S. S. College. Jehanabad (Magadh University)

Department : Physics

Subject : Quantum Mechanics

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Topic: Hydrogen Atom Problem

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Hydrogen Atom Problem

If m is the mass of the particle then its Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad \text{——(1)}$$

and Hamiltonian in spherical coordinates:

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

where

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \qquad \text{——(3)}$$

form eq (2) & (3)

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{\hbar^2 r^2}\right] + V(r)$$

Now, If $H\psi(\vec{r}) = E\psi(\vec{r})$

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

or

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{2m}{\hbar^2}\left[E - V(r)\right]\psi(r,\theta,\phi) = \frac{L^2}{\hbar^2 r^2}\psi(r,\theta,\phi) \qquad \text{——(4)}$$

for Hydrogen atom,

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

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and m is replaced by reduced mass μ,

$$\mu = \frac{mM}{m+M} \quad ; \quad \begin{array}{l} M \to \text{nuclear mass} \\ m \to \text{mass of electron} \end{array}$$

Then equation (4) becomes

$$\Rightarrow \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{2m}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi(r,\theta,\phi) = \frac{L^2}{\hbar^2 r^2}\psi(r,\theta,\phi) \quad \text{--- (5)}$$

and it radial equation

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2}\right]R(r) = 0$$

let $\rho = \left(-\frac{8mE}{\hbar^2}\right)^{1/2} r$, $\quad \lambda = \frac{Ze^2}{4\pi\epsilon_0\hbar}\left(-\frac{m}{2E}\right)^{1/2}$

$$= Z\alpha\left(-\frac{mc^2}{2E}\right)^{1/2}$$

$\alpha = e^2/4\pi\epsilon_0\hbar c \simeq 1/137$

Then

$$\Rightarrow \frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0 \quad \text{--- (6)}$$

In order find the solution of eq (6), we have to examine asymptotic behaviour of $R(\rho)$.

as $\rho \to 0$, then eq (6) reduces to

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$$\Rightarrow \frac{d^2R}{d\rho^2} - \frac{1}{4} R(\rho) = 0 \quad -(7)$$

Then eq (7) solution is given by

$R \propto \exp(\pm \rho/2)$ out of which

$R \propto \exp(-\rho/2)$ is acceptable

Therefore the exact solution must be of the form

$$R(\rho) = e^{-\rho/2} F(\rho)$$

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$$R(\rho) = e^{-\rho/2} F(\rho) \quad —— (8)$$

Now Putting eq (8) in (6), we get

$$\rho^2 \frac{d^2F}{d\rho^2} + \rho(2-\rho)\frac{dF}{d\rho} + [(\lambda-1)\rho - l(l+1)]F(\rho) = 0 \quad —— (9)$$

At $\rho = 0$

$$l(l+1)F(0) = 0$$

$$F(0) = 0 \text{ for } l \neq 0$$

Now form series solution;

$$F(\rho) = \sum_{K=0}^{\infty} a_K \rho^{s+K} \quad —— (10)$$

Putting eq (10) in eq (9), we get

$$\sum_{K=0}^{\infty} a_K [(s+K)(s+K+1) - l(l+1)]\rho^K -$$

$$\sum_{K=0}^{\infty} a_K [s+K+1-\lambda]\rho^{K+1} = 0 \quad —— (11)$$

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Now from equating coefficients ρ^0, we get

$$s(s+1) - l(l+1) = 0$$

$$s = l \text{ or } s = -(l+1) \qquad \text{——(12)}$$

If, $s = -(l+1)$, Then $\rho \to 0$, therefore it is neglected.

$s = l$, Then equating coefficient of ρ^{k+1}

$$a_{k+1}\left[(s+k+1)(s+k+2) - l(l+1)\right] - a_k(s+k+1-\lambda) = 0$$

Putting, $s = l$ we can get ——(13)

$$a_{k+1} = \frac{k+l+1-\lambda}{(k+1)(k+2l+2)} a_k \qquad \text{——(14)}$$

and $$\lim_{k\to\infty} \frac{a_{k+1}}{a_k} = \frac{1}{k}$$

Hence it is similar to our assumption and

$$F(\rho) \simeq \exp(\rho)$$

and

$$R(\rho) \simeq \exp(\rho/2)$$, which is not acceptable as $\rho \to \infty$

$\Rightarrow$ Therefore, λ must be equal to a positive integer n such that

$$\lambda = n = n_r + l + 1 \qquad -(15)$$

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$n_r \rightarrow$ radial quantum number
$n \rightarrow$ Principal quantum number
$l \rightarrow$ angular quantum number

and Energy eigen values from eq (5) & (15)

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} \quad ; n = 1, 2, 3 \ldots$$

Degenaracy :- Each energy level E_n, correspon to more than one distinct state which have the same energy is known as degeneracy. It is given by

$$\sum_{l=0}^{n} (2l+1) = 2\frac{n(n-1)}{2} + n = n^2$$

Spectroscopic Notation

Value of l	0	1	2	3	4	5	- - -
Principal letter	s	p	d	f	g	h	- - -

example :- $n = 4$, $l = 3$, $m_l = 0, \pm l$