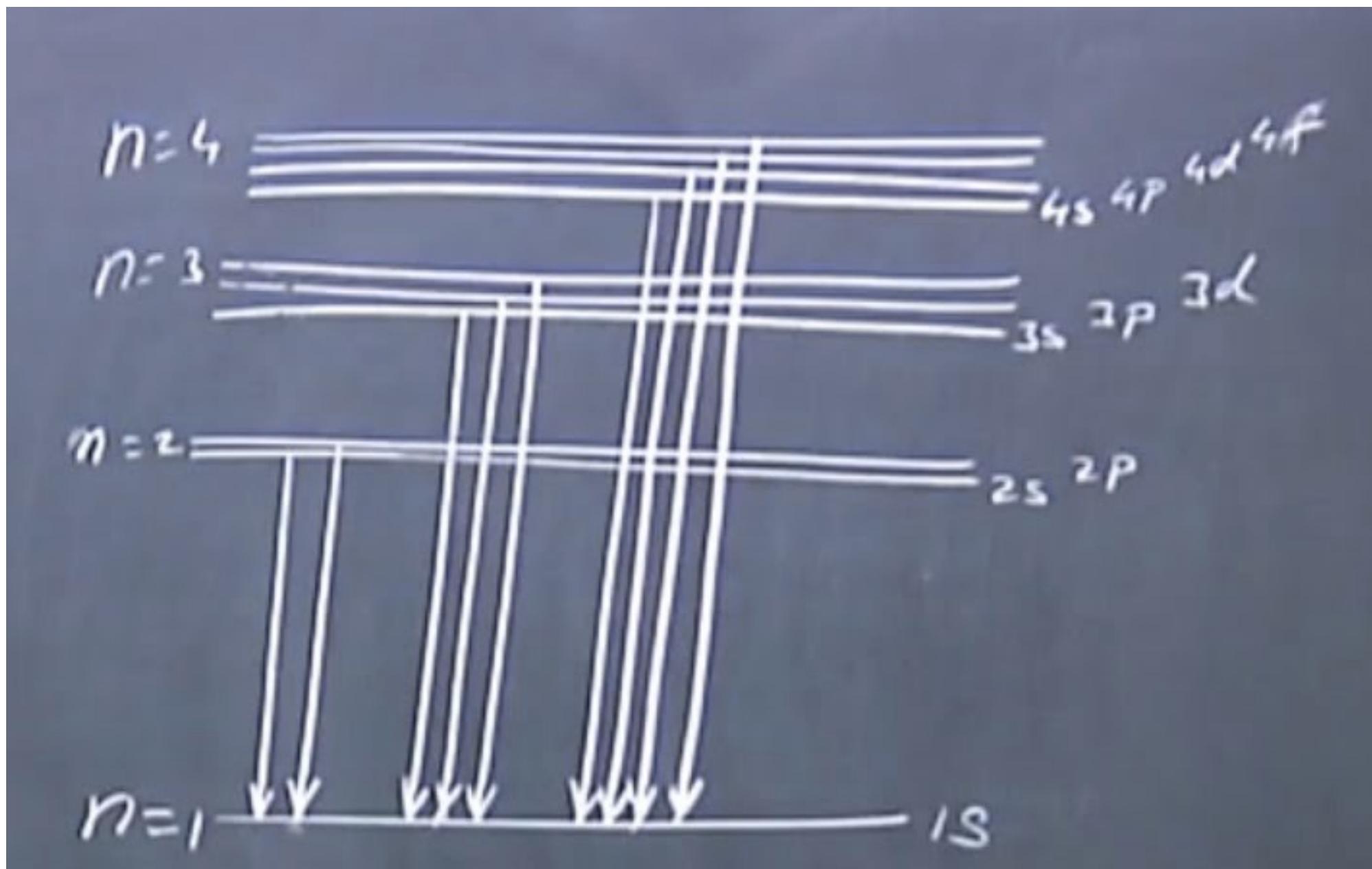
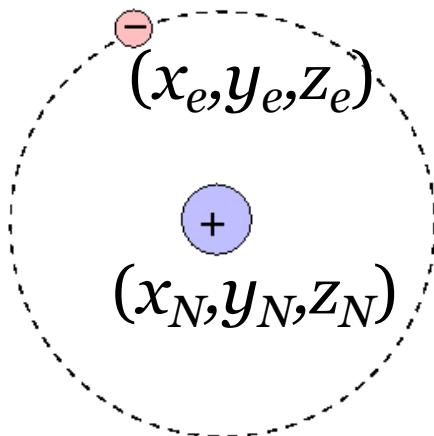


Lecture 6: Quantum numbers of Hydrogen atom



Hydrogen Atom



Two particle central-force problem

Completely solvable – a rare example!

$$\hat{H} = -\frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{1}{4\pi\epsilon_0} \frac{Z_N Z_e e^2}{r_{eN}}$$

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

Hydrogen Atom: Relative Frame of Reference

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



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

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

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

Free particle!
Kinetic energy of the atom

Hydrogen Atom: Electronic Hamiltonian

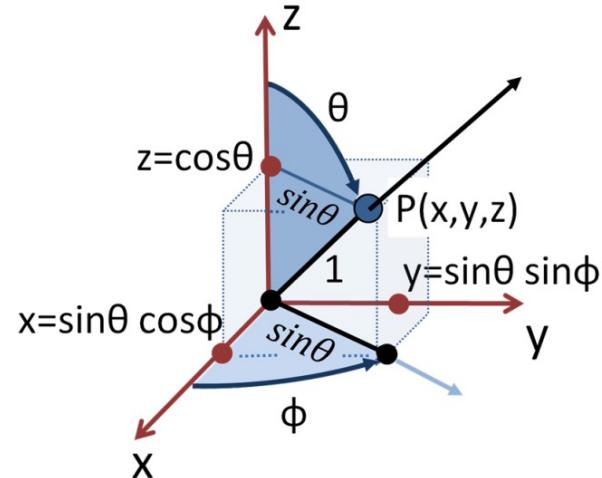
$$\hat{H}_e \cdot \psi_e = \left(-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{QZe^2}{r} \right) \psi_e = E_e \cdot \psi_e$$

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

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

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

Spherical Polar Co-ordinates



$$z = r \cos \theta$$

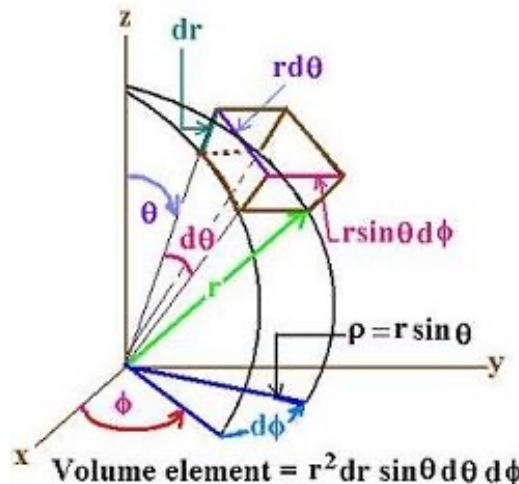
$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

r : 0 to ∞

θ : 0 to π

ϕ : 0 to 2π



Remember

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



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$$r = \sqrt{(x^2 + y^2 + z^2)}$$

$$\theta = \cos^{-1}\left(\frac{z}{r}\right)$$

$$\phi = \tan^{-1}\left(\frac{y}{x}\right)$$

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

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

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

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

The three variables r , θ and ϕ are separated

Solution to ϕ part

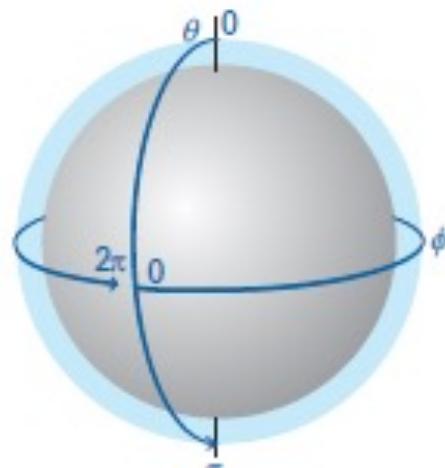
$$\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} + m^2 = 0$$



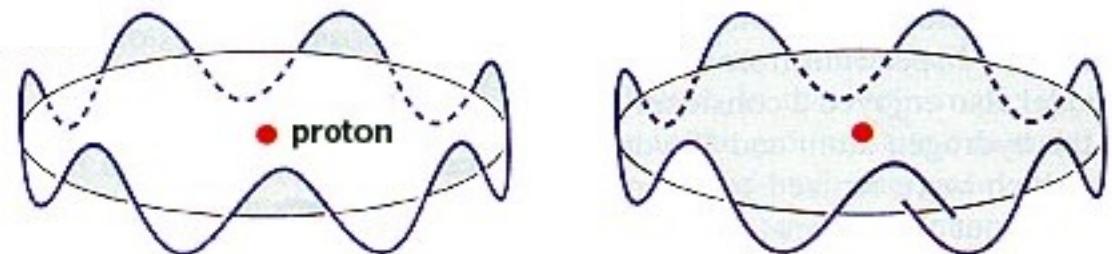
$$\frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = -m^2 \Phi(\phi)$$

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

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



' ϕ ' ranges from 0 to 2π



Wavefunction has to be continuous
 $\Rightarrow \Phi(\phi + 2\pi) = \Phi(\phi)$

Periodic Boundary Condition

Solution to ϕ part

• $\Phi(\phi + 2\pi) = \Phi(\phi)$

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

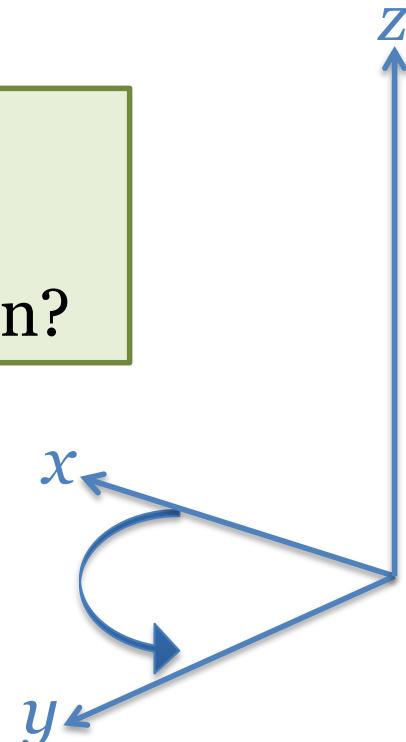
$$e^{im(2\pi)} = 1 \quad \text{and} \quad e^{-im(2\pi)} = 1$$

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

- True only if $m=0, \pm 1, \pm 2, \pm 3, \pm 4, \dots$
- What kind of information does Φ contain?

Change in ϕ : Circular motion in xy plane

z – component of angular momentum?



Angular momentum: from classical to quantum picture

$$\begin{aligned}
 \vec{L} &= \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} & \vec{r} &= x\vec{i} + y\vec{j} + z\vec{k} \\
 &= (yp_z - zp_y)\vec{i} - (xp_z - zp_x)\vec{j} & \vec{p} &= p_x\vec{i} + p_y\vec{j} + p_z\vec{k} \\
 &\quad + (xp_y - yp_x)\vec{k}
 \end{aligned}$$

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

$$\begin{aligned}
 \therefore \widehat{L}_z &= \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \xrightarrow{\textcolor{blue}{\longrightarrow}} \xrightarrow{\textcolor{blue}{\longrightarrow}} \widehat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}
 \end{aligned}$$

Is Φ an eigenfunction?

Moment of truth

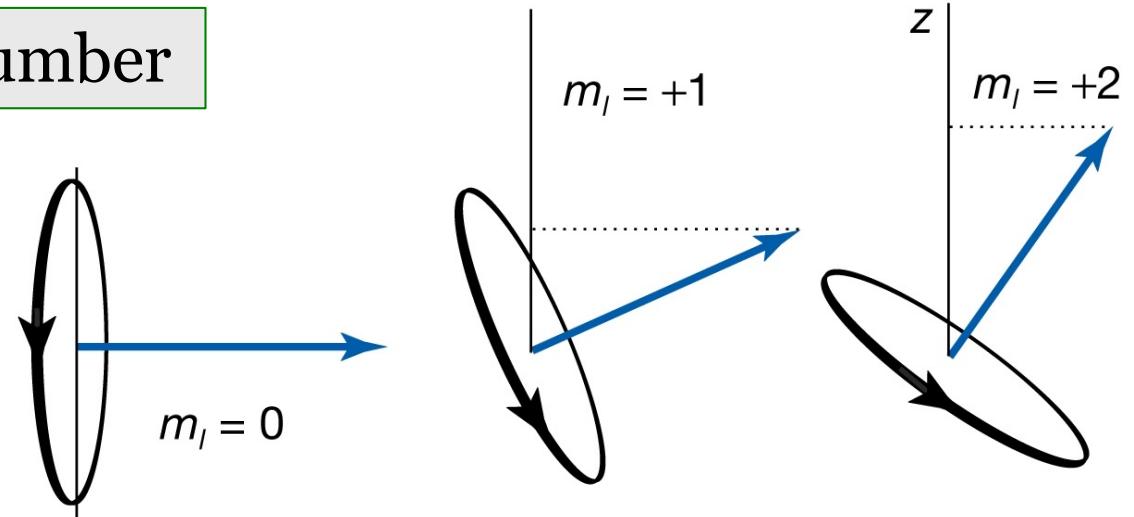
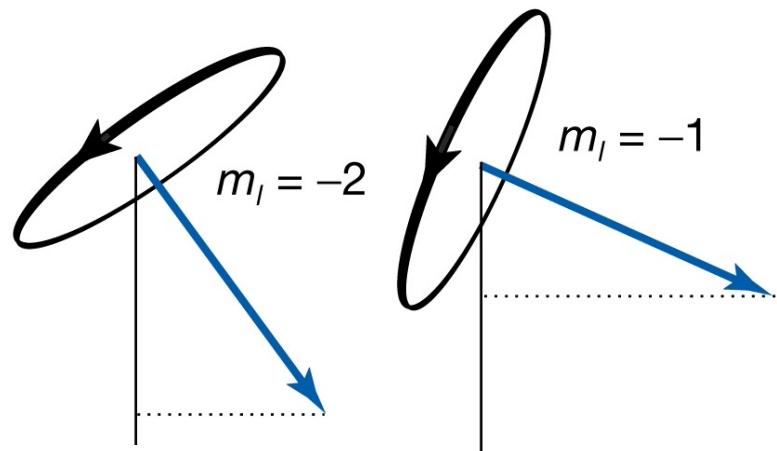
$$\widehat{L_z} = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

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

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

z-component of angular momentum

m: Magnetic Quantum Number



“Space Quantization”

The Θ 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 $\Theta(\theta)$:

$l=0,1,2,3\dots$

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

New quantum number ‘ l ’ : orbital / Azimuthal quantum number

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

The angular ($\Theta \cdot \Phi$) part

The angular part of the solution

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

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

$l=0, 1, 2, 3\dots$

$m=0, \pm 1, \pm 2, \pm 3\dots$ and $|m| \leq l$

The angular ($\Theta\cdot\Phi$) part:

$$\begin{aligned}\vec{L} &= (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k \\ \hat{L}^2 &= \hat{L}_x \cdot \hat{L}_x + \hat{L}_y \cdot \hat{L}_y + \hat{L}_z \cdot \hat{L}_z \\ &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \text{ in spherical polar co-ords.}\end{aligned}$$

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 ($\Theta\cdot\Phi$) part:

$$\begin{aligned}\vec{L} &= (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k \\ \hat{L}^2 &= \hat{L}_x \cdot \hat{L}_x + \hat{L}_y \cdot \hat{L}_y + \hat{L}_z \cdot \hat{L}_z \\ &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \text{ in spherical polar co-ords.}\end{aligned}$$

Angular equation:

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

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

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

The angular (Θ • Φ) part:

$$\begin{aligned}\vec{L} &= (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k \\ \hat{L}^2 &= \hat{L}_x \cdot \hat{L}_x + \hat{L}_y \cdot \hat{L}_y + \hat{L}_z \cdot \hat{L}_z \\ &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \text{ in spherical polar co-ords.}\end{aligned}$$

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

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

The angular (Θ · Φ) part:

$$\begin{aligned}\vec{L} &= (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k \\ \hat{L}^2 &= \hat{L}_x \cdot \hat{L}_x + \hat{L}_y \cdot \hat{L}_y + \hat{L}_z \cdot \hat{L}_z \\ &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \text{ in spherical polar co-ords.}\end{aligned}$$

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

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

What the hell!!!!???????

The angular ($\Theta\cdot\Phi$) part: Total angular momentum

$$\begin{aligned}\vec{L} &= (yp_z - zp_y)\vec{i} + (xp_z - zp_{yx})\vec{j} + (xp_y - yp_x)k \\ \hat{L}^2 &= \hat{L}_x \cdot \hat{L}_x + \hat{L}_y \cdot \hat{L}_y + \hat{L}_z \cdot \hat{L}_z \\ &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]\end{aligned}$$

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

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

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

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

$$a = \frac{\hbar^2}{Qu e^2} = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

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

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

$$E_n = -\frac{2Q^2Z^2\mu e^4}{\hbar^2 n^2} = -\frac{Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{Z^2 e^4}{8\pi\varepsilon_0 a_0 n^2} (\mu \approx m_e)$$

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

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**
Specifies the energy of the electron

- l*** **Orbital Angular Momentum Quantum number**
Specifies the magnitude of the electron's orbital angular momentum

- m*** **Z-component of Angular Momentum Quantum number**
Specifies the orientation of the electron's orbital angular momentum

- s*** **Orbital Angular Momentum Quantum number**
Specifies the orientation of the electron's spin angular momentum

H-Atom: Three Quantum Numbers

$$\boxed{\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{Ze^2}{r} \right)} = \beta(\text{const.})$$



n = principle quantum no

$$\boxed{\frac{m^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right)} = \beta(\text{const.})$$



l = Azimuthal quantum no

$$\boxed{\therefore \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} + m^2 = 0}$$

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