

VIII - 1) Átomo de Hidrogênio

MARCUS AGUIAR

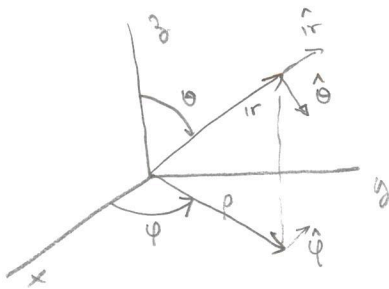
Forças Centrais: $\mathbf{F}(\mathbf{r}) = F(r) \hat{\mathbf{r}} = -\nabla V(r) = -\frac{dV}{dr} \hat{\mathbf{r}}$

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

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

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

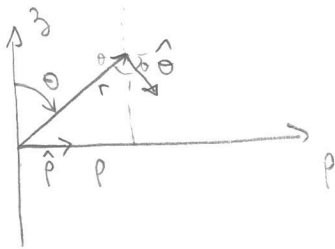
Hamiltonian em Coordenadas Esféricas



$$\begin{cases} x = r \sin\theta \cos\phi \\ y = r \sin\theta \sin\phi \\ z = r \cos\theta \end{cases}$$

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \tan\phi = y/x \\ \tan\theta = \sqrt{x^2 + y^2} / z \end{cases}$$

$$\hat{\mathbf{r}} = \sin\theta \cos\phi \hat{\mathbf{x}} + \sin\theta \sin\phi \hat{\mathbf{y}} + \cos\theta \hat{\mathbf{z}}$$



$$\begin{aligned} \hat{\theta} &= \cos\theta \hat{\rho} - \sin\theta \hat{z} \\ \hat{\rho} &= \cos\phi \hat{x} + \sin\phi \hat{y} \end{aligned}$$

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

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

$$\begin{aligned} \mathbf{r} &= r \hat{\mathbf{r}} \quad ; \quad \dot{\mathbf{r}} = \dot{r} \hat{\mathbf{r}} + \frac{d\hat{\mathbf{r}}}{dt} = \dot{r} \hat{\mathbf{r}} + r(\omega_\theta \cos\phi, \omega_\theta \sin\phi, -\dot{\theta}) \hat{\theta} \\ &\quad + r(-\dot{\phi} \sin\phi, \dot{\phi} \cos\phi, 0) \hat{\phi} \\ &= \dot{r} \hat{\mathbf{r}} + r \dot{\theta} \hat{\theta} + r \sin\theta \dot{\phi} \hat{\phi} \end{aligned}$$

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

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

Moments

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

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

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

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

Note que $L = |\mu r \times v| = \mu r v_\perp =$

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

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

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

ou

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

A Hamiltoniana Quântica

(3)

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

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

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

Como vimos os operadores V , $L^2 = -\hbar^2 \left[\quad \right]$ e assim

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

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

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 $\psi(r, \theta, \varphi)$ que são auto-funções dos 3 operadores:

$$H\psi = E\psi$$

$$L^2\psi = \hbar^2 l(l+1)\psi$$

$$L_z\psi = \hbar m\psi$$

As auto-funções de L^2 e L_3 são do tipo $Y_{\ell}^m(0, \varphi) \Rightarrow$

(4)

$$\psi(r) = R(r) Y_{\ell}^m(0, \varphi) \quad \text{e} \quad H\psi = E\psi \Rightarrow$$

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

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

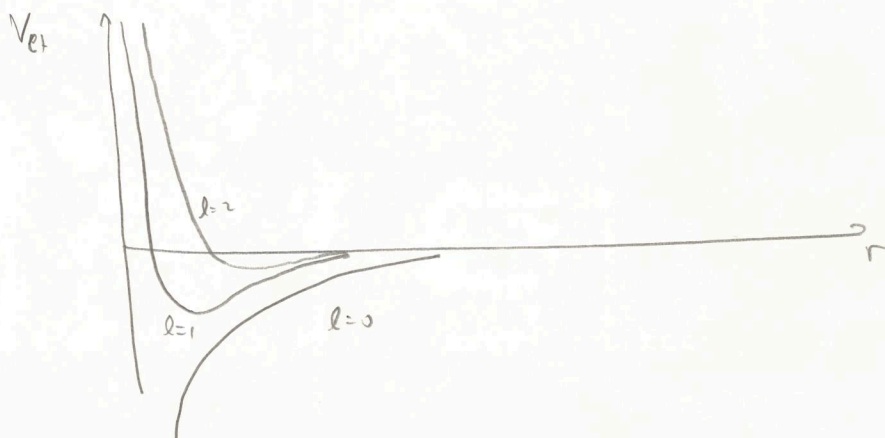
Mudança de variáveis

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

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

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

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



- Componentes próximos da origem

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

$$\frac{1}{r} \frac{d^2}{dr^2} r R \rightarrow C(s+1)s r^{s-2}$$

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

Se $V(r) \xrightarrow{r \rightarrow 0} \sim \frac{1}{r}$ ou vai a infinito ainda mais devagar, $\hbar \omega$

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

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

$$\downarrow$$

$$U_{k,l}(r) \sim C r^{l+1} \quad \text{e} \quad \forall r \rightarrow 0 \quad \boxed{U_{k,l}(0) = 0}$$

AUTOFUNÇÕES

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

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

$\int r^2 d\Omega dr |\Psi_{k,l,m}|^2 = 1$
 $\int r^2 |R_{k,l}|^2 dr = \delta_{k,k'}$
 $\int |U_{k,l}|^2 dr = \delta_{k,k'}$

$$\int_0^\infty r^2 |R_{k,l}(r)|^2 dr = \int_0^\infty |U_{k,l}(r)|^2 dr = 1$$

Se as funções forem de quadrado integrável.

Se k for um índice contínuo, então

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

Como $U(0) = 0$ as integrais convergem se $\int_0^\infty U_{k',l}^*(r) U_{k,l}(r) dr$. A divergência ocorre devido ao...

- Degenerações

- se k e l fixos, $E_{k,l}$ fixo, existe $2l+1$ funções

$\psi_{k,l,m}(r)$ com mesma energia $E_{k,l} \rightarrow$ degen. essencial
(invariância de V por rotações)

- se ocorrer $E_{k',l'} = E_{k,l} \rightarrow$ degen. acidental

PROVA: 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 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- H, L^2, L_z formam um CCOO

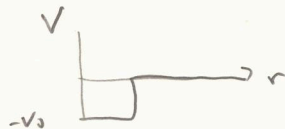
Fixando $E_{k,l}$, l , m , só existe uma auto-função:

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

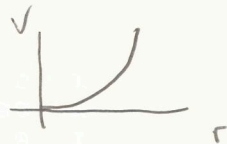
Exemplos

a) $V = 0 \rightarrow$ (funções de Bessel esféricas)

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



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



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



Movimento Relativo e do Centro de Massa

(7)

Mecânica Clássica : $\mathcal{L} = \frac{m_1 \dot{r}_1^2}{2} + \frac{m_2 \dot{r}_2^2}{2} - V(|r_1 - r_2|)$

$$\begin{cases} R_G = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \\ r = r_1 - r_2 \end{cases} \rightarrow \begin{cases} r_1 = R_G + \frac{m_2 r}{m_1 + m_2} \\ r_2 = R_G - \frac{m_1 r}{m_1 + m_2} \end{cases}$$

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

$$\begin{aligned} \mathcal{L} &= \frac{m_1}{2} \left(\dot{r}_G - \frac{m_2 \dot{r}}{M} \right)^2 + \frac{m_2}{2} \left(\dot{r}_G + \frac{m_1 \dot{r}}{M} \right)^2 - V(r) \\ &= \frac{M}{2} \dot{r}_G^2 + \frac{\mu}{2} \dot{r}^2 - V(r) \end{aligned}$$

$$\begin{cases} P_G = \frac{\partial \mathcal{L}}{\partial \dot{r}_G} = M \dot{r}_G = m_1 \dot{r}_1 + m_2 \dot{r}_2 = P_1 + P_2 = \text{momento total.} \\ P_r = \mu \dot{r} = \frac{\mu}{m_1} P_1 - \frac{\mu}{m_2} P_2 \end{cases}$$

$$\begin{cases} P_1 = \frac{\mu}{m_2} P_G + P_r \\ P_2 = \frac{\mu}{m_1} P_G - P_r \end{cases}$$

$$\mathcal{H} = \frac{P_G^2}{2M} + \frac{P_r^2}{2\mu} + V(r)$$

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

$$[X_1, P_{x_1}] = i\hbar$$

$$[X_2, P_{x_2}] = i\hbar \quad \text{etc}$$

$$\begin{cases} R_G = \frac{m_1 R_1 + m_2 R_2}{M} \\ P_G = P_1 + P_2 \end{cases} \quad \begin{cases} R = R_1 - R_2 \\ P = \frac{P_1}{m_1} - \frac{P_2}{m_2} \end{cases}$$

$$[X, P_x] = [X_1 - X_2, \frac{P_1}{m_1} - \frac{P_2}{m_2}] = \frac{P_1}{m_1} i\hbar + \frac{P_2}{m_2} i\hbar$$

$$= i\hbar \mu \frac{m_1 m_2}{m_1 m_2} = i\hbar$$

$$[X_G, P_{x_G}] = [\frac{m_1}{M} X_1 + \frac{m_2}{M} X_2, P_{x_1} + P_{x_2}] = \frac{m_1}{M} i\hbar + \frac{m_2}{M} i\hbar = i\hbar$$

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

$$[H_G, H_R] = 0 \Rightarrow$$

$$H_G |\psi\rangle = E_G |\psi\rangle$$

$$H_R |\psi\rangle = E_R |\psi\rangle$$

$$E = E_R + E_G$$

representação $|r_G, r\rangle \rightarrow \langle r_G, r | \psi \rangle \Rightarrow$ função de 6 variáveis

espaço $E = E_G \otimes E_R$

$$|\psi\rangle = |\chi_G\rangle \otimes |w_r\rangle$$

$$\begin{cases} H_G |\chi_G\rangle = E_G |\chi_G\rangle \\ H_R |w_r\rangle = E_R |w_r\rangle \end{cases}$$

$$\psi(r_G, r) = \langle r_G | \chi_G \rangle \langle r | w_r \rangle$$

$$-\frac{\hbar^2}{2M} \nabla_G^2 \chi_G = E_G \chi_G \rightarrow \chi_G(r_G) = \frac{1}{(m\hbar)^{3/2}} e^{\frac{i}{\hbar} p_G \cdot r_G}$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla_r^2 + V(r) \right] w(r) = E_R w(r)$$

OBS:

$$H|\psi\rangle = (H_G + H_R) [|\chi_G\rangle \otimes |w_r\rangle] = (H_G |\chi_G\rangle) \otimes |w_r\rangle + |\chi_G\rangle \otimes (H_R |w_r\rangle) = (E_G + E_R) |\psi\rangle$$

momento angular

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

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

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

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

O ÁTOMO DE HIDROGÊNIO

(SI)

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

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

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

$$\epsilon_0 = 8.854 \times 10^{-12} \frac{\text{Farad}}{\text{m}}$$

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

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

$$e^2 = \frac{q^2}{4\pi\epsilon_0}$$

Campo Elétrico de 1 elétron a um metro:

$$E = \frac{1}{4\pi\epsilon_0} \frac{q}{r^2} = 1,44 \times 10^9 \text{ V/m}$$

Campo Elétrico de 1 Coulomb a um metro:

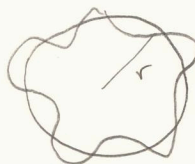
$$E = 8,99 \times 10^9 \text{ V/m}$$

Modelo de Bohr

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

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

- quantização do momento angular:



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

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

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

$$L = n \hbar$$

$$\mu v r = n \hbar$$

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

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

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

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

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

$$a_0 = 0.52 \text{ \AA} = \text{raio d Bohr}$$

$$E_I = 13.6 \text{ eV}$$

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

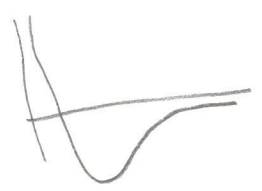
$$\frac{v_0}{c} = 0,0013$$

SOLUÇÃO DA EQUAÇÃO RADIAL

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

$$\psi_{k,l,m}(r) = \frac{u_{k,l}(r)}{r} Y_l^m(\theta, \phi)$$

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



$\rightarrow E < 0$ estados ligados
 $E > 0$ " " " " estados desligados

Novas variáveis

$$\rho = r/a_0 = \frac{\mu e^2 r}{\hbar^2}$$

$$a_0 = \hbar^2 / \mu e^2 \approx 0.52 \text{ \AA} = \text{raio de Bohr}$$

$$\lambda_{k,l}^2 = -\frac{E_{k,l}}{E_I} = -\frac{E_{k,l}}{e^2 \mu} \cdot \frac{2\hbar^2}{\hbar^2}$$

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

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

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

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

COMP. NO INFINITO

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

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

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

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

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

Soluções por série

$$y(p) = p^s \sum_{q=0}^{\infty} C_q p^q$$

$$C_0 \neq 0$$

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

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

$$\frac{l(l+1)y}{p^2} = \sum_{q=0}^{\infty} l(l+1) C_q p^{q+s-2}$$

$$\frac{2y}{p} = \sum_{q=0}^{\infty} 2 C_q p^{q+s-1}$$

$s=1$

$$s(s-1) C_0 - l(l+1) C_0 = 0$$

$$s(s-1) = l(l+1)$$

$$\Rightarrow s = l+1$$

$s = -l$ não pode porque y deve ser regular no origem.

relação geral p^{q+s-1}

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

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

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

$$C_q [lq + q(q+l+1)] = \dots$$

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

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

Pl $q \rightarrow \infty$

$$\lim_{q \rightarrow \infty} \frac{c_q}{c_{q+1}} = \frac{2 [\lambda(q+l) - 1]}{q [q + 2l + 1]} \rightarrow \frac{2\lambda}{q}$$

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

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

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

Impondo que $\lambda = \frac{1}{k+l}$ k inteiro

vemos que $c_k = c_{k+1} = \dots = 0$. Como $c_0 \neq 0$, $k > 1$.

Lembrando a relação de λ com E obtemos

$$E_{k+l} = -\frac{E_I}{(k+l)^2} \quad \text{ou} \quad n = k+l$$

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

$n=1 \rightarrow k=1, l=0$
 $n=2 \rightarrow k=2, l=0$ ou $k=1, l=1$
 etc

Para cada n , $l=0, 1, \dots, n-1$

As funções de onda ficam:

$$y(\rho) = \rho^{l+1} \sum_{q=0}^{k-1} C_q \rho^q$$

$$u(\rho) = e^{-\lambda \rho} y(\rho), \quad \lambda = 1/a_0 \quad e \quad k = n - l$$

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

O coeficiente C_0 é determinado por normalização.

Exemplo 1 $n=1, l=0$ $R_{1,0}(r) = \frac{e^{-r/a_0}}{r} \left(\frac{r}{a_0}\right) C_0 = \frac{C_0}{a_0} e^{-r/a_0}$

$$1 = \int_0^{\infty} r^2 |R_{1,0}|^2 dr = \frac{C_0^2}{a_0^2} \int_0^{\infty} r^2 e^{-2r/a_0} dr = \frac{C_0^2 a_0}{8} \int_0^{\infty} x^2 e^{-x} dx$$

$\underbrace{\int_0^{\infty} x^2 e^{-x} dx}_{= 2}$
 (veja a tabela)

$$= \frac{C_0^2 a_0}{4} \quad e \quad C_0 = \frac{2}{\sqrt{a_0}} ;$$

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

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

Exemplo 2

$$n=2, \quad l=1$$

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

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

4!

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

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

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

APÊNDICE

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

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

$$u = x^n \quad du = n x^{n-1} dx$$
$$e^{-x} dx = dv \quad v = -e^{-x}$$

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

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

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

A equação radial pode ser escrita em termos dos polinômios

$$L_{n+l}^{2l+1}(p) = \sum_{k=0}^{n-l-1} (-1)^{k+2l+1} \frac{[(n+l)!]^2 p^k}{(n-l-1-k)! (2l+1+k)! k!}$$

= polinômios associados de Laguerre.

e

$$R_{nl}(r) = \sqrt{\frac{2}{a_0}} e^{-r/2a_0} \left(\frac{r}{a_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{a_0}\right)$$

$$; \quad p_n = 2 \sqrt{\frac{2k|E|}{\hbar^2}} \quad r = \frac{Z\mu Z e^2 r}{4\pi\epsilon_0 \hbar^2 n}$$

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

ESSAS funções são normalizadas:

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

forma que $\Psi_{n'l'm'}(r, \theta, \phi) = R_{n'l}(r) Y_{l'm'}(\theta, \phi)$ satisfaz

$$\int \Psi_{n'l'm'}^*(r, \theta, \phi) \Psi_{n''l''m''}(r, \theta, \phi) r^2 \sin\theta dr d\theta d\phi = \delta_{nn''} \delta_{ll''} \delta_{mm''}$$

Exemplos de Funções Radiais

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

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

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

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

onde $a_0 = 4\pi\epsilon_0 \frac{\hbar^2}{\mu e^2}$, 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 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 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 $\sqrt{\hbar^2 l(l+1)} = \hbar \sqrt{l(l+1)}$ e l para l grande.

O número quântico m está ligado à projeção de \vec{L} no eixo z , pois como $\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$,

$$\hat{L}_z Y_{lm} = \hat{L}_z^{(0)} \left(\Theta_{lm}(\theta) e^{im\varphi} \right) = \hbar m Y_{lm}$$

Dados n termos $l=0, 1, 2, \dots, n-1$, o estado com $l=n-1$ tem momento angular máximo e vemos que é esféricamente simétrico. Para cada l $m=-l, -l+1, \dots, l-1, l$, como todos tem a mesma energia, a degenerescência do estado com energia E_n é

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

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

Exemplos 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

$$P_{ne}(r) dr = \int_0^\pi \int_0^{2\pi} \Psi_{nem}^*(r, \theta, \varphi) \Psi_{nem}(r, \theta, \varphi) r^2 \sin\theta dr d\theta d\varphi$$

$$= R_{ne}^*(r) R_{ne}(r) r^2 dr \int_0^\pi \int_0^{2\pi} Y_{em}^*(\theta, \varphi) Y_{em}(\theta, \varphi) \sin\theta d\theta d\varphi$$

$$= r^2 R_{ne}^*(r) R_{ne}(r) dr$$

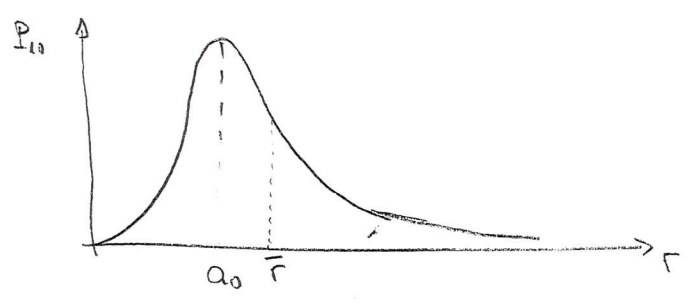
Exemplo Para o estado fundamental ψ_{100} , e $z=1$

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

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.

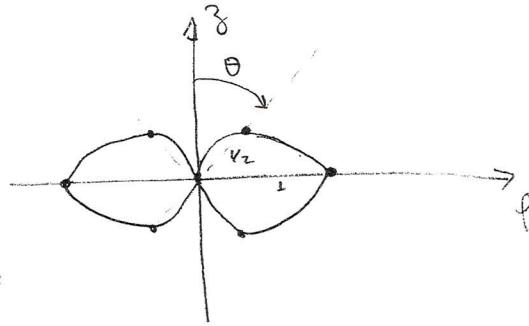
II - Densidade Angular

Podemos escrever

$$|\Psi_{lm}(r, \theta, \varphi)|^2 = \underbrace{R_{nl}^* R_{nl}}_{\frac{P_{nl}}{r^2}} \underbrace{\Theta_{lm}^*(\theta) \Theta_{lm}(\theta)}_{f_{lm}(\theta)} \underbrace{e^{-im\varphi} e^{im\varphi}}_1$$

Para entender o papel de $f_{lm}(\theta)$ 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 $z=0$:

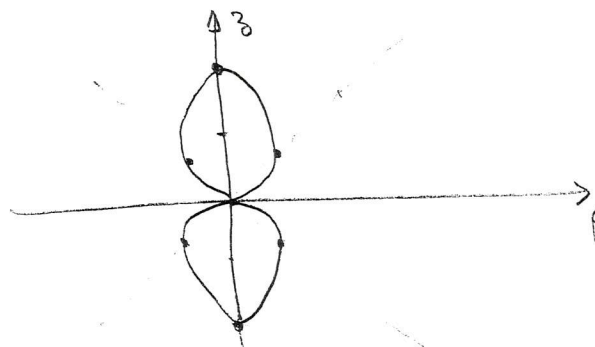
| θ | $f(\theta)$ |
|----------|-------------|
| 0 | 0 |
| $\pi/4$ | $1/2$ |
| $\pi/2$ | 1 |
| $3\pi/4$ | $1/2$ |
| π | 0 |



os pontos são ligados entre si

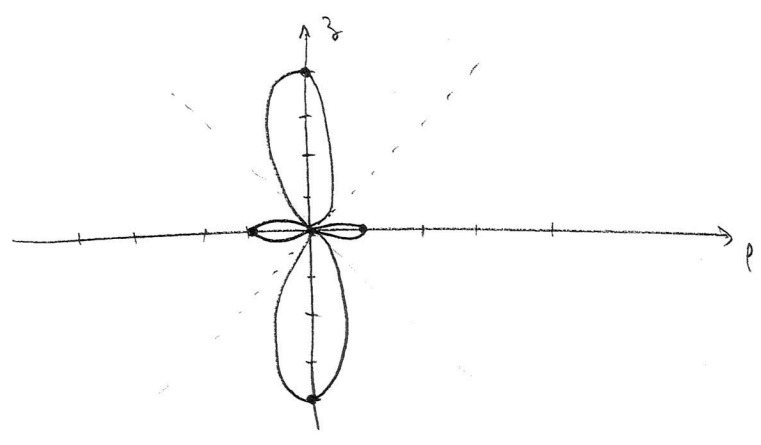
Para $f(\theta) = \cos^2 \theta$ obtemos

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



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

| 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 (ou orbitais) devemos girar a figura em torno do eixo z, formando uma superfície de revolução, e depois multiplicar pela probabilidade radial.

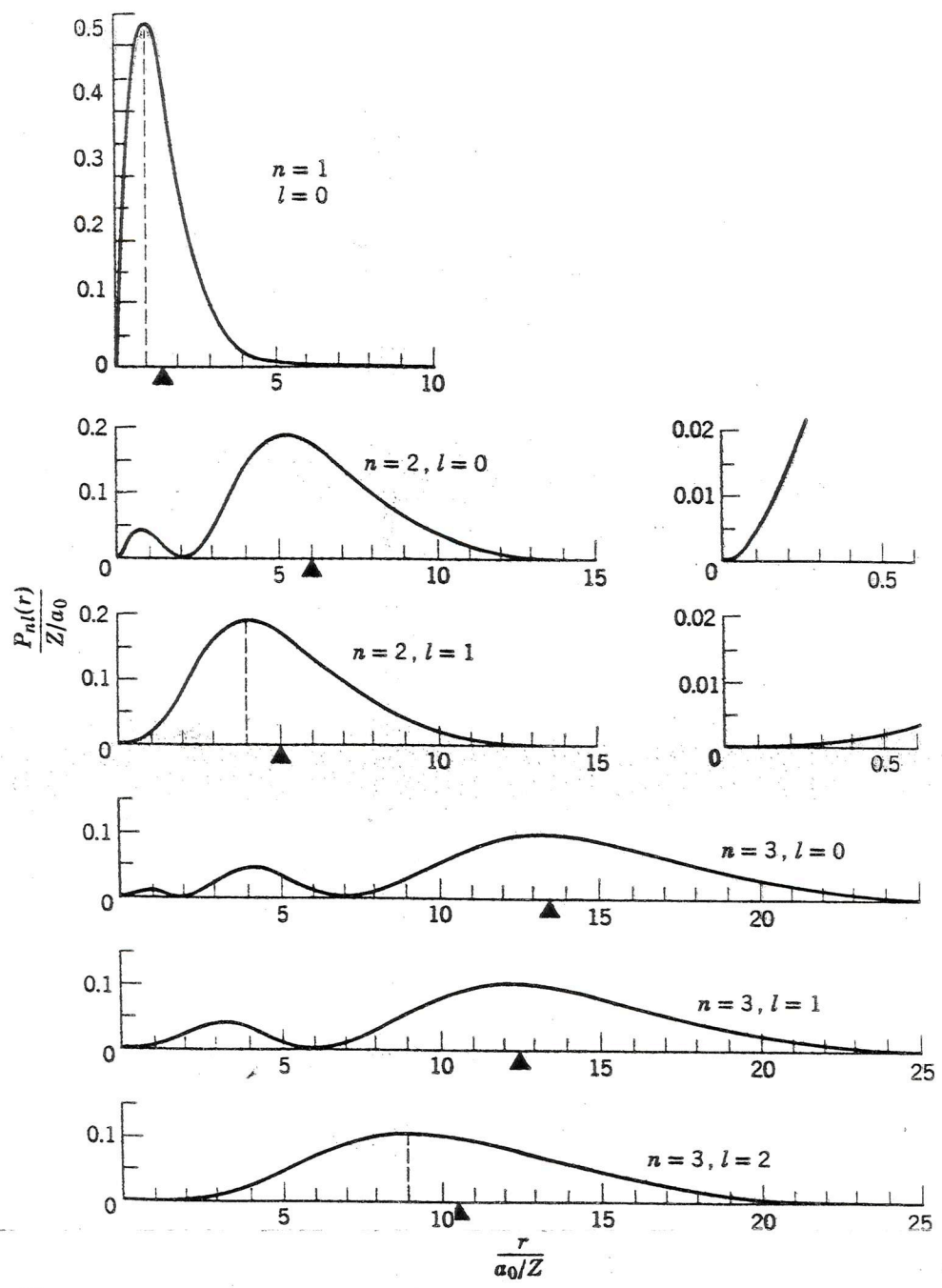


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of l shown. The triangle on each abscissa indicates the value of \bar{r}_{nl} as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor 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 $r_{\text{Bohr}} = n^2 a_0 / Z$, which is indicated by the location of the dashed line.

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

| Quantum Numbers | | Eigenfunctions |
|-----------------|------------|--|
| n | l, m_l | |
| 1 | 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 | $\psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\phi}$ |
| 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 | $\psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \sin \theta e^{\pm i\phi}$ |
| 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 | $\psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$ |
| 3 | 2, ± 2 | $\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2 \theta e^{\pm 2i\phi}$ |

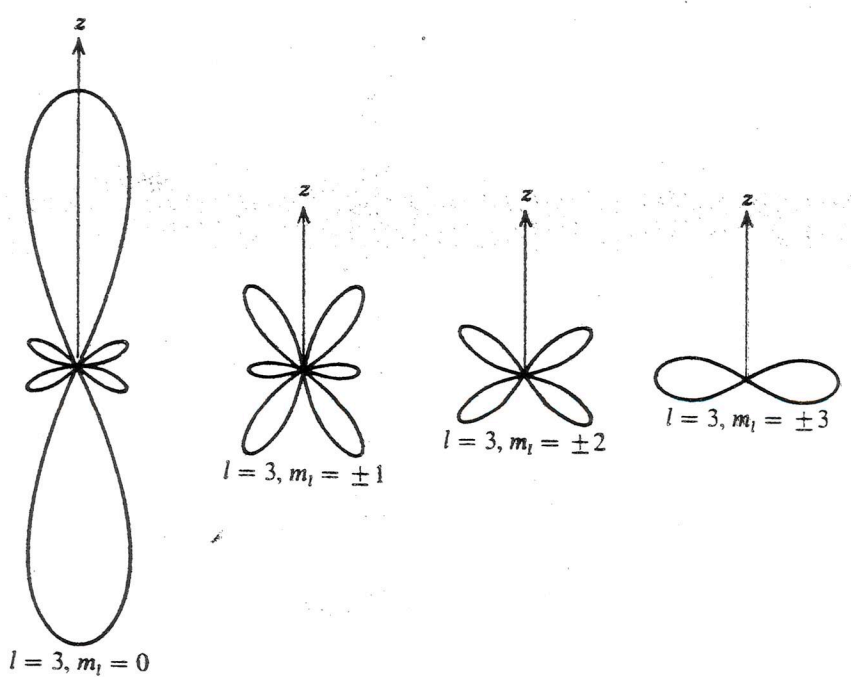
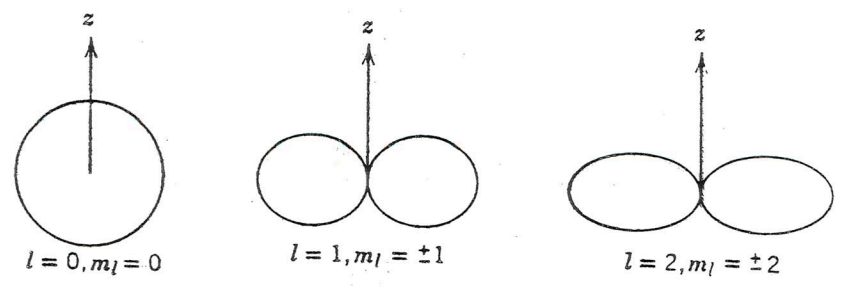


Figure 7-8 Polar diagrams of the directional dependence of the one-electron atom probability densities for $l = 3; m_l = 0, \pm 1, \pm 2, \pm 3$.

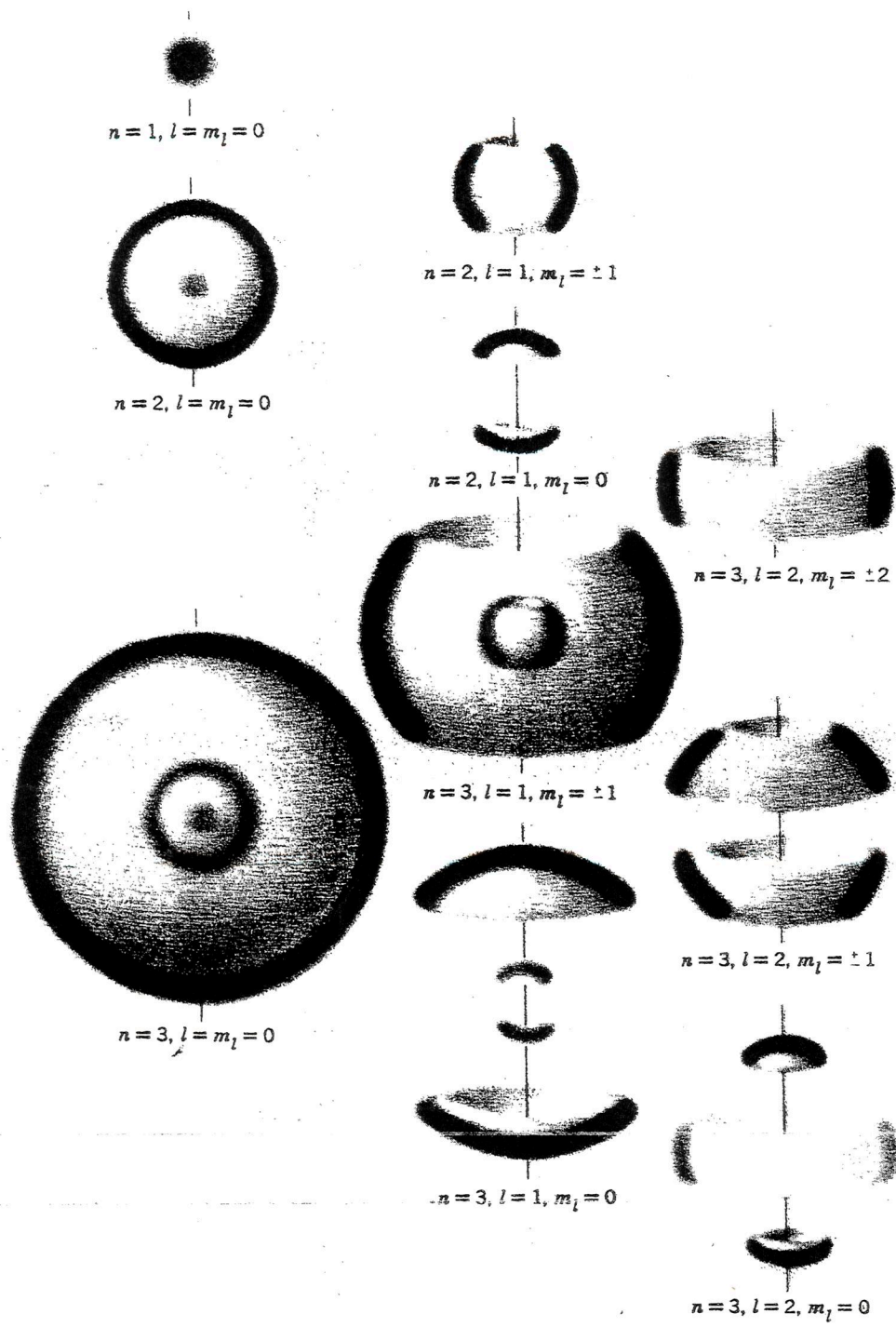


Figure 7-10 An artist's conception of the three-dimensional appearance of several one-electron atom probability density functions. For each of the drawings a line represents the z axis. If all the probability densities for a given n and l are combined, the result is spherically symmetrical.

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

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

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

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

Como calcular: gradiente em cilíndricas

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

$$r = \rho \hat{\rho} + z \hat{z} \quad ; \quad d\vec{r} = d\rho \hat{\rho} + \rho \frac{d\hat{\rho}}{d\rho} d\rho + dz \hat{z} = d\rho \hat{\rho} + \rho d\hat{\rho} + dz \hat{z}$$

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

Espaços Produto

Se E_1 e E_2 são dois espaços com bases $|\varphi_n^1\rangle$ e $|\varphi_n^2\rangle$,
o espaço produto $E = E_1 \otimes E_2$ tem kets da forma

$$|\varphi\rangle = \sum_{nm} c_{nm} |\varphi_n^1\rangle \otimes |\varphi_m^2\rangle \equiv \sum_{n,m} c_{nm} |\varphi_n^1, \varphi_m^2\rangle$$

Na representação $|\varphi_1\rangle \otimes |\varphi_2\rangle \equiv |\varphi_1, \varphi_2\rangle$

$$\langle \varphi_1, \varphi_2 | \varphi \rangle = \sum_{nm} c_{nm} \varphi_n^1(\varphi_1) \varphi_m^2(\varphi_2)$$

Operadores de E_1 são levados à E da forma natural:

$$O_1 \in E_1 \longmapsto O_1 = O_1 \otimes \mathbb{1} \in E$$

$$\Rightarrow O_1 |\varphi\rangle = \sum_{nm} c_{nm} [O_1 |\varphi_n^1\rangle] \otimes |\varphi_m^2\rangle$$

Em particular, se

$$H_1 |\xi_k^1\rangle = E_k^1 |\xi_k^1\rangle$$

$$H_2 |\xi_k^2\rangle = E_k^2 |\xi_k^2\rangle$$

$H = H_1 \otimes \mathbb{1} + \mathbb{1} \otimes H_2$ tem auto-funções $|\xi_{ke}\rangle = |\xi_k^1\rangle \otimes |\xi_e^2\rangle$

e auto-valores $E_{ke} = E_k^1 + E_e^2$