IN 3D $\vec{p} \to -i\hbar\nabla$

$$i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \Psi(\vec{r},t) + V(\vec{r})\Psi(\vec{r},t)$$

Laplacian

Separate variables, time / space
If V does not depend on time, then
there will be a complete set of
States

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$$

Each $\psi_n(\vec{r})$ satisfies the TISE:

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

General solution to TDSE:

$$\Psi(\vec{r},t) = \sum c_n \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$$

Prep. for sep. of variables

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

$$\Rightarrow \quad \nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2}\left[E - V(\vec{r})\right]\psi(\vec{r}) = 0$$

in many interesting cases, the potential depends only on $r = \|\vec{r}\|$ dist. from origin

E.g. H atom where we assume the nucleus is so heavy compared to e^- that it is essentially at rest. in that case

$$\nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2}\left[E - V(r)\right]\psi(\vec{r}) = 0$$

This means we should use spherical coordinates:

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

TISE

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

$$+\frac{2m}{\hbar^2}\left(E-V(r)\right)\psi=0$$

first separate into angular and radial parts

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

standard S. of Var. arguments lead to

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}-\frac{2mr^2}{\hbar^2}\left(V(r)-E\right)\right)$$ Eq. 4.17

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

$f(r) = g(\theta,\varphi)$ must $=$ const.

call this $\ell(\ell+1)$ } cf. 311 discussion

Radial equation

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

angular equation

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

multiply angular eq. by $Y\sin^2\theta$

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

Now separate into θ and ϕ

$$Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$$

⋮ standard arguments

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

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -m^2 \qquad \text{sep. const.}$$

why '$-$' here?

$$\Phi(\varphi) = e^{im\varphi}$$

in order that $\Phi(\varphi) = \Phi(\varphi + 2\pi)$
m must be an integer

$$m = 0, \pm 1, \pm 2, \ldots$$

Θ Eq. becomes

$$\underbrace{\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left[\ell(\ell+1)\sin^2\theta - m^2\right]\Theta = 0}_{\text{Legendre's Equation}}$$

turns out (we will show this on Friday)

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

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

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

Mathematica

$P_0(x) \equiv \text{LegendreP}[0, x] = 1$

$P_1(x) \quad [1, x] = x$

$P_2(x) \quad [2, x] = \frac{1}{2}(3x^2 - 1)$

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

table 4.1 in book

$m=0$

$P_0^0(x) = \text{LegendreP}[0, 0, x] = 1$

$\ell = 0$

$P_1^0(x) = \text{LegendreP}[1, 0, x] = x$

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

$P_1^1(x) = \text{LegendreP}[1, 1, x] = -\sqrt{1-x^2} = -\sin\theta$

$P_1^{-1}(x) = \text{LegendreP}[1, -1, x] = \frac{1}{2}\sqrt{1-x^2} = \frac{1}{2}\sin\theta$

$P_1^0(x) = \text{LegendreP}[1, 0, x] = x = \cos\theta$

slightly different than book, so we must look at mathematica's def.

$$(1-x^2)\frac{d^2y}{dx^2} - 2x\left(\frac{dy}{dx}\right) + n(n+1)\,y = 0$$

our ℓ.

using the change of variables ;

$x = \cos\theta$

$$\frac{d}{dx} = \frac{d}{d(\cos\theta)} = \frac{d}{-\sin\theta \, d\theta}$$

reconcile the book's definition with mathematica's.

---

putting the θ and φ part together we get

$$Y_\ell^m(\theta, \varphi) = C_{\ell m} \, e^{im\varphi} \, P_\ell^m(\cos\theta)$$

$\downarrow$ normalization

$$C_{\ell m} = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}}$$

where $\epsilon = (-1)^m$ for $m \geq 0$

$\epsilon = 1$ for $m < 0$

The Y_ℓ^m are orthog.

$$\int_0^{2\pi}\int_0^{\pi} \left(Y_\ell^m(\theta,\phi)\right)^* \left(Y_{\ell'}^{m'}(\theta,\phi)\right) \sin\theta \, d\theta \, d\phi = \delta_{\ell\ell'}\delta_{mm'}$$

ℓ is called the azimuthal quantum num.

m is the magnetic Q. Number