Radial Equation

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

change variables: $u(r) \equiv r\,R(r)$

$R = \frac{u}{r}$ $\qquad \frac{dR}{dr} = \frac{1}{r}\frac{du}{dr} - \frac{u}{r^2} = \boxed{\frac{r\,(du/dr) - u}{r^2}}$

$$\frac{d}{dr}\left[r^2 \frac{dR}{dr}\right] = \frac{d}{dr}\left[r\frac{du}{dr} - u\right]$$

$$= \frac{du}{dr} + r\frac{d^2u}{dr^2} - \frac{du}{dr} = \boxed{r\frac{d^2u}{dr^2}}$$

the equation becomes

$$r\frac{d^2u}{dr^2} - \frac{2mr^2}{\hbar^2}V\frac{u}{r} - l(l+1)\frac{u}{r} = -\frac{2mr^2}{\hbar^2}E\frac{u}{r}$$

$(\times)\ -\frac{\hbar^2}{2mr}$

$$\hookrightarrow -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]}_{V_{eff}\text{ (effective potential)}}u = Eu$$

Normalization condition: $\int_0^\infty |R|^2 r^2\,dr = \boxed{\int_0^\infty |u|^2\,dr = 1}$

$\boxed{\text{Students go through Example 4.1}} \leftarrow$ HW

Hydrogen Atom

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

Defining

$$K \equiv \frac{\sqrt{-2mE}}{\hbar} \qquad E < 0 \text{ for bound states}$$

$\div$ Eq. (4.53) by E

$$\hookrightarrow \quad \frac{1}{K^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2 K}\frac{1}{Kr} + \frac{l(l+1)}{(Kr)^2}\right]u$$

Introducing

$$\rho \equiv Kr \qquad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2 K}$$

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

Asymptotic solutions

$$\rho \to \infty \Rightarrow \frac{d^2u}{d\rho^2} = u$$

$$u(\rho) = Ae^{-\rho} + \underbrace{Be^{\rho}}$$

blows up for $\rho \to \infty$

$\hookrightarrow B = 0$

$$\boxed{u(\rho) \sim Ae^{-\rho}}$$

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

$$u(\rho) = C\rho^{l+1} + \underbrace{D\rho^{-l}}$$

blows up for $\rho \to 0$

$\hookrightarrow D = 0$

$$\boxed{u(\rho) \sim C\rho^{l+1}}$$

This is done so that now we can write $\boxed{u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)}$ and hope that $v(\rho)$ will be easier to find than $u(\rho)$

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

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

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

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

Putting all together in the radial equation

$$\rho^{l}e^{-\rho}\left\{\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + \left[-2l-2+\cancel{\rho}+\frac{l(l+1)}{\rho} - \rho\left(\cancel{1} - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right)\right]v\right\} = 0$$

$$\Rightarrow \boxed{\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + \left[\rho_0 - 2(l+1)\right]v = 0}$$

Assume the solution $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$ (power series in ρ)

we need to find the coefficients

$$\left\{\begin{array}{l} \dfrac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j \\ \dfrac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1} \end{array}\right\}$$

our goal is to have all terms in the radial eq with the same power: ρ^j

in the radial eq. for v:

can rewrite as $\sum_{j=1}^{\infty} j c_j \rho^j$ and it makes no difference if we include $j=0$ $\rightarrow \sum_{j=0}^{\infty} j c_j \rho^j$

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

Equating the coefficients

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

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j$$ ← recursion formula for c_j

(start with c_0 → found later with normalization)

For large j

$$c_{j+1} \cong \frac{2j}{j(j+1)}\, c_j = \frac{2}{j+1}\, c_j$$

(Obs: could drop 1 in $j+1$; we are keeping it for cleaner expressions)

$$\Rightarrow c_1 = \frac{2}{1} c_0$$

$$c_2 = \frac{2\, c_1}{2} = \frac{2^2}{2.1} c_1$$

$$c_3 = \frac{2}{3} c_2 = \frac{2^3}{3.2.1} c_0 \Rightarrow \boxed{c_j = \frac{2^j}{j!} c_0} \Rightarrow v(\rho) = c_0 \underbrace{\sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j}_{e^{2\rho}}$$

$$\Rightarrow u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) = \boxed{c_0\, \rho^{l+1} e^{\rho}}$$

↳ but it blows up for $\rho \to \infty$

therefore, the series must terminate

$$c_{j_{max}+1} = 0 \Rightarrow \boxed{2(j_{max} + l + 1) - \rho_0 = 0}$$

↓ numerator in the recursion formula

Defining:

$$\boxed{n \equiv j_{max} + l + 1} \Rightarrow \boxed{\rho_0 = 2n}$$

↑ principal quantum number

$\rho_0 = 2n$, $\rho_0 = \dfrac{me^2}{2\pi\epsilon_0 \hbar^2 K}$, $K^2 = -\dfrac{2mE}{\hbar^2}$

$$\Rightarrow \frac{2mE}{\hbar^2} = -\left(\frac{me^2}{2\pi\epsilon_0\hbar^2}\right)^2 \frac{1}{4n^2}$$

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n_2}} \qquad n = 1, 2, 3, \ldots$$

Bohr formula (obtained in 1913 by mixing classical phys.)
(while Schröd. eq. in 1924)

$$\boxed{a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}\,m} \leftarrow \text{Bohr radius} \Rightarrow \begin{cases} \rho_0 = me^2/2\pi\epsilon_0\hbar^2 K \\ \rho_0 = 2/aK = 2n \\ \boxed{K = \dfrac{1}{an}} \end{cases}$$

$$\boxed{\rho = \frac{r}{an}}$$

$\boxed{n=1} \Rightarrow \overline{E_1 = -13.6\,eV}$ ground state

$\boxed{n=2} \Rightarrow E_2 = \dfrac{-13.6\,eV}{4} = \overline{-3.4\,eV}$

$\rightarrow$) Spatial wave functions for hydrogen are labeled by 3 quantum numbers (n, l, m)

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$, $\rho = Kr$, $R(r) = \dfrac{u(r)}{r}$

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

polynomial of degree j_{max} } coefficients determined by recursion formula

Ground state: $\boxed{n=1}$

$$n = j_{max} + l + 1 \qquad \begin{cases} j_{max}, l \geqslant 0 \\ n \geqslant 1 \end{cases}$$

$n=1 \Rightarrow j_{max} = l = 0$

$$\boxed{l=0} \Rightarrow \boxed{m=0}$$

$$\psi_{100}(r,\theta,\phi) = R_{10}(r)\, Y_0^0(\theta,\phi)$$

•) $j_{max} = 0 \Rightarrow v(\rho) = c_0 \longrightarrow R_{10}(r) = \frac{c_0}{r}\rho e^{-\rho}$

$$\rho = Kr = \frac{r}{an} \xRightarrow{(n=1)} \boxed{R_{10}(r) = \frac{c_0}{a} e^{-r/a}}$$

Normalizing

$$\int_0^\infty |R_{10}|^2 r^2\, dr = \frac{|c_0|^2}{a^2}\int_0^\infty e^{-2r/a} r^2\, dr = |c_0|^2 \frac{a}{4} = 1$$

$$\boxed{c_0 = 2/\sqrt{a}}$$

•) $Y_0^0 = 1/\sqrt{4\pi}$

therefore $$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

$E_1 = -13.6$ eV

First excited state(s) $\boxed{n=2}$

$$n = j_{max} + l + 1 \implies \begin{cases} j_{max} = 1, & l = 0 \\ j_{max} = 0, & l = 1 \end{cases}$$

$n \to 2$

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j \qquad \rho_0 = 2n$$

$\boxed{l=0} \Rightarrow \boxed{m=0}$

$\boxed{l=1} \Rightarrow \boxed{m=-1,0,+1}$

four different states with the same energy

∘) $j_{max} = 1, \quad l = 0$

$j = 0, 1$

$$c_1 = \frac{2(0+0+1-2)}{(0+1)(0+0+2)} c_0 \implies \boxed{c_1 = -c_0}$$

$$c_2 = \frac{2(1+0+1-2)}{(1+1)(1+0+2)} c_1 \implies \boxed{c_2 = 0}$$

so

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

$2 \leftarrow n$

$$R_{20}(r) = c_0\left(1 - \frac{r}{2a}\right) \frac{1}{r} \left(\frac{r}{2a}\right)^1 e^{-r/2a}$$

$$\boxed{R_{20}(r) = \frac{c_0}{2a}\left(1 - \frac{r}{2a}\right) e^{-r/2a}} \longrightarrow \text{then normalize to find } c_0$$

∘) $j_{max} = 0, \; l = 1 \longrightarrow v(\rho) = c_0, \quad \rho = r/2a$

$$R_{21}(r) = \frac{c_0}{r}\left(\frac{r}{2a}\right)^{1+1} e^{-r/2a}$$

$$\boxed{R_{21}(r) = \frac{c_0}{4a^2}\, r\, e^{-r/2a}} \longrightarrow \text{normalize to find } c_0$$

HW

Example 4.1

Prob. 4.11, 4.12, 4.13

Prob. 4.21

For arbitrary n

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

For each l

$$m = \underbrace{-l, -l+1, \ldots 0, 1, \ldots l-1, l}_{(2l+1) \text{ values}}$$

$\Rightarrow$ The total degeneracy of the energy level E_n

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = 1 + 3 + 5 + \ldots + (2n-1) = \frac{(\text{initial} + \text{final})\left(\text{number of terms}\right)}{2}$$

(arithmetic series)

$$\boxed{d(n) = n^2}$$

$\rightarrow$ Polynomial $\boxed{v(\rho) = L^{2l+1}_{n-l-1}(2\rho)}$

where $L^{p}_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$ and $L_q(x) \equiv e^{x}\left(\frac{d}{dx}\right)^q (e^{-x}x^q)$

(associated Laguerre polynomial) (Laguerre polynomial)

$\Rightarrow$) Normalized hydrogen wave functions

$$\boxed{\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L^{2l+1}_{n-l-1}(2r/na)\right] Y_l^m(\theta, \phi)}$$

$\Rightarrow$) Wave functions are orthogonal

$$\int \psi^*_{nlm}\, \psi_{n'l'm'}\, r^2 \sin\theta\, dr\, d\theta\, d\phi = \delta_{nn'}\, \delta_{ll'}\, \delta_{mm'}$$