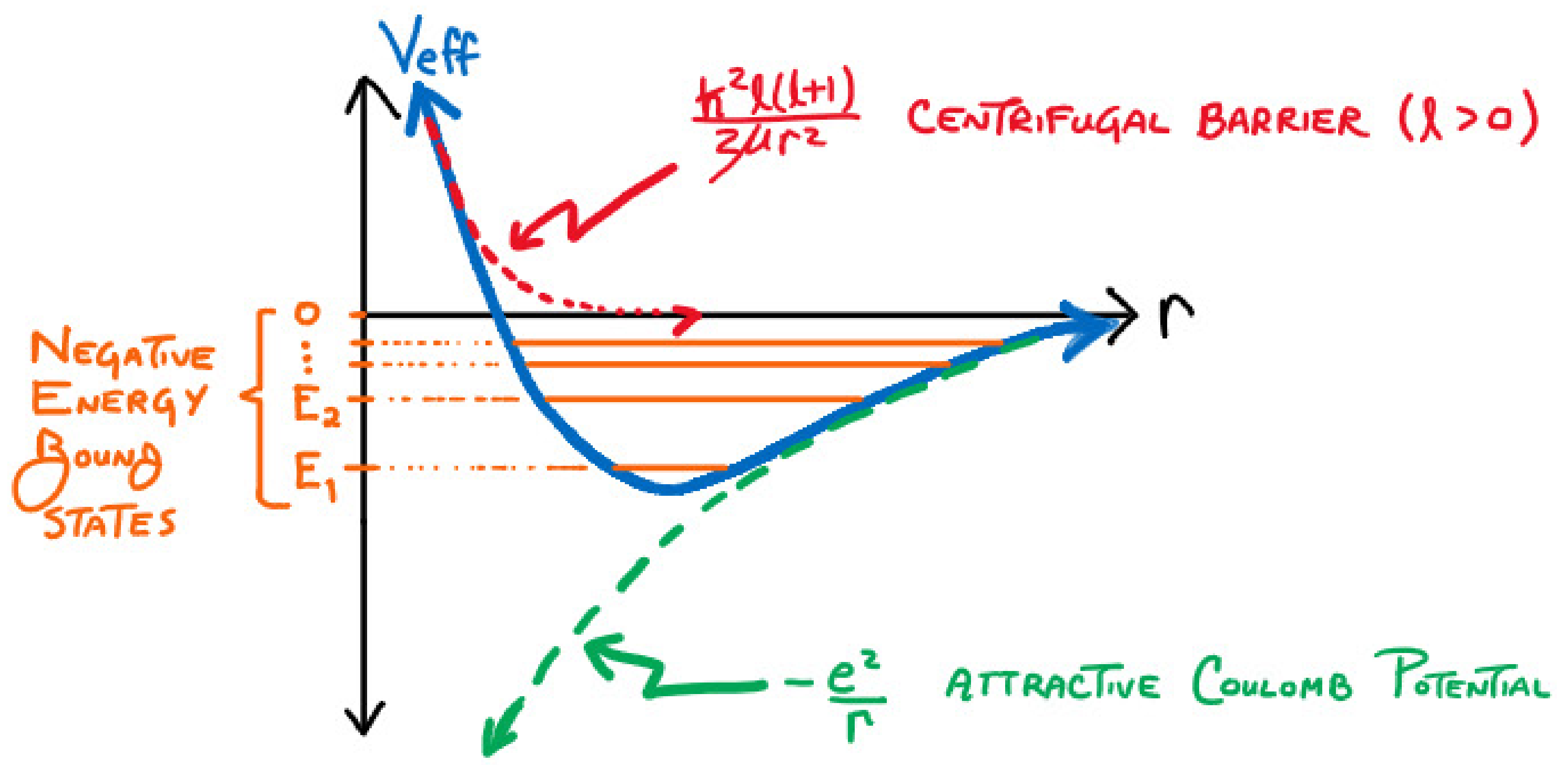
The Hydrogen Atom

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2} + V(r)\right]U_{E\ell} = -|E|\,U_{E\ell}$$ Radial S.E. (Lec. 23, p. 5)

- μ = "Reduced Mass" of electron, proton: $\mu = \frac{m_e m_p}{m_e + m_p} \simeq m_e$, since $m_e \ll m_p$
  - $m_e = 0.511\ \mathrm{MeV}/c^2$
  - $m_p = 938\ \mathrm{MeV}/c^2$

- Attractive Coulomb Potential $V(r) = -\frac{e^2}{r}$

$$\Rightarrow V_{eff}(r) = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{e^2}{r}$$



- We consider Negative-Energy Bound States

$$E = -|E|$$

- **Non-Dimensionalize Diff. Equation**

$$a(|E|) \equiv \frac{\hbar}{\sqrt{2\mu|E|}}$$ characteristic length scale ; $r \equiv a\rho$ (ρ: dimensionless)

$$\Rightarrow \left[-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - \frac{e^2}{|E|a\rho} + 1\right]U_{E\ell} = 0\ ; \quad \frac{e^2}{|E|a} \equiv \frac{1}{\varepsilon}\ \text{(dim.less)}$$

$$\left[-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - \frac{1}{\varepsilon\rho} + 1\right]U_{E\ell} = 0$$

Limits

① $\rho \to \infty$: $\frac{d^2}{d\rho^2}u \simeq u \Rightarrow u = A e^{-\rho} + \cancel{B e^{\rho}}$ unphysical

② $\rho \to 0$: $-\frac{d^2u}{d\rho^2} + \ell(\ell+1)\frac{u}{\rho^2} \simeq 0$; Try $u = c\rho^\alpha$

$\Rightarrow \alpha(\alpha-1) = \ell(\ell+1)$ $\therefore$ $\alpha = \ell+1$ or $\alpha = -\ell$; But: $\lim_{\rho\to 0} U_{E\ell}(\rho) = 0 \Rightarrow \alpha = \ell+1$ (Lec. 23, p. 5)

$$\therefore \quad \lim_{\rho \to 0} U_{E\ell}(\rho) \simeq c\rho^{\ell+1} \qquad (\text{AT LEAST FOR } \ell > 0)$$

- As we did for the SHO, we "Factor Out" the Large-ρ Behavior

$$U_{E\ell}(\rho) \equiv e^{-\rho} V_{E\ell}(\rho) \equiv e^{-\rho} V(\rho)$$

$$\Rightarrow u' = -e^{-\rho}V + e^{-\rho}V' \,, \quad u' \equiv \frac{du}{d\rho} \,; \quad u'' = e^{-\rho}V - 2e^{-\rho}V' + e^{-\rho}V''$$

$$\therefore \left[-V'' + 2V' - \cancel{V} + \frac{\ell(\ell+1)}{\rho^2}V - \frac{1}{\varepsilon\rho}V + \cancel{V} \right] = 0$$

$$\boxed{\left[\frac{d^2}{d\rho^2} - 2\frac{d}{d\rho} + \frac{1}{\varepsilon\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] V = 0}$$

Power Series $\quad V(\rho) \equiv \rho^{\ell+1} \sum_{k=0}^{\infty} C_k \rho^k = \sum_{k=0}^{\infty} C_k \rho^{k+\ell+1}$

- $$\frac{dV}{d\rho} = \sum_{k=0}^{\infty} C_k (k+\ell+1) \rho^{k+\ell}$$

- $$\frac{d^2V}{d\rho^2} = \sum_{k=0}^{\infty} C_k (k+\ell+1)(k+\ell) \rho^{k+\ell-1} \qquad (\ell \geq 1)$$

$$\Rightarrow \sum_{k=0} C_k (k+\ell+1)(k+\ell) \rho^{k+\ell-1} - 2\sum_{k=0} C_k (k+\ell+1) \rho^{k+\ell}$$

$k' \equiv k-1 \Rightarrow k = k'+1$

$$+ \frac{1}{\varepsilon} \sum_{k=0} C_k \rho^{k+\ell} - \ell(\ell+1) \sum_{k=0} C_k \rho^{k+\ell-1} = 0$$

$k' \equiv k-1 \,; \; k = k'+1$

$$\therefore \sum_{k'} C_{k'+1}(k'+\ell+2)(k'+\ell+1)\,\rho^{k'+\ell} - 2\sum_{k} C_k (k+\ell+1)\,\rho^{k+\ell} + \frac{1}{\varepsilon}\sum_{k} C_k\,\rho^{k+\ell} - \ell(\ell+1)\sum_{k'} C_{k'+1}\,\rho^{k'+\ell} = 0$$

We obtain a two-term recursion relation,

$$\boxed{C_{k+1} = C_k \cdot \left[\frac{2(k+\ell+1) - \frac{1}{\varepsilon}}{(k+\ell+2)(k+\ell+1) - \ell(\ell+1)}\right]}$$

NOTE: $\lim_{k\to\infty} \frac{C_{k+1}}{C_k} = \frac{2}{k}$

CLAIM: as in SHO, leads to unacceptable behavior for ∞ series $V(\rho) \sim e^{2\rho}$

$\therefore$ **Series must terminate at some k^*.**

$$C_{k^*+1} = 0 \;\Rightarrow\; 2(k^*+\ell+1) = \frac{1}{\varepsilon}$$

Define **Principle Quantum Number** $n \equiv k^*+\ell+1 \;\Rightarrow\; k^* = n-\ell-1$

$$\varepsilon = \frac{a|E|}{e^2} = \frac{|E|}{e^2}\cdot\frac{\hbar}{\sqrt{2\mu|E|}} = \frac{1}{2n} \quad \text{or} \quad |E| = \frac{e^4}{\hbar^2}\cdot\cancel{2}\mu\cdot\frac{1}{2^{\cancel{2}}n^2}$$

Bound State Energies: $E_n = -\dfrac{R_y}{n^2}$; $R_y \equiv \dfrac{m_e e^4}{2\hbar^2} \simeq 13.6\,\text{eV}$

$n \in 1, 2, 3, \ldots$

"Rydberg" $R_y = \dfrac{m_e e^4}{2\hbar^2} = \dfrac{m_e c^2}{2}\cdot\left(\dfrac{e^2}{\hbar c}\right)^2 = \dfrac{0.511\times 10^6\,\text{eV}}{2} \times \left(\dfrac{1}{137}\right)^2 \simeq 13.6\,\text{eV}$

- Radial WF: $U_{n\ell}(\rho) = e^{-\rho}\,V_{n\ell}(\rho)$; $V_{n\ell}(\rho) = \rho^{\ell+1}\displaystyle\sum_{k=0}^{n-\ell-1} C_k^{(n\ell)}\rho^k$

$\Rightarrow k^* = n-\ell-1 \geq 0 \quad \therefore\; \ell \leq n-1$ angular momentum is bounded by $n-1$.

Series coefficients:

$$C_{k+1}^{(n\ell)} = C_k^{(n\ell)}\cdot 2\left[\frac{(k+\ell+1) - n}{(k+\ell+2)(k+\ell+1) - \ell(\ell+1)}\right]$$

DIMENSIONFUL VERSION: $\rho = \frac{r}{a} = r \cdot \left(\frac{2m_e}{\hbar^2}|E_n|\right)^{\frac{1}{2}} = r \cdot \left(\frac{\cancel{2}m_e}{\hbar^2}\frac{m_e e^4}{\cancel{2}\hbar^2}\frac{1}{n^2}\right)^{1/2} = \frac{r}{n} \cdot \left(\frac{m_e e^2}{\hbar^2}\right)$

BOHR RADIUS: $$a_0 \equiv \frac{\hbar^2}{m_e e^2} = \frac{\hbar c}{m_e c^2} \cdot \left(\frac{\hbar c}{e^2}\right) = \frac{1975\ eV \cdot \text{Å}}{0.511\ MeV} \cdot 137$$

$$\simeq 0.529\ \text{Å}$$

$\therefore \quad \rho = \frac{r}{n a_0}$

THE RADIAL WAVEFUNCTIONS ARE

$$U_{n\ell}(r) = e^{-\frac{r}{n a_0}} \cdot \left(\frac{r}{n a_0}\right)^{\ell+1} \sum_{k=0}^{n-\ell-1} C_k^{(n\ell)} \left(\frac{r}{n a_0}\right)^k, \quad 0 \leq \ell \leq n-1$$

FULL HYDROGEN ATOM WAVE FUNCTIONS

$$\psi_{n\ell m}(r,\theta,\phi) = \frac{U_{n\ell}(r)}{r} \cdot Y_{\ell m}(\theta,\phi) \; ; \quad \begin{array}{c} 0 \leq \ell \leq n-1 \\ -\ell \leq m \leq \ell \end{array}$$

NORMALIZED LOW-n ORBITALS:

1. $n=1, \ell=0$: "S-ORBITAL" ; $E_1 = -R_y = -13.6\,eV$

$$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

← HIGHEST PROBABILITY DENSITY AT $r=0$

2. $n=2, \ell=0,1$: "S, P-ORBITALS" ; $E_2 = -\frac{R_y}{4} \simeq -3.4\,eV$

S-WAVE: $$\psi_{200} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} \cdot \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

P-WAVE: $$\psi_{21\pm1} = \mp\left(\frac{1}{64\pi a_0^3}\right)^{1/2} \cdot \frac{r}{a_0} e^{-r/2a_0} \cdot \sin\theta\, e^{\pm i\phi}$$

$$\psi_{210} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} \cdot \frac{r}{a_0} e^{-r/2a_0} \cdot \cos\theta$$

← P-ORBITALS VANISH AS $r \to 0$.

Degeneracy of Hydrogen Orbitals

- Although $U_{n\ell}(\rho)$ depends on both n and ℓ $(0 \leq \ell \leq n-1)$,

  Energy $E_n = -\dfrac{R_y}{n^2}$, **Independent of ℓ!**

- Total degeneracy for fixed n:

$$\sum_{\ell=0}^{n-1} \underbrace{(2\ell+1)}_{\substack{\#\ m \text{ states} \\ (-\ell \leq m \leq \ell)}} = n^2 = \{1, 4, 9, 16, \ldots\}$$

$n=1$: 1s — 1 state

$n=2$: 2s, 2p — 1+3 states

$n=3$: 3s, 3p, 3d — 1+3+5 states

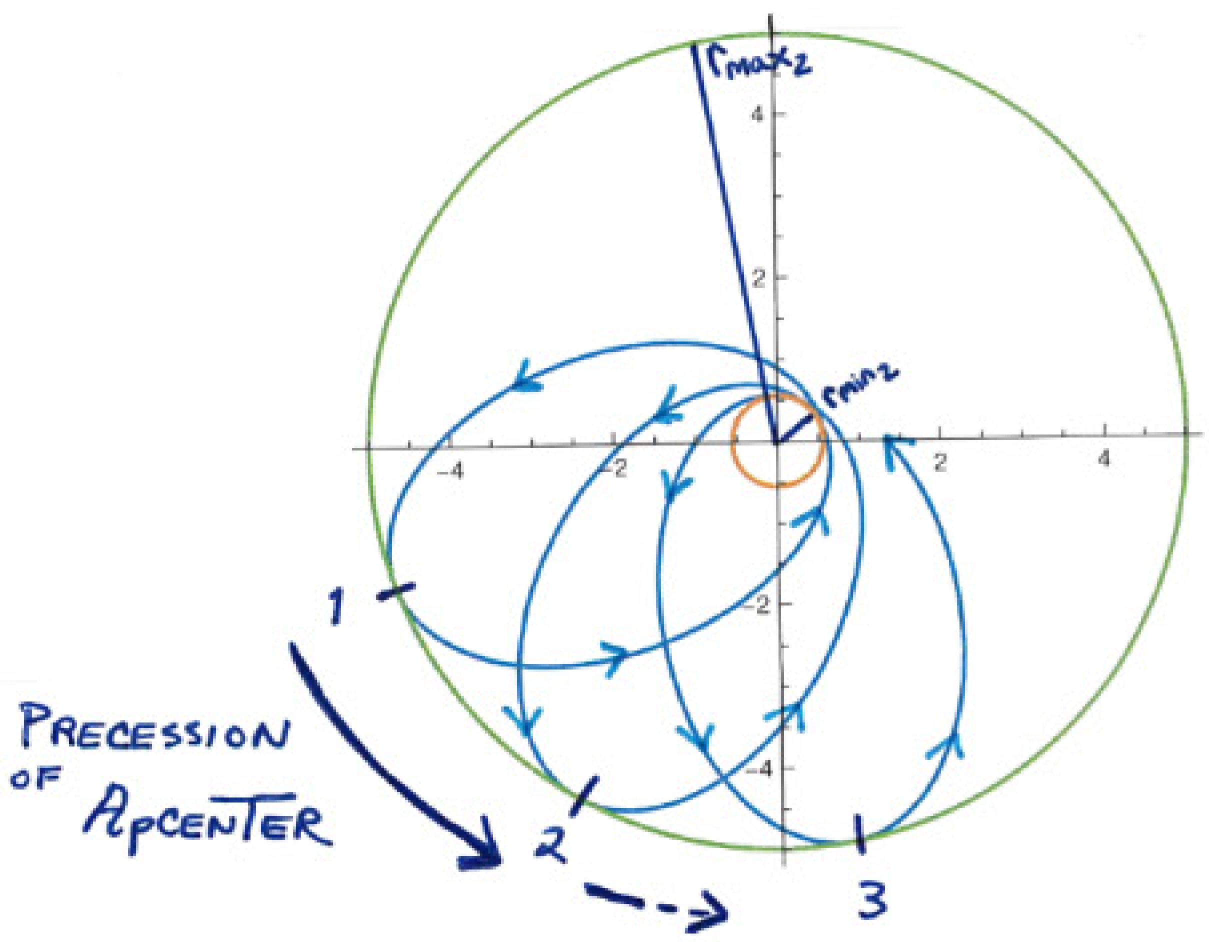
⋮

Why are diff. ℓ-states with same n degenerate?

"Accidental Degeneracy"

- Coulomb $\frac{1}{r}$ potential is special, even in classical case

- Generic Central-Force Motion: Orbit Precesses (not closed)



- Motion in $\frac{1}{r}$ Potential: Bound orbits (Ellipses) are Closed.

- Quantum Version: Degeneracy of different ℓ-orbitals with same n.

Can show that both special features (Closed Classical Orbits, Degenerate ℓ-orbitals) are due to a "Hidden" Symmetry:

$$[\hat{H}, \hat{\vec{N}}] = 0, \quad \hat{\vec{N}} = \frac{1}{2m}\left(\hat{\vec{P}} \times \hat{\vec{L}} - \hat{\vec{L}} \times \hat{\vec{P}}\right) - \frac{e^2 \hat{\vec{X}}}{(\hat{\vec{X}} \cdot \hat{\vec{X}})^{1/2}}$$

"Laplace-Runge-Lenz" Vector

Can build Raising / Lowering operators $\frac{\hat{N}_x \pm i \hat{N}_y}{\sqrt{2}}$

These shift $\ell \to \ell \pm 1$, leaving n unchanged