Orbital Angular Momentum

In classical mechanics, $\vec{L} = \vec{r} \times \vec{p}$.

In QM, we take $\vec{L} = -i\hbar\, \vec{r} \times \vec{\nabla}$, using $\vec{p} = -i\hbar\vec{\nabla}$

This implies the following commutators:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

These commutators say that we cannot determine more than one component of $\vec{L}$ at any time.

For example, the U.C. says
$$\Delta L_x \Delta L_y \geq \frac{\hbar}{2}\langle L_z\rangle.$$
$$\Delta L_y \Delta L_z \geq \frac{\hbar}{2}\langle L_x\rangle$$
$$\Delta L_z \Delta L_x \geq \frac{\hbar}{2}\langle L_y\rangle$$

The only way we can know all three components is when $\vec{L} = \emptyset \Rightarrow$ Then $L_x = L_y = L_z = \emptyset$.

On the other hand, we <u>can</u> determine L^2 <u>and any one component of $\vec{L}$</u>, because

$$[\hat{L}_z, \hat{L}^2] = \emptyset, \quad [\hat{L}_x, \hat{L}^2] = \emptyset, \quad [\hat{L}_y, \hat{L}^2] = \emptyset.$$
where $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

~~Because~~

Because these commutators are zero, $\hat{L}^2$ & $\hat{L}_z$ have ~~eigenfunctions~~ <u>eigenstates in common.</u>

(Just like $[\hat{H}_{free}, \hat{p}] = \emptyset$ implies that $\hat{H}_{free}$ and $\hat{p}$ have common eigenstates.)

Recall that with the SHO, the commutator relation for $[\hat{a}, \hat{a}^+]$ allowed us to determine the eigenvalues for $\hat{H}_{SHO}$ without solving the Schroedinger Eq. (we found that

$$E_n = \hbar\omega_0\left(n + \tfrac{1}{2}\right), n = 0, 1, 2, \ldots$$
$$\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle, \quad \hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

all came from $[\hat{a}, \hat{a}^+] = 1$ & $\hat{H}_{SHO} = \hbar\omega_0(\hat{a}^+\hat{a} + \tfrac{1}{2})$.

We can use a similar strategy to find the eigenvalues for L^2 & L_z.

First Define $\hat{L}_+ \equiv L_x + i\hat{L}_y$, $\hat{L}_- \equiv L_x - i\hat{L}_y$ } these will turn out to be similar to $\hat{a}$ & $\hat{a}^+$.

We can calculate from the definitions:

$$[\hat{L}_z, \hat{L}_+] = \hbar \hat{L}_+, \quad [\hat{L}_z, \hat{L}_-] = -\hbar\hat{L}_-$$

&

$$[\hat{L}^2, \hat{L}_\pm] = \emptyset, \quad [\hat{L}_+, \hat{L}_-] = 2\hbar L_z$$

One more useful expression: $\hat{L}^2 = \hat{L}_\pm \hat{L}_\mp + \hat{L}_z^2 \pm \hbar \hat{L}_z$

We want to find the eigenvalues for $\hat{L}^2$ & $\hat{L}_z$, using the base states that they have in common.

Let $\{|\ell m\rangle\}$ be the name for these common base states.

a label for the $\hat{L}^2$ eigenvalue. (ℓ)

a label for the L_z ~~eigenvalue~~ eigenvalues (m)

Then $\hat{L}_z |\ell m\rangle = (\text{eigenvalue for } L_z) |\ell m\rangle$

Let the eigenvalue be called $\hbar m$, because $\hbar$ has units of angular momentum. We know nothing about m except that it is unitless.

$$\hat{L}_z |\ell m\rangle \equiv \hbar m |\ell m\rangle \leftarrow \text{definition of } m.$$

We can show that m is either $\begin{cases} \text{an integer,} \\ \text{or} \\ \text{an odd multiple of } 1/2 \end{cases}$

Like this:

$$\hat{L}_z \left(\hat{L}_+ |\ell m\rangle \right) = \left(\hbar \hat{L}_+ + \hat{L}_+ \hat{L}_z \right) |\ell m\rangle$$

using $[L_z, L_+] = \hbar L_+$

$$= \left(\hbar \hat{L}_+ + L_+ (\hbar m) \right) |\ell m\rangle$$

$$= \hbar (m+1) \left(\hat{L}_+ |\ell m\rangle \right)$$

$\therefore$ $\hat{L}_+ |\ell m\rangle$ is an unnormalized eigenstate of $\hat{L}_z$, with eigenvalue $\hbar(m+1)$.

$\therefore$

(It turns out that the normalization constant is

$$\hat{L}_\pm |\ell m\rangle = \hbar \sqrt{\ell(\ell+1) - m(m \pm 1)} \; |\ell, m \pm 1\rangle$$

Similarly, $\hat{L}_z \left(\hat{L}_- |\ell m\rangle \right) = \hbar (m-1) \left(\hat{L}_- |\ell m\rangle \right)$,

so $\hat{L}_- |\ell m\rangle$ is an unnormalized eigenstate of $\hat{L}_z$ with eigenvalue $\hbar(m-1)$.

So the L_z eigenvalues are separated by one unit of $\hbar$: $\{ \ldots |\ell, m-2\rangle, |\ell, m-1\rangle, |\ell, m\rangle, |\ell, m+1\rangle \}$

eigenvalues $\hbar(m-2)$, $\hbar(m-1)$, $\hbar m$, $\hbar(m+1)$, ...

Using the $[L^2, L^+]$ commutator, we can also show that

- the eigenvalues for L^2 are $\hbar^2 \ell(\ell+1)$.

$$\Rightarrow \quad L^2 |\ell m\rangle = \hbar^2 \ell(\ell+1) |\ell m\rangle \leftarrow \text{e.v. for } L^2$$

- The allowed values of m run from $-\ell$ to ℓ:

$$m = \{-\ell, -\ell+1, \ldots, \ell-1, \ell\}.$$

- ℓ is either $\begin{cases} \text{an integer } (\ell = 0, 1, 2, 3, \ldots \\ \text{or half integer } (\ell = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots \end{cases}$

$\Rightarrow$ For orbital angular momentum, (Phys 401) ℓ is an integer

$\Rightarrow$ For spin angular momentum (Phys 402), ℓ is half-integer

So our orbital angular momentum states are

$\|\text{state}\rangle$	ℓ	L^2	m	L_z
$\|00\rangle$	0	$\emptyset$	$\emptyset$	
$\|1,-1\rangle, \|1,0\rangle, \|1,1\rangle$	1	$2\hbar^2$	$-1, 0, 1$	$-\hbar, \emptyset, \hbar$
$\|2,-2\rangle, \|2,-1\rangle, \|2,0\rangle, \|2,1\rangle, \|2,2\rangle$	2	$6\hbar^2$	$-2, -1, 0, 1, 2$	$-2\hbar, -\hbar, \emptyset, \hbar, 2\hbar$

These states have a property we call degeneracy. When multiple states have the same eigenvalue, we say they are degenerate. For example, $|1,-1\rangle, |1,0\rangle, |1,1\rangle$ all have $L^2 = 2\hbar^2$. We say they are degenerate in L^2. They are not degenerate with respect to L_z, however. L_z removes the degeneracy

~~Sometimes~~

Orbital Angular momentum

States are $\{|\ell m\rangle\}$, $\ell = 0, 1, 2, 3 \ldots$

$m = \{-\ell, -\ell+1, \ldots 0 \ldots \ell-1, \ell\}$

Eigenvalue Equations

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

$$\hat{L}_z |\ell m\rangle = \hbar m |\ell m\rangle$$

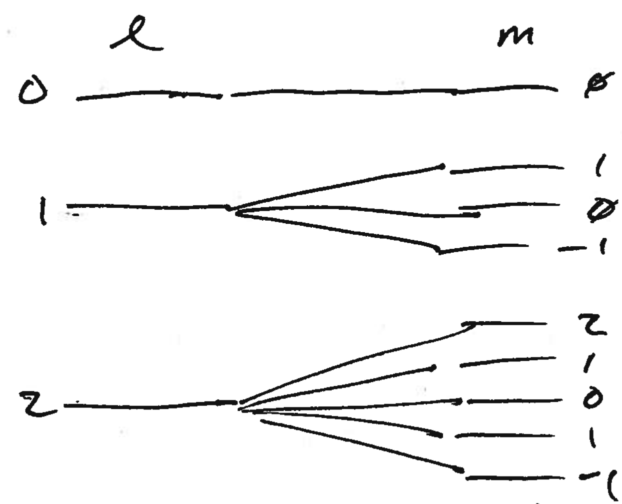
Ladder operators:

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

$$\hat{L}_\pm |\ell m\rangle = \hbar \sqrt{\ell(\ell+1) - m(m\pm1)}\ |\ell, m\pm1\rangle$$

promote or demote the L_z eigenv

These states are "degenerate" with respect to $\hat{L}^2$ $\Rightarrow$ multiple states have the same value of L^2:



These three states all have the same L^2. "triple degeneracy"

"Quintuple degeneracy"

Once L_z is specified (m), then the degeneracy is removed".

However, even when L_z is specified, L_x & L_y are still not known with absolute certainty, because L_x, L_y, & L_z do not commute. $\Rightarrow$ Therefore if we are in an eigenstate of L_z, then L_x & L_y are uncertain:

~~$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$, for example, so~~

~~$\Delta L_z \Delta L_x = \frac{\hbar}{2} \langle L_y \rangle$~~

$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$, for example, so

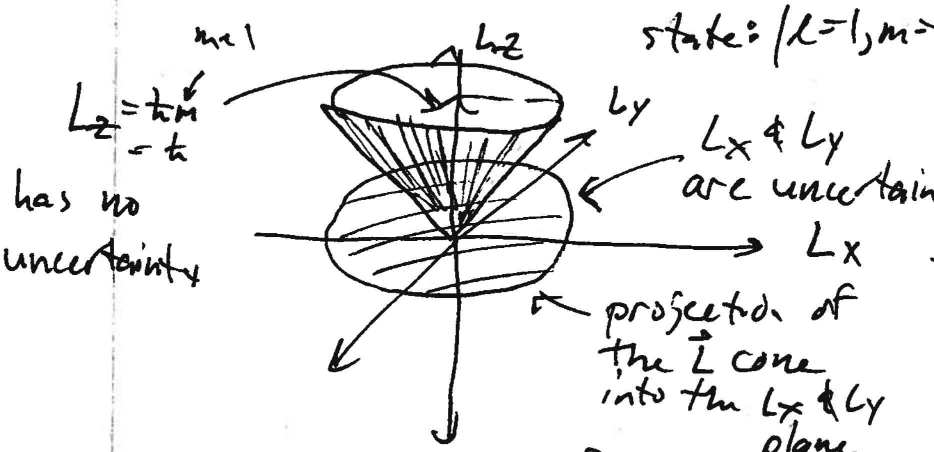
$$\Delta L_x \Delta L_y \geq \frac{\hbar}{2} |\langle L_z \rangle| \quad \text{Uncertainty Relation for } L_x \text{ \& } L_y.$$

Example

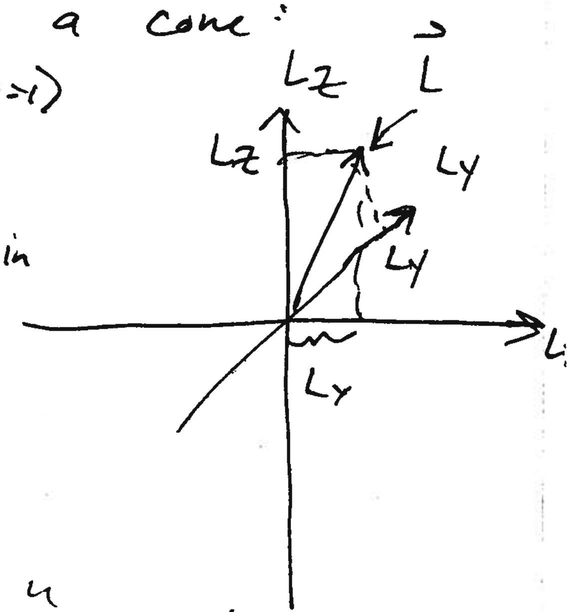
If $|\psi\rangle = |l=1, m=-1\rangle$, then $\langle L_z \rangle = -\hbar$.

Then $\Delta L_x \Delta L_y \geq \left| \frac{-\hbar^2}{2} \right| \geq \frac{\hbar^2}{2}$

We can "picture" these uncertainty relations by picturing the $\vec{L}$ vector as a cone:



"QM view of $\vec{L}$"

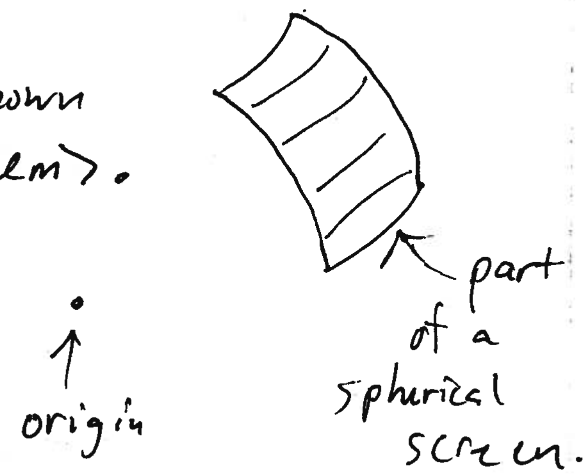


"Classical Mechanics view of L"

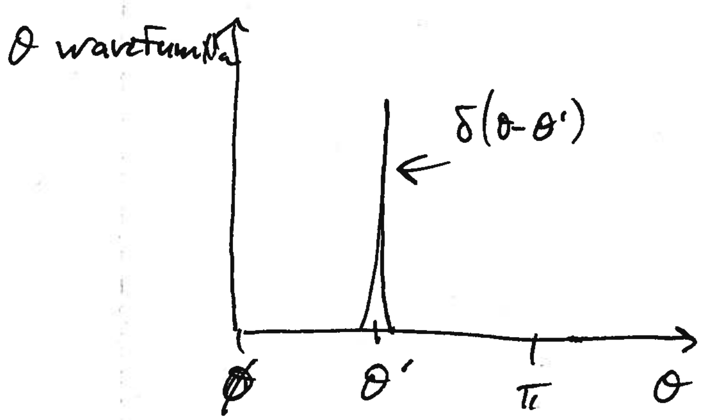
Spatial Wavefunctions for the $\{|lm\rangle\}$

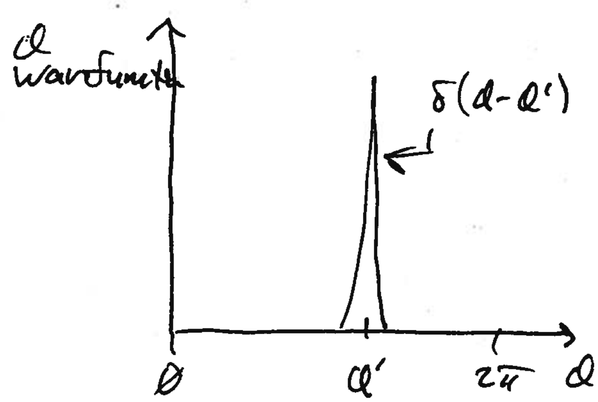
Suppose I have a position measuring device, which measures the θ & ϕ coordinates for a particle. For example, maybe it is a spherical scintillating screen:

Suppose that a particle is known to be in a particular state $|lm\rangle$. Where am I likely to find it on this screen? Where am I unlikely to find it?



We want the amplitude to ~~find~~ observe a particular θ & ϕ for the state $|lm\rangle$. So let $\underline{|\theta\phi\rangle}$ represent a state 100% localized at θ & ϕ:





Then the amplitude to observe $|lm\rangle$ at $|\theta\phi\rangle$ is written $\langle\theta\phi|lm\rangle$ ← QM amplitude to observe θ, ϕ in state $|lm\rangle$

Since θ & ϕ are continuous observables, this is a continuum of amplitudes.

$$\langle\theta,\phi|lm\rangle = \text{continuum of amplitudes} = Y_l^m(\theta,\phi)$$

some complex function

This is analogous to $\langle x|n\rangle = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$ for the 1D particle-in-a-box.

So the $Y_\ell^m(\theta,\phi)$ are the spatial wavefunctions for the $\{|lm\rangle\}$. They tell us where we are likely to find the particle, and where we are unlikely.

The Y_ℓ^m are not simple functions. Here is the complete expression:

"Spherical Harmonics" →
$$Y_\ell^m(\theta,\phi) = e^{im\phi}(-1)^m\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\,\underbrace{P_\ell^m(\cos\theta)}_{\text{"Associated Legendre Functions"}},$$

where
$$P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}\underbrace{P_\ell(x)}_{\text{"Legendre Functions"}},$$

and
$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$$

Explicitly,

$P_0(x) = 1$

$P_1(x) = x$

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

$\vdots$

$Y_0^0(\theta,\phi) = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$

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

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

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

$Y_2^2(\theta,\phi) = \frac{1}{4}\left(\frac{15}{2\pi}\right)^{\frac{1}{2}}\sin^2\theta\, e^{2i\phi}$

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

$\vdots$

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

  $\int_{4\pi} |Y_l^m|^2 \, d\Omega = 1$ 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:** $\sum_{l=0}^{\infty} \sum_{m=-l}^{l} |lm\rangle\langle lm| = 1$

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** $L_z = m\hbar$

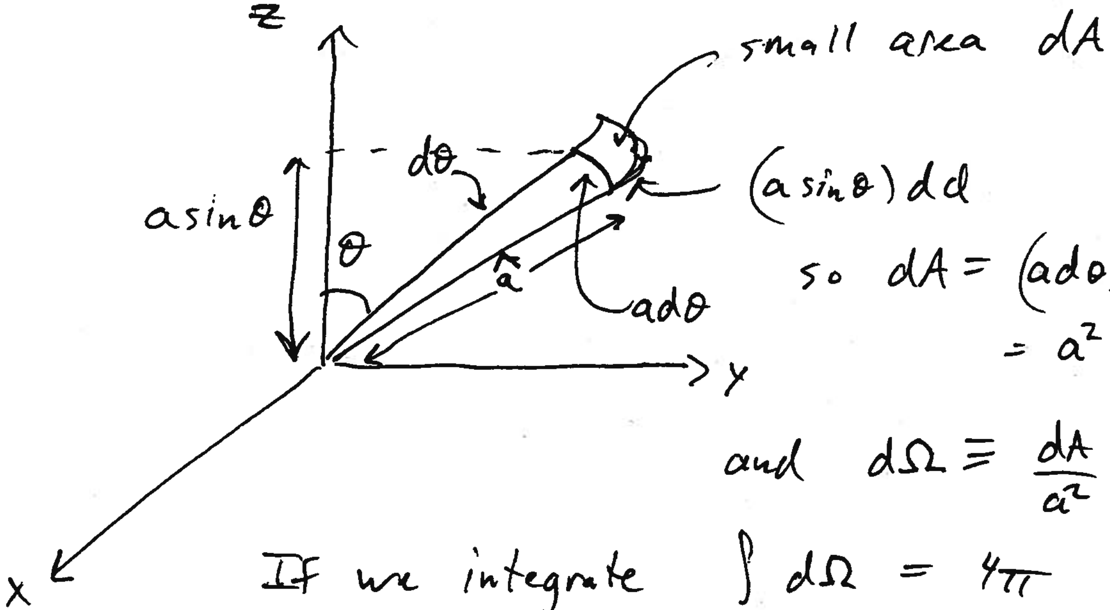
Example Suppose a particle is in state $|\ell m\rangle$.
What is the probability to find it near a particular θ & ϕ?

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

$Y_\ell^m(\theta,\phi)$ ← 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 $\displaystyle\int_{\substack{\text{closed} \\ \text{sphere}}} d\Omega = 4\pi$ ← 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 $\frac{\partial}{\partial\phi}\Phi(\phi) = mi\,\Phi(\phi)$

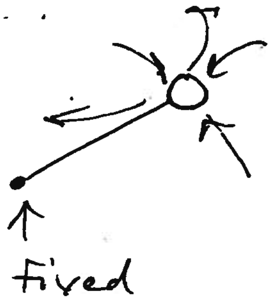
$$\therefore \quad \Phi(\phi) = e^{im\phi} \quad \leftarrow \text{Every spherical harmonic has this factor (when } m\neq 0).$$

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.

What can the angular momentum states describe?

An artificial example: Particle fixed to a rotating rod:



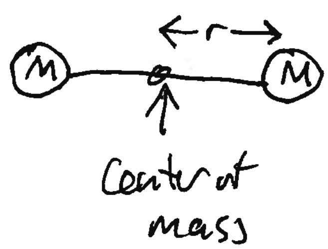
particle free to move in θ & ϕ, but fixed in (r).

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

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



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 $2\ell+1$.

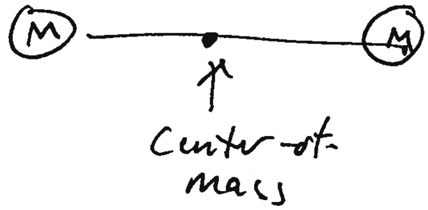
Rotational spectroscopy:

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:

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

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

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

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

← Energy eigenvalues depend on ℓ, but not m

Degeneracy

ℓ		"spectroscopic notation"	Energy	Degeneracy
0	=	"s" ← a name for $\ell = \emptyset$	$\emptyset$	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,

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

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

~~Show that~~

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:

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

then

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

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

$$\Downarrow$$

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

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

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

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

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

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

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

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 $\qquad$ $\uparrow$ 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: $E = \frac{\hbar^2 k^2}{2m}$

In Dirac notation we could say

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

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

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

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

$$\hat{L}_z\,|k\ell m\rangle = m\hbar\,|k\ell m\rangle$$

The spatial wavefunction is the overlap of this state with an eigenstate of r, θ, & ϕ:

$$\langle r\theta\phi\,|\,k\ell m\rangle = A\, j_\ell(kr)\, Y_\ell^m(\theta,\phi)$$

Generalized Time Dependent Schroedinger Eq:

$$i\hbar \frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle \leftarrow \text{Equation of motion for QM.}$$

In a continuous basis, this equation takes the form of a partial differential equation:

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t) \quad \text{in the position basis}$$

$$i\hbar \frac{\partial \Phi(k,t)}{\partial t} = \hat{H}\Phi(k,t) \quad \text{in the momentum basis}$$

In a discrete basis, the equation is a matrix equation:

$$i\hbar \frac{d}{dt} c_i(t) = \sum_j H_{ij} c_j(t) \leftarrow \text{Matrix Mechanics}$$

where $c_i(t) = \langle i|\psi\rangle$, $\hat{H}_{ij} = \langle i|\hat{H}|j\rangle$

Examples of Discrete bases:

- energy, for bound states $\{|n\rangle\}$
- two state system (NH_3): $|up\rangle$, $|down\rangle$
- Angular momentum: $\{|lm\rangle\}$.

In a discrete basis, the state is represented explicitly as a column vector or row vector:

$$|\psi\rangle \sim \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \qquad \langle\psi| \sim (a_1^*, a_2^*, a_3^* \dots)$$

Each component is the overlap of the state with a ~~basis~~ particular basis state: $a_n = \langle n|\psi\rangle$, for example

Interpretation: a_n is a QM amplitude: $P(E_n) = |a_n|^2$

or, if $b_n = \langle up|\psi\rangle$ then $P(up) = |b_n|^2$
or, if $c_n = \langle lm|\psi\rangle$ then $P(l,m) = |c_n|^2$.

In Matrix mechanics, the operators are matrices.
$\langle i|\hat{A}|j\rangle = A_{ij} \equiv$ matrix element in $\{|i\rangle\}$ basis

~~the~~ We can transform from one basis to another:
Let $U_{mi} = \langle m|i\rangle$, $\{|i\rangle\}$ is one basis
$\{|m\rangle\}$ is another basis.

Then we can transform a state vector:
$$|\psi'\rangle = U|\psi\rangle \text{ or } \cancel{b_m = \sum} \; b_m = \sum_i a_i U_{mi}$$
& we can transform a matrix:
$$F' = UFU^{-1} \text{ or } F_{mn} = \sum_{ij} U_{mi} F_{ij} U^{-1}_{jn}$$
An operator is a <u>diagonal</u> matrix when written in its own eigenbasis. Ex: Hamiltonian is diagonal in the energy basis:

$$H = \begin{pmatrix} E_1 & & & \emptyset \\ & E_2 & & \\ & & E_3 & \\ \emptyset & & & \ddots \end{pmatrix} \text{ in energy basis}$$

but ~~the~~ H is non-diagonal in ~~an~~ other basis:

Ex
$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} \leftarrow \text{two state Hamiltonian in up, down basis.}$$

"Rules" for 1D wave mechanics:

- Where $E > V(x)$, ψ oscillates $\Rightarrow \psi = Ae^{ikx} + Be^{-ikx}$
- Where $E < V(x)$, ψ decays $\Rightarrow \psi = Ae^{\kappa x} + Be^{-\kappa x}$
- $k = \frac{\sqrt{2m(E - V(x))}}{\hbar}$, $\kappa = \frac{\sqrt{-2m(E-V(x))}}{\hbar}$
- ψ & ψ' are continuous where V is finite
- For bound states we look for normalizable wavefunction
- For scattering states (continuous), we "live with" unnormalizable states.
- We calculate probability current with $J \equiv \frac{\hbar}{2mi}(\psi^*\psi' - \psi'^*\psi)$
- Ground states have a minimal number of wiggles
- If $V(x)$ is an even function of x, we look for even & odd eigenfunctions.
- Each excited state generally has one more x-axis crossing than the previous

Orbital Angular Momentum

$$[L_x, L_y] = i\hbar L_z \text{ , etc. but } [L_z, L^2] = \emptyset$$

$L_\pm \equiv L_x \pm iL_y$, then $L_\pm|\ell m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m\pm1)}\,|\ell, m\pm1\rangle$

$\ell = 0, 1, 2, 3, \ldots$

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

$L^2|\ell m\rangle = \hbar^2\ell(\ell+1)|\ell m\rangle$ & $L_z|\ell m\rangle = m\hbar|\ell m\rangle$

$\langle\theta\phi|\ell m\rangle = Y_\ell^m(\theta,\phi)$

$\langle\ell m|\ell' m'\rangle = \delta_{\ell\ell'}\delta_{mm'}$ or $\int_{4\pi} (Y_{\ell'}^{m'})^* (Y_\ell^m)^* d\Omega = \delta_{\ell\ell'}\delta_{mm'}$