1

UHF (introducción)

En RHF consideramos

$$|\Psi_{RHF}\rangle = |\psi_1\bar{\psi}_1\ \psi_2\bar{\psi}_2 \cdots\rangle = |x_1 x_2 x_3 \cdots\rangle$$

en donde $x_1 = \psi_1(\vec{r})\alpha(\omega)$, $x_2 = \psi_1(\vec{r})\beta(\omega)$ — electrones de a pares.

En UHF vamos a considerar:

$$|\Psi_{UHF}\rangle = |\psi_1^{\alpha}(\vec{r}_1)\alpha(\omega_1)\ \psi_1^{\beta}(\vec{r}_2)\beta(\omega_2) \cdots\rangle$$

Es decir $\psi_1^{\alpha}(\vec{r}) \neq \psi_1^{\beta}(\vec{r})$ (o no necesariamente $=$)

Habilitamos al sistema para que los e^- α y β ocupen diferentes orbitales espaciales.

Las integrales de 1 y 2 cuerpos se pueden pensar como: (espaciales)

$$h_{ii}^{\alpha} = (\psi_i^{\alpha}|h(1)|\psi_i^{\alpha})$$

$$h_{ii}^{\beta} = (\psi_i^{\beta}|h(1)|\psi_i^{\beta})$$

Coulomb entre un e^- α (i) y otro β (j)

$\downarrow$

α

$$J_{ij}^{\alpha\beta} = J_{ji}^{\beta\alpha} = (\psi_i^\alpha | J_j^\beta | \psi_i^\alpha) = (\psi_j^\beta | J_i^\alpha | \psi_j^\beta)$$

operadores

$$= \int d\bar{r}_2\, \psi_j^{\beta *}(\bar{r}_2) \frac{1}{r_{12}} \psi_j^\beta(\bar{r}_2)$$

$$\int d\bar{r}_2\, \psi_i^{\alpha *}(\bar{r}_2) \frac{1}{r_{12}} \psi_i^\alpha(\bar{r}_2)$$

Coulomb = el mismo spin

$$J_{ij}^{\alpha\alpha} = (\psi_i^\alpha | J_j^\alpha | \psi_i^\alpha) = (\psi_j^\alpha | J_i^\alpha | \psi_j^\alpha) = (ij|ij)$$

idem β

$$(\psi_i^\alpha \psi_i^\alpha | \psi_j^\alpha \psi_j^\alpha)$$

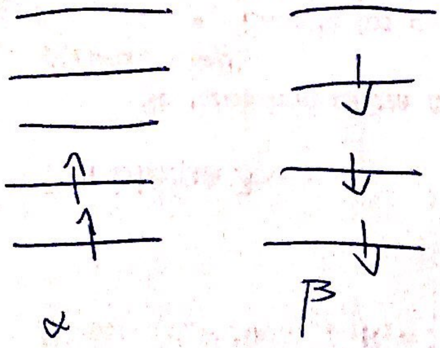
Intercambio

$$K_{ij}^{\alpha\alpha} = (\psi_{i(1)}^\alpha | K_j^\alpha | \psi_i^\alpha) = (\psi_j^\alpha | K_i^\alpha | \psi_j^\alpha) = (ij|ji)$$

$$K_j^\alpha \rightarrow K_j^\alpha(\bar{r}_1)\psi_i^\alpha(\bar{r}_1) = \left[\int d\bar{r}_2\, \psi_j^{\alpha *}(\bar{r}_2) \frac{1}{r_{12}} P_{12}\, \psi_j(\bar{r}_2)\right] \psi_i^\alpha(\bar{r}_1)$$

idem $\beta\beta$

Energy



$$E_0 = \sum_{a=1}^{N_\alpha} h_{aa}^{\alpha} + \sum_{a=1}^{N_\beta} h_{aa}^{\beta}$$

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

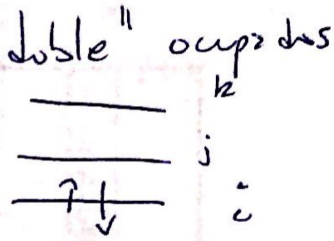
$$+ \frac{1}{2} \sum_{a}^{N_\beta} \sum_{b}^{N_\beta} \left(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} \right)$$

$$+ \sum_{a}^{N_\alpha} \sum_{b}^{N_\beta} J_{ab}^{\alpha\beta}$$

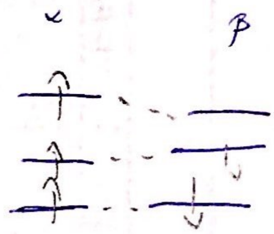
Scanned with CamScanner

Ec. HF: $f(1)\,\chi_i(1) = \varepsilon_i\,\chi_i(1)$

En capa cerrada: $\left[\begin{array}{l} \chi_i = \psi_i(r)\,\alpha(\omega) \\ \chi_{i+1} = \psi_i(r)\,\beta(\omega) \end{array}\right\} \{\psi_i\}_k$



(UHF) $\left[\begin{array}{ll} \chi_i = \psi_i^\alpha(r)\,\alpha(\omega) & \leftarrow \{\psi_i^\alpha\}_k \\ \chi_{i+1} = \psi_i^\beta(r)\,\beta(\omega) & \leftarrow \{\psi_i^\beta\}_k \end{array}\right.$



$$f(1)\,\psi_j^\alpha(r_1)\,\alpha(\omega_1) = \varepsilon_i\,\psi_j^\alpha(r_1)\,\alpha(\omega_1) \quad \leftarrow \int \alpha^*(\omega_1)\,d\omega_1$$

$$\left.\begin{array}{l} f^\alpha(1)\,\psi_j^\alpha(1) = \varepsilon_i^\alpha\,\psi_j^\alpha(1) \\ f^\beta(1)\,\psi_j^\beta(1) = \varepsilon_i^\beta\,\psi_j^\beta(1) \end{array}\right]$$ espaciales.

$$f^\alpha(r_1) = \int d\omega_1\,\alpha^*(\omega_1)\,f(r_1,\omega_1)\,\alpha(\omega_1)$$ idem $f^\beta(1)$

haciendo esta cuenta:

$$f^\alpha(r_1) = h(1) + \sum_a^{N_\alpha}\left[J_a^\alpha(1) - K_a^\alpha(1)\right] + \sum_a^{N_\beta} J_a^\beta(1)$$

acoplados

$$J_a^{\alpha}(1) = \int dr_2 \, \psi_a^{\alpha *}(2) \, r_{12}^{-1} \, \psi_a^{\alpha}(2)$$

$$K_a^{\alpha}(1)\, \psi_i^{\alpha}(1) = \int \left[d\bar{r}_2 \, \psi_a^{\alpha *}(2) \, r_{12}^{-1} \, \psi_i^{\alpha}(2) \right] \psi_a^{\alpha}(1)$$

$$= \int \left[d\bar{r}_2 \, \psi_a^{\alpha *}(2) \, r_{12}^{-1} \, P_{12} \, \psi_a^{\alpha}(2) \right] \psi_i^{\alpha}(1)$$

$$h_{ii}^{\alpha} = \langle \psi_i^{\alpha} | h | \psi_i^{\alpha} \rangle$$

$$J_{ij}^{\alpha\beta} = \langle \psi_i^{\alpha} | J_j^{\beta} | \psi_i^{\alpha} \rangle = J_{ji}^{\beta\alpha}$$

$$K_{ij}^{\alpha\alpha} = \langle \psi_i^{\alpha} \psi_j^{\alpha} | \psi_j^{\alpha} \psi_i^{\alpha} \rangle$$

idem $\beta \leftrightarrow \alpha$

$$E_0 = \sum_a^{N_\alpha} h_{aa}^{\alpha} + \sum_b^{N_\beta} h_{bb}^{\beta} + \frac{1}{2} \sum_a^{N_\alpha} \sum_b^{N_\alpha} \left(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha} \right) + \frac{1}{2} \sum_a^{N_\beta} \sum_b^{N_\beta} \left(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} \right) + \sum_a^{N_\alpha} \sum_b^{N_\beta} J_{ab}^{\alpha\beta}$$

Tomé la = energía planteo y la separé en contribuciones α y β.