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Orbital Optimized MBPT(2) as a Non-local Optimized Effective Potential

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Optimized Effective Potentials in DFT

Kohn-Sham problem:

$$[h(1)+v_s(1)]\,\varphi_i(1)=\varepsilon_i\varphi_i(1)$$

Optimized effective potential condition, require

$$\frac{\delta E}{\delta v_s(1)}=0$$

Leads to equation for the potential

$$\int d2\,X(1,2)v_s(2)=f(1)$$

where $X(1,2)$ is the density-density linear response function

Why a non-local OEP?

- Effort in local OEP is substantial
  - No significant computational advantage to locality
- Since exchange is a non-local operator, focuses on correlation
- Avoids the mathematical problems with inversion
  - $X(1,2)$ is a singular operator
  - Projected in a basis, inversion of $X(1,2)$ requires some form of regularization
- Defines a new set of "optimal" orbitals
- Maybe a step on the way to an OEP for density matrix functional theory (DMFT)

Eigenproblem

Want to have the non-local eigenvalue problem

$$\left[h(1)+\int d2\; v_s(1,2)\right]\varphi_i(1)=\varepsilon_i\varphi_i(1)$$

First-order perturbation theory in the potential yields the following functional derivatives

$$\frac{\delta\varphi_i(3)}{\delta v_s(1,2)}=\sum_b \varphi_b(3)\frac{\varphi_b^*(1)\varphi_i(2)}{\varepsilon_i-\varepsilon_b}+\sum_{j\neq i}\varphi_j(3)\frac{\varphi_j^*(1)\varphi_i(2)}{\varepsilon_i-\varepsilon_j}$$

$$\frac{\delta\varphi_a(3)}{\delta v_s(1,2)}=\sum_{b\neq a} \varphi_b(3)\frac{\varphi_b^*(1)\varphi_a(2)}{\varepsilon_a-\varepsilon_b}+\sum_{j}\varphi_j(3)\frac{\varphi_j^*(1)\varphi_a(2)}{\varepsilon_a-\varepsilon_j}$$

Optimized effective potential condition

$$\frac{\delta E}{\delta v_s(1,2)} = 0$$

or

$$\sum_i \int d3 \, \frac{\delta E}{\delta \varphi_i(3)} \frac{\delta \varphi_i(3)}{\delta v_s(1,2)} + \sum_a \int d3 \, \frac{\delta E}{\delta \varphi_a(3)} \frac{\delta \varphi_a(3)}{\delta v_s(1,2)} + \text{c.c.} = 0$$

Inserting the functional derivatives of the orbitals and rearranging,

$$\sum_{i \neq j} \int d3 \left[\frac{\delta E}{\delta \varphi_i(3)} \varphi_j(3) - \frac{\delta E}{\delta \varphi_j^*(3)} \varphi_i^*(3) \right] \frac{\varphi_j^*(1)\varphi_i(2)}{\varepsilon_i - \varepsilon_j}$$

$$+ \sum_{a \neq b} \int d3 \left[\frac{\delta E}{\delta \varphi_a(3)} \varphi_b(3) - \frac{\delta E}{\delta \varphi_b^*(3)} \varphi_a^*(3) \right] \frac{\varphi_b^*(1)\varphi_a(2)}{\varepsilon_a - \varepsilon_b}$$

$$+ \sum_{ia} \int d3 \left[\frac{\delta E}{\delta \varphi_i(3)} \varphi_a(3) - \frac{\delta E}{\delta \varphi_a^*(3)} \varphi_i^*(3) \right] \frac{\varphi_a^*(1)\varphi_i(2)}{\varepsilon_i - \varepsilon_a} + \text{c.c.} = 0$$

Linear independence

Linear independence of the functions:

$$\int d1\, d2\, \frac{\varphi_p^*(1)\varphi_q(2)}{\varepsilon_p-\varepsilon_q}\frac{\varphi_r(1)\varphi_s^*(2)}{\varepsilon_r-\varepsilon_s} = \frac{\langle p|r\rangle\langle s|q\rangle}{(\varepsilon_p-\varepsilon_q)(\varepsilon_r-\varepsilon_s)} = \frac{\delta_{pr}\delta_{qs}}{(\varepsilon_p-\varepsilon_q)^2}$$

implies that each term in brackets can be set to zero individually:

$$\int d3\, \frac{\delta E}{\delta\varphi_i(3)}\varphi_j(3) - \int d3\, \frac{\delta E}{\delta\varphi_j^*(3)}\varphi_i^*(3) = 0$$

$$\int d3\, \frac{\delta E}{\delta\varphi_a(3)}\varphi_b(3) - \int d3\, \frac{\delta E}{\delta\varphi_b^*(3)}\varphi_a^*(3) = 0$$

$$\int d3\, \frac{\delta E}{\delta\varphi_i(3)}\varphi_a(3) - \int d3\, \frac{\delta E}{\delta\varphi_a^*(3)}\varphi_i^*(3) = 0$$

OO-MBPT(2) and OO-MP2

Writing the energy in the form

$$E = \sum_i h_{ii} + \frac{1}{2}\sum_{ij} \langle ij||ij\rangle + E_{\text{corr}}$$

Straightforward to show simplification to

$$\int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_i(3)}\phi_j(3) - \int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_j^*(3)}\phi_i^*(3) = 0$$

$$\int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_a(3)}\phi_b(3) - \int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_b^*(3)}\phi_a^*(3) = 0$$

$$\int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_i(3)}\phi_a(3) - \int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_a^*(3)}\phi_i^*(3) = \langle i|v_s|a\rangle - \sum_j \langle ij||aj\rangle$$

Two simple choices for E_{corr}:

$$E_{\text{corr}}^{\text{MBPT(2)}} = \sum_{ia} f_{ia} t_i^{a(1)} + \frac{1}{4}\sum_{ijab} \langle ij||ab\rangle\, t_{ij}^{ab(1)},\ E_{\text{corr}}^{\text{MP2}} = \frac{1}{4}\sum_{ijab} \langle ij||ab\rangle\, t_{ij}^{ab(1)}$$

Semi-canonical

Independence of E_{corr} to oo & vv rotations implies

$$\int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_i(3)} \phi_j(3) - \int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_j^*(3)} \phi_i^*(3) = 0$$

$$\int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_a(3)} \phi_b(3) - \int d3\ \frac{\delta E_{\text{corr}}}{\delta \phi_b^*(3)} \phi_a^*(3) = 0$$

are always true. Free to chose

$$\langle i|v_s|j\rangle = \sum_k \langle ik||jk\rangle$$

$$\langle a|v_s|b\rangle = \sum_k \langle ak||bk\rangle$$

$\Rightarrow$ Semi-canonical orbitals.

Final equations for v_s: OO-MBPT(2)

Using the expressions for semi-canonical orbitals,

$$t_i^{a(1)} = \frac{f_{ia}}{f_{ii} - f_{aa}} \qquad t_{ij}^{ab(1)} = \frac{\langle ab||ij\rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}}$$

$$\gamma_{ii} = -\sum_b t_i^{b(1)} t_b^{i\,(1)} - \frac{1}{2}\sum_{jbc} t_{ij}^{bc(1)} t_{bc}^{ij\,(1)}$$

$$\gamma_{aa} = \sum_j t_j^{a(1)} t_a^{j\,(1)} + \frac{1}{2}\sum_{jkb} t_{ab}^{jk\,(1)} t_{jk}^{ab(1)}$$

Then

$$\langle i|v_s^{MBPT(2)}|a\rangle = -h_{ia} + f_{ia}(\gamma_{ii} - \gamma_{aa}) + \sum_{jb}\left[t_j^{b(1)}\langle ji||ba\rangle + t_b^{j\,(1)}\langle bi||ja\rangle\right]$$
$$+ \sum_j \gamma_{jj}\langle ji||ja\rangle + \sum_b \gamma_{bb}\langle bi||ba\rangle + \frac{1}{2}\sum_{jbc} t_{bc}^{ij\,(1)}\langle bc||aj\rangle$$
$$- \frac{1}{2}\sum_{jkb} t_{ab}^{jk\,(1)}\langle ib||jk\rangle$$

Final equations for v_s: OO-MP2

Using the expressions for semi-canonical orbitals,

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

$$\gamma_{ii} = -\frac{1}{2}\sum_{jbc} t_{ij}^{bc(1)}\, t_{bc}^{ij\ (1)} \qquad \gamma_{aa} = \frac{1}{2}\sum_{jkb} t_{ab}^{jk\ (1)}\, t_{jk}^{ab(1)}$$

Then

$$\langle i|v_s^{MP2}|a\rangle = \sum_j \langle ij||aj\rangle + f_{ia}\left(\gamma_{ii}-\gamma_{aa}\right) + \sum_j \gamma_{jj}\langle ji||ja\rangle + \sum_b \gamma_{bb}\langle bi||ba\rangle$$
$$+\frac{1}{2}\sum_{jbc} t_{bc}^{ij\ (1)}\langle bc||aj\rangle - \frac{1}{2}\sum_{jkb} t_{ab}^{jk\ (1)}\langle ib||jk\rangle$$

Implementation

Methods:

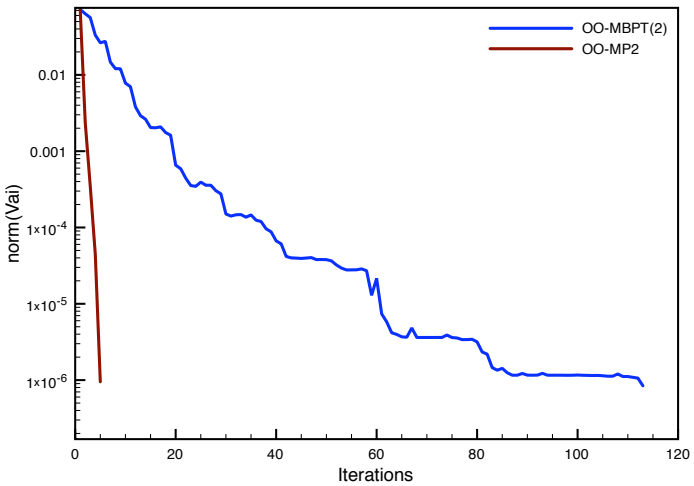
- OO-MBPT(2): Use $E_{\text{corr}}^{\text{MBPT(2)}}$ for optimization and energy
- OO-MP2 (D): Use $E_{\text{corr}}^{\text{MP2}}$ for optimization and energy
- OO-MP2 (S+D): Use $E_{\text{corr}}^{\text{MP2}}$ for optimization and $E_{\text{corr}}^{\text{MBPT(2)}}$ for energy

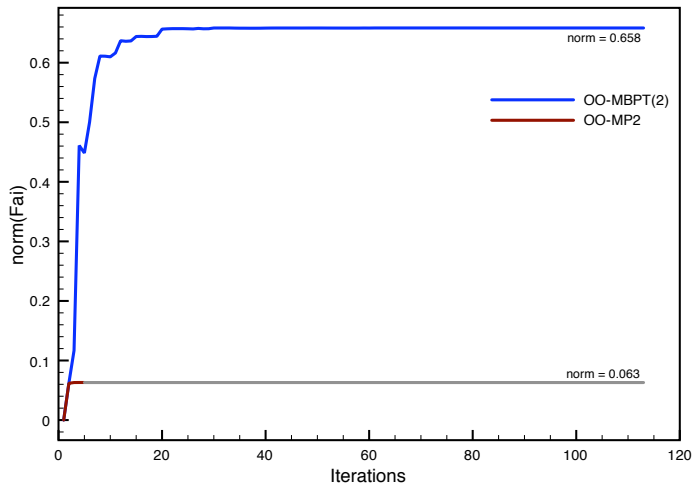
Numerics:

- Iteratively solving for v_s until Frobenius norm of $\langle i|v_s|a\rangle < 10^{-7}$ (matching HF convergence criterion)
- Currently doing integral transformation at every iteration
- Integral transform is rate-determining step

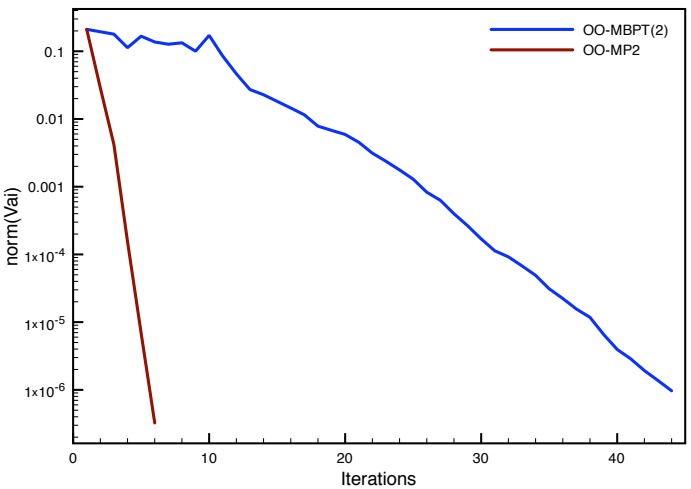
Convergence

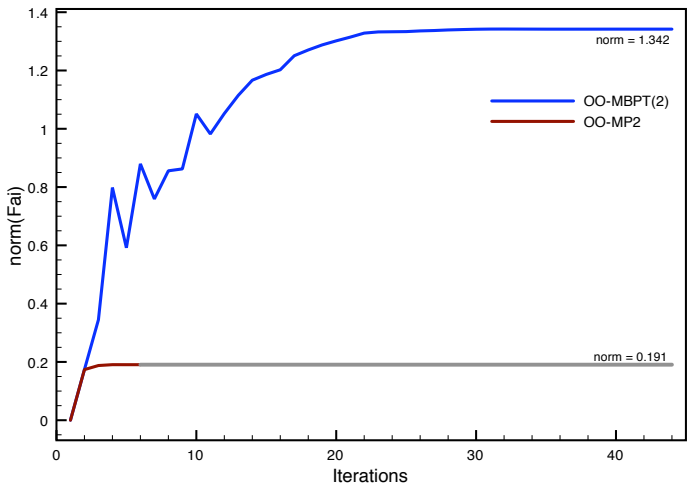
Water, cc-pVDZ





C_2, 6-31G*





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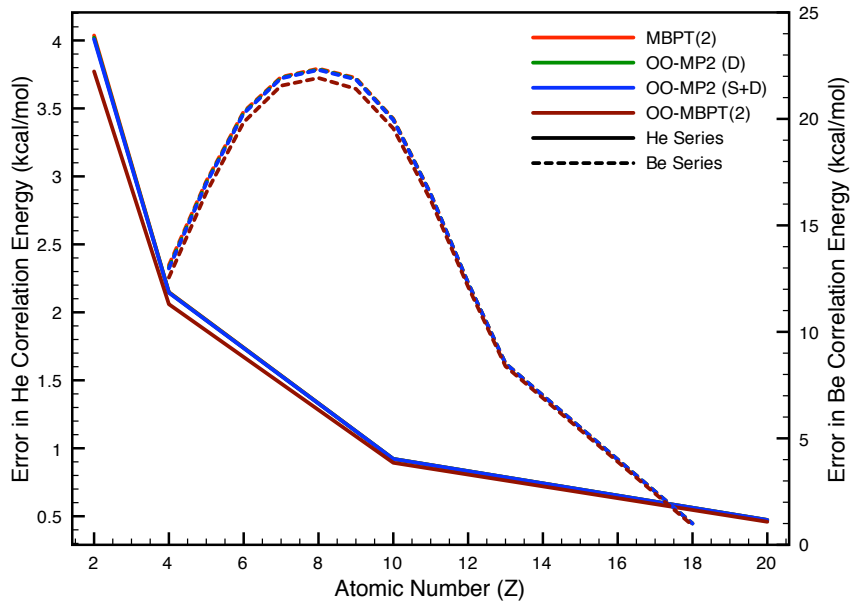
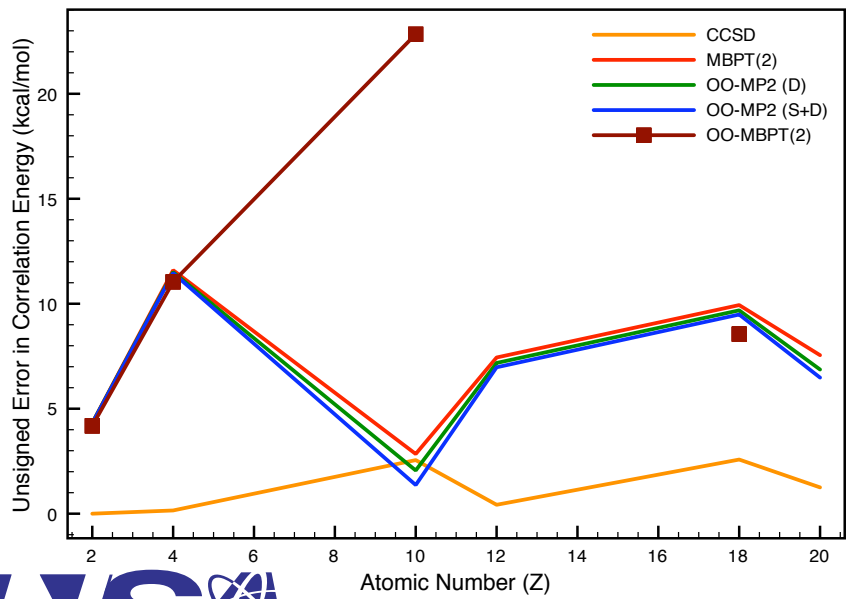
Atomic Species

He Series:
Unc. Roos aug. DZ ANO basis
Relative to FCI

Be Series:
Unc. 7s3p1d basis
Relative to FCI





Neutral Atoms:
Roos aug. DZ ANO basis
Relative to CCSD(T)

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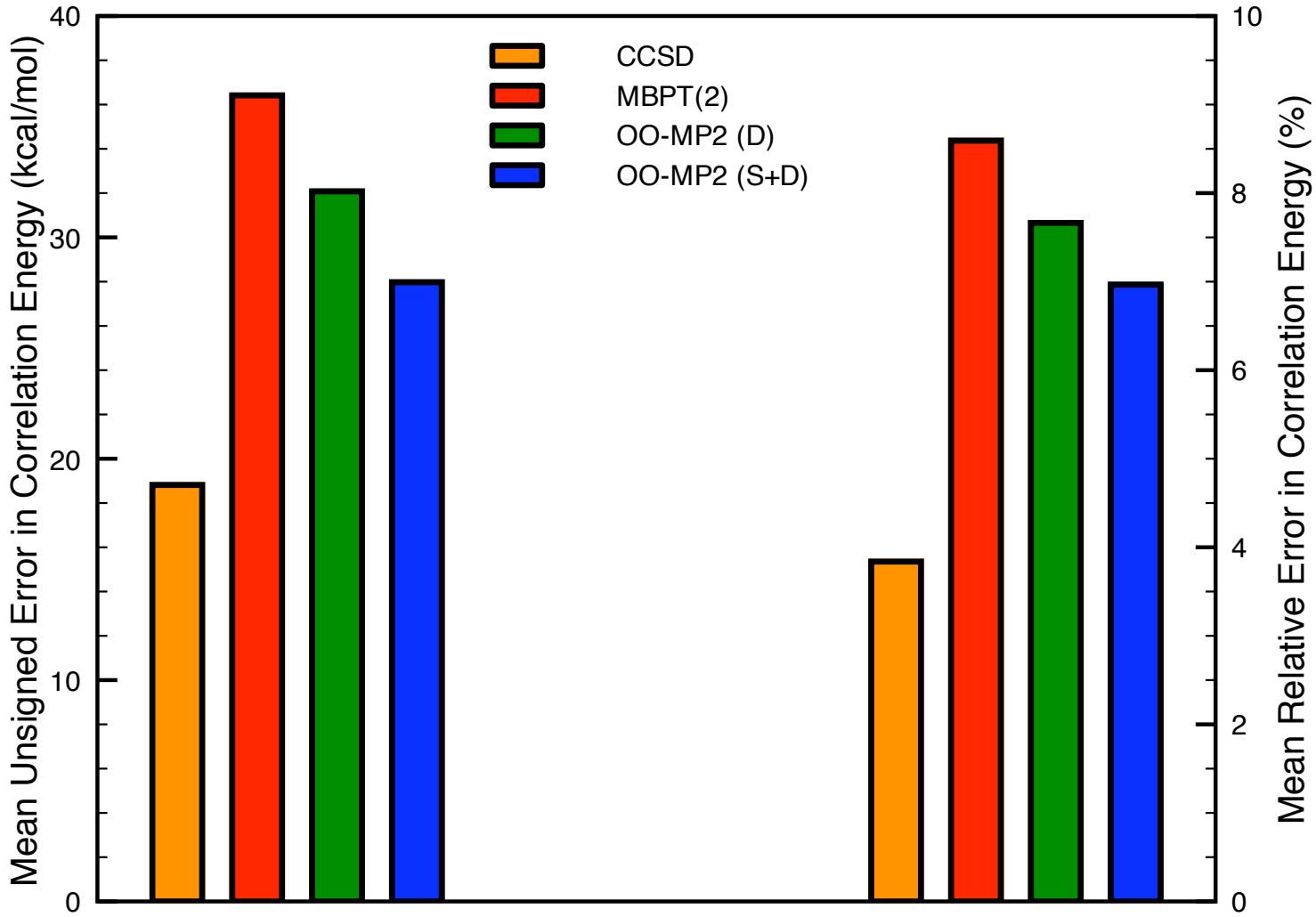
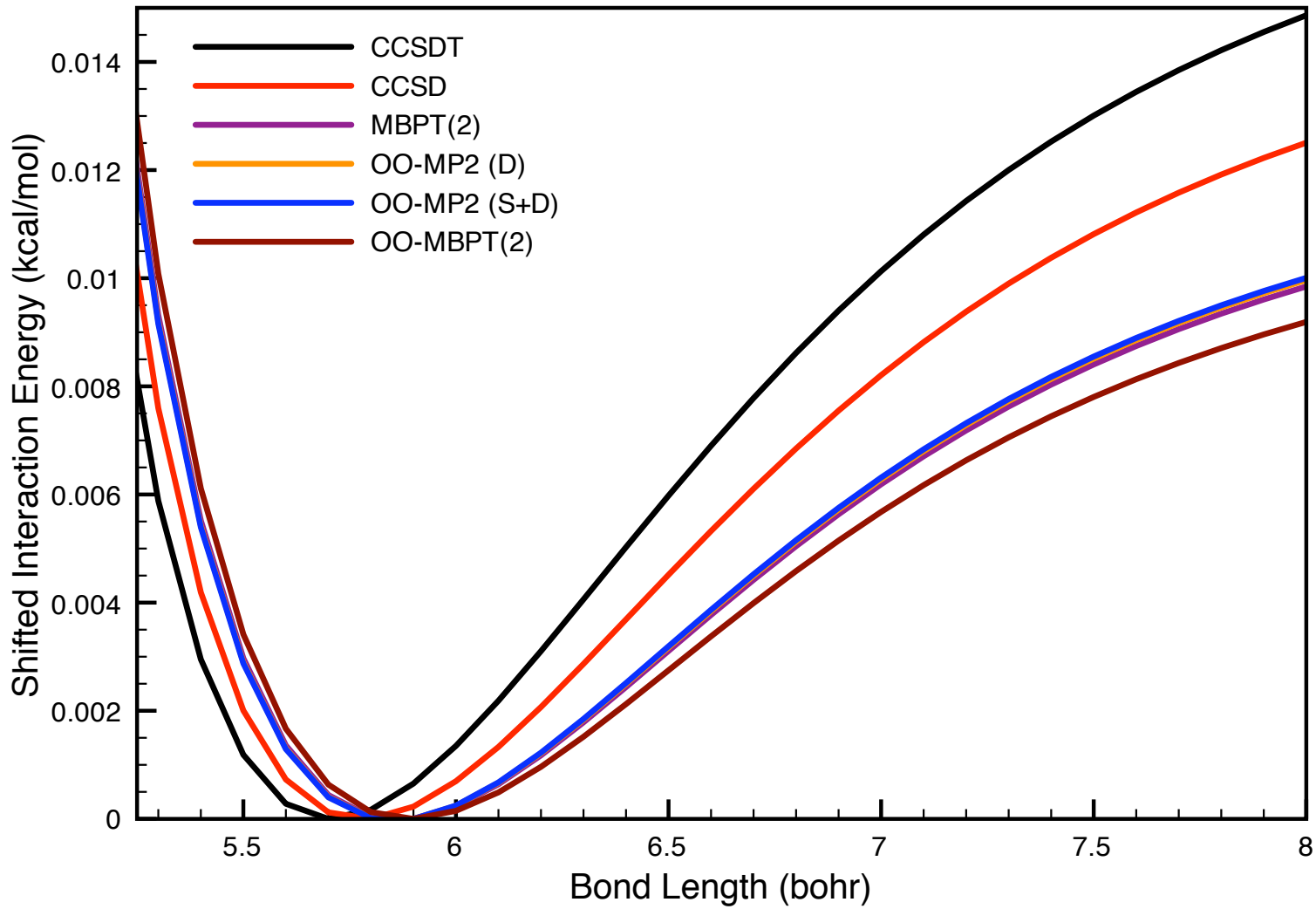
G2-99 Test set

Neutral, singlets, cc-pVTZ basis, relative to CCSD(T)



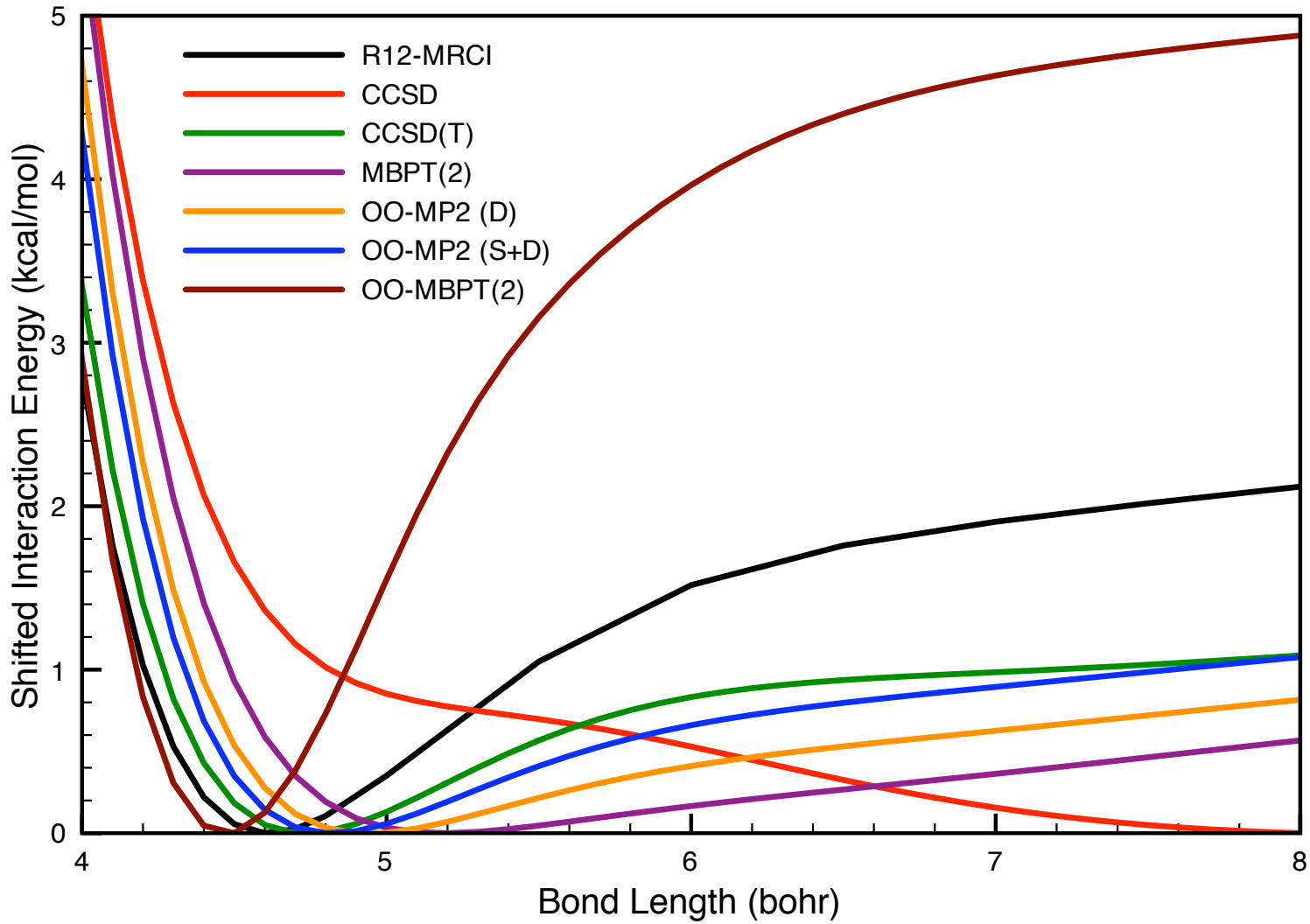
He_2

Uncontracted aug-cc-pVTZ basis



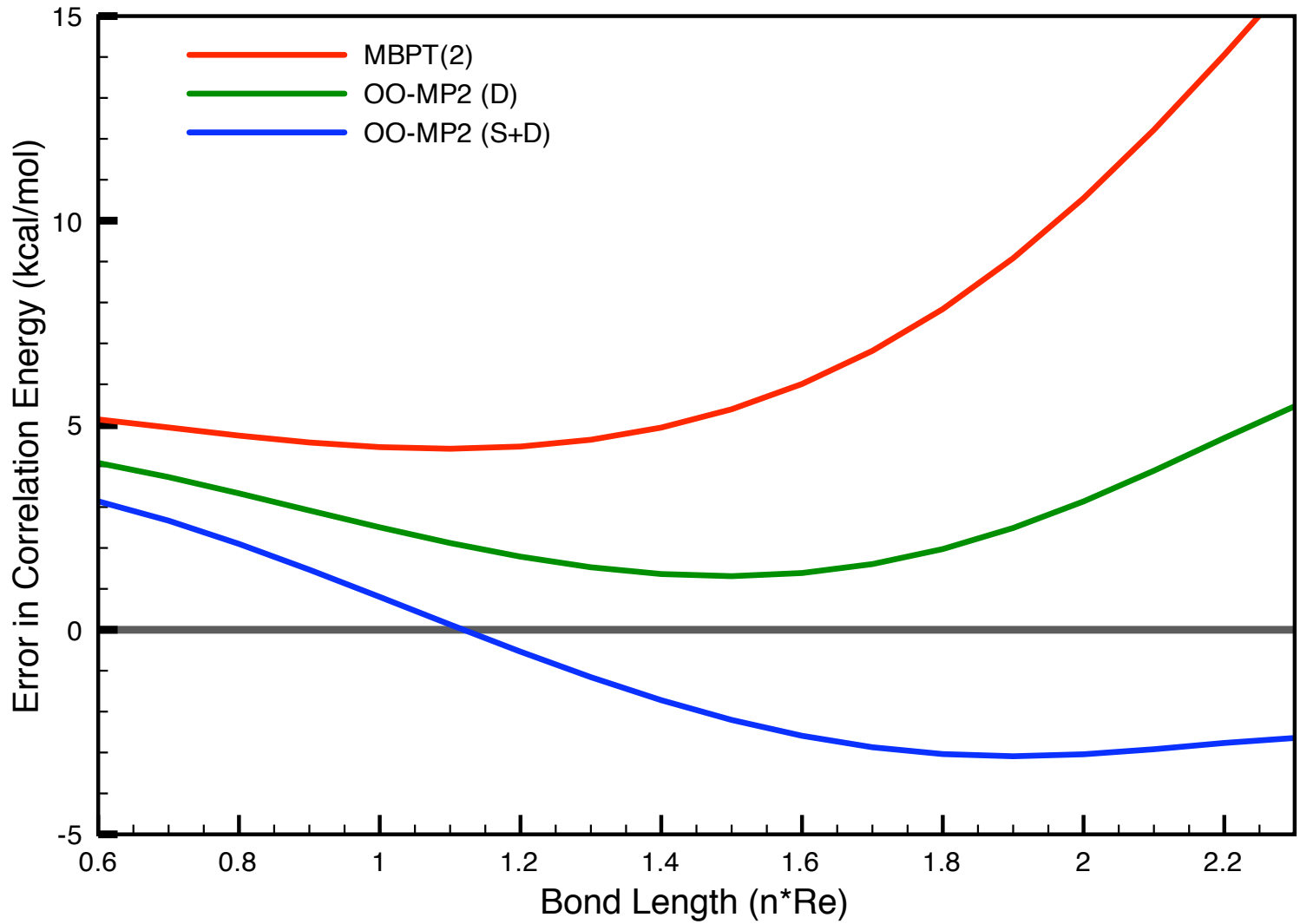
Be_2

Uncontracted aug-cc-pVTZ basis



Hydrogen Fluoride

Roos augmented double-ζ ANO basis, relative to CCSDT



Conclusions

Positives:

- Circumvents problematic inversion of X
- Improves on HF-MBPT(2)
- Easily extendible to other hermitian energy functionals, in particular LinCCSD

Negatives

- Convergence for OO-MBPT(2) is very poor
- Improvement over HF-MBPT(2) is often small
- Requires additional time-consuming iterations

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