base "atómica" $\{\chi_i\} \xrightarrow{HF}$ base "molecular" $\{\phi_i\}$

(no es O.N) (O.N)

HF: es pedir que para un solo det., la energía del fundamental, de N e^-, formado por $\{\phi_i\}$ sea un mínimo variacional. (partiendo de $\{\chi_i\}$)

$$\hat{f}(i)\,\phi_i(x) = \varepsilon_i\,\phi_i(x)$$

ε_r

occ

ε_b

ε_a

$$E_0 = \sum_a^{occ} \langle a|h|a\rangle + \frac{1}{2}\sum_{ab} \langle ab||ab\rangle$$

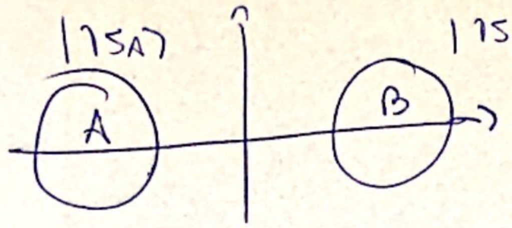
$$\varepsilon_a = \langle a|h|a\rangle + \sum_b^{occ} \langle ab||ab\rangle$$

notar $\sum \varepsilon_a \neq E^0 = \langle \psi|\hat{H}|\psi\rangle$

$$\hat{f}|\phi_a\rangle = \hat{h}(a) + \sum_b^{occ} \hat{J}_b(a) - \hat{K}_b(a) \quad \begin{pmatrix} \hat{f}(a) \\ \hat{f}|\chi_a\rangle \end{pmatrix} ||$$

$$= \hat{h}|a\rangle + \sum_b^{occ} \hat{J}_b|a\rangle - \hat{K}_b|a\rangle$$

H_2 en base mínima



base atom

$$\{1s^A, 1s^B\} \to \{|1\rangle, |2\rangle\}$$
$$\qquad\qquad\qquad \phi_1 \quad \phi_2$$

$$\{\phi_1, \phi_2\} \to \{\phi_1, \bar{\phi}_1, \phi_2, \bar{\phi}_2\}$$

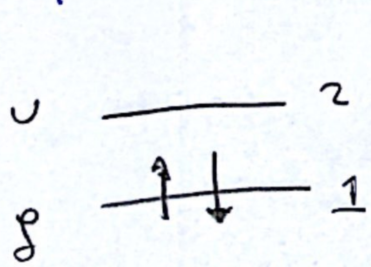
$$|\phi_1\rangle = \frac{1s_A + 1s_B}{(+)} \; ; \; |\phi_2\rangle = \frac{1s_A - 1s_B}{(-)}$$

Paridad:

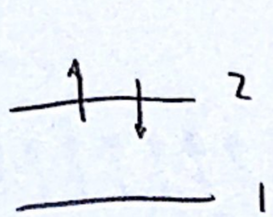
$$\hat{\pi}\,|1\rangle = +|1\rangle \quad \text{"par" } (g)$$

$$\hat{\pi}\,|2\rangle = -|2\rangle \quad \text{"impar" } (u)$$

$$\{|1\bar{1}\rangle, |12\rangle, |1\bar{2}\rangle, |\bar{1}2\rangle, |\bar{1}\bar{2}\rangle, |2\bar{2}\rangle\}$$



$|1\bar{1}\rangle$ par "g"



$|2\bar{2}\rangle$

$E_{1\bar{1}} = 2h_{11} + J_{11}$

$E_{2\bar{2}} = 2h_{22} + J_{22}$

(2

Veamos como se escribe el op de Fock en esta base. $\{|1\rangle, |2\rangle\}$

$$\left.\begin{array}{l}\langle 1|f|1\rangle, \ \langle 1|f|2\rangle = \langle 2|f|1\rangle = 0 \\ \langle 2|f|2\rangle\end{array}\right] ?$$

$\langle 1|f|1\rangle = \varepsilon_1 \quad ; \quad \langle 2|f|2\rangle = \varepsilon_2$

$$\langle 2|f|1\rangle = \langle 2|\left(\hat{h}|1\rangle + \sum_b^{occ} \hat{J}_b|1\rangle - \hat{K}_b|1\rangle\right)$$

b occ $\Rightarrow \{1, \bar{1}\}$

$$= \langle 2|\left[\hat{h}|1\rangle + \hat{J}_1|1\rangle - \hat{K}_1|1\rangle + \hat{J}_{\bar{1}}|1\rangle - \hat{K}_{\bar{1}}|1\rangle\right]$$

$$= \langle 2|\hat{h}|1\rangle + \langle 2|\hat{J}_1|1\rangle - \langle 2|\hat{K}_1|1\rangle + \langle 2|\hat{J}_{\bar{1}}|1\rangle - \langle 2|\hat{K}_{\bar{1}}|1\rangle$$

$\langle a|J_\psi|b\rangle = \langle a\psi|b\psi\rangle$

$\langle a|K_\psi|b\rangle = \langle a\psi|\psi b\rangle$

$$\langle 2|\hat{f}|1\rangle = h_{21} + \cancel{\langle 21|11\rangle} - \cancel{\langle 21|11\rangle}$$

$$+ \langle 2\bar{1}|1\bar{1}\rangle - \langle 2\underbrace{\bar{1}|\bar{1}}_{0\ \times\ \text{spin}}1\rangle$$

$$f_{21} = h_{21} + \langle 21|11\rangle$$

<u>veamos</u>

$2 \to u$

$1 \to g$

$$h_{21} = \int \underset{\substack{\uparrow \\ u}}{\phi_2^*}\ \underset{\substack{\uparrow \\ g}}{\hat{\Theta}(1)}\ \underset{\substack{\uparrow \\ g}}{\phi_1}\ d^3\bar{x} = 0$$

(x sim)

idem $\langle 21|11\rangle$, verlo! (uds)

$$\Rightarrow \hat{F} = \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}$$ en la base $\{|1\rangle, |2\rangle\}$

pero el H_2