Low-Scaling Approximations to the EOM-CCSD Equations

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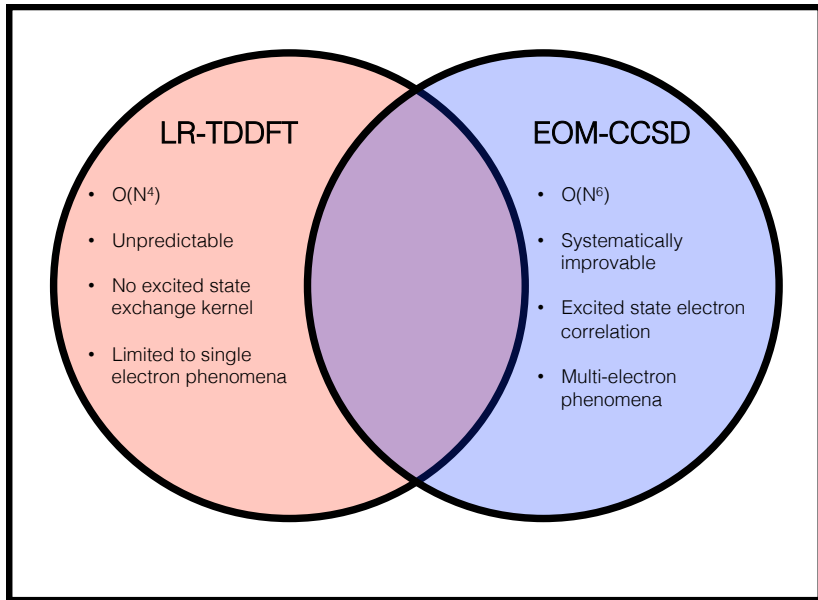
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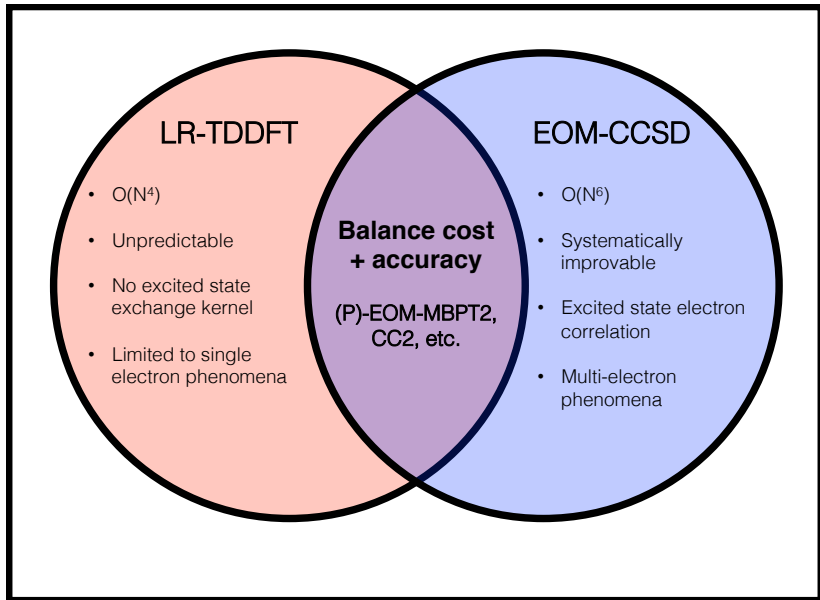
The problem: few competitive wave function alternatives to LR-TDDFT for excited state energies.

Caricato, 2010, regarding TDDFT:

"*Large differences in the results are found between the various functionals...the choice of functional can largely affect the accuracy of a calculation.*"

"*Methods like EOM-CCSD are ... always more reliable than any DFT functional ... [yet] DFT still represents the best compromise between accuracy and computational effort.*"

LR-TDDFT

- $O(N^4)$
- Unpredictable
- No excited state exchange kernel
- Limited to single electron phenomena

EOM-CCSD

- $O(N^6)$
- Systematically improvable
- Excited state electron correlation
- Multi-electron phenomena

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Balance cost + accuracy

(P)-EOM-MBPT2, CC2, etc.

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You can derive MP2 energy equations from CCSD.

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CC has plenty of excited state methods (EOM, LR, etc).

Why can't we derive an MP2 for excited states?

The MBPT equation:

$$\bar{H}_N |\psi_0\rangle = E|\psi_0\rangle$$

$$\bar{H}_N = \left(e^{-\hat{T}} \left(\hat{F}_N + \lambda \hat{V}_N \right) e^{\hat{T}} \right)$$

$$\hat{T} = \lambda \hat{T}^{(1)} + \lambda^2 \hat{T}^{(2)} + \cdots$$

Collect terms through second order

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

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

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

$$\bar{H}_N^{(2)} = \hat{V}_N \hat{T}^{(1)} + \hat{F}_N \hat{T}^{(2)} + \frac{1}{2} \hat{F}_N \hat{T}^{(1)} \hat{T}^{(1)} \cdots$$

EOM-CC is like CI with a CC Hamiltonian.
(In fact, EOM-CCS is equivalent to CIS).

$$\left[\begin{array}{cc} \langle \phi_i^a | \bar{H}_N | \phi_k^c \rangle & \langle \phi_i^a | \bar{H}_N | \phi_{kl}^{cd} \rangle \\ \langle \phi_{ij}^{ab} | \bar{H}_N | \phi_k^c \rangle & \langle \phi_{ij}^{ab} | \bar{H}_N | \phi_{kl}^{cd} \rangle \end{array} \right] \left[\begin{array}{c} R_1 \\ R_2 \end{array} \right] = \omega \left[\begin{array}{c} R_1 \\ R_2 \end{array} \right]$$

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(Rigorously, this is the Jacobian in LR-CC theory,
e.g. derivative of cluster amplitude equations.)

In EOM, the equation matrix elements depend on $\hat{T}$.
Unlike CCSD, we can solve for the $\hat{T}_1$ and $\hat{T}_2$ amplitudes directly:

$$\hat{T}_1 \rightarrow t_i^{a(1)} = 0$$

$$\hat{T}_2 \rightarrow t_{ij}^{ab(1)} = \frac{\langle ij||ab\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

We can solve the equations immediately following SCF (plus integral transform).

$$\left[\begin{array}{cc} \langle \phi_i^a | \bar{H}_N | \phi_k^c \rangle & \langle \phi_i^a | \bar{H}_N | \phi_{kl}^{cd} \rangle \\ \langle \phi_{ij}^{ab} | \bar{H}_N | \phi_k^c \rangle & \langle \phi_{ij}^{ab} | \bar{H}_N | \phi_{kl}^{cd} \rangle \end{array} \right] \left[\begin{array}{c} R_1 \\ R_2 \end{array} \right] = \omega \left[\begin{array}{c} R_1 \\ R_2 \end{array} \right]$$

Bridging the gap between LR-TDDFT and EOM-CCSD

- EOM-CCSD $\to$ O(N^6)
- EOM-MBPT2 $\to$ O(N^6), perturbed $\hat{T}$, smaller prefactor
- P-EOM-MBPT2 $\to$ O(N^5), eliminate O(N^6) terms in DD block
- CC2 $\to$ O(N^5), eliminate O(N^6) terms and most $\hat{T}_2$
- LR-TDDFT $\to$ O(N^4)

Stanton, 1993; Stanton, 1995; Gwaltney, 1996; Christiansen, 1995; Runge, 1984
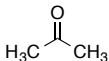
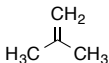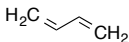MP2 optimized molecules tested (69 states total)
using 6-311(3+,3+)G** (Wiberg, 2002; Caricato, 2010)

log_{10}-log_{10} Plot of computational time as a function of basis size

EOM-CCSD, $y = 5.4x-9.3$, $R^2 = 0.97$
EOM-MBPT2, $y = 5.4x-9.4$, $R^2 = 0.98$
P-EOM-MBPT2, $y = 4.7x-8.5$, $R^2 = 0.99$
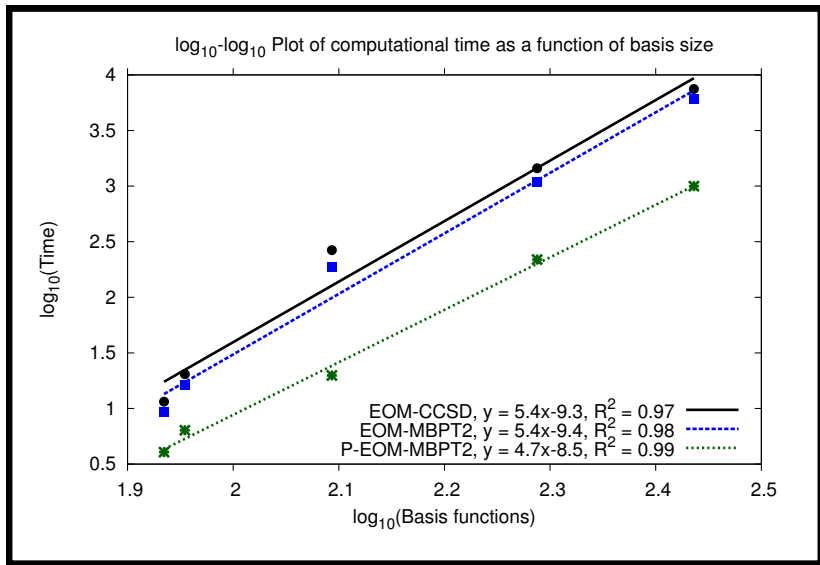
Error compared to experiment (eV)				
All molecules (69 states)				
	Mean AE	RMS	Max AE	MSE
EOM-CCSD	0.27	0.36	1.02	0.20
EOM-MBPT2	0.30	0.43	1.12	0.20
P-EOM-MBPT2	0.47	0.65	1.40	0.41
CC2	0.44	0.53	1.26	-0.19
CIS(D)	0.49	0.61	1.83	-0.04
B3LYP	0.67	0.84	1.82	-0.56
RPA	1.01	1.26	3.63	0.90
CIS	1.07	1.34	3.67	1.01
Average Valence Energy: 5.3 eV				
Average Rydberg Energy: 8.0 eV				

| Error compared to experiment (eV) | | | |
| All molecules, valence states only (30 states) | | | |
	Mean AE	RMS	Max AE	MSE
EOM-CCSD	0.47	0.52	1.02	0.47
EOM-MBPT2	0.56	0.63	1.12	0.51
P-EOM-MBPT2	0.89	0.96	1.40	0.88
CC2	0.36	0.42	1.00	0.20
CIS(D)	0.50	0.59	1.83	0.49
B3LYP	0.20	0.26	0.59	0.06
RPA	1.19	1.44	3.63	1.08
CIS	1.29	1.55	3.67	1.29

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Schreiber, *et al.* (2008) found "CC2 outperforms CCSD in comparisons with CASPT2 and CC3. In general, CCSD seems to overestimate the excitation energies." They studied only valence states.

Error compared to experiment (eV)				
All molecules, Rydberg states only (39 states)				
	Mean AE	RMS	Max AE	MSE
EOM-CCSD	0.11	0.14	0.45	0.00
EOM-MBPT2	0.10	0.14	0.34	-0.05
P-EOM-MBPT2	0.15	0.20	0.55	0.05
CC2	0.50	0.61	1.26	-0.49
CIS(D)	0.49	0.62	1.32	-0.44
B3LYP	1.03	1.09	1.82	-1.03
RPA	0.88	1.11	1.89	0.75
CIS	0.91	1.15	1.94	0.79

Why the difference between MBPT2 and CC2?

Perturbation analysis of Hartree-Fock energy:

▶ Singles second order in wave function, fourth order in energy

▶ Doubles first order in wave function, second order in energy

So it's better we include doubles...right?

Why the difference between MBPT2 and CC2?

When we include an external perturbation:

- Singles first order in perturbation, zeroth order in fluctuation

Singles may be more important than energy analysis suggests. This is especially true for properties.

CC2 and CC3 retain the singles in order to be suitable methods for *properties* (Koch, *et al.* 1997).

Why the difference between MBPT2 and CC2?

EOM-MBPT2: $\hat{T}_2$

CC2: $\hat{T}_1$

- Eliminate all of $\hat{T}_1$, while retaining most $\hat{T}_2$
- $\hat{T}_2$ accounts for pairwise correlation
- Rydberg states — sensitive to electron correlation

- Eliminate most of $\hat{T}_2$, while retaining most $\hat{T}_1$
- $\hat{T}_1$ accounts for orbital rotation/relaxation
- Valence states — sensitive to reference

Thank you to Dr. Xiaosong Li and group.

Thank you to Dr. Marco Caricato.
Thank you to Dr. Michael Frisch.

CC2:

$$\left[\begin{array}{cc} \langle\psi_i^a|e^{-\hat{T}_1-\hat{T}_2}\hat{H}_N e^{\hat{T}_1+\hat{T}_2}|\psi_k^c\rangle & \langle\psi_i^a|e^{-\hat{T}_1-\hat{T}_2}\hat{H}_N e^{\hat{T}_1+\hat{T}_2}|\psi_{kl}^{cd}\rangle \\ \langle\psi_{ij}^{ab}|e^{-\hat{T}_1}\hat{H}_N e^{\hat{T}_1}|\psi_k^c\rangle & \langle\psi_{ij}^{ab}|\hat{F}_N|\psi_{kl}^{cd}\rangle \end{array} \right]$$

P–EOM–MBPT2

$$\left[\begin{array}{cc} \langle\psi_i^a|(e^{-\hat{T}_2}\hat{H}_N e^{\hat{T}_2})^{(2)}|\psi_k^c\rangle & \langle\psi_i^a|(e^{-\hat{T}_2}\hat{H}_N e^{\hat{T}_2})^{(2)}|\psi_{kl}^{cd}\rangle \\ \langle\psi_{ij}^{ab}|(e^{-\hat{T}_2}\hat{H}_N e^{\hat{T}_2})^{(2)}|\psi_k^c\rangle & \langle\psi_{ij}^{ab}|\hat{F}_N|\psi_{kl}^{cd}\rangle \end{array} \right]$$