Hydrogen atom

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

S.W.E. (for radial part, as pot. is central one)

$$\frac{-\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right]u = Eu \quad -(1) \quad \left[\text{here } u = rR_{nl}(r)\right]$$

[for bound state $E < 0$ (in Hydrogen atom e^- is in bound state)]

put $\lambda = \sqrt{\frac{-2\mu|E|}{\hbar^2}}$ (as for bound state $E<0$) $-(2)$

dividing eq^n (1) by E

$$\frac{-\hbar^2}{2\mu E}\frac{d^2u}{dr^2} = \left[1 + \frac{e^2}{4\pi\epsilon_0 E r} - \frac{\hbar^2}{2\mu E}\frac{l(l+1)}{r^2}\right]u$$

now put $\frac{-\hbar^2}{2\mu E} = \frac{1}{\lambda^2} \Rightarrow \lambda^2 = -\frac{2\mu E}{\hbar^2}$, as E is negative due to bound state, so λ^2 is +ve., so $E = -\frac{\lambda^2\hbar^2}{2\mu}$

$$\frac{1}{\lambda^2}\frac{d^2u}{dr^2} = \left[1 - \frac{e^2\, 2\mu}{4\pi\epsilon_0\lambda^2\hbar^2 r} + \frac{l(l+1)}{\lambda^2 r^2}\right]u \quad -(3)$$

let $\rho = \lambda r$, and $\rho_0 = \frac{\mu e^2}{2\pi\epsilon_0\lambda\hbar^2}$

Then eq^n (3) becomes

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u \quad -(4)$$

Asymptotic sol^n of the eq^n (4) in the region where $\rho \to \infty \Rightarrow \frac{d^2u}{d\rho^2} = u \quad -(5)$

general sol^n of eq^n (5) is $u(\rho) = Ae^{-\rho} + Be^{\rho}$

as e^{ρ} blows up (or diverges) so sol^n is $u(\rho) \sim Ae^{-\rho}$.

for $\rho \to 0$ $\frac{l(l+1)}{\rho^2}$ dominates eq^n (4) becomes

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u \quad \exists \text{ sol}^n \quad u(\rho) = C\rho^{l+1} + D\rho^{-l}$$

as ρ^{-l} blows up (diverges) so $u(\rho) \simeq C\rho^{l+1}$

Let the complete sol^n (including asymptotic behaviour)

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad - (6)$$

$$\frac{du}{d\rho} = \rho^{l} e^{-\rho}\left[((l+1)-\rho)v + \rho\frac{dv}{d\rho}\right]$$

$$\frac{d^2u}{d\rho^2} = \rho^{l} e^{-\rho}\left[\left(-2l-2+\rho+\frac{l(l+1)}{\rho}\right)v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right] - (7)$$

So eq^n (4) becomes (after putting eq^n (7))

$$\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + (\rho_0 - 2(l+1))v = 0 \quad - (8)$$

Let (assume) the solution, $v(\rho)$ in power series.

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j \quad \text{(shifting } j \text{ to } j+1) - (9)$$

(differentiate eq (9))

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1} \quad - (10)$$

put eq (9) & (10) into (8)

$$\rho \sum_{j=0}^{\infty} j(j+1)\, c_{j+1}\, \rho^{j-1} + 2(l+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^{j} - 2\rho \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^{j} + (\rho_0 - 2(l+1)) \sum_{j=0}^{\infty} c_j \rho^j = 0$$

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j} + 2(l+1) \sum (j+1) c_{j+1} \rho^{j} \underbrace{- 2 \sum (j+1) c_{j+1} \rho^{j+1}}_{\text{put } j+1 \to j} + (\rho_0 - 2(l+1)) \sum c_j \rho^j = 0$$

this becomes

$$-2 \sum j c_j \rho^j$$

equate the co-efficient of like powers of ρ^j

$$j(j+1)\, c_{j+1} + 2(l+1)(j+1)\, c_{j+1} - 2j c_j + (\rho_0 - 2(l+1))\, c_j = 0$$

$$\Rightarrow c_{j+1} = \left(\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right) c_j \quad \text{— (11)} \quad \text{[Recursion formula]}$$

for $j \to \infty$ $\quad \dfrac{c_{j+1}}{c_j} \to \dfrac{2}{j+1}$

As $e^{2x} = \sum_{n=0}^{\infty} \frac{(2x)^n}{n!}$

$\Rightarrow (n+1)$ term $= \dfrac{(2x)^{n+1}}{(n+1)!}$ $\Rightarrow \dfrac{(n+1)^{th}}{n^{th}}$ term $= \dfrac{2x}{n+1}$

n^{th} term $= \dfrac{(2x)^n}{n!}$

i.e. ratio of $(n+1)^{th}$ to n^{th} term of e^{2x} shows same behaviour as shown by $\dfrac{c_{j+1}}{c_j}$ at $j \to \infty$

So series behave like $e^{2\rho}$

and

$u(\rho) \propto e^{-\rho} \rho^{l+1} e^{2\rho} \sim \rho^{l+1} e^{\rho}$

again it is diverging behaviour

so can't be solution.

So series must be terminated at some finite no. let N.

i.e $\displaystyle\sum_{j=0}^{N} c_j \rho^j \quad \Rightarrow \quad c_{j+1} = 0 = c_{j+2} = \cdots c_{j+n} =$

i.e $N = j_{max}$

eqn (11) becomes

$$c_{j_{max}+1} = \left(\frac{2(j_{max} + l + 1) - \rho_0}{(j_{max}+1)(j_{max} + 2l + 2)} \right) c_{j_{max}}$$

as $C_{j_{maxi}+1} = 0 \Rightarrow 0 = \dfrac{2(j_{max}+l+1) - \rho_0}{(j_{max}+1)(j_{maxi}+2l+2)} C_{j_{maxi}}$

$\Rightarrow \quad 2(j_{maxi}+l+1) - \rho_0 = 0 \quad - (12)$

let $n = j_{maxi} + l + 1$ (n = principal quantum no.)

$2n - \rho_0 = 0 \Rightarrow \rho_0 = 2n \quad - (13)$

as $\rho_0 = \dfrac{\mu e^2}{2\pi \epsilon_0 \lambda \hbar^2} = 2n \Rightarrow \dfrac{\mu^2 e^4}{4\pi^2 \epsilon_0^2 \lambda^2 \hbar^4} = 4n^2$

$\lambda^2 = -\dfrac{2\mu E}{\hbar^2} \Rightarrow -\dfrac{\mu^2 e^4 \hbar^2}{4\pi^2 \epsilon_0^2 2\mu E \hbar^4} = 4n^2$

$E_n = -\dfrac{\mu e^4}{8\pi^2 \epsilon_0^2 \hbar^2 \cdot 4n^2} = -\left[\dfrac{\mu}{2\hbar^2}\left(\dfrac{e^2}{4\pi\epsilon_0}\right)^2\right]\dfrac{1}{n^2} = \dfrac{E_1}{n^2} \quad - (14)$

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

[Also $n = j_{maxi} + l + 1$, as $j_{maxi} = 0, 1, 2, \ldots j_{maxi}$

for $j = 0 \Rightarrow n = l+1$ $\quad l = n-1$

$j = 1 \Rightarrow n = l+2 \Rightarrow l = n-2$

$j = 2 \Rightarrow n = l+3$

i.e if one run up to $j = 3$ then n will run

$l+3, l+2, l+1$ or l will run $\Rightarrow (n-1)(n-2)(n-3)\ldots$

$\Rightarrow$

as $\lambda^2 = \frac{-2\mu E}{\hbar^2}$ $\qquad E_n = -\left[\frac{\mu e^4}{2\hbar^2 16\pi^2 \epsilon_0^2}\right]\frac{1}{n^2}$

$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \Rightarrow a_0^2 = \frac{16\pi^2\epsilon_0^2\hbar^4}{\mu^2 e^4}$

$\lambda^2 = \frac{\cancel{2}\mu}{\hbar^2}\frac{\mu e^4}{\cancel{2}\hbar^2 16\pi^2\epsilon_0^2}\frac{1}{n^2}$ $\qquad = 0.529\times 10^{-10}\,m$

$\lambda^2 = \frac{1}{a_0^2 n^2} \Rightarrow \boxed{\lambda = \frac{1}{a_0 n}}$

as $\rho = \lambda r = \frac{r}{a_0 n}$

as

$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho) \Rightarrow R_{nl}(r) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho)$

here $v(\rho)$ is a polynomial of degree $J_{max} = n-l-1$ in ρ, where

co-efficients are determined by recursion formula

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}c_j$$

and power series $\sum_{j=0}^{N=j_{max}} c_j\rho^j$ [use eq^n 11 where $\rho_0 = 2n$]

$R_{nl}(r) = \frac{u(\rho)}{r} = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho)$ $\qquad v(\rho) = c_0\rho^0 = c_0$

as $N = j_{max} = 1$ for $n=1, l=0$.

$R_{10}(r) = \frac{1}{r}(\lambda r)^{l+1}e^{-\lambda r}v(\rho)$

$R_{10}(r) = \lambda^{l+1}r^l e^{-r/na_0}c_0$

$R_{10}(r) = \frac{1}{a_0}e^{-r/a_0}c_0$

as $\int_0^\infty r^2|R_{nl}(r)|^2 dr = 1 \Rightarrow \int_0^\infty r^2\frac{c_0^2}{a_0^2}e^{-2r/a_0}dr = 1$

using Gamma fun $\int_0^\infty x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$

$\frac{c_0^2}{a_0^2}\int_0^\infty r^2 e^{-2r/a_0}dr = 1 \Rightarrow \frac{c_0^2}{a_0^2}\frac{2!}{\left(\frac{2}{a_0}\right)^3} = 1 \Rightarrow \frac{c_0^2\,\cancel{2}a_0}{\cancel{8}4} = 1 \Rightarrow \boxed{c_0 = \frac{2}{\sqrt{a_0}}}$

$$R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

For $R_{20}(r) = \lambda^{l+1} r^{l} e^{-r/na_0} v(\rho)$

$$v(\rho) = \sum_{j=0}^{N=j_{max}} c_j \rho^j = \quad \text{as } n=2,\ l=0,\ j_{max} = 2-0-1 = 1$$

$$= c_0\rho^0 + c_1\rho \Rightarrow c_0 + c_1\rho = c_0 + \lambda r c_1$$

c_1 can be find using recursion relation.

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j = \quad \text{as for } c_1 = c_{j+1} \Rightarrow j=0$$

$$c_{0+1} = \frac{2(0+0+1-2)}{(0+1)(0+0+2)} c_0 = \frac{\cancel{2}(-1)}{\cancel{2}} c_0 \Rightarrow c_1 = -c_0$$

$$c_1 = -\frac{2}{\sqrt{a_0}}$$

$$v(\rho) = c_0(1 - \lambda r) = c_0\left(1 - \frac{r}{2a_0}\right)$$

$$R_{20}(r) = \frac{c_0}{2a_0}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0} = \boxed{\cancel{\frac{2}{\sqrt{a_0}\cdot 2a_0}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}}}$$

$$\boxed{\cancel{R_{20}(r) = \frac{1}{(a_0)^{3/2}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}}}$$ and so on.

Render one has to be normalized again to find c_0 (for every fun c_0 is different)

Normalizing $\int_0^\infty |R_{20}(r)|^2 r^2 dr = 1$

$$\frac{|c_0|^2}{4a_0^2}\int_0^\infty r^2\cdot\left(1 + \frac{r^2}{4a_0^2} - \frac{r}{a_0}\right)e^{-r/a_0} dr \quad \text{using Gamma fun.}$$

$$\frac{|c_0|^2}{4a_0^2}\left[\frac{2!}{\left(\frac{1}{a_0}\right)^3} + \frac{4!}{4a_0^2\left(\frac{1}{a_0}\right)^5} - \frac{3!}{a_0\left(\frac{1}{a_0}\right)^4}\right] = 1 \Rightarrow |c_0|^2\left[\frac{a_0}{2} + \frac{3}{2}a_0 - \frac{3}{2}a_0\right] = 1$$

$$\Rightarrow c_0 = \sqrt{\frac{2}{a_0}} \quad \text{for } R_{20}(r)$$

hence

$$R_{20}(r) = \sqrt{\frac{2}{a_0}}\ \frac{1}{2a_0}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$$

$$= \sqrt{\frac{1}{2a_0^{3/2}}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$$

and so on one can find R_{21}, R_{30} ---.

Second approach for $R_{nl}(r)$

The recursion relation given by eq^n 11

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}\,c_j$$

is fun of well known associated Laguerre fun.

Note. we have taken

$$\int_0^\infty r^2 |R_{n0}(r)|^2 dr = 1$$

This comes for $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_l^m(\theta,\phi)$

$$\int_0^\infty |\psi_{nlm}(r,\theta,\phi)|^2 dV = 1$$ here $dV = r^2\sin\theta\, d\theta\, d\phi\, dr$

For R_{n0} this becomes $R_{n0}(r)\,Y_0^0(\theta,\phi)$ and $Y_0^0(\theta,\phi) = \frac{1}{(4\pi)^{1/2}}$

So, $$\int |\psi|^2 dV = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} |R_{n0}(r)|^2 |Y_0^0(\theta,\phi)|^2 r^2 \sin\theta\, d\theta\, d\phi\, dr$$

$$\int_0^\infty |R_{n0}(r)|^2 r^2 dr \underbrace{\int_0^{\pi}\int_0^{2\pi}\frac{1}{(4\pi)}\cdot \sin\theta\, d\theta\, d\phi}_{1}$$

as $\int_0^{2\pi} d\phi = 2\pi$

$\int_0^{\pi}\sin\theta\, d\theta = \cos\theta\Big]_0^{\pi} = 2$

& we have $\boxed{\int_0^\infty r^2 |R_{n0}(r)|^2 dr = 1 = \int |\psi|^2 dV}$ only for R_{n0}

So to find $R_{21} \Rightarrow R_{nl}$ one has to solve

$\int |\psi|^2 dV \Rightarrow$ for R_{21}, $l=1$, $m=0$ i.e $Y_1^0(\theta,\phi)$

$$Y_1^0(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta .$$

$$\int_0^\infty |R_{21}|^2 r^2 dr \underbrace{\int_0^\pi \int_0^{2\pi} \frac{3}{4\pi} \cdot \cos^2\theta \sin\theta \, d\theta \, d\phi}_{\frac{3}{4\pi} \cdot 2\pi \int_0^\pi \underbrace{\cos^2\theta \sin\theta \, d\theta}_{\frac{2}{3}}} = 1$$

$$\int_0^\infty |R_{21}|^2 r^2 dr \, [1] = 1 \Rightarrow \text{hence}$$

$$\boxed{\iiint_0^\infty |\psi_{nlm}|^2 dV = 1 = \int_0^\infty |R_{nl}(r)|^2 r^2 dr}$$

for $R_{21}(r) \Rightarrow R_{nl}(r) = \frac{1}{r}(\lambda r)^{l+1} e^{-\lambda r} C_0$ $\left[\begin{array}{l} n=2 \\ l=1 \end{array} \Rightarrow j_{max} = n-l-1 = 0. \right.$

so $\sum C_j \rho^j = C_0$.

$$R_{21}(r) = \frac{1}{r}\left(\frac{r}{2a_0}\right)^2 e^{-r/2a_0} C_0$$

$$\int_0^\infty |R_{21}(r)|^2 r^2 dr = |C_0|^2 \int_0^\infty \frac{r^4}{4a_0^4} e^{-r/a_0} dr = 1$$

$$\frac{|C_0|^2}{4a_0^4} \frac{4!}{\left(\frac{1}{a_0}\right)^5} = 1 \Rightarrow |C_0| = 1/\sqrt{6a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{6a_0^3}} \frac{1}{2}\left(\frac{r}{2a_0}\right) e^{-r/2a_0} = \frac{1}{\sqrt{24 a_0^3}} \left(\frac{r}{2a_0}\right) e^{-r/2a_0}$$