

- Formal derivation of Hartree-Fock method under the first quantization.

After separate the nuclear and electronic motion (i.e. B.O. approx.), we deal with electronic motion only.

→

$$\hat{H}_e |\psi_e\rangle = E |\psi_e\rangle$$

$\hat{H}_e = \underbrace{\hat{T}_e}_{1e^- \text{ term}} + \underbrace{\hat{V}_{Ne}}_{1e^- \text{ term}} + \underbrace{\hat{V}_{ee}}_{2e^- \text{ term}}$

$|\psi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)\rangle \approx \underbrace{\chi_1(1) \cdot \chi_2(2) \dots \chi_N(N)}_{\text{Hartree product, approx!}}$

* Configuration: the way to arrange electrons into spin-orbitals.

∴ electrons are fermions (i.e. spin = $\frac{1}{2}$)

∴ obey ① antisymmetry

② Pauli exclusion principle

∴ $|\psi_e\rangle =$ single Slater determinant.

$$|\psi_e\rangle \approx |\psi_{SD}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{r}_1) & \chi_2(\vec{r}_1) & \dots & \chi_N(\vec{r}_1) \\ \chi_1(\vec{r}_2) & \chi_2(\vec{r}_2) & \dots & \chi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{r}_N) & \chi_2(\vec{r}_N) & \dots & \chi_N(\vec{r}_N) \end{vmatrix}$$

row: same electrons

column: same spin-orbital.

$$= |\chi_1 \chi_2 \dots \chi_N\rangle$$

$$= |1, 2, \dots, N\rangle$$

→ After adopt above approximations (B.O., Hartree-product, SD approx.), we want to find the minimum electronic energy (E_{\min} , i.e. ground state energy) by varying electronic wavefunction (i.e. variational)

$$E^{HF} = \min_{\psi_{SD}} \langle \psi_{SD} | \hat{H}_e | \psi_{SD} \rangle$$

The processes are the same in the simplified version.

HF-SCF → Lagrange undetermined multiplier

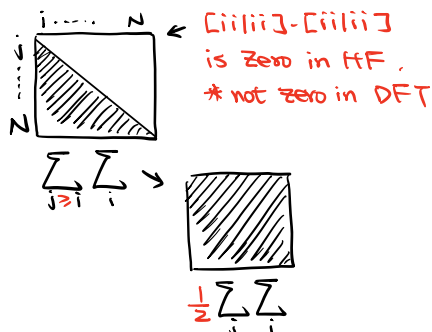
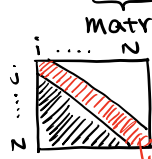
→ Fock equation

→ self-consistent-field (SCF)

→ $E = \langle \psi_{SD} | \hat{H}_e | \psi_{SD} \rangle$

$$= \langle i, j, \dots, N | \sum_i \hat{h}_i + \sum_{j>i} \sum_i \frac{1}{r_{ij}} | i, j, \dots, N \rangle$$

$$= \sum_i \langle i | \hat{h} | i \rangle + \sum_{j>i} \sum_i \langle ij || ji \rangle$$



$$\langle ij || ji \rangle = \langle ij | ij \rangle - \langle ij | ji \rangle$$

physicist's notation

chemist's notation

$$= [ii|jj] - [ij|ij]$$

$$\int d^3r_1 d^3r_2 \cdot \chi_i^*(r_1) \chi_j^*(r_2) \frac{1}{r_{12}} \chi_i(r_1) \chi_j(r_2)$$

$$= \int d^3r_1 d^3r_2 \cdot \underbrace{\chi_i^*(r_1) \chi_i(r_1)}_{|\chi_i|^2 : \text{electronic density}} \frac{1}{r_{12}} \chi_j^*(r_2) \chi_j(r_2)$$

$$= \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N \{ \underbrace{[ii|jj]}_{J_{ij}} - \underbrace{[ij|ij]}_{K_{ij}} \}$$

J_{ij} : Coulomb integral

K_{ij} : Exchange integral

$$\Rightarrow E^{HF} = \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N [J_{ij} - K_{ij}]$$

$$\langle ij | \rangle = \delta_{ij} \rightarrow \text{Lagrange multiplier } (\mathcal{L})$$

$$\mathcal{L} \rightarrow \mathcal{L} + \delta \mathcal{L}$$

$$\chi_i \rightarrow \chi_i + \delta \chi_i$$

$$\rightarrow \mathcal{L}[\chi] = E^{HF}[\chi] - \sum_j \varepsilon_j (\langle i | j \rangle - \delta_{ij})$$

$$\delta \mathcal{L}[\chi] = \underbrace{\delta E^{HF}[\chi]}_{\delta \left\{ \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N [ii|jj] - [ij|ij] \right\}} - \sum_j \overbrace{\varepsilon_j (\delta \langle i | j \rangle + \langle i | \delta j \rangle + \langle \delta j | i \rangle)}^{\varepsilon_j (\delta \langle i | j \rangle)} = 0$$

$$\because \delta^2 \ll \delta$$

$$= \sum_i [\langle \delta i | \hat{h} | i \rangle - \langle i | \hat{h} | \delta i \rangle]$$

$$+ \frac{1}{2} \sum_{i,j} \{ [\delta i | i | j j] + [i | \delta i | j j] + [i i | j \delta j] + [i i | j j \delta j] \}$$

$$- \frac{1}{2} \sum_{i,j} \{ [\delta i j | i j] - [i \delta j | i j] + [i j | \delta i j] + [i j | i j \delta j] \}$$

$$- \sum_{i,j} \{ \varepsilon_j (\langle \delta i | j \rangle - \langle i | \delta j \rangle) \}$$

trick 1. play

with dummy indices, i and j . eg. $[\delta_{ii} | j j]$ $\xrightarrow[\substack{i \rightarrow j, j \rightarrow i}]{\text{rename orb.}}$ $\{ \delta_{jj} | i i \}$ $\xrightarrow{\text{swap}}$ $[i i | \delta_{jj}]$

\therefore combine \blacktriangle terms

$$= \sum_i [\langle \delta_{ii} | \hat{h} | i \rangle + \langle i | \hat{h} | \delta_{ii} \rangle]$$

$$+ \sum_{i,j} \{ [\delta_{ii} | j j] + [i \delta_{ii} | j j] \} - \{ [\delta_{ij} | j i] + [i \delta_{ij} | j i] \}$$

$$- \sum_{i,j} [\epsilon_{ij} \cdot (\langle \delta_{ii} | j \rangle + \langle i | \delta_{ij} \rangle)]$$

trick 2, take complex conjugate twice

eg. $(\boxed{\text{A}})^* = \boxed{\text{A}}$, take \blacktriangle as an example

$$(\epsilon_{ij} \langle i | \delta_{ij} \rangle^*)^* = (\epsilon_{ij}^* \langle \delta_{ij} | i \rangle)^*$$

\downarrow trick 1, $i \rightarrow j, j \rightarrow i$

$$= (\epsilon_{ji}^* \langle \delta_{ii} | j \rangle)^*$$

$$= \epsilon_{ji} \langle j | \delta_{ii} \rangle$$

\downarrow Hermitian ($A^\dagger = A$)

$$= \epsilon_{ij} \langle i | \delta_{ij} \rangle$$

$$\delta \mathcal{L}[i] = \sum_i \langle \delta_{ii} | \hat{h} | i \rangle + \sum_{i,j} ([\delta_{ii} | j j] - [\delta_{ij} | j i] - \epsilon_{ij} \langle \delta_{ii} | j \rangle)$$

$$+ \text{complex conjugate (c.c.)} = 0$$

to be clear, take δx_i^* out of this integro-differential eqn.

$$\begin{aligned} \rightarrow \delta \mathcal{L} &= \sum_i \int d\mathbf{r}_1 \cdot \delta x_i^*(\mathbf{r}_1) \cdot [(\hat{h}(\mathbf{r}_1) \cdot x_i(\mathbf{r}_1)) \\ &\quad + (\sum_j x_i(\mathbf{r}_1) \int d\mathbf{r}_2 \frac{1}{r_{12}} x_j^*(\mathbf{r}_2) x_j(\mathbf{r}_2)) \\ &\quad - (\sum_j x_j(\mathbf{r}_1) \int d\mathbf{r}_2 \frac{1}{r_{12}} x_j^*(\mathbf{r}_2) x_i(\mathbf{r}_2)) \\ &\quad - (\sum_j \epsilon_{ij} x_j(\mathbf{r}_1)] + \text{c.c.} = 0 \end{aligned}$$

$$\rightarrow \sum_i \int d\mathbf{r}_1 \cdot \delta x_i^*(\mathbf{r}_1) \cdot [(\hat{h}(\mathbf{r}_1) \cdot x_i(\mathbf{r}_1))$$

$$+ \left(\sum_j^N \chi_j(r_1) \int dr_2 \frac{1}{r_{12}} |\chi_j^*(r_2)|^2 \right) \hat{J}_j(r_1)$$

electron 1 "feels" the potential generated by electron 2.

$$- \left(\sum_j^N \chi_j(r_1) \int dr_2 \frac{1}{r_{12}} \chi_j^*(r_2) \chi_i(r_2) \right) \hat{K}_j(r_1)$$

$$= \sum_j^N \epsilon_{ij} \cdot \chi_j(r_1)$$

$$\rightarrow \underbrace{\left[\hat{h}(r_1) + \sum_j \hat{J}_j(r_1) - \sum_j \hat{K}_j(r_1) \right]}_{\hat{f}(r_1) \text{ Fock operator}} \chi_i(r_1) = \sum_j \epsilon_{ij} \chi_j(r_1)$$

have freedom by changing basis such that make the matrix ϵ_{ij} become diagonal

$$\rightarrow \underbrace{\hat{f}(r_1)} \chi_i(r_1) = \epsilon_i \chi_i(r_1) \quad \text{Hartree-Fock equation}$$

$$\therefore \hat{f} = f(\chi_i) \quad \rightarrow \text{eigenvalue equation}$$

\therefore self-consistent-field.

→ Chose atomic orbitals (pre-selected basis) as a basis set, we transform Hartree-Fock eqn. into Hartree-Fock-Roothaan equations.

$$\chi_i = \sum_u C_{ui} \underbrace{\tilde{\chi}_u}_{\text{A.O.}}$$

$$\rightarrow \text{matrix form.} \quad \sum_\nu F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu} C_{\nu i}$$

$$FC = SC\epsilon \quad \#$$