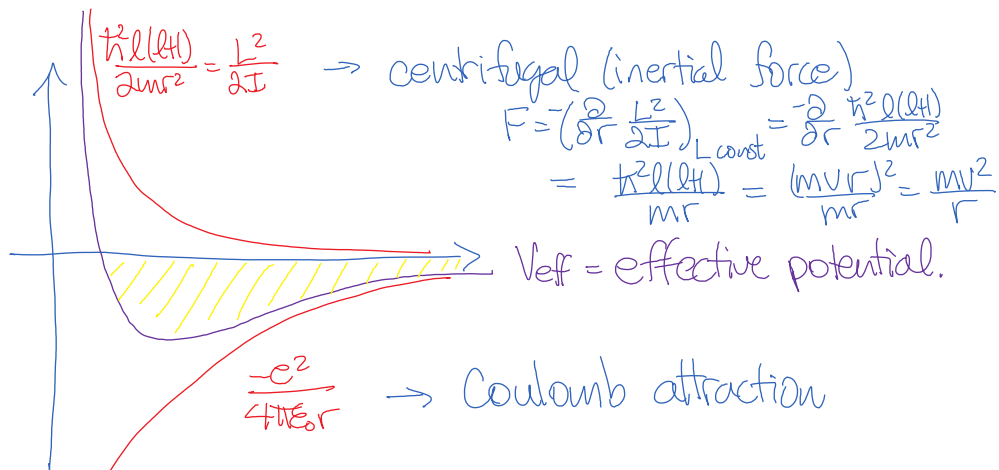


* Radial Equation

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r, \theta, \phi) \quad V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

$$= \left[-\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{l(l+1)}{r^2} \right) - \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{u(r)}{r} Y_{lm}(\theta, \phi)$$

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



- effective "wave number" κ (decay const. κ as $r \rightarrow \infty$) $E = -\frac{\hbar^2 \kappa^2}{2m}$

$$\frac{d^2 u}{d(r\kappa)^2} = \left(1 - \frac{e^2}{4\pi\epsilon_0 r} \frac{1}{\hbar^2 \kappa^2} + \frac{l(l+1)}{(r\kappa)^2} \right) u$$

- normalize coordinates: $\rho = \kappa r$ $V/E = \rho_0/\rho = \frac{2me^2}{4\pi\epsilon_0 \hbar^2 \kappa^2}$ $\rho_0 = \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa}$

$$\frac{d^2 u}{d\rho^2} = \left(\underbrace{1 - \frac{\rho_0}{\rho}}_{r \rightarrow \infty} + \underbrace{\frac{l(l+1)}{\rho^2}}_{r \rightarrow 0} \right) u$$

- asymptotic dependence:

as $r \rightarrow \infty$: $\frac{d^2 u}{d\rho^2} \approx u \rightarrow u(\rho) \sim e^{-\rho}$ [similar to STO]

as $r \rightarrow 0$: $\frac{d^2 u}{d\rho^2} \approx \frac{l(l+1)}{\rho^2} u \rightarrow u(\rho) \sim \rho^{l+1}$ [like square well]

thus let $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$
 $u'(\rho) = \left[\left(\frac{l+1}{\rho} - 1 \right) v + v' \right] e^{-\rho}$

$$\rho v'' + \underbrace{2(\ell H - \rho)}_{\text{doesn't vanish!}} v' + (\rho_0 - 2(\ell H)) v = 0 \quad (*)$$

$f_n(x)$	index	a	b	wdx	$+p$ $-p$	$+q$ $-q$	$- \lambda$ λ	h_n	wave type
$L_k^{(2)}(x)$	$k=0,1,2,\dots$	$0 < x < \infty$	$x^2 e^{-x} dx$	$x^{a+1} e^{-x}$	0	k	$\frac{\Gamma(a+1+k)}{k!}$	(Harmonic osc.) (Coulomb potential)	

$$x L'' + (2+1-x) L' + k L = 0 \quad k=0,1,2,\dots \quad \text{let } v(\rho) = L_k^{(2)}(x=2\rho)$$

$$\psi_{nlm} = N \rho^l e^{-\rho} L_{n-l-1}^{2l+1}(2\rho) Y_{lm}(\theta, \phi) \quad \text{where } \rho = Kr \quad E = -\frac{\hbar^2 k^2}{2m}$$

* series solution: let $v = \sum_{j=0}^{\infty} c_j p^j$

$$v'' = \sum_{j=2}^{\infty} c_j (j)(j-1) \rho^{j-2} \quad \rho v'' = \sum_{j=1}^{\infty} c_{j+1} (j+1)(j) \rho^j$$

relabel indices to get all terms like $\sum_{j \in I} \dots p^j$

$$C_{\text{in}} = -2i + (0 - 2(0+i)) \quad \gamma(0+i) = 0 \quad \text{as } i \rightarrow \infty \quad 2$$

$$\frac{C_{j+1}}{C_j} = - \frac{-2j + (\rho_0 - 2(l+1))}{(j+1)j + 2(l+1)(j+1)} = \frac{2(l+1+j) - \rho_0}{(2l+2+j)(j+1)} \xrightarrow{\text{as } j \rightarrow \infty} \frac{2}{j+1}$$

* quantization of energy E_n

This is the series for $v = e^{2\rho} = \sum_{j=0}^{\infty} \frac{(2\rho)^j}{j!} \xrightarrow{\text{as } \rho \rightarrow \infty} \infty$

Thus the series must truncate: $C_{j+1} = 0$ for some $j_{\max}$

i.e. $\rho_0 = 2(l+1+j_{\max})$ where $j_{\max} = 0, 1, 2, \dots$

$$E = -\frac{\hbar^2 k^2}{2m} = -\frac{\hbar^2}{2m} \left(\frac{me^2}{2\pi\epsilon_0 \hbar^2 \rho_0} \right)^2 = \frac{-me^4}{2(4\pi\epsilon_0 \hbar)^2 (l+1+j_{\max})^2}$$

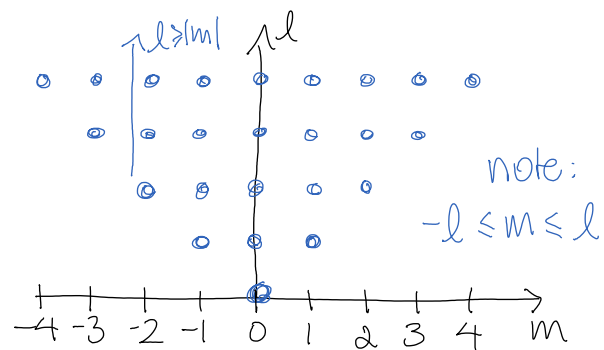
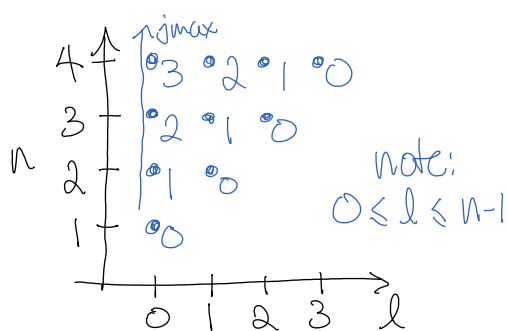
$$E_n = -\frac{1}{2} \underbrace{mc^2}_{\text{rest mass of electron}} \left(\underbrace{\frac{e^2}{4\pi\epsilon_0 \hbar c}}_{\alpha \approx 1/137 = \text{electric quantum}} \right)^2 \frac{1}{n^2}$$

define $n \equiv l+1+j_{\max}$

We recovered the Bohr formula "legally"!

* Quantum numbers of H atom: 3: n, l, m

note: $j_{\max} = \text{level for } l^{\text{th}} \text{ angular state} = \# \text{ of radial lobes}$



at a given $l > 0$, the first radial mode $R_{nl}(r)$ is already in an excited energy state

at a given $m \neq 0$ the first polar mode $P_l^m(\cos\theta)$ already has nonzero (azimuthal) ang. momentum.

-switching order of quantum numbers:

$$\begin{aligned}
 n &= 0, 1, 2, \dots, \infty && \text{"shells, energy levels"} \\
 l &= 0 \text{ "s"}, 1 \text{ "p"}, 2 \text{ "d"}, 3 \text{ "f"}, 4 \text{ "g"}, \dots, n-1 && \text{"ang. mom. orbitals"} \\
 m &= -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l && \text{"magnetic substates"}
 \end{aligned}$$

- degeneracy: $g_l = 2l+1$ # of m substates
 $g_n = \sum_{l=0}^{n-1} 2l+1 = n^2$ # of energy substates

* Spectrum:

$$\begin{aligned}
 \frac{hc}{\lambda} &= h\nu = E_{if} = -E_0 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\
 \frac{1}{\lambda} &= \frac{E_0}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) && R_\infty = E_0/hc = \frac{mc^2}{2hc} \cdot \alpha^2 \quad \text{"Rydberg constant"} \\
 &&& = 10973731 \text{ /m}
 \end{aligned}$$