The Hartree-Fock energy (Take 4)

Problem: Core Hamiltonian

"Show that $\langle \Psi_{HF} | \mathbf{O}_1 | \Psi_{HF} \rangle = \sum_{i=1}^{N} h_i$ *for the same system"*

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"Show that $\langle \Psi_{HF} | \mathbf{O}_1 | \Psi_{HF} \rangle = \sum_{i=1}^{N} h_i$ for the same system"

Solution

$$\mathbf{O}_1 = h(1) + h(2)$$

$$\begin{aligned}
&\langle \Psi_{\text{HF}} | h(1) + h(2) | \Psi_{\text{HF}} \rangle \\
&\quad = \frac{1}{2} \langle \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1) | h(1) + h(2) | \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1) \rangle \\
&\quad = \frac{1}{2} \Big[\langle \chi_1(1)\chi_2(2) | h(1) + h(2) | \chi_1(1)\chi_2(2) \rangle - \langle \chi_1(1)\chi_2(2) | h(1) + h(2) | \chi_2(1)\chi_1(2) \rangle \\
&\quad - \langle \chi_2(1)\chi_1(2) | h(1) + h(2) | \chi_1(1)\chi_2(2) \rangle + \langle \chi_2(1)\chi_1(2) | h(1) + h(2) | \chi_2(1)\chi_1(2) \rangle \Big] \\
&\quad = \frac{1}{2} \Big[h_1 + h_2 - 0 - 0 + h_2 + h_1 \Big] = h_1 + h_2
\end{aligned}$$

The Hartree-Fock energy (Take 5)

Problem: Two-electron Hamiltonian

"Show that $\langle \Psi_{HF} | \mathbf{O}_2 | \Psi_{HF} \rangle = \sum_{i<j}^{N} \left(\mathcal{J}_{ij} - \mathcal{K}_{ij} \right)$ *for the same system and write down the HF energy"*

The Hartree-Fock energy (Take 5)

Problem: Two-electron Hamiltonian

"Show that $\langle \Psi_{HF} | \mathbf{O}_2 | \Psi_{HF} \rangle = \sum_{i<j}^{N} (\mathcal{J}_{ij} - \mathcal{K}_{ij})$ for the same system and write down the HF energy"

Solution

$$\mathbf{O}_2 = r_{12}^{-1}$$

$$\begin{aligned}
\langle \Psi_{\text{HF}} | r_{12}^{-1} | \Psi_{\text{HF}} \rangle &= \frac{1}{2} \langle \chi_1\chi_2 - \chi_2\chi_1 | r_{12}^{-1} | \chi_1\chi_2 - \chi_2\chi_1 \rangle \\
&= \frac{1}{2} \Big[\langle \chi_1\chi_2 | r_{12}^{-1} | \chi_1\chi_2 \rangle - \langle \chi_1\chi_2 | r_{12}^{-1} | \chi_2\chi_1 \rangle \\
&\quad - \langle \chi_2\chi_1 | r_{12}^{-1} | \chi_1\chi_2 \rangle + \langle \chi_2\chi_1 | r_{12}^{-1} | \chi_2\chi_1 \rangle \Big] \\
&= \frac{1}{2} \Big[\mathcal{J}_{12} - \mathcal{K}_{12} - \mathcal{K}_{12} + \mathcal{J}_{12} \Big] = \mathcal{J}_{12} - \mathcal{K}_{12}
\end{aligned}$$

Remember that $\langle \chi_2\chi_1 | r_{12}^{-1} | \chi_2\chi_1 \rangle = \langle \chi_1\chi_2 | r_{12}^{-1} | \chi_1\chi_2 \rangle$

$$\boxed{E_{\text{HF}} = h_1 + h_2 + \mathcal{J}_{12} - \mathcal{K}_{12}}$$

The Hartree-Fock energy (Take 6)

@home: Three-electron system

"Find the HF energy of a three-electron system composed by the spin orbitals χ_1, χ_2 and χ_3"

Solution

$$\mathbf{O}_1 = h(1) + h(2) + h(3)$$
$$\mathbf{O}_2 = r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}$$

$$\vdots$$

$$\boxed{E_{\text{HF}} = h_1 + h_2 + h_3 + \mathcal{J}_{12} + \mathcal{J}_{13} + \mathcal{J}_{23} - \mathcal{K}_{12} - \mathcal{K}_{13} - \mathcal{K}_{23}}$$

HF energy of He

Singlet $1s^2$ state of the He atom

$$\chi_1 = \alpha\,\psi_1 \qquad \chi_2 = \beta\,\psi_1$$

$$E_{\text{HF}}(\text{singlet}) = h_1 + h_2 + \mathcal{J}_{12} - \mathcal{K}_{12} = 2h_1 + J_{11}$$

$$\begin{aligned}\mathcal{J}_{12} &= \langle \chi_1\chi_2|\chi_1\chi_2\rangle \\ &= \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle\langle\psi_1\psi_1|\psi_1\psi_1\rangle = J_{11}\end{aligned}$$

$$\begin{aligned}\mathcal{K}_{12} &= \langle \chi_1\chi_2|\chi_2\chi_1\rangle \\ &= \langle\alpha|\beta\rangle\langle\beta|\alpha\rangle\langle\psi_1\psi_1|\psi_1\psi_1\rangle = 0\end{aligned}$$

Triplet $1s2s$ state of the He atom

$$\chi_1 = \alpha\,\psi_1 \qquad \chi_2 = \alpha\,\psi_2$$

$$E_{\text{HF}}(\text{triplet}) = h_1 + h_2 + \mathcal{J}_{12} - \mathcal{K}_{12} = h_1 + h_2 + J_{12} - K_{12}$$

Singlet-triplet energy splitting

$$\begin{aligned}\Delta E_{\text{HF}} &= E_{\text{HF}}(\text{triplet}) - E_{\text{HF}}(\text{singlet}) \\ &= \underbrace{(h_2 - h_1)}_{>0} + \underbrace{(J_{12} - J_{11})}_{<0} - K_{12}\end{aligned}$$

HF Energy of Atoms

Problem 1: HF energy of the Li atom

"Find the HF energy of the Li atom in terms of the spatial MOs"

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Problem 2: HF energy of the B atom

"Find the HF energy of the B atom' in terms of the spatial MOs'

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$$E_{\text{HF}} = 2h_1 + h_2 + J_{11} + 2J_{12} - K_{12}$$

Problem 2: HF energy of the B atom

"Find the HF energy of the B atom' in terms of the spatial MOs'

Solution 2:

$$E_{\text{HF}} = 2h_1 + 2h_2 + h_3 + J_{11} + 4J_{12} + J_{22} - 2K_{12} + 2J_{13} + 2J_{23} - K_{13} - K_{23}$$