Formulari de Física Atòmica i Radiació

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I. Àtoms d'un Electró

$$\mu = \frac{\mathrm{m_e} M}{\mathrm{m_e} + M} \quad \mathbf{r} = \mathbf{r_2} - \mathbf{r_1} \quad \mathbf{R} = \frac{M\mathbf{r}_1 + \mathrm{m_e}\mathbf{r}_2}{M + \mathrm{m_e}}$$

Hamiltonià:

$$\mathcal{H} = -\frac{\hbar^2}{2(M+\mathrm{m_e})}\nabla^2_{\mathbf{R}_{\mathrm{CM}}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(r) = \mathcal{H}_{\mathrm{CM}} + \mathcal{H}_{\mathbf{r}}$$

Moment angular orbital:

$$\mathbf{L} = \frac{1}{\hbar}\mathbf{r}\times\mathbf{p} = -i\mathbf{r}\times\boldsymbol{\nabla} \quad [L_i, L_j] = i\epsilon_{ijk}L_k \quad [L^2, L_i] = 0$$

$$L^2 Y_{\ell m} = \ell(\ell+1)Y_{\ell m} \quad L_z Y_{\ell m} = m Y_{\ell m}$$

$$\langle Y_{\ell' m'} | Y_{\ell m}\rangle = \delta_{\ell\ell'}\delta_{mm'}$$

$$Y^*_{\ell m} = (-1)^m Y_{\ell -m} \quad Y_{\ell m}(\theta,\phi) = (-1)^\ell Y_{\ell m}(\pi-\theta, \pi+\phi)$$

Camp central:

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi) \qquad P_{n\ell}(r) = rR_{n\ell}(r)$$

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 P_{n\ell}(r)}{\mathrm{d}r^2} + \left[\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right]P_{n\ell}(r) = E_{n\ell}P_{n\ell}(r)$$

$$\langle P_{n\ell}(r) | P_{n'\ell}(r)\rangle = \delta_{nn'} \quad n_r = n-\ell-1 \quad E_n = -\frac{Z^2}{2n^2}\mathrm{m_e}c^2\alpha^2$$

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

Teorema del virial:

$$2\langle T\rangle - \langle \mathbf{r}\cdot\boldsymbol{\nabla}V\rangle = 0$$

$$2\langle T\rangle + \langle V\rangle = 0 \quad \langle T\rangle = -E_n \quad \langle V\rangle = 2E_n$$

$$\frac{\langle v^2\rangle^{1/2}}{c} = \frac{Z}{n}\alpha$$

Àtoms de Rydberg

$$Z_{\mathrm{ef}} = 1 \quad \langle r\rangle_n \approx n^2 a_0 \quad \Delta E_{n,n+1} \approx \frac{2|E_1|}{n^3}$$

Efecte de massa finita del nucli:

$$E_n = -\frac{Z^2}{2n^2}(\mu\alpha^2c^2) = \frac{\mu}{\mathrm{m_e}}E_n(M=\infty)$$

$$a_\mu = \frac{\hbar^2}{\mu e^2} = \frac{\mathrm{m_e}}{\mu}a_0 \qquad E_\mu = \frac{\mu}{\mathrm{m_e}}E_h$$

Efecte de tamany finit del nucli:

$$\Delta E = \frac{Z^4 e^2}{n^3 a_\mu^3}\frac{2}{5}R_N^2\delta_{\ell,0} = \frac{Z^4}{n^3}\frac{2}{5}\left(\frac{R_N}{a_\mu}\right)^2 E_\mu\delta_{\ell,0}$$

Àtoms exòtics:

(i) **Positroni** (e^+, e^-): $\mu = \frac{\mathrm{m_e}}{2}$, $a_\mu = 2a_0$
(ii) **Muoni** (μ^+, e^-)
(iii) **Àtoms muònics** $(e^- \leftrightarrow \mu^-)$
(iv) **Àtoms hadrònics** $(e^- \leftrightarrow \text{hadró}^-)$

Moment angular d'spin

$$\mathbf{S} = \frac{\boldsymbol{\sigma}}{2} \qquad \chi_{m_s} \equiv |s, m_s\rangle$$

$$S^2|s,m_s\rangle = s(s+1)|s,m_s\rangle \quad S_z|s,m_s\rangle = m_s|s,m_s\rangle$$

Moment angular generalitzat

$$J^2|j,m\rangle = j(j+1)|j,m\rangle \quad J_z|j,m\rangle = m|j,m\rangle$$

Acoblament de dos moments angulars:

$$J^2 = J_1^2 + J_2^2 + 2\mathbf{J}_1\cdot\mathbf{J}_2 \quad J_z = J_{1z} + J_{2z}$$

$$m = m_1 + m_2 \quad j = |j_1 - j_2|, \ldots, j_1 + j_2 \quad m = -j, \ldots, j$$

$$|j_1, j_2, m_1, m_2\rangle \to |j_1, j_2, j, m\rangle$$

Acoblament de L i S:

$$|\ell, s, m_\ell, m_s\rangle = Y_{\ell m_\ell}\chi_{sm_s}$$

$$[J^2, L_z + S_z] = 0 \quad [J^2, L_z] \neq 0 \quad [J^2, S_z] \neq 0$$

$$|l, s, j, m\rangle \equiv \Omega^\ell_{jm}(\theta,\phi) \qquad \left\langle \Omega^{\ell'}_{j'm'} \middle| \Omega^\ell_{jm}\right\rangle = \delta_{jj'}\delta_{mm'}\delta_{\ell\ell'}$$

$$\mathbf{L}\cdot\mathbf{S}|j,m\rangle = \frac{1}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]|j,m\rangle$$

Moments dipolars magnètics:

$$\boldsymbol{\mu}_L = -\mu_B\mathbf{L} \quad \boldsymbol{\mu}_S = -g_s\mu_B\mathbf{S} \quad U = -\boldsymbol{\mu}\cdot\mathbf{B}$$

Equació de Pauli

$$\mathcal{H}_P = \frac{1}{2\mathrm{m}}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 - e\varphi - \boldsymbol{\mu}_S\cdot\mathbf{B}$$

$$\psi_{n\ell m_\ell m_S}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi)\chi_{m_S}$$

Estructura fina:

$$\mathcal{H}_D = \boldsymbol{\alpha}\cdot(\mathbf{p}c - q\mathbf{A}) + \beta mc^2 + q\varphi$$

$$\mathcal{H}_{\mathrm{m}} = -\frac{-p^4}{8\mathrm{m}^3c^2}\mathbb{I}_2 \quad \mathcal{H}_{SO} = -\frac{e\hbar}{2\mathrm{m}^2c^2}\mathbf{S}\cdot(\boldsymbol{\nabla}\varphi\times\mathbf{p})$$

$$H_{Dw} = -\frac{e\hbar}{2\mathrm{m}^2c^2}\nabla^2\varphi\mathbb{I}_2 = \frac{\pi\hbar^2e^2Z}{2\mathrm{m}^2c}\delta(\mathbf{r})\mathbb{I}_2$$

Total:

$$\Delta E_{nj} = E_n\left(\frac{Z\alpha}{n}\right)^2\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) < 0$$

$$\left|\frac{\Delta E_{nj}}{E_n}\right| \approx 5\times10^{-5}\frac{Z^2}{n^2} \qquad j = \ell \pm \frac{1}{2} \quad Z \leq 30$$

Particulars:

$$\Delta E_{\rm m} = E_n \left(\frac{Z\alpha}{n}\right)^2 \left(\frac{n}{\ell+\frac{1}{2}} - \frac{3}{4}\right)$$

$$\Delta E_{Dw} = -\frac{Z\alpha^2}{n} E_n \delta_{\ell,0}$$

$$\Delta E_{SO} = -E_n \frac{(Z\alpha)^2}{2n\left(j+\frac{1}{2}\right)\left(\ell+\frac{1}{2}\right)} \cdot \begin{cases} +1 & j=\ell+\dfrac{1}{2} \\ 0 & j=0 \\ -1 & j=\ell-\dfrac{1}{2} \end{cases}$$

Estructura hiperfina:

$$\boldsymbol{\mu} = g_I \mu_N \mathbf{I} \qquad \mathbf{F} = \mathbf{J} + \mathbf{I} \quad F = |j-I|, \ldots, j+I$$

$$\Delta E_{\rm hip} = C\langle \mathbf{J}\cdot\mathbf{I}\rangle = C\frac{1}{2}\left[F(F+1) - j(j+1) - I(I+1)\right]$$
$$\Delta E_{F+1} - \Delta E_F = C(F+1)$$

II. Àtoms multielectrònics

$$\mathcal{H} = -\frac{\hbar^2}{2\mathrm{m}}\nabla^2_{\mathbf{R}_0} - \sum_{i=1}^{N}\frac{\hbar^2}{2\mathrm{m_e}}\nabla^2_{\mathbf{R}_i} - \sum_{i=1}^{N}\frac{Ze^2}{r_i} + \sum_{i<j}\frac{e^2}{r_{ij}}$$

$$\mathcal{H}_{CM} = -\frac{\hbar^2}{2(M+N\mathrm{m_e})}\nabla^2_{\mathbf{R}}$$

$$\mathcal{H}_{\rm rel} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i} - \frac{\hbar^2}{2M}\sum_{i<j}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j} - \sum_{i=1}^{N}\frac{Ze^2}{r_i} + \sum_{i<j}\frac{e^2}{r_{ij}}$$

Sistema de partícules idèntiques

$$[T_{ij}, \mathcal{H}] = 0 \quad T_{ij}\psi = \pm\psi$$
$$[\mathcal{H}, P] = 0$$

TS: $T_{ij}\psi_S = \psi_S \ \forall i,j \ \Leftrightarrow \ P\psi_S = \psi_S \ \ \forall P$
TA: $T_{ij}\psi_A = -\psi_A \ \forall i,j \ \Leftrightarrow \ P\psi_A = (-1)^P\psi_A \ \ \forall P$

$$S_N = \sum_p \frac{p}{N!} = S_N^\dagger = S_N^2 \quad A_N = \sum_p (-1)^p \frac{p}{N!} = A_N^\dagger = A_N^2$$

Fermions sense interacció

$$\mathcal{H}_0\varphi_i = E_i\varphi_i \Rightarrow E = \sum_i E_i \quad \psi = \prod_i \varphi_i$$

Determinant d'Slater:

$$\psi_A(x_1,...,x_N) = \frac{1}{\sqrt{N!}}\sum_p (-1)^p \varphi_1(x_{p1})\cdots\varphi_N(x_{pN})$$

Model de partícules independents per l'àtom (MPI)

$$\mathcal{H}^{\rm MPI} = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2\mu}\nabla_i^2 + V_{\rm ef}(r)\right) \quad V_{\rm ef}(r) = -\frac{Ze^2}{r} + S(r)$$

Potencial de ionització (per un e^- de valència ns^1)

$$I_p = \frac{Z_{\rm ef}^2}{2n^2}E_h$$

Àtom d'Heli

$$\mathcal{H} \simeq \left(-\frac{\hbar^2}{2\mathrm{m}}\nabla_1^2 - \frac{Ze^2}{r_1}\right) + \left(-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze^2}{r_2}\right) + \frac{e^2}{r_{ij}}$$

Estat fonamental $1s^2$

Sense interacció: $E = E_{n=1} + E_{n=1}$

Teoria de pertorbacions: $\Delta E = \frac{5}{8}Z$

Mètode variacional: $E = Z_{\rm ef}^2 - 2Z_{\rm ef}Z + \frac{5}{8}Z_{\rm ef}$
$Z_{\rm ef} = Z - \frac{5}{16}$

Nivells excitats $(1s, n\ell)$

$$\Psi = \psi_+\chi_{00} \quad \Psi = \psi_-\chi_{1M_S}$$

$$\psi_\pm(\mathbf{r_1},\mathbf{r_2}) = \frac{1}{\sqrt{2}}[u_{1s}(\mathbf{r_1})u_{nlm}(\mathbf{r_2}) \pm u_{nlm}(\mathbf{r_1})u_{1s}(\mathbf{r_2})]$$

Sense interacció: $E = E_{1s} + E_{nl} = -\frac{Z^2}{2}\left(1 + \frac{1}{n^2}\right)$

Teoria de pertorbacions: $\Delta E = J \pm K$

$$J = \iint |\varphi_{100}(\mathbf{r}_1)|^2 \frac{e^2}{r_{12}} |\varphi_{n\ell m_L}(\mathbf{r}_2)|^2 \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

$$K = \iint \varphi^*_{100}(\mathbf{r}_1)\varphi^*_{n\ell m_L}(\mathbf{r}_2)\frac{e^2}{r_{12}}\varphi_{100}(\mathbf{r}_2)\varphi_{n\ell m_L}(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

Mètode variacional: $E = I^{(Z_{1s})} + I^{(Z_{nl})} + J + K$

Degeneració

$$D(n\ell; q) = \binom{2(2\ell+1)}{q} = \frac{[2(2\ell+1)]!}{[2(2\ell+1)-q]!q!}$$

$$^{2S+1}L \Rightarrow D = \sum_{LS}(2L+1)(2S+1)$$

$$^{2S+1}L_J \Rightarrow D = 2J+1$$

Acoblament LS (o acoblament de Russell-Sanders)

$$\Delta E_{so} = \frac{1}{2}T_\alpha(L,S)[J(J+1) - L(L+1) - S(S+1)]$$

Capa menys que semiplena: $T_\alpha > 0$

Capa més que semiplena: $T_\alpha < 0$

Capa semiplena $T_\alpha = 0$

Regla de l'interval de Landé:

$$E(J+1)-E(J) = T_\alpha(J+1) \Rightarrow \frac{E(J+1)-E(J)}{E(J)-E(J-1)} = \frac{J+1}{J}$$

Paritat

$$\text{Paritat} = (-1)^{\sum_i l_i}$$

III. Àtoms en Camps Externs
(Efecte Zeeman)

$$\mathcal{H} = -\frac{\hbar^2}{2\mathrm{m}}\nabla^2 - \frac{Ze^2}{r} + \mu_B B(L_z + 2S_z) + \frac{\hbar^2}{2\mathrm{m}_\mathrm{e}^2 c^2}\frac{Ze^2}{r^3}\mathbf{L}\cdot\mathbf{S}$$

Situació en què $\mathcal{H}_B \gg \mathcal{H}_{\mathrm{SO}}$
Zeeman Normal

$$E = E_n + \Delta E_{m_\ell + 2m_s} = E_n + \mu_B B(m_\ell + 2m_s)$$

Paschen-Back

$$E_{n\ell m_\ell m_s} = E_n + \Delta E_{m_\ell+2m_s} - E_n\frac{Z^2\alpha^2}{n}\frac{m_\ell m_s}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}(1-\delta_{\ell 0})$$

Situació en què $\mathcal{H}_B \ll \mathcal{H}_{\mathrm{SO}}$
Sense pertorbar:

$$\Delta E_{SO} = -E_n\frac{(Z\alpha)^2}{2n\left(j+\frac{1}{2}\right)\left(\ell+\frac{1}{2}\right)}\cdot\begin{cases} +1 & j=\ell+\dfrac{1}{2} \\ 0 & j=0 \\ -1 & j=\ell-\dfrac{1}{2}\end{cases}$$

Efecte Zeeman Anòmal:

$$\Delta E_B = \mu_B B m_j\left(\frac{2j+1}{2\ell+1}\right) = \mu_b B g_j m_j$$

Fórmula de Landé:

$$g_j = g_\ell\frac{j(j+1)+\ell(\ell+1)-s(s+1)}{2j(j+1)} + g_s\frac{j(j+1)+s(s+1)-\ell(\ell+1)}{2j(j+1)}$$

Àtoms multielectrònics

$$\mathcal{H}'_B = \mu_B B(L_z + 2S_z)$$

Camp B intens:

- Z.N.: $\Delta E_B = \mu_B B(M_L + 2M_S)$
- P.B.: $\Delta E_B = \mu_B B(M_L + 2M_S) + \Delta E_{SO}(B \neq 0)$

Camp B feble:

$$\Delta E_B = g_J \mu_B B M_J$$

Fórmula de Landé:

$$g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

IV. Radiació

Regles de selecció (dipolar elèctric):
Estructura grossa:

$$\Delta\ell = \pm1, \quad \Delta m_\ell = 0, \pm1 \quad \Delta m_s = 0$$

Estructura fina:

$$\Delta\ell = \pm1, \quad \Delta j = 0, \pm1 \quad \Delta m_j = 0, \pm1$$

Multielectrònics:

$$\Delta J = 0, \pm1, \quad \Delta M_J = 0, \pm1 \quad \pi_f = -\pi_i$$

A. Constants i Unitats

$$\alpha = \frac{e^2}{\hbar c} = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137,036}$$

$$\mathrm{m}_\mathrm{e}c^2\alpha^2 = \frac{e^2}{a_0} = \frac{\mathrm{m}_\mathrm{e}e^4}{\hbar^2} = 27,2114\ \mathrm{eV} \equiv E_h$$

$$a_0 = \frac{\hbar^2}{\mathrm{m}_\mathrm{e}e^2} = 5,2918\times10^{-11}\ \mathrm{m}$$

$$\mu_B = \frac{e\hbar}{2\mathrm{m}_\mathrm{e}c} = \frac{1}{2c} = \frac{\alpha}{2}$$

$$\mu_N = \frac{e\hbar}{2\mathrm{m}_\mathrm{e}c} = \frac{\mu_B}{1836,15}$$

$$1\ \mathrm{cm}^{-1} = 1,23984\times10^{-4}\ \mathrm{eV}$$

$$1\ \mathrm{eV} = 8065,54\ \mathrm{cm}^{-1}$$

$$1\ \mathrm{cm}^{-1} = 2,988\times10^4\ \mathrm{MHz}$$

B. Teoria de Pertorbacions

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \qquad E \approx E_n + \Delta E$$

Sense degeneració: $\Delta E = \langle\psi_0|\,\mathcal{H}'\,|\psi_0\rangle$
Amb degeneració: $\Delta E = \langle\psi_{0\beta}|\,\mathcal{H}'\,|\psi_{0\alpha}\rangle$

C. Mètode Variacional

$$H\,|\psi_n\rangle = E_n\,|\psi_n\rangle \quad |\phi\rangle = |\psi_n\rangle \quad E_0 \leq E[\phi] = \frac{\langle\phi|\,H\,|\phi\rangle}{\langle\phi|\,\phi\rangle}$$

$$\delta E[\phi] = 0$$