Hydrogen Atom

$V(r) = \frac{-Ze^2}{r} \Rightarrow \frac{-Ze^2}{4\pi\epsilon_0 r}$ dropping $\frac{1}{4\pi\epsilon_0}$ & $Z=1$ hydrogen

Potential depends only on r

we have previously studied the angular part of Schrodinger's Eq. $\Rightarrow$ angular momentum

also looked at free particle $V(r) = 0$

so now look at case where $V(r) \neq 0$ and look at radial part of Schrodinger Equation

Previously we showed the following

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

with $V(r) = \frac{-Ze^2}{r}$

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

similar to what we have done earlier $\Rightarrow$ change of variables $\Rightarrow$ general solution independent of mass and charge

Define $\rho^2 = \frac{8m|E|}{\hbar^2} r^2$ note $E<0$ Bound state

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}}\, r \qquad d/dr = \frac{d\rho}{dr}\, d/d\rho = \sqrt{\frac{8m|E|}{\hbar^2}}\, d/d\rho$$

$$\left[\frac{-\hbar^2}{2m}\left\{\frac{8m|E|}{\hbar^2}\frac{1}{\rho^2}\sqrt{\frac{8m|E|}{\hbar^2}}\, d/d\rho\left(\rho^2 \frac{\hbar^2}{8m|E|}\sqrt{\frac{8m|E|}{\hbar^2}}\, d/d\rho\right) - \frac{l(l+1)}{\rho^2}\frac{8m|E|}{\hbar^2}\right\} - Ze^2\sqrt{\frac{8m|E|}{\hbar^2}}\frac{1}{\rho}\right] R = ER$$

$$-4|E|\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d}{d\rho}\right)+\frac{4|E|\,l(l+1)}{\rho^2}-Ze^2\sqrt{\frac{8m|E|}{\hbar^2}}\,\frac{1}{\rho}\Bigg]R=ER$$

Divide by $+4|E|$

$$-\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d}{d\rho}\right)+\frac{l(l+1)}{\rho^2}-Ze^2\sqrt{\frac{m}{|E|2\hbar^2}}\,\frac{1}{\rho}\Bigg]R=-\frac{1}{4}R$$

since $E<0$ + using $|E|$ in ρ definition

$$\text{let } \lambda=\frac{Ze^2}{\hbar}\sqrt{\frac{m}{2|E|}}$$

$$-\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d}{d\rho}\right)+\frac{l(l+1)}{\rho^2}-\frac{\lambda}{\rho}\Bigg]R(\rho)=-\frac{1}{4}R(\rho)$$

now similar to what we did for a free particle

let $u=\rho R$

$R=u/\rho \qquad \frac{dR}{d\rho}=\frac{\rho\, du/d\rho-u}{\rho^2} \qquad \rho^2\frac{dR}{d\rho}=\rho\frac{du}{d\rho}-u$

$$d/d\rho\left(\rho^2\frac{dR}{d\rho}\right)=d/d\rho\left(\rho\frac{du}{d\rho}-u\right)=\rho\frac{d^2u}{d\rho^2}+\cancel{\frac{du}{d\rho}}-\cancel{\frac{du}{d\rho}}=\frac{d^2u}{d\rho^2}\rho$$

so we get

$$-\frac{1}{\cancel{\rho}}\frac{d^2u}{d\rho^2}+\frac{l(l+1)}{\rho^2}\frac{u}{\cancel{\rho}}-\frac{\lambda}{\rho}\frac{u}{\cancel{\rho}}=-\frac{1}{4}\frac{u}{\cancel{\rho}}$$

$$-\frac{d^2u}{d\rho^2}+\frac{l(l+1)}{\rho^2}u-\frac{\lambda u}{\rho}+\frac{1}{4}u=0$$

$$* \quad \boxed{\frac{d^2u}{d\rho^2}-\left[\frac{l(l+1)}{\rho^2}-\frac{\lambda}{\rho}+\frac{1}{4}\right]u=0}$$

need to solve this equation

1st look at asymptotic behavior

ρ small $\frac{1}{\rho^2}$ much larger than $\frac{1}{\rho}$ so neglect $\frac{1}{\rho}$ terms

$$\Rightarrow \frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u = 0$$

Try series solution

$$u = \sum_{m=0}^{\infty} a_m \rho^{s+m}$$

$$\sum_{m=0}^{\infty} a_m (s+m)(s+m-1)\rho^{s+m-2} - \ell(\ell+1)\sum_{m=0}^{\infty} a_m \rho^{s+m-2} = 0$$

for $m=0$

$$a_0\{(s)(s-1) - \ell(\ell+1)\} = 0 \quad a_0\{s^2 - s - \ell^2 - \ell\} = 0$$

$a_0 \neq 0$

if $s = -\ell \Rightarrow \{\ell^2 + \ell - \ell^2 - \ell\} = 0$ ✓

if $s = \ell+1 \Rightarrow \{\ell^2 + 2\ell + 1 - \ell - 1 - \ell^2 - \ell\} = 0$ ✓

Since series is $\rho^s \sum_{m=0}^{\infty} a_m \rho^m$ and ρ small ρ^1, ρ^2, ρ^3 small so only $m=0$ term matters so

$$u = a_0 \rho^s = \begin{cases} a_0 \rho^{-\ell} \\ a_0 \rho^{\ell+1} \end{cases}$$

$$R = \frac{u}{\rho} \Rightarrow R = \begin{cases} a_0 \rho^{-\ell-1} \\ a_0 \rho^{\ell} \end{cases}$$ ← goes to ∞ at origin so discard

$R(\rho) \Rightarrow \rho^\ell$ for small ρ $\quad (s = \ell+1)$

for ρ large $\frac{1}{\rho^2}$ small + $\frac{1}{\rho}$ small so we get

$$\frac{d^2u}{d\rho^2} - \frac{1}{4}u = 0 \qquad u = e^{\pm \rho/2}$$

$u^{\rho/2} \to \infty$ for free potential so discard

$$u = e^{-\rho/2}$$

$$R \Rightarrow \frac{e^{-\rho/2}}{\rho} \qquad \rho \text{ large}$$

since we know $u \propto e^{-\rho/2}$ use this information to solve problem

$$\text{let } u = y(\rho)e^{-\rho/2}$$

substitute into $*$

$$\frac{du}{d\rho} = \frac{dy}{d\rho}e^{-\rho/2} + y(\rho)e^{-\rho/2}(-1/2)$$

$$\frac{d^2u}{d\rho^2} = \frac{d^2y}{d\rho^2}e^{-\rho/2} + \frac{dy}{d\rho}e^{-\rho/2}(-1/2) - \frac{dy}{d\rho}e^{-\rho/2}\left(\frac{1}{2}\right) + y(\rho)e^{-\rho/2}\left(\frac{1}{4}\right)$$

so we get

$$\cancel{e^{-\rho/2}}\left(\frac{d^2y}{d\rho^2} - \frac{dy}{d\rho} + \cancel{y(\rho)\frac{1}{4}}\right) - \left[\frac{\ell(\ell+1)}{\rho^2} - \frac{\lambda}{\rho} + \cancel{\frac{1}{4}}\right]y(\rho)\cancel{e^{-\rho/2}} = 0$$

$$\star \quad \boxed{\frac{d^2y}{d\rho^2} - \frac{dy}{d\rho} - \left(\frac{\ell(\ell+1)}{\rho^2} - \frac{\lambda}{\rho}\right)u(\rho) = 0}$$

from earlier we know that $u(\rho) = \rho^s \sum_{m=0}^{\infty} a_m \rho^m \quad s = \ell+1$

so guess solution

$$y(\rho) = \rho^{\ell+1}\sum_{m=0}^{\infty} a_m \rho^m = \sum_{m=0}^{\infty} a_m \rho^{m+\ell+1}$$

substitute into ☆

$$\sum_{m=0}^{\infty} a_m (m+\ell+1)(m+\ell)\, \rho^{m+\ell-1} - \sum a_m (m+\ell+1)\, \rho^{m+\ell} - \sum a_m\, \ell(\ell+1)\, \rho^{m+\ell-1} - \sum a_m \lambda\, \rho^{m+\ell} = 0$$

$$\sum_{m=0}^{\infty} a_m \left[(m+\ell+1)(m+\ell) - \ell(\ell+1)\right] \rho^{m+\ell-1} - \sum_{m=0}^{\infty} a_m \left[(m+\ell+1) - \lambda\right] \rho^{m+\ell} = 0$$

linearly independent so lowest power of $\rho = 0 \Rightarrow \rho^{m+\ell-1}$

for $m=0$ we find

$$a_0 \left[(\ell+1)(\ell) - \ell(\ell+1)\right] = 0$$
$$a_0 [0] = 0 \checkmark \quad \text{so } a_0 \text{ can be anything}$$

note since $m=0$ term is 0 in first sum we can start sum from $m=1$

1st term

$$\sum_{m=1}^{\infty} a_m \left[(m+\ell+1)(m+\ell) - \ell(\ell+1)\right] \rho^{m+\ell-1} \qquad \text{let } k = m-1, \quad m = k+1$$

$$\sum_{k=0}^{\infty} a_{k+1} \left[(k+\ell+2)(k+\ell+1) - \ell(\ell+1)\right] \rho^{k+\ell} \qquad k \text{ is a dummy index, let } k \to m$$

so entire eq. becomes

$$\sum_{m=0}^{\infty} a_{m+1} \left[(m+\ell+2)(m+\ell+1) - \ell(\ell+1)\right] \rho^{m+\ell} - \sum_{m=0}^{\infty} a_m \left[(m+\ell+1) - \lambda\right] \rho^{m+\ell} = 0$$

$$\sum_{m=0}^{\infty} \underbrace{\left\{ a_{m+1} \left[(m+\ell+2)(m+\ell+1) - \ell(\ell+1)\right] - a_m \left[(m+\ell+1) - \lambda\right] \right\}} \rho^{m+\ell} = 0$$

if true for all ρ term in $\{\}$ must be 0

$$a_{m+1} \left[(m+\ell+2)(m+\ell+1) - \ell(\ell+1)\right] - a_m \left[(m+\ell+1) - \lambda\right] = 0$$

so

$$\boxed{a_{m+1} = \frac{(m+\ell+1) - \lambda}{(m+\ell+2)(m+\ell+1) - \ell(\ell+1)}\, a_m}$$

$a_0 \neq 0$ once a_0 known all other $a_1, a_2 \ldots$ known

normalization

look at asymptotic behavior for large m

$\frac{a_{m+1}}{a_m}$ as $m \to \infty \approx \frac{m}{m^2} = \frac{1}{m}$

note $e^{\rho} = 1 + \rho + \rho^2/2 + \rho^3/6 + \dots$

$a_0 = 1$ $\quad \frac{a_1}{a_0} = 1$

$a_1 = 1$ $\quad \frac{a_2}{a_1} = 1/2 \Rightarrow \frac{a_{m+1}}{a_m} = \frac{1}{m}$

$a_2 = \frac{1}{2}$

$a_3 = 1/6$ $\quad \frac{a_3}{a_2} = 1/3$

so for large m our series $\approx e^{\rho}$

recall $u(\rho) = y(\rho) e^{-\rho/2} = e^{\rho} e^{-\rho/2} = e^{\rho/2}$

so this has form of increasing exponential which does not converge so series must terminate at some point (to be normalizable)

counting variable

this occurs if $(m+l+1) - \lambda = 0$ or $\lambda = m+l+1$

recall $\lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{m}{2|E|}}$ mass

I used "m" for counting & "m" for mass so redefine counting variable as j

so $(j+l+1) - \lambda = 0$ or $\lambda = j+l+1$

$\frac{Ze^2}{\hbar}\sqrt{\frac{m}{2|E|}} = j+l+1 \Rightarrow \frac{Z^2e^4}{\hbar^2}\frac{m}{2|E|} = (j+l+1)^2$

so $E = \frac{-Z^2e^4}{\hbar^2}\frac{m}{2(j+l+1)^2}$ $\quad j = 0, 1, 2 \dots$

E degenerate for different values of j, l

note $j = 0, 1, 2 \ldots$

is this the principle quantum # you are familiar with?

for $Z=1$ $\quad E = \frac{-13.6\,eV}{n^2}$

no! principle quantum # starts from $n=1$

so redefine $\quad n = j + l + 1 \quad$ principle quantum #

$$\boxed{E = \frac{-Z^2 e^4 m}{2\hbar^2 n^2} = \frac{-13.6\,eV\ Z^2}{n^2} \qquad n = 1, 2, 3, \ldots}$$

return to $R(\rho)$

$$R(\rho) = \frac{u(\rho)}{\rho} = \frac{y(\rho)}{\rho} e^{-\rho/2} = \frac{1}{\rho} \rho^{l+1} \sum a_m \rho^m e^{-\rho/2}$$

$$\Rightarrow \quad R(\rho) = \underbrace{\rho^l \sum_{m=0}^{n-l-1} a_m \rho^m}_{\text{associated Lagerre polynomials}} e^{-\rho/2}$$