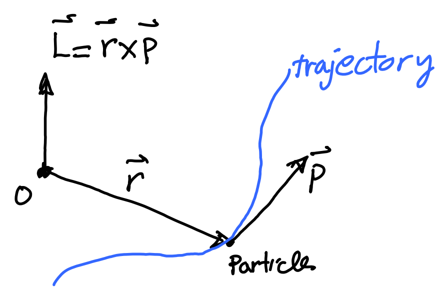
Note Title 5/2/2008

Angular Momentum

Classical Mechanics

Conservation of:
- Energy, E
- Linear Momentum, $\vec{p} = m\vec{v}$
- Angular Momentum, $\vec{L} = \vec{r} \times \vec{p}$

Angular momentum:



unit is $J\,s$

$$\vec{L} = \vec{r} \times \vec{p} = m\,\vec{r} \times \vec{v} = m\left(\vec{r} \times \left(\vec{\omega} \times \vec{r}\right)\right)$$

$$a \times (b \times c) = (a \cdot c)\,b - (a \cdot b)\,c$$

$$\vec{L} = m\left(r^2\vec{\omega} - \vec{r}\,(\vec{r} \cdot \vec{\omega})\right) = \overbrace{m\left(\vec{r}^{\,2}\vec{1} - \vec{r}\,\vec{r}\right)}^{I}\,\vec{\omega}$$

If $\vec{n}$ is a unit vector in the direction of $\vec{\omega}$:

$$I = m\left(r^2 - (\vec{r} \cdot \vec{n})^2\right)$$ moment of inertia

If r is measured from the principle axis of rotation:

$$\vec{r} \cdot \vec{n} = 0 \implies I = mr^2$$

The kinetic energy of the rotating rigid body is:

$$E = \frac{1}{2} I\omega^2 = \frac{L^2}{2I}$$

Cartesian components of $\vec{L} = \vec{r} \times \vec{p}$

$$(L_x, L_y, L_z) = (\vec{x}, \vec{y}, \vec{z}) \times (\vec{p}_x, \vec{p}_y, \vec{p}_z)$$

$$= (y p_z - z p_y$$

$$z p_x - x p_z$$

$$x p_y - y p_x)$$

Angular Momentum Operator in QM

$$\hat{p} = -i\hbar \nabla$$

$$(\hat{p}_x, \hat{p}_y, \hat{p}_z) = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - x\hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

or:
$$\boxed{\vec{L} = -i\hbar \left(\hat{r} \times \vec{\nabla} \right)}$$

Commutators

$$[L_x, L_y] = L_x L_y - L_y L_x = [(y p_z - z p_y), (z p_x - x p_z)]$$

$$= [y p_z, z p_x] - \underbrace{[y p_z, x p_z]}_{\underbrace{[y, x]}_{0} p_z} - \underbrace{[z p_y, z p_x]}_{z \underbrace{[p_y, p_x]}_{0}} + [z p_y, x p_z]$$

$$= y p_z z p_x - z p_x y p_z + z p_y x p_z - x p_z z p_y$$

$$= \underbrace{p_z z y p_x - z p_z \overbrace{p_x y}^{= y p_x}}_{} + \underbrace{z p_z \overbrace{p_y x}^{= x p_y} - p_z z x p_y}_{}$$

$$= \underbrace{[p_z, z]}_{-i\hbar} y p_x + \underbrace{[z, p_z]}_{i\hbar} x p_y$$

$$= i\hbar (\overbrace{x p_y - y p_x}^{\hat{L}_z}) = i\hbar \hat{L}_z$$

Recall

$[x, p_x] = i\hbar$

$[x, p_y] = 0$

$[x, p_z] = 0$

$$\boxed{\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned}}$$

The fact that the commutator of two components of angular momentum is not zero, dictates that no two components of L can be measured to arbitrary accuracy.

Total angular momentum operator:

$$\hat{L} = \hat{L}_x + \hat{L}_y + \hat{L}_z$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

However, $\hat{L}^2$ can be simultaneously be measured by any of L_x, L_y, or L_z to arbitrary accuracy. Because: $[L_x, L^2] = [L_y, L^2] = [L_z, L^2] = 0$

Proof:

$$[L_z, L^2] = [L_z, L_x^2 + L_y^2 + L_z^2]$$

$$= [L_z, L_x^2] + [L_z, L_y^2] + \overbrace{[L_z, L_z^2]}^{=0}$$

$$= L_x \overbrace{[L_z, L_x]}^{i\hbar L_y} + \overbrace{[L_z, L_x]}^{i\hbar L_y} L_x + L_y \overbrace{[L_z, L_y]}^{-i\hbar L_x} + \overbrace{[L_z, L_y]}^{-i\hbar L_x} L_y$$

$$= i\hbar \left(L_x L_y + L_y L_x - L_y L_x - L_x L_y \right)$$

$$= 0$$

$$\Rightarrow [\hat{L}_x, \hat{L}^2] = [\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0$$

And $[\hat{L}, L^2] = 0$

Recall: If two operator commute, they have a simoltaneous eigenfunction.

In following we pick z as our reference.

Eigenvalues of $\hat{L}_z$ and $\hat{L}^2$

Let's define creation and annihilation operators for angular momentum:

$$\hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y$$

$$\rightarrow \quad L_x = \frac{1}{2}(L_+ + L_-) \rightarrow L_x^2 = \frac{1}{4}[L_+^2 + L_+L_- + L_-L_+ + L_-^2]$$

$$L_y = \frac{1}{2i}(L_+ - L_-) \rightarrow L_y^2 = -\frac{1}{4}[L_+^2 - L_+L_- - L_-L_+ + L_-^2]$$

Since $[\hat{L}^2, L_{x,y}] = 0 \rightarrow [\hat{L}^2, \hat{L}_\pm] = 0$

$$[\hat{L}_+, \hat{L}_-] = [L_x + iL_y, L_x - iL_y]$$

$$= [L_x, -iL_y] + [iL_y, L_x]$$

$$= (-i)(i\hbar L_z) + (i)(-i\hbar L_z)$$

$$= 2\hbar \hat{L}_z$$

$$[L_z, \hat{L}_\pm] = [L_z, L_x \pm iL_y] = [L_z, L_x] \pm i[L_z, L_y]$$

$$= i\hbar L_y \pm i(-i\hbar)L_x = \hbar(\pm L_x + iL_y]$$

$$= \pm\hbar(L_x \pm iL_y]$$

$$= \pm\hbar \hat{L}_\pm$$

$[\hat{L}^2, \hat{L}_z] = 0 \Rightarrow$ They have simoltaneus eigenfunction(s).

say $\psi_{\lambda m}$:

$$\hat{L}^2 \psi_{\lambda m} = \hbar^2 \lambda \psi_{\lambda m}$$

$$\hat{L}_z \psi_{\lambda m} = \hbar m \psi_{\lambda m}$$

Since $[\hat{L}_z, L_\pm] = \pm\hbar \hat{L}_\pm \neq 0$, $\psi_{\lambda m}$ is not an eigenstate of $L_\pm$.

But we can show that $L_\pm \psi_{\lambda m}$ is an eigenstate of L_z:

$$\hat{L}_z(L_\pm \psi_{\lambda m}) = (L_\pm L_z \pm \hbar L_\pm)\psi_{\lambda m} = L_\pm \overbrace{L_z \psi_{\lambda m}}^{m\hbar\psi_{\lambda m}} \pm \hbar L_\pm \psi_{\lambda m}$$

$$= \hbar(m\pm 1)(L_\pm \psi_{\lambda m})$$

So $L_\pm \psi_{\lambda m}$ is an eigenfunction of L_z with eigenvalue $\hbar(m\pm1)$.

But L_z commutes with $\hat{L}^2$. So $(L_\pm \psi_{\lambda m})$ must be the eigenfunction of $\hat{L}^2$ too $\Rightarrow$

$$\left\{\begin{array}{ll} \hat{L}_z(L_\pm \psi_{\lambda m}) = \hbar(m\pm1)(L_\pm \psi_{\lambda m}) & \rightarrow L_\pm \text{ increases or decreases the quantum number } m. \\ \hat{L}^2(L_\pm \psi_{\lambda m}) = \hbar^2\lambda(L_\pm \psi_{\lambda m}) & \rightarrow L_\pm \text{ does not affect } \lambda. \end{array}\right.$$

So we can write: $\quad L_\pm \psi_{\lambda m} = A^\pm_{\lambda m}\psi_{\lambda, m\pm1}$

$A^\pm_{\lambda m}$ from normalization of $\psi_{\lambda m}$: $\quad A_{\lambda m} = \hbar\sqrt{\lambda - m(m\pm1)}$

Let's find out what values m can take:

Since $\hat{L}^2 = L_x^2 + L_y^2 + L_z^2 \rightarrow L^2 - L_z^2 = L_x^2 + L_y^2 \geq 0 \rightarrow$

$$\langle \psi_{\lambda m} | L^2 - L_z^2 | \psi_{\lambda m}\rangle = \hbar^2(\lambda - m^2) \geq 0 \Rightarrow m^2 \leq \lambda$$

$$\Rightarrow -\lambda \leq m \leq \lambda$$

So, for a given λ, there is a maximum value that m can take, m_{max}.

$\Rightarrow \quad \hat{L}_+ \psi_{\lambda m_{max}} = 0 \quad$ Since there is no $\psi_{\lambda m_{max}+1}$

Also, notice that:

$$\hat{L}_-\hat{L}_+ = (L_x - iL_y)(L_x + iL_y) = L_x^2 + L_y^2 + i\underbrace{(L_xL_y - L_yL_x)}^{i\hbar L_z}$$

$$= L_x^2 + L_y^2 - \hbar \hat{L}_z$$

$$= L^2 - L_z^2 - \hbar L_z$$

$$\rightarrow \quad \hat{L}_-\hat{L}_+\Psi_{\lambda m_{max}} = (L^2 - L_z^2 - \hbar L_z)\Psi_{\lambda m_{max}}$$

$$= \hbar^2(\lambda - m_{max}^2 - m_{max})\Psi_{\lambda m_{max}} = 0$$

$$\Rightarrow \quad \lambda = m_{max}^2 + m_{max} = m_{max}(m_{max}+1)$$

Similarly, there is a minimum for m: m_{min}

$$\hat{L}_-\Psi_{\lambda m_{min}} = 0 \Rightarrow \lambda = m_{min}(m_{min} - 1)$$

$$\Rightarrow \quad m_{max}(m_{max}+1) = m_{min}(m_{min}-1)$$

$$\Rightarrow \quad m_{max} = -m_{min}$$

Let's define $\ell \equiv m_{max} \rightarrow \lambda = \ell(\ell+1)$

which we call it orbital angular momentum.

$$L^2\Psi_{\lambda m} = \hbar\lambda\Psi_{\lambda m} = \hbar\ell(\ell+1)\Psi_{\ell m}$$

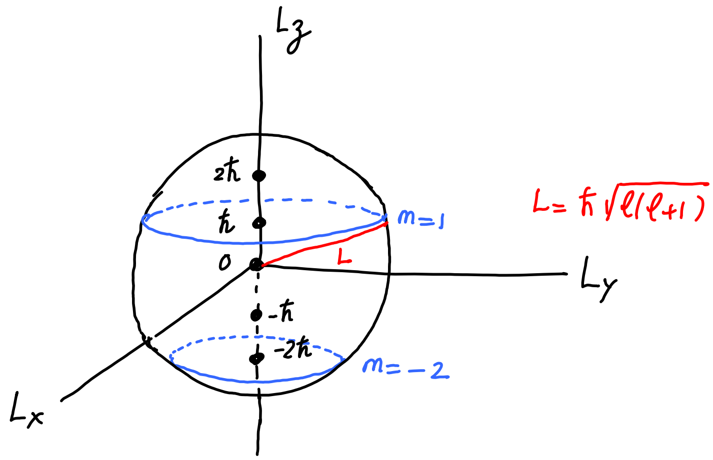
$$\boxed{\begin{aligned} L^2|\ell, m\rangle &= \hbar\ell(\ell+1)\,|\ell, m\rangle \\ L_z|\ell, m\rangle &= \hbar m\,|\ell, m\rangle \end{aligned}}$$

$\ell = 0, 1, 2, \ldots$

$m = -\ell, -\ell+1, \ldots, \ell-1, \ell$

$(-\ell \le m \le \ell)$

Example $l=2 \Rightarrow m=-2,-1,0,1,2$



Uncertainty for L_x and L_y:

$$\Delta A \, \Delta B \geq \frac{i}{2} \langle [\hat{A}, \hat{B}] \rangle$$

$$\Delta L_x \Delta L_y \geq \frac{i}{2} \langle \underbrace{[L_x, L_y]}_{i\hbar L_z} \rangle$$

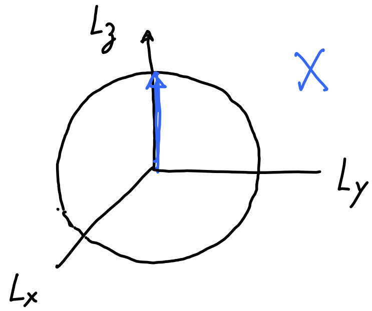
↳ eigenvalue of L_z is $m\hbar$

$$\geq \frac{i}{2}(i\hbar)(m\hbar)$$

$$\geq \frac{m\hbar^2}{2}$$

So the only state that can be simultaneously known is $|l=0, m=0\rangle$.

Notice that it is not possible to have:



because then we would know exactly $L_x = L_y = 0$ and $L_z = L$ that violates the uncertainty.

Spherical harmonics

Spherical coordinate: $x = r\sin\theta\cos\phi$

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

$z = r\cos\theta$

So the angular momentum components in spherical coordinate are:

$$\hat{L}_x = i\hbar\left(\sin(\phi)\frac{\partial}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\right) \quad \text{(See Excercise 11.1)}$$

$$\hat{L}_y = i\hbar\left(-\cos(\phi)\frac{\partial}{\partial\theta} + \cot(\theta)\sin(\phi)\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$L^2 = -\hbar^2\left(\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The eigenfunction solutions for these operators are

Spherical harmonics $Y_\ell^m(\theta,\varphi)$:

$$\hat{L}^2 Y_\ell^m = \hbar^2\ell(\ell+1)Y_\ell^m$$

$$\hat{L}_z Y_\ell^m = \hbar m Y_\ell^m \quad \rightarrow \quad \overbrace{-i\hbar\frac{\partial}{\partial}}^{\hat{L}_z} Y_\ell^m = \hbar m Y_\ell^m$$

$$\rightarrow \frac{\partial}{\partial\varphi}Y_\ell^m = im Y_\ell^m$$

$$Y_\ell^m(\theta,\varphi) = \Phi_m(\varphi)\,\Theta_m^\ell(\theta) \quad \rightarrow \quad \frac{\partial}{\partial\varphi}\Phi_m(\varphi) = im\Phi_m(\varphi)$$

$$\Rightarrow \Phi_m(\varphi) = A e^{im\varphi}$$

normaliz $\int_0^{2\pi} |\Phi_m|^2 d\varphi = 1 \rightarrow A = \frac{1}{\sqrt{2\pi}}$

Since physically we must have: $\Phi_m(\varphi) = \Phi_m(\varphi + 2\pi) \rightarrow$

$$e^{im\varphi} = e^{im(\varphi+2\pi)} \rightarrow e^{im2\pi} = 1 \rightarrow m = 0, \pm 1, \pm 2, \ldots$$

$Y_\ell^m = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \Theta_\ell^m(\theta)$ Substitute in :

$$L^2 Y_\ell^m = \hbar \ell(\ell+1) Y_\ell^m \rightarrow$$

$$\underbrace{\frac{1}{\sin\theta} \frac{d}{d\theta}}_{-d\mu} \left(\sin\theta \frac{d}{d\theta} \Theta_\ell^m(\theta) \right) + \left(\ell(\ell+1) - \frac{m^2}{\sin^2(\theta)} \right) \Theta_\ell^m(\theta) = 0$$

$\mu \equiv \cos\theta \Rightarrow d\mu = -\sin\theta d\theta$

$$\frac{1}{d\mu} \left[(1-\mu^2) \frac{d}{d\mu} \Theta_\ell^m(\theta) \right] + \left[\ell(\ell+1) - \frac{m^2}{1-\mu^2} \right] \Theta_\ell^m(\theta) = 0$$

Legendre polynomials are the solution for integral values of ℓ and m:

$$P_\ell(\mu) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\mu^\ell} (\mu^2 - 1)^\ell$$

which can be written as:

$$P_\ell(\mu) = \sum_{k=0}^{\ell} \frac{(-1)^k (\ell+k)!}{(\ell-k)!\,(k!)^2\, 2^{k+1}} \left[(1-\mu)^k + (-1)^\ell (1+\mu)^k \right]$$

$$P_0(\mu) = 1 \qquad (\mu = \cos\theta \text{ for us})$$

$$P_1(\mu) = \mu$$

$$P_2(\mu) = \frac{1}{2}(3\mu^2 - 1)$$

$$\vdots$$

Check the normalization of the spherical harmonics:

$$\int |\underbrace{Y_\ell^m}_{\frac{e^{im\varphi}}{\sqrt{2\pi}}\Theta_\ell^m(\mu)}|^2 \sin\theta \, d\theta \, d\varphi = \underbrace{\int_0^{2\pi} d\varphi \left| \frac{e^{im\varphi}}{\sqrt{2\pi}} \right|^2}_{=1} \int_{-1}^{1} d\mu \, |\Theta_\ell^m(\mu)|^2 = 1$$

$$\Rightarrow \int_{-1}^{1} d\mu \, |\Theta_\ell^m(\mu)|^2 = 1 \rightarrow$$

$$\Theta_\ell^m(\mu) = \left(\frac{2\ell+1}{2} \frac{(\ell-m)!}{(\ell+m)!} \right)^{1/2} P_\ell^m(\mu)$$

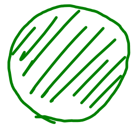
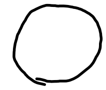
$$\boxed{Y_\ell^m(\theta,\varphi) = \left(\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!} \right)^{1/2} P_\ell^m(\cos\theta) \, e^{im\varphi}}$$

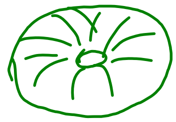
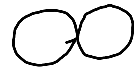
Spherical harmonics are orthogonal and complete:

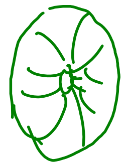
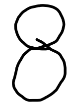
$$\langle Y_\ell^m \, Y_{\ell'}^{m'} \rangle = \int_0^\pi d\theta \int_0^{2\pi} d\varphi \, Y_\ell^{m*} Y_{\ell'}^{m'} \sin\theta = \delta_{\ell\ell'} \delta_{mm'}$$

Also, they have the property that:

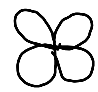
$$\sum_{m=-\ell}^{m=\ell} |Y_\ell^m(\theta,\varphi)|^2 = \frac{2\ell+1}{4\pi}$$

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$  $|Y_0^0|$ 

$$Y_1^1 = -\frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \sin\theta\, e^{i\varphi}$$  $|Y_1^1|$ 

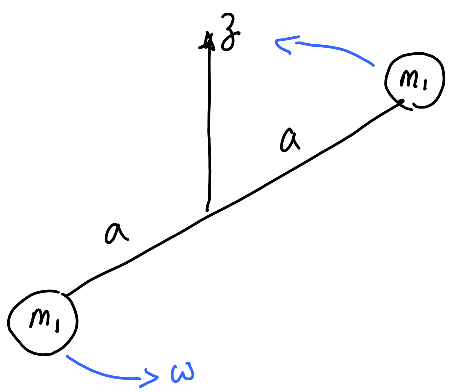
$$Y_1^0 = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} \cos\theta$$  $|Y_1^0|$ 

$$Y_1^{-1} = \frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \sin(\theta)\, e^{-i\varphi}$$

$$Y_2^1 = -\frac{1}{2}\left(\frac{15}{2\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{i\varphi}$$  $|Y_2^1|$ 

$\vdots$

The rigid rotator



In classical mechanics: $E = \frac{1}{2} I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$

where: $I = \sum m r^2 = 2 m_1 a^2$

In QM: $L^2 \longrightarrow \hat{L}^2$

$$H\Psi_{\ell m} = E_\ell \Psi_{\ell m} = \frac{\hat{L}^2}{2I}\Psi_{\ell m} = \frac{\hbar^2 \ell(\ell+1)}{2I}\Psi_{\ell m}$$

The solutions are clearly $\psi_{\ell m} = Y_\ell^m(\theta, \varphi)$

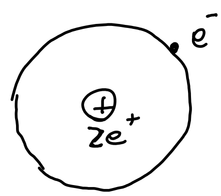
and the energy eigenvalues are $(2\ell+1)$-fold degenerate

(because there are $m = -\ell, -\ell+1, \dots, 0, \dots, \ell$ states for each energy level)

So the particle may be in a superposition of these same energy states.

The Hydrogen atom, H

$$V(r) = \frac{1}{4\pi\epsilon_r\epsilon_0} \frac{Ze^2}{r^2}$$



For an isolated atom $\epsilon_r = 1$.

$$H = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V(r_e - r_p)$$

In center of mass coordinate:

$$\vec{r} = \vec{r}_e - \vec{r}_p$$

$M = m_e + m_p$ total mass

$m_r = \frac{m_e m_p}{m_e + m_p}$ reduced mass

$$\rightarrow \quad \hat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m_r}\nabla_r^2 + V(r)$$

$\hat{H}\psi(R, r) = E\psi(R, r) \rightarrow \psi(r_e, r_p) = f(R)\psi(r) \rightarrow$

$$\begin{cases} -\frac{\hbar^2}{2M}\nabla_R^2 f(R) = E_k f(R) \longrightarrow f(R) = \frac{1}{\sqrt{V}} e^{i\vec{K}\cdot\vec{R}}, \quad E_K = \frac{\hbar^2 K^2}{2M} \\ \left(-\frac{\hbar^2}{2m_r}\nabla_r^2 + V(r)\right)\psi(r) = E_n \psi(r) \\ E = E_K + E_n \quad \text{total energy} \end{cases}$$

To find E_n, Solve :

$$\left(-\frac{\hbar^2}{2m}\nabla_r^2 + \frac{1}{4\pi\epsilon_r\epsilon_0}\frac{e^2}{r}\right)\psi(r) = E_n \psi(r)$$

where;

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

using separation of variables :

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\underbrace{\Theta_m^l(\theta)\,\Phi_m(\varphi)}_{\text{Spherical Harmonics}} \rightarrow$$

$$\boxed{\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\,Y_l^m(\theta,\varphi)}$$

Substitute ψ_{nlm} in schrodinger equation :

$$-\frac{\hbar^2}{2m}\left[\frac{Y_l^m}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R_{nl}}{\partial r}\right) + \frac{R_{nl}}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_l^m}{\partial\theta}\right) + \frac{R_{nl}}{r^2\sin^2\theta}\frac{\partial^2 Y_l^m}{\partial\varphi^2}\right] + V(r)R_{nl}Y_l^m = E_n R_{nl} Y_l^m$$

multiply both sides by $\frac{-2r^2 m_r}{\hbar^2} \frac{1}{R_{n\ell} Y_\ell^m}$ =>

$$\overbrace{\left(\frac{1}{R_{n\ell}}\frac{d}{dr}\left(r^2 \frac{dR_{n\ell}}{dr}\right) - \frac{2r^2 m_r}{\hbar^2}(V(r) - E_n)\right)}^{\text{function of only } r} +$$

$$\underbrace{\frac{1}{Y_\ell^m}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y_\ell^m}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} Y_\ell^m\right)}_{\text{function of only } \theta \text{ and } \varphi} = 0$$

$$\rightarrow \begin{cases} \frac{1}{R_{n\ell}}\frac{d}{dr}\left(r^2 \frac{dR_{n\ell}}{dr}\right) - \frac{2r^2 m_r}{\hbar^2}(V(r) - E_n) = \lambda & \text{I} \\ \underbrace{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y_\ell^m}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} Y_\ell^m}_{-\frac{\hat{L}^2}{\hbar^2} Y_\ell^m} = -\lambda Y_\ell^m & \text{II} \end{cases}$$

II $\Rightarrow$ $\hat{L}^2 Y_\ell^m = \hbar^2 \lambda Y_\ell^m \rightarrow \lambda = \ell(\ell+1)$

I $\times \frac{\hbar^2}{2m} \frac{R_{n\ell}}{r^2}$ =>

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR_{n\ell}}{dr}\right) + \left(\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} + V(r)\right) R_{n\ell} = E_n R_{n\ell}$$

Define: $\alpha^2 \equiv \frac{-2mE}{\hbar^2}$, $\lambda = \frac{me^2}{4\pi\epsilon_0 \hbar^2 \alpha}$, $\rho = 2\alpha r$ =>

$$\underbrace{\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d}{d\rho}R_{nl}\right)} + \left(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right)R_{nl} = 0$$

$$= \frac{d^2}{d\rho^2}R_{nl} + \frac{2}{\rho}\frac{d}{d\rho}R_{nl}$$

In the limit of $\rho \to \infty$, we have:

$$\frac{d^2 R_{nl}}{d\rho^2} - \frac{1}{4}R_{nl} = 0$$

$$\frac{d^2 R_{nl}}{d\rho^2} = \frac{1}{4}R_{nl} \longrightarrow R_{nl}(\rho \to \infty) = e^{-\rho/2}$$

(Note that the other solution $e^{\rho/2}$ is not acceptable as it diverges at infinity)

So the general solution has the form:

$$R_{nl}(\rho) = e^{-\rho/2}F(\rho)$$

Substitute $\Rightarrow$

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left(\frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} - \frac{1}{\rho}\right)F = 0$$

F must be in this form to avoid singularity at $\rho = 0$:

$$F(\rho) = \rho^l L(\rho)$$

$$= \rho^l \sum_\nu a_\nu \rho^\nu = \rho^l(a_0 + a_1\rho + a_2\rho^2 + \cdots)$$

Substitute to get:

$$\rho \frac{d^2L}{d\rho^2} + [2(l+1)-\rho]\frac{dL}{d\rho} + (\lambda-1-l)L = 0$$

$$\rho\Big(\sum_{\nu=2}\nu(\nu-1)a_\nu\rho^{\nu-2}\Big) + [2(l+1)-\rho]\sum_{\nu=1}\nu a_\nu\rho^{\nu-1} + (\lambda-1-l)\sum_{\nu=0}a_\nu\rho^\nu = 0$$

$$\sum_{\nu=2}\nu(\nu-1)a_\nu\rho^{\nu-1} + 2(l+1)\sum_{\nu=1}\nu a_\nu\rho^{\nu-1} - \sum_{\nu=1}\nu a_\nu\rho^\nu + (\lambda-1-l)\sum_{\nu=0}a_\nu\rho^\nu = 0$$

$$\underbrace{\sum_{\nu=2}\big(\nu a_\nu(\nu-1+2l+2)\big)\rho^{\nu-1}}_{\sum_{\nu=1}(\nu+1)a_{\nu+1}(\nu+2l+2)\rho^\nu} + 2(l+1)a_1 - \sum_{\nu=1}a_\nu(-\nu+\lambda-1-l)\rho^\nu + a_0(\lambda-1-l)=0$$

$$\begin{cases}(\lambda-1-l)a_0 + 2(l+1)a_1 = 0\\ (\nu+1)(\nu+2l+2)a_{\nu+1} + a_\nu(\nu+l+1-\lambda) = 0 \Rightarrow a_{\nu+1} = -\dfrac{(\nu+l+1-\lambda)}{(\nu+1)(\nu+2l+2)}a_\nu\end{cases}$$

To ensure the wavefunction goes to zero as $\rho \to \infty$, at som $\nu = n'$, we must have:

$$\nu + l + 1 - \lambda = n' + l + 1 - \lambda = 0$$

Define the principle quantum number as $n \equiv \lambda \Rightarrow$

$$n = n' + l + 1$$

n': radial quantum number

l: orbital quantum number

Polynomial $L(\rho)$ is called associated Laguerre polynomial:

$$L^{2l+1}_{n+1}(\rho) = \sum_{k=0}^{n-l-1}(-1)^{k+2l+1}\frac{((n+1)!)^2(\rho)^k}{(n-l-1-k)!\,(2l+1+k)!\,k!}$$

n	l	$L_{n+l}^{2l+1}(\rho)$
1	0	-1
2	0	$-4+2\rho$
2	1	$-18+6\rho-3\rho^2$
3	0	-6
3	1	$-96+24\rho$
3	2	-120

$l \leq n-1$

The energy eigenvalue E_n is now calcuted knowing $\lambda = n$:

recall: $E_n = \dfrac{-\hbar^2\alpha^2}{2m}$, $\lambda = \dfrac{me^2}{4\pi\epsilon_0\hbar^2\alpha}$ $\rightarrow$ $E_n = \dfrac{-me^2}{2(4\pi\epsilon_0)^2\hbar^2 n^2}$ (m: reduced mass)

The characteristic inverse length scale is:

$$\alpha = \frac{me^2}{4\pi\epsilon_0\hbar^2 n} \qquad m = \frac{m_p m_e}{m_p + m_e} \simeq m_e \quad \text{since } m_p \gg m_e$$

$$\Rightarrow a_B \equiv \frac{1}{\alpha} \Rightarrow \boxed{a_B = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \cong 0.529\ \text{Å}}$$ Bohr radius

Rydberg constant for the hydrogen atom is:

$$R_y = \frac{\hbar^2\alpha^2}{2m} = \frac{m_e e^2}{2(4\pi\epsilon_0)^2\hbar^2} = 13.6058\ \text{eV}$$

which is E_1.

$$\Rightarrow \boxed{E_n = \frac{-m_e e^2}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2} = -\frac{R_y}{n^2} \cong \frac{-13.6\,(\text{eV})}{n^2}} \quad n = 1, 2, \ldots$$

Hydrogen atom wavefunction

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi)$$

$$= -\left(\frac{2Z}{na_B}\right)^{3/2}\left(\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right)^{1/2} e^{-\frac{Zr}{na_B}}\left(\frac{2Zr}{na_B}\right)^{\ell} L_{n+\ell}^{2\ell+1}\left(\frac{2Zr}{na_B}\right)$$

For example:

$$\psi_{100} = R_{10}Y_0^0 = 2\left(\frac{Z}{a_B}\right)^{3/2} e^{-Zr/a_B}\left(\frac{1}{4\pi}\right)^{1/2}$$

$$\psi_{200} = R_{20}Y_0^0 = 2\left(\frac{Z}{2a_B}\right)^{3/2}\left(1-\frac{Zr}{2a_B}\right) e^{-Zr/2a_B}\left(\frac{1}{4\pi}\right)^{1/2}$$

$$\psi_{210} = R_{21}Y_1^0 = \frac{2}{\sqrt{3}}\left(\frac{Z}{2a_B}\right)^{3/2}\left(\frac{Zr}{2a_B}\right) e^{-Zr/2a_B}\left(\frac{3}{\pi}\right)^{1/2}\cos\theta$$

$$\vdots$$

Quantum numbers of Hydrogen atom

Principle, n	1	2			3	
orbital angular momentum, ℓ	0	0	1	0	1	2
m	0	0	$-1,0,1$	0	$-1,0,1$	$-2,-1,0,1,2$
notation	1s	2s	2p	3s	3p	3d