H_2^+ variacional

$\psi = c_a \phi_a + c_b \phi_b$ $\{\phi_a, \phi_b\}$ base atómica (NO ON!)

$S = \langle a | b \rangle \neq 0$! (ojo)

La funcional a minimizar es:

$$\mathcal{L}(\psi) = \langle \psi | H | \psi \rangle - \lambda (\langle \psi | \psi \rangle + 1)$$

buscamos el set de coeficientes (c_a, c_b) que minimizan $\mathcal{L}$.

$$\underline{\langle \psi | H | \psi \rangle} = (c_a^* \phi_a^* + c_b^* \phi_b^*) \hat{H} (c_a \phi_a + c_b \phi_b)$$

$$= |c_a|^2 \langle a | H | a \rangle + |c_b|^2 \langle b | H | b \rangle$$

$$+ c_a^* c_b \langle a | H | b \rangle + c_a c_b^* \langle b | H | a \rangle$$

(base real)

$$\left[= c_a^2 h_{aa} + c_b^2 h_{bb} + 2 c_a c_b h_{ab} \right]$$

$$\langle\psi|\psi\rangle = \left(c_a^{*}\phi_a + c_b^{*}\phi_b\right)\left(c_a\phi_a + c_b\phi_b\right)$$

$$\left[= c_a^2 + 2c_ac_bS_{ab} + c_b^2\right]$$

$$\Rightarrow \mathcal{L}(\psi) = c_a^2 h_{aa} + c_b^2 h_{bb} + 2c_ac_b h_{ab}$$

$$- \lambda\left(c_a^2 + 2c_ac_bS_{ab} + c_b^2 - 1\right)$$

<u>Ahora</u> $\dfrac{\partial \mathcal{L}}{\partial c_a} = 0, \quad \dfrac{\partial \mathcal{L}}{\partial c_b} = 0$

$$\Rightarrow 2h_{aa}\underset{\neq}{c_a} + 2\underset{=}{c_b}h_{ab} - 2\lambda \underset{\neq}{c_a} - 2\lambda \underset{=}{c_b} S_{ab} = 0$$

$$2h_{bb}\underset{=}{c_b} + 2\underset{\neq}{c_a}h_{ab} - 2\lambda \underset{=}{c_b} - 2\lambda \underset{\neq}{c_a} S_{ab} = 0$$

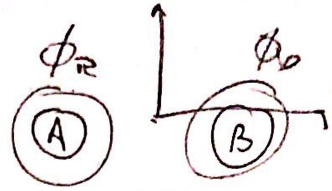
$(\lambda \in \mathbb{R})$

$$\cancel{2}h_{aa}c_a + \cancel{2}h_{ab}c_b = \cancel{2}\lambda\left(c_a + c_bS_{ab}\right)$$

$$\cancel{2}h_{ab}c_a + \cancel{2}h_{bb}c_b = \cancel{2}\lambda\left(c_b + c_aS_{ab}\right)$$

$$\begin{pmatrix} h_{aa} & h_{ab} \\ h_{ab} & h_{bb} \end{pmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix} = \lambda \begin{pmatrix} 1 & S_{ab} \\ S_{ab} & 1 \end{pmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix}$$

$$\det\begin{pmatrix} h_{aa}-\lambda & h_{ab}-\lambda S_{ab} \\ h_{ab}-\lambda S_{ab} & h_{bb}-\lambda \end{pmatrix} = 0$$



$\langle a|h|a\rangle = \langle b|h|b$

$$(h_{aa}-\lambda)(h_{bb}-\lambda) - (h_{ab}-\lambda S_{ab})(h_{ab}-\lambda S_{ab}) = 0$$

$S_{ab} \equiv S$

$h_{aa} = h_{bb} \equiv E_h$

$$\boxed{(E_h-\lambda)^2 - (h_{ab}-\lambda S)^2 = 0}$$

Wolfram

$$\lambda_1 = \frac{h_{ab}-E_h}{S-1} \quad (S \neq 1)$$

$$\lambda_2 = \frac{h_{ab}+E_h}{S+1} \quad (S+1 \neq 0)$$

λ son las energías

$$v_1 = (1,1), \quad v_2 = (-1,1)$$

$$\{\underbrace{\{\,,\,\}}_{\text{filas}},\{\,,\,\}\}$$

7.7

Acomodando

$$d_1 = \frac{h_{ab} - h_{aa}}{S-1} \quad , \quad d_2 = \frac{h_{ab} + h_{aa}}{S+1}$$

Veamos, $\boxed{h_{aa} \Rightarrow}$ $\langle a|H|a\rangle$, pero $\hat{H} = \hat{t} - \hat{v}_a - \hat{v}_b$

$$\hat{H}|a\rangle = (\hat{t} - \hat{v}_a)|a\rangle - \hat{v}_b|a\rangle$$

$$= E_H|a\rangle - \hat{v}_b|a\rangle \quad \alpha$$

$$\Rightarrow \langle \hat{a}|H|\hat{a}\rangle = E_H - \langle a|\hat{v}_b|a\rangle = E_H - V_1$$

idem con h_{bb}

$$\boxed{h_{ab} \Rightarrow \langle b|H|a\rangle} = \overset{\alpha}{}$$

$$= \langle b|\left(E_H|a\rangle - \hat{v}_b|a\rangle\right)$$

$$= E_H \underbrace{\langle b|a\rangle}_{S} - \overbrace{\langle b|V_b|a\rangle}^{V_2} = E_H S - V_2$$

$$\Rightarrow \boxed{h_{ab} = E_H S - V_2}$$

Volvemos

$$d_1 = \frac{h_{ab} - h_{aa}}{S-1} = \frac{\overbrace{E_H S - V_2}^{h_{ab}} - E_H + V_1}{S-1}$$

$$= E_H \frac{(S-1)}{(S-1)} - \frac{V_2 - V_1}{S-1} = E_H - \left(\frac{V_1 - V_2}{1-S}\right)$$

$$d_2 = \frac{h_{ab} + h_{aa}}{1+S} = \frac{E_H S - V_2 + E_H - V_1}{1+S}$$

$$= E_H \frac{(S+1)}{(S+1)} - \frac{V_1 + V_2}{1+S} = E_H - \left(\frac{V_1 + V_2}{1+S}\right)$$

Perfecto