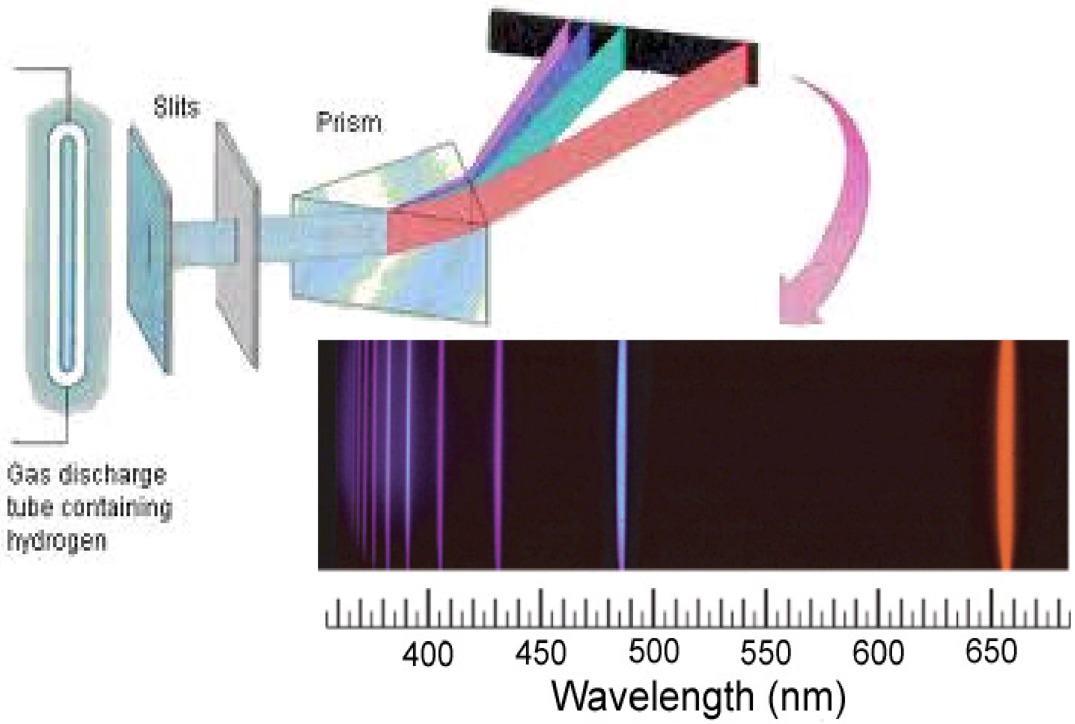
Atomic spectrum of Hydrogen



Rydberg:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad n_1, n_2 = 1, 2, 3 \ldots$$

"Rydberg constant" $\sim 10^5\ cm^{-1}$

$$\lambda\nu = c$$

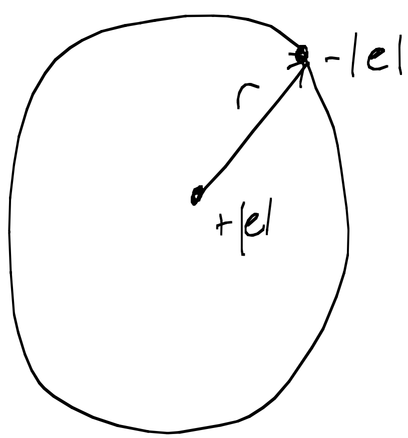
$$\lambda(h\nu) = hc$$

$$E = h\nu = \frac{hc}{\lambda} = \frac{1240\,nm\,eV}{\lambda}$$

$$R_y \rightarrow hcR \sim 13.6\,eV$$

"Rydberg"

Classical Rutherford model



$$E_{tot} = E_{kinetic} + E_{potential} = \frac{1}{2}mv^2 + \left(-\frac{e^2}{4\pi\epsilon_0 r}\right) = \frac{1}{2}mv^2 - mv^2 = -\frac{1}{2}mv^2$$

$$F_{centripetal} = F_{electrostatic} \rightarrow \frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \rightarrow r = \frac{e^2}{4\pi\epsilon_0 m v^2}$$

acceleration: $\frac{v^2}{r}$ $\longrightarrow$ EM radiation and finite lifetime of atom!

"Semiclassical" Bohr atom

deBroglie: $\lambda = \frac{h}{p}$

Bohr: circumference of orbit $= 2\pi r = n\lambda$ $\quad n = 1, 2, 3 \ldots$

$$= n\frac{h}{mv}$$

$$\rightarrow mvr = L = n\frac{h}{2\pi} = n\hbar$$

$$= mv\frac{e^2}{4\pi\epsilon_0 mv^2} = \frac{e^2}{4\pi\epsilon_0 v} = n\hbar \rightarrow v = \frac{e^2}{4\pi\epsilon_0 n\hbar}$$

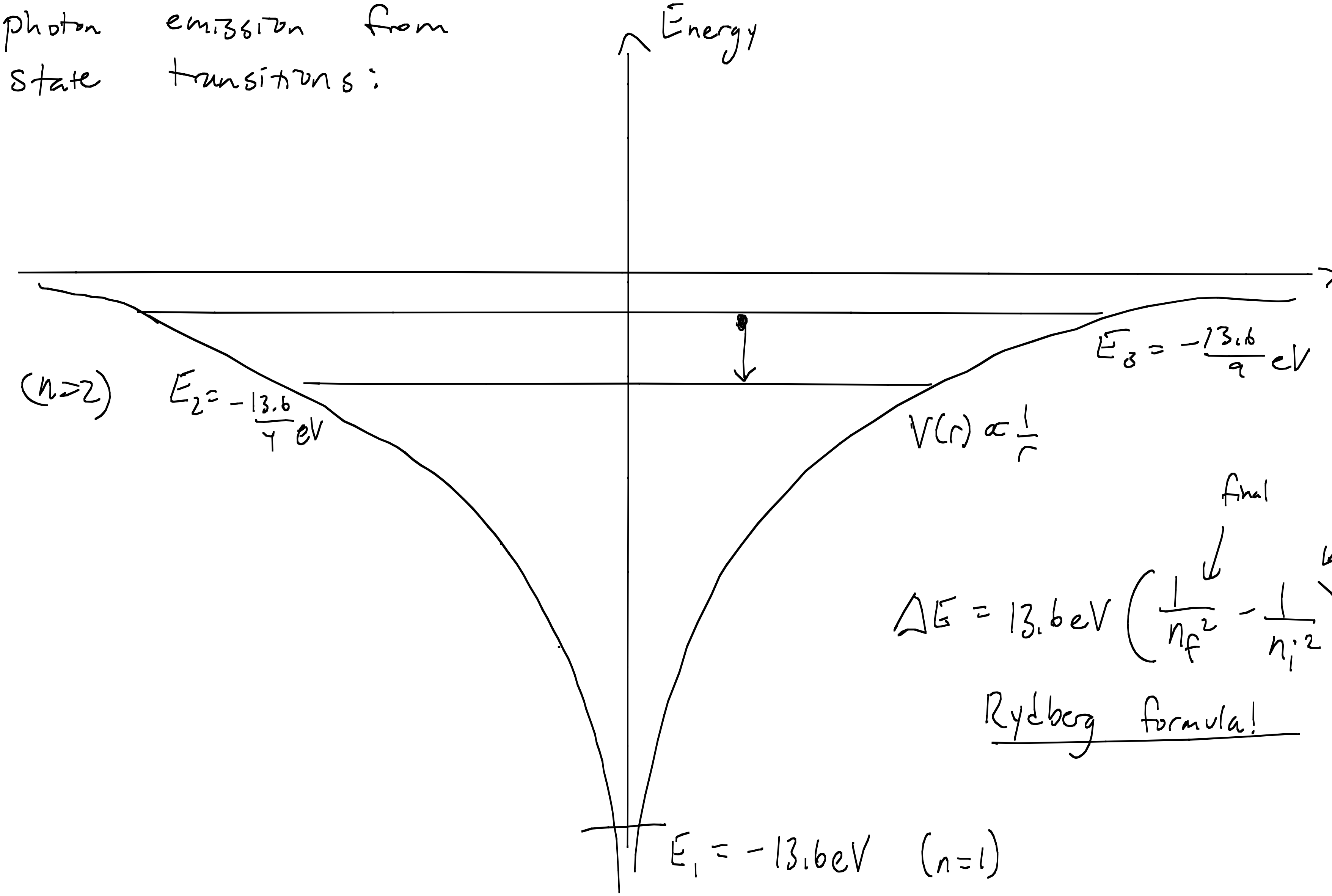
$$E_{tot} = -\frac{1}{2}mv^2 = -\frac{1}{2}m\left(\frac{e^2}{4\pi\epsilon_0 n\hbar}\right)^2 \cong \frac{-13.6\text{ eV}}{n^2}$$

$$r = \frac{e^2}{4\pi\epsilon_0 mv^2} = \frac{4\pi\epsilon_0\hbar^2 n^2}{me^2} = a_0 n^2$$

"Bohr radius" $\sim 0.5\,\text{Å}$ (5×10^{-9} cm)

Hydrogen spectrum

photon emission from state transitions:



final, initial

$$\Delta E = 13.6\,\text{eV}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Rydberg formula!

Problems w/ Bohr's model of hydrogen

1. Orbit w/ definite radius violates uncertainty principle!

2. Angular momentum of ground state is nonzero!

3. Fails to explain:

   a. Spectra of larger atoms w/ >1 electron

   b. multiplets (zero-field splitting of spectral lines)

   c. magnetic field-induced spectral line splitting (Zeeman effect)

Quantum mechanics of Hydrogen atom

$V(r) = \dfrac{-e^2}{4\pi\epsilon_0 r}$ (spherically symmetric) $\longrightarrow$ $\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\phi)$

Radial equation: $-\dfrac{\hbar^2}{2m}\dfrac{d^2u}{dr^2} + \left[-\dfrac{e^2}{4\pi\epsilon_0 r} + \dfrac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]u = Eu$, $u(r) \equiv rR(r)$

$$K^2 \equiv -\frac{2mE}{\hbar^2}$$

$$\frac{1}{K^2}\frac{d^2u}{dr^2} + \left[\frac{e^2}{4\pi\epsilon_0 r \frac{\hbar^2 K^2}{2m}} - \frac{\ell(\ell+1)}{K^2 r^2} - 1\right]u = 0$$

$\rho \equiv Kr \rightarrow d\rho = K\,dr$

$$\frac{d^2u}{d\rho^2} + \left[\left(\frac{2me^2}{4\pi\epsilon_0 \hbar^2 K}\right)\frac{1}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - 1\right]u = 0$$

$$\frac{d^2u}{d\rho^2} + \left[\frac{\rho_0}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - 1\right]u = 0$$

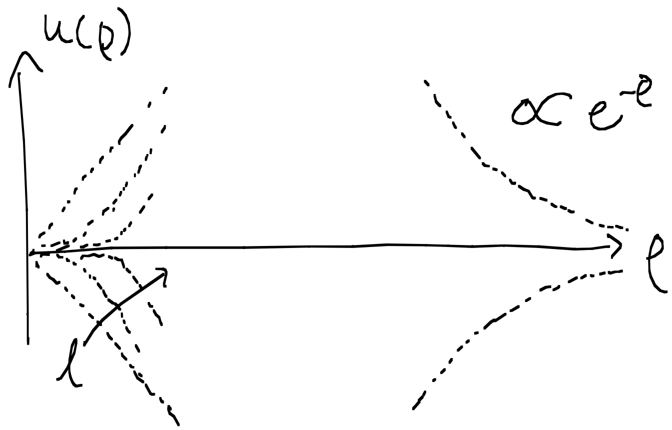
Asymptotic behavior of $u(\rho)$

$\rho \to \infty$: $\sim \frac{d^2u}{d\rho^2} - u = 0 \longrightarrow u(\rho) = Ae^{-\rho} + \cancel{B}e^{+\rho}$ $\to 0$ for normalizable wavefunction

Boundary condition @ $\rho \to \infty$

$\rho \to 0$: $\sim \frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u = 0 \longrightarrow u(\rho) = C\rho^{\ell+1} + \cancel{D}\rho^{-\ell}$ $\to 0$

Boundary condition @ $\rho = 0$



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