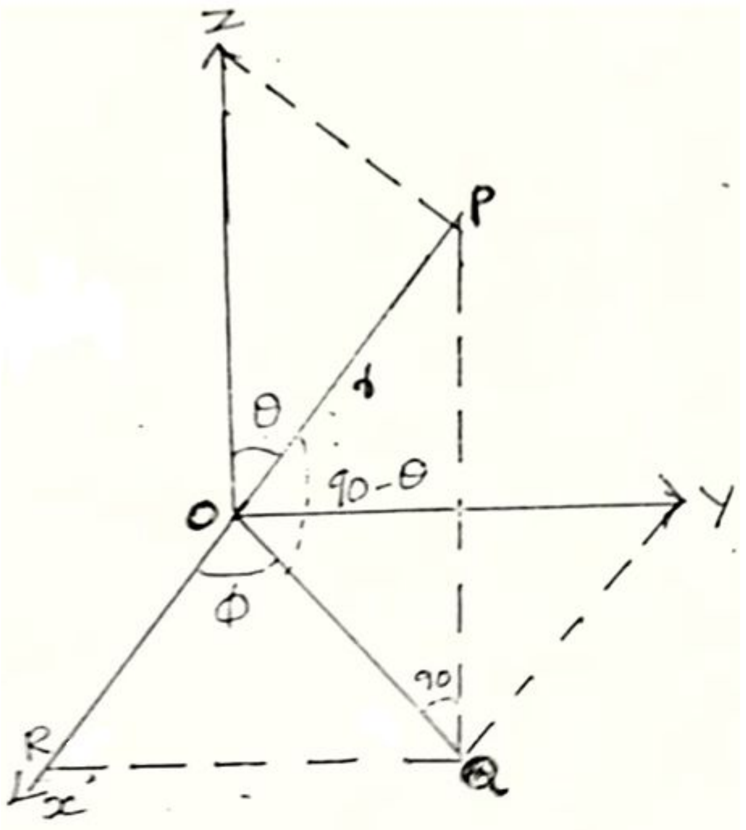
Quantum Mechanics of Rotational Motion

→ Motion of an electron around the nucleus of an atom is an example of rotational motion.

SPHERICAL COORDINATES

Consider a particle at point P with coordinates (x, y, z) or $[r, \theta, \phi]$ at a distance 'r' from the central point 'O'. r is called the radius vector as its direction is changing continuously.



The rotation of the particle P about z axis makes a cone with angle θ which is called the solid angle. The projection of P on xy plane makes another angle ϕ with x axis which is the angle of projection. Thus the point P can be represented by one distance 'r' and two angles θ and ϕ ie $P[r, \theta, \phi]$.

$\phi \rightarrow$ varies from 0 to 2π, $\theta \rightarrow$ varies from 0 to π.

Consider the Δ OQR, $\sin\phi = \dfrac{QR}{OQ} = \dfrac{\text{opposite side}}{\text{Hypotenuse}}$

Since QR is ||el to y axis, $QR = y$

$$\sin\phi = \frac{y}{OQ}, \quad y = OQ \sin\phi \quad \text{——} \; ①$$

$$\cos\phi = \frac{\text{adjacent side}}{\text{Hypotenuse}} = \frac{OR}{OQ} = \frac{x}{OQ}$$

(since OR is ||el to x axis)

$$\therefore x = OQ\cos\phi \quad \text{---} \; (2)$$

Consider the ΔOPQ

$$\cos[90-\theta] = \frac{OQ}{OP}$$

$$\sin\theta = \frac{OQ}{OP} = \frac{OQ}{r} \qquad \because \cos[90-\theta] = \sin\theta$$

$$OQ = r\sin\theta \quad \text{---} \; (3)$$

$$\therefore x = r\sin\theta\cos\phi \quad \text{---} \; (4)$$

$$y = r\sin\theta\sin\phi \quad \text{---} \; (5)$$

Consider ΔOPQ

$$\sin(90-\theta) = \frac{PQ}{OP}$$

$$\cos\theta = \frac{PQ}{r} = \frac{z}{r} \qquad \text{[PQ is ||el to z axis]}$$

$$z = r\cos\theta \quad \text{---} \; (6)$$

$$\tan\phi = \frac{\sin\phi}{\cos\phi} = \frac{y/r\sin\theta}{x/r\sin\theta} = \frac{y}{x} \quad \text{---} \; (7)$$

[From equations 4 and 5]

Also $r^2 = x^2+y^2+z^2$ ——— (8)

Transformation of ∇^2 to spherical coordinates.

When dealing with problems involving a center of symmetry, so that we use spherical coordinates, we express ∇^2 in terms of spherical coordinates rather than cartesian coordinates.

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

$$\frac{\delta}{\delta x} = \frac{\delta}{\delta r} \times \frac{\delta r}{\delta x} + \frac{\delta}{\delta \theta}\,\frac{\delta \theta}{\delta x} + \frac{\delta}{\delta \phi}\cdot\frac{\delta \phi}{\delta x}$$

a) $x^2+y^2+z^2 = r^2$

Differentiating w.r.t x.

$$2x = 2r\frac{\delta r}{\delta x}$$

$$\text{or} \quad \frac{\delta r}{\delta x} = \frac{x}{r} = \frac{r \sin\theta \cos\phi}{r} = \sin\theta\cos\phi$$

b) $\cos\theta = \frac{z}{r}$

Differentiating w.r.t x

$$-\sin\theta\,\frac{\delta\theta}{\delta x} = \frac{r\frac{\delta z}{\delta x} - z\frac{\delta r}{\delta x}}{r^2}$$

$$\boxed{\frac{d}{dx}\left[\frac{u}{v}\right] = \frac{v\cdot\frac{d}{dx}u - u\cdot\frac{d}{dx}v}{v^2}}$$

$$= \frac{-2\frac{\delta r}{\delta x}}{r^2} = \frac{-2 \times \frac{x}{r}}{r^2}$$

ie $$-\sin\theta \frac{\delta\theta}{\delta x} = \frac{-2 \times x}{r^3}$$

$$\frac{\delta\theta}{\delta x} = \frac{-\cancel{r}\cos\theta \times \cancel{r}\,\cancel{\sin\theta}\cos\phi}{-\cancel{\sin\theta} \times r\cancel{3}}$$

$$= \frac{\cos\theta\cos\phi}{r}$$

c) $$\tan\phi = \frac{y}{x}$$

Differentiating w.r.t x.

$$\sec^2\phi \frac{\delta\phi}{\delta x} = \frac{x \cdot \frac{\delta y}{\delta x} - y\frac{\delta x}{\delta x}}{x^2}$$

$$= \frac{-y}{x^2} = \frac{-r\sin\theta\sin\phi}{r^2\sin^2\theta\cos^2\phi}$$

$$\therefore \frac{\delta\phi}{\delta x} = \frac{-\cancel{r}\,\cancel{\sin\theta}\sin\phi}{\cancel{r^2}\sin^{\cancel{2}}\theta\,\cancel{\cos^2\phi}} \times \frac{1}{\cancel{\cos^2\phi}} = -\frac{\sin\phi}{r\sin\theta}$$

$$\therefore \frac{\delta}{\delta x} = \frac{\delta}{\delta r}\frac{\delta r}{\delta x} + \frac{\delta}{\delta \theta}\frac{\delta \theta}{\delta x} + \frac{\delta}{\delta \phi}\frac{\delta \phi}{\delta x}$$

$$= \frac{\delta}{\delta r}\sin\theta\cos\phi + \frac{\delta}{\delta \theta}\frac{\cos\theta\cos\phi}{r} + \frac{\delta}{\delta \phi}\frac{-\sin\phi}{r\sin\theta}$$

$$\frac{\delta}{\delta x} = X = 0 - \frac{\sin\theta\cos\phi}{r} - \frac{\cos\phi}{r\sin\theta}$$

$$\frac{\delta ?}{\delta x^2} = \frac{\delta(X)}{\delta x} = \frac{\delta X}{\delta r}\cdot\frac{\delta r}{\delta x} + \frac{\delta X}{\delta \theta}\cdot\frac{\delta \theta}{\delta x} + \frac{\delta X}{\delta \phi}\cdot\frac{\delta \phi}{\delta x}$$

$$\rightarrow \quad \frac{\delta X}{\delta r}\cdot\frac{\delta r}{\delta x} = \left(\frac{\sin\theta\cos\phi}{r^2} + \frac{\cos\phi}{r^2\sin\theta}\right]\sin\theta\cos\phi$$

$$= \frac{\sin^2\theta\cos^2\phi}{r^2} + \frac{\cos^2\phi}{r^2}$$

$$= \frac{\cos^2\phi}{r^2}\left[\sin^2\theta + 1\right]$$

Similarly $\dfrac{\delta x}{\delta \theta} \cdot \dfrac{\delta \theta}{\delta x}$

$$= \left(-\frac{\cos\theta\cos\phi}{r} + \frac{\cos\phi}{r}\ \text{cosec}\,\theta\cot\theta\right) \frac{\cos\theta\cos\phi}{r}$$

$\because \dfrac{d}{dx}\text{cosec}\,\theta = -\text{cosec}\,\theta\cot\theta$

$$= -\frac{\cos^2\theta\cos^2\phi}{r^2} + \frac{\cos^2\phi}{r^2}\cos\theta\ \text{cosec}\,\theta\cot\theta$$

$$= -\frac{\cos^2\theta\cos^2\phi}{r^2} + \frac{\cos^2\phi}{r^2} \cdot \cos\theta\,\frac{1}{\sin\theta}\,\frac{\cos\theta}{\sin\theta}$$

$$= -\frac{\cos^2\theta\cos^2\phi}{r^2} + \frac{\cos^2\theta\cos^2\phi}{r^2\sin^2\theta}$$

$$= \frac{\cos^2\theta\cos^2\phi}{r^2}\left[\frac{1}{\sin^2\theta} - 1\right]$$

$\rightarrow$ $\dfrac{\delta x}{\delta \phi} \cdot \dfrac{\delta \phi}{\delta x}$

$$= \left(\frac{\sin\theta\sin\phi}{r} + \frac{\sin\phi}{r\sin\theta}\right) - \frac{\sin\phi}{r\sin\theta}$$

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

∇^2 in spherical coordinates can be obtained by calculating $\frac{\delta Y}{\delta y}$ and $\frac{\delta Z}{\delta z}$, then by adding the three and simplifying as

$$\nabla^2 = \frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta}{\delta r}\right] + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\delta}{\delta\theta}\left(\sin\theta\frac{\delta}{\delta\theta}\right] + \frac{1}{\sin^2\theta}\frac{\delta^2}{\delta\phi^2}\right\}$$

The first term represents the linear or radial part and the second term represents the angular part.

$$\nabla^2 = \frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta}{\delta r}\right] + \frac{1}{r^2}\Lambda$$

where $\Lambda = \frac{1}{\sin\theta}\frac{\delta}{\delta\theta}(\sin\theta\, \delta/\delta\theta) + \frac{1}{\sin^2\theta}\frac{\delta^2}{\delta\phi^2}$

The Schrödinger equation $\hat{H}\Psi = E\Psi$ becomes

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\left[\frac{\delta}{\delta r}\left(r^2\frac{\delta}{\delta r}\right) + \Lambda\right]\Psi_{(r,\theta,\phi)} = E\Psi_{r,\theta,\phi}$$

$$\frac{-\hbar^2}{2I}\left[\frac{\delta}{\delta r}\left[r^2\,\delta/\delta r\right] + \Lambda\right]\Psi_{(r,\theta,\phi)} = E\Psi_{(r,\theta,\phi)}$$

where $I = mr^2 \Rightarrow$ moment of inertia of the rotating body

The equation can be applied to any system where V is zero.

PARTICLE IN A RING MODEL

Consider a particle of mass m rotating in a circle of radius r in the xy plane.

SW equation for a rotating body in polar / spherical coordinates is

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta}{\delta r}\right]+\frac{1}{r^2\sin\theta}\frac{\delta}{\delta\theta}\sin\theta\frac{\delta}{\delta\theta}+\frac{1}{r^2\sin^2\theta}\frac{\delta^2}{\delta\phi^2}\right]\Psi_{r,\theta,\phi}$$

$$= E\Psi(r,\theta,\phi)$$

ie $$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\delta}{\delta r}\left(r^2\frac{\delta}{\delta r}\right)+\frac{1}{r^2}\Lambda\right]\Psi_{r,\theta,\phi} = E\Psi_{r,\theta,\phi}$$

Since r is a constant, the linear part becomes zero and the equation reduces to

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\Lambda\Psi_{r,\theta,\phi} = E\Psi_{r,\theta,\phi}$$

Since the particle is in rotation in the xy plane ie ⊥r to the z axis, $\theta = 90$

$$\sin\theta = \sin 90 = 1$$

$$\therefore \Lambda = \frac{1}{\sin\theta}\frac{\delta}{\delta\theta}\sin\theta\,\delta/\delta\theta + \frac{1}{\sin^2\theta}\,\delta/\delta\phi^2$$

$\wedge = \frac{\delta^2}{\delta \phi^2}$ ie θ terms are zero.

The S.W equation becomes

$$\left(\frac{-\hbar^2}{2m} \cdot \frac{1}{r^2} \wedge \right) \psi_\phi = E \psi_\phi$$

$$\frac{-\hbar^2}{2I} \frac{\delta^2 \psi_\phi}{\delta \phi^2} = E \psi_\phi$$

$$\frac{\delta^2 \psi_\phi}{\delta \phi^2} = -\frac{2IE}{\hbar^2} \psi_\phi$$

ie $$\frac{\delta^2 \psi_\phi}{\delta \phi^2} + \frac{2IE}{\hbar^2} \psi_\phi = 0 \qquad \text{——— (1)}$$

$$\frac{\delta^2 \psi_\phi}{\delta \phi^2} + m^2 \psi_\phi = 0 \qquad \text{where } m^2 = \frac{2IE}{\hbar^2}$$

The above equation is similar to the equation of a particle in 1D box. The possible solutions of eq. 1 are

i) $\psi_1 = C_1 \cos m\phi$
ii) $\psi_2 = C_2 \sin m\phi$
iii) $\psi_3 = C_3 e^{im\phi}$
iv) $\psi_4 = C_4 e^{-im\phi}$

The most general solutions are equation (iii) and (iv). and the complete solution is $\boxed{\psi_\phi = C_3 e^{im\phi}}$

Proof

$$\psi_\phi = A_m e^{im\phi} \text{ and } \psi_\phi = A_{-m} e^{-im\phi}$$

The functions are finite and continuous for all values of ϕ and m. They are single valued too; since the angles ϕ and $\phi + 2\pi$ represent the same point. The requirement that ψ_ϕ be a single valued function of ϕ is

$$\psi(\phi + 2\pi) = \psi_\phi$$

ie the initial state of the system is ψ_ϕ when the angle is ϕ and after one revolution, the state will be $\psi(\phi+2\pi)$.

$$A_m e^{im(\phi+2\pi)} = A_m e^{im\phi} \quad \text{— ②}$$

$$A_{-m} e^{-im(\phi+2\pi)} = A_{-m} e^{-im\phi} \quad \text{— ③}$$

Considering ②

$$A_m e^{im(\phi+2\pi)} = A_m e^{im\phi} \cdot e^{im2\pi}$$

$$= \psi_\phi e^{im2\pi}$$

$$e^{im2\pi} = \frac{A_m e^{im(\phi+2\pi)}}{\psi_\phi} = \frac{\psi_{\phi+2\pi}}{\psi_\phi} = \frac{\psi_\phi}{\psi_\phi} = 1$$

Thus ② and ③ together imply that

$$e^{\pm i2\pi m} = 1 \quad \text{———— ④}$$

In terms of cosines and sines, eq ④ becomes

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

which implies that $m = 0, \pm 1, \pm 2 \ldots$ because $\cos 2\pi m = 1$ ⑥
and $\sin 2\pi m = 0$ for $m = 0, \pm 1, \pm 2 \ldots$

Hence one equation can be obtained as

$$\boxed{\psi_\phi = A_m e^{im\phi}} \quad \text{where } m = 0, \pm 1, \pm 2 \quad \text{—— ⑤}$$

or $\psi_\phi = c_3 e^{im\phi}$

Applying normalisation condition

$$\int \phi \, \phi^* \, d\phi = 1 \quad \text{ie}$$

$$\int_0^{2\pi} A_m e^{im\phi} A_{-m} e^{-im\phi} \, d\phi = 1$$

$$|A_m|^2 \int_0^{2\pi} d\phi = 1$$

$$|A_m|^2 [\phi]_0^{2\pi} = 1$$

$$|A_m|^2 \times 2\pi = 1$$

$$A_m = \left(\frac{1}{2\pi}\right)^{1/2}$$

$$\boxed{\therefore \; \psi_\phi = \left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi} \quad \text{where } m = 0, \pm 1, \pm 2, \ldots}$$

Energy of the rotating body

$$m^2 = \frac{2IE}{\hbar^2}$$

$$E = \frac{\hbar^2 m^2}{2I} = \frac{m^2 h^2}{8\pi^2 I}$$

Value of m	$\psi_m = \left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi}$	$E_m = \frac{m^2 h^2}{8\pi^2 I}$
$m = 0$	$\psi_0 = \left(\frac{1}{2\pi}\right)^{1/2}$	$E_0 = 0$
$m = \pm 1$	$\psi_{-1} = \left(\frac{1}{2\pi}\right)^{1/2} e^{-i\phi}$ $\psi_1 = \left(\frac{1}{2\pi}\right)^{1/2} e^{i\phi}$	$E_{\pm 1} = \frac{h^2}{8\pi^2 I}$
$m = \pm 2$	$\psi_{-2} = \left(\frac{1}{2\pi}\right)^{1/2} e^{-2i\phi}$ $\psi_2 = \left(\frac{1}{2\pi}\right)^{1/2} e^{2i\phi}$	$E_{\pm 2} = \frac{4h^2}{8\pi^2 I}$

Rotating particle does not have zero point energy, since for $m = 0$, $E = 0$

PARTICLE ON A SPHERE → 3D model

S.W equation for a rotating body is

$$\frac{-\hbar^2}{2m}\left[\frac{\delta}{\delta r}\left[r^2\frac{\delta}{\delta r}\right] + \Lambda\right]\Psi_{r,\theta,\phi} = E\,\Psi_{r,\theta,\phi}$$

Since r is constant, the first term in the above equation containing r is neglected and the equation reduces to

$$\frac{-\hbar^2}{2I}\,\Lambda\,\Psi(\theta,\phi) = E\,\Psi_{\theta,\phi}$$

$$\frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\delta}{\delta\theta}\left(\sin\theta\frac{\delta}{\delta\theta}\right) + \frac{1}{\sin^2\theta}\frac{\delta^2}{\delta\phi^2}\right]\Psi_{\theta,\phi} = E\,\Psi_{\theta,\phi} \quad \text{—} (1)$$

This equation contains two variables which has to be seperated to solve

Seperation of variables

Let $\Psi_{(\theta,\phi)} = H_\theta \times \Phi_\phi$

Substituting in (1)

$$\frac{-\hbar^2}{2I}\left[\Phi_\phi\frac{1}{\sin\theta}\frac{\delta}{\delta\theta}\left(\sin\theta\frac{\delta}{\delta\theta}H_\theta\right) + \frac{H_\theta}{\sin^2\theta}\frac{\delta^2}{\delta\phi^2}\Phi_\phi\right] = E\,H_\theta\,\Phi_\phi$$

Dividing throughout by $H_\theta\,\Phi_\phi$

$$\frac{-\hbar^2}{2I}\left[\frac{1}{H_\theta\sin\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta}{\delta\theta}H_\theta\right] + \frac{1}{\Phi_\phi\sin^2\theta}\frac{\delta^2\Phi_\phi}{\delta\phi^2}\right] = E$$

Multiplying throughout by $\sin^2\theta$

$$-\frac{\hbar^2}{2I}\left[\frac{\sin\theta}{H_\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta}{\delta\theta}H_\theta\right]+\frac{1}{\Phi_\phi}\frac{\delta^2\Phi_\phi}{\delta\phi^2}\right]=E\sin^2\theta$$

$$\frac{\sin\theta}{H_\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta}{\delta\theta}H_\theta\right]+\frac{1}{\Phi_\phi}\frac{\delta^2\Phi_\phi}{\delta\phi^2}=-\frac{2IE}{\hbar^2}\sin^2\theta$$

Put $\frac{2IE}{\hbar^2}=\alpha^2$

$$\frac{\sin\theta}{H_\theta}\delta/\delta\theta\left[\sin\theta\,\delta/\delta\theta\,H_\theta\right]+\frac{1}{\Phi_\phi}\frac{\delta^2\Phi_\phi}{\delta\phi^2}=-\alpha^2\sin^2\theta$$

On rearranging.

$$\frac{\sin\theta}{H_\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta}{\delta\theta}H_\theta\right]+\alpha^2\sin^2\theta=-\frac{1}{\Phi_\phi}\frac{\delta^2\Phi_\phi}{\delta\phi^2}$$

Equating L.H.S and R.H.S into another constant m^2, we get

$$\frac{\sin\theta}{H_\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta}{\delta\theta}H_\theta\right]+\alpha^2\sin^2\theta=m^2$$

$$\text{and}\quad -\frac{1}{\Phi_\phi}\frac{\delta^2\Phi_\phi}{\delta\phi^2}=m^2 \quad -②$$

<u>To solve the ϕ equation</u>

② becomes $\frac{\delta^2\Phi_\phi}{\delta\phi^2}=-m^2\Phi_\phi$ ie $\frac{\delta^2\Phi_\phi}{\delta\phi^2}+m^2\Phi_\phi=0$

This equation is similar to that of particle in a ring

$$\boxed{\Phi_\phi=(1/2\pi)^{1/2}e^{im\phi}}$$

To solve θ equation

$$\frac{\sin\theta}{H_\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta}{\delta\theta}H_\theta\right]+\alpha^2\sin^2\theta = m^2 \quad \text{———} \ (1)$$

In order to solve this equation, H_θ is converted to a function in terms of x

$(\sin^2\theta+\cos^2\theta=1)$
$(\sin^2\theta = 1-x^2)$
if $x=\cos\theta$
$\sin\theta = (1-x^2)^{1/2}$

Let $H_\theta = P_x$

Put $x=\cos\theta$, $\sin\theta = (1-x^2)^{1/2}$

$$\frac{d}{d\theta} = \frac{d}{dx}\cdot\frac{dx}{d\theta}$$

$$= -\sin\theta\, d/dx = -(1-x^2)^{1/2}\frac{d}{dx}$$

Substituting in eq. (1)

$$\frac{(1-x^2)^{1/2}\times(-)(1-x^2)^{1/2}}{P_x}\left[\frac{d}{dx}(1-x^2)^{1/2}\times(-)(1-x^2)^{1/2}\frac{d}{dx}P(x)\right]+\alpha^2(1-x^2)=m^2$$

$$\frac{(1-x^2)}{P_x}\frac{d}{dx}(1-x^2)\frac{d}{dx}P_x+\alpha^2(1-x^2)-m^2=0$$

Multiplying throughout by $\frac{P_x}{1-x^2}$

$$\frac{d}{dx}\left[(1-x^2)\frac{d}{dx}P_x\right]+\alpha^2\cancel{(1-x^2)}\frac{P_x}{\cancel{(1-x^2)}}-m^2\times\frac{P_x}{(1-x^2)}=0$$

$$\frac{d}{dx}\left[(1-x^2)\frac{d}{dx}P_x\right]+\alpha^2 P_x-m^2\times\frac{P_x}{(1-x^2)}=0$$

$$\frac{d}{dx}\left[(1-x^2)\frac{d}{dx}P_x\right]+\left(\alpha^2-\frac{m^2}{(1-x^2)}\right]P_x=0$$

$$\frac{d}{dx}\left[(1-x^2)\,P'_x\right]+\left[\alpha^2-\frac{m^2}{(1-x^2)}\right]P_x=0$$

$$(1-x^2)\,P''_x+P'_x\,x-2x+\left[\alpha^2-\frac{m^2}{(1-x^2)}\right]P_x=0$$

$$(1-x^2)\,P''_x-2x\,P'_x+\left[\alpha^2-\frac{m^2}{(1-x^2)}\right]P_x=0 \quad \text{—} \; (2)$$

Equation (2) is the Legendre differential equation and is a well-known equation in classical Physics. Such equations are solved using polynomial method and the solution of this equation is known as Legendre polynomial. LP is represented as $P_l^{|m|}x$

When $m=0$ and l an integer, the polynomial is called Legendre Polynomial and when m and l are integers, then it is associated lengendre Polynomial. The Solutions are mostly easily discussed by considering the $m=0$ case.

$P_l x \rightarrow$ The Legendre Polynomial

$P_l^m(x) \rightarrow$ Associated Legendre Polynomial

$$P_x = a_0 x^0 + a_1 x^1 + a_2 x^2 + a_3 x^3 + \cdots\cdots$$

$$P'x = a_1 x^0 + 2a_2 x^1 + 3a_3 x^2 + 4a_4 x^3 + \cdots\cdots$$

$$P''x = (1\times 2) a_2 x^0 + (2\times 3) a_3 x + (3\times 4) a_4 x^2 + \cdots\cdots$$

Substituting in the equation ② and equating the coefficients of powers of $x = 0$, the Legendre equation can be solved substituting $m = 0$.

$$(1-x^2)\left\{(1\times 2) a_2 x^0 + (2\times 3) a_3 x^1 + (3\times 4) a_4 x^2\right\}$$

$$-2x\left\{a_1 x^0 + 2a_2 x^1 + 3a_3 x^2 + \cdots\right\}$$

$$+\alpha^2\left\{a_0 x^0 + a_1 x^1 + a_2 x^2 + a_3 x^3 + \cdots\cdots\right\}$$

Equating the coefficients

$$x^0 \rightarrow (1\times 2)a_2 + \alpha^2 a_0 = 0$$

$$x^1 \rightarrow (2\times 3)a_3 - 2a_1 + \alpha^2 a_1 = 0$$

$$x^2 \rightarrow (3\times 4)a_4 - (1\times 2)a_2 - (2\times 2)a_2 + \alpha^2 a_2 = 0$$

ie $(3\times 4)a_4 - 2a_2 - 4a_2 + \alpha^2 a_2 = 0$

$$(3\times 4)a_4 - \underset{(2\times 3)}{6}a_2 + \alpha^2 a_2 = 0$$

$$x^3 \rightarrow [(4\times 5)a_5 - (2\times 3)a_3 - (2\times 3)a_3 + \alpha^2 a_3] = 0$$

$$4\times 5 - \underset{(3\times 4)}{12}a_3 + \alpha^2 a_3 = 0$$

$$x^4 \longrightarrow (5\times 6)a_6 - (3\times 4)a_4 - (2\times 4)a_4 + \alpha^2 a_4 = 0$$

$$(5\times 6)a_6 - \underset{(4\times 5)}{20}a_4 + \alpha^2 a_4 = 0$$

$x^K \rightarrow (k+1)(k+2)a_{k+2} - K(K+1)a_K + \alpha^2 a_K = 0$

ie $(k+1)(k+2)a_{k+2} = K(K+1)a_K - \alpha^2 a_K$

$$\boxed{a_{k+2} = \frac{K(K+1)a_K - \alpha^2 a_K}{(k+1)(k+2)}}$$

This is the recursion formula of associated Legendre Polynomial

For a real system the polynomial cannot be extended up to infinity. It must be terminated at a point. Let it be l.

Then the recursion formula becomes,

$$a_{l+2} = \frac{l(l+1) - \alpha^2}{(l+1)(l+2)} a_l$$

All coefficients beyond a_l are zero ie $a_{l+2} = 0$

$$\frac{l(l+1) - \alpha^2}{(l+1)(l+2)} a_l = 0$$

a_l cannot be zero, so $l(l+1) - \alpha^2 = 0$

$$\alpha^2 = l(l+1)$$

$$\alpha^2 = \frac{2IE}{\hbar^2}$$

$$\boxed{E = \frac{\alpha^2 \lambda^2}{8\pi^2 I} = \frac{\lambda^4}{8\pi^2 I} l(l+1)}$$

where $l = 0, 1, 2$

Normalisation Factor

The θ function is H_θ. Applying the normalisation condition

$$N^2 \int_0^\pi H_\theta^2 \, d\theta = 1$$

$$N = \frac{1}{\sqrt{\int_0^\pi H_\theta^2 \, d\theta}}$$

The value of N is obtained as $\left[\frac{2l+1}{2} \frac{l-|m|!}{l+|m|!} \right]^{1/2}$

$$H_\theta(l,m) = \underbrace{N \, (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x)}_{ALP}$$

$$\Phi_{\phi \, m_l} = \left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi}$$

The total/complete wavefunction of the particle on a sphere is

$$\Psi(\theta, \phi) = H_\theta(l,m) \times \Phi_{\phi(m_l)}$$

$$\boxed{\Psi(\theta,\phi) = \left[\frac{2l+1}{2} \frac{l-|m|!}{l+|m|!} \right]^{1/2} (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x) \times \left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi}}$$

The wavefunction is a function of θ and ϕ, the two angles in spherical coordinates and hence the wavefunction is called spherical harmonics.

$\psi(\theta,\phi)$ contains the term $\frac{d^{|m|}}{dx^{|m|}} P_l(x)$. When $m>l$, the term becomes zero. If that is the case, $\psi(\theta,\phi)$ becomes zero which is not possible as long as the particle is present. Therefore a restriction is imposed where $m \le l$ and $m>l$ cannot exist.

l and m are identified with the quantum numbers of energy and angular momentum.

ROTATION OF DIATOMIC MOLECULES

– RIGID ROTATOR / RIGID ROTOR

→ The rotation of a diatomic molecule can be described by a rigid rotator

→ A rigid rotor consists of two spherical particles attached together but are seperated by finite fixed distance and capable of rotating about an axis passing through the centre of mass and normal to the plane containing the two particles

There are two types of rigid rotors

1) 2D Rigid rotor — diatomic molecule rotating in a plane
Planar Rigid rotor/
(fixed axis) → Particle in a ring model.

2) 3D rigid rotor → rotation in space [free axis]
 - Particle on a sphere model

→ Wavefunction of a 3D rigid rotor is called spherical harmonics.

→ It is represented by $Y_{l m_l}(\theta, \phi)$

→ $Y_{l m_l}(\theta, \phi) = \psi(\theta, \phi) = H_{\theta(l,m)} \times \Phi_{\phi\, m_l}$

where θ is dependent on l and m and ϕ is dependent only on m_l.

Rodrigues formula for LP and ALP

The associated Legendre polynomial $P_l^m(x)$ is obtained by differentiating the Legendre polynomial $P_l(x)$ m times and $m \le l$.

Rodrigues formula for LP

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2-1)^l$$

→ When $l = 0$

$$P_0(x) = \frac{1}{2^0 0!} \frac{d^0}{dx^0} (x^2-1)^0$$

$$= 1$$

→ when $l = 1$

$$P_1(x) = \frac{1}{2^1 1!} \frac{d^1}{dx^1} (x^2-1)^1$$

$$= \frac{1}{2} \cdot 2x = x = \cos\theta$$ [Page 284 McQuarrie]

→ when $l = 2$

$$P_2(x) = \frac{1}{2^2 2!} \frac{d^2}{dx^2} (x^2-1)^2$$

$$= \frac{1}{8} \frac{d}{dx} 2x \cdot 2(x^2-1)$$

$$= \frac{1}{8} \cdot 4 \frac{d}{dx} (x^2-1)\, x$$

$$= \frac{1}{2} [x^2-1 + x \cdot 2x] = \frac{1}{2} [3x^2-1]$$

→ When $l = 3$

$$P_3(x) = \frac{1}{2^3 \times 3!} \frac{d^3}{dx^3} (x^2-1)^3$$

$$= \frac{1}{48} \frac{d^2}{dx^2} 3(x^2-1)^2 \cdot 2x$$

$$= \frac{1}{48} \times 6 \frac{d^2}{dx^2} [x^2-1]^2 \cdot x$$

$$= \frac{1}{8} \frac{d}{dx} [(x^2-1)^2 \cdot 1 + x \cdot 2[x^2-1] \times 2x]$$

$$= \frac{1}{8} [2(x^2-1)\, 2x + 4[x^2 \cdot 2x + (x^2-1) \times 2x]]$$

$$= \frac{1}{8} (4x[x^2-1] + 4[2x^3 + 2x^3 - 2x]]$$

$$= \frac{1}{8} [4x^3 - 4x + 8x^3 + 8x^3 - 8x]$$

$$= \frac{1}{8} [20x^3 - 12x]$$

$$= \frac{5}{2} x^3 - \frac{3}{2} x$$

Rodrigue's formula for ALP

$$P_l^m(x) = \left[\frac{2l+1}{2}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} (1-x^2)^{|m|/2}\,\frac{d^m}{dx^m}\,P_l(x)$$

→ When $l=0$, $m=0$

$$P_0^0(x) = \left[\frac{2\times 0+1}{2}\,\frac{(0-0)!}{(0+0)!}\right]^{1/2} (1-x^2)^{0/2}\,\frac{d^0}{dx^0}\,P_0(x)$$

$$= \frac{1}{\sqrt{2}}$$

→ When $l=1$, $m=0$

$$P_1^0(x) = \left[\frac{2\times 1+1}{2}\,\frac{(1-0)!}{(1+0)!}\right]^{1/2} (1-x^2)^{\frac{|0|}{2}}\,\frac{d^0}{dx^0}\,P_1(x)$$

$$= \left(\frac{3}{2}\right)^{1/2}\cdot x$$

→ When $l=1$, $m=1$

$$P_1^1(x) = \left[\frac{2\times 1+1}{2}\,\frac{(1-1)!}{(1+1)!}\right]^{1/2} (1-x^2)^{1/2}\,\frac{d^1}{dx^1}\,P_1(x)$$

$$= \left(\frac{3}{4}\right)^{1/2} (1-x^2)^{1/2}$$

Spherical Harmonics — $Y_{lm_l}(\theta, \phi) = H_\theta \, \Phi_\phi$

a) $l = 0, \; m = 0$

$$H_\theta = \frac{1}{\sqrt{2}} \; , \quad \Phi_\phi = \left(\frac{1}{2\pi}\right)^{1/2}$$

$$Y_{lm_l}(\theta, \phi) = \frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{2\pi}} = \frac{1}{2\sqrt{\pi}}$$

b) $l = 1, \; m = 0$

$$H_\theta = \left(\frac{3}{2}\right)^{1/2} x \quad \text{and} \quad \Phi_\phi = \left(\frac{1}{2\pi}\right)^{1/2}$$

$$Y_{lm_l}(\theta, \phi) = \left(\frac{3}{2}\right)^{1/2} x \times \left(\frac{1}{2\pi}\right)^{1/2}$$

$$= \frac{\sqrt{3}}{2\sqrt{\pi}} x = \frac{\sqrt{3}}{2\sqrt{\pi}} \cos\theta$$

c) $l = 1, \; m = 1$

$$Y_{lm_l}(\theta, \phi) = \left(\frac{3}{4}\right)^{1/2} (1 - x^2)^{1/2} \left(\frac{1}{2\pi}\right)^{1/2} e^{i\phi}$$

d) $l = 1, \; m = -1$

$$Y_{lm_l}(\theta, \phi) = \left(\frac{3}{4}\right)^{1/2} (1 - x^2)^{1/2} \left(\frac{1}{2\pi}\right)^{1/2} e^{-i\phi}$$