COUPLED CLUSTER THEORY

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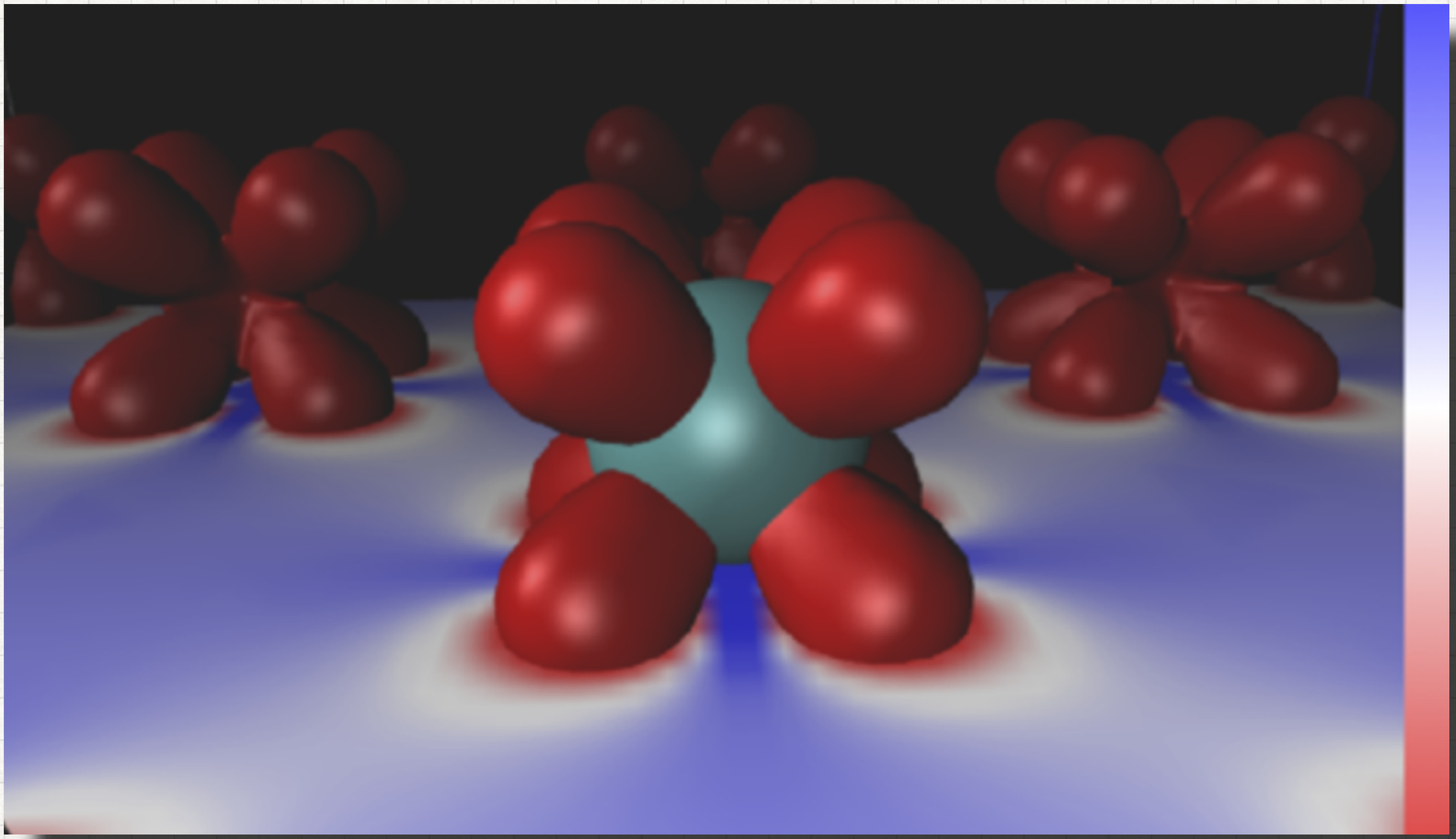


Coester and Kümmel adopted the name "exp-S method", after the form of the wave function (2) and the symbol S for the cluster operation. Cizek and Paldus introduced the term "Coupled-Pair Many Electron Theory" (CPMET), and extended CPMET, from their emphasis on $T \simeq T_2$, explicit equations for which 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).

THE COUPLED CLUSTER EQUATIONS

- So far, we have derived several key expressions for coupled cluster theory:

CC Wave Function: $$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle$$

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

CC Amplitudes: $$0 = \langle\Phi_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle$$

Similarity-transformed Hamiltonian:

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + \left[\hat{H},\hat{T}\right] + \frac{1}{2!}\left[\left[\hat{H},\hat{T}\right],\hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right],\hat{T}\right]$$

- Our next goal is to convert these equations to algebraic form in terms of the cluster amplitudes and the one- and two-electron integrals that comprise the electronic Hamiltonian.

NORMAL ORDERING

- Evaluation of matrix elements of second-quantized operators between determinants is easier when those operators are written in "normal order." In general, this means that all annihilation or creation operators that would give zero when acting on the "vacuum state" are moved to the right in a given string.
- In quantum chemistry the "vacuum state" is conveniently chosen to be the Hartree-Fock reference state, $|\Phi_0\rangle$, which contains a set of *N* occupied orbitals (the "Fermi vacuum"):

$$a_i^\dagger|\Phi_0\rangle = 0 \qquad a_a|\Phi_0\rangle = 0$$

- Thus, our definition of normal ordering requires us to move all operators such as $a_i^\dagger$ and a_a to the right of operators such as a_i and $a_a^\dagger$.
- One way to achieve this ordering would be to use the anti-commutation relations of the annihilation and creation operators:

$$a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq} \qquad a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger = 0 \qquad a_p a_q + a_q a_p = 0$$

- A better way is through Wick's theorem…

OPERATOR CONTRACTIONS

- We define a "contraction" between two adjacent annihilation/creation operators as:

$$\overbrace{AB} \equiv AB - \{AB\}$$

where the $\{\}$ around a string implies that the operators may be rearranged at will, while still keeping up with changes in sign.

- This leads us to four possible contractions in accord with the Fermi vacuum:

$$\overbrace{a_i^\dagger a_j} = a_i^\dagger a_j - \{a_i^\dagger a_j\} = a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij}$$

$$\overbrace{a_a a_b^\dagger} = a_a a_b^\dagger - \{a_a a_b^\dagger\} = a_a a_b^\dagger + a_b^\dagger a_a = \delta_{ab}$$

$$\overbrace{a_a^\dagger a_b} = \overbrace{a_i a_j^\dagger} = 0$$

- Contractions between operators in ***different*** orbital spaces are zero.

WICK'S THEOREM

- Wick's theorem provides a mechanism for expressing a given string of annihilation/creation operators as a linear combination of normal-ordered strings:

$$ABC\ldots XYZ = \{ABC\ldots XYZ\} + \sum_{\text{singles}} \{\overbrace{A\ldots}^{}BC\ldots XYZ\}$$

$$+ \sum_{\text{doubles}} \{\overbrace{A\ldots\ldots}^{}\overbrace{BC\ldots XYZ}^{}\} + \ldots$$

- In the case of a product of normal-ordered strings (the case we'll most often encounter), Wick's theorem also helps:

$$\{ABC\ldots\}\{XYZ\ldots\} = \{ABC\ldots XYZ\ldots\} + \sum_{\text{singles}} \{\overbrace{ABC\ldots XYZ}^{}\ldots\}$$

$$+ \sum_{\text{doubles}} \{\overbrace{ABC\ldots\ldots XYZ}^{}\ldots\} + \ldots$$

- A contraction takes a negative sign if an odd number of operators stand between the two under contraction, and a positive sign otherwise.

THE NORMAL-ORDERED HAMILTONIAN

- Let's apply Wick's theorem to the second-quantized Hamiltonian:

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

- The second-quantized string in the one-electron term becomes:

$$a_p^\dagger a_q = \{a_p^\dagger a_q\} + \{\overbrace{a_p^\dagger a_q}\} = \{a_p^\dagger a_q\} + \delta_{pq}\delta_{p\in i}$$

where the notation $p \in i$ means that p must be an occupied orbital.

- Thus, the one-electron term becomes:

$$\sum_{pq} h_{pq} a_p^\dagger a_q = \sum_{pq} h_{pq} \{a_p^\dagger a_q\} + \boxed{\sum_i h_{ii}}$$

- The last term, which contains no second-quantized operators, is the one-electron contribution to the Hartree-Fock energy.

THE NORMAL-ORDERED HAMILTONIAN

- The two-electron term involves more components:

$$a_p^\dagger a_q^\dagger a_s a_r = \{a_p^\dagger a_q^\dagger a_s a_r\} + \{\overbrace{a_p^\dagger a_q^\dagger} a_s a_r\} + \{a_p^\dagger \overbrace{a_q^\dagger a_s} a_r\} + \{\overbrace{a_p^\dagger a_q^\dagger a_s a_r}\}$$
$$+ \{a_p^\dagger \overbrace{a_q^\dagger a_s a_r}\} + \{\overbrace{a_p^\dagger a_q^\dagger a_s} a_r\} + \{\overbrace{a_p^\dagger \overbrace{a_q^\dagger a_s} a_r}\}$$

- Now evaluate the contractions:

$$a_p^\dagger a_q^\dagger a_s a_r = \{a_p^\dagger a_q^\dagger a_s a_r\} - \delta_{p\in i}\delta_{ps}\{a_q^\dagger a_r\} + \delta_{q\in i}\delta_{qs}\{a_p^\dagger a_r\} + \delta_{p\in i}\delta_{pr}\{a_q^\dagger a_s\}$$
$$- \delta_{q\in i}\delta_{qr}\{a_p^\dagger a_s\} - \delta_{p\in i}\delta_{ps}\delta_{q\in j}\delta_{qr} + \delta_{p\in i}\delta_{pr}\delta_{q\in j}\delta_{qs}$$

- Insert this back into the expression for $\hat{V}$ and change the summations:

$$\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} - \frac{1}{4}\sum_{qri}\langle iq||ri\rangle\{a_q^\dagger a_r\}$$
$$+ \frac{1}{4}\sum_{pri}\langle pi||ri\rangle\{a_p^\dagger a_r\} + \frac{1}{4}\sum_{qsi}\langle iq||is\rangle\{a_q^\dagger a_s\} - \frac{1}{4}\sum_{psi}\langle pi||is\rangle\{a_p^\dagger a_s\}$$
$$- \frac{1}{4}\sum_{ij}\langle ij||ji\rangle + \frac{1}{4}\sum_{ij}\langle ij||ij\rangle$$

Two-electron contribution to the Hartree-Fock energy

THE NORMAL-ORDERED HAMILTONIAN

- The four terms involving only two annihilation/creation operators are identical and can be combined into one:

$$-\frac{1}{4}\sum_{qri}\langle iq||ri\rangle\{a_q^\dagger a_r\}+\frac{1}{4}\sum_{pri}\langle pi||ri\rangle\{a_p^\dagger a_r\}+\frac{1}{4}\sum_{qsi}\langle iq||is\rangle\{a_q^\dagger a_s\}-\frac{1}{4}\sum_{psi}\langle pi||is\rangle\{a_p^\dagger a_s\}=\sum_{pqi}\langle pi||qi\rangle\{a_p^\dagger a_q\}$$

- The two terms with no annihilation/creation operators are identical and can also be combined into one:

$$-\frac{1}{4}\sum_{ij}\langle ij||ji\rangle+\frac{1}{4}\sum_{ij}\langle ij||ij\rangle=\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

- Bringing all the one- and two-electron terms together we have:

$$\hat{H}=\sum_i h_{ii}+\frac{1}{2}\sum_{ij}\langle ij||ij\rangle+\sum_{pq}h_{pq}\{a_p^\dagger a_q\}+\sum_{pri}\langle pi||qi\rangle\{a_p^\dagger a_q\}+\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\}$$

The Hartree-Fock energy

The Fock operator

- Final form:

$$\hat{H}=\langle\Phi_0|\hat{H}|\Phi_0\rangle+\sum_{pq}f_{pq}\{a_p^\dagger a_q\}+\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\}$$

THE NORMAL-ORDERED HAMILTONIAN

- We can thus define the normal-ordered Hamiltonian to be the original second-quantized Hamiltonian minus its (Fermi) vacuum expectation value:

$$\begin{aligned}\hat{H}_N &= \hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle \\ &= \sum_{pq} f_{pq}\{a_p^\dagger a_q\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} \\ &= \hat{F}_N + \hat{V}_N\end{aligned}$$

- We may therefore think of the normal-ordered Hamiltonian as a ***correlation operator*** in that the contributions to the Hartree-Fock energy have been removed. This is the form of the Hamiltonian we use from this point forward.
- This is a general result: The normal-ordered form of an operator is the operator itself minus its vacuum/reference expectation value.
- *A key corollary: The vacuum/reference expectation value of a normal-ordered operator is* ***zero****.*

NORMAL-ORDERED CLUSTER OPERATORS

- In the previous lecture, we defined the cluster operators as:

$$\hat{T}_1 = \sum_{ia} t_i^a a_a^\dagger a_i \qquad \text{and} \qquad \hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

or, more generally:

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{ij\ldots ab\ldots}^{n} t_{ij\ldots}^{ab\ldots} a_a^\dagger a_b^\dagger \ldots a_j a_i$$

- Recall that our definition of normal ordering relative to the Fermi vacuum means that all $a_i^\dagger$ and a_a must stand to the right of all $a_a^\dagger$ and a_i. This is already the case with the excitation operators, so we may trivially write:

$$\hat{T}_1 = \sum_{ia} t_i^a \{a_a^\dagger a_i\} \qquad \hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\}$$

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{ij\ldots ab\ldots}^{n} t_{ij\ldots}^{ab\ldots} \{a_a^\dagger a_b^\dagger \ldots a_j a_i\}$$

- Again: the $\{\}$ means that we may rearrange the operators at will, as long as we keep up with the sign.

SIMPLIFYING THINGS (A BIT)

- We can now modify the Hausdorff expansion to use only normal-ordered operators:

$$e^{-\hat{T}}\hat{H}_N e^{\hat{T}} = \hat{H}_N + \left[\hat{H}_N, \hat{T}\right] + \frac{1}{2!}\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] + \ldots$$

- This leads to another important property of the commutator expansion:

> *Only those terms from the Wick's theorem evaluation of the commutators in the Hausdorff expansion in which the Hamiltonian contracts at least once with every cluster operator on its right can make a non-zero contribution.*

- We will illustrate this property using two of the simplest terms from the expansion:

$$\left[\hat{F}_N, \hat{T}_1\right] \qquad \text{and} \qquad \frac{1}{2}\left[\left[\hat{F}_N, \hat{T}_1\right], \hat{T}_1\right]$$

SIMPLIFYING THINGS (A BIT)

- First, write the linear commutator explicitly in terms of second-quantized operators:

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pq}\sum_{ia} f_{pq} t_i^a \left[\{a_p^\dagger a_q\}, \{a_a^\dagger a_i\}\right]$$

$$= \sum_{pq}\sum_{ia} f_{pq} t_i^a \left(\{a_p^\dagger a_q\}\{a_a^\dagger a_i\} - \{a_a^\dagger a_i\}\{a_p^\dagger a_q\}\right)$$

- Next, use Wick's theorem to evaluate the each of the products:

$$\{a_p^\dagger a_q\}\{a_a^\dagger a_i\} = \{a_p^\dagger a_q a_a^\dagger a_i\} + \{\overbracket{a_p^\dagger a_q a_a^\dagger} a_i\} + \{a_p^\dagger \overbracket{a_q a_a^\dagger} a_i\} + \{\overbracket{a_p^\dagger a_q a_a^\dagger} a_i\}$$

$$= \boxed{\{a_p^\dagger a_q a_a^\dagger a_i\}} + \delta_{pi}\{a_q a_a^\dagger\} + \delta_{qa}\{a_p^\dagger a_i\} + \delta_{pi}\delta_{qa}$$

$$\{a_a^\dagger a_i\}\{a_p^\dagger a_q\} = \boxed{\{a_a^\dagger a_i a_p^\dagger a_q\}}$$

- We can recognize that the uncontracted terms in both products are ***identical*** because we may rearrange the operators within the $\{\}$. Thus, they exactly cancel in the commutator, leaving only terms in which $\hat{F}_N$ has at least one contraction with $\hat{T}_1$ on its right.

SIMPLIFYING THINGS (A BIT)

- The quadratic commutator may be expanded into three terms:

$$\frac{1}{2}\left[\left[\hat{F}_N,\hat{T}_1\right],\hat{T}_1\right] = \frac{1}{2}\left(\hat{F}_N\hat{T}_1^2 - 2\hat{T}_1\hat{F}_N\hat{T}_1 + \hat{T}_1^2\hat{F}_N\right)$$
$$= \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq}t_i^a t_j^b \left(\{a_p^\dagger a_q\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\} - 2\{a_a^\dagger a_i\}\{a_p^\dagger a_q\}\{a_b^\dagger a_j\} + \{a_a^\dagger a_i\}\{a_b^\dagger a_j\}\{a_p^\dagger a_q\}\right)$$

- Wick's theorem for each product gives:

$$\{a_p^\dagger a_q\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\} = \{a_p^\dagger a_q a_a^\dagger a_i a_b^\dagger a_j\} + \{\overbrace{a_p^\dagger a_q a_a^\dagger} a_i a_b^\dagger a_j\} + \{\overbrace{a_p^\dagger a_q a_a^\dagger a_i a_b^\dagger} a_j\}$$
$$+ \{a_p^\dagger \overbrace{a_q a_a^\dagger} a_i a_b^\dagger a_j\} + \{a_p^\dagger \overbrace{a_q a_a^\dagger a_i a_b^\dagger} a_j\} + \{\overbrace{a_p^\dagger a_q} a_a^\dagger a_i a_b^\dagger a_j\}$$
$$+ \{\overbrace{a_p^\dagger a_q} a_a^\dagger \overbrace{a_i a_b^\dagger} a_j\} + \{\overbrace{a_p^\dagger a_q a_a^\dagger} a_i \overbrace{a_b^\dagger} a_j\} + \{\overbrace{a_p^\dagger a_q a_a^\dagger a_i a_b^\dagger} a_j\}$$

$$-2\{a_a^\dagger a_i\}\{a_p^\dagger a_q\}\{a_b^\dagger a_j\} = -2\left(\{a_a^\dagger a_i a_p^\dagger a_q a_b^\dagger a_j\} + \{a_a^\dagger a_i \overbrace{a_p^\dagger a_q a_b^\dagger} a_j\} + \{a_a^\dagger a_i a_p^\dagger \overbrace{a_q a_b^\dagger} a_j\}\right.$$
$$\left. + \{a_a^\dagger a_i \overbrace{a_p^\dagger a_q} a_b^\dagger \overbrace{a_j}\}\right)$$

$$\{a_a^\dagger a_i\}\{a_b^\dagger a_j\}\{a_p^\dagger a_q\} = \{a_a^\dagger a_i a_b^\dagger a_j a_p^\dagger a_q\}$$

- The only contributions that don't cancel are terms 7 and 8 from the first product!

SIMPLIFYING THINGS (A BIT)

- The uncontracted terms are clearly identical:

$$\{a_p^\dagger a_q a_a^\dagger a_i a_b^\dagger a_j\} - 2\{a_a^\dagger a_i a_p^\dagger a_q a_b^\dagger a_j\} + \{a_a^\dagger a_i a_b^\dagger a_j a_p^\dagger a_q\} = 0$$

- We can see that the singly contracted terms are also identical when we convert the summations to the same patterns, *e.g.*:

$$\frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\{\overbrace{a_p^\dagger a_q a_a^\dagger} a_i a_b^\dagger a_j\} + \{\overbrace{a_p^\dagger a_q a_a^\dagger a_i a_b^\dagger} a_j\} - 2\{a_a^\dagger a_i \overbrace{a_p^\dagger a_q a_b^\dagger} a_j\} \right)$$

$$= \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\delta_{pi}\{a_q a_a^\dagger a_b^\dagger a_j\} + \delta_{pj}\{a_q a_a^\dagger a_i a_b^\dagger\} - 2\delta_{pj}\{a_a^\dagger a_i a_q a_b^\dagger\} \right)$$

$$= \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(\sum_q f_{iq}\{a_q a_a^\dagger a_b^\dagger a_j\} + \sum_q f_{jq}\{a_q a_a^\dagger a_i a_b^\dagger\} - 2\sum_q f_{jq}\{a_a^\dagger a_i a_q a_b^\dagger\} \right)$$

$$= \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(\sum_q f_{jq}\{a_q a_b^\dagger a_a^\dagger a_i\} + \sum_q f_{jq}\{a_q a_a^\dagger a_i a_b^\dagger\} - 2\sum_q f_{jq}\{a_a^\dagger a_i a_q a_b^\dagger\} \right)$$

$$= 0$$

SIMPLIFYING THINGS (A BIT)

- The doubly contracted terms in which the Fock operator shares both of its indices with only one of the two $\hat{T}_1$ operators are also zero:

$$\frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq}t_i^a t_j^b \left(\{\overbrace{a_p^\dagger a_q \overbrace{a_a^\dagger a_i}} a_b^\dagger a_j\} + \{\overbrace{a_p^\dagger a_q \overbrace{a_a^\dagger a_i a_b^\dagger}} a_j\} - 2\{a_a^\dagger a_i \overbrace{a_p^\dagger a_q \overbrace{a_b^\dagger a_j}}\} \right)$$

$$= \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \sum_{pq} f_{pq} \left(\delta_{pi}\delta_{qa}\{a_b^\dagger a_j\} + \delta_{pj}\delta_{qb}\{a_a^\dagger a_i\} - 2\delta_{pj}\delta_{qb}\{a_a^\dagger a_i\} \right)$$

$$= \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(f_{ia}\{a_b^\dagger a_j\} + f_{jb}\{a_a^\dagger a_i\} - 2f_{jb}\{a_a^\dagger a_i\} \right)$$

$$= \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(f_{jb}\{a_a^\dagger a_i\} + f_{jb}\{a_a^\dagger a_i\} - 2f_{jb}\{a_a^\dagger a_i\} \right)$$

$$= 0$$

SIMPLIFYING THINGS (A BIT)

- The only non-zero contributions arise from the double contractions in which the Fock operator shares an index with each of the two $\hat{T}_1$ operators to its right, leading to a rather compact final result:

$$\frac{1}{2}\left[\left[\hat{F}_N, \hat{T}_1\right], \hat{T}_1\right] = \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\{ \overbrace{a_p^\dagger a_q \overbrace{a_a^\dagger a_i \overbrace{a_b^\dagger a_j}}}\} + \{ \overbrace{a_p^\dagger \overbrace{a_q a_a^\dagger \overbrace{a_i a_b^\dagger}}} a_j \} \right)$$

$$= \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\delta_{pj}\delta_{qa}\{a_i a_b^\dagger\} - \delta_{pi}\delta_{qb}\{a_a^\dagger a_j\} \right)$$

$$= \sum_{ia}\sum_{jb} f_{ja} t_i^a t_j^b \{a_i a_b^\dagger\}$$

Only those terms from the Wick's theorem evaluation of the commutators in the Hausdorff expansion in which the Hamiltonian contracts at least once with every cluster operator on its right can make a non-zero contribution.

- We can summarize this important finding using a relatively simple notation:

$$e^{-\hat{T}} \hat{H}_N e^{\hat{T}} = \left(\hat{H}_N e^{\hat{T}} \right)_c$$

THE CCSD ENERGY EQUATION

- We now have the tools necessary to derive an algebraic expression for the CCSD energy, starting from our formal equation:

$$E_{\mathrm{CC}} = \langle \Phi_0 | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle = \langle \Phi_0 | \left(\hat{H}_N e^{\hat{T}} \right)_c | \Phi_0 \rangle$$

recognizing from our earlier analysis that we need only consider up to terms that are quadratic in $\hat{T}$:

$$E_{\mathrm{CC}} = \langle \Phi_0 | \left(\hat{H}_N \left[1 + \hat{T} + \frac{1}{2}\hat{T}^2 \right] \right)_c | \Phi_0 \rangle$$

- The leading term vanishes because the reference expectation value of a normal-ordered operator is zero:

$$\langle \Phi_0 | \hat{H}_N | \Phi_0 \rangle = 0$$

- The linear term contains four contributions:

$$\langle \Phi_0 | \left(\hat{H}_N \hat{T} \right)_c | \Phi_0 \rangle = \langle \Phi_0 | \left(\hat{F}_N \hat{T}_1 + \hat{V}_N \hat{T}_1 + \hat{F}_N \hat{T}_2 + \hat{V}_N \hat{T}_2 \right)_c | \Phi_0 \rangle$$

- Let's deal with each of these in order using the techniques we've learned…

THE CCSD ENERGY EQUATION

- Given that the reference expectation value of a normal-ordered operator is zero, ***only fully contracted terms*** from Wick's theorem can give non-zero results:

$$\langle\Phi_0|\left(\hat{F}_N\hat{T}_1\right)_c|\Phi_0\rangle = \sum_{pq}\sum_{ia} f_{pq}t_i^a\langle\Phi_0|\{a_p^\dagger a_q\}\{a_a^\dagger a_i\}|\Phi_0\rangle$$

$$= \sum_{pq}\sum_{ia} f_{pq}t_i^a\langle\Phi_0|\{\overbrace{a_p^\dagger a_q a_a^\dagger}a_i\}|\Phi_0\rangle$$

$$= \sum_{pq}\sum_{ia} f_{pq}t_i^a\langle\Phi_0|\delta_{pi}\delta_{qa}|\Phi_0\rangle$$

$$= \sum_{ia} f_{ia}t_i^a$$

- For the $\left(\hat{V}_N\hat{T}_1\right)_c$ term, however, it is not possible to generate fully contracted terms, and so it makes no contribution to the energy:

$$\langle\Phi_0|\left(\hat{V}_N\hat{T}_1\right)_c|\Phi_0\rangle = \frac{1}{4}\sum_{pqrs}\sum_{ia}\langle pq||rs\rangle t_i^a\langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_i\}|\Phi_0\rangle = 0$$

THE CCSD ENERGY EQUATION

- Similarly, the $\left(\hat{F}_N\hat{T}_2\right)_c$ cannot yield a fully contracted expression, and also vanishes:

$$\langle\Phi_0|\left(\hat{F}_N\hat{T}_2\right)_c|\Phi_0\rangle = \frac{1}{4}\sum_{pq}\sum_{ijab} f_{pq}t_{ij}^{ab}\langle\Phi_0|\{a_p^\dagger a_q\}\{a_a^\dagger a_b^\dagger a_j a_i\}|\Phi_0\rangle = 0$$

- The $\left(\hat{V}_N\hat{T}_2\right)_c$ term is the only remaining non-zero linear contribution:

$$\langle\Phi_0|\left(\hat{V}_N\hat{T}_2\right)_c|\Phi_0\rangle = \frac{1}{16}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_b^\dagger a_j a_i\}|\Phi_0\rangle$$

$$= \frac{1}{16}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_{ij}^{ab}\Big(\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} +$$

$$\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\}\Big)$$

$$= \frac{1}{16}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_{ij}^{ab}\left(\delta_{pi}\delta_{qj}\delta_{ra}\delta_{sb} + \delta_{pj}\delta_{qi}\delta_{rb}\delta_{sa} - \delta_{pj}\delta_{qi}\delta_{ra}\delta_{sb} - \delta_{pi}\delta_{qj}\delta_{rb}\delta_{sa}\right)$$

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

THE CCSD ENERGY EQUATION

- Among the six components of the energy expression involving $\hat{T}^2$, only one can yield fully contracted terms:

$$\frac{1}{2}\langle\Phi_0|\left(\hat{V}_N\hat{T}_1^2\right)_c|\Phi_0\rangle = \frac{1}{8}\sum_{pqrs}\sum_{ia}\sum_{jb}\langle pq||rs\rangle t_i^a t_j^b\langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\}|\Phi_0\rangle$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b \Bigg(\{\overbrace{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\} + \{\overbrace{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\} +$$

$$\{\overbrace{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\} + \{\overbrace{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\} \Bigg)$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b \left(-\delta_{pj}\delta_{qi}\delta_{ra}\delta_{sb} + \delta_{pj}\delta_{qi}\delta_{rb}\delta_{sa} + \delta_{pi}\delta_{qj}\delta_{ra}\delta_{sb} - \delta_{pi}\delta_{qj}\delta_{rb}\delta_{sa}\right)$$

$$= \frac{1}{2}\sum_{aibj}\langle ij||ab\rangle t_i^a t_j^b$$

- We can now bring all of the non-zero terms together to obtain the final CCSD energy expression:

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

THE CCSD AMPLITUDE EQUATIONS

- The derivation of algebraic expressions for the cluster amplitudes is similar to that of the energy equation. In the CCSD approximation, the single-and double-excitation amplitudes are determined from, respectively:

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

- Key concept: Although each of these expressions does not immediately appear to involve reference expectation values, they can be converted to this form by recognizing that the excited determinants on the left can be written as:

$$\langle \Phi_i^a | = \langle \Phi_0 | \{ a_i^\dagger a_a \} \qquad \text{and} \qquad \langle \Phi_{ij}^{ab} | = \langle \Phi_0 | \{ a_i^\dagger a_j^\dagger a_b a_a \}$$

- For example the leading $\hat{H}_N$ contribution to the single-excitation amplitude equations is:

$$\langle \Phi_i^a | \hat{F}_N | \Phi_0 \rangle = \sum_{pq} f_{pq} \langle \Phi_0 | \{ a_i^\dagger a_a \} \{ a_p^\dagger a_q \} | \Phi_0 \rangle = \sum_{pq} f_{pq} \{ \overbrace{a_i^\dagger a_a}^{} \overbrace{a_p^\dagger a_q}^{} \} = \sum_{pq} f_{pq} \delta_{iq} \delta_{ap} = f_{ai}$$

THE CCSD AMPLITUDE EQUATIONS

- Similarly, the leading $\hat{H}_N$ contribution to the double-excitation amplitude equations is:

$$\langle \Phi_{ij}^{ab} | \hat{V}_N | \Phi_0 \rangle = \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \langle \Phi_0 | \{a_i^\dagger a_j^\dagger a_b a_a\} \{a_p^\dagger a_q^\dagger a_s a_r\} | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \Bigg(\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} +$$

$$\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} \Bigg)$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \left(\delta_{pa}\delta_{qb}\delta_{ri}\delta_{sj} - \delta_{pb}\delta_{qa}\delta_{ri}\delta_{sj} - \delta_{pa}\delta_{qb}\delta_{rj}\delta_{si} + \delta_{pb}\delta_{qa}\delta_{rj}\delta_{si}\right)$$

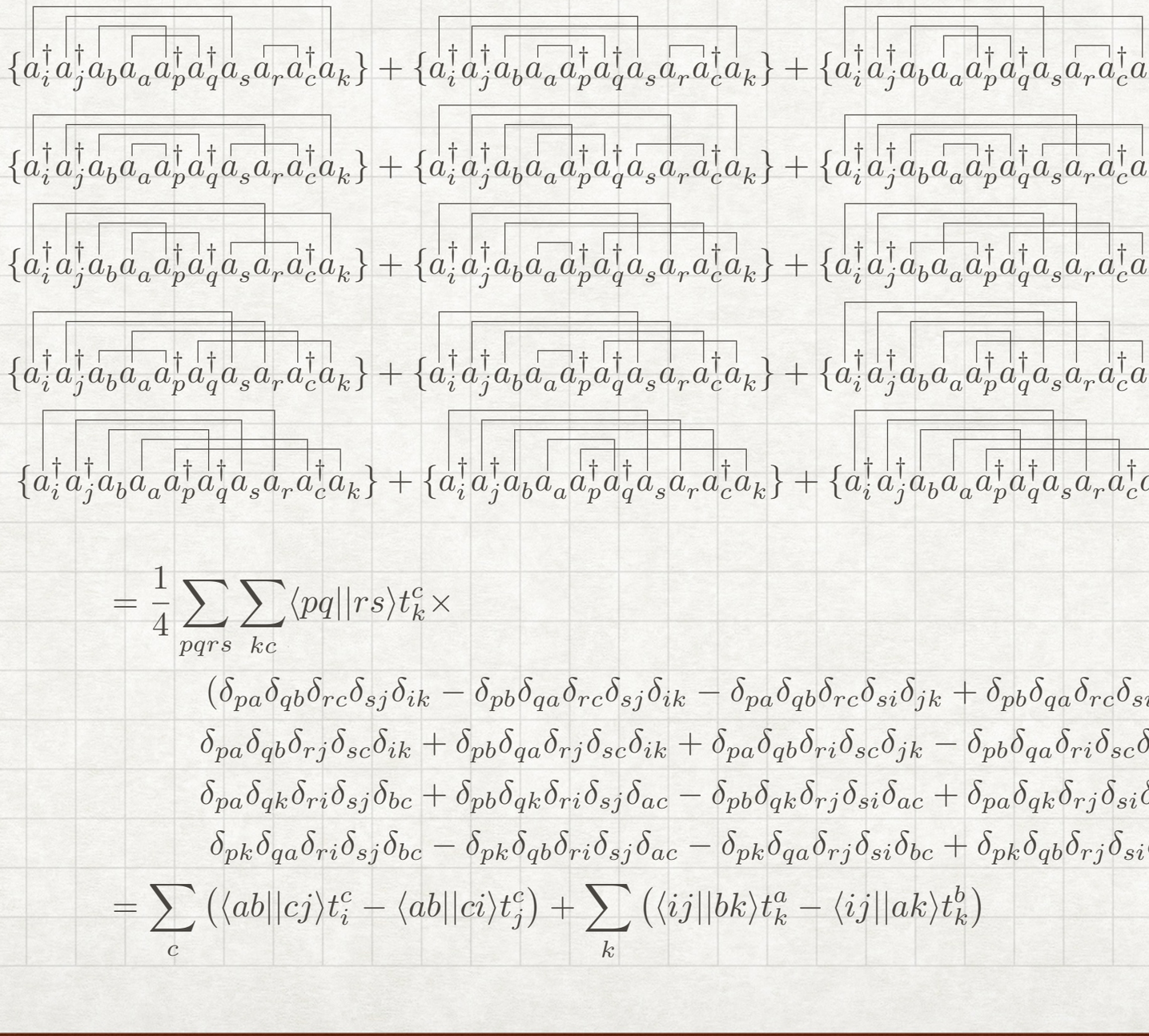
$$= \langle ab||ij\rangle$$

THE CCSD AMPLITUDE EQUATIONS

- And a term that I include here mainly because it looks so awesome:

$$\langle \Phi_{ij}^{ab}| \left(\hat{V}_N \hat{T}_1\right)_c |\Phi_0\rangle = \frac{1}{4}\sum_{pqrs}\sum_{kc}\langle pq||rs\rangle t_k^c \langle \Phi_0|\{a_i^\dagger a_j^\dagger a_b a_a\}\left(\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_c^\dagger a_k\}\right)_c|\Phi_0\rangle$$

$$= \frac{1}{4}\sum_{pqrs}\sum_{kc}\langle pq||rs\rangle t_k^c \Bigg(\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\} +$$



$$= \frac{1}{4}\sum_{pqrs}\sum_{kc}\langle pq||rs\rangle t_k^c \times$$

$$(\delta_{pa}\delta_{qb}\delta_{rc}\delta_{sj}\delta_{ik} - \delta_{pb}\delta_{qa}\delta_{rc}\delta_{sj}\delta_{ik} - \delta_{pa}\delta_{qb}\delta_{rc}\delta_{si}\delta_{jk} + \delta_{pb}\delta_{qa}\delta_{rc}\delta_{si}\delta_{jk} -$$
$$\delta_{pa}\delta_{qb}\delta_{rj}\delta_{sc}\delta_{ik} + \delta_{pb}\delta_{qa}\delta_{rj}\delta_{sc}\delta_{ik} + \delta_{pa}\delta_{qb}\delta_{ri}\delta_{sc}\delta_{jk} - \delta_{pb}\delta_{qa}\delta_{ri}\delta_{sc}\delta_{jk} -$$
$$\delta_{pa}\delta_{qk}\delta_{ri}\delta_{sj}\delta_{bc} + \delta_{pb}\delta_{qk}\delta_{ri}\delta_{sj}\delta_{ac} - \delta_{pb}\delta_{qk}\delta_{rj}\delta_{si}\delta_{ac} + \delta_{pa}\delta_{qk}\delta_{rj}\delta_{si}\delta_{bc} +$$
$$\delta_{pk}\delta_{qa}\delta_{ri}\delta_{sj}\delta_{bc} - \delta_{pk}\delta_{qb}\delta_{ri}\delta_{sj}\delta_{ac} - \delta_{pk}\delta_{qa}\delta_{rj}\delta_{si}\delta_{bc} + \delta_{pk}\delta_{qb}\delta_{rj}\delta_{si}\delta_{ac})$$

$$= \sum_c \left(\langle ab||cj\rangle t_i^c - \langle ab||ci\rangle t_j^c\right) + \sum_k \left(\langle ij||bk\rangle t_k^a - \langle ij||ak\rangle t_k^b\right)$$

THE $\hat{T}_1$ AMPLITUDE EQUATIONS

- Using a great deal of mental (and physical!) fortitude, one can apply Wick's theorem to all of the terms from the Hausdorff expansion and obtain the following expression for the single-excitation amplitudes:

$$0 = f_{ai} + \sum_c f_{ac} t_i^c - \sum_k f_{ki} t_k^a + \sum_{kc} \langle ka||ci\rangle t_k^c + \sum_{kc} f_{kc} t_{ik}^{ac} + \frac{1}{2} \sum_{kcd} \langle ka||cd\rangle t_{ki}^{cd} -$$
$$\frac{1}{2} \sum_{klc} \langle kl||ci\rangle t_{kl}^{ca} - \sum_{kc} f_{kc} t_i^c t_k^a - \sum_{klc} \langle kl||ci\rangle t_k^c t_l^a + \sum_{kcd} \langle ka||cd\rangle t_k^c t_i^d -$$
$$\sum_{klcd} \langle kl||cd\rangle t_k^c t_i^d t_l^a + \sum_{klcd} \langle kl||cd\rangle t_k^c t_{li}^{da} - \frac{1}{2} \sum_{klcd} \langle kl||cd\rangle t_{ki}^{cd} t_l^a - \frac{1}{2} \sum_{klcd} \langle kl||cd\rangle t_{kl}^{ca} t_i^d$$

THE $\hat{T}_2$ AMPLITUDE EQUATIONS

$$
\begin{aligned}
0 = {} & \langle ab||ij\rangle + \sum_c \left(f_{bc}t_{ij}^{ac} - f_{ac}t_{ij}^{bc}\right) - \sum_k \left(f_{kj}t_{ik}^{ab} - f_{ki}t_{jk}^{ab}\right) + \frac{1}{2}\sum_{kl}\langle kl||ij\rangle t_{kl}^{ab} + \frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_{ij}^{cd} \\
& + P(ij)P(ab)\sum_{kc}\langle kb||cj\rangle t_{ik}^{ac} + P(ij)\sum_c\langle ab||cj\rangle t_i^c - P(ab)\sum_k\langle kb||ij\rangle t_k^a + \frac{1}{2}P(ij)P(ab)\sum_{klcd}\langle kl||cd\rangle t_{ik}^{ac}t_{lj}^{db} \\
& + \frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_{ij}^{cd}t_{kl}^{ab} - P(ab)\frac{1}{2}\sum_{klcd}\langle kl||cd\rangle t_{ij}^{ac}t_{kl}^{bd} - P(ij)\frac{1}{2}\sum_{klcd}\langle kl||cd\rangle t_{ik}^{ab}t_{jl}^{cd} + P(ab)\frac{1}{2}\sum_{kl}\langle kl||ij\rangle t_k^a t_l^b \\
& + P(ij)\frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_i^c t_j^d - P(ij)P(ab)\sum_{kc}\langle kb||ic\rangle t_k^a t_j^c + P(ab)\sum_{kc} f_{kc}t_k^a t_{ij}^{bc} + P(ij)\sum_{kc} f_{kc}t_i^c t_{jk}^{ab} \\
& - P(ij)\sum_{klc}\langle kl||ci\rangle t_k^c t_{lj}^{ab} + P(ab)\sum_{kcd}\langle ka||cd\rangle t_k^c t_{ij}^{db} + P(ij)P(ab)\sum_{kcd}\langle ak||dc\rangle t_i^d t_{jk}^{bc} \\
& + P(ij)P(ab)\sum_{klc}\langle kl||ic\rangle t_l^a t_{jk}^{bc} + P(ij)\frac{1}{2}\sum_{klc}\langle kl||cj\rangle t_i^c t_{kl}^{ab} - P(ab)\frac{1}{2}\sum_{kcd}\langle kb||cd\rangle t_k^a t_{ij}^{cd} \\
& - P(ij)P(ab)\frac{1}{2}\sum_{kcd}\langle kb||cd\rangle t_i^c t_k^a t_j^d + P(ij)P(ab)\frac{1}{2}\sum_{klc}\langle kl||cj\rangle t_i^c t_k^a t_l^b - P(ij)\sum_{klcd}\langle kl||cd\rangle t_k^c t_i^d t_{lj}^{ab} \\
& - P(ab)\sum_{klcd}\langle kl||cd\rangle t_k^c t_l^a t_{ij}^{db} + P(ij)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_i^c t_j^d t_{kl}^{ab} + P(ab)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_k^a t_l^b t_{ij}^{cd} \\
& + P(ij)P(ab)\sum_{klcd}\langle kl||cd\rangle t_i^c t_l^b t_{kj}^{ad} + P(ij)P(ab)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_i^c t_k^a t_j^d t_l^b
\end{aligned}
$$

- The permutation operator maintains antisymmetry of the resulting terms:

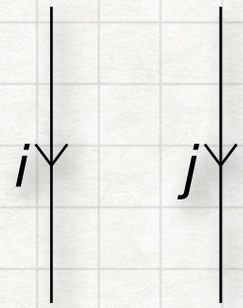
$$P(pq)f(p,q) = f(p,q) - f(q,p)$$

A FEW OBSERVATIONS

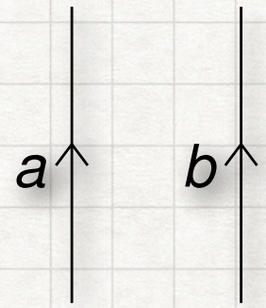
- Wick's theorem is certainly superior to application of the raw anti-commutation relations, but it still involves substantial tedium and numerous opportunities for error.
- For most terms, the result obtained from Wick's theorem still contains many redundancies that can only be reduced by further algebraic manipulation, *e.g.* re-indexing of summations, permutation of indices, etc.
- If we were to continue this approach to higher-order excitations (*i.e.*, triples, quadruples, etc.), the number of algebraic manipulations required by Wick's theorem becomes insurmountable if completed by hand.
- Computer algorithms exist to automate this process, and they have been quite successful even for higher excitations.[a]
- However, another approach exists that streamlines the process and offers a topological perspective on the various terms in the coupled cluster equations: ***diagrams!***

[a] See for example: S. Hirata, "Tensor contraction engine: Abstraction and automated parallel implementation of configuration-interaction, coupled-cluster, and many-body perturbation theories," J. Phys. Chem. A, 107, 9887 (2003).

DIAGRAMS: THE BASICS

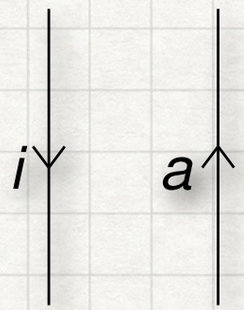


Holes
(Occupied Orbitals)



Particles
(Virtual Orbitals)

The Fermi Vacuum
(Empty Space)

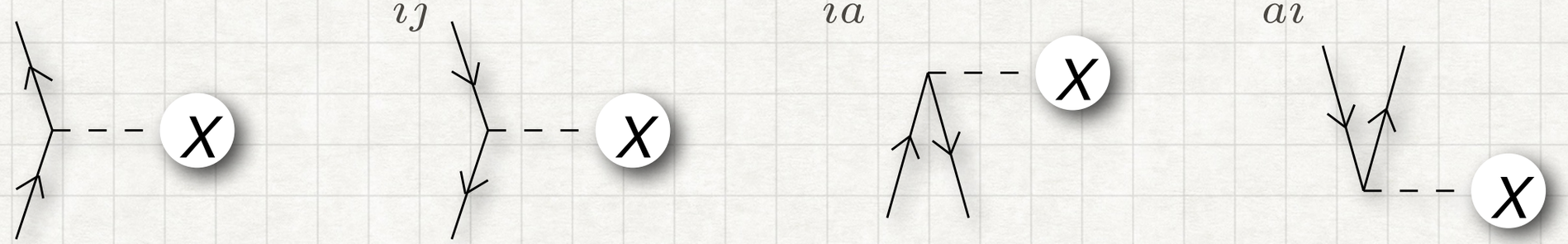


A Singly Excited
Determinant, $|\Phi_i^a\rangle$

DIAGRAMS: THE BASICS

- Diagrammatic representation of the Fock operator

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



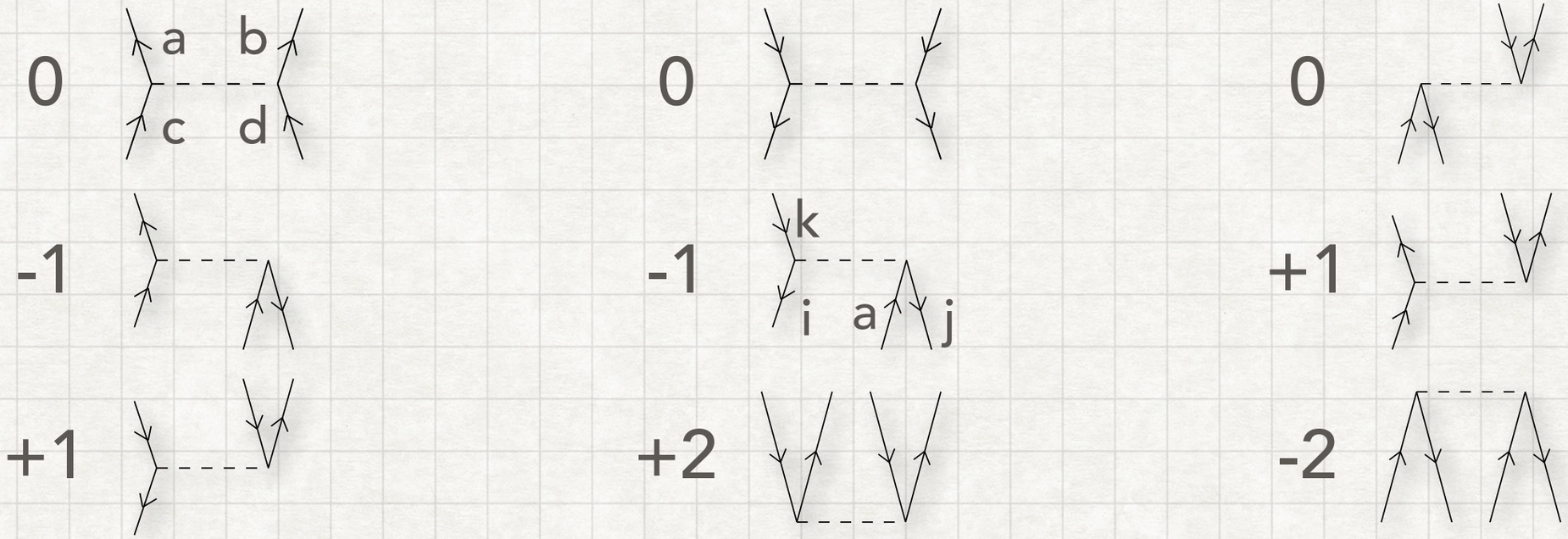
Excitation Level: 0 0 -1 +1

- The dotted horizontal line is called the "interaction line", and the upward- and downward-directed lines emanate from "vertices" and represent the annihilation/creation operators. Each vertex can connect to two directed lines, at most.
- The outward-directed line from a vertex corresponds to the left-hand orbital index in the integral, and the inward-directed line to the right-hand index.
- Directed lines above the interaction line 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 creation and annihilation operators divided by 2.

DIAGRAMS: THE BASICS

- Diagrammatic representation of the two-electron Hamiltonian component:

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



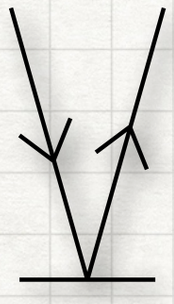
- For two-electron operators/integrals, the ordering of indices is:

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

DIAGRAMS: THE BASICS

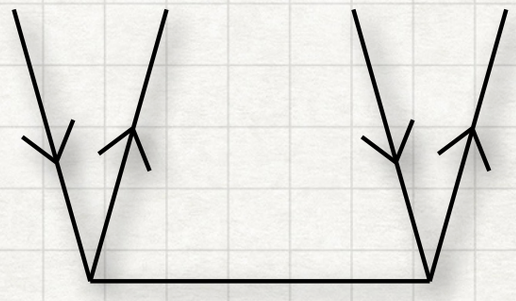
- Diagrammatic representation of cluster operators:

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



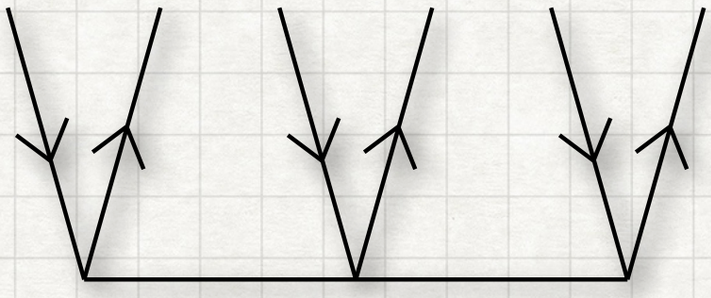
+1

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



+2

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



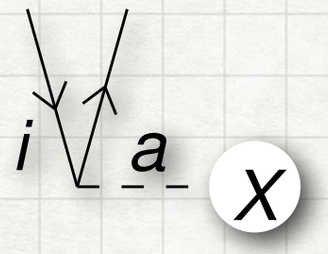
+3

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

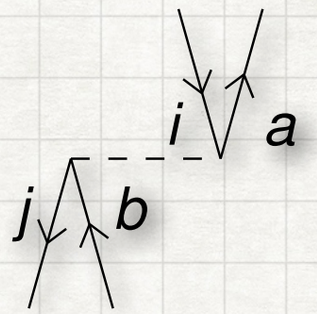
DIAGRAMS: MATRIX ELEMENTS

- 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:

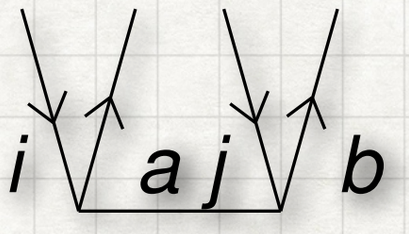
$$\langle \Phi_i^a | \hat{F}_N | \Phi_0 \rangle =$$



$$\langle \Phi_i^a | \hat{V}_N | \Phi_j^b \rangle =$$

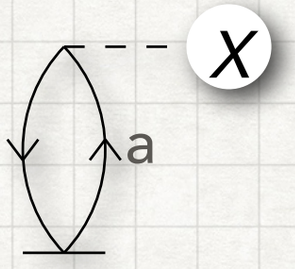


$$\langle \Phi_{ij}^{ab} | \hat{T}_2 | \Phi_0 \rangle =$$



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 $\hat{T}_1$:

$$\langle \Phi_0 | \left(\hat{F}_N \hat{T}_1 \right)_c | \Phi_0 \rangle =$$ 

$$= \sum_{ia} f_{ia} t_i^a$$

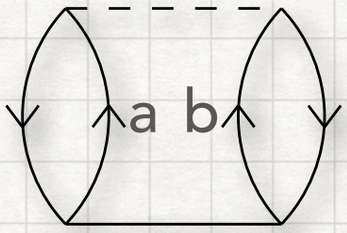
- To interpret this algebraically:
  1. Label all directed lines with appropriate indices: *i*, *j*, *k*, …; *a*, *b*, *c*, …
  2. Interpret the lines connected to the Fock operator vertex as:

$$f_{\text{left-out right-in}}$$

  3. Include summations for all "internal" lines (those that begin and end at interaction lines). "External" lines start at an interaction line and extend above of below the diagram.
  4. The sign of the diagram is $(-1)^{h+l}$, where *h* is the number of hole lines and *l* is the number of "loops" – a route along a series of directed lines that either returns to its beginning or starts at an external line and ends at another.

DIAGRAMS: THE CC ENERGY

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

$$\langle \Phi_0 | \left(\hat{H}_N \hat{T}_2 \right)_c | \Phi_0 \rangle =$$ 

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

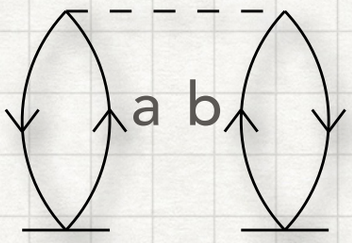
- To interpret this algebraically:
  1. Label all directed lines with appropriate indices: *i*, *j*, *k*, …; *a*, *b*, *c*, …
  2. Interpret the lines connected to the $\hat{V}_N$ operator vertex as:

     ⟨left-out right-out||left-in right-in⟩
  3. Interpret the lines connected to the $\hat{T}_2$ operator from left to right.
  4. Include summations for all "internal" lines.
  5. The sign of the diagram is $(-1)^{h+l}$.
  6. Paris of "equivalent" lines begin at the same interaction line and end at the same interaction line. For each such pair, multiply the expression by 1/2.

DIAGRAMS: THE CC ENERGY

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

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

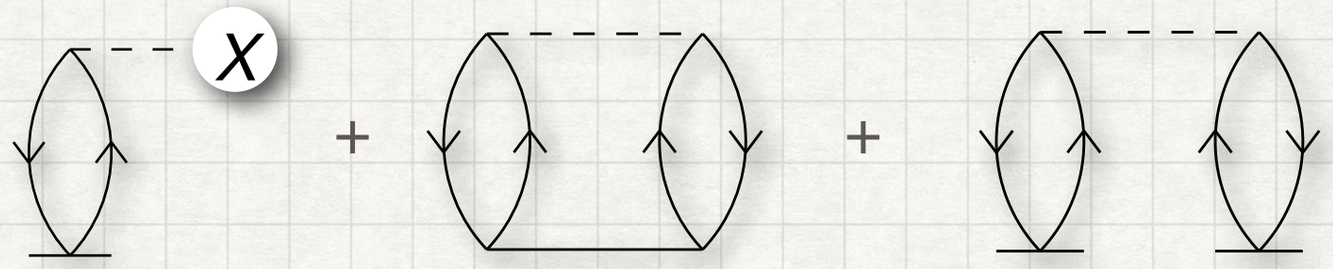


$$= \frac{1}{2} \sum_{ijab} \langle ij||ab \rangle t_i^a t_j^b$$

- 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:

$$E_{CCSD} =$$



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

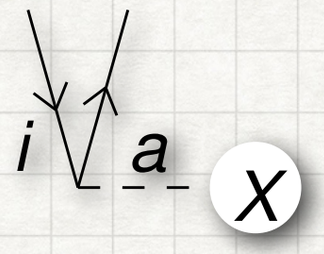
DIAGRAMS: THE CC AMPLITUDE EQUATIONS

- Next we consider the amplitude equations:

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

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

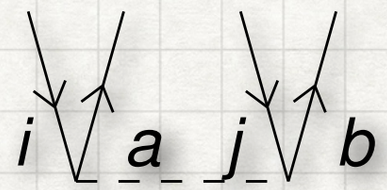
$$\langle \Phi_i^a | \hat{F}_N | \Phi_0 \rangle =$$



$$= f_{ai}$$

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

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

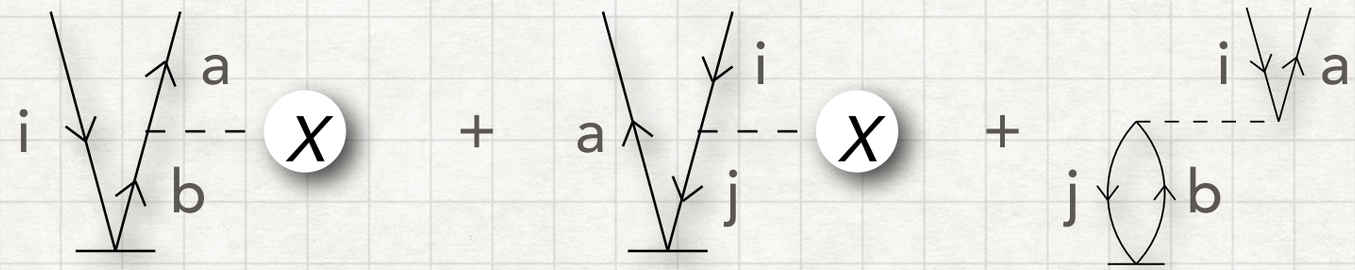


$$= \langle ab || ij \rangle$$

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

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

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

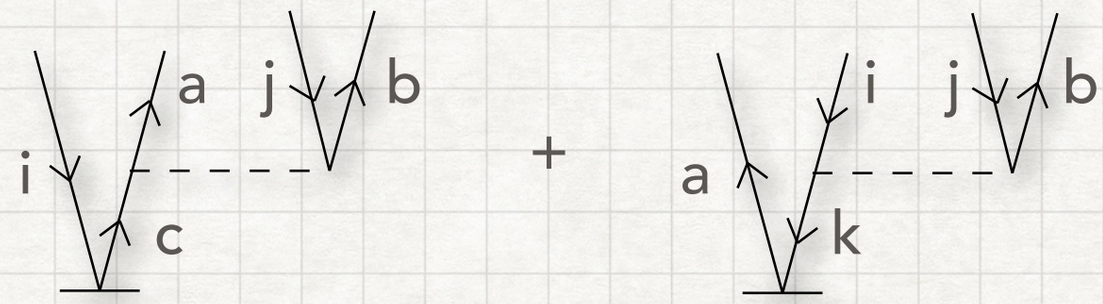


$$= \sum_b f_{ab} t_i^b - \sum_j f_{ji} t_j^a + \sum_{jb} \langle ja||bi\rangle t_j^b$$

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 interaction lines), external hole or particle lines introduces a permutation operator, $P(pq)$, to ensure antisymmetry of the final expression.

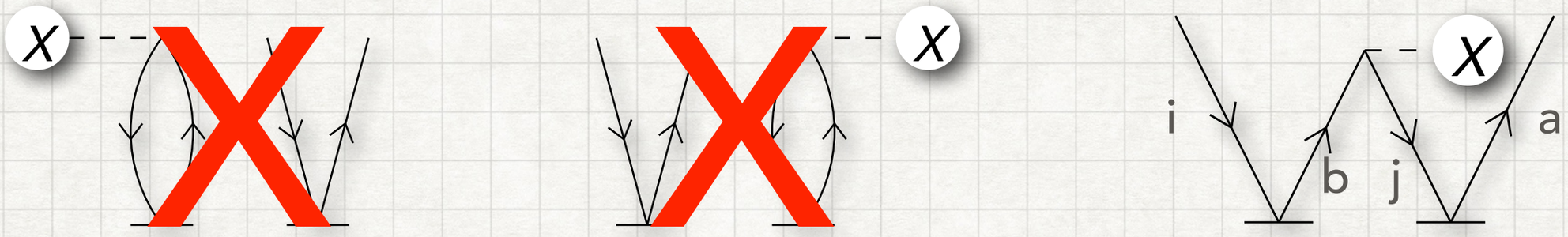
- This rule, in conjunction with our previous rules, gives:

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

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.

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

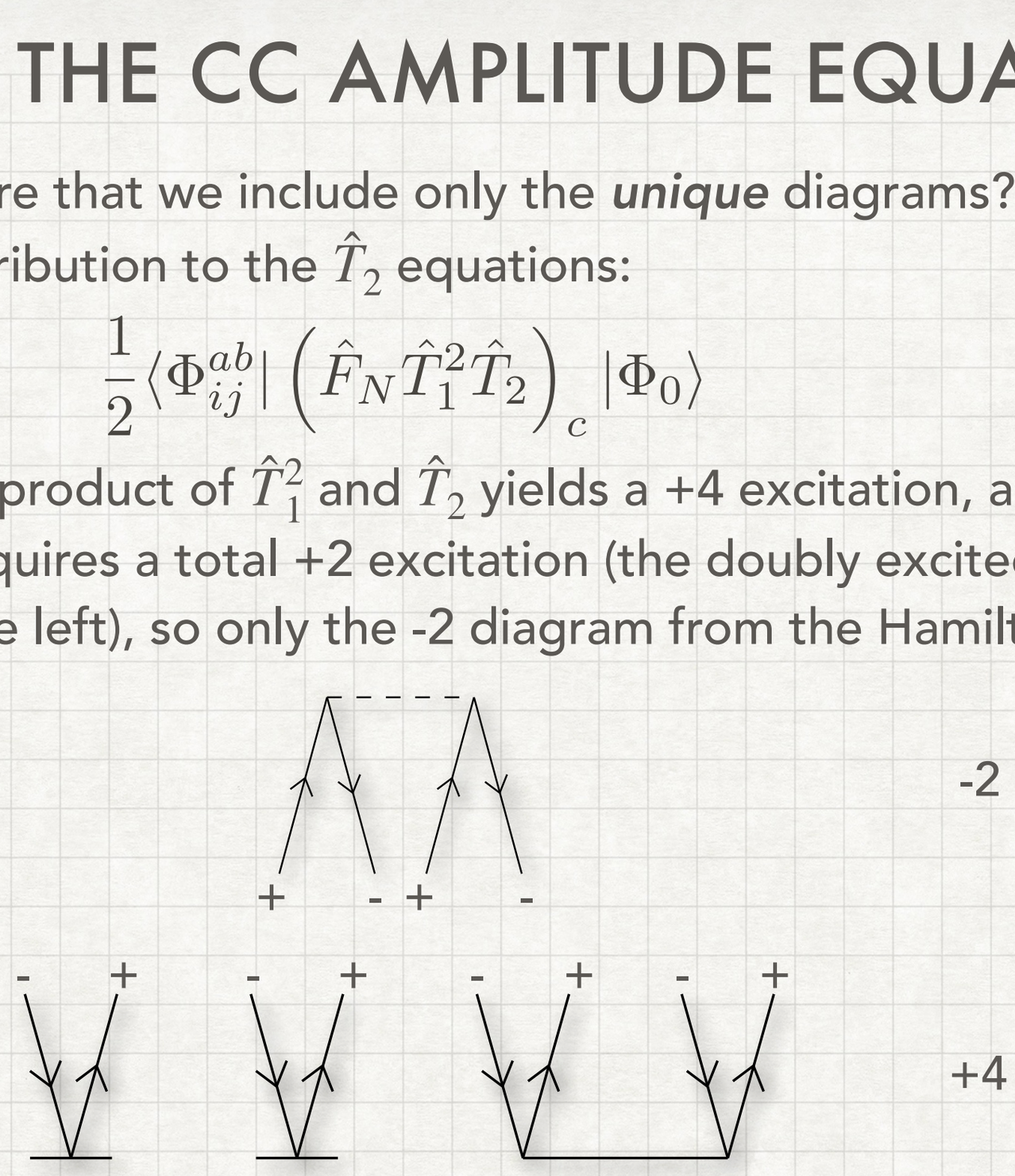
- Note that the factor of 1/2 in the expression on the left is automatically accounted for in the diagram.

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:

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

- 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:



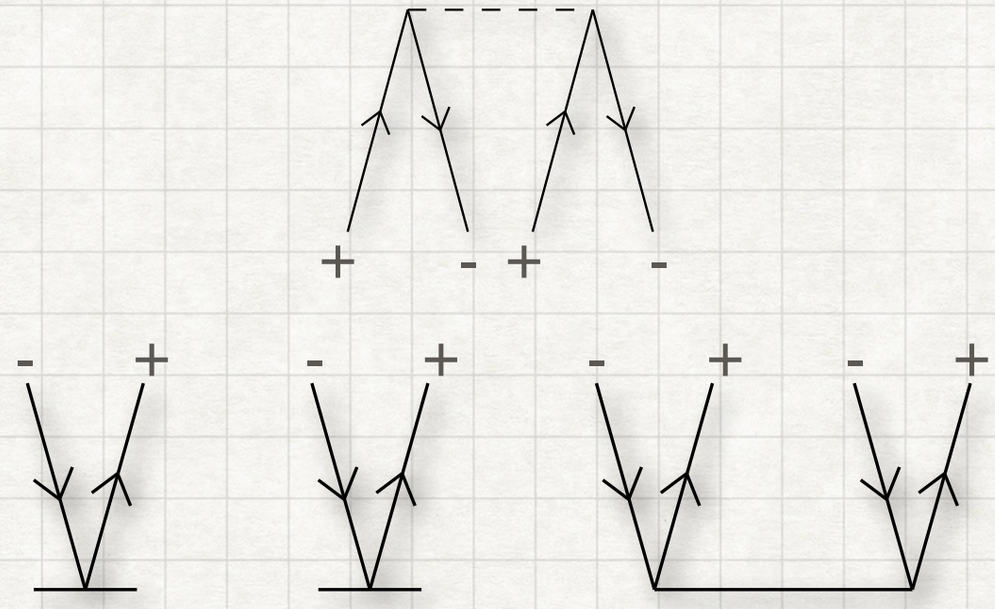
- The Kucharski-Bartlett "sign sequence": Assign "+" to each particle line and "-" to each hole line from all operators and select all unique combinations that take at least one connection from each $\hat{T}$ operator.

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

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

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

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

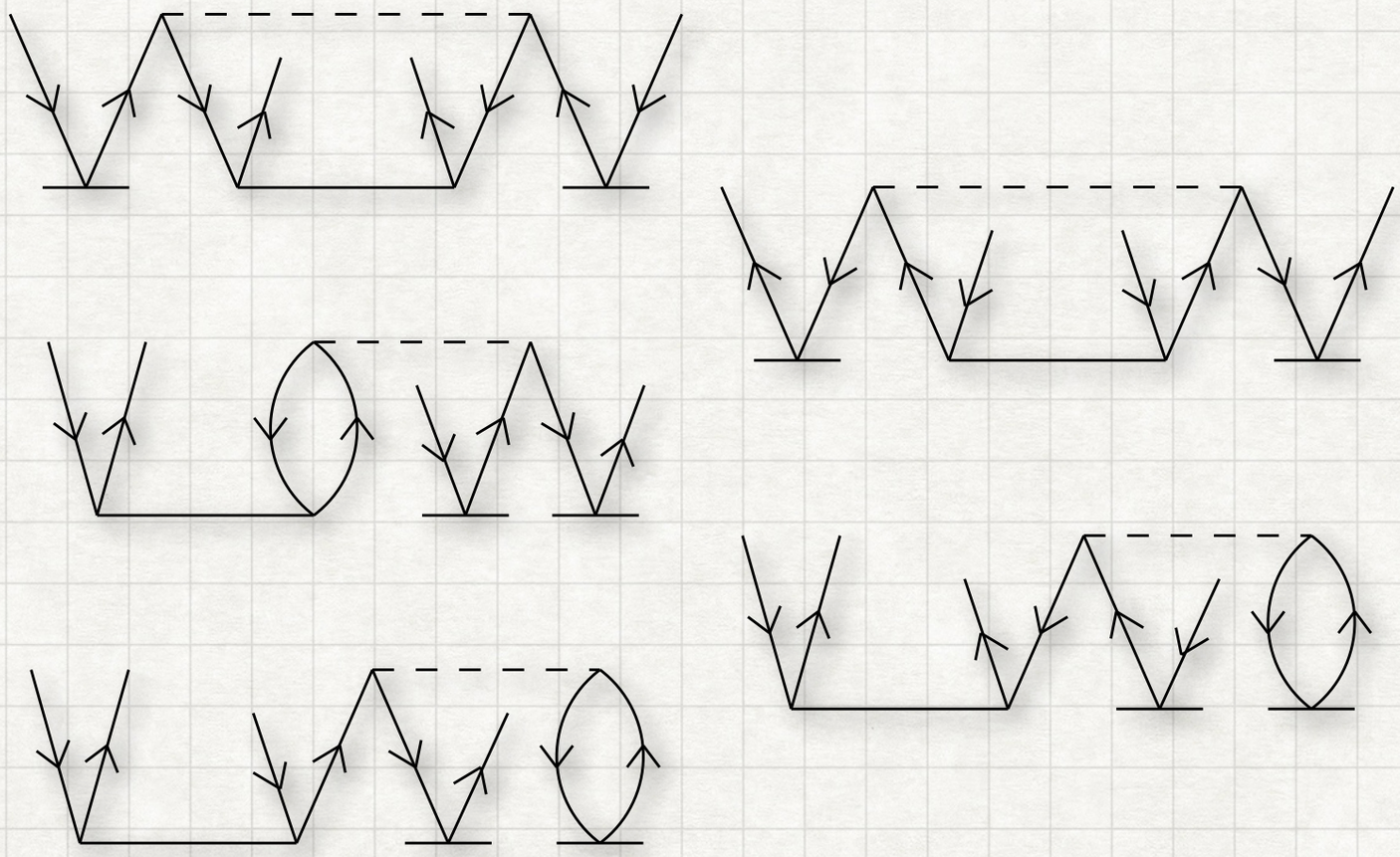


- There are only five unique combinations, leading to five unique diagrams.

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

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

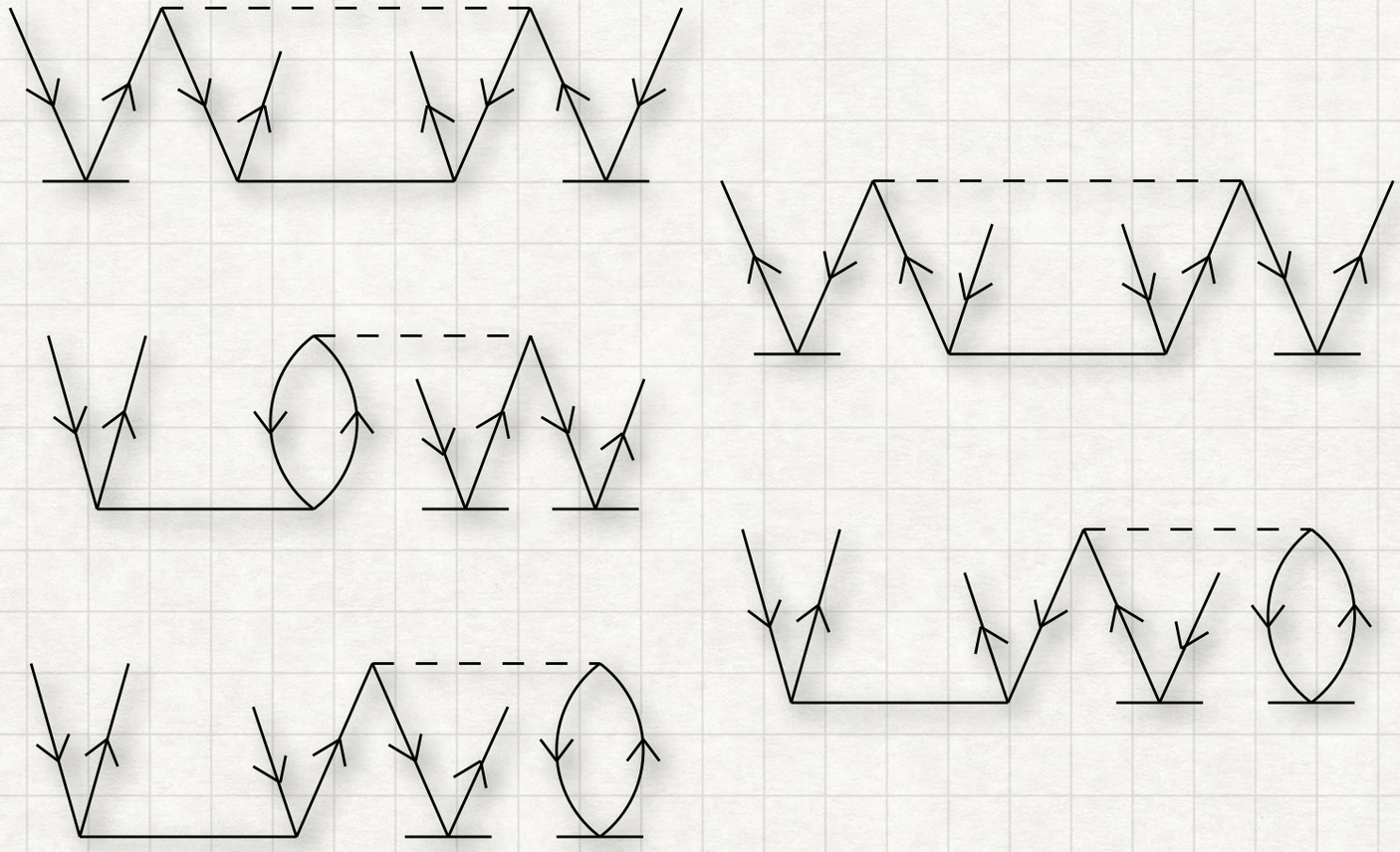
$\hat{T}_1$	$\hat{T}_1$	$\hat{T}_2$
+	+	– –
–	–	+ +
+	–	+ –
+ –	+	–
+ –	–	+



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

DIAGRAMS: THE CC AMPLITUDE EQUATIONS

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



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

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

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

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

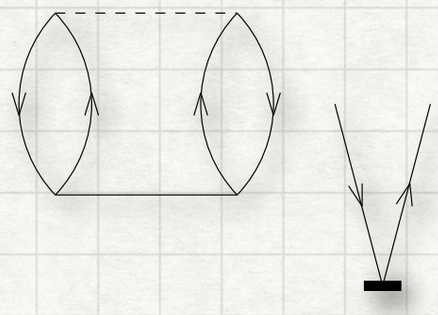
$$E c_{ij\ldots}^{ab\ldots} = \langle \Phi_{ij\ldots}^{ab\ldots} | \hat{H} \left(1 + \hat{C} \right) | \Phi_0 \rangle$$

Coupled Cluster

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

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

- 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.

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