

Física atómica

pod

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1. Átomos hidrogenoides

$$p''(r) = \frac{2\mu}{\hbar^2} [U_l(r) - E] p(r) \quad , \quad U_l(r) = V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} \quad , \quad n = n_r + l + 1 \quad , \quad (\alpha)_k = \alpha \cdot (\alpha + k - 1)$$

$${}_1F_1(\alpha, \beta, z) = \sum_{k=0}^{\infty} \frac{(\alpha)_k z^k}{(\beta)_k k!} \quad , \quad p_{nl}(r) = a_0^{-1/2} \left(\frac{2Zr}{na_0} \right)^{l+1} e^{-\frac{Zr}{na_0}} {}_1F_1 \left(l+1-n, 2l+2, \frac{2Zr}{na_0} \right)$$

$$\psi_{nlm}(\vec{r}) = \frac{p_{nl}(r)}{r} Y_{ml}(\hat{r}) \quad , \quad E = -\frac{Z^2 m e^4}{2n^2 \hbar^2} \quad , \quad \int_0^{\infty} r^n e^{-ar} dr = \frac{n!}{a^{n+1}} \quad , \quad \psi^{(Z)} = Z^{3/2} \psi^{(1)} \quad , \quad \langle r^k \rangle^{(Z)} = \frac{\langle r^k \rangle^{(1)}}{Z^k}$$

$$H_m = -\frac{1}{8m^3 c^2} p^4 = -\frac{\alpha^2}{2} \left(H_p + \frac{Z}{r} \right)^2 \quad , \quad \alpha = \frac{e^2}{\hbar c} = 1/137,0035$$

$$H_{so} = -\frac{e\hbar}{8m^2 c^2} \vec{\sigma} \cdot \vec{\nabla} \varphi \times \vec{p} = \frac{\alpha^2}{2} \frac{1}{r} \frac{dV}{dr} \vec{L} \vec{S} = \xi(r) \vec{L} \vec{S} \quad , \quad \xi(r) = \frac{Z\alpha^2}{2} \frac{1}{r^3}$$

$$H_{DW} = -\frac{e\hbar}{8m^2 c^2} \nabla^2 \varphi = \frac{Z\alpha^2}{2} \pi \delta(\vec{r})$$

$$\langle H_{so} \rangle = -E_n \frac{(Z\alpha)^2}{2n} \frac{j(j+1) - l(l+1) - 3/4}{l(l+1/2)(l+1)} (1 - \delta_{l0})$$

$$\langle H_m \rangle = -E_n \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{3}{4} - \frac{n}{l+1/2} \right]$$

$$\langle H_{DW} \rangle = -E_n \frac{(Z\alpha)^2}{n} \delta_{l0}$$

$$\Delta E_{nlj} = E_n \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{n}{j+1/2} - \frac{3}{4} \right] \quad , \quad j = l \pm 1/2$$

$$\text{Vol. finito } \Delta E = \frac{Z^4}{n^3} \left(\frac{M}{M+1} \right)^3 \frac{2}{5} R^2 \delta_{l0} \quad , \quad R = A^{1/3} 2,3 \times 10^{-5} a_0$$

$$\text{massa fin. } E(M) = \frac{M}{M+m} E(\infty) \quad , \quad \Delta E = E(M) - E(\infty)$$

2. Átomos multieletrónicos

$$\vec{R} = \frac{\sum_i m_e \vec{r}_{e_i} + M_N \vec{r}_N}{M_n + N m_e}, \quad \vec{r}_i = \vec{r}_{e_i} - \vec{r}_N, \quad T = -\frac{\hbar^2}{2(M_N + N m_e)} \nabla_R^2 - \frac{\hbar^2}{2\mu} \sum \nabla_i^2 - \frac{\hbar^2}{2M_n} \sum \vec{\nabla}_i \cdot \vec{\nabla}_j$$

$$V = -\sum_{i=1}^N \frac{1}{r_i} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad S_N = \frac{1}{N!} \sum_{p \in S_N} P, \quad A_N = \frac{1}{N!} \sum_{p \in S_N} (-1)^p P, \quad A^\dagger = A^2 = A, \quad AS = SA = 0$$

$$F(x_1, \dots, x_N) = \sum_i f(x_i), \quad G(x_1, \dots, x_N) = \sum_{i<j} g(x_i, x_j), \quad E \sim n+l \sim n, \quad D_{eq} = \binom{2(2l+1)}{n}$$

$$\langle \psi | F | \psi \rangle = \sum_{i=1}^N \int \phi_i^* f \phi_i d^3 r, \quad \langle \psi_{1,2,\dots} | F | \psi_{\bar{1},\bar{2},\dots} \rangle = \int \phi_1^* f \tilde{\phi}_1 d^3 r$$

$$\langle \psi | G | \psi \rangle = \sum_{i<j} \left(\iint \phi_i^*(x_1) \phi_j^*(x_2) g(x_1 x_2) \phi_i(x_1) \phi_j(x_2) - \iint \phi_i^*(x_1) \phi_j^*(x_2) g(x_1 x_2) \phi_i(x_2) \phi_j(x_1) \right)$$

$$\langle \psi_{12\dots} | G | \psi_{\bar{1}\bar{2}\dots} \rangle = \sum_{j=2} \left(\iint \phi_1^*(x_1) \phi_j^*(x_2) g(x_1 x_2) \tilde{\phi}_1(x_1) \phi_j(x_2) - \iint \phi_1^*(x_1) \phi_j^*(x_2) g(x_1 x_2) \tilde{\phi}_1(x_2) \phi_j(x_1) \right)$$

$$\langle \psi_{12\dots} | G | \psi_{\bar{1}\bar{2}\dots} \rangle = \left(\iint \phi_1^*(x_1) \phi_2^*(x_2) g(x_1 x_2) \tilde{\phi}_1(x_1) \tilde{\phi}_2(x_2) - \iint \phi_1^*(x_1) \phi_2^*(x_2) g(x_1 x_2) \tilde{\phi}_1(x_2) \tilde{\phi}_2(x_1) \right)$$

$$\left[\frac{-\hbar^2}{2m} \nabla^2 - \frac{Z e^2}{r} \right] \varphi_i + \underbrace{\sum_j \left[\int \varphi_j^*(\vec{r}') \frac{e^2 d^3 r'}{|\vec{r} - \vec{r}'|} \varphi_j(\vec{r}') \right]}_{V_D \varphi_i \text{ Hartree}} \varphi_i - \underbrace{\sum_j \left[\delta_{m_{s_i} m_{s_j}} \int \varphi_j^*(\vec{r}') \frac{e^2 d^3 r'}{|\vec{r} - \vec{r}'|} \varphi_i(\vec{r}') \right]}_{V_{\text{ech}} \varphi_i \text{ Hartree-Fock}} \varphi_j = E_i \varphi_i$$

$$f(x) \varphi_i(x) + \left[\sum_{j=1}^N \int dx' \varphi_j^*(x') g(x, x') \varphi_j(x') \right] \varphi_i(x) - \sum_{j=1}^N \left[\int dx' \varphi_j^*(x') g(x, x') \varphi_i(x') \right] \varphi_j(x) = E_i \varphi_i(x)$$

$$E = \langle \psi | H | \psi \rangle = \sum_i I(i) + \frac{1}{2} \sum_{ij} (J(ij) - K(ij)) = \sum_i E_i - \frac{1}{2} \sum_{ij} (J(ij) - K(ij))$$

3. Átomo de helio

$$E_{\text{tdp},(1s)^2} = \left(-Z^2 + \frac{5}{8} Z \right) Z_{\text{eff}} = Z - \frac{5}{16} \quad . \quad n^{2s+1} L, \quad E \sim (2s+1)^{-1}$$

$$\Delta E = \left\langle \psi \left| \frac{e^2}{r_{12}} \right| \psi \right\rangle = e \sum_{l=0}^{\infty} C^l(00,00) C^l(00,00) F^L(10,10), \quad C^L(00,00) = \delta^{L0}$$

$$F^0(10,10) = \int dr_1 dr_2 \frac{1}{r_{>}} [p_{10}(r_1) p_{10}(r_2)]^2 = \frac{5}{8} \frac{Z}{a_0}$$

4. Interacción con campos externos

4.1. Efecto stark

$$\vec{A} = 0, \phi = -\varepsilon, H' = e\varepsilon \sum_i z_i, E_{100}^{(1)} = 0, E_{100}^{(2)} = -\frac{9}{4} \frac{a_0^3}{Z^4},$$

$$\langle nl'm' | H' | nlm \rangle = 0 \text{ si } l-l' = \text{par, o } m \neq m', \langle \vec{D} \rangle = \alpha \vec{\varepsilon}, \alpha = \frac{-1}{\varepsilon} \frac{\partial E_0^{(2)}}{\partial \varepsilon},$$

$$E_0^{(2)} = \sum_{k \neq 0} \frac{|\langle 0 | H' | k \rangle|^2}{E_0 - E_k} E_0^{(2)} \approx \frac{e^2 \varepsilon^2}{E_0} \sum_i \langle 0 | z_i^2 | 0 \rangle_{\text{esf}} = \frac{e^2 \varepsilon^2}{E_0} \frac{N}{3} \langle r^2 \rangle$$

$$E_0^{(2)} \geq \frac{-1}{E_1 - E_0} \sum_{k \neq 0} |\langle 0 | H' | k \rangle|^2 = \frac{-e^2 \varepsilon^2}{E_1 - E_0} \sum_i \langle z^2 \rangle = \frac{-e^2 \varepsilon^2 N / 3}{E_1 - E_0} \langle r^2 \rangle,$$

4.2. Efecto Zeeman

$$\phi = 0, \vec{A} = \frac{1}{2} \vec{B} \times \vec{r}, H' = \frac{e}{mc} \vec{A} \vec{p} + \mu_B \vec{\sigma} \vec{B} = \mu_B \vec{B} (\vec{L} + 2\vec{S}) = -(\vec{M}_L + \vec{M}_S) \vec{B}, \vec{M}_i = -g_i \mu_B \vec{J}_i$$

- $H' \gg H_{\text{so}}$ Paschen-Back $E = E_n + \mu_B B(m_l + 2m_s), \Delta E_{\text{so}} = -E_n \frac{\alpha^2 Z^2}{n} \frac{m_l m_s}{l(l+1/2)(l+1)} (1 - \delta_{l0})$

$$\langle \gamma L S M'_L M'_J | H_{\text{so}} | \gamma L S M_L M_J \rangle = T_{\gamma L S M_L M_S} \delta_{M'_L M_L} \delta_{M'_S M_S}, \Delta E = \mu_B (M_L + 2M_S) + T_{\gamma L S M_L M_S}$$

- $H_{\text{so}} \gg H'$ Z. anómalo $g_J = g_L \frac{J^2 + L^2 - S^2}{2J^2} + g_S \frac{J^2 + S^2 - L^2}{2J^2} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$

$$H' = g_J \mu_B B J_z, \Delta E = g_J \mu_B B M_J$$

5. Espectroscopias atómicas

$$\psi = \sum_n C_n(t) e^{-iE_n t / \hbar} \langle \phi_n \rangle, \dot{C}_f^{(0)} = 0, \dot{C}_f^{(1)} = -\frac{i}{\hbar} \sum_n C_n^{(0)} H'_{fn} e^{i\omega_{fn} t}, C_f^{(t)} = \frac{-i}{\hbar} \int_0^t dt' H'_{fi} e^{i\omega_{fi} t'}$$

$$W_{fi}^{\text{est}} = n(\omega_{fi}) 4\pi \frac{e^2}{3\hbar} \omega_{fi} |\langle f | \vec{r} | i \rangle|^2, W_{fi}^S = \frac{4e^2}{3\hbar c^3} \omega_{fi}^3 |\langle f | \vec{r} | i \rangle|^2, \frac{N_1}{N_2} = e^{-\frac{E_1 - E_2}{kT}}, n = \frac{\omega^2}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1}$$

$$\dot{N}_{1 \rightarrow 2} = W^{\text{est}} N_1, \dot{N}_{2 \rightarrow 1} = W^{\text{est}} N_2 + W^S N_2; \Delta l = \pm 1, \Delta m_l = 0, \pm 1, \pi_i = -\pi_f, \Delta m_s = 0$$

$$W^{\text{est}} = n(\omega_{fi}) \frac{2\pi e^2}{mc^2 \hbar \omega_{fi}} \left| \left\langle f \left| e^{i\vec{k}\vec{r}} \hat{\varepsilon} \left[\vec{p} + i \frac{\hbar}{2} \vec{\sigma} \times \vec{k} \right] \right| i \right\rangle \right|^2, F_{fi}^{E1} \approx \frac{eA_0}{mc} \langle f | \hat{\varepsilon} \vec{p} | i \rangle$$

$$\text{est. fina } \Delta j = 0, \pm 1, \Delta m_l = 0, \pm 1, \pi_f = -\pi_i$$

$$\text{multi. } \Delta J = 0, \pm 1 (\text{no } L = L' = 0), \Delta M = 0, \pm 1, \pi_f = -\pi_i, \Delta S = 0$$

$$W_{fi} = \frac{4\alpha}{3c^2} \omega_{fi}^3 |\langle f | \vec{r} | i \rangle|^2$$

6. Varios

$$\langle Y_{l_1 m_1} | C_{LM} | Y_{l_2 m_2} \rangle = \sqrt{\frac{2l_2 + 1}{2l_1 + 1}} \langle Ll_2 00 | l_1 0 \rangle \langle Ll_2 M m_2 | l_1 m_1 \rangle, \quad C_{LM} = \sqrt{\frac{4\pi}{2L + 1}} Y_{LM}$$

$$\int_0^\infty dr p_{n, l-1} p_{nl} r = -\frac{3n}{2Z} \sqrt{n^2 - l^2} a_0,$$

$$a_0 = \frac{\hbar^2}{me^2} = 0,529177 \text{ \AA}$$

$$t_0 = \frac{\hbar^3}{me^4} = 2,41888 \times 10^{-17} \text{ s}$$

$$E_h = \frac{me^4}{\hbar^2} = 27,2114 \text{ eV}$$

$$c = \frac{1}{\alpha} \quad \mu_B = \alpha/2$$

$$1 \text{ cm}^{-1} = 1,2398 \times 10^{-4} \text{ eV}$$

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

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

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

$$\langle r^{-2} \rangle = \frac{Z^2}{a_0^2} \frac{1}{n^3(l+1/2)}$$

$$\langle r^{-1} \rangle = \frac{Z}{a_0} \frac{1}{n^2}$$

$$\langle r \rangle = \frac{a_0}{Z} \frac{1}{2} (3n^2 - l(l+1))$$

$$\langle r^2 \rangle = \frac{a_0^2}{Z^2} \frac{n^2}{2} (5n^2 + 1 - 3l(l+1))$$

$$\vec{L} = \frac{1}{\hbar} \vec{r} \times \vec{p}, \quad \nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r) - \frac{\vec{L}^2}{r^2}, \quad \frac{1}{r_{12}} = \sum_{l=0} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} \sum_{m=-l} l Y_{lm}^*(\hat{r}_1) Y_{lm}(\hat{r}_2)$$

$$\langle Y_{l_3 m_3} | Y_{l_1 m_1} | Y_{l_2 m_2} \rangle = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l_3 + 1)}} \langle l_1 l_2 00 | l_3 0 \rangle \langle l_1 l_2 m_1 m_2 | l_3 m_3 \rangle$$

$$[J_i, J_j] = i\epsilon_{ijk} J_k, \quad J_{\pm 1} = \mp \frac{1}{\sqrt{2}} (J_x \pm iJ_y), \quad J_0 = J_z, \quad J^2 = -J_{+1}J_{-1} + J_0^2 - J_{-1}J_{+1}$$

$$J_{\pm 1} |jm\rangle = \mp \sqrt{\frac{1}{2} (j(j+1) - m(m \pm 1))} |j, m \pm 1\rangle, \quad A_i = |\vec{A}| C_{1i}, \quad C_{LM} = \sqrt{\frac{4\pi}{2L+1}} Y_{LM}$$

$$\left\langle j_1, \frac{1}{2}, m - m_2, m_2 = \pm \frac{1}{2} \middle| jm \right\rangle = \begin{cases} j = j_1 + 1/2 & \left(\frac{j_1 \pm m + 1/2}{2j_1 + 1}\right)^{1/2} \\ j = j_1 + 1/2 & \mp \left(\frac{j_1 \mp m + 1/2}{2j_1 + 1}\right)^{1/2} \end{cases}$$

$$C^1(l'm'_l, lm_l)\delta_{q, m'_l - m_l} = \int_{4\pi} d\hat{r} Y_{l'm'_l}^*(\hat{r}) C_{1q}(\hat{r}) Y_{lm}(\hat{r}) = \sqrt{\frac{2l+1}{2l'+1}} \langle l100 | l'0 \rangle \langle l1m_l, m'_l - m_l | l'm'_l \rangle$$

$$C^k(l'm'; lm) = \int Y_{l'm'}^* C_{k, m' - m} Y_{lm}, \quad \sum_{m'} |C^1(l'm'; lm)|^2 = \begin{cases} \frac{l+1}{2l+1} & \text{si } l' = l + 1 \\ \frac{l}{2l+1} & \text{si } l' = l - 1 \end{cases}$$