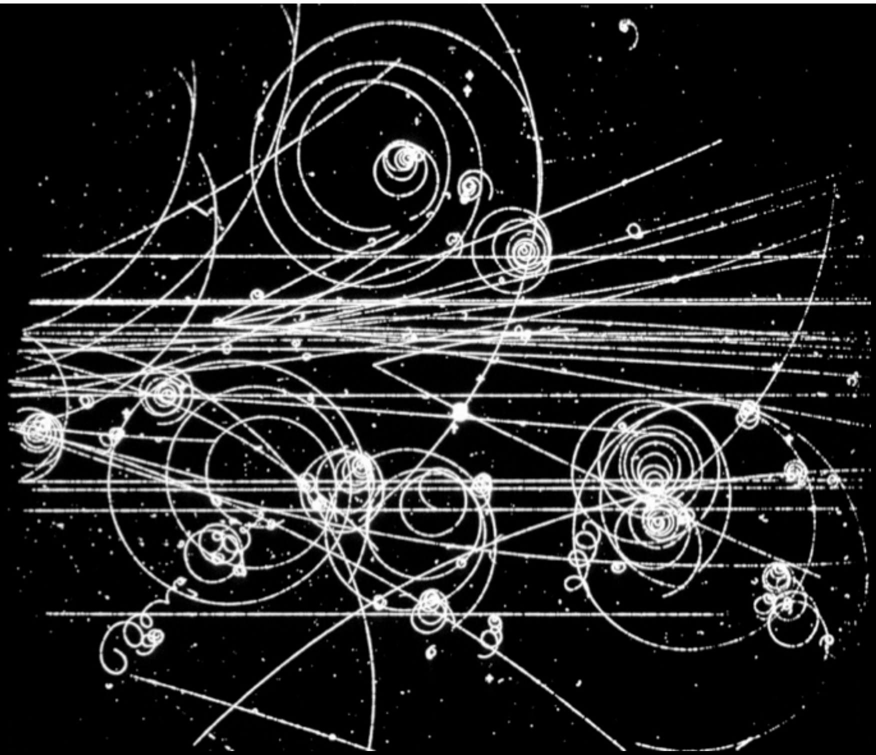
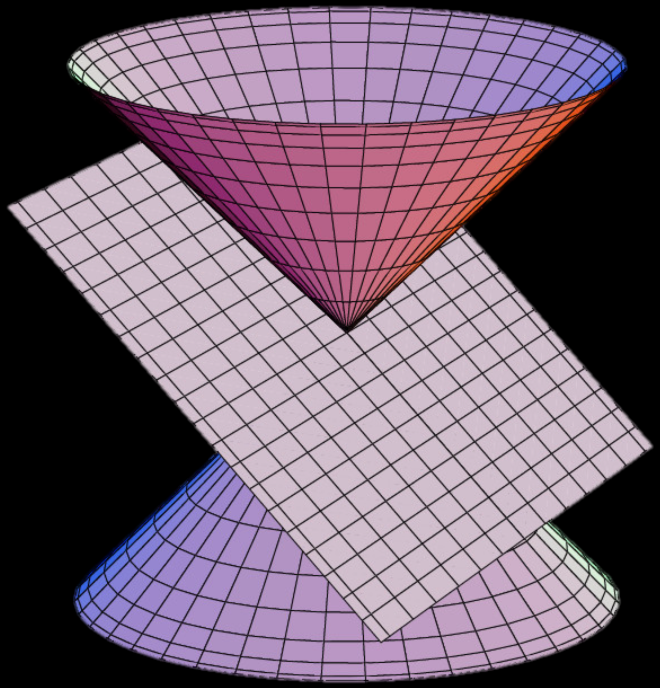
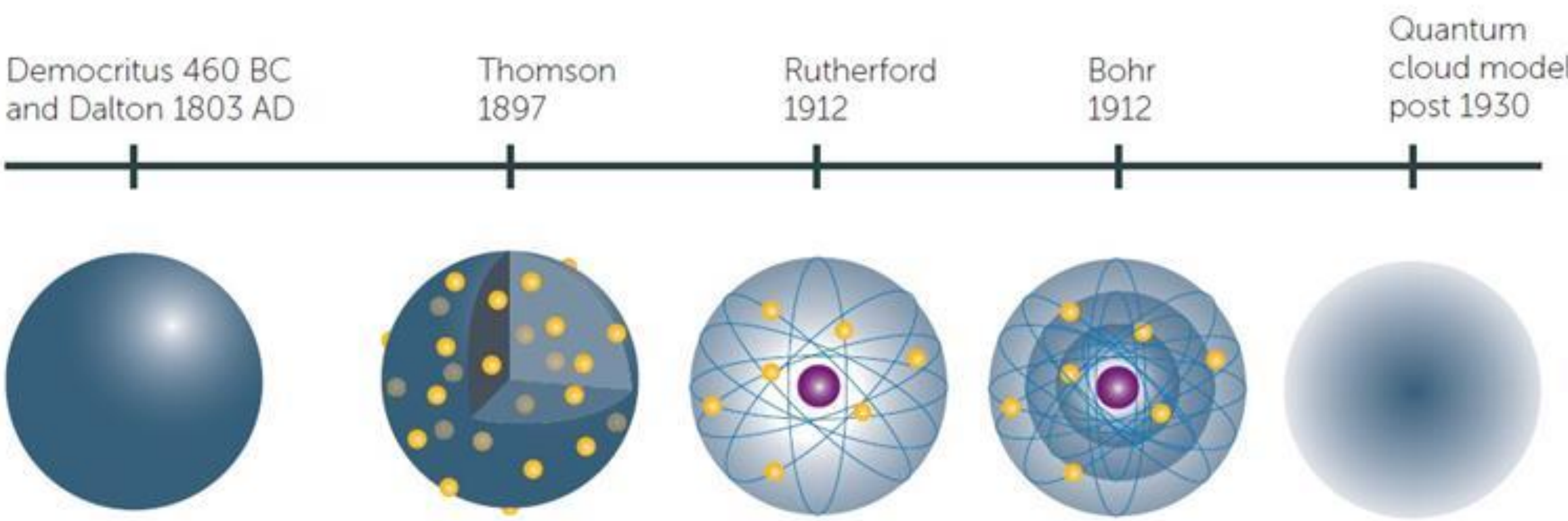




Modern Physics (Phys. IV): 2704

Professor Jasper Halekas
Van Allen 70
MWF 12:30-1:20 Lecture

Models of the Atom



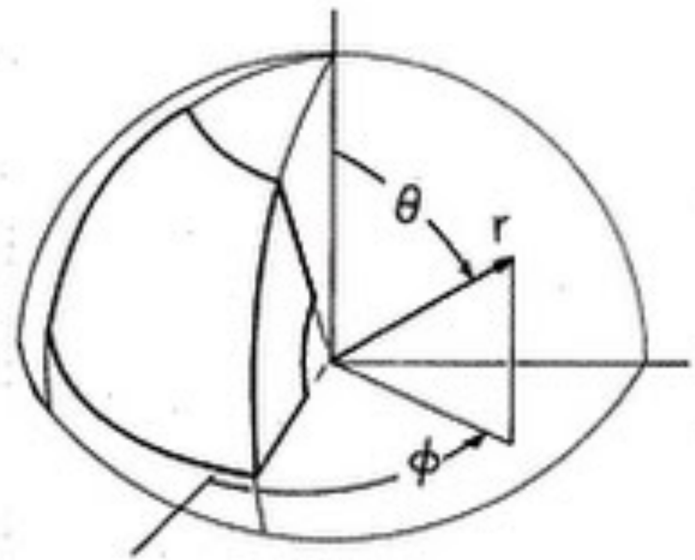
Schrödinger Equation for Hydrogen

$$E\psi = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\varepsilon}\frac{1}{r}\psi$$

$$-\frac{\hbar^2}{2m_r}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi(r,\theta,\phi)$$

$$-\frac{q^2}{4\pi\varepsilon_0 r}\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

Laplacian in Spherical Coordinates



$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin(\theta)}\frac{\partial}{\partial \theta}\left(sin(\theta)\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 sin^2(\theta)}\frac{\partial^2}{\partial \varphi^2}$$

Concept Check

- Given an equation f(x) = g(y) that is true for all values of the independent variables x and y, what ***must*** be true of the functions f and g?

A. Both functions are equal to zero
B. Both functions are polynomials
C. Both functions are constant
D. This equation cannot be solved

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Hydrogen Atom

Time - Independent Schrödinger Eq.

1-d: $-\hbar^2/2m \; d^2\psi/dx^2 + U(x)\psi(x) = E\psi(x)$

3-d: $-\hbar^2/2m \; \nabla^2\psi + U(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$

cartesian: $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$

spherical: $\nabla^2 = 1/r^2 \; \partial/\partial r \, (r^2 \partial/\partial r)$
$+ 1/(r^2 \sin\theta) \; \partial/\partial\theta \, (\sin\theta \; \partial/\partial\theta)$
$+ 1/(r^2 \sin^2\theta) \; \partial^2/\partial\varphi^2$

H atom $\quad U(\vec{r}) = - e^2/4\pi\varepsilon_0 r$

$\Rightarrow -\hbar^2/(2mr^2) [\partial/\partial r \, (r^2 \, \partial\psi/\partial r) + \frac{1}{\sin\theta} \partial/\partial\theta \, (\sin\theta \, \partial\psi/\partial\theta)$
$+ 1/\sin^2\theta \; \partial^2\psi/\partial\varphi^2]$
$- e^2/4\pi\varepsilon_0 r \; \psi = E\psi$

Use separation of variables

$\psi(r, \theta, \varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$

$\Rightarrow -\hbar^2/2mr^2 \, [\partial/\partial r \, (r^2 \partial R/\partial r) \, \Theta\Phi$
$+ 1/\sin\theta \; \partial/\partial\theta \, (\sin\theta \, \partial\Theta/\partial\theta) \cdot R \cdot \Phi$
$+ 1/\sin^2\theta \; \partial^2\Phi/\partial\varphi^2 \cdot R\Theta]$
$- e^2/4\pi\varepsilon_0 r \cdot R\Theta\Phi = E R\Theta\Phi$

- Divide by $R\Theta\Phi$
- Multiply by $2mr^2/\hbar^2$

$$-\left[\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}\right]-\frac{me^2r}{2\pi\varepsilon_0\hbar^2}=\frac{2mE}{\hbar^2}r^2$$

$$\Rightarrow \frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{me^2r}{2\pi\varepsilon_0\hbar^2}-\frac{2mE}{\hbar^2}r^2 = -\left[\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}\right]$$

- LHS depends only on r
- RHS depends on θ, φ
- True for all r, θ, φ
  $\Rightarrow$ both sides must be constant

Write constant $= C_\ell$

$$\Rightarrow \frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2} = -C_\ell$$

$$\Rightarrow \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -C_\ell\sin^2\theta$$

$$\Rightarrow \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+C_\ell\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}$$

LHS depends on θ, RHS on φ, so both are constant

- Write second constant $= C_m$

- Three ODEs for R, Θ, Φ

$$\frac{1}{R}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{me^2 r}{2\pi\varepsilon_0\hbar^2} + \frac{2mE}{\hbar^2} r^2 = C_\ell$$

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + C_\ell \sin^2\theta = C_m$$

$$-\frac{1}{\Phi}\frac{\partial^2 \Phi}{\partial\varphi^2} = C_m$$

Azimuthal Wave Function

$$\frac{\partial^2 \Phi}{\partial\varphi^2} = -C_m \Phi$$

Rewrite $C_m = m_\ell^2$

$$\frac{\partial^2 \Phi}{\partial\varphi^2} = -m_\ell^2 \Phi$$

$$\Rightarrow \boxed{\Phi(\varphi) = A e^{i m_\ell \varphi}}$$

To satisfy continuity

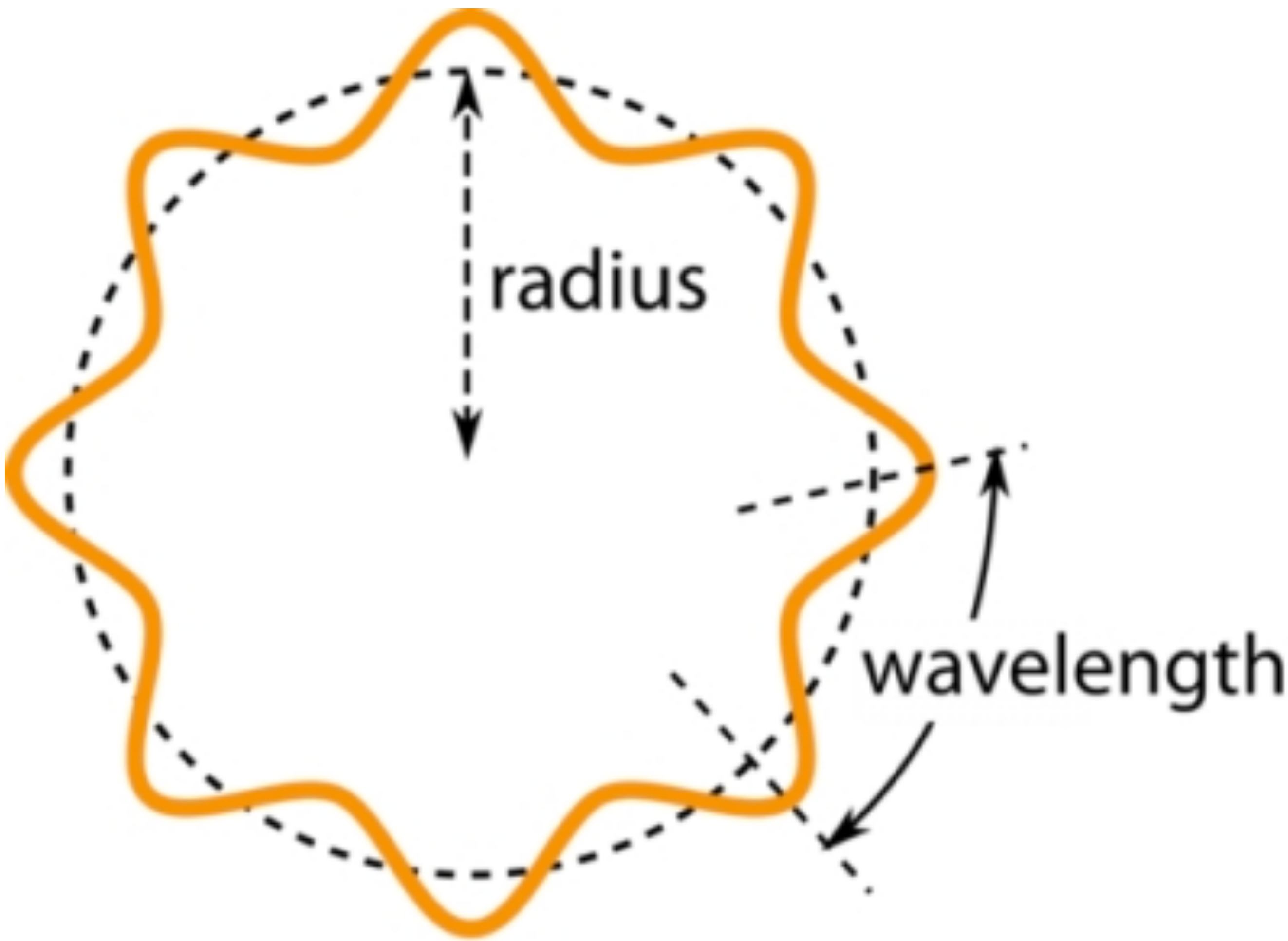
$$\Phi(\varphi) = \Phi(\varphi + 2\pi)$$

$$\Rightarrow \boxed{m_\ell = 0, \pm 1, \pm 2, \ldots}$$

Normalization: $\int_0^{2\pi} |\Phi|^2 d\varphi = \int_0^{2\pi} A e^{i m_\ell \varphi} e^{-i m_\ell \varphi} d\varphi$
$= 2\pi A^2 = 1$

$$\Rightarrow \boxed{\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i m_\ell \varphi}}$$

Azimuthal Wave Function



Azimuthal symmetry of wave functions

- Azimuthal wave function $e^{im\phi}$
- Azimuthal probability density $e^{im\phi}e^{-im\phi} = 1$
- Probability of finding electron is azimuthally symmetric for pure wave function
- Same as for the circular orbits of the Bohr model!

Polar Wave Function

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + C_\ell \sin^2\theta = C_m$$
$$= m_\ell^2$$

$$\Rightarrow \frac{1}{\sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) - \frac{m_\ell^2 \Theta}{\sin^2\theta} + C_\ell \Theta = 0$$

Solutions are $A P_\ell^m(\cos\theta)$

- P_ℓ^m are Legendre Polynomials
- For valid solution

$$C_\ell = \ell(\ell+1)$$
and $m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell$

$$\Theta(\theta) = A P_\ell^m(\cos\theta)$$

(A determined by normalization
$\int_0^\pi |\Theta|^2 d\theta = 1$

Legendre Polynomials

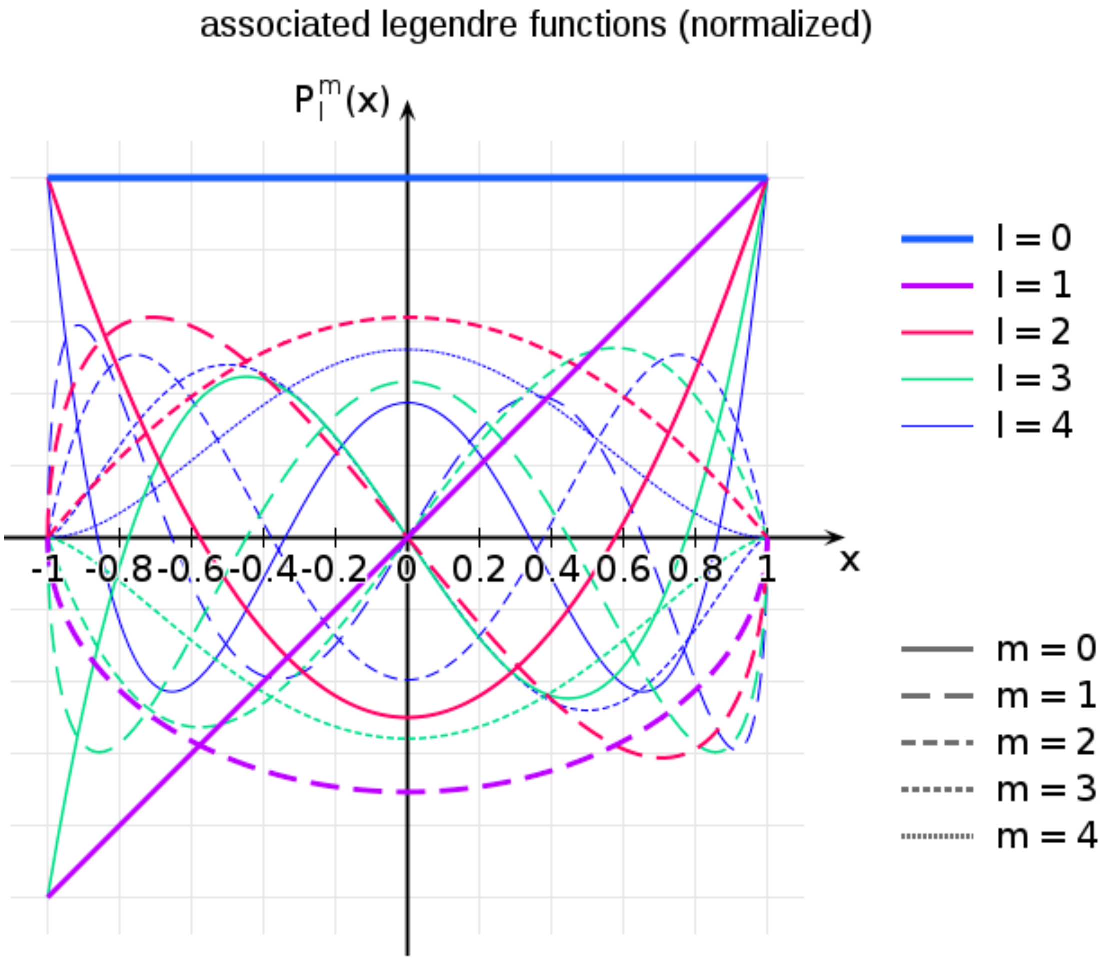


Table 6-2

The First Few Associated Legendre Functions $P_l^{|m|}(x)$

$P_0^0(x) = 1$

$P_1^0(x) = x = \cos\theta$

$P_1^1(x) = \sqrt{1 - x^2} = \sin\theta$

$P_2^0(x) = 1/2(3x^2 - 1) = 1/2(3\cos^2\theta - 1)$

$P_2^1(x) = 3x\sqrt{1 - x^2} = 3\cos\theta\ \sin\theta$

$P_2^2(x) = 3(1 - x^2) = 3\sin^2\theta$

$P_3^0(x) = 1/2(5x^3 - 3x) = 1/2(5\cos^3\theta - 3\cos\theta)$

$P_3^1(x) = 3/2(5x^2 - 1)(1 - x^2)^{1/2} = 3/2(5\cos^2\theta - 1)\sin\theta$

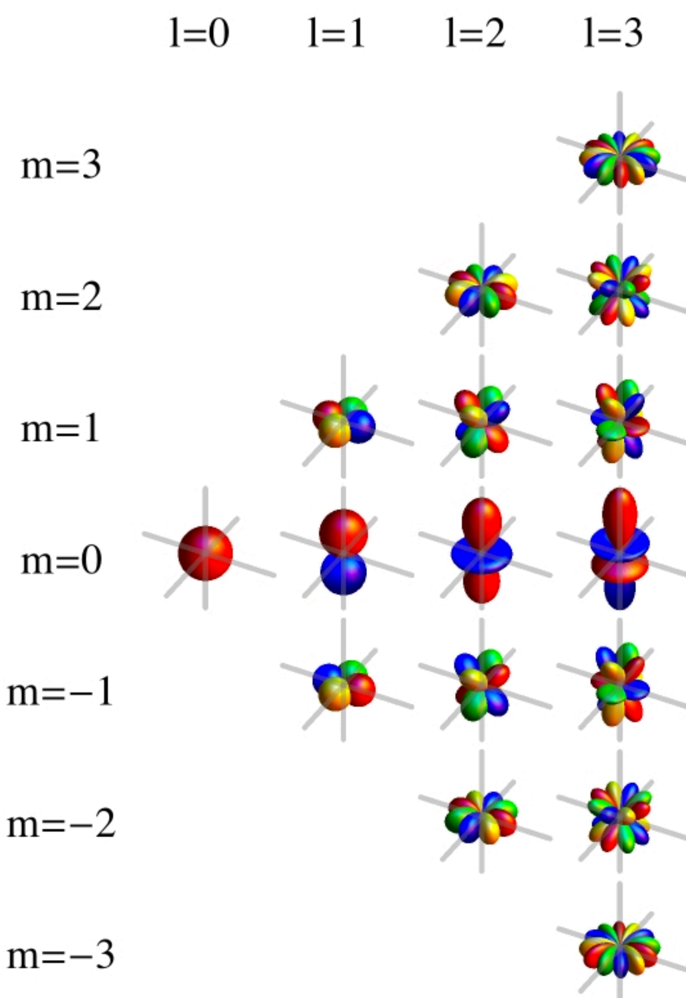
$P_3^2(x) = 15x(1 - x^2) = 15\cos\theta\ \sin^2\theta$

$P_3^3(x) = 15(1 - x^2)^{3/2} = 15\sin^3\theta$

<u>Not normalized</u>

Spherical Harmonics

-real
+real
-imaginary
+imaginary



ℓ	m_ℓ	$Y_{\ell m_l}(\theta,\phi) = \Theta_{\ell m_l}(\theta)\Phi_{m_l}(\phi)$
0	0	$(1/4\pi)^{1/2}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
1	± 1	$\mp(3/8\pi)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta - 1)$
2	± 1	$\mp(15/8\pi)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$
2	± 2	$(15/32\pi)^{1/2}\sin^2\theta e^{\pm 2i\phi}$

$$\Phi_{m_\ell}(\phi) = \frac{1}{\sqrt{2\pi}} e^{i m_\ell \phi}$$

$$\Theta_{\ell m_\ell}(\theta) = \left[\frac{2\ell+1}{2}\frac{(\ell - m_\ell)!}{(\ell + m_\ell)!}\right]^{1/2} P_\ell^{m_\ell}(\theta)$$

$P_\ell^{m_\ell}(\theta) = associated\ \ Legendre\ \ polynomial$

Angular Probability Density

s: l = 0

p: l = 1

d: l = 2

f: l = 3