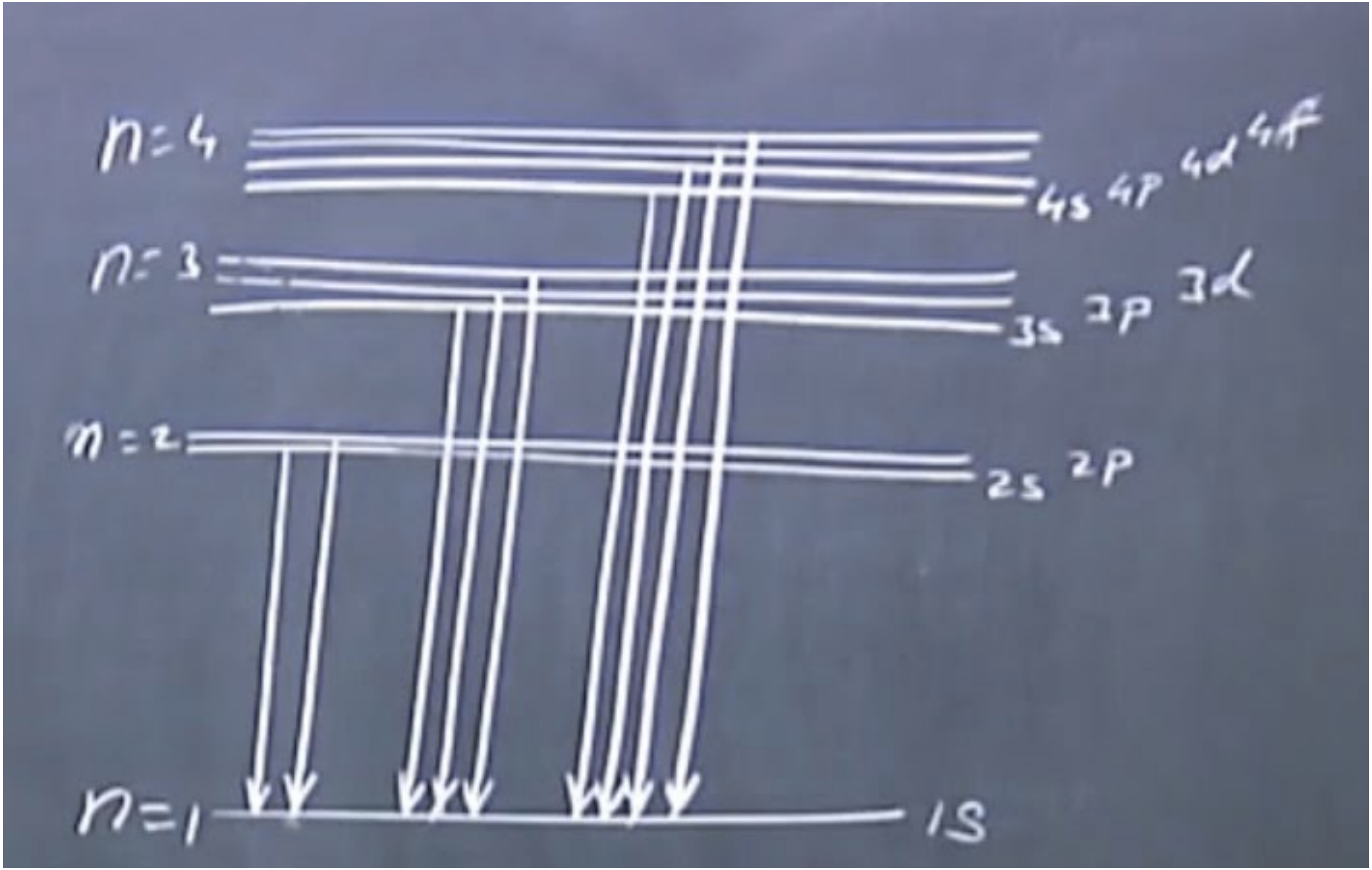
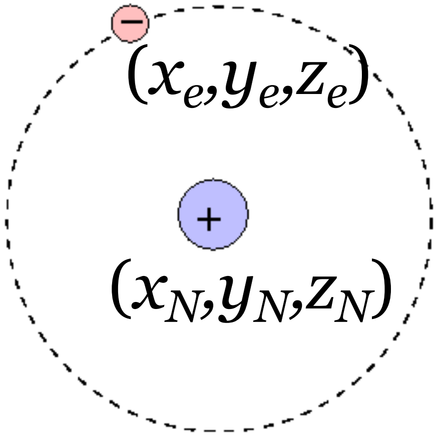
# Lecture 6: Quantum numbers of Hydrogen atom



# Hydrogen Atom




Two particle central-force problem

Completely solvable – a rare example!

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{Z_N Z_e e^2}{r_{eN}}$$

$$\nabla_N^2 = \frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_N^2} + \frac{\partial^2}{\partial z_N^2} \qquad \nabla_e^2 = \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}$$

# Hydrogen Atom: Relative Frame of Reference

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N^2-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{QZe^2}{r_{eN}}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

$$\Downarrow$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{QZe^2}{r}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

where $M=m_e+m_N$ and $\mu=\dfrac{m_e m_N}{m_e+m_N}$

$$\widehat{H}_N\chi_N=\left(-\frac{\hbar^2}{2M}\nabla_R^2\right)\chi_N=E_N\chi_N$$

Free particle!
Kinetic energy of the atom

# Hydrogen Atom: Electronic Hamiltonian

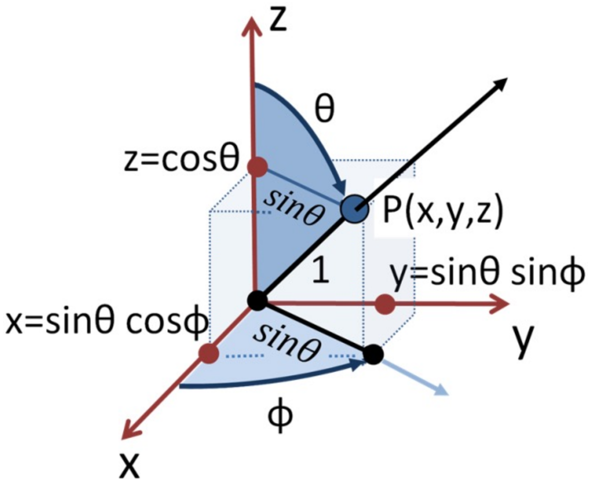
$$\widehat{H}_e \cdot \psi_e = \left( -\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{QZe^2}{r} \right)\psi_e = E_e \cdot \psi_e$$

$$\psi_e \Rightarrow \psi_e(x,y,z)$$

$$-\frac{\hbar^2}{2\mu}\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)\psi_e(x,y,z) - \frac{QZe^2}{\sqrt{\left(x^2+y^2+z^2\right)}}\psi_e(x,y,z) = E_e \cdot \psi_e(x,y,z)$$

Not possible to separate out into three different co-ordinates.
Need a new co-ordinate system

# Spherical Polar Co-ordinates

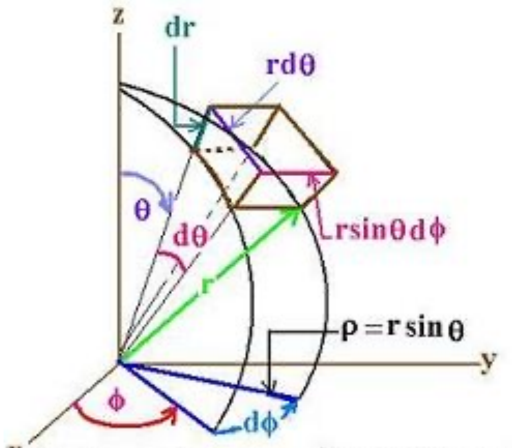



$$z = r\cos\theta$$
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$


$r$:0 to ∞

θ: 0 to π

ϕ: 0 to 2π




Volume element = $r^2 dr \sin\theta\, d\theta\, d\phi$

$$r = \sqrt{\left(x^2 + y^2 + z^2\right)}$$
$$\theta = \cos^{-1}\left(\frac{z}{r}\right)$$
$$\phi = \tan{-1}\left(\frac{y}{x}\right)$$

$$d\tau = dx \cdot dy \cdot dz = r^2 \cdot dr \cdot \sin\theta \cdot d\theta \cdot d\phi$$

# Schrodinger equation for the electronic part in Spherical Polar Co-ordinates

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_e}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_e}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_e}{\partial\phi^2}\right]$$

$$-\frac{QZe^2}{r}\psi_e=E_e\psi_e$$

# Separation of variables

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

The three variables $r$, $\theta$ and $\phi$ are separated

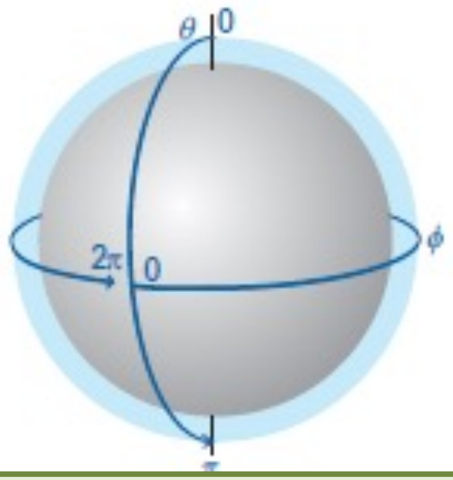
# Solution to $\phi$ part

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+m^2=0$$

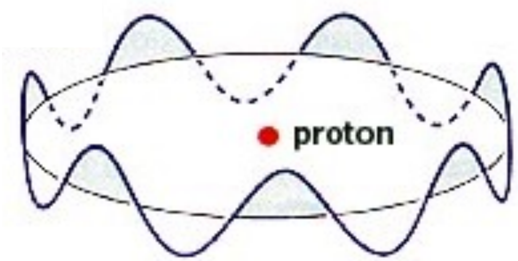
$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2\Phi(\phi)$$

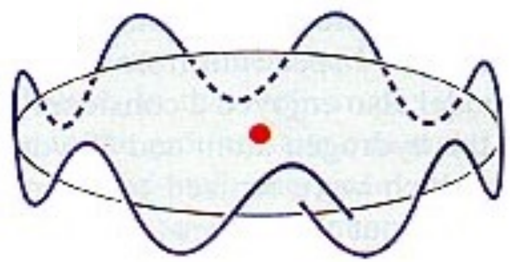
Trial solution: $\Phi(\phi)=Ae^{\pm im\phi}$

$$\frac{\partial\Phi}{\partial\phi}=\pm im\Phi$$




‘ϕ’ ranges from 0 to 2π



Wavefunction has to be continuous

$$\Rightarrow\Phi(\phi+2\pi)=\Phi(\phi)$$

**Periodic Boundary Condition**

## Solution to $\phi$ part

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

$$A_m e^{im(\phi+2\pi)} = A_m e^{im(\phi)} \quad \text{and} \quad A_{-m} e^{-im(\phi+2\pi)} = A_{-m} e^{-im(\phi)}$$

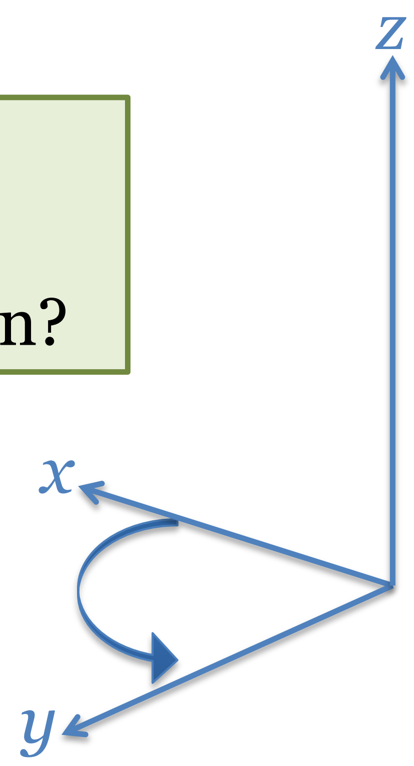
$$e^{im(2\pi)} = 1 \quad \text{and} \quad e^{-im(2\pi)} = 1$$

$$\cos(2\pi m) \pm i \sin(2\pi m) = 1$$

- True only if $m$=0, ±1, ±2, ±3, ±4,....
- What kind of information does $\Phi$ contain?

Change in $\phi$: Circular motion in $xy$ plane

$z$ – component of angular momentum?



# Angular momentum: from classical to quantum picture

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$$

$$\vec{p} = p_x\vec{i} + p_y\vec{j} + p_z\vec{k}$$

$$= (yp_z - zp_y)\vec{i} - (xp_z - zp_x)\vec{j} + \underbrace{(xp_y - yp_x)}_{L_z}\vec{k}$$

$$\boxed{\widehat{p_y} = \frac{\hbar}{i}\frac{\partial}{\partial y}; \qquad \widehat{p_x} = \frac{\hbar}{i}\frac{\partial}{\partial x}}$$

$$\therefore \widehat{L_z} = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \longrightarrow \longrightarrow \boxed{\widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}}$$

Is $\Phi$ an eigenfunction?

# Moment of truth

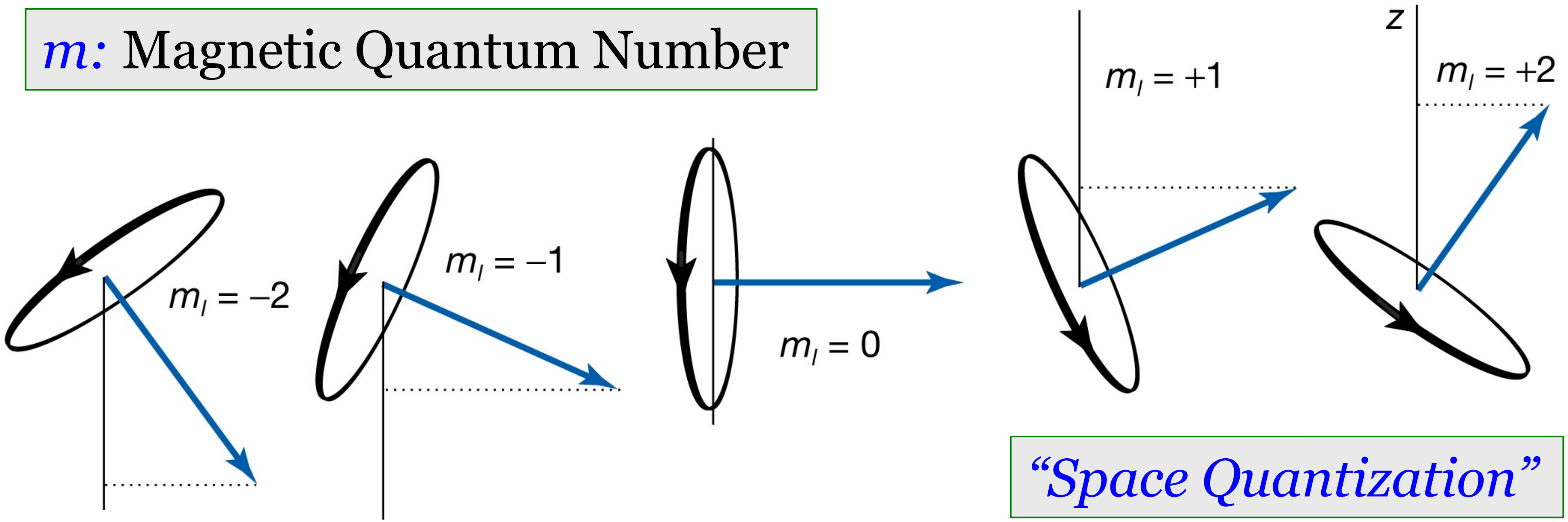
$$\widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$$\Phi(\phi) = Ae^{\pm im\phi}$$

$$\widehat{L_z}\Phi = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi = \frac{\hbar}{i}\, im\,\Phi = \boxed{m\hbar}\,\Phi$$

*z*-component of angular momentum

*m:* Magnetic Quantum Number




*"Space Quantization"*

# The $\Theta$ and the $R$ part

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial R(r)}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{QZe^2}{r} + E_e\right)R(r) - \beta R(r) = 0$$

Solve to get $R(r)$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\Theta(\theta) + \beta\Theta(\theta) = 0$$

Solve to get $\Theta(\theta)$

**Need serious mathematical skill to solve these two equations.**
**We only look at solutions**

## The Θ part

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}\Theta(\theta)+\beta\Theta(\theta)=0$$

Solution to $\Theta(\theta)$ :

*l*=0,1,2,3...

$P_l^m(\cos\theta)$:Associated Legendre Polynomials

New quantum number '*l*' : orbital / Azimuthal quantum number

Restriction on $m \le l$
is due to this equation

# The angular (Θ·Φ) part

The angular part of the solution

$Y_l^m(\theta,\phi) \Rightarrow \Theta(\theta)\cdot\Phi(\phi)$ are called spherical harmonics

$$Y_l^m(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}$$

*l*=0,1,2,3…

*m*=0, ±1, ±2, ±3… and $|m| \le l$

## The angular (Θ·Φ) part:

$$\vec{L} = (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k$$

$$\widehat{L^2} = \widehat{L_x}.\widehat{L_x} + \widehat{L_y}.\widehat{L_y} + \widehat{L_z}.\widehat{L_z}$$

$$= -\hbar^2 \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$ in spherical polar co-ords.

**Angular equation:**

$$-\left[ \frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} \right] = \beta$$

Multiply by

$$Y(\theta, \phi) = \Theta\Phi$$

## The angular (Θ·Φ) part:

$$\vec{L} = (yp_z - zp_y)\vec{\imath} + (xp_z - zp_{yx})\vec{\jmath} + (xp_y - yp_x)k$$

$$\widehat{L^2} = \widehat{L_x}.\widehat{L_x} + \widehat{L_y}.\widehat{L_y} + \widehat{L_z}.\widehat{L_z}$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

in spherical polar co-ords.

**Angular equation:**

$$-\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] = \beta$$

Multiply by

$$Y(\theta,\phi) = \Theta\Phi$$

$$-\quad\left[\qquad\qquad\qquad\right] = \beta\,\Phi\Theta$$

## The angular (Θ·Φ) part:

$$\vec{L} = (yp_z - zp_y)\vec{\imath} + (xp_z - zp_{yx})\vec{\jmath} + (xp_y - yp_x)k$$

$$\widehat{L^2} = \widehat{L_x}.\widehat{L_x} + \widehat{L_y}.\widehat{L_y} + \widehat{L_z}.\widehat{L_z}$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$ in spherical polar co-ords.

**Angular equation:** $$\boxed{-\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] = \beta}$$

Multiply by $Y(\theta,\phi) = \Theta\Phi$

$$-\hbar^2\left[\frac{\Phi}{\sin\theta}\frac{\partial\Theta}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta} + \frac{\Theta}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] = \hbar^2\beta\,\Phi\Theta$$

## The angular (Θ·Φ) part:

$$\vec{L} = (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k$$

$$\widehat{L^2} = \widehat{L_x}.\widehat{L_x} + \widehat{L_y}.\widehat{L_y} + \widehat{L_z}.\widehat{L_z}$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$ in spherical polar co-ords.

**Angular equation:** $$-\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] = \beta$$

Multiply by $Y(\theta,\phi) = \Theta\Phi$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Phi\Theta = \hbar^2\beta\,\Phi\Theta$$

## The angular (Θ·Φ) part:Total angular momentum

$$\vec{L} = (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k$$

$$\widehat{L^2} = \widehat{L_x}.\widehat{L_x} + \widehat{L_y}.\widehat{L_y} + \widehat{L_z}.\widehat{L_z}$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

in spherical polar co-ords.

**Angular equation:**

$$-\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] = \beta$$

Multiply by

$Y(\theta,\phi) = \Theta\Phi$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = \hbar^2\beta Y(\theta,\phi)$$

$$\widehat{L}^2 Y(\theta,\phi) = \hbar^2 l(l+1) Y(\theta,\phi)$$

## The *R* part

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{QZe^2}{r}+E_e\right)R(r)-\beta R(r)=0$$

Solution to R(r) are

$$a=\frac{\hbar^2}{Q\mu e^2}=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$$R_{nl}(r)=-\left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2}r^l e^{-Zr/na_0}L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$$

Restriction on $l<n$

Where $L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$ are called associated *Laguerre* functions

The new quantum number is '*n*' called principal quantum number

# Energy of the Hydrogen Atom

$$E_n = -\frac{2Q^2 Z^2 \mu e^4}{\hbar^2 n^2} = -\frac{Z^2 \mu e^4}{8\varepsilon_o^2 h^2 n^2} = -\frac{Z^2 e^4}{8\pi\varepsilon_o a_o n^2} \left(\mu \approx m_e\right)$$

$$E_n = \frac{-13.6eV}{n^2}$$

Energy is dependent only on '*n*'

Energy obtained by full quantum mechanical treatment is equal to Bohr energy

Potential energy term is only dependent on the ***Radial*** part and has no contribution from the ***Angular*** parts

# Quantum Numbers of Hydrogen Atom

| | |
|---|---|
| ***n*** | **Principal Quantum number**<br>Specifies the energy of the electron |
| ***l*** | **Orbital Angular Momentum Quantum number**<br>Specifies the magnitude of the electron's orbital angular momentum |
| ***m*** | **Z-component of Angular Momentum Quantum number**<br>Specifies the orientation of the electron's orbital angular momentum |
| ***s*** | **Orbital Angular Momentum Quantum number**<br>Specifies the orientation of the electron's spin angular momentum |

# H-Atom: Three Quantum Numbers

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)} = \beta(const.)$$ → **n = principle quantum no**

$$\boxed{\frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)} = \beta(const.)$$ → **l = Azimuthal quantum no**

$$\therefore \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+m^2=0$$ → **$m_l$ = magnetic quantum no**

**3 Quantum Numbers needed to describe the 3D system completely**

**Unlike PIB three Quantum Numbers are INTER-RELATED in H-Atom**