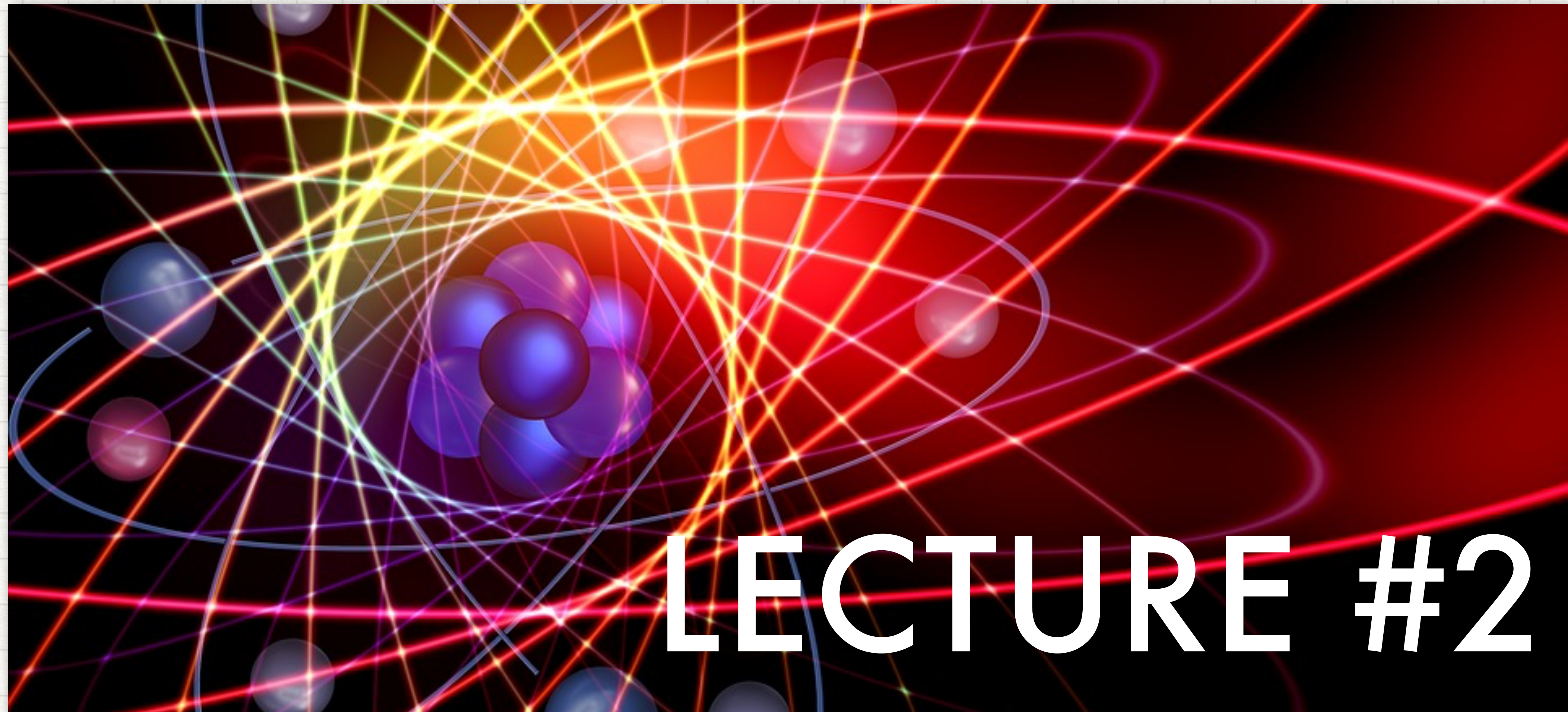


COUPLED CLUSTER THEORY

PROF. T. DANIEL CRAWFORD, VIRGINIA TECH



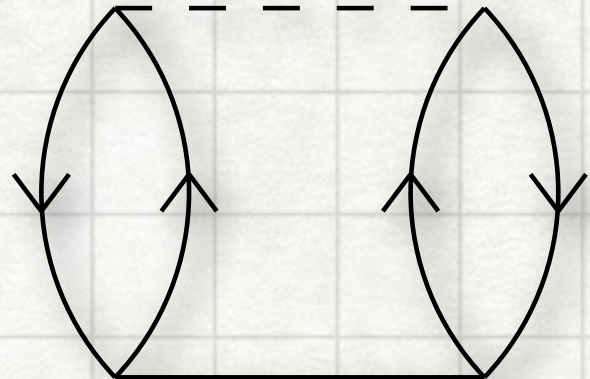
LECTURE #2

Coester and Kümmel adopted the name “exp- S method”, after the form of the wave function (2) and the symbol S for the cluster operation. Cizek and Paldus introduced the term “Coupled-Pair Many Electron Theory” (CPMET), and extended CPMET, from their emphasis on $T \simeq T_2$, explicit equations for which were first obtained by Cizek [3a]. We prefer the denotation **Coupled-Clutter Method (CCM)** since it suggests most vividly the central features of admissibility of general-sized clusters and coupling of them in a nonlinear fashion. It is worth pointing out that Eq. (28) represents not a unitary but rather a similarity transformation. This is unlike the situation in work like that of Westhaus [8], as it voids the termination of the commutator series but preserves the Hermiticity of the transformed Hamiltonian.

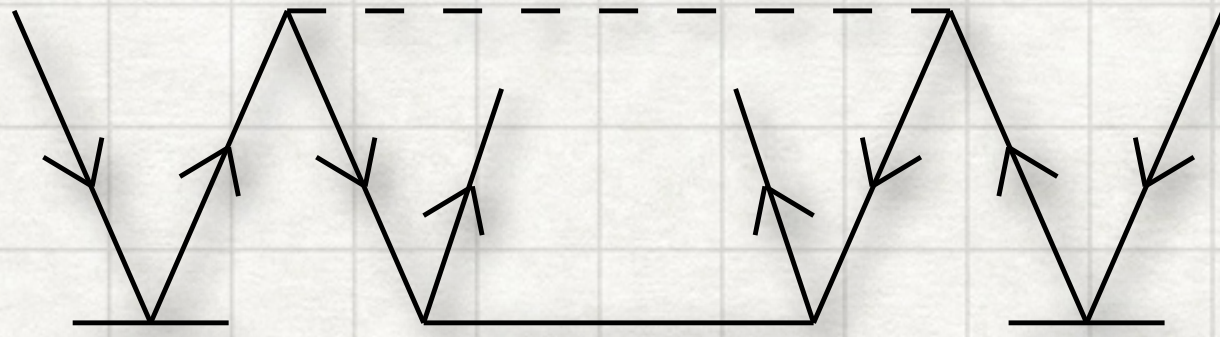
H.J. Monkhorst, “Calculation of properties with the coupled-cluster method”,
Int. J. Quantum Chem. Symp., 11, 421-432 (1977).

DIAGRAMS: THE BASICS

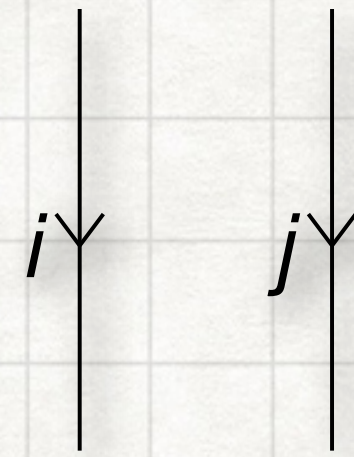
Diagrammatic methods are designed to simplify the derivation of the programmable equations for coupled cluster theory and other many-electron methods. They provide topological representations of the necessary operators, wave functions, and matrix elements that we may interpret algebraically using a relatively simple set of rules.

$$\langle \Phi_0 | \left(\hat{H}_N \hat{T}_2 \right)_c | \Phi_0 \rangle = \text{Diagram} = \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}$$


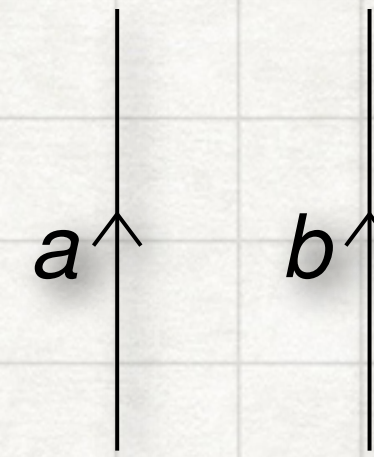
$$\frac{1}{2} \langle \Phi_i^a | \left(\hat{F}_N \hat{T}_1^2 \right)_c | \Phi_0 \rangle = \text{Diagram} = - \sum_{jb} f_{jb} t_i^b t_j^a$$


$$\frac{1}{2} \langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1^2 \hat{T}_2 \right)_c | \Phi_0 \rangle \rightarrow \text{Diagram} = \frac{1}{4} P(ij) \sum_{klcd} \langle kl || cd \rangle t_{kl}^{cd} t_i^c t_j^d$$


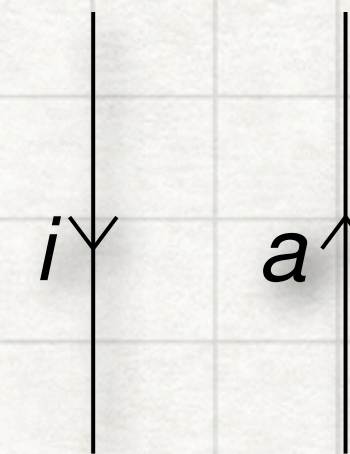
DIAGRAMS: THE BASICS



Holes
(Occupied Orbitals)



Particles
(Virtual Orbitals)



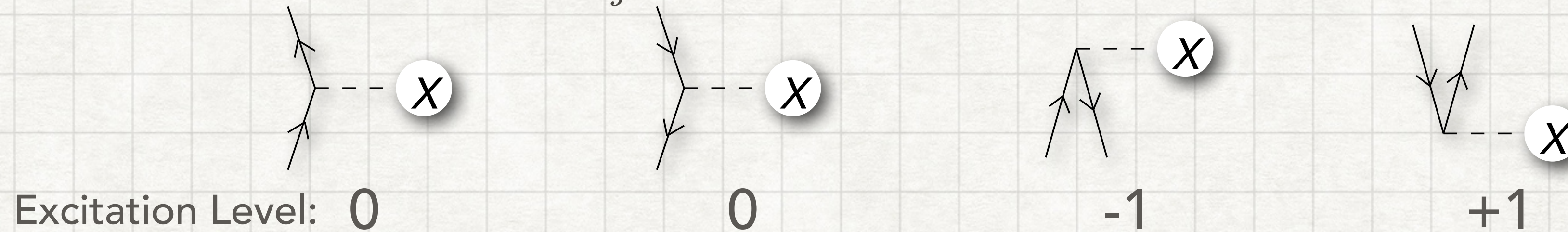
The Fermi Vacuum, $|\Phi_0\rangle$
(Empty Space)

A Singly Excited
Determinant, $|\Phi_i^a\rangle$

DIAGRAMS: THE BASICS

- Diagrammatic representation of the Fock operator

$$\hat{F}_N = \sum_{ab} f_{ab} \{a_a^\dagger a_b\} + \sum_{ij} f_{ij} \{a_i^\dagger a_j\} + \sum_{ia} f_{ia} \{a_i^\dagger a_a\} + \sum_{ai} f_{ai} \{a_a^\dagger a_i\}$$

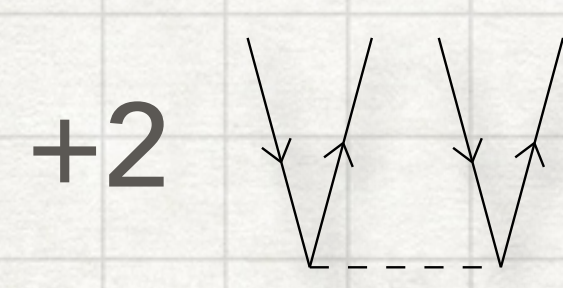
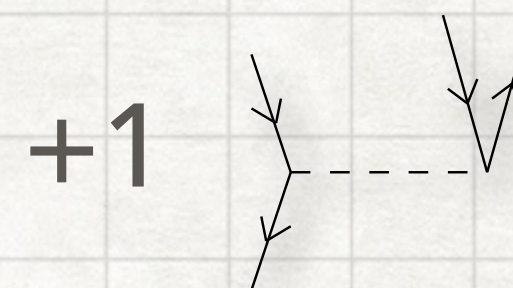
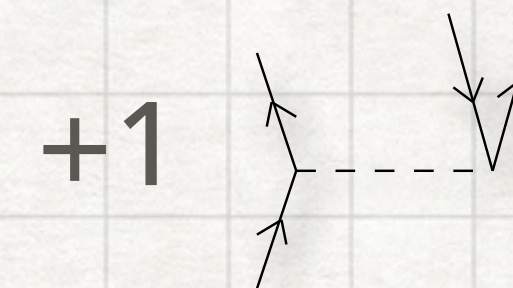
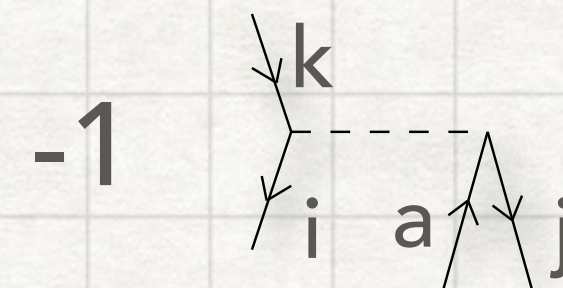
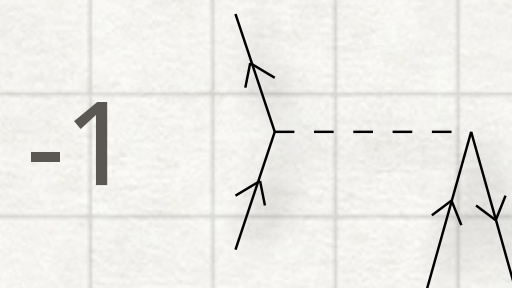
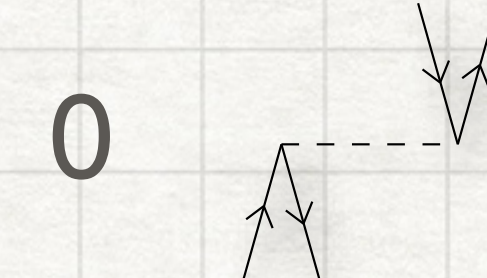
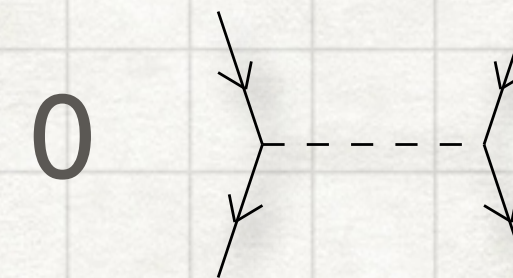
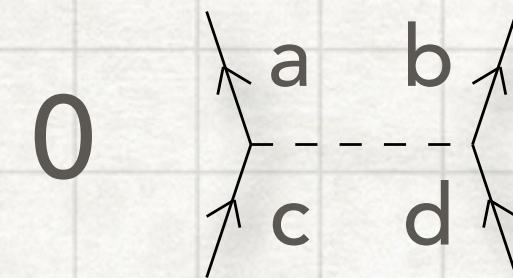


- The dashed horizontal line represents the Fock operator (the "interaction line").
- The directed lines (arrows) connect to the "vertices" and represent the annihilation/creation operators. Each vertex can connect to two directed lines, at most.
- The outgoing/incoming lines at the vertex are the left-/right-hand orbital indices in the integral.
- Directed lines above the operator are "quasiparticle creation operators" ($a_a^\dagger$ or a_i), and those below are "quasiparticle annihilation operators" (a_a or $a_i^\dagger$).
- The excitation level of a diagram is the difference in the number of lines above and below the operator line divided by 2.

DIAGRAMS: THE BASICS

Diagrammatic representation of the two-electron Hamiltonian component:

$$\begin{aligned}\hat{V}_N = & \frac{1}{4} \sum_{abcd} \langle ab || cd \rangle \{a_a^\dagger a_b^\dagger a_d a_c\} + \frac{1}{4} \sum_{ijkl} \langle ij || kl \rangle \{a_i^\dagger a_j^\dagger a_l a_k\} + \sum_{iabj} \langle ia || bj \rangle \{a_i^\dagger a_a^\dagger a_j a_b\} \\ & + \frac{1}{2} \sum_{aibc} \langle ai || bc \rangle \{a_a^\dagger a_i^\dagger a_c a_b\} + \frac{1}{2} \sum_{ijka} \langle ij || ka \rangle \{a_i^\dagger a_j^\dagger a_a a_k\} + \frac{1}{2} \sum_{abci} \langle ab || ci \rangle \{a_a^\dagger a_b^\dagger a_i a_c\} \\ & + \frac{1}{2} \sum_{iajk} \langle ia || jk \rangle \{a_i^\dagger a_a^\dagger a_k a_j\} + \frac{1}{4} \sum_{abij} \langle ab || ij \rangle \{a_a^\dagger a_b^\dagger a_j a_i\} + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle \{a_i^\dagger a_j^\dagger a_b a_a\}\end{aligned}$$



- For two-electron operators/integrals, the ordering of indices is:

$\langle \text{left-out right-out} || \text{left-in right-in} \rangle$

DIAGRAMS: THE BASICS

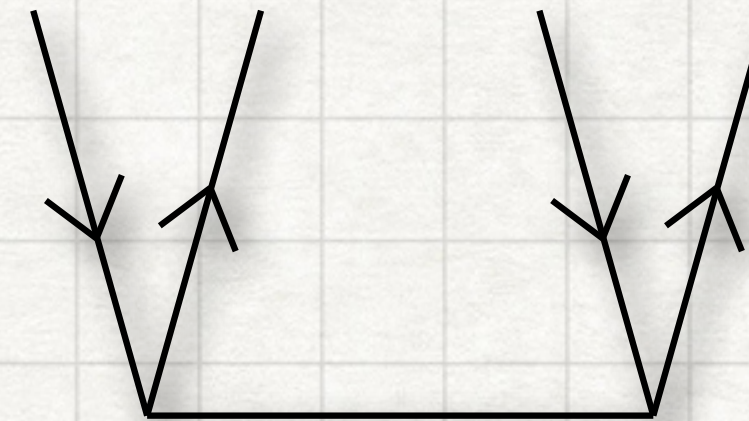
Diagrammatic representation of cluster operators:

$$\hat{T}_1 = \sum_{ia} t_i^a \{a_a^\dagger a_i\}$$



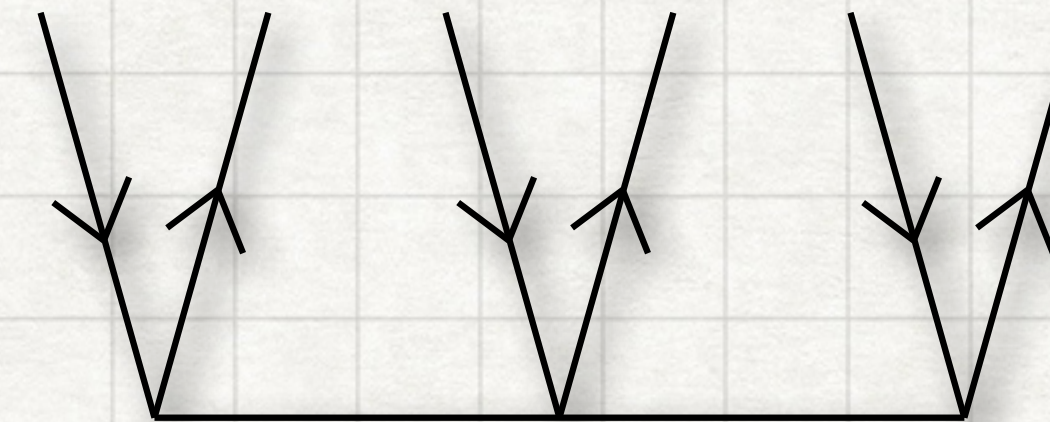
+1

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\}$$



+2

$$\hat{T}_3 = \frac{1}{36} \sum_{ijkabc} t_{ijk}^{abc} \{a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i\}$$



+3

- We choose a solid (rather than dashed) interaction line to distinguish the $\hat{T}_n$ from $\hat{F}_N$ and $\hat{V}_N$.
- All lines are quasiparticle creation lines in this case because these are excitation operators.

DIAGRAMS: MATRIX ELEMENTS

We usually interpret our diagrams as matrix elements of second-quantized operators (or products of such operators) between Slater determinants:

- Right-to-left in a matrix element corresponds to bottom-to-top in a given diagram.
- Examples:

$$\langle \Phi_i^a | \hat{F}_N | \Phi_0 \rangle = \text{Diagram: A vertex with two incoming lines from the left labeled } i \text{ and } a, \text{ and two outgoing lines to the right. A circle with an } X \text{ is to the right of the vertex.}$$

$$\langle \Phi_i^a | \hat{V}_N | \Phi_j^b \rangle = \text{Diagram: Two vertices connected by a horizontal dashed line. The left vertex has two incoming lines from the left labeled } j \text{ and } b. \text{ The right vertex has two incoming lines from the left labeled } i \text{ and } a.$$

$$\langle \Phi_{ij}^{ab} | \hat{T}_2 | \Phi_0 \rangle = \text{Diagram: Two vertices connected by a horizontal solid line. The left vertex has two incoming lines from the left labeled } i \text{ and } a. \text{ The right vertex has two incoming lines from the left labeled } j \text{ and } b.$$

DIAGRAMS: THE CC ENERGY

- We are now ready to construct diagrams representing the components of the coupled cluster energy equation. We'll start with the simplest term that is linear in $\hat{T}_1$:

$$\langle \Phi_0 | \left(\hat{F}_N \hat{T}_1 \right)_c | \Phi_0 \rangle = i \text{ (diagram: a loop with a dashed line and an 'X' in a circle) } = \sum_{ia} \sum_{ia} f_{ia} t_{ia}^a$$

- To interpret this algebraically:
 - Label all directed lines with appropriate indices: $i, j, k, \dots; a, b, c, \dots$
 - Include summations for all "internal" lines (those that begin and end at operator lines). "External" lines start at an operator line and extend above or below the diagram.
 - Interpret the lines connected to the Fock operator and $\hat{T}_1$ vertices as:

$$f_{\text{left-out right-in}} \quad t_{\text{in}}^{\text{out}}$$

- The sign of the diagram is $(-1)^{h+l}$, where h is the number of internal hole lines and l is the number of "loops" – a route along a series of directed lines that returns to its beginning.

DIAGRAMS: THE CC ENERGY

- Next consider the terms linear in $\hat{T}_2$:

$$\langle \Phi_0 | \left(\hat{H}_N \hat{T}_2 \right)_c | \Phi_0 \rangle = i \text{ (diagram) } = \sum_{i,j,a,b} \frac{1}{2} \frac{1}{i!j!} \langle \Phi_0 | \hat{H}_N | \Phi_0 \rangle \langle \Phi_0 | \hat{T}_2 | \Phi_0 \rangle$$

The diagram shows a vertex labeled $\hat{H}_N$ with two incoming lines (left and right) and two outgoing lines (top and bottom). The top line is dashed, and the bottom line is solid. The vertex is connected to a $\hat{T}_2$ operator, which is represented by a box with two incoming lines (left and right) and two outgoing lines (top and bottom). The lines are labeled with indices: i, j, a, b .

- To interpret this algebraically:
 1. Label all directed lines with appropriate indices: $i, j, k, \dots; a, b, c, \dots$
 2. Include summations for all "internal" lines.
 3. Interpret the lines connected to the $\hat{V}_N$ operator vertex as:
 $\langle \text{left-out right-out} | | \text{left-in right-in} \rangle$
 4. Interpret the lines connected to the $\hat{T}_2$ operator from left to right:
 $t \begin{matrix} \text{left-out right-out} \\ \text{left-in right-in} \end{matrix}$
 5. The sign of the diagram is $(-1)^{h+l}$.
 6. Pairs of "equivalent" lines begin at the same operator line and end together at another operator line. For each such pair, multiply the expression by 1/2.

DIAGRAMS: THE CC ENERGY

- Next consider the terms quadratic in $\hat{T}_1$:

$$\langle \Phi_0 | \left(\frac{1}{2} \hat{H}_N \hat{T}_1^2 \right)_c | \Phi_0 \rangle = \text{diagram} = \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b$$

- This diagram may be interpreted using the previous rules, as appropriate, but now we have one additional rule:
 - A pair of “equivalent vertices” is given when two identical operators connect to the Hamiltonian in exactly the same way. For n equivalent vertices, multiply the expression by $1/n!$.
- Putting all three diagrams together gives us our final expression:

$$E_{CCSD} = \text{diagram 1} + \text{diagram 2} + \text{diagram 3}$$

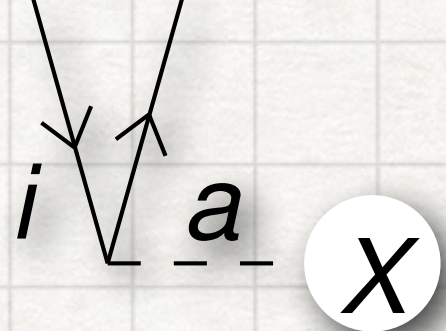
$$= \sum_{ia} f_{ia} t_i^a + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b$$

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

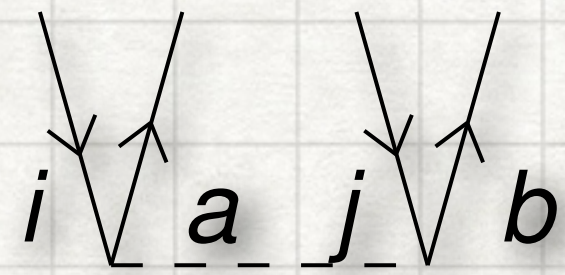
- Next we consider the amplitude equations:

$$0 = \langle \Phi_i^a | \left(\hat{H}_N e^{\hat{T}} \right)_c | \Phi_0 \rangle \quad \text{and} \quad 0 = \langle \Phi_{ij}^{ab} | \left(\hat{H}_N e^{\hat{T}} \right)_c | \Phi_0 \rangle$$

- The leading term in the $\hat{T}_1$ equation is:

$$\langle \Phi_i^a | \hat{F}_N | \Phi_0 \rangle = \text{diagram} = f_{ai}$$


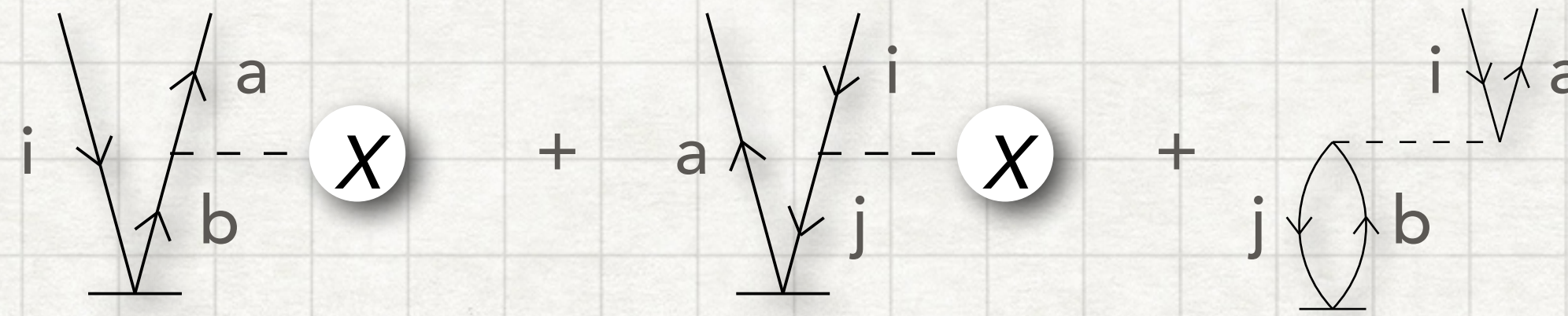
- The leading term in the $\hat{T}_2$ equation is:

$$\langle \Phi_{ij}^{ab} | \hat{V}_N | \Phi_0 \rangle = \text{diagram} = \langle ab || ij \rangle$$


DIAGRAMS: THE CC AMPLITUDE EQUATIONS

- The linear $\hat{T}_1$ contributions to the singles equation are:

$$\langle \Phi_i^a | \left(\hat{F}_N \hat{T}_1 \right)_c | \Phi_0 \rangle + \langle \Phi_i^a | \left(\hat{V}_N \hat{T}_1 \right)_c | \Phi_0 \rangle =$$

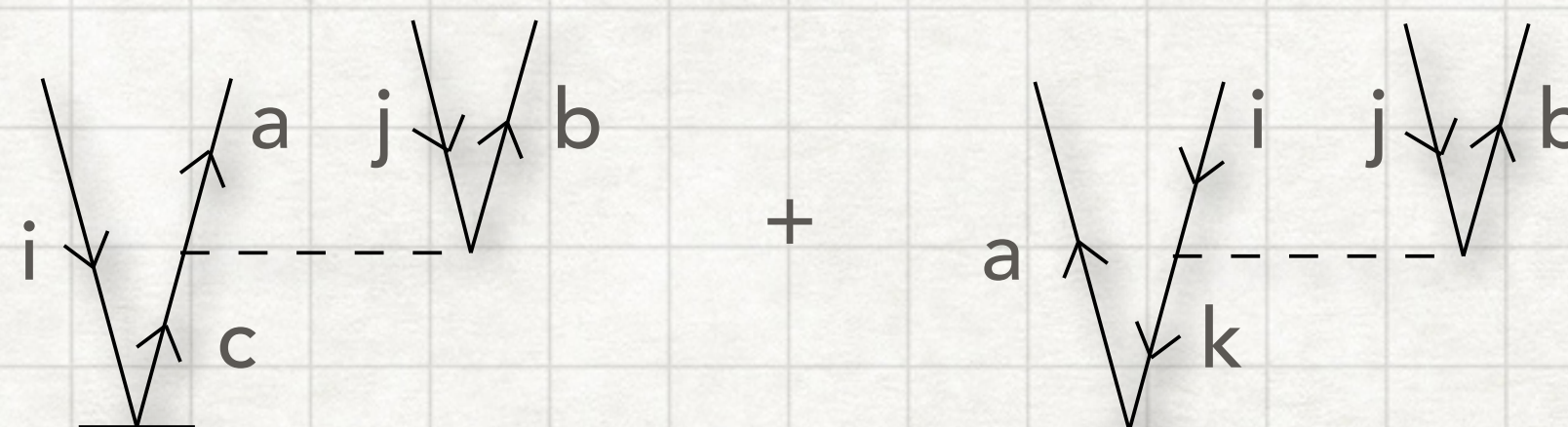


$$= \sum_b f_{ab} t_i^b - \sum_j f_{ji} t_j^a + \sum_{jb} \langle ja || bi \rangle t_j^b$$

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

- The linear $\hat{T}_1$ contribution of $\hat{V}_N$ to the doubles equation is:

$$\langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1 \right)_c | \Phi_0 \rangle =$$



- For these diagrams, we need a new rule:

Each pair of unique (*i.e.*, connecting to different operator lines), external hole or particle lines introduces a permutation operator, $P(pq)$, to ensure antisymmetry of the final expression.

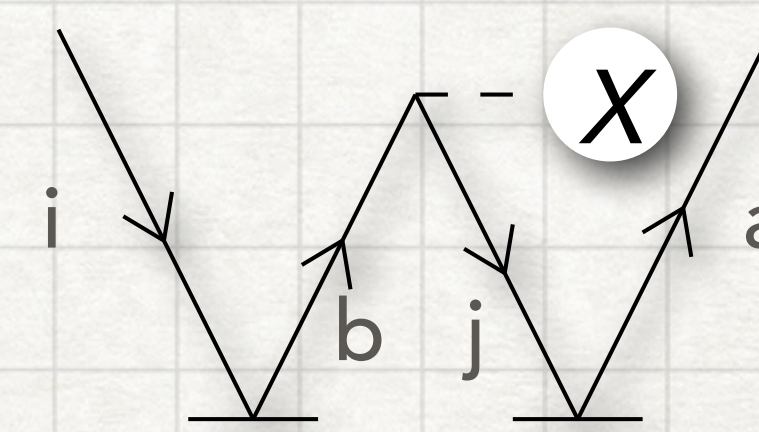
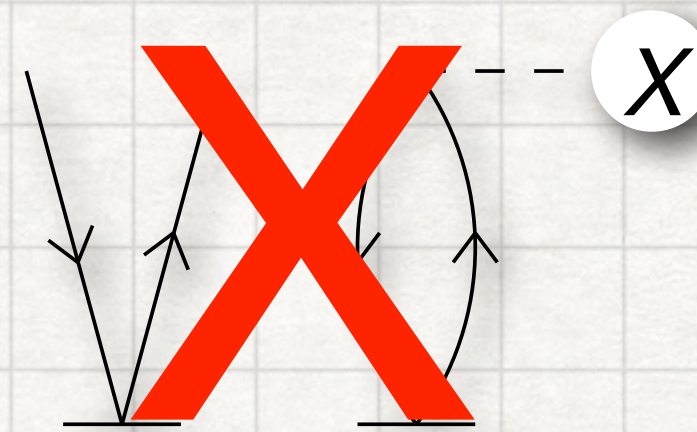
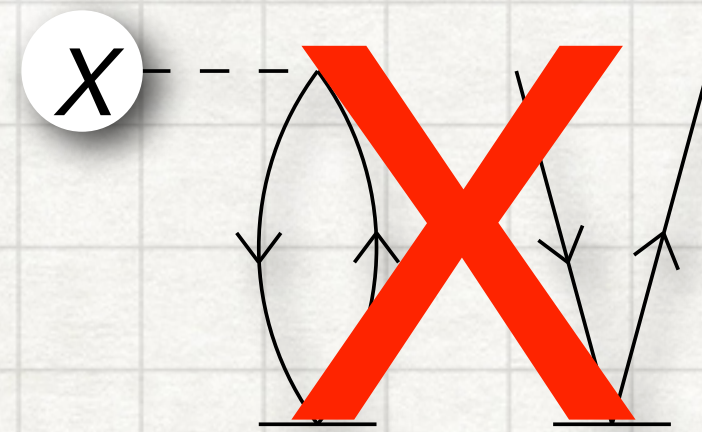
- This rule, in conjunction with our previous rules, gives:

$$\langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1 \right)_c | \Phi_0 \rangle = P(ij) \sum_c \langle ab || cj \rangle t_i^c - P(ab) \sum_k \langle kb || ij \rangle t_k^a$$

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

- The quadratic $\hat{T}_1$ contribution of $\hat{F}_N$ to the singles equation is:

$$\frac{1}{2} \langle \Phi_i^a | \left(\hat{F}_N \hat{T}_1^2 \right)_c | \Phi_0 \rangle =$$



- Only those diagrams in which the Hamiltonian fragment has at least one connection/contraction with every $\hat{T}$ operator can contribute.

$$\frac{1}{2} \langle \Phi_i^a | \left(\hat{F}_N \hat{T}_1^2 \right)_c | \Phi_0 \rangle = - \sum_{jb} f_{jb} t_i^b t_j^a$$

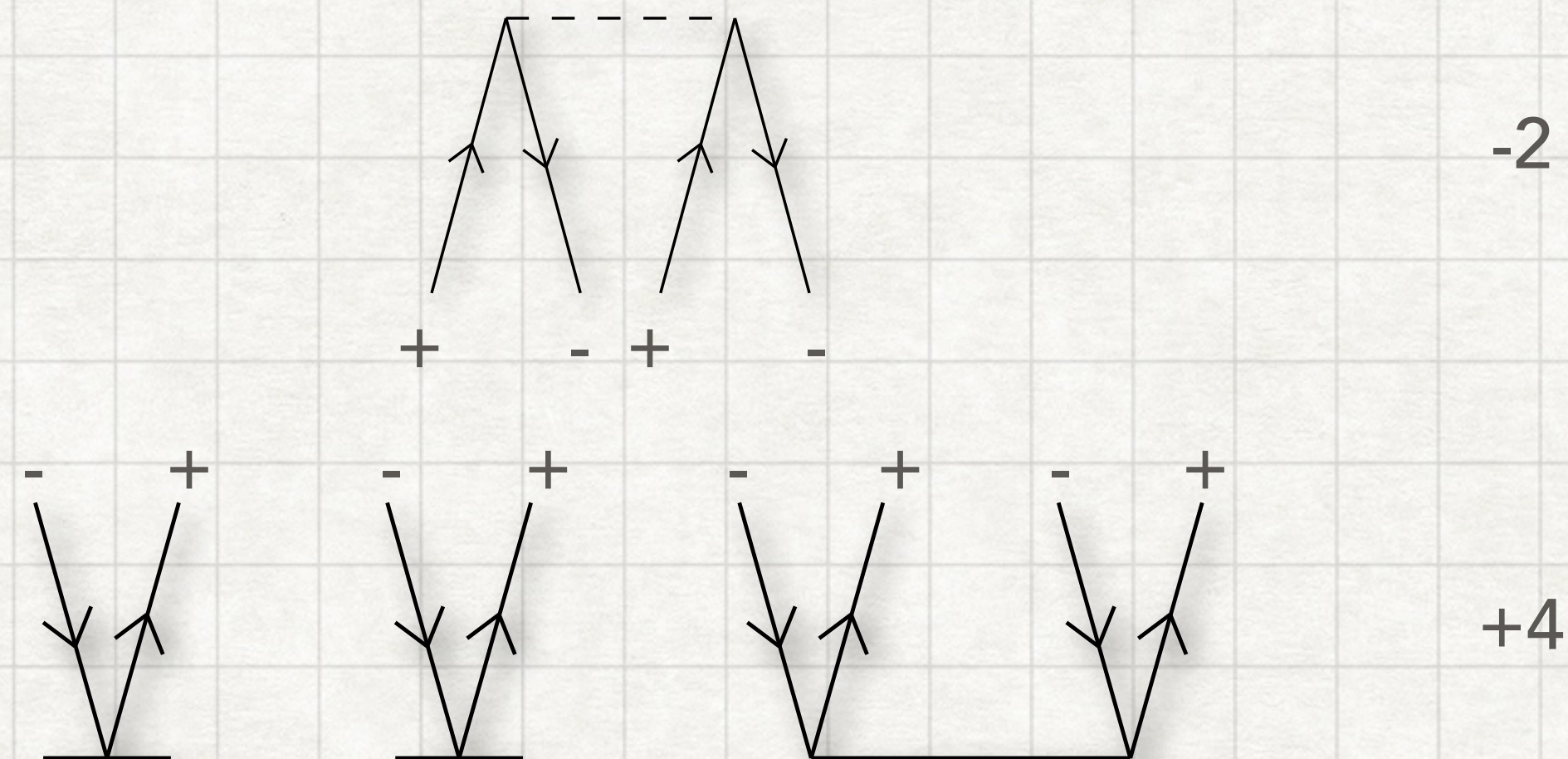
- Note that the factor of 1/2 in the expression on the left is automatically accounted for in the diagram.

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

- How can we be sure that we include only the *unique* diagrams? Consider the following contribution to the $\hat{T}_2$ equations:

$$\frac{1}{2} \langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1^2 \hat{T}_2 \right)_c | \Phi_0 \rangle$$

- We know that the product of $\hat{T}_1^2$ and $\hat{T}_2$ yields a +4 excitation, and the matrix element requires a total +2 excitation (the doubly excited determinant on the left), so only the -2 diagram from the Hamiltonian will work:



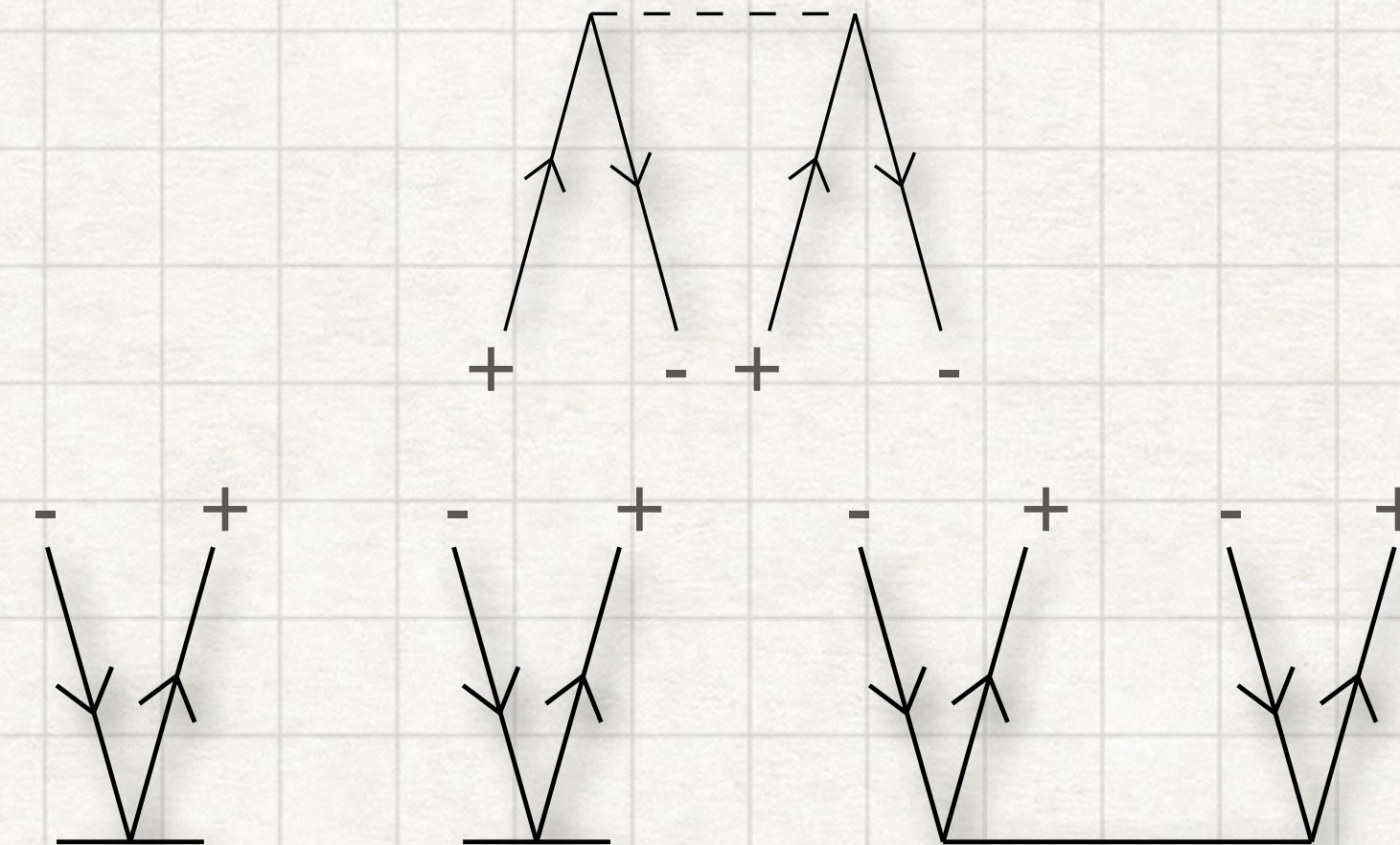
- The Kucharski-Bartlett "sign sequence": Assign "+" to each particle line and "-" to each hole line from all operators and select all unique combinations that take at least one connection from each $\hat{T}$ operator.

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

$$\frac{1}{2} \langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1^2 \hat{T}_2 \right)_c | \Phi_0 \rangle$$

- Since there can be only four connections (+-+ -), we choose up to four +/- signs from each of the three cluster operators:

$\hat{T}_1$	$\hat{T}_1$	$\hat{T}_2$
+	+	--
-	-	++
+	-	+ -
+ -	+	-
+ -	-	+

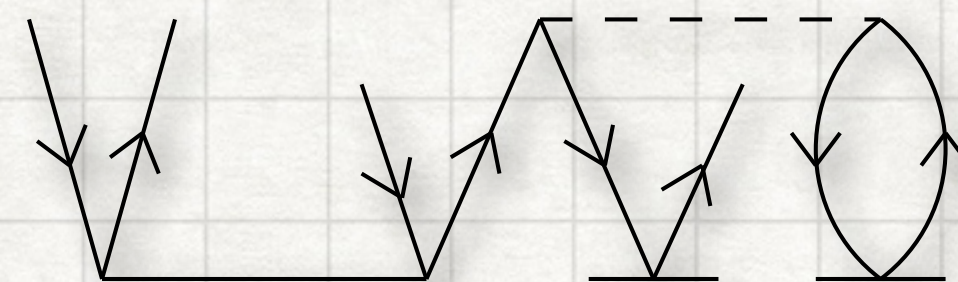
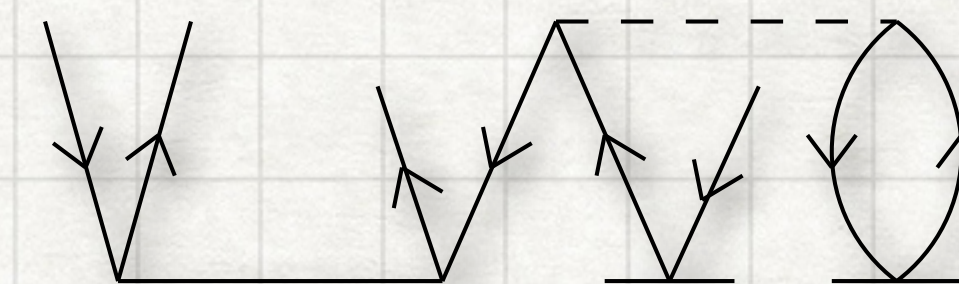
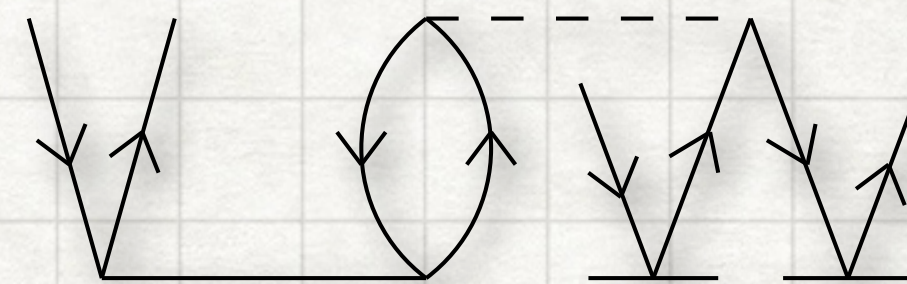
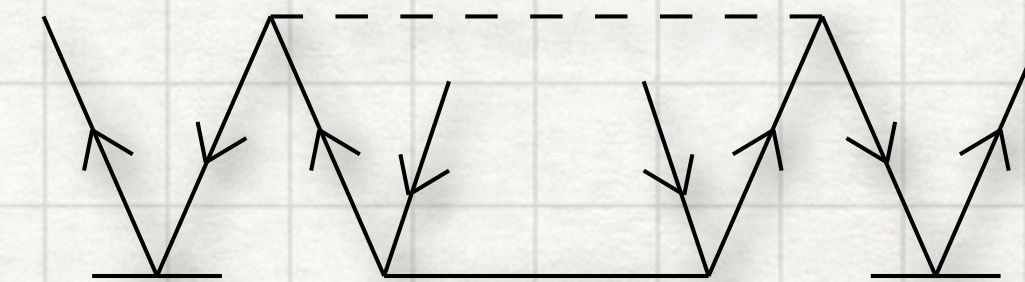
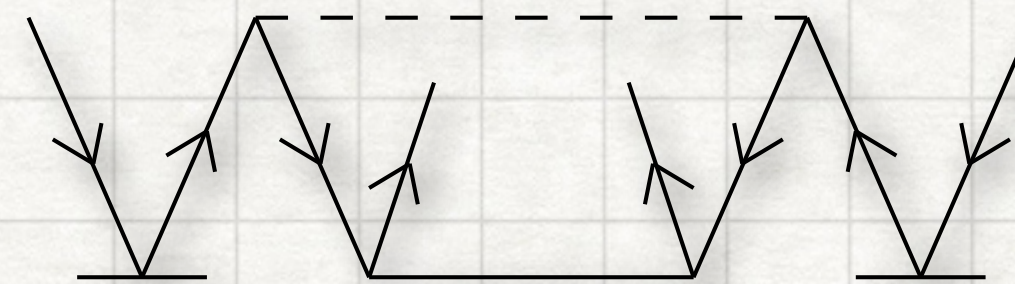


- There are only five unique combinations, leading to five unique diagrams.

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

$$\frac{1}{2} \langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1^2 \hat{T}_2 \right)_c | \Phi_0 \rangle$$

$\hat{T}_1$	$\hat{T}_1$	$\hat{T}_2$
+	+	--
-	-	+ +
+	-	+ -
+ -	+	-
+ -	-	+



- There are only five unique combinations, leading to five unique diagrams.

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

$$\frac{1}{2} \langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1^2 \hat{T}_2 \right)_c | \Phi_0 \rangle =$$

- Applying our rules, we have the complete algebraic interpretation:

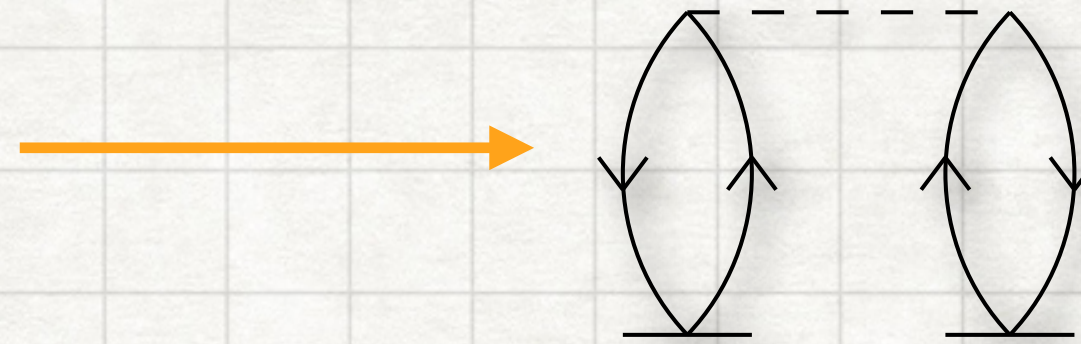
$$\begin{aligned} \frac{1}{2} \langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_1^2 \hat{T}_2 \right)_c | \Phi_0 \rangle = & + \frac{1}{4} P(ij) \sum_{klcd} \langle kl || cd \rangle t_{kl}^{ab} t_i^c t_j^d + \frac{1}{4} P(ab) \sum_{klcd} \langle kl || cd \rangle t_{ij}^{cd} t_k^a t_l^b \\ & - P(ij) P(ab) \sum_{klcd} \langle kl || cd \rangle t_{ik}^{ac} t_j^d t_l^b - P(ij) \sum_{klcd} \langle kl || cd \rangle t_{ik}^{ab} t_j^c t_l^d - P(ab) \sum_{klcd} \langle kl || cd \rangle t_{ij}^{ac} t_k^b t_l^d \end{aligned}$$

COMMON DIAGRAM TERMINOLOGY

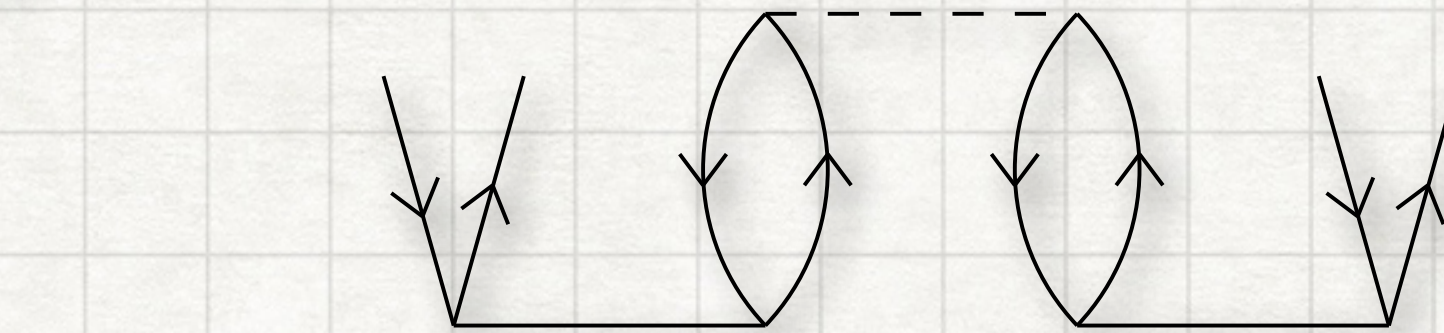
- **Open** – contains external lines



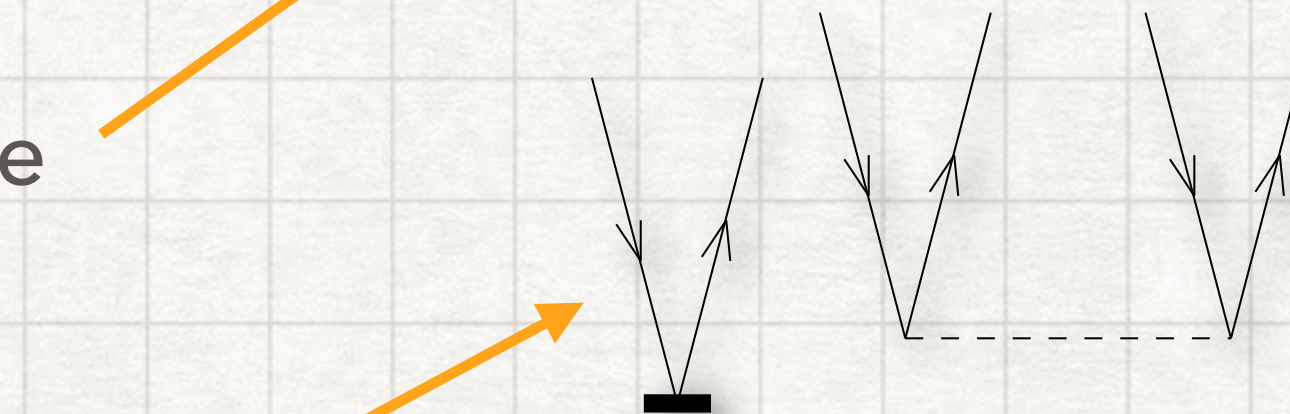
- **Closed** – no external lines



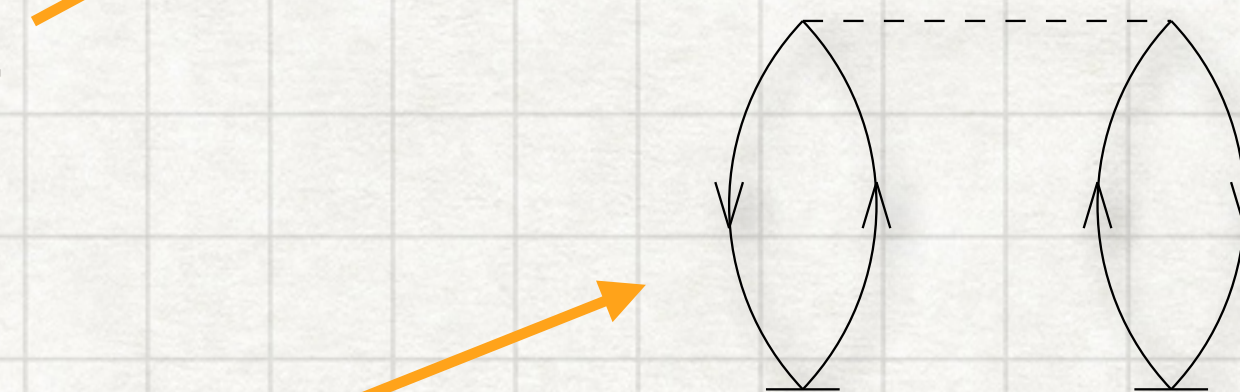
- **Connected** – all parts of the diagram are connected to one another via directed lines



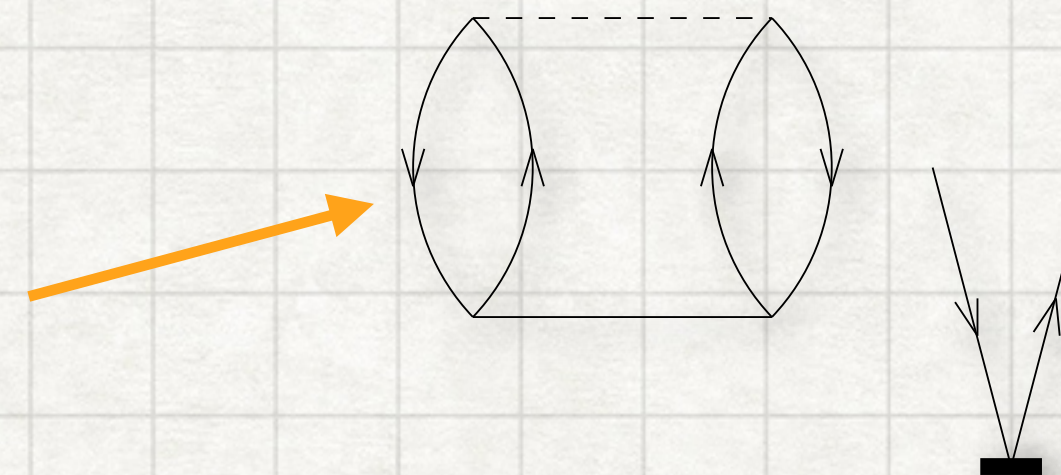
- **Disconnected** – some components of the diagram are not connected via directed lines



- **Linked** – contains closed components that are connected



- **Unlinked** – contains closed components that are not connected



SIZE EXTENSIVITY

- This term was developed by Bartlett in 1978^a and refers to the correct physical (linear) scaling of the energy with the number of electrons.

Configuration Interaction

$$E = \langle \Phi_0 | \hat{H} (1 + \hat{C}) | \Phi_0 \rangle$$

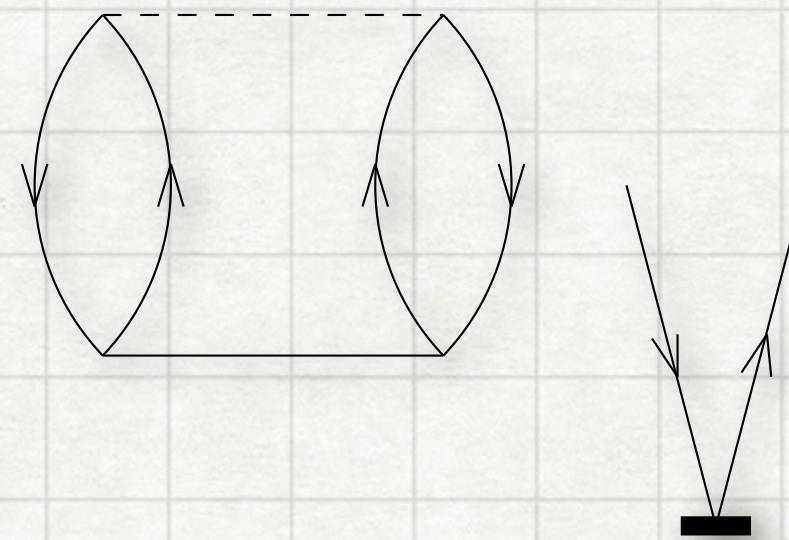
$$E_{C_{ij}^{ab}\dots} = \langle \Phi_{ij}^{ab}\dots | \hat{H} (1 + \hat{C}) | \Phi_0 \rangle$$

Coupled Cluster

$$E = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle$$

$$0 = \langle \Phi_{ij}^{ab}\dots | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle$$

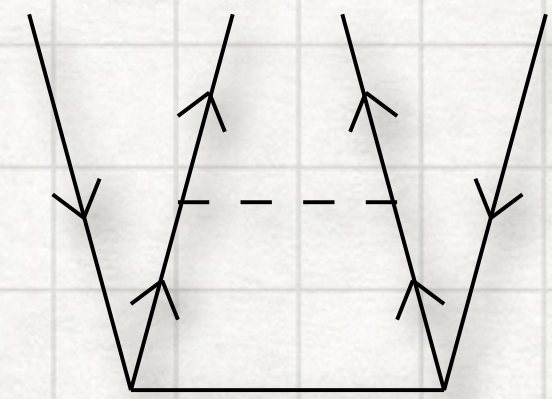
- The (unavoidable) appearance of the energy in the CI amplitude equations leads to "unlinked" diagrams such as:



- The scaling of the "closed" component of the diagram, which represents the CI energy, scales independently from the open component, leading to non-linear scaling of the CI energy with the size of the system.
- Such terms cannot appear in the coupled cluster equations, and thus the CC energy scales correctly (linearly) with the number of electrons.

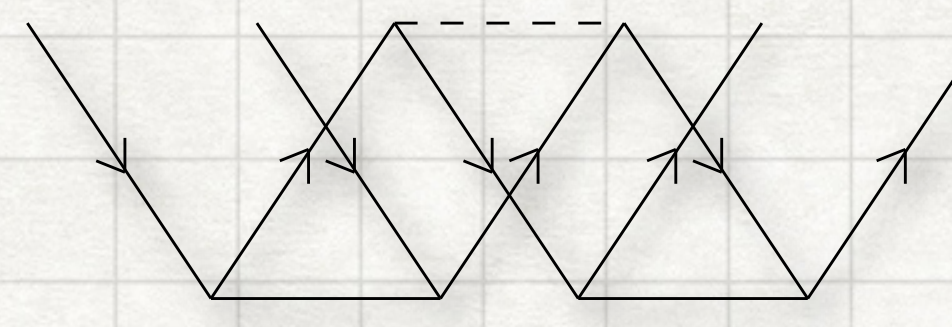
COMPUTATIONAL COST

- Now that we have algebraic and diagrammatic representations of the many terms of the CC equations, we may examine their computational cost in detail. The most expensive term in the CCSD equations is the particle-particle ladder:



$$= \frac{1}{2} \sum_{ef} \langle ab || ef \rangle t_{ij}^{ef} \quad \text{Cost: } \mathcal{O}(n_o^2 n_v^4) \quad \left. \vphantom{\sum_{ef}} \right\} \begin{array}{l} \text{This is typically} \\ \text{simplified} \\ \text{to } \mathcal{O}(N^6) \end{array}$$

- However, if you look closely at the $\hat{T}_2$ amplitude equations we saw earlier, you'll find terms that appear to be even more expensive, e.g.:



$$= \frac{1}{4} \sum_{mnef} t_{ij}^{ef} t_{mn}^{ab} \langle mn || ef \rangle \quad \mathcal{O}(n_o^4 n_v^4)$$

- Such terms, which involve products of $\hat{T}$ operators, may be factorized into less expensive terms:

$$\frac{1}{4} \sum_{mnef} t_{ij}^{ef} t_{mn}^{ab} \langle mn || ef \rangle = \frac{1}{4} \sum_{mn} t_{mn}^{ab} \left(\sum_{ef} t_{ij}^{ef} \langle mn || ef \rangle \right) \quad 2 \times \mathcal{O}(n_o^4 n_v^2)$$