THE SCHRODINGER EQUATION IN SPHERICAL COORDINATES

Depending on the symmetry of the problem it is sometimes more convenient to work with a coordinate system that best simplifies the problem. For example, the hydrogen atom can be most conveniently described by using spherical coordinates since the potential energy U(r) and force F(r) both depend on the radial distance ‘r’ of the electron from the nucleus (proton).

$$U(r) = -\frac{Zke^2}{r}, \ \ (Z=1)$$

$$F(r) = -\frac{dU(r)}{dr} = \frac{Zke^2}{r^2}$$

Since the force is a conservative force, then the energy (kinetic + potential) remains constant and we will show that it is quantized. Since the energy is quantized, it leads to stationary states where,

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-i\omega t}$$

where $E=\hbar\omega$ is the particle energy

Where $\psi(\mathbf{r})$ is the solution to the Time Independent Schrodinger Equation in spherical coordinates:

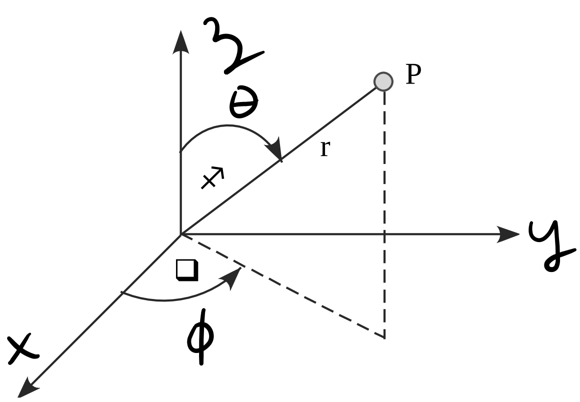
$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + U(\mathbf{r})\psi(r) = E\psi(\mathbf{r})$$

Where,

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

is the Laplacian Operator in spherical coordinates. Recall that in spherical coordinates:

$$r: \ \ 0 \to \infty$$
$$\theta: \ \ 0 \to \pi$$
$$\phi: \ \ 0 \to 2\pi$$



Thus, In spherical coordinates $\psi(r) = \psi(r,\theta,\phi)$. Substituting the Laplacian Operator in the TISE we get:

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

We will show that the solution to this equation will demonstrate the quantization of ENERGY and ANGULAR MOMENTUM! The solution will also show the origin and physical meaning of the quantum numbers:

n = principal quantum number (describes the size and energy of an orbital)
ℓ = orbital quantum number (describes the shape of the orbital)
m$_\ell$ = magnetic quantum number (describes the orientation of orbital in space)

Using separation of variable,

$\boxed{\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi)}$ substitute into the TISE:

$$-\frac{\hbar^2}{2m}\left(\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial\phi^2}\right)=(E-U)Rfg$$

Multiply by r^2 and divide by $-\dfrac{\hbar^2}{2m}$:

$$fg\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{Rg}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{Rf}{\sin^2\theta}\frac{\partial^2 g}{\partial\phi^2}=-\frac{2m}{\hbar^2}(E-U)r^2Rfg$$

Divide both sides by Rfg:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{1}{g\sin^2\theta}\frac{\partial^2 g}{\partial\phi^2}=-\frac{2m}{\hbar^2}(E-U)r^2$$

Rearranging:

$$\boxed{\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\frac{2mr^2}{\hbar^2}(E-U)=-\left[\frac{1}{f(\theta)\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df(\theta)}{d\theta}\right)+\frac{1}{g(\phi)\sin^2\theta}\frac{d^2g(\phi)}{d\phi^2}\right]}$$

Note that the LHS is a function of *r* only and the RHS is a function of θ and Φ only. Since the variables are independent, changes in *r* cannot effect the RHS and changes in θ and Φ cannot effect the LHS. Thus, the two sides must be equal to the same constant, which we will call $\ell(\ell+1)$

SOLUTION TO THE ANGULAR DEPENDENCE

$$\left[\frac{1}{f(\theta)\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df(\theta)}{d\theta}\right)+\frac{1}{g(\phi)\sin^2\theta}\frac{d^2g(\phi)}{d\phi^2}\right]=-\ell(\ell+1)$$

$$\frac{1}{g(\phi)}\frac{d^2g(\phi)}{d\phi^2}=-\ell(\ell+1)\sin^2\theta-\frac{\sin\theta}{f(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{df(\theta)}{d\theta}\right)$$

Setting both sides equal to the constant $-m^2$:

LHS

$$\frac{1}{g(\phi)}\frac{d^2g(\phi)}{d\phi^2}=-m^2$$

$$\frac{d^2g(\phi)}{d\phi^2}+m^2g(\phi)=0$$

$$g(\phi)=e^{im\phi}$$

Since $\psi(r,\theta,\phi)$ must be single-valued, then:

$$g(\phi)=g(\phi+2\pi)$$

$$e^{im\phi}=e^{im(\phi+2\pi)}$$

$$e^{im\phi}=e^{im\phi}e^{i2\pi m}$$

$$e^{i2\pi m}=1$$

$$e^{i2\pi m}=\cos(2\pi m)+i\sin(2\pi m)$$

$\boxed{m=0,\pm1,\pm2,......}$ magnetic quantum number

RHS

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

Solution:

$$f_\ell^m(\theta)=\frac{(\sin\theta)^{|m|}}{2^\ell\ell!}\left[\frac{d}{d(\cos\theta)}\right]^{\ell+1}(\cos^2\theta-1)^\ell \quad \text{(Associated Legendre Functions)}$$

$$\boxed{\begin{array}{l}\ell=0,1,2,3.....\\ m=0,\pm1,\pm2,...,\pm\ell\end{array}}$$

ℓ = angular momentum quantum number

$$\boxed{\begin{aligned} f_0^0 &= 1 \\ f_1^0 &= 2\cos\theta \\ f_1^1 &= \sin\theta \\ f_2^0 &= 4(3\cos^2\theta - 1) \end{aligned}}$$

Some Associated Legendre Functions

The product of the angular dependence are called the Spherical Harmonics:

$\boxed{Y_\ell^m(\theta,\phi) = f_\ell^m(\theta) g_m(\phi)}$ Spherical Harmonics

$$\boxed{\begin{aligned} Y_0^0 &= \frac{1}{\sqrt{4\pi}} \\ Y_1^0 &= \frac{1}{2}\sqrt{\frac{3\cos\theta}{\pi}} \\ Y_1^{\pm 1} &= \pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi} \end{aligned}}$$

Some Spherical Harmonics

<u>SOLUTION TO THE RADIAL DEPENDENCE</u>

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

$$\text{multiply by: -}\frac{\hbar^2}{2mr^2}$$

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

For the hydrogen atom $U(r) = -\dfrac{Zke^2}{r}$ where $(Z = 1)$

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

The solution to this equation is:

$$R_{n\ell} = \frac{a_o e^{-(\frac{r}{a_o})n}}{r} L_{n\ell}(r/a_o)$$

where $L_{n\ell}(r/a_o) =$ Laguerre Polynomials

The result for the energy of the Hydrogen atom is as expected, same as the Bohr Theory!!!

$\boxed{E_n = -\frac{ke^2}{2a_o}\left(\frac{Z}{n}\right)^2}$ Energy of Hydrogen Atom

Where n=1,2,3…. and n > ℓ. $\ell = 0,1,2,3,\cdots\cdots(n-1)$

<u>THE COMPLETE WAVEFUNCTION FOR THE HYDROGEN ATOM</u>

$$\psi_{n\ell m}(r,\theta,\phi) = C_{n\ell m} R_{n\ell}(r) Y_\ell^m(\theta,\phi)$$

Where $C_{n\ell m}$ is a constant determined by the normalization conditions.