Atome d'Hélium

2 électrons : si on néglige leur interaction de Coulomb

États propres imperturbés $\mathcal{H}_0 = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$

$$E_{n_1 n_2} = -Z^2 R_y \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \leftarrow \quad Z = 2$$

$n_1, n_2 = 1, 2, \ldots$

$$\Psi^{(\pm)}_{\substack{n_1 l_1 m_1 \\ n_2 l_2 m_2}}(\vec{r}_1, \sigma_1 ; \vec{r}_2 \sigma_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1 l_1 m_1}(\vec{r}_1)\,\psi_{n_2 l_2 m_2}(\vec{r}_2) \pm \psi_{n_2 l_2 m_2}(\vec{r}_1)\,\psi_{n_1 l_1 m_1}(\vec{r}_2)\right]$$

$\langle \sigma_1 \sigma_2 \mid S, M_S \rangle$

$S_1^z \quad S_2^z$

état de la somme des deux spins

$S = 0$ singulet $(+)$

$S = 1$ 3 triplets $(-)$

$$\langle \sigma_1 \sigma_2 \mid S = 0, M_S = 0 \rangle = \frac{\delta_{\sigma_1 \uparrow}\,\delta_{\sigma_2 \downarrow} - \delta_{\sigma_2 \uparrow}\,\delta_{\sigma_1 \downarrow}}{\sqrt{2}}$$

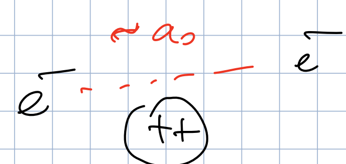
Fondamental

$n_1 = n_2 = 1$

$$E_{11} = -8 R_y \longrightarrow \Psi^{(+)}$$

traitement de l'interaction $e^- - e^-$ en perturbation

$$\mathcal{H} = \mathcal{H}_0 + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$



$$\Delta E_{\text{Coul.}} \sim \frac{e^2}{4\pi\varepsilon_0 a_0} = 2 R_y \approx 27\ \text{eV} \quad \text{estimation}$$

$$\Delta E_{Coul.} = \langle \Psi^{(+)}_{100} \,|\, \frac{e^2}{4\pi\epsilon_0 r_{12}} \,|\, \Psi^{(+)}_{100} \rangle$$

$$= \int d^3r_1 \, d^3r_2 \; |\psi_{100}(\vec{r}_1)|^2 \, |\psi_{100}(\vec{r}_2)|^2 \; \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$= \dots = \underline{34 \text{ eV}}$$

<u>États excités</u> : perturbation due à $\frac{e^2}{4\pi\epsilon_0 r_{12}}$

n_1, n_2

états excités "<u>intéressants</u>" $\longrightarrow$ états excités de He proprement dit

$$\boxed{n_1 = 1 \qquad n_2 \geq 2}$$

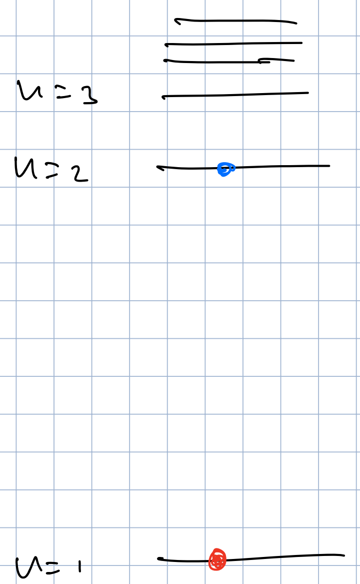
en dehors de cette famille :

$$E_{22} = -4 R_y \left(\frac{1}{4} + \frac{1}{4} \right) = \underline{-2 R_y}$$

comparer à l'<u>énergie d'ionisation</u> de He

$$E_{1\infty} = -4 R_y \left(1 + \cancel{\frac{1}{\infty}}^{\,0} \right) = -4 R_y$$

$$E_{22} > E_{1\infty} = E(He^+)$$



$n_1 l_1 m_1 = 100$

$$\Psi^{(\pm)}_{n\,l\,m,\,S M_S}(\vec r_1 \sigma_1 ; \vec r_2 \sigma_2)$$

$$= \left[\psi_{100}(\vec r_1)\, \psi_{nlm}(\vec r_2) \pm \psi_{nlm}(\vec r_1)\, \psi_{100}(\vec r_2) \right]$$

$$\langle \sigma_1 \sigma_2 | S M_S \rangle$$

$$E_{n_1=1,\, n_2=n} = - Z^2 R_y \left(1 + \frac{1}{n^2}\right)$$

<u>perturber</u> ces états excités avec $\frac{e^2}{4\pi\varepsilon_0 r_{12}}$

$\Psi^{(\pm)}_{nlm}$ dégénérés

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

$m = -l, \dots, l$

$\pm \longrightarrow S = 1, \quad M_S = 0, \pm 1$

$\hookrightarrow S = 0$

matrice des perturbations $\qquad \epsilon = \pm 1$

$$\left\langle \Psi^{(\epsilon')}_{n l' m', S' M_S'} \right| \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\uparrow} \left| \Psi^{(\epsilon)}_{n l m, S M_S} \right\rangle \sim \delta_{SS'}\ \delta_{M_S M_S'}$$

$$\vec S = \vec S_1 + \vec S_2 \longrightarrow \hbar^2 S(S+1)$$

$$\vec L = \vec L_1 + \vec L_2 \longrightarrow \hbar^2 L(L+1) \qquad L = l \qquad \begin{array}{l} l_1 = 0 \\ l_2 = l \end{array}$$

$$L = |l_1 - l_2|, \dots, l_1 + l_2$$

$$L^z = L_1^z + L_2^z \rightarrow \hbar M = \hbar(m_1 + m_2) = \hbar m$$

$\rightarrow \left| \Psi^{(\pm)}_{nlm,sM_s} \right\rangle$ état propre de $\vec{L}^2$, L^z, $\vec{S}^2$, S^z

opérateur d'échange $\hat{P}_{12}$ pour la partie spatiale

$$\hat{P}_{12} \underbrace{\psi_1(\vec{r}_1)\,\psi_2(\vec{r}_2)} = \underbrace{\psi_1(\vec{r}_2)\,\psi_2(\vec{r}_1)}$$

$$\hat{P}_{12} \left| \Psi^{(\pm)}_{nlm\,sM_s} \right\rangle = \pm \left| \Psi^{(\pm)}_{nlm\,sM_s} \right\rangle$$

$\dfrac{e^2}{4\pi\varepsilon_0 |\vec{r}_{12}|} \rightarrow$ invariant sous rotations

$$r_{12} = |\vec{r}_1 - \vec{r}_2|$$

$$\left[\vec{L}^2, \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right] = \left[L^z, \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]$$

$$= \left[\frac{e^2}{4\pi\varepsilon_0 r_{12}}, P_{12}\right] = 0$$

$$\left\langle \Psi^{(\varepsilon')}_{nl'm',s'M_s'} \right| \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}} \left| \Psi^{(\varepsilon)}_{nlm,sM_s} \right\rangle \sim \delta_{ss'}\,\delta_{M_sM_s'}\,\delta_{ll'}\,\delta_{mm'}\,\delta_{\varepsilon\varepsilon'}$$

$$= \Delta E^{(\pm)}_{nl\cancel{m}}$$

$$\left|\Psi^{(\pm)}_{nlm;\,SM_S}\right\rangle = \frac{1}{\sqrt{2}}\Big(|100\rangle\,|nlm\rangle \pm |nlm\rangle\,|100\rangle\Big)\,|SM_S\rangle$$

$$\Delta E^{(\pm)}_{nl} = \frac{1}{2}\Big[\big(\langle 100|\langle nlm| \pm \langle nlm|\langle 100|\big)\,\frac{e^2}{4\pi\epsilon_0 r_{12}}\,\big(|100\rangle|nlm\rangle \pm |nlm\rangle|100\rangle\big)\Big]$$

$$= \cancel{\frac{1}{2}}\;\langle 100|\langle nlm|\,\frac{e^2}{4\pi\epsilon_0 r_{12}}\,|100\rangle|nlm\rangle\; +$$

intégrale directe

$$J_{nl} = \int d^3r_1\, d^3r_2\,(-e)|\psi_{100}(\vec r_1)|^2(-e)|\psi_{nlm}(\vec r_2)|^2\,\frac{1}{4\pi\epsilon_0 r_{12}}$$

$$\pm\;\langle 100|\langle nlm|\,\frac{e^2}{4\pi\epsilon_0 r_{12}}\,|nlm\rangle|100\rangle$$

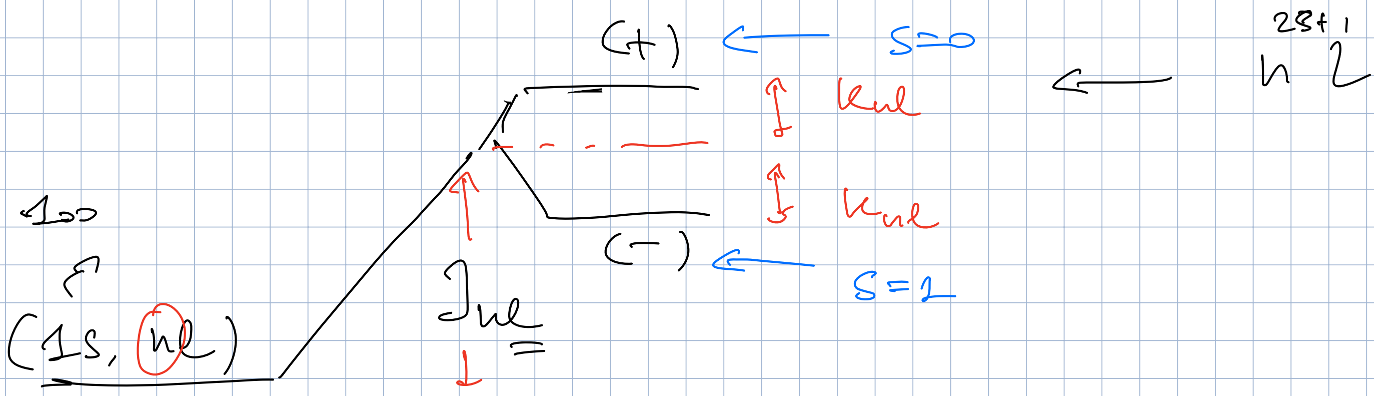
$$\int d^3r_1\, d^3r_2\;\psi^*_{100}(\vec r_1)\,\psi^*_{nlm}(\vec r_2)\,\psi_{100}(\vec r_2)\,\psi_{nlm}(\vec r_1)\,\frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$= K_{nl}$$

intégrale d'échange

$$\Delta E^{(\pm)}_{nl} = J_{nl} \pm K_{nl}$$

$$K_{nl} > 0\,.$$



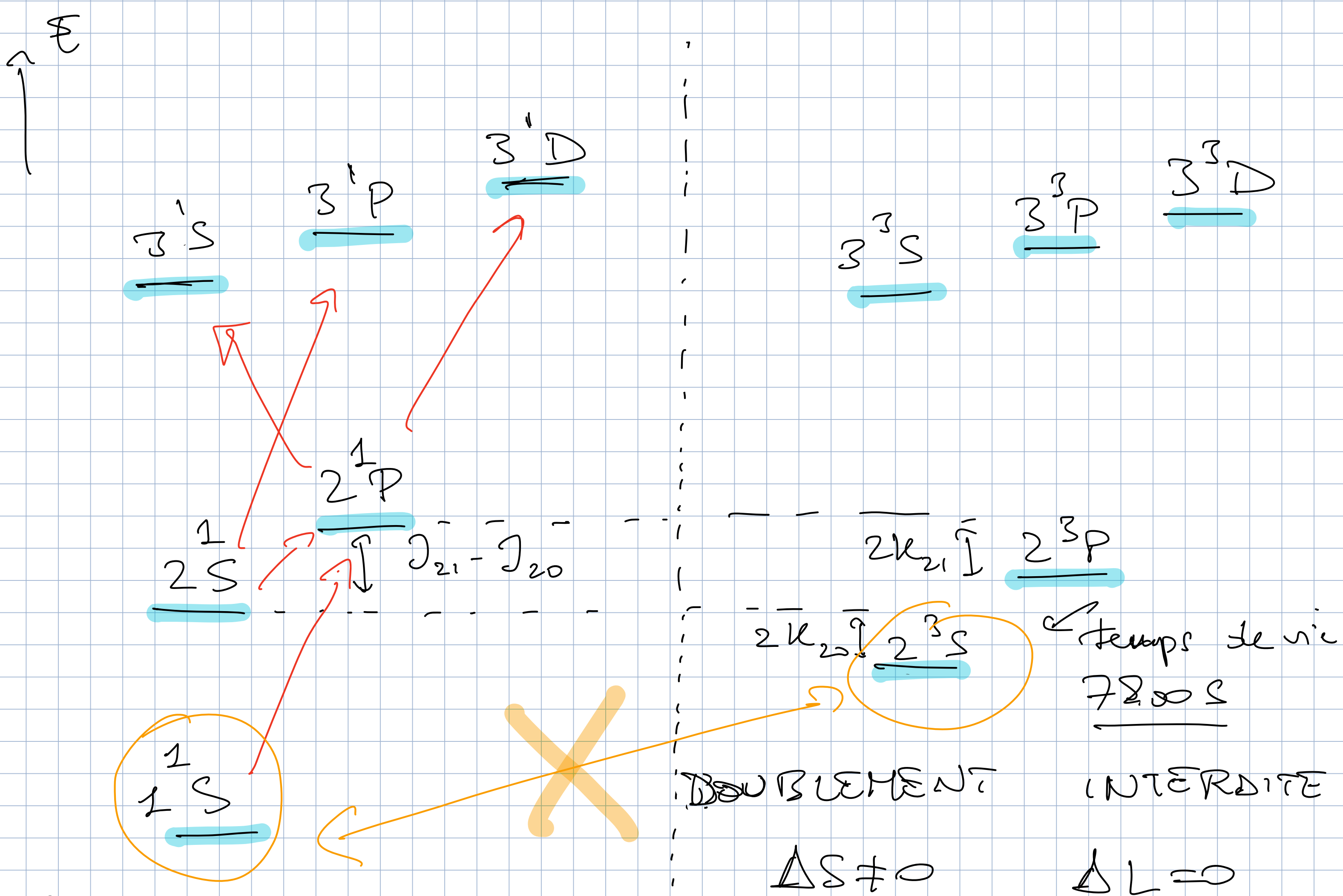
Niveaux d'énergie de He : notation spectroscopique

$$n^{2S+1}L \quad \begin{cases} n^1L & S=0 \\ n^3L & S=1 \end{cases}$$

$L \to l$

Spectre de He

$E^{(S)}_{nl} \rightarrow n\,^{2S+1}L$



(PARA-HELIUM)

$L = \quad 0 \quad 1 \quad 2 \ \ldots$

$S = 0$

(ORTHO-HELIUM)

$L = \quad 0 \quad 1 \quad 2 \ \ldots$

$S = 1$

- - - -

Règles de sélection (en approximation de dipôle)

$$\langle \Psi_{n l_i m_i S M_S} | \vec{E} \cdot \vec{D} | \Psi_{n l m_l S M_S} \rangle \neq 0$$

indépendant du spin

$$\vec{D} = -e\,(\vec{r}_1 + \vec{r}_2)$$

$\Delta n = n' - n =$ quelconque

$\Delta \ell =$

$\Rightarrow \Delta L = \cancel{0}, \pm 1$

$\Delta m = q$

$\Delta S = 0$

$\Delta M_S = 0$

$\sim$ Wigner-Eckart

$\ell 1$

$m q ; \ell' m'$

$$\vec{\varepsilon} \cdot \underline{\vec{D}} = \underline{D_q}$$

$$\vec{\varepsilon} = \vec{u}_q = \begin{cases} \vec{w} = \vec{e}_z \\ \vec{u}_{\pm 1} = \dfrac{\vec{e}_x \pm i\vec{e}_y}{\sqrt{2}} \end{cases}$$

$$\langle \Psi_{n'\ell'm' s' M_s'} | (-e)(r_{1q} + r_{2q}) | \Psi_{n\ell m s M_s} \rangle$$

$$= (-e)\, \delta_{SS'}\, \delta_{M_s M_s'} \frac{1}{2} \left(\langle 100| \langle n'\ell'm'| \pm \langle n'\ell'm'| \langle 100| \right) \underline{(r_{1q} + r_{2q})} \left(|100\rangle |n\ell m\rangle \pm |n\ell m\rangle |100\rangle \right)$$

$$= (-e)\, \delta_{SS'}\, \delta_{M_s M_s'} \frac{1}{2} \left[\langle n'\ell'm' | r_{1q} | n\ell m\rangle + (1 \to 2) \right]$$

atome d'hydrogène

$\Delta \ell = 0$

Atomes à N électrons

problème à N-corps

$$\mathcal{H} = \underbrace{-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{N}\frac{1}{r_i}} + \underbrace{\sum_{i<j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}}$$

$$= \sum_{i=1}^{N}\left[\frac{\hbar^2}{2m}\nabla_i^2 + V_{eff}(\vec{r}_i)\right] \longrightarrow \mathcal{H}_{CFA}$$

"champ moyen" vu par l'électron

$$\underbrace{+ \sum_{i=1}^{N}\left(-\frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{j(\neq i)}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} - V_{eff}(\vec{r}_i)\right)}_{\mathcal{H}_I}$$

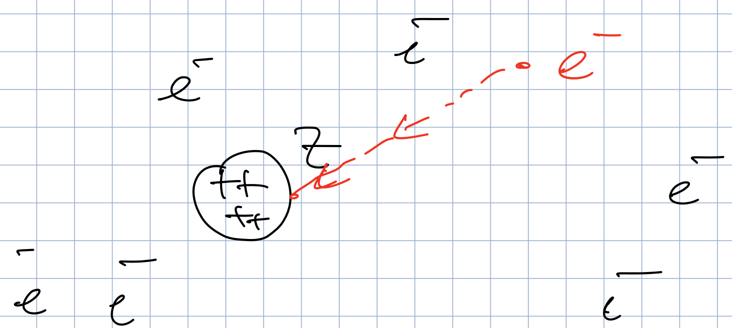
$\mathcal{H}_I$ perturbation de $\mathcal{H}_{CFA}$

"Central field approximation"

$$V_{eff}(\vec{r}_i) = V_{eff}(r_i)$$

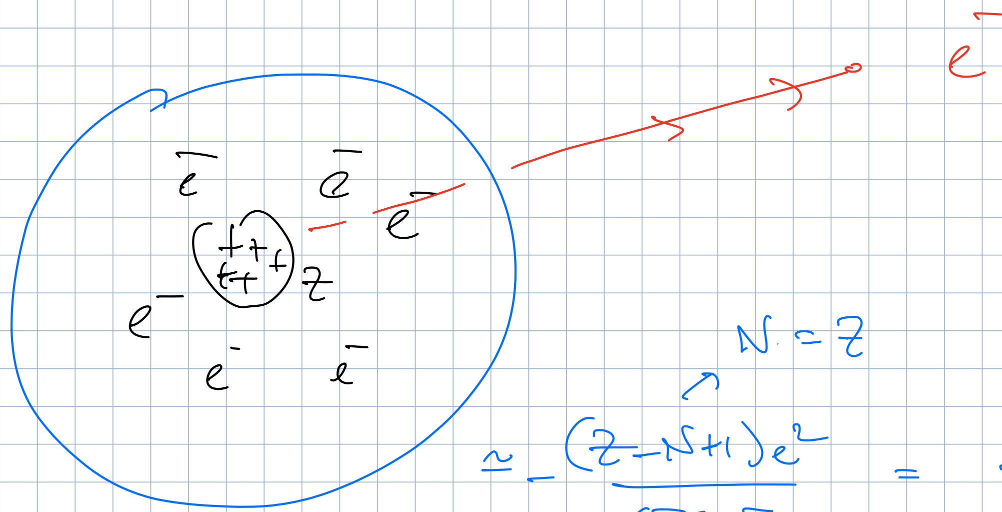
Image simple de $V_{eff}(r_i)$

$(r_i \to 0)$



$$V_{eff}(r) \simeq -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$(r_i \to \infty)$



$N = Z$

$$\simeq -\frac{(Z-N+1)e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{4\pi\epsilon_0 r}$$

$V_{eff}(r)\,\frac{4\pi\epsilon_0 r}{e^2}$