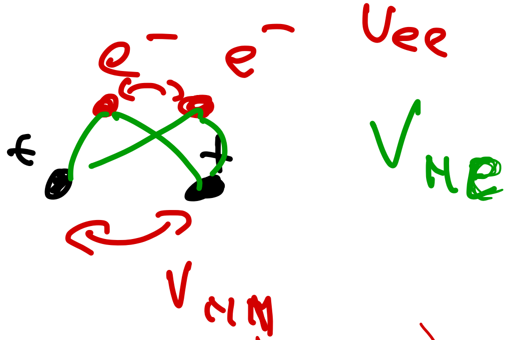
Chap 2 : opérateurs mono e^-



I Introduction

$$\hat{H} = \sum_{N}^{\text{noyaux}} \underbrace{T(N)}_{\phi} + \sum_{i}^{e^-} T(i) + \sum_{i}^{e^-} \sum_{N} V_{Ne}(i) + \sum_{N} \sum_{N'} V_{NN'} + \underbrace{\sum_{i} \sum_{j} V_{ee}(i,j)}$$

négligé ds 1e temps

$$\sum_{i} \sum_{j} \frac{1}{r_{ij}}$$

$$\hat{H} = \sum_{i} \overbrace{\Big(\underbrace{T(i) + \sum_{N} V_{Ne}(i)}_{\hat{h}(i)} \Big)} + \sum_{N} \sum_{N'} V_{NN'} + \sum_{i} \sum_{j} \frac{1}{r_{ij}}$$

$\hat{h}(i) \Leftarrow$ monoélectronique

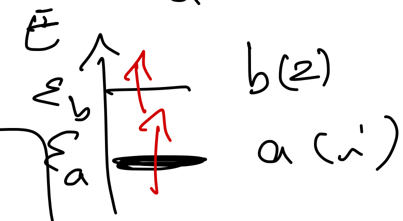
on appelle $H_{el} = \sum_{i}^{e^-} \hat{h}(i)$

$$\boxed{\hat{H} = \hat{H}_{el} + \sum_{N} \sum_{N'} \hat{V}_{NN'} + \sum_{i} \sum_{j} \frac{1}{r_{ij}}}$$

I Application de $\hat{H}_{el} = \sum_i \hat{h}(i)$

une orbitale (spin) est fonction propre de $\hat{h}(i)$: $\hat{h}(i)\, a(i) = \varepsilon_a\, a(i)$

$$\hat{h}(i)\,|a(i)\rangle = \varepsilon_a\,|a(i)\rangle$$



1) $\Psi(1,2) = a(1)\,b(2)$

$\hat{H}(1,2) = \hat{h}(1) + \hat{h}(2)$

$\hat{H}(1,2)\,\Psi(1,2) = [\hat{h}(1) + \hat{h}(2)]\,(a(1)\,b(2))$

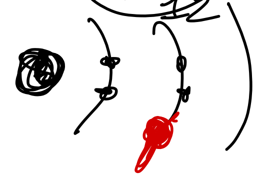
un opérateur n'agit que sur son e^-

$= \hat{h}(1)\,a(1)\,b(2) + a(1)\,h(2)\,b(2)$

$= \varepsilon_a\,a(1)\,b(2) + a(1)\,\varepsilon_b\,b(2)$

$$\boxed{[\hat{h}(1) + \hat{h}(2)]\,a(1)\,b(2) = (\varepsilon_a + \varepsilon_b)\;a(1)\,b(2)}$$

Hückel
Slater
(ce non)
($1/r_{12}$)



2) $\Psi(1,2) = |a\;b| = \dfrac{1}{\sqrt{2}}\left[a(1)\,b(2) - b(1)\,a(2)\right]$

$H(1,2)\,|a\,b|$ — déjà fait

— $[h(1) + h(2)]\;b(1)\,a(2) = (\varepsilon_b + \varepsilon_a)\,(b(1)\,a(2))$

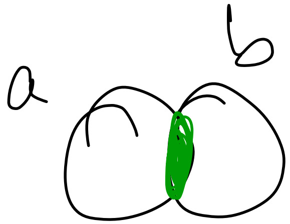
$H(1,2)\,|a\,b| = \dfrac{1}{\sqrt{2}}\left[(\varepsilon_a + \varepsilon_b)\,a(1)\,b(2) - (\varepsilon_a + \varepsilon_b)\,b(1)\,a(2)\right]$

$= (\varepsilon_a + \varepsilon_b)\left[\dfrac{1}{\sqrt{2}}\,(a(1)\,b(2) - b(1)\,a(2))\right] = \boxed{(\varepsilon_a + \varepsilon_b)\,|a\,b|}$

3) ces applications sur $a(1)\,b(2)$ et $|a\,b|$

se font pareil sur $|a(1)\,b(1)\rangle$ et $|\,|a\,b|\,\rangle$

les kets.



$$S_{ab} = \int_{E} a^*(1)\, b(1)\, \boxed{dv} = \langle a(1) | b(1) \rangle = \langle a | b \rangle$$

Intégrale monoélectronique h_{aa}, h_{ab}

$$\langle a(1) | \hat{h}(1) | a(1) \rangle = \langle a(1) | E_a | a(1) \rangle$$

$$= E_a \langle a(1) | a(1) \rangle$$

$$\alpha \qquad h_{aa} \qquad = E_a$$

$$h_{ab} = \langle a(1) | h(1) | b(1) \rangle = \langle a(1) | E_b | b(1) \rangle$$

$$= E_b \langle a(1) | b(1) \rangle = E_b\, S_{ab}$$

$$I = \langle a(1)\bar{a}(2)b(3) \,\|\, c(1)d(2)e(3) \rangle$$

$$I = \langle a(1)|c(1)\rangle \langle \bar{a}(2)|d(2)\rangle \langle b(3)|e(3)\rangle$$

$\{a, b, c, d, e\}$ normées mais $S_{ab} \neq 0$

$$= S_{ac} \times \langle a(2)\beta(2) | d(2)\alpha(2)\rangle \times S_{be}$$

$$= S_{ac} \times \langle a(2)|d(2)\rangle \langle \beta(2)|\alpha(2)\rangle \times S_{be}$$

$$= S_{ac} \times S_{ad} \times 0 \times S_{be}$$

$$= 0$$

$$\langle a(1)\alpha(1) | c(1)\alpha(1)\rangle$$

$$\langle a(1)|c(1)\rangle \underbrace{\langle \alpha(1)|\alpha(1)\rangle}_{1}$$

II Opérateurs de Spin (TD 3)

$$\vec{\hat{S}}(1) = \hat{S}_x(1)\,\vec{i} + \hat{S}_y(1)\,\vec{j} + \hat{S}_z(1)\,\vec{k}$$

$\hookrightarrow$ $\hat{S}_z(1)$ et $\underbrace{\hat{S}^2(1) = \vec{\hat{S}}(1)\cdot\vec{\hat{S}}(1)}$

II-1 $\hat{S}_z(1)\,|\alpha(1)\rangle = m_s(1)\,|\alpha(1)\rangle$

$\hat{S}_z(1)$ et $\hat{S}^2(1)$ agissent sur la variable de Spin de (1)

$$\hat{S}_z(1)\,|\alpha(1)\,\alpha(1)\rangle = |\alpha(1)\quad \hat{S}_z(1)\,\alpha(1)\rangle$$

$$= +\frac{1}{2}\,|\alpha(1)\,\alpha(1)\rangle$$

$$\hat{S}_z(1)\,|\alpha(1)\rangle = +\frac{1}{2}\,|\alpha(1)\rangle \quad \Big\| \quad \hat{S}_z(1)\,|\beta(1)\rangle = -\frac{1}{2}\,|\beta(1)\rangle$$

$\alpha(1)$ et $\beta(1)$ sont fonctions propres de $\hat{s}_z(1)$ avec les v. p^res $+1/2$ et $-1/2$

$$\boxed{\hat{S}_z(1,2,3) = \hat{s}_z(1) + \hat{s}_z(2) + \hat{s}_z(3)}$$

$\uparrow$ b

$\uparrow\downarrow$ a

$$\hat{S}_z(1,2,3)\,|a(1)\,\bar{a}(2)\,b(3)|$$

$$\left[\hat{s}_z(1) + \hat{s}_z(2) + \hat{s}_z(3)\right]\left(a(1)\,\bar{a}(2)\,b(3)\right)$$

$$= \hat{s}_z(1)\,a(1)\alpha(1)\,a(2)\beta(2)b(3)\alpha(3) + a(1)\,\hat{s}_z(2)a(2)\beta(2)\,b(3)$$

$$= +\frac{1}{2}\,a(1)\alpha(1)a(2)\beta(2)b(3)\alpha(3) + \left(-\frac{1}{2}\right)a(1)\,\bar{a}(2)\,b(3)$$

$$+\frac{1}{2}\,a(1)\bar{a}(2)\,b(3)$$

$$= \left(+\frac{1}{2} - \frac{1}{2} + \frac{1}{2}\right)a(1)\,\bar{a}(2)\,b(3)$$

$S_z(1,2,3)$ s'applique de la même façon sur det. Slater

$$S_z(1,2,3)\,|a\bar{a}b| = \left(+\frac{1}{2} - \frac{1}{2} + \frac{1}{2}\right)|a\bar{a}b|$$

$$= +\frac{1}{2}\,|a\bar{a}b|$$

II-2. $\hat{S}^2$ et $\hat{s}^2$

$$\hat{s}^2 = \vec{\hat{s}}\cdot\vec{\hat{s}} = \left(\hat{s}_x \vec{i} + \hat{s}_y \vec{j} + \hat{s}_z \vec{k}\right)\left(\hat{s}_x \vec{i} + \hat{s}_y \vec{j} + \hat{s}_z \vec{k}\right)$$

$$= \underbrace{\hat{s}_x^2 + \hat{s}_y^2}_{} + \underbrace{\hat{s}_z^2}_{}$$

$$\hat{s}_z^2(1)\,\bar{a}(1) = \hat{s}_z(1)\left(\hat{s}_z(1)\,\bar{a}(1)\right) = \hat{s}_z(1)\left(-\frac{1}{2}\,\bar{a}(1)\right)$$

$$= -\frac{1}{2}\,\hat{s}_z(1)\left(\bar{a}(1)\right)$$

$$= -\frac{1}{2} \times -\frac{1}{2}\,\bar{a}(1)$$

$$\boxed{\hat{s}_z^2\,\bar{a}(1) = +\frac{1}{4}\,\bar{a}(1)}$$

$$S_z^2(1,2,3) = \left(\hat{s}_z^2(1) + \hat{s}_z^2(2) + \hat{s}_z^2(3)\right)\left(a(1)\,\bar{a}(2)\,b(3)\right)$$

$$= \frac{1}{4}\,a(1)\,\bar{a}(2)\,b(3) + \frac{1}{4}\,a(1)\,\bar{a}(2)\,b(3) + \frac{1}{4}\,a(1)\,\bar{a}(2)\,b(3)$$

$$= 3/4\;a(1)\,\bar{a}(2)\,b(3)$$

$\hat{S}_x^2$ et $\hat{S}_y^2$ nécessitent de passer par $\hat{S}_+$ et $\hat{S}_-$

$\hat{s}_x$ et $\hat{s}_y$ —— $\hat{s}_+$ $\hat{s}_-$

$$\hat{s}_+(1) = \hat{s}_x(1) + i\,\hat{s}_y(1)$$

$$\hat{s}_-(1) = \hat{s}_x - i\,\hat{s}_y(1)$$

$$\left\{\begin{array}{l} \hat{s}_+(1)|\alpha(1)\rangle = 0 \\ \hat{s}_+(1)|\beta(1)\rangle = |\alpha(1)\rangle \end{array}\right. \qquad \begin{array}{l} s_-(1)|\alpha(1)\rangle = |\beta(1)\rangle \\ s_-(1)|\beta(1)\rangle = 0 \end{array}$$

matrice de Pauli :

$$\begin{array}{c|cc} \hat{s}_+ & |\alpha(1)\rangle & |\beta(1)\rangle \\ \hline \langle\alpha(1)| & 0 & \boxed{1} \\ \langle\beta(1)| & \boxed{0} & \boxed{0} \end{array}$$

$\boxed{}$ $\langle\beta(1)|\hat{s}_+|\alpha(1)\rangle$

$\boxed{}$ $\langle\alpha(1)|s_+|\beta(1)\rangle$

$\boxed{}$ $\langle\beta(1)|s_+(1)|\beta(1)\rangle$

$\langle\beta(1)|\alpha(1)\rangle$

$$S_+(1,2,3) = s_+(1) + s_+(2) + s_+(3)$$

On peut montrer que $\hat{s}^2 = \underbrace{\frac{1}{2}\left(\hat{s}_+ \cdot \hat{s}_- + \hat{s}_- \hat{s}_+\right)}_{(s_x^2 + s_y^2)} + s_z^2$

$$\hat{S}^2 = \frac{1}{2}\left(\hat{S}_+ \cdot \hat{S}_- + \hat{S}_- \hat{S}_+\right) + \hat{S}_z^2$$

$$S_+(1,2,3)\,|a\,\bar{a}\,b| = \underbrace{\cancel{|0\,\bar{a}\,b|}}_{0} + \underbrace{|a\,a\,b|}_{0} + \underbrace{|a\,\bar{a}\,0|}_{0}$$

$$S_-(1,2,3)\,|a\,\bar{a}\,b| = \underbrace{\cancel{|\bar{a}\,\bar{a}\,b|}}_{0} + \underbrace{|a\,0\,b|}_{0} + |a\,\bar{a}\,\bar{b}|$$