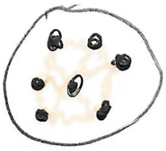
# 第八章：Hartree-Fock 方法





How to solve a many-body system ? [fermions]

Hamiltonian : $H$ (已知)

State : $|\Psi\rangle$ (未知)

Energy : $E_{[\Psi]} = \dfrac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$

* Ritz 变分原理： any state making the functional $E[\Psi]$ stationary, when $|\Psi\rangle$ is allowed to vary over the whole Hilbert space, is an eigenstate of the hamiltonian $H$ belong to the eigenvalue $E$.

$H|\Psi\rangle = E|\Psi\rangle$

证明：$\langle\Psi| \longrightarrow \langle\Psi| + \langle\delta\Psi|$ 无穷小的变化

相应能量变化：$\delta E = \delta\left(\dfrac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}\right) = \dfrac{\langle\delta\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$

Stationary $\Rightarrow$ $\delta E = 0$ $\Rightarrow$ $\begin{cases} \langle\delta\Psi|H|\Psi\rangle = 0 \\ \langle\Psi|\Psi\rangle = 1 \quad \text{归一化条件} \end{cases}$ $\Rightarrow \langle\delta\Psi|H-E|\Psi\rangle = 0 \quad (1)$

($E$：保证归一化)

方程(1)对任意$\langle\delta\Psi|$成立，则有 $(H-E)|\Psi\rangle = 0$

即 $H|\Psi\rangle = E|\Psi\rangle$

* 另一种表述方式： The energy expectation value $E[\Psi]$ in any state $|\Psi\rangle$ is larger than or equal to the ground state energy, the equality arising only if $|\Psi\rangle = |\Psi_{g.s.}\rangle$. 即： $E[\Psi] \geq E[\Psi_0]$ , or $\dfrac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq \dfrac{\langle\Psi_0|H|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}$

## Ritz变分原理:(波函数展开)

假设 $|\Phi_k\rangle$ 是 H 的本征态,则有: $H|\Phi_k\rangle = E_k|\Phi_k\rangle$

所有 $|\Phi_k\rangle$ 构成一个完备基 (Hillbert 空间)

试探波函数 $|\Psi\rangle = \sum_{k=0}^{\infty} C_k|\Phi_k\rangle$ , $\langle\Phi_k|\Phi_{k'}\rangle = \delta_{kk'}$

$$\langle\Psi|\Psi\rangle = \sum_k |C_k|^2 = 1$$

$$\Rightarrow \langle\Psi|H|\Psi\rangle = \sum_{k=0}^{\infty} |C_k|^2 E_k = E_0 + \sum_{k=1}^{\infty} |C_k|^2 (E_k - E_0)$$

$$\left(\left( |C_0|^2 E_0 + \sum_{k=1}^{\infty} |C_k|^2 E_k \right)\right)$$

$$\left(\left( E_0\left(1 - \sum_{k=1}^{\infty}|C_k|^2\right) + \sum_{k=1}^{\infty}|C_k|^2 E_k \right)\right)$$

由于 $E_k \geq E_0$, 则 $\langle\Psi|H|\Psi\rangle \geq E_0$, $\boxed{\text{"="仅当 } C_0=1,\ C_{k>0}=0}$

因此,只要 $|\Psi\rangle$ 混合了 $|\Psi_k\rangle, k>0$ 成份, $\langle\Psi|H|\Psi\rangle > E_0$

$\Rightarrow \delta\langle\Psi|H|\Psi\rangle = 0 \Rightarrow$ true ground state w.f.

加上附加条件 $\langle\Psi|\Psi\rangle = 1 \Rightarrow \delta\left(\langle\Psi|\hat{H}|\Psi\rangle - E\langle\Psi|\Psi\rangle\right) = 0$

$$\Rightarrow H|\Psi\rangle = E|\Psi\rangle$$

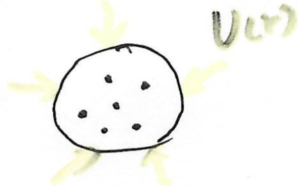

* Caution:

① trial wave function $|\Psi\rangle$ 应该选择为方便计算 $\langle\Psi|H|\Psi\rangle$
试探波函数

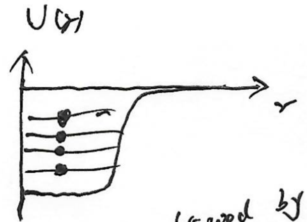
② 真实的基态波函数一般很复杂，不在试探波函数的参数空间，

则 $\delta E[\Psi]=0$ 得到的 $|\Psi\rangle$ 不会是 $H$ 的本征态！

比如：试探波函数选为 HF 态，只有一个 Slater 行列式！




## 二. Hartree-Fock 近似.



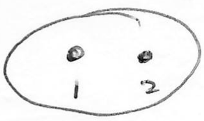

particles trapped by a mean field U(r)!

* 试探波函数选取为一个 Slater 行列式:

$$|\Psi\rangle = a_1^+ a_2^+ \cdots a_A^+ |0\rangle = \prod_{i=1}^{A} a_i^+ |0\rangle$$

$i$ 对应单粒子态，波函数 $\phi_i(r)$

例子:




两粒子波函数: $|\psi(\vec r_1)\rangle|\psi(\vec r_2)\rangle$ (独立粒子)

$|\Psi_{12}(\vec r_1,\vec r_2)\rangle$ ① 不考虑反对称性 忽略相互作用

在 $\vec r_1$ 处找到 1 粒子，$\vec r_2$ 处 … 2 粒子 几率 $|\psi(\vec r_1)|^2|\psi(\vec r_2)|^2$ (无关联)

② 考虑反对称性 但仍忽略相互作用

$$\frac{1}{\sqrt2}\begin{vmatrix}\psi_1(\vec r_1) & \psi_1(\vec r_2)\\ \psi_2(\vec r_1) & \psi_2(\vec r_2)\end{vmatrix}$$

$$|\Psi_{12}(\vec r_1,\vec r_2)\rangle = \frac{1}{\sqrt2}\left[\,|\psi_1(\vec r_1)\rangle|\psi_2(\vec r_2)\rangle - |\psi_2(\vec r_1)\rangle|\psi_1(\vec r_2)\rangle\,\right]$$

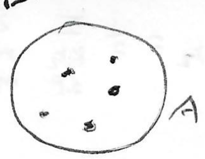
几率

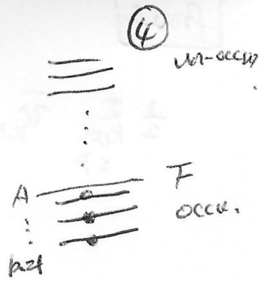
$$|\Psi_{12}(\vec r_1,\vec r_2)|^2 = \frac12\Big[\,|\psi_1(\vec r_1)|^2|\psi_2(\vec r_2)|^2 + |\psi_2(\vec r_1)|^2|\psi_1(\vec r_2)|^2 - \psi_1^*(\vec r_1)\psi_2^*(\vec r_2)\psi_1(\vec r_2)\psi_2(\vec r_1) - \psi_1^*(\vec r_2)\psi_2^*(\vec r_1)\psi_1(\vec r_1)\psi_2(\vec r_2)\Big]$$

$$|\Psi_{12}(\vec r_1,\vec r_2)\rangle = a_1^+ a_2^+ |0\rangle \quad (\text{二次量子化})$$

# 三. Hartree-Fock Theory (Approximation)

独立粒子近似



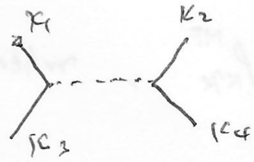

④

* Basic assumption (approximation)

$$|\Psi\rangle \simeq |\Phi_{HF}\rangle = \prod_k a_k^+ |0\rangle, \quad \phi_k(\vec r) \text{ single-particle w.f. (unknown)}$$

* Consider a $H$ with interaction term up to two body.

$$H = \underbrace{\sum_{k_1k_2} t_{k_1k_2} a_{k_1}^+ a_{k_2}}_{\text{单体}} + \underbrace{\frac{1}{4}\sum_{k_1k_2k_3k_4} \bar v_{k_1k_2k_3k_4} a_{k_1}^+ a_{k_2}^+ a_{k_4} a_{k_3}}_{\text{两体}}$$


* Energy

$$E[\Phi_{HF}] = \frac{\langle \Phi | H | \Phi\rangle}{\langle \Phi | \Phi \rangle}$$

HF: determine the $\phi_i(\vec r)$ with the variational principle,

即最小化 $E[\Phi_{HF}]$!

* Basis expansion method

We expand the s.p. w.f. $\phi_i(\vec r)$ in terms of a known basis (H.O.)

$$\phi_k(\vec r) = \sum_m C_{km} \varphi_m(\vec r)$$

$\varphi_m$: H.O. w.f.

$C_{km}$: unknown parameters to be determined!

$$\boxed{\begin{array}{c}\text{正交归一} \\ \langle \varphi_m | \varphi_{m'}\rangle = \delta_{mm'}\end{array}}$$

$$E[\Phi] = \langle HF | \sum_{k_1k_2} t_{k_1k_2} a_{k_1}^+ a_{k_2} | HF\rangle + \frac{1}{4}\sum_{k_1k_2k_3k_4} \langle HF | \bar v_{k_1k_2k_3k_4} a_{k_1}^+ a_{k_2}^+ a_{k_4} a_{k_3} | HF\rangle$$

$$= \sum_{k_1k_2} t_{k_1k_2} \underbrace{\langle HF | a_{k_1}^+ a_{k_2} | HF\rangle}_{\delta_{k_1k_2}} + \frac{1}{4}\sum_{k_1k_2k_3k_4} \bar v_{k_1k_2k_3k_4} \underbrace{\langle HF | a_{k_1}^+ a_{k_2}^+ a_{k_4} a_{k_3} | HF\rangle}_{\langle a_{k_1}^+ a_{k_3}\rangle\langle a_{k_2}^+ a_{k_4}\rangle - \langle a_{k_1}^+ a_{k_4}\rangle\langle a_{k_2}^+ a_{k_3}\rangle}$$

$$= \sum_{k_1 \le F} t_{k_1k_1} + \frac{1}{2}\sum_{k_1k_2 \le F} \bar v_{k_1k_2k_1k_2}$$

代入 $\phi_k = \sum_m C_{km} \varphi_m$ $\quad \left( a_k^\dagger |0\rangle = \sum_m C_{km} d_m^\dagger |0\rangle \right)$

$$E[\Phi_{HF}] = \sum_{k_1 \le F} \sum_{m_1 m_2} C^*_{k_1 m_1} C_{k_1 m_2} t_{m_1 m_2} + \frac{1}{2} \sum_{\substack{k_1 k_2 \\ \le F}} \sum_{\substack{m_1 m_2 \\ m_3 m_4}} C^*_{k_1 m_1} C^*_{k_2 m_2} C_{k_1 m_3} C_{k_2 m_4} \bar{v}_{m_1 m_2 m_3 m_4}$$

单粒子波函数归一化： $* \ \langle k|k'\rangle = \sum_{mm'} \overbrace{C^*_{km} C_{k'm'}}^{\langle m|m'\rangle} = \delta_{kk'}$

$$\overset{k=k'}{\Rightarrow} \sum_{mm'} \overbrace{C^*_{km} C_{km'}}^{\langle m|m'\rangle} = 1 \quad \Big\} \Rightarrow \boxed{\sum_m C^*_{km} C_{km} = 1}$$

$* \ \langle m|m' = \delta_{mm'}$

The unknown parameters $C_{km}$ are determined by variational principle.

$$F[\Phi_{HF}] = E[\Phi_{HF}] - \sum_{k_1 \le F} \varepsilon_{k_1} \sum_{m_1} C^*_{k_1 m_1} C_{k_1 m_1}$$

$$\frac{\delta F[\Phi_{HF}]}{\delta C^*_{k_1 m_1}} = \sum_{m_2} C_{k_1 m_2} t_{m_1 m_2}$$

$$+ \sum_{k_2 \le F} \sum_{m_2 m_3 m_4} C^*_{k_2 m_2} C_{k_1 m_3} C_{k_2 m_4} \bar{v}_{m_1 m_2 m_3 m_4}$$

$$- \varepsilon_{k_1} C_{k_1 m_1} = 0$$

Replacing the indice in the summations: $m_2 \Leftrightarrow m_3$ of the second line,

$$\sum_{m_2} t_{m_1 m_2} C_{k_1 m_2} + \sum_{k_2 \le F} \sum_{m_2 m_3 m_4} C^*_{k_2 m_3} C_{k_2 m_4} \bar{v}_{m_1 m_3 m_2 m_4} C_{k_1 m_2} = \varepsilon_{k_1} C_{k_1 m_1}$$

$$\Rightarrow \sum_{m_2} \underbrace{\left[ t_{m_1 m_2} + \sum_{k_2 \le F} \sum_{m_3 m_4} C^*_{k_2 m_3} C_{k_2 m_4} \bar{v}_{m_1 m_3 m_2 m_4} \right]}_{= h^{HF}_{m_1 m_2}} C_{k_1 m_2} = \varepsilon_{k_1} C_{k_1 m_1}$$

$$\Rightarrow \boxed{\sum_{m_2} h^{HF}_{m_1 m_2} C_{k_1 m_2} = \varepsilon_{k_1} C_{k_1 m_1}} \quad \Longleftrightarrow \quad \boxed{h^{HF} \phi_{k_1} = \varepsilon_{k_1} \phi_{k_1}}$$

HF equation!

Introducing Density Matrix: $\rho^{HF}_{m_1 m_2} = \langle HF | d^\dagger_{m_2} d_{m_1} | HF \rangle$

From the relation: $a_k^\dagger = \sum_m C_{km} d_m^\dagger \Rightarrow a_k = \sum_m C^*_{km} d_m$

$$\Rightarrow \begin{pmatrix} a \\ a^\dagger \end{pmatrix}_k = \begin{pmatrix} C^* & 0 \\ 0 & C \end{pmatrix}_{km} \begin{pmatrix} d \\ d^\dagger \end{pmatrix}_m \Rightarrow \begin{pmatrix} d \\ d^\dagger \end{pmatrix} = \begin{pmatrix} C^T & 0 \\ 0 & C^\dagger \end{pmatrix} \begin{pmatrix} a \\ a^\dagger \end{pmatrix}$$

$$\Rightarrow \begin{cases} d_m = \sum_k C_{km}\, a_m \\ d_m^+ = \sum_k C_{km}^*\, a_m^+ \end{cases} \Rightarrow \rho^{HF}_{m_1 m_2} \equiv \langle HF | d^+_{m_2} d_{m_1} | HF \rangle$$

$$= \sum_{k_1 k_2} C^*_{k_2 m_2} C_{k_1 m_1} \langle HF | a^+_{k_2} a_{k_1} | HF \rangle$$

$$\langle HF | a^+_{k_2} a_{k_1} | HF \rangle = \begin{cases} \delta_{k_1 k_2}, & k_1 k_2 \le F \\ 0, & k_1 k_2 > F \end{cases} \equiv n_{k_1} \delta_{k_1 k_2}$$

where $n_{k_1} = \begin{cases} 1, & k_1 \le F \\ 0, & k_1 > F \end{cases}$

$$\boxed{\rho^{HF}_{m_1 m_2} = \sum_{k \le F} C^*_{k m_2} C_{k m_1}}$$

In terms of $\rho$:
$$h^{HF}_{m_1 m_2} = t_{m_1 m_2} + \sum_{m_3 m_4} \rho_{m_4 m_3} \bar{v}_{m_1 m_3 m_2 m_4}$$

For Conenience, the so-called ph field $\Gamma$ is introduced.

$$\boxed{\Gamma_{m_1 m_2} = \sum_{m_3 m_4} \bar{v}_{m_1 m_3 m_2 m_4} \rho_{m_4 m_3}}$$

Then,
$$\boxed{h^{HF}_{m_1 m_2} = t_{m_1 m_2} + \Gamma_{m_1 m_2}}$$

Solution: Iterative method

① Guess $C_{km}$

② Calculate $\rho$ and $\Gamma[\rho]$, $h[\rho]$ with $C_{km}$

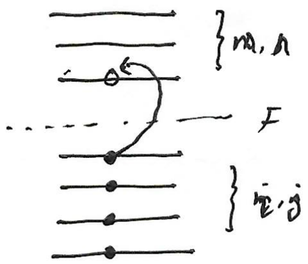
③ Solve the HF equation $\Rightarrow$ $\boxed{\varepsilon_k, C_{km}}$

④ Repeat ② until $\boxed{\varepsilon_k, C_{km}}$ do not change significantly.

* Total energy:
$$E[\Phi^{HF}] = \sum_{k \le F} t_{kk} + \frac{1}{2} \sum_{k_1 k_2 \le F} \bar{v}_{k_1 k_2 k_1 k_2}$$
$$= \sum_{k \le F} (t + \Gamma)_{kk} + \boxed{\frac{1}{2} \sum_{k_1 k_2 \le F} \bar{v}_{k_1 k_2 k_1 k_2} - \sum_{k \le F} \Gamma_{kk}}$$
$$= \sum_{k \le F}^{A} \varepsilon_k - \frac{1}{2} \sum_{k_1 k_2 \le F}^{A} \bar{v}_{k_1 k_2 k_1 k_2} \quad \text{(Homework)}$$

It demonstrates that the total energy is NOT simply given by the first term, i.e. the sum of the individual s.p. energies!

## 四. HF 对激发态的描述.




*. g.s. $|HF\rangle = \prod_{k=1}^{A} a_k^{+} |0\rangle$

* Ex. states:

1 particle-1 hole excitation: (1p-1h) $\quad a_m^{+} a_i |HF\rangle \equiv |mi\rangle \longrightarrow |\Phi_i^m\rangle$

2p-2h : $\quad a_m^{+} a_n^{+} a_i a_j |HF\rangle \equiv |mn;ij\rangle \longrightarrow |\Phi_{ij}^{mn}\rangle$

* Energy of excited configs:

$$E_i^m \equiv \langle \Phi_i^m | H | \Phi_i^m \rangle$$

$$= \langle HF | a_i^{+} a_m H a_m^{+} a_i | HF \rangle, \quad H = \sum_k \varepsilon_k a_k^{+} a_k - \frac{1}{2}\sum_{k_1 k_2} \bar{v}_{k_1 k_2 k_1 k_2} a_{k_1}^{+} a_{k_2}^{+} a_{k_1} a_{k_2}$$

$$\boxed{K : \text{HF basis } \left( \langle HF | a_k^{+} a_{k'} | HF \rangle = \delta_{kk'} \begin{cases} \text{for } k,k' \le F \\ =0, \text{ for } k,k' > F \end{cases} \right) \equiv n_k \delta_{kk'}}$$

$$= E_{HF} + \varepsilon_m - \varepsilon_i - \bar{v}_{mimi}$$

(证明见后面推导)

* 正规乘积 (Normal ordering) 与 Wick 定理

① Choose a reference state, $|\Phi\rangle = |0\rangle$ or $|HF\rangle$

② Introduce brackets "$\{\cdots\}$" indicating "normal ordering", w.r.t. the ref. state $|\Phi\rangle$ $\quad \langle\Phi|\{\cdots\}|\Phi\rangle \equiv 0$

and $\overline{a_i^{+} a_j} \equiv \langle \Phi | a_i^{+} a_j | \Phi \rangle$ indicating "Contraction"

③ $$a_i^{+} a_j \equiv \{a_i^{+} a_j\} + \overline{a_i^{+} a_j}$$

$$a_{i_1}^{+} a_{i_2}^{+} \cdots a_{i_A}^{+} a_{j_A} \cdots a_{j_2} a_{j_1} \equiv \{a_{i_1}^{+} \cdots a_{i_A} a_{j_A} \cdots a_{j_1}\}$$
$$+ \overline{a_{i_1}^{+} a_{j_1}} \{a_{i_2}^{+} \cdots a_{i_A}^{+} a_{j_A} \cdots a_{j_2}\} - \overline{a_{i_1}^{+} a_{j_2}} \{a_{i_2}^{+} \cdots a_{j_1}\}$$
$$+ \cdots$$
$$+ \text{full Contractions.}$$

e.g. $H = \sum_{k_1k_2} t_{k_1k_2} a^\dagger_{k_1} a_{k_2} + \frac{1}{4}\sum_{k_1k_2k_3k_4} \bar{v}_{k_1k_2k_3k_4} a^\dagger_{k_1} a^\dagger_{k_2} a_{k_4} a_{k_3}$ , Ref. state $|HF\rangle$

$$= \sum_{k_1k_2} t_{k_1k_2} \left( \{a^\dagger_{k_1} a_{k_2}\} + \overline{a^\dagger_{k_1} a_{k_2}} \right)$$

$$+ \frac{1}{4}\sum_{k_1k_2k_3k_4} \bar{v}_{k_1k_2k_3k_4} \Big( \{a^\dagger_{k_1} a^\dagger_{k_2} a_{k_4} a_{k_3}\} + \{a^\dagger_{k_1} a^\dagger_{k_2}\} \overline{a_{k_4} a_{k_3}} + \overline{a^\dagger_{k_1} a^\dagger_{k_2}} \{a_{k_4} a_{k_3}\}$$

$$- \overline{a^\dagger_{k_1} a_{k_4}} \{a^\dagger_{k_2} a_{k_3}\} + \overline{a^\dagger_{k_2} a_{k_3}} \{a^\dagger_{k_1} a_{k_4}\} + \{a^\dagger_{k_1} a_{k_3}\} \overline{a^\dagger_{k_2} a_{k_4}} - \{a^\dagger_{k_2} a_{k_4}\} \overline{a^\dagger_{k_1} a_{k_3}}$$

$$+ \overline{a^\dagger_{k_1} a_{k_3}}\, \overline{a^\dagger_{k_2} a_{k_4}} - \overline{a^\dagger_{k_1} a_{k_4}}\, \overline{a^\dagger_{k_2} a_{k_3}} \Big)$$

代入
$$\begin{cases} \rho^{HF}_{k_2k_1} \equiv \overline{a^\dagger_{k_1} a_{k_2}} = \langle HF | a^\dagger_{k_1} a_{k_2} | HF \rangle = \begin{cases} \delta_{k_1k_2}, & k_1k_2 \le F \\ 0, & k_1k_2 > F \end{cases} \\ \overline{a^\dagger_{k_1} a^\dagger_{k_2}} = \overline{a_{k_4} a_{k_3}} = 0 \end{cases}$$

$$\Rightarrow H = \sum_{k_1k_2} t_{k_1k_2} \{a^\dagger_{k_1} a_{k_2}\} \underbrace{\phantom{x}}_{+\sum_{k_1k_2} t_{k_1k_2}\rho_{k_2k_1}} + \frac{1}{4}\sum_{k_1k_2k_3k_4} \bar{v}_{k_1k_2k_3k_4} \{a^\dagger_{k_1} a^\dagger_{k_2} a_{k_4} a_{k_3}\}$$

$$+ \frac{1}{4}\sum_{k_1k_2k_3k_4} \bar{v}_{k_1k_2k_3k_4} \begin{pmatrix} -\rho_{k_4k_1}\{a^\dagger_{k_2} a_{k_3}\} + \rho_{k_3k_2}\{a^\dagger_{k_1} a_{k_4}\} \\ +\rho_{k_4k_2}\{a^\dagger_{k_1} a_{k_3}\} - \rho_{k_3k_1}\{a^\dagger_{k_2} a_{k_4}\} \\ +\rho_{k_4k_2}\rho_{k_3k_1} - \rho_{k_4k_1}\rho_{k_3k_2} \end{pmatrix}$$

$$\equiv E_0 + \sum_{k_1k_2} f_{k_1k_2} \{a^\dagger_{k_1} a_{k_2}\} + \frac{1}{4}\sum_{k_1k_2k_3k_4} \Gamma_{k_1k_2k_3k_4} \{a^\dagger_{k_1} a^\dagger_{k_2} a_{k_4} a_{k_3}\}$$

where
$$\begin{cases} E_0 = \sum_k t_{kk} + \frac{1}{2}\sum_{k_1k_2} \bar{v}_{k_1k_2k_1k_2} = \langle HF | H | HF \rangle \\ f_{k_1k_2} = t_{k_1k_2} + \sum_{k_3k_4 \le F} \bar{v}_{k_1k_3k_2k_4}\rho_{k_4k_3} = \sum_{k \le F} \bar{v}_{k_1kk_2k} + t_{k_1k_2} = h_{k_1k_2} \\ \Gamma_{k_1k_2k_3k_4} = \bar{v}_{k_1k_2k_3k_4} \end{cases}$$

Wick 定理 :
$$\{a^\dagger_{i_1} \cdots a^\dagger_{i_N} a_{j_N} \cdots a_{j_1}\}\{a^\dagger_{k_1} \cdots a^\dagger_{k_M} a_{l_M} \cdots a_{l_1}\}$$
$$= (-1)^{M\cdot N}\{a^\dagger_{i_1} \cdots a^\dagger_{i_N} a^\dagger_{k_1} \cdots a^\dagger_{k_M} a_{j_N} \cdots a_{j_1} a_{l_M} \cdots a_{l_1}\}$$
$$+ (-1)^{M\cdot N}\overline{a^\dagger_{i_1} a_{l_1}}\{a^\dagger_{i_2} \cdots a^\dagger_{i_N} a^\dagger_{k_1} \cdots a^\dagger_{k_M} a_{j_N} \cdots a_{j_1} a_{l_M} \cdots a_{l_2}\}$$
$$+ \cdots$$
$$+ (\text{siglets}) + (\text{doublets}) + \cdots$$

* e.g.

$$\{a_i^+ a_j\}\{a_k^+ a_l\} = -\{a_i^+ a_k^+ a_j a_l\} + \{a_i^+ a_l\}\,\overbracket{a_j\, a_k^+} + \overbracket{a_i^+ a_l}\,\{a_j\, a_k^+\} + \overbracket{a_i^+ a_l}\;\overbracket{a_j\, a_k^+}$$

$$= \{a_i^+ a_k^+ a_l a_j\} - \underset{\sim\sim}{\overbracket{a_i^+ a_l}}\,\{a_k^+ a_j\} + \overbracket{a_j\, a_k^+}\,\{a_i^+ a_l\} + \overbracket{a_i^+ a_l}\;\overbracket{a_j a_k^+}$$

$$= \{a_i^+ a_k^+ a_l a_j\} - \delta_{il}\, n_i \{a_k^+ a_j\} + \bar{n}_j\, \delta_{jk} \{a_i^+ a_l\} + n_i \bar{n}_j\, \delta_{il}\, \delta_{jk}$$

where $\bar{n}_j \equiv \overbracket{a_j\, a_j^+} \equiv \langle HF | a_j\, a_j^+ | HF \rangle$
$= 1 - \langle HF | a_j^+ a_j | HF \rangle \equiv 1 - n_j$

For convenience, we introduce a notation:

$$A^i_j \equiv a_i^+ a_j \quad \text{and} \quad \{A^i_j\} \equiv \{a_i^+ a_j\}, \quad \{A^{ik}_{jl}\} \equiv \{a_i^+ a_k^+ a_l a_j\}$$

Then.

$$\{A^i_j\}\{A^k_l\} = \{A^{ik}_{jl}\} - n_i\, \delta_{il} \{A^k_j\} + \bar{n}_j\, \delta_{jk} \{A^i_l\} + n_i \bar{n}_j\, \delta_{il}\, \delta_{jk}$$

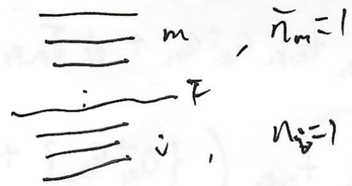
Similary, one finds,

$$\{A^a_b\}\{A^{kl}_{mn}\} = \{A^{akl}_{bmn}\} + (1-\hat{P}_{mn})\, n_a\, \delta_{an} \{A^{kl}_{bm}\} + (1-\hat{P}_{kl})\, \bar{n}_b\, \delta_{bk} \{A^{al}_{mn}\} + (1-\hat{P}_{kl})(1-\hat{P}_{mn})\, n_a\, \delta_{an}\, \bar{n}_b\, \delta_{bk} \{A^l_m\}$$

where $\hat{P}_{mn}$ represents exchange $m \leftrightarrow n$!

证明

$$E_{mi} \equiv \langle HF|\, a_i^\dagger a_m \hat{H}\, a_m^\dagger a_i \,|HF\rangle = E_0 + \varepsilon_m - \varepsilon_i - \Gamma_{mimi}$$




$i \le F,\ m > F$

① ~~zero~~-body part $\quad \hat{H}^{(0)} = E_0$

$$E^{(0)}_{mi} = \langle HF|\, a_i^\dagger a_m E_0\, a_m^\dagger a_i \,|HF\rangle ,$$

$$= E_0 \langle HF|\, a_i^\dagger a_m a_m^\dagger a_i \,|HF\rangle = E_0$$

② one-body part $\quad \hat{H}^{(1)} = \sum_{k_1k_2} f_{k_1k_2}\{A^{k_1}_{k_2}\}$

$$a_i^\dagger a_m = \{a_i^\dagger a_m\} + \langle HF|a_i^\dagger a_m|HF\rangle = \{A^i_m\}$$

$$a_m^\dagger a_i = \{a_m^\dagger a_i\} + \langle HF|a_m^\dagger a_i|HF\rangle = \{A^m_i\}$$

$\Rightarrow$ $E^{(1)}_{mi} = \sum_{k_1k_2}\langle HF|\, \underbrace{\{A^i_m\}\{A^{k_1}_{k_2}\}}\{A^m_i\}\,|HF\rangle f_{k_1k_2}$ ，只有全部收缩项非零

$$= \sum_{k_1k_2}^{f_{k_1k_2}} \langle HF| \Big(\{A^{ik_1}_{mk_2}\} - n_i\delta_{ik_2}\{A^{k_1}_m\} + \bar n_m \delta_{mk_1}\{A^i_{k_2}\} + \underbrace{n_i\bar n_m\delta_{ik_2}\delta_{mk_1}\Big)\{A^m_i\}|HF\rangle}_{0}$$

$$= \sum_{k_1k_2}\Big[\bar n_m\delta_{mk_1}\langle HF|\,\{A^i_{k_2}\}\{A^m_i\}\,|HF\rangle - n_i\delta_{ik_2}\langle HF|\,\{A^{k_1}_m\}\{A^m_i\}\,|HF\rangle\Big] f_{k_1k_2}$$

$$= \sum_{k_1k_2}\Big[\bar n_m\delta_{mk_1} n_i\bar n_{k_2}\delta_{ii}\delta_{mk_2} - n_i\delta_{ik_2} n_i\delta_{k_1 i}\bar n_m\delta_{mm}\Big]$$

$$= \underbrace{\bar n_m n_i \bar n_m}_{1} f_{mm} - \underbrace{n_i n_i \bar n_m}_{1} f_{ii} = f_{mm} - f_{ii} = \varepsilon_m - \varepsilon_i$$

③ two-body part $\quad \hat{H}^{(2)} = \frac{1}{4}\sum_{k_1k_2k_3k_4}\Gamma_{k_1k_2k_3k_4}\{A^{k_1k_2}_{k_3k_4}\}$

$$E^{(2)}_{mi} = \frac{1}{4}\sum_{k_1k_2k_3k_4}\Gamma_{k_1k_2k_3k_4}\langle HF|\,\underbrace{\{A^i_m\}\{A^{k_1k_2}_{k_3k_4}\}}_{\text{only NO1B contributes}}\{A^m_i\}\,|HF\rangle$$

$$= \frac{1}{4}\sum_{k_1k_2k_3k_4}\Gamma_{k_1k_2k_3k_4}(-1)(1-\hat P_{k_1k_2})(1-\hat P_{k_3k_4})\, n_i\bar n_m\delta_{ik_4}\delta_{mk_1}\{A^{k_2}_{k_3}\}\{A^m_i\}|HF\rangle$$

$$= -\sum_{k_1k_2k_3k_4}\Gamma_{k_1k_2k_3k_4} n_i\bar n_m\delta_{ik_4}\delta_{mk_1} n_i\bar n_m\delta_{k_2 i}\delta_{mk_3} = -\Gamma_{mimi} n_i^2\bar n_m^2 = -\Gamma_{mimi}$$