Section 6.3.5: The Hydrogen Atom

The Hydrogen atom consists of an electron and a proton. let us label the electron by #1 and the proton by #2, where their positions are given by $\vec{r_e} = \vec{r_1}$ and $\vec{r_p} = \vec{r_2}$ and their momenta are given by $\vec{P_e} = \vec{P_1}$ and $\vec{P_p} = \vec{P_2}$. so the state of the two particles is described by $\Psi(\vec{r_1}, \vec{r_2}, t)$.

$\Rightarrow$ the time evolution of the wave function Ψ is determined by the schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \;; \quad \text{where } H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V(\vec{r_1}, \vec{r_2}, t)$$

$$= -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r_1}, \vec{r_2}, t)$$

$\Downarrow$

for time-independent potentials, (i.e $V(\vec{r_1}, \vec{r_2})$), the solution of schrodinger equation can be written as

$$\Psi(\vec{r_1}, \vec{r_2}, t) = \psi(\vec{r_1}, \vec{r_2})\, e^{-\frac{iE}{\hbar}} \;; \quad E \text{ is the total energy of the two particles}$$

- Now for central fields, the interaction potential depends on the distance between the two particles

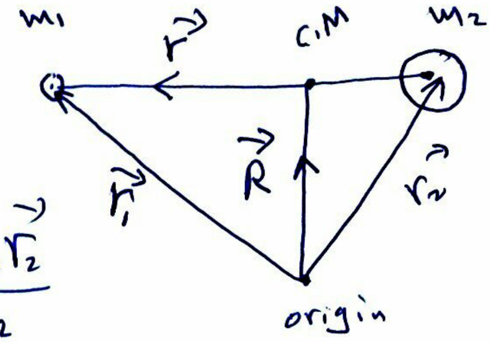
$$V(\vec{r_1}, \vec{r_2}) = V(\vec{r}) = V(|\vec{r}|) = \underbrace{V(r)}_{\text{shortly}}$$

when $\vec{r}$ is the relative distance vector of the two particles

$$\vec{r} = \vec{r_1} - \vec{r_2}$$

since V does not depend on time and depends only on relative distance, then schrodinger equation can be separated into two parts, one part describes the motion of the center of mass, and the other part describes the relative motion of the two particles. we proceeds as follows

let us first change the variables from $\vec{r_1}, \vec{r_2}$ to $\vec{r}$ and $\vec{R}$



$$\vec{r} = \vec{r_1} - \vec{r_2} \quad \text{and} \quad \vec{R} = \frac{m_1\vec{r_1} + m_2\vec{r_2}}{m_1 + m_2}$$

$$= \frac{m_1\vec{r_1} + m_2\vec{r_2}}{M} \quad ; \quad M = m_1 + m_2$$

let us introduce the reduced mass $m = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_1 m_2}{M}$

$$\vec{R} = \frac{m_1\vec{r_1} + m_2\vec{r_2}}{M} \Rightarrow M\vec{R} = m_1\vec{r_1} + m_2(\vec{r_1} - \vec{r})$$

$$M\vec{R} = m_1\vec{r_1} + m_2\vec{r_1} - m_2\vec{r}$$

$$M\vec{R} = (m_1 + m_2)\vec{r_1} - m_2\vec{r}$$

$$M\vec{R} = M\vec{r_1} - m_2\vec{r}$$

$$\Rightarrow \boxed{\vec{r_1} = \vec{R} + \frac{m_2}{M}\vec{r}}$$

similarly, we have $\boxed{\vec{r_2} = \vec{R} - \frac{m_1}{M}\vec{r}}$

now we have $\vec{P_1} = -i\hbar\vec{\nabla}_1$; $\vec{P_2} = -i\hbar\vec{\nabla}_2$

define the total momentum (Momentum of center of mass) as

$$\vec{P} = \vec{P_1} + \vec{P_2} \quad \text{----} \quad *$$

and the relative momentum as $\vec{p} = m\dot{\vec{r}} = m(\dot{\vec{r_1}} - \dot{\vec{r_2}})$

where $\vec{P_1} = m_1\dot{\vec{r_1}}$ and $\vec{P_2} = m_2\dot{\vec{r_2}}$

$$= m\dot{\vec{r_1}} - m\dot{\vec{r_2}}$$

$$= m(\vec{P_1}/m_1) - m(\vec{P_2}/m_2)$$

$$= \frac{m}{m_1}\vec{P_1} - \frac{m}{m_2}\vec{P_2}$$

but $m = \frac{m_1 m_2}{M} \Rightarrow \frac{m}{m_1} = \frac{m_2}{M}$ and $\frac{m}{m_2} = \frac{m_1}{M}$

$$\Rightarrow \boxed{\vec{P} = \frac{m_2}{M}\vec{P_1} - \frac{m_1}{M}\vec{P_2}} \quad \text{----} \quad **$$

solving eq (*) and (**) for $\vec{P_1}$ and $\vec{P_2}$, we end up with

$$\vec{P_1} = \frac{m_1}{M}\vec{P} + \vec{P} \quad \text{and} \quad \vec{P_2} = \frac{m_2}{M}\vec{P} - \vec{P}$$

so our original Hamiltonian becomes

$$H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V(r)$$

$$= \frac{\left(\frac{m_1}{M}\vec{P} + \vec{P}\right)^2}{2m_1} + \frac{\left(\frac{m_2}{M}\vec{P} - \vec{P}\right)^2}{2m_2} + V(r)$$

cross terms cancel each others

$$= \frac{\vec{P}^2}{2m_1} + \frac{\vec{P}^2}{2m_2} + \frac{m_1^2}{2M^2 m_1}\vec{P}^2 + \frac{m_2^2}{2M^2 m_2}\vec{P}^2 + V(r)$$

$$= \frac{\vec{P}^2}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right) + \frac{\vec{P}^2}{2M^2}(m_1 + m_2) + V(r) \; ; \quad \frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2}$$

$$= \frac{\vec{P}^2}{2m} + \frac{\vec{P}^2}{2M} + V(r) \; ; \quad M = m_1 + m_2$$

$$= \underbrace{\frac{\vec{P}^2}{2M}}_{\text{motion of c.m}} + \underbrace{\frac{\vec{p}^2}{2m} + V(r)}_{\text{relative motion}} \; ; \text{ when } \vec{P} = -i\hbar\vec{\nabla}_R, \quad p = -i\hbar\nabla_r$$

$$= -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + V(r)$$

Recall that our original Schrodinger equation is
↳ time-independent

$$H\,\Psi(\vec{r_1},\vec{r_2}) = E\,\Psi(\vec{r_1},\vec{r_2})$$

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V(r)\psi = E\psi$$

Now using the new coordinates system this equation ends up with

$$-\frac{\hbar^2}{2M}\nabla_R^2\Psi(\vec{R},r) - \frac{\hbar^2}{2m}\nabla_r^2\Psi(\vec{R},\vec{r}) + V(r)\Psi(\vec{R},\vec{r}) = E\Psi(\vec{R},r)$$

let us solve this eq^n by the separation of variables

let $\Psi(\vec{R},\vec{r}) = \Psi_R(\vec{R})\,\Psi_r(\vec{r})$

substitute this into Schrodinger equation and divide by $\Psi = \Psi_R\Psi_r$, we end up with

$$\left[-\frac{\hbar^2}{2M}\frac{1}{\Psi_R}\nabla_R^2\Psi_R\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{\Psi_r}\nabla_r^2\Psi_r + V(r)\right] = E$$

the first bracket depends only on $\vec{R}$ and the second bracket depends only on $\vec{r}$. since $\vec{R}$ and $\vec{r}$ are independent vectors, so each bracket must be a constant; let us call them E_R and E_r

$$-\frac{\hbar^2}{2M}\nabla_R^2\Psi_R = E_R\Psi_R \qquad \text{with} \qquad E_R + E_r = E$$

$$-\frac{\hbar^2}{2m}\nabla_r^2\Psi_r + V(r)\Psi_r = E_r\Psi_r$$

for the equation of C.M, we have

$$\nabla_R^2 \psi_R + \frac{2M E_R}{\hbar^2} \psi_R = 0 \quad , \quad \text{free particle motion}$$

$$\psi_R(\vec{R}, t) = e^{\frac{i}{\hbar}\vec{P}\cdot\vec{R}} \, e^{-\frac{i}{\hbar}E_R t} \longrightarrow E_R = \frac{\hbar^2 k^2}{2M} = \text{constant}$$

- for the relative motion, the equation represents a particle of mass m moving in a central potential V(r)

$$-\frac{\hbar^2}{2m}\nabla_r^2 \psi_r + V(r)\psi_r = E_r \psi$$

however, we can scale our new coordinates such that the origen is chosen to be at the location of center of mass i.e $\Rightarrow E = \cancelto{0}{E_{C.M}} + E_r = E_r$

for H atom the second equation (relative one) is called the radial equation with $\psi_r = \psi(r)$ and $E_r = E$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = E\,\psi(r)$$

Notice that H is spherically symmetric, therefore the solution is expected to be spherically symmetric

i.e $\psi(\vec{r}) = \psi(r)$

The radial equation of the H atom

the radial eq^n is $\dfrac{d^2u}{dr^2} + k_l^2(r)\, u = 0$; $u = r R(r)$

where $k_l^2(r) = \dfrac{2m}{\hbar^2}\left[E - V(r) - \dfrac{\hbar^2 l(l+1)}{2mr^2}\right]$; m: reduced mass

for Hydrogen atom $V(r) = -\dfrac{Ze^2}{r}$ (Gaussian units)

and for bound states, we have $E < 0$

let $E = -\mathcal{E}$; $\mathcal{E} > 0$

$$\Rightarrow k_l^2(r) = \frac{2m}{\hbar^2}\left[-\mathcal{E} + \frac{Ze^2}{r} - \frac{\hbar^2 l(l+1)}{2mr^2}\right]$$

$$= -\frac{2m\mathcal{E}}{\hbar^2} + \frac{Ze^2}{r}\frac{2m}{\hbar^2} - \frac{l(l+1)}{r^2}$$

$$\Rightarrow \frac{d^2u}{dr^2} + \left[-\frac{2m\mathcal{E}}{\hbar^2} + \frac{Ze^2}{r}\frac{2m}{\hbar^2} - \frac{l(l+1)}{r^2}\right]u = 0$$

let $x^2 = \dfrac{2m\mathcal{E}}{\hbar^2}$ and $\rho = xr \Rightarrow \dfrac{\partial}{\partial r} = \dfrac{\partial \rho}{\partial r}\dfrac{\partial}{\partial \rho} = x\dfrac{\partial}{\partial \rho}$

$$\frac{\partial^2}{\partial r^2} = \frac{\partial}{\partial r}\frac{\partial}{\partial r} = \frac{\partial \rho}{\partial r}\frac{\partial}{\partial \rho}\left(x\frac{\partial}{\partial \rho}\right) = x^2\frac{\partial^2}{\partial \rho^2}$$

$$\Rightarrow x^2\frac{d^2u}{d\rho^2} + x^2\left[-1 + \frac{Ze^2}{x^2 r}\frac{2m}{\hbar^2} - \frac{l(l+1)}{x^2r^2}\right]u = 0$$

divide by x^2

$$\frac{d^2u}{d\rho^2} + \left[-1 + \frac{2mZe^2}{\hbar^2 x}\frac{1}{\rho} - \frac{l(l+1)}{\rho^2}\right]u = 0$$

where $\alpha = \dfrac{2mZe^2}{\hbar^2 x}$

$$\frac{d^2u}{d\rho^2} + \left[-1 + \frac{\alpha}{\rho} - \frac{l(l+1)}{\rho^2}\right]u = 0 \; ; \quad \text{------ (10)}$$

let us look at the Asymptotic behavior of eq^n (10)

i) as $\rho \to 0$ $\quad \frac{l(l+1)}{\rho^2} >> \frac{\alpha}{\rho}$ and $\frac{l(l+1)}{\rho^2} >> 1$

$$\Rightarrow \frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u = 0 \qquad \text{Euler equation}$$

$$u(\rho) = \underbrace{A\rho^{l+1}}_{\text{regular}} + \underbrace{B\rho^{-l}}_{\text{irregular solution}}$$

$B=0$, since $u(r) = r R(r)$ has to vanish at $r=0$ as the potential there is infinite ($V(r) = -e^2/r$)

$\Rightarrow u(\rho) = A\rho^{l+1}$ only the regular solution survives

ii) as $\rho \to \infty$, equation (10) goes to

$$\frac{d^2u}{d\rho^2} - u = 0$$

; for bound state solution, we expect the wavefunction vanish at as $\rho \to \infty$

i.e $u \sim e^{-\rho}$

so the general solution of the Euler equation can be written as

$$u(\rho) = \rho^{l+1} e^{-\rho} \underbrace{v(\rho)}_{\text{function of } \rho} \quad \text{----- (11)}$$

let us substitute this solution into the euler equation, but before that let us find u' and u''

$$u' = (l+1)\rho^{l}e^{-\rho}v(\rho) - \rho^{l+1}e^{-\rho}v(\rho) + \underbrace{\rho^{l+1}e^{-\rho}}_{= \frac{u(\rho)}{v(\rho)}} v'(\rho)$$

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

$$= \left(\frac{l+1}{\rho}u - u - \frac{u}{v}v'\right) = \left(\frac{l+1}{\rho} - 1 + \frac{v'}{v}\right)u'$$

and $u'' = \left(-\frac{(l+1)}{\rho^2} + \frac{1}{V}V'' - \frac{V'^2}{V^2} \right) u + \left(\frac{l+1}{\rho} - 1 + \frac{V'}{V} \right) u'$

$$= \left(-\frac{(l+1)}{\rho^2} + \frac{1}{V}V'' - \frac{V'^2}{V^2} \right) u + \left(\frac{l+1}{\rho} - 1 + \frac{V'}{V} \right)^2 u$$

$\Rightarrow$ the Euler eq^n becomes

$$\left[-\frac{l+1}{\rho^2} + \frac{V''}{V} - \frac{V'^2}{V^2} + \frac{(l+1)^2}{\rho^2} + 1 + \frac{V'^2}{V^2} - 2\,\frac{l+1}{\rho} - 2\frac{V'}{V} + 2\frac{l+1}{\rho}\frac{V'}{V} \right] u$$

$$+ \left[-1 + \frac{\alpha}{\rho} - \frac{l(l+1)}{\rho^2} \right\} u = 0$$

$$\Big[\underbrace{-\frac{l+1}{\rho^2}}_{1} + \frac{V''}{V} \cancel{- \frac{V'^2}{V^2}} + \underbrace{\frac{(l+1)^2}{\rho^2}}_{1} \cancel{+1} \cancel{+ \frac{V'^2}{V^2}} - 2\,\frac{(l+1)}{\rho} - 2\frac{V'}{V} + 2\,\frac{(l+1)}{\rho}\frac{V'}{V}$$

$$\cancel{-1} + \frac{\alpha}{\rho} - \underbrace{\frac{l(l+1)}{\rho^2}}_{1} \Big\} u = 0$$

terms labeled by 1 cancel each others

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

$\hookrightarrow$ becomes $\frac{V''}{V} + 2\left(\frac{l+1}{\rho} - 1\right)\frac{V'}{V} + [\alpha - 2(l+1)]\frac{1}{\rho} = 0$

multiply by ρV

$$\boxed{\rho V'' + 2(l+1-\rho)V' + [\alpha - 2(l+1)]V = 0} \quad \text{--- (12)}$$

2^{nd} order linear diff eq^n with no singularities

let us try to use series to solve this eq^n

let $V(\rho) = \sum_{k=0}^{\infty} C_k \rho^k$; $V' = \sum_{k=0}^{\infty} k C_k \rho^{k-1}$; $V'' = \sum_{k=0}^{\infty} k(k-1) C_k \rho^{k-2}$

substitute in (12)

$$\sum_k C_k \left[k(k-1)\rho^{k-1} + 2(l+1)k\rho^{k-1} - 2k\rho^k + (\alpha - 2(l+1))\rho^k \right\} = 0$$

$$C_{k+1}(k+1)k + 2(l+1)(k+1)C_{k+1} - 2kC_k + [\alpha - 2(l+1)]C_k = 0$$

$$C_{k+1}\left[(k+1)k + 2(l+1)(k+1)\right] = C_k\left[2k + 2(l+1) - \alpha\right]$$

$$C_{k+1}(k+1)\left[k + 2l + 2\right] = C_k\left[2(k+l+1) - \alpha\right]$$

$$C_{k+1} = C_k \frac{2(k+l+1) - \alpha}{(k+1)(k+2l+2)} \quad \text{recurrence relation}$$

for $k \gg 1$ $\quad C_{k+1} \approx C_k \dfrac{2k}{k^2} = C_k \dfrac{2}{k} \Rightarrow \dfrac{C_{k+1}}{C_k} = \dfrac{2}{k}$

but the $C_{k+1}/C_k = \dfrac{2}{k}$ is the same as the limiting behavior of $e^{2\rho}$; let us check ?!

$$e^{2\rho} = \sum_{k=0}^{\infty} \frac{(2\rho)^k}{k!} = \sum \frac{2^k}{k!}\rho^k ; \Rightarrow C_k = \frac{2^k}{k!}$$

$$C_{k+1} = \frac{2^{k+1}}{(k+1)!}$$

$$\Rightarrow \frac{C_{k+1}}{C_k} = \frac{2^{k+1}}{(k+1)!}\,\frac{k!}{2^k}$$

$$= \frac{\cancel{2^k}\,2\,\cancel{k!}}{(k+1)\cancel{k!}\,\cancel{2^k}} = \frac{2}{k+1} \quad ; \text{so for } k \gg 1 \Rightarrow \frac{C_{k+1}}{C_k} \approx \frac{2}{k}$$

$$\therefore \; v(\rho) = e^{2\rho}$$

$$\Rightarrow u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) = \rho^{l+1} e^{-\rho} e^{2\rho} = \rho^{l+1} e^{\rho}$$

but this result is unphysical as u does not vanish as $\rho \to \infty$. to obtain a physical solution, the series $v(\rho)$ must terminate at a certain power N; hence the function $v(\rho)$ becomes a polynomial of order N

$$\Rightarrow v(\rho) = \sum_{k=0}^{N} C_k \rho^k$$

This requires that all coefficients $C_{N+1}, C_{N+2}, \dots$ have to vanish $\Rightarrow$ so

$$C_{N+1} = 0 = C_N \frac{2(N+l+1)-\alpha}{(N+1)(N+2l+2)} = 0$$

Now $C_N \neq 0 \Rightarrow 2(N+l+1)-\alpha = 0$

$$\Rightarrow \alpha = 2(N+l+1)$$

let us define the main quantum # n as

$n = N+l+1 \Rightarrow \alpha = 2n$, when $\alpha = \frac{2mZe^2}{\hbar^2 \varkappa}$

$\therefore \alpha = 2n$ and $\varkappa^2 = \frac{2m\mathcal{E}}{\hbar^2}$

$$\frac{2mZe^2}{\hbar^2\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}} = 2n \Rightarrow \frac{m^2Z^2e^4}{\hbar^2\, 2m\mathcal{E}} = n^2$$

$$\Rightarrow \mathcal{E}_n = \frac{mZ^2e^4}{2\hbar^2 n^2} \text{ ; Bhor spectrum}$$

$$E_n = -\mathcal{E}_n = -\frac{mZ^2e^4}{2\hbar^2n^2} = -\frac{1}{2}e^2\frac{me^2}{\hbar^2}\frac{1}{n^2}$$; when $a_0 = \frac{\hbar^2}{me^2}$ Bhor radius

for H atom ($Z=1$) $= -\frac{e^2}{2a_0}\frac{1}{n^2}$

Now since $N = 0, 1, 2, 3, \dots \Rightarrow n = l+1, l+2, l+3, \dots$

so for a given value of n, l takes values between 0 and $n-1$

n: $l = 0, 1, 2, 3, \dots, n-1$

$\Rightarrow$ Remember that N is the order of the Polynomial which must be an integer

- for H like atoms $E_n = \frac{-e^2Z^2}{2a_0}\frac{1}{n^2} = -\frac{Z^2 \mathcal{E}_0}{n^2}$; $\mathcal{E}_0 = \frac{e^2}{2a_0} = 13.6\text{ eV}$

The radial wave functions: of the H atom

we found that $n = N + l + 1$; n: principle quantum #

N: radial " "

l: orbital " " ;

i) consider the ground state of the H atom $(n=1)$,

$\Rightarrow N = l = 0$; the G.S is unique and has one state

$$\underbrace{R_{10}(r)\, Y_{00}(\theta,\phi)}_{\Psi_{100}(r,\theta,\phi)} \quad ; \text{ where } Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$

let us find $R_{10}(r)$?

Now $U_{nl}(\rho) \approx \rho^{l+1} e^{-\rho} V(\rho) \Longrightarrow U_{10}(\rho) \approx \rho e^{-\rho} V(\rho)$

$\Rightarrow U_{10}(\rho) = A_{10}\, \rho e^{-\rho} V(\rho)$; when $V(\rho) = \sum_{k=0}^{N} C_k \rho^k$; $N=0$

$\Rightarrow U_{10}(\rho) = A_{10} C_0\, \rho e^{-\rho}$ $\qquad = \sum_{k=0}^{0} C_k \rho^k = C_0$

$R_{10}(\rho) = \frac{U_{10}(\rho)}{\rho} = A_{10} C_0 e^{-\rho}$

let us find out first what is ρ for G.S

$\varkappa r = \rho$; $\varkappa = \sqrt{\frac{2m\mathcal{E}}{\hbar^2}}$; $\mathcal{E}_n = \frac{e^2}{2a_0}\frac{1}{n^2}$; $\mathcal{E}_0 = \frac{e^2}{2a_0}$; $a_0 = \frac{\hbar^2}{me^2}$

$$\varkappa = \sqrt{\frac{2m}{\hbar^2}\frac{e^2}{2a_0}} = \sqrt{\frac{1}{a_0}\frac{me^2}{\hbar^2}} = \sqrt{\frac{1}{a_0}\frac{1}{a_0}} = \sqrt{\frac{1}{a_0^2}} = \frac{1}{a_0}$$

$\Rightarrow \rho = r/a_0$ this for G.S

- for first excited state $(n=2)$ $\quad \varkappa = \sqrt{\frac{2m\mathcal{E}_1}{\hbar^2}}$; $\mathcal{E}_1 = \frac{e^2}{2a_0}\frac{1}{4}$

$\Rightarrow \rho = r/2a_0$ $\qquad = \sqrt{\frac{2m}{\hbar^2}\frac{1}{4}\frac{e^2}{2a_0}} = \sqrt{\frac{me^2}{\hbar^2}\frac{1}{4a_0}}$

- for state (n) in general $\qquad = \sqrt{\frac{1}{4a_0^2}} = \frac{1}{2a_0}$

$$\boxed{\rho = r/na_0}$$

$\therefore$ $R_{10}(r) = A_{10} C_0 e^{-r/a_0}$, to find $A_{10} C_0$ we normalize

$$\int_0^\infty r^2 |R_{nl}(r)|^2 dr = 1 \quad \Rightarrow \quad (A_{10} C_0)^2 \int_0^\infty r^2 e^{-2r/a_0} dr = 1$$

using $\int_0^\infty x^n e^{-ax} = \frac{n!}{(a)^{n+1}}$

$$(A_{10} C_0)^2 \frac{2}{(2/a_0)^3} = 1$$

$$A_{10} C_0 = 2 (1/a_0)^{3/2}$$

$$\therefore \boxed{R_{10}(r) = 2 (1/a_0)^{3/2} e^{-r/a_0}}$$

(ii) first excited state $(n=2)$; $n = N + l + 1$

two possibilities for $n=2$ $\begin{cases} N=1, l=0 & \text{singlet (1)} \quad R_{20} Y_{00} \\ N=0, l=1 & \text{triplet (3)} \quad R_{21} Y_{11}, R_{21} Y_{10}, R_{21} Y_{1-1} \end{cases}$

so the $n=2$ state is four fold degenerate (4- states)

Notice that degeneracy is $= n^2 = 2^2 = 4$ (without spin)

Now let us find the functions $R_{21}(r)$ and $R_{20}(r)$

$R_{21}(r)$?: $\quad U_{21}(\rho) = A_{21} \rho^2 e^{-\rho} v(\rho)$ with $l=1$ and $N=0$

$$\Rightarrow v(\rho) = \sum_{k=0}^{N} C_k \rho^k = C_0 \Rightarrow U_{21}(\rho) = A_{21} C_0 \rho^2 e^{-\rho}$$

$$\Rightarrow R_{21}(\rho) = \frac{U_{21}(\rho)}{\rho} = A_{21} C_0 \rho e^{-\rho} \quad ; \quad \text{but } \rho = r/2a_0$$

$$= A_{21} C_0 (r/2a_0) e^{-r/2a_0}$$

Normalize $\left(\frac{A_{21} C_0}{2a_0}\right)^2 \underbrace{\int_0^\infty r^4 e^{-r/a_0} dr}_{4!/(1/a_0)^5} = 1 \Rightarrow A_{21} C_0 = \frac{1}{\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2}$

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

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

Now $R_{20}(r)$?

$$u_{20}(\rho) = A_{20}\rho^{l+1} e^{-\rho} v(\rho) \overset{l=0}{=} A_{20}\, \rho e^{-\rho} v(\rho) \quad ; \quad N=1$$

$$v(\rho) = \sum_{k=0}^{1} C_k \rho^k = C_0 + C_1 \rho \implies$$

$$u_{20}(\rho) = A_{20}\, \rho e^{-\rho} (C_0 + C_1 \rho)$$

Now C_1 can be found from $C_{k+1} = C_k \dfrac{2(k+l+1)-2n}{(k+1)(k+2l+2)}$ (in term of C_0)

where $n=2,\ k=0,\ l=0$

$$C_1 = C_0 \frac{2-4}{2} = -C_0$$

$$\therefore\ u_{20}(\rho) = A_{20} C_0\, \rho e^{-\rho}(1-\rho)$$

$$R_{20}(\rho) = \frac{u_{20}(\rho)}{\rho} = A_{20} C_0\, e^{-\rho}(1-\rho) \ ;$$

$$= \underline{A_{20} C_0}\, e^{-r/2a_0}(1 - r/2a_0) \ ; \text{ when } \rho = r/2a_0$$

Normalize

$$(A_{20} C_0)^2 \int_0^\infty r^2 \left(1 - \frac{r}{2a_0}\right)^2 e^{-r/a_0}\, dr = 1$$

$$(A_{20} C_0)^2 \left[\int_0^\infty r^2 \left(1 + \frac{r^2}{4a_0^2} - \frac{r}{a_0}\right) e^{-r/a_0}\, dr \right] = 1$$

$$(A_{20} C_0)^2 \left[\int_0^\infty r^2 e^{-r/a_0}\, dr + \frac{1}{4a_0^2} \int_0^\infty r^4 e^{-r/a_0}\, dr - \frac{1}{a_0} \int_0^\infty r^3 e^{-r/a_0}\, dr \right] = 1$$

$$(A_{20} C_0)^2 \left[\frac{2}{(1/a_0)^3} + \frac{1}{4a_0^2} \frac{4!}{(1/a_0)^5} - \frac{1}{a_0} \frac{3!}{(1/a_0)^4} \right] = 1$$

$$\implies A_{20} C_0 = 2\left(\frac{1}{2a_0}\right)^{3/2}$$

$$\therefore\ \boxed{R_{20}(r) = 2\left(\frac{1}{2a_0}\right)^{3/2} e^{-r/2a_0} (1 - r/2a_0)}$$

following the same procedure & we find for $n=3$

R_{30}, R_{31}, R_{32}, ...

for $n=3$; $n = N + l + 1$

$$\begin{cases} N=2,\ l=0 & \text{singlet (1)} \quad R_{30} Y_{00} \\ N=1,\ l=1 & \text{triplet (3)} \quad R_{31} Y_{11},\ R_{31} Y_{10},\ R_{31} Y_{1,-1} \\ N=0,\ l=2 & \text{fivet (5)} \quad R_{32} Y_{22},\ R_{32} Y_{21},\ R_{32} Y_{20},\ R_{32} Y_{2,-1},\ R_{32} Y_{2,-2} \end{cases}$$

so we have 9 states

$d = n^2 = 3^2 = 9$ (again without spin)

so for H atom $d = \sum_{l=0}^{n-1} (2l+1) = n^2$

Remark: if we take the spin of electron into account, the electron's state is specified by 4 quantum numbers (n, l, m_l, m_s) where

$$n = 1, 2, 3, \ldots$$
$$l = 0, 1, 2, \ldots, n-1$$
$$m_l = -l, -l+1, \ldots, +l$$
$$m_s = \pm 1/2$$

$\Rightarrow$ the total wave function is then

$$\Psi_{nlm_lm_s}(\vec{r}) = \psi_{nlm_l}(r,\theta,\phi) \left| \tfrac{1}{2}, \pm \tfrac{1}{2} \right\rangle$$
$$= R_{nl}(r)\, Y_{lm}(\theta,\phi) \left| 1/2, \pm 1/2 \right\rangle$$

for spin up $\quad \psi_{nlm_l 1/2}(\vec{r}) = \psi_{nlm_l}(r,\theta,\phi) \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

for spin down $\quad \psi_{nlm_l -1/2}(\vec{r}) = \psi_{nlm_l}(r,\theta,\phi) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

- when the spin of electron is considered, the degeneracy of each level is $d = 2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$

H Spectrum $\quad V(r) = -e^2/r$

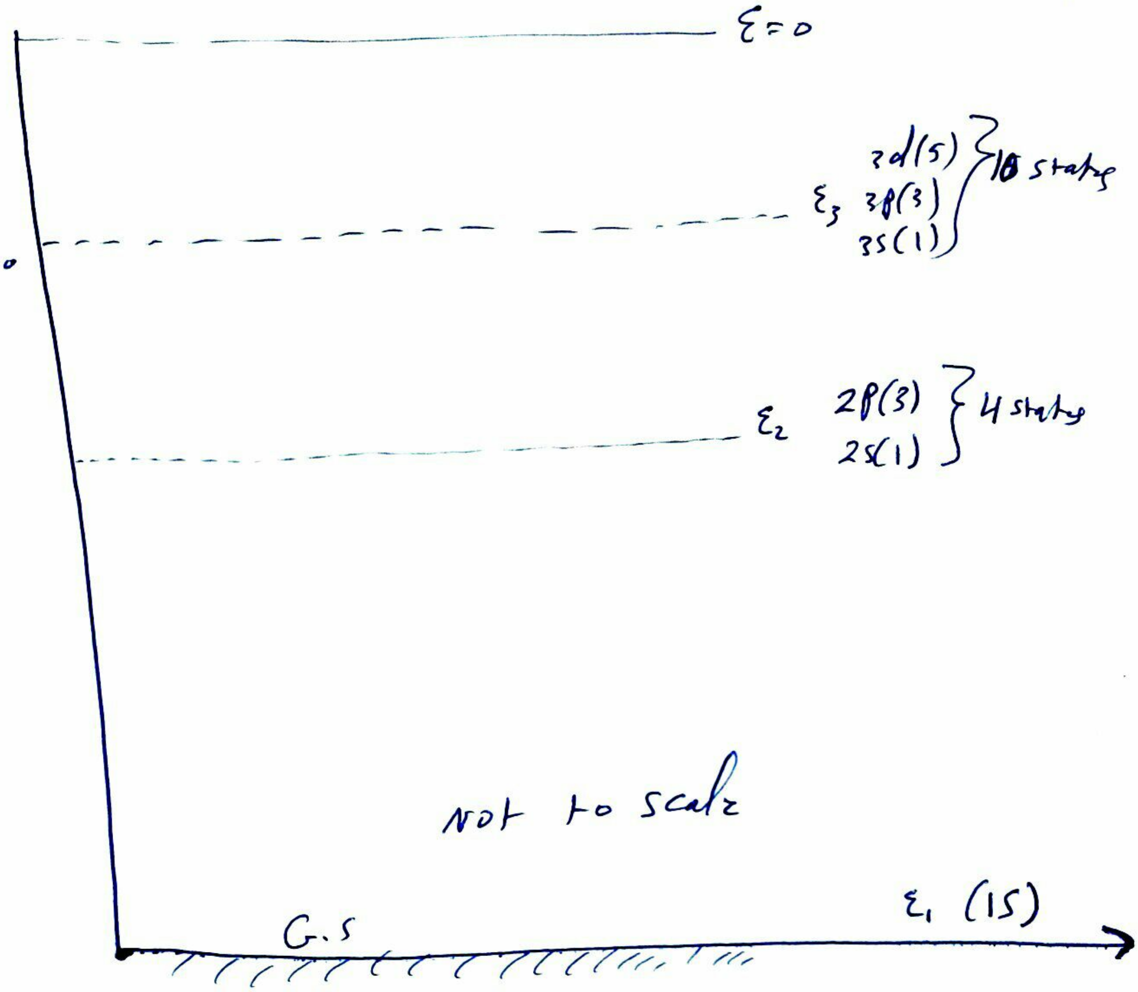
$G_n = -\mathcal{E}_n$; $\mathcal{E}_n = +\dfrac{e^2}{2a_0}\dfrac{1}{n^2} = \dfrac{\mathcal{E}_1}{n^2} = \dfrac{13.6\ \text{eV}}{n^2}$; $\mathcal{E}_2 = \dfrac{\mathcal{E}_1}{4}$

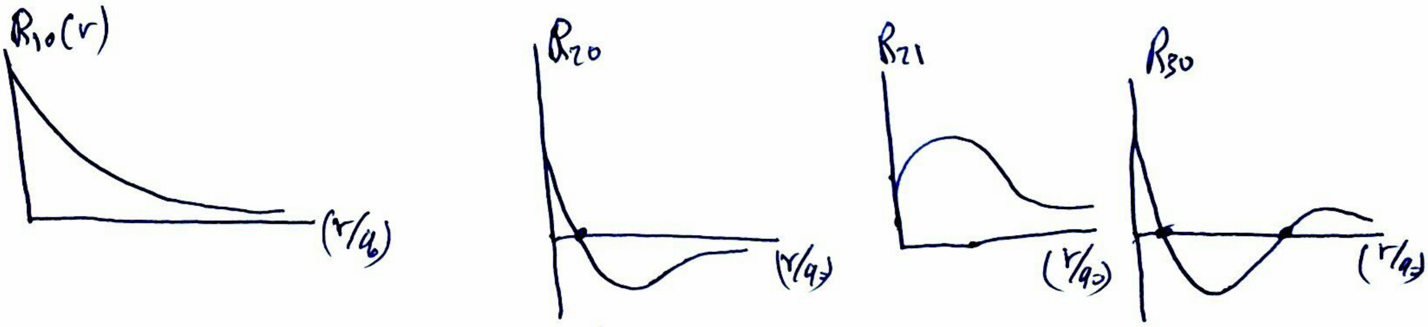
$\mathcal{E}_3 = \dfrac{\mathcal{E}_1}{9}$

$n=3,\ N=0,\ l=2$
$n=3,\ N=1,\ l=1$
$n=3,\ N=2,\ l=0$

$n=2,\ N=0,\ l=1$
$n=2,\ N=1,\ l=0$

$n=1,\ N=0,\ l=0$





$R_{nl}(r)$ has $(n-l-1)$ nodes

- the total wave function is $\psi_{nlm}(\vec{r}) = R_{nl}(r)\, Y_{lm}(\theta, \varphi)$

the normalization condition is

$$\int |\psi|^2 d^3r = 1 \quad \Rightarrow \int |\psi^2|\, r^2 dr\, d\Omega = \int_0^\infty |R_{nl}(r)|^2 r^2 dr \underbrace{\int_0^{4\pi} |Y_{lm}(\theta\varphi)|^2 d\Omega}_{=1}$$

$$\therefore \int_0^\infty |R_{nl}(r)|^2 r^2 dr \int_0^{4\pi} |Y_{lm}(\theta\varphi)|^2 d\Omega = 1$$

it is convenient to normalize R and Y separately

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1 \quad \text{and} \quad \int_0^{2\pi} d\phi \int_0^\pi |Y_{lm}(\theta,\phi)|^2 \sin\theta \, d\theta = 1$$

$$\Downarrow$$

$$\text{or} \quad \int |Y_{lm}(\theta,\phi)|^2 d\Omega = 1$$

the quantity $P_{nl}(r) = r^2 |R_{nl}(r)|^2$

is called the probability distribution function or the probability of finding the electron in a spherical shell $r \to r+dr$

so $\int_0^a r^2 |R_{nl}(r)|^2 dr$ = the probability of finding the electron in a sphere of radius a centered about the origin

$\int_a^b r^2 |R_{nl}(r)|^2 dr$ = the probability of finding the electron in ~~a sheri~~ a spherical shell of inner radius (a) and outer radius b

- now let us find the average values of the various powers of r. since $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi)$, we can see that the average of r^k is independent of the azimuthal quantum # m

i.e $$\langle nlm | r^k | nlm \rangle = \int r^k |\psi_{nlm}(r,\theta,\phi)|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \int_0^\infty r^{k+2} |R_{nl}(r)|^2 dr \underbrace{\int d\Omega |Y_{lm}(\theta,\phi)|^2}_{=1}$$

$$= \int_0^\infty r^{k+2} |R_{nl}(r)|^2 dr = \langle nl | r^k | nl \rangle$$

Example: Find $\langle r \rangle$ and $\langle r^2 \rangle$ for the electron in the Ground state of the H atom

Using $\langle r^k \rangle = \int_0^\infty r^{k+2} |R_{nl}(r)|^2 dr$

we have $\langle r \rangle = \int_0^\infty r^3 |R_{10}(r)|^2 dr$; $R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

$$= 4\left(\frac{1}{a_0}\right)^3 \int_0^\infty r^3 e^{-2r/a_0} dr = 4\left(\frac{1}{a_0}\right)^3 \frac{3!}{(2/a_0)^4} = \frac{3}{2} a_0$$

and $\langle r^2 \rangle = \int_0^\infty r^4 |R_{10}(r)|^2 dr = 4\left(\frac{1}{a_0}\right)^3 \int_0^\infty r^4 e^{-2r/a_0} dr$

$$= 4\left(1/a_0\right)^3 \frac{4!}{(2/a_0)^5} = 3a_0^2$$

- Calculate the value of r at which the radial probability density of the G.S of the H atom reaches its maximum

$$P_{10}(r) = r^2 |R_{10}(r)|^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

the maximum occurs when $\frac{dP}{dr} = 0 \Rightarrow 2r - \frac{2r^2}{a_0} = 0 \Rightarrow \boxed{r = a_0}$

- Now let us see how to calculate $\langle \frac{1}{r} \rangle$ and $\langle \frac{1}{r^2} \rangle$

the radial eq^n of the H atom reads

$$\frac{d^2 u_{nl}}{dr^2} + \left[\frac{-me^4}{\hbar^4 n^2} + \frac{2me^2}{\hbar^2 r} - \frac{l(l+1)}{r^2}\right] u_{nl} = 0$$

or $$\frac{u_{nl}''}{u_{nl}} = \frac{l(l+1)}{r^2} - \frac{2me^2}{\hbar^2 r} + \frac{m^2 e^4}{\hbar^4 n^2} \quad \text{---} \quad (13)$$

Now let us treat l as a continuous variable and take the first derivative of the last eq^n w.r.t l

$$\frac{\partial}{\partial l}\left[\frac{u_{nl}''}{u_{nl}}\right] = \frac{2l+1}{r^2} - \frac{2m^2e^4}{\hbar^4 n^3} \quad ; \text{ where } \quad n = N+l+1$$

$$\frac{\partial n}{\partial l} = 1$$

Now using $\int_0^\infty u_{nl}^2(r)\,dr = \int_0^\infty r^2 R_{nl}^2(r)\,dr = 1$

~~we have~~ multiply the last eq^n with $u_{nl}^2(r)$ and integrate over r, we have

$$\underbrace{\int_0^\infty u_{nl}^2(r)\frac{\partial}{\partial l}\left[\frac{u_{nl}''}{u_{nl}}\right]dr}_{L.H.S} = \underbrace{(2l+1)\int_0^\infty u_{nl}^2(r)\frac{1}{r^2}\,dr - \frac{2m^2e^4}{\hbar^4 n^3}\int_0^\infty u_{nl}^2(r)\,dr}_{R.H.S}$$

$$R.H.S = (2l+1)\langle nl|\frac{1}{r^2}|nl\rangle - \frac{2m^2e^4}{\hbar^4 n^3}\underbrace{\langle nl|nl\rangle}_{1}$$

$$= (2l+1)\langle nl|\frac{1}{r^2}|nl\rangle - \frac{2m^2e^4}{\hbar^4 n^3}$$

$$L.H.S ; \quad \frac{\partial}{\partial l}\left[u_{nl}''\frac{1}{u_{nl}}\right] = \frac{1}{u_{nl}}\frac{\partial u_{nl}''}{\partial l} + u_{nl}''\frac{\partial}{\partial l}\left(\frac{1}{u_{nl}}\right)$$

$$= \frac{1}{u_{nl}}\frac{\partial u_{nl}''}{\partial l} - u_{nl}''\frac{1}{u_{nl}^2}\frac{\partial u_{nl}}{\partial l}$$

$$\therefore L.H.S = \int_0^\infty u_{nl}(r)\frac{\partial u_{nl}''}{\partial l}\,dr - \int_0^\infty u_{nl}''\frac{\partial u_{nl}}{\partial l}\,dr = 0$$

as $u(r)$ has to vanish at $r=0$ $\left(u \propto \rho^{l+1} = (\varkappa r)^{l+1}\right)$ and at $r=\infty$ $\left(u(\rho)\sim e^{-\rho}\right)$

$$\langle nl|\frac{1}{r^2}|nl\rangle = \frac{1}{(2l+1)}\frac{2m^2e^4}{\hbar^4 n^3} = \frac{2}{n^3(2l+1)a_0^2}$$

Now to find $\langle \frac{1}{r} \rangle$, let us treat the electrons charge e in eqn (13) as a continuous variable

$$\frac{\partial}{\partial e}\left[\frac{u''_{nl}}{u_{nl}}\right] = -\frac{4me}{\hbar^2 r} + \frac{4m^2e^3}{\hbar^4 n^2}$$

multiply by $u^2_{nl}(r)$ and integrate over r,

$$\underbrace{\int_0^\infty u^2_{nl}\frac{\partial}{\partial e}\left[\frac{u''_{nl}}{u_{nl}}\right]dr}_{\text{zero}} = -\frac{4me}{\hbar^2}\int_0^\infty u^2_{nl}(r)\frac{1}{r}\,dr + \frac{4m^2e^3}{\hbar^4 n^2}\int_0^\infty u^2_{nl}(r)\,dr$$

$$= -\frac{4me}{\hbar^2}\left\langle \frac{1}{r}\right\rangle + \frac{4m^2e^3}{\hbar^4 n^2}$$

$$\Rightarrow \left\langle \frac{1}{r}\right\rangle = \frac{me^2}{\hbar^2 n^2} = \frac{1}{a_0 n^2}$$

now we can use Kramer's recursion relation to find $\langle r\rangle$, $\langle \frac{1}{r}\rangle$ $\langle r^2\rangle$, ...

$$\frac{k+1}{n^2}\langle nl|r^k|nl\rangle - (2k+1)a_0\langle nl|r^{k-1}|nl\rangle + \frac{k a_0^2}{4}\left[(2l+1)^2-k^2\right]\langle nl|r^{k-2}|nl\rangle = 0 \quad *$$

take $k=0 \Rightarrow \langle nl|\frac{1}{r}|nl\rangle = \frac{1}{a_0 n^2}$

take $k=1 \Rightarrow \langle nl|r|nl\rangle = \frac{1}{2}\left[3n^2 - l(l+1)\right]a_0$

// $k=2 \Rightarrow \langle nl|r^2|nl\rangle = \frac{1}{2}n^2\left[5n^2+1-3l(l+1)\right]a_0^2$

// $k=-1 \Rightarrow \langle nl|\frac{1}{r^3}|nl\rangle = \frac{2}{n^3 l(l+1)(2l+1)a_0^3}$

// $k=-2 \Rightarrow$

Note $\langle nl|r^0|nl\rangle = 1$