~~DM's treatment~~

DM's treatment

The radial Equation is:

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

$$A=\ell(\ell+1)$$

Multiply the Equation by $\frac{\hbar^2}{2\mu r^2}R(r)$,

$$\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+ER(r)-V(r)R(r)=\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)R(r)$$

$$\left[-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+V(r)R(r)+\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)R(r)\right]=ER(r)$$

$$\left[-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+V(r)+\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)\right]R(r)=ER(r)$$

$$V_{eff}=V(r)+\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)$$

For hydrogenic Atoms.

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

The radial differential Equation becomes

$$\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{\hbar^2}{2\mu r^2}\ell(\ell+1)\right]R = 0$$

Which can be written as

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

Step 1

It is customary to define a characteristic Length scale α such that the dimensionless radius ρ is.

$$\rho = \frac{r}{\alpha} \Rightarrow dr = \alpha\, d\rho$$

We can rewrite the differential Equation for $R(\rho)$

$$\frac{1}{\alpha^2}\frac{d^2R}{d\rho^2} + \frac{2}{\alpha^2\rho}\frac{dR}{d\rho} + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_0\alpha\rho} - \frac{\hbar^2}{2\mu\alpha^2\rho^2}\ell(\ell+1)\right]R = 0$$

multiplying by α^2.

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{2\mu\alpha^2}{\hbar^2}E + \left(\frac{\mu Ze^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{2\alpha}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]R = 0$$

Note that

$$\left[\frac{2\mu\alpha^2}{\hbar^2}E + \left(\frac{\mu Z e^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{2\alpha}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right] \text{ is dimensionless.}$$

$\frac{2\mu\alpha^2}{\hbar^2}E = -\nu^2$

Define

$$\frac{1}{Z}a_0 = \frac{1}{Z}\left(\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}\right) \longrightarrow \text{length} \qquad a_0 = a_0 \approx 0.529\ \text{nm} = 0.529\ \text{Å}$$

$$\alpha \equiv \frac{4\pi\varepsilon_0\hbar^2}{\mu Z e^2} = \frac{a_0}{Z}$$

$$-\nu^2 = \frac{E}{\left(\frac{\hbar^2}{2\mu\alpha^2}\right)} \quad ; \boxed{\nu > 0} \quad \text{(dimensionless)} \quad \text{or} \quad \boxed{E = -\nu^2\frac{\hbar^2}{2\mu\alpha^2}}$$

Because we are only interested in bounded solutions., $E<0$

Using these dimensionless constants, ρ & ν, we write the radial Equation as:

$$\boxed{\frac{-d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\nu^2 + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]R = 0}$$

Ask what is the Range of ρ

$\rho \in (0, +\infty)$

Step 2. study the asymptotic form of the solutions

(a) $\rho \to \infty \Rightarrow$

$$\frac{d^2R}{d\rho^2} - \nu^2 R = 0 \quad \text{and} \quad R = \cancel{Ae^{\nu\rho}} + Be^{-\nu\rho}$$

$Ae^{\nu\rho}$ blows up at Large ρ

Thus for Large ρ

$$\boxed{R(\rho) \sim e^{-\nu\rho}}$$

(b): $\rho \to 0 \Rightarrow$

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

and:

$$R(\rho) = A\rho^{\ell} + B\cancel{\frac{1}{\rho^{\ell+1}}}$$

this tem blows up at small ρ

Thus for small ρ.

$$\boxed{R(\rho) \sim \rho^{\ell}}$$

~~Step~~

step 3 Seperate out the asymptotic behavior.

$$\boxed{R(\rho) = e^{-\nu\rho}\rho^{l} H(\rho)}$$

$$\frac{dR}{d\rho} = e^{-\nu\rho}\rho^{l} H(\rho)(-\nu) + l e^{-\nu\rho}\rho^{l-1} H(\rho) + e^{-\nu\rho}\rho^{l} H'(\rho)$$

$$= \underline{e^{-\nu\rho}\rho^{l-1}}\left[l H(\rho) - \nu\rho H(\rho) + \rho H(\rho)\right]$$

$$\frac{d^2R}{d\rho^2} = \rho^{l-1} e^{-\nu\rho}\left[(2-2\nu-2\nu l)H(\rho) + (2+2l-2\nu\rho)H'(\rho) + \rho H''(\rho)\right]$$

With these, we can obtain the DE for $H(\rho)$.

$$\boxed{\rho\frac{d^2H}{d\rho^2} + 2(l+1-\nu\rho)\frac{dH}{d\rho} + 2(1-\nu-\nu l)H(\rho) = 0}$$

step 4.

Power series solution to the Radial Equation..

$$\rho \frac{d^2H}{d\rho^2} + 2(l+1-\gamma\rho)\frac{dH}{d\rho} + 2(1-\gamma-\gamma l)H(\rho) = 0$$

Look for the solution $H(\rho)$ of the following form:

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

the 1st term $= 0$

$$\frac{dH}{d\rho} = \sum_{j=0}^{+\infty} j\, c_j \rho^{j-1} = \sum_{j=0}^{+\infty} (j+1) c_{j+1} \rho^j$$

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

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

$$\boxed{2\gamma \sum_{j=0}^{+\infty} j\, c_j \rho^j}$$

The coefficients for each power of ρ must vanish:

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

Thus we have the following recurrence ~~relationship~~ relation

$$c_{j+1} = \frac{2\nu(j+\ell+1)-2}{(j+1)(j+2\ell+2)} c_j \qquad j \geq 0$$

The asymptotic behavior of the Radial Solution Requires that

$$2\nu(j_{max}+\ell+1)-2=0$$

Define $n = j_{max}+\ell+1$

$$\Rightarrow \nu = \frac{1}{j_{max}+\ell+1}$$

① n is the principle Quantum number of a hydrogenic Atom.

$$n = 0, 1, 2, 3 \cdots +\infty$$

② $\nu = \frac{1}{n}$ and is discrete

③
$$E = -\frac{1}{n^2}\frac{\hbar^2}{2\mu\alpha^2} = -\frac{1}{n^2}\frac{\hbar^2}{2\mu}\cdot\left(\frac{\mu Z e^2}{4\pi\varepsilon_0\hbar^2}\right)^2$$

$$= -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{\mu}{\hbar^2}$$

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

(3): The Angular momentum quantum number is limited to a finite set of values for every n.

$$n = j_{max} + l + 1 \Rightarrow l = n - j_{max} - 1$$

~~It can be established~~

It can be easily established that

$$l = 0, 1, 2, \ldots (n-1)$$

$\Leftarrow$ $l \geq 0$

$j_{max} \geq 0$

To Summerize, we now have obtained three quantum numbers.

$n = 1, 2, \ldots +\infty$

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

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

In David M's Book the radial solution is of this form

$$R(\rho) = \rho^{l} e^{-\nu\rho} H(\rho) \quad \text{where } \rho = \frac{r}{a} = \frac{Zr}{a_0}$$

the radial Equation in terms of $H(\rho)$ is:

$$\rho \frac{d^2H(\rho)}{d\rho^2} + 2(l+1-\nu\rho)\frac{dH(\rho)}{d\rho} + 2(1-\gamma-\nu l)H(\rho) = 0$$

$\nu = \frac{1}{n}$

$$\rho \frac{d^2H}{d\rho^2} + 2\left(l+1-\frac{\rho}{n}\right)\frac{dH}{d\rho} + 2\left(1-\frac{1}{n}-\frac{l}{n}\right)H(\rho) = 0$$

Let $x = \frac{2\rho}{n}$, the radial Equation in term of $H(x)$ is.

$$\frac{dH(\rho)}{d\rho} = \frac{dH(x)}{dx}\frac{dx}{d\rho} = \frac{2}{n}\frac{dH(x)}{dx}$$

$$\left(\frac{nx}{2}\right)\frac{2}{n}\frac{d}{dx}\left(\frac{2}{n}\frac{dH(x)}{dx}\right) + 2\left(l+1-\frac{x}{2}\right)\frac{2}{n}\frac{dH(x)}{dx} + \frac{2}{n}\left(n-l-1\right)H(x) = 0$$

$$x\frac{d^2H(x)}{dx^2} + (2l+1+1-x)\frac{dH(x)}{dx} + (n-l-1)H(x) = 0$$

The solution is $H(x) = L_{n-l-1}^{2l+1}(x)$

~~$H(x) = H(x) = (-1)^{2l+1} L_{n-l-1} \frac{d}{dx}$~~

~~$H(x) = L_{n-l-1}^{2l+1}(x)$~~

~~$H(\rho) = L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right) = L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$~~

Review

Via the change of variable $\rho = \frac{r}{\alpha} = \frac{Zr}{\alpha_0}$

$$\downarrow$$

$$R(\rho) = \rho^{\ell} e^{-\nu\rho} H(\rho)$$

$$\downarrow \quad x = \frac{2}{n}\rho$$

$$H(\rho) = L^{2\ell+1}_{n-\ell-1}\left(\frac{2}{n}\rho\right)$$

Putting Everything together:

$$R(\rho) = \rho^{\ell} e^{-\nu\rho} H(\rho)$$

$$= \rho^{\ell} e^{-\nu\rho} L^{2\ell+1}_{n-\ell-1}\left(\frac{2}{n}\rho\right)$$

$$\downarrow$$

$$R_{n\ell}(r) = \left(\frac{Zr}{\alpha_0}\right)^{\ell} e^{-Zr/n\alpha_0} L^{2\ell+1}_{n-\ell-1}\left(\frac{2Zr}{n\alpha_0}\right)$$

$$\psi(r,\theta,\phi) = -\underbrace{\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right\}^{1/2}}_{\text{For normalization purpose}} e^{-Zr/na_0} \left(\frac{2Zr}{na_0}\right)^{\ell} L_{n-\ell-1}^{2\ell+1}\left(\frac{2Zr}{na_0}\right) Y_{\ell}^{m}(\theta,\phi)$$