Hydrogen Atom:

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} \frac{-e^2}{4\pi\varepsilon_0 r} \right) u(r) = E\, u(r)$$

MKS units

$$\int_0^\infty dr\, (u(r))^2 = 1$$

(1) Switch to dimensionless units:

$$\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} - \frac{2me^2}{4\pi\varepsilon_0 \hbar^2} \frac{1}{r} \right) u(r) = \frac{2mE}{\hbar^2} u(r)$$

$\rightarrow a_0 = \dfrac{\hbar^2}{m \cdot \frac{e^2}{4\pi\varepsilon_0}}$ has the units of length (Bohr radius)

$$\approx \frac{(1 \times 10^{-34} J \cdot s)^2}{(9.1 \times 10^{-31} kg)} \frac{(9 \times 10^9 N \cdot m^2/C^2)^{-1}}{(1.6 \times 10^{-19} C)^2}$$

$\approx 0.52 \mathring{A}$, where $1 \mathring{A} = 10^{-10} m$

$$\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} - \frac{1}{a_0} \frac{2}{r} \right) u(r) = \frac{2mE}{\hbar^2} u(r)$$

$$\left(-a_0^2 \frac{d^2}{dr^2} + \frac{a_0^2 \ell(\ell+1)}{r^2} - \frac{2a_0}{r} \right) u(r) = \frac{2ma_0^2}{\hbar^2} u(r)$$

Rydberg energy; I here means ionization.

$$\rightarrow E_I = \frac{\hbar^2}{2ma_0^2} = \frac{\hbar^2}{2m} \left(\frac{m}{\hbar^2} \right)^2 \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 = \frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2$$

$$= \frac{(9.1 \times 10^{-31} kg)}{2(1 \times 10^{-34} J \cdot s)^2} (1.6 \times 10^{-19} C)^4 (9 \times 10^9 N \cdot m^2/C^2)^2$$

$\approx 13.6 eV$

Let $\rho = r/a_0$ and $\lambda = \sqrt{-E/E_I}$ $(E<0)$.

$$\rightarrow \left(-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho} - \frac{2}{\rho}\right)u = -\lambda^2 u$$

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

(2) Asymptotic behavior as $r \to \infty$.

For large r (or ρ),

$$\left[\frac{d^2}{d\rho^2} - \lambda^2\right]u(\rho) \approx 0$$

$\rightarrow \rho \approx e^{\pm\lambda\rho}$; however, $e^{+\lambda\rho}$ is unphysical because it is not normalizable.

$\rightarrow \rho \sim e^{-\lambda\rho}$ as $\rho \to \infty$.

Let $u(\rho) = e^{-\lambda\rho}\, y(\rho)$

$$\frac{du}{d\rho} = -\lambda u + e^{-\lambda\rho}\frac{dy(\rho)}{d\rho}$$

$$\frac{d^2u}{d\rho^2} = \lambda^2 u - 2\lambda e^{-\lambda\rho}\frac{dy}{d\rho} + e^{-\lambda\rho}\frac{d^2y}{d\rho^2}$$

$$\rightarrow \lambda^2 u - 2\lambda e^{-\lambda\rho}\frac{dy}{d\rho} + e^{-\lambda\rho}\frac{d^2y}{d\rho^2}$$

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

$$\rightarrow \boxed{\frac{d^2y}{d\rho^2} - 2\lambda\frac{dy}{d\rho} + \left(\frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right)y = 0}$$

(3) Series Solution:

Let ρ^s be the behavior of $y(\rho)$ near $\rho = 0$ $(r=0)$.
Look for a solution of the form

$$y(\rho) = \rho^s \sum_{q=0}^{\infty} c_q \rho^q$$

$$= \sum_{q=0} c_q \rho^{q+s}$$

as $\rho \to 0$

$$\frac{dy}{d\rho} = \sum_{q=0}^{\infty} c_q(q+s)\rho^{q+s-1} \qquad \sim c_0 s \rho^{s-1}$$

$$\frac{d^2y}{d\rho^2} = \sum_{q=0}^{\infty} c_q(q+s)(q+s-1)\rho^{q+s-2} \qquad \sim c_0 s(s-1)\rho^{s-2}$$

$$\frac{1}{\rho}y = \sum_{q=0}^{\infty} c_q \rho^{q+s-1} \qquad \sim c_0 \rho^{s-1}$$

$$\frac{1}{\rho^2}y = \sum_{q=0}^{\infty} c_q \rho^{q+s-2} \qquad \sim c_0 \rho^{s-2}$$

Compare the most singular terms:

$$c_0 s(s-1)\rho^{s-2} - \ell(\ell+1) c_0 \rho^{s-2} = 0$$

$$\rightarrow s(s-1) = \ell(\ell+1) \rightarrow s = \ell+1 \text{ or } -\ell \quad (\text{or } c_0 = 0)$$

Look at the other terms:

$$\frac{d^2y}{d\rho^2} - 2\lambda\frac{dy}{d\rho} + \left(\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)y = \sum_{q=1}^{\infty} c_q (q+s)(q+s-1)\rho^{q+s-2}$$
$$-2\lambda \sum_{q=0}^{\infty} c_q (q+s)\rho^{q+s-1}$$
$$+2\sum_{q=0}^{\infty} c_q \rho^{q+s-1}$$
$$-\ell(\ell+1)\sum_{q=1}^{\infty} c_q \rho^{q+s-2}$$

$$= \sum_{q=0}^{\infty} c_{q+1}(q+s+1)(q+s)\rho^{q+s-1}$$
$$-2\lambda c_q (q+s)\rho^{q+s-1}$$
$$+2c_q\rho^{q+s-1}$$
$$-\ell(\ell+1)c_{q+1}\rho^{q+s-1}$$

$$\rightarrow \left[(q+s+1)(q+s) - \ell(\ell+1)\right]c_{q+1} + 2\left[1-\lambda(q+s)\right]c_q$$

$$\rightarrow c_{q+1} = \frac{2\left[\lambda(q+s)-1\right]}{(q+s+1)(q+s) - \ell(\ell+1)}\, c_q$$

Since $\int_0^\infty dr\,(u(r))^2 = 1$,

$$\int_0^\infty d\rho\,(u(\rho))^2 = \int_0^\infty d\rho\,(y(\rho))^2 e^{-2\lambda\rho} \text{ is finite.}$$

$\rightarrow y(\rho) \sim \rho^{-l}$ is not physical for $l = 1, 2, 3, \ldots$

For $l = 0$, $y(\rho) \sim \rho^{-l} = \rho^0 = 1$.

$$\left(\frac{d^2}{d\rho^2} - 2\lambda\frac{d}{d\rho} + \frac{2}{\rho}\right)1 = \frac{2}{\rho} \neq 0, \text{ which is a contradiction}$$

$\rightarrow y(\rho) \sim \rho^{-l}$ is also not physical for $l = 0$.

$$\Rightarrow \boxed{s = l + 1}$$

The recursion relation now becomes

$$c_{q+1} = \frac{2[\lambda(q+l+1) - 1]}{(q+1)(q+1+2l+1)} c_q$$

since $\underbrace{(q+l+2)}_{(q+1)+(l+1)}\underbrace{(q+l+1)}_{(q+1)+l} - l(l+1) =$

$= (q+1)^2 + (q+1)(2l+1)$

$= (q+1)(q+1+2l+1)$.

$$\rightarrow \boxed{c_q = \frac{2[\lambda(q+l) - 1]}{q(q+2l+1)} c_{q-1}} \quad q = 1, 2, 3, \ldots$$

For large q, $\frac{c_q}{c_{q-1}} \approx \frac{2\lambda}{q}$.

Compare this to

$$e^{2\rho\lambda} = \sum_{q=0}^{\infty} \frac{1}{q!}(2\rho\lambda)^q = \sum_{q=0}^{\infty} d_q \rho^q, \text{ where } d_q = \frac{(2\lambda)^q}{q!}$$

$$\rightarrow \frac{d_q}{d_{q-1}} = \frac{2\lambda}{q}.$$

Thus, $\sum_{q=0}^{\infty} c_q \rho^q \sim e^{2\rho\lambda}$ <u>unless</u> $c_q = 0$ for $q \geq k$.

Since $u(\rho) = e^{-\lambda\rho} y(\rho)$, this would imply $u(\rho) \sim \rho^s e^{-\lambda\rho} e^{2\lambda\rho} = \rho^s e^{\lambda\rho}$, which is not normalizable. $\Rightarrow c_q = 0$ for $q > q_0$.

$\rightarrow \lambda(k+l) - 1 = 0$ for some $k = 1, 2, 3, \ldots$

$$\rightarrow \boxed{\begin{array}{l} \lambda = \frac{1}{n} \text{ for } n = 1, 2, 3, \ldots \\ \\ l = n - k = 0, 1, 2, \ldots, n-1 \end{array}}$$

(4) Energies and degeneracies:

$$E = -\lambda^2 E_I = \frac{-1}{n^2} E_I$$

For a given n the allowed ℓ values a $0, 1, \ldots, n-1$.
The degeneracy for angular momentum ℓ is $(2\ell+1)$.
$\rightarrow$ The total number of states for a given n is

$$\sum_{\ell=0}^{n-1} (2\ell+1) = 2\,\frac{n(n-1)}{2} + n = n^2.$$

(5) Wave functions: $u(\rho) = y(\rho) e^{-\lambda\rho}$

$$a_0 \int_0^\infty d\rho\, (u(\rho))^2 = 1$$

$\underline{n=1, \ell=0:}$ $\quad k = n - \ell = 1, \quad \lambda = \frac{1}{n} = 1$

$$u(\rho) = \rho c_0 e^{-\lambda\rho}$$

$$a_0 \int_0^\infty d\rho\, \rho^2 c_0^2 e^{-2\lambda\rho} = \frac{2 a_0 c_0^2}{(2\lambda)^2} = \frac{a_0 c_0^2}{4} = 1$$

$$\rightarrow c_0 = \frac{2}{\sqrt{a_0}}$$

$$R(r) = \frac{u(r)}{r} = \frac{2}{\sqrt{a_0}} \frac{1}{r} \left(\frac{r}{a_0}\right) e^{-r/a_0} = \boxed{\frac{2}{(a_0)^{3/2}} e^{-r/a_0}} = R_{\underset{n}{1},\underset{\ell}{0}}(r)$$