F 789 – Mecânica Quântica II

1º Semestre de 2023

15/03/2023

Aula 4

Aulas passadas

Potencial central $V(r)$: Quantidades conservadas - $[H,L^2]=[H,L_z]=0$.
$\{H, L^2, L_z\}$ podem ser diagonalizadas simultaneamente e formam um C.C.O.C:

$$H\varphi_{k,l,m}(\mathbf{r}) = E_{k,l}\varphi_{k,l,m}(\mathbf{r})$$
$$L^2\varphi_{k,l,m}(\mathbf{r}) = l(l+1)\hbar^2\varphi_{k,l,m}(\mathbf{r})$$
$$L_z\varphi_{k,l,m}(\mathbf{r}) = m\hbar\varphi_{k,l,m}(\mathbf{r})$$

- As auto-funções simultâneas de $\{H, L^2, L_z\}$ são do tipo:

$$\varphi_{k,l,m}(\mathbf{r}) = R_{k,l}(r)\,Y_{l,m}(\theta,\phi) = \frac{1}{r}u_{k,l}(r)\,Y_{l,m}(\theta,\phi)$$

- $Y_{l,m}(\theta,\phi)$ são os harmônicos esféricos.
- Funções radiais:

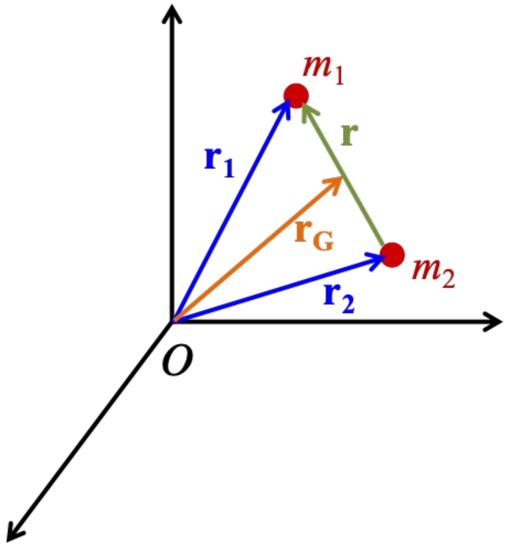
$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right]R_{k,l}(r) = E_{k,l}R_{k,l}(r)$$
$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \underbrace{\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)}_{V_{eff}(r)}\right]u_{k,l}(r) = E_{k,l}u_{k,l}(r)$$

- Comportamento na origem: $R_{k,l}(r) \to r^l,\ u_{k,l}(r) \to r^{(l+1)}$ quando $r \to 0$

Aula passada

Problema de dois corpos clássico. Pode ser separado em dois problemas desacoplados

- O movimento do centro de massa → partícula livre
- O movimento relativo → partícula de massa μ (massa efetiva) num potencial central.



$$\mathbf{r}_G = \frac{m_1}{M}\mathbf{r}_1 + \frac{m_2}{M}\mathbf{r}_2, \ (M = m_1 + m_2)$$
$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2,$$
$$\mathbf{p}_G = \mathbf{p}_1 + \mathbf{p}_2,$$
$$\mathbf{p} = \mu\dot{\mathbf{r}} = \frac{m_2}{M}\mathbf{p}_1 - \frac{m_2}{M}\mathbf{p}_2. \ \left(\mu = \frac{m_1 m_2}{M}\right)$$

Dinâmica Hamiltoniana: $H = H_G + H_r$

$$H_G = \frac{\mathbf{p}_G^2}{2M},$$
$$H_r = \frac{\mathbf{p}^2}{2\mu} + V(r).$$

Aula passada

Dinânica quântica: os operadores do setor do centro de massa comutam com os operadores do setor do movimento relativo.

A função de onda total é um produto de um função de onda do centro de massa, $\chi(\mathbf{r}_G)$ (de partícula livre), por uma função de onda do movimento relativo, $\varphi_r(\mathbf{r})$, que descreve uma partícula de massa μ num potencial central.

$$[H_G, H_r] = 0$$

$$H\psi(\mathbf{r}_G,\mathbf{r}) = (H_G + H_r)\,\psi(\mathbf{r}_G,\mathbf{r}) = E\psi(\mathbf{r}_G,\mathbf{r})$$

$$\boxed{\Rightarrow \psi(\mathbf{r}_G,\mathbf{r}) = \chi(\mathbf{r}_G)\,\varphi_r(\mathbf{r})}$$

$$H_G\chi(\mathbf{r}_G) = -\frac{\hbar^2}{2M}\nabla_G^2\chi(\mathbf{r}_G) = E_G\chi(\mathbf{r}_G) \Rightarrow \chi_{\mathbf{p}_G}(\mathbf{r}_G) = \frac{e^{i\mathbf{p}_G\cdot\mathbf{r}_G/\hbar}}{(2\pi\hbar)^{3/2}},\;\; E_G = \frac{\mathbf{p}_G^2}{2M},$$

$$H_r\varphi_r(\mathbf{r}) = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]\varphi_r(\mathbf{r}) = E_r\varphi_r(\mathbf{r})$$

$$\boxed{E = (E_G + E_r)}$$

Aula passada

Átomo de hidrogênio: um próton e um elétron com atração coulombiana

$$m_e = 9.1 \times 10^{-31} \text{ kg}$$
$$m_p = 1.7 \times 10^{-27} \text{ kg} \approx 1800\ m_e$$
$$q_p = -q_e \equiv q = 1.6 \times 10^{-19} \text{ C}$$
$$\mu \approx m_e$$

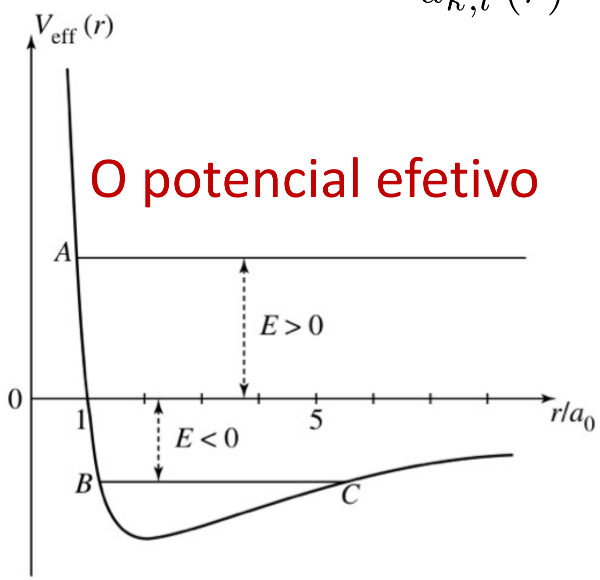
$$V(r) = -\frac{q^2}{4\pi\epsilon_0}\frac{1}{r} \equiv -\frac{e^2}{r}$$

$$\boxed{\text{Núcleo de carga } Zq \rightarrow \quad V(r) = -\frac{Ze^2}{r}}$$

$e^2 \rightarrow Ze^2$

Equação radial: $$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right] u_{k,l}(r) = E_{k,l} u_{k,l}(r)$$

$$u_{k,l}(r) \rightarrow r^{(l+1)} \text{ quando } r \rightarrow 0$$



$E>0$: função de quadrado não integrável, espectro contínuo.
$E<0$: função de quadrado integrável, espectro discreto.

Aula passada

Escalas de comprimento e energia do problema:

$$a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.52\ \text{Å} \ \ (\text{raio de Bohr})$$

$$E_I = \frac{\mu e^4}{2\hbar^2} \approx 13.6\ \text{eV}$$

Núcleo de carga Zq →

$$a_0 = \frac{\hbar^2}{Z\mu e^2} \approx \frac{0.52}{Z}\ \text{Å}$$

$$E_I = \frac{\mu Z^2 e^4}{2\hbar^2} \approx 13.6 Z^2\ \text{eV}$$

Definindo quantidades adimensionais ($E_{k,l}<0$): $\lambda_{k,l} = \sqrt{\frac{|E_{k,l}|}{E_I}},$

$$\rho = \frac{r}{a_0}.$$

Equação radial adimensional:

$$\boxed{\left[\frac{d^2}{d\rho^2} - \frac{l\,(l+1)}{\rho^2} + \frac{2}{\rho} - \lambda_{k,l}^2\right] \bar{u}_{k,l}(\rho) = 0}$$

$$\bar{u}_{k,l}(\rho) \sim \rho^{(l+1)} \ \ (\rho \to 0)$$

$u_{k,l}(r) = \bar{u}_{k,l}\left(\frac{r}{a_0}\right)$

Análise assintótica

$\rho \to \infty$:

$$\left[\frac{d^2}{d\rho^2} - \lambda_{k,l}^2\right] u_{k,l}(\rho) = 0$$

$$\Rightarrow \quad u_{k,l}(\rho) = C_\pm e^{\pm \lambda_{k,l} \rho}$$

NORMALIZÁVEL : $\Longrightarrow \quad u_{k,l}(\rho) \propto e^{-\lambda_{k,l} \rho}$

Solução por série de potências

CHUTE: $u_{k,\ell}(\rho) = e^{-\lambda_{k,\ell}\rho}\, y_{k,\ell}(\rho)$

LEVO NA EQ. RADIAL:

$$\frac{du}{d\rho} = -\lambda e^{-\lambda\rho} y + e^{-\lambda\rho} y' = [-\lambda y + y'] e^{-\lambda\rho}$$

$$\frac{d^2u}{d\rho^2} = \lambda^2 e^{-\lambda\rho} y - \lambda e^{-\lambda\rho} y' - \lambda e^{-\lambda\rho} y' + e^{-\lambda\rho} y''$$

$$= [\lambda^2 y - 2\lambda y' + y''] e^{-\lambda\rho}$$

$$\left[(\cancel{\lambda^2 y} - 2\lambda y' + y'')\cancel{e^{-\lambda\rho}} - \frac{\ell(\ell+1)}{\rho^2}\cancel{e^{-\lambda\rho}} y + \frac{2}{\rho}\cancel{e^{-\lambda\rho}} y \cancel{- \lambda^2 y e^{-\lambda\rho}} \right] = 0$$

$$\left\{ \frac{d^2}{d\rho^2} - 2\lambda_{k,\ell}\frac{d}{d\rho} + \left[\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right] \right\} y_{k,\ell}(\rho) = 0$$

$$y_{k,\ell}(\rho \to 0) \sim \rho^{(\ell+1)}$$

$$y_{k,\ell}(\rho) = \sum_{q=0}^{\infty} c_q \, \rho^{(q+\ell+1)} \qquad (c_0 \neq 0)$$

$$= c_0 \, \rho^{(\ell+1)} + c_1 \, \rho^{(\ell+2)} + c_2 \cdots \xrightarrow[\rho \to 0]{} c_0 \, \rho^{(\ell+1)}$$

$$\frac{dy}{d\rho} = \sum_{q=0}^{\infty} c_q (q+\ell+1) \, \rho^{(q+\ell)}$$

$$\frac{d^2y}{d\rho^2} = \sum_{q=0}^{\infty} c_q (q+\ell+1)(q+\ell) \, \rho^{(q+\ell-1)}$$

$$\sum_{q=0}^{\infty} c_q \Big[(q+\ell+1)(q+\ell) \, \rho^{(q+\ell-1)} \underbrace{- 2\lambda_{k,\ell}(q+\ell+1)\rho^{(q+\ell)} + 2\rho^{(q+\ell)}}_{q \to q-1}$$

$$- \ell(\ell+1) \, \rho^{(q+\ell-1)} \Big] = 0$$

$$\sum_{q=0}^{\infty} c_q \left[(q+\ell+1)(q+\ell) - \ell(\ell+1) \right] \rho^{(q+\ell-1)}$$

$$\sum_{q=1}^{\infty} 2 \, c_{q-1} \left[1 - \lambda_{k,\ell}(q+\ell) \right] \rho^{(q+\ell-1)} = 0$$

$$c_0\left[\cancel{\ell(\ell+1)-\ell(\ell+1)}^{\,0}\right]\rho^{(\ell-1)}$$

$$+\sum_{q=1}^{\infty}\left\{c_q\left[(q+\ell+1)(q+\ell)-\ell(\ell+1)\right]+2c_{q-1}\left[1-\lambda_{k,\ell}(q+\ell)\right]\right\}\rho^{(q+\ell-1)}=0$$

PARA QUE TODOS OS COEFICIENTES SE ANULEM:

$$c_q\left[q^2+q(2\ell+1)\right]=2c_{q-1}\left[\lambda_{k,\ell}(q+\ell)-1\right]$$

DADO C_0, ACHA-SE C_1, DEPOIS C_2, ...

CONVERGÊNCIA DA SÉRIE INFINITA:

$$\lim_{q\to\infty}\left|\frac{c_q}{c_{q-1}}\right|=\frac{1}{R}$$

SE O LIMITE FOR FINITO

R = RAIO DE CONVERGÊNCIA

$$\frac{c_q}{c_{q-1}}=\frac{2\left[\lambda_{k,\ell}(q+\ell)-1\right]}{q^2+q(2\ell+1)}\xrightarrow[q\to\infty]{}\frac{2q\lambda_{k,\ell}}{q^2}=\frac{2\lambda_{k,\ell}}{q}\to 0$$

$R\to\infty \Rightarrow$ CONVERGE $\forall\ \rho$

QUAL É O COMPORTAMENTO ASSINTÓTICO ($\xi \to \infty$)?

SEJA A SÉRIE DA FUNÇÃO $e^{2\lambda_{k,\ell}\xi}$:

$$e^{2\lambda_{k,\ell}\xi} = \sum_{q=0} \frac{(2\lambda_{k,\ell})^q}{q!}\xi^q \equiv \sum_{q=0} d_q \xi^q$$

$$d_q = \frac{(2\lambda_{k,\ell})^q}{q!}$$

$$\Rightarrow \frac{d_q}{d_{q-1}} = \frac{(2\lambda_{k,\ell})^q}{q!}\,\frac{(q-1)!}{(2\lambda_{k,\ell})^{(q-1)}} = \frac{2\lambda_{k,\ell}}{q}$$

QUE É O MESMO COMPORTAMENTO ASSINTÓTICO DO NOSSO PROBLEMA DE INTERESSE. PODE-SE MOSTRAR QUE SEGUE QUE AS DUAS SÉRIES TÊM O MESMO COMPORTAMENTO ASSINTÓTICO.

$$\Rightarrow y_{k,\ell}(\xi) \propto e^{2\lambda_{k,\ell}\xi} \Rightarrow u_{k,\ell}(\xi) = e^{\lambda_{k,\ell}\xi} \xrightarrow[\xi \to \infty]{} \infty$$

NÃO É DE $\square$-INTEGRÁVEL

A ÚNICA MANEIRA DE EVITAR ESSA FUNÇÃO NÃO NORMALIZÁVEL É IMPOR QUE A SÉRIE SEJA FINITA:

$$C_q\left[q^2+q(2\ell+1)\right]=2\,C_{q-1}\left[\lambda_{k,\ell}(q+\ell)-1\right]$$

SE ESCOLHERMOS: $\boxed{\lambda_{k,\ell}=\dfrac{1}{k+\ell} \quad k\geq 1}$

O TERMO $C_k=0$ E A SÉRIE TERÁ APENAS $(k-1)$ TERMOS

$$C_k\left[k^2+k(2\ell+1)\right]=2\,C_{k-1}\left[\overbrace{\lambda_{k,\ell}(k+\ell)}^{1}-1\right]=0$$

PARA CADA $\underline{\ell}$, $k=1,2,3,\ldots$

$$\lambda_{k,\ell} = \sqrt{\frac{|E_{k,\ell}|}{E_I}} \Rightarrow E_{k,\ell} = -E_I \lambda_{k,\ell}^2 = -\frac{E_I}{(k+\ell)^2} \quad (k = 1, 2, 3, \ldots)$$

OS COEFICIENTES PODEM SER OBTIDOS EM TERMOS DE C_0. $y_{k,\ell}(\rho)$ SERÁ UM POLINÔMIO (POLINÔMIO DE LAGUERRE).

$$u_{k,\ell}(\rho) = e^{-\lambda_{k,\ell}(\rho)} \, y_{k,\ell}(\rho)$$

$u_{k,\ell}\left(\rho = \frac{r}{a_0}\right)$, C_0 É DETERMINADO POR NORMALIZAÇÃO

$$R_{k,\ell}(r) = \frac{u_{k,\ell}(r/a_0)}{r}$$

As primeiras funções radiais

$$R_{k=1,l=0}(r) = 2(a_0)^{-3/2}\,\mathrm{e}^{-r/a_0}$$

$$R_{k=2,l=0}(r) = 2(2a_0)^{-3/2}\left(1 - \frac{r}{2a_0}\right)\mathrm{e}^{-r/2a_0}$$

$$R_{k=1,l=1}(r) = (2a_0)^{-3/2}\,\frac{1}{\sqrt{3}}\,\frac{r}{a_0}\,\mathrm{e}^{-r/2a_0}$$

Já normalizadas: $\int_0^{\infty} \left|R_{k,l}\,(r)\right|^2 r^2 dr = 1$

As primeiras auto-funções

Núcleo de carga Zq

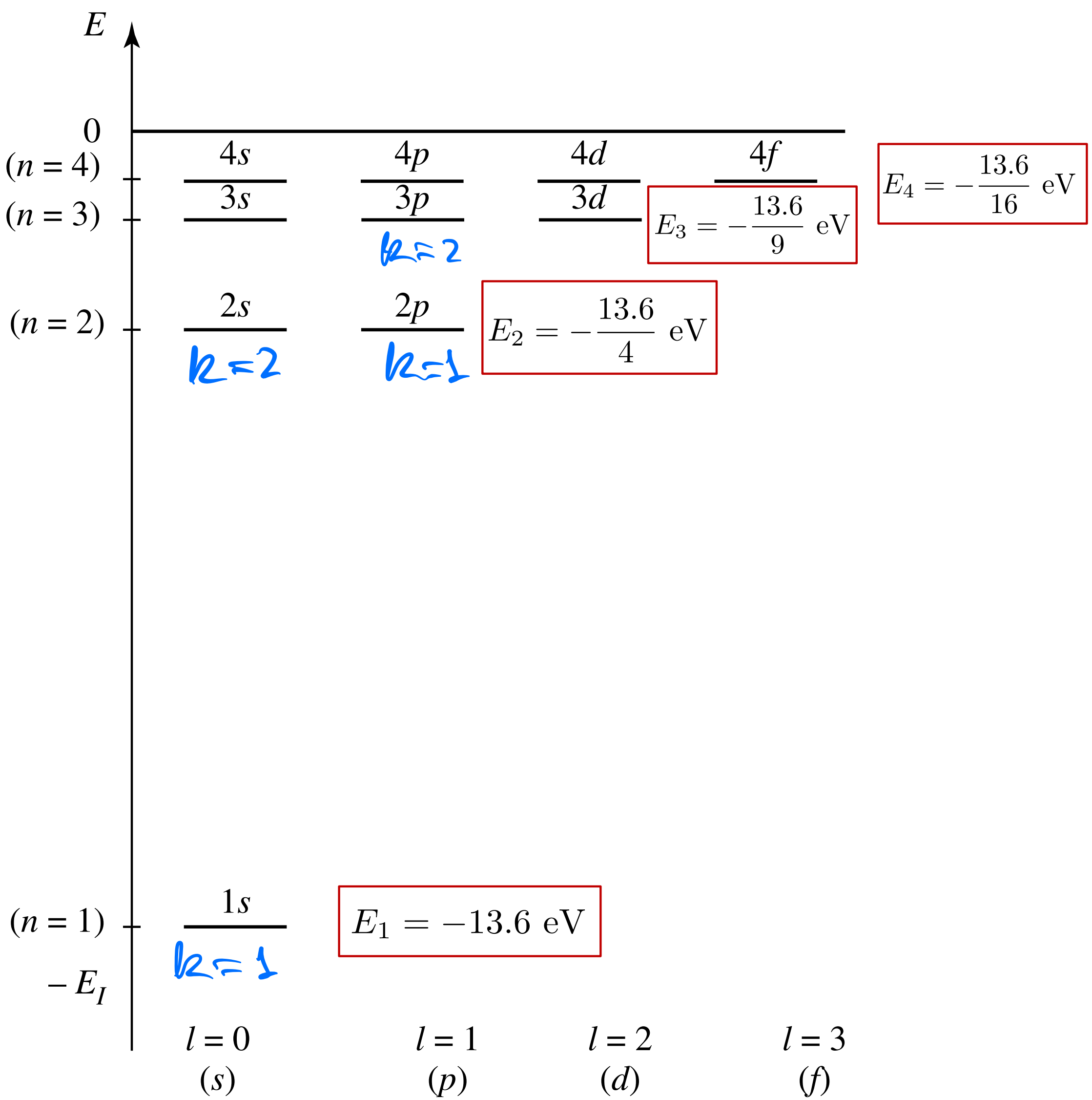
$\boxed{n=k+l}$

$E_{k,l} \equiv E_{n,l} = -\frac{E_I}{n^2}$

$k = n - l$

Quantum Numbers n	l	m_l	Eigenfunctions	
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	$k=1$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	$k=2$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$	$k=1$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta \, e^{\pm i\varphi}$	$k=1$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$	
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta$	
3	1	± 1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \sin\theta \, e^{\pm i\varphi}$	
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} (3\cos^2\theta - 1)$	
3	2	± 1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin\theta \cos\theta \, e^{\pm i\varphi}$	
3	2	± 2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2\theta \, e^{\pm 2i\varphi}$	

Níveis de energia



Notação espectroscópica:

l=0 (s)
l=1 (p)
l=2 (d)
l=3 (f)
l=4 (g)
l=5 (h)
l=6 (i)
l=7 (j)
⋮

n (ℓ)

Degenerescências

As auto-energias só dependem de $k+l=n$.

$k = 1, 2, 3, \ldots$

$l = 0, 1, 2, 3, \ldots$

Valores possíveis de l para um n fixo:

$$l = n - k = \underbrace{\{n-1,\ n-2,\ \ldots\ \underbrace{n=0}_{k=n}\}}_{n \text{ VALORES POSSÍVEIS DE } l}$$

$l = 0, 1, 2, \ldots, (n-1)$

$n = 1, 2, 3, 4, \ldots$

ALÉM DISSO, PARA (n, l) FIXOS,

$m = -l, -l+1, \ldots, l-1, l \rightarrow (2l+1)$ VALORES POSSÍVEIS DE m

(n, ℓ, m) : $n = 1, 2, 3, \ldots$ Nº QUÂNTICO PRINCIPAL

$\ell = 0, 1, \ldots, n-1$ Nº " AZIMUTAL

$m = -\ell, \ldots, \ell$ " " MAGNÉTICO

PARA O NÍVEL $\underline{n}$:

$$g_n = \sum_{\ell=0}^{(n-1)} (2\ell+1) = n^2$$

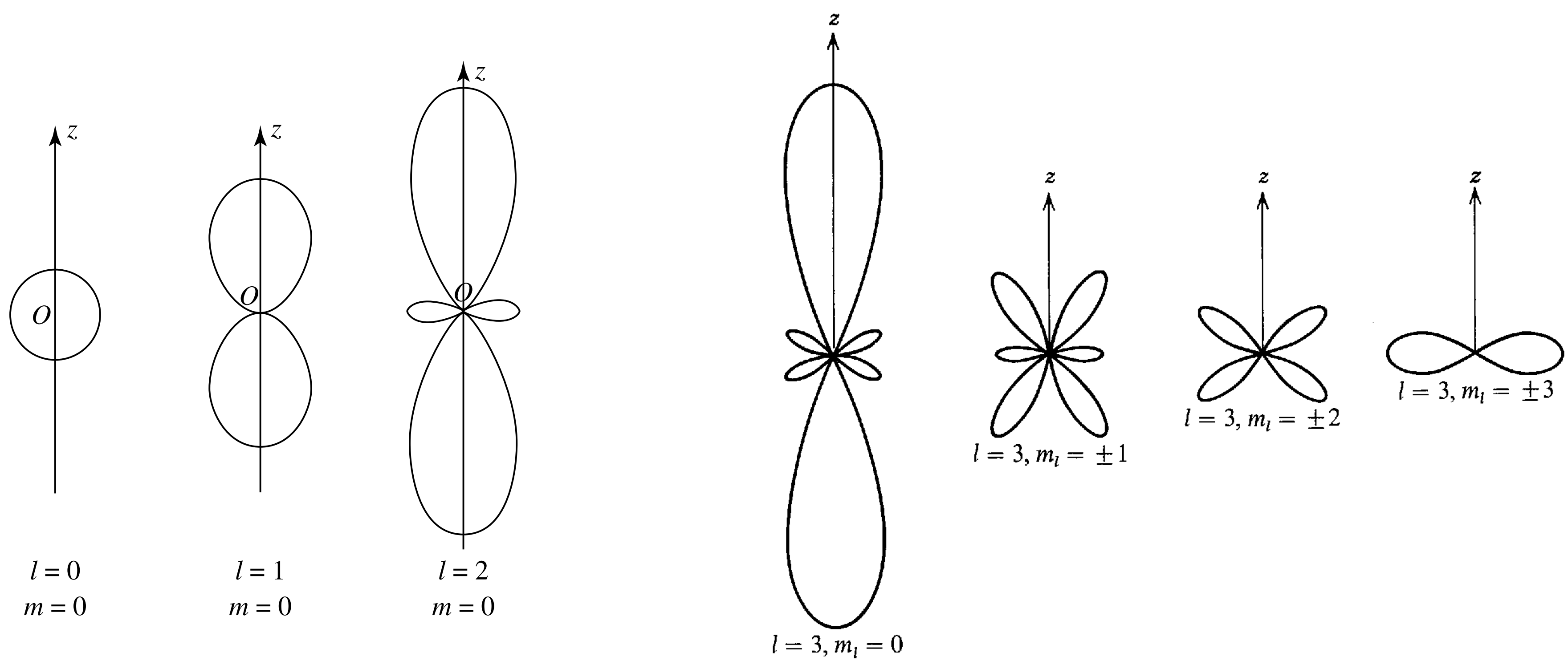
+ O SPIN DO ELÉTRON $\longrightarrow g_n = 2n^2$

As auto-funções

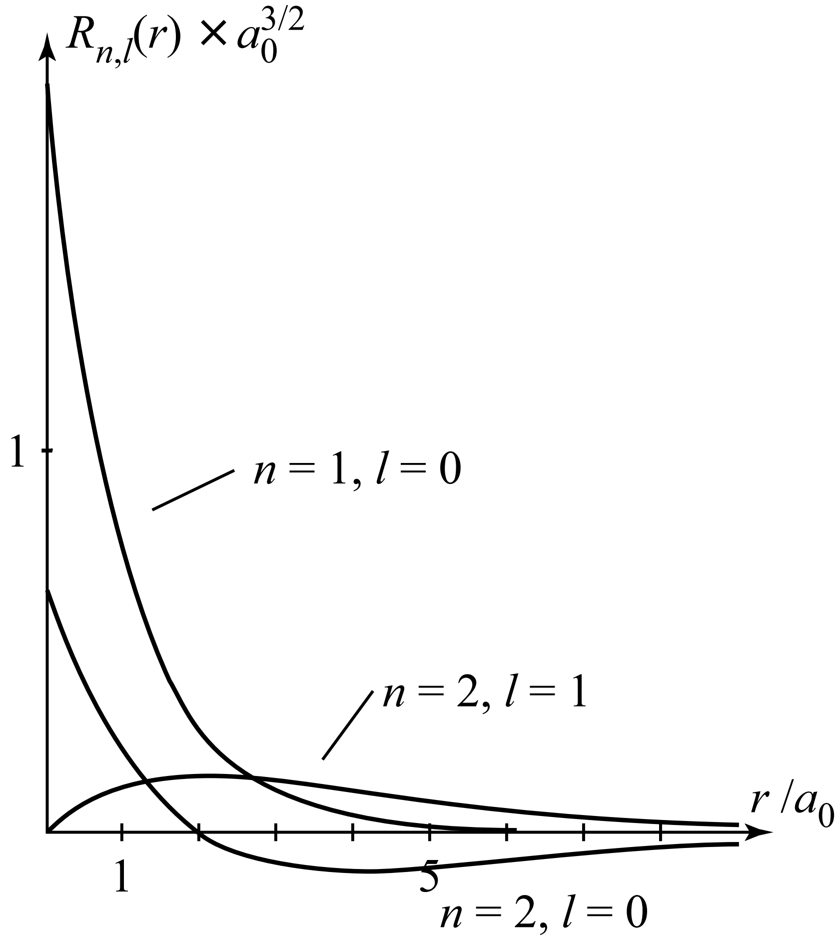
Densidade de probabilidade: $\left|\varphi_{n,l,m}(\mathbf{r})\right|^2 = \left|R_{n,l}(r)\right|^2 \left|Y_{l,m}(\theta,\phi)\right|^2 \propto \left|R_{n,l}(r)\right|^2 \left|Z_{l,m}(\theta)\right|^2$

$$Y_{lm}(\theta,\phi) = Z_{lm}(\theta)\,\frac{e^{im\phi}}{\sqrt{2\pi}}$$

Dependência angular: gráfico polar de $\left|Z_{l,m}(\theta)\right|^2$



Função radial: $R_{n,l}(r)$



$$R_{k=1,l=0}(r) = 2(a_0)^{-3/2}\,\mathrm{e}^{-r/a_0} \qquad n=1$$

$$R_{k=2,l=0}(r) = 2(2a_0)^{-3/2}\left(1 - \frac{r}{2a_0}\right)\mathrm{e}^{-r/2a_0} \qquad n=2$$

$$R_{k=1,l=1}(r) = (2a_0)^{-3/2}\,\frac{1}{\sqrt{3}}\,\frac{r}{a_0}\,\mathrm{e}^{-r/2a_0} \qquad n=2$$

$$R_{n,\ell}(r) \sim r^{\ell} \quad (r \to 0)$$

$$\ell = 0 \qquad R_{n\ell}(r) \xrightarrow[r \to 0]{} \text{CONST.}$$

Densidade de probabilidade radial

$$dP_{n,\ell,m}(r,\theta,\phi) = |R_{n,\ell}(r)|^2 \, |Y_{\ell,m}(\theta,\phi)|^2 \, d^3r$$

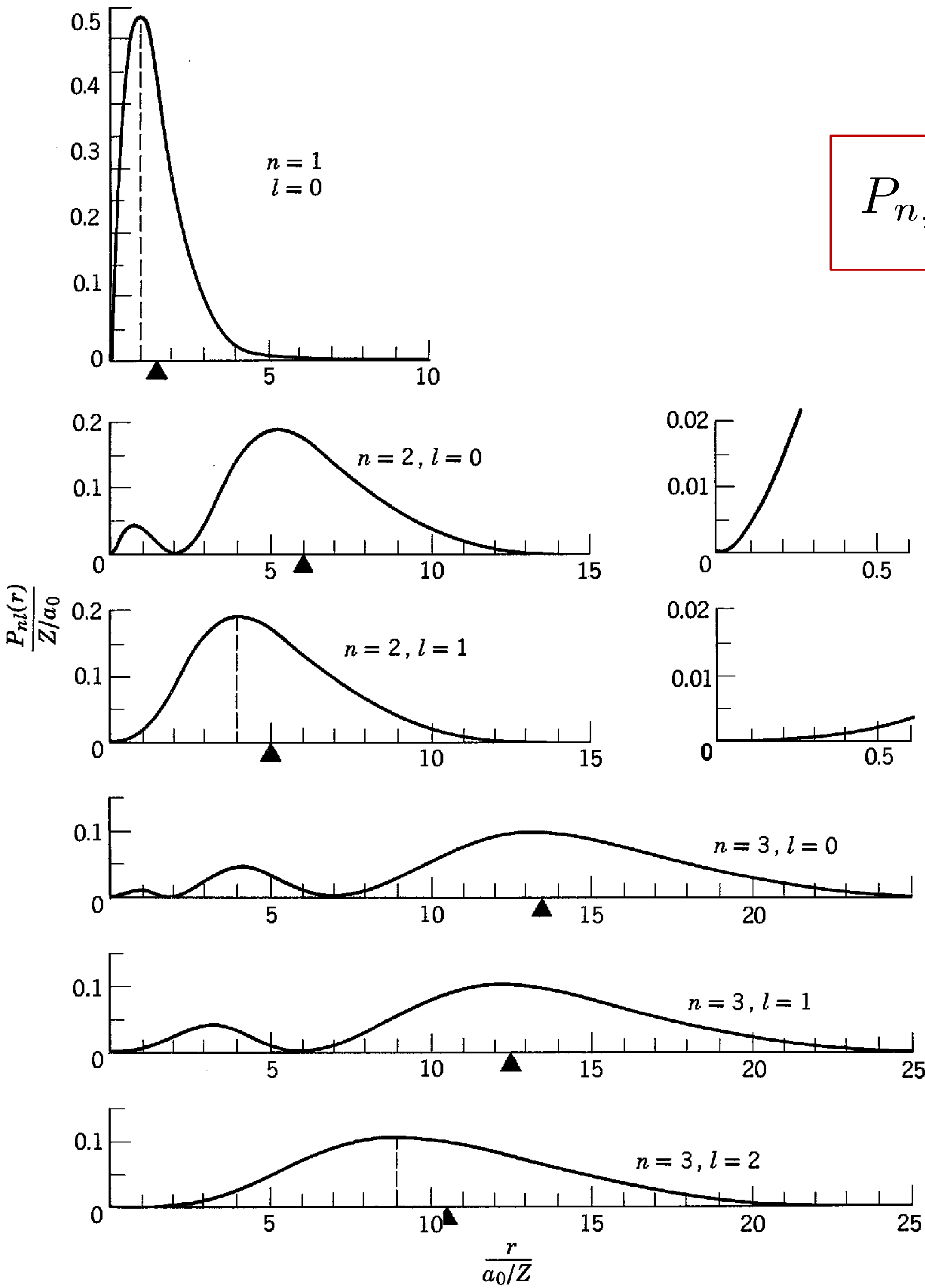
$$= |R_{n,\ell}(r)|^2 \, |Y_{\ell,m}(\theta,\phi)|^2 \, r^2 dr \, \underbrace{d\Omega}_{\sin\theta \, d\theta \, d\phi}$$

DENS. DE PROB. RADIAL:

PROBABILIDADE DO ELÉTRON ESTAR NUMA CASCA ESFÉRICA ENTRE r E $r+dr$

$$dP^{(r)}(r) = \int_{d\Omega} |R_{n,\ell}(r)|^2 \, |Y_{\ell m}(\theta,\phi)|^2 \, r^2 dr \, d\Omega$$

$$dP^{(r)}_{n,\ell}(r) = \underbrace{|R_{n,\ell}(r)|^2 \, r^2}_{\frac{dP^{(r)}_{n,\ell}}{dr} \, = \text{ DENS. DE PROB. RADIAL}} dr$$



$$\boxed{P_{n,l}(r) = r^2 \left|R_{n,l}(r)\right|^2}$$

O triângulo dá o valor médio $\langle r \rangle$

$$\langle r \rangle = \int_0^\infty r \left[r^2 \left|R_{n,l}(r)\right|^2 \right] dr$$