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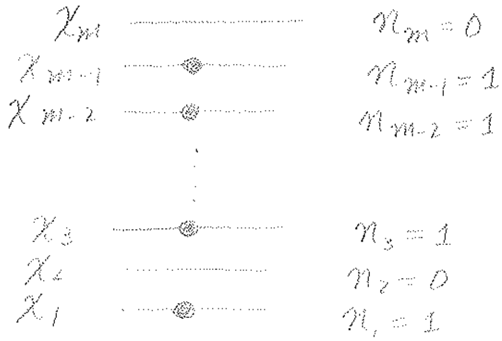
iii) Second quantization (Quantum Field Theory!)

A Slater determinant can be specified by its spinorbital occupancy



$$\longrightarrow \begin{array}{l} \quad m{:}\ 1 \quad 2 \quad 3 \quad \cdots \quad m-2 \quad m-1 \quad m \\ |n_1\, n_2\, n_3 \cdots n_{m-2}\, n_{m-1}\, n_m\rangle \\ |1\ 0\ 1 \cdots 1\ 1\ 0\rangle \end{array}$$

we no longer have/need info about which electron occupies which orbital

But how do we make sure $|n_1 \cdots n_m\rangle$ is antisym wrt electron interchange?

Creation operator

$$\hat{a}_p^\dagger |n_1 \cdots \overset{\text{no electron}}{0_p} \cdots n_m\rangle = (-1)^{\eta_p} |n_1 \cdots \overset{\text{now there's an electron}}{1_p} \cdots n_m\rangle \qquad \eta_p = \sum_{q=1}^{p-1} n_q$$

$$\hat{a}_p^\dagger |n_1 \cdots 1_p \cdots n_m\rangle = 0 \quad \text{(double creation not allowed)}$$

Annihilation operator

$$\hat{a}_p |n_1 \cdots 1_p \cdots n_m\rangle = (-1)^{\eta_p} |n_1 \cdots 0_p \cdots n_m\rangle$$

$$\hat{a}_p |n_1 \cdots 0_p \cdots n_m\rangle = 0 \quad \text{(double annihilation not allowed)}$$

Adjoint

when acting to the left the meaning of operator reversed

$$\langle n_1 \cdots 0_p \cdots n_m| \hat{a}_p = (-1)^{\eta_p} \langle n_1 \cdots 1_p \cdots n_m|$$

$$\langle n_1 \cdots 1_p \cdots n_m| \hat{a}_p = 0$$

$$\langle n_1 \cdots 1_p \cdots n_m| \hat{a}_p^\dagger = (-1)^{\eta_p} \langle n_1 \cdots 0_p \cdots n_m|$$

$$\langle n_1 \cdots 0_p \cdots n_m| \hat{a}_p^\dagger = 0$$

Vacuum $|0_1, 0_2, \cdots, 0_m\rangle$ $\qquad \langle 0_1, 0_2 \cdots 0_m | 0_1 0_2 \cdots 0_m\rangle = 1$ (normalized)

Anti symmetry ...

B electron A $\quad n_2 = 1$

$$\hat{a}_2^\dagger \hat{a}_1^\dagger |0_1, 0_2\rangle = \hat{a}_2^\dagger |1_1, 0_2\rangle = (-1)^1 |1_1, 1_2\rangle$$

first

$n_2 = 0$

$$\hat{a}_1^\dagger \hat{a}_2^\dagger |0_1, 0_2\rangle = \hat{a}_1^\dagger |0_1, 1_2\rangle = |1_1, 1_2\rangle$$

first

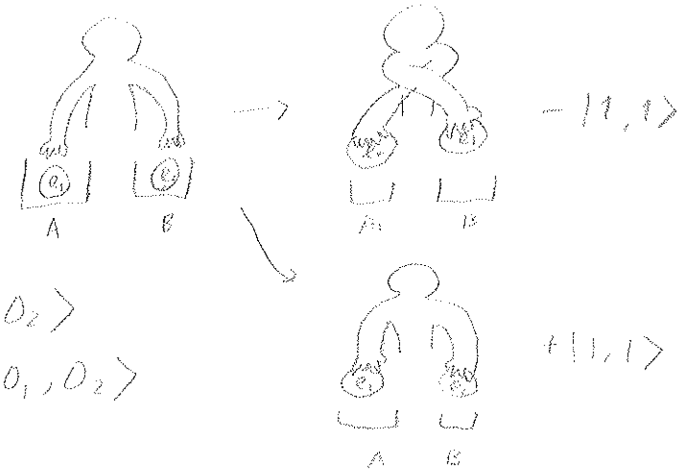
sign change

... is built into the rules of action of c/a operators.

Adding them together,

$$(\hat{a}_1^\dagger \hat{a}_2^\dagger + \hat{a}_2^\dagger \hat{a}_1^\dagger)|0_1, 0_2\rangle = 0$$

Think how we interchange electrons!



Similarly

$$\hat{a}_2 \hat{a}_1 |1_1, 1_2\rangle = \hat{a}_2 |0_1, 1_2\rangle = |0_1, 0_2\rangle$$
$$\hat{a}_1 \hat{a}_2 |1_1, 1_2\rangle = -\hat{a}_1 |1_1, 0_2\rangle = -|0_1, 0_2\rangle$$

$$(\hat{a}_1 \hat{a}_2 + \hat{a}_2 \hat{a}_1)|1_1, 1_2\rangle = 0$$

It is possible to prove that these relationship hold for any determinants, therefore

$$\hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = 0$$
$$\hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0$$

physically they signify antisymmetry (order of creations or of annihilations causes sign change, thus "+")

These are true for $p = q$ also because

$$\hat{a}_p^\dagger \hat{a}_p^\dagger = 0 \quad \text{(double creation)}$$
$$\hat{a}_p \hat{a}_p = 0 \quad \text{(double annihilation)}$$

Furthermore, if $p \neq q$,

$$\hat{a}_p^\dagger \hat{a}_q |\underbrace{\cdots}_{\eta_1} 1_q \underbrace{\cdots}_{\eta_2} 0_p \cdots\rangle = (-1)^{\eta_1} \hat{a}_p^\dagger |\underbrace{\cdots}_{\eta_1} 0_q \underbrace{\cdots}_{\eta_2} 0_p \cdots\rangle$$

$$= (-1)^{\eta_1}(-1)^{\eta_1}(-1)^{\eta_2} |\cdots 0_q \cdots 1_p \cdots\rangle$$

$$= (-1)^{\eta_2} |\cdots 0_q \cdots 1_p \cdots\rangle$$

$$\hat{a}_q \hat{a}_p^\dagger |\underbrace{\cdots}_{\eta_1} 1_q \underbrace{\cdots}_{\eta_2} 0_p \cdots\rangle = (-1)^{\eta_1+1+\eta_2} \hat{a}_q |\underbrace{\cdots}_{\eta_1} 1_q \underbrace{\cdots}_{\eta_2} 1_p \cdots\rangle$$

$$= (-1)^{\eta_1+1+\eta_2}(-1)^{\eta_1} |\cdots 0_q \cdots 1_p \cdots\rangle$$

$$= -(-1)^{\eta_2} |\cdots 0_q \cdots 1_p \cdots\rangle$$

$$\hat{a}_p^\dagger \hat{a}_q + \hat{a}_q \hat{a}_p^\dagger = 0 \quad (p \neq q) \qquad \text{(physically antisym)}$$

if $p = q$,

$$\left.\begin{aligned} \hat{a}_p^\dagger \hat{a}_p |\underbrace{\cdots}_{\eta} 1_p \cdots\rangle &= (-1)^{\eta} \hat{a}_p^\dagger |\underbrace{\cdots}_{\eta} 0_p \cdots\rangle \\ &= (-1)^{\eta}(-1)^{\eta} |\cdots 1_p \cdots\rangle \\ &= |\cdots 1_p \cdots\rangle \\ \hat{a}_p \hat{a}_p^\dagger |\underbrace{\cdots}_{\eta} 1_p \cdots\rangle &= 0 \end{aligned}\right\} \begin{array}{l} \hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_p^\dagger = 1 \\ \text{if } 1_p \end{array}$$

$$\left.\begin{aligned} \hat{a}_p^\dagger \hat{a}_p |\underbrace{\cdots}_{\eta} 0_p \cdots\rangle &= 0 \\ \hat{a}_p \hat{a}_p^\dagger |\underbrace{\cdots}_{\eta} 0_p \cdots\rangle &= (-1)^{\eta} \hat{a}_p |\underbrace{\cdots}_{\eta} 1_p \cdots\rangle \\ &= (-1)^{\eta}(-1)^{\eta} |\cdots 0_p \cdots\rangle \\ &= |\cdots 0_p \cdots\rangle \end{aligned}\right\} \begin{array}{l} \hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_p^\dagger = 1 \\ \text{if } 0_p \end{array}$$

$$\hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_p^\dagger = 1 \qquad \text{(physically, an orbital has an electron or none)}$$

Anti commutation relations

$$\hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = 0 \quad , \quad \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0, \quad \hat{a}_p^\dagger \hat{a}_q + \hat{a}_q \hat{a}_p^\dagger = \delta_{pq}$$

(I) (II) (III)

Hamiltonian

order!

$$\hat{H} = \sum_{p,q} \langle p|\hat{h}|q\rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{p,q,r,s} \langle pq|rs\rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

$1^* 2^* \; 1\, 2 \qquad 1^* \; 2^* \; 2 \; 1$

$$= \sum_{p,q} \langle p|\hat{h}|q\rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{p,q,r,s} \langle pq||rs\rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

coefficients

We shall verify that this is consistent w/ Slater-Condon.

Example 1.

$$\langle \Phi_0| \sum_{p,q} \langle p|\hat{h}|q\rangle \hat{a}_p^\dagger \hat{a}_q |\Phi_0\rangle = \sum_{p,q} \langle p|\hat{h}|q\rangle\langle \Phi_0|\hat{a}_p^\dagger \hat{a}_q|\Phi_0\rangle$$

Since $\hat{a}_a|\Phi_0\rangle = 0$, $\langle \Phi_0|\hat{a}_a^\dagger = 0$
(virtual electron annihilation)

$$= \sum_{i,j} \langle i|\hat{h}|j\rangle\langle \Phi_0|\hat{a}_i^\dagger \hat{a}_j|\Phi_0\rangle$$

$$= \sum_{i,j} \langle i|\hat{h}|j\rangle\langle \Phi_0|\delta_{ij} - \hat{a}_j \hat{a}_i^\dagger|\Phi_0\rangle$$

double creation

$$= \sum_{i,j} \langle i|\hat{h}|j\rangle \delta_{ij} \langle \Phi_0|\Phi_0\rangle$$

$$= \sum_i \langle i|\hat{h}|i\rangle$$

$$\hat{a}_i^\dagger|\Phi_0\rangle = \langle \Phi_0|\hat{a}_i = \hat{a}_a|\Phi_0\rangle = \langle \Phi_0|\hat{a}_a^\dagger = 0$$

Example 2.

$$\langle \Phi_0 | \frac{1}{4} \sum_{p,q,r,s} \langle pq||rs\rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | \Phi_0 \rangle = \frac{1}{4} \sum_{p,q,r,s} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | \Phi_0 \rangle$$

$$\underbrace{\hat{a}_s \hat{a}_a | \Phi_0 \rangle}_{\text{double annihilation}} = 0 \qquad \hat{a}_a \hat{a}_r | \Phi_0 \rangle = -\underbrace{\hat{a}_r \hat{a}_a | \Phi_0 \rangle}_{\text{double ann.}} = 0 \longrightarrow \hat{a}_s \hat{a}_r | \Phi_0 \rangle = \hat{a}_l \hat{a}_k | \Phi_0 \rangle$$

$$\underbrace{\langle \Phi_0 | \hat{a}_a^\dagger}_{\text{double ann.}} \hat{a}_q^\dagger = 0 \qquad \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_a^\dagger = -\langle \Phi_0 | \hat{a}_a^\dagger \hat{a}_p^\dagger = 0 \longrightarrow \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q^\dagger = \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_j^\dagger$$

$$= \frac{1}{4} \sum_{i,j,k,l} \langle ij||kl\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{i,j,k,l} \langle ij||kl\rangle \langle \Phi_0 | \hat{a}_i^\dagger (\delta_{jl} - \hat{a}_l \hat{a}_j^\dagger) \hat{a}_k | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{i,j,k} \langle ij||kj\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_k | \Phi_0 \rangle - \frac{1}{4} \sum_{i,j,k,l} \langle ij||kl\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_l \hat{a}_j^\dagger \hat{a}_k | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{i,j,k} \langle ij||kj\rangle \langle \Phi_0 | \delta_{ik} - \underbrace{\hat{a}_k \hat{a}_i^\dagger | \Phi_0 \rangle}_{0} - \frac{1}{4} \sum_{i,j,k,l} \langle ij||kl\rangle \langle \Phi_0 | (\delta_{il} - \hat{a}_l \hat{a}_i^\dagger)(\delta_{jk} - \hat{a}_k \hat{a}_j^\dagger) | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{i,j} \langle ij||ij\rangle - \frac{1}{4} \sum_{i,j,k,l} \langle ij||kl\rangle \langle \Phi_0 | \delta_{il} \delta_{jk} | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{i,j} \langle ij||ij\rangle - \frac{1}{4} \sum_{i,j} \langle ij||ji\rangle = \frac{1}{2} \sum_{i,j} \langle ij||ij\rangle$$

Example 3.

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = ?$$

$$= \sum_{p,q} \langle p|\hat{h}|q\rangle \langle \Phi_0 | \overbrace{\hat{a}_i^\dagger \hat{a}_a}^{\langle \Phi_i^a|} \hat{a}_p^\dagger \hat{a}_q \overbrace{\hat{a}_b^\dagger \hat{a}_j | \Phi_0\rangle}^{|\Phi_j^b\rangle} \quad \cdots (A)$$

$$+ \frac{1}{4} \sum_{p,q,r,s} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_a \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \hat{a}_b^\dagger \hat{a}_j | \Phi_0 \rangle \quad \cdots (B)$$

strategy

- swap operators with anticomm.
- (I), (II) → change sign, (III) → spawn a new term w/ δ and change sign
- move $\hat{a}_i^\dagger, \hat{a}_a$ to right to use $\hat{a}_i^\dagger|\Phi_0\rangle = 0$, $\hat{a}_a|\Phi_0\rangle = 0$
- move $\hat{a}_i, \hat{a}_a^\dagger$ to left to use $\langle\Phi_0|\hat{a}_i = 0$, $\langle\Phi_0|\hat{a}_a^\dagger = 0$

$$(A) = \sum_{p,q} \langle p|\hat{h}|q\rangle \langle \Phi_0 | \hat{a}_i^\dagger (\delta_{ap} - \hat{a}_p^\dagger \underset{\text{going right}}{\hat{a}_a})(\delta_{bq} - \underset{\text{going left}}{\hat{a}_b^\dagger} \hat{a}_q) \hat{a}_j | \Phi_0 \rangle$$

$$= \langle a|\hat{h}|b\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_j | \Phi_0 \rangle \qquad \delta_{ij} - \hat{a}_j \hat{a}_i^\dagger$$

$$- \sum_p \langle p|\hat{h}|b\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_p^\dagger \hat{a}_a \hat{a}_j | \Phi_0 \rangle \qquad -\hat{a}_j \hat{a}_a$$

$$- \sum_q \langle a|\hat{h}|q\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_b^\dagger \hat{a}_q \hat{a}_j | \Phi_0 \rangle \qquad -\hat{a}_b^\dagger \hat{a}_i^\dagger$$

$$+ \sum_{p,q} \langle p|\hat{h}|q\rangle \langle \Phi_0 | \underbrace{\hat{a}_i^\dagger \hat{a}_p^\dagger}_{-\hat{a}_p^\dagger \hat{a}_i^\dagger} \underbrace{\hat{a}_a \hat{a}_b^\dagger}_{\delta_{ab} - \hat{a}_b^\dagger \hat{a}_a} \underbrace{\hat{a}_q \hat{a}_j}_{-\hat{a}_j \hat{a}_q} | \Phi_0 \rangle$$

$$= \langle a|h|b\rangle \delta_{ij} + \sum_{p,q} \langle p|\hat{h}|q\rangle \langle \Phi_0 | \hat{a}_p^\dagger \underbrace{\hat{a}_i^\dagger \hat{a}_j}_{\delta_{ij} - \hat{a}_j \hat{a}_i^\dagger} \hat{a}_q | \Phi_0 \rangle \delta_{ab} - \sum_{p,q} \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_i^\dagger \hat{a}_b^\dagger \underbrace{\hat{a}_a \hat{a}_j}_{-\hat{a}_j \hat{a}_a} \hat{a}_q | \Phi_0 \rangle$$

$$= \langle a|h|b\rangle \delta_{ij} + \underbrace{\sum_{p,q} \langle p|\hat{h}|q\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q | \Phi_0 \rangle \delta_{ab}}_{\sum_k \langle k|\hat{h}|k\rangle} \delta_{ij} - \sum_{p,q} \langle p|\hat{h}|q\rangle \langle \Phi_0 | \underbrace{\hat{a}_p^\dagger \hat{a}_j}_{\delta_{jp} - \hat{a}_j \hat{a}_p^\dagger} \underbrace{\hat{a}_i^\dagger \hat{a}_q}_{\delta_{iq} - \hat{a}_q \hat{a}_i^\dagger} | \Phi_0 \rangle \delta_{ab} \quad \hat{a}_q \hat{a}_a = 0$$

$= 0$ $\qquad$ $= 0$

$$= \langle a|\hat{h}|b\rangle \delta_{ij} + \sum_k \langle k|\hat{h}|k\rangle \delta_{ab}\delta_{ij} - \langle j|\hat{h}|i\rangle \delta_{ab}$$

(B) $= \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_a \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \hat{a}_b^\dagger \hat{a}_j | \Phi_0\rangle$

$$(\delta_{ap} - \hat{a}_p^\dagger \hat{a}_a) \quad (\delta_{br} - \hat{a}_b^\dagger \hat{a}_r)$$

0 contrib.

$$= \frac{1}{4}\sum_{qs} \langle aq||bs\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_j | \Phi_0\rangle - \frac{1}{4}\sum_{pqs} \langle pq||bs\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_p^\dagger \hat{a}_a \hat{a}_q^\dagger \hat{a}_s \hat{a}_j | \Phi_0\rangle$$

$$(-\hat{a}_q^\dagger \hat{a}_i^\dagger)(\hat{a}_j \hat{a}_s) \qquad (-\hat{a}_p^\dagger \hat{a}_i^\dagger)(\delta_{aq} - \hat{a}_q^\dagger \hat{a}_a)(-\hat{a}_j \hat{a}_s)$$

$$- \frac{1}{4}\sum_{qrs} \langle aq||rs\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_b^\dagger \hat{a}_r \hat{a}_j | \Phi_0\rangle + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_p^\dagger \hat{a}_a \hat{a}_q^\dagger \hat{a}_s \hat{a}_b^\dagger \hat{a}_r \hat{a}_j | \Phi_0\rangle$$

$$(-\hat{a}_q^\dagger \hat{a}_i^\dagger)(\delta_{sb} - \hat{a}_b^\dagger \hat{a}_s)(-\hat{a}_j \hat{a}_r) \qquad (-\hat{a}_p^\dagger \hat{a}_i^\dagger)(\delta_{aq} - \hat{a}_q^\dagger \hat{a}_a)(\delta_{sb} - \hat{a}_b^\dagger \hat{a}_s)(-\hat{a}_j \hat{a}_r)$$

0 cont.

$$= \frac{1}{4}\sum_{k} \langle ak||bk\rangle \delta_{ij} - \frac{1}{4}\langle aj||bi\rangle - \frac{1}{4}\sum_{ps} \langle pa||bs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_i^\dagger \hat{a}_j \hat{a}_s | \Phi_0\rangle$$

$$(\delta_{ij} - \hat{a}_j \hat{a}_i^\dagger)$$

$$- \frac{1}{4}\sum_{qr} \langle aq||rb\rangle \langle \Phi_0 | \hat{a}_q^\dagger \hat{a}_i^\dagger \hat{a}_j \hat{a}_r | \Phi_0\rangle + \frac{1}{4}\sum_{pr} \langle pa||rb\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_i^\dagger \hat{a}_j \hat{a}_r | \Phi_0\rangle$$

$$(\delta_{ij} - \hat{a}_j \hat{a}_i^\dagger) \qquad (\delta_{ij} - \hat{a}_j \hat{a}_i^\dagger)$$

$$- \frac{1}{4}\sum_{prs} \langle pa||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_i^\dagger \hat{a}_b^\dagger \hat{a}_s \hat{a}_j \hat{a}_r | \Phi_0\rangle - \frac{1}{4}\sum_{pqr} \langle pq||rb\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_i^\dagger \hat{a}_q^\dagger \hat{a}_a \hat{a}_j \hat{a}_r | \Phi_0\rangle$$

0 cont. 0 cont.

$$+ \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_i^\dagger \hat{a}_q^\dagger \hat{a}_a \hat{a}_b^\dagger \hat{a}_s \hat{a}_j \hat{a}_r | \Phi_0\rangle$$

$$= \frac{1}{4}\sum_{k} \langle ak||bk\rangle \delta_{ij} - \frac{1}{4}\langle aj||bi\rangle - \frac{1}{4}\sum_{k} \langle ka||bk\rangle \delta_{ij} + \frac{1}{4}\sum_{ps} \langle pa||bs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_j \hat{a}_i^\dagger \hat{a}_s | \Phi_0\rangle_{\to 0}$$

$$0 \quad (\delta_{pj} - \hat{a}_j \hat{a}_p^\dagger)(\delta_{is} - \hat{a}_s \hat{a}_i^\dagger)$$

$$- \frac{1}{4}\sum_{k} \langle ak||kb\rangle \delta_{ij} + \frac{1}{4}\sum_{qr} \langle aq||rb\rangle \langle \Phi_0 | \hat{a}_q^\dagger \hat{a}_j \hat{a}_i^\dagger \hat{a}_r | \Phi_0\rangle_{\to 0} + \frac{1}{4}\sum_{k} \langle ka||kb\rangle \delta_{ij} - \frac{1}{4}\sum_{pr} \langle pa||rb\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_j \hat{a}_i^\dagger \hat{a}_r | \Phi_0\rangle$$

$$0 \quad (\delta_{qj} - \hat{a}_j \hat{a}_q^\dagger)(\delta_{ir} - \hat{a}_r \hat{a}_i^\dagger) \qquad (\delta_{jp} - \hat{a}_j \hat{a}_p^\dagger) \quad (\delta_{ir} - \hat{a}_r \hat{a}_i^\dagger)$$

$$+ \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_i^\dagger \hat{a}_a \hat{a}_b^\dagger \hat{a}_j \hat{a}_s \hat{a}_r | \Phi_0\rangle$$

$$(\delta_{ab} - \hat{a}_b^\dagger \hat{a}_a) \quad 0$$

$$= \sum_{k} \langle ak||bk\rangle \delta_{ij} - \langle aj||bi\rangle + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_i^\dagger \hat{a}_j \hat{a}_s \hat{a}_r | \Phi_0\rangle \delta_{ab}$$

$$(\delta_{ij} - \hat{a}_j \hat{a}_i^\dagger)$$

$$= \sum_{k} \langle ak||bk\rangle \delta_{ij} - \langle aj||bi\rangle + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | \Phi_0\rangle \delta_{ij}\delta_{ab}$$

$$- \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_j \hat{a}_i^\dagger \hat{a}_s \hat{a}_r | \Phi_0\rangle \delta_{ab}$$

$$(\delta_{qj} - \hat{a}_j \hat{a}_q^\dagger)(\delta_{is} - \hat{a}_s \hat{a}_i^\dagger)$$

$$= \sum_{k} \langle ak||bk\rangle \delta_{ij} - \langle aj||bi\rangle + \frac{1}{2}\sum_{kl} \langle kl||kl\rangle \delta_{ij}\delta_{ab}$$

$$- \frac{1}{4}\sum_{pr} \langle pj||ri\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_r | \Phi_0\rangle^{\delta_{ab}} + \frac{1}{4}\sum_{prs} \langle pj||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_s \hat{a}_i^\dagger \hat{a}_r | \Phi_0\rangle^{\delta_{ab}}_{\to 0}$$

$$(\delta_{ir} - \hat{a}_r \hat{a}_i^\dagger)$$

$$+ \frac{1}{4}\sum_{pqr} \langle pq||ri\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_j \hat{a}_q^\dagger \hat{a}_r | \Phi_0\rangle \delta_{ab} - \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \hat{a}_p^\dagger \hat{a}_j \hat{a}_q^\dagger \hat{a}_s \hat{a}_i^\dagger \hat{a}_r | \Phi_0\rangle^{0} \delta_{ab}$$

$$0 \quad (\delta_{pj} - \hat{a}_j \hat{a}_p^\dagger) \qquad 0 \quad (\delta_{pj} - \hat{a}_j \hat{a}_p^\dagger) \quad (\delta_{ir} - \hat{a}_r \hat{a}_i^\dagger)$$

$$= \sum_k \langle ak||bk\rangle \delta_{ij} - \langle aj||bi\rangle + \frac{1}{2}\sum_{kl} \langle kl||kl\rangle \delta_{ij}\delta_{ab}$$

$$- \sum_k \langle jk||ik\rangle \delta_{ab}$$

Fock operator

$\langle a|\hat{f}|b\rangle$

$$A + B = \delta_{ij}\left(\langle a|\hat{h}|b\rangle + \sum_k \langle ak||bk\rangle\right)$$

$\langle j|\hat{f}|i\rangle$

$$- \delta_{ab}\left(\langle j|\hat{h}|i\rangle + \sum_k \langle jk||ik\rangle\right)$$

E_{HF}

$$+ \delta_{ab}\delta_{ij}\left(\sum_k \langle k|h|k\rangle + \frac{1}{2}\sum_{k,l} \langle kl||kl\rangle\right)$$

$$- \langle aj||bi\rangle$$

Still extremely tedious!

$$= E_{HF}\,\delta_{ab}\delta_{ij} + \delta_{ij}\langle a|\hat{f}|b\rangle - \delta_{ab}\langle j|\hat{f}|i\rangle - \langle aj||bi\rangle$$

Observations.

1) Only nonzero contributions come from δ_{pq} ($\hat{a}_p^\dagger a_p$ or $\hat{a}_p\hat{a}_p^\dagger$)
2) All other swaps are to lead to $\hat{a}_i^\dagger|\Phi_0\rangle$, $\langle\Phi_0|a_i$, $\hat{a}_a|\Phi_0\rangle$, $\langle\Phi_0|\hat{a}_a^\dagger$. and hence zero contrib.
3) Final results tend to be well organized into E_{HF}, $\langle p|\hat{f}|q\rangle$ and $\langle pq||rs\rangle$. In other words, E_{HF}, $\hat{f}$ have some fundamental significance.
4) $\hat{a}_p^\dagger \to \hat{p}^\dagger$, $\hat{a}_p \to \hat{p}$ to simplify the notation.

There must be an expedient way to enumerate all $\hat{p}^\dagger p$, $\hat{p}\hat{p}^\dagger$ type pairing and to remove all vanishing contributions, recognizing the natural organization of results in terms of E_{HF}, $\langle p|\hat{f}|q\rangle$ and $\langle pq||rs\rangle$!