Hydrogen atom

Schrödinger time independent equation

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

$$\Rightarrow \nabla^2\psi + \frac{2\mu}{\hbar^2}(E-V)\psi = 0.$$

For Hydrogen atom, $V(r) = -\frac{Z}{r}$.

(in SI units, $Z = \frac{|e|}{4\pi\epsilon_0}$.)

Useful to write ∇^2 in spherical-polar co-ordinates.

& $\psi \equiv \psi(r,\theta,\varphi)$.

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

$$+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{2\mu}{\hbar^2}(E-V)\psi = 0.$$

Use $\psi(r,\theta,\varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$, substitute in above equation, multiply by $\frac{r^2\sin^2\theta}{R\Theta\Phi}$ and rearrange

$$\Rightarrow -\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta\,(E-V)$$

$$-\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) = \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}. \qquad \text{(I)}$$

L.H.S. is a function of r & θ

R.H.S. is a function of φ alone

Let both sides equal $-m_l^2$ (a negative definite quantity)

$$\Rightarrow \boxed{\frac{d^2\Phi}{d\varphi^2} = -m_l^2\,\Phi} \quad \text{—— (II)}$$

Rearranging (I) (using (II)),

$$\Rightarrow \frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2(E-V)}{\hbar^2}$$

$$= \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right).$$

L.H.S. is a function of r, while, R.H.S. is a function of θ. Thus, both sides equal a constant.

Let that constant be $l(l+1)$

(inspired by the existing standard differential eqns for Laguerre & Legendre polynomials)

$$\Rightarrow \boxed{\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + \frac{2\mu}{\hbar^2}\left[E - V - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = 0.} \quad \text{—— (III)}$$

$$\& \quad \boxed{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right)\Theta = 0.} \quad \text{—— (IV)}$$

$$\Theta(\theta)\,\Phi(\varphi) \equiv Y_l^{m_l}(\theta, \varphi)$$

Spherical Harmonics.

$$R(r) \equiv R_{n,l}(r).$$

Laguerre functions.

Typical $R_{n,l}(r)$

n	l	$R_{n,l}(r)$
1	0	$\frac{2}{(a_0)^{3/2}}\, e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\left(\frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{\sqrt{3}\,(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0}\, e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{1}{81\sqrt{30}} \frac{r^2}{a_0^2}\, e^{-r/3a_0}$

Here, $\boxed{a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}}$.

Typical $Y_l^{m_l}(\theta, \varphi)$

l	m_l	$Y_l^{m_l}(\theta, \varphi)$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	± 1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\varphi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	± 1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\varphi}$
2	± 2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\varphi}$

Note: $\Phi(\varphi + 2\pi) = \Phi(\varphi)$.

Typical case

$\ell = 0\ ,\ m_\ell = 0$

Radial equation: $\dfrac{d^2R}{dr^2} + \dfrac{2}{r}\dfrac{dR}{dr} + \dfrac{2\mu}{\hbar^2}\left(E + \dfrac{e^2}{4\pi\epsilon_0 r}\right)R = 0$

Try $R = Ae^{-r/a_0}$

$$\Rightarrow \left(\frac{1}{a_0^2} + \frac{2\mu}{\hbar^2}E_{n=1,\ell=0,m_\ell=0}\right)$$

$$+\left(\frac{2\mu e^2}{4\pi\epsilon_0\hbar^2} - \frac{2}{a_0}\right)\frac{1}{r} = 0.$$

$$\Rightarrow \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}.$$

$$\& \quad E_{n=1,\ell=0,m_\ell=0} = -\frac{\hbar^2}{2\mu a_0^2}$$

$$= -\frac{\mu e^4}{2(4\pi\epsilon_0\hbar)^2}$$

$$= -E_0.$$