VIII. Spherically Symmetric Potential Energy Functions: $U(\vec{r}) = U(r)$

- 3D TISE $(\hat{H}\psi = E\psi)$ Problems
- $U(\vec{r}) = U(x,y,z) = U(r,\theta,\phi)$ in general [Hard to do!]
- Many useful $U(\vec{r})$ in physics are spherically symmetric

$$U(\vec{r}) = U(r,\theta,\phi) = U(r) \quad \text{depends on } r \text{ only}$$

- Induced us to use spherical coordinates
- Separation of variables should work [r-equation, θ-equation, ϕ-equation]
- Energy eigenvalues and properties of energy eigenstates?
- Be aware of degeneracy

A. $U(\vec{r})$ of Hydrogen Atom is Spherically Symmetric

$U(\vec{r})$ = potential energy of an electron [-e charge] at $\vec{r}$ due to $\underbrace{\text{nucleus}}^{[+e \text{ charge}]}$ at origin

$$\underset{\substack{\uparrow \\ \text{Potential energy} \\ \uparrow \\ \text{Go into } \hat{H}}}{U(\vec{r})} = (-e)\cdot\underbrace{\left(\frac{e}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right)}_{\text{electric potential due to +e charge at origin}} = \underbrace{\frac{-e^2}{4\pi\varepsilon_0 r}}_{}$$

[Coulomb potential energy function]

$\boxed{U(x,y,z) \text{ in Cartesian coordinates}}$

- Inspect $U(x,y,z)$
- Hopeless to separate variables using Cartesian Coordinates

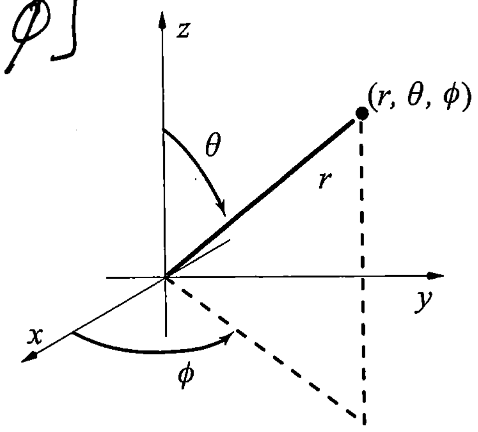
$\boxed{U(r,\theta,\phi) \text{ in spherical coordinates} = U(r) \text{ [depends on } r \text{ only]}}$

- Separation of Variables should work using Spherically coordinates

B. Spherical Symmetric $U(\vec{r})$ is more general than Coulomb form

Definition: $U(\vec{r}) = U(r)$ only [independent of θ, ϕ]

Spherical symmetric potential energy function



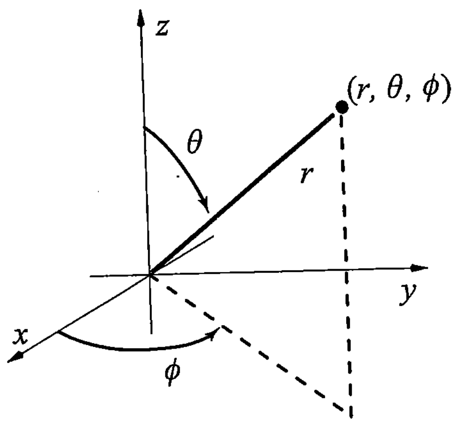
[Origin: Central Force (c.f. classical mechanics)]

(Force in radial $\hat{r}$ direction only

- 3D isotropic oscillator $U(r,\theta,\phi) = U(r) = \frac{1}{2} m\omega_0^2 r^2$
- 3D infinite well $U(r,\theta,\phi) = U(r) = \begin{cases} 0 & r < a \\ \infty & r \geq a \end{cases}$ (useful in nuclear physics & Quantum Dots)
- 3D finite well

- Following discussion is good for general $U(r)$, until we explicit plug in $U_{Coulomb}(r)$

C. Spherical Coordinates and Laplacian ∇^2



Cartesian (x, y, z) $\longleftrightarrow$ Spherical (r, θ, ϕ)

$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases} \qquad \begin{cases} r = \sqrt{x^2+y^2+z^2} \\ \theta = \cos^{-1}\dfrac{z}{\sqrt{x^2+y^2+z^2}} \\ \phi = \tan^{-1}\dfrac{y}{x} \end{cases}$$

[Partial derivatives needed]

∇^2 in spherical coordinates† (2 forms)

$$\nabla^2\psi = \begin{cases} \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial\psi}{\partial r}\right) + \dfrac{1}{r^2\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial\psi}{\partial\theta}\right) + \dfrac{1}{r^2\sin^2\theta}\dfrac{\partial^2\psi}{\partial\phi^2} \\ \dfrac{1}{r}\dfrac{\partial^2}{\partial r^2}(r\psi) + \dfrac{1}{r^2\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial\psi}{\partial\theta}\right) + \dfrac{1}{r^2\sin^2\theta}\dfrac{\partial^2\psi}{\partial\phi^2} \end{cases}$$

† See Chapter on "Partial Differentiation" in "All you wanted to know about Mathematics but were afraid to ask" by Lyons. See also Griffiths' book on electrodynamics.

D. TISE and Separation of Variables

TISE: $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + U(r)\psi(\vec{r}) = E\psi(\vec{r})$

- Only $U(\vec{r}) = U(r)$
- $\psi(r,\theta,\phi)$ is a 3D wavefunction, thus depends on r, θ, ϕ

$$\boxed{\text{Aim: Solve for allowed } E \text{ and } \psi(\vec{r}) = \psi(r,\theta,\phi)}$$

TISE in Spherical Coordinates

$$\boxed{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}\big(E-U(r)\big)\psi = 0} \qquad (1)$$

[This is the starting equation for all problems of $U(r)$]

Separation of Variables:

$$\psi(\vec{r}) = \psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{function of } r \text{ only}} \cdot \underbrace{Y(\theta,\phi)}_{\text{fn of } \theta \text{ and } \phi \text{ only}} = R(r)\cdot\underbrace{\Theta(\theta)}_{\text{function of } \theta \text{ only}}\cdot\underbrace{\Phi(\phi)}_{\text{function of } \phi \text{ only}}$$

- <u>Find equations</u> satisfied by $R(r)$ and $Y(\theta,\phi)$

Subst. $\psi(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi)$ into TISE (1) (Ex.)

$$\underbrace{\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}(E-U(r))\right]}_{\substack{\text{depends on } r \text{ only} \\ \parallel \\ +\lambda \text{ (a constant)}}} + \underbrace{\left[\frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]}_{\substack{\text{depends on } \theta,\phi \text{ only} \\ \parallel \\ -\lambda \text{ (a constant)}}} = 0$$

Only Possible if

holds for any r,θ,ϕ

$+\lambda$ (a constant) $+$ $-\lambda$ (a constant) $= 0$ [OK]

(2 equations are found)

$$\boxed{\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}(E-U(r))R = \lambda R} \quad (2)$$

<u>Radial Equation for $R(r)$</u>

- $U(r)$ enters here
- Another eigenvalue problem

$$\boxed{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = -\lambda Y} \quad (3)$$

<u>θ-ϕ Equation for $Y(\theta,\phi)$</u>

- Doesn't depend on $U(r)$
- Same Eq. (3) [same $Y(\theta,\phi)$] for <u>ALL</u> $U(r)$

E. Solutions to the θ-ϕ Equation are Spherical Harmonics $Y_{\ell m_\ell}(\theta,\phi)$

(i) Knowing Key Features of Solutions to θ-ϕ Equation

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = -\lambda Y \qquad (3)$$

- Solutions are called spherical harmonics $Y_{\ell,m_\ell}(\theta,\phi)$
- Well-behaved $\psi(r,\theta,\phi) \Rightarrow$ Well-behaved $Y(\theta,\phi)$
- To be well-behaved, must have

$$\lambda = \ell(\ell+1) \qquad \text{with } \ell = 0, 1, 2, \ldots$$

and $-\ell \leq m_\ell \leq +\ell$ (thus $m_\ell = 0, \pm 1, \pm 2, \ldots$) (4)

- ℓ, m_ℓ are quantum numbers labelling $Y_{\ell,m_\ell}(\theta,\phi)$
- Same $Y_{\ell m_\ell}(\theta,\phi)$ work for all spherically symmetric $U(r)$

(ii) Understanding Spherical Harmonics

- What is the ϕ-dependence in $Y(\theta,\phi)$?

$$\boxed{\text{Ans: } Y(\theta,\phi) \sim \Theta(\theta)\cdot e^{im_\ell \phi}}$$

Let's see why.

- Write $Y(\theta,\phi) = \Theta(\theta)\cdot\Phi(\phi)$ [Further separate θ and ϕ in Eq.(3)]

Eq.(3):

$$\underbrace{\left[\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \lambda\sin^2\theta\right]}_{\substack{\text{depends on } \theta \text{ only} \\ \parallel \\ m_\ell^2 \text{ (a constant)}}} + \underbrace{\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi}{\partial\phi^2}}_{\substack{\text{depends on } \phi \text{ only} \\ \parallel \\ -m_\ell^2}} = 0$$

holds for all θ and ϕ

$\Downarrow$

$$\boxed{\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\sin^2\theta\cdot\Theta - m_\ell^2\cdot\Theta = 0} \quad (5)$$

$\underline{\theta\text{-Equation for } \Theta(\theta)}$

$\Downarrow$

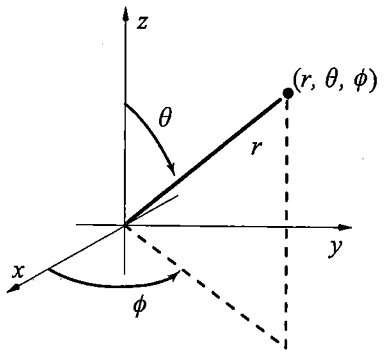
$$\boxed{\frac{d^2\Phi}{d\phi^2} + m_\ell^2\Phi = 0} \quad (6)$$

$\underline{\phi\text{-Equation for } \Phi(\phi)}$

"Azimuthal Equation"

$$\frac{d^2\Phi}{d\phi^2} + m_\ell^2 \Phi = 0 \quad \Rightarrow \quad \Phi(\phi) = A\, e^{im_\ell\phi} \quad \left[\text{actually } e^{\pm i m_\ell \phi}\right]$$

$\psi(r,\theta,\phi)$ must be single-valued [one value at a position in space]



$$\therefore \Phi(\phi+2\pi) = \Phi(\phi) \quad [\because \text{Same place}]$$

$$e^{im_\ell\phi} e^{im_\ell 2\pi} = e^{im_\ell\phi}$$

$$\Rightarrow e^{i2\pi m_\ell} = 1 \Rightarrow m_\ell = \text{integer (positive, negative, zero)}$$

$$m_\ell = 0, \pm 1, \pm 2, \pm 3, \cdots$$

$$\boxed{\Phi(\phi) = \underbrace{\frac{1}{\sqrt{2\pi}}}\, e^{im_\ell\phi}, \quad m_\ell = 0, \pm 1, \pm 2, \cdots} \qquad (7)$$

Normalization [ϕ's range is 0 to 2π]

ϕ-equation solved

After considering ϕ only, we have:

$$Y(\theta,\phi) \sim \Theta(\theta) \cdot e^{im_\ell\phi}$$

Next Question: What is $\Theta(\theta)$?

Back to Θ-Equation: $\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \lambda \sin^2\theta \, \Theta - m_\ell^2 \, \Theta = 0$ (5)

[Recall: $m_\ell = 0, \pm 1, \pm 2, \ldots$. There is one Eq. for every value of $|m_\ell|$]

Outline of Mathematical steps and Key Results

- Change variable to $v \equiv \cos\theta$; $\Theta(\theta) \rightarrow P(v)$

$$\frac{d}{d\theta} \rightarrow -\sqrt{1-v^2}\,\frac{d}{dv}$$

- Eq.(5) becomes

$$\boxed{\frac{d}{dv}\left[(1-v^2)\frac{dP}{dv}\right] + \left[\lambda - \frac{m_\ell^2}{1-v^2}\right]P = 0} \qquad (8)$$

This is the associated Legendre differential Equation (1752-1833)

This special $m_\ell = 0$ case of (8) is the Legendre differential Equation

Solutions[+] to Eq. (8) for well-behaved $\Theta(\theta)$

- λ must be of the form $\boxed{\lambda = l(l+1) \text{ with } l = 0,1,2,\cdots}$ for well-behaved Θ

Solutions to Eq. (8) →
$$\underbrace{P_l^{|m_l|}(v)}_{\text{associated Legrendre Polynomial}} = (1-v^2)^{|m_l|/2} \underbrace{\left(\frac{d}{dv}\right)^{|m_l|}}_{\text{differentiate } |m_l| \text{ times}} \underbrace{P_l(v)}_{\text{Legrendre Polynomial } P_l(\cos\theta)} \quad (9)$$

$\because$ $P_l(v)$ is a polynomial of highest degree v^l $\Rightarrow$ $\boxed{\left(\frac{d}{dv}\right)^{|m_l|} P_l(v) = 0 \text{ for } |m_l| > l}$

then $\psi = 0$ → bad!

$$\boxed{\begin{array}{l} \text{For given } l \ (=0,1,2,\cdots), \\ m_l = \underbrace{-l, -l+1, \cdots; -1, 0, +1, \cdots; l-1, l}_{(2l+1) \text{ values of } m_l \text{ for a given value of } l} \end{array}} \quad (10)$$

[+] We shall not work out the details on solving Eq. (8). The math. form of solutions $Y_{l,m_l}(\theta,\phi)$ is more important than their derivations.

<u>Summary on θ-φ Equation</u>: $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}=-\lambda Y$

- $\lambda = \ell(\ell+1)$ for acceptable behavior
- $$\boxed{\begin{array}{l}\text{Solutions are:}\quad Y_{\ell m_\ell}(\theta,\phi)\sim P_\ell^{|m_\ell|}(\cos\theta)\cdot e^{im_\ell\phi}\\ \qquad\text{where } \ell=0,1,2,\cdots\\ \qquad m_\ell=-\ell,\cdots,0,\cdots,+\ell\ \ [-\ell\le m_\ell\le\ell]\ \text{for a given } \ell\end{array}}\qquad(11)$$
- Thus, $Y_{\ell m_\ell}(\theta,\phi)$ (called <u>spherical harmonics</u>) satisfies

$$\boxed{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_{\ell m_\ell}}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{\ell m_\ell}}{\partial\phi^2}=-\ell(\ell+1)Y_{\ell,m_\ell}}\qquad(12)$$

For a given ℓ value on RHS, there are $(2\ell+1)$ functions $Y_{\ell m_\ell}(\theta,\phi)$ that satisfy Eq.(12). Eq.(12) is important in <u>QM orbital angular momentum</u>.

There are tables for $Y_{\ell m_\ell}(\theta,\phi)$ [Google]

$\boxed{\ell=0}$ $Y_{00} = \sqrt{\frac{1}{4\pi}}$; $\boxed{\ell=1}$ $Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$, $Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$

$\boxed{\ell=2}$ $Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$, $Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta\, e^{\pm i\phi}$, $Y_{2\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm i2\phi}$

and many more...

- They are normalized as $\displaystyle\int_0^{2\pi}\int_0^{\pi} |Y_{\ell m_\ell}(\theta,\phi)|^2 \overbrace{\sin\theta\, d\theta\, d\phi}^{d\Omega} = 1$

- They are orthogonal $\displaystyle\int_0^{2\pi}\int_0^{\pi} Y_{\ell m_\ell}(\theta,\phi)\, Y_{\ell' m_\ell'}(\theta,\phi)\, d\Omega = \delta_{\ell\ell'}\delta_{m_\ell m_\ell'}$

Polar Plot is a way to illustrate $Y_{\ell m_\ell}(\theta, \phi)$

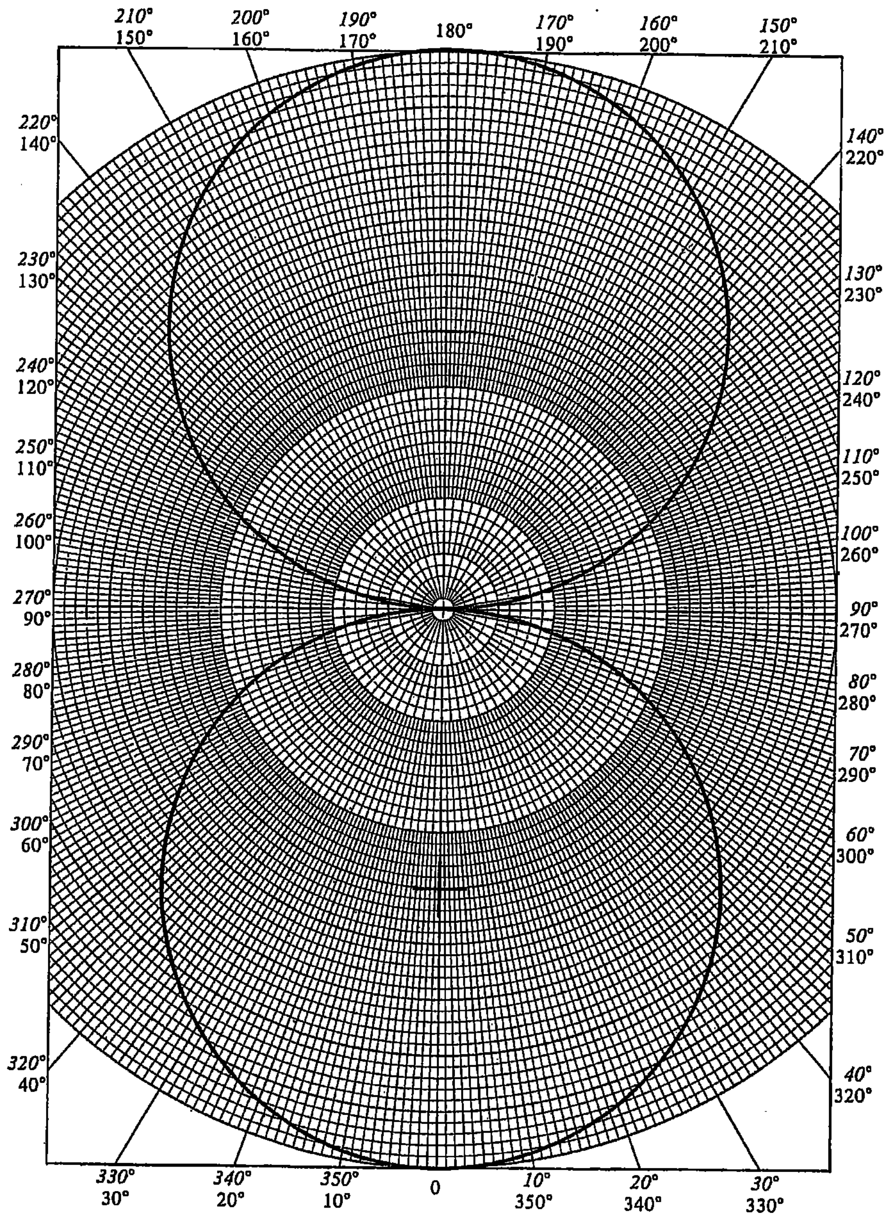
How to show $f(\theta) = \cos\theta$?

This is related to

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta \, e^{i0\phi}$$

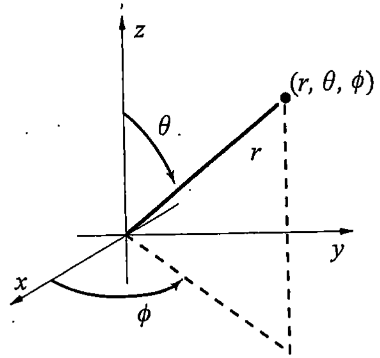
$$= \sqrt{\frac{3}{4\pi}} \cos\theta$$

- Can think of this as a cut at $y=0$ OR equivalently a plot on x-z plane
- Take θ, calculate $\cos\theta$, draw $|\cos\theta|$ as a distance from origin and make a dot
- Go through values of θ

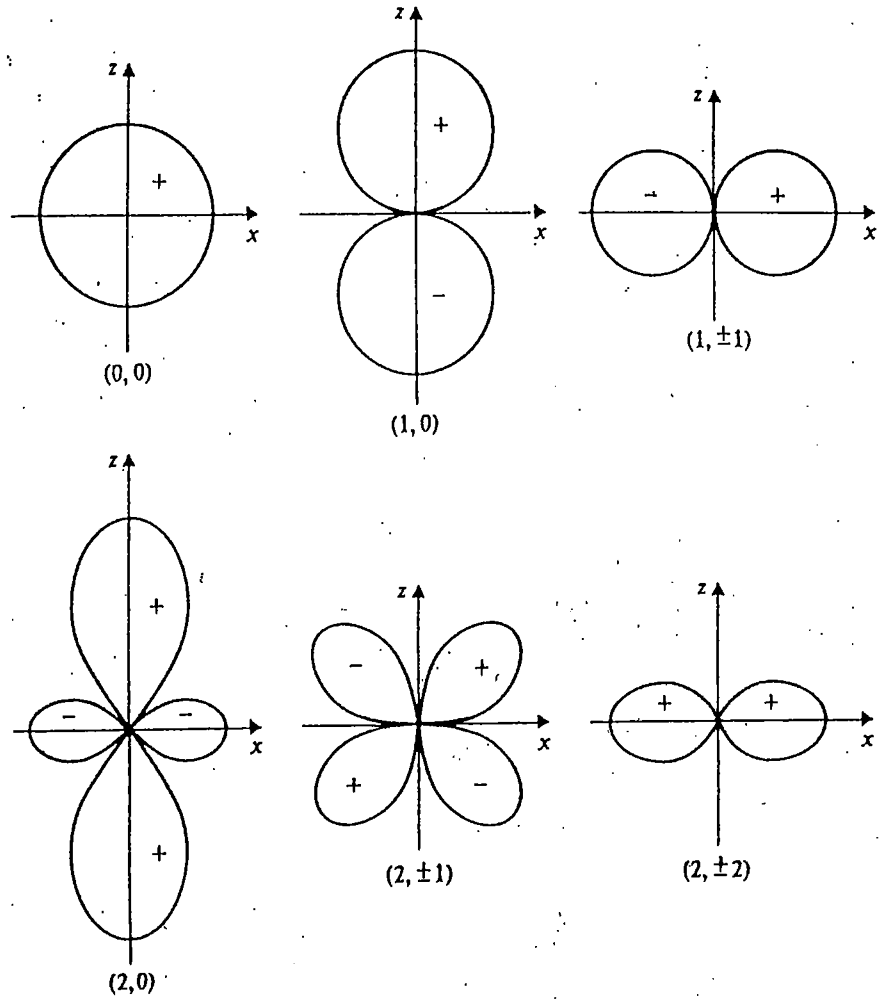


A polar plot of $f(\theta) = \cos\theta$. To construct such a plot, mark off the distance $f(\theta)$ along the radial line labeled by the angle θ.

Polar Plots of $Y_{\ell m_\ell}(\theta,\phi)$ [on x-z plane] ($\phi=0$)



- x-z plane ($y=0$) corresponds to $\phi=0$
- To think about $\underbrace{|Y_{\ell m_\ell}(\theta,\phi)|^2}_{\text{related to } |\psi|^2}$
  - Square the lengths from origin (in your mind) $\Rightarrow$ similar shape
  - $|Y_{\ell m_\ell}(\theta,\phi)|^2$ has no ϕ-dependence
  - $|Y_{\ell m_\ell}(\theta,\phi)|^2$ ~ Rotate shape along z-axis



Polar plots of the sections at $y=0$ through the spherical harmonics with quantum numbers (l,m). The distance from the origin of a point on a curve is proportional to the magnitude of the function in that direction. The sign of the function in each region of space is also indicated.

Go To Appendix A

For those mathematically inclined students who want to know how to solve the θ-equation for the special case of $m_\ell = 0$, i.e. $\frac{d}{dv}\left[(1-v^2)\frac{dP}{dv}\right] + \lambda P = 0$

Go to appendix A. The solutions Legendre polynomials, are useful also in solving EM problems (Laplace Equation).

Students may also skip Appendix A. But the key features of $Y_{\ell m_\ell}(\theta,\phi)$ are needed for subsequent discussions.