

# Hartree-Fock

Mean-field theory to solve the electronic Schrödinger equation

$$\left[ -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}} \right] \Psi(\mathbf{r}; \mathbf{R}) = E_{el} \Psi(\mathbf{r}; \mathbf{R})$$

$$\left[ \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) \right] \Psi(\mathbf{r}; \mathbf{R}) = E_{el} \Psi(\mathbf{r}; \mathbf{R})$$

Assuming non-interacting electrons yields Hartree product

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \cdots \chi_N(\mathbf{x}_N)$$

But this approach does not satisfy the antisymmetry principle

$$\chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1) = -\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)$$

With a Slater determinant however, it is.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Slater determinant:

- Electrons are indistinguishable
- Every electron in every orbital
- Equivalent to mean field treatment
- Satisfies Pauli exclusion

Electronic energy expression

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle$$

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i < j} v(i, j) + V_{NN}$$

$$h(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \quad v(i, j) = \frac{1}{r_{ij}}$$

Can be cast in integral form

$$E_{HF} = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} [ii|jj] - \underbrace{[ij|ji]}$$

Anti-Symmetry

$$\langle i | h | j \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$[ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2)$$

Solution

$$h(\mathbf{x}_1)\chi_i(\mathbf{x}_1) + \sum_{j \neq i} \left[ \int d\mathbf{x}_2 |\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1} \right] \chi_i(\mathbf{x}_1) - \sum_{j \neq i} \left[ \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2) r_{12}^{-1} \right] \chi_j(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$



Coulomb term

$$\mathcal{J}_j(\mathbf{x}_1) = \int d\mathbf{x}_2 |\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1}$$



Exchange term

$$\mathcal{K}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \left[ \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_i(\mathbf{x}_2) \right] \chi_j(\mathbf{x}_1)$$

Solution

$$\left[ h(\mathbf{x}_1) + \sum_{j \neq i} \mathcal{J}_j(\mathbf{x}_1) - \sum_{j \neq i} \mathcal{K}_j(\mathbf{x}_1) \right] \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

$$[\mathcal{J}_i(\mathbf{x}_1) - \mathcal{K}_i(\mathbf{x}_1)] \chi_i(\mathbf{x}_1) = 0$$

$$\left[ h(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1) \right] \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

Solved numerically by optimizing orthonormal orbitals



Fock operator  $f$

Take

$$\left[ h(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1) \right] \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

And solve in a basis set

$$\chi_i = \sum_{\mu=1}^K C_{\mu i} \tilde{\chi}_{\mu} \qquad f(\mathbf{x}_1) \sum_{\nu} C_{\nu i} \tilde{\chi}_{\nu}(\mathbf{x}_1) = \epsilon_i \sum_{\nu} C_{\nu i} \tilde{\chi}_{\nu}(\mathbf{x}_1)$$

$$\sum_{\nu} C_{\nu i} \int d\mathbf{x}_1 \tilde{\chi}_{\mu}^*(\mathbf{x}_1) f(\mathbf{x}_1) \tilde{\chi}_{\nu}(\mathbf{x}_1) = \epsilon_i \sum_{\nu} C_{\nu i} \int d\mathbf{x}_1 \tilde{\chi}_{\mu}^*(\mathbf{x}_1) \tilde{\chi}_{\nu}(\mathbf{x}_1)$$

Fock matrix  $F_{\mu\nu}$

Overlap matrix  $S_{\mu\nu}$

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}$$

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

