Probleme 12

$$\varepsilon_i^\alpha = \langle \chi_i^\alpha | f_i^\alpha | \chi_i^\alpha \rangle$$

$$\varepsilon_i^\beta = \langle \chi_i^\beta | f_i^\beta | \chi_i^\beta \rangle$$

$$\varepsilon_i^\alpha = \langle \chi_i^\alpha | f_i^\alpha | \chi_i^\alpha \rangle =$$

$$= \langle \chi_i^\alpha | h(\bar{r}_1) | \chi_i^\alpha \rangle +$$

$$+ \sum_{b=1}^{N_\alpha} \langle \chi_i^\alpha | J_b^\alpha(1) | \chi_i^\alpha \rangle - \langle \chi_i^\alpha | K_b^\alpha | \chi_i^\alpha \rangle +$$

$$+ \sum_{b=1}^{N_\beta} \langle \chi_i^\alpha | J_b^\beta | \chi_i^\alpha \rangle$$

Obs:

$$\langle \chi_i^\alpha | J_b^\alpha | \chi_i^\alpha \rangle = \langle \chi_i^\alpha \left| \left(\int \chi_b^{\alpha *}(2)\, r_{12}^{-1}\, \chi_b^\alpha(2)\, d2 \right) \right| \chi_i^\alpha \rangle$$

$$= \int \psi_i^{*\alpha}(1)\, \alpha^*(1)\, \psi_b^{*\alpha}(2)\, \alpha^*(2)\, r_{12}^{-1}\, \psi_i^\alpha(1)\, \alpha(1)\, \psi_b^\alpha(2)\, \alpha(2)\, d\omega_1 d\omega_2 d\bar{r}_1 d\bar{r}_2$$

$$= \int \psi_i^{\alpha *}(1)\, \psi_b^{\alpha *}(2)\, r_{12}^{-1}\, \psi_i^\alpha(1)\, \psi_b^\alpha(2) = J_{ib}^{\alpha\alpha}$$

$$\langle \chi_i^\alpha | J_b^\beta | \chi_i^\alpha \rangle$$

$$= \langle \chi_i^\alpha | \int \chi_b^{*\beta}(2)\, r_{12}^{-1}\, \chi_b^\beta(2)\, dz \,|\, \chi_i^\alpha \rangle$$

$$= \int \psi_i^{\alpha *}(1)\,\alpha^*(1)\, \psi_b^{\beta *}(2)\,\beta^*(2)\, r_{12}^{-1}\, \psi_b^\beta(2)\,\beta(2)\, \psi_i^\alpha(1)\,\alpha(1)\, d\omega_1 d\omega_2 dr_1 dr_2$$

$$= \int \psi_i^{\alpha *}(1)\, \psi_b^{\beta *}(2)\, r_{12}^{-1}\, \psi_b^\beta(2)\, \psi_i^\alpha(1)\, dr_1 dr_2 = J_{ib}^{\alpha\beta}$$

•)

$$\langle \chi_i^\alpha | K_b^\alpha | \chi_i^\alpha \rangle = \langle \chi_i^\alpha | \int \chi_b^{\alpha *}(1)\, r_{12}^{-1}\, \chi_i^\alpha(2)\, dz \,|\, \chi_b^\alpha \rangle$$

$$= \int \psi_i^{\alpha *}(1)\,\alpha(1)\, \psi_b^{\alpha *}(2)\,\alpha(2)\, r_{12}^{-1}\, \psi_i^\alpha(2)\,\alpha(2)\, \psi_b^\alpha(1)\,\alpha(1)\, d\omega_1 d\omega_2 dr_1 dr_2$$

$$= \int \psi_i^{\alpha *}(1)\, \psi_b^{\alpha *}(2)\, r_{12}^{-1}\, \psi_b^\alpha(1)\, \psi_i^\alpha(2)\, dr_1 dr_2 = K_{ib}^{\alpha\alpha}$$

•)

$$\Rightarrow \boxed{\varepsilon_i^\alpha = h_{ii}^{\alpha\alpha} + \sum_{b=1}^{N_\alpha} \left(J_{ib}^{\alpha\alpha} - K_{ib}^{\alpha\alpha} \right) + \sum_{b=1}^{N_\beta} J_{ib}^{\alpha\beta}}$$

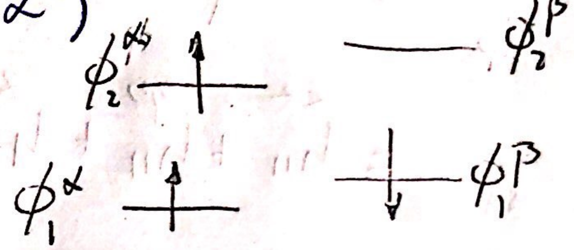
haciendo lo mismo intercambiando $\alpha \leftrightarrow \beta$

$$\varepsilon_i^\beta = h_{ii}^{\beta\beta} + \sum_{b=1}^{N_\beta} \left(J_{ib}^{\beta\beta} - K_{ib}^{\beta\beta} \right) + \sum_{b=1}^{N_\alpha} J_{ib}^{\beta\alpha}$$

Problema 13

Atomo de litio ($3e^-$)

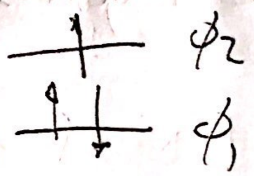
$$|\Psi_0\rangle = |\phi_1^{\alpha}\alpha, \phi_1^{\beta}\beta, \phi_2^{\alpha}\alpha\rangle$$



$N=3$, $N_\alpha = 2$, $N_\beta = 1$

- caso restricto:

$$|\Psi_0^{RHF}\rangle = |1\bar{1}2\rangle$$



$N_\alpha : \{\phi_1^{\alpha}, \phi_2^{\alpha}\}$

$N_\beta : \{\phi_1^{\beta}\}$

$$E^0_{RHF} = 2h_{11} + J_{11} + 2J_{12} - K_{12} + h_{22}$$

$$E^0_{UHF} = \sum_{i=1}^{N_\alpha} h_{ii} + \sum_{i=1}^{N_\beta} h_{ii} + \frac{1}{2}\sum_{a}^{\overset{2}{N_\alpha}} \sum_{b}^{\overset{2}{N_\alpha}} \left(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}\right)$$

$$+ \frac{1}{2}\sum_{a}^{N_\beta}\sum_{b}^{N_\beta}\left(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}\right) + \sum_{a,b}^{N_\alpha N_\beta} J_{ab}^{\alpha\beta}$$

$$= h_{11}^{\alpha\alpha} + h_{11}^{\beta\beta} + h_{22}^{\alpha\alpha} + \frac{1}{2}\Big(\cancel{J_{11}^{\alpha\alpha} - K_{11}^{\alpha\alpha}} + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha}$$

$$+ J_{21}^{\alpha\alpha} - K_{21}^{\alpha\alpha} + \cancel{J_{22}^{\alpha\alpha} - K_{22}^{\alpha\alpha}}\Big) + \frac{1}{2}\left(\cancel{J_{11}^{\beta\beta} - K_{11}^{\beta\beta}}\right) +$$

$$+ J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}$$

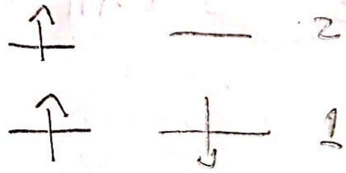
$$E^{0}_{UAF} = h_{11}^{\alpha\alpha} + h_{11}^{\beta\beta} + h_{22}^{\alpha\alpha} +$$

$$+ \frac{1}{2}\left(J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{21}^{\alpha\alpha} - K_{21}^{\alpha\alpha}\right) + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}$$

$$= h_{11}^{\alpha\alpha} + h_{11}^{\beta\beta} + h_{22}^{\alpha\alpha} + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}$$

Se ve fácil que podemos recuperar el caso restricto

ii) Arranco el e^- menos energético



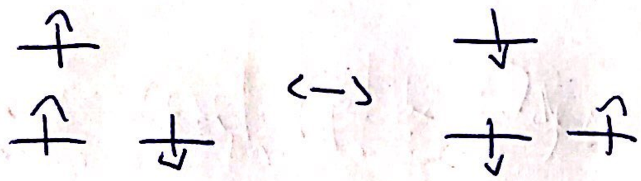
$$IP = -\varepsilon_i \Rightarrow -\varepsilon_2^{\alpha}$$

ó

$$-\varepsilon_1^{\beta}$$

iii) Sacar un $\bar{e}$ (el) electrón del segundo nivel $\Rightarrow IP = -\varepsilon_2^\alpha$

(iv) $|\Psi_1\rangle = |\phi_1^\alpha \beta, \phi_1^\beta \alpha, \phi_2^\alpha \beta\rangle$

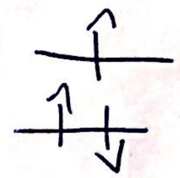


$|\Psi_0\rangle$ $|\Psi_1\rangle$

(v) Aplicar $\hat{S}^2 |\Psi_0\rangle$

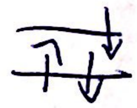
Probleme 14

$$|\psi_1\rangle = |\phi_1, \bar{\phi}_1, \phi_2\rangle$$



(= energie)

$$|\psi_2\rangle = |\phi_1, \bar{\phi}_1, \bar{\phi}_2\rangle$$



$$\Rightarrow |\psi_0^{trial}\rangle = c.l \{ |\psi_1\rangle, |\psi_2\rangle \}$$