

# Low-Rank Tensor Factorizations in Coupled-Cluster Theory

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## Abstract

Coupled-cluster theory is one of the most accurate and reliable black-box electronic structure methods for the prediction of molecular properties. The primary limitation of this method is its enormous computational cost; the coupled-cluster singles and doubles (CCSD) method scales with the sixth-power of system size,  $O(N^6)$ , and the storage requirements for the wavefunction grow as  $O(N^4)$ . Here, we present approximate formulations of CC methods based on compression of the wavefunction coefficients and tensor hypercontraction (THC) approximations to the electron repulsion integrals and amplitudes.

## Coupled-Cluster Theory

Coupled-cluster (CC) theory is defined by its exponential ansatz for the wavefunction and the resulting CC Schrödinger equation.

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Phi_0\rangle$$

Typically, the CC energy and  $t$ -amplitudes are defined by a projective series of nonlinear equations.

$$\langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{CC}$$

$$\langle\Phi_{ij}^{ab\dots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0$$

In EOM-CC, excited states are obtained by introducing a linear excitation operator and solving for the eigenstates of the similarity transformed Hamiltonian.

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}\hat{R}_n|\Phi_0\rangle = E_{EOM-CC}\hat{R}_n|\Phi_0\rangle$$

$$\hat{R}_n = \frac{1}{(n!)^2} \sum_{ijab\dots} a_i^\dagger a_a^\dagger \dots a_j a_i r_{ij}^{ab\dots}$$

The CCSD and EOM-CCSD methods are defined by truncating the  $\hat{T}$  and  $\hat{R}$  operators at the level of singles and doubles.

## Tensor HyperContraction

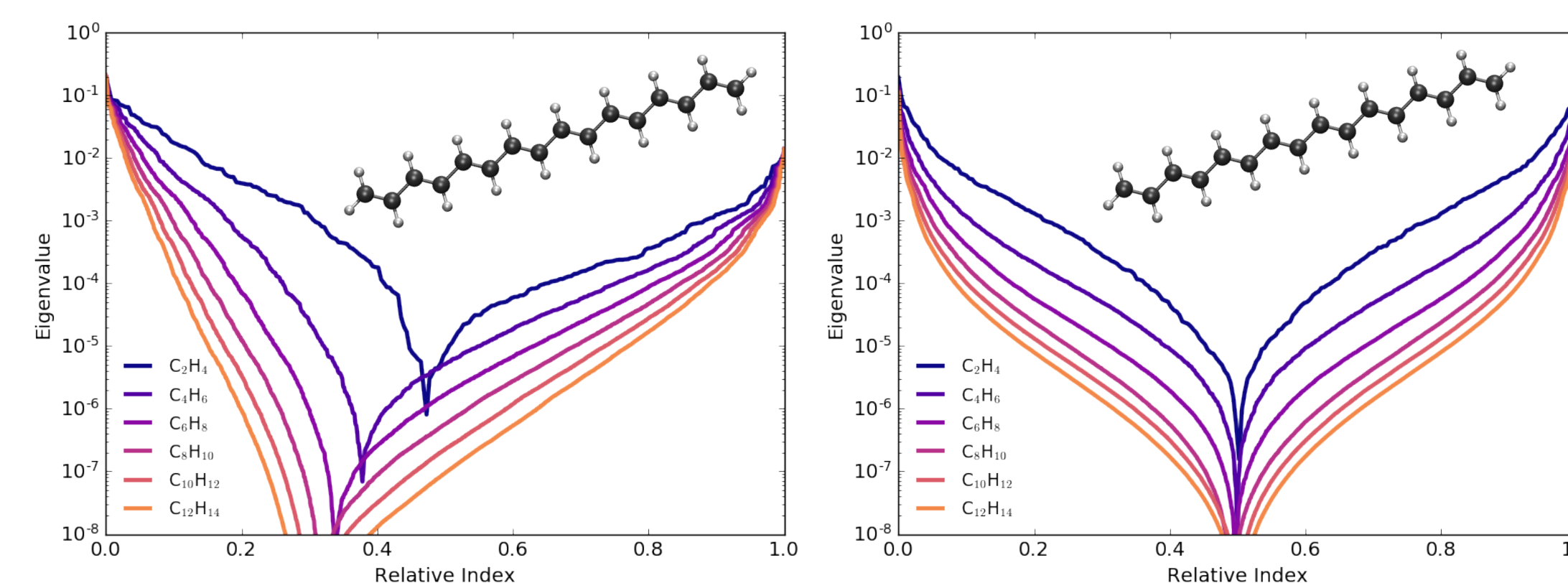
The ubiquitous electron repulsion integral tensor emits a low-rank factorization that can be exploited in many contexts in electronic structure theory. The density fitting approximation,

$$(pq|rs) \approx \sum_{AB} (pq|A)[J^{-1}]_{AB}(B|rs)$$

is a common strategies for building such a low-rank representation. However, these approaches leave the indices in the bra and ket "pinned," which limits the available algebraic flexibility. The Tensor HyperContraction factorization, however, exposes all available flexibility and represents the ideal factorization of such a fourth-order tensor.

$$(pq|rs) \approx \sum_{PQ} X_p^P X_q^P Z^{PQ} X_r^Q X_s^Q$$

## Motivation



**Fig. 1** The absolute value of the eigenvalues of the  $t$ -amplitudes (left) of CCSD and  $r$ -amplitudes (right) is plotted against the relative index of the eigenvalue: the most positive eigenvalue has an index of 0 and the most negative eigenvalue has an index of 1. Computations were performed for a series of linear alkenes using a cc-pVDZ basis set.

## Rank-Reduced Coupled-Cluster

Motivated by the rank sparsity of the doubles amplitudes in CC (seen in Fig. 1), we assert a low-rank decomposition of the doubles amplitudes and develop a reformulation of the CC theory to operate directly in terms of these compressed quantities.

$$t_{ij}^{ab} = \sum_{PQ} U_{ia}^P T^{PQ} U_{jb}^Q \quad r_{ij}^{ab} = \sum_{PQ} U_{ia}^P R^{PQ} U_{jb}^Q$$

To that end, we introduce the linear de-excitation operators that appear in the  $\Lambda$ -equations commonly used to define CC gradients and properties and treat the  $\lambda$ -amplitudes as low-rank quantities.

$$\hat{\Lambda} = \sum_{ia} a_i^\dagger a_a \lambda_a^i + \frac{1}{4} \sum_{ijab} a_i^\dagger a_j^\dagger a_b a_a \lambda_{ij}^{ab}$$

$$\lambda_{ab\dots}^{ij\dots} = \sum_{PQ} U_{ia}^P \Lambda^{PQ} U_{jb}^Q$$

We now may define the RR-CC wavefunction from the perspective of the CC energy functional.

$$E_{CC} = \langle\Phi_0|(1 + \hat{\Lambda})e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle$$

The RR-CC doubles amplitude equations are generated by setting the partial derivative of the CC energy functional with respect to  $\Lambda^{PQ}$  to zero.

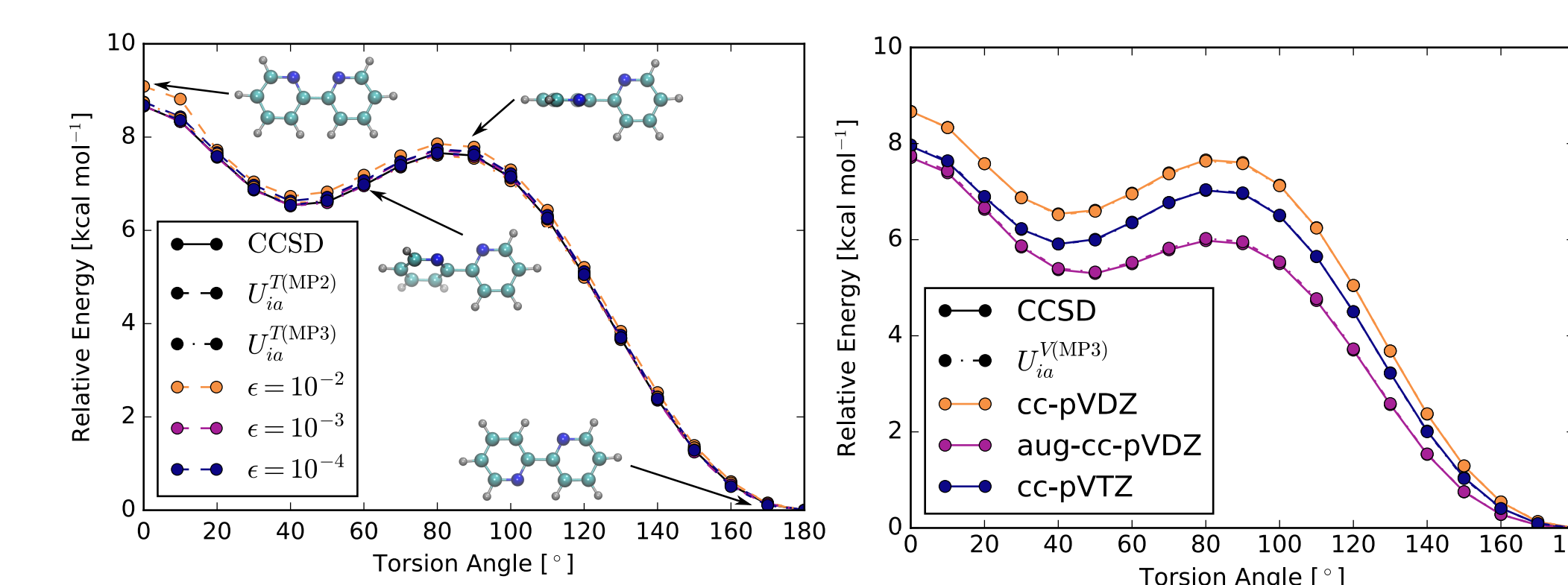
$$\frac{\partial}{\partial \Lambda^{PQ}} \langle\Phi_0|(1 + \hat{\Lambda})e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0$$

Generalization of this procedure to EOM-CCSD is straightforward. The question that remains is how to best choose the  $U_{ia}^P$  quantities. We consider the eigendecomposition of more approximate doubles amplitudes such as those obtained from MP2 or MP3.

Projectors for RR-EOM-CCSD must be state specific. Here, we use a form of the doubles amplitudes reminiscent of CIS(D).

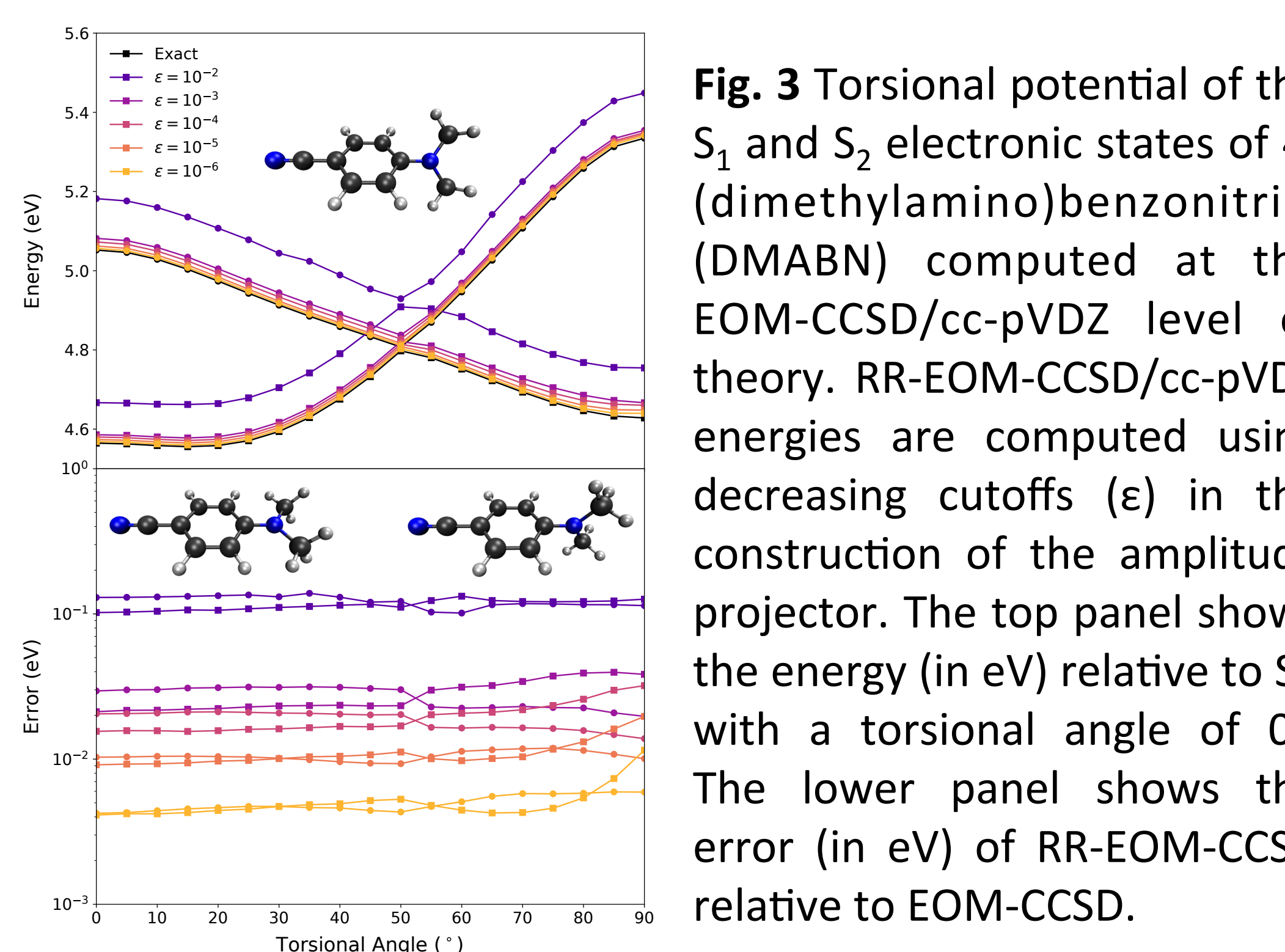
$$r_{ij}^{ab} = \langle\Phi_{ij}^{ab}|[\hat{H}, \hat{R}_1]|\Phi_0\rangle / (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j - \omega)$$

## Results: Rank-Reduced CCSD



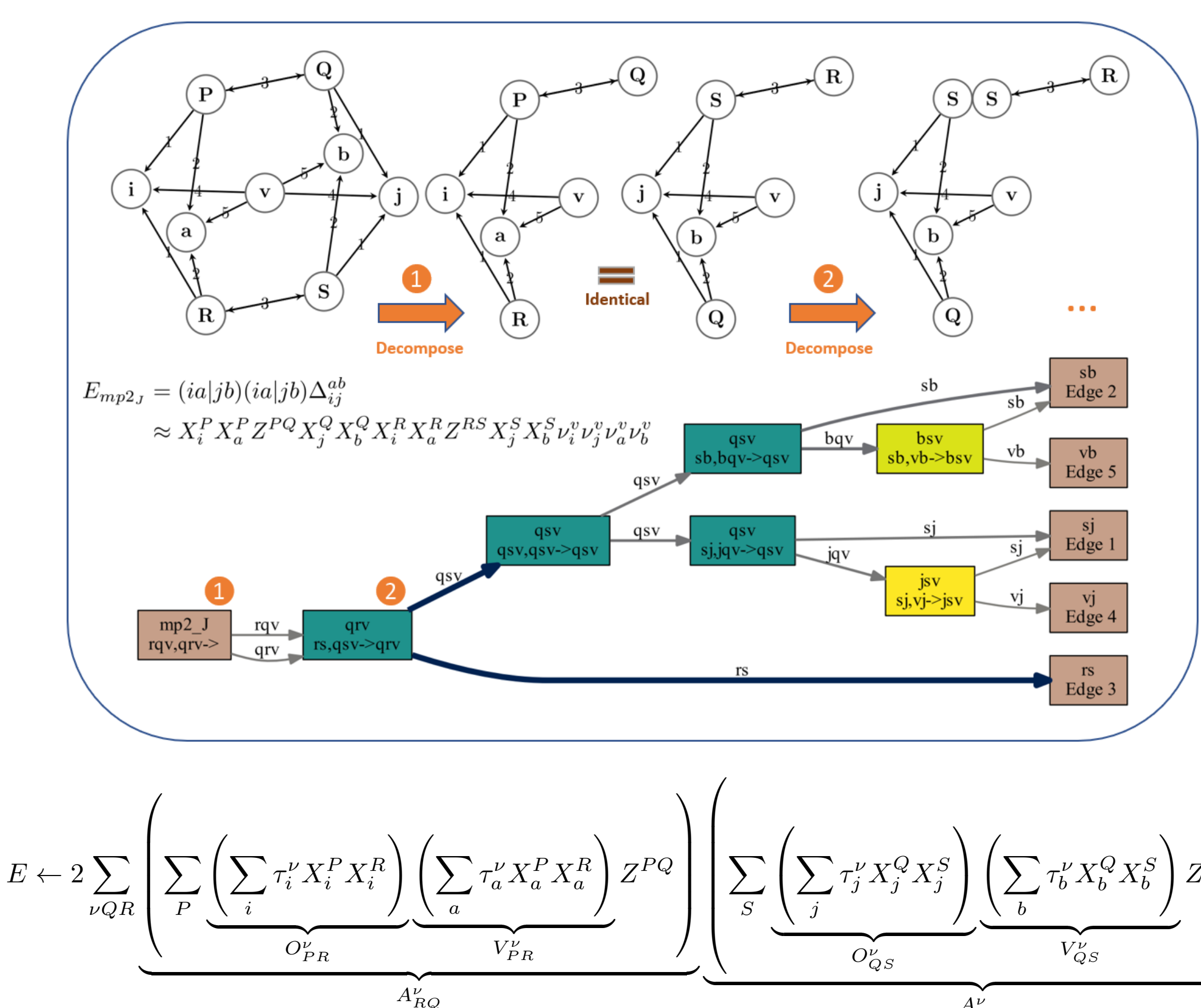
**Fig. 2** Accuracy of RR-CCSD for the torsional potential of bipyridine using various projectors in a cc-pVDZ basis (left). RR-CCSD using an MP3 projector with an eigenvalue cutoff of  $10^{-3}$ .

## Results: Rank-Reduced EOM-CCSD

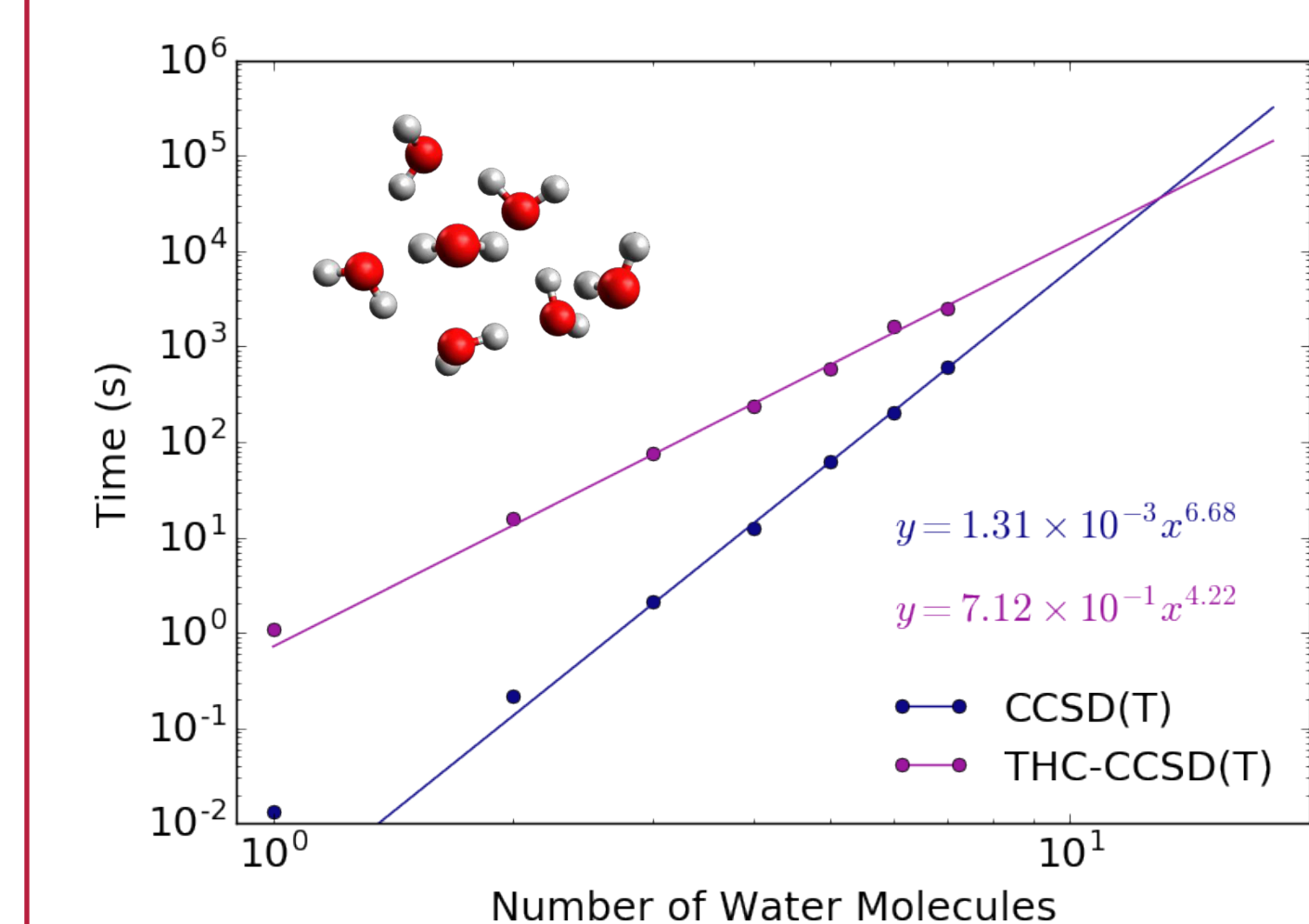


**Fig. 3** Torsional potential of the  $S_1$  and  $S_2$  electronic states of 4-(dimethylamino)benzonitrile (DMABN) computed at the EOM-CCSD/cc-pVDZ level of theory. RR-EOM-CCSD/cc-pVDZ energies are computed using decreasing cutoffs ( $\epsilon$ ) in the construction of the amplitude projector. The top panel shows the energy (in eV) relative to  $S_0$  with a torsional angle of  $0^\circ$ . The lower panel shows the error (in eV) of RR-EOM-CCSD relative to EOM-CCSD.

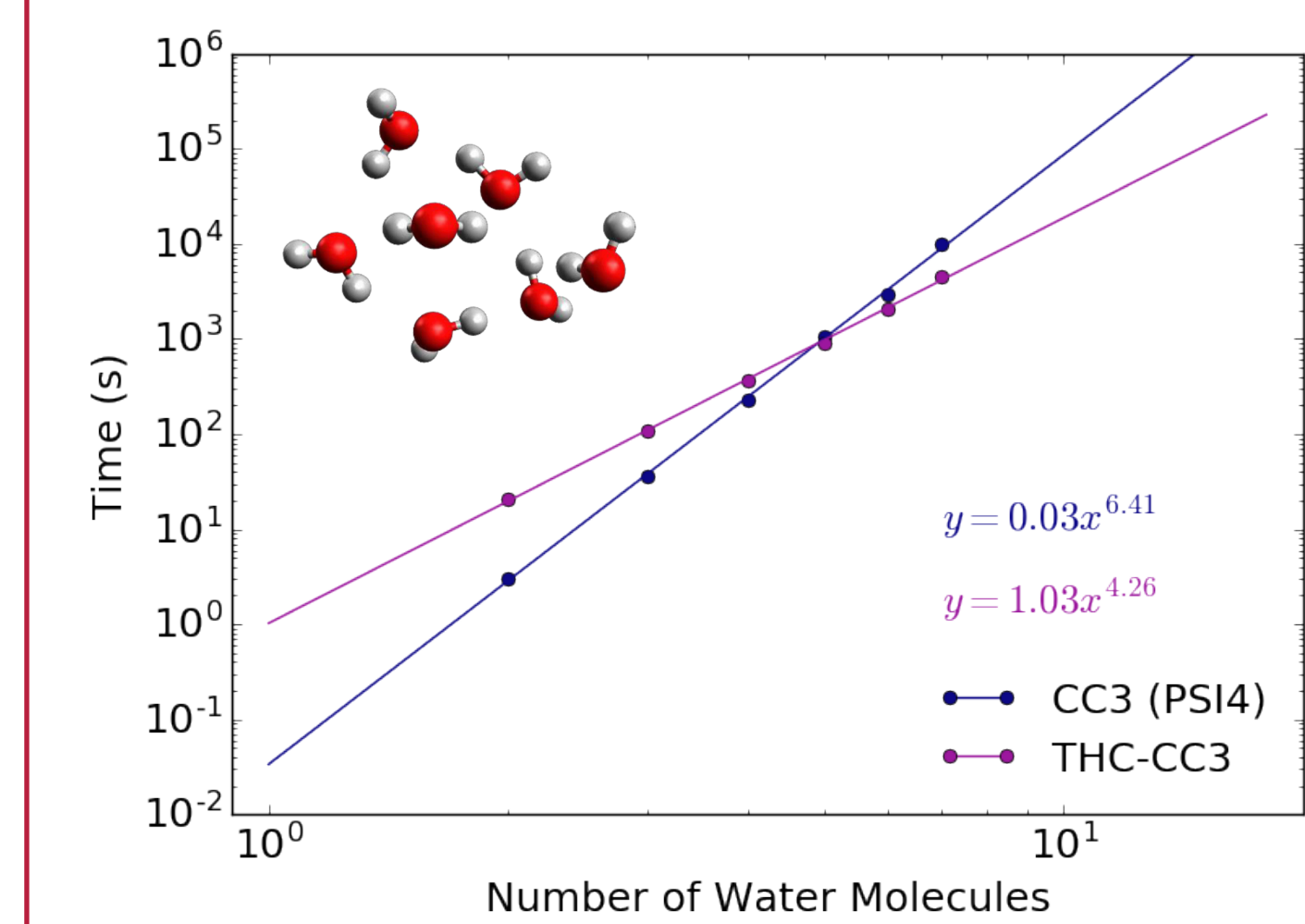
## Automatic Code Generation



## Factorized Triples Corrections with THC



**Fig. 4** Timing of the CCSD(T)/cc-pVDZ perturbative triples correction with and without the application of THC approximations to clusters of water molecules. Crossover is estimated for systems with containing more than 13 water molecules.



**Fig. 5** Timing of one iteration of CC3/cc-pVDZ with and without the application of THC approximations. Timings for CC3 use the implementation in the PSI4 package.

## Conclusions and Future Directions

We have demonstrated that our rank-reduced reformulation of CCSD and EOM-CCSD allows chemical accuracy in the correlation energy and excitation energy to be achieved with a compressed representation of the wavefunction. What remains is to fully realize the potential improvements in efficiency that result from combining these ideas with tensor hypercontraction (THC) representations of the electron repulsion integrals and low-rank projectors. The compressed representation of wavefunctions and operators makes these approaches amenable to high performance distributed memory implementations.

**Fig. 6** Timings of a fully factorized implementation of rank-reduced linearized coupled-cluster doubles (RR-LCCD) for a series of water clusters in a cc-pVDZ basis set. Note that the method shows lower than  $O(N^5)$  scaling.

