Chap 4 : Termes bi electroniques / méthode (HF)

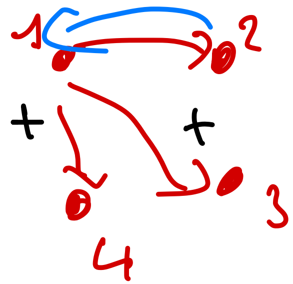
I Intro

(à noyaux fixes $\hat{T}_N = 0$)

$$\hat{H} = \sum_{i}^{e^-} \underbrace{h(i)}_{\text{monoé}} + \overbrace{\sum_{A}\sum_{B>A} V_{AB}}^{\text{noyaux}} + \sum_{i}^{e^-}\sum_{j>i} \frac{1}{r_{ij}}$$

évite double comptage

$$\sum_{i=1}^{4}\sum_{j>i}^{4} \frac{1}{r_{ij}} = \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}}$$



$\langle b(1)|\hat{h}(1)|\bar{b}(1)\rangle = 0$

↳ $\langle b(1)\alpha(1)|\hat{h}(1)|b(1)\beta(1)\rangle$

$= \langle b(1)|\hat{h}(1)|b(1)\rangle\langle\alpha(1)|\beta(1)\rangle$

$= \varepsilon_b \times 0$

$= 0$

$\hat{h}(i)|a(i)\alpha(i)\rangle$ agit sur espace $\frac{1}{r_{ij}}$

$\hat{S}_z(i)|a(i)\alpha(i)\rangle$ agit sur spin.

II Intégrales biélectroniques J_{ab} et K_{ab}

J_{ab} : coulomb — K_{ab} : échange

$\boxed{\text{Hückel} \neq \left| \begin{matrix} \alpha \\ \beta \end{matrix} \right.}$

II-1 coulomb J_{ab}

$$\boxed{\Psi_{(1,2)} = a(1)\, b(2)} \qquad \boxed{\langle a | b \rangle = 0}$$

$$\hat{H}_{el} = \sum_i h(i) + \underbrace{\sum_i \sum_{j>i} \frac{1}{r_{ij}}}$$

$$\langle \Psi(1,2) | \hat{H}_{el} | \Psi(1,2) \rangle = \langle a(1)\, b(2) | h(1) + h(2) + \frac{1}{r_{12}} | a(1)\, b(2) \rangle$$

$$= \underbrace{\langle a(1) | h(1) | a(1) \rangle}_{h_{aa}} \underbrace{\langle b(2) | b(2) \rangle}_{1} + \underbrace{\langle a(1) | a(1) \rangle}_{1} \underbrace{\langle b(2) | h(2) | b(2) \rangle}_{h_{bb}}$$

$$+ \underbrace{\langle a(1)\, b(2) | \frac{1}{r_{12}} | a(1)\, b(2) \rangle}$$

$$J_{ab} = \langle a b \overset{1/r_{12}}{|} a b \rangle$$

$\widehat{\frac{1}{r_{12}}}$ agit sur espace : $J_{ab} = J_{a\bar{b}} = J_{\bar{a}b} = J_{\bar{a}\bar{b}} = J_{ba} = J_{b\bar{a}} = J_{\bar{b}a} = J_{\bar{b}\bar{a}}$

$$\langle a(1)\, b(2) | \widehat{\frac{1}{r_{12}}} | a(1)\, b(2) \rangle = \langle a(1)\alpha(1)\, b(2)\alpha(2) | \widehat{\frac{1}{r_{12}}} | a(1)\alpha(1)\, b(2)\alpha(2) \rangle$$

$$= \underbrace{\langle a(1) b(2) | \widehat{\frac{1}{r_{12}}} | a(1) b(2) \rangle}_{J_{ab}\,(\text{espace})} \underbrace{\langle \alpha(1) | \alpha(1) \rangle}_{1} \underbrace{\langle \alpha(2) | \alpha(2) \rangle}_{1}$$

$$J_{a\bar{b}} = \langle a\bar{b} | a\bar{b} \rangle = \langle a(1)\alpha(1)\, b(2)\beta(2) | \widehat{\frac{1}{r_{12}}} | a(1)\alpha(1)\, b(2)\beta(2) \rangle$$

$$= \underbrace{\langle a(1) b(2) | \widehat{\frac{1}{r_{12}}} | a(1) b(2) \rangle}_{J_{ab}} \underbrace{\langle \alpha(1) | \alpha(1) \rangle}_{1} \underbrace{\langle \beta(2) | \beta(2) \rangle}_{1}$$

$J_{ab} = J_{ba}$ car les $\bar{e}$ (1) et (2) sont indiscernables

$$\langle ab | ab \rangle = \langle ba | ba \rangle$$

$$J_{ab} = \iint_{\varepsilon_1, \varepsilon_2} a^*(1)\, b^*(2)\, \frac{1}{r_{12}}\, a(1)\, b(2)\, dv_1\, dv_2\, d\omega_1\, d\omega_2$$

II-2 intégrale biel sur det Slater : K_{ab}

$$\Psi(1,2) = |a\, b| = \frac{1}{\sqrt{2}}\big(a(1)\, b(2) - b(1)\, a(2)\big)$$

$$\langle a(1) | h(1) | b(1) \rangle = 0$$

$$\langle \Psi(1,2) | \hat{H}_{el} | \Psi(1,2) \rangle = \frac{1}{2} \left\langle a(1)b(2) - b(1)a(2) \left| h(1) + h(2) + \frac{1}{r_{12}} \right| a(1)b(2) - b(1)a(2) \right\rangle$$

$$= \frac{1}{2}\Big\{ h_{aa} + h_{bb} + J_{ab} + h_{bb} + h_{aa} + J_{ba} - \langle a(1)b(2) | \cancel{h(1)} + \cancel{h(2)} + \frac{1}{r_{12}} | b(1)\, a(2) \rangle - \langle b(1)\, a(2) | \frac{1}{r_{12}} | a(1)\, b(2) \rangle$$

$$- \langle a(1) b(2) | \frac{1}{r_{12}} | b(1)\, a(1) \rangle$$

$$- K_{ab} \qquad\qquad - K_{ba}$$

$$\langle |ab| | \hat{H}_{el} | |ab| \rangle = \frac{1}{2}\Big\{ 2h_{aa} + 2h_{bb} + 2J_{ab} \boxed{- 2K_{ab}} \Big\}$$

terme stabilisant (Hund)

II-3 : intégrale d'échange K_{ab}

$$K_{ab} = K_{ba} = K_{\bar{a}\bar{b}} = K_{\bar{b}\bar{a}} \quad \Big\| \quad K_{a\bar{b}} = 0 = K_{\bar{a}b}$$

des termes stabilisants disparaissent si $\uparrow\downarrow$

$$J_{a\bar{b}} = \langle a\bar{b} | a\bar{b} \rangle$$

$$K_{a\bar{b}} = \langle a\bar{b} | \bar{b}a \rangle = \langle a(1)\bar{b}(2) | \frac{1}{r_{12}} | \bar{b}(1)a(2) \rangle$$

$$= \langle a(1)\alpha(1)b(2)\beta(2) | \frac{1}{r_{12}} | b(1)\beta(1)a(2)\alpha(2) \rangle$$

$$= \langle a(1)b(2) | \frac{1}{r_{12}} | b(1)a(2) \rangle \underbrace{\langle \alpha(1) | \beta(1) \rangle}_{0} \times \underbrace{\langle \beta(2) | \alpha(2) \rangle}_{0}$$

$$= K_{ab} \times 0 \times 0$$

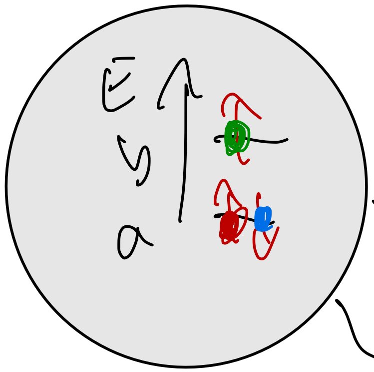
III Énergie d'un déterminant / configuration

Formules de Slater entre déterminants bâtis sur base $\{a, b, \dots\}$ orthonormées.

D : déterminant $|ab\dots|$

$N_é = n_{el}$

$$E_D = \langle D|\hat{H}_{el}|D\rangle = \sum_{a=1}^{N}\left(h_{aa} + \sum_{b>a}^{N}(J_{ab} - K_{ab})\right)$$



$|a\bar{a}b|$

$$E(|a\bar{a}b|) = h_{aa} + J_{a\bar{a}} - K_{a\bar{a}} + J_{ab} - K_{ab} + h_{\bar{a}\bar{a}} + J_{\bar{a}b} - K_{\bar{a}b} + h_{bb}$$

$$= 2h_{aa} + h_{bb} + J_{aa} + 2J_{ab} - K_{ab}$$

autres règles de Slater : déterminants en coïncidence max

- si D_2 diffère de D_1 par 1 spin orb

$D_1 = |\dots m \dots|$

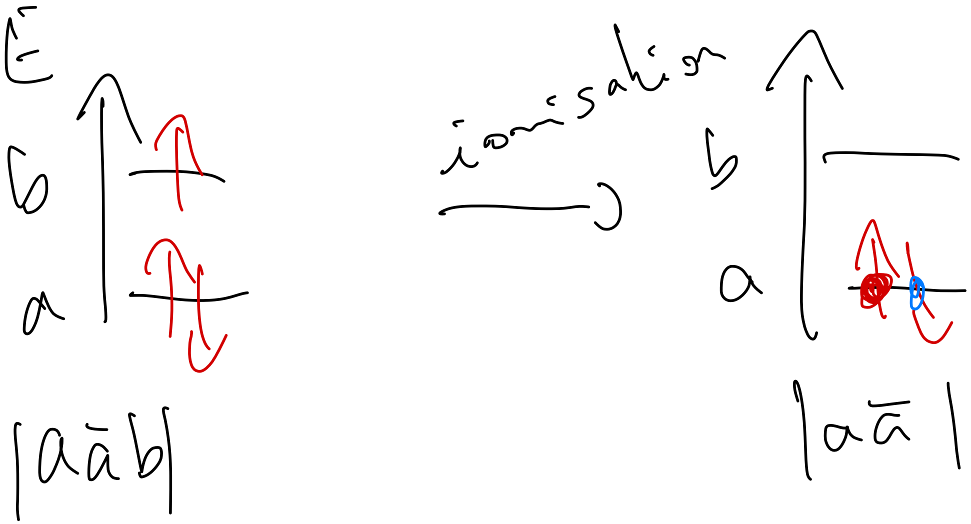
$D_2 = |\dots p \dots|$

$$\langle D_1|\hat{H}_{el}|D_2\rangle = h_{mp} + \sum_{a}^{N}\langle ma|pa\rangle - \langle ma|ap\rangle$$

- si D_2 diff. de D par 2 spin orb

$$\left\{ \begin{array}{l} D_1 = |\cdots mn \cdots| \\ D_2 = |\cdots pq \cdots| \end{array} \right. \qquad \langle D_1 | H_{ee} D_2 \rangle = \langle mn|pq\rangle - \langle mn|qp\rangle$$

IV Potentiel d'ionisation, Koopmans, Energie d'une orbitale.



$$E_{|a\bar{a}|} = h_{aa} + J_{a\bar{a}} - \cancel{K_{a\bar{a}}} + h_{\bar{a}\bar{a}}$$

$$= 2h_{aa} + J_{aa}$$

$$E_{(|a\bar{a}b|)} = 2h_{aa} + h_{bb} + J_{aa} + 2J_{ab} - K_{ab}$$

Koopmans : de $PI_1 = -\varepsilon_{\text{orbitale}}$ $\|$ $PI_1 = E(M^+) - E(M)$

ici $PI_1 = \cancel{2h_{aa}} + \cancel{J_{aa}} - \cancel{2h_{aa}} - h_{bb} - \cancel{J_{aa}} - 2J_{ab} + K_{ab}$

$PI_b = -h_{bb} - 2J_{ab} + K_{ab}$

Koopmans $\rightarrow$ $\boxed{\varepsilon_b = h_{bb} + 2J_{ab} - K_{ab}}$

généralisation :

$|\cdots a \cdots|$

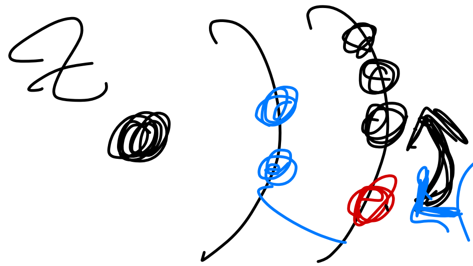
N électrons

$$\boxed{\varepsilon_a = h_{aa} + \sum_{k}^{N} J_{ak} - K_{ak}}$$

Car $J_{aa} = K_{aa} \rightarrow J_{aa} - K_{aa} = 0$

Pas d'auto répulsion (self interaction)

Rq: le modèle d'écrantage de Slater inclut $J_{ij} - K_{ij} = \frac{1}{r_{ij}}$ dans les constantes d'écran σ_{ij}



$\frac{1}{r_{12}}$

$$Z^{eff.} = Z - \underbrace{\sigma_{12} - \sigma_{22}}_{J - K}$$

écrantage $\Leftrightarrow$ biel.