Coupled cluster theory: Fundamentals

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Outline

- The coupled cluster wave functions
- The coupled cluster Schrödinger equation
- Evaluating the CCSD energy
- Optimizing the coupled cluster wave function
- The $\mathcal{T}_1$ diagnostic
- Size consistency
- Coupled cluster perturbation theory
- The coupled cluster Lagrangian
- The $2n+1$ rule
- The CC2 and CC3 hybrid models
- The CCSD(T) noniterative method

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Coulomb correlation

- We take Hartree-Fock as the zeroth order reference.
  - This takes care of Fermi correlation.
- The correlation energy is then defined as the remaining deviation from the exact energy.

$$E = E_{\text{HF}} + E_{\text{corr}}$$

- When the HF reference is a good approximation to the wave function, coupled-cluster methods accurately describe the correction due to dynamic Coulomb correlation.
- We use the language of second quantization to discuss coupled-cluster methods.

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Pair Clusters

- The wave function for the motion of non-interacting fermions is described by a slater determinant of occupied spin-orbitals $I = 1, N$.

$$|\mathbf{H}F\rangle = \left[\prod_{I=1}^{N} a_I^\dagger\right] |\text{vac}\rangle$$

- Allowing for instantaneous Coulomb repulsion, the motion of two electrons in spin orbitals I and J is disturbed

$$a_I^\dagger a_J^\dagger \rightarrow a_I^\dagger a_J^\dagger + \sum_{A>B} t_{IJ}^{AB} a_A^\dagger a_B^\dagger.$$

- The disturbance is represented by excitations into virtual spin orbitals A and B with probabilities t_{IJ}^{AB}.
- This is known as a *pair cluster* or *two-electron cluster*.

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- Let us introduce an operator that describes this correlation process

$$\hat{\tau}_{IJ}^{AB} = a_A^\dagger a_I a_B^\dagger a_J$$

- We may write the pair cluster IJ as

$$\left[\prod_{A>B}(1 + t_{IJ}^{AB}\hat{\tau}_{IJ}^{AB})\right] a_I^\dagger a_J^\dagger|\text{vac}\rangle = a_I^\dagger a_J^\dagger|\text{vac}\rangle + \sum_{A>B} t_{IJ}^{AB} a_A^\dagger a_B^\dagger|\text{vac}\rangle.$$

- Allowing each pair of electrons to interact, we arrive at a *coupled cluster* wave function

$$|\text{CCD}\rangle = \left[\prod_{A>B,I>J}(1 + t_{IJ}^{AB}\hat{\tau}_{IJ}^{AB})\right]|\text{HF}\rangle.$$

- Note that all $\hat{\tau}_{IJ}^{AB}$ commute with each other.

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General coupled clusters

- Pair clusters account for the (dominant) two-electron interactions.
- The simultaneous interaction of three or more electrons also occurs, and in addition each orbital relaxes.
- We introduce a generalized excitation operator

$$\hat{\tau}_\mu = \hat{\tau}_{IJK\ldots}^{ABC\ldots} = a_A^\dagger a_I a_B^\dagger a_J a_C^\dagger a_K \ldots$$

- The generalized coupled cluster wave function is

$$|\text{CC}\rangle = \left[\prod_\mu (1 + t_\mu \hat{\tau}_\mu)\right]|\text{HF}\rangle.$$

- Note the product form, in contrast to the CI wave function.

$$|\text{CI}\rangle = \left(1 + \sum_\mu C_\mu \hat{\tau}_\mu\right)|\text{HF}\rangle.$$

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The exponential ansatz

- Since the spin-orbital excitation operators satisfy

$$\hat{\tau}_\mu^2 = 0,$$

- then

$$(1 + t_\mu \hat{\tau}_\mu) = \exp(t_\mu \hat{\tau}_\mu).$$

- and

$$|\mathrm{CC}\rangle = \left[\prod_\mu (1 + t_\mu \hat{\tau}_\mu)\right] |\mathrm{HF}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle,$$

- with

$$\hat{T} = \sum_\mu t_\mu \hat{\tau}_\mu.$$

- The order of the operators does not matter, $[\hat{\tau}_\mu, \hat{\tau}_\nu] = 0$
- This exponential formulation affords significant simplifications later on.

The hierarchy of excitation levels

- We may classify the excitation operators according to the level of excitation

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N$$

- where $\hat{T}_1$ contains excitations involving one electron only

$$\hat{T}_1 = \sum_{AI} t_I^A a_A^\dagger a_I = \sum_{AI} t_I^A \hat{\tau}_I^A$$

- and $\hat{T}_2$ contains excitations involving two electrons only etc.

$$\begin{aligned} \hat{T}_2 &= \sum_{\substack{A>B \\ I>J}} t_{IJ}^{AB} a_A^\dagger a_I a_B^\dagger a_J \\ &= \tfrac{1}{4} \sum_{AIBJ} t_{IJ}^{AB} a_A^\dagger a_I a_B^\dagger a_J = \tfrac{1}{4} \sum_{AIBJ} t_{IJ}^{AB} \hat{\tau}_{IJ}^{AB} \end{aligned}$$

- The truncation of the excitation operator $\hat{T}$ defines the coupled cluster method

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N$$

CCS	$\hat{T}_1$
CCSD	$\hat{T}_1 + \hat{T}_2$
CCSDT	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3$
CCSDTQ	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$
	$\vdots$

- Excitations $\hat{T}_N$ are able to account for the simultaneous interaction of N electrons.
- This series rapidly converges if the HF wave function is a good zeroth order reference.

Coupled cluster convergence towards full CI

- The difference between the cc-pVDZ energies of H_2O from the full CI limit of various coupled-cluster methods (E_h). The HOH angle is 110.565^o and $R_{\text{ref}} = 1.84345$ a_0.

method	$R = R_{\text{ref}}$	$R = 2R_{\text{ref}}$
RHF	0.217822	0.363954
CCSD	0.003744	0.022032
CCSDT	0.000493	-0.001405
CCSDTQ	0.000019	-0.000446
CCSDTQ5	0.000003	

- The series converges very fast at equilibrium and slower at stretched geometry where there a higher multi-reference character.

Connected and disconnected clusters

- Expanding $|\mathrm{CC}\rangle$, we obtain

$$\begin{aligned}\exp(\hat{T})|\mathrm{HF}\rangle &= \left(1+\sum_{\mu} t_\mu \hat{\tau}_\mu + \sum_{\mu>\nu} t_\mu t_\nu \hat{\tau}_\mu \hat{\tau}_\nu + \cdots\right)|\mathrm{HF}\rangle \\ &= |\mathrm{HF}\rangle + \sum_{\mu} t_\mu |\mu\rangle + \sum_{\mu>\nu} t_\mu t_\nu + \cdots |\mu\nu\rangle.\end{aligned}$$

- Note that each excitation $\hat{\tau}_\mu$ occurs only once in $\hat{T}$.
- Collecting determinants we see that a given determinant is generated in several ways

$$\exp(\hat{T})|\mathrm{HF}\rangle = \sum_i \hat{C}_i|\mathrm{HF}\rangle$$

$$\begin{aligned}\hat{C}_0 &= 1 \\ \hat{C}_1 &= \hat{T}_1 \\ \hat{C}_2 &= \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 \\ \hat{C}_3 &= \hat{T}_3 + \hat{T}_1\hat{T}_2 + \tfrac{1}{6}\hat{T}_1^3\end{aligned}$$

- E.g., the determinant with orbitals IJ replaced by AB

$$(t_{IJ}^{AB})^{\mathrm{total}}|_{IJ}^{AB}\rangle = t_{IJ}^{AB}\hat{\tau}_{IJ}^{AB}|\mathrm{HF}\rangle + t_I^A t_J^B \hat{\tau}_I^A \hat{\tau}_J^B|\mathrm{HF}\rangle - t_I^B t_J^A \hat{\tau}_I^B \hat{\tau}_J^A|\mathrm{HF}\rangle$$

- t_{IJ}^{AB} are *connected cluster amplitudes*
- $t_I^A t_J^B$ and $t_I^B t_J^A$ are *disconnected cluster amplitudes*

- The maximum excitation in $\hat{T}$ determines the maximum connected amplitude.
- All possible excitations are included in $|\mathrm{CC}\rangle$, the amplitudes of all higher excitations are determined by products of connected amplitudes.
- Whereas each determinant is parameterized in CI theory, in CC theory the excitation process is parameterized. We shall see that this leads to size consistency.

The coupled cluster Schrödinger equation

- We wish to solve $\hat{H}|\mathrm{CC}\rangle = E|\mathrm{CC}\rangle$.
- What happens if we apply the variational principle?

$$E_{\mathrm{min}} = \min_{t_\mu} \frac{\langle \mathrm{CC}|\hat{H}|\mathrm{CC}\rangle}{\langle \mathrm{CC}|\mathrm{CC}\rangle}$$

- $|\mathrm{CC}\rangle$ depends on t_μ in a non-linear way:

$$\frac{\partial}{\partial t_\mu}|\mathrm{CC}\rangle = \left[\prod_\nu (1 + t_\nu \hat{\tau}_\nu)\right] |\mu\rangle$$

- The variational condition results in an intractable set of nonlinear equations for the amplitudes.

$$\langle\mu| \left[\prod_\nu (1 + t_\nu \hat{\tau}_\nu^\dagger)\right] \hat{H}|\mathrm{CC}\rangle = E_{\mathrm{min}} \langle\mu| \left[\prod_\nu (1 + t_\nu \hat{\tau}_\nu^\dagger)\right] |\mathrm{CC}\rangle$$

The projected coupled cluster equations

- In a given orbital basis, the full coupled cluster wave function that includes all $\binom{M}{N} - 1$ excitations satisfies

$$\hat{H} \exp(\hat{T})|\mathrm{HF}\rangle = E \exp(\hat{T})|\mathrm{HF}\rangle$$

- We may set up $\binom{M}{N}$ equations to find the energy and amplitudes by left projecting by each determinant.

$$\begin{aligned} \langle \mathrm{HF}|\hat{H} \exp(\hat{T})|\mathrm{HF}\rangle &= E \\ \langle \mu|\hat{H} \exp(\hat{T})|\mathrm{HF}\rangle &= E\langle \mu| \exp(\hat{T})|\mathrm{HF}\rangle \end{aligned}$$

- The are the *projected coupled cluster equations* and must be solved self consistently.

- For truncated cluster operator $\hat{T}_N$ the Schrödinger equation is never satisfied.

$$\hat{H}\exp(\hat{T}_N)|\mathrm{HF}\rangle = \exp(\hat{T}')|\mathrm{HF}\rangle \neq E_N \exp(\hat{T}_N)|\mathrm{HF}\rangle$$

- For a cluster operator that includes n-tuple excitations we project the Schrödinger equation onto the manifold of all n-tuple excited determinants.

$$\begin{aligned}\langle \mathrm{HF}|\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E \\ \langle \mu_n|\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E\langle \mu_n|\exp(\hat{T})|\mathrm{HF}\rangle\end{aligned}$$

- Solving self consistently yields approximate amplitudes and an approximate energy, which may be above or below the exact energy.
- The error in the amplitudes is due to the missing interactions with the excitations absent from $\hat{T}_N$.

The similarity transformed Hamiltonian

- Since $\langle \mathrm{HF}|\exp(-\hat{T}) = \langle \mathrm{HF}|$, we may left multiply by $\exp(-\hat{T})$.

$$\begin{aligned}\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E\exp(\hat{T})|\mathrm{HF}\rangle \\ \exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E|\mathrm{HF}\rangle\end{aligned}$$

- The projected energy and amplitude equations are then decoupled.

$$\begin{aligned}\langle \mathrm{HF}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E \\ \langle \mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= 0\end{aligned}$$

- We define the *similarity transformed Hamiltonian*:

$$\hat{H}^T = \exp(-\hat{T})\hat{H}\exp(\hat{T})$$

- $\hat{H}^T$ may been seen as an effective Hamiltonian and is non-Hermitian.

The BCH expansion

- The similarity transformed Hamiltonian may be simplified through the Baker-Campbell-Hausdorff (BCH) expansion.
- We Taylor expand $\hat{H}^{\lambda T}$ around $\lambda = 0$

$$\begin{aligned}
\hat{H}^{\lambda T} &= \exp(-\lambda\hat{T})\hat{H}\exp(\lambda\hat{T}) \\
&= \hat{H}^{\lambda T}\Big|_{\lambda=0} + \lambda\frac{d\hat{H}^{\lambda T}}{d\lambda}\Big|_{\lambda=0} + \tfrac{1}{2!}\lambda^2\frac{d^2\hat{H}^{\lambda T}}{d\lambda^2}\Big|_{\lambda=0} + \cdots \\
\frac{d\hat{H}^{\lambda T}}{d\lambda} &= \exp(-\lambda\hat{T})[\hat{H},\hat{T}]\exp(\lambda\hat{T}) \\
\frac{d^2\hat{H}^{\lambda T}}{d\lambda^2} &= \exp(-\lambda\hat{T})[[\hat{H},\hat{T}],\hat{T}]\exp(\lambda\hat{T})
\end{aligned}$$

- Setting $\lambda = 1$ we obtain the BCH expansion

$$\hat{H}^T = \hat{H} + [\hat{H},\hat{T}] + \tfrac{1}{2!}[[\hat{H},\hat{T}],\hat{T}] + \tfrac{1}{3!}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \cdots$$

- In fact, the BCH expansion of $\hat{H}^T$ terminates after only four nested commutators.

$$\begin{aligned}
\hat{H}^T = \hat{H} &+ [\hat{H},\hat{T}] + \tfrac{1}{2!}[[\hat{H},\hat{T}],\hat{T}] + \tfrac{1}{3!}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] \\
&+ \tfrac{1}{4!}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]
\end{aligned}$$

- We recall that a commutator $[\hat{A},\hat{B}]$ has a rank one less than the operator $\hat{A}\hat{B}$, reducing the rank of the $\hat{A}$ and $\hat{B}$ contributions by one half. e.g.

$$[a_P^\dagger a_Q, a_A^\dagger a_I] = \delta_{QA}a_P^\dagger a_I - \delta_{PI}a_A^\dagger a_Q$$

- Since the Hamiltonian is a rank 2 operator, four successive commutations removes the contribution from $\hat{H}$ leaving only the excitation operator contributions, which always commute, $[a_A^\dagger a_I, a_B^\dagger a_J] = 0$.

The coupled cluster energy

- Applying BCH to the projected energy expression,

$$\begin{aligned} E &= \langle \mathrm{HF}|\hat{H}|\mathrm{HF}\rangle + \langle \mathrm{HF}|[\hat{H},\hat{T}]|\mathrm{HF}\rangle + \tfrac{1}{2!}\langle \mathrm{HF}|[[\hat{H},\hat{T}],\hat{T}]|\mathrm{HF}\rangle \\ &+ \tfrac{1}{3!}\langle \mathrm{HF}|[[[\hat{H},\hat{T}],\hat{T}],\hat{T}]|\mathrm{HF}\rangle + \tfrac{1}{4!}\langle \mathrm{HF}|[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]|\mathrm{HF}\rangle \end{aligned}$$

  - This simplifies considerably, since $\langle \mathrm{HF}|\hat{T} = 0$
  - and since $\hat{H}$ is a two particle operator, it can de-excite a maximum of 2 electrons: $\langle \mathrm{HF}|\hat{H}\hat{T}_i|\mathrm{HF}\rangle = 0$ for $i > 2$
  - also $\langle \mathrm{HF}|\hat{H}\hat{T}_1|\mathrm{HF}\rangle = 0$ due to the Brillouin theorem.

- The projected energy expression is simply

$$E = E_{HF} + \langle \mathrm{HF}|[\hat{H},\hat{T}_2]|\mathrm{HF}\rangle + \tfrac{1}{2}\langle \mathrm{HF}|[[\hat{H},\hat{T}_1],\hat{T}_1]|\mathrm{HF}\rangle$$

- Only singles and doubles amplitudes contribute directly to the energy, but the singles and doubles amplitudes depend on all the other amplitudes.

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The coupled cluster amplitude equations

- Applying the BCH expansion to the projected amplitude equations

$$\begin{aligned} 0 &= \langle \mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle \\ &= \langle \mu|\hat{H}|\mathrm{HF}\rangle + \langle \mu|[\hat{H},\hat{T}]|\mathrm{HF}\rangle + \tfrac{1}{2!}\langle \mu|[[\hat{H},\hat{T}],\hat{T}]|\mathrm{HF}\rangle \\ &+ \tfrac{1}{3!}\langle \mu|[[[\hat{H},\hat{T}],\hat{T}],\hat{T}]|\mathrm{HF}\rangle + \tfrac{1}{4!}\langle \mu|[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]|\mathrm{HF}\rangle \end{aligned}$$

- These form coupled a set of nonlinear equations, at most quartic in the amplitudes.
- In fact, except for singles and doubles, the amplitudes for the highest excitation level only occur linearly.
- Further simplifications arise for specific coupled cluster models. We shall now examine the closed shell CCSD model in more detail.

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Evaluating the CCSD energy

- For CCSD $\hat{T} = \hat{T}_1 + \hat{T}_2$
- For closed shell systems we use the spin free excitation operators

$$\begin{aligned}
\hat{T}_1 &= \sum_{ai} t_i^a E_{ai} = \sum_{ai} t_i^a (a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta}) \\
\hat{T}_2 &= \tfrac{1}{2} \sum_{aibj} t_{ij}^{ab} E_{ai} E_{bj} \\
&= \tfrac{1}{2} \sum_{aibj} t_{ij}^{ab} \begin{pmatrix} a_{a\alpha}^\dagger a_{i\alpha} a_{b\alpha}^\dagger a_{j\alpha} + a_{a\alpha}^\dagger a_{i\alpha} a_{b\beta}^\dagger a_{j\beta} \\ + a_{a\beta}^\dagger a_{i\beta} a_{b\alpha}^\dagger a_{j\alpha} + a_{a\beta}^\dagger a_{i\beta} a_{b\beta}^\dagger a_{j\beta} \end{pmatrix}
\end{aligned}$$

- These excitation operators commute with $\hat{S}_\pm$ and $\hat{S}_z$ and do not alter the spin state of the closed shell HF reference.

- The closed shell CCSD energy is then

$$\begin{aligned}
E &= E_{HF} + \tfrac{1}{2} \sum_{aibj} t_{ij}^{ab} \langle \mathrm{HF} | [\hat{H}, E_{ai} E_{bj}] | \mathrm{HF} \rangle \\
&\quad + \tfrac{1}{2} \sum_{aibj} t_i^a t_j^b \langle \mathrm{HF} | [[\hat{H}, E_{ai}], E_{bj}] | \mathrm{HF} \rangle
\end{aligned}$$

- Since $\langle \mathrm{HF} | E_{ai} = 0$ we may write this in the form

$$E = E_{HF} + \tfrac{1}{2} \sum_{aibj} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \langle \mathrm{HF} | [[\hat{H}, E_{ai}], E_{bj}] | \mathrm{HF} \rangle$$

- In general it is useful to derive general expressions for commutators of this type since they occur frequently.
- However, here we will only consider the term required for the expectation value, $\langle \mathrm{HF} | \hat{H} E_{ai} E_{bj} | \mathrm{HF} \rangle$.

- We use Wick's theorem to normal order the operator string $\hat{H}E_{ai}E_{bj}$ with respect to the HF state. Only the fully contracted terms contribute to the expectation value.
- We recall that the normal ordered spin free Hamiltonian in canonical orbitals is

$$\hat{H} = E_{HF} + \sum_p \varepsilon_p :E_{pp}: + \tfrac{1}{2}\sum_{pqrs} g_{pqrs} :E_{pq}E_{rs} - \delta_{qr}E_{ps}:$$

- Excitation operators are always normal ordered since they contain only q-creation operators $a_A^\dagger$ and a_I. We therefore use the generalized Wicks theorem

$$\begin{aligned} :ABC...::XYZ...: \;&=\; :ABC...XYZ...: \\ &+ \sum_{\text{singles}} :\overbrace{ABC...XY}Z... : \\ &+ \sum_{\text{doubles}} :\overbrace{ABC...X\overbrace{YZ}...}: \quad + \quad ... \end{aligned}$$

- The only fully contracted terms arise from the quadruple contractions of the term

$$\tfrac{1}{2}\sum_{pqrs} g_{pqrs} :E_{pq}E_{rs}::E_{ai}E_{bj}: =$$

$$\tfrac{1}{2}\sum_{\mu\nu\sigma\tau}\sum_{pqrs} g_{pqrs} :a^\dagger_{p\mu}a_{q\mu}a^\dagger_{r\nu}a_{s\nu}::a^\dagger_{a\sigma}a_{i\sigma}a^\dagger_{b\tau}a_{j\tau}:$$

$$\langle \text{HF}| :a^\dagger_{p\mu}a_{q\mu}a^\dagger_{r\nu}a_{s\nu}::a^\dagger_{a\sigma}a_{i\sigma}a^\dagger_{b\tau}a_{j\tau}: |\text{HF}\rangle =$$

$$\langle \text{HF}| \overbrace{a^\dagger_{p\mu}a_{q\mu}a^\dagger_{r\nu}a_{s\nu}a^\dagger_{a\sigma}a_{i\sigma}a^\dagger_{b\tau}a_{j\tau}} + \overbrace{a^\dagger_{p\mu}a_{q\mu}a^\dagger_{r\nu}a_{s\nu}a^\dagger_{a\sigma}a_{i\sigma}a^\dagger_{b\tau}a_{j\tau}}$$

$$+ \quad \overbrace{a^\dagger_{p\mu}a_{q\mu}a^\dagger_{r\nu}a_{s\nu}a^\dagger_{a\sigma}a_{i\sigma}a^\dagger_{b\tau}a_{j\tau}} + \overbrace{a^\dagger_{p\mu}a_{q\mu}a^\dagger_{r\nu}a_{s\nu}a^\dagger_{a\sigma}a_{i\sigma}a^\dagger_{b\tau}a_{j\tau}} |\text{HF}\rangle$$

$$\begin{aligned} = \quad &\langle \text{HF}|\delta_{pi}\delta_{qa}\delta_{rj}\delta_{sb}\delta_{\mu\sigma}\delta_{\nu\tau} - \delta_{pi}\delta_{qb}\delta_{rj}\delta_{sa}\delta_{\mu\sigma}\delta_{\mu\tau}\delta_{\nu\tau}\delta_{\nu\sigma} \\ &-\delta_{pj}\delta_{qa}\delta_{ri}\delta_{sb}\delta_{\mu\tau}\delta_{\mu\sigma}\delta_{\nu\sigma}\delta_{\nu\tau} + \delta_{pj}\delta_{qb}\delta_{ri}\delta_{sa}\delta_{\mu\tau}\delta_{\nu\sigma}|\text{HF}\rangle \end{aligned}$$

- Performing the summation we arrive at

$$\begin{aligned}\frac{1}{2}\sum_{\mu\nu\sigma\tau}\sum_{pqrs} g_{pqrs}\langle \mathrm{HF}|&\delta_{pi}\delta_{qa}\delta_{rj}\delta_{sb}\delta_{\mu\sigma}\delta_{\nu\tau} - \delta_{pi}\delta_{qb}\delta_{rj}\delta_{sa}\delta_{\mu\sigma}\delta_{\mu\tau}\delta_{\nu\tau}\delta_{\nu\sigma} \\ &-\delta_{pj}\delta_{qa}\delta_{ri}\delta_{sb}\delta_{\mu\tau}\delta_{\mu\sigma}\delta_{\nu\sigma}\delta_{\nu\tau} + \delta_{pj}\delta_{qb}\delta_{ri}\delta_{sa}\delta_{\mu\tau}\delta_{\nu\sigma}|\mathrm{HF}\rangle \\ &= \tfrac{1}{2}(4g_{iajb} - 2g_{ibja} - 2g_{jaib} + 4g_{jbia}) \\ &= (4g_{iajb} - 2g_{ibja}) = 2L_{iajb}\end{aligned}$$

- This is the only contribution to the term $\langle \mathrm{HF}|\hat{H}E_{ai}E_{bj}|\mathrm{HF}\rangle$ and the closed shell CCSD energy is given by

$$E = E_{HF} + \sum_{aibj}\left(t_{ij}^{ab} + t_i^a t_j^b\right) L_{iajb}$$

- Since the energy only ever depends on the singles and doubles amplitudes, this equation is valid for all closed shell coupled cluster methods.

The CCSD singles amplitude equations

- The singles amplitude expressions for CCSD are

$$\langle \mu_1|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle = 0$$

- Applying the BCH expansion we arrive at

$$\begin{aligned}\langle \mu_1|\hat{H}|\mathrm{HF}\rangle &+ \langle \mu_1|[\hat{H},\hat{T}_1]|\mathrm{HF}\rangle \\ +\langle \mu_1|[\hat{H},\hat{T}_2]|\mathrm{HF}\rangle &+ \tfrac{1}{2}\langle \mu_1|[[\hat{H},\hat{T}_1],\hat{T}_1]|\mathrm{HF}\rangle \\ +\langle \mu_1|[[[\hat{H},\hat{T}_1],\hat{T}_2]|\mathrm{HF}\rangle &+ \tfrac{1}{6}\langle \mu_1|[[[\hat{H},\hat{T}_1],\hat{T}_1],\hat{T}_1]|\mathrm{HF}\rangle = 0\end{aligned}$$

- This is cubic in the $\hat{T}_1$ amplitudes, but only linear in the $\hat{T}_2$ amplitudes.
- The evaluation of these commutators follows the same principals as for the energy.

The CCSD doubles amplitude equations

- The doubles amplitude equations for CCSD are

$$\langle \mu_2 | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle = 0$$

- Applying the BCH expansion we arrive at

$$\begin{aligned}
\langle \mu_2 | \hat{H} | \mathrm{HF} \rangle + \langle \mu_2 | [\hat{H}, \hat{T}_1] | \mathrm{HF} \rangle \\
+ \langle \mu_2 | [\hat{H}, \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mu_2 | [[\hat{H}, \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle \\
+ \langle \mu_2 | [[\hat{H}, \hat{T}_1], \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mu_2 | [[\hat{H}, \hat{T}_2], \hat{T}_2] | \mathrm{HF} \rangle \\
+ \tfrac{1}{6} \langle \mu_2 | [[[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle \\
+ \tfrac{1}{2} \langle \mu_2 | [[[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{T}_2] | \mathrm{HF} \rangle \\
+ \tfrac{1}{24} \langle \mu_2 | [[[[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle = 0
\end{aligned}$$

- The singles amplitudes appear to fourth order but the doubles only appear quadratically.

The $T1$-transformed Hamiltonian

- The expressions for the amplitudes are much simplified if we introduce a $T1$-transformed Hamiltonian. Writing the similarity transformed Hamiltonian

$$\exp(-\hat{T}_2 - \hat{T}_1) \hat{H} \exp(\hat{T}_1 + \hat{T}_2) = \exp(-\hat{T}_2) \tilde{\hat{H}} \exp(\hat{T}_2)$$

- The singles and double amplitude expressions are then

$$\begin{aligned}
\langle \mu_1 | \tilde{\hat{H}} | \mathrm{HF} \rangle + \langle \mu_1 | [\tilde{\hat{H}}, \hat{T}_2] | \mathrm{HF} \rangle &= 0 \\
\langle \mu_2 | \tilde{\hat{H}} | \mathrm{HF} \rangle + \langle \mu_2 | [\tilde{\hat{H}}, \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mu_2 | [[\tilde{\hat{H}}, \hat{T}_2], \hat{T}_2] | \mathrm{HF} \rangle &= 0
\end{aligned}$$

- and are equivalent to the CCD model.

- The $T1$ transformation has the effect of rotating the orbitals.
- This means that the $T1$-transformed Hamiltonian is expressed in terms of a new set of creation and annihilation operators, which relate to the new orbitals.

$$\tilde{\hat{H}} = \sum_{PQ} \tilde{h}_{PQ} \tilde{a}_P^\dagger \tilde{a}_Q + \tfrac{1}{2} \sum_{PQRS} \tilde{g}_{PQRS} \tilde{a}_P^\dagger \tilde{a}_R^\dagger \tilde{a}_S \tilde{a}_Q + h_{\mathsf{nuc}}$$

- The new $\tilde{a}_P$, $\tilde{a}_P^\dagger$ are simply linear combinations of the original ones.

$$\begin{aligned} \tilde{a}_I^\dagger &= a_I^\dagger - \sum_A t_I^A a_A^\dagger \qquad \tilde{a}_A^\dagger = a_A^\dagger \\ \tilde{a}_A &= a_A + \sum_I t_I^A a_A \qquad \tilde{a}_I = a_I \end{aligned}$$

- Note that the $T1$-transformed integrals are not symmetric to permutation of the orbital indices, but the permutational symmetry upon electron permutation is retained.

Optimizing the coupled cluster wave function

- We intend to find the amplitudes such that

$$\langle \mu | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \mathsf{HF} \rangle = 0$$

- For an arbitrary set of amplitudes $\mathbf{t}$, we have the vector function $\boldsymbol{\Omega}(\mathbf{t})$:

$$\Omega_\mu(\mathbf{t}) = \langle \mu | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \mathsf{HF} \rangle$$

- We may expand $\boldsymbol{\Omega}(\mathbf{t})$ around the current best guess $\mathbf{t} = \mathbf{t}^n$.

$$\boldsymbol{\Omega}(\mathbf{t}) = \boldsymbol{\Omega}^0(\mathbf{t}^n) + \frac{\partial \boldsymbol{\Omega}^0(\mathbf{t}^n)}{\partial \mathbf{t}} \boldsymbol{\Delta}\mathbf{t} + \cdots$$

- Improving the amplitudes $\mathbf{t}^{n+1} = \mathbf{t}^n + \boldsymbol{\Delta}\mathbf{t}^n$ (Newton):

$$\boldsymbol{\Omega}^1(\mathbf{t}^n) \boldsymbol{\Delta}\mathbf{t}^n = -\boldsymbol{\Omega}^0(\mathbf{t}^n)$$

The Jacobian matrix $\Omega^1_{\mu\nu}(\mathbf{t})$

- The *Jacobian matrix* details how the vector of residuals of the amplitude equations $\boldsymbol{\Omega}^0(\mathbf{t})$, responds to a change in the amplitudes.

$$\begin{aligned}
\Omega^0_\mu(\mathbf{t}) &= \langle\mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle \\
\Omega^0_\mu(\mathbf{t}) &= \langle\mu|\left[\prod_\nu(1-t_\nu\hat{\tau}_\nu)\right]\hat{H}\left[\prod_\nu(1+t_\nu\hat{\tau}_\nu)\right]|\mathrm{HF}\rangle \\
\frac{\partial\Omega^0_\mu(\mathbf{t})}{\partial t_\nu} &= \langle\mu|\exp(-\hat{T})\hat{H}\hat{\tau}_\nu\exp(\hat{T})|\mathrm{HF}\rangle \\
&\quad -\langle\mu|\exp(-\hat{T})\hat{\tau}_\nu\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle
\end{aligned}$$

- Note that $\hat{\tau}^2_\nu = 0$.

$$\Omega^1_{\mu\nu}(\mathbf{t}^n) = \frac{\partial\Omega^0_\mu(\mathbf{t}^n)}{\partial t_\nu} = \langle\mu|\exp(-\hat{T})[\hat{H},\hat{\tau}_\mu]\exp(\hat{T})|\mathrm{HF}\rangle$$

The quasi-Newton method

- Newton's method involves solving a set of linear equations in each iteration.

$$\boldsymbol{\Omega}^1(\mathbf{t}^n)\boldsymbol{\Delta}\mathbf{t}^n = -\boldsymbol{\Omega}^0(\mathbf{t}^n)$$

- The quasi-Newton method avoids this expense.

$$\begin{aligned}
\Omega^0_\mu(\mathbf{t}^n) &= \varepsilon_\mu t^n_\mu + \langle\mu|\exp(-\hat{T}^n)\hat{\Phi}\exp(\hat{T}^n)|\mathrm{HF}\rangle \\
\Omega^1_{\mu\nu}(\mathbf{t}^n) &= \varepsilon_\mu\delta_{\mu\nu} + \langle\mu|\exp(-\hat{T}^n)[\hat{\Phi},\hat{\tau}_\nu]\exp(\hat{T}^n)|\mathrm{HF}\rangle
\end{aligned}$$

- The diagonal part is from the HF contribution.
- The nondiagonal part from the fluctuation potential is small.
- Improving the amplitudes $\mathbf{t}^{n+1} = \mathbf{t}^n + \boldsymbol{\Delta}\mathbf{t}^n$ (quasi-Newton):

$$\varepsilon_\mu\Delta t^n_\mu = -\Omega^0_\mu(\mathbf{t}^n)$$

The $\mathcal{T}_1$ diagnostic

- It is important to judge the reliability of a CC calculation.
  - Basis set convergence aside, the convergence with the level of excitation is much slower if the HF determinant is not a good zeroth order reference. In this case the CCSD method would be inappropriate.
- Simplest diagnostic is to examine the coefficients of the CSFs in ψ. Multireference character is indicated by a small HF coefficient or large coefficients for certain CSFs.
- Another useful indicator is the $\mathcal{T}_1$ diagnostic.

$$\mathcal{T}_1 = |\mathbf{t}_1|/\sqrt{N}$$

  - The norm of the vector of $\hat{T}_1$ amplitudes, scaled to be independent of the number of correlated electrons N.
  - Empirically, if $\mathcal{T}_1$ is less than 0.02 then a CCSD result is considered reliable.
  - Higher order excitation levels can correct for some amount of multireference character.

Size consistency

- Defined as the property that $E(AB) = E(A) + E(B)$, if the subsystems A and B do not interact.
- Coupled cluster methods are size consistent (in contrast to truncated CI).
- Assume that $|\mathrm{CC}_A\rangle$ and $|\mathrm{CC}_B\rangle$ are known.
- The energies of subsystems A and B are

$$\begin{aligned} E_A &= \langle \mathrm{HF}_A|\hat{H}_A|\mathrm{CC}_A\rangle = \langle \mathrm{HF}_A|\hat{H}_A^T|\mathrm{HF}_A\rangle \\ E_B &= \langle \mathrm{HF}_B|\hat{H}_B|\mathrm{CC}_B\rangle = \langle \mathrm{HF}_B|\hat{H}_B^T|\mathrm{HF}_B\rangle \end{aligned}$$

- The amplitudes defining $|\mathrm{CC}_A\rangle$ and $|\mathrm{CC}_B\rangle$ fulfill the projected equations

$$\begin{aligned} \langle \mu_A|\hat{H}_A^T|\mathrm{HF}_A\rangle &= 0 \\ \langle \mu_B|\hat{H}_B^T|\mathrm{HF}_B\rangle &= 0 \end{aligned}$$

- Recall that $\hat{H}^T = \exp(-\hat{T})\hat{H}\exp(\hat{T})$.

- For the combined system AB, where A and B do not interact, we have $\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$and

$$\begin{aligned} |\mathrm{HF}_{AB}\rangle &= |\mathrm{HF}_A\mathrm{HF}_B\rangle \\ |\mathrm{CC}_{AB}\rangle &= \exp(\hat{T}_A + \hat{T}_B)|\mathrm{HF}_{AB}\rangle \end{aligned}$$

- Note that

$$\begin{aligned} \hat{H}^T_{AB} &= \exp(-\hat{T}_A - \hat{T}_B)(\hat{H}_A + \hat{H}_B)\exp(\hat{T}_A + \hat{T}_B) \\ &= \exp(-\hat{T}_A)\hat{H}_A\exp(\hat{T}_A) + \exp(-\hat{T}_B)\hat{H}_B\exp(\hat{T}_B) \\ &= \hat{H}^T_A + \hat{H}^T_B \end{aligned}$$

- $|\mathrm{CC}_{AB}\rangle$ fulfills the amplitude equations for the system AB.

$$\begin{aligned} \langle\mu_{AB}|\hat{H}^T_{AB}|\mathrm{HF}_{AB}\rangle &= 0 \\ \langle\mu_A\mathrm{HF}_B|\hat{H}^T_A + \hat{H}^T_B|\mathrm{HF}_A\mathrm{HF}_B\rangle &= \langle\mu_A|\hat{H}^T_A|\mathrm{HF}_A\rangle = 0 \\ \langle\mathrm{HF}_A\mu_B|\hat{H}^T_A + \hat{H}^T_B|\mathrm{HF}_A\mathrm{HF}_B\rangle &= \langle\mu_B|\hat{H}^T_B|\mathrm{HF}_B\rangle = 0 \\ \langle\mu_A\mu_B|\hat{H}^T_A + \hat{H}^T_B|\mathrm{HF}_A\mathrm{HF}_B\rangle &= 0 \end{aligned}$$

- For size consistency we require that $E_{AB} = E_A + E_B$.

$$\begin{aligned} E_{AB} &= \langle\mathrm{HF}_{AB}|\hat{H}^T_{AB}|\mathrm{HF}_{AB}\rangle \\ &= \langle\mathrm{HF}_A\mathrm{HF}_B|\hat{H}^T_A + \hat{H}^T_B|\mathrm{HF}_A\mathrm{HF}_B\rangle \\ &= \langle\mathrm{HF}_A|\hat{H}^T_A|\mathrm{HF}_A\rangle + \langle\mathrm{HF}_B|\hat{H}^T_B|\mathrm{HF}_B\rangle \\ &= E_A + E_B \end{aligned}$$

- Using the same arguments one finds that all of the terms in the coupled cluster equations are size consistent. e.g.

$$[[\hat{H}_{AB}, \hat{T}_{1AB}], \hat{T}_{1AB}] = [[\hat{H}_A, \hat{T}_{1A}], \hat{T}_{1A}] + [[\hat{H}_B, \hat{T}_{1B}], \hat{T}_{1B}]$$

- This coupled cluster formalism is in fact *term-wise size extensive* – size extensivity requires that the correlation energy scales correctly with the size of the system.
- The expressions arising from the non-similarity transformed Hamiltonian are not term-wise size-extensive.

Coupled cluster and perturbation theory

- In perturbation theory we split the Hamiltonian into two parts, a zeroth order reference and a small perturbation.

$$\hat{H} = \hat{H}_0 + \hat{U}$$

- The solution to $\hat{H}_0|0^{(0)}\rangle = E^{(0)}|0^{(0)}\rangle$ is known.
- In Møller Plesset perturbation theory the Fock operator $\hat{f}$ is the zeroth order Hamiltonian and the perturbation is known as the *fluctuation potential* $\hat{\Phi}$.

$$\begin{aligned}
\hat{H} &= \hat{f} + \hat{\Phi} + h_{\mathsf{nuc}} \\
\hat{H} &= \sum_{PQ} h_{pq} a_P^\dagger a_Q + \tfrac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q + h_{\mathsf{nuc}} \\
\hat{f} &= \sum_{P} \varepsilon_P a_P^\dagger a_P \\
\hat{\Phi} &= \hat{H} - \hat{f} - h_{\mathsf{nuc}}
\end{aligned}$$

Møller Plesset perturbation theory

- We expand terms of the Schrödinger equation $\hat{H}|0\rangle = E|0\rangle$, in orders of the perturbation

$$(\hat{f} + \hat{\Phi}) \left(\sum_{k=0}^{\infty} |0^{(k)}\rangle \right) = \left(\sum_{l=0}^{\infty} E^{(k)} \right) \left(\sum_{k=0}^{\infty} |0^{(k)}\rangle \right)$$

$$\begin{aligned}
E &= E^{(0)} + E^{(1)} + E^{(2)} + \cdots \\
|0\rangle &= |0^{(0)}\rangle + |0^{(1)}\rangle + |0^{(2)}\rangle + \cdots
\end{aligned}$$

- Collecting terms in each order we obtain

$$\begin{aligned}
E^{(0)}|0^{(0)}\rangle &= \hat{f}|0^{(0)}\rangle \\
E^{(1)}|0^{(0)}\rangle &= (\hat{f} - E^{(0)})|0^{(1)}\rangle + \hat{\Phi}|0^{(0)}\rangle \\
E^{(2)}|0^{(0)}\rangle &= (\hat{f} - E^{(0)})|0^{(2)}\rangle + (\hat{\Phi} - E^{(1)})|0^{(1)}\rangle
\end{aligned}$$

- We expand $|0^{(n)}\rangle$ in terms of the eigenstates of the Fock operator, the excited state determinants

$$|0^{(n)}\rangle = \sum_{\mu} C_{\mu}^{(n)} |\mu\rangle$$

- Note the intermediate normalization $\langle 0^{(n)}|0^{(0)}\rangle = 0$.
- Projecting the first order equations by $\langle \mathrm{HF}| = \langle 0^{(0)}|$ and $\langle \mu|$ we obtain the energy and amplitude expressions

$$\begin{aligned} E^{(1)} &= \langle \mathrm{HF}|\hat{\Phi}|\mathrm{HF}\rangle \\ \varepsilon_{\mu} C_{\mu}^{(1)} &= -\langle \mu|\hat{\Phi}|\mathrm{HF}\rangle \end{aligned}$$

- The equations for the second order energy and amplitude are more complicated.

$$\begin{aligned} E^{(2)} &= \langle \mathrm{HF}|\hat{\Phi}|0^{(1)}\rangle \\ \varepsilon_{\mu} C_{\mu}^{(2)} &= -\langle \mu|\hat{\Phi} - E^{(1)}|0^{(1)}\rangle \end{aligned}$$

Coupled cluster perturbation theory

- In coupled cluster theory the Schrödinger equation is

$$\begin{aligned} \hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E\exp(\hat{T})|\mathrm{HF}\rangle \\ \exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E|\mathrm{HF}\rangle \\ (\hat{f}^{T} + \hat{\Phi}^{T})|\mathrm{HF}\rangle &= E|\mathrm{HF}\rangle \end{aligned}$$

- We expand terms of the Schrödinger equation in orders of the perturbation.

$$\hat{T} = \sum_{n=1}^{\infty} \hat{T}^{(n)} \qquad \hat{\Phi}^{T} = \sum_{n=1}^{\infty} [\hat{\Phi}^{T}]^{(n)}$$

$$E = \sum_{n=0}^{\infty} E^{(n)} \qquad \hat{f}^{T} = \hat{f} + \sum_{n=1}^{\infty} \sum_{\mu} \varepsilon_{\mu} t_{\mu}^{(n)} \hat{\tau}_{\mu}$$

- Note that e.g. $\hat{T}_2 = \hat{T}_2^{(1)} + \hat{T}_2^{(2)} + \cdots$

- The Schrödinger equation becomes

$$\left(\hat{f} + \sum_{n=1}^{\infty}\left[\sum_{\mu}\varepsilon_\mu t_\mu^{(n)}\hat{\tau}_\mu + [\hat{\Phi}^T]^{(n)}\right]\right)|\mathrm{HF}\rangle \quad = \quad \left(\sum_{n=0}^{\infty} E^{(n)}\right)|\mathrm{HF}\rangle$$

- Collecting terms of order (n) in the perturbation we have

$$\begin{aligned} E^{(0)}|\mathrm{HF}\rangle &= \hat{f}|\mathrm{HF}\rangle \\ E^{(n)}|\mathrm{HF}\rangle &= \sum_{\mu}\varepsilon_\mu t_\mu^{(n)}\hat{\tau}_\mu|\mathrm{HF}\rangle + [\hat{\Phi}^T]^{(n)}|\mathrm{HF}\rangle \quad n > 0 \end{aligned}$$

- Projecting onto $\langle\mathrm{HF}|$ and $\langle\mu|$ we obtain the coupled cluster perturbation expressions for the energy and amplitudes.

$$\begin{aligned} E^{(n)} &= \langle\mathrm{HF}|[\hat{\Phi}^T]^{(n)}|\mathrm{HF}\rangle \\ \varepsilon_\mu t_\mu^{(n)} &= -\langle\mu|[\hat{\Phi}^T]^{(n)}|\mathrm{HF}\rangle \end{aligned}$$

- Note the similarity to the usual coupled cluster equations.

Perturbation order and excitation levels

- The excitations present at each order of perturbation is determined by the amplitude expressions

$$\varepsilon_\mu t_\mu^{(n)} = -\langle\mu|[\hat{\Phi}^T]^{(n)}|\mathrm{HF}\rangle$$

- Applying the BCH expansion to $\hat{\Phi}^T = \exp(-\hat{T})\hat{\Phi}\exp(\hat{T})$

$$\begin{aligned} \hat{\Phi}^T = \; & \hat{\Phi} + [\hat{\Phi},\hat{T}] + \tfrac{1}{2!}[[\hat{\Phi},\hat{T}],\hat{T}] + \tfrac{1}{3!}[[[\hat{\Phi},\hat{T}],\hat{T}],\hat{T}] \\ & + \tfrac{1}{4!}[[[[\hat{\Phi},\hat{T}],\hat{T}],\hat{T}],\hat{T}] \end{aligned}$$

- and expanding $\hat{T} = \hat{T}^{(1)} + \hat{T}^{(2)} + \hat{T}^{(3)} + \cdots$, we obtain

$$\begin{aligned} \varepsilon_\mu t_\mu^{(1)} &= -\langle\mu|\hat{\Phi}|\mathrm{HF}\rangle \\ \varepsilon_\mu t_\mu^{(2)} &= -\langle\mu|[\hat{\Phi},\hat{T}^{(1)}]|\mathrm{HF}\rangle \\ \varepsilon_\mu t_\mu^{(3)} &= -\langle\mu|[\hat{\Phi},\hat{T}^{(2)}]|\mathrm{HF}\rangle - \langle\mu|[[\hat{\Phi},\hat{T}^{(1)}],\hat{T}^{(1)}]|\mathrm{HF}\rangle \end{aligned}$$

- To nth order in the perturbation the wave function is

$$|0^{(n)}\rangle = [\exp(\hat{T})]^{(n)}|\mathrm{HF}\rangle$$

- To first order only doubles excitations enter the wave function since $\hat{\Phi}$ is a rank 2 operator and $\langle\mu_1|\hat{\Phi}|\mathrm{HF}\rangle = 0$

$$\begin{aligned}
\varepsilon_{\mu_2} t^{(1)}_{\mu_2} &= -\langle\mu_2|\hat{\Phi}|\mathrm{HF}\rangle \\
|0^{(1)}\rangle &= [\exp(\hat{T})]^{(1)}|\mathrm{HF}\rangle = \hat{T}^{(1)}_2|\mathrm{HF}\rangle
\end{aligned}$$

- To second order singles doubles and triples excitations enter the wave function since $[\hat{\Phi}, \hat{T}^{(1)}_2]$ is a rank 3 operator

$$\begin{aligned}
\varepsilon_\mu t^{(2)}_\mu &= -\langle\mu|[\hat{\Phi}, \hat{T}^{(1)}_2]|\mathrm{HF}\rangle \\
|0^{(2)}\rangle &= [\exp(\hat{T})]^{(2)}|\mathrm{HF}\rangle = \left(\hat{T}^{(2)} + \tfrac{1}{2}\hat{T}^{(1)}\hat{T}^{(1)}\right)|\mathrm{HF}\rangle \\
&= \hat{T}^{(2)}_1|\mathrm{HF}\rangle + \hat{T}^{(2)}_2|\mathrm{HF}\rangle + \hat{T}^{(2)}_3|\mathrm{HF}\rangle + \tfrac{1}{2}\hat{T}^{(1)}_2\hat{T}^{(1)}_2|\mathrm{HF}\rangle
\end{aligned}$$

- The third order wave function contains connected quadruple excitations, and corrections to the singles, doubles and triples amplitudes.

$$\begin{aligned}
\varepsilon_\mu t^{(3)}_\mu &= -\langle\mu|[\hat{\Phi}, \hat{T}^{(2)}]|\mathrm{HF}\rangle - \langle\mu|[[\hat{\Phi}, \hat{T}^{(1)}], \hat{T}^{(1)}]|\mathrm{HF}\rangle \\
|0^{(3)}\rangle &= \left(\hat{T}^{(3)} + \hat{T}^{(2)}\hat{T}^{(1)} + \tfrac{1}{6}\hat{T}^{(1)}\hat{T}^{(1)}\hat{T}^{(1)}\right)|\mathrm{HF}\rangle \\
&= \hat{T}^{(3)}_1|\mathrm{HF}\rangle + \hat{T}^{(3)}_2|\mathrm{HF}\rangle + \left(\hat{T}^{(3)}_3 + \hat{T}^{(2)}_1\hat{T}^{(1)}_2\right)|\mathrm{HF}\rangle \\
&\quad + \left(\hat{T}^{(3)}_4 + \hat{T}^{(2)}_2\hat{T}^{(1)}_2\right)|\mathrm{HF}\rangle + \hat{T}^{(2)}_3\hat{T}^{(1)}_2|\mathrm{HF}\rangle \\
&\quad + \hat{T}^{(1)}_2\hat{T}^{(1)}_2\hat{T}^{(1)}_2|\mathrm{HF}\rangle
\end{aligned}$$

- In general, the nth order excitations enter to order $n-1$.
- The only exception is the singles, which enter at second order due to the Brillouin theorem.
- These results are the same as for MPPT, but they have been derived much more easily.

The CCPT Energies

- Currently $E^{(n)}$ requires knowledge of $t_\mu^{(n-1)}$.

$$E^{(n)} = \langle \mathrm{HF}|[\hat{\Phi}^T]^{(n)}|\mathrm{HF}\rangle$$

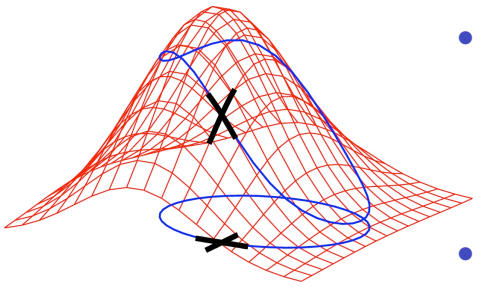
- Wigner's $2n+1$ rule states that $E^{(2n+1)}$ only requires the wave function to nth order.
- We note that the coupled cluster equations represent a minimization of the energy subject to the constraint that the amplitudes fulfill the projected amplitude equation.

$$\begin{aligned}\langle \mathrm{HF}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E \\ \langle \mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= 0\end{aligned}$$

- To derive efficient CCPT energy expressions, we transform the constrained minimization to a free variational minimization using the technique of *Lagrange multipliers*.

Constrained optimization and the Lagrangian

- Let $f(x,y)$ be a function that we would like to minimize subject to the constraint that $g(x,y)=0$.



- The gradient of $f(x,y)$ may be expressed in two components

$$f'(x,y) = \varepsilon g'_{\parallel}(x,y) + \epsilon g'_{\perp}(x,y)$$

- At the minimum (x_0,y_0), $\epsilon = 0$.

- We define the Lagrangian $L(x,y) = f(x,y) - \varepsilon g(x,y)$, which we minimize with respect to x, y, ε without constraint

$$\begin{aligned}\frac{\partial L}{\partial \varepsilon} &= g(x,y) = 0 \\ \frac{\partial L}{\partial x} &= \frac{\partial f}{\partial x} - \varepsilon\frac{\partial g}{\partial x} = 0 \\ \frac{\partial L}{\partial y} &= \frac{\partial f}{\partial y} - \varepsilon\frac{\partial g}{\partial y} = 0\end{aligned}$$

- Ensures that the constraint is satisfied at the minimum: $L(x_0,y_0) = f(x_0,y_0)$.
- Determines the Lagrange multiplier ε, which is the component of $f'(x,y)$ in the path of the constraint.

The coupled cluster Lagrangian

- The coupled cluster Lagrangian depends on amplitudes $\mathbf{t}$ and Lagrange multipliers $\bar{\mathbf{t}}$.

$$
\begin{aligned}
L(\mathbf{t},\bar{\mathbf{t}}) &= \langle \mathrm{HF}|\hat{f}^T + \hat{\Phi}^T|\mathrm{HF}\rangle + \sum_\mu \bar{t}_\mu \langle \mu|\hat{f}^T + \hat{\Phi}^T|\mathrm{HF}\rangle \\
&= E_0 + \langle \mathrm{HF}|\hat{\Phi}^T|\mathrm{HF}\rangle + \sum_\mu \varepsilon_\mu t_\mu \bar{t}_\mu + \sum_\mu \bar{t}_\mu \langle \mu|\hat{\Phi}^T|\mathrm{HF}\rangle \\
\bar{L}_\mu &= \frac{\partial L}{\partial \bar{t}_\mu} = 0 = \varepsilon_\mu t_\mu + \langle \mu|\hat{\Phi}^T|\mathrm{HF}\rangle \\
L_\mu &= \frac{\partial L}{\partial t_\mu} = 0 = \varepsilon_\mu \bar{t}_\mu + \langle \mathrm{HF}|\hat{\Phi}^T|\mu\rangle + \sum_\mu \bar{t}_\mu \langle \mu|[\hat{\Phi}^T, \hat{\tau}_\mu]|\mathrm{HF}\rangle
\end{aligned}
$$

- Note that $\hat{\Phi}^T$ is not Hermitian: $\langle \mathrm{HF}|\hat{\Phi}^T|\mu\rangle \neq \langle \mu|\hat{\Phi}^T|\mathrm{HF}\rangle$

The CCPT Lagrangian

- Solving the CCPT equations is equivalent to expanding the coupled cluster Lagrangian in orders of the perturbation and minimizing each $L^{(n)}$ separately.

$$
\begin{aligned}
L &= E_0 + \langle \mathrm{HF}|\hat{\Phi}^T|\mathrm{HF}\rangle + \sum_\mu \varepsilon_\mu t_\mu \bar{t}_\mu + \sum_\mu \bar{t}_\mu \langle \mu|\hat{\Phi}^T|\mathrm{HF}\rangle \\
L &= L^{(0)} + L^{(1)} + L^{(2)} + \cdots \\
L^{(n)} &= E^{(0)}\delta_{n,0} + \langle \mathrm{HF}|[\hat{\Phi}^T]^{(n)}|\mathrm{HF}\rangle + \sum_\mu \sum_{k=1}^{n-1} \varepsilon_\mu t_\mu^{(k)} \bar{t}_\mu^{(n-k)} \\
&\quad + \sum_\mu \sum_{k=1}^{n-1} \bar{t}_\mu^{(k)} \langle \mu|[\hat{\Phi}^T]^{(n-k)}|\mathrm{HF}\rangle
\end{aligned}
$$

- With $\frac{\partial L^{(n)}}{\partial t_\mu} = \frac{\partial L^{(n)}}{\partial \bar{t}_\mu} = 0$

- t_μ and $\bar{t}_\mu$ have been expanded in orders of the perturbation strength α

$$\begin{aligned} t_\mu &= \alpha t_\mu^{(1)} + \alpha^2 t_\mu^{(2)} + \alpha^3 t_\mu^{(3)} + \cdots \\ \frac{\partial L^{(n)}}{\partial t_\mu} &= 0 = \alpha \frac{\partial L^{(n)}}{\partial t_\mu^{(1)}} + \alpha^2 \frac{\partial L^{(n)}}{\partial t_\mu^{(2)}} + \alpha^3 \frac{\partial L^{(n)}}{\partial t_\mu^{(3)}} + \cdots \end{aligned}$$

- Since this holds for any value of α, $L^{(n)}$ must be stationary with respect to all $t_\mu^{(k)}$ and $\bar{t}_\mu^{(k)}$

$$\frac{\partial L^{(n)}}{\partial t_\mu^{(k)}} = \frac{\partial L^{(n)}}{\partial \bar{t}_\mu^{(k)}} = 0$$

- We may eliminate terms in $L^{(n)}$ that are linear in $t_\mu^{(k)}$ or $\bar{t}_\mu^{(k)}$.
- $L^{(2n)}$ and $L^{(2n+1)}$ are linear in vectors $\bar{t}_\mu^{(k)}$ for all k.
- $L^{(2n)}$ and $L^{(2n+1)}$ are linear in vectors $t_\mu^{(k)}$ for $k > n$.

$$\begin{aligned} L^{(n)} = {} & E^{(0)}\delta_{n,0} + \sum_\mu \sum_{k=1}^{n-1} \varepsilon_\mu t_\mu^{(k)} \bar{t}_\mu^{(n-k)} + \langle \mathsf{HF}|\hat{\Phi}|\mathsf{HF}\rangle \delta_{n,1} \\ & + \langle \mathsf{HF}|[\hat{\Phi}, \hat{T}^{(n-1)}]|\mathsf{HF}\rangle + \sum_{k=1}^{n-1} \langle \mathsf{HF}|[[\hat{\Phi}, \hat{T}^{(k)}], \hat{T}^{(n-k-1)}]|\mathsf{HF}\rangle \\ & + \sum_\mu \bar{t}_\mu^{(n-1)} \langle \mu|\hat{\Phi}|\mathsf{HF}\rangle + \sum_\mu \sum_{k=1}^{n-2} \bar{t}_\mu^{(k)} \langle \mu|[\hat{\Phi}, \hat{T}^{(n-k-1)}]|\mathsf{HF}\rangle \\ & + \sum_\mu \sum_{k=1}^{n-3} \sum_{l=1}^{n-k-2} \bar{t}_\mu^{(k)} \langle \mu|[[\hat{\Phi}, \hat{T}^{(l)}], \hat{T}^{(n-k-l-1)}]|\mathsf{HF}\rangle + \cdots \end{aligned}$$

- For $L^{(2n+1)}$ we may eliminate all $t_\mu^{(k)}$ or $\bar{t}_\mu^{(k)}$ with $k > n$.
- For $L^{(2n)}$ we may eliminate all $t_\mu^{(k)}$ with $k > n$ and all $\bar{t}_\mu^{(k)}$ with $k > n - 1$ ($2n + 2$ rule for the multipliers).

The CCPT energies

- We have now arrived at expressions for $E^{(2n+1)}$ that depend only on $t_\mu^{(k)}$ and $\bar{t}_\mu^{(k)}$ with $k \leq n$. Starting with

$$E^{(n)} = L^{(n)} = E^{(0)}\delta_{n,0} + \langle \mathsf{HF}|[\hat{\Phi}^T]^{(n)}|\mathsf{HF}\rangle + \sum_\mu \sum_{k=1}^{n-1} \varepsilon_\mu t_\mu^{(k)} \bar{t}_\mu^{(n-k)} + \sum_\mu \sum_{k=1}^{n-1} \bar{t}_\mu^{(k)} \langle \mu|[\hat{\Phi}^T]^{(n-k)}|\mathsf{HF}\rangle$$

- and eliminating terms that do not obey the $(2n+1)$ and $(2n+2)$ rules, we obtain

$$\begin{aligned} E^{(1)} &= \langle \mathsf{HF}|\hat{\Phi}|\mathsf{HF}\rangle \\ E^{(2)} &= \langle \mathsf{HF}|[\hat{\Phi}, \hat{T}_2^{(1)}]|\mathsf{HF}\rangle \end{aligned}$$

- We note that $L_\mu^{(1)} = \bar{L}_\mu^{(1)} = 0$ implies that $t_\mu^{(1)} = \bar{t}_\mu^{(1)}$.

The CCPT energies

- The third order energy is given by

$$\begin{aligned} L^{(3)} = &\sum_\mu \varepsilon_\mu t_\mu^{(1)} \bar{t}_\mu^{(2)} + \sum_\mu \varepsilon_\mu t_\mu^{(2)} \bar{t}_\mu^{(1)} + \langle \mathsf{HF}|[\hat{\Phi}, \hat{T}^{(2)}]|\mathsf{HF}\rangle \\ &+ \tfrac{1}{2}\langle \mathsf{HF}|[[\hat{\Phi}, \hat{T}_2^{(1)}], \hat{T}_2^{(1)}]|\mathsf{HF}\rangle + \sum_\mu \bar{t}_{\mu_2}^{(1)} \langle \mu_2|[\hat{\Phi}, \hat{T}_2^{(1)}]|\mathsf{HF}\rangle \\ &+ \sum_\mu \bar{t}_\mu^{(2)} \langle \mu|\hat{\Phi}|\mathsf{HF}\rangle \end{aligned}$$

- Recall that only double excitations enter to first order.
- After elimination of the terms linear in $t_\mu^{(2)}$ and $\bar{t}_\mu^{(2)}$

$$E^{(3)} = \sum_\mu \bar{t}_{\mu_2}^{(1)} \langle \mu_2|[\hat{\Phi}, \hat{T}_2^{(1)}]|\mathsf{HF}\rangle$$

The CCPT energies

- The fourth and fifth order energy corrections may be obtained similarly

$$
\begin{aligned}
E^{(4)} &= \sum_{\mu} \bar{t}^{(1)}_{\mu_2} \langle \mu_2 | [\hat{\Phi}, \hat{T}^{(2)}] | \mathsf{HF} \rangle + \tfrac{1}{2} \sum_{\mu} \bar{t}^{(1)}_{\mu_2} \langle \mu_2 | [[\hat{\Phi}, \hat{T}^{(1)}_2], \hat{T}^{(1)}_2] | \mathsf{HF} \rangle \\
E^{(5)} &= \tfrac{1}{2} \langle \mathsf{HF} | [[\hat{\Phi}, \hat{T}^{(2)}], \hat{T}^{(2)}] | \mathsf{HF} \rangle + \sum_{\mu} \bar{t}^{(1)}_{\mu_2} \langle \mu_2 | [[\hat{\Phi}, \hat{T}^{(2)}], \hat{T}^{(1)}_2] | \mathsf{HF} \rangle \\
&\quad + \sum_{\mu} \bar{t}^{(2)}_{\mu} \langle \mu | [\hat{\Phi}, \hat{T}^{(2)}] | \mathsf{HF} \rangle + \tfrac{1}{2} \sum_{\mu} \bar{t}^{(2)}_{\mu} \langle \mu | [[\hat{\Phi}, \hat{T}^{(1)}_2], \hat{T}^{(1)}_2] | \mathsf{HF} \rangle
\end{aligned}
$$

Coupled cluster *vs* perturbation theory

- In CC the amplitude equations are solved *self consistently* for a given excitation level N_{CC} and associated projection manifold.

$$
\begin{aligned}
\varepsilon_{\mu_n} t_{\mu_n} &= -\langle \mu_n | \hat{\Phi}^{T_{[N_{\mathsf{CC}}]}} | \mathsf{HF} \rangle \qquad n \leq N_{\mathsf{CC}} \\
\hat{T}_{N_{\mathsf{CC}}} &= \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_{N_{\mathsf{CC}}}
\end{aligned}
$$

- In CCPT the amplitude equations are solved *recursively* up to a given order N_{PT} in the fluctuation potential. No excitations are ignored, but only the amplitudes that contribute to order N_{PT} are non zero.

$$
\varepsilon_{\mu} t_{\mu} = -\langle \mu | [\hat{\Phi}^T]^{(n)} | \mathsf{HF} \rangle \qquad n \leq N_{\mathsf{PT}}
$$

- To what order in the fluctuation potential are the CC amplitudes and energy correct?

Perturbation orders in coupled cluster terms

- Recall that in CCPT the amplitudes for n-tuple excitations t_{μ_n} first occur at order $n-1$ in the fluctuation potential.
- In the CC equations the n-tuple excitations t_{μ_n} first occur when the cluster operator is truncated at n-tuple excitations $N_{\text{CC}} = n$.
- The inclusion t_{μ_n} in the self consistent CC equations affects the amplitudes $t_{\mu_{n-1}}$ and $t_{\mu_{n-2}}$ directly. E.g.

$$\varepsilon_{\mu_{n-1}} t_{\mu_{n-2}} \quad = \quad -\langle \mu_{n-2} | [\hat{\Phi}, \hat{T}_n] | \text{HF} \rangle + \cdots$$

- These corrections to $t_{\mu_{n-1}}$ and $t_{\mu_{n-2}}$ are of order n in $\hat{\Phi}$.
- The lower excitations are affected indirectly through the changes in $t_{\mu_{n-1}}$ and $t_{\mu_{n-2}}$ and the corrections are of order $n+1$ in $\hat{\Phi}$.

- We introduce the shorthand notation $R_n^N = -\langle \mu_n | \hat{\Phi}^{T_N} | \text{HF} \rangle$.
- Let us first examine CCS

$$\varepsilon_{\mu_1} t_{\mu_1} = R_1^1 \quad = \quad -\langle \mu_1 | \tilde{\hat{\Phi}} | \text{HF} \rangle$$

- where $\tilde{\hat{\Phi}}$ is the *T1-transformed* fluctuation potential.

$$\tilde{\hat{\Phi}} = \exp(-\hat{T}_1) \hat{\Phi} \exp(\hat{T}_1) = \hat{\Phi} + [\hat{\Phi}, \hat{T}_1] + \tfrac{1}{2}[[\hat{\Phi}, \hat{T}_1], \hat{T}_1] + \cdots$$

- The order to which t_{μ_1} are correct is determined by the order of the correction introduced by CCSD.
- For CCSD we have

$$\begin{aligned}
\varepsilon_{\mu_1} t_{\mu_1} = R_1^2 \quad &= \quad R_1^1 - \langle \mu_1 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \text{HF} \rangle && = R_1^1 + O(2) \\
\varepsilon_{\mu_2} t_{\mu_2} = R_2^2 \quad &= \quad -\langle \mu_2 | \tilde{\hat{\Phi}} | \text{HF} \rangle - \langle \mu_2 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \text{HF} \rangle \\
&\quad\; -\tfrac{1}{2} \langle \mu_2 | [[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_2] | \text{HF} \rangle && = O(1)
\end{aligned}$$

- The CCS singles amplitudes are correct to first order in $\hat{\Phi}$.

- For CCSDT we have

$$
\begin{aligned}
\varepsilon_{\mu_1} t_{\mu_1} = R_1^3 &= R_1^2 - \langle \mu_1 | [\tilde{\hat{\Phi}}, \hat{T}_3] | \mathrm{HF} \rangle &= R_1^2 + O(3) \\
\varepsilon_{\mu_2} t_{\mu_2} = R_2^3 &= R_2^2 - \langle \mu_2 | [\tilde{\hat{\Phi}}, \hat{T}_3] | \mathrm{HF} \rangle &= R_2^2 + O(3) \\
\varepsilon_{\mu_3} t_{\mu_3} = R_3^3 &= -\langle \mu_3 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \mathrm{HF} \rangle & \\
&\quad -\langle \mu_3 | [\tilde{\hat{\Phi}}, \hat{T}_3] | \mathrm{HF} \rangle & \\
&\quad -\tfrac{1}{2} \langle \mu_3 | [[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_2] | \mathrm{HF} \rangle & \\
&\quad -\mu_3 | [[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_3] | \mathrm{HF} \rangle &= O(2)
\end{aligned}
$$

- The CCSD singles and doubles are therefore correct to second order in $\hat{\Phi}$.
- The CCSD wave function is correct to first order, due to the lack of second order triples corrections.
- The CCSD wave function is more accurate than that of MP1, which is only correct to first order in the singles and doubles.

- From CCSDTQ we see that the CCSDT wave function is correct to second order due to the quadruples.

$$
\begin{aligned}
\varepsilon_{\mu_1} t_{\mu_1} = R_1^4 &= R_1^3 \\
\varepsilon_{\mu_2} t_{\mu_2} = R_2^4 &= R_2^3 + O(4) \\
\varepsilon_{\mu_3} t_{\mu_3} = R_3^4 &= R_3^3 + O(4) \\
\varepsilon_{\mu_4} t_{\mu_4} = R_4^4 &= O(3)
\end{aligned}
$$

- The CCSDT doubles and triples are therefore correct to third order. The singles are indirectly affected by the fourth order change in the doubles through $\langle \mu_1 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \mathrm{HF} \rangle$. The correction to the singles is fifth order and the CCSDT singles are are correct to fourth order.
- The energy only depends on the singles and doubles. The CCSDT energy is correct to fourth order due to third order doubles correction in CCSDTQ.

Hybrid coupled cluster and perturbation models

- Let us examine the CCSD equations again

$$\begin{aligned}\varepsilon_{\mu_1} t_{\mu_1} &= -\langle \mu_1 | \tilde{\hat{\Phi}} | \mathrm{HF} \rangle - \langle \mu_1 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \mathrm{HF} \rangle \\ \varepsilon_{\mu_2} t_{\mu_2} &= -\langle \mu_2 | \tilde{\hat{\Phi}} | \mathrm{HF} \rangle - \langle \mu_2 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \mathrm{HF} \rangle - \tfrac{1}{2} \langle \mu_2 | [[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_2] | \mathrm{HF} \rangle\end{aligned}$$

- The last two terms of the doubles amplitude equations scale as n^6 with the basis set. The remaining terms scale as n^5 or less.
- These terms represent second and higher order corrections to the doubles amplitudes.
- Noting that the doubles are anyway only correct to second order, we may approximate the doubles to first order by discarding the last two terms, reducing the cost of the calculation.

The CC2 hybrid model

- The iterative solution of the resulting equations is the hybrid CC2 model.

$$\begin{aligned}\varepsilon_{\mu_1} t_{\mu_1} &= -\langle \mu_1 | \tilde{\hat{\Phi}} | \mathrm{HF} \rangle - \langle \mu_1 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \mathrm{HF} \rangle \\ \varepsilon_{\mu_2} t_{\mu_2} &= -\langle \mu_2 | \tilde{\hat{\Phi}} | \mathrm{HF} \rangle\end{aligned}$$

- The quality of the CC2 wave function is intermediate between the MP1 and CCSD wave functions.
- Since the doubles are correct to first order, the CC2 energy is correct to second order and is expected to be of similar quality to the MP2 energy.

$$E = \langle \mathrm{HF} | \hat{\Phi} | \mathrm{HF} \rangle + \langle \mathrm{HF} | [\hat{\Phi}, \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mathrm{HF} | [[\hat{\Phi}, \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle$$

- Note that the CCSD energy is correct to third order.

The CC3 hybrid model

- For CCSDT the third and higher order corrections to the triples amplitudes are the most expensive.

$$\begin{aligned}\varepsilon_{\mu_3} t_{\mu_3} &= -\langle \mu_3 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \mathrm{HF} \rangle - \langle \mu_3 | [\tilde{\hat{\Phi}}, \hat{T}_3] | \mathrm{HF} \rangle \\ &\quad -\tfrac{1}{2} \langle \mu_3 | [[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_2] | \mathrm{HF} \rangle - \mu_3 | [[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_3] | \mathrm{HF} \rangle\end{aligned}$$

- In CCSDT the triples are correct to third order. Retaining only the first term, we approximate t_{μ_3} to second order and solve the resulting CC3 hybrid expressions iteratively.

$$\begin{aligned}\varepsilon_{\mu_1} t_{\mu_1} &= R_1^2 - \langle \mu_1 | [\tilde{\hat{\Phi}}, \hat{T}_3] | \mathrm{HF} \rangle \\ \varepsilon_{\mu_2} t_{\mu_2} &= R_2^2 - \langle \mu_2 | [\tilde{\hat{\Phi}}, \hat{T}_3] | \mathrm{HF} \rangle \\ \varepsilon_{\mu_3} t_{\mu_3} &= -\langle \mu_3 | [\tilde{\hat{\Phi}}, \hat{T}_2] | \mathrm{HF} \rangle\end{aligned}$$

- The quality of the CC3 wave function is intermediate between the MP2 and CCSDT wave functions.
- In both CC3 and CCSDT the doubles are correct to third order, the energy is correct to fourth order.

CCSD(T): a noniterative hybrid method

- The $2n + 1$ rule states that we only require the second order ψ to obtain an energy correct to fourth order in $\hat{\Phi}$.
- The CCSD wave function is correct to second order in $\hat{T}_1$ and $\hat{T}_2$, but is missing the second order connected triples.
- In CCPT the $\hat{T}_3^{(2)}$ amplitudes are obtained from the $\hat{T}_2^{(1)}$ amplitudes.
- The CCSD(T) method consists of a perturbative (noniterative) correction to the CCSD energy.
  - Utilizing the expressions from perturbation theory, approximate second order triples amplitudes ${}^*\hat{T}_3^{(2)}$ are generated from the CCSD $\hat{T}_2$ amplitudes (rather than from first order amplitudes).
  - The second order corrected wave function is then used to compute the fourth and fifth order energy corrections, which are added to the CCSD energy.

- The forth and fifth order energy terms that contain the connected triples amplitudes are

$$
\begin{aligned}
E_T^{(4)} &= \sum_{\mu_2} \bar{t}_{\mu_2}^{(1)} \langle \mu_2 | [\hat{\Phi}, \hat{T}_3^{(2)}] | \mathsf{HF} \rangle \\
E_T^{(5)} &= \sum_{\mu_1} \bar{t}_{\mu_1}^{(2)} \langle \mu_1 | [\hat{\Phi}, \hat{T}_3^{(2)}] | \mathsf{HF} \rangle + \sum_{\mu_2} \bar{t}_{\mu_2}^{(2)} \langle \mu_2 | [\hat{\Phi}, \hat{T}_3^{(2)}] | \mathsf{HF} \rangle \\
&+ \sum_{\mu_3} \bar{t}_{\mu_3}^{(2)} \langle \mu_3 | [\hat{\Phi}, \hat{T}_3^{(2)}] | \mathsf{HF} \rangle + \sum_{\mu_3} \bar{t}_{\mu_4}^{(2)} \langle \mu_4 | [\hat{\Phi}, \hat{T}_3^{(2)}] | \mathsf{HF} \rangle \\
&+ \sum_{\mu_3} \bar{t}_{\mu_3}^{(2)} \langle \mu_3 | [\hat{\Phi}, \hat{T}^{(2)}] | \mathsf{HF} \rangle + \tfrac{1}{2} \sum_{\mu_3} \bar{t}_{\mu_3}^{(2)} \langle \mu_3 | [[\hat{\Phi}, \hat{T}_2^{(1)}], \hat{T}_2^{(1)}] | \mathsf{HF} \rangle
\end{aligned}
$$

- The first two terms of $E_T^{(5)}$ arise from projection onto the singles and doubles manifold. Of the five, only these two are included in the CCSD(T) correction, which becomes

$$
\Delta E^{\mathsf{CCSD(T)}} = \sum_{\mu_1} \bar{t}_{\mu_1} \langle \mu_1 | [\hat{\Phi},^* \hat{T}_3^{(2)}] | \mathsf{HF} \rangle + \sum_{\mu_2} \bar{t}_{\mu_2} \langle \mu_2 | [\hat{\Phi},^* \hat{T}_3^{(2)}] | \mathsf{HF} \rangle
$$

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