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V) Diagrams

excitation operator

Suppose a wavefunction $|\Psi\rangle = \hat{C}_1|\Phi_0\rangle = \sum_i \sum_a C_i^a |\Phi_i^a\rangle$

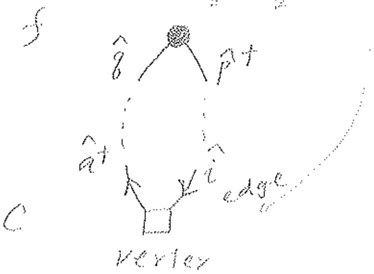
$= \sum_i \sum_a C_i^a \{\hat{a}^\dagger \hat{i}\}|\Phi_0\rangle$ (note, $\hat{a}^\dagger \hat{i} = \{\hat{a}^\dagger \hat{i}\}$)

no external contraction ?

$\langle \Phi_0 | \hat{H} | \Psi \rangle = \langle \Phi_0 | E_{HF} \sum_i \sum_a C_i^a \{\hat{a}^\dagger \hat{i}\} | \Phi_0 \rangle \longrightarrow 0$

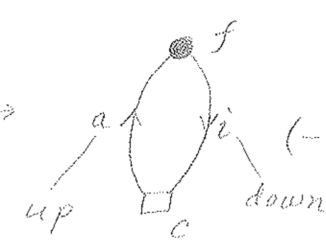
$+ \sum_{p,q} \sum_{i,a} \langle p|\hat{f}|q\rangle C_i^a \langle \Phi_0 | \{\hat{p}^\dagger \hat{q}\}\{\hat{a}^\dagger \hat{i}\} | \Phi_0 \rangle$

$+ \frac{1}{4} \sum_{p,q,r,s} \cdots \langle \Phi_0 | \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\}\{\hat{a}^\dagger \hat{i}\} | \Phi_0 \rangle \longrightarrow 0$



excitation $\longrightarrow$ C

$\longrightarrow$



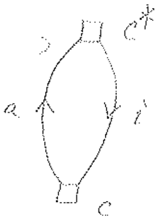
$(-1)^{1+1} \sum_{a,i} \langle i|\hat{f}|a\rangle C_i^a$

\# loops, \# occ. hole lines; out, in

see Appendix 10A March et al. "The Many-Body Problem in Quantum Mechanics"

$\langle \Psi | \hat{H} | \Psi \rangle = E_{HF} \sum_{i,a,j,b} C_i^{a*} C_j^b \langle \Phi_0 | \{\hat{i}^\dagger \hat{a}\}\{\hat{b}^\dagger \hat{j}\} | \Phi_0 \rangle$

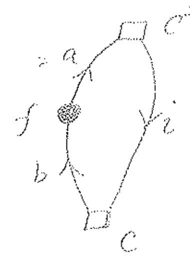
de excitation $\hat{C}_1^\dagger$



$(-1)^{1+1} \sum_{a,i} C_i^{a*} C_i^a$

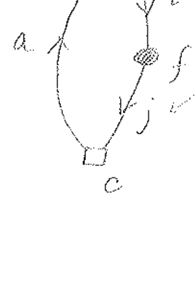
\# loops, \# hole lines; out

$+ \sum_{p,q} \sum_{i,a} \sum_{j,b} C_i^{a*} C_j^b \langle \Phi_0 | \{\hat{i}^\dagger \hat{a}\}\{\hat{p}^\dagger \hat{q}\}\{\hat{b}^\dagger \hat{j}\} | \Phi_0 \rangle$



$(-1)^{1+1} \sum_{a,b,i} \langle a|\hat{f}|b\rangle C_i^{a*} C_i^b$

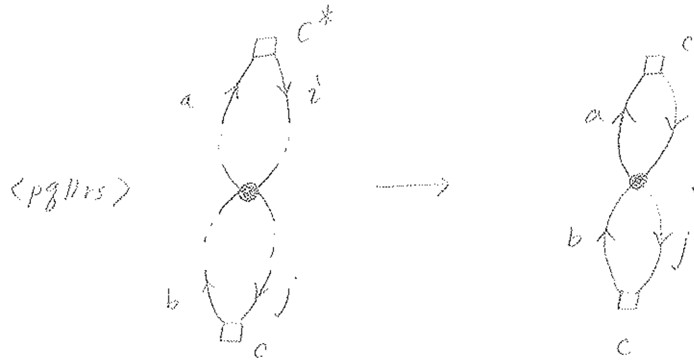
out, in



$(-1)^{1+2} \sum_{i,j,a} \langle j|\hat{f}|i\rangle C_i^{a*} C_j^a$

out, in

$$+\frac{1}{4}\sum_{p,q,r,s}\sum_{i,a}\sum_{j,b} C_i^{a*} C_j^{b} \langle pq||rs\rangle \langle\Phi_0|\{\hat{i}^\dagger \hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\,\hat{r}\}\{\hat{b}^\dagger \hat{j}\}|\Phi_0\rangle$$

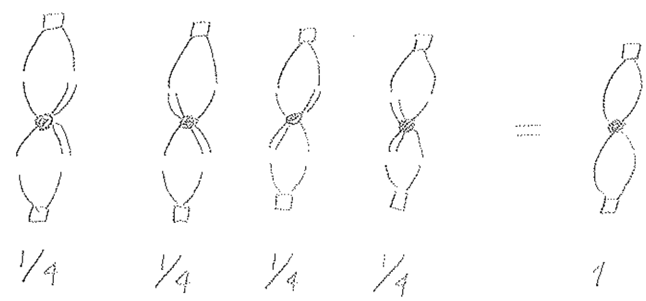


$\langle aj||bi\rangle = \langle$ left out, right out $||$ l. in, r. in $\rangle$

#loops, #holes

$$(-1)^{1+2}\sum_{\substack{a,i\\ b,j}} \langle aj||bi\rangle C_i^{a*} C_j^{b}$$

4 different ways of contractions are consolidated into one topologically distinct contribution. with the correct coefficient $1/4 \times 4 = 1$



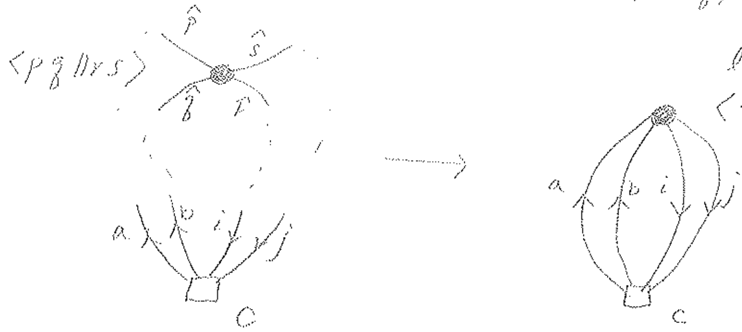
$C_{ij}^{ab} = -C_{ij}^{ba} = -C_{ji}^{ab} = C_{ji}^{ba}$ same as $\hat{a}^\dagger \hat{b}^\dagger \hat{j}\,\hat{i}$

Suppose $|\Psi\rangle = \hat{C}_2|\Phi_0\rangle = \sum_{i<j}\sum_{a<b} C_{ij}^{ab}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\,\hat{i}\}|\Phi_0\rangle$ note the order convention

$$= \frac{1}{4}\sum_{i,j}\sum_{a,b} C_{ij}^{ab}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\,\hat{i}\}|\Phi_0\rangle$$

$$\langle\Phi_0|\hat{H}|\Psi\rangle = \frac{1}{4}\cdot\frac{1}{4}\sum_{p,q,r,s}\sum_{i,j,a,b} \langle pq||rs\rangle C_{ij}^{ab} \langle\Phi_0|\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\,\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\,\hat{i}\}|\Phi_0\rangle$$

(obviously E_{HF} and $\langle p|\hat{f}|q\rangle$ cannot fully contract)

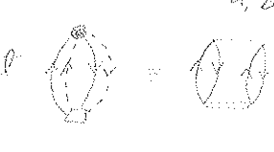


#loops, #holes, #equivalent pairs (i,j) (a,b) same type same origin dest.

$$(-1)^{2+2}\left(\frac{1}{2}\right)^{2}\sum_{\substack{i,j\\ a,b}} \langle ij||ab\rangle C_{ij}^{ab}$$

always connect

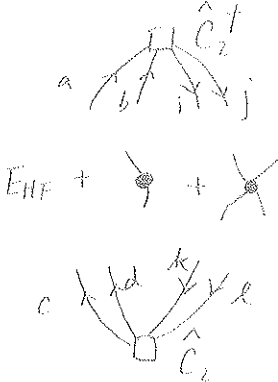
Loop: left-in to left out, right-in to right out

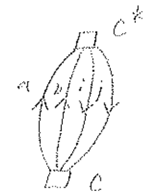


Example. 1

$$\langle \Phi_0 | \hat{C}_2^{\dagger} \hat{H} \hat{C}_2 | \Phi_0 \rangle = \left(\frac{1}{4}\right)^2 \sum_{\substack{ij \\ a,b}} \sum_{\substack{k,l \\ c,d}} C_{ij}^{ab*} C_{kl}^{cd} \langle \Phi_0 | \{ \hat{i}^{\dagger} \hat{j}^{\dagger} \hat{b} \hat{a} \} \hat{H} \{ \hat{c}^{\dagger} \hat{d}^{\dagger} \hat{l} \hat{k} \} | \Phi_0 \rangle$$

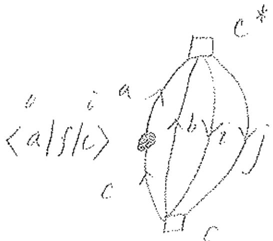
$\hat{H} = E_{HF} +$  $\langle p|\hat{f}|q\rangle +$  $\langle pq||rs\rangle$



$\longrightarrow$ E_{HT} 

(i, j) equivalence
(a, b)

$$(-1)^{2+2}\left(\frac{1}{2}\right)^{2} \sum_{\substack{a,b \\ i,j}} C_{ij}^{ab*} C_{ij}^{ab} E_{HT}$$

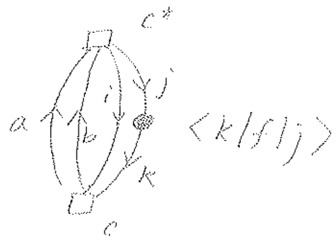


(i,j) equivalence

loro

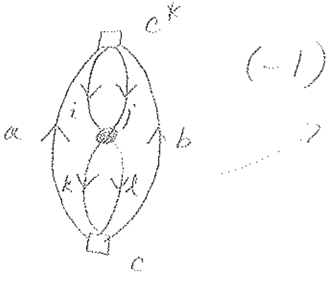
$$(-1)^{2+2}\left(\frac{1}{2}\right)^{1} \sum_{\substack{a,b,c \\ i,j}} C_{ij}^{ab*} C_{ij}^{cb} \langle a|f|c\rangle$$

lori



i, j, k

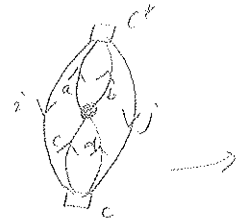
$$(-1)^{2+3}\left(\frac{1}{2}\right)^{1} \sum_{\substack{a,b \\ i,j,k}} C_{ij}^{ab*} C_{ik}^{ab} \langle k|f|i\rangle$$



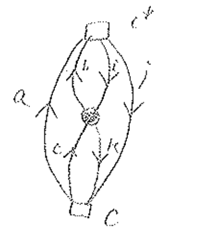
(i, j)
(k, l)
(a, b)

lorolihi

$$(-1)^{2+4}\left(\frac{1}{2}\right)^{3} \sum_{\substack{a,b \\ i,j \\ k,l}} C_{ij}^{ab*} C_{kl}^{ab} \langle kl||ij\rangle$$



$$\longrightarrow (-1)^{2+2}\left(\frac{1}{2}\right)^{3} \sum_{\substack{a,b \\ c,d \\ i,j}} C_{ij}^{ab*} C_{kl}^{cd} \langle ab||cd\rangle$$



$$(-1)^{2+3} \sum_{\substack{a,b,c \\ i,j,k}} C_{ij}^{ab*} C_{kj}^{ac} \langle bk||ci\rangle$$

Diagrammatic rules

— Bartlett "Coupled-Cluster theory: An Overview of Recent Developments" in Modern Electronic Structure Theory, Part I, ed. David R. Yarkony

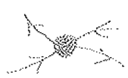
— March et al. "The Many-Body Problems in Quantum Mechanics"

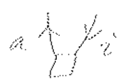
— Shavitt and Bartlett "Many-Body Methods in Chemistry and Physics"

Closed diagrams

1) label ↑ particle (a, b, c..) and ↓ hole (i, j, k..) lines (edges).

2) associate  one-particle vertex with $\langle out | \hat{f} | in \rangle$.

3) associate  two-particle vertex with $\langle$left out, right out$||$l.i, r.i$\rangle$.

4) associate  with C_i^a,  C_{ij}^{ab}, etc.

5) sum all internal line labels.

6) associate $\left(\frac{1}{2}\right)$ for each pair of equivalent lines (same type, same origin, same destination).

7) associate $\left(\frac{1}{2}\right)$ for each pair of equivalent vertexes.

8) multiply $(-1)^{l+h}$, where l is the number of loops, h is the number of hole lines.

Open diagrams

1) label external lines

2) Sum over all distinct permutations of external lines with $(-1)^p$

3) fictitious loops count as loops