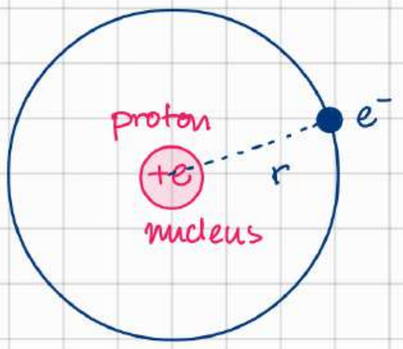
The Hydrogen Atom



The nucleus consists of a proton with charge $+e$

An electron revolves in orbits around the nucleus.

Potential Energy of the system :

$$V(r) = \frac{(+e)(-e)}{4\pi\epsilon_0 r} = \frac{-e^2}{4\pi\epsilon_0 r}$$

I shall execute the quantum mechanical treatment of the hydrogen atom with the following steps :-

Step I : Write the Hamiltonian of the system.

The classical Hamiltonian for this system is :

$$H = K.E. + P.E.$$

$$= \frac{p^2}{2m} + \left(\frac{-e^2}{4\pi\epsilon_0 r} \right)$$

$$= \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0}$$

Step II : Write the Schrödinger equation in spherical polar co-ordinates

Time-independent -

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

In spherical polar co-ordinates (r,θ,ϕ) the Laplacian takes the form :

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

So the time-independent Schrödinger equation reads :

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

$\longrightarrow$ eq^n 1

Uhff !! This is a complicated looking equation !

Can we attack it by simplifying or breaking up the equation into managable parts ?

The answer is — yes, we can !

Our line of attack will be the separation of variable technique.

Also, keep in mind that our potential $\frac{-e^2}{4\pi\epsilon_0 r}$ is dependent only on r and not on θ and ϕ.

$$\therefore \; V(r,\theta,\phi) \equiv V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

This takes us to the third step :

Step III : Separation of variable technique.

Suppose $\psi(r,\theta,\phi)$ is composed of two other functions :- $R(r)$ and $Y(\theta,\phi)$

Such that $\psi(r,\theta,\phi)$ may be written as

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

Let's put it into equation 1

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}(RY)\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}(RY)\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}(RY)\right)\right] + VRY = ERY$$

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

Dividing both sides by RY ,

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

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

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

The first term depends only on R,

The second term depends only on θ, ϕ

So each term must individually be a constant.

Let's say,

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

$\longrightarrow$ eq^n 2

So to get 0, the other term must be $-l(l+1)$

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

$\longrightarrow$ eq^n 3

Equation 2 is called the radial equation.

Note that it contains $V(r)$ as well as E.
So, we can be sure that the energy states in the Hydrogen atom are dependent only on 'r' and not on θ and ϕ.

Equation 3 is called the angular equation.
You will see later that this equation will give us the concept of atomic orbitals.

Step IV :

Let's keep aside the radial equation for now and attack the angular equation.

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

Multiplying both sides by $Y\sin^2\theta$,

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

Let's employ the separation of variable technique again to separate out θ and ϕ dependent parts.

$$\text{Let}\quad Y(\theta,\phi)=A(\theta)B(\phi)$$

Putting it in the above equation,

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

$$\Rightarrow B\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial A}{\partial\theta}\right)+A\frac{\partial^2 B}{\partial\phi^2}+l(l+1)AB\sin^2\theta=0$$

Dividing both sides by AB,

$$\left[\frac{\sin\theta}{A}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial A}{\partial\theta}\right)+l(l+1)\sin^2\theta\right]+\left[\frac{1}{B}\frac{\partial^2 B}{\partial\phi^2}\right]=0$$

We see that the first term depends only on θ and the second term depends only on ϕ

So each must be equal to some constant.

Let's say,

$$\frac{\sin\theta}{A}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial A}{\partial\theta}\right)+l(l+1)\sin^2\theta = m^2$$

$\longrightarrow$ eq^n (4)

So, the other term must be $-m^2$

$$\therefore \frac{1}{B}\frac{\partial^2 B}{\partial\phi^2} = -m^2$$

Since, B depends only on ϕ i.e. $B(\phi)$

$\therefore$ partial derivative may be converted to a total derivative.

$$\frac{\partial^2 B}{\partial\phi^2} \rightarrow \frac{d^2 B}{d\phi^2}$$

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

$$\Rightarrow \frac{d^2B}{d\phi^2} = -Bm^2$$

$$\Rightarrow \frac{d^2B}{d\phi^2} + Bm^2 = 0$$

The solution to this equation is simple :

$$\boxed{B(\phi) = K_1 e^{im\phi}}$$

K_1 is a constant that may later be absorbed into the normalisation constant.

'm' can take both positive & negative values.

Let's try to solve the other equation i.e. eq^n 4

$$\frac{\sin\theta}{A}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial A}{\partial\theta}\right) + l(l+1)\sin^2\theta = m^2$$

Since A is a function of θ alone, so we can replace the partial derivative with total derivative

$$\frac{\sin\theta}{A}\frac{d}{d\theta}\left(\sin\theta\frac{dA}{d\theta}\right)+l(l+1)\sin^2\theta = m^2$$

$$\Rightarrow \sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dA}{d\theta}\right)+l(l+1)\sin^2\theta A = m^2 A$$

$$\Rightarrow \sin^2\theta\frac{d^2A}{d\theta^2}+\sin\theta\cos\theta\frac{dA}{d\theta}+l(l+1)\sin^2\theta A = m^2A$$

$$\Rightarrow \frac{d^2A}{d\theta^2}+\cot\theta\frac{dA}{d\theta}+\left[l(l+1)-\frac{m^2}{\sin^2\theta}\right]A = 0$$

Let, $x = \cos\theta$

$$\Rightarrow \theta = \cos^{-1}x$$

$$\Rightarrow d\theta = \frac{-1}{\sqrt{1-x^2}}dx$$

$$\Rightarrow \frac{d}{d\theta} = -\sqrt{1-x^2}\frac{d}{dx}$$

$$\Rightarrow \frac{d^2}{d\theta^2} = -\sqrt{1-x^2}\frac{d}{dx}\left(-\sqrt{1-x^2}\frac{d}{dx}\right)$$

$$= \sqrt{1-x^2}\sqrt{1-x^2}\frac{d^2}{dx^2}+\frac{\sqrt{1-x^2}(-2x)}{2\sqrt{1-x^2}}\frac{d}{dx}$$

$$= (1-x^2)\frac{d^2}{dx^2}-x\frac{d}{dx}$$

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

$$\Rightarrow (1-x^2)\frac{d^2A}{dx^2} - x\frac{dA}{dx} + \cot\theta\left(-\sqrt{1-x^2}\right)\frac{dA}{dx}$$

$$+ \left[l(l+1) - \frac{m^2}{1-\cos^2\theta} \right] A = 0$$

$$\Rightarrow (1-x^2)\frac{d^2A}{dx^2} - x\frac{dA}{dx} - \frac{\cos\theta}{\sin\theta}\sqrt{1-\cos^2\theta}\,\frac{dA}{dx}$$

$$+ \left[l(l+1) - \frac{m^2}{1-\cos^2\theta} \right] A = 0$$

$$\Rightarrow (1-x^2)\frac{d^2A}{dx^2} - x\frac{dA}{dx} - \cos\theta\,\frac{dA}{dx}$$

$$+ \left[l(l+1) - \frac{m^2}{1-x^2} \right] A = 0$$

$$\Rightarrow (1-x^2)\frac{d^2A}{dx^2} - 2x\frac{dA}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2} \right] A = 0$$

This equation is known as the Associated Legendre's differential equation.

Homework : try to find out the Legendre's differential equation and the Associated Legendre's differential equation in any Mathematical Physics books and see how to solve these equations.

Anyways, the solution to the Associated Legendre's differential equation is the associated Legendre function -

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

$P_l(x)$ is the Legendre Polynomial defined by

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

But we considered $\cos\theta = x$.

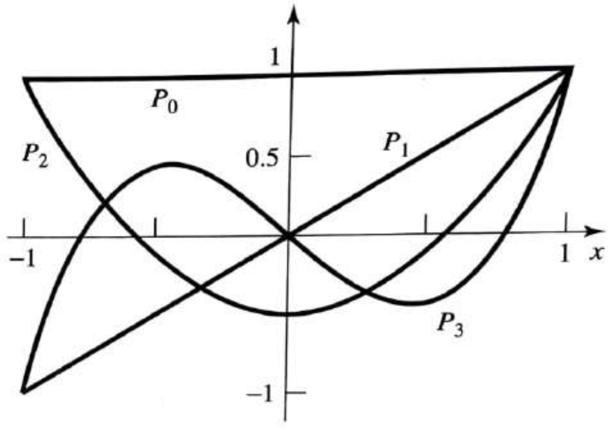
$\therefore$ The solution that we want is.

$$A(\theta) = P_l^m(\cos\theta) = (1-\cos^2\theta)^{\frac{|m|}{2}} \left(\frac{d}{d\cos\theta}\right)^{|m|} \left\{ \frac{1}{2^l l!} \left(\frac{d}{d\cos\theta}\right)^l (\cos^2\theta - 1)^l \right\}$$

TABLE 4.1: The first few Legendre polynomials, $P_l(x)$: (a) functional form, (b) graphs.

$P_0 = 1$
$P_1 = x$
$P_2 = \frac{1}{2}(3x^2 - 1)$
$P_3 = \frac{1}{2}(5x^3 - 3x)$
$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$
$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$

(a)

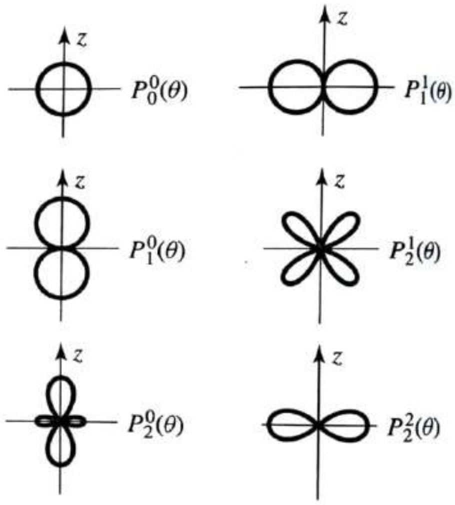


(b)

TABLE 4.2: Some associated Legendre functions, $P_l^m(\cos\theta)$: (a) functional form, (b) graphs of $r = P_l^m(\cos\theta)$ (in these plots r tells you the magnitude of the function in the direction θ; each figure should be rotated about the z-axis).

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\ \cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\ \cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

(a)



(b)

TABLE 4.3: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2}\sin\theta\,(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta e^{\pm 3i\phi}$

Remember the quantum numbers n, l, m that you read about while studying atomic models?

$$n = 1, 2, 3, \ldots$$

$$l = 0, 1, 2, \ldots$$

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

We are now ready to analyze why these quantum numbers takes these particular values:

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

Notice this formula. For this formula to make sense, l must be a non-negative number.

$$\therefore \quad l = 0, 1, 2, \ldots$$

Also notice the formula below:

$$P_l^m(\cos\theta) = \left(1 - \cos^2\theta\right)^{\frac{|m|}{2}} \left(\frac{d}{d\cos\theta}\right)^{|m|} \left\{ \frac{1}{2^l l!}\left(\frac{d}{d\cos\theta}\right)^l \left(\cos^2\theta - 1\right)^l \right\}$$

If $|m| > l$ then we find that successive diffirentiation $\left(\frac{d}{d\cos\theta}\right)^{|m|}$ gives $P_l^m(\cos\theta) = 0$.

so, $|m| \geqslant l$

$\therefore$ the value of m goes from $-l$ to l.

$m = -l, -l+1, -l+2, \ldots -1, 0, 1, \ldots, l-2, l-1, l$

So, we are in a position to construct our angular equation solution.

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

However, this solution is not normalised. We can normalize this using a normalisation constant.

The normalised solution is :

$$\boxed{Y_m^l(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)\,(l-|m|)!}{4\pi\,(l+|m|)!}}\; P_l^m(\cos\theta)\, e^{im\phi}}$$

$$\epsilon = (-1)^m \quad \text{for} \quad m > 0$$
$$= 1 \quad \text{for} \quad m \leqslant 0$$

Step V :

We have solved the angular equation and obtained $Y^{l}_{m}(\theta, \phi)$ as the solution.

Now it is our turn to solve the radial equation i.e. equation 2

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

Since $R(r)$ and $V(r)$ are dependent on r alone so we can replace the partial derivative with a total derivative.

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

We shall make a cleaver substitution :

$$u(r) = r\,R(r)$$

$$\Rightarrow R = \frac{u}{r}$$

$$\Rightarrow \frac{dR}{dr} = \frac{r\frac{du}{dr} - u}{r^2}$$

So, the above equation becomes :

$$\frac{1}{R}\frac{d}{dr}\left(r^2\,\frac{r\frac{du}{dr}-u}{r^2}\right)-\frac{2mr^2}{\hbar^2}\left(V(r)-E\right)=l(l+1)$$

$$\Rightarrow \frac{d}{dr}\left(r\frac{du}{dr}-u\right)-\frac{2mr^2}{\hbar^2}\left(V(r)-E\right)R=l(l+1)R$$

$$\Rightarrow r\frac{d^2u}{dr^2}+\frac{du}{dr}-\frac{du}{dr}-\frac{2mr^2}{\hbar^2}\left(V(r)-E\right)R$$

$$=l(l+1)R$$

$$\Rightarrow \frac{d^2u}{dr^2}-\frac{2mr^2}{\hbar^2}\left(V(r)-\frac{\hbar^2}{2mr^2}l(l+1)\right)\frac{R}{r}$$

$$=-\frac{2mr^2}{\hbar^2}E\frac{R}{r}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]Rr=ERr$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u=Eu.$$

This is the radial form of the Schrödinger equation for a r-dependent potential $V(r)$

The potential for the Hydrogen atom was

$$V(r)=-\frac{e^2}{4\pi\epsilon_0 r}$$

So, the radial Schrödinger equation for the H-atom has the form :

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

We shall try to solve this equation in the next class.