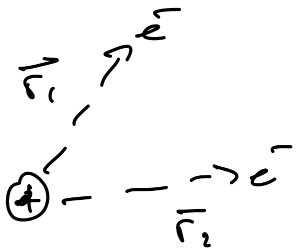
$$\langle \gamma' ; j' m' | V_q | \gamma ; j m \rangle$$

$$= \langle \gamma' ; j' \| V \| \gamma ; j \rangle \quad C^{1j}_{mq;\, j'm'}$$

$$\vec{V}$$

Hélium

$$H = \overbrace{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}^{H_0}$$



$$+ \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{H_{int}}$$

Spectre de H_0

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

État fondamental

$$E_{1\,1} = -8 R_y = \underline{-109 \text{ eV}} \qquad Z = 2$$

et → état spatial

$$|\Psi^{(\pm)}_{n_1 l_1 m_1;\, n_2 l_2 m_2}\rangle$$

$$\frac{1}{\sqrt{2}}\left(|n_1 l_1 m_1\rangle \otimes |n_2 l_2 m_2\rangle \pm |n_2 l_2 m_2\rangle \otimes |n_1 l_1 m_1\rangle\right)$$

$$\otimes |\chi^{(\mp)}\rangle$$

$$|\chi^{(-)}\rangle = \frac{|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle}{\sqrt{2}} = |S_{tot}=0, M_S=0\rangle$$

$$|\chi^{(+)}\rangle = \begin{cases} |\uparrow\uparrow\rangle & |S_{tot}=1, M_S=1\rangle \\ (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2} & 0 \\ |\downarrow\downarrow\rangle & -1 \end{cases}$$

État fondamental

$$\left(|100\rangle \otimes |100\rangle\right) \otimes |\chi^{(-)}\rangle$$

$$\Delta E_{int} = \langle 100| \otimes \langle 100| \frac{e^2}{4\pi\epsilon_0 r_{12}} |100\rangle \otimes |100\rangle$$

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

$$= \ldots = \underline{\underline{34\ eV}}$$

États excités

État symétrisé pour 2 particules indiscernables

$$|100\rangle \otimes |100\rangle \longrightarrow |100\rangle \otimes |n\ell m\rangle$$

$(1s,\ n\ell)$

« configuration électronique »

$$|\tilde{\Psi}^{(\pm)}_{n\ell m}\rangle \otimes |\chi^{(\mp)}\rangle \qquad \sigma\sigma' = -$$

$$|\tilde{\Psi}^{(\pm)}_{n\ell m}\rangle = \frac{1}{\sqrt{2}}\left[|100\rangle \otimes |n\ell m\rangle \pm |n\ell m\rangle \otimes |100\rangle\right]$$

$|\tilde{\Psi}^{(\pm)}_{n\ell m}\rangle$ → $S_{tot} = 0$ si $+$

↳ $S_{tot} = 1$ si $-$

$E_{1,n}$ → états symétrisés dégénérés

$2\ n^2$

$(\pm)\ (\ell m)$

perturber avec $\underbrace{\mathcal{H}_{int} = \dfrac{e^2}{4\pi\epsilon_0 r_{12}}}$

$$\langle \Psi^{(\sigma')\,*}_{n\ell' m'} | \mathcal{H}_{int} | \Psi^{(\sigma)}_{n\ell m} \rangle \underbrace{\langle \chi^{(\sigma')} | \chi^{(\sigma)} \rangle}$$

$$\sim \delta_{\ell\ell'}\ \delta_{mm'}\ \delta_{\sigma\sigma'}$$

$$\vec{L} = \vec{L}_1 + \vec{L}_2$$

$$\left[L^z,\ \dfrac{e^2}{4\pi\epsilon_0 r_{12}} \right] = 0$$

$\mathcal{H}_{int}$

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

$$\underbrace{\hat{U}_z(\vartheta) = e^{-\frac{i}{\hbar}\vartheta \hat{L}^z}}$$

$$[L^x, \mathcal{H}_{int}] = 0$$

$$[L^y, \mathcal{H}_{int}] = 0$$

$$[\vec{L}^2, \mathcal{H}_{int}] = 0$$

$\underline{\mathcal{H}_{int},\ \vec{L}^2,\ L^z}$ admettent une base commune

$$l=0$$

$$\rightarrow \left(|100\rangle \otimes |nlm\rangle \pm |nlm\rangle \otimes |100\rangle\right)$$

$$\underbrace{\vec{L}_1^2,\ L_1^z \qquad \vec{L}_2^2,\ L_2^z}_{} \qquad \vec{L}_1^2,\ L^z \qquad \vec{L}_2^2,\ L_2^z$$

$$\underbrace{\vec{L} = \vec{L}_1 + \vec{L}_2}_{}$$

$$\vec{L}^2 \rightsquigarrow \hbar^2 l(l+1)$$

$$\begin{cases} \vec{L}^2 \, |\Psi^{(\pm)}_{nlm}\rangle = \hbar^2 l(l+1) \, |\Psi^{(\pm)}_{nlm}\rangle \\ L^z \, |\Psi^{(\pm)}\rangle = \hbar m \, |\Psi^{(\pm)}\rangle \end{cases}$$

$$\Delta E^{\overset{d}{(\pm)}}_{nl} = \langle \Psi^{\overset{L}{(\pm)}}_{nlm} | \frac{e^2}{4\pi\epsilon_0 r_{12}} | \Psi^{(\pm)}_{nlm} \rangle$$

$$= \frac{1}{2}\left[\langle 100| \otimes \langle nlm| \pm \langle nlm| \otimes \langle 100|\right] \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$\left[|100\rangle \otimes |nlm\rangle \pm |nlm\rangle \otimes |100\rangle\right]$$

$$= \cancel{\frac{1}{2}}\left[\cancel{2}\langle 100| \otimes \langle nlm| \frac{e^2}{4\pi\epsilon_0 r_{12}} |100\rangle \otimes |nlm\rangle\right.$$

$$\sum \langle nlm| \otimes \langle 100| \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}} |nlm\rangle} \otimes |100\rangle$$

$$\pm \sum \langle 100| \otimes \langle nlm| \frac{e^2}{4\pi\epsilon_0 r_{12}} |nlm\rangle \otimes |100\rangle \Big]$$

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

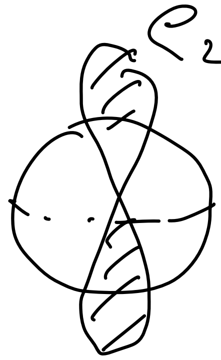
$$\pm \underbrace{\int d^3r_1\, d^3r_2\, \psi^*_{100}(\vec r_1)\, \psi^*_{nlm}(\vec r_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_{nlm}(\vec r_1)\, \psi_{100}(\vec r_2)}_{K_{nl}}$$

J_{nl} = intégrale directe

$$= \int d^3r_1 \int d^3r_2 \frac{\rho_1(\vec r_1)\, \rho_2(\vec r_2)}{4\pi\epsilon_0 r_{12}}$$

$\rho_1 = -e|\psi_{100}(\vec r_1)|^2$

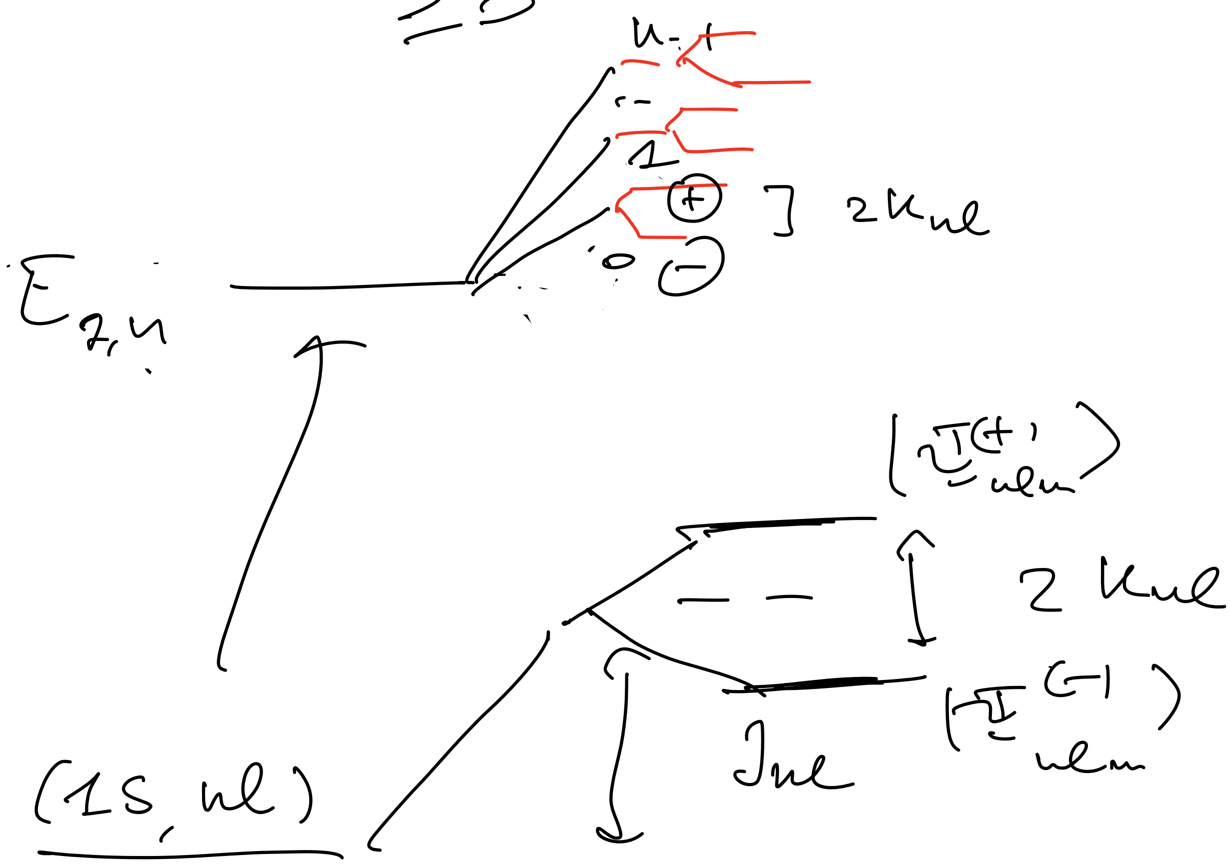
$\rho_2 = -e|\psi_{nlm}(\vec r_2)|^2$



K_{nl} = intégrale d'échange

croît avec l

$$\Delta E^{(\pm)}_{nl} = \underset{\geq 0}{\underline{J_{nl}}} \pm \underset{\geq 0}{\underline{K_{nl}}}$$



$({}^3\Psi^{(-)}_{nlm})$: empêche aux deux électrons d'être au même endroit spatial

$$|\,\Phi^{(\pm)}_{nlm}\rangle \otimes |\chi^{(\mp)}\rangle$$

états propres de $\vec{L}^2$, $\vec{S}^2$

$l \qquad S = 0, 1$

<u>niveau d'énergie :</u> $n\,{}^{2S+1}L$

$S, P, D, \ldots$

$l=0 \quad l=1 \quad l=2$

"termes spectroscopiques LS"
"termes de Russell–Saunders"
"couplage LS"

Etats excités $(nl, n'l')$

$n > 1, \quad n' > 1$

trop énergétiques

$n = 2$
$n' = 2$

$$E_{2,2} = -Z^2 R_y \left(\frac{1}{4} + \frac{1}{4}\right)$$

$$= -2 R_y$$

$$E_{2,2} > E_{n=1} + \text{électron libre}$$

$$= -4 R_y$$

Règles de sélection en approxim. de dipôle

$$n\,^{2S+1}L \longrightarrow n'\,^{2S'+1}L'$$

$(1s, nl)$

$$\vec{\varepsilon} \cdot \vec{D}$$

$$\vec{D} = -e(\vec{r}_1 + \vec{r}_2) \rightarrow D_q = -e(r_{1,q} + r_{2,q})$$

$$\langle \underset{=}{\Psi^{(\sigma')}_{n'l'm'}} | \otimes \langle \chi^{(\sigma')} | (r_{1q} + r_{2q}) | \Psi^{(\sigma)}_{nlm} \rangle \otimes | \chi^{(\sigma)} \rangle$$

$$\delta_{\sigma\sigma'}$$

$$r_{1q} \to r_{1q} \otimes \mathbb{1}$$

$$\quad\;\; 1 \qquad 2$$

$\Delta S = S' - S = 0$

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

$r_{2q} \to \underline{\mathbb{1}} \otimes r_{2q}$

$$= \frac{1}{2}\left(\langle 100| \otimes \langle n'l'm'| \pm \langle n'l'm'| \otimes \langle 100|\right) \underbrace{(r_{1q} + r_{2q})}$$

$$\left(|100\rangle \otimes |nlm\rangle \pm |nlm\rangle \otimes |100\rangle\right)$$

$$= \frac{1}{2}\Big[\cancel{\langle 100| r_{1q} |100\rangle}^{0} + \langle n'l'm'| r_{2q} | nlm\rangle$$

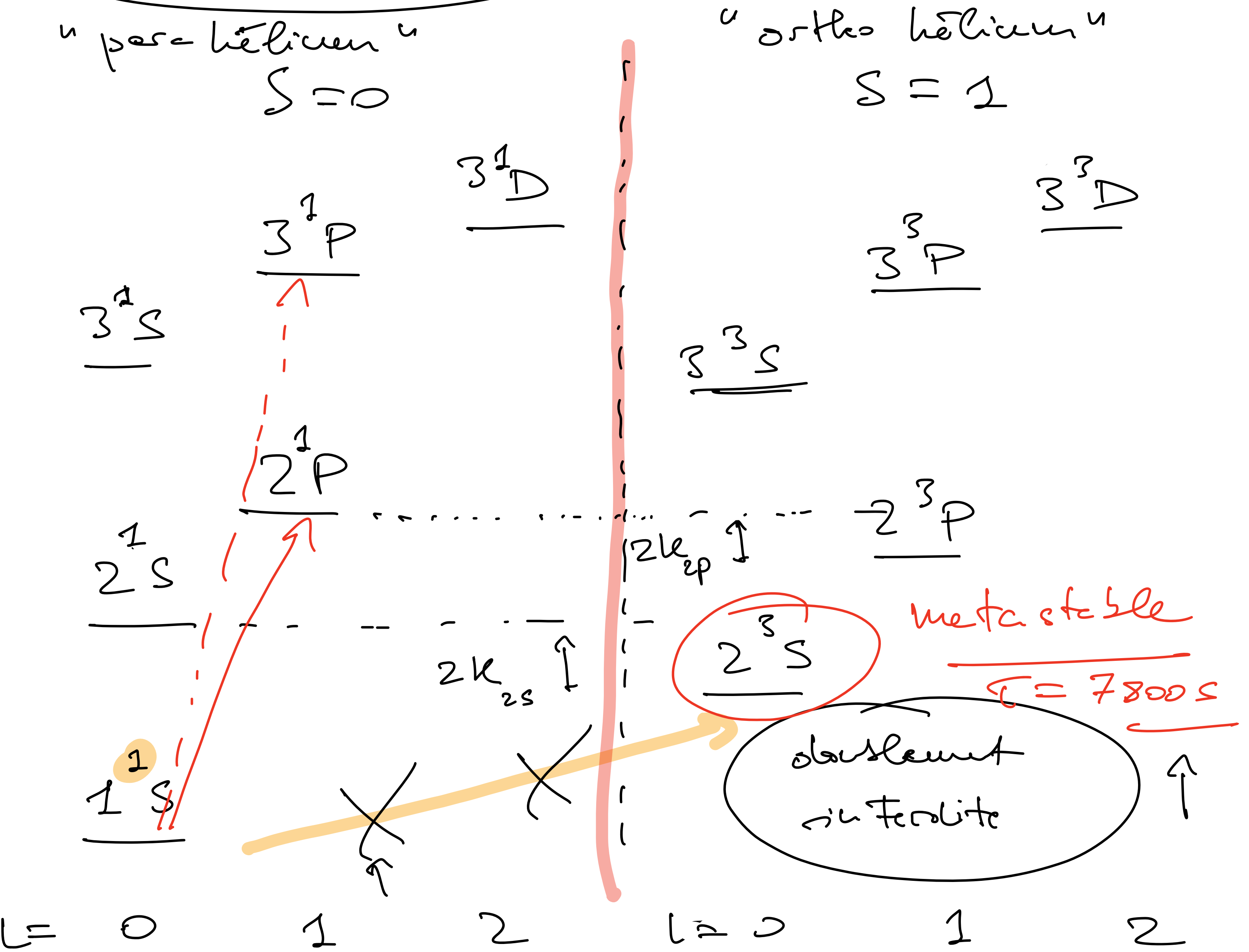
$$+ \underbrace{\langle n'l'm'| r_{1q} | nlm\rangle}\Big]$$

$$\Delta m = m' - m = q$$

$$\Delta l = l' - l = \pm 1$$

$$\Delta l = \pm 1$$

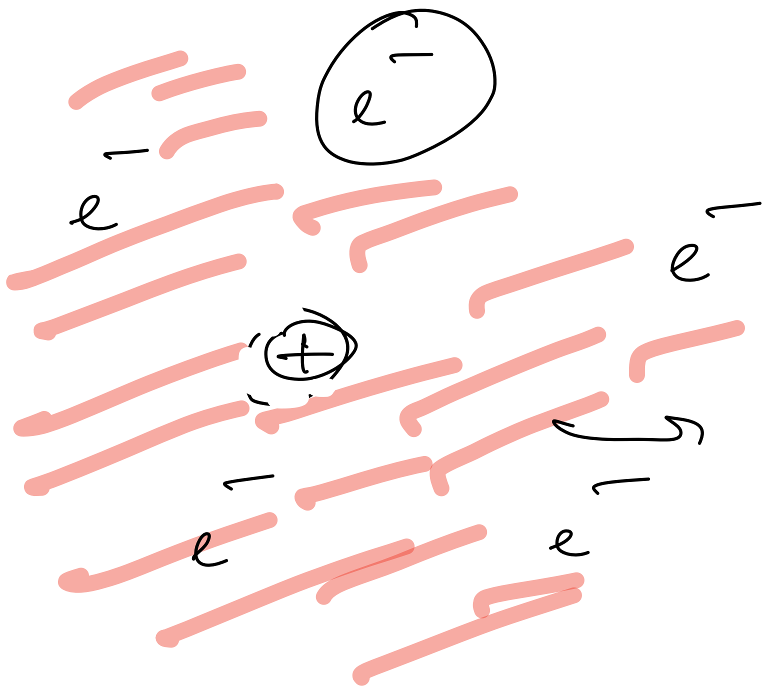
$$\Delta S = 0$$



Atomes à N électrons

$$\mathcal{H} = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{r_i} \right)$$

$$+ \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\varepsilon_0 \, r_{ij}}$$



distribution moyenne de charge associée à N−1 électrons

$$\mathcal{H}_{eff} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} + S(\vec{r})$$

écrantage → "screen"

$$\mathcal{H} = \underbrace{\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + S(|\vec{r}_i|)\right]}_{\mathcal{H}_{CF}} + \underbrace{\left(\frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i S(\vec{r}_i)\right)}_{\mathcal{H}_I}$$

$\mathcal{H}_{CF}$: Hamiltonien en approximation de champ central

H_I : Hamiltonien d'interaction

↳ perturbation de H_{CF}