Notes on Hartree-Fock method

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Two electron system

e.g. He atom $\qquad$ x : general variable

Hamiltonian

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dx_1^2} - \frac{1}{2}\frac{d^2}{dx_2^2} + \frac{1}{|x_1 - x_2|} - \frac{2}{|x_1 - \tau_1|} - \frac{2}{|x_2 - \tau_1|} \quad \text{---- (1)}$$

$$= \underbrace{-\frac{1}{2}\frac{d^2}{dx_1^2} - \frac{2}{|x_1 - \tau_1|}}_{\hat{V}_1(x_1)} \underbrace{-\frac{1}{2}\frac{d^2}{dx_1^2} - \frac{2}{|x_2 - \tau_1|}}_{\hat{V}_1(x_2)} + \underbrace{\frac{1}{|x_1 - x_2|}}_{\hat{V}_2(x_1 x_2)}$$

Thus,

$$\hat{H} = \hat{V}_1(x_1) + \hat{V}(x_2) + \hat{V}_2(x_1 x_2)$$

$$= V_1 + V_2 \quad \text{----- (2)}$$

where

$$V_1 = \sum_{i=1}^{2} \hat{V}_1(x_i) \quad , \quad V_2 = \frac{1}{2}\sum_{i \neq j = 1}^{2} \hat{V}_2(x_i x_j)$$

Due to the indistinctiveness of electrons,

$$|\Phi(x_1 x_2)|^2 = |\Phi(x_2 x_1)|^2$$

$$\longrightarrow \quad \Phi(x_1 x_2) = e^{i\alpha}\Phi(x_2 x_1) = e^{i2\alpha}\Phi(x_1 x_2) \quad \text{--- (3)}$$

$e^{i2\alpha}$ should be I $\longrightarrow$ $e^{i\alpha} = \pm 1$ $\quad$ $+1$ Boson

-1 Fermion

---- (4)

Slater determinant

$$\Phi(x_1\, x_2) = \frac{1}{\sqrt{2}}\left\{\varphi_\ell(x_1)\varphi_{\ell'}(x_2) - \varphi_{\ell'}(x_1)\varphi_\ell(x_2)\right\} \quad \text{--- (5)}$$

variable change

↓

$$\Phi(x_2\, x_1) = \frac{1}{\sqrt{2}}\left\{\varphi_\ell(x_2)\varphi_{\ell'}(x_1) - \varphi_{\ell'}(x_2)\varphi_\ell(x_1)\right\} \quad \text{--- (6)}$$

Comparing Eqs. (5) and (6), we have

$$\Phi(x_1\, x_2) = -\Phi(x_2\, x_1) \quad \text{--- (7)}$$

the property is consistent with Eq. (4).

Also, Eq. (5) can be written by the determinant

$$\Phi(x_1\, x_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_\ell(x_1) & \varphi_{\ell'}(x_1) \\ \varphi_\ell(x_2) & \varphi_{\ell'}(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left|\varphi_\ell\, \varphi_{\ell'}\right| \quad \text{--- (8)}$$

↑ simplified notation.

It is also noted that

If $\varphi_\ell = \varphi_{\ell'}$

$$\Phi(x_1\, x_2) = 0$$

This is easily confirmed from Eq. (5) as

$$\Phi(x_1\, x_2) = \frac{1}{\sqrt{2}}\left\{\varphi_\ell(x_1)\varphi_\ell(x_2) - \varphi_\ell(x_1)\varphi_\ell(x_2)\right\}$$

$$= 0 \quad \text{--- (9)}$$

Thus, the slater determinant satisfies Pauli's exclusion principle automatically.

Hartree - Fock method

A single Slater determinant is used to evaluate the total energy.

$$E = \frac{\langle \Phi | \hat{H} | \Phi \rangle \quad \text{numerator}}{\langle \Phi | \Phi \rangle \quad \text{denominator}} \qquad \cdots \quad (10)$$

$$\langle \Phi | \Phi \rangle = \frac{1}{2} \int dx_1 \int dx_2 \left(\varphi_l^*(x_1) \varphi_{l'}^*(x_2) - \varphi_{l'}^*(x_1) \varphi_l^*(x_2) \right) \times \left(\varphi_l(x_1) \varphi_{l'}(x_2) - \varphi_{l'}(x_1) \varphi_l(x_2) \right)$$

$$= \frac{1}{2} \underbrace{\int dx_1\, \varphi_l^*(x_1) \varphi_l(x_1)}_{1} \underbrace{\int dx_2\, \varphi_{l'}^*(x_2) \varphi_{l'}(x_2)}_{1}$$

$$- \frac{1}{2} \underbrace{\int dx_1\, \varphi_l^*(x_1) \varphi_{l'}(x_1)}_{0} \underbrace{\int dx_2\, \varphi_{l'}^*(x_2) \varphi_l(x_2)}_{0}$$

$$- \frac{1}{2} \underbrace{\int dx_1\, \varphi_{l'}^*(x_1) \varphi_l(x_1)}_{0} \underbrace{\int dx_2\, \varphi_l^*(x_2) \varphi_{l'}(x_2)}_{0}$$

$$+ \frac{1}{2} \underbrace{\int dx_1\, \varphi_{l'}^*(x_1) \varphi_{l'}(x_1)}_{1} \underbrace{\int dx_2\, \varphi_l^*(x_2) \varphi_l(x_2)}_{1} = \frac{1}{2} + \frac{1}{2} = 1$$

$$\cdots \quad (11)$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \frac{1}{2} \int dx_1 \int dx_2 \left(\varphi_l^*(x_1) \varphi_{l'}^*(x_2) - \varphi_{l'}^*(x_1) \varphi_l^*(x_2) \right) \times \hat{H} \times \left(\varphi_l(x_1) \varphi_{l'}(x_2) - \varphi_{l'}(x_1) \varphi_l(x_2) \right)$$

$$= \frac{1}{2} \iint dx_1 dx_2\, \varphi_l^*(x_1) \varphi_{l'}^*(x_2)\, \hat{H}\, \varphi_l(x_1) \varphi_{l'}(x_2) \qquad \cdots \quad (A)$$

$$- \frac{1}{2} \iint dx_1 dx_2\, \varphi_l^*(x_1) \varphi_{l'}^*(x_2)\, \hat{H}\, \varphi_{l'}(x_1) \varphi_l(x_2) \qquad \cdots \quad (B)$$

$$- \frac{1}{2} \iint dx_1 dx_2\, \varphi_{l'}^*(x_1) \varphi_l^*(x_2)\, \hat{H}\, \varphi_l(x_1) \varphi_{l'}(x_2) \qquad \cdots \quad (C)$$

$$+ \frac{1}{2} \iint dx_1 dx_2\, \varphi_{l'}^*(x_1) \varphi_l^*(x_2)\, \hat{H}\, \varphi_{l'}(x_1) \varphi_l(x_2) \qquad \cdots \quad (D)$$

$$(A) = \frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,\hat{H}\,\varphi_l(x_1)\varphi_{l'}(x_2)$$

$$= \frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,V_1\,\varphi_l(x_1)\varphi_{l'}(x_2) \quad \text{---} (A1)$$

$$+ \frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,V_2\,\varphi_l(x_1)\varphi_{l'}(x_2) \quad \text{---} (A2)$$

---- (13)

$$(A1) = \frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,\hat{V}_1(x_1)\,\varphi_l(x_1)\varphi_{l'}(x_2)$$

$$+ \frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,\hat{V}_1(x_2)\,\varphi_l(x_1)\varphi_{l'}(x_2)$$

$$= \frac{1}{2}\int dx_1\, \varphi_l^*(x_1)\,\hat{V}_1(x_1)\,\varphi_l(x_1) + \frac{1}{2}\int dx_2\, \varphi_{l'}^*(x_2)\,\hat{V}_1(x_2)\,\varphi_{l'}(x_2)$$

--- (14)

$$(A2) = \frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_l(x_1)\,\frac{1}{|x_1 - x_2|}\,\varphi_{l'}^*(x_2)\varphi_{l'}(x_2)$$

---- (15)

$$(B) = -\frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,\hat{H}\,\varphi_{l'}(x_1)\varphi_l(x_2)$$

$$= -\frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,V_1\,\varphi_{l'}(x_1)\varphi_l(x_2) \quad \text{---} (B1)$$

$$- \frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}^*(x_2)\,V_2\,\varphi_{l'}(x_1)\varphi_l(x_2) \quad \text{---} (B2)$$

---- (16)

$$(B1) = -\frac{1}{2}\int dx_1\, \varphi_l^*(x_1)\,\hat{V}_1(x_1)\,\varphi_{l'}(x_1)\underbrace{\int dx_2\, \varphi_{l'}^*(x_2)\varphi_l(x_2)}_{0}$$

$$- \frac{1}{2}\underbrace{\int dx_1\, \varphi_l^*(x_1)\varphi_{l'}(x_1)}_{0}\int dx_2\, \varphi_{l'}^*(x_2)\,\hat{V}_1(x_2)\,\varphi_l(x_2) = 0$$

---- (17)

$$(B2) = -\frac{1}{2}\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}(x_1)\,\frac{1}{|x_1 - x_2|}\,\varphi_{l'}^*(x_2)\varphi_l(x_2)$$

---- (18)

$$(C) = -\frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\, \varphi_{l}^{*}(x_2)\, \hat{H}\, \varphi_{l}(x_1)\, \varphi_{l'}(x_2)$$

$$= -\frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\, \varphi_{l}^{*}(x_2)\, V_1\, \varphi_{l}(x_1)\, \varphi_{l'}(x_2) \quad \cdots (C1)$$

$$-\frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\, \varphi_{l}^{*}(x_2)\, V_2\, \varphi_{l}(x_1)\, \varphi_{l'}(x_2) \quad \cdots (C2)$$

$$\cdots (19)$$

$$(C1) = -\frac{1}{2}\int dx_1\, \varphi_{l'}^{*}(x_1)\, \hat{V}_1(x_1)\, \varphi_{l}(x_1) \int dx_2\, \underbrace{\varphi_{l}^{*}(x_2)\, \varphi_{l'}(x_2)}_{=0}$$

$$-\frac{1}{2}\int dx_1\, \underbrace{\varphi_{l'}^{*}(x_1)\, \varphi_{l}(x_1)}_{0} \int dx_2\, \varphi_{l}^{*}(x_2)\, \hat{V}_1(x_2)\, \varphi_{l'}(x_2) = 0$$

$$\cdots (20)$$

$$(C2) = -\frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\, \varphi_{l}(x_1)\, \frac{1}{|x_1 - x_2|}\, \varphi_{l}^{*}(x_2)\, \varphi_{l'}(x_2)$$

$$\cdots (21)$$

$$(D) = \frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\varphi_{l}^{*}(x_2)\, \hat{H}\, \varphi_{l'}(x_1)\, \varphi_{l}(x_2)$$

$$= \frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\varphi_{l}^{*}(x_2)\, V_1\, \varphi_{l'}(x_1)\, \varphi_{l}(x_2) \quad \cdots (D1)$$

$$+ \frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\varphi_{l}^{*}(x_2)\, V_2\, \varphi_{l'}(x_1)\, \varphi_{l}(x_2) \quad \cdots (D2)$$

$$\cdots (22)$$

$$(D1) = \frac{1}{2}\int dx_1\, \varphi_{l'}^{*}(x_1)\, \hat{V}_1(x_1)\, \varphi_{l'}(x_1) \int dx_2\, \underbrace{\varphi_{l}^{*}(x_2)\, \varphi_{l}(x_2)}_{1}$$

$$+ \frac{1}{2}\int dx_1\, \underbrace{\varphi_{l'}^{*}(x_1)\, \varphi_{l'}(x_1)}_{1} \int dx_2\, \varphi_{l}^{*}(x_2)\, \hat{V}_1(x_2)\, \varphi_{l}(x_2)$$

$$= \frac{1}{2}\int dx_1\, \varphi_{l'}^{*}(x_1)\, \hat{V}_1(x_1)\, \varphi_{l'}(x_1) + \frac{1}{2}\int dx_2\, \varphi_{l}^{*}(x_2)\, \hat{V}_1(x_2)\, \varphi_{l}(x_2)$$

$$\cdots (23)$$

$$(D2) = \frac{1}{2}\iint dx_1 dx_2\, \varphi_{l'}^{*}(x_1)\, \varphi_{l'}(x_1)\, \frac{1}{|x_1 - x_2|}\, \varphi_{l}^{*}(x_2)\, \varphi_{l}(x_2)$$

$$\cdots (24)$$

Therefore, the total energy by the HF method is given by

$$E_{HF} = \begin{matrix} (A1) & & (A2) & & (B2) \\ + & + & + & + & + \\ (D1) & & (D2) & & (C2) \end{matrix} \quad \cdots (25)$$

One-particle energy

$$(A1) + (D1) = \int dx\, \varphi_l^*(x)\, \hat{V}_1(x)\, \varphi_l(x) + \int dx\, \varphi_{l'}(x)\, \hat{V}_1(x)\, \varphi_{l'}(x) \quad \cdots (26)$$

Hartree energy

$$(A2) + (D2) = \iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_l(x_1) \frac{1}{|x_1 - x_2|} \varphi_{l'}^*(x_2)\varphi_{l'}(x_2) \quad \cdots (27)$$

Exchange energy

$$(B2) + (C2) = -\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}(x_1) \frac{1}{|x_1 - x_2|} \varphi_l(x_2)\varphi_{l'}^*(x_2) \quad \cdots (28)$$

For a N-electron system, the total energy is given by

$$\boxed{\begin{aligned} E_{HF} = {} & \sum_{l=1}^{N} \int dx\, \varphi_l^*(x)\, \hat{V}_1(x)\, \varphi_l(x) \\ & + \frac{1}{2}\sum_{l=1}^{N}\sum_{l'=1}^{N} \Big[\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_l(x_1) \frac{1}{|x_1 - x_2|} \varphi_{l'}^*(x_2)\varphi_{l'}(x_2) \\ & \qquad - \iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}(x_1) \frac{1}{|x_1 - x_2|} \varphi_l(x_2)\varphi_{l'}^*(x_2) \Big] \end{aligned}} \quad \cdots (29)$$

In case of $l = l'$, two terms cancel out.

Hartree - Fock equation

Under the condition of orthonormality between one-particle wave functions, φ, E_{HF} is variationally optimized using Lagrange's multiplier method.

$$F = E_{HF} - \sum_{l}\sum_{l'} \varepsilon_{ll'} \left(\int \varphi_l^*(x)\, \varphi_{l'}(x)\, dx - \delta_{ll'} \right) \quad \text{--- (30)}$$

Let us consider the discretization of F

$$F = \sum_{l=1}^{N} \Delta x \sum_i \varphi_l^*(x^{(i)})\, \hat{V}_1(x^{(i)})\, \varphi_l(x^{(i)})$$

$$+ \frac{1}{2} \sum_l \sum_{l'} (\Delta x)^2 \sum_i \sum_j \varphi_l^*(x_1^{(i)})\, \varphi_l(x_1^{(i)}) \frac{1}{|x_1^{(i)} - x_2^{(j)}|} \varphi_{l'}^*(x_2^{(j)})\, \varphi_{l'}(x_2^{(j)})$$

$$- \frac{1}{2} \sum_l \sum_{l'} (\Delta x)^2 \sum_i \sum_j \varphi_l^*(x_1^{(i)})\, \varphi_{l'}(x_1^{(i)}) \frac{1}{|x_1^{(i)} - x_2^{(j)}|} \varphi_l(x_2^{(j)})\, \varphi_{l'}^*(x_2^{(j)})$$

$$- \sum_l \sum_{l'} \varepsilon_{ll'} \left(\Delta x \sum_i \varphi_l^*(x^{(i)})\, \varphi_{l'}(x^{(i)}) - \delta_{ll'} \right) \quad \text{--- (31)}$$

The partial derivative of F with respect to φ_k^* at $x^{(p)}$ is given by

$$\frac{\partial F}{\partial \varphi_k^*(x^{(p)})} = \Delta x\, \hat{V}_1(x^{(p)})\, \varphi_k(x^{(p)})$$

$$+ \sum_{l'} (\Delta x)^2 \varphi_k(x_1^{(p)}) \sum_j \frac{1}{|x_1^{(p)} - x_2^{(j)}|} \varphi_{l'}^*(x_2^{(j)})\, \varphi_{l'}(x_2^{(j)})$$

$$- \sum_{l'} (\Delta x)^2 \varphi_{l'}(x_1^{(p)}) \sum_j \frac{1}{|x_1^{(p)} - x_2^{(j)}|} \varphi_k(x_2^{(j)})\, \varphi_{l'}^*(x_2^{(j)})$$

$$- \sum_{l'} \varepsilon_{kl'}\, \Delta x\, \varphi_{l'}(x^{(p)}) \quad \text{--- (32)}$$

Now we consider the continuation of Eq. (32), then we get

$$\frac{\partial F}{\partial \varphi_k^*(x)} = \Delta x\, \hat{V}_1(x)\, \varphi_k(x)$$
$$+ \Delta x \left[\sum_{l'} \int dx' \frac{1}{|x-x'|} \varphi_{l'}^*(x')\, \varphi_{l'}(x')\right] \varphi_k(x)$$
$$- \Delta x \left[\sum_{l'} \int dx' \frac{1}{|x-x'|} \varphi_k(x')\, \varphi_{l'}^*(x')\right] \varphi_{l'}(x)$$
$$- \Delta x \sum_{l'} \varepsilon_{kl'}\, \varphi_{l'}(x) \qquad \text{--- (33)}$$

Let $\frac{\partial F}{\partial \varphi_k^*(x)}$ be zero, we have

$$\hat{V}_1(x)\, \varphi_k(x) + \left[\sum_{l'=1}^{N} \int dx' \frac{1}{|x-x'|} \varphi_{l'}^*(x')\varphi_{l'}(x')\right] \varphi_k(x)$$
$$- \left[\sum_{l'=1}^{N} \int dx' \frac{1}{|x-x'|} \varphi_k(x')\, \varphi_{l'}^*(x')\right] \varphi_{l'}(x) = \sum_{l'} \varepsilon_{kl'}\, \varphi_{l'}(x)$$

--- (34)

Equation (34) can be written by a matrix form:

$$\begin{pmatrix} & & \\ & F & \\ & & \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_N \end{pmatrix} = \begin{pmatrix} & & \\ & \varepsilon & \\ & & \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_N \end{pmatrix} \qquad \text{--- (35)}$$

Noting that ε is Hermitian, so ε can be diagonalized

$$U^{+} \varepsilon\, U = \varepsilon_d \rightarrow \varepsilon = U \varepsilon_d U^{+} \qquad \text{--- (36)}$$

$$F\varphi = \varepsilon\varphi \rightarrow F\varphi = U\varepsilon_d U^{+}\varphi$$
$$\rightarrow U^{+}F\varphi = \varepsilon_d U^{+}\varphi$$
$$\rightarrow U^{+}FUU^{+}\varphi = \varepsilon_d U^{+}\varphi$$

By renaming $U^{+}\varphi \rightarrow \varphi$, $U^{+}FU \rightarrow F$, We obtain $\boxed{F\varphi = \varepsilon_d\varphi}$ --- (37)

Exchange energy

Let us consider the exchange energy again.

$$E_x = -\iint dx_1 dx_2\, \varphi_l^*(x_1)\varphi_{l'}(x_1)\frac{1}{|x_1 - x_2|}\varphi_l(x_2)\varphi_{l'}^*(x_2)$$

φ is given by a product of a real space function ϕ and a spin space function η (eta) as

$$\varphi_l(x) = \phi_l(r)\,\eta_l(\sigma) \qquad \text{----} \quad (38)$$

Then, the exchange energy is expressed by

$$E_x = -\iiiint dr_1 d\sigma_1\, dr_2 d\sigma_2$$

No! No!

$$\times\ \phi_l^*(r_1)\eta_l^*(\sigma_1)\,\phi_{l'}^*(r_1)\eta_{l'}^*(\sigma_1)\frac{1}{|r_1 - r_2|}\phi_l(r_2)\eta_l(\sigma_2)\,\phi_{l'}^*(r_2)\eta_{l'}^*(\sigma_2)$$

$$= -\int d\sigma_1\, \eta_l^*(\sigma_1)\eta_{l'}(\sigma_1)\int d\sigma_2\, \eta_l^*(\sigma_2)\eta_{l'}(\sigma_2)$$

No!

$$\times \iint dr_1 dr_2\, \phi_l^*(r_1)\phi_{l'}^*(r_1)\frac{1}{|r_1 - r_2|}\phi_l(r_2)\phi_{l'}^*(r_2) \qquad \text{----} \quad (39)$$

---

if $\eta_l \neq \eta_{l'}$

$$E_x = 0 \qquad \text{----} \quad (40)$$

The exchange energy takes a quantum mechanical interaction among the same spin into account.

Second quantization

> There is a way which simplifies the notation and treatment of the many electron system.

In general, the Hamiltonian of many electron system is given by

$$\hat{H} = V_1 + V_2 \,, \qquad V_1 = \sum_{i=1}^{N} \hat{V}_1(x_i) \,, \qquad V_2 = \frac{1}{2}\sum_{i \neq j = 1}^{N} \hat{V}_2(x_i\ x_j) \qquad \cdots (41)$$

The many electron wave function is given by

$$\Psi(x_1 x_2 \cdots x_N) = \sum_{l_1 l_2 \cdots l_N} f(l_1 l_2 \cdots l_N) \left| \varphi_{l_1} \varphi_{l_2} \cdots \varphi_{l_N} \right| \qquad \cdots (42)$$

If we take a single Slater determinant in the summation of Eq. (42) as an approximation, this corresponds to the $\boxed{\text{Hartree-Fock method}}$

One-particle operator, V_1

We analyze how V_1 operates the Slater determinant.

For a two electron system,

$$V_1 \left| \varphi_{l_1} \varphi_{l_2} \right| = \sum_{i=1}^{2} \hat{V}_1(x_i) \Big(\varphi_{l_1}(x_1)\varphi_{l_2}(x_2) - \varphi_{l_1}(x_2)\varphi_{l_2}(x_1) \Big)$$

$$= \hat{V}_1(x_1)\varphi_{l_1}(x_1)\varphi_{l_2}(x_2) - \varphi_{l_1}(x_2)\hat{V}_1(x_1)\varphi_{l_2}(x_1)$$
$$+ \varphi_{l_1}(x_1)\hat{V}_1(x_2)\varphi_{l_2}(x_2) - \hat{V}_1(x_2)\varphi_{l_1}(x_2)\varphi_{l_2}(x_1)$$

$$= \begin{vmatrix} \hat{V}_1(x_1)\varphi_{l_1}(x_1) & \varphi_{l_2}(x_1) \\ \hat{V}_1(x_2)\varphi_{l_1}(x_2) & \varphi_{l_2}(x_2) \end{vmatrix} + \begin{vmatrix} \varphi_{l_1}(x_1) & \hat{V}_1(x_1)\varphi_{l_2}(x_1) \\ \varphi_{l_1}(x_2) & \hat{V}_1(x_2)\varphi_{l_2}(x_2) \end{vmatrix}$$

$$= \left| \hat{V}_1\varphi_{l_1}\ \varphi_{l_2} \right| + \left| \varphi_{l_1}\ \hat{V}_1\varphi_{l_2} \right| \qquad \cdots (43)$$

In general,

$$V_1 |\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_i}\cdots\varphi_{\ell_N}| = |\hat{V}_1\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_i}\cdots\varphi_{\ell_N}|$$
$$+ |\varphi_{\ell_1}\hat{V}_1\varphi_{\ell_2}\cdots\varphi_{\ell_i}\cdots\varphi_{\ell_N}|$$
$$\cdots$$
$$+ |\varphi_{\ell_1}\varphi_{\ell_2}\cdots\hat{V}_1\varphi_{\ell_i}\cdots\varphi_{\ell_N}|$$
$$\cdots$$
$$+ |\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_i}\cdots\hat{V}_1\varphi_{\ell_N}| \quad \cdots (44)$$

It is important to note

$$\hat{V}_1\varphi_{\ell_i} = \sum_m |\varphi_m\rangle\langle\varphi_m|\hat{V}_1|\varphi_{\ell_i}\rangle \quad \cdots (45)$$

where the completeness of one-particle wave function is given by

$$\sum_m |\varphi_m\rangle\langle\varphi_m| = 1 \quad \cdots (46)$$

so, we can write as

$$|\varphi_{\ell_1}\varphi_{\ell_2}\cdots\hat{V}_1\varphi_{\ell_i}\cdots\varphi_{\ell_N}| = \sum_m \langle\varphi_m|\hat{V}_1|\varphi_{\ell_i}\rangle |\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_m\cdots\varphi_{\ell_N}| \quad \cdots (47)$$

The operation in Eq. (47) can be treated by introducing a destruction and creation operators, a and $a^\dagger$ in algebraic form.

<u>Definition</u>

「destruction operator」

$$a_{\ell_i}|\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_i}\cdots\varphi_{\ell_N}|$$
$$= a_{\ell_i}(-1)^{i-1}|\varphi_{\ell_i}\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_{i-1}}\varphi_{\ell_{i-2}}\cdots\varphi_{\ell_N}|$$
$$= (-1)^{i-1}|\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_{i-1}}\varphi_{\ell_{i-2}}\cdots\varphi_{\ell_N}| \quad \cdots (48)$$

「creation operator」

$$a_m^\dagger|\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_{i-1}}\varphi_{\ell_{i+1}}\cdots\varphi_{\ell_N}|$$
$$= |\varphi_m\varphi_{\ell_1}\varphi_2\cdots\varphi_{\ell_{i-1}}\varphi_{\ell_{i+1}}\cdots\varphi_{\ell_N}| \quad \cdots (49)$$
$$= (-1)^{i-1}|\varphi_{\ell_1}\varphi_{\ell_2}\cdots\varphi_{\ell_{i-1}}\varphi_m\varphi_{\ell_{i+1}}\cdots\varphi_{\ell_N}|$$

Therefore

$$a_m^+ a_{\ell_i} \left| \varphi_{\ell_1} \varphi_{\ell_2} \cdots \varphi_{\ell_i} \cdots \varphi_{\ell_N} \right| = \left| \varphi_{\ell_1} \varphi_{\ell_2} \cdots \varphi_m \cdots \varphi_{\ell_N} \right| \quad \cdots (50)$$

By comparing Eqs. (47) and (50),

we can write as

$$\left| \varphi_{\ell_1} \varphi_{\ell_2} \cdots \hat{V}_1 \varphi_{\ell_i} \cdots \varphi_{\ell_N} \right| \longrightarrow \sum_m \langle \varphi_m | \hat{V}_1 | \varphi_{\ell_i} \rangle a_m^+ a_{\ell_i} \left| \varphi_{\ell_1} \varphi_{\ell_2} \cdots \varphi_{\ell_i} \cdots \varphi_{\ell_N} \right| \quad \cdots (51)$$

Returning Eq. (44), it turns out that

the operation of V_1 can be expressed by

the operators as

$$V_1 \left| \varphi_{\ell_1} \varphi_{\ell_2} \cdots \varphi_{\ell_i} \cdots \varphi_{\ell_N} \right| \longrightarrow \sum_\mu \sum_\nu \langle \varphi_\mu | \hat{V}_1 | \varphi_\nu \rangle a_\mu^+ a_\nu \left| \varphi_{\ell_1} \varphi_{\ell_2} \cdots \varphi_{\ell_N} \right| \quad \cdots (52)$$

where the suffixes μ and ν run all the one-particle states no matter whether the states exist or not.

Thus, V_1 is expressed by

$$V_1 = \sum_\mu \sum_\nu \langle \varphi_\mu | \hat{V}_1 | \varphi_\nu \rangle a_\mu^+ a_\nu \quad \cdots (53)$$

Two-particle operator

Next, we analyze how V_2 operates the Slater determinant.

For a two electron system,

$$V_2 |\varphi_{l_1}\varphi_{l_2}| = \frac{1}{2}\sum_{i\neq j=1}^{2} \hat{V}_2(x_i\, x_j)\Big(\varphi_{l_1}(x_1)\varphi_{l_2}(x_2) - \varphi_{l_1}(x_2)\varphi_{l_2}(x_1)\Big)$$

$$= \frac{1}{2}\Big(\hat{V}_2(x_1\, x_2)\varphi_{l_1}(x_1)\varphi_{l_2}(x_2) - \hat{V}_2(x_1\, x_2)\varphi_{l_1}(x_2)\varphi_{l_2}(x_1)\Big)$$

$$+ \frac{1}{2}\Big(\hat{V}_2(x_2\, x_1)\varphi_{l_1}(x_1)\varphi_{l_2}(x_2) - \hat{V}_2(x_2\, x_1)\varphi_{l_1}(x_2)\varphi_{l_2}(x_1)\Big) \quad \text{----- (54)}$$

It is important to note that

$$\hat{V}_2(x_1\, x_2)\varphi_{l_1}(x_1)\varphi_{l_2}(x_2)$$

$$= \overbrace{\Big(\sum_m |\varphi_m(x_1)\rangle\langle\varphi_m(x_1)|\Big)}^{1}\overbrace{\Big(\sum_{m'} |\varphi_{m'}(x_2)\rangle\langle\varphi_{m'}(x_2)|\Big)}^{1}$$

$$\times\ \hat{V}_2(x_1\, x_2)\,|\varphi_{l_1}(x_1)\rangle\,|\varphi_{l_2}(x_2)\rangle$$

$$= \sum_m\sum_{m'} \varphi_m(x_1)\varphi_{m'}(x_2)\underbrace{\iint dx_1 dx_2\, \varphi_m^*(x_1)\varphi_{m'}^*(x_2)\hat{V}_2(x_1\, x_2)\varphi_{l_1}(x_1)\varphi_{l_2}(x_2)}_{A} \quad \text{---- (55)}$$

$$\hat{V}_2(x_1\, x_2)\varphi_{l_1}(x_2)\varphi_{l_2}(x_1) = \sum_{m\, m'}\varphi_m(x_1)\varphi_{m'}(x_2)\underbrace{\iint dx_1 dx_2\, \varphi_m^*(x_1)\varphi_{m'}^*(x_2)\hat{V}_2(x_1\, x_2)\varphi_{l_1}(x_2)\varphi_{l_2}(x_1)}_{B} \quad \text{---- (56)}$$

$$\hat{V}_2(x_2\, x_1)\varphi_{l_1}(x_1)\varphi_{l_2}(x_2) = \sum_{m, m'}\varphi_m(x_2)\varphi_{m'}(x_1)\underbrace{\iint dx_1 dx_2\, \varphi_m^*(x_2)\varphi_{m'}^*(x_1)\hat{V}_2(x_2\, x_1)\varphi_{l_1}(x_1)\varphi_{l_2}(x_2)}_{B} \quad \text{---- (57)}$$

$$\hat{V}_2(x_2\, x_1)\varphi_{l_1}(x_2)\varphi_{l_2}(x_1) = \sum_{m, m'}\varphi_m(x_2)\varphi_{m'}(x_1)\underbrace{\iint dx_1 dx_2\, \varphi_m^*(x_2)\varphi_{m'}^*(x_1)\hat{V}_2(x_2, x_1)\varphi_{l_1}(x_2)\varphi_{l_2}(x_1)}_{A} \quad \text{--- (58)}$$

putting Eqs. (55) − (58) into Eq. (54),

we obtain

$$V_2\,|\varphi_{l_1}\varphi_{l_2}| = \frac{1}{2}\sum_{m,m'}\iint dx_1 dx_2\, \varphi_m^*(x_1)\varphi_{m'}^*(x_2)\,\hat{V}_2(x_1,x_2)\,\varphi_{l_1}(x_1)\varphi_{l_2}(x_2)\,|\varphi_m\varphi_{m'}|$$

$$+\frac{1}{2}\sum_{m,m'}\iint dx_1 dx_2\, \varphi_m^*(x_1)\varphi_{m'}(x_2)\,\hat{V}_2(x_1,x_2)\,\varphi_{l_2}(x_1)\varphi_{l_1}(x_1)\,|\varphi_{m'}\varphi_m| \qquad \text{---- (59)}$$

For the general case, we notice

$$V_2\,|\varphi_{l_1}\varphi_{l_2}\ \cdots\ \varphi_{l_N}| = \frac{1}{2}\sum_{\gamma}\sum_{\delta}\sum_{\mu}\sum_{\nu}\overbrace{\iint dx_1 dx_2\, \varphi_\gamma^*(x_1)\varphi_\delta^*(x_2)\,\hat{V}_2(x_1,x_2)\,\varphi_\mu(x_1)\varphi_\nu(x_2)}^{\langle\varphi_\gamma\varphi_\delta|\hat{V}_2|\varphi_\mu\varphi_\nu\rangle}$$

$$\times\,|\ \cdots\ \varphi_\gamma\ \cdots\ \varphi_\delta\ \cdots\ | \qquad \text{--- (60)}$$

Let us show that the operation of V_2

Can be treated using the operators, a and a^+

$$\boxed{\underbrace{1\ 2\ 3\ 4}_{4}\ 5\ \underbrace{6\ 7\ 8}_{3}\ 9 \qquad (-1)^{4+3+1}}$$

First, noting that

$$\therefore\ a_\delta^+ a_\gamma^+ a_\mu a_\nu\,|\underbrace{\cdots\cdots}_{N'}\ \varphi_\mu\ \underbrace{\cdots\cdots}_{N''}\ \varphi_\nu\ \cdots\cdots|$$

$$= a_\delta^+ a_\gamma^+ a_\mu\,(-1)^{N'+N''+1}\,|\underbrace{\cdots\cdots}_{N'}\ \varphi_\mu\ \underbrace{\cdots\cdots}_{N''}\ *\ \cdots\cdots|$$

$$= a_\delta^+ a_\gamma^+\,(-1)^{N'\cancel{+1}}(-1)^{N'+N''+1}\,|\underbrace{\cdots\cdots}_{N'}\ *\ \underbrace{\cdots\cdots}_{N''}\ *\ \cdots\cdots$$

$$= a_\delta^+\,(-1)^{N''+1}\,|\varphi_\gamma\ \underbrace{\cdots\cdots}_{N'}\ *\ \underbrace{\cdots\cdots}_{N''}\ *\ \cdots\cdots|$$

$$= a_\delta^+\,(-1)^{N''+1}(-1)^{N'}\,|\underbrace{\cdots\cdots}_{N'}\ \varphi_\gamma\ \underbrace{\cdots\cdots}_{N''}\ *\ \cdots\cdots|$$

$$= (-1)^{N'+N''+1}\,|\varphi_\delta\ \underbrace{\cdots\cdots}_{N''}\ \varphi_\gamma\ \underbrace{\cdots\cdots}_{N''}\ *\ \cdots\cdots|$$

$$= (-1)^{N'+N''+1}(-1)^{N'+N''+1}\,|\underbrace{\cdots\cdots}_{N'}\ \varphi_\gamma\ \underbrace{\cdots\cdots}_{N''}\ \varphi_\delta\ \cdots\cdots| \qquad \text{---- (61)}$$

$$= |\underbrace{\cdots\cdots}_{N'}\ \varphi_\gamma\ \underbrace{\cdots\cdots}_{N''}\ \varphi_\delta\ \cdots\cdots|$$

we see

$a_\delta^+ a_\gamma^+ a_\mu a_\nu$ operates as follows

ϕ_ν and ϕ_μ are destructed, and ϕ_δ and ϕ_γ are inserted into the same place where ϕ_ν and ϕ_μ were initially located.

By comparing Eqs. (60) and (61), we can express as

$$V_2 = \frac{1}{2} \sum_\gamma \sum_\delta \sum_\mu \sum_\nu \langle \varphi_\gamma \varphi_\delta | \hat{V}_2 | \varphi_\mu \varphi_\nu \rangle a_\delta^+ a_\gamma^+ a_\mu a_\nu \quad \text{---- (62)}$$

We are now ready to write the Hamiltonian of many electron system using the operators.

Using Eqs. (52) and (62),

$$\boxed{\hat{H} = \sum_\mu \sum_\nu \langle \varphi_\mu | \hat{V}_1 | \varphi_\nu \rangle a_\mu^+ a_\nu + \frac{1}{2} \sum_\gamma \sum_\delta \sum_\mu \sum_\nu \langle \varphi_\gamma \varphi_\delta | \hat{V}_2 | \varphi_\mu \varphi_\nu \rangle a_\delta^+ a_\gamma^+ a_\mu a_\nu} \quad \text{---- (63)}$$

This is so called <u>the second quantized Hamiltonian</u>.

In this case, the Slater determinant can be replaced by an abstract occupation number state vector.

e.g. $$|\phi_1 \phi_3 \phi_5 \phi_9 \cdots | \longrightarrow |1011010 \cdots\rangle \quad \text{--- (64)}$$

In general

$$|\varphi_{l_1} \varphi_{l_2} \cdots \varphi_{l_N}| \longrightarrow |n_1 n_2 \cdots n_\infty\rangle \quad \text{--- (65)}$$

The single particle quantum number $l_1, l_2 \cdots l_N$ are assumed to be ordered $l_1 < l_2 < \cdots < l_N$

It should be noted that using the abstract state vector, a many electron wave function is given by

$$|\psi\rangle = \sum_{n_1 n_2 \cdots n_\infty} f(n_1 n_2 \cdots n_\infty)\, | n_1 n_2 \cdots n_\infty \rangle \quad \cdots (66)$$

we only have to count the occupation number in the abstract states.

The properties of the destruction and creation operators

Based on the definitions Eqs. (48) and (49), we see

$$a_s | \cdots n_s \cdots \rangle = \begin{cases} (-1)^{S_s} (n_s)^{\frac{1}{2}} | \cdots n_s - 1 \cdots \rangle & \text{if } n_s = 1 \\ 0 & \text{otherwise} \end{cases}$$

$$a_s^{+} | \cdots n_s \cdots \rangle = \begin{cases} (-1)^{S_s} (n_s + 1)^{\frac{1}{2}} | \cdots n_s + 1 \cdots \rangle & \text{if } n_s = 0 \\ 0 & \text{otherwise} \end{cases} \quad \cdots (67)$$

The square root is just due to the consistency to the formula for boson

where

$$S_s = n_1 + n_2 + \cdots + n_{s-1} \quad \cdots (68)$$

Let us check $a_s^+ a_s$

$$a_s^+ a_s | \cdots n_s \cdots \rangle$$
$$= a_s^+ (-1)^{S_s} (n_s)^{\frac{1}{2}} | \cdots n_s - 1 \cdots \rangle$$
$$= (-1)^{S_s} (n_s)^{\frac{1}{2}} (-1)^{S_s} (n_s)^{\frac{1}{2}} | \cdots n_s \cdots \rangle$$
$$= n_s | \cdots n_s \cdots \rangle$$

So, we see

$$\boxed{a_s^+ a_s | \cdots n_s \cdots \rangle = n_s | \cdots n_s \cdots \rangle} \quad \cdots (69)$$

Therefore $a_s^+ a_s$ is called "number operator".

proof of $\{a_r, a_s^+\} = a_r a_s^+ + a_s^+ a_r = \delta_{rs}$

For $n_s = 0$

$$a_s^+ | \cdots n_s \cdots \rangle$$

$$= (-1)^{S_s} (n_s+1)^{\frac{1}{2}} | \cdots n_s+1 \cdots \rangle \quad \cdots (70)$$

$$a_r a_s^+ | \cdots n_s \cdots \rangle$$

* $r<s$ & $n_r = 1$

$$= (-1)^{S_s} (n_s+1)^{\frac{1}{2}} (-1)^{S_r} (n_r)^{\frac{1}{2}} | \cdots n_r - 1 \cdots n_s+1 \cdots \rangle \quad \cdots (71)$$

* $r=s$

$$= (-1)^{S_s} (n_s+1)^{\frac{1}{2}} (-1)^{S_s} (n_s+1)^{\frac{1}{2}} | \cdots n_s \cdots \rangle$$
$$= (1-n_s) | \cdots n_s \cdots \rangle \quad \cdots (72)$$

* $r>s$ & $n_r = 1$

$$= (-1)^{S_r} (n_s+1)^{\frac{1}{2}} (-1) (-1)^1 (n_r)^{\frac{1}{2}} | \cdots n_s+1 \cdots n_r - 1 \cdots \rangle \quad \cdots (73)$$

* otherwise

$$a_r a_s^+ | \cdots n_s \cdots \rangle = 0 \quad \cdots (74)$$

For $n_r = 1$

$$a_r | \cdots n_r \cdots \rangle$$

$$= (-1)^{S_r} (n_r)^{\frac{1}{2}} | \cdots n_r - 1 \cdots \rangle \quad \cdots (75)$$

$$a_s^+ a_r | \cdots n_r \cdots \rangle$$

* $r<s$ & $n_s = 0$

$$= (-1)^{S_r} (n_r)^{\frac{1}{2}} (-1)^{S_s} (-1)^{-1} (n_s+1)^{\frac{1}{2}} | \cdots n_r - 1 \cdots n_s+1 \cdots \rangle \quad \cdots (76)$$

* $r=s$

$$= (-1)^{S_r} (n_r)^{\frac{1}{2}} (-1)^{S_r} (n_r)^{\frac{1}{2}} | \cdots n_r \cdots \rangle$$

$$= n_s | \cdots n_s \cdots \rangle \quad \cdots (77)$$

* $r>s$

$$= (-1)^{S_r} (n_r)^{\frac{1}{2}} (-1)^{S_s} (n_s+1)^{\frac{1}{2}} | \cdots n_s+1 \cdots n_r - 1 \cdots \rangle \quad \cdots (78)$$

* otherwise

$$a_s^+ a_r | \cdots n_r \cdots \rangle = 0$$

We see that "$r \neq s$" always gives $a_r a_s^+ + a_s^+ a_r = 0$, and that for "$r=s$" $a_r a_s^+ + a_s^+ a_r = 1$, Thus. it was proved. //