3ª Lista QFL1242 2016

(1) $\int \Psi^* \Psi \, d\tau = 1$

$\hookrightarrow \int_0^\infty r^2 dr \int_0^\pi \mathrm{sen}\theta \, d\theta \int_0^{2\pi} d\phi$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$\hookrightarrow a = 2/a_0$
$n = 2$

p/ estado fundamental

$$\int_0^\infty \left(N_1 e^{-r/a_0}\right)^2 r^2 dr \int_0^\pi \mathrm{sen}\theta \, d\theta \int_0^{2\pi} d\phi = 1 \Rightarrow 4\pi N_1^2 \int_0^\infty r^2 e^{-2r/a_0} dr = 1$$

$$\cancel{4}\pi N_1^2 \cdot \frac{\cancel{2}! \cdot a_0^3}{\cancel{8}} = 1 \Rightarrow \boxed{N_1 = \sqrt{\frac{1}{a_0^3 \cdot \pi}}}$$

p/ estado excitado

$$\int_0^\infty \left[N_2 \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}\right]^2 r^2 dr \cdot \int_0^\pi \mathrm{sen}\theta \, d\theta \int_0^{2\pi} d\phi = 1$$

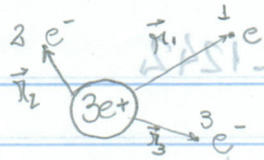
$$N_2^2 \cdot 4\pi \int_0^\infty \left(4 - \frac{4r}{a_0} + \frac{r^2}{a_0^2}\right) e^{-r/a_0} r^2 dr = 1$$

$$4\pi N_2^2 \left[4 \int_0^\infty r^2 e^{-r/a_0} dr - \frac{4}{a_0} \int_0^\infty r^3 e^{-r/a_0} dr + \frac{1}{a_0^2} \int_0^\infty r^4 e^{-r/a_0} dr\right] = 1$$

$$4\pi N_2^2 \left[4 \cdot 2! \, a_0^3 - \frac{4}{\cancel{a_0}} 3! \, a_0^{\cancel{4}\,3} + \frac{1}{\cancel{a_0^2}} 4! \, a_0^{\cancel{5}\,3}\right] = 1$$

$$4\pi a_0^3 N_2^2 \left(8 - \cancel{24} + \cancel{24}\right) = 1 \Rightarrow \boxed{N_2 = \frac{1}{\sqrt{32\pi a_0^3}}}$$

(2) Átomo Li



$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{R}) = E\,\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{R})$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{3}\nabla_{r_i}^2 - \sum_{i=1}^{3}\frac{3e^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{3}\sum_{j>i}\frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|}$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left[\nabla_1^2 + \nabla_2^2 + \nabla_3^2\right] + \frac{e^2}{4\pi\varepsilon_0}\left[\frac{-3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \underbrace{\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}}_{\text{Não separa variáveis}}\right]$$

(3) $E = -\frac{1}{n^2} hcR_H$

a.) $n = 1$ $\quad l = 0$ $\quad g = $ degenerescência $= 1$

b.) $n = 3$ $\quad l = 0 \quad m = 0,$

$l = 1 \quad m = 0, \pm 1$

$l = 2 \quad m = 0, \pm 1, \pm 2$ $\quad g = 9$

$\boxed{g = n^2}$

c.) $n = 5$

$l = 0 \quad m = 0 \quad 1$

$l = 1 \quad m = 0, \pm 1 \quad 3$

$l = 2 \quad m = 0, \pm 1, \pm 2 \quad 5$

$l = 3 \quad m = 0, \pm 1, \pm 2, \pm 3 \quad 7$

$l = 4 \quad m = 0, \pm 1, \pm 2, \pm 3, \pm 4 \quad 9$

$g = 25$

(4) Orbitais 2p

$$\begin{cases} \Psi_{210} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} \frac{r}{a_0}\, e^{-r/2a_0} \cos\theta \rightarrow p_z \\ \Psi_{21\pm1} = \left(\frac{1}{64\pi a_0^3}\right)^{1/2} \frac{r}{a_0} \cdot e^{-r/2a_0}\, \text{sen}\,\theta\, e^{\pm i\phi} \end{cases}$$

$2p_x = \Psi_{211} - \Psi_{21-1}$

Ver Wolfram

$2p_y = \Psi_{211} + \Psi_{21-1}$

Ortogonalidade $\int \Psi_i^* \Psi_j \, d\tau = 0$

$$\int (\Psi_{211} - \Psi_{21-1})^* (\Psi_{211} + \Psi_{21-1}) \, d\tau = \int \underbrace{\Psi_{211}^* \Psi_{211}}_{1} + \Psi_{211}^* \Psi_{21-1} - \Psi_{21-1}^* \Psi_{211} - \underbrace{\Psi_{21-1}^* \Psi_{21-1}}_{1} \, d\tau$$

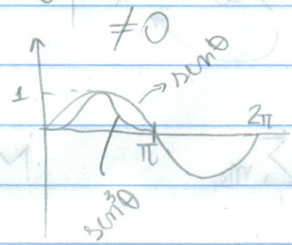
$$= 1 + N_{211} N_{21-1} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{r}{a_0} e^{-r/2a_0} \, \text{sen}\theta \, e^{-i\phi} \, \frac{r}{a_0} e^{-r/2a_0} \, \text{sen}\theta \, e^{-i\phi} \, r^2 \, dr \, \text{sen}\theta \, d\theta \, d\phi$$

$$- N_{21-1} N_{211} \iiint \frac{r}{a_0} e^{-r/2a_0} \, \text{sen}\theta \, e^{i\phi} \, \frac{r}{a_0} \, \text{sen}\theta \, e^{i\phi} \, r^2 \, dr \, \text{sen}\theta \, d\theta \, d\phi - 1$$

$$= \frac{N_{211} N_{21-1}}{a_0^2} \int_0^{\infty} r^4 e^{-r/a_0} \, dr \int_0^{\pi} \text{sen}^3\theta \, d\theta \underbrace{\int_0^{2\pi} e^{-2i\phi} \, d\phi}_{\text{zero}} \qquad \int_0^{2\pi} \cos(-2\phi) + i\,\text{sen}(2\phi) \, d\phi \quad \text{sen}(-2\phi)\Big|_0^{2\pi} - i\cos(2\phi)\Big|_0^{2\pi}$$

$$- \frac{N_{21-1} N_{211}}{a_0^2} \int_0^{\infty} r^4 e^{-r/a_0} \, dr \int_0^{\pi} \text{sen}^3\theta \, d\theta \underbrace{\int_0^{2\pi} e^{2i\phi} \, d\phi}_{\text{zero}} \qquad \int_0^{2\pi} \cos(2\phi) - i\,\text{sen}(2\phi) \, d\phi \quad \text{sen}(2\phi)\Big|_0^{2\pi} + i\cos(2\phi)\Big|_0^{2\pi}$$

$\neq 0$ $\qquad\qquad$ $\neq 0$



$$e^{ia\phi} = \cos(a\phi) - i\,\text{sen}(a\phi)$$

$$\boxed{\therefore \int_0 2p_x^* \, 2p_y \, d\tau = 0}$$

(5) $|\Psi|^2$ = densidade de probabilidade $\quad \Psi = \left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$

$|\Psi|^2 \, d\tau$ = Probabilidade em intervalo infinitesimal

Distância mais provável = Máximo de $P \Rightarrow dP/dr = 0$

tem vários r / $P' = 0$

$$P = 4\pi r^2 |\Psi|^2 = \frac{\cancel{4\pi} r^2}{8\,\cancel{32}\cancel{\pi} a_0^3}\left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} = \frac{1}{8a_0^3}\left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right) e^{-r/a_0}$$

$$\frac{dP}{dr} = \frac{1}{8a_0^3}\left[\left(8r - \frac{12r^2}{a_0} + \frac{4r^3}{a_0^2}\right) e^{-r/a_0} + \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right)\left(-\frac{1}{a_0}\right) e^{-r/a_0}\right] = 0$$

$$\frac{1}{8a_0^3}\left[\left(8r - \frac{12-4}{a_0} r^2 + \frac{4+4}{a_0^2} r^3 - \frac{r^4}{a_0^3}\right) e^{-r/a_0}\right] = 0$$

$$=\frac{1}{8a_0^3}\left[\left(8-\frac{16r}{a_0}+\frac{8r^2}{a_0^2}-\frac{r^3}{a_0^3}\right)r\cdot e^{-r/a_0}\right]=0$$

Eq. cúbica completa! Procurar "solve cubic equation" no google e achar um site que resolva p/ você!

$e^{-r/a_0}=0$ ou $\boxed{r=0}$ ou $8-\frac{16r}{a_0}+\frac{8r^2}{a_0^2}-\frac{r^3}{a_0^3}=0$

$\cancel{\exists}\ r\ /\ e^{-r/a_0}=0$

ou $\frac{r}{a_0}=x$ $\quad -x^3+8x^2-16x+8=0$ $\quad (=(-1)^3,\ (2)^3)$

$(-x+2)^3=(-x+2)(x^2-4x+4)=-x^3+6x^2-12x+8$

$\therefore\ -x^3+8x^2-16x+8=(-x^3+6x^2-12x+8)+2x^2-4x=0$

$\Rightarrow (-x+2)(-x+2)^2-2x(-x+2)=0$

$\Rightarrow (-x+2)[(-x+2)^2-2x]=0$

$-(x-2)(x^2-6x+4)=0$

$x=2$ ou $6\pm\sqrt{36-16}\,/2$ $\quad x=3\pm\sqrt{5}$

FINAL:

$$\boxed{\begin{aligned}&\frac{r}{a_0}=0\\&\frac{r}{a_0}=3-\sqrt{5}\\&r/a_0=2\\&r/a_0=3+\sqrt{5}\leftarrow\end{aligned}}$$

⑥ $S=\sum_i s_i$ $\qquad M_s=\sum_i m_{s_i}$ $\qquad M_s=-S,\dots 0,\dots +S$

p/ 2 elétrons: ↑↑ ↑↓ ↓↑ ↓↓ $\qquad S=0,1$ $\qquad 2S+1=1,3$

M_s: 1 0 0 −1

p/ 3 elétrons: ↑↑↑ ↑↑↓ ↑↓↓ ↓↓↓ (1) (3) (3) (1) $=8\ (2\times2\times2)$ $\qquad S=\frac{3}{2},\frac{1}{2}$ (×2)

M_s: $\frac{3}{2}$ $\frac{1}{2}$ $-\frac{1}{2}$ $-\frac{3}{2}$

$2S+1=4,2$

p/ 4 elétrons: ↑↑↑↑ ↑↑↑↓ ↑↑↓↓ ↑↓↓↓ ↓↓↓↓ (1) (4) (6) (4) (1) $=16$ $\qquad S=2,1,0$ (×3) (×2)

M_s: 2 1 0 −1 −2 $\qquad 2S+1=5,3,0$

p/ 5 elétrons: ↑↑↑↑↑ ↑↑↑↑↓ ↑↑↑↓↓ ↑↑↓↓↓ ↑↓↓↓↓ ↓↓↓↓↓ (1) (5) (10) (10) (5) (1) $=2^5=32$ $\qquad S=\frac{5}{2},\frac{3}{2},\frac{1}{2}$ (×4) (×5)

M_s: 5/2 3/2 1/2 −1/2 −3/2 −5/2

⑦ ^{28}Ni $Ni^{+} = 26$ elétrons $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

d^8 ⇅ ⇅ ⇅ ↑ ↑ M_S 1 $S = 1, 0$

↑ ↓ 0

↓ ↑ 0

↓ ↓ −1

⑧ a.) Sc [Ar] $3d^1 4s^2$ 10 microestados

$M_L = m_l = 2, 1, 0, -1, -2$ $L = l = 2$ $^2D_{5/2}$, $^2D_{3/2}$

$M_S = m_s = 1/2, -1/2$ $S = s = 1/2$

b.) Br [Ar] $3d^{10} 4s^2 4p^5$

$p^5 = p^1$ $M_L = m_l = -1, 0, 1$ $L = l = 1$ $^2P_{3/2}$ $^2P_{1/2}$

$M_s = m_s = -1/2, 1/2$ $S = s = 1/2$

⑨ ^3D $L = 2$ $S = 1$ $J = 3, 2, 1$

p/ $J = 3$ $M_J = 0, \pm1, \pm2, \pm3$ = 7

p/ $J = 2$ $M_J = 0, \pm1, \pm2$ = 5

p/ $J = 1$ $M_J = 0, \pm1$ = 3

^4D $L = 2$ $S = 3/2$ $J = \overset{8}{\frac{7}{2}}, \overset{6}{\frac{5}{2}}, \overset{4}{\frac{3}{2}}, \overset{2}{\frac{1}{2}}$

p/ $J = 7/2$ $M_J = \pm 7/2, \pm 5/2, \pm 3/2, \pm 1/2$

^2G $L = 4$ $S = 1/2$ $J = \overset{10}{9/2}, \overset{8}{7/2}$

⑩ $\Delta l = 1$ Δl

a.) $2s \to 1s$ proibida 0

b.) $2p \to 1s$ permitida +1

c.) $3d \to 2p$ permitida −1

d.) $5d \to 2s$ proibida −2

e.) $5p \to 3s$ permitida −1

f.) $6p \to 4f$ proibida +2

(11) $\hat{H} = \hat{H}^{(0)} + \hat{H}'$

a) Oscilador Harmônico

$$E_v^{(0)} = h\nu(v + 1/2) \qquad \Psi_v = N_v H_v \, e^{-\alpha x^2/2}$$

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{k}{2}x^2$$

$$H^{(1)} = \frac{\gamma}{6}x^3 + \frac{b}{24}x^4$$

b) Partícula na caixa

$$E_n^{(0)} = \frac{n^2h^2}{8m_e a^2} \qquad \Psi_n = A \operatorname{sen}(n\pi x/a)$$

$$H^{(0)} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\hat{H}^{(1)} = \begin{cases} 0 & 0 < x < a/2 \\ b & a/2 < x < a \end{cases}$$

c) Átomo de Hidrogênio

$$E_n^{(0)} = -\frac{Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} \qquad \Psi^{(0)} = \text{orbitais produto } \psi_1(r_1)\psi_2(r_2)$$

$$H^{(0)} = \hat{H}_H(1) + \hat{H}_H(2) = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze}{4\pi\varepsilon_0 r_1} - \frac{Ze}{4\pi\varepsilon_0 r_2}$$

$$\hat{H}^{(1)} = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

(12) $E^{(1)} = \int \Psi_n H' \Psi_n \, d\tau$

$$\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad \alpha = \left(k\mu/\hbar^2\right)^{1/2}$$

$$H' = \frac{\gamma}{6}x^3 + \frac{b}{24}x^4$$

$$E^{(1)} = \int_{-\infty}^{+\infty} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}\left[\frac{\gamma}{6}x^3 + \frac{b}{24}x^4\right]\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}\, dx$$

$$\left\{ \int_0^{\infty} x^4 e^{-bx^2}dx = \frac{3}{8b^2}\sqrt{\frac{\pi}{b}} \right.$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2}\left[\cancel{\int_{-\infty}^{+\infty} \frac{\gamma}{6}\overset{\text{impar}}{x^3} e^{-\alpha x^2}dx}^{\,\to 0} + \int_{-\infty}^{+\infty}\frac{b}{24}\overset{\text{par}}{x^4} e^{-\alpha x^2}dx\right]$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \cdot \frac{b}{24} \cdot 2 \cdot \frac{3}{8\alpha^2}\sqrt{\frac{\pi}{\alpha}} = \frac{b}{32\alpha^2}$$

$$\boxed{E^{(1)} = \frac{b}{32\alpha^2}}$$

(13) $\Psi_1 = \left(\frac{2}{a}\right)^{1/2} \operatorname{sen}\left(\frac{\pi x}{a}\right) \qquad H' = b \qquad a/2 < x < a$

$$E^{(1)} = \int_0^{a/2} \Psi_1^* \overset{\text{zero}}{H'} \Psi_1 \, dx + \int_{a/2}^{a}\left(\frac{2}{a}\right)^{1/2}\operatorname{sen}\left(\frac{\pi x}{a}\right)\cdot b \cdot\left(\frac{2}{a}\right)^{1/2}\operatorname{sen}\left(\frac{\pi x}{a}\right)dx$$

$$E^{(1)} = \frac{2b}{a}\int_{a/2}^{a}\operatorname{sen}^2\left(\frac{\pi x}{a}\right)dx \qquad \left\{ \int \operatorname{sen}^2 bx = \frac{x}{2} - \frac{\operatorname{sen} 2bx}{4b} \right\}$$

$$E^{(1)} = \frac{2b}{a}\left[\frac{x}{2} - \frac{\operatorname{sen}\frac{2\pi x}{a}}{4(\pi/a)}\right]_{x=a/2}^{x=a} = \frac{2b}{a}\left[\frac{a}{2} - \frac{a}{4} - \frac{\cancel{\operatorname{sen} 2\pi}^{\,0}}{4\pi/a} + \frac{\cancel{\operatorname{sen}\pi}^{\,0}}{4\pi/a}\right]$$

$$\boxed{E^{(1)} = \frac{2b}{a}\cdot\frac{a}{4} = \frac{b}{2}}$$

(14) $H^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{k}{2}x^2$

$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$

$H = H^{(0)} + H' \Rightarrow H' = H - H^{(0)}$

$H' = cx^4 - \frac{kx^2}{2}$

$$\int_0^{\infty} x^4 e^{-bx^2}dx = \frac{3}{8b^2}\left(\frac{\pi}{b}\right)^{1/2}$$

$$\int_0^{\infty} x^2 e^{-bx^2}dx = \frac{1}{4}\left(\frac{\pi}{b^3}\right)^{1/2}$$

$$E^{(1)} = \int_{-\infty}^{+\infty}\left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha x^2/2}\left[cx^4 - \frac{kx^2}{2}\right]e^{-\alpha x^2/2}\,dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2}\left[\int_{-\infty}^{+\infty} cx^4 e^{-\alpha x^2}dx - \frac{k}{2}\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2}dx\right]$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2}\left[c\cdot 2\cdot\frac{3}{8\alpha^2}\left(\frac{\pi}{\alpha}\right)^{1/2} - \frac{k}{2}\cdot 2\cdot\frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{1/2}\right]$$

$$\boxed{E^{(1)} = \frac{3}{4}\frac{c}{\alpha^2} - \frac{k}{4\alpha}}$$