Diagrammatic techniques in Coupled-Cluster Theory

Advanced Lecture Series in Electronic Structure Theory, Fall 2010

K. Sahan Thanthiriwatte
School of Chemistry and Biochemistry,
Georgia Institute of Technology.

August 17, 2010

References

- T. D. Crawford, and H. F. Schaefer "An Introduction to Coupled Cluster Theory for Computational Chemists", *In* Reviews of Computational Chemistry; Lipkowitz, K. B., Boyd, D. B., Eds., Vol. 14, Chapter 2, pp 33-136, VCH Publishers: New York, **2000**.
- I. Shavitt and R. J. Bartlett "Many-body Methods in Chemistry and Physics", Cambridge University Press, Cambridge, **2009**.
- S. A. Kucharski and R. J. Bartlett, "Fifth-order many-body perturbation theory and its relationship to various coupled-cluster approaches" *Adv. Quantum Chem.*, **1986**, *18*, 281.

Introduction

- Diagrammatic notation originated in quantum field theory, in the form of Feynman diagrams , in an explicit time-dependent format.
- Initial applications to RSPT were also in time-dependent form.
- Time-independent non-relativistic non-degenerate Feynman diagrams are referred as **Goldstone diagrams**.
- Antisymmetrized Goldstone diagram formalism adapted and popularized by Kucharski and Bartlett[1]

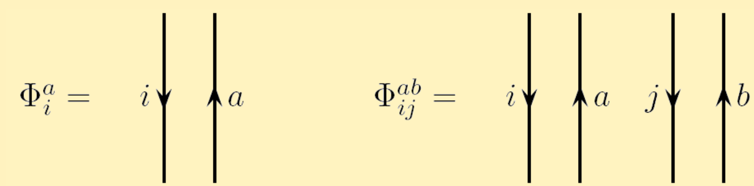
The purposes of the diagrammatic notation are:

- To make it easy to list all non-vanishing distinct terms in CC equations.
- To bring out certain cancellation in these sums.
- To provide certain systematics for manipulation of the various surviving terms.
- To construct the CC energy and amplitude equations far more quickly than by direct application of Wick's theorem.

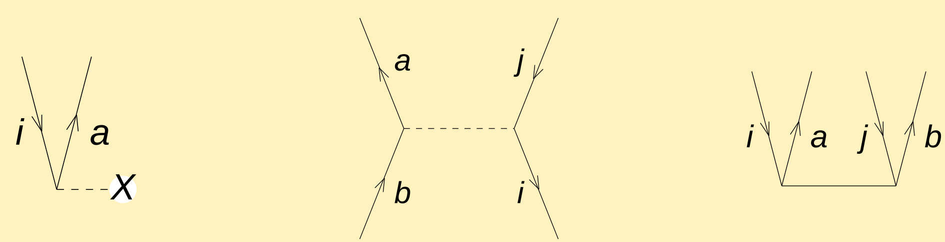
[1] S. A. Kucharski and R. J. Bartlett, "Fifth-order many-body perturbation theory and its relationship to various coupled-cluster approaches" *Adv. Quantum Chem.*, **1986**, *18*, 281.

Slater Determinant

- The reference state (the Fermi vacuum) $|\Phi_0\rangle$ is represented by nothing.
- Drawing upward and downward directed lines that identify those orbitals which differ from those in the reference determinant.
- Downward directed lines represent hole states (orbitals occupied in the reference).
- Upward directed lines represent particle states (orbitals unoccupied in the reference).

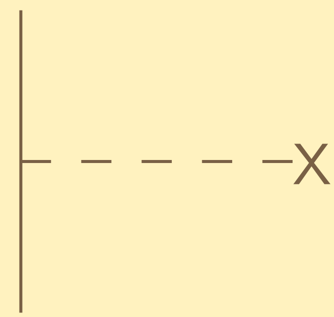


- Dashed line (- - -) indicates components of the electronic Hamiltonian.
- Solid line (—) indicates cluster operators $\hat{T}_1$, $\hat{T}_2$, etc.
- q-creation operators lie above the interaction line, whereas q-annihilation lines lie below the interaction line.



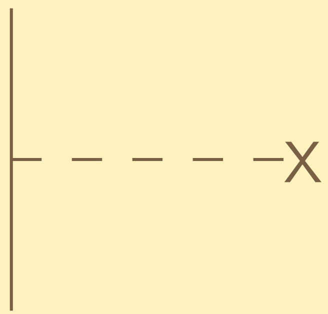
One Particle Operators

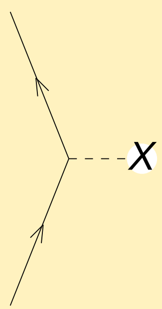
$$\sum_{pq} f_{pq} \{\hat{a}_p^\dagger \hat{a}_q\} =$$



One Particle Operators

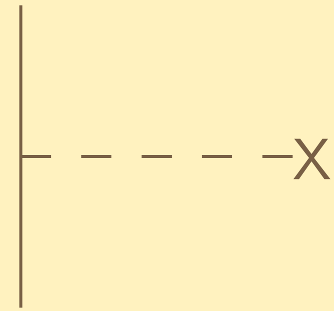
$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$

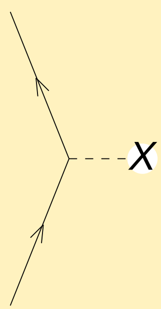


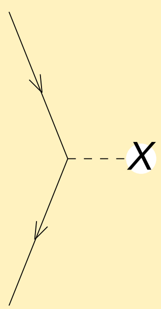


One Particle Operators

$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$

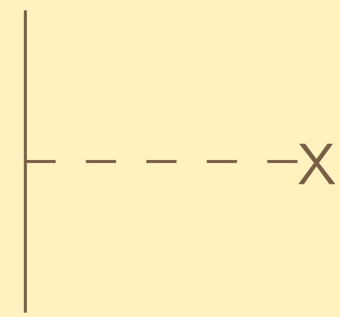


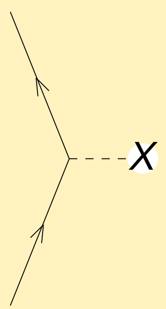


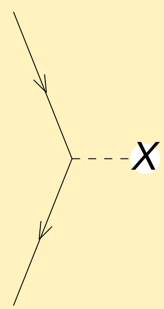


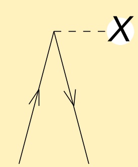
One Particle Operators

$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$



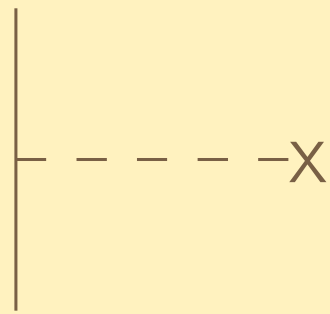






One Particle Operators

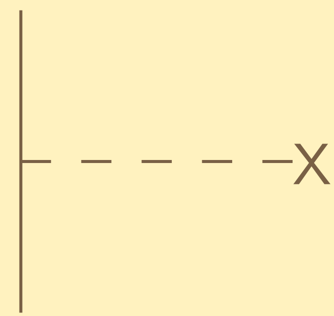
$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$



The Sherrill Group

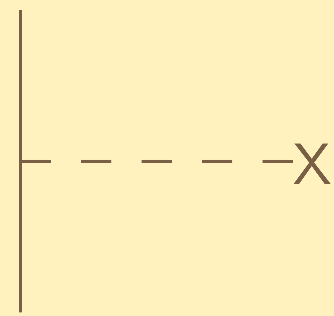
One Particle Operators

$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$



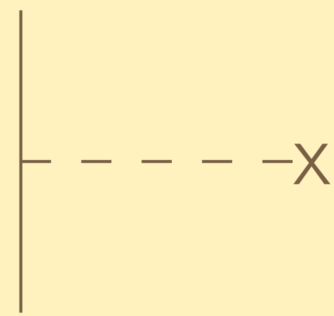
One Particle Operators

$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$



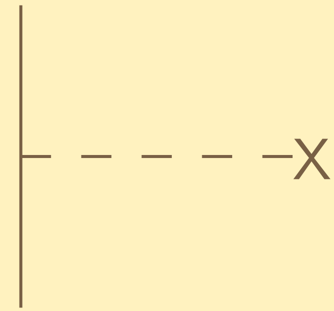
One Particle Operators

$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$



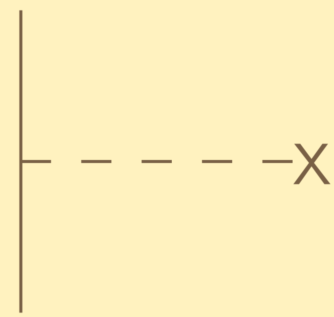
One Particle Operators

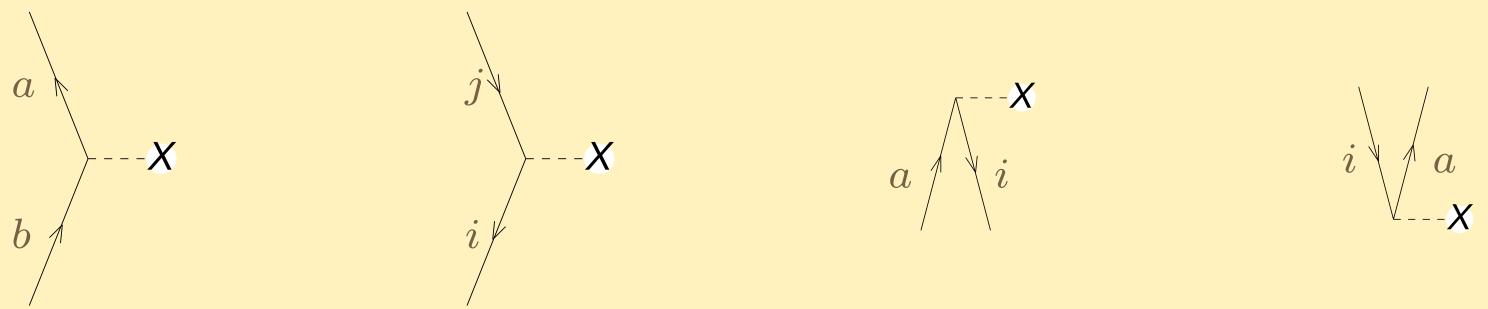
$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$



One Particle Operators

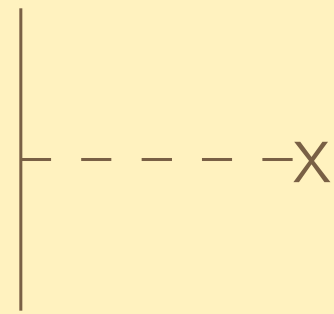
$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$





One Particle Operators

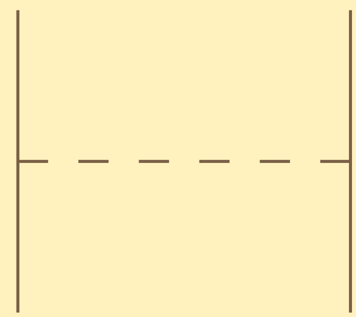
$$\sum_{pq} f_{pq}\{\hat{a}_p^\dagger \hat{a}_q\} =$$

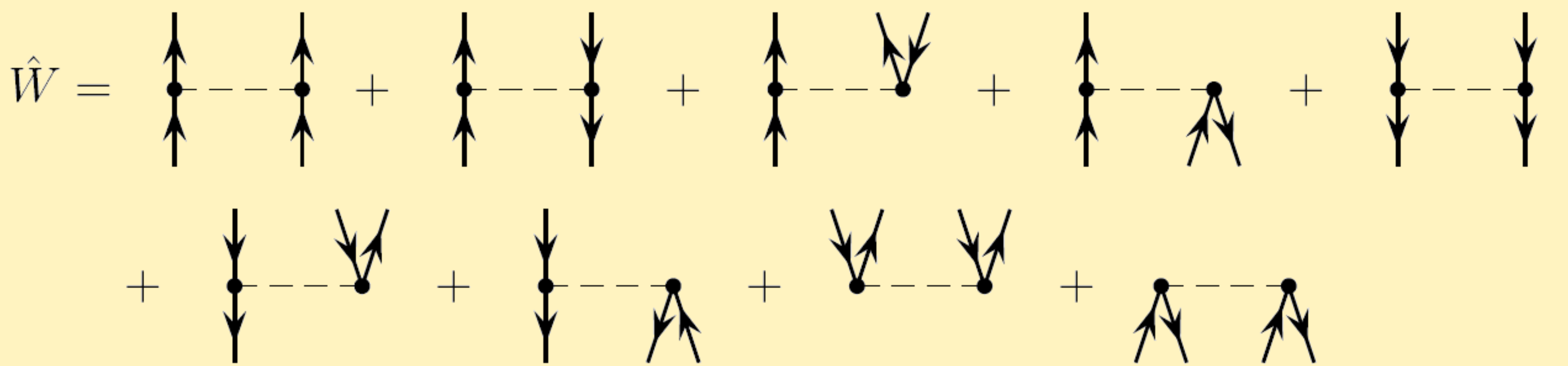


0 0 -1 $+1$

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$





The integral indices associated with a two-body vertex are assigned according to the scheme

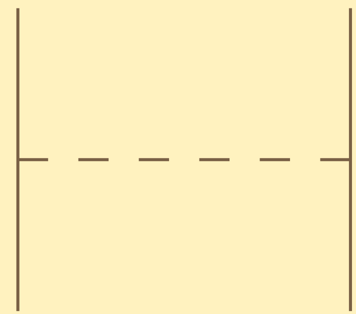
- $\langle$ left-out right-out $||$ left-in right-in $\rangle$

while the corresponding operator product can be described by

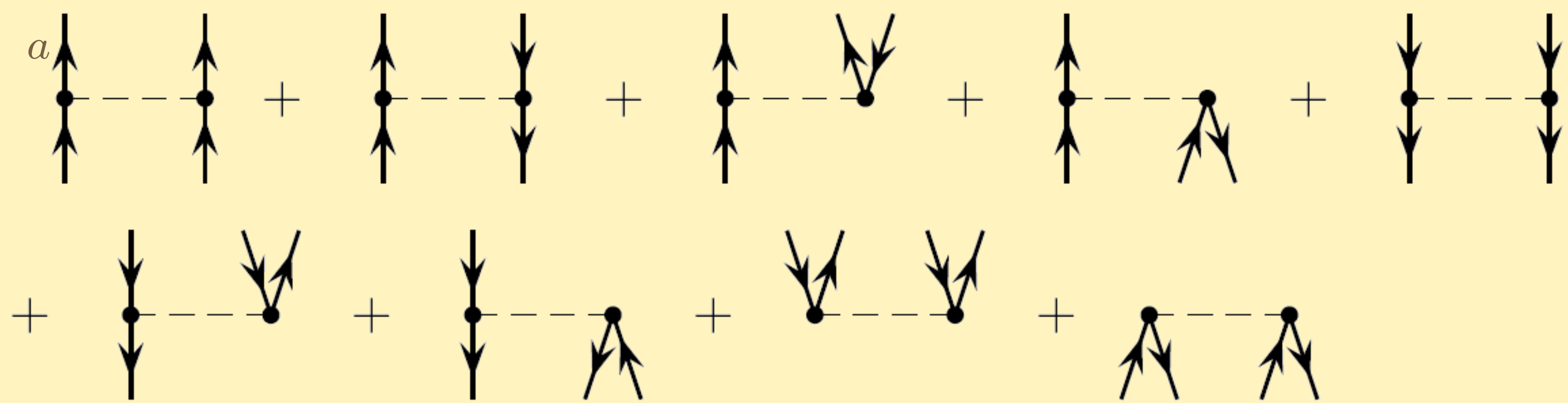
- $\{$(left-out)†(right-out)†(right-in)(left-in)$\}$

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$\hat{W} =$



The integral indices associated with a two-body vertex are assigned according to the scheme

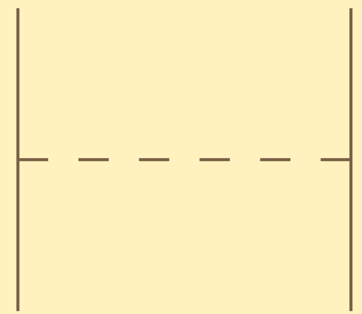
- ⟨ left-out right-out || left-in right-in ⟩

while the corresponding operator product can be described by

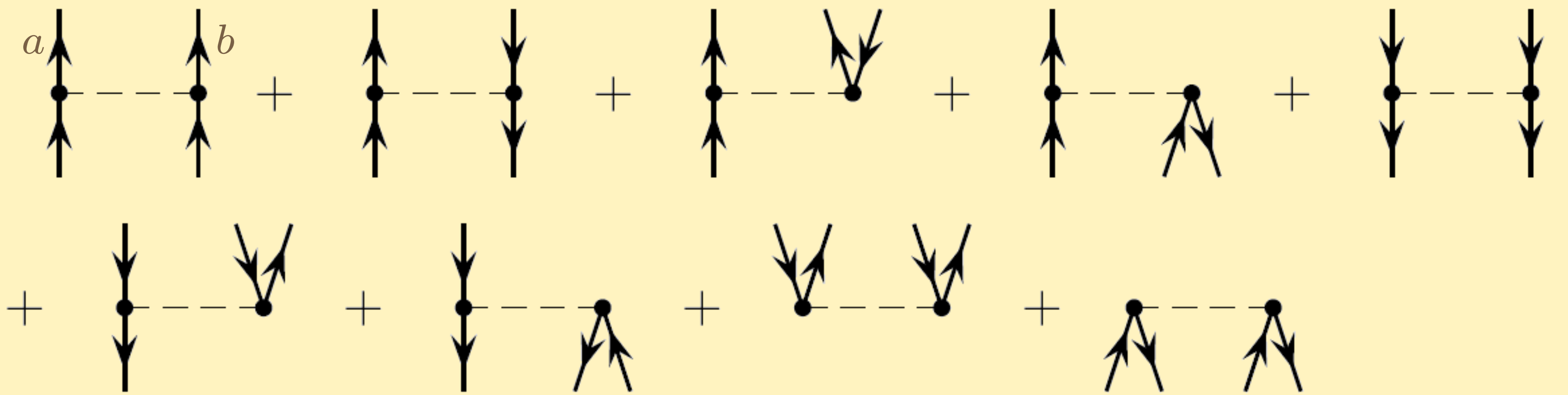
- {(left-out)†(right-out)†(right-in)(left-in)}

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$$\hat{W} =$$



The integral indices associated with a two-body vertex are assigned according to the scheme

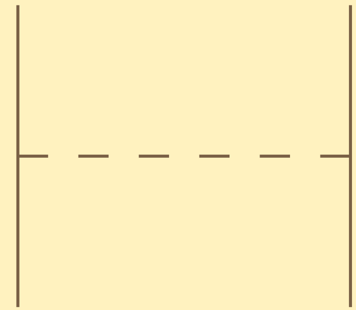
- ⟨ left-out right-out || left-in right-in ⟩

while the corresponding operator product can be described by

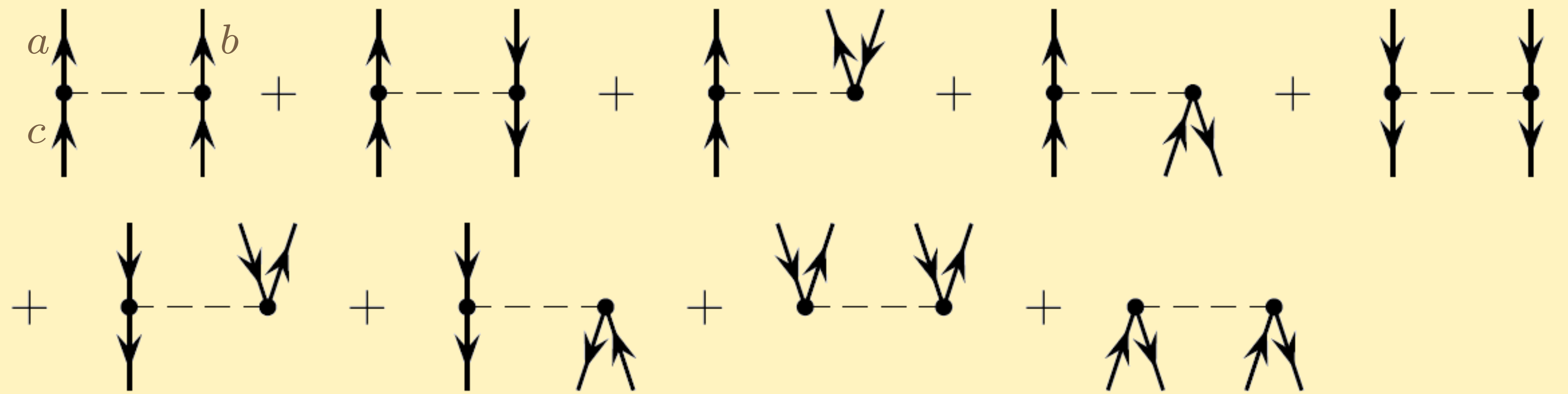
- {(left-out)†(right-out)†(right-in)(left-in)}

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$$\hat{W} =$$



The integral indices associated with a two-body vertex are assigned according to the scheme

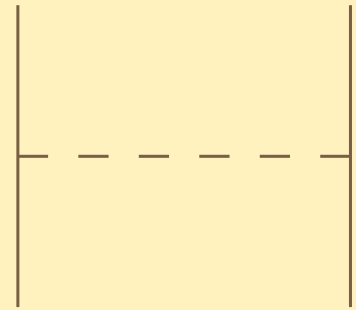
- ⟨ left-out right-out || left-in right-in ⟩

while the corresponding operator product can be described by

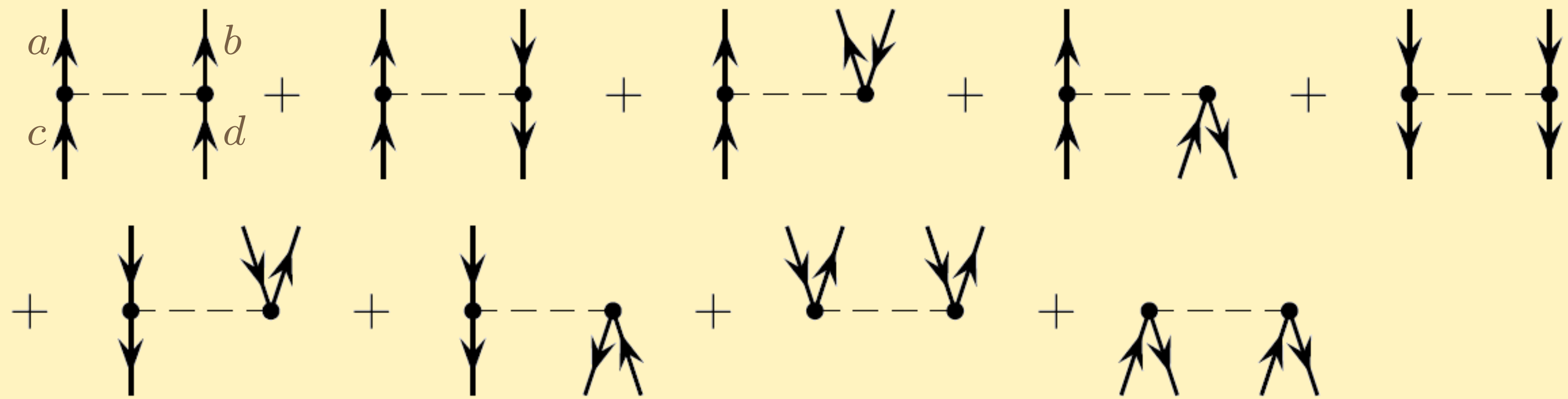
- {(left-out)†(right-out)†(right-in)(left-in)}

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$$\hat{W} =$$



The integral indices associated with a two-body vertex are assigned according to the scheme

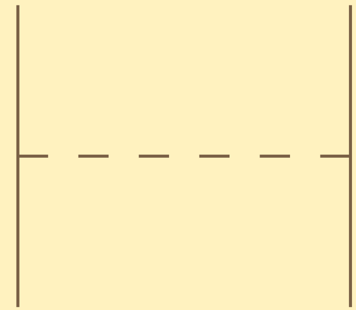
- ⟨ left-out right-out || left-in right-in ⟩

while the corresponding operator product can be described by

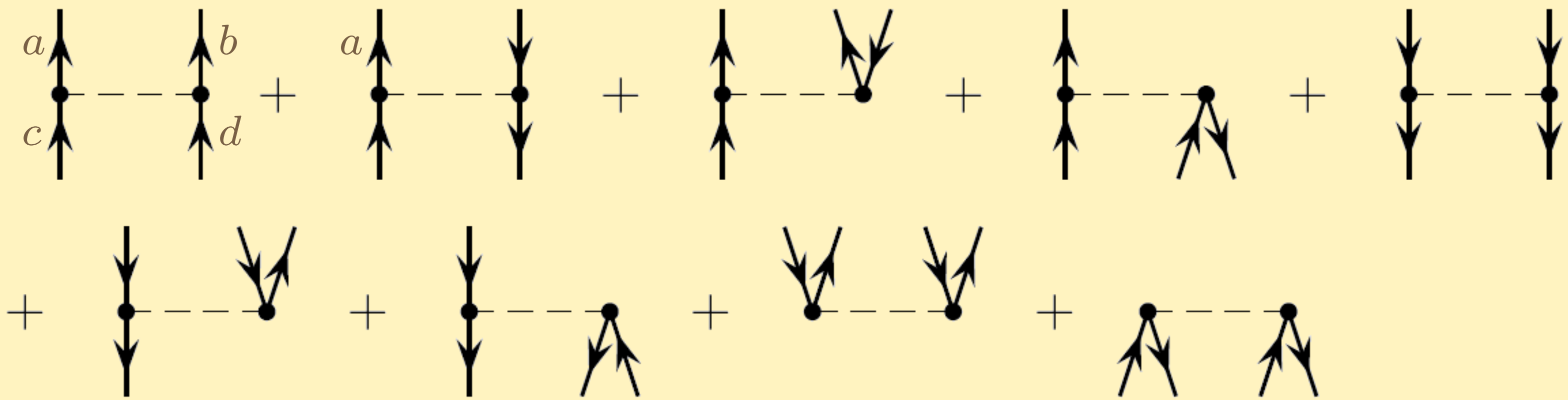
- {(left-out)†(right-out)†(right-in)(left-in)}

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$\hat{W} =$



The integral indices associated with a two-body vertex are assigned according to the scheme

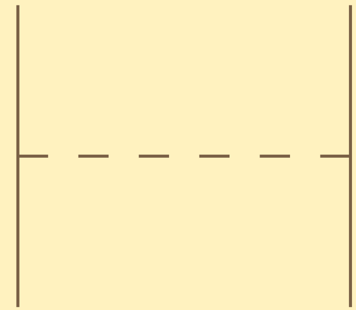
- $\langle$ left-out right-out $||$ left-in right-in $\rangle$

while the corresponding operator product can be described by

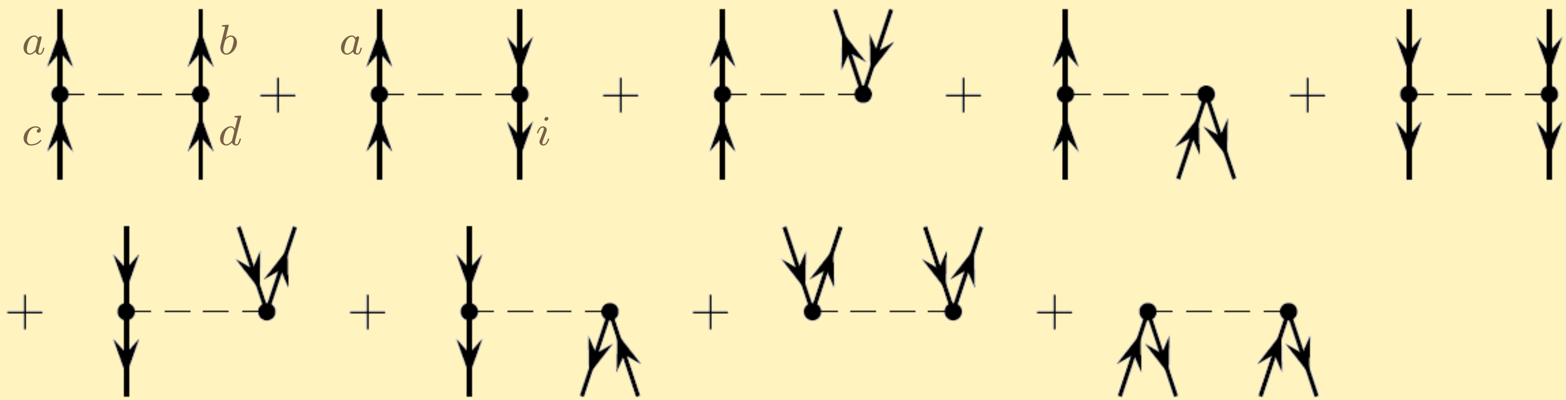
- $\{(\text{left-out})^\dagger(\text{right-out})^\dagger(\text{right-in})(\text{left-in})\}$

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$\hat{W} =$



The integral indices associated with a two-body vertex are assigned according to the scheme

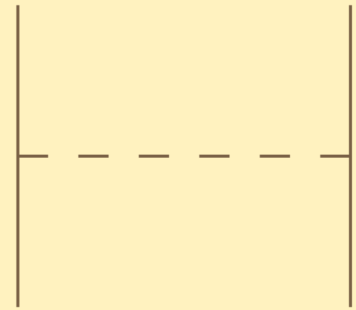
- ⟨ left-out right-out || left-in right-in ⟩

while the corresponding operator product can be described by

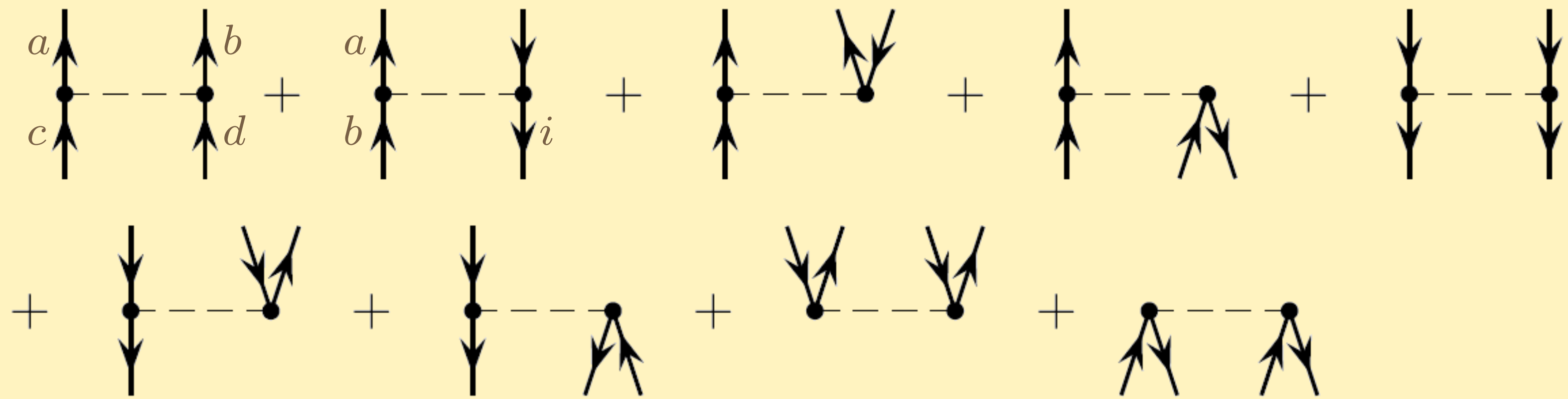
- {(left-out)†(right-out)†(right-in)(left-in)}

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$$\hat{W} =$$



The integral indices associated with a two-body vertex are assigned according to the scheme

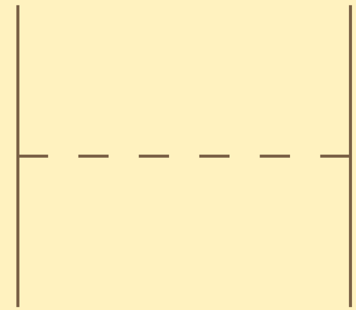
- ⟨ left-out right-out || left-in right-in ⟩

while the corresponding operator product can be described by

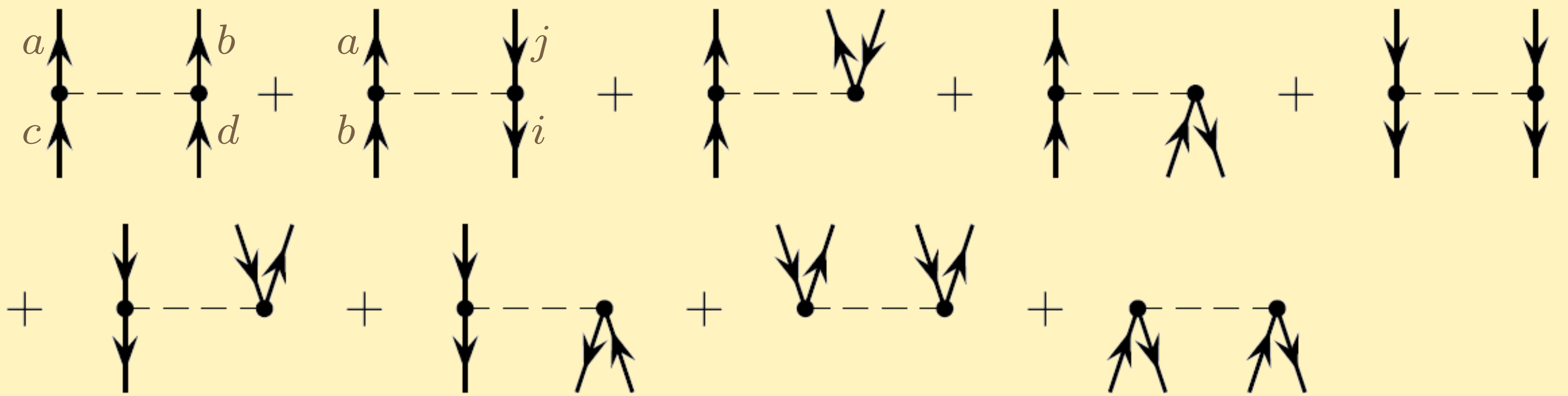
- {(left-out)†(right-out)†(right-in)(left-in)}

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$\hat{W} =$



The integral indices associated with a two-body vertex are assigned according to the scheme

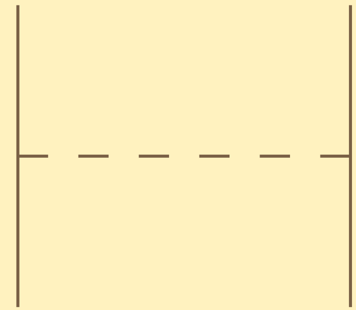
- ⟨ left-out right-out || left-in right-in ⟩

while the corresponding operator product can be described by

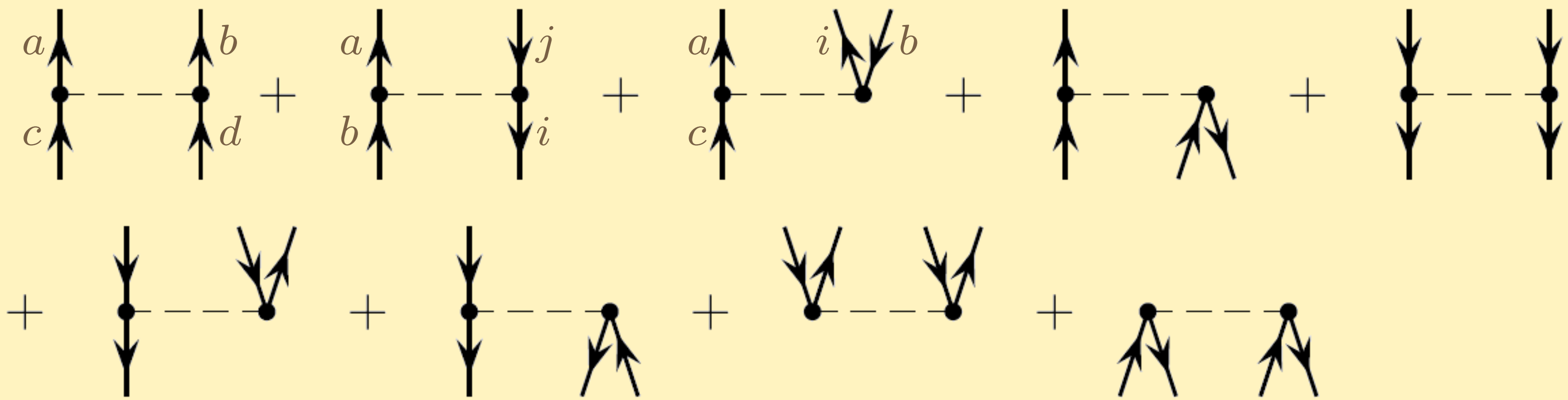
- {(left-out)†(right-out)†(right-in)(left-in)}

Two Particle Operators

$$\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} =$$



$\hat{W} =$



The integral indices associated with a two-body vertex are assigned according to the scheme

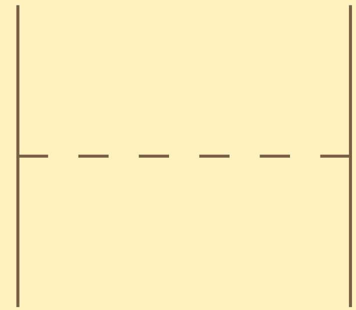
- $\langle$ left-out right-out $||$ left-in right-in $\rangle$

while the corresponding operator product can be described by

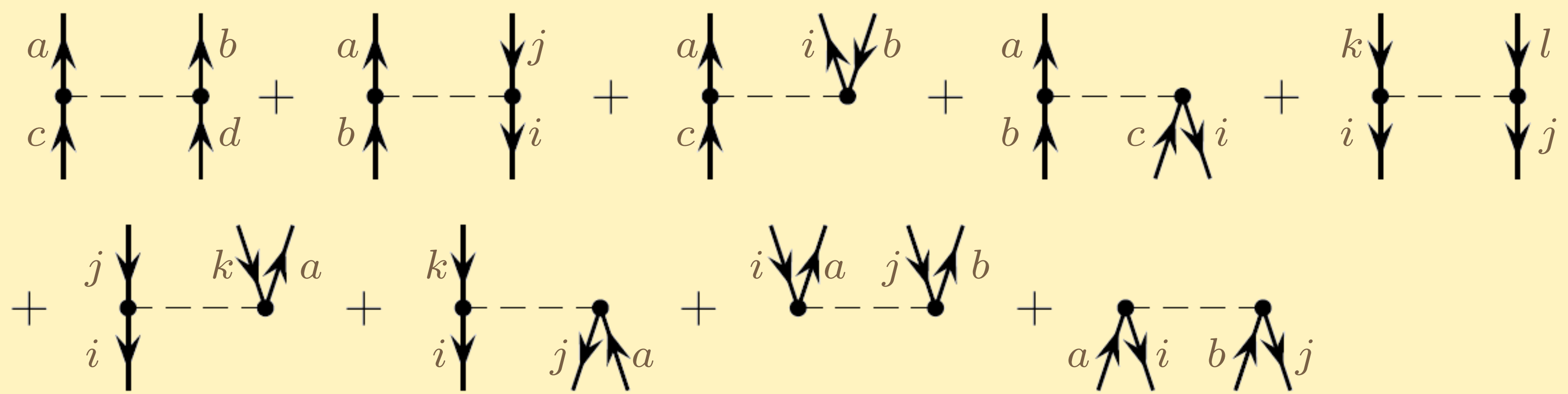
- $\{$(left-out)†(right-out)†(right-in)(left-in)$\}$

Two Particle Operators

$$\sum_{pqrs}\langle pq||rs\rangle\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\} =$$



$\hat{W} =$



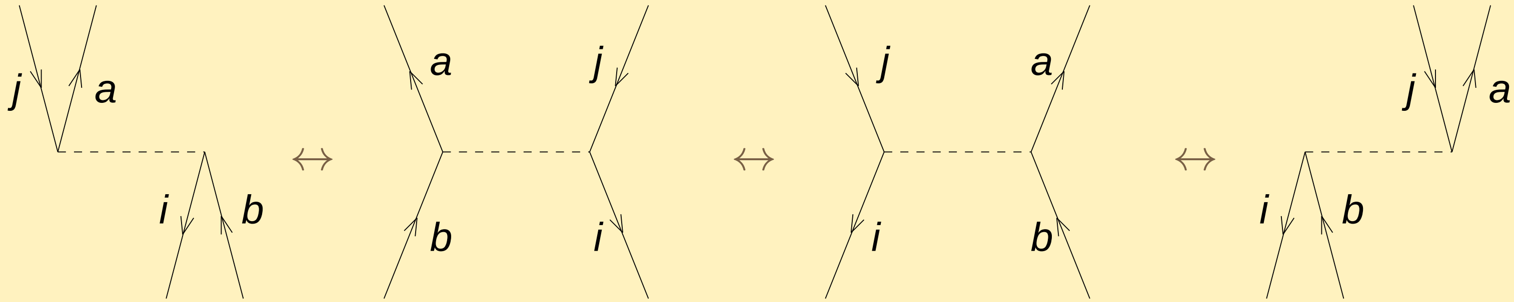
The integral indices associated with a two-body vertex are assigned according to the scheme

- ⟨ left-out right-out || left-in right-in ⟩

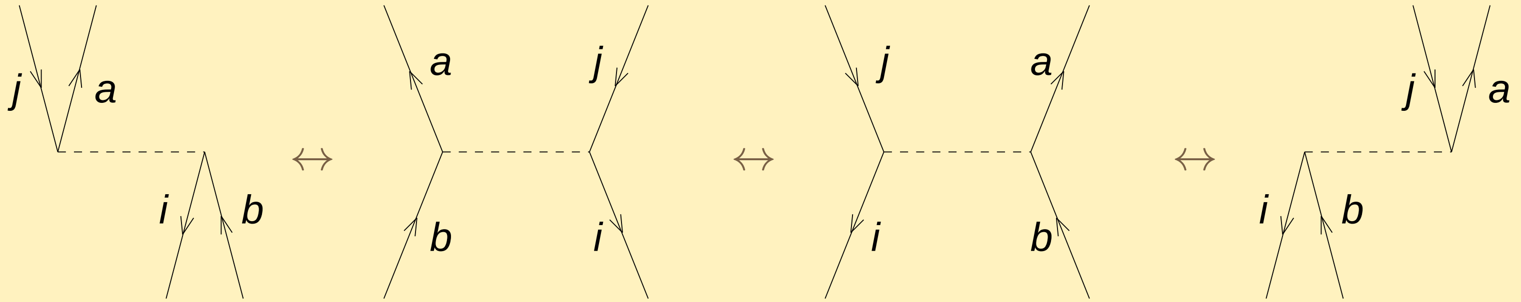
while the corresponding operator product can be described by

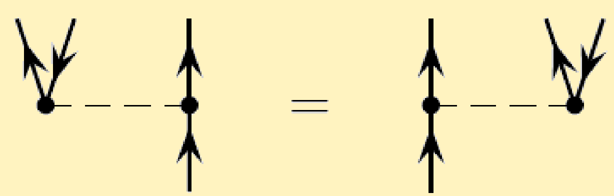
- {(left-out)†(right-out)†(right-in)(left-in)}

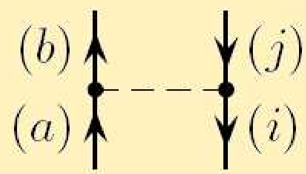
Two Particle Operators



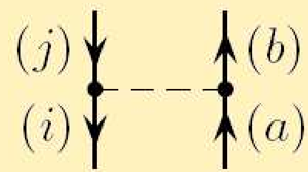
Two Particle Operators





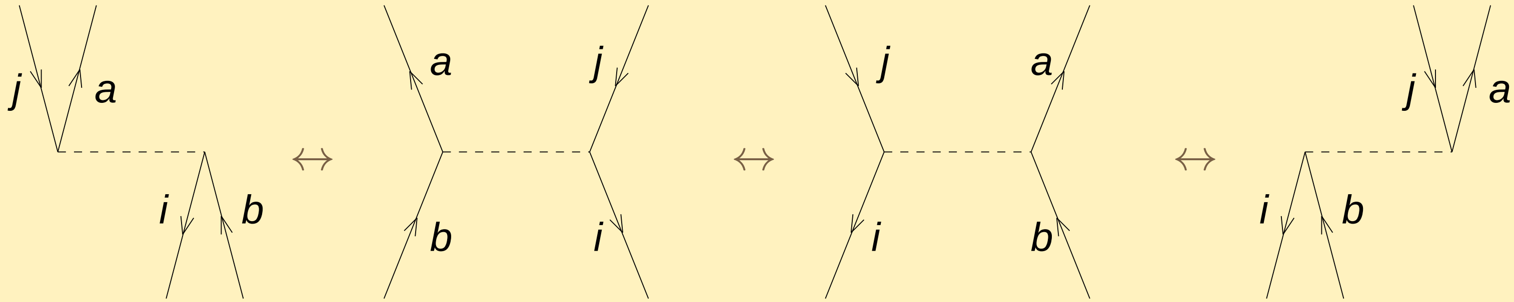


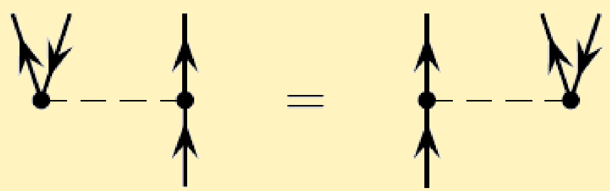
$$= \frac{1}{2}\sum_{abij}\langle bi|aj\rangle\{\hat{b}^\dagger\hat{i}^\dagger\hat{j}\hat{a}\}$$

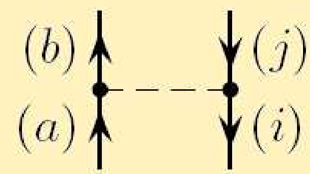


$$= \frac{1}{2}\sum_{abij}\langle ib|ja\rangle\{\hat{i}^\dagger\hat{b}^\dagger\hat{a}\hat{j}\}$$

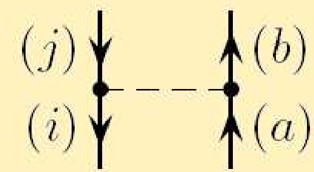
Two Particle Operators





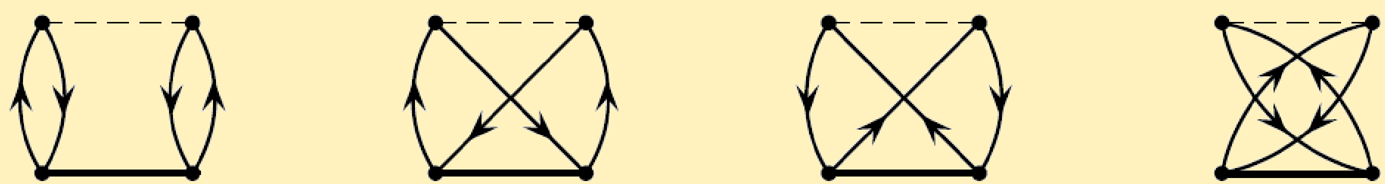


$$= \frac{1}{2}\sum_{abij}\langle bi|aj\rangle\{\hat{b}^\dagger\hat{i}^\dagger\hat{j}\hat{a}\}$$

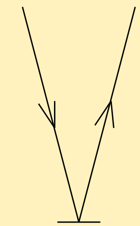


$$= \frac{1}{2}\sum_{abij}\langle ib|ja\rangle\{\hat{i}^\dagger\hat{b}^\dagger\hat{a}\hat{j}\}$$

- the weight factor

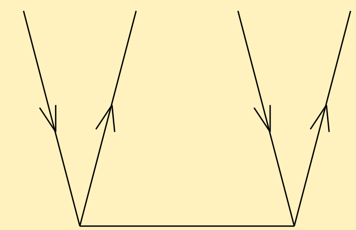


$$\hat{T}_1 = \sum_{ia} t_i^a \{\hat{a}_a^\dagger \hat{a}_i\} =$$



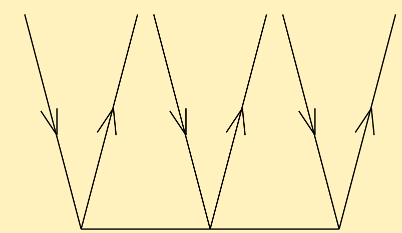
+1

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \{\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i\} =$$



+2

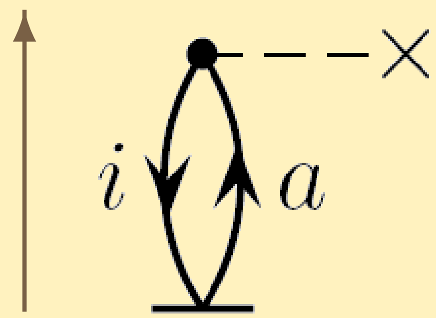
$$\hat{T}_3 = \frac{1}{36} \sum_{ijkabc} t_{ijk}^{abc} \{\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_k \hat{a}_j \hat{a}_i\} =$$



+3

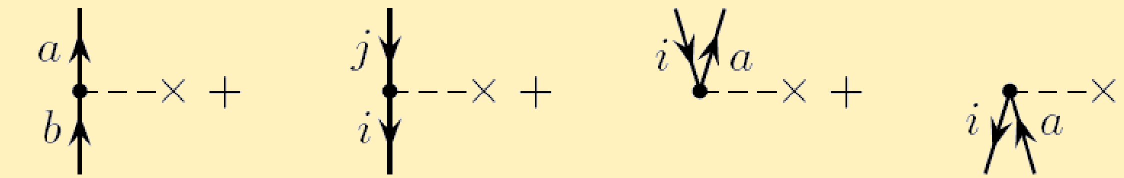
Time ordering

1. **Fictitious time**



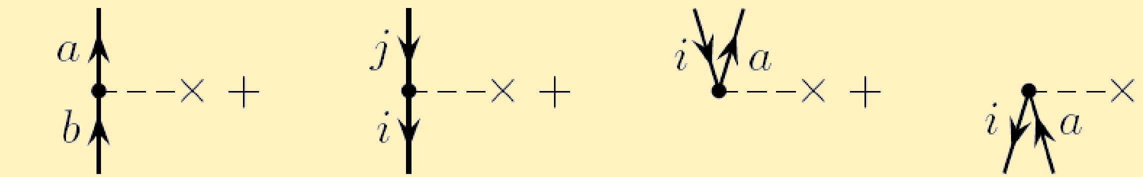
$$\sum_{ai} \langle 0 | f_{ia} \{ \hat{a}_i^\dagger \hat{a}_a \} t_i^a \{ \hat{a}_a^\dagger \hat{a}_i \} | 0 \rangle \qquad (1)$$

Systematic generation of CC diagrams

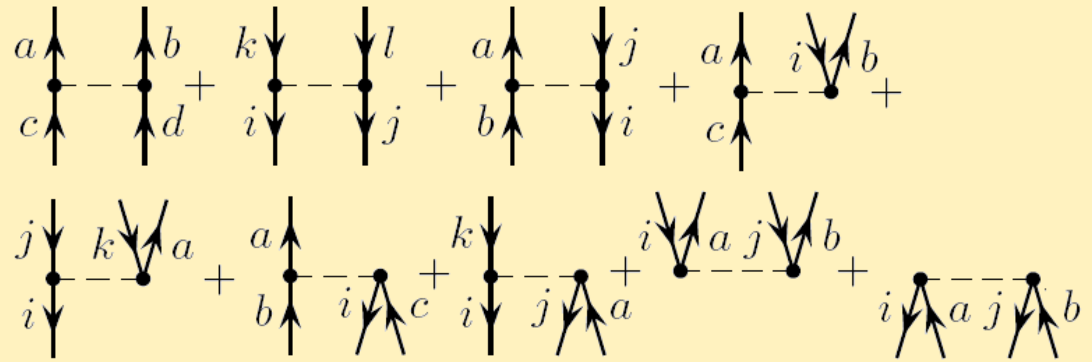
$\hat{F}_{\mathrm{N}} =$ 

Systematic generation of CC diagrams

$\hat{F}_{\mathrm{N}} =$

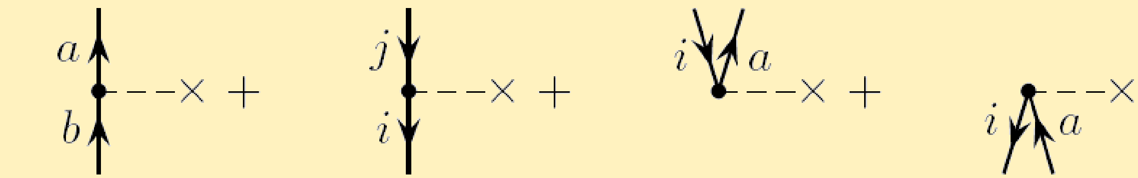


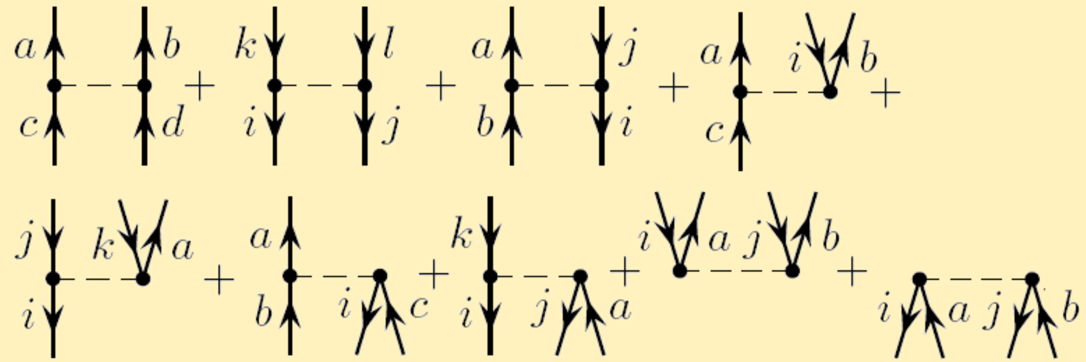
$\hat{W} =$

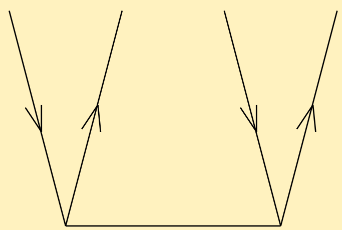
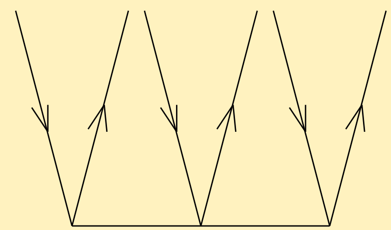


The Sherrill Group

Systematic generation of CC diagrams

$\hat{F}_{\mathrm{N}} =$ 

$\hat{W} =$ 

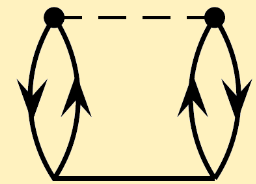
$T_1 =$  , $T_2 =$  , $T_3 =$ 

Diagrammatic derivation of the CCD equations

The CCD energy is given by

$$\langle 0|\hat{H}_N \hat{T}_2|0\rangle \tag{2}$$

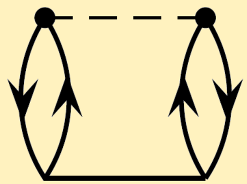
$$\Delta E_{\mathrm{CCD}} =$$

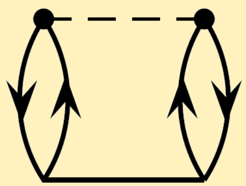


Diagrammatic derivation of the CCD equations

The CCD energy is given by

$$\langle 0|\hat{H}_N \hat{T}_2|0\rangle \tag{2}$$

$$\Delta E_{\text{CCD}} =$$ 

 $$= \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}$$

The Sherrill Group

CCD from Algebraic Method

$$
\begin{aligned}
\left(\hat{F}_N \hat{T}_2\right)_c &= \frac{1}{4} \sum_{pq} \sum_{aibj} f_{pq} t_{ij}^{ab} \{a_p^\dagger a_q\}\{a_a^\dagger a_b^\dagger a_j a_i\} \\
&= \frac{1}{4} \sum_{pq} \sum_{aibj} f_{pq} t_{ij}^{ab} \Big(\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \\
&\quad \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \\
&\quad \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\} \Big) .
\end{aligned}
$$

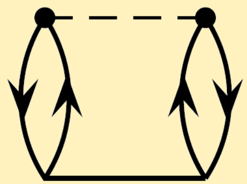
$$
\begin{aligned}
\langle \Phi_0 | \left(\hat{V}_N \hat{T}_2\right)_c | \Phi_0 \rangle &= \frac{1}{16} \sum_{pqrs} \sum_{aibj} \langle pq||rs \rangle t_{ij}^{ab} \langle \Phi_0 | \{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_b^\dagger a_j a_i\} | \Phi_0 \rangle \\
&= \frac{1}{16} \sum_{pqrs} \sum_{aibj} \langle pq||rs \rangle t_{ij}^{ab} \Big(\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} + \\
&\qquad \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} \Big) \\
&= \frac{1}{16} \sum_{pqrs} \sum_{aibj} \langle pq||rs \rangle t_{ij}^{ab} \left(\delta_{pi}\delta_{qj}\delta_{ra}\delta_{sb} + \delta_{pj}\delta_{qi}\delta_{rb}\delta_{sa} - \delta_{pj}\delta_{qi}\delta_{ra}\delta_{sb} - \delta_{pi}\delta_{qj}\delta_{rb}\delta_{sa} \right) \\
&= \frac{1}{4} \sum_{aibj} \langle ij||ab \rangle t_{ij}^{ab} .
\end{aligned}
$$

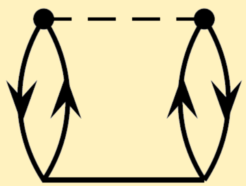
Diagrammatic derivation of the CCD equations

The CCD energy is given by

$$\langle 0|\hat{H}_N \hat{T}_2|0\rangle \tag{3}$$

$$\Delta E_{\mathrm{CCD}} =$$





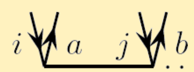
$$= \frac{1}{4}\sum_{ijab} \langle ij\|ab\rangle t_{ij}^{ab}$$

Interpretation rules for coupled-cluster diagrams

1. Up-going lines are labeled with a “particle” and are labeled with $a, b, c, d, \ldots$; down-going lines are holes and are labeled with $i, j, k, l, \ldots$ particle lines with $a, b, c, d, \ldots$.

2. One-particle interaction vertices should be interpreted as the integral $\langle$ out(left) $|$ operator $|$ in (right) $\rangle$.

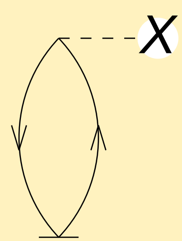
3. Two particle vertices corresponds to the antisymmetrized integrals $\langle$ left-out right-out $||$ left-in right-in $\rangle$.

4. With every T_m vertex 

associate an amplitude $t_{ij\ldots}^{ab\ldots}$

5. Sum over all internal line labels, i. e., lines terminating below the last $\hat{H}_N$.

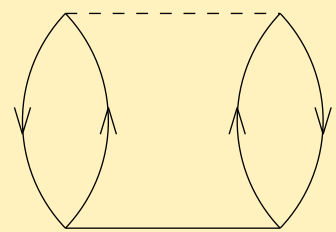
6. The sign of the diagram is $(-1)^{h+l}$, where h is the number of hole lines and l is the number of loops. (for open diagrams fictitious external loop should be included).



$$= \sum_{ia} f_{ia} t_i^a, \qquad (4)$$

Interpretation rules for coupled-cluster diagrams

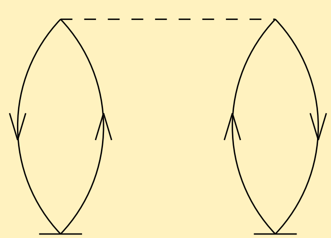
7. The weight factor for diagrams is specified by $\left(\frac{1}{2}\right)^m$, wher m is the number of pairs of "equivalent" lines. (Two internal lines are considered equivalent if they connect the same two vertices, going in the same direction.)



$$= \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}. \tag{5}$$

8. To maintain full antisymmetry of an amplitude, the algebraic expression for a diagram should be preceded by a permutation operator permuting the open lines in all distinct ways, $\sum_p(-1)^p\hat{P}(ij\ldots|ab\ldots)$

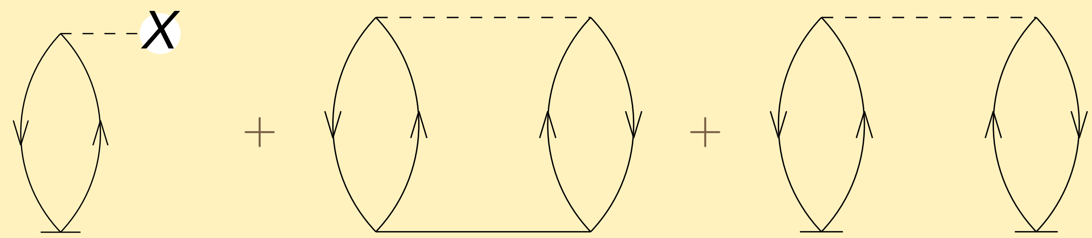
9. *For energy diagrams* include a factor of $\left(\frac{1}{2}\right)$ for each "equivalent" vertices. (if there are n equivalent vertices in the diagram, they contribute a prefactor of $\frac{1}{n!}$ to the final expression.)



$$= \frac{1}{2}\sum_{ijab}\langle ij||ab\rangle t_i^a t_j^b. \tag{6}$$

CCSD Energy Diagrams

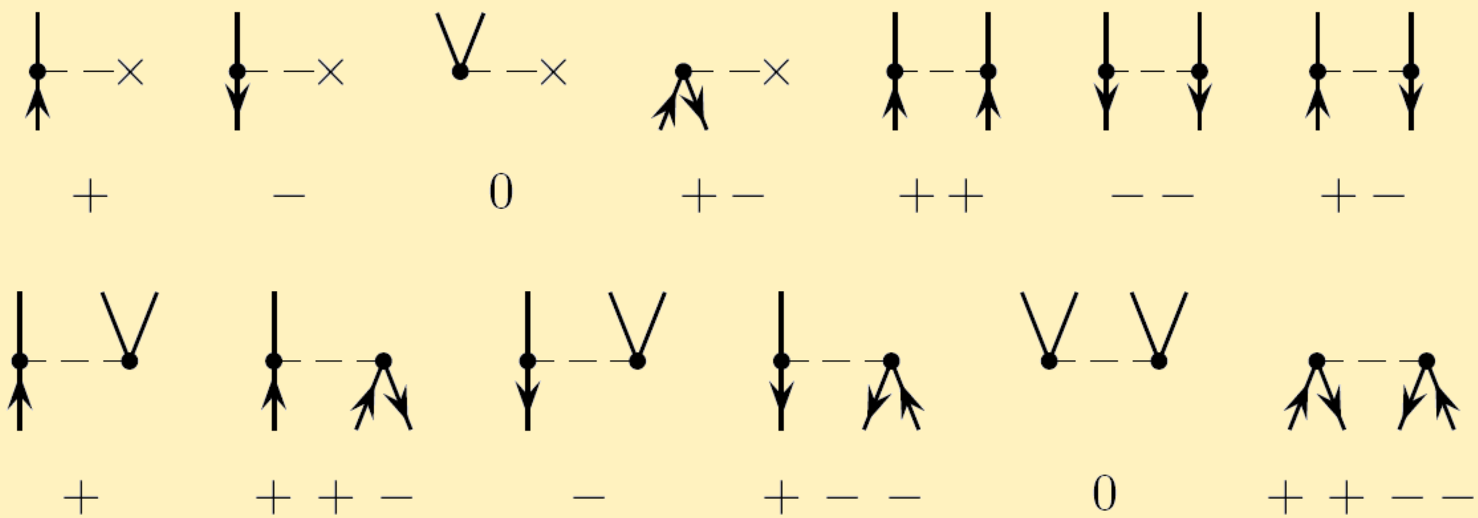
$$E_{\mathrm{CCSD}} - E_0 =$$



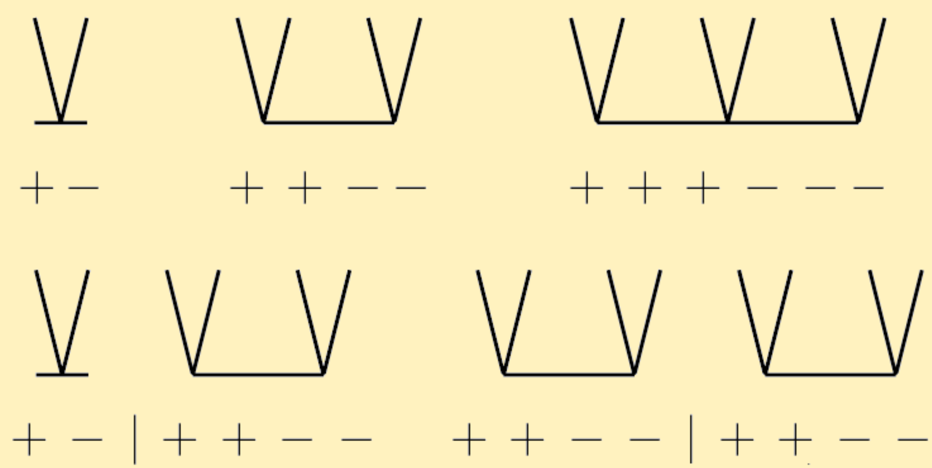
$$= \sum_{ia} f_{ia} t_i^a + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b, \quad (7)$$

Systematic generation of CC diagrams

The Hamiltonian-operator vertices are assigned following labels

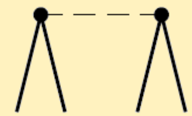


The cluster-operator vertices are given the following labels:



Systematic generation of CC diagrams

- $\langle \Psi_{ij}^{ab} | (\hat{T}_2)^2 | 0 \rangle$ Term as an example



$$+ + - -$$

$$+ + - - \,|\, + + - -$$

The contraction patterns that connect both $(\hat{T}_2)^2$ vertices to the interaction vertex:

$$+ + \,|\, - - \qquad + - \,|\, + - \qquad + + - \,|\, - \qquad + - - \,|\, +$$