Físca atómica

pod

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1. Átomos hidrogenoides

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

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

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

$$\begin{aligned}
H_m &= -\frac{1}{8m^3c^2}p^4 = -\frac{\alpha^2}{2}\left(H_p + \frac{Z}{r}\right)^2 \quad , \ \alpha = \frac{e^2}{\hbar c} = 1/137{,}0035 \\
H_{so} &= -\frac{e\hbar}{8m^2c^2}\vec{\sigma}\cdot\vec{\nabla}\varphi\times\vec{p} = \frac{\alpha^2}{2}\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\vec{L}\vec{S} = \xi(r)\vec{L}\vec{S} \ , \ \xi(r) = \frac{Z\alpha^2}{2}\frac{1}{r^3} \\
H_{DW} &= -\frac{e\hbar}{8m^2c^2}\nabla^2\varphi = \frac{Z\alpha^2}{2}\pi\delta(\vec{r})
\end{aligned}$$

$$\begin{aligned}
\langle H_{so}\rangle &= -E_n\frac{(Z\alpha)^2}{2n}\frac{j(j+1) - l(l+1) - 3/4}{l\,(l+1/2)\,(l+1)}(1-\delta_{l0}) \\
\langle H_m\rangle &= -E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{3}{4} - \frac{n}{l+1/2}\right] \\
\langle H_{DW}\rangle &= -E_n\frac{(Z\alpha)^2}{n}\delta_{l0} \\
\Delta E_{nlj} &= E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{n}{j+1/2} - \frac{3}{4}\right] \quad , \ j = l\pm 1/2
\end{aligned}$$

$$\text{Vol. finito } \Delta E = \frac{Z^4}{n^3}\left(\frac{M}{M+1}\right)^3\frac{2}{5}R^2\delta_{l0} \ , \ R = A^{1/3}\,2{,}3\times10^{-5}a_0$$

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

2. Átomos multielectrònicos

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

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

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

$$\begin{aligned}
\langle\psi|F|\psi\rangle &= \sum_{i=1}^{N}\int\phi_i^*f\phi\mathrm{d}^3r \quad , \quad \left\langle\psi_{1,2,\ldots}\middle|F\middle|\psi_{\tilde{1},2,\ldots}\right\rangle=\int\phi_1^*f\tilde{\phi}_1\mathrm{d}^3r\\
\langle\psi|G|\psi\rangle &= \sum_{i<j}\left(\iint\varphi_i^*(x_1)\varphi_j^*(x_2)g(x_1x_2)\varphi_i(x_1)\varphi_j(x_2)-\iint\varphi_i^*(x_1)\varphi_j^*(x_2)g(x_1x_2)\varphi_i(x_2)\varphi_j(x_1)\right)\\
\langle\psi_{12\ldots}|G|\psi_{\tilde{1}2\ldots}\rangle &= \sum_{j=2}\left(\iint\varphi_1^*(x_1)\varphi_j^*(x_2)g(x_1x_2)\tilde{\varphi}_1(x_1)\varphi_j(x_2)-\iint\varphi_i^*(x_1)\varphi_j^*(x_2)g(x_1x_2)\tilde{\varphi}_1(x_2)\varphi_j(x_1)\right)\\
\langle\psi_{12\ldots}|G|\psi_{\tilde{1}\tilde{2}\ldots}\rangle &= \left(\iint\varphi_1^*(x_1)\varphi_2^*(x_2)g(x_1x_2)\tilde{\varphi}_1(x_1)\tilde{\varphi}_2(x_2)-\iint\varphi_i^*(x_1)\varphi_2^*(x_2)g(x_1x_2)\tilde{\varphi}_1(x_2)\tilde{\varphi}_2(x_1)\right)
\end{aligned}$$

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

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

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

3. Átomo de helio

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

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

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

4. Interacción con campos externos

4.1. Efecto stark

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

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

$$E_0^{(2)}=\sum_{k\neq0}\frac{|\langle0|H'|k\rangle|^2}{E_0-E_k}E_0^{(2)}\approx\frac{e^2\varepsilon^2}{E_0}\sum_i\left\langle0|z_i^2|0\right\rangle\underset{\text{esf}}{=}\frac{e^2\varepsilon^2}{E_0}\frac{N}{3}\left\langle r^2\right\rangle$$

$$E_0^{(2)}\geq\frac{-1}{E_1-E_0}\sum_{k\neq0}|\langle0|H'|k\rangle|^2=\frac{-e^2\varepsilon^2}{E_1-E_0}\sum_i\left\langle z^2\right\rangle=\frac{-e^2\varepsilon^2N/3}{E_1-E_0}\left\langle r^2\right\rangle\ ,$$

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 $E=E_n+\mu_BB(m_l+2m_s)\ ,\ \Delta E_{\text{so}}=-E_n\dfrac{\alpha^2Z^2}{n}\dfrac{m_lm_s}{l(l+1/2)(l+1)}(1-\delta_{l0})$

$$\langle\gamma LSM_L'M_J'|H_{\text{so}}|\gamma LSM_LM_J\rangle=T_{\gamma LS}M_LM_S\,\delta_{M_L'M_L}\,\delta_{M_S'M_S}\ ,\ \Delta E=\mu_B(M_L+2M_S)+T_{\gamma LS}M_LM_S$$

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

$$H'=g_J\mu_BBJ_z\ ,\ \Delta E=g_J\mu_BBM_J$$

5. Espectroscopias atómicas

$$\psi=\sum_n C_n(t)\mathrm{e}^{-iE_nt/\hbar}\langle\phi_n\rangle\ ,\ \dot{C}_f^{(0)}=0\ ,\ \dot{C}_f^{(1)}=-\frac{i}{\hbar}\sum_n C_n^{(0)}H'_{fn}\mathrm{e}^{i\omega_{fn}t}\ ,\ C_f^{(t)}\underset{t=0\to|n\rangle}{=}-\frac{i}{\hbar}\int_0^t\mathrm{d}t'H'_{fi}\mathrm{e}^{i\omega_{fi}}$$

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

$$\dot{N}_{1\to2}=W^{\text{est}}N_1\ ,\ \dot{N}_{2\to1}=W^{\text{est}}N_2+W^{\text{s}}N_2\ ;\ \Delta l=\pm1\ ,\ \Delta m_l=0,\pm1\ ,\ \pi_i=-\pi_f\ ,\ \Delta m_s=0$$

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

$$\text{est.fina } \Delta j=0,\pm1\ ,\ \Delta m_l=0,\pm1\ ,\ \pi_f=-\pi_i$$

$$\text{multi. } \Delta J=0,\pm1(\text{no } L=L'=0)\ ,\ \Delta M=0,\pm1\ ,\ \pi_f=-\pi_i\ ,\ \Delta S=0$$

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

6. Varios

$$\langle Y_{l_1m_1}|C_{LM}|Y_{l_2m_2}\rangle = \sqrt{\frac{2l_2+1}{2l_1+1}}\,\langle Ll_200|l_10\rangle\,\langle Ll_2Mm_2|l_1m_1\rangle \;,\; C_{LM}=\sqrt{\frac{4\pi}{2L+1}}Y_{LM}$$

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

$$\begin{aligned}
a_0 &= \frac{\hbar^2}{me^2} = 0{,}529177\,\mathrm{\mathring{A}} \\
t_0 &= \frac{\hbar^3}{me^4} = 2{,}41888\times 10^{-17}s \\
E_h &= \frac{me^4}{\hbar^2} = 27{,}2114eV \\
c &= \frac{1}{\alpha} \qquad \mu_B = \alpha/2 \\
1\mathrm{cm}^{-1} &= 1{,}2398\times 10^{-4}\mathrm{eV}
\end{aligned}$$

$$\begin{aligned}
p_{10}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} 2r\mathrm{e}^{-Zr/a_0} \\
p_{20}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{2}}\left[1-\frac{1}{2}\frac{Zr}{a_0}\right]\mathrm{e}^{-Zr/2a_0} \\
p_{21}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{2\sqrt{6}}\frac{Zr^2}{a_0}\mathrm{e}^{-Zr/2a_0}
\end{aligned}$$

$$\begin{aligned}
\langle r^{-2}\rangle &= \frac{Z^2}{a_0^2}\frac{1}{n^3(l+1/2)} \\
\langle r^{-1}\rangle &= \frac{Z}{a_0}\frac{1}{n^2} \\
\langle r\rangle &= \frac{a_0}{Z}\frac{1}{2}\left(3n^2-l(l+1)\right) \\
\langle r^2\rangle &= \frac{a_0^2}{Z^2}\frac{n^2}{2}\left(5n^2+1-3l(l+1)\right)
\end{aligned}$$

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

$$\langle Y_{l_3m_3}|Y_{l_1m_1}|Y_{l_2m_2}\rangle = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}}\,\langle l_1l_200|l_30\rangle\,\langle l_1l_2m_1m_2|l_3m_3\rangle$$

$$[J_i,J_j] = i\epsilon_{ijk}J_k\;,\; J_{\pm1} = \mp\frac{1}{\sqrt{2}}\left(J_x\pm iJ_y\right)\;,\; J_0 = J_z\;,\; J^2 = -J_{+1}J_{-1}+J_0^2-J_{-1}J_{+1}$$

$$J_{\pm1}\,|jm\rangle = \mp\sqrt{\frac{1}{2}\Big(j(j+1)-m(m\pm1)\Big)}\;,\; A_i = |\vec{A}|\,C_{1i}\;,\; C_{LM} = \sqrt{\frac{4\pi}{2L+1}}Y_{LM}$$

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

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

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