Coordinate-Free Schrödinger Eq.

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

Separation of Variables

$f(\vec{r}) = \psi(\vec{r})$

$$\Psi(x,y,z,t) = \boxed{f_1(x) \cdot f_2(y) \cdot f_3(z)} \cdot g(t)$$

$Y(\theta,\varphi)$

$$\Psi(r,\theta,\varphi,t) = R(r) \cdot \boxed{T(\theta) \cdot F(\varphi)} \cdot g(t)$$

$$g(t) = g_0\, e^{\frac{-itE}{\hbar}}$$

E is separation constant.

solution to $\dfrac{\dot{g}(t)}{g(t)} = -E$

Laplacian Operator in Spherical Polar Coord's

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

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

Time-independent S.E.

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

$$f(\vec{r}) = R(r)\, Y(\theta,\varphi)$$

S. E.

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)Y(\theta,\varphi)}{\partial r}\right)\right.$$

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

$$\left.+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 R(r)Y(\theta,\varphi)}{\partial\varphi^2}\right\}+V(\vec{r})R(r)Y(\theta,\varphi)=E R(r)Y(\theta,\varphi)$$

divide both sides by $R(r)\,Y(\theta,\varphi)$

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{R(r)}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}R(r)\right)\right.$$

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

$$\left.\frac{1}{Y(\theta,\varphi)}\frac{1}{r^2\sin^2\theta}\frac{\partial^2 Y(\theta,\varphi)}{\partial\varphi^2}\right\}+V(r)-E=0$$

function of r, not θ φ

multiply by r^2, divide by $-\frac{\hbar^2}{2m}$

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

$$+\left[\frac{1}{Y(\theta,\varphi)}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y(\theta,\varphi)\right)\right.$$

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

$$\underbrace{\omega(r)}_{\substack{= C \\ \ell(\ell+1)}} + \underbrace{B(\theta,\varphi)}_{\substack{= -C \\ -\ell(\ell+1)}} = 0 \quad \forall\, r,\theta,\varphi$$

$\leftarrow$ for later convenience

Radial Equation

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

Angular Equation

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

Ansatz: $Y(\theta,\varphi) = T(\theta)\cdot F(\varphi)$

multiply by $\sin^2\theta$

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

$$+ \underbrace{\frac{1}{F(\varphi)} \frac{d^2 F(\varphi)}{d\varphi^2}}_{= -m^2} = 0 \quad \forall \theta, \varphi$$

O.D.E. $\dfrac{\sin\theta}{T(\theta)} \dfrac{d}{d\theta}\left[\sin\theta \dfrac{dT(\theta)}{d\theta}\right] + \ell(\ell+1)\sin^2\theta = m^2$

$\Rightarrow$ $T(\theta)$ will be stamped by ℓ, m

$$T_\ell^m(\theta) = T_{\ell m}(\theta)$$

Associated Legendre Diff. Eq.

O.D.E. $\dfrac{F''(\varphi)}{F(\varphi)} = -m^2$

$$\begin{aligned} F(\varphi) &= A\sin(m\varphi) + B\cos(m\varphi) \\ &= A'\sin(m\varphi + B') \\ &= A''\cos(m\varphi + B'') \\ &= Ce^{im\varphi} + De^{-im\varphi} \end{aligned}$$