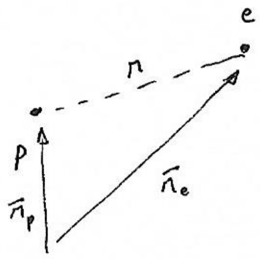
# Átomo de hidrogênio






$$\left[ -\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r)\right]\Psi(\vec{r}_p,\vec{r}_e) = E_T\,\Psi(\vec{r}_p,\vec{r}_e)$$

- $-\frac{\hbar^2}{2m_p}\nabla_p^2$: cinética próton
- $-\frac{\hbar^2}{2m_e}\nabla_e^2$: cinética elétron
- $V(r)$: interação coulombiana $\left(-\frac{e^2}{r}\right)$
- $E_T$: energia total do sistema

$$\begin{cases} \vec{r} = \vec{r}_e - \vec{r}_p \\ \vec{R} = \dfrac{m_p\vec{r}_p + m_e\vec{r}_e}{m_p+m_e} \end{cases}$$

$$\Psi(\vec{r}_p,\vec{r}_e) = \Psi(\vec{R},\vec{r}) = \Psi_p(\vec{R})\,\Psi_e(\vec{r})$$

$$\Downarrow$$

$$\underbrace{\frac{1}{\Psi_p(\vec{R})}\left[-\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\right]\Psi_p(\vec{R})}_{E_{cm}\ \left(\text{partícula livre c/ massa } M\right)} + \underbrace{\frac{1}{\Psi_e(\vec{r})}\left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(r)\right]\Psi_e(\vec{r})}_{E\ \left(\text{mov. elétron em relação ao próton}\right)} = E_T$$

$$\begin{cases} M = m_e + m_p & \text{(massa total)} \\ \dfrac{1}{m} = \dfrac{1}{m_e} + \dfrac{1}{m_p} & \text{(massa reduzida)} \end{cases}$$

$$m \simeq m_e$$

## Mov. eletrônico

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right)\Psi(\vec{r}) = E\,\Psi(\vec{r})$$

$$\nabla^2(r,\theta,\phi) = \nabla_r^2 - \frac{L^2(\theta,\phi)}{\hbar^2 r^2}$$

$\Downarrow$ coord. esféricas

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + \frac{L^2(\theta,\phi)}{2mr^2} - \frac{e^2}{r}\right]\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$

$$\begin{cases} \nabla_r^2 = \dfrac{\partial^2}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial}{\partial r} = \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial}{\partial r}\right) \\ L^2 = -\hbar^2\left(\dfrac{\partial^2}{\partial\theta^2} + \cot g\,\theta\dfrac{\partial}{\partial\theta} + \dfrac{1}{\operatorname{sen}^2\theta}\dfrac{\partial^2}{\partial\phi^2}\right) \\ \quad = -\hbar^2\dfrac{1}{\operatorname{sen}\theta}\dfrac{\partial}{\partial\theta}\left(\operatorname{sen}\theta\dfrac{\partial}{\partial\theta}\right) + \dfrac{1}{\operatorname{sen}^2\theta}\dfrac{\partial^2}{\partial\phi^2} \end{cases}$$

$$\boxed{\Psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)}$$

$$\underbrace{\frac{2mr^2}{\hbar^2}\,\frac{1}{R(r)}\left[\frac{\hbar^2}{2m}\nabla_r^2 + \frac{e^2}{r} + E\right]R(r)}_{\text{parte radial}} = \underbrace{\frac{1}{Y(\theta,\phi)}\left[\frac{L^2(\theta,\phi)}{\hbar^2}\right]Y(\theta,\phi)}_{\text{parte angular}} = \boxed{\lambda_\ell^2 \geq 0}$$

<u>Parte angular</u>

$$\frac{L^2(\theta,\phi)}{\hbar^2}\,Y(\theta,\phi) = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial Y}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = \lambda_\ell^2\,Y(\theta,\phi)$$

$$\boxed{Y(\theta,\phi) = P(\theta)\,\chi(\phi)}$$

$$\left[\frac{1}{P(\theta)}\,\frac{1}{\sin\theta}\,\frac{d}{d\theta}\left(\sin\theta\,\frac{dP}{d\theta}\right) + \lambda_\ell^2\right]\sin^2\theta = \frac{-1}{\chi(\phi)}\,\frac{d^2\chi}{d\phi^2} = \lambda_m^2 \geq 0 \qquad \boxed{\lambda_m^2 \leq \lambda_\ell^2}$$

$$\begin{cases} L_z = -i\hbar\,\dfrac{\partial}{\partial\phi} \\ L_z^2 = -\hbar^2\,\dfrac{\partial^2}{\partial\phi^2} \end{cases}$$

$$\Downarrow$$

$$\chi_m(\phi) \sim e^{im\phi} \qquad (m = 0, \pm 1, \pm 2, \ldots)$$

↳ autofunção de $L_z$ c/ autovalor $m\hbar$

$$\boxed{\lambda_m^2 = m^2}$$

$$\boxed{\left[\frac{1}{\sin\theta}\,\frac{d}{d\theta}\left(\sin\theta\,\frac{d}{d\theta}\right) + \lambda_\ell^2 - \frac{m^2}{\sin^2\theta}\right]P_\ell^m(\theta) = 0}$$

eq. associada de Legendre

$$\boxed{Y_\ell^m(\theta,\phi) = P_\ell^m(\theta)\,\chi_m(\phi)}$$

<u>esféricos harmônicos</u>

↳ $P_\ell^m$: polinômios associados de Legendre

$$\boxed{x = \cos\theta} \implies \frac{d}{dx}\left[(1-x^2)\frac{dP_\ell^m}{dx}\right] + \left[\lambda_\ell^2 - \frac{m^2}{1-x^2}\right]P_\ell^m(\theta) = 0 \qquad (-1 < x < 1)$$

$$\begin{cases} \lambda_\ell^2 = \ell(\ell+1) \\ m^2 \leq \lambda_\ell^2 \end{cases} \implies m \leq \pm\sqrt{\ell(\ell+1)} \implies |m| \leq \ell \qquad \begin{cases} \ell = 0, 1, 2, \dots \\ m = 0, \pm 1, \dots \pm \ell \end{cases}$$

$$P_\ell^m(x) = (1-x^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_\ell(x) \qquad (\ell \geq |m|) \qquad P_\ell(x) = P_\ell^0(x) \qquad P_\ell^m(\theta) = (\operatorname{sen}\theta)^{|m|} \frac{d^{|m|}}{d\cos\theta^{|m|}} P_\ell(\theta)$$

($P_\ell(x)$ → polinómios de Legendre)

não-normalizados

| $\ell$ | $P_\ell(x)$ | $P_\ell(\cos\theta)$ | $m$ | $P_\ell^m(\theta)$ |
|---|---|---|---|---|
| 0 | 1 | 1 | 0 | 1 |
| 1 | $x$ | $\cos\theta$ | 0 | $\cos\theta$ |
| | | | 1 | $\operatorname{sen}\theta$ |
| 2 | $\frac{1}{2}(3x^2-1)$ | $\frac{1}{2}(3\cos^2\theta - 1)$ | 0 | $\frac{1}{2}(3\cos^2\theta - 1)$ |
| | | | 1 | $3\operatorname{sen}\theta\cos\theta$ |
| | | | 2 | $3\operatorname{sen}^2\theta$ |

$$\boxed{Y_\ell^m(\theta,\phi) = \frac{A_{\ell m}}{\sqrt{2\pi}} P_\ell^m(\theta) e^{im\phi}}$$

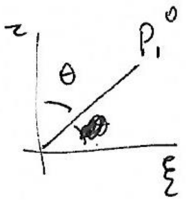
$(\ell = 0, 1, 2, \dots \quad m = 0, \pm 1, \dots \pm \ell)$

## Normalização

$$\int \Psi^*(r,\theta,\phi)\,\Psi(r,\theta,\phi)\, r^2 dr \sin\theta\, d\theta\, d\phi = \underbrace{\int \overbrace{|R(r)|^2}^{|u(r)|^2} r^2 dr}_{1}\ \underbrace{\int |P_\ell^m(\theta)|^2 \sin\theta\, d\theta}_{1}\ \underbrace{\int_0^{2\pi} |A_\phi \underbrace{e^{im\phi}}_{1}|^2 d\phi}_{1} = 1 \Rightarrow A_\phi = \frac{1}{\sqrt{2\pi}}$$

## Representação polar

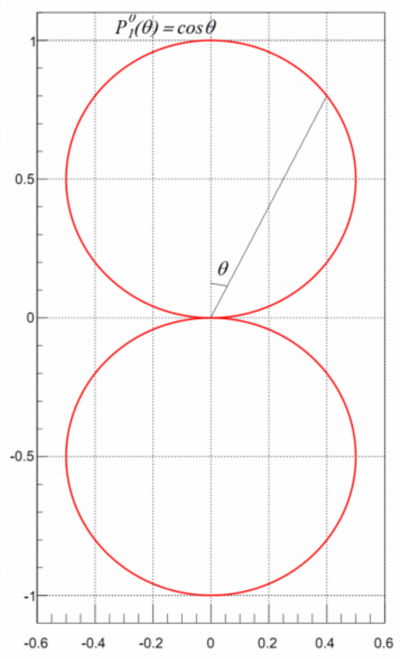
$P_1^0 = \cos\theta$




$$\begin{cases} |z| = P_1^0 \cos\theta = \cos^2\theta = \dfrac{1+\cos 2\theta}{2} \\ \xi = P_1^0 \sin\theta = \sin\theta\cos\theta = \dfrac{\sin 2\theta}{2} \end{cases}$$

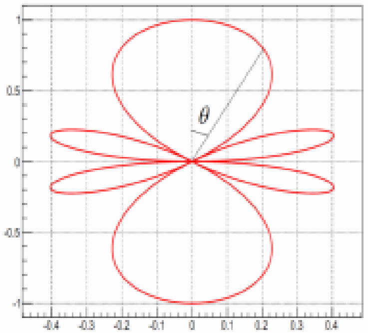
$$\Rightarrow \sin^2 2\theta + \cos^2 2\theta = (2\xi)^2 + (2z \mp 1)^2 = 1$$

$$\left(\frac{\xi}{1/2}\right)^2 + \left(\frac{z \mp 1/2}{1/2}\right)^2 = 1$$

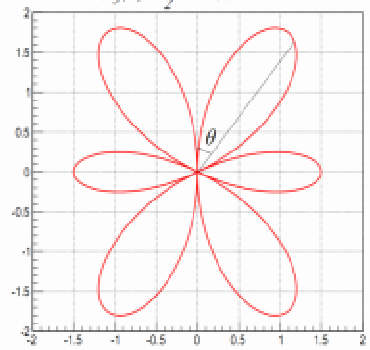


# Representações polares das funções associadas de Legendre

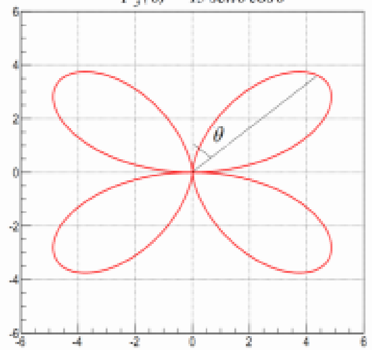
$P_3^0(\theta) = \frac{1}{2} sen\theta (5cos^2\theta - 3)$



$P_3^{\pm 1}(\theta) = \frac{3}{2} sen\theta (5cos^2\theta - 1)$



$P_3^{\pm 2}(\theta) = 15 sen^2\theta cos\theta$



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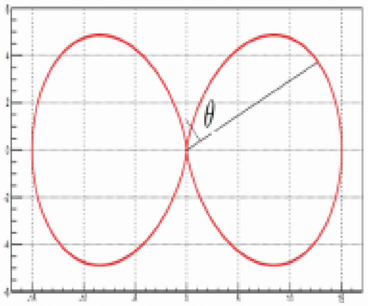
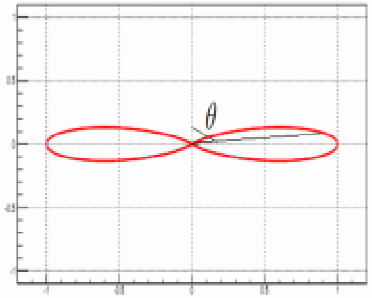
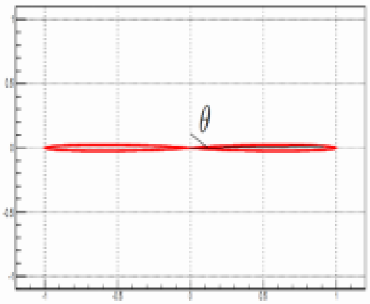
$P_3^{\pm 3}(\theta) = 15 sen^3\theta$



$P_{20}^{\pm 20}(\theta) = (sen\theta)^{20}$

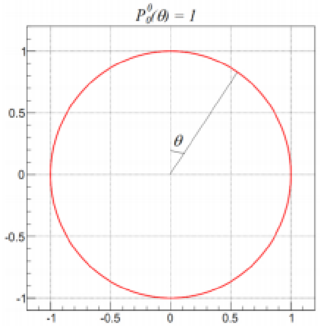


$P_{500}^{\pm 500}(\theta) = (sen\theta)^{500}$

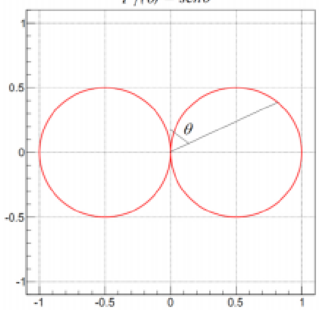


movimento prat plano (clássico)

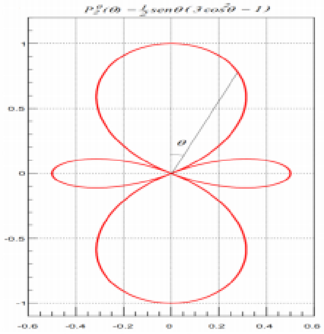
$P_0^0(\theta) = 1$



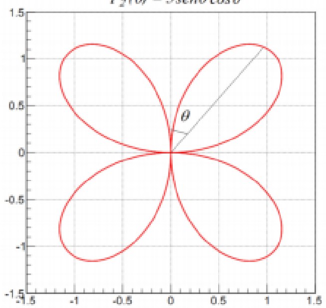
$P_1^{\pm 1}(\theta) = sen\theta$



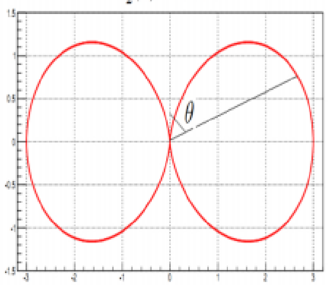
$P_2^0(\theta) = \frac{1}{2} sen\theta (3cos^2\theta - 1)$



$P_2^{\pm 1}(\theta) = 3 sen\theta cos\theta$



$P_2^{\pm 2}(\theta) = 3 sen^2\theta$



<u>parte radial</u> $\psi(r,\theta,\phi) = R(r)\, Y_\ell^m(\theta,\phi)$

$$\frac{2mr^2}{\hbar^2}\frac{1}{R(r)}\left[\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{e^2}{r} + E\right]R(r) = \overbrace{\ell(\ell+1)}^{\lambda_\ell^2}$$

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

$$r = \rho\, a_B = \rho\left(\frac{\hbar^2}{me^2}\right)$$

$$\boxed{a_B \simeq 0.5\ \text{Å}}$$

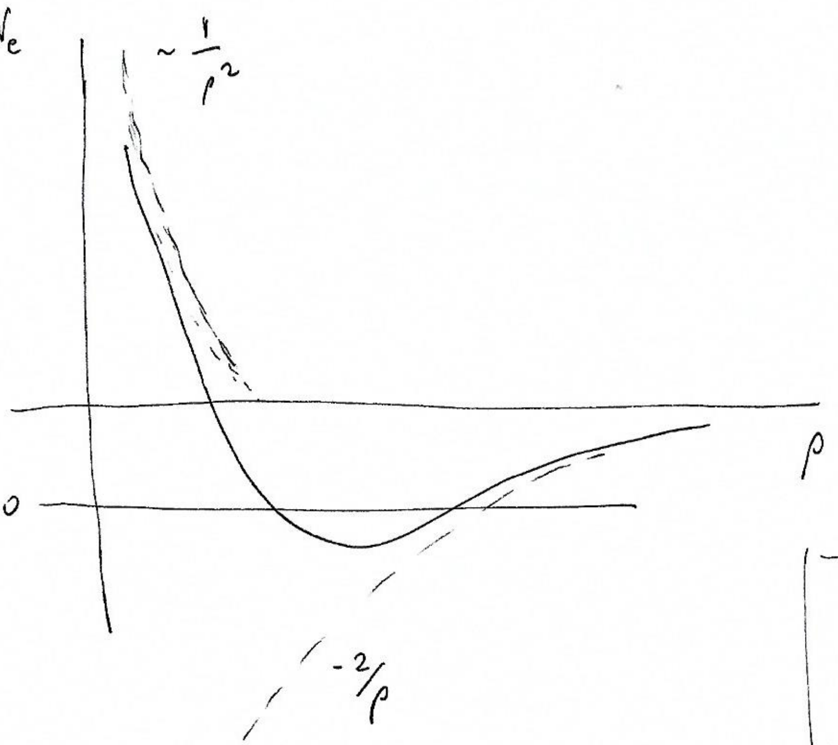
$$\underbrace{\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)}_{\frac{1}{\rho}\frac{d^2}{d\rho^2}(\rho R)} + \left[\underbrace{\frac{E}{E_R}}_{\varepsilon} + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]R(\rho) = 0$$

$$\boxed{E_R = \frac{e^2}{2a_B} \simeq 13{,}6\,\text{eV}}$$

$$\boxed{\frac{d^2u(\rho)}{d\rho^2} + \left\{\varepsilon - \underbrace{\left[\frac{\ell(\ell+1)}{\rho^2} - \frac{2}{\rho}\right]}_{V_\ell(\rho)\ \to\ \text{potencial efetivo}}\right\}u(\rho) = 0}$$

$$u(\rho) = \rho\, R(\rho)$$

$V_\ell(\rho) \to$ potencial efetivo




(estados ligados) $V_{min} < E < 0$

$R = \dfrac{u}{\rho}$ finita na origem

$\Downarrow$

$$\boxed{u(0) = 0 \qquad u(\infty) = 0} \text{ (estados ligados)}$$

condições de contorno

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

eq. radial

$$\boxed{\varepsilon = \frac{E}{E_R}} < 0$$

negativo espectro

normalização

$$\int_0^\infty |R(r)|^2 r^2 \, dr = \boxed{\int_0^\infty |u(r)|^2 dr = 1} \quad (r = \rho a_B) \qquad u(r) = r R(r) \Rightarrow u(\rho) = a_B \underbrace{\rho R(\rho)}_{u(\rho)}$$

$\to dr = a_B \, d\rho$

$$\boxed{\int_0^\infty |u(\rho)|^2 d\rho = \frac{1}{a_B^3}}$$

comportamento assintótico

$$\rho \to \infty \Rightarrow \frac{d^2u_\infty}{d\rho^2} - |\varepsilon| u_\infty = 0 \Rightarrow u_\infty = e^{-\sqrt{|\varepsilon|}\,\rho}$$

$$\rho \to 0 \Rightarrow \frac{d^2u_0}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2} u_0 = 0 \Rightarrow u_0 = \rho^{\ell+1}$$

$$\Rightarrow u(\rho) = \rho^{\ell+1} e^{-\alpha\rho} v(\rho) \qquad \boxed{\alpha^2 = -\varepsilon}$$

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

$$v(\rho) = \sum_{j=0}^{\infty} b_j \rho^j \Rightarrow b_{j+1} = \frac{2\alpha\left[j + (\ell+1) - 1/\alpha\right]}{(j+1)(j+2\ell+2)} b_j \to 2\frac{\alpha}{j} b_j \quad (j \gg 1) \text{ diverge p/ } \rho \to \infty$$

$$\Downarrow$$

$$j_{máx} = k$$

$$j_{máx} = k \Rightarrow \overbrace{k+\ell+1}^{n} - 1/\alpha_n = 0 \Rightarrow \boxed{\alpha_n = \frac{1}{n}} \Rightarrow \boxed{\varepsilon_n = -\frac{1}{n^2}}$$

$$v_{n\ell}(\rho) = \sum_{j=0}^{k} b_j \rho^j \quad (k, \ell \leq n-1)$$

$$\boxed{E_n = -\frac{E_R}{n^2} = -\frac{e^2}{2a_B}\frac{1}{n^2}}$$

$n = 1, 2, 3$

$\ell = 0, 1, 2, \ldots, n-1$

$m_\ell = 0, \pm 1, \pm 2, \ldots \pm \ell$

$$u_{n\ell}(\rho) = \rho^{\ell+1} e^{-\alpha_n\rho} v_{n\ell}(\rho) \Rightarrow R_{n\ell}(\rho) = \rho^{\ell} e^{-\alpha_n\rho} v_{n\ell}(\rho)$$

$$\boxed{\psi_{n,\ell,m}(r,\theta,\phi) = \left(\frac{u_{n\ell}(r)}{r}\right) P_\ell^m(\theta)\, e^{im\phi}}$$

$$\left(\frac{u_{n\ell}(r)}{r}\right) \to R_{n\ell}(r)$$

• estado fundamental : $n=1$ $(\alpha_1 = 1)$, $k=0$, $l=0$, $m=0$

$$v_{10}(r) = b_0 \Rightarrow u_{10} = b_0 \, r \, e^{-r/a_B}$$

$$b_0^2 \underbrace{\int_0^\infty r^2 e^{-2r/a_B} dr}_{a_B^3/4} = 1 \quad \text{(normalização)}$$

$$\Downarrow$$

$$b_0 = \frac{2}{a_B^{3/2}} \Rightarrow \boxed{u_{10} = \frac{2}{a_B^{3/2}} \, r \, e^{-r/a_B}}$$

$$\boxed{u_{10} = \frac{2}{\sqrt{a_B}} \left(\frac{r}{a_B}\right) e^{-r/a_B}}$$

$$\boxed{\mathcal{E}_1 = -\frac{e^2}{2a_B} = -13{,}6 \, eV}$$

$$\boxed{\alpha_n = \frac{1}{n} \Rightarrow \varepsilon_n = -\frac{1}{n^2}}$$

$$\boxed{\mathcal{E}_n = -\frac{E_R}{n^2} = -\frac{e^2}{2a_B} \frac{1}{n^2}}$$

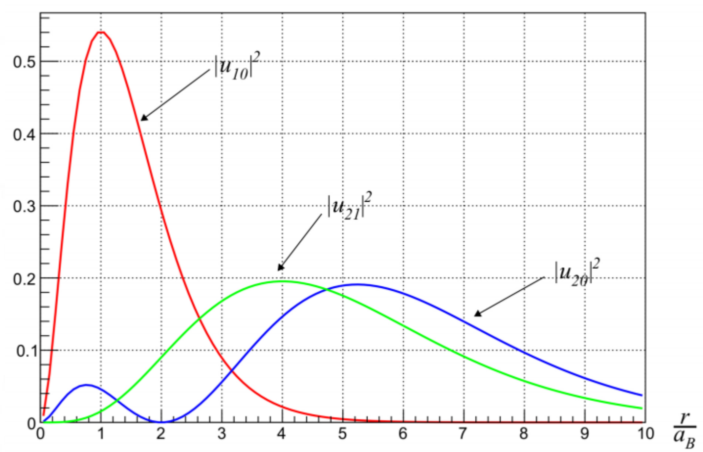
$$\begin{cases} b_{j+1} = 2\alpha_n \dfrac{(j + l + 1 - 1/\alpha_n)}{(j+1)(j+2l+2)} b_j \\ j_{máx} = k \Rightarrow \underbrace{k + l + 1}_{n} - \dfrac{1}{\alpha_n} = 0 \end{cases}$$

$$\begin{cases} v_{nl} = \sum_{j=0}^{k} b_j \left(\dfrac{r}{a_B}\right)^j \\ u_{nl} = r^{l+1} e^{-\alpha_n r/a_B} v_{nl}(r) \end{cases}$$

$$I(\lambda) = \int_0^\infty e^{-\lambda r} dr = \frac{1}{\lambda} \quad (\lambda = 2/a_B)$$

$$I'(\lambda) = \int_0^\infty -r \, e^{-\lambda r} dr = -\frac{1}{\lambda^2}$$

$$I''(\lambda) = \int_0^\infty r^2 e^{-\lambda r} dr = \frac{2}{\lambda^3} = \frac{a_B^3}{4}$$




Distribuições de probabilidades radiais para os autoestados de energias $(1,0)$ $(2,0)$ e $(2,1)$

$n \swarrow \quad \searrow l$

- $\underline{n=2}\ (\alpha_2 = 1/2) \implies \begin{cases} l=0, & k=1 \\ \text{ou} & \\ l=1, & k=0 \end{cases}$

$$\int_0^\infty e^{-\lambda x}\,dx = \frac{1}{\lambda}$$
$$\int x\,e^{-\lambda x}\,dx = \frac{1}{\lambda^2}$$
$$\int x^2 e^{-\lambda x}\,dx = \frac{2}{\lambda^3}$$
$$\int x^3 e^{-\lambda x}\,dx = \frac{6}{\lambda^4}$$
$$\int x^4 e^{-\lambda x}\,dx = \frac{24}{\lambda^5}$$

$\underline{l=0\ ,\ k=1}$

$$\begin{cases} v_{20}(r) = b_0 + b_1 \dfrac{r}{a_B} \implies u_{20}(r) = \left(b_0 + b_1 \dfrac{r}{a_B}\right) r\, e^{-\frac{r}{2a_B}} \\ b_1 = \alpha_2\left(1 - \dfrac{1}{\alpha_2}\right) b_0 = \dfrac{-b_0}{2} \implies u_{20}(r) = \left(1 - \dfrac{r}{2a_B}\right) b_0\, r\, e^{-r/2a_B} \end{cases}$$

normalização

$$a_B^3 b_0^2 \int_0^\infty \left(1 - \frac{r}{2a_B}\right)^2 \left(\frac{r}{a_B}\right)^2 e^{-r/a_B}\,\frac{dr}{a_B} = a_B^3 b_0^2 \left[\underbrace{\int_0^\infty \left(\frac{r}{a_B}\right)^2 e^{-r/a_B}\frac{dr}{a_B}}_{2} - \underbrace{\int_0^\infty \left(\frac{r}{a_B}\right)^3 e^{-r/a_B}\frac{dr}{a_B}}_{6} + \frac{1}{4}\underbrace{\int_0^\infty \left(\frac{r}{a_B}\right)^4 e^{-r/a_B}\frac{dr}{a_B}}_{24 \to 6}\right] = 1$$

$$b_0 = \left(\frac{1}{2a_B^3}\right)^{1/2}$$

$\Downarrow$

$$\boxed{u_{20} = \left(\frac{1}{2a_B}\right)^{1/2}\left(1 - \frac{r}{2a_B}\right)\left(\frac{r}{a_B}\right) e^{-r/2a_B}}$$

• $\underline{n = 2}$ $(\alpha_2 = 1/2)$

$\underline{l = 1,\ k = 0}$ : $\quad v_{21}(r) = b_0 \implies u_{21} = b_0\, r^2\, e^{-r/2a_B}$

$$a_B^5\, b_0^2 \underbrace{\int_0^\infty \frac{r^4}{a_B^4}\, e^{-r/a_B}\, \frac{dr}{a_B}}_{24} = 1 \implies \left(\frac{1}{24 a_B^5}\right)^{1/2} = b_0$$

$$\implies \boxed{u_{21} = \left(\frac{1}{24 a_B}\right)^{1/2} \left(\frac{r}{a_B}\right)^2 e^{-r/2a_B}}$$

$$\boxed{u_{21} = \left(\frac{2}{3 a_B}\right)^{1/2} \left(\frac{r}{2 a_B}\right)^2 e^{-r/2a_B}}$$