The Fock matrix

Using the variational principle, one can show that, to minimise the energy, the MOs need to diagonalise the Fock operator

$$\boxed{f(1) = h(1) + \sum_{j}^{\text{occ}} [\mathcal{J}_j(1) - \mathcal{K}_j(1)]}$$

For a closed-shell system (i.e. two electrons in each orbital)

$$f(1) = h(1) + \sum_{j}^{N/2} [2J_j(1) - K_j(1)] \quad \text{(closed shell)}$$

These orbitals are called canonical molecular orbitals (= eigenvectors):

$$\boxed{f(1)\,\chi_i(1) = \varepsilon_i(1)\,\chi_i(1)}$$

and ε_i are called the MO energies (= eigenvalues)

Introduction of a basis

Expansion in a basis

$$\psi_i(\boldsymbol{r}) = \sum_{\mu}^{K} C_{\mu i}\phi_\mu(\boldsymbol{r}) \qquad \equiv \qquad |i\rangle = \sum_{\mu}^{K} C_{\mu i}|\mu\rangle$$

K AOs gives K MOs: $N/2$ are occupied MOs and $K - N/2$ are vacant/virtual MOs

Roothaan-Hall equations

$$f|i\rangle = \varepsilon_i|i\rangle \quad \Rightarrow \quad f\sum_{\nu} C_{\nu i}|\nu\rangle = \varepsilon_i \sum_{\nu} C_{\nu i}|\nu\rangle$$

$$\Rightarrow \quad \langle\mu|f\sum_{\nu} C_{\nu i}|\nu\rangle = \varepsilon_i\langle\mu|\sum_{\nu} C_{\nu i}|\nu\rangle$$

$$\Rightarrow \quad \sum_{\nu} C_{\nu i}\langle\mu|f|\nu\rangle = \sum_{\nu} C_{\nu i}\varepsilon_i\langle\mu|\nu\rangle \quad \Rightarrow \quad \boxed{\sum_{\nu} F_{\mu\nu}C_{\nu i} = \sum_{\nu} S_{\mu\nu}C_{\nu i}\varepsilon_i}$$

Introduction of a basis (Take 2)

Matrix form of the Roothaan-Hall equations

$$\boxed{\mathbf{F}\,\mathbf{C} = \mathbf{S}\,\mathbf{C}\,\mathbf{E} \quad \Leftrightarrow \quad \mathbf{F}'\,\mathbf{C}' = \mathbf{C}'\,\mathbf{E}}$$

$$\mathbf{F}' = \mathbf{X}^\dagger\,\mathbf{F}\,\mathbf{X} \qquad \mathbf{C} = \mathbf{X}\,\mathbf{C}' \qquad \mathbf{X}^\dagger\,\mathbf{S}\,\mathbf{X} = \mathbb{I}$$

- Fock matrix $F_{\mu\nu} = \langle \mu | f | \nu \rangle$ and Overlap matrix $S_{\mu\nu} = \langle \mu | \nu \rangle$
- We need to determine the coefficient matrix $\mathbf{C}$ and the orbital energies $\mathbf{E}$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \qquad \mathbf{E} = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \varepsilon_K \end{pmatrix}$$

Self-consistent field (SCF) procedure

$$\mathbf{F}(\mathbf{C})\,\mathbf{C} = \mathbf{S}\,\mathbf{C}\,\mathbf{E}$$ **How do we solve these HF equations?**

Expression of the Fock matrix

"Find the expression of the Fock matrix in terms of the one- and two-electron integrals"

Expression of the Fock matrix

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$$F_{\mu\nu} = \langle \mu | h + \sum_j^{\text{occ}} (\mathcal{J}_j - \mathcal{K}_j) | \nu \rangle = H_{\mu\nu} + \sum_j^{\text{occ}} \langle \mu | \mathcal{J}_j - \mathcal{K}_j | \nu \rangle$$

$$= H_{\mu\nu} + \sum_j^{\text{occ}} (\langle \mu\chi_j | r_{12}^{-1} | \nu\chi_j \rangle - \langle \mu\chi_j | r_{12}^{-1} | \chi_j\nu \rangle)$$

$$= H_{\mu\nu} + \sum_j^{\text{occ}} \sum_{\lambda\sigma} C_{\lambda j} C_{\sigma j} (\langle \mu\lambda | r_{12}^{-1} | \nu\sigma \rangle - \langle \mu\lambda | r_{12}^{-1} | \sigma\nu \rangle)$$

$$= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu\lambda | \nu\sigma \rangle - \langle \mu\lambda | \sigma\nu \rangle)$$

$$= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu\lambda || \nu\sigma \rangle = H_{\mu\nu} + G_{\mu\nu}$$

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu\lambda | \nu\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \sigma\nu \rangle) \quad \text{(closed shell)}$$

Density matrix & Chemists vs Physicists

Density matrix **P**

$$\boxed{P_{\mu\nu} = \sum_{i}^{\text{occ}} C_{\mu i} C_{\nu i}} \qquad \text{or} \qquad P_{\mu\nu} = 2 \sum_{i}^{\text{N/2}} C_{\mu i} C_{\nu i} \quad \text{(closed shell)}$$

Physicist's notation for two-electron integrals

$$\langle \mu\nu | \lambda\sigma \rangle = \iint \phi_\mu(1) \phi_\nu(2) \frac{1}{r_{12}} \phi_\lambda(1) \phi_\sigma(2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$\langle \mu\nu || \lambda\sigma \rangle = \langle \mu\nu | \lambda\sigma \rangle - \langle \mu\nu | \sigma\lambda \rangle$$

Chemist's notation for two-electron integrals

$$(\mu\nu | \lambda\sigma) = \iint \phi_\mu(1) \phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2) \phi_\sigma(2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$(\mu\nu || \lambda\sigma) = (\mu\nu | \lambda\sigma) - (\mu\sigma | \lambda\nu)$$

How to perform a HF calculation in practice?

The SCF algorithm

1. Specify molecule $\{\boldsymbol{R}_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$
2. Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle\mu\nu|\lambda\sigma\rangle$
3. Diagonalize $\mathbf{S}$ and compute $\mathbf{X}$
4. Obtain guess density matrix for $\mathbf{P}$
   1. Calculate $\mathbf{G}$ and then $\mathbf{F} = \mathbf{H} + \mathbf{G}$
   2. Compute $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$
   3. Diagonalize $\mathbf{F}'$ to obtain $\mathbf{C}'$ and $\mathbf{E}$
   4. Calculate $\mathbf{C} = \mathbf{X} \mathbf{C}'$
   5. Form a new density matrix $\mathbf{P} = \mathbf{C} \mathbf{C}^\dagger$
   6. Am I converged? If not go back to 1.
5. Calculate stuff that you want, like E_{HF} for example

How to calculate $\mathbf{X}$?

Different orthogonalizations

1. Symmetric orthogonalization

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U}\,\mathbf{s}^{-1/2}\,\mathbf{U}^{\dagger}$$

Is it working?

$$\mathbf{X}^{\dagger}\,\mathbf{S}\,\mathbf{X} = \mathbf{S}^{-1/2}\,\mathbf{S}\,\mathbf{S}^{-1/2} = \mathbf{I}$$

2. Canonical orthogonalization (when you have linear dependencies)

$$\mathbf{X} = \mathbf{U}\,\mathbf{s}^{-1/2}$$

Is it working?

$$\mathbf{X}^{\dagger}\,\mathbf{S}\,\mathbf{X} = \mathbf{s}^{-1/2}\,\mathbf{U}^{\dagger}\,\mathbf{S}\,\mathbf{U}\,\mathbf{s}^{-1/2} = \mathbf{s}^{-1/2}\,\mathbf{s}\,\mathbf{s}^{-1/2} = \mathbf{I}$$

3. Gram-Schmidt orthogonalization

How to obtain a good guess for the MOs or density matrix?

Possible initial density matrix

1. We can set $\mathbf{P} = \mathbf{0} \Rightarrow \mathbf{F} = \mathbf{H}$ (core Hamiltonian approximation):
   $\Rightarrow$ Usually a poor guess but easy to implement
2. Use EHT or semi-empirical methods (cf previous lectures):
   $\Rightarrow$ Out of fashion
3. Using tabulated atomic densities:
   $\Rightarrow$ "SAD" guess in QChem/IQmol
4. Read the MOs of a previous calculation:
   $\Rightarrow$ Very common and very useful

How do I know I have converged (or not)?

Convergence in SCF calculations

1. You can check the energy and/or the density matrix:
   $\Rightarrow$ The energy/density **should not** change at convergence

2. You can check the commutator $\mathbf{FPS} - \mathbf{SPF}$:
   $\Rightarrow$ At convergence, we have $\mathbf{FPS} - \mathbf{SPF} = \mathbf{0}$

3. The DIIS (direct inversion in the iterative subspace) method is usually used to speed up convergence:
   $\Rightarrow$ Extrapolation of the Fock matrix using previous iterations

$$\mathbf{F}_{m+1} = \sum_{i=m-k}^{m} c_i \mathbf{F}_i$$

Expression of the HF energy

"Find the expression of the HF energy in terms of the one- and two-electron integrals?"

Expression of the HF energy

"Find the expression of the HF energy in terms of the one- and two-electron integrals?"

$$E_{\text{HF}} = \sum_i h_i + \frac{1}{2}\sum_{ij}(\mathcal{J}_{ij} - \mathcal{K}_{ij}) \quad \text{(cf few slides ago)}$$

$$= \sum_i \langle \sum_\mu c_{\mu i}\phi_\mu | h | \sum_\nu c_{\nu i}\phi_\nu \rangle$$

$$+ \frac{1}{2}\sum_{ij} \langle (\sum_\mu c_{\mu i}\phi_\mu)(\sum_\lambda c_{\lambda j}\phi_\lambda) || (\sum_\nu c_{\nu i}\phi_\nu)(\sum_\sigma c_{\sigma j}\phi_\sigma) \rangle$$

$$= \sum_{\mu\nu} P_{\mu\nu} \left[H_{\mu\nu} + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu\lambda || \nu\sigma \rangle \right]$$

$$\boxed{E_{\text{HF}} = \frac{1}{2}\text{Tr}[\mathbf{P}\,(\mathbf{H} + \mathbf{F})]}$$