Deriving The 3D QM Solutions From Scratch

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The 3D TISE is

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

The spherical Laplacian is

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

Presuming ψ separates in spherical coordinates as $\psi = R(r)Y(\theta,\phi)$, the TISE is

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right] + VRY = ERY$$

$$\Leftrightarrow \left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2mr^2}{\hbar^2}[E-V]\right\} + \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = 0$$

This separates the equation; the left side depends solely on r, and the right only on θ,ϕ, implying each term is constant, as if the left term varies in r, the right term cannot vary to compensate and keep the whole equation equal to zero.

We therefore reduce this to the system

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2mr}{\hbar^2}[E-V] = \ell(\ell+1),$$

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

First, we consider the angular equation: expanding,

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

We separate again. Presuming $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$,

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

Dividing by Y and moving the term on the right over,

$$\left\{\frac{\sin\theta}{\Theta}\left(\cos\theta\frac{\partial\Theta}{\partial\theta}+\sin\theta\frac{\partial^2\Theta}{\partial\theta^2}\right)+\ell(\ell+1)\sin^2\theta\right\}+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi}=0$$

This is clearly separated, so the angular equation reduces to two equations

$$\frac{\sin\theta}{\Theta}\left(\cos\theta\frac{\partial\Theta}{\partial\theta}+\sin\theta\frac{\partial^2\Theta}{\partial\theta^2}\right)+\ell(\ell+1)=m^2,$$

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

The second is trivial: the ansatz $e^{k\phi}$ yields auxiliary equation $k^2+m^2=0 \Leftrightarrow k=\pm im$. Allowing $m<0$, this is just $k=im$, so $\Phi(\phi)=e^{im\phi}$.

The first equation is a standard result (I guess),

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

where

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

and

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

are the Legendre polynomials.