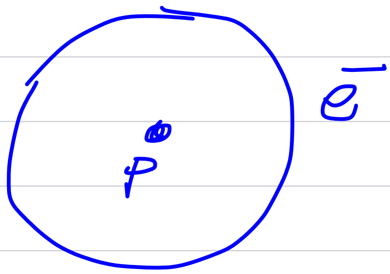
Atomo di idrogeno.

$$H = \frac{p^2}{2\mu} - \frac{e^2}{r}$$

$$\Psi = R_e(r)\, Y_{e,m}(\theta,\varphi)$$



$$H = \frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} - \frac{e^2}{r} \qquad r = |r_e - r_p|,$$

$$R = \frac{m_e r_e + m_p r_p}{m_e + m_p} \quad ; \quad r = r_e - r_p$$

$$-\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2,$$

$$M = m_1 + m_2 \,; \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \simeq m_e$$

$$H = H_{CM} + H^{(rel)}$$

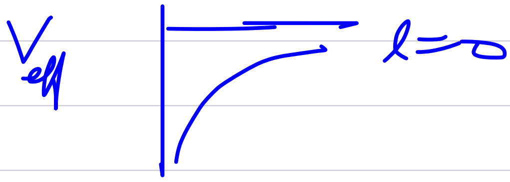
$$H_{CM} = \frac{P_{CM}^2}{2M} \,; \quad \boxed{H^{rel} = \frac{p^2}{2\mu} - \frac{e^2}{r}}$$

$$\mu = \frac{m_e m_p}{m_e + m_p} \simeq m_e\left(1 + O\left(10^{-3}\right)\right)$$

$m_e \sim 0.5\,\mathrm{MeV}$; $m_p \sim 940\,\mathrm{MeV}$.

Equazione Radiale. $\quad \Psi = R_\ell(r)\, Y_{\ell m}(\theta,\varphi) \Rightarrow$

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} + \frac{2m}{\hbar^2}\left(E+\frac{e^2}{r}\right)\right]R_\ell = 0 \quad (*)$$



L'eq. scala come $\frac{1}{r^2}$ $\quad \left[\frac{me}{\hbar^2}\right] \to \left[\frac{1}{r}\right]$

$r_B \equiv \frac{\hbar^2}{me^2}$ = raggio di Bohr.

$r_B^2 \times (*)$, $\quad r/r_B \equiv \tilde{r} \to r \quad (r_B = 1)$

$$\frac{2mE}{\hbar^2} = \frac{2mE}{\hbar^2}\cdot\left(\frac{\hbar^2}{me^2}\right)^2 = 2\left(\frac{r_B}{e^2}\right)E = 2E/(e^2/r_B)$$

$$= 2\tilde{E} \Rightarrow 2E. \quad \left(\frac{e^2}{r_B} = 1 = E_{u.a}\right)$$

{ E in unità di e^2/r_B
r " " r_B

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} + 2\left(E+\frac{1}{r}\right)\right]R = 0$$

oppure $\quad -E = \epsilon > 0$

$$\left\{\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} + 2\left(-\epsilon+\frac{1}{r}\right)\right\}R = 0$$

$$R'' + \frac{2}{r}R' - \frac{\ell(\ell+1)}{r^2}R + 2\left(-\epsilon+\frac{1}{r}\right)R = 0 \quad (**)$$

$r \to \infty \qquad R'' - 2\epsilon R \simeq 0$

$\therefore \quad R \sim e^{-\sqrt{2\epsilon}\, r}$

Poniamo $\sqrt{2\epsilon}\, r \equiv \rho \qquad r = \dfrac{\rho}{\sqrt{2\epsilon}}$ $\qquad \dfrac{2}{2\epsilon r} = \dfrac{2}{\sqrt{2\epsilon}\,\rho} = \sqrt{\dfrac{2}{\epsilon}}\,\dfrac{1}{\rho}$

$\dfrac{1}{2\epsilon}(**) \Rightarrow$

$d^2/d\rho^2 \Rightarrow$

$$R'' + \frac{2}{\rho}R' + \left(-1 + \frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right)R = 0 \qquad = \beta/\rho$$

$$\beta \equiv \sqrt{\frac{2}{\epsilon}}$$

l'unico parametro oltre a l

$\rho \to 0 \qquad R_l(\rho) \sim \rho^l$

$\rho \to \infty \qquad R_l(\rho) \sim e^{-\rho}$

$$R_l(\rho) = \left(\rho^l e^{-\rho}\right) w_l(\rho)$$

$$R_l'(\rho) = \left(\frac{l}{\rho} - 1\right)\rho^l e^{-\rho} w_l + \rho^l e^{-\rho} w_l'$$

$$R_l'' = \rho^l e^{-\rho} w_l'' + 2\left(\frac{l}{\rho} - 1\right)\rho^l e^{-\rho} w_l' + \left\{\left(\frac{l}{\rho} - 1\right)^2 - \frac{l}{\rho^2}\right\}\rho^l e^{-\rho} w_l$$

$\Rightarrow$

$$\rho^l e^{-\rho} w_l'' + 2\left(\frac{l}{\rho}-1\right)\rho^l e^{-\rho} w_l'$$

$$+\left\{\left(\frac{l}{\rho}-1\right)^2 - \frac{l}{\rho^2}\right\}\rho^l e^{-\rho} w_l$$

$$+\frac{2}{\rho}\left[\left(\frac{l}{\rho}-1\right)\rho^l e^{-\rho} w_l + \rho^l e^{-\rho} w_l'\right]$$

$$+\left[-1+\frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right]\rho^l e^{-\rho} w_l = 0$$

$$\Rightarrow \quad w_l'' + 2\left(\frac{l}{\rho}-1\right) w_l'$$

$$+\left[\left(\frac{l}{\rho}-1\right)^2 - \frac{l}{\rho^2}\right] w_l$$

$$+\frac{2}{\rho}\left[\left(\frac{l}{\rho}-1\right) w_l + w_l'\right]$$

$$+\left\{-1+\frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right\} w_l = 0$$

$$\Rightarrow \quad w_l'' + \left(\frac{2l+2}{\rho}-2\right) w_l' + \frac{\beta-2-2l}{\rho} w_l$$

$$\boxed{\rho w_l'' + (2l+2-2\rho) w_l' + (\beta-2l-2) w_l = 0}$$

Metodo di Frobenius

Poniamo

$$w_\ell(\rho) = \sum_{k=0}^{\infty} a_k \cdot \rho^k$$

$$w_\ell' = \sum a_k \cdot k \cdot \rho^{k-1} = \sum (k+1) a_{k+1} \rho^k$$

$$\rho w_\ell' = \sum k a_k \rho^k$$

$$w_\ell'' = \sum_k k(k-1) a_k \rho^{k-2} = \sum_k (k+2)(k+1) a_{k+2} \rho^k$$

$$\rho w_\ell'' = \sum (k+1) k a_{k+1} \rho^k$$

$\Rightarrow \rho^k$: $(k+1) k a_{k+1} + (2\ell+2)(k+1) a_{k+1} - 2k a_k$

$+ (\beta - 2\ell - 2) a_k = 0$

$$\boxed{(2\ell+2+k)(k+1) a_{k+1} + (\beta - 2(\ell+k+1)) a_k = 0}$$

$a_0 \neq 0, \to a_1 \to a_2 \to \dots$

Se non termina $\quad \frac{a_{k+1}}{a_k} \overset{k\to\infty}{\sim} \frac{2}{k}$

$$\therefore a_{k+1} \sim \frac{2}{k} \frac{2}{k-1} \cdots \sim \frac{2^k}{k!}$$

$$\therefore w = \sum a_k \rho^k \sim \frac{2^k \rho^k}{k!} \sim e^{2\rho} \quad \therefore R \sim e^{+\rho} !$$

$\therefore$ La serie deve terminare. $\Rightarrow$

$\exists_k$ tale che

$$\beta - 2(\ell+k+1) = 0 \ ;$$

questo è possibile se e solo se

$$\beta = 2n \ , \ (n=1,2,3,\dots)$$

perché $\quad \ell = 0, 1, 2 \dots$

$\qquad\qquad k = 0, 1, 2, \dots$

Più precisamente, per soluzioni con ℓ $\left(\begin{matrix} \mathbb{L}^2 = \\ \ell(\ell+1) \end{matrix}\right)$

$$\beta = 2n, \qquad n \geq \ell + 1$$

$$\therefore \quad \beta = \sqrt{\frac{2}{\epsilon}} \quad \therefore \quad \frac{2}{\epsilon} = (2n)^2 = 4n^2$$

$$\epsilon = \frac{1}{2n^2} \Rightarrow E = -\frac{1}{2n^2}$$

$$\Rightarrow E = -\frac{e^2}{2n^2 r_B} \quad ! \ (\text{Bohr})$$

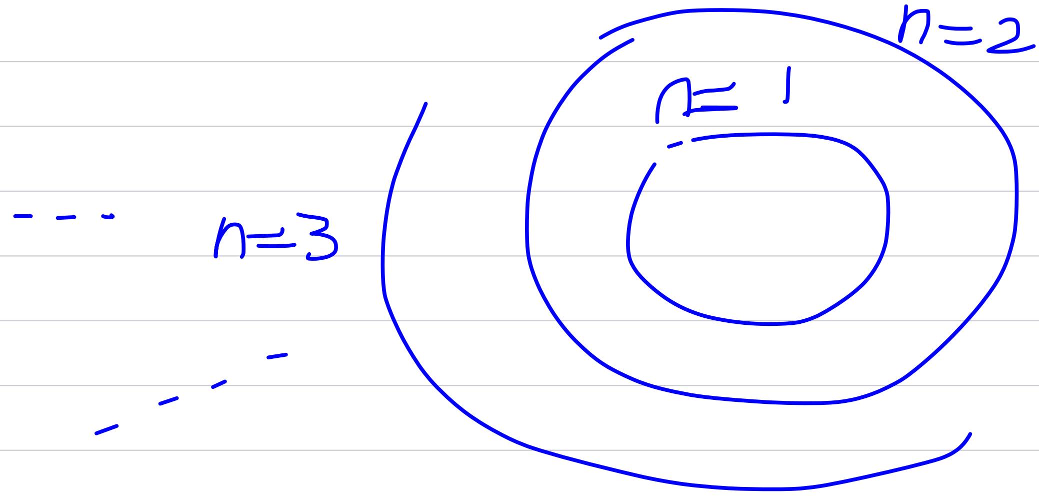
$$n = 1, 2, 3, \dots$$

Per il livello n, $\quad \ell = 0, 1, 2, \dots, n-1$!

$$R_\ell(r) = \rho^\ell e^{-\rho} w_\ell(\rho) \rightarrow \text{polinomio}$$

$$\rho = \sqrt{2\epsilon}\, r = \sqrt{\frac{2}{2n^2}}\, r = \frac{r}{n} = \frac{r}{n\, r_B}$$

$$\therefore\ R_{n,\ell}(r) \sim e^{-r/n r_B}$$



Un atomo di idrogeno di raggio ~ 1m?

$$r_B \sim 0.5\,\mathring{A} = 0.5\cdot 10^{-8}\,cm \sim 0.5\cdot 10^{-10}\,m$$

$$n\, r_B \sim 1\,m \Rightarrow n \sim 10^{10}\ !$$

In generale, un atomo con $n \gg 1$

~ atomi di Rydberg

Degenerazione

$n: \quad l = 0, 1, 2 \dots, n-1$

$$\# = \sum_0^{n-1} (2l+1) = (n-1)n + n$$
$$= n^2 \quad !$$

Lo stato fondamentale di H.

$\left.\begin{array}{l} n=1 \\ l=0 \end{array}\right\}$ $R_{10}(r) = 2e^{-r} = 2 r_B^{-3/2} e^{-r/r_B}$

$$\int_0^\infty dr\, r^2 (R_{10})^2 = 4\int dr\, r^2 e^{-2r} = \frac{4}{8}\Gamma(3)$$
$$= 1 \quad \text{OK}.$$

$$\psi_{100}(r) = R_{10}(r) Y_{00}(\theta,\varphi) = \frac{2}{\sqrt{4\pi}} e^{-r} = \frac{1}{\sqrt{\pi}} e^{-r}$$

Stati eccitati $\quad n = 2.$ $\begin{cases} l=0 \\ l=1 \end{cases}$

$n = l + k + 1$

$\Rightarrow l = 0, \ k = 1.$ Eq. $k=0 \quad 2a_1 + 2a_0 = 0$

$k=1 \quad a_2 = 0 \quad \therefore a_1 = -a_0$

$$R_{2,0} = a_0(1-\rho)e^{-\rho} = a_0\left(1-\frac{r}{2}\right)e^{-r/2}. \quad \rho =$$
$$= a_0\left(1-\frac{r}{r_B}\right) e^{-r/2r_B} \quad \times \ Y_{00} = \frac{1}{\sqrt{4\pi}}.$$

Sol. con $\ell = 1$, $k = 0$.

$k = 0 \quad a_2 = 0$.

$$R_{2,1}(r) = \rho e^{-\rho} = \frac{r}{2} e^{-r/2} = \frac{r}{2r_B} e^{-r/2r_B}$$

$$\psi_{2,\ell,m} = R_{2,1}(r) \cdot Y_{1,m}(\theta,\varphi) \quad \left(m = \pm 1, 0 \right)$$

La funzione d'onda $R_{n,\ell}(r)$

$$R_{n,\ell} = \rho^{\ell} e^{-\rho} W_{\ell}(\rho) \qquad \rho \equiv \frac{r}{n r_B} \quad - \quad \beta = 2n$$

$$\boxed{\rho W_{\ell}'' + (2\ell+2-2\rho) W_{\ell}' + (2n-2\ell-2) W_{\ell} = 0} \quad (*)$$

Sol. polinomiale:

$$W_{n,\ell}(\rho) = L_{n+\ell}^{2\ell+1}(2\rho) \qquad \text{Polinomi associati di Laguerre}$$

Polinomi di Laguerre sono generati da:

$$U(x,s) = \frac{e^{-xs/1-s}}{1-s} = \sum_{k=0}^{\infty} \frac{L_k(x)}{k!} s^k$$

$$\frac{\partial}{\partial x}, \frac{\partial}{\partial s} \Rightarrow x L_k'' + (1-x) L_k' + k L_k = 0 \quad (**)$$

$$L_k^p \equiv \frac{d^p}{dx^p} L_k(x) \quad \text{soddisfa:}$$

$$\Rightarrow x L_k^{p\,\prime\prime} + (p+1-x) L_k^{p\,\prime} + (k-p) L_k^p = 0 \quad (***)$$

$$(*) \Longleftrightarrow (***) \quad ?$$

$$2\rho = z, \quad \rho = \frac{z}{2}, \quad \frac{d}{d\rho} = 2\frac{d}{dz}, \quad \Rightarrow$$

$$z w_\ell'' + (2\ell+2-z) w_\ell' + (n-1-\ell) w_\ell = 0$$

$(\cancel{xxxx})$

Ora $(\cancel{x}) \equiv (\cancel{xxxx})$, ponendo

$$\left.\begin{aligned} p+1 &= 2\ell+2 \\ k-p &= n-\ell-1 \end{aligned}\right\} \Rightarrow \begin{aligned} p &= 2\ell+1 \\ k &= \ell+n \end{aligned}$$

$$\therefore\ w_\ell(r) = L^{2\ell+1}_{n+\ell}(z) = L^{2\ell+1}_{n+\ell}(2\rho), \qquad \rho = \frac{r}{n r_B}$$

L^p_k generati da:

$$U_p(\rho, s) = (-)^p \frac{s^p}{(1-s)^{p+1}} e^{-\rho s/1-s} = \sum_k \frac{L^p_k(\rho)\, s^k}{k!}$$

$$\therefore\ R_{n,\ell}(r) = C_{n,\ell} (2\rho)^\ell e^{-\rho} L^{2\ell+1}_{n+\ell}(2\rho)$$

$$= C_{n,\ell} \left(\frac{2r}{n r_B}\right)^\ell e^{-r/n r_B} L^{2\ell+1}_{n+\ell}\left(2r/n r_B\right)$$

$$C_{n,\ell} = -\frac{2}{n^2} r_B^{-3/2} \sqrt{\frac{(n-\ell-1)!}{\{(n+\ell)!\}^3}}$$

$r_B = 1$

$$R_{1,0}(r) = 2r e^{-r}$$

$$R_{2,0} = \frac{1}{2\sqrt{2}}(2-r) e^{-r/2} = \frac{r_B^{-3/2}}{2\sqrt{2}}\left(2 - \frac{r}{r_B}\right) e^{-r/2r_B},$$

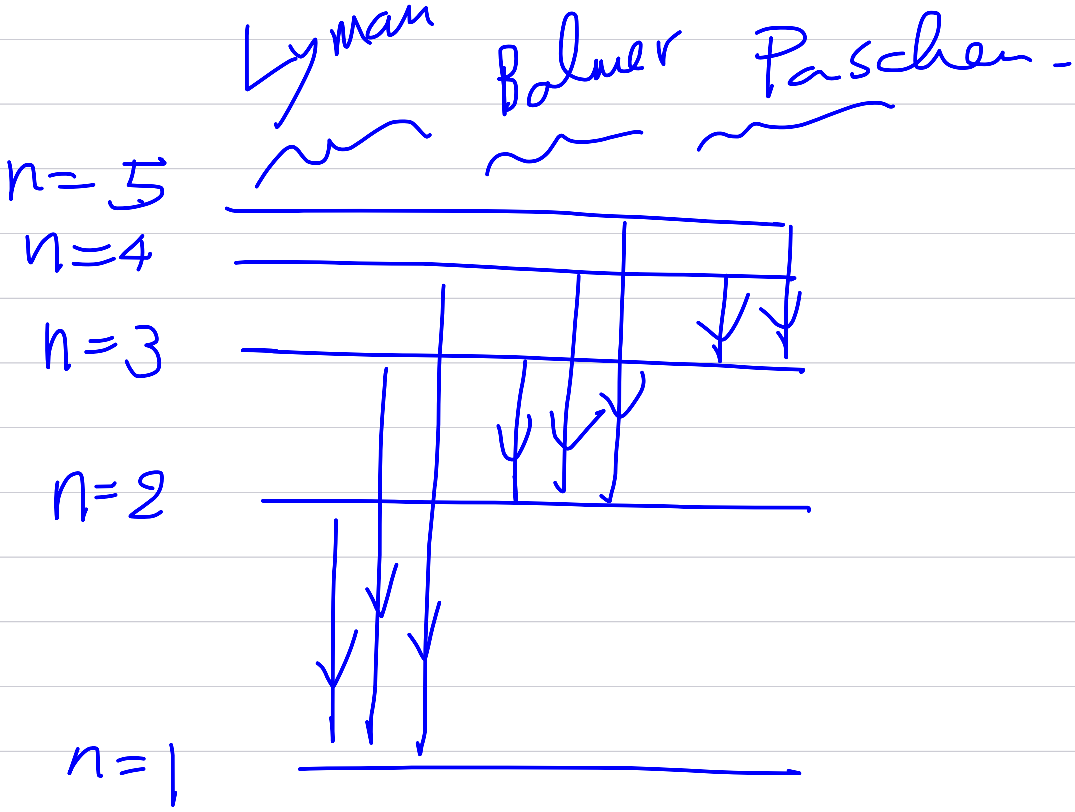
$$R_{2,1} = \frac{1}{2\sqrt{6}}\, r e^{-r/2} = \frac{r_B^{-3/2}}{2\sqrt{6}} \frac{r}{r_B} \cdot e^{-r/2r_B},$$

Le serie spettrali $\Leftrightarrow$ transizioni $n_1 \to n_2$

Lyman: $n_2 = 1$, $n_1 = 2, 3, 4 \dots$

Balmer: $n_2 = 2$, $n_1 = 3, 4, 5, \dots$

Paschen: $n_3 = 3$, $n_1 = 4, 5, \dots$



$$E_{n_1} - E_{n_2} = -\frac{e^2}{2r_B}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= h\nu = hc/\lambda$$

$$\lambda = hc \cdot \frac{r_B}{e^2} \sim \left(\frac{hc}{e^2}\right) r_B \sim \frac{r_B}{1/137}$$

$\gg r_B$

$$\frac{e^2}{\hbar c} \equiv \alpha \simeq \frac{1}{137} \quad \text{(costante di struttura fine)}$$

$$\langle p^2 \rangle_{100} = 2m \left\langle \frac{p^2}{2m} \right\rangle = 2m \left\langle H + \frac{e^2}{r} \right\rangle$$

$$= 2m \left(E_{100} + \left\langle \frac{e^2}{r} \right\rangle_{100} \right)$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{r_B} .$$

$$2m \left(-\frac{e^2}{2r_B} + \frac{e^2}{r_B} \right) = \frac{me^2}{r_B} = \frac{m^2 e^4}{\hbar^2}$$

$$\simeq m^2 v^2$$

$$\therefore \quad v \sim \frac{e^2}{\hbar} = c \cdot \frac{e^2}{\hbar c}$$

$$\sim O\left(\frac{1}{100}\right) \cdot c . \qquad !$$

$v \ll c$ (l'appr. non relativistico OK. ma non troppo ...)