Serie 5:	Distribución Electrónica - RDM	HOJA FECHA

1. Aproximación de Hartree-Fock de capa cerrada; entonces:

$$|\Phi\rangle = |\Psi_0\rangle = |\chi_1 \chi_2 \ldots \chi_N\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \ldots \psi_N \bar{\psi}_N\rangle$$

i. $\quad {}^1D_i^k =$

en HF

$${}^1D_{ik} = \langle \Phi^N | a_k^\dagger a_i | \Phi^N \rangle = \langle \Psi_0 | a_k^\dagger a_i | \Psi_0 \rangle$$

$$= \langle {}^2\Psi_0 | \delta_{ik} - a_i a_k^\dagger | {}^2\Psi_0 \rangle = \delta_{ik} - \underbrace{\langle {}^2\Psi_0 | a_i a_k^\dagger | \Psi_0 \rangle}_{\text{nulo salvo si } i=k \text{ y } k \in \{occ\} \Rightarrow {}^1D_{ik} = 0}$$

$${}^1D_{ik} = \delta_{ik} \nu_i \quad \text{donde } \nu_i = \begin{cases} 1 & i \in \{occ\} \\ 0 & i \notin \{occ\} \end{cases}$$

$${}^1D_{i\sigma}^{k\sigma'} = \delta_{i\sigma\, k\sigma'} \nu_i = \delta_{ik} \delta_{\sigma\sigma'} \nu_i$$ ← le metemos el spin

$${}^1D_{ik} = \langle \psi_1 \bar{\psi}_1 \ldots \psi_{\frac{N}{2}} \bar{\psi}_{\frac{N}{2}} | a_{k\sigma}^\dagger a_{i\sigma'} | \psi_1 \bar{\psi}_1 \ldots \psi_{\frac{N}{2}} \bar{\psi}_{\frac{N}{2}} \rangle$$

Este es el aspecto en la base 'restricted' [con capa cerrada]

$${}^1D_{ik} = \sum_{\sigma,\sigma'}^{occ} {}^1D_{i\sigma}^{k\sigma'} = \sum_{\sigma\sigma'}^{N/2} \delta_{ik} \nu_i \delta_{\sigma\sigma'} = \nu_i \delta_{ik} \sum_{\sigma\sigma'}^{N/2} \delta_{\sigma\sigma'}$$

$$\delta_{\alpha\alpha} + \delta_{\beta\beta} + \delta_{\alpha\beta} + \delta_{\beta\alpha} = 2$$

$$\boxed{{}^1D_{ik} = 2\nu_i \delta_{ik}}$$

ii.

$${}^1D = \sum_{ij} {}^1D_{ij} |\chi_i\rangle\langle\chi_j| \Rightarrow {}^1D(x,x') = \sum_{ij} {}^1D_{ij} \chi_i(x) \chi_j^*(x') \quad [1]$$

$${}^1D = \sum_{ij} \nu_i \delta_{ij} |i\rangle\langle j| = \sum_i |i\rangle\langle i|$$

$${}^1D(x,x') = \langle x | \left(\sum_a^{occ} |a\rangle\langle a| \right) | x' \rangle = \sum_a^{occ} \chi_a(x) \chi_a^*(x')$$

$${}^1D(x,x') = 2 \sum_a^{occ} \psi_a(x) \psi_a^*(x') = 2 \sum_{a,\mu,\nu} c_\mu^a \phi_\mu(x) c_\nu^{a*} \phi_\nu^*(x')$$

porque aparecen en este caso,

$$\sum_a^{occ} \left(\psi_a \alpha \psi_a^* \alpha + \psi_a \beta \psi_a^* \beta \right)$$

$$= \sum_{a\mu\nu} 2 c_\mu^a c_\nu^{a*} \phi_\mu(x) \phi_\nu(x')$$

$$= \sum_{\mu\nu} \phi_\mu(x) \phi_\nu(x') \underbrace{\sum_a 2 c_\mu^a c_\nu^{a*}}_{{}^1D_{\mu\nu}}$$

⇒ por comparación con [1] →

NOTA

$$\boxed{{}^1D_{\mu\nu} = 2 \sum_a c_\mu^a c_\nu^{a*}}$$

III.

$$^2D^{ij}_{kl} = \frac{1}{2}\langle \Psi | a_i^{\dagger} a_j^{\dagger} a_l a_k | \Psi \rangle$$

sea $|\Psi\rangle = |\chi_1 \chi_2 \dots \chi_N\rangle$ un estado HF $\rightarrow$ $|\Psi\rangle = |\Psi_0\rangle$

$$= \frac{1}{2}\langle \Psi_0 | a_i^{\dagger} (\delta_{jl} - a_l a_j^{\dagger}) a_k | \Psi_0 \rangle$$

$$\delta_{jl} a_i^{\dagger} a_k - a_i^{\dagger} a_l a_j^{\dagger} a_k$$

$$\delta_{jl}(\delta_{ik} - a_k a_i^{\dagger}) - (\delta_{il} - a_l a_i^{\dagger})(\delta_{jk} - a_k a_j^{\dagger})$$

$$\delta_{jl}\delta_{ik} - \underset{①}{\delta_{jl} a_k a_i^{\dagger}} - \delta_{il}\delta_{jk} + \underset{②}{\delta_{jk} a_l a_i^{\dagger}} + \underset{③}{\delta_{il} a_k a_j^{\dagger}} - a_l a_i^{\dagger} a_k a_j^{\dagger}$$

$$- a_l(\delta_{ik} - a_k a_i^{\dagger}) a_j^{\dagger}$$

$$- \underset{④}{\delta_{ik} a_l a_j^{\dagger}} + \underset{⑤}{a_l a_k a_i^{\dagger} a_j^{\dagger}}$$

$$^2D^{ij}_{kl} = \frac{1}{2}\left[\delta_{jl}\delta_{ik} - \delta_{il}\delta_{jk}\right.$$

① $-\langle \Psi_0 | \delta_{jl} a_k a_i^{\dagger} | \Psi_0 \rangle = -\delta_{jl} \underbrace{\langle \Psi_0 | a_k a_i^{\dagger} | \Psi_0 \rangle}_{=0}$; y para idem con las otras restantes porque intentan crear algún spin-orbital ya presente $\Rightarrow$

$$^2D^{ij}_{kl} = \frac{1}{2}\left[\delta_{jl}\delta_{ik} - \delta_{il}\delta_{jk}\right]$$

$$= \frac{1}{2}\left[\delta_{jl}\nu_j \,\delta_{ik}\nu_i - \delta_{il}\nu_i\,\delta_{jk}\nu_j\right]$$

$$\boxed{^2D^{ij}_{kl} = \frac{1}{2}\nu_i\nu_j\left[\delta_{jl}\delta_{ik} - \delta_{il}\delta_{jk}\right]}$$

◀ Habría que chequear el enunciado otra vez por el error de tipeo

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4.

$$\Psi(x) = \sum_k \phi_k(x)\, a_k$$

$$\Psi^{+}(x) = \sum_j \phi_j^{*}(x)\, a_j^{+} \qquad \{\phi_i\} \text{ conjunto completo}$$

NOTA
Esta definición es sólo válida para estados puros

$${}^{N}D = |\Psi^N\rangle\langle\Psi^N|$$

¡en general NO tengo estados puros sino CL de estados

$$\Psi^{+}(x')\,\Psi(x) =$$

$$\sum_{ij} \phi_j^{*}(x')\, a_j^{+}\, \phi_i(x)\, a_i$$

$$\sum_{ij} \phi_j^{*}(x')\, \phi_i(x)\, a_j^{+} a_i$$

$\Rightarrow$ bracketeando

$$\langle\Psi|\,\Psi^{+}(x')\,\Psi(x)\,|\Psi\rangle$$

$$= \sum_{ij} \phi_j^{*}(x')\, \phi_i(x)\, \langle\Psi|\, a_j^{+} a_i\, |\Psi\rangle$$

$$= \sum_{ij} \phi_j^{*}(x')\, \phi_i(x)\, {}^{1}D_{ij}$$

$$= \sum_{ij} \phi_i(x)\, {}^{1}D_{ij}\, \phi_j^{*}(x')$$

$$= \sum_{ij} \langle x|\phi_i\rangle\, {}^{1}D_{ij}\, \langle\phi_j|x'\rangle$$

$$= \langle x|\underbrace{\left(\sum_{ij} {}^{1}D_{ij}\, |\phi_i\rangle\langle\phi_j|\right)}|x'\rangle$$

$$\langle x|\,{}^{1}D\,|x'\rangle = {}^{1}D(x,x') \Rightarrow$$

$$\boxed{{}^{1}D(x,x') = \langle\Psi|\,\Psi^{+}(x')\,\Psi(x)\,|\Psi\rangle}$$

$$\Psi^{+}(x_1')\,\Psi^{+}(x_2')\,\Psi(x_2)\,\Psi(x_1) =$$

$$\sum_{ijkl} \phi_i^{*}(x_1')\, a_i^{+}\, \phi_j^{*}(x_2')\, a_j^{+}\, \phi_k(x_2)\, a_k\, \phi_l(x_1)\, a_l \Rightarrow$$ bracketeando se tiene

$$\langle{}^{2}\Psi|\sum_{ijkl} \phi_i^{*}(x_1')\, \phi_j^{*}(x_2')\, \phi_k(x_2)\, \phi_l(x_1)\; a_i^{+} a_j^{+} a_k a_l\; |{}^{2}\Psi\rangle$$

$$\sum_{ijkl} \phi_i^{*}(x_1')\, \phi_j^{*}(x_2')\, \phi_k(x_2)\, \phi_l(x_1)\, \underbrace{\langle{}^{2}\Psi|\, a_i^{+} a_j^{+} a_k a_l\, |{}^{2}\Psi\rangle}_{2\cdot{}^{2}D_{lk}^{ij}}$$

$$\sum_{ijkl} \langle x_2|\phi_k\rangle\langle x_1|\phi_l\rangle\langle\phi_i|x_1'\rangle\langle\phi_j|x_2'\rangle\; {}^{2}D_{lk}^{ij}\; 2$$

NOTA

$$\sum_{ijkl} \langle x_1|\phi_l\rangle\langle x_2|\phi_k\rangle {}^2D^{ij}_{lk}\, 2\langle\phi_i|x_1'\rangle\langle\phi_j|x_2'\rangle$$

$$\langle x_2 x_1|\phi_l\phi_k\rangle\, {}^2D^{ij}_{lk}\, 2\langle\phi_j\,\phi_i|x_1' x_2'\rangle$$

$$\langle x_2 x_1|\ \sum_{ijkl} 2\cdot {}^2D^{ij}_{lk}\ |\phi_l\phi_k\rangle\langle\phi_j\,\phi_i|\ \ |x_1' x_2'\rangle$$

$$\langle x_2 x_1|\left(2\sum_{ijkl} {}^2D^{ij}_{lk}\ \phi_l^+\phi_k^+\,|\,\rangle\langle\,|\,\phi_j\phi_i\right)|x_1' x_2'\rangle$$

$$\boxed{\langle x_2 x_1|\,{}^2D\,|x_1' x_2'\rangle = {}^2D(x_1 x_2|x_1' x_2')}$$

NOTA BRA-Space

$|x_1' x_2'\rangle$

$\langle x_2' x_1'|$

pues

$a_1^+ a_2^+|\ \rangle$

$\langle\ |a_2 a_1$

$\langle x_2 x_1|$

Usamos que:

$${}^2D = 1/2\sum_{ijkl} |ij\rangle\langle ji|\,{}^2D\,|lk\rangle\langle kl|$$

$${}^2D = 1/2\sum_{ijkl} {}^2D^{lk}_{ij}\, a_i^+ a_j^+ a_k a_l = \sum_{ijkl} {}^2D^{ij}_{lk}\, a_l^+ a_k^+ a_j a_i$$

índices MUDOS

Hay un temita con el factor 2

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6.

$\mathcal{O}_1 = \sum_i^N h(i)$ $\quad\mathcal{O}_1$ = operador monoelectrónico

$h(i)$ = operador de un electrón

$$\langle \Phi^1 | \mathcal{O}_1 | \Phi^1 \rangle = \left(\sum_\mu c_\mu^* \langle \phi_\mu|\right) \mathcal{O}_1 \left(\sum_\nu c_\nu |\phi_\nu\rangle\right)$$

$${}^1D = \sum_i n_i |\varphi_i\rangle\langle\varphi_i| \qquad \sum_i^N h(i) \left(\sum_\nu c_\nu |\phi_\nu\rangle\right)$$

pero como $\quad {}^1D(x,x') = \langle x|\Phi^1\rangle\langle\Phi^1|x'\rangle = \langle x|{}^1D|x'\rangle = \langle x|\left(\sum_{ij} \langle i|{}^1D|j\rangle |i\rangle\langle j|\right)|x'\rangle$

$$= \langle x| \left(\sum_\mu c_\mu |\phi_\mu\rangle\right)\left(\sum_\nu c_\nu^* \langle\phi_\nu|\right)|x'\rangle \qquad \sum_{ij} {}^1D_{ij}\, \phi_i(x)\, \phi_j^*(x')$$

$$\sum_{\mu\nu} \underbrace{c_\mu c_\nu^*} \langle x|\phi_\mu\rangle\langle\phi_\nu|x'\rangle$$

$$= \sum_{\mu\nu} {}^1D_{\mu\nu}\, \phi_\mu(x)\, \phi_\nu^*(x') \quad \rightarrow \quad c_\mu c_\nu^* = {}^1D_{\mu\nu}$$

también sale de acá $\longrightarrow$

$$tr(h\,{}^1D) = \langle \Phi^1 | \mathcal{O}_1 | \Phi^1 \rangle = \langle \mathcal{O}_1 \rangle$$

$$\sum_{ij} h_{ij}\,{}^1D_{ji} = \sum_{ij} \langle i|h|j\rangle\,{}^1D_{ij} = \langle \Phi^N | \mathcal{O}_1 | \Phi^N \rangle$$

$$\sum \left(\sum_\nu c_\nu^{*i} \langle\nu|\right) h \left(\sum_\mu c_\mu^i |\mu\rangle\right) {}^1D_{ij}$$

, pero h es independiente del spin

NOTA