SE in Spherical Coordinates

+

Spherical Harmonics

Consider a radial potential $V(r)$ which implies a central force.

<u>SE</u>

$$\frac{-\hbar^2}{2m}\nabla^2\phi + V(r)\phi = E\phi$$

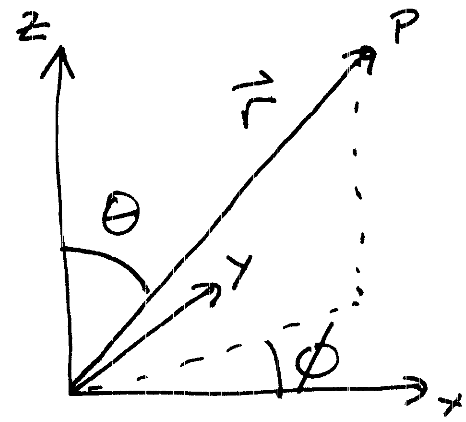
Write the Laplacian in spherical coordinates, using Griffiths E+M front cover as always.

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

$$+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

While I like ϕ for the energy eigenstate wavefunction, when in spherical coordinates we will use ψ.

Spherical Coordinate System



Coordinate transformations also in Griffiths E+M.

TISE in Spherical Coordinates

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

As usual, try separation of variables.

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$$

$$-\frac{\hbar^2}{2m}\left(\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)\right.$$

$$\left. + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right) + RYV(r) = ERY$$

<u>Divide by ψ</u> and multiply by $-2mr^2/\hbar^2$

$$\frac{1}{R}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\right) - \frac{2mr^2}{\hbar^2}\left(V(r)-E\right)$$

$$+\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right) = 0$$

Introduce Separation Constant $\ell(\ell+1)$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r)-E\right) = \ell(\ell+1)$$

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

$$= -\ell(\ell+1)$$

Work on the second equation and try separation again

$$Y(\theta,\phi) = T(\theta)\,\Phi(\phi)$$

Naturally it works yielding, after multiplication by $\sin^2\theta$

$$\frac{1}{T}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right) + \ell(\ell+1)\sin^2\theta\right]$$

$$+ \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = 0$$

<u>Introduce separation constant m^2</u>

$$\frac{1}{\Phi}\frac{d^2\Phi}{d^2\phi} = -m^2$$

$$\frac{1}{T}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{dT}{d\theta}\right) + l(l+1)\sin^2\theta\right] = m^2$$

Solve Φ eqn

$$\Phi = e^{im\phi}$$

Work on T eqn

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{dT}{d\theta}\right) + \left[l(l+1)\sin^2\theta - m^2\right]T = 0$$

Solutions to T eqn are the associated Legendre polynomials, P_l^m

$$P_l^m = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x)$$

$$T = P_l^m(\cos\theta)$$

Dfn $P_l(x)$ - Legendre Polynomial

$$P_l(x) = \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l$$

<u>Examples</u>

$P_0 = 1$ $\qquad P_1 = x$ $\qquad P_2 = \frac{1}{2}(3x^2-1)$

$$P_3 = \frac{1}{2}(5x^3 - 3x)$$

So the complete solution to the angular part of the seprated SE is

$$Y_l^m(\theta,\phi) = A\, e^{im\phi} P_l^m(\cos\theta)$$

Normalization in Spherical Coordinates

$$1 = \int_0^\infty dr \int_0^\pi r\,d\theta \int_0^{2\pi} r\sin\theta\,d\phi \;\psi^*\psi$$

Normalize the radial and angular pieces separately

$$1 = \int_0^\infty R^*(r)\,R(r)\,r^2\,dr$$

$$1 = \int_0^\pi d\theta \int_0^{2\pi} d\phi \,\sin\theta\; Y^* Y$$

Normalized Spherical Harmonics

$$Y_\ell^m(\theta,\phi) = \varepsilon \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi\,(\ell+|m|)!}}\; e^{im\phi}\,P_\ell^m(\cos\theta)$$

$$\varepsilon \equiv (-1)^m \quad m \geq 0 \qquad\qquad \varepsilon = 1 \quad m < 0$$

$l \equiv$ Azimuthal Quantum Number

$m \equiv$ Magnetic Quantum Number

$$m = l, l-1 \;\cdots\; -l$$

<u>Examples</u>

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

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \qquad Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \cos\theta \sin\theta \, e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right) \sin^2\theta \, e^{\pm 2i\phi}$$

The spherical harmonics are an orthonormal set,

Orthogonality

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \; Y^{*m}_{l} \, Y^{m'}_{l'} \sin\theta = \delta_{ll'} \, \delta_{mm'}$$

Since they are orthogonal, all the old tricks work

Ex Suppose $\psi = A r (1 + \cos\theta)$, what possible values of l and m could be observed?

$$1 = \sqrt{4\pi}\, Y^0_0$$

$$\cos\theta = \sqrt{\frac{4\pi}{3}}\, Y^0_1$$

$$\psi = A r \left(\sqrt{4\pi}\, Y^0_0 + \sqrt{\frac{4\pi}{3}}\, Y^0_1 \right)$$

$$= A' r \left(Y^0_0 + \sqrt{\frac{1}{3}}\, Y^0_1 \right)$$

Normalize the angular part,

$$\sqrt{1^2 + \frac{1}{3}} = \frac{2}{\sqrt{3}}$$

$$(\,) \rightarrow \frac{\sqrt{3}}{2} Y_0^0 + \frac{1}{2} Y_1^0$$

Observed	Prob
$l = 0$, $m = 0$	$3/4$
$l = 1$, $m = 0$	$1/4$