Átomo de hidrogênio (sem spin)

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]}\psi(r,\theta,\varphi) = E\,\psi(r,\theta,\varphi)$$

$$H = -\frac{\hbar^2}{2m}\nabla_r^2 + \frac{L^2}{2mr^2} - \frac{e^2}{r} \implies \begin{cases} [H, L^2] = 0 \\ [H, L_z] = [L^2, L_z] = 0 \end{cases}$$

- Estados estacionários caracterizados por 3 n.ºs quânticos (n,ℓ,m)

$$\begin{cases} n = 1, \dots \\ \ell = 0, 1, \dots \\ m = 0, \pm 1, \dots \pm \ell \end{cases}$$

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\,Y_\ell^m(\theta,\varphi) = \frac{u_{n\ell}(r)}{r}\,P_\ell^m(\theta)\,\frac{e^{im\varphi}}{\sqrt{2\pi}}$$

$$\begin{cases} \langle E\rangle_{n,\ell,m} = -\dfrac{13{,}6}{n^2}\,(\text{eV}) & R_y = \dfrac{e^2}{2a_B} = 13{,}6\,\text{eV} \qquad a_B = \dfrac{\hbar^2}{\cancel{2}me^2} = 0{,}529\,\text{Å} \\ \langle L^2\rangle_{n,\ell,m} = \ell(\ell+1)\hbar^2 & \langle L_z\rangle_{n,\ell,m} = m\hbar \end{cases}$$

- normalização :

$$\int_0^{2\pi}\!\!\int_0^{\pi}\!\!\int_0^{\infty}\psi^*(r,\theta,\varphi)\,\psi(r,\theta,\varphi)\,r^2 dr\,\operatorname{sen}\theta\, d\theta\, d\varphi = \overbrace{\int_0^{\infty}|R_{n\ell}(r)|^2 r^2 dr}^{1}\;\overbrace{\int_\pi^0 |P_\ell^m(\cos\theta)|^2\, d(\cos\theta)}^{1}\;\overbrace{\int_0^{2\pi}\frac{d\varphi}{2\pi}}^{1}$$

$$\int_0^{\infty}|R_{n\ell}(r)|^2 r^2 dr = \int_0^{\infty}|u_{n\ell}(r)|^2 dr = 1 \implies \boxed{|u_{n\ell}(r)|^2 = \rho(r)}$$

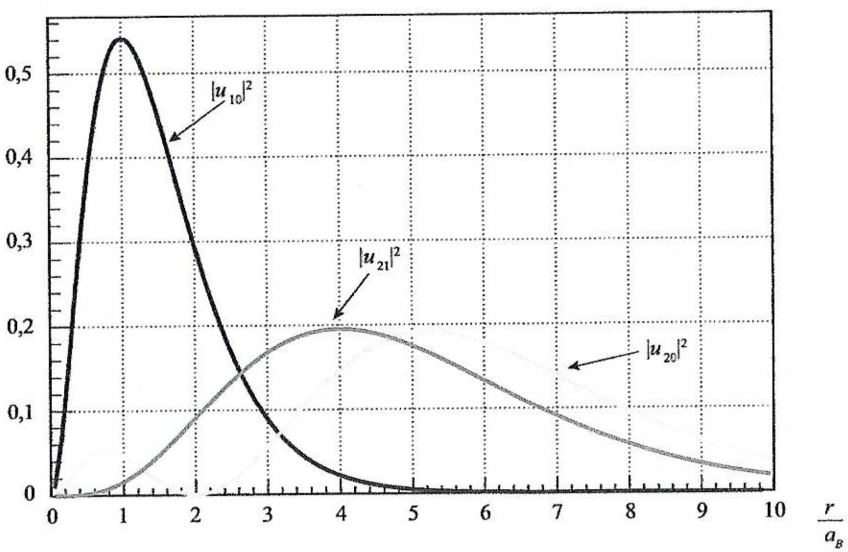
→ densidade de probabilidade de presença radial.

$$\boxed{u_{n\ell}(r) = r\,R_{n\ell}(r)}$$

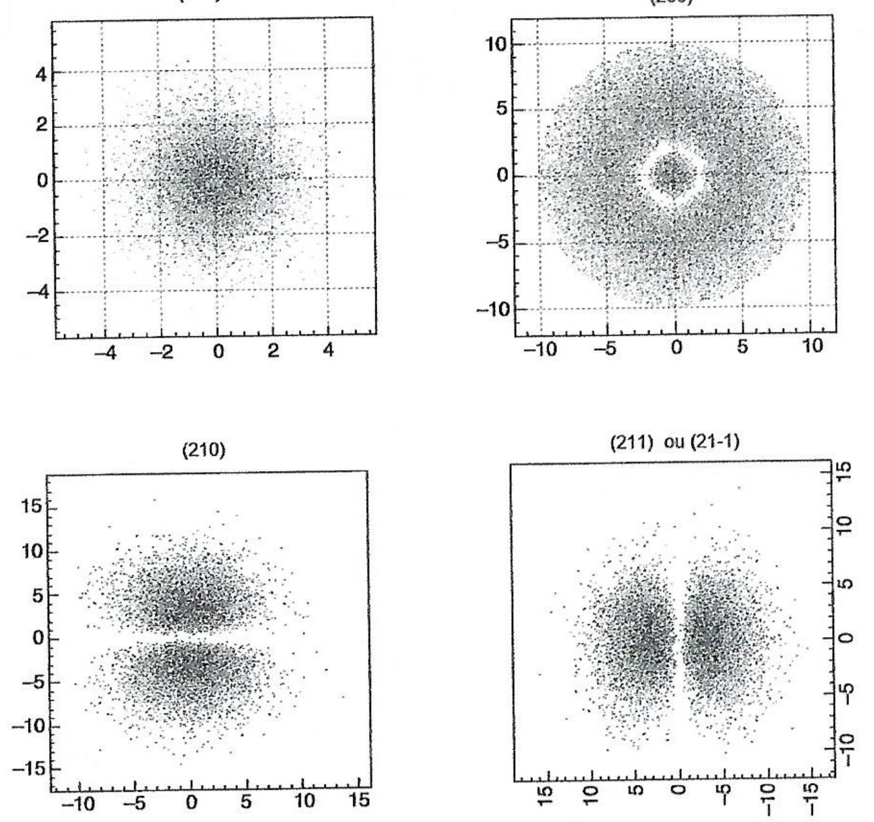
Os primeiros estados estacionários

notação espectroscópica	$(n\ l\ m)$	$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\, P_l^m(\theta)\, e^{im\varphi}$	$\lvert u_{nl}(r)\rvert^2\, \lvert P_l^m(\theta)\rvert^2$	$E_n = \frac{-13{,}6}{n^2}$ (eV)
1s	100	e^{-r/a_B}	$r^2\, e^{-2r/a_B}$	$-13{,}6$
2s	200	$\left(1 - \frac{r}{2a_B}\right) e^{-r/2a_B}$	$r^2\left(1 - r/2a_B\right)^2 e^{-\frac{r}{a_B}}$	
2p	210	$r\, e^{-r/2a_B} \cos\theta$	$r^4\, e^{-r/a_B} \cos^2\theta$	$-3{,}4$
	21 ± 1	$r\, e^{-r/2a_B} \operatorname{sen}\theta\, e^{\pm i\varphi}$	$r^4\, e^{-r/a_B} \operatorname{sen}^2\theta$	

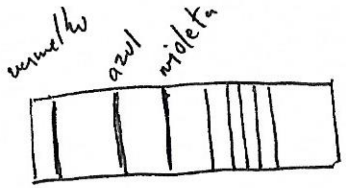
distribuições de probab. de presença radial



diagramas polares das distrib. de probabilidades



Espectro do hidrogénio



$$\lambda = 3645{,}6 \, \frac{n^2}{n-4} \, (\text{Å})$$ → Balmer (1885)

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$ → Rydberg (1888) $\boxed{R_H \sim 10^5 \, \text{cm}^{-1}}$

cte de Rydberg

$$c = \lambda \nu \implies \nu_{mn} = (c R_H) \left| \frac{1}{m^2} - \frac{1}{n^2} \right|$$ → q.q. linha (freq.) é dada pela diferença entre 2 termos espectrais (Ritz)

Bohr (1913) → $$E_n = -\frac{e^2}{2a_B} \frac{1}{n^2}$$ (espectro de energia do hidrogénio)

$$\Downarrow$$

$$\nu_{nm} = \frac{|E_n - E_m|}{h} = \underbrace{\frac{e^2}{2a_B h}}_{cR_H} \left| \frac{1}{n^2} - \frac{1}{m^2} \right|$$

frequências emitidas ou absorvidas

$$\implies R_H = \frac{e^2}{4\pi a_B c \hbar} = \frac{(4{,}8)^2 \times 10^{-20}}{4\pi \times 0{,}5 \times 10^{-8} \times 3 \times 10^{10} \times 10^{-27}} \sim 10^5 \, \text{cm}^{-1}$$

Transições e regras de seleção

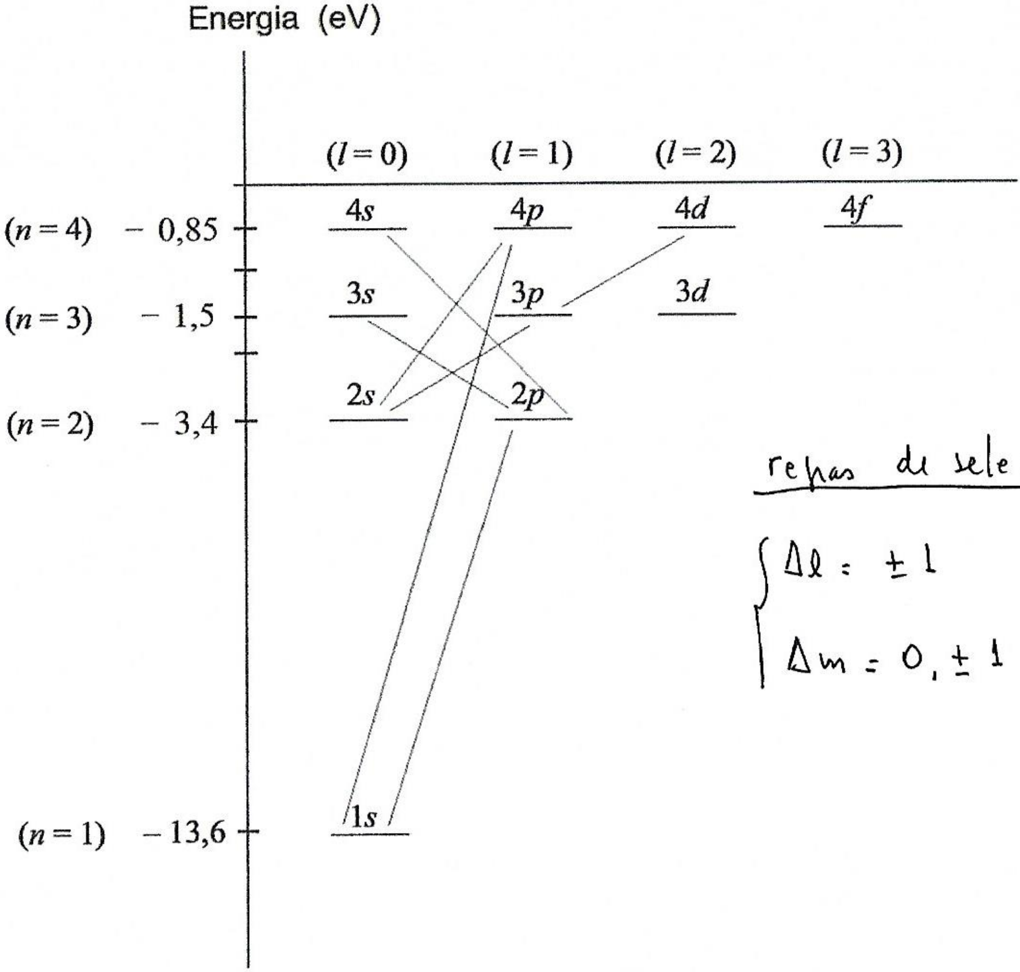
$\nu_{nl} \sim \left| \frac{1}{n^2} - \frac{1}{m^2} \right|$ → correspondem a transições entre os níveis de energia

↓

frequências emitidas ou absorvidas

$$\begin{cases} 4p \to 2s & 4s \to 2p \\ 4p \to 1s & 4d \to 3p \\ 3p \to 2s & \text{(permitidas)} \end{cases}$$

$$\begin{cases} 4d \to 2s & 4s \to 2s \\ 3d \to 1s & 3s \to 1s \\ 4p \to 3p & \text{(proibidas)} \end{cases}$$



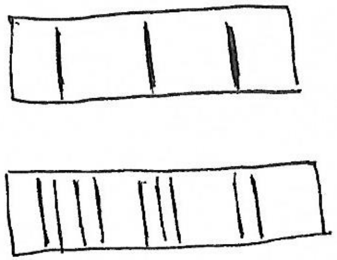
regras de seleção

$$\begin{cases} \Delta l = \pm 1 \\ \Delta m = 0, \pm 1 \end{cases}$$ (transições permitidas)

Efeito Zeeman – desdobramento das linhas espectrais em um campo magnético

s/campo

c/campo



$$\begin{cases} \text{normal} \rightarrow 2 \text{ ou } 3 \text{ linhas (momentum angular orbital} \\ \text{anômalo} - > 3 \text{ linhas (orbital + ?)} \end{cases}$$

interação momento dipolar c/ campo magnético

$$\boxed{\begin{aligned} V &= -\vec{\mu}_\ell \cdot \vec{B} \\ &= \gamma_\ell \, \vec{L} \cdot \vec{B} \end{aligned}}$$

$[\mu_\ell] = J/T$ (joule/tesla)

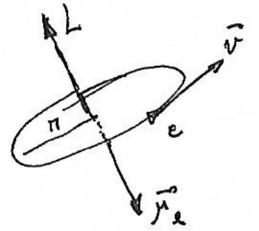
(energia potencial da interação)

(quântico)

$$\vec{B} = B_z \hat{k} \Rightarrow \begin{cases} \mu_z = \gamma_\ell L_z \\ L_z = m_\ell \hbar \text{ (autovalor de } L_z) \end{cases} \Longrightarrow \mu_z = m_\ell \underbrace{(\hbar \gamma_\ell)}_{\mu_B \text{ (magneton de Bohr)}}$$

$$\boxed{\mu_B = \frac{e\hbar}{2m}} \sim 10^{-23} \, J/T$$

momento dipolar orbital $(\vec{\mu}_\ell)$



$$\begin{cases} L = mvr \\ \mu_\ell = iA \end{cases}$$

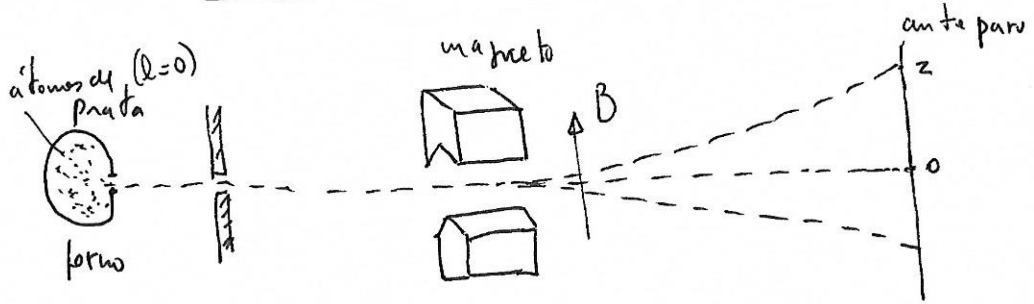
$$i = \frac{e}{T} = \frac{e}{2\pi}\omega = \frac{ev}{2\pi r} \Rightarrow iA = \frac{evr}{2}$$

$$\boxed{\vec{\mu}_\ell = -\underbrace{\left(\frac{e}{2m}\right)}_{\gamma_\ell} \vec{L}}$$

$\gamma_\ell \sim 10^{11} \, T^{-1} s^{-1}$

razão giromagnética

Experimento de Stern-Gerlach (1921)



$$V = -\mu_z B$$

$$F_z = -\frac{\partial V}{\partial z} = \mu_z \frac{\partial B}{\partial z}$$

resultados esperados:
- q.q. valor de z (contínuo) - clássico
- $(2l+1)$ traços $(\mu_z = m_l \mu_B)$ - quântico

resultado do experimento:
- 2 traços
- μ_z: μ_B, $-\mu_B$

p/ $l = 0 \Rightarrow$ 1 traço (esperado)

Spin (1925) - Uhlenbeck - Goudsmit

$$\mu_{lz} = \gamma L_z = \gamma m_l \hbar = m_l \mu_B$$

μ_B, 0, $-\mu_B$ $(l=1)$

$2\mu_B$, μ_B, 0, $-\mu_B$, $-2\mu_B$ $(l=2)$

$$\mu_{sz} = 2\gamma S_z = 2\gamma m_s \hbar = 2 m_s \mu_B$$

μ_B, $-\mu_B$ $\quad s = 1/2 \quad m_{s_z}$: $1/2$, $-1/2$

spin do elétron

$$\Rightarrow \boxed{\vec{\mu}_s = -2\gamma \vec{S} = -\left(\frac{e}{m}\right)\vec{S}}$$

Propriedades algébricas do momentum angular

momentum angular orbital

$$L^2 \underbrace{Y_\ell^{m_\ell}}_{|\ell, m_\ell\rangle} = \ell(\ell+1)\hbar^2 \underbrace{Y_\ell^{m_\ell}}_{|\ell, m_\ell\rangle} \qquad \ell = 0, 1, 2, \ldots$$

$|\ell, m_\ell\rangle$ → autoestados de L^2 e L_z

$$[L_x, L_y] = i\hbar L_z \quad \text{(cíclica)}$$

$$L_z |\ell, m_\ell\rangle = m_\ell \hbar |\ell, m_\ell\rangle \qquad m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell \quad (2\ell+1)$$

momentum angular intrínseco do elétron (spin)

redundante

autoestado de S^2 e S_z

$$S^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle = \frac{3}{4}\hbar^2 |s, m_s\rangle \qquad s = 1/2$$

$$[S_x, S_y] = i\hbar S_z \quad \text{(cíclica)}$$

$$S_z |s, m_s\rangle = m_s \hbar |s, m_s\rangle \begin{cases} \frac{\hbar}{2} |s, \cancel{1/2}\rangle \\ -\frac{\hbar}{2} |s, \cancel{-1/2}\rangle \end{cases} \qquad m_s = 1/2, -1/2$$

notações usuais p/ autoestados do spin

$$\begin{cases} |1/2, 1/2\rangle = |+\rangle = |up\rangle = |\uparrow\rangle = |+1/2\rangle = \chi_+ \\ |1/2, -1/2\rangle = |-\rangle = |down\rangle = |\downarrow\rangle = |-1/2\rangle = \chi_- \end{cases}$$

$$\begin{cases} S^2 |\pm\rangle = \frac{3}{4}\hbar^2 |\pm\rangle \\ S_z |\pm\rangle = \pm\frac{\hbar}{2} |\pm\rangle \end{cases}$$

Matrizes de Pauli (1927)

$$S_x = \frac{\hbar}{2} \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\sigma_x} \qquad S_y = \frac{\hbar}{2} \underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\sigma_y} \qquad S_z = \frac{\hbar}{2} \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\sigma_z}$$

$$[\sigma_x, \sigma_y] = 2i\sigma_z \qquad\qquad \vec{\sigma} = \sigma_x \hat{i} + \sigma_y \hat{j} + \sigma_z \hat{k}$$

- determine os autovalores de σ_x, σ_y, σ_z e σ^2
- determine os autovetores de σ_x, σ_y, σ_z e σ^2