Hydrogen Atom

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

$$\begin{aligned}
\alpha &= \frac{e^2}{4\pi\epsilon_0\hbar c} \\
&= \frac{\left(1.6\times10^{-19}\,C\right)^2}{4\pi\,8.85\times10^{-12}\,C^2/Nm^2\,1.055\times10^{-34}\,Js\,3\times10^8 m/s} \\
&\approx \frac{1}{137}
\end{aligned}$$

$$\mu = \frac{m_e\,m_p}{m_e+m_p}$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left(-\frac{\hbar c\alpha}{r} + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right)u = E\,u$$

Hydrogen Atom

- continuum unbound states: $E > 0$
- bound states: $E < 0$

$$\kappa = \frac{\sqrt{-2\mu E}}{\hbar}$$

divide Schrödinger Eq. by E

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} + \left(\frac{\hbar c\alpha}{\kappa^2 r}\frac{2\mu}{\hbar^2} - \frac{1}{\kappa^2}\frac{\ell(\ell+1)}{r^2}\right)u = u$$

$$\rho = \kappa r, \;\; \rho_0 = \frac{2\mu c\alpha}{\hbar\kappa}$$

$$\frac{d^2u}{d\rho^2} = u\left(1 - \frac{2\mu c\alpha}{\hbar\kappa\rho} + \frac{\ell(\ell+1)}{\rho^2}\right) = u\left(1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right) \qquad *$$

Asymptotic Forms

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

$$u \approx A\,e^{-\rho} + B\,e^{+\rho}$$

$$B = 0$$

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

$$u = C\rho^{\ell+1} + D\rho^{-\ell}$$

$$\begin{aligned}
\frac{du}{d\rho} &= C(\ell+1)\rho^{\ell} - D\ell\rho^{-\ell-1} \\
\frac{d^2u}{d\rho^2} &= C(\ell+1)\ell\rho^{\ell-1} + D\ell(\ell+1)\rho^{-\ell-2} \\
&= \ell(\ell+1)\frac{\left(C\rho^{\ell+1}+D\rho^{-\ell}\right)}{\rho^2}
\end{aligned}$$

$$D = 0$$

Asymptotic Form

$$u = \rho^{\ell+1} e^{-\rho} v(\rho)$$

$$\begin{aligned}
\frac{du}{d\rho} &= (\ell+1)\rho^{\ell} e^{-\rho} v - \rho^{\ell+1} e^{-\rho} v + \rho^{\ell+1} e^{-\rho} \frac{dv}{d\rho} \\
\frac{d^2u}{d\rho^2} &= (\ell+1)\ell\rho^{\ell-1} e^{-\rho} v - 2(\ell+1)\rho^{\ell} e^{-\rho} v \\
&\quad + 2(\ell+1)\rho^{\ell} e^{-\rho} \frac{dv}{d\rho} + \rho^{\ell+1} e^{-\rho} v \\
&\quad -2\rho^{\ell+1} e^{-\rho} \frac{dv}{d\rho} + \rho^{\ell+1} e^{-\rho} \frac{d^2v}{d\rho^2} \\
\frac{d^2u}{d\rho^2} &= \rho^{\ell} e^{-\rho} \left[\left(\frac{\ell(\ell+1)}{\rho} + \rho - 2(\ell+1) \right) v \right. \\
&\qquad \left. + 2(\ell+1-\rho) \frac{dv}{d\rho} + \rho \frac{d^2v}{d\rho^2} \right]
\end{aligned}$$

$$\frac{d^2u}{d\rho^2} = u \left(1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right)$$

$$\rho \frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + (\rho_0 - 2(\ell+1))\, v \qquad *$$

Asymptotic Form

$$u = \rho^{\ell+1}\, e^{-\rho}\, v(\rho)$$

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Power Series Solution

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

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

$$c_{j+1}\left[(j+1)j + 2(\ell+1)(j+1)\right] = c_j\left[2j + 2(\ell+1) - \rho_0\right]$$

$$c_{j+1} = c_j \frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)} \quad *$$

large j: $\quad c_{j+1} \approx c_j \frac{2j}{j(j+1)} \approx c_j \frac{2}{(j+1)}$

Power Series Solution

$$\text{if} \quad c_{j+1} = c_j \frac{2}{(j+1)}$$

$$\text{then} \quad c_j = c_0 \frac{2^j}{j!}$$

$$v = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

$$u = \rho^{\ell+1} e^{-\rho} v(\rho) = c_0 \rho^{\ell+1} e^{\rho}$$

series must terminate

$$c_{j_{\max}+1} = 0$$

$$2(j_{\max} + \ell + 1) - \rho_0 = 0$$

$$n \equiv j_{\max} + \ell + 1 \qquad *$$

Principle Quantum Number

$$n \equiv j_{\max} + \ell + 1$$

$$\rho_0 = 2n = \frac{2\mu c\alpha}{\hbar\kappa}$$

$$\begin{aligned} E &= -\frac{\hbar^2\kappa^2}{2\mu} = -\frac{\hbar^2}{2\mu}\left(\frac{2\mu c\alpha}{\hbar 2n}\right)^2 \\ &= -\frac{\alpha^2\mu c^2}{2n^2} \\ &= -\frac{13.6 \text{ eV}}{n^2} \end{aligned}$$

$$\kappa = \frac{\mu c\alpha}{\hbar n} \equiv \frac{1}{an}$$

Bohr radius : $a = \frac{\hbar}{\alpha\mu c} = 0.0529 \text{ nm}$

$$\rho = \kappa r = \frac{r}{a\,n}$$

Hydrogen Wavefunction

$$\psi(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$$

$$R_{n\ell}(r) \propto \tfrac{1}{r}\rho^{\ell+1}\, e^{-\rho}\, v(\rho)$$

$v(\rho)$ is a polynomial of degree $j_{\max} = n - \ell - 1$