$\langle \theta\phi | lm \rangle \equiv Y_l^m(\theta,\phi) =$ "Spherical Harmonics"

$\langle \theta\phi | lm \rangle$: QM amplitude to observe a particular θ & ϕ for a particle in state l,m

$Y_l^m(\theta,\phi)$: a complex function = spatial wavefunction for state l,m.

Properties of the Y_l^m

- **Normalized**: $\langle lm | lm \rangle = 1$ in Dirac Notation

$$\int_{4\pi} |Y_l^m|^2 \, d\Omega = 1 \quad \text{in position space}$$

or equivalently

$$\int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\phi \, |Y_{lm}|^2 = 1$$

- **Orthogonal**: $\langle l'm' | lm \rangle = \delta_{l'l}\delta_{mm'}$ in Dirac Notation

or

$$\int_{4\pi} \left(Y_{l'}^{m'}\right)^* Y_l^m \, d\Omega = \delta_{l'l}\delta_{mm'}$$

or

$$\int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\phi \left(Y_{l'}^{m'}\right)^* Y_l^m = \delta_{l'l}\delta_{m'm}$$

- **Complete**: $\displaystyle\sum_{l=0}^{\infty} \sum_{m=-l}^{l} |lm\rangle\langle lm| = 1$

Consequence: any reasonable function of θ,ϕ can be expanded in terms of the Y_l^m:

$$\psi(\theta,\phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} Y_l^m(\theta,\phi)$$

$\psi(\theta,\phi)$: any arbitrary function of θ,ϕ

a_{lm}: some appropriate set of coefficients $\{a_{lm}\}$.

How do we find the $\{a_{\ell m}\}$ for a particular $\psi(\theta,\phi)$?

Answer: As always, $a_{\ell m}$ = overlap of Y_ℓ^m with ψ:

$$a_{\ell m} = \langle \ell m | \psi \rangle = \int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\phi \, \left(Y_\ell^m\right)^* \psi$$

Proof: As always, use orthogonality:

$$|\psi\rangle \equiv \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} a_{\ell m} |\ell m\rangle \leftarrow \text{by definition of } \{a_{\ell m}\}.$$

Then multiply with $\langle \ell' m' |$:

$$\langle \ell' m' | \psi \rangle = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} a_{\ell m} \underbrace{\langle \ell' m' | \ell m \rangle}_{\delta_{\ell\ell'}\delta_{mm'}} = a_{\ell' m'}$$

$$\therefore \quad \boxed{a_{\ell m} = \langle \ell m | \psi \rangle}$$

What is the meaning of the $\{a_{\ell m}\}$?

As always, $\langle \ell m | \psi \rangle = a_{\ell m}$ is the amplitude to measure ℓ & m from an arbitrary state ψ:

$$\underbrace{\text{Prob}(\ell, m)}_{} = |a_{\ell m}|^2$$

Probability to measure $L^2 = \hbar^2 \ell(\ell+1)$ and $L_z = m\hbar$

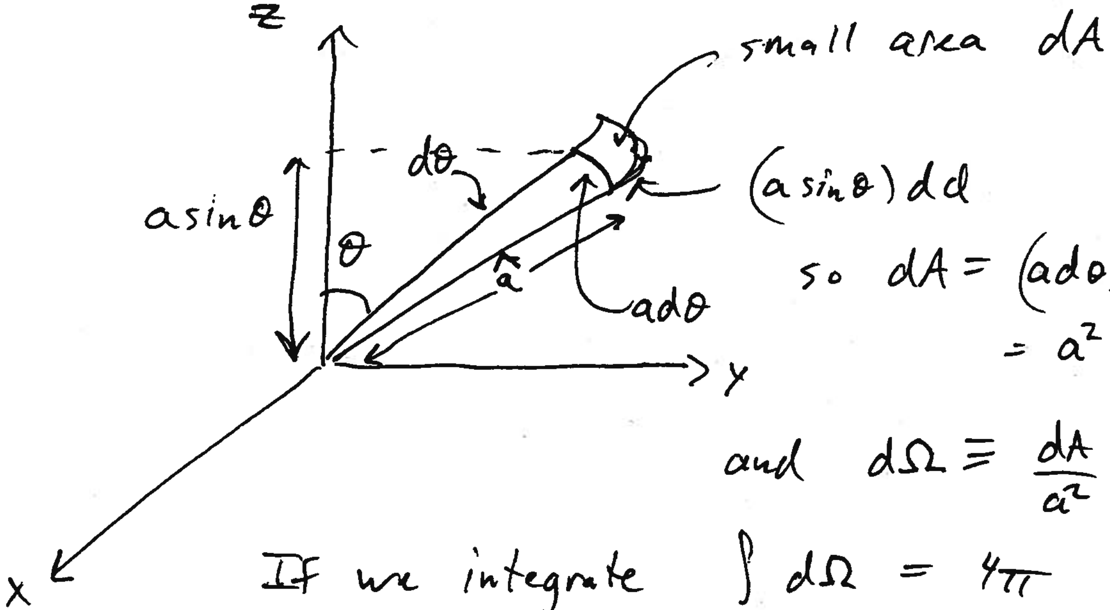
<u>Example</u> Suppose a particle is in state $|\ell m\rangle$.
What is the probability to find it near a particular θ & ϕ?

Answer:
$$\underbrace{P(\theta,\phi)}_{\text{probability density}} \, \underset{\substack{\uparrow \\ \text{small solid angle near } \theta,\phi}}{d\Omega} = \left| Y_\ell^m(\theta,\phi)\right|^2 d\Omega$$

$\uparrow$ QM amplitude

(Just like $P(x)dx = |\psi(x)|^2 dx$.)

What is $d\Omega$? $\Longrightarrow$ Recall definition of solid angle:



so $dA = (a\,d\theta)(a\sin\theta\,d\phi)$
$= a^2 \sin\theta\, d\theta\, d\phi$

and $d\Omega \equiv \dfrac{dA}{a^2} = \sin\theta\, d\theta\, d\phi$

If we integrate $\displaystyle\int_{\substack{\text{closed}\\ \text{sphere}}} d\Omega = 4\pi$

$\uparrow$ area of a unit sphere.

Finding the Y_ℓ^m Functions

The Y_ℓ^m are the solutions to

$$\hat{L}^2 Y_\ell^m(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta,\phi)$$
$$\& \quad \hat{L}_z Y_\ell^m(\theta,\phi) = \hbar m Y_\ell^m(\theta,\phi)$$

In spherical coordinates,

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi} \quad \& \quad L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

The Y_ℓ^m are the solutions to the two eigenvalue equation:

$$L^2 \text{ eq} \Rightarrow -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] Y_\ell^m(\theta,\phi) = \hbar^2\ell(\ell+1) Y_\ell^m(\theta,\phi)$$

$$L_z \text{ eq} \Rightarrow \quad -i\hbar\frac{\partial}{\partial\phi} Y_\ell^m(\theta,\phi) = \hbar m Y_\ell^m(\theta,\phi).$$

The L^2 equation is tricky to solve, but the L_z equation is simple. Assume seperation of variables:

$$Y_\ell^m(\theta,\phi) \equiv \Phi(\phi)\,\Theta(\theta)$$

The L_z equation says $\quad \frac{\partial}{\partial\phi}\Phi(\phi) = mi\,\Phi(\phi)$

$$\therefore \quad \Phi(\phi) = e^{im\phi} \quad \leftarrow \text{Every spherical harmonic has this factor (when } m \neq 0).$$

Also, we can see that m should be an integer so that the wavefunction is single valued when $\phi \to \phi + 2\pi$.
We already concluded that m is an integer based on the operator algebra.

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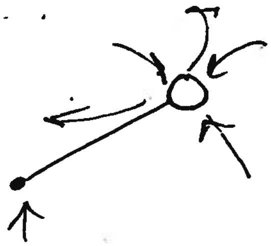
What can the angular momentum states describe?

An artificial example: Particle fixed to a rotating rod:



particle free to move in θ & ϕ, but fixed in (r).

fixed

$$\psi(\theta,\phi) = \underbrace{\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} a_{\ell m} Y_\ell^m}$$

because Y_ℓ^m are complete on the sphere, we can always find a set of $\{a_{\ell m}\}$ that satisfies this.

A more physical, realistic example: Diatomic Molecule

Example: H_2

$\leftarrow r \rightarrow$

Center of mass

Molecule can:

1. Vibrate $\Rightarrow$ Approximately SHO
2. Translate its center of mass $\Rightarrow$ Free particle, plane wave
3. Rotate about center of mass

Ignore 1 & 2 for the moment, and consider 3.

* Classically the KE will be $KE = \frac{L^2}{2I}$, $I = 2Mr^2$

I = moment of inertia about the center of mass

L = angular momentum.

So we might guess $\hat{H} = \frac{\hat{L}^2}{2I}$, for a region where $V(\vec{r}) = \emptyset$.

Obviously, $[\hat{H}, \hat{L}] = \emptyset$ for this system, so the stationary states and angular momentum states are in common..

$$\hat{H}\, \psi_{\ell m} = E_{\ell m}\, \psi_{\ell m}, \quad \psi_{\ell m} = \text{stationary state} = Y_\ell^m(\theta, \phi)$$

$$\frac{1}{2I} L^2 \psi_{\ell m} = E_{\ell m}\, \psi_{\ell m}$$

$$\frac{1}{2I} \hbar^2 \ell(\ell+1) = E_{\ell m}\, \psi_{\ell m}$$

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

actually, E only depends on ℓ:

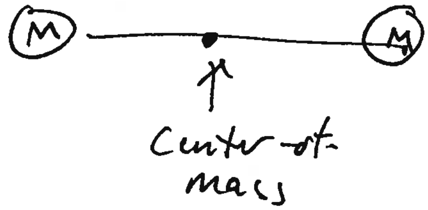
$$E_\ell = \frac{\hbar^2 \ell(\ell+1)}{2I}$$

What's the degeneracy? Every ℓ state has $2\ell+1$ m states so degeneracy is $2\ell+1$.

Rotational spectoscopy:

ℓ		"spectroscopic notation"	Energy	Degeneracy
0	=	"s"	0	1
1	=	"p"	$2\hbar^2/2I$	3
2	=	"d"	$6\hbar^2/2I$	5
3	=	"f"	$12\hbar^2/2I$	7
4	=	"g"	$20\hbar^2/2I$	9
⋮		⋮		

Diatomic Molecule



$$\hat{H} = \frac{\hat{L}^2}{2I}, \quad I = \text{moment of inertia}$$

from classical mechanics

Since $[\hat{H}, \hat{L}] = \emptyset$, the energy eigenstates are the same as the angular momentum states:

$$\cancel{\frac{1}{2I}\hat{L}^2 \psi_{lm}} \qquad \psi_{lm} = Y_l^m$$

$$\frac{1}{2I}\hat{L}^2 \psi_{lm} = E_{lm}\psi_{lm}$$

$$\frac{1}{2I}\hbar^2 l(l+1) = E_{lm}\psi_{lm}$$

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

← Energy eigenvalues depend on l, but not m

Degeneracy

l		"spectroscopic notation"	Energy	Degeneracy
0	=	"s" ← a name for $l=\emptyset$	$\emptyset$	1
1	=	"p"	$2\hbar^2/2I$	3
2	=	"d"	$6\hbar^2/2I$	~~3~~ 5
3	=	"f"	$12\hbar^2/2I$	7
4	=	"g"	$20\hbar^2/2I$	9
⋮		⋮	⋮	⋮

Central Potential

Suppose a particle moves in 3 dimension in a potential field which depends only on r:

$$\vec{V}(\vec{r}) = V(r)$$

The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

In Spherical Coordinates,

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}\Bigg[\underbrace{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}_{-\hat{L}^2/\hbar^2}\Bigg]$$

$$= \frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{\hat{L}^2}{\hbar^2 r^2}$$

~~Since What~~

Question: ~~What is~~ Does $\hat{H}$ commute with $\hat{L}^2$?

Answer: $\hat{L}^2$ depends only on θ & ϕ, Therefore

$$\left[\frac{1}{r}\frac{\partial^2}{\partial r^2} r, \hat{L}^2\right] = \emptyset, \quad \left[\frac{\hat{L}^2}{r^2}, \hat{L}^2\right] = \emptyset \quad \& \quad \left[V(r), \hat{L}^2\right] = \emptyset$$

$\therefore$ $[\hat{H}, \hat{L}^2] = \emptyset$ for a central potential $V(r)$.

Consequences

- The stationary states will be in common with the angular momentum states.
- Angular momentum will be conserved:

$$\frac{d\langle \hat{L}^2\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H}, \hat{L}^2]\rangle = \emptyset.$$

In position space, this means that we can use separation of variables:

If $$\hat{H} = \frac{-\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right] + \frac{1}{2mr^2}\hat{L}^2 + V(r)$$

then $$\psi(r,\theta,\phi) = R(r)\underbrace{Y_\ell^m(\theta,\phi)}_{\substack{\text{Angular momentum}\\ \text{States}\\ = \text{Spherical Harmonics}}}$$ ← Separation of r from θ,ϕ

where $\hat{H}\psi = E\psi$

$$\Downarrow$$

$$\left\{\frac{-\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right] + \frac{1}{2mr^2}\hat{L}^2 + V(r)\right\}R(r)Y_\ell^m(\theta,\phi)$$

$$= E\,R(r)Y_\ell^m(\theta,\phi)$$

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

so $$\underbrace{\left\{\frac{-\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right] + \frac{\hbar^2\ell(\ell+1)}{2mr^2} + V(r)\right\}}_{\substack{\text{none of these operators acts}\\ \text{on } Y_\ell^m(\theta,\phi)\text{, so it}\\ \text{divides out:}}}R(r)Y_\ell^m(\theta,\phi) = E\,R(r)Y_\ell^m(\theta,\phi)$$

"Radial Equation for $R(r)$"

$$\boxed{\left(\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right) + \frac{\hbar^2\ell(\ell+1)}{2mr^2} + V(r)\right)R(r) = E\,R(r)}$$

To solve any central potential problem, we solve this equation for $R(r)$, then the full solution is

$$\psi(r,\theta,\phi) = R(r)\,Y_\ell^m(\theta,\phi).$$

Simplify by changing variables: $u(r) \equiv r\,R(r)$.

Then
$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]u(r) = E\,u(r).}$$

This equation has the same form as the usual 1D-Schroedinger Eq, if we consider $V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}$ to be an *effective potential*.

Simplest potential: ~~Spherical well:~~ $V(r) = \emptyset$ = free particle

$$\cancel{V(r) = \begin{cases} 0 & \text{for } r \le a \\ \infty & \text{for } r > a \end{cases}}$$

~~Then $u(r) = 0$ for $r > a \Rightarrow R(r) = 0$ for $r > a$~~

~~For $r \le a$, we have~~

$$\frac{d^2u}{dr^2} = \left(\frac{\ell(\ell+1)}{r^2} - k^2\right)u \quad , \quad k^2 \equiv \frac{2mE}{\hbar^2}$$

Solutions are $u(r) = A\,r\,j_\ell(kr)$, where

$j_\ell(x)$ = spherical Bessel function of order ℓ
$$= (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \left(\frac{\sin x}{x}\right)$$

$$j_0(kr) = \frac{\sin kr}{kr} \quad , \quad j_1(kr) = \frac{\sin(kr)}{(kr)^2} - \frac{\cos(kr)}{kr}$$

$\uparrow$ ℓ value $\qquad\qquad \uparrow$ ℓ value

Then $R(r) = \frac{u}{r} = A\,j_\ell(kr)$

Complete Solution is $\psi_{k\ell m}(r,\theta,\varphi) = j_\ell(kr)\,Y_\ell^m(\theta,\varphi)$

Energy eigenvalues are a continuum: $E = \frac{\hbar^2k^2}{2m}$

In Dirac notation we could say

let $\{|k\ell m\rangle\}$ be free particle states in spherical coordinates

Then measurement of E^2 gives $\frac{\hbar^2 k^2}{2m}$

or $$\hat{H}\,|k\ell m\rangle = \frac{\hbar^2 k}{2m}\,|k\ell m\rangle$$

& $$\hat{L}^2\,|k\ell m\rangle = \hbar^2 \ell(\ell+1)\,|k\ell m\rangle$$
$$\hat{L}_z\,|k\ell m\rangle = m\hbar\,|k\ell m\rangle$$

The spatial wavefunction is the overlap of this state with an eigenstate of r, θ, & ϕ:
$$\langle r\theta\phi\,|\,k\ell m\rangle = A\, j_\ell(kr)\, Y_\ell^m(\theta,\phi)$$