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iv) Normal ordering and Wick's theorem

In second quantization, we aim at achieving

$$\hat{i}^\dagger |\Phi_0\rangle = \hat{a}|\Phi_0\rangle = 0, \quad \langle\Phi_0|\hat{i} = \langle\Phi_0|\hat{a}^\dagger = 0$$

double creation — double annihilation — double creation (adjoint) — double annihilation (adjoint)

to erase vanishing terms from an expectation value.

The "normal order" of an operator sequence is in which $\hat{i}^\dagger$ and $\hat{a}$ are always placed to the right of $\hat{i}$ and $\hat{a}^\dagger$.

We use $\{\cdots\}$ to indicate that the operator sequence in the braket is normal orderd. More specifically $\{$sequence$\}$ is equal to the normal ordered sequence times $(-1)^{\#\text{swaps needed to reorder}}$.

$$\{\hat{i}^\dagger \hat{j}\} = \underset{\text{because of one swap}}{(-)}\underset{\text{to left}}{\hat{j}}\ \underset{\text{to right}}{\hat{i}^\dagger}$$

$$\{\hat{a}\hat{b}^\dagger\} = -\underset{\text{left}}{\hat{b}^\dagger}\ \underset{\text{right}}{\hat{a}}$$

$$\{\underbrace{\hat{i}^\dagger \hat{a}}_{\text{no preference}}\} = \hat{i}^\dagger \hat{a} = -\hat{a}\hat{i}^\dagger$$

either is normal ordered.

Normal ordered and the original operator sequences generally differ from each other because the order of operations matters. We call this difference "a contraction".

$$\hat{x}\hat{y} - \{\hat{x}\hat{y}\} = \overbrace{\hat{x}\hat{y}} \quad (\text{contraction})$$

$$\overbracket{\hat{i}^\dagger \hat{j}} = \hat{i}^\dagger \hat{j} - \{\hat{i}^\dagger \hat{j}\} = \hat{i}^\dagger \hat{j} - (-\hat{j}\,\hat{i}^\dagger) = \hat{i}^\dagger \hat{j} + \hat{j}\,\hat{i}^\dagger = \delta_{ij}$$

anticomm. relation

$$\overbracket{\hat{a}\,\hat{b}^\dagger} = \hat{a}\,\hat{b}^\dagger - \{\hat{a}\,\hat{b}^\dagger\} = \hat{a}\,\hat{b}^\dagger - (-\hat{b}^\dagger \hat{a}) = \hat{a}\,\hat{b}^\dagger + \hat{b}^\dagger \hat{a} = \delta_{ab}$$

All the other contractions (including $\overbracket{\hat{i}\,\hat{j}^\dagger}$ and $\overbracket{\hat{a}^\dagger \hat{b}}$) are zero.

(confirm this). $\overbracket{\hat{i}\,\hat{j}}$, $\overbracket{\hat{i}\,\hat{a}}$, $\overbracket{\hat{i}\,\hat{j}^\dagger}$, $\overbracket{\hat{a}^\dagger \hat{b}} = ?$

The main benefit of normal ordering lies in the fact

$$\langle \Phi_0 | \hat{x}\,\hat{y} | \Phi_0 \rangle = \langle \Phi_0 | \overbracket{\hat{x}\,\hat{y}} | \Phi_0 \rangle + \underbrace{\langle \Phi_0 | \{\hat{x}\,\hat{y}\} | \Phi_0 \rangle}_{0}$$

0 (because of inevitable double creation/annih.)

$$\overbracket{\hat{x}\,\hat{y}} = \begin{cases} \delta_{ij} & (\text{if } \hat{x} = \hat{i}^\dagger,\ \hat{y} = \hat{j}) \\ \delta_{ab} & (\text{if } \hat{x} = \hat{a},\ \hat{y} = \hat{b}^\dagger) \\ 0 & (\text{otherwise}) \end{cases}$$

Let us define a contraction of a long operator sequence

$$\{\hat{x}_1 \hat{x}_2 \cdots \hat{x}_p \cdots \hat{x}_q \cdots \hat{x}_r \cdots \hat{x}_s \cdots\} = (-1)^\eta\, \overbracket{\hat{x}_p \hat{x}_r}\,\overbracket{\hat{x}_q \hat{x}_s}\, \{\hat{x}_1 \hat{x}_2 \cdots\}$$

swaps to reorder to

$(-1)^\eta$ is equal to $(-1)^{\#\text{intersections}}$ if full contraction

full contraction, $\{\overbracket{\hat{w}\,\hat{x}}\,\overbracket{\hat{y}\,\hat{z}}\}$, etc. is a number $0, \pm 1$

partial contraction, $\{\overbracket{\hat{w}\,\hat{x}}\,\hat{y}\,\hat{z}\}$, etc. is an operator

$$\{\hat{x}_1 \hat{x}_2 \cdots \hat{x}_n\} = (-1)^\eta \underbrace{\hat{x}_m \cdots \hat{x}_\ell}_{\text{in normal order}}$$

$\overleftarrow{\hat{i}, \hat{a}^\dagger}$ $\quad$ $\overrightarrow{\hat{i}^\dagger, \hat{a}}$

Wick's theorem:

an operator sequence is the sum of its normal-ordered sequence and all partial and full contraction.

Proof → see Shavitt & Bartlett "Many-Body Methods in Chemistry and Physics".

normal

$$\hat{w}\hat{x}\hat{y}\hat{z} = \{\hat{w}\hat{x}\hat{y}\hat{z}\} + \{\overbracket{\hat{w}\hat{x}}\hat{y}\hat{z}\} + \{\overbracket{\hat{w}\hat{x}\hat{y}}\hat{z}\} + \{\overbracket{\hat{w}\hat{x}\hat{y}\hat{z}}\} \quad \text{partial}$$

$$+ \{\hat{w}\overbracket{\hat{x}\hat{y}}\hat{z}\} + \{\hat{w}\overbracket{\hat{x}\hat{y}\hat{z}}\} + \{\hat{w}\hat{x}\overbracket{\hat{y}\hat{z}}\} + \{\overbracket{\hat{w}\hat{x}}\overbracket{\hat{y}\hat{z}}\} \quad \text{full}$$

$$+ \{\overbracket{\hat{w}\hat{x}\hat{y}}\hat{z}\} + \{\overbracket{w\overbracket{xy}z}\}$$

$$\langle\Phi_0|\hat{w}\hat{x}\hat{y}\hat{z}|\Phi_0\rangle = \langle\Phi_0|\{\overbracket{\hat{w}\hat{x}}\overbracket{\hat{y}\hat{z}}\}|\Phi_0\rangle + \langle\Phi_0|\{\overbracket{\hat{w}\hat{x}\hat{y}}\hat{z}\}|\Phi_0\rangle + \langle\Phi_0|\{\overbracket{\hat{w}\overbracket{\hat{x}\hat{y}}\hat{z}}\}|\Phi_0\rangle$$

only full contractions can contribute

Products of normal-ordered sequences:

$$\hat{w}\hat{x}\hat{y}\hat{z} = (\hat{w}\hat{x})(\hat{y}\hat{z}) = (\overbracket{\hat{w}\hat{x}} + \{\hat{w}\hat{x}\})(\overbracket{\hat{y}\hat{z}} + \{\hat{y}\hat{z}\})$$

$$= \overbracket{\hat{w}\hat{x}}\,\overbracket{\hat{y}\hat{z}} + \overbracket{\hat{w}\hat{x}}\{\hat{y}\hat{z}\} + \overbracket{\hat{y}\hat{z}}\{\hat{w}\hat{x}\} + \{\hat{w}\hat{x}\}\{\hat{y}\hat{z}\}$$

($\overbracket{\hat{y}\hat{z}}$ is a number and commutative)

Compare

$$\{\hat{w}\hat{x}\}\{\hat{y}\hat{z}\} = \{\hat{w}\hat{x}\hat{y}\hat{z}\} + \{\overbracket{\hat{w}\hat{x}\hat{y}}\hat{z}\} + \{\overbracket{\hat{w}\hat{x}\hat{y}\hat{z}}\} + \{\hat{w}\overbracket{\hat{x}\hat{y}}\hat{z}\}$$

$$+ \{\hat{w}\overbracket{\hat{x}\hat{y}\hat{z}}\} + \{\overbracket{\hat{w}\hat{x}\hat{y}}\hat{z}\} + \{\overbracket{\hat{w}\overbracket{\hat{x}\hat{y}}\hat{z}}\} \longrightarrow \text{survive in } \langle\Phi_0|\{\hat{w}\hat{x}\}\{\hat{y}\hat{z}\}|\Phi_0\rangle$$

= same as $\hat{w}\hat{x}\hat{y}\hat{z}$ minus "internal contractions" such as $\{\overbracket{\hat{w}\hat{x}}\}\{\hat{y}\hat{z}\}$, $\{\hat{w}\hat{x}\}\{\overbracket{\hat{y}\hat{z}}\}$.

Hamiltonian

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

reorganized

$$\hat H = E_{HF} + \sum_{p,q}\langle p|\underline{f}|q\rangle\{p^\dagger q\} + \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\{p^\dagger q^\dagger s r\} \quad \cdots \quad (\times)$$

Fock operator $\langle p|\hat f|q\rangle = \langle p|\hat h|q\rangle + \sum_i \langle pi||qi\rangle$

$$\sum_{p,q}\langle p|\hat h|q\rangle \hat p^\dagger \hat q = \sum_{p,q}\langle p|\hat h|q\rangle \overline{\hat p^\dagger \hat q} + \sum_{p,q}\langle p|\hat h|q\rangle\{\hat p^\dagger \hat q\} = \sum_i \langle i|\hat h|i\rangle + \sum_{p,q}\langle p|\hat h|q\rangle\{p^\dagger q\}$$

only way this is non zero is $\overline{\hat i^\dagger \hat j} = \delta_{ij}$

only way non zero $\overline{\hat i^\dagger \hat j} = \delta_{ij}$

$$\frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle \hat p^\dagger \hat q^\dagger \hat s \hat r = \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\Big(\{\hat p^\dagger \hat q^\dagger \hat s \hat r\} + \{\hat p^\dagger \hat q^\dagger \hat s \hat r\} + \{\hat p^\dagger \hat q^\dagger \hat s \hat r\}$$
$$+ \{\hat p^\dagger \hat q^\dagger s r\} + \{\hat p^\dagger \hat q^\dagger \hat s \hat r\} + \{\hat p^\dagger \hat q^\dagger \hat s \hat r\}$$
$$+ \{\hat p^\dagger \hat q^\dagger \hat s \hat r\}\Big)$$

swap q, s to $\overline{ps}\{qr\}$

$$= \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\{\hat p^\dagger \hat q^\dagger \hat s \hat r\} - \frac{1}{4}\sum_{q,r}\sum_i \langle iq||ri\rangle\{\hat q^\dagger \hat r\}$$
$$+ \frac{1}{4}\sum_{q,s}\sum_i \langle iq||is\rangle\{\hat q^\dagger \hat s\} + \frac{1}{4}\sum_{p,r}\sum_i \langle pi||ri\rangle\{\hat p^\dagger \hat r\}$$
$$- \frac{1}{4}\sum_{p,s}\sum_i \langle pi||is\rangle\{\hat p^\dagger \hat s\} - \frac{1}{4}\sum_{i,j}\langle ij||ji\rangle + \frac{1}{4}\sum_{i,j}\langle ij||ij\rangle$$

1 intersection in full contraction

$$= \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\{\hat p^\dagger \hat q^\dagger \hat s r\} + \sum_{p,q}\sum_i \langle pi||qi\rangle\{\hat p^\dagger \hat q\} + \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle$$

Adding together we get $(\times)$

Example 1

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \langle \Phi_0 | E_{HF} | \Phi_0 \rangle + \sum_{p,q} \langle p | \hat{f} | q \rangle \underbrace{\langle \Phi_0 | \{ \hat{p}^\dagger \hat{q} \} | \Phi_0 \rangle}_{0} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \underbrace{\langle \Phi_0 | \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \} | \Phi_0 \rangle}_{0}$$

$$= E_{HF} \ !$$

Example 2

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = \langle \Phi_0 | \hat{i}^\dagger \hat{a} \ \hat{H} \ \hat{b}^\dagger \hat{j} | \Phi_0 \rangle$$

$$= \langle \Phi_0 | \{ \hat{i}^\dagger \hat{a} \} \hat{H} \{ \hat{b}^\dagger \hat{j} \} | \Phi_0 \rangle$$

$$= E_{HF} \overbrace{\langle \Phi_0 | \{ \hat{i}^\dagger \hat{a} \} \{ \hat{b}^\dagger \hat{j} \} | \Phi_0 \rangle}^{\delta_{ij} \delta_{ab}} + \sum_{p,q} \langle p | \hat{f} | q \rangle \overbrace{\underbrace{\langle \Phi_0 | \{ \hat{i}^\dagger \hat{a} \} \{ \hat{p}^\dagger \hat{q} \} \{ \hat{b}^\dagger \hat{j} \} | \Phi_0 \rangle}_{- \delta_{iq} \delta_{ab} \delta_{pj}}}^{\delta_{ij} \delta_{ap} \delta_{qb}}$$

$$+ \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \overbrace{\underbrace{\langle \Phi_0 | \{ \hat{i}^\dagger \hat{a} \} \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \} \{ \hat{b}^\dagger \hat{j} \} | \Phi_0 \rangle}_{\delta_{ir} \delta_{ap} \delta_{qj} \delta_{sb}}}^{- \delta_{is} \delta_{ap} \delta_{qj} \delta_{rb}}$$

$$\overbrace{\underbrace{\langle \Phi_0 | \{ \hat{i}^\dagger \hat{a} \} \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \} \{ \hat{b}^\dagger \hat{j} \} | \Phi_0 \rangle}_{- \delta_{ir} \delta_{aq} \delta_{sb} \delta_{pj}}}^{\delta_{is} \delta_{aq} \delta_{rb} \delta_{pj}}$$

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