- **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.

→ $\hat{H}_e |\Psi_e\rangle = E |\Psi_e\rangle$

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

$1e^-$ term:

$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{R_{Ai}}$

$2e^-$ term:

$\hat{V}_{ij} = \frac{1}{r_{ij}}$

$|\Psi_e(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N)\rangle \approx \chi_1(1) \cdot \chi_2(2) \dots \chi_N(N)$ (spin-orbital)

↓ Hartree product, approx!

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

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

∴ obey ① antisymmetry

② Pauli exclusion principle

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

$$|\Psi_e\rangle \approx |\Psi_{SD}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{r}_1) & \chi_2(\vec{r}_1) & \cdots & \chi_N(\vec{r}_1) \\ \chi_1 & & & \vdots \\ \vdots & & & \\ & & & \chi_N(\vec{r}_N) \end{vmatrix}$$

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 energe (Emin, i.e. ground state energy) by varifying electronic wavefunction (i.e. vorational)

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

The processes are the same in the simplied version.

HF-SCF → Lagrange undetermined multiplier

→ Fock equation

→ self-consistent-field (SCF)

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

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

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

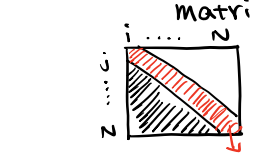
physicist's notation

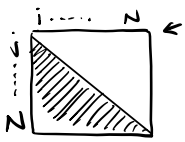
$\langle ij \| ji\rangle = \langle ij|ij\rangle - \langle ij|ji\rangle$ (① ② ① ②)

chemist's notation

$= [ii|jj] - [ij|ij]$ (① ① ② ②)

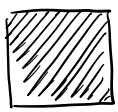
matrix





$[ii|ii]-[ii|ii]$ is zero in HF, * not zero in DFT

$\sum_{j>i}\sum_i$



$\frac{1}{2}\sum_j\sum_i$

$$\int d\vec{r}_1 d\vec{r}_2 \cdot \chi_i^*(r_1)\chi_j^*(r_2)\frac{1}{r_{12}}\chi_i(r_1)\chi_j(r_2)$$

$$= \int d\vec{r}_1 d\vec{r}_2 \cdot \underbrace{\chi_i^*(r_1)\chi_i(r_1)}_{|\chi_i|^2:\text{electronic density}}\frac{1}{r_{12}}\chi_j^*(r_2)\chi_j(r_2)$$

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

J_{ij} : Columb integral

K_{ij} : Exchange integral

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

$\langle i|j\rangle = \delta_{ij}$ → Lagrange multiplier ($\mathcal{L}$)

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

$\chi_i \to \chi_i + \delta\chi_i$

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

$\varepsilon_{ij}(\langle\delta i|j\rangle + \langle i|\delta j\rangle + \langle\delta i|\delta j\rangle)$

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

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

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

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

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

$$- \sum_{ij}\{\varepsilon_{ij}(\langle\delta i|j\rangle - \langle i|\delta j\rangle)\}$$

trick 1. play

with dummy indices, i and j.

eg. $[\delta_{ii}|_{jj}]$ (① ① ② ②) $\xrightarrow[i\to j,\ j\to i]{\text{rename orb.}} \{\delta_{jj}|_{ii}\}$ (② ② ① ①) $\xrightarrow{\text{swap}} [_{ii}|\delta_{jj}]$ (① ① ② ②)

$\therefore$ combine ▲ terms

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

$$+ \sum_{i,j} \{[\delta_{ii}|_{jj}] + [_i\delta_i|_{jj}]\} - \{[\delta_{ij}|_{ji}] + [_i\delta_j|_{ji}]\}$$

$$- \sum_{i,j} [\varepsilon_{ij}\cdot(\langle\delta_i|j\rangle + \langle i|\delta_j\rangle)]$$

trick 2. take complex conjugate twice

eg. $(\blacksquare^*)^* = \blacksquare$; take ▲ as an example

$$(\varepsilon_{ij}\langle i|\delta_j\rangle^*)^* = (\varepsilon_{ij}^*\langle\delta_j|i\rangle)^*$$

↓ trick 1. $i\to j$, $j\to i$

$$= (\varepsilon_{ji}^*\langle\delta_i|j\rangle)^*$$

$$= \varepsilon_{ji}\langle j|\delta_i\rangle$$

↓ Hermitian ($A^\dagger = A$)

$$= \varepsilon_{ij}\langle i|\delta_j\rangle$$

$$\delta\mathcal{L}[i] = \sum_i \langle\delta_i|\hat{h}|i\rangle + \sum_{i,j}\left([\delta_{ii}|_{jj}] - [\delta_{ij}|_{ji}] - \varepsilon_{ij}\langle\delta_i|j\rangle\right)$$

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

to be clear, take $\delta\chi_i^*$ out of this integro-differential eqn.

$$\rightarrow \delta\mathcal{L} = \sum_i^N \int d\mathbf{r}_1 \cdot \delta\chi_i^*(\mathbf{r}_1)\cdot\Big[\left(\hat{h}(\mathbf{r}_1)\cdot\chi_i(\mathbf{r}_1)\right)$$

$$+ \left(\sum_j^N \chi_i(\mathbf{r}_1)\int d\mathbf{r}_2\,\frac{1}{r_{12}}\chi_j^*(\mathbf{r}_2)\chi_j(\mathbf{r}_2)\right)$$

$$- \left(\sum_j^N \chi_j(\mathbf{r}_1)\int d\mathbf{r}_2\,\frac{1}{r_{12}}\chi_j^*(\mathbf{r}_2)\chi_i(\mathbf{r}_2)\right)$$

$$- \left(\sum_j^N \varepsilon_{ij}\cdot\chi_j(\mathbf{r}_1)\Big]\right. + \text{c.c.} = 0$$

$$\rightarrow \sum_i^N \int d\mathbf{r}_1 \cdot \delta\chi_i^*(\mathbf{r}_1)\cdot\Big[\left(\hat{h}(\mathbf{r}_1)\cdot\chi_i(\mathbf{r}_1)\right)$$

$$+\left(\sum_j^N \chi_i(\mathbf{r}_1)\int d\mathbf{r}_2 \frac{1}{r_{12}}|\chi_j^*(\mathbf{r}_2)|^2\right) \quad \hat{J}_j(\mathbf{r}_1)$$

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

$$-\left(\sum_j^N \chi_j(\mathbf{r}_1)\int d\mathbf{r}_2 \frac{1}{r_{12}}\chi_j^*(\mathbf{r}_2)\chi_i(\mathbf{r}_2)\right)\Big] \quad \hat{K}_j(\mathbf{r}_1)$$

$$= \sum_j^N \varepsilon_{ij}\chi_j(\mathbf{r}_1)$$

$$\rightarrow \underbrace{\left[\hat{h}(\mathbf{r}_1) + \sum_j \hat{J}_j(\mathbf{r}_1) - \sum_j \hat{K}_j(\mathbf{r}_1)\right]}_{\hat{f}(\mathbf{r}_1)} \chi_i(\mathbf{r}_1) = \sum_j^N \varepsilon_{ij}\chi_j(\mathbf{r}_1)$$

$\hat{f}(\mathbf{r}_1)$ Fock operator

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

$$\rightarrow \underbrace{\hat{f}(\mathbf{r}_1)}\chi_i(\mathbf{r}_1) = \varepsilon_i\chi_i(\mathbf{r}_1)$$

Hartree-Fock equation

$\because \hat{f} = f(\chi_i)$ → eigenvale 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.

$$\chi_i = \sum_\mu C_{\mu i}\underbrace{\tilde{\chi}_\mu}_{\text{A.O.}}$$

→ matrix form. $\sum_\nu F_{\mu\nu}C_{\nu i} = \varepsilon_i\sum_\nu S_{\mu\nu}C_{\nu i}$

$$FC = SC\varepsilon \quad \#$$