Physics 492: Quantum Mechanics II
Lecture 8: Position Representation of Angular Momentum

We have seen in Lecture 7, that we can express the total kinetic energy as

$$\frac{\hat{\vec{P}}^2}{2m} = \frac{\hat{P}_r^2}{2m} + \frac{\hat{L}^2}{2m\hat{r}^2} \qquad \hat{P}_r = \text{radial momentum}, \quad \hat{\vec{L}} = \text{angular momentum}$$

In position representation:

$$\hat{\vec{P}} \doteq \frac{\hbar}{i}\vec{\nabla}, \quad \hat{P}^2 \doteq -\hbar^2\nabla^2 = -\hbar^2\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\ \ ) + \frac{1}{r^2\sin\theta}\left(\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\ \ \right)\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

where I have expressed the Laplacian is spherical coordinates

$$\Rightarrow \hat{P}_r^2 \doteq -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\ \ ), \quad \hat{L}^2 \doteq -\hbar^2\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\ \ \right)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

The angular momentum operator acts on the angular coordinates (θ, ϕ)
By transforming between Cartesian and spherical coordinates, we can show

$$\hat{L}_x = \hat{y}\hat{P}_z - \hat{z}\hat{P}_y \doteq \frac{\hbar}{i\sin\theta}\left[-\sin\theta\sin\phi\frac{\partial}{\partial\theta} - \cos\theta\cos\phi\frac{\partial}{\partial\phi}\right]$$

$$\hat{L}_y = \hat{z}\hat{P}_x - \hat{x}\hat{P}_z \doteq \frac{\hbar}{i\sin\theta}\left[+\sin\theta\cos\phi\frac{\partial}{\partial\theta} - \cos\theta\sin\phi\frac{\partial}{\partial\phi}\right]$$

$$\hat{L}_z = \hat{x}\hat{P}_y - \hat{y}\hat{P}_x \doteq \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

We seek the common eigenfunctions of $\hat{L}^2$ & $\hat{L}_z$, i.e. the position representation of $\underbrace{|l,m\rangle \doteq Y_{l,m}(\theta,\phi)}$. These are known as the <u>spherical harmonics</u>

We already have found the eigenfunctions of $\hat{L}_z \propto e^{im\phi}$. The operator $\hat{L}^2$ is almost separable in θ, ϕ, but not quite. But we can separate according to the ansatz:

$$Y_{l,m}(\theta,\phi) = \Theta_{l,m}(\theta)\, e^{im\phi}$$

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

$$\Rightarrow -\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Theta_{\ell,m}(\theta)\,e^{im\phi} = \ell(\ell+1)\,\Theta_{\ell,m}(\theta)\,e^{im\phi}$$

$$\overset{\circ}{=} \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_{\ell,m}}{d\theta}\right) + \left(\ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right)\Theta_{\ell,m}(\theta) = 0$$

Now we change coordinates: Let $\mu = \cos\theta$ $\Rightarrow$ $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta} = -\frac{\partial}{\partial(\cos\theta)} = -\frac{\partial}{\partial\mu}$

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

Let $\Theta_{\ell,m}(\theta) = P_\ell^m(\cos\theta)$

$$\Rightarrow \boxed{\frac{d}{d\mu}\left[(1-\mu^2)\frac{dP_\ell^m}{d\mu}\right] + \left(\ell(\ell+1) - \frac{m^2}{1-\mu^2}\right)P_\ell^m(\mu) = 0}$$

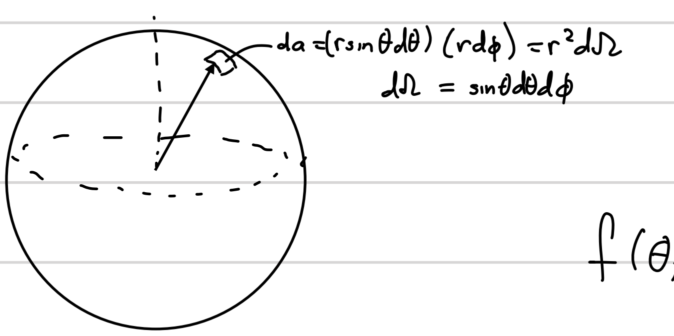
This is known as <u>Legendre's equations</u> and the solutions are the associated <u>Legendre polynomials</u>

$$\Rightarrow \boxed{Y_{\ell,m}(\theta,\phi) = \underbrace{N_{\ell,m}}_{\text{Normalization}}\, P_\ell^m(\cos\theta)\, e^{im\phi}}$$

<u>Boundary conditions require</u> $\ell = 0,1,2\ldots$ $\quad -\ell \le m \le \ell$ integer steps

The normalization is $\langle \ell,m|\ell m\rangle = \int_{4\pi} d\Omega\, |Y_{\ell,m}(\theta,\phi)|^2 = 1$

where $\underbrace{\int_{4\pi} d\Omega}_{\text{solid angle}} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta = \int_0^{2\pi} d\phi \int_{-1}^{1} d\mu \quad (\mu = \cos\theta)$



The spherical harmonics form a complete set of function over the surface of a sphere for a fixed r.

$$f(\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} C_{\ell,m}\, Y_{\ell,m}(\theta,\phi)$$

$$C_{\ell,m} = \langle \ell,m|f\rangle = \int d\Omega\, Y^*_{\ell,m}(\theta,\phi)\, f(\theta,\phi)$$

We are familiar with such expansions as the multipole expansions of a charge distribution.

Table of first few spherical harmonics

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1,\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi} = \mp\sqrt{\frac{3}{8\pi}}\left(\frac{x\pm iy}{r}\right)$$

$$Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\left(\frac{z}{r}\right)$$

$$Y_{2,\pm2}(\theta,\phi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}}\left(\frac{x\pm iy}{r}\right)^2$$

$$Y_{2,\pm1}(\theta,\phi) = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\phi} = \mp\sqrt{\frac{15}{8\pi}}\left(\frac{x\pm iy}{r}\right)\left(\frac{z}{r}\right)$$

$$Y_{2,0}(\theta,\phi) = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right) = \sqrt{\frac{5}{16\pi}}\left(3\left(\frac{z}{r}\right)^2 - 1\right)$$

Here I used $\frac{x\pm iy}{r} = \sin\theta\, e^{\pm i\phi}$, $\frac{z}{r} = \cos\theta$, the so-called "spherical basis"

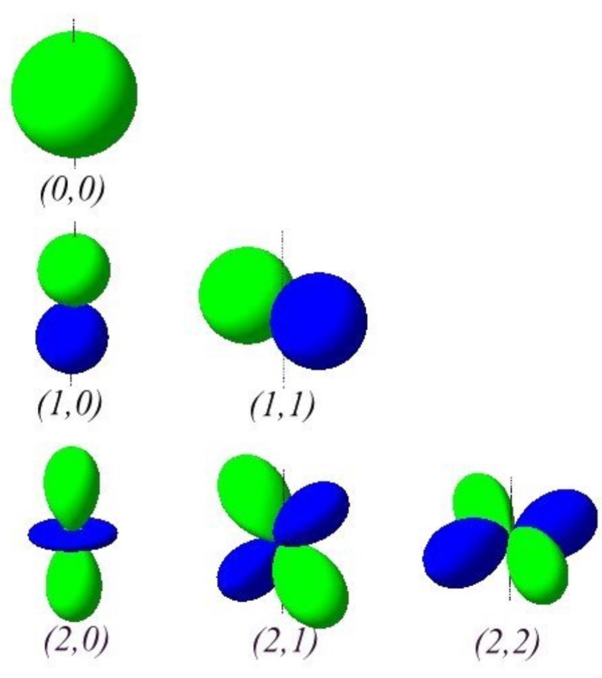
The $Y_{l,m}$'s are l^{th} order polynomials in these components that are eigenfunctions of rotation around the z-axis, with eigenvalue m.

Graphically, we represent the spherical harmonics as a "polar plot"

$l=0$: "s orbital"

$l=1$: "p orbital"

$l=2$: "d orbital"



Here we plotted the real part only. The $Y_{l,0}$ are real.

$$\mathrm{Re}(Y_{l,m}) = \frac{Y_{l,m} + (-1)^m Y_{l,-m}}{2}$$

Since $Y^*_{l,m} = (-1)^m Y_{l,-m}$

The label of "s, p, d" for the orbitals is ancient history, relating to the description of spectral lines: s = sharp, p = principle, d = diffuse. But this arcane notation persists today, so we're stuck with it..

Let us now return to the solution to the Schrödinger equation (time independent) with spherical symmetry. We can express the Hamiltonian as

$$\hat{H} = \frac{\hat{P}_r^2}{2m} + \frac{\hat{L}^2}{2m\hat{r}^2} + V(\hat{r})$$

We seek the solutions to $\hat{H}|\psi\rangle = E|\psi\rangle$

A C.S.C.O. is $\{\hat{H}, \hat{L}^2, \hat{L}_z\}$. Thus we can completely specify an eigenvectors with eigenvalues $|E, l, m\rangle$. We will particular be interested is bound states, in which case E will be discrete.

In position representation is spherical coordinates

$$\frac{-\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(r\psi(r,\theta,\phi)\right) + \frac{\hat{L}^2_{\theta\phi}\psi(r,\theta,\phi)}{2mr^2} = E\psi(r,\theta,\phi)$$

Here, I have not written out the differential operator for $\hat{L}^2$ but emphasize that $\hat{L}^2_{\theta,\phi}$ is an operator that acts only of θ + ϕ coordinates.

This problem isn't completely separable in angular and radial motion because of the dependence of r in the angular components of kinetic energy. However, as in the $Y_{l,m}$'s we can separate with an ansatz

$$\psi(r,\theta,\phi) = \underbrace{R_{E,l}(r)}_{\text{Radial wave function}}\, Y_{lm}(\theta,\phi)$$

$\rightarrow$ eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}\left(rR_{E,l}(r)\right) + \frac{\hbar^2 l(l+1)}{2mr^2}R_{E,l}(r) + V(r)R_{E,l}(r) = E\,R_{E,l}(r)$$

$$\boxed{\begin{aligned} &\Rightarrow -\frac{d^2}{dr^2}\left(rR_{El}(r)\right) + \left(V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right)\left(rR_{El}(r)\right) = E\left(rR_{El}(r)\right) \\ &-\frac{d^2}{dr^2}u_{E,l}(r) + \left(V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right)u_{El}(r) = E\,u_{El}(r) \end{aligned}}$$

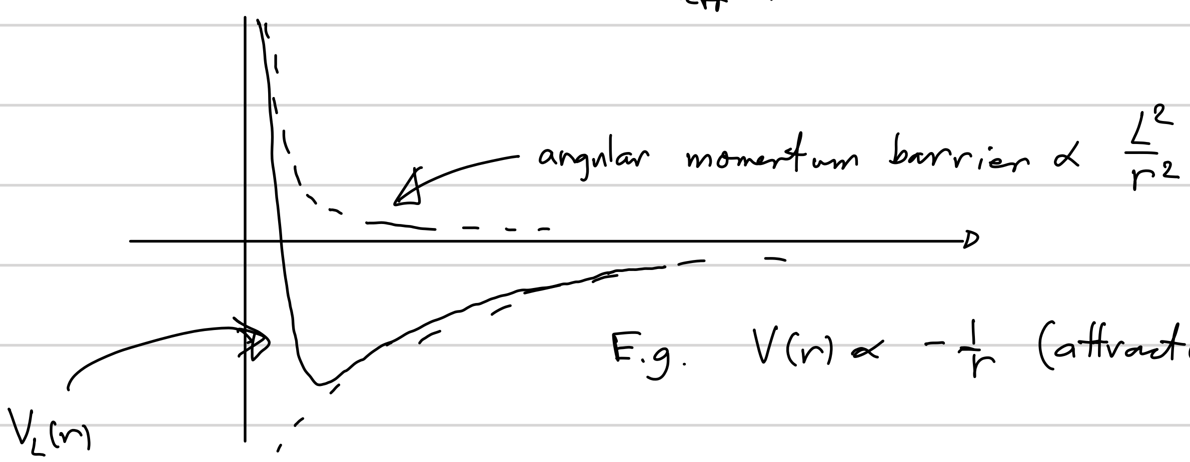
This equation is known as the "radial equation", and $u_{El}(r) = r\,R_{El}(r)$ is known as the "reduced" radial wavefunction. The reduced radial wave function satisfies a 1D Schrodinger equation with an effective potential

$$V_{eff}^{(\ell)}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}.$$

The second term is the "angular momentum barrier"

Recall from classical dynamics, in a central potential

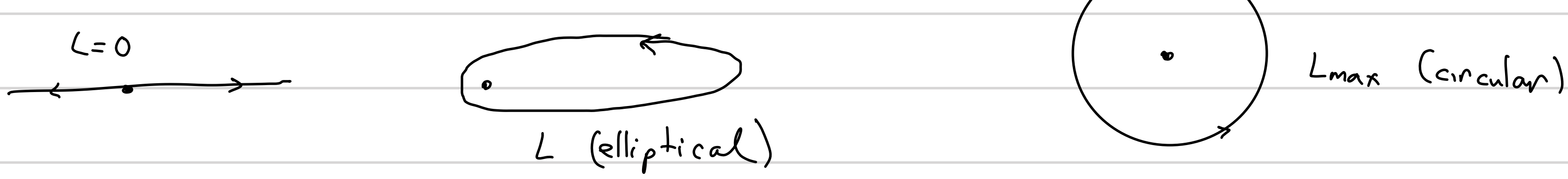
$$H = \frac{p_r^2}{2m} + \underbrace{\frac{L^2}{2mr^2} + V(r)}_{V_{eff}^{L}(r)}. \qquad |\vec{L}| \text{ is conserveved}$$



E.g. $V(r) \propto -\frac{1}{r}$ (attractive potential

The angular momentum barrier keeps the particle from "penetrating" to the origin.

E.g. Keppler orbits:



<u>Boundary conditions and the radial equation</u>

The radial wave function is defined only on the <u>half-line</u>

$$0 \leq r < \infty$$

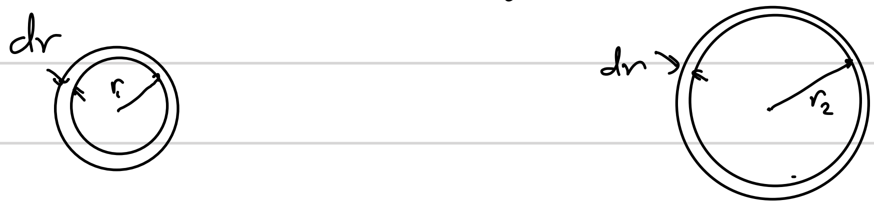
The wave function normalization $\int d^3r \, |\psi_{E,\ell,m}(r,\theta,\phi)|^2 = \int_0^\infty dr \, r^2 |R_{E,\ell}(r)| \underbrace{\int d\Omega \, |Y_{\ell,m}(\theta,\phi)|^2}_{=1}$

$$\Rightarrow \int_0^\infty dr \, r^2 |R_{E,\ell}(r)|^2 = \int_0^\infty dr \, |u_{E\ell}(r)|^2 = 1$$

Thus, the probability to find the particle between radial r an $r+dr$ is

$$P = r^2 |R_{E,\ell}(r)|^2 \, dr = |u_{E\ell}(r)|^2 \, dr$$

The factor r^2 is geometric. It represents how the volume of a shell grows as a function of r.



$r_2 > r_1$

As $r \to 0$ the probabity to find the particle must shrink to <u>zero</u>.
Thus, we have an extra boundary condition: $r^2 |R(r)|^2 \to 0$ as $r \to 0$
$\Rightarrow$ $|R_{E\ell}(r)|$ cannot blow up faster than $\frac{1}{r}$ as $r \to 0$, or equivalently, $|u_{E\ell}(r)| \to 0$ at least like r as $r \to 0$. The the 1D radial equation for $u_{E\ell}(r)$ has extra "hard wall" boundary condition at $r = 0$

<u>Degeneracy and spherical symmetry in quantum mechanics</u>

In general, the energy depends explicitly on ℓ, with higher ℓ yielding higher energy. However, the energy is independent of $\hat{L}_z$. We know this because there is spherical symmetry — <u>no axis is special</u>! Thus for spherical symmetry there is always <u>at least</u> a $2\ell+1$ degenercal is the energy levels.
The energies are independent of the m quantum number.

Now, as we will see, there can be additional degeneracies that are "accidental" or due to addition symmetries. The hydrogen atom is one such case due to the special nature of the Coulomb potential, as we will see