H ion

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right]\Psi(\vec{r}) = E\Psi(\vec{r}),$$

where $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$.

Let $\Psi(\vec{r}) = R(r)\Theta(\theta)\Phi(\phi)$, then

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R\Theta\Phi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial R\Theta\Phi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 R\Theta\Phi}{\partial\phi}\right] - \frac{e^2}{r}R\Theta\Phi = ER\Theta\Phi$$

$$-\frac{\hbar^2}{2m}\left[\frac{\Theta\Phi}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{dR}{dr}\right) + \frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi}\right] - \frac{e^2}{r}R\Theta\Phi = ER\Theta\Phi$$

$\times\ -2mr^2\sin^2\theta / R\Theta\Phi\hbar^2$,

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{2mre^2\sin^2\theta}{\hbar^2} = -\frac{2mr^2E\sin^2\theta}{\hbar^2}$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2}{\hbar^2}mr^2\sin^2\theta\left(\frac{e^2}{r}+E\right)$$

Both sides are independent & $\therefore$ equal to some constant, $-m_\ell^2$,

$$\Rightarrow \frac{d^2\Phi}{d\phi^2} = -m_\ell^2\Phi \Rightarrow \Phi(\phi) = e^{im_\ell\phi}.$$

Furthermore, $\Phi(\phi) = \Phi(\phi+2\pi)$,

$\Rightarrow m_\ell \in \mathbb{Z}$, and

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2}{\hbar^2}mr^2\sin^2\theta\left(\frac{e^2}{r}+E\right) = m_\ell^2$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2}{\hbar^2}mr^2\left(\frac{e^2}{r}+E\right) = \frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

Both sides again independent, $\therefore$ equal to some constant $\ell(\ell+1)$;

$\rightarrow$

$\rightarrow \quad \Rightarrow \frac{m_\ell^2 \Theta}{\sin^2\theta} - \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) = \ell(\ell+1)\Theta,$ and ①

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2mR}{\hbar^2}\left(\frac{e^2}{r} + E\right) = \ell(\ell+1)\frac{R}{r^2}. \quad ②$$

Solving ① ;

Let $z = \cos\theta$, $\therefore \frac{dz}{d\theta} = -\sin\theta$, ~~$\therefore \sin\theta\, d\theta$~~ $\frac{d\theta}{dz} = -\frac{1}{\sin\theta}$,
$\frac{d}{dz} = \frac{d}{d\theta}\cdot\frac{d\theta}{dz} = -\frac{1}{\sin\theta}\frac{d}{d\theta}$, and $\frac{d}{d\theta} = -\sin\theta\frac{d}{dz}$

$$\therefore ① \Rightarrow \frac{m_\ell^2 \Theta}{\cancel{\sin^2\theta}\, 1-z^2} + \frac{d}{dz}\left(-(1-z^2)\frac{d\Theta}{dz}\right) = \ell(\ell+1)\Theta$$
$$\frac{d}{dz}\left((1-z^2)\frac{d\Theta}{dz}\right) + \left(\ell(\ell+1) - \frac{m_\ell^2}{1-z^2}\right)\Theta = 0.$$

This has sol^{n} $\Theta_{\ell, m_\ell}(z) = (1-z^2)^{\frac{|m_\ell|}{2}} \frac{d^{|m_\ell|}P_\ell(z)}{dz^{|m_\ell|}}$,
where $P_\ell(z)$ satisfies
$(1-z^2)\frac{d^2P_\ell}{dz^2} - 2z\frac{dP_\ell}{dz} + \ell(\ell+1)P_\ell = 0.$
Let $P_\ell(z) = \sum_{k=0}^{\infty} a_k z^k$, then

$$(1-z^2)\sum_{k=0}^{\infty} k(k-1)a_k z^{k-2} - 2z\sum_{k=0}^{\infty} k a_k z^{k-1}$$
$$+ \ell(\ell+1)\sum_{k=0}^{\infty} a_k z^k = 0$$

$$\sum_{k=0}^{\infty}\left[k(k-1)a_k z^{k-2} - \left\{k(k+1)\cancel{a_k} \cancel{+2k} - \ell(\ell+1)\right\}a_k z^k\right] = 0$$

$$\sum_{k=0}^{\infty}\left[(k+2)(k+1)a_{k+2} - \left\{k(k+1) - \ell(\ell+1)\right\}a_k\right]z^k = 0$$

For this to be true $\forall z$, coefficient of z^k must $= 0$,

$$\Rightarrow a_{k+2} = \frac{k(k+1) - \ell(\ell+1)}{(k+2)(k+1)} a_k,$$

Hence $P_\ell(z) = \sum_{k=0}^{\infty} a_k \cancel{z^k} z^k$ split into two series of even & odd powers, where a_k determined by arbitrary constants a_0 & a_1.

$\rightarrow$

→ As $k \to \infty$, $a_k \to a_{k+2}$ $\Rightarrow$ series diverges for $|z| = 1$.
By setting $l = 0, 1, 2, 3, \ldots,$ one of these series can be terminated at the lth term, and the other can have $a_0/a_1 = 0$, depending on if l is even or odd.

This ~~means~~ means that $P_l(z)$ will be a polynomial in z of degree l, hence

$$|m_l| \leq l,$$

otherwise

$$\Theta_{l,m_l}(z) = (1-z^2)^{\frac{|m_l|}{2}} \frac{d^{|m_l|} P_l(z)}{dz^{|m_l|}} = 0$$

Changing back to θ,

$$\Theta_{l,m_l}(\theta) = \sin^2\theta^{\frac{|m_l|}{2}} \cdot \frac{d^{|m_l|}}{d(\cos\theta)^{|m_l|}} \left(\sum_{k=0}^{l} a_k \cos^k\theta \right)$$

$$= \sin^{|m_l|}\theta \cdot \frac{d^{|m_l|}}{d(\cos\theta)^{|m_l|}} \left(\sum_{k=0}^{l} a_k \cos^k\theta \right),$$

where

$$a_{k+2} = \frac{k(k+1) - l(l+1)}{(k+2)(k+1)} a_k$$

and if l is odd, $a_0 = 0$, if l even, $a_1 = 0$.

Solving ② ;

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mR}{\hbar^2}\left(\frac{e^2}{r} + E\right) = l(l+1)\frac{R}{r^2},$$

where $l = 0, 1, 2, 3, \ldots$

Let $\rho = 2\beta r$, where $\beta^2 = \frac{2mE}{\hbar^2}$, and
let $\gamma = \frac{me^2}{\hbar^2\beta}$, then
$\frac{d\rho}{dr} = 2\beta$, $\frac{d}{d\rho} = \frac{d}{dr}\cdot\frac{dr}{d\rho} = \frac{1}{2\beta}\frac{d}{dr}$, and $\frac{d}{dr} = 2\beta\frac{d}{d\rho}$,

$$\Rightarrow \frac{2\beta}{r^2}\frac{d}{d\rho}\left(2\beta r^2\frac{dR}{d\rho}\right) + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right)R = l(l+1)\frac{R}{r^2}$$

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) + \left(-\frac{l(l+1)}{\rho^2} + \frac{\gamma}{\rho} - \frac{1}{4}\right)R = 0$$

Consider the case of ~~$\frac{1}{\rho}$~~ $\rho \to \infty$, then the above reduces to

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) = \frac{R}{4},$$ which has a solution

$$R(\rho) = e^{-\frac{\rho}{2}},$$ suggesting original eq^{n} has form

$R(\rho) = e^{-\frac{\rho}{2}}F(\rho)$. Substituting, this gives

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\gamma-1}{\rho} - \frac{l(l+1)}{\rho^2}\right]F = 0$$

Let $F(\rho) = \rho^s\sum_{k=0}^{\infty}a_k\rho^k$, ~~then~~ $s \geq 0$, then

$$\left.\begin{aligned}&\sum_{k=0}^{\infty}k(k-1)a_k\rho^{k+s-2} + \sum_{k=0}^{\infty}ka_k\rho^{k+s-1}\left(\frac{2}{\rho}-1\right)\\ &+ \sum_{k=0}^{\infty}\left(\frac{\gamma-1}{\rho} - \frac{l(l+1)}{\rho^2}\right)a_k\rho^{k+s} = 0\end{aligned}\right\}\text{incorrect}$$

$$\sum_{k=0}^{\infty}\left[\{(s+k)(s+k+1) - l(l+1)\}a_k\rho^{s+k-2} - \{s+k+1-\gamma\}a_k\rho^{s+k-1}\right] = 0$$

→

$\rightarrow \quad \Rightarrow \left[s(s+1) - l(l+1)\right] a_0 \rho^{s-2}$
$+ \sum_{k=0}^{\infty} \left[\{ (s+k+1)(s+k+2) - l(l+1) \} a_{k+1} - \{ s+k+1-\gamma \} a_k \right] \rho^{s+k-1}$
$= 0$

$\Rightarrow \quad s(s+1) - l(l+1) = 0$, and
$$a_{k+1} = \frac{(s+k+1-\gamma)}{(s+k+1)(s+k+2) - l(l+1)} a_k$$

First result indicates $s = l$ $(s \neq -(l+1) \because s \geq 0)$, giving

$$a_{k+1} = \frac{(k+l+1-\gamma)}{(k+l+1)(k+l+2) - l(l+1)} a_k$$

Clearly, as $k \to \infty$, $a_{k+1} \to \frac{a_k}{k}$, i.e. same as series expansion of e^{ρ}, hence $R(\rho) = e^{-\frac{\rho}{2}} F(\rho) \to \infty$ as $\rho \to \infty$ if $F(\rho)$ is an infinite series. To prevent this, can terminate $F(\rho)$ series by requiring

$$\gamma = n, \quad \text{where } n = l+1,\ l+2,\ l+3 \ldots$$

Causing recurrence relation to terminate at $[n-(l+1)]$th term,
$\therefore$ $F(\rho)$ will be polynomial of order $n-1$.
Can also find energies of each n from previous relations;

$$n^2 = \gamma^2 = \frac{m^2 e^4}{\hbar^4 \beta^2}, \quad \text{where } \beta^2 = \frac{2mE}{\hbar^2},$$

$$\Rightarrow \quad n^2 = \frac{me^4}{2E\hbar^2} \quad \Rightarrow \quad E_n = \frac{me^4}{2\hbar^2 n^2}$$
$n = 1, 2, 3, \ldots$

$R(\rho) = e^{-\frac{\rho}{2}} F(\rho)$, $\quad F(\rho) = \rho^l \sum_{k=0}^{n-(l+1)} a_k \rho^k$, where
$a_{k+1} = (k+l+1-n)/\ldots \cdot a_k$
where $\rho = 2\beta r = \frac{\sqrt{8mE}}{\hbar} r$

$$\therefore \quad R(r) = e^{-\frac{\sqrt{2mE}}{\hbar} r} \left(\frac{\sqrt{8mE}}{\hbar} r \right)^l \sum_{k=0}^{n-(l+1)} a_k \left(\frac{\sqrt{8mE}}{\hbar} r \right)^k$$

$n \in \mathbb{N}\setminus\{0\}$, i.e. $n = 1, 2, 3, \ldots$

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

$m_l = -l, -(l-1), \ldots, 0, \ldots, l-1, l.$

$$\Psi(r, \theta, \phi) = \alpha R(r)\Theta(\theta)\Phi(\phi), \text{ where}$$

$\cancel{\Phi(\phi) =}$

$$\Phi_{m_l}(\phi) = e^{i m_l \phi},$$

$$\Theta_{l,m_l}(\theta) = \sin^{|m_l|}\theta \cdot \frac{d^{|m_l|}}{d(\cos\theta)^{|m_l|}}\left(\sum_{k=0}^{l} a_k \cos^k\theta\right),$$

where

$$a_{k+2} = \frac{k(k+1) - l(l+1)}{(k+2)(k+1)} a_k, \text{ and}$$

if l odd $\Rightarrow a_0 = 0$, l even $\Rightarrow a_1 = 0$.

$$R_{n,l}(r) = e^{-\frac{\sqrt{2mE}}{\hbar}r} \cdot \sum_{k=0}^{n-(l+1)} a_k \left(\frac{\sqrt{8mE}}{\hbar} r\right)^{k+l}$$

where

$$a_{k+1} = \frac{(k+l+1-n)a_k}{(k+l+1)(k+l+2) - l(l+1)}$$

Normalisation then requires that $\iiint_{r,\theta,\phi} |\Psi(r,\theta,\phi)|^2 = 1$,

$$\therefore \iiint_{r\,\theta\,\phi} \alpha^2 |R|^2 |\Theta|^2 |\Phi|^2 = 1$$

$$\Rightarrow \alpha = \left[\int_0^\infty |R|^2 dr \int_0^{2\pi} |\Phi|^2 d\phi \int_0^\pi |\Theta|^2 d\theta\right]^{-\frac{1}{2}},$$

where $\int_0^{2\pi} |\Phi|^2 d\phi = 2\pi$ simply.