Here we consider the problem of a particle confined to the surface of a sphere of radius R. The problem of a mass confine to a sphere is often called the rigid rotor problem.

Consider a particle of mass μ confine to move on a sphere of radius R. The wave Function is independent of r, so the derivatives with respect to r are zero. And the energy eigenvalue equation reduce to

$$-\frac{\hbar^2}{2\mu R^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\theta,\phi)=E\psi(\theta,\phi)$$

$$\frac{\hat{L}^2}{2I}\psi(\theta,\phi)=E\psi(\theta,\phi)$$

Is a wave function for $\hat{L}^2$

$$I=\mu R^2$$

Rotational kinetic energy operator in three dimension spherical coordinate

The angular momentum in this case is not confined to the z-direction because The particle can move anywhere on the sphere.

- To solve the above equation we used the separation of variable method. We assume the wave function by the form

$$\psi(\theta,\phi) = f(\theta)\Phi(\phi)$$

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]f(\theta)\Phi(\phi) = Ef(\theta)\Phi(\phi)$$

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

$$\boxed{\lambda = \frac{2IE}{\hbar^2}}$$

$$\boxed{\frac{\sin\theta}{f(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}f(\theta)\right)+\lambda\sin^2\theta}=\boxed{-\frac{1}{\Phi(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi(\phi)}=m^2$$

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

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

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

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

$$\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$m=0,\pm1,\pm2,\cdots$$

The wave function of

$\hat{L}_z$

Here we have no restriction on the values of m,
The restriction will come later !

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

$$x=\cos\theta$$

$$\sin^2\theta=1-x^2$$

$$dx=-\sin\theta d\theta$$

$$d\theta=\frac{-dx}{\sin\theta}$$

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

$$\frac{\partial}{\partial x}\left(1-x^2\right)\frac{\partial}{\partial x}f(x)+\left(\lambda-\frac{m^2}{1-x^2}\right)f(x)=0$$

$$\boxed{\left(1-x^2\right)\frac{\partial^2}{\partial x^2}f(x)-2x\frac{\partial}{\partial x}f(x)+\left(\lambda-\frac{m^2}{1-x^2}\right)f(x)=0}$$

$$\boxed{\left(1-x^2\right)\frac{\partial^2}{\partial x^2}f(x)-2x\frac{\partial}{\partial x}f(x)+\left(\lambda-\frac{m^2}{1-x^2}\right)f(x)=0}$$

For m=0

compare $$\left\{\begin{aligned}&\left(1-x^2\right)\frac{\partial^2}{\partial x^2}f(x)-2x\frac{\partial}{\partial x}f(x)+\lambda f(x)=0\\&\left(1-x^2\right)P_l''(x)-2xP_l'(x)+l(l+1)P_l(x)=0\end{aligned}\right.$$

If $\longrightarrow \lambda=l(l+1)$

then $\longrightarrow f(x)\to P_l(x)$

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

$\uparrow$

Legendre Polynomials

Legendre polynomials

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

$$P_0(\cos\theta) = 1$$

$$P_1(\cos\theta) = \cos\theta$$

$$P_2(\cos\theta) = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$\int_0^\pi P_l(\cos\theta) P_{l'}(\cos\theta) \sin\theta d\theta = \frac{2}{2l+1} \delta_{ll'}$$

General case

$$\boxed{\left(1-x^2\right)\frac{\partial^2}{\partial x^2}f(x)-2x\frac{\partial}{\partial x}f(x)+\left(\lambda-\frac{m^2}{1-x^2}\right)f(x)=0}$$

compare

$$\left(1-x^2\right)\frac{\partial^2}{\partial x^2}P_l^{|m|}(x)-2x\frac{\partial}{\partial x}P_l^{|m|}(x)+\left(l(l+1)-\frac{m^2}{1-x^2}\right)P_l^{|m|}(x)=0$$

if → $\lambda \to l(l+1)$ Than $f(x)\to P_l^{|m|}(x)$

l is called orbital angular momentum quantum number. Its values restricted to 0,1,2,3,4,………

Since P_l is a polynomial of degree, l, its $|m|th$ derivative, and hence $P_l^{|m|}$ will vanish if $|m|>l$

Therefore $\boxed{|m| \le l}$

Restriction on the values of m

Hence for a fixed value of l there are (2l+1) allowed values of m given by

$$\begin{aligned} l &= 0,1,2,3,\cdots \\ m &= 0,\pm 1,\pm 2,\cdots,\pm l \end{aligned} \qquad (2l+1)$$

We understand this restriction as follows: Since Lx, Ly, Lz are hermitian operators i.e their eigenvalues are real.

$$\left\langle L^2 \right\rangle = \left\langle L_x^2 \right\rangle + \left\langle L_y^2 \right\rangle + \left\langle L_z^2 \right\rangle$$

$$\boxed{\begin{gathered} \left\langle L^2 \right\rangle \geq \left\langle L_z^2 \right\rangle \\ l(l+1) \geq m^2 \end{gathered}}$$

The component of a vector in any direction can not exceed the magnitude of the vector

Associate Legendre polynomials

$$x = \cos(\theta)$$

$$f(\theta) = P_l^{|m|}(\cos\theta)$$

$$P_l^{|m|}(x) = (1 - x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x)$$

$$m = 0, \pm 1, \pm 2, \cdots, \pm l$$

$$\int_0^{\pi} P_l^m(\cos\theta) P_{l'}^m(\cos\theta) \sin\theta d\theta = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ll'}$$

$$f_{lm}(\theta) = \left(-1\right)^{(m+|m|)/2}\left[\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)$$

$$\boxed{\psi_{lm}(\theta,\phi) = f_{lm}(\theta)\Phi_m(\phi) = Y_{lm}(\theta,\phi)}$$

$$Y_{lm}(\theta,\phi) = (-1)^{(m+|m|)/2}\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}$$

$$\int_0^{\pi}\int_0^{2\pi} Y_{l'm'}^{*}(\theta,\phi)Y_{lm}(\theta,\phi)\sin(\theta)\,d\theta d\phi = \delta_{ll'}\delta_{mm'}$$

Some important relation

- 1 $$Y_{lm}(\theta,\phi) = (-1)^m Y^*_{l,-m}(\theta,\phi)$$

- 1I Under parity operator $\vec{r} \rightarrow -\vec{r}$

Under this operation the spherical polar coordinates transform to

$$r \rightarrow r$$

$$\theta \rightarrow \pi - \theta$$

$$\phi \rightarrow \phi + \pi$$

$$P\left[Y_{lm}(\theta,\phi)\right] = Y_{lm}(\pi - \theta, \phi + \pi)$$

$$P_l^{|m|}\left[\cos(\pi - \theta)\right] = P_l^{|m|}\left[-\cos\theta\right] = (-1)^{l-|m|} P_l^{|m|}\left[-\cos\theta\right]$$

$$\Phi_m(\phi + \pi) = (-1)^m \Phi_m(\phi)$$

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta,\phi)$$

$$P\left[Y_{lm}(\theta,\phi)\right]=\left(-1\right)^{l}Y_{lm}(\theta,\phi)$$

So $Y_{lm}(\theta,\phi)$ has party of l, Even for even l and odd for odd l.

Y_{lm} Form a complete set, so that a function f(theta, phi) can be expand In terms of them as

$$f\left(\theta,\phi\right)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}a_{lm}Y_{lm}\left(\theta,\phi\right)$$

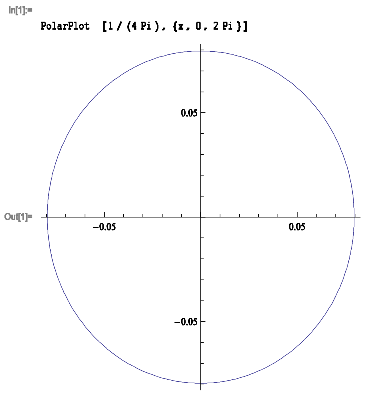
$$a_{lm}=\int Y_{lm}^{*}\left(\theta,\phi\right)f\left(\theta,\phi\right)d\Omega$$

Addition theorem of the spherical harmonics: if R1 and R2 are two vectors have Ploar angles $(\theta_1,\phi_1),(\theta_1,\phi_1)$,respectively, and let theta be the angle Between them. than

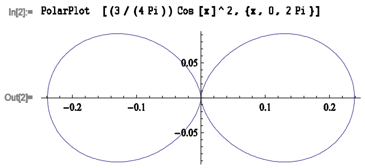
$$P_l(\cos\theta)=\frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_{lm}^{*}(\theta_1,\phi_1)Y_{lm}(\theta_1,\phi_1)$$

Polarplot for $\left|Y_{lm}(\theta,\phi)\right|^2$

Since the probability density does not depend on ϕ at all, the full angular probability densities can be obtained by rotating these figures around the *z-axis.*



```
In[1]:=
PolarPlot  [1 / (4 Pi ), {x, 0, 2 Pi }]
```



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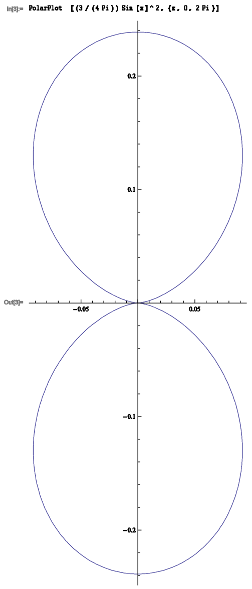
In[2]:= PolarPlot  [(3 / (4 Pi )) Cos [x]^2, {x, 0, 2 Pi }]
```



```
In[3]:= PolarPlot  [(3 / (4 Pi )) Sin [x]^2, {x, 0, 2 Pi }]
```

$$E_l = \frac{\hbar^2}{2I} l(l+1)$$

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

Notice that: $E = \dfrac{L^2}{2I}$

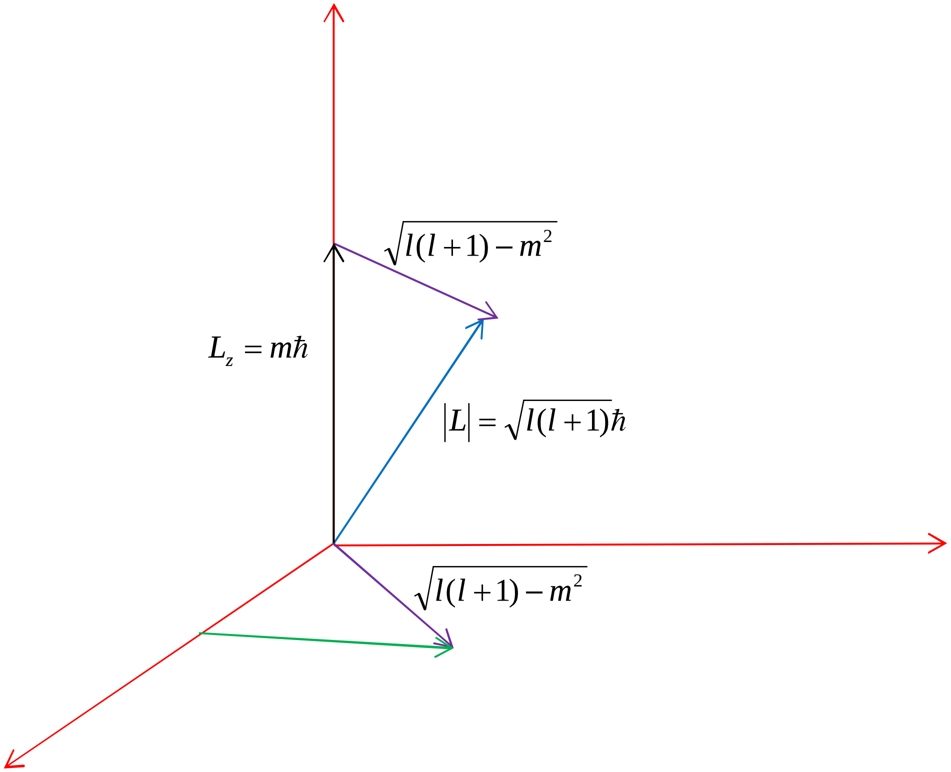
So the eigenvalue for $\hat{L}^2$ is

$$l(l+1)\hbar^2$$

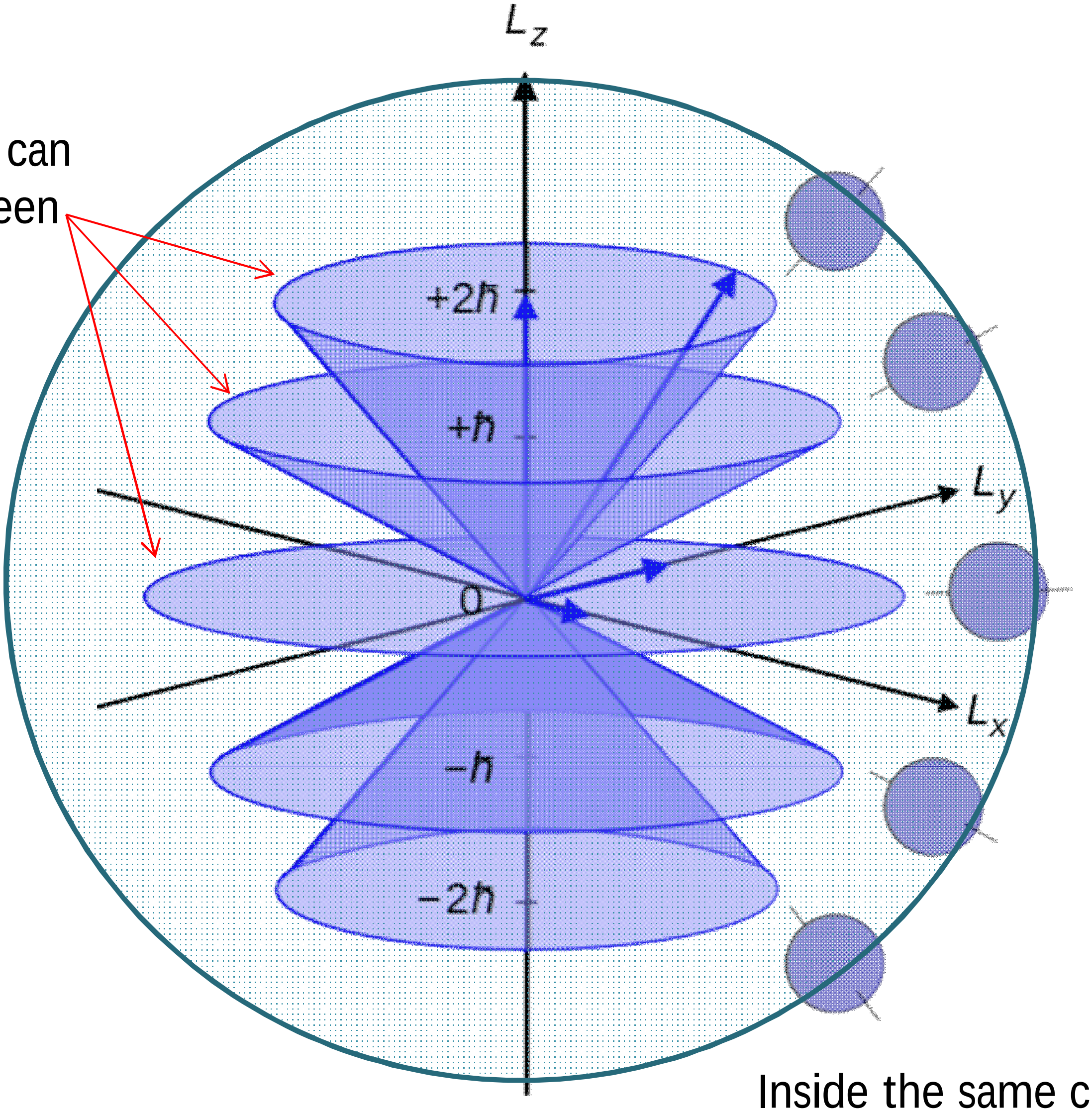
or $\boxed{|L| = \sqrt{l(l+1)}\hbar}$

As you well see in the H.W

$$\left\langle L_x^2 \right\rangle = \left\langle L_y^2 \right\rangle = \frac{1}{2}\left[l(l+1) - m^2\right]\hbar^2$$



The energy does not differentiate between any of these directions, it depend only on the Magnitude of the radius i.e the absolute value of L.



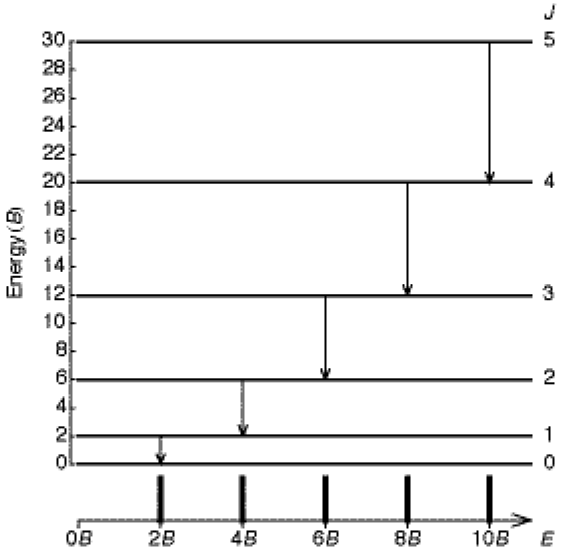
The wave function can Differentiate between

Inside the same cone the wave Function can not diffrentiate between The states

$$E_l = \frac{\hbar^2}{2I} l(l+1)$$

The energy is independent on the quantum number m. therefore the
(2l+1) eigenfunctions with m=-l,-l+1,….,l. corresponding to the same energy.
So that the energy level is (2l+1)-fold degenerate.
This degeneracy because the Hamiltonian of the rigid rotator commutes
With the orbital angular momentum operator L, therefore it is invariant under
Rotations. Hence for this system all directions of space are physically equivalent.
So, the energy levels cannot depend on the magnitude of the component of L in
Any particular direction.

Example: rotational energy level of hydrogen chloride Hcl



Equilibrium bound length R is: 0.127 nm

$$\hbar c = 197.3 \ eV.nm$$

$$\mu = \frac{m_H m_{cl}}{(m_H + m_{cl})} = \frac{1 \times 35}{1+35} \cong 0.97 \text{ a.m.u}$$

$$\text{a.m.u} \approx 938 \text{ MeV}$$

$$\Delta E = E_{l+1} - E_l = B2(l+1) = B(2,4,6,\cdots)$$

$$B = \frac{\hbar^2}{2I} = \frac{(197.3)^2 \ (\text{ev.nm})^2}{2(0.97 \times 938 \times 10^6 \text{ ev})(0.127 \text{ nm})^2} = 1.32 \text{ meV}$$

Experiments on Hcl give B=1.28 meV

To solve problem 9 you may need the following relation

$$\left(1-x^2\right)\frac{dP_l^{|m|}(x)}{dx}=\sqrt{1-x^2}\,P_l^{|m|+1}(x)-|m|\,xP_l^{|m|}(x)$$