VIII – O Átomo de Hidrogênio

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Forças Centrais :

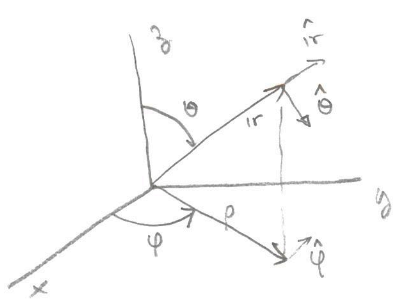
$$\mathbb{F}(\mathbb{r}) = F(r)\,\hat{\mathbb{r}} = -\nabla V(r) = -\frac{dV}{dr}\,\hat{\mathbb{r}}$$

$$\Rightarrow \quad F(r) = -\frac{dV}{dr}$$

Momento angular $\vec{\mathcal{L}} = \mathbb{r} \times \mathbb{p}$ é conservado:

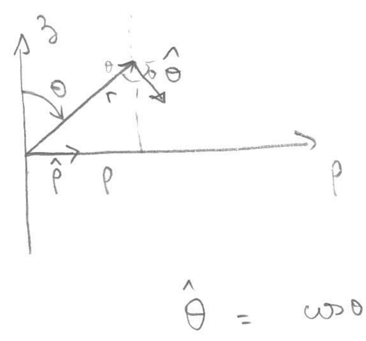
$$\frac{d\vec{\mathcal{L}}}{dt} = \underbrace{\dot{\mathbb{r}} \times \mathbb{p}}_{=0} + \mathbb{r} \times \frac{d\mathbb{p}}{dt} = \mathbb{r} \times \mathbb{F} = 0 \Rightarrow \text{movimento plano.}$$

Hamiltoniana em Coordenadas Esféricas



$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases} \qquad \begin{cases} r = \sqrt{x^2+y^2+z^2} \\ tg\varphi = y/x \\ tg\theta = \sqrt{x^2+y^2}\,/z \end{cases}$$

$$\hat{\mathbb{r}} = \sin\theta\cos\varphi\,\hat{x} + \sin\theta\sin\varphi\,\hat{y} + \cos\theta\,\hat{z}$$



$$\hat{\theta} = \cos\theta\,\hat{\rho} - \sin\theta\,\hat{z}$$

$$\hat{\rho} = \cos\varphi\,\hat{x} + \sin\varphi\,\hat{y}$$

$$\hat{\theta} = \cos\theta\cos\varphi\,\hat{x} + \cos\theta\sin\varphi\,\hat{y} - \sin\theta\,\hat{z}$$

$$\hat{\varphi} = -\sin\varphi\,\hat{x} + \cos\varphi\,\hat{y}$$

$$\mathbb{r} = r\,\hat{\mathbb{r}} \quad ; \quad \dot{\mathbb{r}} = \dot{r}\,\hat{\mathbb{r}} + \frac{d\hat{\mathbb{r}}}{dt} = \dot{r}\,\hat{\mathbb{r}} + r(\cos\theta\cos\varphi, \cos\theta\sin\varphi, -\sin\theta)\,\dot{\theta} + r(-\sin\theta\sin\varphi, \sin\theta\cos\varphi, 0)\,\dot{\varphi}$$

$$= \dot{r}\,\hat{\mathbb{r}} + r\dot{\theta}\,\hat{\theta} + r\sin\theta\,\dot{\varphi}\,\hat{\varphi}$$

$$L = \frac{\mu \dot{\mathbf{r}}^2}{2} - V(r)$$

$$= \frac{\mu}{2}\left[\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\varphi}^2\right] - V(r)$$

Momentos

$$p_r = \frac{\partial \mathcal{L}}{\partial \dot{r}} = \mu \dot{r} \quad \rightarrow \quad \dot{r} = p_r/\mu$$

$$p_\theta = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = \mu r^2 \dot{\theta} \quad \rightarrow \quad \dot{\theta} = \frac{p_\theta}{\mu r^2}$$

$$p_\varphi = \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = \mu r^2 \sin^2\theta\, \dot{\varphi} \quad \rightarrow \quad \dot{\varphi} = \frac{p_\varphi}{\mu r^2 \sin^2\theta}$$

$$H = \frac{1}{2\mu}\left[p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\varphi^2}{r^2\sin^2\theta}\right] + V(r) = \sum_i p_i \dot{q}_i - L = T + V$$

Note que $\mathcal{L} = |\mu \mathbf{r} \times \mathbf{v}| = \mu r v_\perp =$

$$\mathcal{L}^2 = \mu^2 r^2 v_\perp^2 = \mu^2 r^2\left[r^2\dot{\theta}^2 + r^2\dot{u}^2\sin^2\varphi\right]$$

$$= \mu^2 r^2\left[\frac{p_\theta^2}{\mu^2 r^2} + \frac{p_\varphi^2}{\mu^2 r^2 \sin^2\theta}\right] = p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}$$

$$\boxed{H = \frac{p_r^2}{2\mu} + \frac{\mathcal{L}^2}{2\mu r^2} + V(r)}$$

ou

$$H = \frac{p_r^2}{2\mu} + V_{ef}(r) \quad ; \quad V_{ef}(r) = V(r) + \frac{\mathcal{L}^2}{2\mu r^2} \quad \text{com } \mathcal{L} = \text{const.}$$

– A Hamiltoniana Quântica

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \varphi(\mathbf{r}) = E\, \varphi(\mathbf{r})$$

Em coor. retangulares $\nabla^2 = \sum \frac{\partial^2}{\partial x_i^2}$

Em esféricas $\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}\left[\frac{\partial^2}{\partial \theta^2} + \frac{1}{\operatorname{tg}\theta}\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \varphi^2} \right]$

Como vimos no capítulo VI, $L^2 = -\hbar^2 [\ \ ]$ e assim

$$\boxed{H = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{2\mu r^2} L^2 + V(r)}$$

$$H\, \varphi(r,\theta,\varphi) = E\, \varphi(r,\theta,\varphi)$$

– AUTOFUNÇÕES

Como o operador $\vec{L}$ só envolve θ e φ, $[H, \vec{L}] = [H, L^2] = 0$

Conjunto completo de operadores que comutam: H, L^2, L_z e procuramos funções $\varphi(r,\theta,\varphi)$ que são auto-funções dos 3 operadores:

$$H\varphi = E\varphi$$
$$L^2\varphi = \hbar^2 \ell(\ell+1)\,\varphi$$
$$L_z\varphi = \hbar m\, \varphi$$

As auto-funções de L^2 e L_3 são do tipo $Y_\ell^m(\theta,\varphi)$ $\Rightarrow$

$$\psi(\mathbf{r}) = R(r)\, Y_\ell^m(\theta,\varphi) \qquad e \qquad H\psi = E\psi \Rightarrow$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(rR\right) + \frac{\hbar^2}{2\mu r^2}\ell(\ell+1)R + V(r)R = ER$$

$\Rightarrow$ eq. não depende de $\underline{\underline{m}}$. Para cada ℓ dado acharemos alguns valores de E, $\Rightarrow$ $E \to E_{k,\ell}$ e a degenerescência será $(2\ell+1)$ para um dado k e ℓ. Faremos t.b. $R(r) \to R_{k,\ell}(r)$.

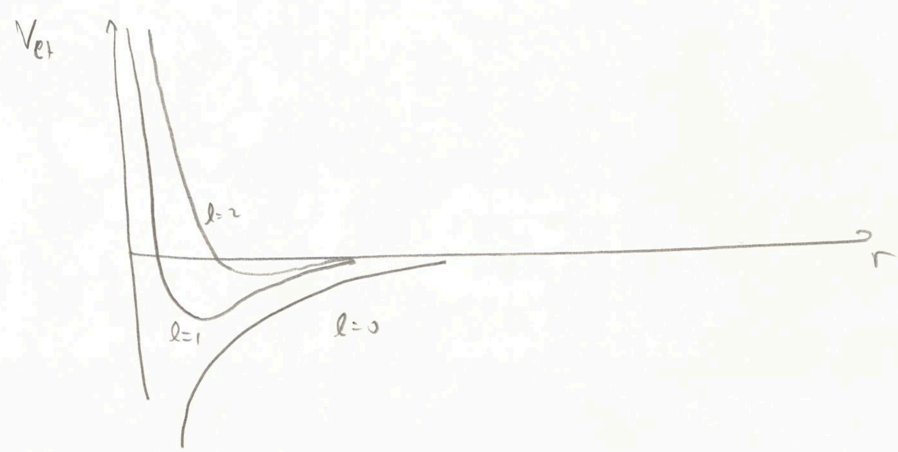
Mudança de variáveis

$$R_{k,\ell}(r) = \frac{1}{r}u_{k,\ell}(r)$$

$$-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2}u_{k,\ell} + \frac{\hbar^2}{2\mu}\ell(\ell+1)\frac{u_{k,\ell}}{r^3} + V(r)\frac{u_{k,\ell}}{r} = \frac{E_{k,\ell}u_{k,\ell}}{r}$$

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 u_{k,\ell}}{\partial r^2} + \frac{\hbar^2}{2\mu r^2}\ell(\ell+1)u_{k,\ell} + V(r)u_{k,\ell} = E_{k,\ell}u_{k,\ell}$$

$\Rightarrow$ problema uni-dimensional com $V_{ef}(r) = V(r) + \dfrac{\hbar^2\ell(\ell+1)}{2\mu r^2}$



- Comportamento próximo da origem

$$R_{k,l}(r) \underset{r\to 0}{\sim} C\, r^{s}$$

$$\frac{1}{r}\frac{d^2}{dr^2} rR \to C(s+1)s\; r^{s-2}$$

$$-\frac{\hbar^2}{2\mu} s(s+1)\, r^{s-2} + \frac{\hbar^2\, l(l+1)}{2\mu}\, r^{s-2} + V(r)\, r^{s} = E\, r^{s}$$

se $V(r) \xrightarrow[r\to 0]{} \sim \frac{1}{r}$ ou vai a infinito ainda mais devagar, então

$$-s(s+1) + l(l+1) \simeq 0 \quad \Rightarrow \quad \begin{array}{l} s = l \\ \text{ou} \\ s = -(l+1) \leftarrow \text{diverge} \end{array}$$

$$\Rightarrow \quad R_{k,l}(r) \sim C\, r^{l}$$

$$\downarrow$$

$$u_{k,l}(r) \sim C\, r^{l+1} \quad \text{e p/ } r\to 0 \quad \boxed{u_{kl}(0) = 0}$$

- AUTOFUNÇÕES

- $\varphi_{k,l,m}(r,\theta,\varphi) = R_{k,l}(r)\, Y_l^m(\theta,\varphi) = \frac{1}{r} u_{k,l}(r)\, Y_{l,m}(\theta,\varphi)$

- $\int r^2 d\Omega\, dr\, |\varphi|^2 = \int |Y_l^m(\theta,\varphi)|^2 d\Omega \int r^2 |R_{kl}|^2 dr = 1$

$$\int r^2 d\Omega\, dr\, \varphi^*_{k'l'm'}\, \varphi_{klm} = \delta_{kk'}\delta_{ll'}\dots$$

$$\downarrow$$

$$\int r^2 R^*_{k'l} R_{kl}\, dr = \delta_{kk'}$$

$$\downarrow$$

$$\int u^*_{k'l}\, u_{kl}\, dr = \delta_{kk'}$$

$$\downarrow$$

$$\int_0^\infty r^2 |R_{k,l}(r)|^2 dr = \int_0^\infty |u_{k,l}(r)|^2 dr = 1 \leftarrow \text{se as funções forem de quadrado integrável.}$$

Se k for um índice contínuo, então

- $\int_0^\infty r^2 R^*_{k',l}(r)\, R_{k,l}(r) = \int_0^\infty u^*_{k',l}(r)\, u_{k,l}(r)\, dr = \delta(k-k')$

Como $u(0)=0$ as integrais convergem se $\int_0^{\bar r} u^*_{k'l}(r)\, u_{k,l}(r)\, dr$. A divergência ocorre

- Degenerescências

- p/ K e l fixos, $E_{K,l}$ fixo, existe $2l+1$ funções $\varphi_{K,l,m}(r)$ com mesma energia $E_{K,l}$ → degen. essencial

  (invariança de V por rotações)

- se ocorrer de $E_{K',l'} = E_{K,l}$ → deg. acidental

- H, L^2, L_3 formam um CCOC

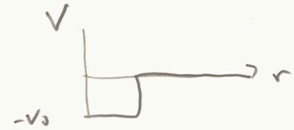
Fixando $E_{K,l}$, l, m, só existe uma auto-função:

- l fixa a equação radial
- $E_{K,l}$ fixa uma solução $R_{K,l}(r)$ dessa equação.
- l e m fixam $Y_l^m(\theta,\varphi)$

Exemplos

a) $V = 0$ → (funções de Bessel esféricas)

b) $V = \begin{cases} -V_0 & \text{se } r < a \\ 0 & \text{se } r > a \end{cases}$



c) $V = \frac{K}{2} r^2$

d) $V = \frac{-Ze^2}{r}$

Movimento Relativo e do Centro de Massa

Mecânica Clássica

: $\mathcal{L} = \frac{m_1 \dot{\mathbf{r}}_1^2}{2} + \frac{m_2 \dot{\mathbf{r}}_2^2}{2} - V(|\mathbf{r}_1 - \mathbf{r}_2|)$

$$\begin{cases} \mathbf{r}_G = \dfrac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \\ \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \end{cases} \rightarrow \begin{cases} \mathbf{r}_1 = \mathbf{r}_G + \dfrac{m_2 \mathbf{r}}{m_1 + m_2} \\ \mathbf{r}_2 = \mathbf{r}_G - \dfrac{m_1 \mathbf{r}}{m_1 + m_2} \end{cases}$$

$$\begin{cases} M = m_1 + m_2 \\ \mu = \dfrac{m_1 m_2}{m_1 + m_2} \end{cases}$$

$$\mathcal{L} = \frac{m_1}{2}\left(\dot{\mathbf{r}}_G - \frac{m_2 \dot{\mathbf{r}}}{M}\right)^2 + \frac{m_2}{2}\left(\dot{\mathbf{r}}_G + \frac{m_1 \dot{\mathbf{r}}}{M}\right)^2 - V(r)$$

$$= \frac{M}{2} \dot{\mathbf{r}}_G^2 + \frac{\mu}{2} \dot{\mathbf{r}} - V(r)$$

$$\begin{cases} \mathbf{P}_G = \dfrac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_G} = M \dot{\mathbf{r}}_G = m_1 \dot{\mathbf{r}}_1 + m_2 \dot{\mathbf{r}}_2 = \mathbf{P}_1 + \mathbf{P}_2 = \text{momento total.} \\ \mathbf{P}_r = \mu \dot{\mathbf{r}} = \dfrac{\mu}{m_1} \mathbf{P}_1 - \dfrac{\mu}{m_2} \mathbf{P}_2 \end{cases}$$

$$\begin{cases} \mathbf{P}_1 = \dfrac{\mu}{m_2} \mathbf{P}_G + \mathbf{P}_r \\ \mathbf{P}_2 = \dfrac{\mu}{m_1} \mathbf{P}_G - \mathbf{P}_r \end{cases}$$

$$\mathcal{H} = \frac{\mathbf{P}_G^2}{2M} + \frac{\mathbf{P}_r^2}{2\mu} + V(r)$$

Como $\dot{\mathbf{P}}_G = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_G} = 0 \rightarrow \mathbf{P}_G = \text{const.}$

Mec. Quântica

$$[X_1, P_{x_1}] = i\hbar$$
$$[X_2, P_{x_2}] = i\hbar \qquad \text{etc}$$

$$\begin{cases} \mathbb{R}_G = \dfrac{m_1 \mathbb{R}_1 + m_2 \mathbb{R}_2}{M} \\ \mathbb{P}_G = \mathbb{P}_1 + \mathbb{P}_2 \end{cases} \qquad \begin{cases} \mathbb{R} = \mathbb{R}_1 - \mathbb{R}_2 \\ \dfrac{\mathbb{P}}{\mu} = \dfrac{\mathbb{P}_1}{m_1} - \dfrac{\mathbb{P}_2}{m_2} \end{cases}$$

$$[X, P_x] = \left[X_1 - X_2, \frac{\mu}{m_1} P_{1x} - \frac{\mu}{m_2} P_{2x}\right] = \frac{\mu}{m_1} i\hbar + \frac{\mu}{m_2} i\hbar$$
$$= i\hbar \mu \frac{m_1 + m_2}{m_1 m_2} = i\hbar$$

$$[X_G, P_{xG}] = \left[\frac{m_1}{M} X_1 + \frac{m_2}{M} X_2, P_{1x} + P_{2x}\right] = \frac{m_1}{M} i\hbar + \frac{m_2}{M} i\hbar = i\hbar$$

$$H = \frac{\mathbb{P}_G^2}{2M} + \frac{\mathbb{P}^2}{2\mu} + V(\mathbb{R}) \equiv H_G + H_R$$

$$[H_G, H_R] = 0 \Rightarrow \qquad H_G|\varphi\rangle = E_G|\varphi\rangle$$
$$H_R|\varphi\rangle = E_R|\varphi\rangle$$

$$E = E_R + E_G$$

representação $|\mathbb{r}_G, \mathbb{r}\rangle \rightarrow \langle \mathbb{r}_G, \mathbb{r}|\varphi\rangle \Rightarrow$ função de 6 variáveis

espaço $\mathcal{E} = \mathcal{E}_G \otimes \mathcal{E}_r \qquad |\varphi\rangle = |\chi_G\rangle \otimes |w_r\rangle$

$$\begin{cases} H_G|\chi_G\rangle = E_G|\chi_G\rangle \\ H_r|w_r\rangle = E_r|w_r\rangle \end{cases} \qquad \varphi(\mathbb{r}_G, \mathbb{r}) = \langle \mathbb{r}_G|\chi_G\rangle \langle \mathbb{r}|w_r\rangle$$

$$-\frac{\hbar^2}{2M} \nabla_G^2 \chi_G = E_G \chi_G \rightarrow \chi_G(\mathbb{r}_G) = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar} \mathbb{p}_G \cdot \mathbb{r}_G}$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbb{r}}^2 + V(\mathbb{r})\right] w(\mathbb{r}) = E_r\, w(\mathbb{r})$$

OBS:
$$H|\varphi\rangle = (H_G + H_R)\left[|\chi_G\rangle \otimes |w_R\rangle\right] = \left(H_G|\chi_G\rangle\right) \otimes |w_R\rangle$$
$$+ |\chi_G\rangle \otimes \left(H_R|w_R\rangle\right) = (E_G + E_R)|\varphi\rangle$$

Momento Angular

$$\mathbb{J} = \mathbb{L}_1 + \mathbb{L}_2 = \mathbb{R}_1 \times \mathbb{P}_1 + \mathbb{R}_2 \times \mathbb{P}_2$$

$$= \left[\mathbb{R}_G + \frac{m_2 \mathbb{R}}{M} \right] \times \left[\frac{\mu}{m_2} \mathbb{P}_G + \mathbb{P} \right] + \left[\mathbb{R}_G - \frac{m_1 \mathbb{R}}{M} \right] \times \left[\frac{\mu}{m_1} \mathbb{P}_G - \mathbb{P} \right]$$

$$= \left(\frac{\mu}{m_2} + \frac{\mu}{m_1} \right) (\mathbb{R}_G \times \mathbb{P}_G) + \left(\frac{m_2}{M} + \frac{m_1}{M} \right) (\mathbb{R} \times \mathbb{P})$$

$$= \mathbb{R}_G \times \mathbb{P}_G + \mathbb{R} \times \mathbb{P} = \mathbb{L}_G + \mathbb{L}$$

O Átomo do Hidrogênio

(SI)

$m_p = 1.6726 \times 10^{-27}$ Kg

$m_e = 0.9109 \times 10^{-30}$ Kg

$q = 1.6022 \times 10^{-19}$ C

$\varepsilon_0 = 8.854 \times 10^{-12} \ \frac{\text{Farad}}{\text{m}}$

$\mu = \frac{m_p m_e}{m_p + m_e} = 0.9104 \times 10^{-30}$ Kg

$$V(r) = -\frac{q^2}{4\pi\varepsilon_0} \frac{1}{r} \equiv -\frac{e^2}{r}$$

$$e^2 = \frac{q^2}{4\pi\varepsilon_0}$$

Campo Elétrico de 1 elétron à um metro:

$$\bar{E} = \frac{1}{4\pi\varepsilon_0} \frac{q}{r^2} = 1,44 \times 10^{-9} \ V/m$$

Campo Elétrico de 1 Coulomb à um metro:

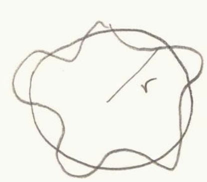
$$E = 8,99 \times 10^{9} \ V/m$$

Modelo de Bohr

- $E = \frac{1}{2} \mu v^2 - \frac{e^2}{r}$

- movimento circular $\mu \frac{v^2}{r} = \frac{e^2}{r^2}$

- quantização do momento angular:



$\lambda = \frac{h}{p}$

$$2\pi r = n\lambda = \frac{n 2\pi \hbar}{\mu v}$$

$$\downarrow$$

$$\boxed{\mu v r = n\hbar}$$

$$\downarrow$$

$$L = n\hbar$$

$\mu v r = n\hbar$

$\mu v^2 = \frac{e^2}{r} \rightarrow \quad r = \frac{e^2}{\mu v^2} \qquad \cancel{\mu}\cancel{v}\frac{e^2}{\mu v^2} = n\hbar$

$v = \frac{e^2}{n\hbar}$ ou $\boxed{v_n = \frac{v_0}{n} \; ; \quad v_0 = e^2/\hbar}$

$r = \frac{e^2}{\mu v^2} = \frac{e^2 n^2 \hbar^2}{\mu e^4} \rightarrow \boxed{r_n = a_0 n^2 \qquad a_0 = \frac{\hbar^2}{\mu e^2}}$

$$E = \frac{\mu}{2}\frac{v_0^2}{n^2} - \frac{e^2}{a_0 n^2} = \frac{1}{n^2}\left[\frac{\mu}{2}\cdot\frac{e^4}{\hbar^2} - \frac{e^2 \mu e^2}{\hbar^2}\right] = -\frac{1}{2}\frac{e^4\mu}{\hbar^2 n^2}$$

$$\boxed{E_n = -\frac{E_I}{n^2} \qquad E_I = \frac{e^4\mu}{2\hbar^2}}$$

$a_0 = 0.52\ \text{Å} =$ raio de Bohr

$E_I = 13.6\ \text{eV}$

$v_0 = 3{,}8 \times 10^5\ \text{m/s} = 380\ \text{km/s}$

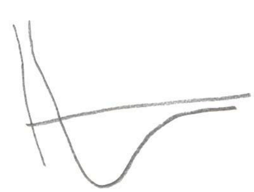
$\frac{v_0}{c} = 0{,}0013$

SOLUÇÃO DA EQUAÇÃO RADIAL

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r}\right]\varphi(\mathbf{r}) = E\,\varphi(\mathbf{r})$$

$$\varphi_{k,l,m}(\mathbf{r}) = \frac{u_{kl}(r)}{r} Y_l^m(\theta,\varphi)$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u_{k,l} + \underbrace{\left(\frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right)}_{}u_{k,l} = E_{k,l}\,u_{k,l}$$



$\rightarrow E < 0$ estados ligados

$E > 0$ " de espalhamento

Novas variáveis

$$\rho = r/a_0 = \frac{\mu e^2 r}{\hbar^2} \qquad a_0 = \hbar^2/\mu e^2 \simeq 0.52\ \text{Å} = \text{raio de Bohr}$$

$$\lambda_{k,l}^2 = -\frac{E_{k,l}}{E_I} = -\frac{E_{k,l}\cdot 2\hbar^2}{e^4\mu} \qquad E_I = \frac{e^4\mu}{2\hbar^2} \simeq 13.6\ eV = \text{energia de ionização.}$$

$$\left[-\frac{\hbar^2}{2\mu a_0^2}\frac{d^2}{d\rho^2} + \frac{l(l+1)\hbar^2}{a_0^2 2\mu\rho^2} - \frac{e^2}{a_0\rho}\right]u_{k,l} = -E_I\lambda_{k,l}^2 u$$

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{e^2 2\mu a_0}{\hbar^2\,\rho}\right]u_{k,l} = +\frac{e^4\mu}{2\hbar^2}\cdot\frac{2\mu}{\hbar^2}\,\cancel{\frac{\hbar^4}{\mu^2e^4}}\,\lambda_{k,l}^2\, u$$

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

COMP. no infinito

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

$$u_{k,l}(\rho) \equiv e^{-\lambda_{k,l}\rho}\, y_{k,l}(\rho)$$

$$\frac{du}{d\rho} = \left[-\lambda_{k,l}\, y + \frac{dy_{k,l}}{d\rho}\right]e^{-\lambda_{k,l}\rho}$$

$$\frac{d^2u}{d\rho^2} = \left[-2\lambda_{k,l}\frac{dy}{d\rho} + \frac{d^2y_{k,l}}{d\rho^2} + \lambda_{k,l}^2\, y\right]e^{-\lambda_{k,l}\rho}$$

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

Solução por série

$$y(\rho) = \rho^s \sum_{q=0}^{\infty} C_q \rho^q \qquad \boxed{C_0 \neq 0}$$

$$y'' = \sum_{q=0}^{\infty} (q+s)(q+s-1) C_q \rho^{q+s-2}$$

$$y' = \sum_{q=0}^{\infty} (q+s) C_q \rho^{q+s-1}$$

$$\frac{l(l+1) y}{\rho^2} = \sum_0^{\infty} l(l+1) C_q \rho^{q+s-2}$$

$$\frac{2y}{\rho} = \sum_0^{\infty} 2 C_q \rho^{q+s-1}$$

$\boxed{s-2}$ $$s(s-1) C_0 - l(l+1) C_0 = 0 \qquad s(s-1) = l(l+1)$$

$$\Rightarrow \boxed{s = l+1}$$

$s=-l$ não pode porque y deve ser regular na origem.

potência geral ρ^{q+s-2}

$$(q+s)(q+s-1) C_q - 2\lambda(q-1+s) C_{q-1} - l(l+1) C_q + 2 C_{q-1} = 0$$

$$C_q\left[(q+s)(q+s-1) - l(l+1)\right] = C_{q-1}\left[2\lambda(q-1+s) - 2\right]$$

$$C_q\left[(q+l+1)(q+l) - l(l+1)\right] = 2 C_{q-1}\left[\lambda(q+l) - 1\right]$$

$$C_q\left[lq + q(q+l+1)\right] = \text{''}$$

$$\boxed{q\left[q+2l+1\right] C_q = 2\left[\lambda(q+l)-1\right] C_{q-1}}$$

$$C_q = \frac{2\left[\lambda(q+l)-1\right]}{q\left[q+2l+1\right]} C_{q-1}$$

p/ $q \to \infty$

$$\lim_{q\to\infty} \frac{c_q}{c_{q-1}} = \frac{2\left[\lambda(q+\ell)-1\right]}{q\left[q+2\ell+1\right]} \longrightarrow \frac{2\lambda}{q}$$

Note que $\quad e^{2\lambda\rho} = \sum_{n=0}^{\infty} \frac{(2\lambda\rho)^n}{n!} \equiv \sum d_n \rho^n \quad ; \quad d_n = \frac{(2\lambda)^n}{n!}$

e $\quad \frac{d_n}{d_{n-1}} = \frac{(2\lambda)^n}{n!} \cdot \frac{(n-1)!}{(2\lambda)^{n-1}} = \frac{2\lambda}{n}$

Assim $\; y(q) \rightsquigarrow e^{2\lambda\rho}$, que diverge mesmo quando multiplicado por $e^{-\lambda\rho}$. Temos que truncar a série p/ garantir convergência:

Impondo que $\quad \boxed{\lambda = \frac{1}{k+\ell}} \qquad k$ inteiro

vemos que $\quad C_k = C_{k+1} = \dots = 0$. Como $C_0 \neq 0$, $k \geq 1$.

Lembrando a relação de λ com E obtemos

$$E_{k,\ell} = \frac{-E_I}{(k+\ell)^2} \qquad \text{ou} \qquad \boxed{n = k+\ell}$$

$$\boxed{E_n = -\frac{E_I}{n^2}}$$

$n=1 \longrightarrow k=1, \; \ell=0$

$n=2 \longrightarrow k=2, \; \ell=0 \quad$ ou $\quad k=1, \; \ell=1$

etc

$\boxed{\text{Para cada } n, \quad \ell = 0, 1, \dots, n-1}$

As funções de onda ficam:

$$y_{k,l}(\rho) = \rho^{l+1} \sum_{q=0}^{k-1} c_q \rho^q$$

$$u(\rho) = e^{-\lambda\rho}\, y(\rho) \quad , \quad \lambda = 1/n \quad e \quad k = n-l$$

$$\boxed{R_{n,l}(r) = \frac{e^{-r/na_0}}{r} \left(\frac{r}{a_0}\right)^{l+1} \sum_{q=0}^{n-l-1} c_q \left(\frac{r}{a_0}\right)^q}$$

O coeficiente c_0 é determinado por normalização.

Exemplo 1 $\quad n=1, \; l=0 \qquad R_{1,0}(r) = \dfrac{e^{-r/a_0}}{r}\left(\dfrac{r}{a_0}\right) c_0 = \dfrac{c_0}{a_0} e^{-r/a_0}$

$$1 = \int_0^\infty r^2 |R_{10}|^2 dr = \frac{c_0^2}{a_0^2}\int_0^\infty r^2 e^{-2r/a_0} dr = \frac{c_0^2 a_0}{8} \underbrace{\int_0^\infty x^2 e^{-x} dx}_{=2}$$

(veja adiante)

$$= \frac{c_0^2 a_0}{4} \quad e \quad c_0 = \frac{2}{\sqrt{a_0}} \quad ;$$

$$\boxed{R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}}$$

$$\Psi_{1,0,0}(r,\theta,\varphi) = R_{10}(r)\, Y_{00}(\theta,\varphi) = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$$

Exemplo 2

$n=2, \quad l=1$

$$R_{21}(r) = \frac{e^{-r/2a_0}}{r}\left(\frac{r}{a_0}\right)^2 C_0 = \frac{C_0}{a_0^2}\, r\, e^{-r/2a_0}$$

$$1 = \int_0^\infty r^2 |R_{21}|^2 dr = \frac{C_0^2}{a_0^4}\int_0^\infty r^4 e^{-r/a_0} dr = C_0^2 a_0 \underbrace{\int_0^\infty x^4 e^{-x} dx}_{4!}$$

$$= 24\, a_0 C_0^2 \rightarrow \quad C_0 = \frac{1}{2\sqrt{6a_0}}$$

$$\boxed{R_{21}(r) = \frac{1}{2\sqrt{6a_0^3}}\left(\frac{r}{a_0}\right) e^{-r/2a_0}}$$

$$\Psi_{21m}(r,\theta,\varphi) = R_{21}(r)\, Y_{1m}(\theta,\varphi)$$

APÊNDICE $\quad I_n = \int_0^\infty x^n e^{-x} dx$

Temos que $I_0 = 1$. Integrando por partes:

$u = x^n \qquad du = n x^{n-1} dx$

$e^{-x} dx = dv \qquad v = -e^{-x}$

$$I_n = -x^n e^{-x}\Big|_0^\infty + n\int_0^\infty x^{n-1} e^{-x} dx = n I_{n-1}$$

$$I_n = n I_{n-1} = n(n-1) I_{n-2} = n(n-1)(n-2)\dots 2 I_1$$

$$\Rightarrow \boxed{I_n = n!}$$

A equação radial pode ser escrita em termos dos polinômios

$$L^{2\ell+1}_{n+\ell}(\rho) = \sum_{k=0}^{n-\ell-1} (-1)^{k+2\ell+1} \frac{[(n+\ell)!]^2 \rho^k}{(n-\ell-1-k)!\,(2\ell+1+k)!\,k!}$$

= polinômios Associados de Laguerre.

e

$$\boxed{R_{n\ell}(\rho) = \sqrt{\ } \, e^{-\rho/2} \rho_n^{\ell} L^{2\ell+1}_{n+\ell}(\rho_n)}$$; $\rho_n = 2\sqrt{\frac{2\mu|E|}{\hbar^2}}\, r = \frac{2\mu Z e^2 r}{4\pi\varepsilon_0 \hbar^2 n}$

$= \frac{2r}{na_0}$

Essas funções são normalizadas:

$$\int_0^\infty R_{n'\ell}(r) R_{n\ell}(r) r^2 dr = \delta_{nn'}$$

, forma que $\varphi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r) Y_{\ell m}(\theta,\varphi)$ satisfaz

$$\int \varphi^*_{n'\ell'm'}(r,\theta,\varphi)\, \varphi_{n\ell m}(r,\theta,\varphi)\, r^2 \sin\theta\, dr\, d\theta\, d\varphi = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}$$

Exemplos de Funções Radiais

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0}\, e^{-Zr/2a_0}$$

$$R_{30}(r) = 2\left(\frac{Z}{3a_0}\right)^{3/2}\left[1 - \frac{2Zr}{3a_0} + \frac{2Z^2r^2}{27a_0^2}\right] e^{-Zr/3a_0}$$

onde $$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \quad , \quad \text{de forma que } \rho = \frac{2Z}{n}\frac{r}{a_0}$$

A tabela 7.2, do livro de Eisberg-Resnick mostra algumas auto-funções completas.

DEGENERESCÊNCIAS

Os níveis de energia só dependem do número quântico $\underline{n}$. Existem portanto vários estados distintos com a mesma energia. Dizemos que esses estados são degenerados.

Vimos na página 8 que $-l \leq m \leq l$ e na página 11 que $n \geq l+1$, ou $l \leq n-1$. O número quântico $\underline{l}$ está relacionado ao momento angular, pois

$$\hat{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

O módulo do momento angular quântico é $\sqrt{\hbar^2 l(l+1)} = \hbar\sqrt{l(l+1)} \simeq \hbar l$ para $\underline{l}$ grande. O número quântico $\underline{m}$ está ligado à projeção de $\vec{L}$ no eixo z, pois como $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$,

$$\hat{L}_z Y_{lm} = \Theta_{lm}(\theta)\left(-i\hbar\frac{\partial}{\partial\varphi} e^{im\varphi}\right) = \hbar m Y_{lm}$$

Dado $\underline{n}$ temos $l = 0, 1, 2, \ldots, n-1$. O estado com $l = n-1$ tem momento angular máximo e veremos que é esfericamente simétrico. Para cada $\underline{l}$ $m = -l, -l+1, \ldots, l-1, l$. Como todos tem a mesma energia, a degenerescência do estado com energia E_n é

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

$$= 2\,(0 + n - 1)\,\frac{n}{2} + n = n^2$$

Exemplo Para $n = 3$ temos

$$\psi_{300},\ \psi_{310},\ \psi_{311},\ \psi_{31-1},\ \psi_{320},\ \psi_{321},\ \psi_{32-1},\ \psi_{322},\ \psi_{32-2}$$

DENSIDADE DE PROBABILIDADES

I - DENSIDADE RADIAL

$$P_{nl}(r)\,dr = \int_0^{\pi}\int_0^{2\pi} \psi^*_{nlm}(r,\theta,\varphi)\,\psi_{nlm}(r,\theta,\varphi)\, r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

$$= R^*_{nl}(r)\, R_{nl}(r)\, r^2\, dr \int_0^{\pi}\int_0^{2\pi} Y^*_{lm}(\theta,\varphi)\, Y_{lm}(\theta,\varphi)\, \sin\theta\, d\theta\, d\varphi$$

$$= r^2 R^*_{nl}(r)\, R_{nl}(r)\, dr$$

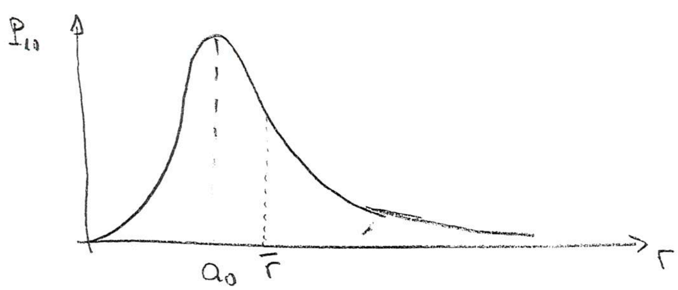
Exemplo: Para o estado fundamental ψ_{100}, e $Z = 1$

$$P_{10}(r) = r^2 \, 4\left(\frac{1}{a_0}\right)^3 e^{-2r/a_0} = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

Máximo: $\frac{\partial P_{10}}{\partial r} = 0 \Rightarrow 2r e^{-2r/a_0} - \frac{2r^2}{a_0} e^{-2r/a_0} = 0$ e $\boxed{r = a_0}$

Valor médio: $$\bar{r} = \int_0^\infty \frac{4r^3}{a_0^3} e^{-2r/a_0} dr = \frac{4}{a_0^3}\left(\frac{a_0}{2}\right)^4 \int_0^\infty u^3 e^{-u} du$$

$$= \frac{4 a_0^4}{16 a_0^3} \cdot 6 = \frac{3}{2} a_0$$



A figura 7.5 mostra algumas probabilidades radiais. Veja que a_0 = raio de Bohr. Pode-se mostrar que quando $l = n-1$ o máximo de $P_{n,l}$ ocorre em $a_0 n^2$, como previsto pelo velho modelo de Bohr para órbitas circulares.

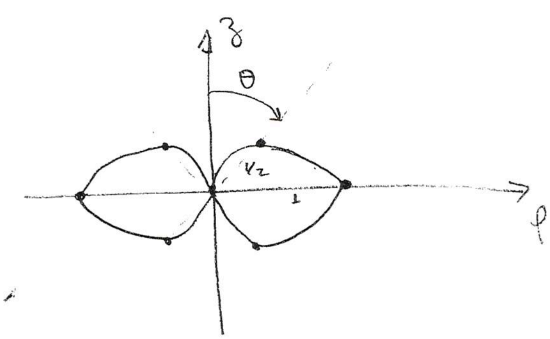
II – Densidade Angular

Podemos escrever

$$|\Psi_{\ell n m}(r,\theta,\varphi)|^2 = \underbrace{R^*_{n\ell}\, R_{n\ell}}_{\frac{P_{n\ell}}{r^2}}\ \underbrace{\Theta^*_{\ell m}(\theta)\, \Theta_{\ell m}(\theta)}_{f_{\ell m}(\theta)}\ \underbrace{e^{-im\varphi}\, e^{im\varphi}}_{1}$$

Para entender o papel de $f_{\ell m}(\theta)$ faremos gráficos polares. Como exemplo tomamos $f(\theta) = \sin^2\theta$. Para cada valor de θ calculamos $f(\theta)$ e marcamos esse valor como um raio no plano z-ρ:

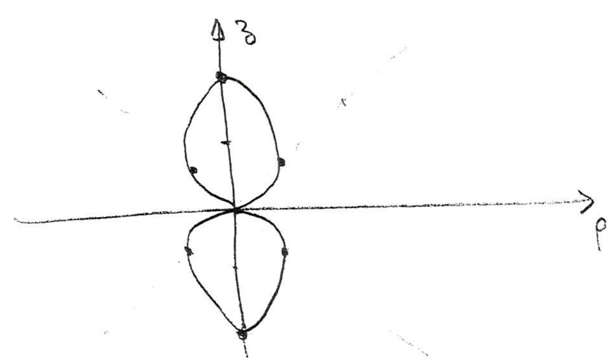
θ	$f(\theta)$
0	0
$\pi/4$	1/2
$\pi/2$	1
$3\pi/4$	1/2
π	0



os pontos são ligados entre si

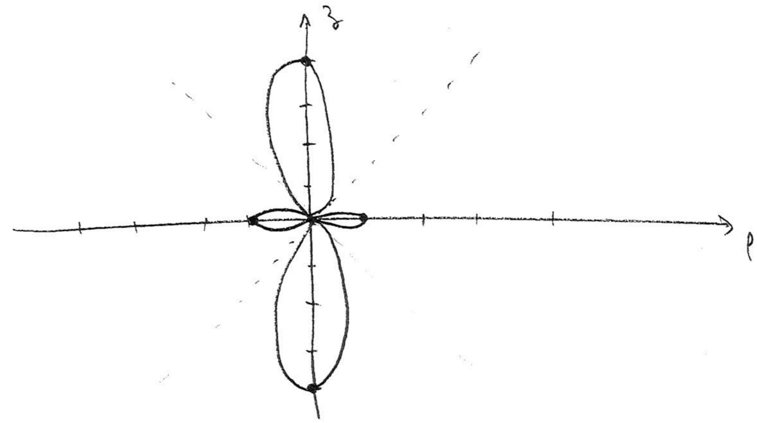
Para $f(\theta) = \cos^2\theta$ obtemos

θ	$f(\theta)$
0	1
$\pi/4$	1/2
$\pi/2$	0
$3\pi/4$	1/2
π	1



Para $f_{20}(\theta) = \Theta^{*}_{20}(\theta)\,\Theta_{20}(\theta) = (3\cos^2\theta - 1)^2 = \left(\frac{1}{2} + \frac{3}{2}\cos 2\theta\right)^2$

θ	f_{20}
0	4
45	1/4
70,5	0
90	1
109,5	0
135	1/4
180	4



A figura 7.8 mostra mais configurações, e a 7.10 mostra a combinação da densidade radial com a angular para alguns estados.

Para obter a distribuição de probabilidades completa (os orbitais) devemos girar a figura em torno do eixo z, formando uma superfície de revolução, e depois multiplicar pela probabilidade radial.

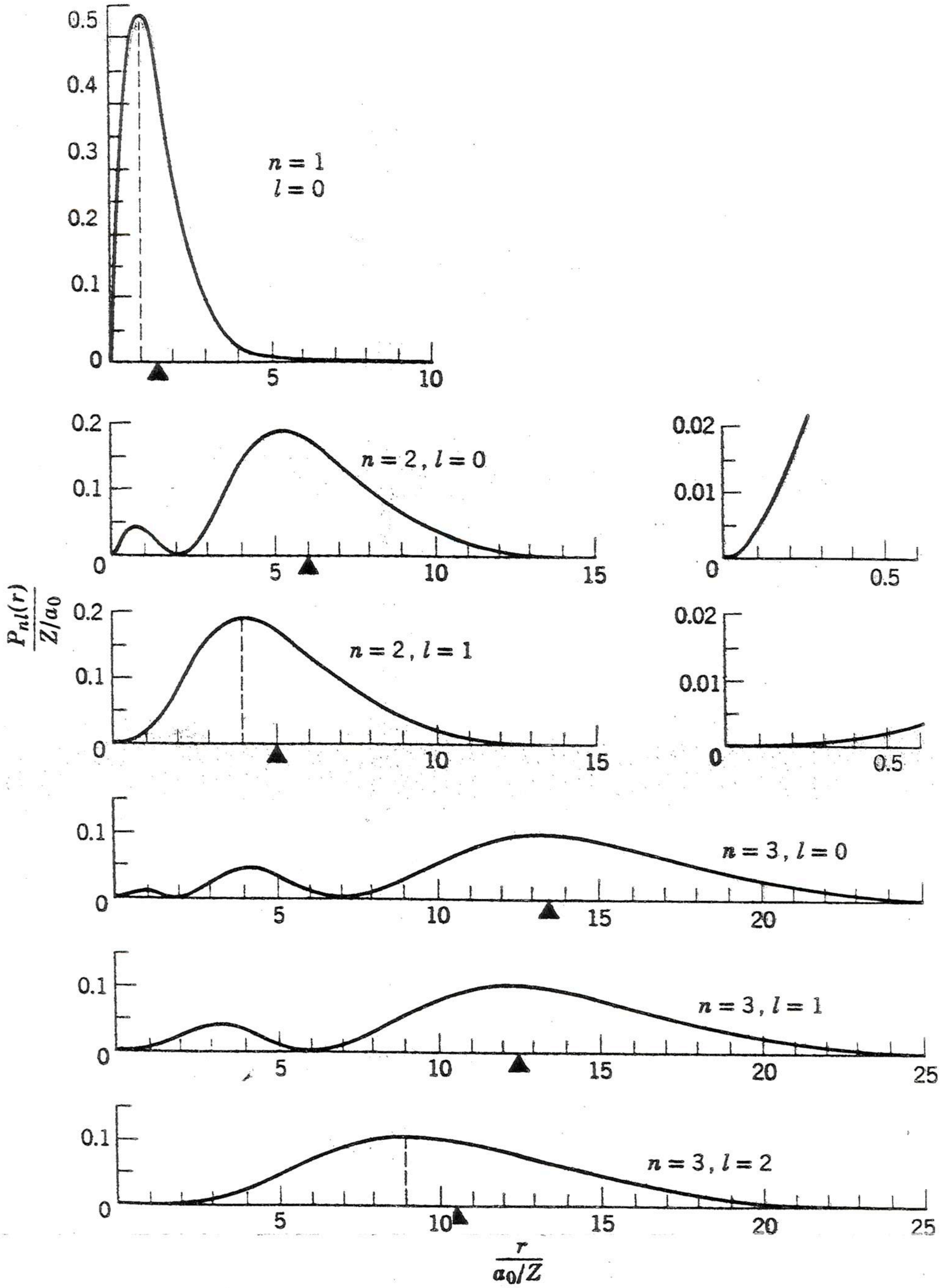


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of l shown. The triangle on each abscissa indicates the value of $\overline{r_{nl}}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{Bohr} = n^2 a_0/Z$, which is indicated by the location of the dashed line.

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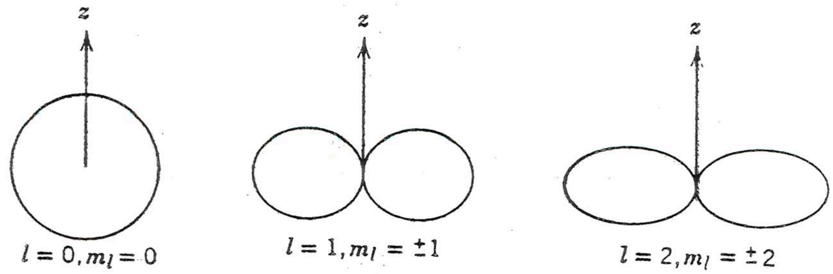
Table 7-2 Some Eigenfunctions for the One-Electron Atom

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



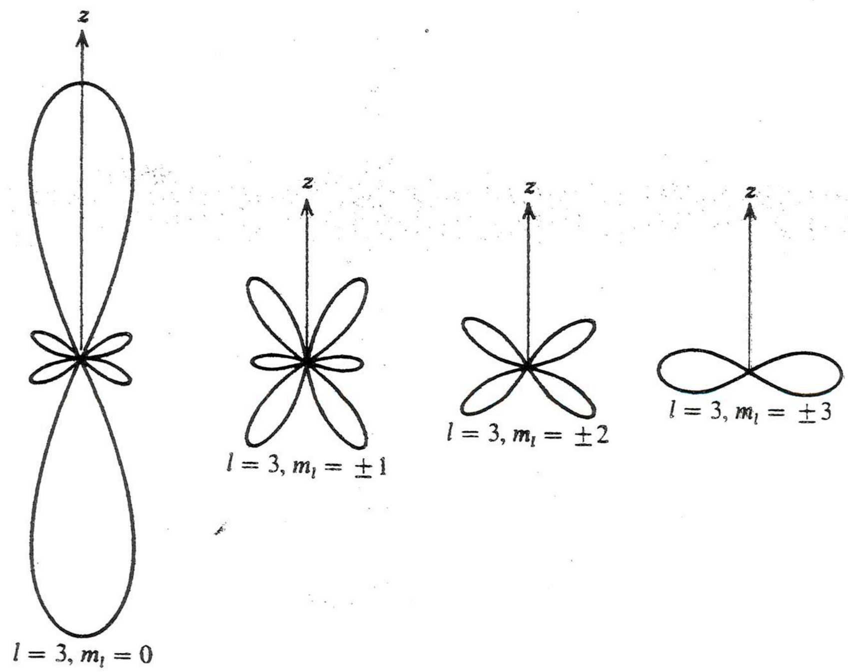


Figure 7-8 Polar diagrams of the directional dependence of the one-electron atom probability densities for $l = 3$; $m_l = 0, \pm 1, \pm 2, \pm 3$.

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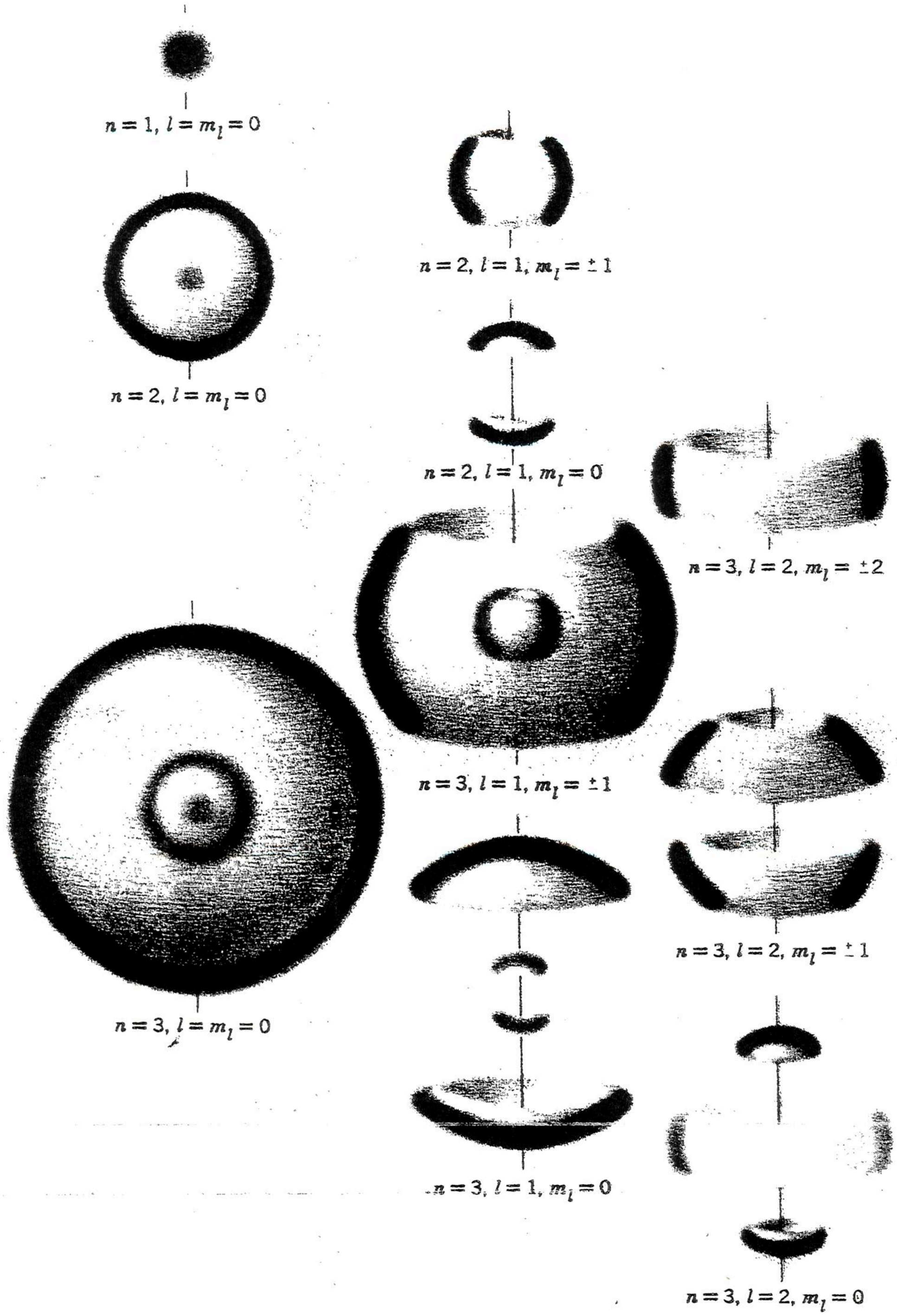

Figure 7-10 An artist's conception of the three-dimensional appearance of several one-electron atom probability density functions. For each of the drawings a line represents the z axis. If all the probability densities for a given n and l are combined, the result is spherically symmetrical.

Coordenadas Cilíndricas

$$\nabla V = \frac{\partial V}{\partial \rho}\hat{\rho} + \frac{1}{\rho}\frac{\partial V}{\partial \varphi}\hat{\varphi} + \frac{\partial V}{\partial z}\hat{z}$$

$$\nabla \cdot \vec{u} = \frac{1}{\rho}\left[\frac{\partial}{\partial \rho}(\rho u_\rho) + \frac{\partial}{\partial \varphi}(u_\varphi) + \frac{\partial}{\partial z}(\rho u_z)\right]$$

$$\nabla^2 V = \frac{1}{\rho}\left[\frac{\partial}{\partial \rho}\left(\rho\frac{\partial V}{\partial \rho}\right) + \frac{\partial}{\partial \varphi}\left(\frac{1}{\rho}\frac{\partial V}{\partial \varphi}\right) + \frac{\partial}{\partial z}\left(\rho\frac{\partial V}{\partial z}\right)\right]$$

Coordenadas Esféricas

$$\nabla V = \frac{\partial V}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial V}{\partial \theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial V}{\partial \varphi}\hat{\varphi}$$

$$\nabla \cdot \vec{u} = \frac{1}{r^2\sin\theta}\left[\frac{\partial}{\partial r}(r^2\sin\theta\, u_r) + \frac{\partial}{\partial \theta}(r\sin\theta\, u_\theta) + \frac{\partial}{\partial \varphi}(r u_\varphi)\right]$$

$$\nabla^2 V = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial V}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial V}{\partial \varphi}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 V}{\partial \varphi^2}$$

Como calcular: gradiente em cilíndricas

$$\nabla V \cdot d\mathbf{r} = dV = \frac{\partial V}{\partial \rho}d\rho + \frac{\partial V}{\partial \varphi}d\varphi + \frac{\partial V}{\partial z}dz$$

$$\mathbf{r} = \rho\hat{\rho} + z\hat{z} \quad ; \quad d\mathbf{r} = d\rho\,\hat{\rho} + \rho\frac{d\hat{\rho}}{d\varphi} + dz\,\hat{z} = d\rho\,\hat{\rho} + \rho\, d\varphi\,\hat{\varphi} + dz\,\hat{z}$$

$$\Rightarrow \nabla V = \frac{\partial V}{\partial \rho}\hat{\rho} + \frac{1}{\rho}\frac{\partial V}{\partial \varphi}\hat{\varphi} + \frac{\partial V}{\partial z}\hat{z}$$

Espaços Produto

Se $\mathcal{E}_1$ e $\mathcal{E}_2$ são dois espaços com bases $|\varphi^1_n\rangle$ e $|\varphi^2_n\rangle$, o espaço produto $\mathcal{E} = \mathcal{E}_1 \otimes \mathcal{E}_2$ tem kets da forma

$$|\psi\rangle = \sum_{nm} c_{nm} |\varphi^1_n\rangle \otimes |\varphi^2_m\rangle \equiv \sum_{n,m} c_{nm} |\varphi^1_n, \varphi^2_m\rangle$$

Na representação $|\mathbf{r}_1\rangle \otimes |\mathbf{r}_2\rangle \equiv |\mathbf{r}_1, \mathbf{r}_2\rangle$

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \psi\rangle = \sum_{nm} c_{nm} \varphi^1_n(\mathbf{r}_1)\, \varphi^2_m(\mathbf{r}_2)$$

Operadores de $\mathcal{E}_1$ são levados à $\mathcal{E}$ da forma natural:

$$\mathcal{O}_1 \in \mathcal{E}_1 \longmapsto \mathcal{O}_1 = \mathcal{O}_1 \otimes \mathbb{1} \in \mathcal{E}$$

$$\Rightarrow \quad \mathcal{O}_1 |\psi\rangle = \sum_{nm} c_{nm} \left[\mathcal{O}_1 |\varphi^1_n\rangle\right] \otimes |\varphi^2_m\rangle .$$

Em particular, se

$$H_1 |\xi^1_k\rangle = \epsilon^1_k |\xi^1_k\rangle$$
$$H_2 |\xi^2_k\rangle = \epsilon^2_k |\xi^2_k\rangle$$

$H = H_1 \otimes \mathbb{1} + \mathbb{1} \otimes H_2$ tem auto-funções $|\xi_{k\ell}\rangle = |\xi^1_k\rangle \otimes |\xi^2_\ell\rangle$

e auto-valores $\epsilon_{k\ell} = \epsilon^1_k + \epsilon^2_\ell$