Diagrammatic representation of operators. / normal order

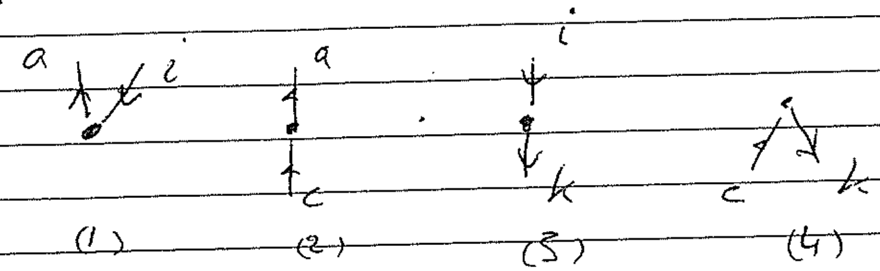
We have seen before that using the normal ordered operators reduces the complexity of equations.
It is still tedious to derive equations, however. Nowadays computers are often used to derive equations. There is another tool to derive equations: drawing diagrams and translating them into algebra. This approach originates in the famous Feynman diagrams of quantum electrodynamics. Here we focus on the use of diagrams in Quantum Chemistry.

To represent operators we have
- vertex : a symbol representing the operator
- outgoing lines : creation op.
- ingoing lines : annihilation
- lines pointing upwards : virtual
- lines pointing downwards : occupied

as a consequence:
- line below vertex: q-annihilation
- line above vertex: q-creation

Examples: one-electron operators

$\hat{f} \rightarrow$ ● vertex



$$\hat{f} = \sum_{a,i} f_{ai}\{a^+ i\} \quad (1)$$

$$+ \sum_{a,c} f_{ac}\{a^+ c\} \quad (2)$$

$$+ \sum_{i,k} f_{ki}\{k^+ i\} \quad (3)$$

$$+ \sum_{c,k} f_{kc}\{k^+ c\} \quad (4)$$

You can verify: $f_{out,\,in}\{\hat{out}^+ \, \hat{in}\}$

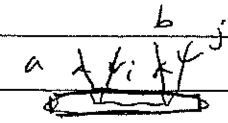
labels a, i above the vertex
$\Rightarrow$ q-creation operators

labels c, k: below the vertex
$\Rightarrow$ q-annihilation operators

$$\hat{f}|0\rangle \rightarrow \sum_{a,i} f_{ai}\{a^+ i\}|0\rangle$$

all other terms vanish!

Example (2) : <u>Excitation operator</u>



rectangular boxes.

(1) (2)

$$\hat{C} = \sum_{i,a} C_i^a \{a^+ i\}$$

$$+ \frac{1}{4} \sum_{i,j,a,b} C_{ij}^{ab} \{a^+ i \; b^+ j\}$$

$$\left[\text{or} \quad C_{ij}^{ab} \{a^+ b^+ j i\} \right]$$

It only matters ~~which~~ which lines go into and out of vertex.

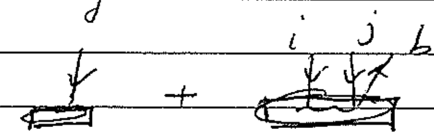
To keep track of signs, I draw $\sim$ inside the vertex this indicates 'particle labels'

$$\ell_1 \sim \ell_2$$

$$\underset{(1)}{C_i^a} \; \underset{(2)}{{}^{b}_{j}} \quad \{ \underset{1}{a^+ i} \;\; \underset{2}{b^+ j} \}$$

This is important to keep track of signs.

<u>Ionization</u>



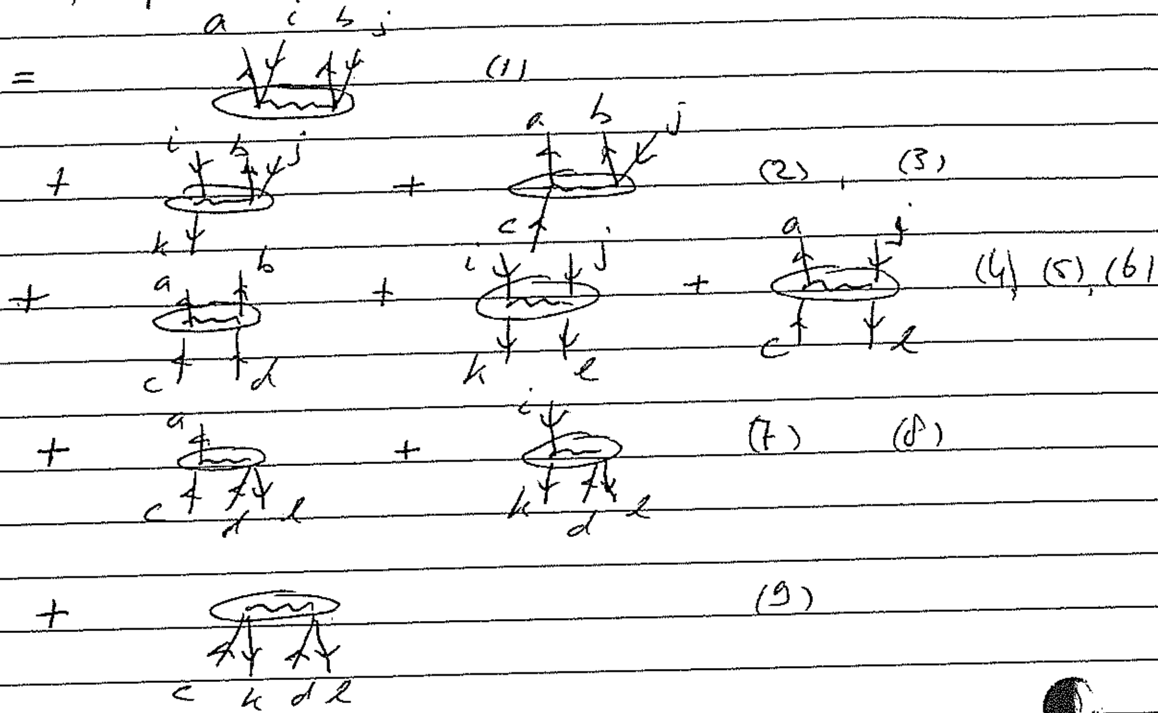
$$\sum_i C_i \{\hat{i}\} + \sum_{i,j,b} C_{ij}^{b} \{i \, b^+_j\}$$

$$= C_{ji}^{b} \{b^+ j i\}$$

I indicated empty spot with $\circ$ (for clarity)

Example: 2-electron integrals.

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



$$\hat{V} = \sum_{\ldots} \frac{1}{4} \langle ab||ij\rangle \{a^\dagger i\, b^\dagger j\} \quad (1)$$

$$+ \frac{1}{2} \langle kb||ij\rangle \{k^\dagger i\, b^\dagger j\} \quad (2)$$

$$+ \frac{1}{2} \langle ab||cj\rangle \{a^\dagger c\, b^\dagger j\} \quad (3)$$

$$+ \frac{1}{4} \langle ab||cd\rangle \{a^\dagger c\, b^\dagger d\} \quad (4)$$

$$+ \frac{1}{4} \langle kl||ij\rangle \{k^\dagger i\, l^\dagger j\} \quad (5)$$

$$+ \langle al||cj\rangle \{a^\dagger c\, l^\dagger j\} \quad (6)$$

$$+ \frac{1}{2} \langle al||cd\rangle \{a^\dagger c\, l^\dagger d\} \quad (7)$$

$$+ \frac{1}{2} \langle kl||id\rangle \{k^\dagger i\, l^\dagger d\} \quad (8)$$

$$+ \frac{1}{4} \langle kl||cd\rangle \{k^\dagger c\, l^\dagger d\} \quad (9)$$

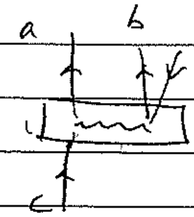
$\langle pq||rs\rangle$ left out, right out, left in, right in.

$\{p^\dagger r\, q^\dagger s\}$

or $\{p^\dagger q^\dagger s r\}$

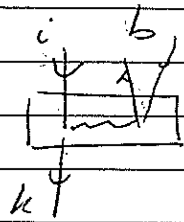
I only listed the unique contributions. The factors ~~half~~ $\frac{1}{4}$, $\frac{1}{2}$ etc. indicate if indices are equivalent.

We can also have operators like



$$\frac{1}{2}\sum_{..} S^{ab}_{cj} \{a^{+}c\; b^{+}j\}$$

or



$$\frac{1}{2}\sum_{..} S^{kb}_{ij} \{k^{+}i\; b^{+}j\}$$

They arise in multi reference theories.

Notation of labels (my convention)

q-creation	a, b	virtuals
	i, j	occupied
q-annihilation	c, d	virtual
	k, l	occupied

I always pair up ~~in~~ ~~[illegible]~~
(a, i, k, c) and
(b, j, l, d)
"particle 1" and "particle 2"

Diagrams and Wick's theorem.

Before we saw $\{\hat{A}\}\{\hat{B}\} =$
$$\{\hat{A}\hat{B}\} + \{\hat{A}\hat{B}\} + \{\hat{A}\hat{B}\} + \cdots$$
$$\{\hat{A}\hat{B}\} \text{ maximally contracted.}$$

This we can easily represent diagrammatically;
Draw $\hat{A}$ above $\hat{B}$.
join lines to represent contractions.
We can draw operators diagrams such that the external operator lines have a particular particle-hole character.

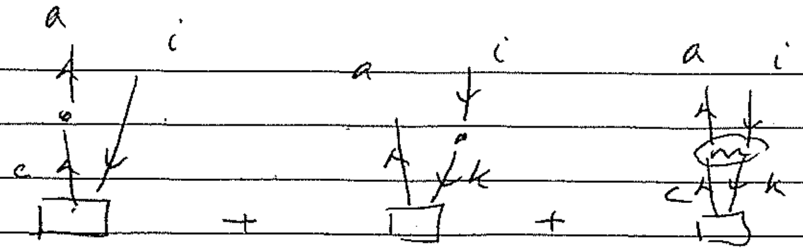
Let's do some examples

CI singles:

$$\langle HF| a_i^{+} \hat{H} \hat{C}_1 |HF\rangle$$

$$\Rightarrow \left(\hat{H}\hat{C}_1\right)_i^a$$

Draw diagrams such that the overall excitation operator looks like $a^+ i$



rules to translate to formula.

1) Sum over internal (contracted) lines

2) include a minus sign for each internal hole line

3) include a minus sign for each closed loop.

4) Include a symmetry factor + permutation to avoid double counting (delicate)

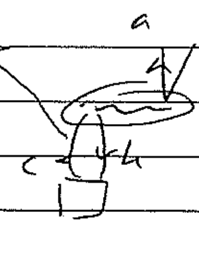
$$(HC_1)_i^a = \sum_c f_{ac} C_i^c - \sum_k f_{ki} C_k^a$$

$$- \sum_{k,c} \langle ak||ci\rangle C_k^c$$

[Connect to matrix for CIS]

I could have drawn last term as

closed loop.



$$\rightarrow \sum_{c,k} (-)^2 \cdot \langle ka||ci\rangle C_k^c$$

$$= - \sum_{c,k} \langle ak||ci\rangle C_k^c$$

Same formula in the end.

I will not derive / justify diagrammatic rules here.

rule 4) is a little complicated. We get a factor of $\frac{1}{n!}$ for each set of n equivalent internal lines.

In the end we should permute over all external labels, as we draw only one unique diagram (examples later). If permuted diagram is the same we need to correct for double counting.

Our goal at present is to get a first introduction.

We can learn to draw diagrams systematically:

a) Draw all unique skeleton diagrams (no arrows)

b) include arrows in all possible ways

c) formula: labels / signs add labels to diagram.

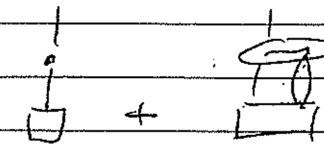
d) include equivalence factor.

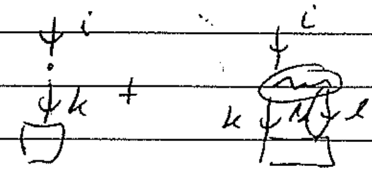
Example ionization CI IPCI

In the excersises you are asked to derive the expressions using the "matrix-element method".

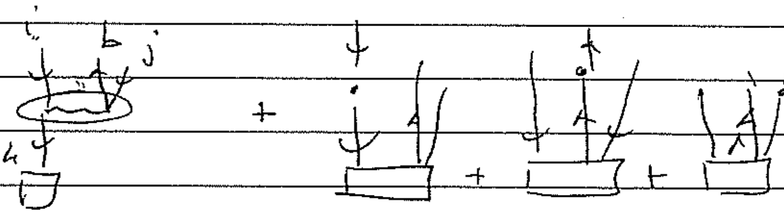
Let us now draw the diagrams

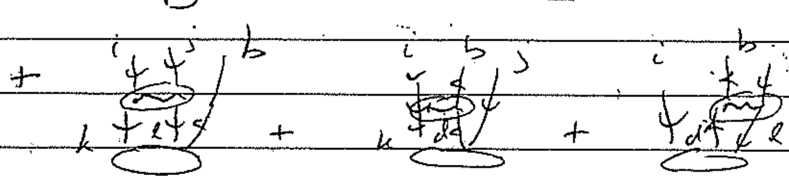
$\hat{C} =$ 

$(\hat{H}\hat{C})_i =$  (skeletons)

$\Rightarrow$  (full diagrams)

$$(HC)_i = -\sum_k f_{ki} c_k - \sum_{k,l,d} \cancel{\tfrac{1}{2}} \langle kl||id\rangle c_{kl}^{d}$$

$(\hat{H}\hat{C})_{ij}^{b} =$ 



$$(HC)_{ij}^{b} = \sum_k -\langle kb||ij\rangle c_k$$

$$-\sum_k f_{ki} c_{kj}^{b} - \sum_l f_{lj} c_{il}^{b} + \sum_d f_{bd} c_{ij}^{d}$$

$$+\cancel{\tfrac{1}{2}} \sum_{kl} \langle kl||ij\rangle c_{kl}^{b} - \langle kb||id\rangle c_{kj}^{d} - \sum \langle bl||dj\rangle c_{il}^{d}$$

from these equations we can extract the matrix equations

$$
\begin{array}{c|cc}
 & k & kl^{d} \\
\hline
i & -f_{ki} & -\langle kb\|id\rangle \\
i_j^{b} & -\langle kb\|ij\rangle & \downarrow
\end{array}
\begin{pmatrix} C_k \\ C_{kld} \end{pmatrix}
$$

$$
\langle i_j^{b} | H | kl^{d} \rangle =
$$

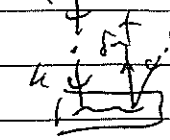
$$
- f_{ki}\, \delta_{jl}\, \delta_{bd} - f_{jl}\, \delta_{ik}\, \delta_{bd}
$$

$$
+ f_{bd}\, \delta_{ik}\, \delta_{jl} + \langle kl\|ij\rangle\, \delta_{bd}
$$

$$
- \langle kb\|id\rangle\, \delta_j^{l} - \langle bl\|dj\rangle\, \delta_{ik}
$$

Lines ~~that~~ from $\hat{C}$ that go directly to external index acquire a δ-function.

example



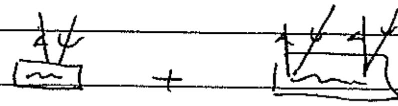
$$
\sum_{kdl} - f_{ki}\, \delta_{bd}\, \delta_{jl}\, C_{kl}^{d}
$$

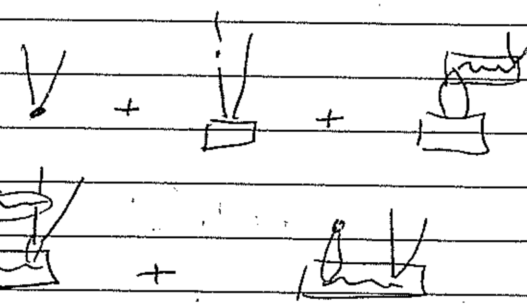
$$
= - \sum_{k} f_{ki}\, C_{kj}^{b}
$$

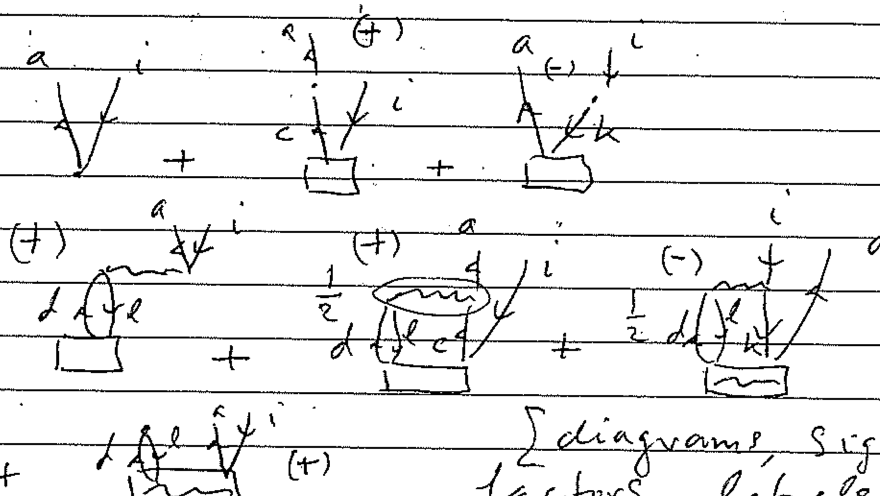
other terms are analogous.

Let me give one more example to illustrate systematic drawing of diagrams.

$\boxed{\text{CI SD}}$

$C = 1 +$ 

$(HC)_i^a =$  (skeletons)

$=$ 

{diagrams, signs, factors, labels}

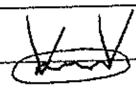
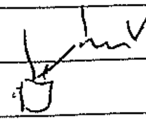
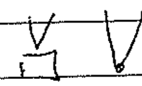
<u>Formula</u>: $f_{ai} + \sum_c f_{ac} c_i^c - \sum_k f_{ki} c_k^a$

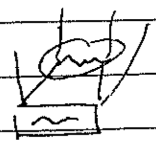
$+ \sum_{l,d} \langle la||di\rangle c_l^d + \frac{1}{2} \sum_{l,d,c} \langle la||dc\rangle c_{li}^{dc}$

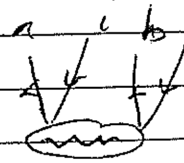
$- \frac{1}{2} \sum_{l,k,d} \langle lk||di\rangle c_{lk}^{da}$

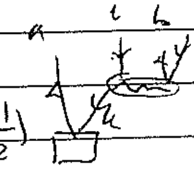
$+ \sum_{l,d} f_{ld} c_{di}^{da}$

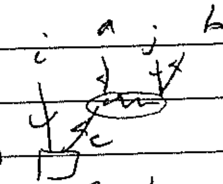
$$(HC)_{ij}^{ab} = (1-P_{ij})(1-P_{ab}) \quad \{\text{permutations}\}$$

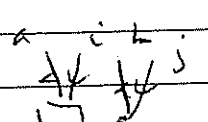
 +  + 

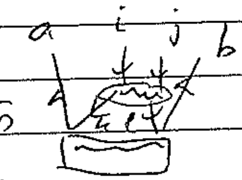
\+  ~~spx~~ skeletons

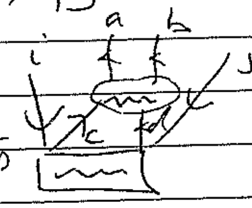
$\frac{1}{4}$ 

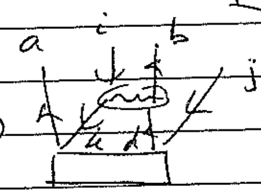
$+(-\frac{1}{2})$ 

$+(\frac{1}{2})$ 

\+ 1 · 

$+\frac{1}{8}$ 

$+\frac{1}{8}$ 

$+(-)$ 

$$(HC)_{ij}^{ab} = (1-P_{ij})(1-P_{ab}) \Big[$$

$$\frac{1}{4}\langle ab||ij\rangle - \frac{1}{2}\sum_k \langle kb||ij\rangle C_k^a$$

$$+ \frac{1}{2}\sum_c \langle ab||cj\rangle C_i^c + f_{ai} C_j^b$$

$$+ \frac{1}{8}\sum_{k,l} \langle kl||ij\rangle C_{kl}^{ab} + \frac{1}{8}\sum_{c,d} \langle ab||cd\rangle C_{ij}^{cd}$$

$$- \sum_{k,d} \langle kb||id\rangle C_{kj}^{ad} \Big]$$

Symmetry factor: $\frac{1}{2}$ for each pair of equivalent lines.