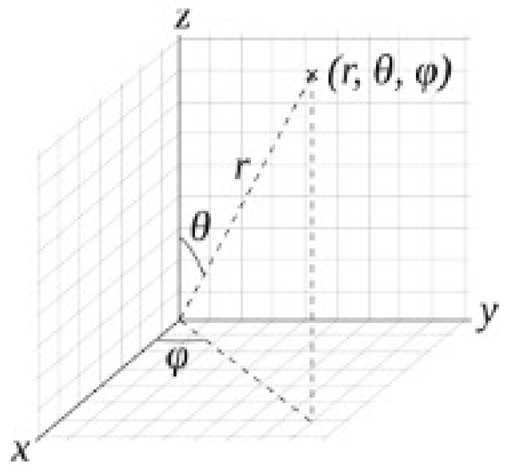
Orbital Angular Momentum in 3D: Part 2, Position Basis, Sph. Harmonics

Spherical Polar Coordinates



$$x = r\cos\phi\,\sin\theta \qquad\qquad r = (x^2+y^2+z^2)^{1/2}$$
$$y = r\sin\phi\,\sin\theta \quad \Rightarrow \quad \phi = \tan^{-1}(y/x)$$
$$z = r\cos\theta \qquad\qquad \theta = \tan^{-1}\left(\frac{\sqrt{x^2+y^2}}{z}\right)$$

Eigenstates of Orbital Ang. Mom.: $\hat{L}_z |l,m\rangle = \hbar m|l,m\rangle$; $\hat{L}^2 |l,m\rangle = \hbar^2 l(l+1)|l,m\rangle$; $-l \le m \le l$

Lec. 15 : $\hat{L}_z \Rightarrow -i\hbar(x\partial_y - y\partial_x) = -i\hbar\,\partial_\phi$; $-i\hbar\partial_\phi\, e^{im\phi} = m\hbar\, e^{im\phi}$, $m \in \mathbb{Z}$ (Periodic Boundary Cond.)

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \Rightarrow -i\hbar\left[(y\partial_z - z\partial_y) \pm i(z\partial_x - x\partial_z)\right]$$

$$= -i\hbar\left[\mp i(x \pm iy)\partial_z \pm iz(\partial_x \pm i\partial_y)\right]$$

We need to convert these diff. operators to Spherical Polar Coordinates

$$\frac{\partial}{\partial x_i} = \frac{\partial r}{\partial x_i}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x_i}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x_i}\frac{\partial}{\partial \phi}, \quad x_i \in \{x, y, z\}$$

Results (HW!):

① $$\partial_x = \cos\phi\left[\sin\theta\,\partial_r + \frac{1}{r}\cos\theta\,\partial_\theta\right] - \frac{1}{r\sin\theta}\sin\phi\,\partial_\phi$$

② $$\partial_y = \sin\phi\left[\sin\theta\,\partial_r + \frac{1}{r}\cos\theta\,\partial_\theta\right] + \frac{1}{r\sin\theta}\cos\phi\,\partial_\phi$$

③ $$\partial_z = \cos\theta\,\partial_r - \frac{\sin\theta}{r}\partial_\theta$$

$$\Rightarrow \partial_x \pm i\partial_y = e^{\pm i\phi}\left[\sin\theta\,\partial_r + \frac{1}{r}\cos\theta\,\partial_\theta\right] \pm \frac{i}{r\sin\theta} e^{\pm i\phi}\partial_\phi$$

$$\hat{L}_\pm \Rightarrow \cancel{-i}\hbar\left[\mp\cancel{i}\, r\sin\theta\, e^{\pm i\phi}\left(\cancel{\cos\theta\,\partial_r} - \frac{\sin\theta}{r}\partial_\theta\right) \pm \cancel{i}\, r\cos\theta\, e^{\pm i\phi}\left(\cancel{\sin\theta\,\partial_r} + \frac{1}{r}\cos\theta\,\partial_\theta\right) + i\frac{\cancel{r}\cos\theta}{\cancel{r}\sin\theta}e^{\pm i\phi}\partial_\phi\right]$$

$$= \hbar e^{\pm i\phi}\left[\pm\sin^2\theta\,\partial_\theta \pm \cos^2\theta\,\partial_\theta + i\cot\theta\,\partial_\phi\right]$$

FINALLY,

ORBITAL ANGULAR MOMENTUM GENERATORS — SPH. POLAR

$$\hat{L}_\pm \Rightarrow \hbar e^{\pm i\phi}\left[i\cot\theta\,\partial_\phi \pm \partial_\theta\right] \quad ; \quad \hat{L}_z \Rightarrow -i\hbar\partial_\phi$$

CHECK: ① $[\hat{L}_z, \hat{L}_\pm] = \left[-i\hbar\partial_\phi, \hbar e^{\pm i\phi}(i\cot\theta\,\partial_\phi \pm \partial_\theta)\right]$

$$= \pm\hbar\hat{L}_\pm \checkmark$$

② $[\hat{L}_+, \hat{L}_-] = 2\hbar\hat{L}_z$ (HW !)

GEN. REPRESENTATION THEORY (LEC. 21)

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

$$\Downarrow$$

$-\ell \le m \le \ell$ ($2\ell+1$ STATES) ; $-i\hbar\frac{\partial}{\partial\phi}\psi_{\ell m}(r,\theta,\phi) = m\hbar\,\psi_{\ell m}(r,\theta,\phi)$

LEC. 15, P.4: PERIODIC BOUNDARY CONDITIONS

$$\Downarrow$$

$$\psi_{\ell m}(r,\theta,\phi) = \psi_{\ell m}(r,\theta)\, e^{im\phi} \; ; \; m \in \mathbb{Z}$$

- $\ell \equiv$ ANGULAR MOMENTUM QUANTUM NUMBER
- $m \equiv$ MAGNETIC QUANTUM NUMBER

$\therefore\; \ell \in \{0, 1, 2, 3, \ldots\}$

HALF-INTEGER ℓ (OR m) EXCLUDED FOR ORBITAL ANG. MOMENTUM

CONSIDER A 3D WAVEFUNCTION THAT CORRESPONDS TO A HIGHEST WEIGHT STATE

HWS : $m = \ell$

$$\langle\vec{r}|\ell,\ell\rangle \equiv U_{\ell\ell}(r)\,\psi_{\ell\ell}(\theta)\,e^{i\ell\phi} \; ; \; U_{\ell\ell}(r) = \text{RADIAL W.F.} — \underline{\text{INDEPT.}}$$

OF ORBITAL ANGULAR MOMENTUM

(I.E., DOESN'T CHANGE UNDER ROTATIONS)

$$\hat{L}_+ |\ell\ell\rangle = 0 \Rightarrow \hbar\, e^{+i\phi}\left[i\cot\theta\,\partial_\phi + \partial_\theta\right]\psi_{\ell\ell}(\theta)\, e^{i\ell\phi} = 0$$

$$\left[-\ell\cot\theta + \frac{d}{d\theta}\right]\psi_{\ell\ell}(\theta) = 0 \quad \text{or} \quad \frac{d\psi_{\ell\ell}}{\psi_{\ell\ell}} = \ell\cot\theta\, d\theta$$

$$\int \frac{d\psi_{\ell\ell}}{\psi_{\ell\ell}} = \ln\left[\frac{\psi_{\ell\ell}(\theta)}{\underset{\uparrow}{c}}\right] = \ell\int\cot\theta\, d\theta = \ell\ln(\sin\theta)$$

INTEGRATION CONST.

$$\therefore \quad \psi_{\ell\ell}(\theta) = c\,(\sin\theta)^\ell \quad ; \quad \langle\vec{r}|\ell\ell\rangle = u_{\ell\ell}(r)\,(\sin\theta)^\ell\, e^{i\ell\phi}$$

- CAN CHECK:

$$\hat{L}^2 (\sin\theta)^\ell e^{i\ell\phi} = \hbar^2\ell(\ell+1)\cdot(\sin\theta)^\ell e^{i\ell\phi}$$

(HW!)

; LEC 23: $\vec{\nabla}^2\psi = \left[\frac{1}{r^2}\partial_r(r^2\partial_r\psi) - \frac{1}{r^2\hbar^2}\hat{L}^2\psi\right]$

ANGULAR PART OF SPHERICAL LAPLACIAN IS $\propto \hat{L}^2$!

DEFINE: HIGHEST WEIGHT SPHERICAL HARMONIC

$\equiv$ ANGULAR PART OF 3D WAVE FUNCTION WITH TOTAL ANG. MOMENTUM ℓ, $\hat{L}_z$ EIGENVALUE IS $m\hbar = \ell\cdot\hbar$ (MAXIMUM)

$$Y_{\ell,\ell}(\theta,\phi) \equiv A_{\ell\ell}\,(\sin\theta)^\ell\, e^{i\ell\phi} \quad ; \quad A_{\ell\ell} = \underbrace{(-1)^\ell}_{\text{CONVENTION}}\underbrace{\left[\frac{(2\ell+1)!}{4\pi}\right]^{1/2}\cdot\frac{1}{2^\ell\,\ell!}}_{\text{NORMALIZES } \langle\ell\ell|\ell\ell\rangle = 1 \text{ OVER THE UNIT SPHERE}}$$

WE CAN VIEW THIS AS A NORMALIZED WAVE FUNCTION OVER THE UNIT SPHERE

$$Y_{\ell\ell}(\theta,\phi) = \langle\theta\phi|\ell\ell\rangle$$

$$\langle\ell\ell|\ell\ell\rangle = \underbrace{\int_0^{2\pi} d\phi\int_0^\pi d\theta\,\sin\theta}_{\text{USUAL AREA MEASURE FOR UNIT SPHERE}}\;\langle\ell\ell|\theta\phi\rangle\langle\theta\phi|\ell\ell\rangle = A_{\ell\ell}^2\int_0^{2\pi}d\phi\int_0^\pi d\theta\,\sin\theta\,(\sin\theta)^{2\ell}$$

$$\int_0^{2\pi}d\phi\int_0^\pi d\theta\,\sin\theta = 4\pi \checkmark$$

$$= 2\pi A_{\ell\ell}^2\int_0^\pi d\theta\,(\sin\theta)^{2\ell+1}$$

$$= 1$$ (CLAIM — e.g., MATHEMATICA)

OTHER $|\ell, m\rangle$ WITH $m < \ell$ (DESCENDANT STATES)?

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

$\Rightarrow$ THUS $\quad |\ell,\ell-1\rangle = \dfrac{1}{C^{(-)}_{\ell\ell}}\,\hat{L}_-|\ell\ell\rangle = \dfrac{1}{\hbar\sqrt{\ell(\cancel{\ell}+1) - \cancel{\ell^2}+\ell}}\,\hat{L}_-|\ell\ell\rangle = \dfrac{1}{\hbar\sqrt{2\ell}}\,\hat{L}_-|\ell\ell\rangle$

$$\therefore\; Y_{\ell,\ell-1}(\theta,\phi) = \langle\theta\phi|\ell\,\ell-1\rangle = \frac{A_{\ell\ell}}{\cancel{\hbar}\sqrt{2\ell}}\cdot\cancel{\hbar}\,e^{-i\phi}\underbrace{\left[i\cot\theta\,\partial_\phi - \partial_\theta\right](\sin\theta)^{\ell}\,e^{i\ell\phi}}_{= -2\ell\,\cos\theta\,(\sin\theta)^{\ell-1}\,e^{i\ell\phi}}$$

$$= -\sqrt{2\ell}\,A_{\ell\ell}\,\cos\theta\cdot(\sin\theta)^{\ell-1}\,e^{i(\ell-1)\phi}$$

CAN KEEP GOING...

RESULT: FOR $m \geq 0$,

$$Y_{\ell m}(\theta,\phi) = A_{\ell\ell}\left[\frac{(\ell+m)!}{(2\ell)!\,(\ell-m)!}\right]^{1/2} e^{im\phi}\cdot(\sin\theta)^{-m}\,\frac{d^{\ell-m}}{d(\cos\theta)^{\ell-m}}\,(\sin\theta)^{2\ell}$$

"SPHERICAL HARMONICS"

FOR NEGATIVE MAGNETIC QUANTUM NUMBERS: $\quad Y_{\ell,-m}(\theta,\phi) = (-1)^m\left(Y_{\ell m}(\theta,\phi)\right)^*$

ORTHOGONALITY CONDITION:

$$\langle\ell m|\ell' m'\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta\,\sin\theta\,\langle\ell m|\theta\phi\rangle\langle\theta\phi|\ell' m'\rangle$$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta\,\sin\theta\; Y^*_{\ell m}(\theta,\phi)\,Y_{\ell' m'}(\theta,\phi) = \delta_{\ell\ell'}\,\delta_{m,m'}$$

AS EXPECTED FOR ANG. MOM. EIGENKETS WITH DIFFERENT QUANTUM NUMBERS.

We can expand a generic state $\psi_{(\vec{r})} = \psi_{(r,\theta,\phi)}$ in an infinite series including all spherical harmonics, with (ℓ,m)-dependent coefficients:

$$\psi_{(r,\theta,\phi)} \equiv \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} C_{\ell m}(r)\, Y_{\ell m}(\theta,\phi) \;;$$

$$C_{\ell m}(r) = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\; Y^*_{\ell m}(\theta,\phi)\, \psi_{(r,\theta,\phi)}$$ using orthonormality of $\{|\ell,m\rangle\}$

State Normalization

$$\langle\psi|\psi\rangle = \int d^3\vec{r}\; \psi^*_{(\vec{r})}\, \psi_{(\vec{r})} = \int_0^{\infty} r^2 dr \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\; \psi^*_{(r,\theta,\phi)}\, \psi_{(r,\theta,\phi)}$$

$$= \int_0^{\infty} r^2 dr \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \sum_{\ell,m} \sum_{\ell',m'} C^*_{\ell m}(r)\, C_{\ell' m'}(r)\, Y^*_{\ell m}(\theta,\phi)\, Y_{\ell' m'}(\theta,\phi)$$

$$= \sum_{\ell,m} \int_0^{\infty} r^2 dr\, |C_{\ell m}(r)|^2$$

Explicit Formulae: Low-ℓ Spherical Harmonics

$\ell = 0$ ("s-wave")

① $Y_{00}(\theta,\phi) = \dfrac{1}{\sqrt{4\pi}}$ Constant, spherically symmetric $\Rightarrow$ invariant under rotations (as expected for $\ell = 0$)

$\ell = 1$ ("p-wave")

② $Y_{11}(\theta,\phi) = -\left(\dfrac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta\, e^{i\phi}$

③ $Y_{10}(\theta,\phi) = \left(\dfrac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta$

④ $Y_{1-1}(\theta,\phi) = \left(\dfrac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta\, e^{-i\phi}$

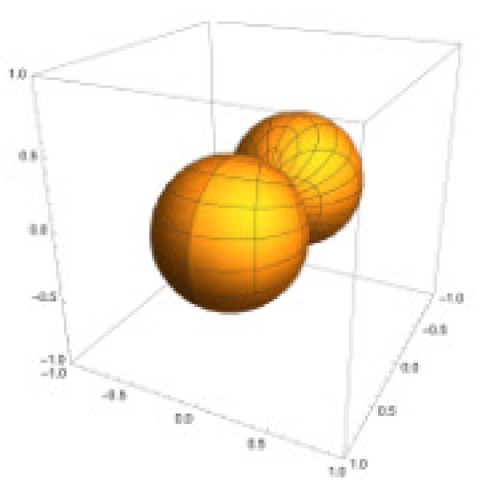
Note: Y_{11}, Y_{1-1} are complex-valued; $|Y_{1\pm1}|^2(\theta,\phi) = |Y_{1\pm1}|^2(\theta)$, Indept. of ϕ

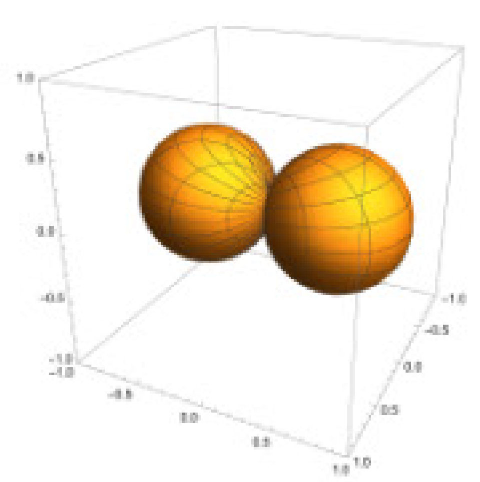
$\Rightarrow$ Probability Distribution $|Y_{\ell m}|^2(\theta)$ is <u>Axially Symmetric</u> for <u>any</u> (ℓ, m),
i.e. Invariant under Rigid Z-Rotation $\phi \to \phi + \phi_0$

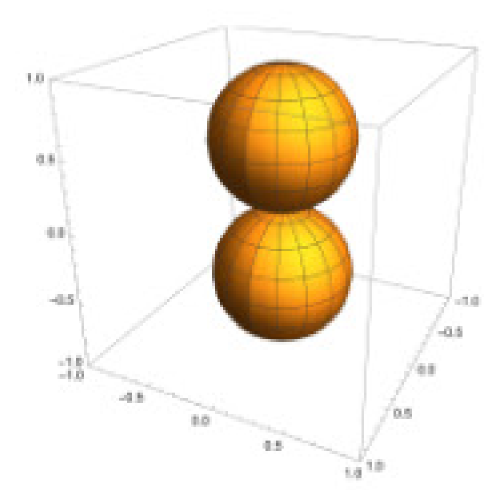
- This is because $Y_{\ell m}(\theta,\phi)$'s are **Eigenstates of** $\hat{R}_z(\phi_0) = e^{-i\frac{\hat{L}_z}{\hbar}\phi_0}$

$$e^{-i\frac{\hat{L}_z}{\hbar}\phi_0} Y_{\ell m}(\theta,\phi) = \underbrace{e^{-im\phi_0}}_{\text{E'value of unitary Rot. Operator, Pure Phase}} Y_{\ell m}(\theta,\phi) = Y_{\ell m}(\theta, \phi - \phi_0)$$

What is the Connection to $P_{x,y}$ Orbitals in Chemistry?

P_x : 

P_y : 

P_z : 

$|\psi_{P_x}|^2(\theta,\phi)$, $|\psi_{P_y}|^2(\theta,\phi)$ <u>**NOT**</u> Axially Symmetric!

Answer: Basis Change, as in Spin-1 (Lec. <u>10</u>)

- $|P_x\rangle, |P_y\rangle, |P_z\rangle \longleftrightarrow |\vec{n}_x\rangle, |\vec{n}_y\rangle, |\vec{n}_z\rangle$ "Real" unit vectors along x, y, z.

- $|Y_{11}\rangle, |Y_{10}\rangle, |Y_{1-1}\rangle \longleftrightarrow^{*} \frac{|\vec{n}_x\rangle + i|\vec{n}_y\rangle}{\sqrt{2}}, |\vec{n}_z\rangle, \frac{|\vec{n}_x\rangle - i|\vec{n}_y\rangle}{\sqrt{2}}$ $\hat{L}_z$ E'states.

* up to overall phase

Explicitly,

$$\frac{-Y_{11} + Y_{1-1}}{\sqrt{2}} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\phi \sin\theta = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{x}{r}$$

$$\frac{i(Y_{11} + Y_{1-1})}{\sqrt{2}} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \sin\phi \sin\theta = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{y}{r}$$

$$Y_{10} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{z}{r}$$

$\ell = 2$ ("d-wave")

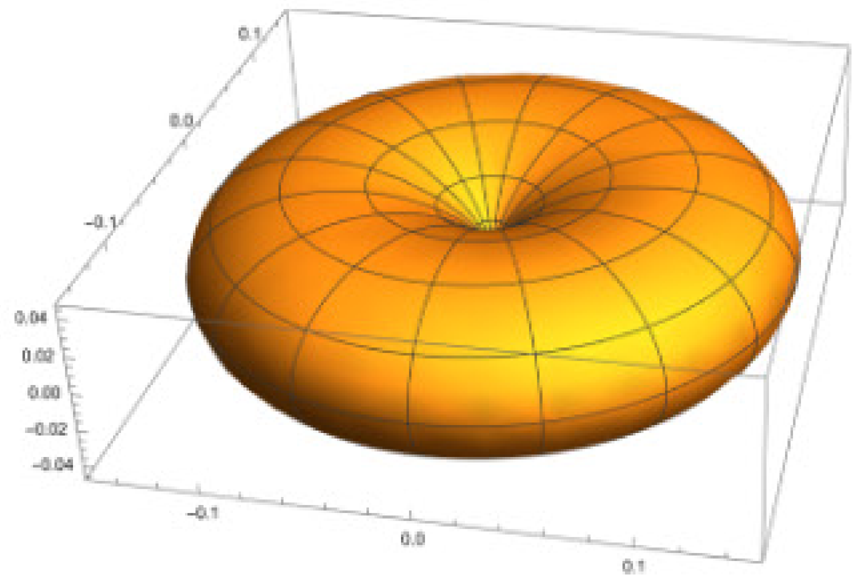
(5.) $Y_{2,\pm 2}(\theta,\phi) = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta \; e^{\pm 2i\phi}$

(6.) $Y_{2,\pm 1}(\theta,\phi) = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta \; e^{\pm i\phi}$

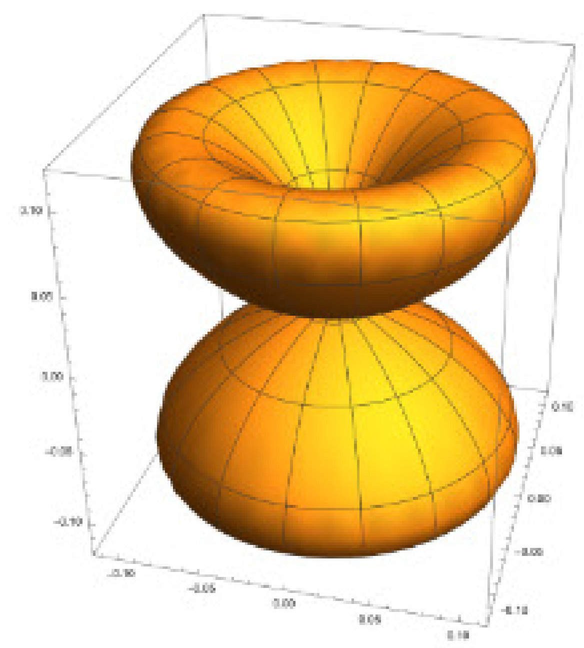
(7.) $Y_{2,0}(\theta,\phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$

VIA SphericalPlot3D[...] IN MATHEMATICA:

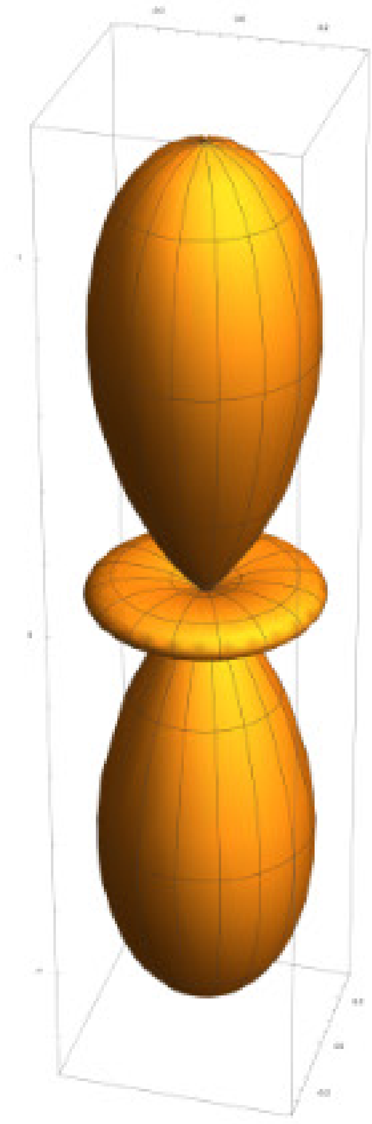
$|Y_{2\pm2}|^2(\theta)$



$|Y_{2\pm1}|^2(\theta)$



$|Y_{20}|^2(\theta)$



- $|Y_{2\pm2}|^2$ CONCENTRATES PROBABILITY IN THE XY PLANE, AS EXPECTED CLASSICALLY FOR A STATE ORBITING AROUND THE ORIGIN $x = y = z = 0$ WITH HIGH L_z ANGULAR MOMENTUM

- $|Y_{20}|^2$ CONCENTRATES PROBABILITY ALONG $\theta = 0, \pi$ DIRECTIONS (POLES), SENSIBLE FOR A STATE WITH $L_z = 0$.