

Simplified Equation of Motion Coupled Cluster for Excited States

Joshua Goings

Department of Chemistry

University of Washington, Seattle

✉ jjgoings@uw.edu  [jjgoings](https://github.com/jjgoings)

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.

Helgaker, Trygve, et al. "Recent advances in wave function-based methods of molecular-property calculations." *Chemical Reviews* 112.1 (2012): 543-631.

We form an exact excited state from the exact ground state

$$|\Psi_e\rangle = R|\Psi_g\rangle$$

$$R = R_1 + R_2 + \dots = r_i^a a_a^\dagger a_i + r_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \dots$$

Likewise, we can generate the exact ground state

$$|\Psi_g\rangle = e^T |\Psi_0\rangle$$

$$T = T_1 + T_2 + \dots = t_i^a a_a^\dagger a_i + t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \dots$$

$$He^T R_m |\Psi_0\rangle = E_m e^T R_m |\Psi_0\rangle \quad \text{or} \quad HR_m |CC\rangle = E_m R_m |CC\rangle$$

Stanton, John F., and Rodney J. Bartlett. "The equation of motion coupled cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties." The Journal of chemical physics 98 (1993): 7029.

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:

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

or simply

$$H_N = F + V$$

Shavitt, Isaiah, and Rodney J. Bartlett. *Many-body methods in chemistry and physics: MBPT and coupled-cluster theory*. Cambridge University Press, 2009.

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

$$\begin{aligned}\bar{H}_N &= e^{-T} H_N e^T \\ &= H_N + [H_N, T] + \frac{1}{2} [[H_N, T], T] + \dots \text{(infinitely more!)} \\ &\dots \text{a bit of work} \dots \\ &= H_N + H_N T_1 + H_N T_2 + \frac{1}{2} H_N T_1^2 + \dots \text{(only 11 more terms!)} \\ &= (H_N e^T)_c\end{aligned}$$

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

Crawford, T. Daniel, and H. F. Schaefer. “An introduction to coupled cluster theory for computational chemists.” *Reviews in computational chemistry* 14 (2000): 33-136.

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

$$\begin{aligned} [\bar{H}, R_m]|0\rangle &= \bar{H}R_m|0\rangle - R_m\bar{H}|0\rangle \\ &= E_m R_m|0\rangle - E_0 R_m|0\rangle \\ &= \omega R_m|0\rangle \end{aligned}$$

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

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

Bartlett, Rodney J. "Coupled cluster theory and its equation-of-motion extensions." Wiley Interdisciplinary Reviews: Computational Molecular Science 2.1 (2012): 126-138.

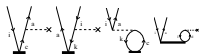
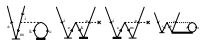
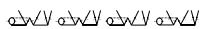
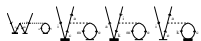
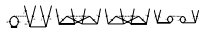
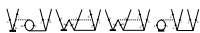
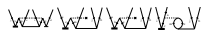
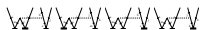
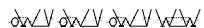
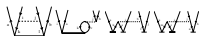
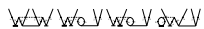
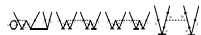
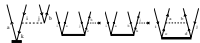
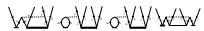
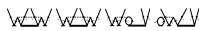
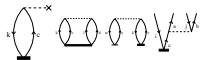
Let's use EOM-CCSD as an example.

$$T = T_1 + T_2$$

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 λ

$$H_N = F + \lambda V$$

Similarly, we expand the T operator perturbatively

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

$$\begin{aligned}
(H_N e^T)_c |\Psi_0\rangle &= H_N |\Phi_0\rangle + H_N T |\Phi_0\rangle + \frac{1}{2} H_N T^2 |\Phi_0\rangle + \dots \\
&= (F + \lambda V) |\Phi_0\rangle \\
&+ (F + \lambda V)(\lambda T^{(1)} + \lambda^2 T^{(2)} + \dots) |\Phi_0\rangle \\
&+ \frac{1}{2} (F + \lambda V)(\lambda T^{(1)} + \lambda^2 T^{(2)} + \dots)^2 |\Phi_0\rangle + \dots
\end{aligned}$$

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

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

$$\bar{H}_N^{(1)} = V + FT^{(1)}$$

$$\bar{H}_N^{(2)} = VT^{(1)} + FT^{(2)} + \frac{1}{2} FT^{(1)} T^{(1)}$$

Unlike CCSD, we can solve for the T_1 and T_2 amplitudes directly:

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

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

$$\begin{aligned}\langle \Phi_{ij}^{ab} | \bar{H}^{(1)} | \Phi_0 \rangle &= 0 \\ &= \langle ij || ab \rangle - (f_{ii} + f_{jj} - f_{aa} - f_{bb}) t_{ij}^{ab(1)} \\ t_{ij}^{ab(1)} &= \frac{\langle ij || ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}\end{aligned}$$

For our reference, this gives the MP2 energy expression back directly (sanity check!)

Finally plugging in terms, we have three new methods to try

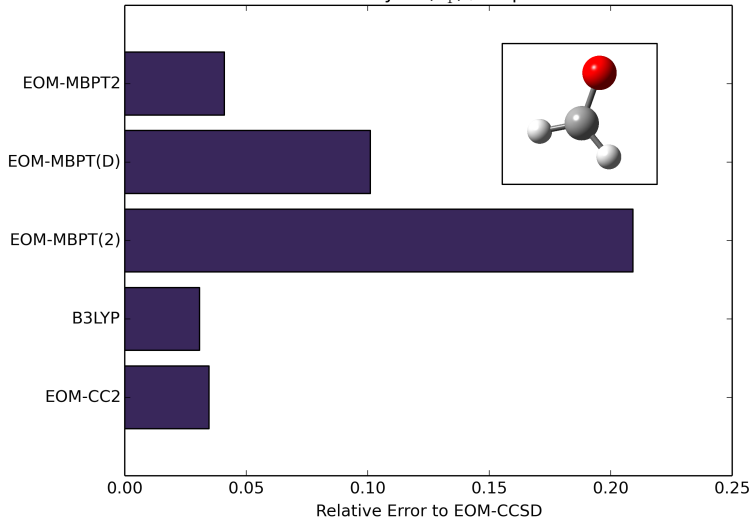
$$\text{EOM-MBPT2} = \begin{bmatrix} \langle S | \bar{H}^{(0 \rightarrow 2)} | S \rangle & \langle S | \bar{H}^{(0 \rightarrow 2)} | D \rangle \\ \langle D | \bar{H}^{(0 \rightarrow 2)} | S \rangle & \langle D | \bar{H}^{(0 \rightarrow 2)} | D \rangle \end{bmatrix}$$

$$\text{EOM-MBPT(D)} = \begin{bmatrix} \langle S | \bar{H}^{(0 \rightarrow 2)} | S \rangle & \langle S | \bar{H}^{(0 \rightarrow 2)} | D \rangle \\ \langle D | \bar{H}^{(0 \rightarrow 2)} | S \rangle & \langle D | \bar{H}^{(0 \rightarrow 1)} | D \rangle \end{bmatrix}$$

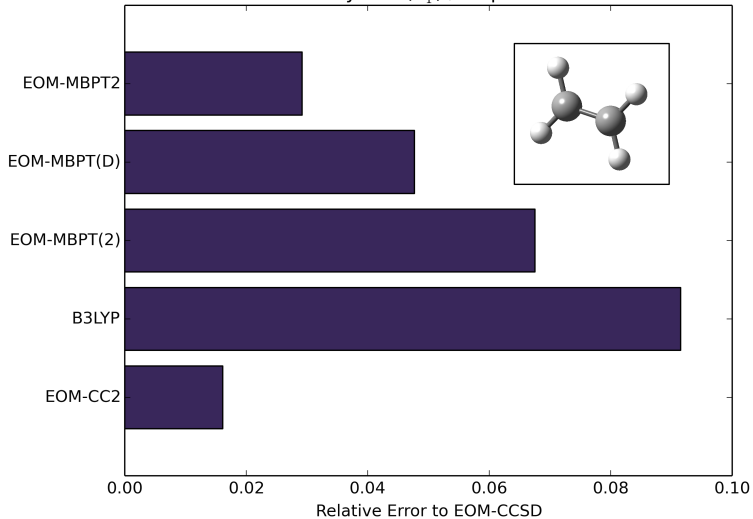
$$\text{EOM-MBPT(2)} = \begin{bmatrix} \langle S | \bar{H}^{(0 \rightarrow 2)} | S \rangle & \langle S | \bar{H}^{(0 \rightarrow 1)} | D \rangle \\ \langle D | \bar{H}^{(0 \rightarrow 1)} | S \rangle & \langle D | \bar{H}^{(0 \rightarrow 1)} | D \rangle \end{bmatrix}$$

(In fact, we can derive CIS and the CIS(D) families of equations this way!)

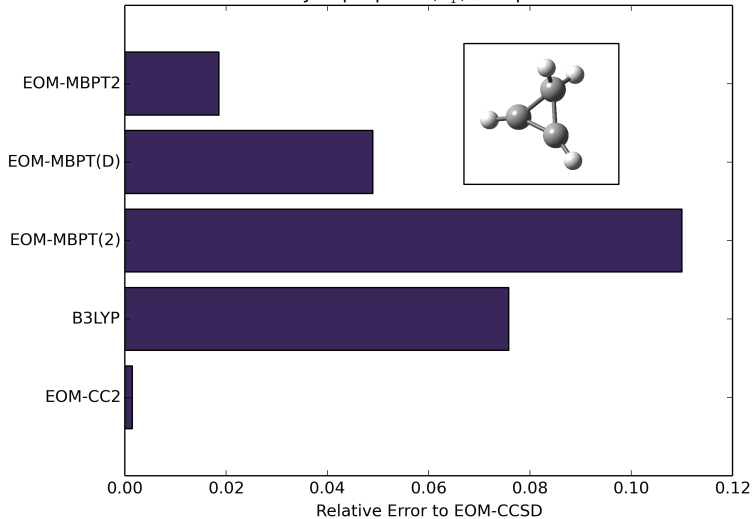
Formaldehyde (S_1) / cc-pVDZ



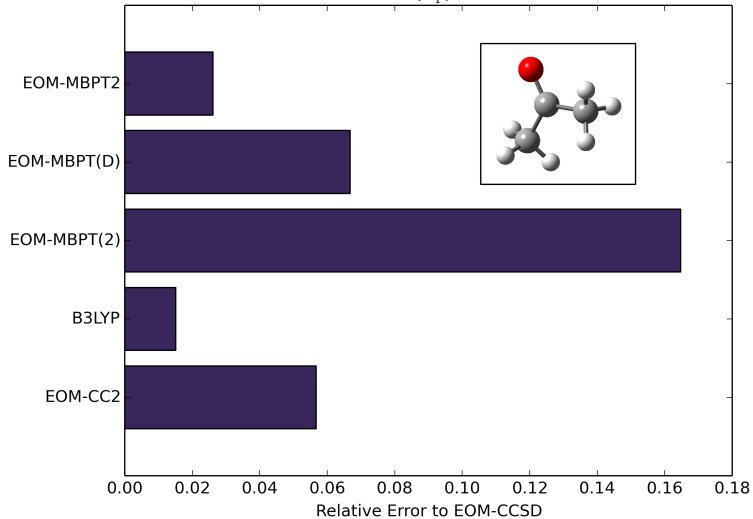
Ethylene (S_1) / cc-pVDZ



Cyclopropene (S_1) / cc-pVDZ



Acetone (S_1) / 6-31G



Why is this method promising?

- ▶ Non-iterative solution for amplitudes
- ▶ Far smaller prefactor
- ▶ Lowers scaling by a factor

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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