Simplified Equation of Motion
Coupled Cluster for Excited States

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Molecular properties:
Linear response (LR) or equation of motion (EOM)
Calculation of (most) properties require:

- Response theory due to perturbation
- Approximation to the wavefunction

The order in which theory is applied matters!

\[
\text{LR-CC} = \text{CC} + \text{LR}
\]
\[
\text{EOM-CC} = \text{LR} + \text{CC}
\]

We will focus on EOM methods.

We form an exact excited state from the exact ground state

\[ |\Psi_e\rangle = R|\Psi_g\rangle \]

\[ R = R_1 + R_2 + \cdots = r_i^a a^\dagger_a a_i + r_{ij}^{ab} a^\dagger_a a^\dagger_b a_j a_i + \cdots \]

Likewise, we can generate the exact ground state

\[ |\Psi_g\rangle = e^T|\Psi_0\rangle \]

\[ T = T_1 + T_2 + \cdots = t_i^a a^\dagger_a a_i + t_{ij}^{ab} a^\dagger_a a^\dagger_b a_j a_i + \cdots \]

\[ He^TR_m|\Psi_0\rangle = E_m e^TR_m|\Psi_0\rangle \quad \text{or} \quad HR_m|CC\rangle = E_m R_m|CC\rangle \]

It is convenient to use the *normal-ordered Hamiltonian*, $H_N$.

\[ H_N = H - \langle 0 | H | 0 \rangle \]

In other words, $H_N$ is now a "correlation operator". In second quantization this gives:

\[ H_N = \sum_p f_{pq} \{ a_p^\dagger a_q \} + \frac{1}{4} \langle pq || rs \rangle \{ a_p^\dagger a_q^\dagger a_s a_r \} \]

or simply

\[ H_N = F + V \]

In addition to normal ordered operators, we use Wick’s Theorem to simplify the CC equations.

\[
\bar{H}_N = e^{-T} H_N e^T
\]

\[
= H_N + [H_N, T] + \frac{1}{2} [[H_N, T], T] + \cdots \text{(infinitely more!)}
\]

\[\cdots \text{a bit of work} \cdots\]

\[
= H_N + H_N T_1 + H_N T_2 + \frac{1}{2} H_N T_1^2 + \cdots \text{(only 11 more terms!)}
\]

\[
= (H_N e^T)_c
\]

Turns out all the \(T\) operators must share an index with \(H_N\) (“connected cluster”), and the expression truncates naturally.

One final result before we continue. We can solve for excitations directly:

\[
[H, R_m]|0\rangle = \bar{H}R_m|0\rangle - R_m\bar{H}|0\rangle \\
= E_m R_m|0\rangle - E_0 R_m|0\rangle \\
= \omega R_m|0\rangle
\]

where \(\omega_m = E_m - E_0\). Applying Wick’s theorem, we keep connected \(R\) and \(\bar{H}\) terms, giving us a final expression of

\[
(\bar{H}_N R)_c|0\rangle = \omega R|0\rangle
\]

Let’s use EOM-CCSD as an example.

\[ T = T_1 + T_2 \]

The actual solution requires diagonalizing \( \bar{H} \) in the space of singly and doubly excited determinants

\[
\begin{pmatrix}
    \langle \Phi_i^a | \bar{H} | \Phi_k^c \rangle & \langle \Phi_i^a | \bar{H} | \Phi_{kl}^{cd} \rangle \\
    \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_k^c \rangle & \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_{kl}^{cd} \rangle
\end{pmatrix}
\]

The matrix elements are evaluated using diagrammatic techniques.
The diagrams are numerous, and scale as bad as $O(N^6)$. We want to use the tools of perturbation theory to simplify the equations. Introducing a scalar ordering parameter $\lambda$

$$H_N = F + \lambda V$$

Similarly, we expand the $T$ operator perturbatively

$$T = \lambda T^{(1)} + \lambda^2 T^{(2)} + \lambda^3 T^{(3)} + \cdots$$
\[(H_N e^T)_c |\Psi_0\rangle = H_N |\Phi_0\rangle + H_N T |\Phi_0\rangle + \frac{1}{2} H_N T^2 |\Phi_0\rangle + \cdots
\]
\[= (F + \lambda V) |\Phi_0\rangle
\]
\[+ (F + \lambda V)(\lambda T^{(1)} + \lambda^2 T^{(2)} + \cdots) |\Phi_0\rangle
\]
\[+ \frac{1}{2} (F + \lambda V)(\lambda T^{(1)} + \lambda^2 T^{(2)} + \cdots)^2 |\Phi_0\rangle + \cdots
\]

Collecting terms of like order \(\lambda\) yields, with \(\bar{H}_N = (H_N e^T)_c\)

\[\bar{H}_N^{(0)} = F\]
\[\bar{H}_N^{(1)} = V + FT^{(1)}\]
\[\bar{H}_N^{(2)} = V T^{(1)} + FT^{(2)} + \frac{1}{2} FT^{(1)} T^{(1)}\]
Unlike CCSD, we can solve for the $T_1$ and $T_2$ amplitudes directly:

$$\langle \Phi_i^a | H^{(1)} | \Phi_0 \rangle = 0 = \sum_b f_{ab} t_i^b(1) - \sum_j f_{ij} t_i^a(1)$$

By the diagonal nature of the canonical Fock matrix elements, $t_i^a(1) = 0$. In a similar manner,

$$\langle \Phi_{ij}^{ab} | H^{(1)} | \Phi_0 \rangle = 0 = \langle ij|ab \rangle - (f_{ii} + f_{jj} - f_{aa} - f_{bb}) t_{ij}^{ab(1)}$$

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

For our reference, this gives the MP2 energy expression back directly (sanity check!)
Finally plugging in terms, we have three new methods to try

\[
\begin{align*}
\text{EOM-MBPT2} &= \begin{bmatrix}
\langle S| \bar{H}^{(0\rightarrow2)} | S \rangle & \langle S| \bar{H}^{(0\rightarrow2)} | D \rangle \\
\langle D| \bar{H}^{(0\rightarrow2)} | S \rangle & \langle D| \bar{H}^{(0\rightarrow2)} | D \rangle 
\end{bmatrix} \\
\text{EOM-MBPT(D)} &= \begin{bmatrix}
\langle S| \bar{H}^{(0\rightarrow2)} | S \rangle & \langle S| \bar{H}^{(0\rightarrow2)} | D \rangle \\
\langle D| \bar{H}^{(0\rightarrow2)} | S \rangle & \langle D| \bar{H}^{(0\rightarrow1)} | D \rangle 
\end{bmatrix} \\
\text{EOM-MBPT(2)} &= \begin{bmatrix}
\langle S| \bar{H}^{(0\rightarrow2)} | S \rangle & \langle S| \bar{H}^{(0\rightarrow1)} | D \rangle \\
\langle D| \bar{H}^{(0\rightarrow1)} | S \rangle & \langle D| \bar{H}^{(0\rightarrow1)} | D \rangle 
\end{bmatrix}
\end{align*}
\]

(In fact, we can derive CIS and the CIS(D) families of equations this way!)
Formaldehyde ($S_1$) / cc-pVDZ

- EOM-MBPT2
- EOM-MBPT(D)
- EOM-MBPT(2)
- B3LYP
- EOM-CC2

Relative Error to EOM-CCSD
Ethylene ($S_1$) / cc-pVDZ

- EOM-MBPT2
- EOM-MBPT(D)
- EOM-MBPT(2)
- B3LYP
- EOM-CC2

Relative Error to EOM-CCSD
Why is this method promising?
  ▶ Non-iterative solution for amplitudes
  ▶ Far smaller prefactor
  ▶ Lowers scaling by a factor
Why is this method promising?

- Non-iterative solution for amplitudes
- Far smaller prefactor
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Why might this method fail?

- Total neglect of single excitations (Thouless 1960)
- Neglect of higher excitation character
- Cost/benefit of accuracy versus speed