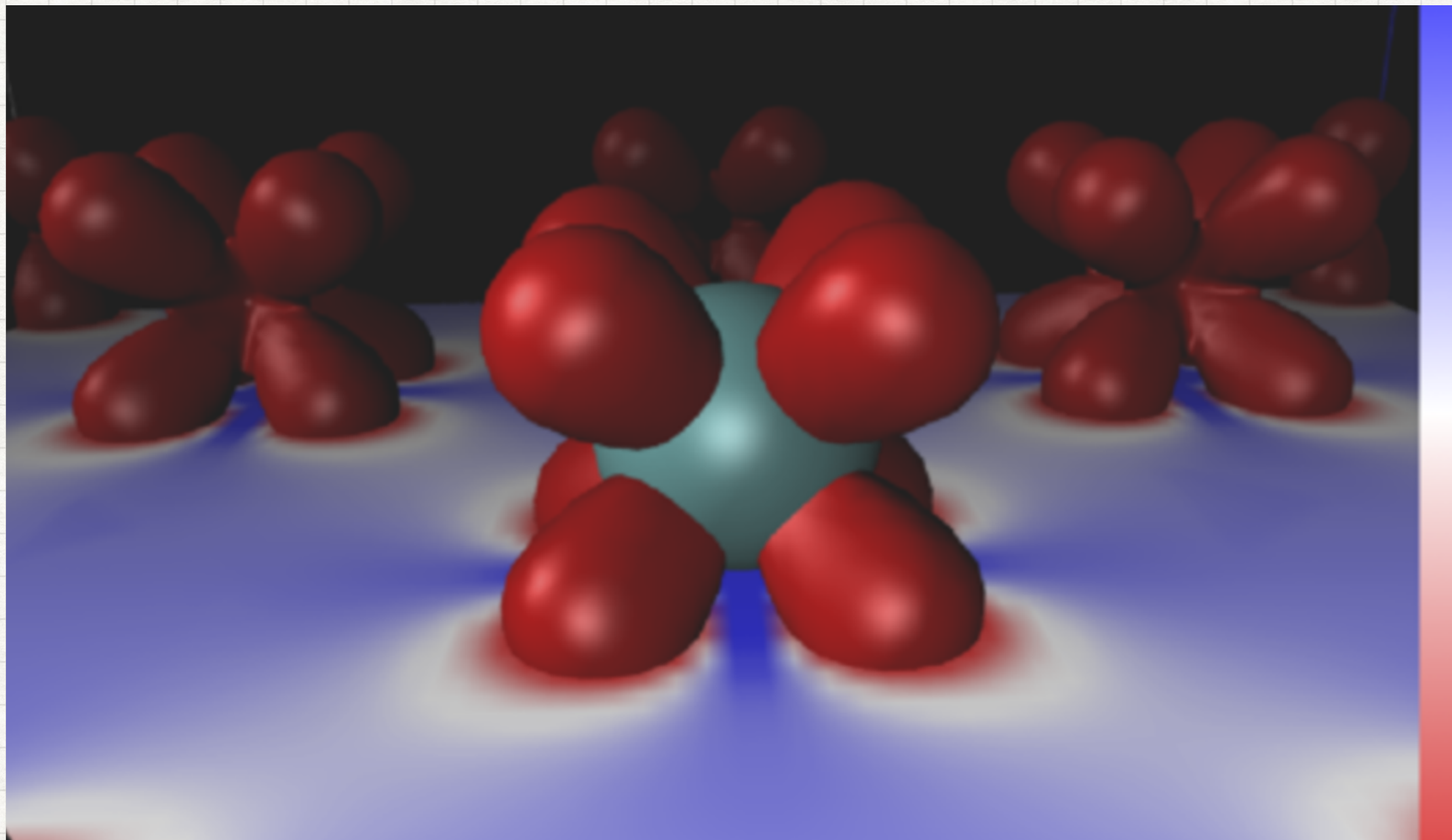


# COUPLED CLUSTER THEORY

PROF. T. DANIEL CRAWFORD, VIRGINIA TECH



# COMPUTATIONAL COST

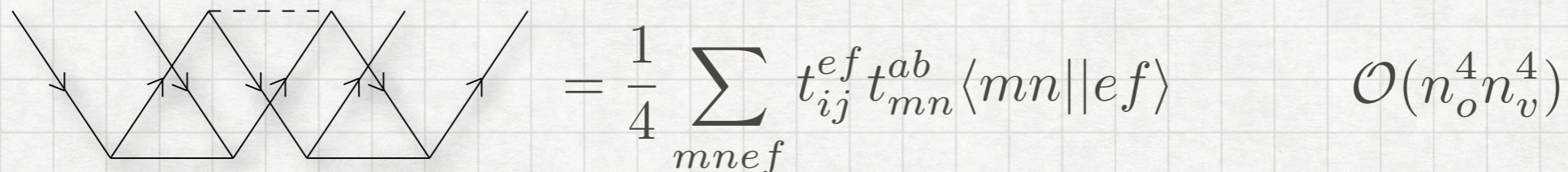
- Now that we have algebraic and diagrammatic representations of the many terms of the CC equations, we may examine their computational cost in detail. The most expensive term in the CCSD equations is the particle-particle ladder:



$$= \frac{1}{2} \sum_{ef} \langle ab || ef \rangle t_{ij}^{ef} \quad \text{Cost: } \mathcal{O}(n_o^2 n_v^4)$$

This is typically simplified to  $\mathcal{O}(N^6)$

- 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:

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

# PERTURBATION THEORY

- Rayleigh-Schrödinger perturbation theory involves four key steps:
  1. Partition the Hamiltonian into a zeroth-order component and a perturbation/fluctuation potential:

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}$$

2. Expand the wave function and energy into orders of  $\lambda$ :

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

3. Expand each perturbed wave function as a linear combination of a set of zeroth-order wave functions:

$$|\Psi_0^{(n)}\rangle = \sum_{I \neq 0} c_I^{(n)} |\Psi_I^{(0)}\rangle$$

which are often taken to be eigenfunctions of the zeroth-order Hamiltonian:

$$\hat{H}^{(0)} |\Psi_I^{(0)}\rangle = E_I^{(0)} |\Psi_I^{(0)}\rangle$$

4. Insert these expressions into the Schrödinger equation, collect terms by order of  $\lambda$ , and set  $\lambda=1$  to obtain separate equations for each order.

# MANY-BODY PERTURBATION THEORY

- In electronic-structure theory, we partition the second-quantized Hamiltonian into a zeroth-order component extracted from the Fock operator:

$$\hat{H}^{(0)} = \hat{F}_N = \sum_{ij} f_{ij} \{a_i^\dagger a_j\} + \sum_{ab} f_{ab} \{a_a^\dagger a_b\} = \sum_i \epsilon_i \{a_i^\dagger a_i\} + \sum_a \epsilon_a \{a_a^\dagger a_a\}$$

and place the remainder into the perturbation:

$$\hat{H}^{(1)} = \hat{V}_N = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\}$$

where we have assumed canonical Hartree-Fock orbitals.

- With this choice, a natural candidate for the ground-state zeroth-order wave function is the Hartree-Fock determinant:

$$|\Psi_0^{(0)}\rangle = |\Phi_0\rangle$$

and the other zeroth-order wave functions are excited determinants:

$$\{|\Psi_I^{(0)}\rangle\} = \{|\Phi_{ij\dots}^{ab\dots}\rangle\}$$

# MANY-BODY PERTURBATION THEORY

- This partitioning and choice of zeroth-order functions leads to the usual Møller-Plesset perturbational series, where the Hartree-Fock energy is the sum of the zeroth- and first-order energies:

$$E_{\text{HF}} = \langle \Phi_0 | \hat{H}_N | \Phi_0 \rangle = \langle \Phi_0 | \left( \hat{H}^{(0)} + \hat{H}^{(1)} \right) | \Phi_0 \rangle = E_0^{(0)} + E_0^{(1)}$$

- The first-order Møller-Plesset wave function automatically includes only double excitations:

$$|\Phi_0^{(1)}\rangle = \frac{1}{4} \sum_{ijab} (t_{ij}^{ab})^{(1)} |\Phi_{ij}^{ab}\rangle = \frac{1}{4} \sum_{ijab} (t_{ij}^{ab})^{(1)} \{a_a^\dagger a_b^\dagger a_j a_i\} |\Phi_0\rangle = \hat{T}_2^{(1)} |\Phi_0\rangle$$

where the first-order amplitudes have a concise form:

$$(t_{ij}^{ab})^{(1)} = \frac{\langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- And the second-order (MP2) energy is:

$$E_{\text{MP2}} = E_0^{(2)} = \frac{1}{4} \sum_{ijab} (t_{ij}^{ab})^{(1)} \langle ij || ab \rangle = \frac{1}{4} \sum_{ijab} \frac{\langle ij || ab \rangle \langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- Note that only doubles appear in the first-order wave function, whereas singles, triples, and quadruples appear in the second-order wave function.

# PERTURBATIONAL CC THEORY

- The contribution of excited determinants to various orders of perturbation theory suggests that we may decompose the cluster operators into perturbational orders:

$$\hat{T}_n = \hat{T}_n^{(1)} + \hat{T}_n^{(2)} + \hat{T}_n^{(3)} + \dots$$

where only  $\hat{T}_2$  includes a non-zero first-order term.

- We will adopt a common notation for the similarity-transformed Hamiltonian to simplify our equations somewhat:

$$\bar{H} = e^{-\hat{T}} \hat{H}_N e^{\hat{T}}$$

- The order-by-order expansion of  $\hat{T}$  and the partitioning of  $\hat{H}_N$  lead to a corresponding expansion of  $\bar{H}$ :

$$\bar{H} = \bar{H}^{(0)} + \bar{H}^{(1)} + \bar{H}^{(2)} + \dots$$

- The lowest few orders are:

$$\bar{H}^{(0)} = \hat{F}_N$$

$$\bar{H}^{(1)} = \hat{V}_N + \left( \hat{F}_N \hat{T}_2^{(1)} \right)_c$$

$$\bar{H}^{(2)} = \left( \hat{F}_N \hat{T}_1^{(2)} + \hat{F}_N \hat{T}_2^{(2)} + \hat{V}_N \hat{T}_2^{(1)} + \frac{1}{2} \hat{F}_N (\hat{T}_2^{(1)})^2 \right)_c$$

# PERTURBATIONAL CC THEORY

- In this formulation, we can construct  $n$ -th order Schrödinger equations as:

$$\bar{H}^{(n)} |\Phi_0\rangle = E^{(n)} |\Phi_0\rangle$$

and then project these onto appropriate determinants to obtain energies and perturbed amplitudes.

- The perturbed energies arise from projection onto the Hartree-Fock state:

$$E^{(n)} = \langle \Phi_0 | \bar{H}^{(n)} | \Phi_0 \rangle$$

- The second-order energy, for example is:

$$E^{(2)} = \langle \Phi_0 | \bar{H}^{(2)} | \Phi_0 \rangle = \langle \Phi_0 | \left( \hat{F}_N \hat{T}_1^{(2)} + \hat{F}_N \hat{T}_2^{(2)} + \hat{V}_N \hat{T}_2^{(1)} + \frac{1}{2} \hat{F}_N (\hat{T}_2^{(1)})^2 \right)_c | \Phi_0 \rangle$$

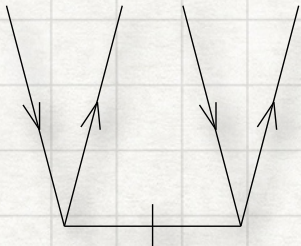
- However, the second and fourth terms on the right cannot contribute, because the Fock operator cannot cancel the +2 and +4 excitations produced by the cluster operators.
- Furthermore, the leading term is also zero, because only the  $f_{ia}$  component of  $\hat{F}_N$  can connect with  $\hat{T}_1^{(2)}$ , and this term is zero by Brillouin's theorem.

# THE SECOND-ORDER ENERGY

- The simplified equation for the second-order (MP2) energy is:

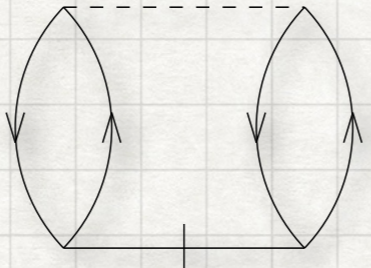
$$E^{(2)} = \langle \Phi_0 | \left( \hat{V}_N \hat{T}_2^{(1)} \right)_c | \Phi_0 \rangle$$

- We may write the first-order  $\hat{T}_2$  operator as:

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


where we indicate the order on the diagram using a hash mark on the interaction line.

- Then the second-order energy is similar to what we derived before for CCSD:



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

- Now we need an expression for the first-order doubles.

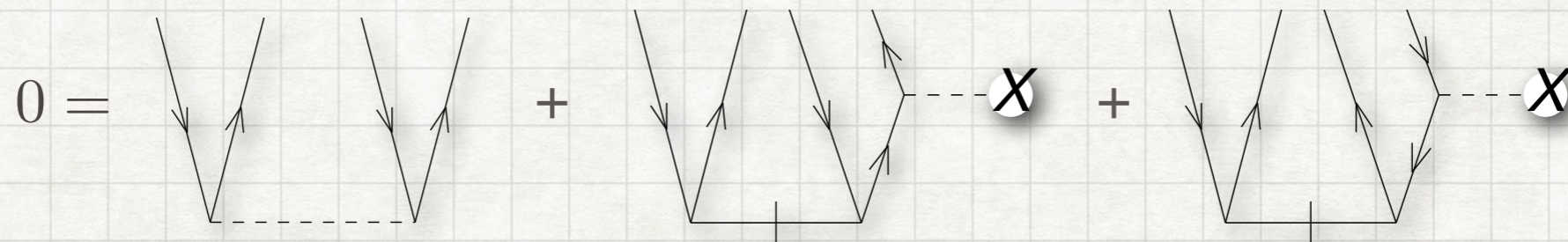


# THE FIRST-ORDER WAVE FUNCTION

- We may obtain an equation for the  $\hat{T}_2^{(1)}$  amplitudes by projecting the first-order Schrödinger equation onto the doubly excited Slater determinants:

$$0 = \langle \Phi_{ij}^{ab} | \bar{H}^{(1)} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{V}_N | \Phi_0 \rangle + \langle \Phi_{ij}^{ab} | \left( \hat{F}_N \hat{T}_2^{(1)} \right)_c | \Phi_0 \rangle$$

- Diagrammatically:



- Evaluating these diagrams gives:

$$0 = \langle ab || ij \rangle + P(ab) \sum_e f_{be} t_{ij}^{ae(1)} - P(ij) \sum_m f_{mj} t_{im}^{ab(1)}$$

- If the orbitals are canonical:

$$0 = \langle ab || ij \rangle + (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) t_{ij}^{ab(1)}$$

- We may rearrange this to something familiar:

$$t_{ij}^{ab(1)} = \frac{\langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

# THE SECOND-ORDER ENERGY (AGAIN)

- With an expression for the first-order doubles, we may write the second-order energy in its final form:

$$E_0^{(2)} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab(1)} \langle ij || ab \rangle = \frac{1}{4} \sum_{ijab} \frac{\langle ij || ab \rangle \langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- This is identical to the MP2 expression we examined earlier, but was derived entirely via the coupled cluster equations.
- A notational convenience is to incorporate the energy denominator directly into the diagram for  $\hat{T}_2^{(1)}$  as a horizontal line:

$$\text{Diagram} = t_{ij}^{ab(1)} = \frac{\langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} = \text{Diagram with horizontal line}$$

- This also leads to a modified diagram for the second-order energy:

$$\text{Diagram with horizontal line} = \text{Diagram with dashed lines}$$

# HIGHER EXCITATIONS

- As noted earlier, if we go beyond the CCSD approximation to include triples via CCSDT, the cost of the computation becomes unmanageable for chemically significant systems. Can we incorporate the effects of triples without making an investment in the full triples equations?
- For this analysis, we'll choose  $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$  (CCSDT), which gives us a similarity-transformed Hamiltonian:

$$\bar{H}_{\text{CCSDT}} = e^{-\hat{T}_1 - \hat{T}_2 - \hat{T}_3} \hat{H}_N e^{\hat{T}_1 + \hat{T}_2 + \hat{T}_3}$$

- Triple excitations first appear in the second-order wave function and the fourth-order energy (MP4). That gives us a starting point for approximating the effects of full triples:

$$E_T^{(4)} = \langle \Phi_0 | \bar{H}^{(4)} | \Phi_0 \rangle = \langle \Phi_0 | \left( \hat{V}_N \hat{T}_2^{(3)} \right)_c | \Phi_0 \rangle$$

# HIGHER EXCITATIONS

- The third-order doubles equation is:

$$0 = \langle \Phi_{ij}^{ab} | \bar{H}^{(3)} | \Phi_0 \rangle$$

$$= \langle \Phi_{ij}^{ab} | \left( \hat{F}_N \hat{T}_2^{(3)} + \hat{V}_N \hat{T}_1^{(2)} + \hat{V}_N \hat{T}_2^{(2)} + \hat{V}_N \hat{T}_3^{(2)} + \frac{1}{2} \hat{V}_N (\hat{T}_2^{(1)})^2 \right)_c | \Phi_0 \rangle$$

and only contribution we don't already have is  $\hat{V}_N \hat{T}_3^{(2)}$ .

- The contribution of  $\hat{T}_3^{(2)}$  to  $\hat{T}_2^{(3)}$  may be written as:

$$-\langle \Phi_{ij}^{ab} | \left( \hat{F}_N \hat{T}_2^{(3)} \right)_c | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \left( \hat{V}_N \hat{T}_3^{(2)} \right)_c | \Phi_0 \rangle$$

- We need second-order  $\hat{T}_3^{(2)}$  for this expression, which comes from:

$$-\langle \Phi_{ijk}^{abc} | \left( \hat{F}_N \hat{T}_3^{(2)} \right)_c | \Phi_0 \rangle = \langle \Phi_{ijk}^{abc} | \left( \hat{V}_N \hat{T}_2^{(1)} \right)_c | \Phi_0 \rangle$$

- So the chain of perturbational levels we need to compute the contribution of  $\hat{T}_3$  to the fourth-order energy is:

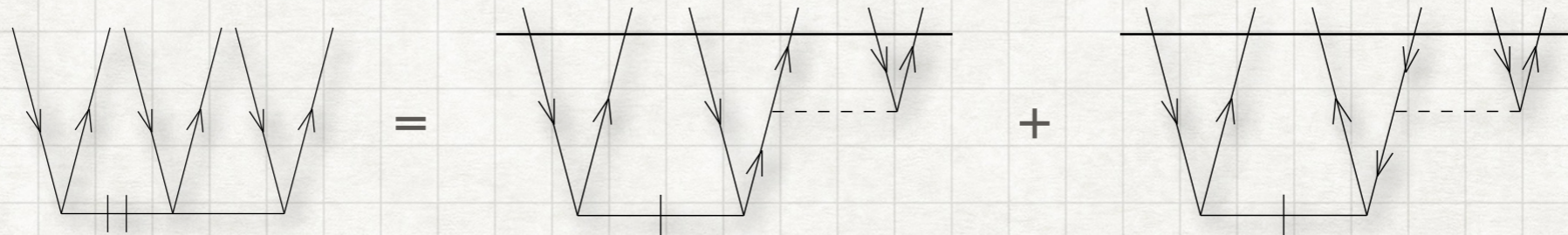
$$E_T^{(4)} \leftarrow \hat{T}_2^{(3)} \leftarrow \hat{T}_3^{(2)} \leftarrow \hat{T}_2^{(1)}$$

# HIGHER EXCITATIONS

- The contribution of  $\hat{T}_2^{(1)}$  to  $\hat{T}_3^{(2)}$  is:

$$-\langle \Phi_{ijk}^{abc} | \left( \hat{F}_N \hat{T}_3^{(2)} \right)_c | \Phi_0 \rangle = \langle \Phi_{ijk}^{abc} | \left( \hat{V}_N \hat{T}_2^{(1)} \right)_c | \Phi_0 \rangle$$

- Diagrammatically:



- Algebraically:

$$D_{ijk}^{abc} t_{ijk}^{abc(2)} = P(k/ij)P(a/bc) \sum_d \langle bc || dk \rangle t_{ij}^{ad(1)} - P(i/jk)P(c/ab) \sum_l \langle lc || jk \rangle t_{il}^{ab(1)}$$

- The permutation operators are defined as:

$$P(p/qr) f(pqr) = f(pqr) - f(qpr) - f(rqp)$$

- The energy denominators are defined as:

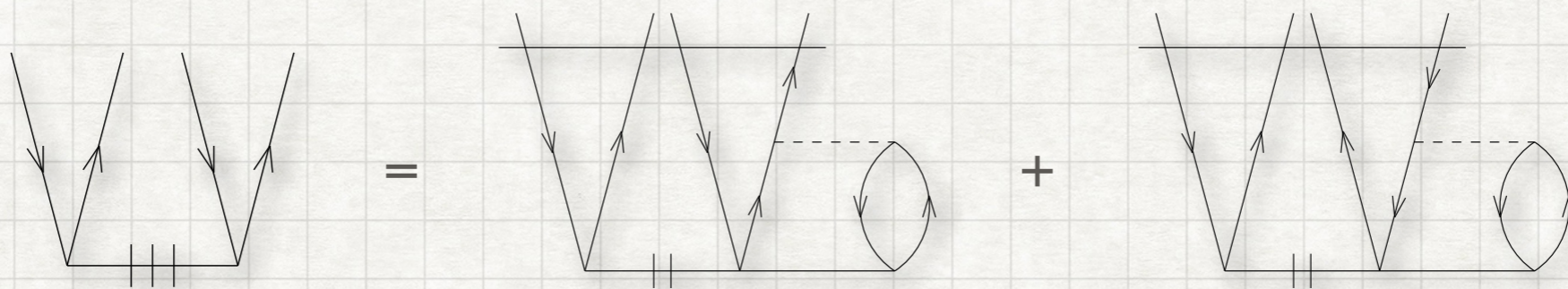
$$D_{ijk}^{abc} \equiv \epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c$$

# HIGHER EXCITATIONS

- The contribution of  $\hat{T}_3^{(2)}$  to  $\hat{T}_2^{(3)}$  may be written as:

$$-\langle \Phi_{ij}^{ab} | \left( \hat{F}_N \hat{T}_2^{(3)} \right)_c | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \left( \hat{V}_N \hat{T}_3^{(2)} \right)_c | \Phi_0 \rangle$$

- Or, diagrammatically as:



- And algebraically:

$$D_{ij}^{ab} t_{ij}^{ab(3)} = \frac{1}{2} P(ab) \sum_{mef} \langle bm || ef \rangle t_{ijm}^{aef(2)} - \frac{1}{2} P(ij) \sum_{mne} \langle mn || jb \rangle t_{imn}^{abe(2)}$$

# HIGHER EXCITATIONS

- Finally, the contribution of  $\hat{T}_2^{(3)}$  to  $E_T^{(4)}$  is:

$$E_T^{(4)} = \langle \Phi_0 | \left( \hat{V}_N \hat{T}_2^{(3)} \right)_c | \Phi_0 \rangle = \text{Diagram} = \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab(3)}$$

- Thus, we have a recipe for including the effects of triple-excitations via fourth-order perturbation theory. A few important observations are:
  - This approach is referred to as the CCSD+T(4) method.
  - Given that we are correcting  $E_{\text{CCSD}}$ , we already have the converged and  $\hat{T}_2$  amplitudes. Thus, we can use them rather than  $\hat{T}_2^{(1)}$ , which gives the CCSD+T(CCSD) = CCSD[T] method.
  - It is not necessary to compute and store all the  $t_{ijk}^{abc(2)}$  amplitudes. They are computed in batches, which are then immediately applied to the computation of  $t_{ij}^{ab(3)}$ , which is easier to store. ***This is key to the success of these methods.***

# CCSD(T)

- In 1989, Raghavachari *et al.* recognized that, in addition to  $E_T^{(4)}$ , a particular fifth-order energy contribution involving  $\hat{T}_1$  was important:

$$E_{ST}^{(5)} = \frac{1}{4} \sum_{ijkabc} \langle jk || bc \rangle t_i^a t_{ijk}^{abc}$$

- They combined this term with  $E_T^{(4)}$  (both computed using converged  $\hat{T}_1$  and  $\hat{T}_2$  amplitudes) to obtain the famous (T) correction:

$$E_{CCSD(T)} = E_{CCSD} + E_T^{(4)} + E_{ST}^{(5)}$$

- The computational cost of the CCSD(T) approach is a non-iterative  $\mathcal{O}(n_o^3 n_v^4)$  step in addition to the iterative  $\mathcal{O}(n_o^2 n_v^4)$  cost of CCSD.
- Due to its high accuracy, but significantly reduced cost (relative to the full CCSDT approach), CCSD(T) is widely regarded as the "gold standard" of coupled cluster theory.



# OTHER APPROXIMATE TRIPLES METHODS

CCSDT-1

Similar in structure to (T), but iterative.

CCSDT-2

Adds  $\hat{T}_2^2$  terms to CCSDT-1 (iterative).

CCSDT-3

Adds  $\hat{T}_1$ ,  $\hat{T}_1^2$ , and,  $\hat{T}_1^3$  terms to CCSDT-2 (iterative).

CC3

Similar to CCSDT-1, but includes all  $\hat{T}_1$  terms at zeroth-order (iterative).

CCSDR(3)

Similar to CC3, but is non-iterative.

- All of these methods have  $\mathcal{O}(N^7)$  cost, but vary in their prefactors and whether they are iterative or non-iterative. None require storage of the complete vector of  $\hat{T}_3$  amplitudes.