Normal order, with respect to single determinant, e.g. $|HF\rangle$

In quantum ~~chem~~ chemistry we have a number of methods in which we want to evaluate

$$\langle HF| \hat{A} \hat{B} \hat{C} |HF\rangle$$

e.g. $\langle HF| (b^+ s) (\hat{H}) (r_a^\dagger) |HF\rangle$ (CIS)

Here $\hat{A}, \hat{B}, \hat{C}$ are expressed using strings of second quantized annihilation and creation operators.

We can use the anticommutation relations to move operators around.

$$\hat{A}\hat{B}\hat{C} = \hat{O}.$$

a very convenient way to order operators in $\hat{O}$ is so-called normal order.

We define:

quasiparticle annihilation $\hat{c}_p |HF\rangle = 0$

quasiparticle creation $c_q^\dagger |HF\rangle = 0$

Let me use notation for orbitals that is most widely used in the literature.

occupied orbitals: i, j, k, l
virtual orbitals: a, b, c, d
general orbitals: p, q, r, s

This is different from the S&O naming convention. Let us make the switch.

q-annihilation: $\hat{a}\,|HF\rangle = 0$
$\hat{i}^{+}\,|HF\rangle = 0$

q-creation $\langle HF|\,a^{+} = 0$
$\langle HF|\,\hat{i} = 0$

If one would organize the operators in $\hat{O} = \hat{A}\hat{B}\hat{C}$ such that:
all q-annihilation operators to the right
all q-creation operators to the left
then results would simplify enormously.
This is referred to as writing an operator in normal order.

Normal ordered operator $\hat{O}$

$$\{\hat{O}\} = \Sigma \underbrace{(\cdots\cdots)}_{q\text{-creation}} \underbrace{(\cdots\cdots)}_{q\text{-annihilation}}$$

within the $(\cdots\cdots)_{q\text{-creation}}$ part operators anti commute, e.g.

$$(a^{+} i\, b^{+} c^{+} j) = \pm (a^{+} b^{+} c^{+} \cdots i j)$$

Likewise within q-annihilation part operators anti commute

$$(i^{+} a\, j^{+} b c) \sim \pm (b a i^{+} c j^{+})$$

Within a normal ordered string we can take all operators to anticommute.

$$\{p^{+} q^{+} r s^{+}\} = \pm \{p^{+} r s^{+} q^{+}\}$$

However to evaluate action as a conventional string, ~~(~~ the operators always act such that $\{\hat{O}\} = (\quad)_{q\text{-creation}} (\text{---})_{q\text{-ann.}}$

as a result:

$\{\hat{O}\} |HF\rangle = 0$ when $\{\hat{O}\}$ contains <u>any</u> q-annihilation ops

$\langle HF | \{\hat{O}\} = 0$ when $\{\hat{O}\}$ contains any q-creation operators

$\langle HF | \{\hat{O}\} | HF \rangle = 0$ if $\{\hat{O}\}$ contains any operators at all

$\Rightarrow$ only constant term in $\{\hat{O}\}$ contributes to $\langle HF | \{\hat{O}\} | HF \rangle$.

Normal ordering is a very useful bookkeeping device

Let us consider a string of two operators. We can define a <u>contraction</u> as follows

$$p^+ q = \{p^+ q\} + \overline{p^+ q}$$

or $$\overline{p^+ q} = p^+ q - \{p^+ q\}$$

Likewise $$\overline{q p^+} = q p^+ - \{q p^+\}$$

<u>Hence</u>

$$\overline{i^+ j} = i^+ j - \{i^+ j\} = i^+ j + j i^+ = \delta_{ij}$$
$$\overline{i^+ a} = i^+ a - \{i^+ a\} = i^+ a - i^+ a = 0$$
$$\overline{a^+ i} = a^+ i - \{a^+ i\} = a^+ i - a^+ i = 0$$
$$\overline{a^+ b} = a^+ b - \{a^+ b\} = a^+ b - a^+ b = 0$$

$$\overline{i j^\dagger} = i j^\dagger - \{i j^\dagger\} = i j^\dagger - i j^\dagger = 0$$

$$\overline{a i^\dagger} = \cdots = 0$$

$$\overline{i a^\dagger} = \ldots 0$$

$$\overline{a b^\dagger} = a b^\dagger - \{a b^\dagger\} = a b^\dagger + b^\dagger a = \delta_{ab}$$

There are only two non-zero contractions:

$$\overline{i^\dagger j} = \delta_{ij}$$

$$\overline{a b^\dagger} = \delta_{ab}$$

I could have done this differently.

$$\langle HF| \overline{p^\dagger q} |HF\rangle = \langle HF|p^\dagger q|HF\rangle - \cancel{\langle HF|\{p^\dagger q\}|HF\rangle}$$

$$= \langle HF|p^\dagger q|HF\rangle$$

$$= \delta_{pq} \text{ if } p \text{ is occupied}$$

$$\Rightarrow \overline{i^\dagger j} = \delta_{ij} \qquad \text{others are } 0.$$

$$\langle HF| \overline{q p^\dagger} |HF\rangle = \langle HF|q p^\dagger|HF\rangle - \cancel{\langle HF|\{q p^\dagger\}|HF\rangle}$$

$$= \langle HF|q p^\dagger|HF\rangle = \delta_{pq} \text{ if } p \text{ is virtual}$$

$$\overline{a b^\dagger} = \delta_{ab} \qquad \text{all others are zero.}$$

The use of contractions follows from <u>Wick's</u> theorem

$$\{A\}\{B\} = \{A\,B\}$$ no contraction

$$+ \{A\,B\}$$ one contraction between op. in $\hat{A}$, $\hat{B}$

$$+ \{A\,B\}$$ two contractions between operators in $\hat{A}$ and $\hat{B}$

$$+ \cdots$$

$$+ \{A\,B\}$$ maximum number of contractions

To apply Wick's theorem we first express operators themselves in normal order.

A very important consequence is

$$\langle HF|\{A\}\{B\}|HF\rangle$$

$$= \langle HF|\,A\,B\,|HF\rangle$$ fully contracted

all operators are to be contracted since

$$\langle HF|\{\hat{O}\}|HF\rangle = 0$$

if $\{\hat{O}\}$ contains any operators.

A contraction within a normal ordered product is defined using that operators in N-O.P. anticommute: eg.,

$$\{p^\dagger q^\dagger s r\} = -\{\overbrace{p^\dagger s}\, q^\dagger r\}$$

$$= -\overbrace{p^\dagger s}\,\{q^\dagger r\}$$

Once contracted operators are adjacent, they can be removed as a pair (no sign change)

a contraction is always just a number (could be a function). It is not an operator.

One has to deal with signs correctly.

Normal ordered form of H

$$\hat{h} = \sum_{p,q} h_{pq}\, p^\dagger q$$

$$= \sum_{p,q} h_{pq} \left(\{p^\dagger q\} + \overline{p^\dagger q} \right)$$

$$= \sum_{p,q} h_{pq} \{p^\dagger q\} + \sum_{i} h_{ii}$$

$$= \langle HF | \hat{h} | HF \rangle + \sum_{p,q} h_{pq} \{p^\dagger q\}$$

$$= h_0 + \sum_{p,q} h_{pq} \{p^\dagger q\}$$

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

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

remember $\overline{p^\dagger q} = \delta_{pq}$, p/q - occupied.

$\Rightarrow$ (Do excercise)

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

In total we get

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

This is a very convenient way to write the Hamiltonian.

$$E_{HF} = \sum_{i\ occ} h_{ii} + \frac{1}{2} \sum_{i,j} \langle ij||ij\rangle$$

$$f_{pq} = h_{pq} + \sum_{\substack{i \\ occ.}} \langle pi||qi\rangle$$

Let us revisit some matrix elements

- Koopmans IP

$\langle HF | i^\dagger (E_{HF} + \hat{F} + \hat{V}) j | HF \rangle$

$= E_{HF} \delta_{ij} + f_{pq} \langle HF | i^\dagger \{p^\dagger q\} j | HF \rangle$

$+ \langle HF | i^\dagger \{p^\dagger q^\dagger s r\} j | HF \rangle$

$= E_{HF} \delta_{ij} - f_{ji}$

- Likewise Koopmans EA

- $\boxed{\text{CIS}}$

$\langle HF | j^\dagger b \; (E_{HF} + \hat{F} + \hat{V}) \; a^\dagger i | HF \rangle$

$= \langle HF | j^\dagger b \; E_{HF} \; a^\dagger i | HF \rangle$

$+ \sum_{p,q} f_{pq} \langle HF | j^\dagger b \; \{p^\dagger q\} \; a^\dagger i | HF \rangle + \langle j^\dagger b \; p^\dagger q \; a^\dagger i \rangle$

$+ \frac{1}{4} \sum_{p,q,r,s} \langle HF | j^\dagger b \; \{p^\dagger q^\dagger s r\} \; a^\dagger i | HF \rangle \quad (\times 4)$

$= E_{HF} \delta_{ab} \delta_{ij}$

$+ \delta_{ij} f_{ab} - \delta_{ab} f_{ij}$

$- \langle bi || aj \rangle$

Normal ordering has more uses than just $\langle HF | \hat{A} \hat{O} \hat{B} | HF \rangle$.