Tensor Hypercontraction Form of (T) Energy in Coupled-Cluster Theory

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Presentation Overview

Introduction to CC Theory

- Coupled-cluster theory provides size extensive and systematic convergence to the FCI energy and wavefunction of a molecule, through the exponential ansatz:

$$|\Psi\rangle = e^{T}|\Psi\rangle \tag{1}$$

- For chemically-reliable predictions ($<$ 1 kcal/mol error), all electronic excitations up to triples need to be considered
- However, the cost of considering triples in the coupled-cluster equations scale at least $\mathcal{O}(N^7)$
- Solution: Let's change the equations then!

Tensor Hypercontraction of ERIs

- Density-fitting (DF/RI) and Cholesky Decomposition (CD) provides an approximation to electron-repulsion integrals (ERIs)

$$(pq|rs) \approx B_{pq}^{Q} B_{rs}^{Q} \tag{2}$$

  with linear-scaling auxiliary index Q.
- Tensor Hypercontraction (THC) is an extension to density-fitting developed by Ed Hohenstein and Rob Parrish, and uses two linear-scaling auxiliary indices [Hohenstein 2012]

$$(pq|rs) \approx x_p^I x_q^I Z^{IJ} x_r^J x_s^J \tag{3}$$

- CANDECOMP/PARAFAC (CP) Decomposition of the B_{pq}^{Q} intermediate is used to provide extra auxiliary index

Tensor Hypercontraction of CC Amplitudes

- Similarly, Parrish and Hohenstein also developed a similar form for doubles amplitudes in coupled-cluster theory

$$t_{ij}^{ab} \approx y_i^X y_a^X T^{XY} y_j^Y y_b^Y \tag{4}$$

- Recently, they published a paper where they combined the THC form of ERIs and doubles amplitudes to derive an $O(N^4)$ version of the CCSD algorithm [Hohenstein 2022]
- But CCSD is not enough for chemical accuracy... so we will attempt to apply this to the (T) correction

Tensor Hypercontraction of Triples Amplitude

- We can derive a THC form for the triples amplitude [Jiang 2022]

$$t_{ijk}^{abc} \approx z_i^X z_a^X z_j^Y z_b^Y z_k^Z z_c^Z T^{XYZ} \tag{5}$$

- This can be achieved through the rank-reduction for the (T) amplitude, using the HO-OI approach of Lesiuk [Lesiuk 2022]. This takes $\mathcal{O}(N^5)$ time.

$$t_{ijk}^{abc} \approx V_{ia}^A V_{jb}^B V_{kc}^C T^{ABC} \tag{6}$$

- Followed by a CP decomposition of the V orthogonal projectors

$$V_{ia}^A \approx y_i^X y_a^X \theta^{AX} \tag{7}$$

Working Equations for Traditional CCSD(T)

- Traditional CCSD(T) Equations

$$E^{(T)} = t_{ijk}^{abc} \cdot \left(\frac{4}{3} V_{ijk}^{abc} - 2V_{ijk}^{cba} + \frac{2}{3} V_{ijk}^{cab}\right) \tag{8}$$

- Evaluation of t_{ijk}^{abc} takes $\mathcal{O}(N^7)$, and V_{ijk}^{abc} takes $\mathcal{O}(N^6)$

Working Equations for THC-CCSD(T)

$$E^{(T)} \mathrel{+}= 8 \cdot \overline{U}^{VX} \overline{D}^{VQY} \overline{B}^{QZ} t_{XYZ} \tag{9}$$

$$E^{(T)} \mathrel{+}= 4 \cdot \overline{t_1}^{X} \overline{B}^{QY} \overline{B}^{QZ} t_{XYZ} \tag{10}$$

$$E^{(T)} \mathrel{-}= 4 \cdot \widetilde{U}^{VXZ} \overline{D}^{VQY} \widetilde{B}^{QZX} t_{XYZ} \tag{11}$$

$$E^{(T)} \mathrel{-}= 4 \cdot \widetilde{U}^{VXZ} \widetilde{D}^{VQZX} \overline{B}^{QY} t_{XYZ} \tag{12}$$

$$E^{(T)} \mathrel{-}= 4 \cdot \overline{U}^{VX} \widetilde{D}^{VQXZ} \widetilde{B}^{QZX} t_{XYZ} \tag{13}$$

$$E^{(T)} \mathrel{-}= 4 \cdot \widetilde{t_1}^{XZ} \widetilde{B}^{QZX} \overline{B}^{QY} t_{XYZ} \tag{14}$$

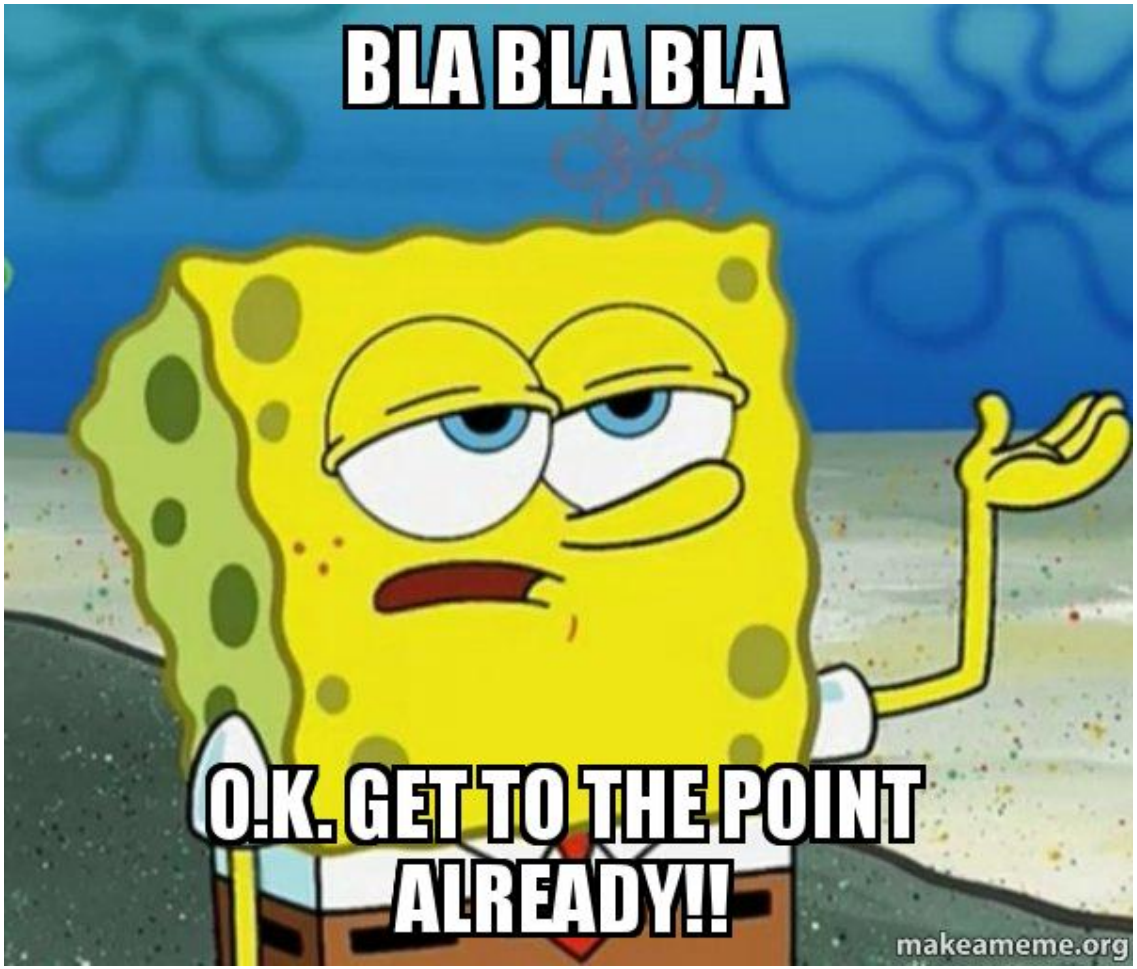
$$E^{(T)} \mathrel{-}= 2 \cdot \overline{t_1}^{Y} \widetilde{B}^{QXZ} \widetilde{B}^{QZX} t_{XYZ} \tag{15}$$

$$E^{(T)} \mathrel{+}= 2 \cdot \widetilde{U}^{VXZ} \widetilde{D}^{VQYX} \widetilde{B}^{QZY} t_{XYZ} \tag{16}$$

$$E^{(T)} \mathrel{+}= 2 \cdot \widetilde{U}^{VXZ} \widetilde{D}^{VQZY} \widetilde{B}^{QYX} t_{XYZ} \tag{17}$$

$$E^{(T)} \mathrel{+}= 2 \cdot \widetilde{t_1}^{XZ} \widetilde{B}^{QYX} \widetilde{B}^{QZY} t_{XYZ} \tag{18}$$

Working Equations for THC-CCSD(T)



Analysis and Implementation Details

- All these contributions to the (T) energy can be evaluated in $\mathcal{O}(N^5)$ time or less
- Compare this to $\mathcal{O}(N^7)$ for traditional CCSD(T) and $\mathcal{O}(N^6)$ for Lesiuk's RR-CCSD(T) [Lesiuk 2022]
- This code is implemented as a plugin of Psi4, and uses Dr. Justin Turney's EinsumsInCpp package for the tensor contractions and the CP Decomposition

Energy Convergence with Eigenvalue Tolerance

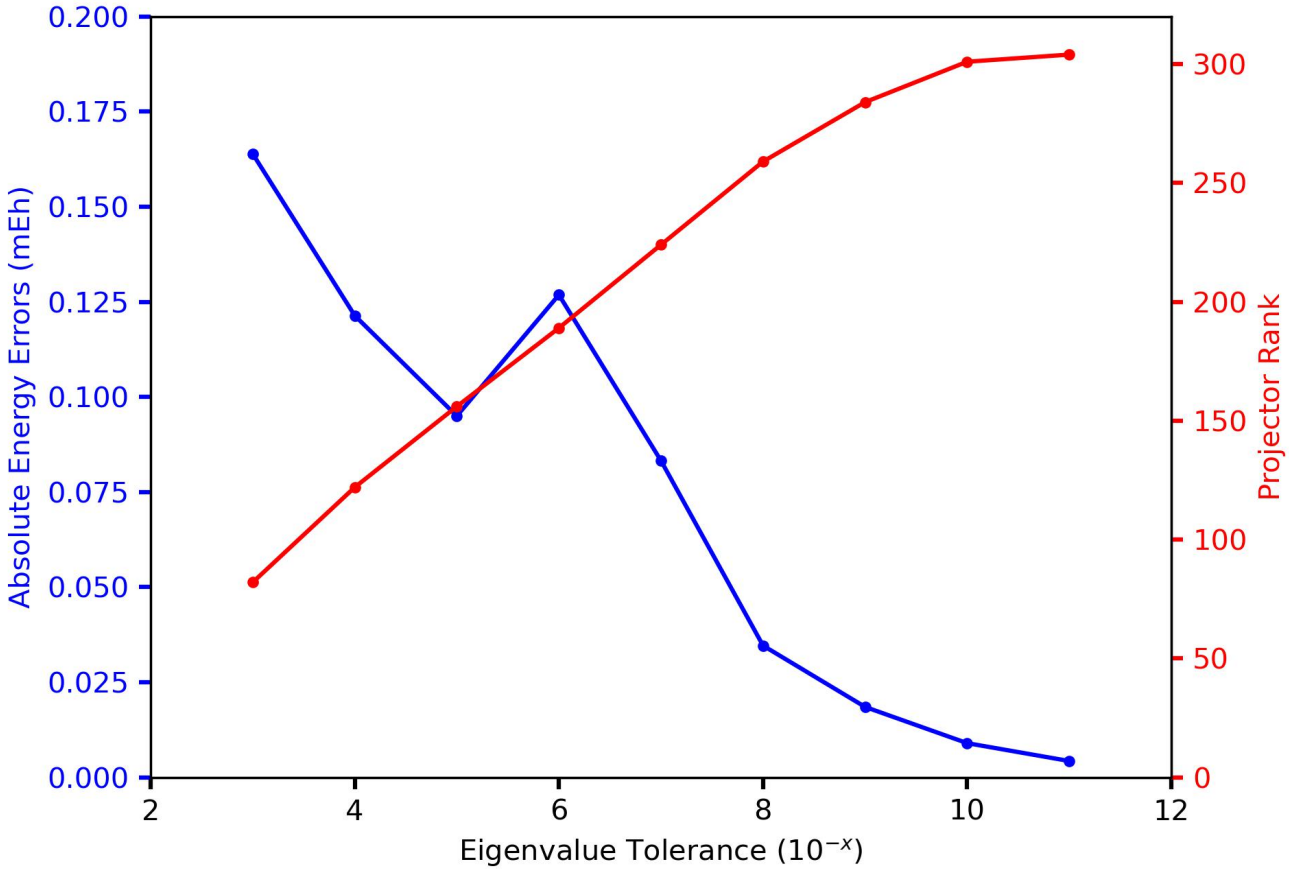


Figure: THC-CCSD(T) errors relative to eigenvalue tolerance for a water dimer, cc-pVDZ basis, projector rank describes the size of the THC auxiliary index

Conformation Energies

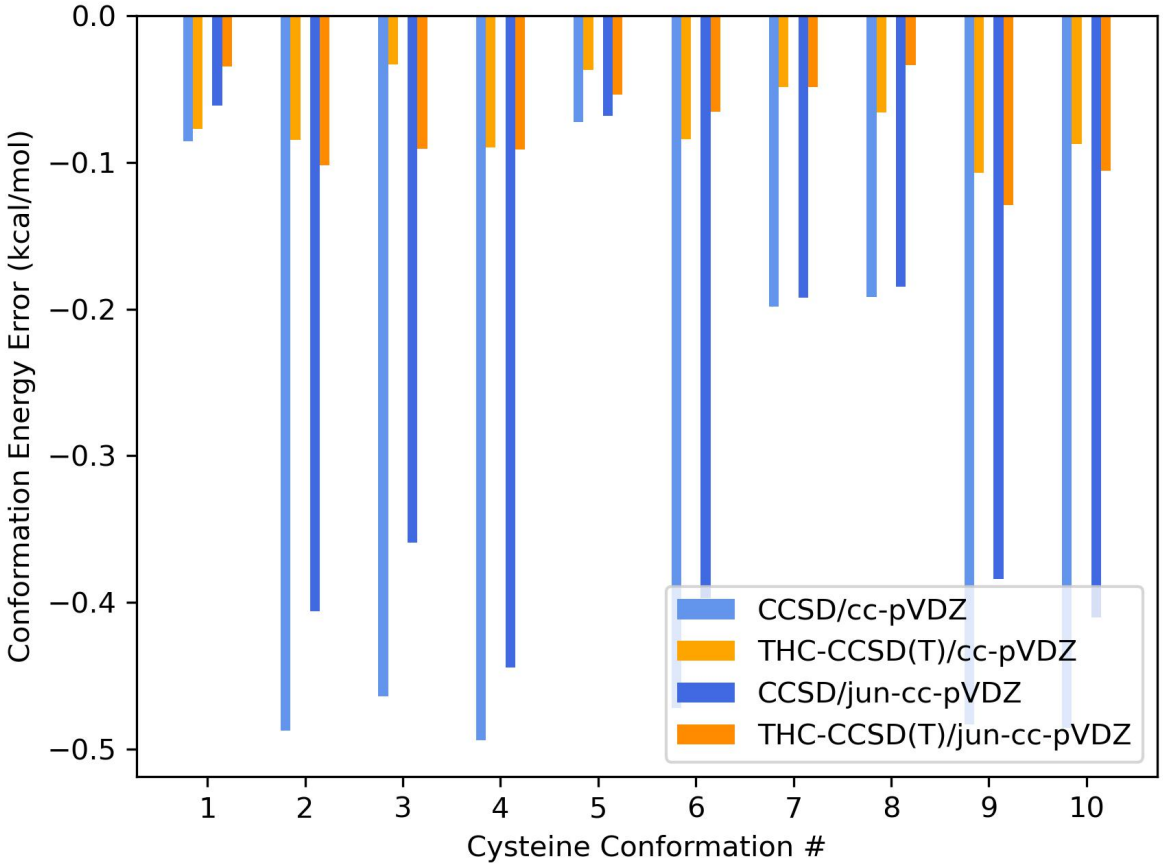


Figure: THC-CCSD(T) Errors relative to CCSD(T) for the CYCONF data set, CCSD results are included for reference, errors typically less than 0.1 kcal/mol, 10^{-4} eigenvalue tolerance

Potential Energy Surface

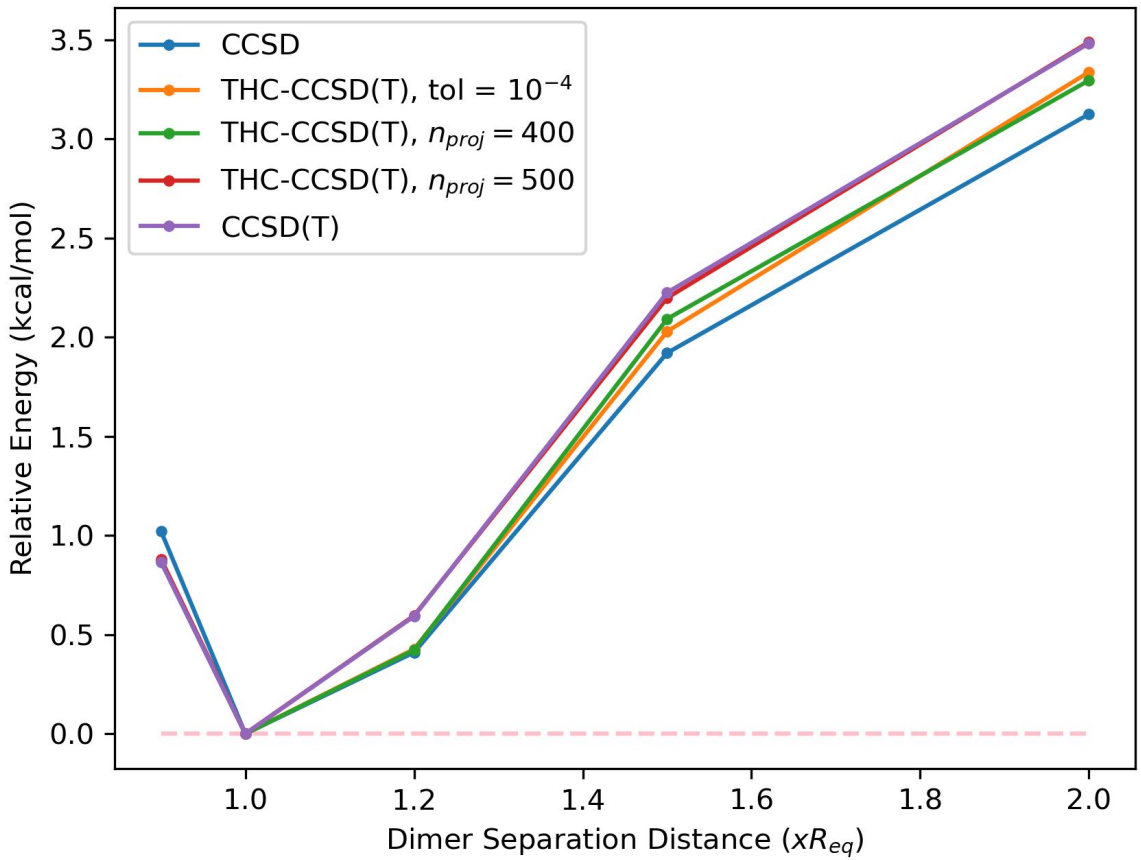


Figure: Potential energy surface of benzene-HCN dimer from S22, evaluated with CCSD(T), THC-CCSD(T), and CCSD

Potential Energy Surface (Cont.)

Method	ME	MAE	RMSE
CCSD	-0.138	0.200	0.236
THC-CCSD(T) (10^{-4})	-0.100	0.103	0.132
THC-CCSD(T) (400)	-0.098	0.098	0.128
THC-CCSD(T) (500)	-0.001	0.010	0.014

Table: Errors in potential energy surface compared to CCSD(T) reference (kcal/mol), for CCSD and THC-CCSD(T) calculations with varying parameters

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The End

Questions? Comments?