

Abstract

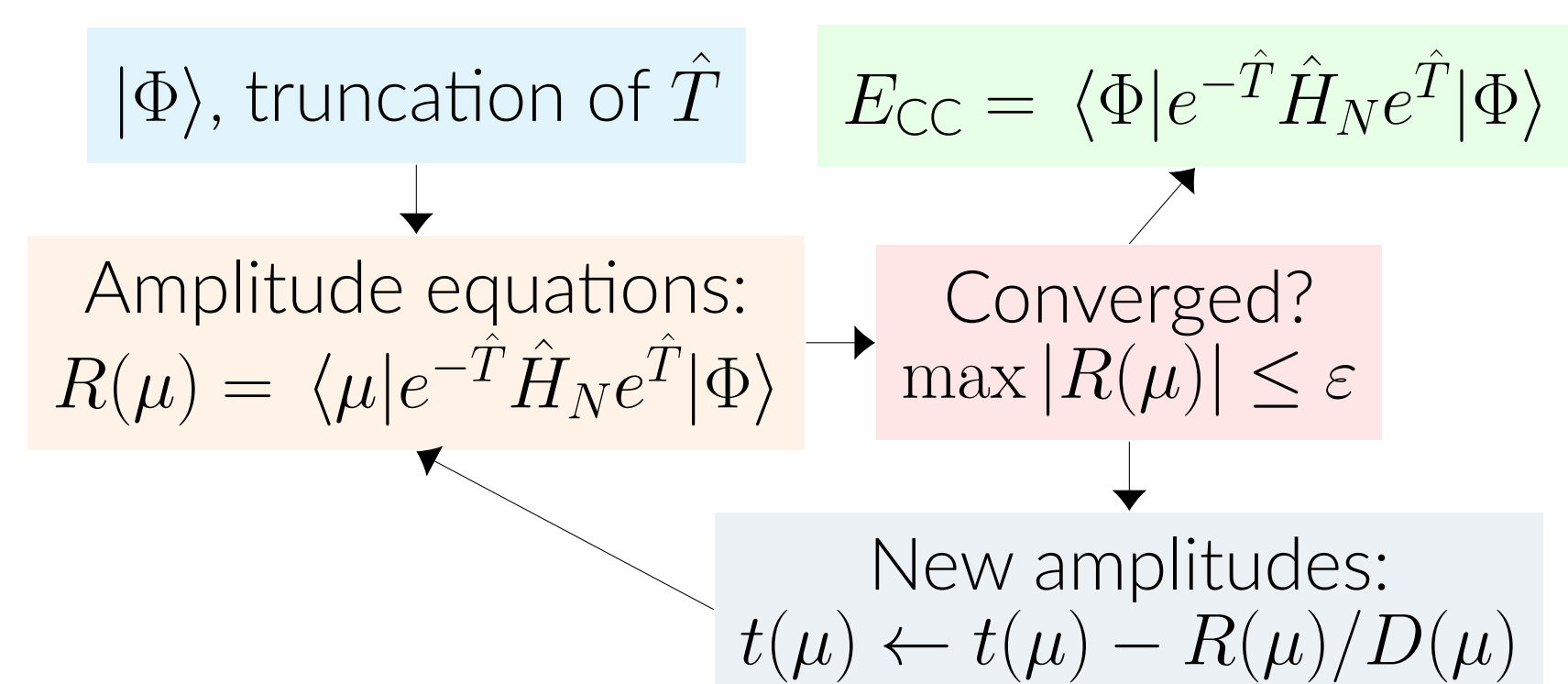
Excited states can be studied using a variety of methods, each with its own advantages and drawbacks. Coupled-cluster (CC) theory is one such approach that provides accurate results at high order, overcoming the lack of size extensivity of configuration-interaction (CI) methods. The usual way of targeting excited states via the equation-of-motion (EOM) or linear-response (LR) formalism has proven its effectiveness.[1] However, high-order CC methods come with a high computational cost that limits the system size that can be studied. Additionally, lower-order CC methods may encounter difficulties in certain cases. Furthermore, EOM-CC and LR-CC methods compute excited states based on the results of the ground-state calculation, which introduces a bias toward the latter. To address these challenges, we explore state-specific CC approaches to study excited states. Specifically, we rely on CCSD and two-determinant CCSD (TD-CCSD) that we have implemented in the open-source software **QUANTUM PACKAGE**, which is freely accessible on github at <https://quantumpackage.github.io/qp2>.

Single-reference coupled cluster

Single-reference CC methods rely on an exponential ansatz of the wave function

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Phi\rangle \quad (1)$$

with $|\Phi\rangle$ a reference Slater determinant, often chosen as the Hartree-Fock determinant, and \hat{T} an excitation operator.



Targeting excited states

For excited states, the usual EOM-CC approach builds $\bar{H} = e^{-\hat{T}} \hat{H}_N e^{\hat{T}}$ and diagonalizes it in a CI basis. A different approach consists of using a non-Aufbau determinant as a reference to directly target a given excited state.

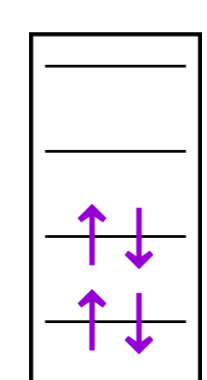
Pros

- state-specific orbitals
- access to higher-lying excited states
- access to doubly-excited states at CCSD level

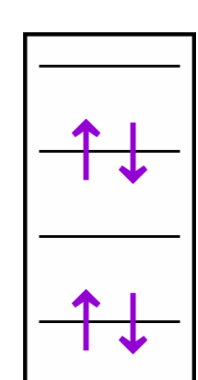
Cons

- for "single-reference" states only
- can be hard to converge
- difficult to aim/end up on the right state

Double excitations



(a) Closed-shell ground state



(b) Closed-shell doubly-excited state

While EOM-CCSD is not adequate for doubly-excited states, Δ CCSD can circumvent this problem by performing state-specific calculations.[2, 3]

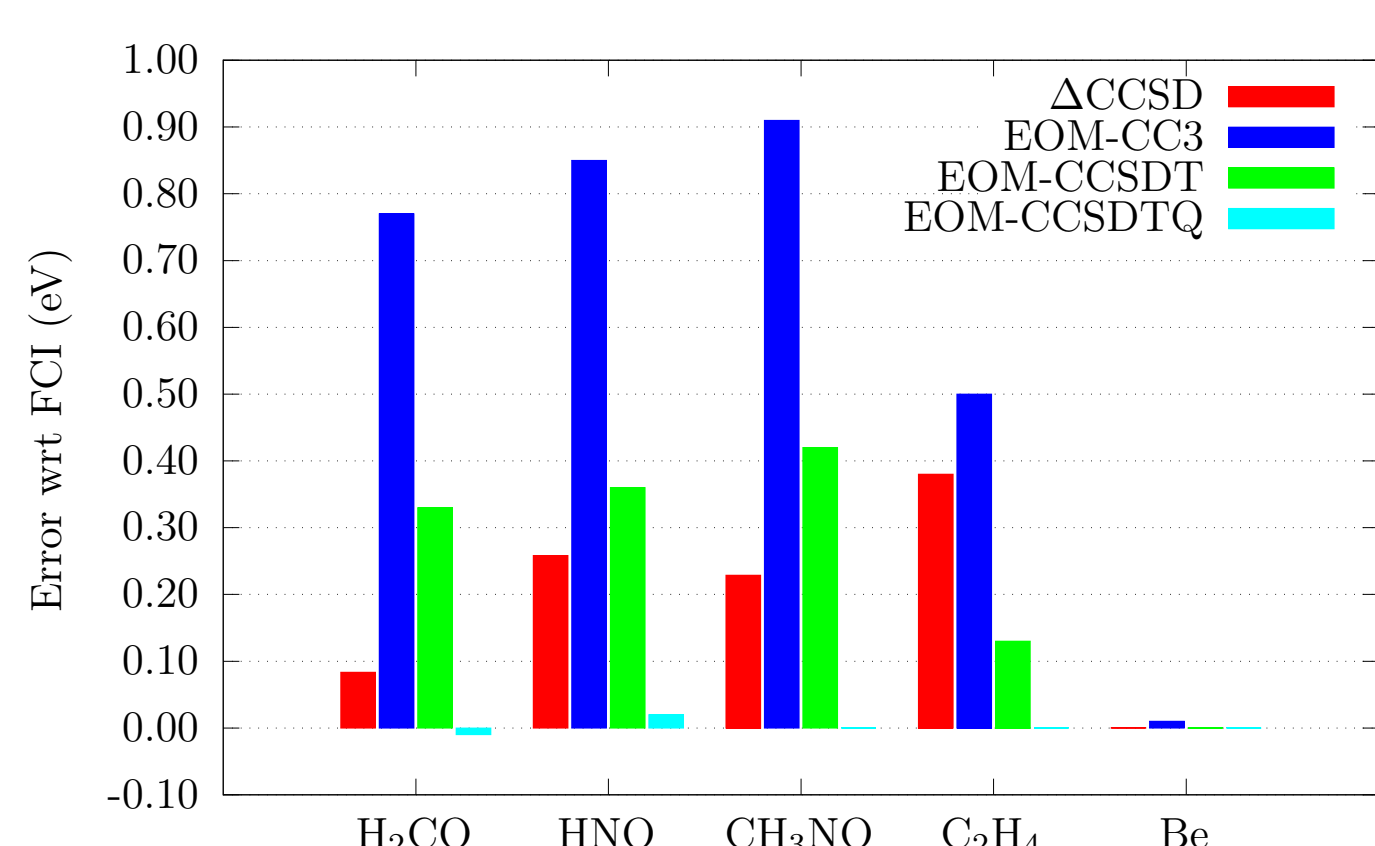
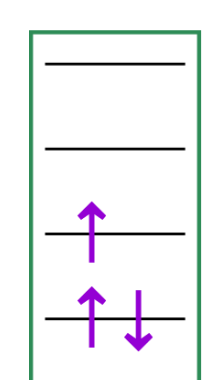
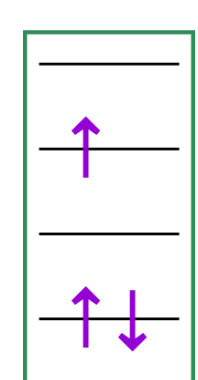


Figure 2. Error in excitation energy for double excitations (aug-cc-pVDZ).

Doublet-doublet transitions



(a) Doublet ground state



(b) Doublet excited state

The same strategy can be applied to doublet-doublet transitions as both ground and excited states are single references.

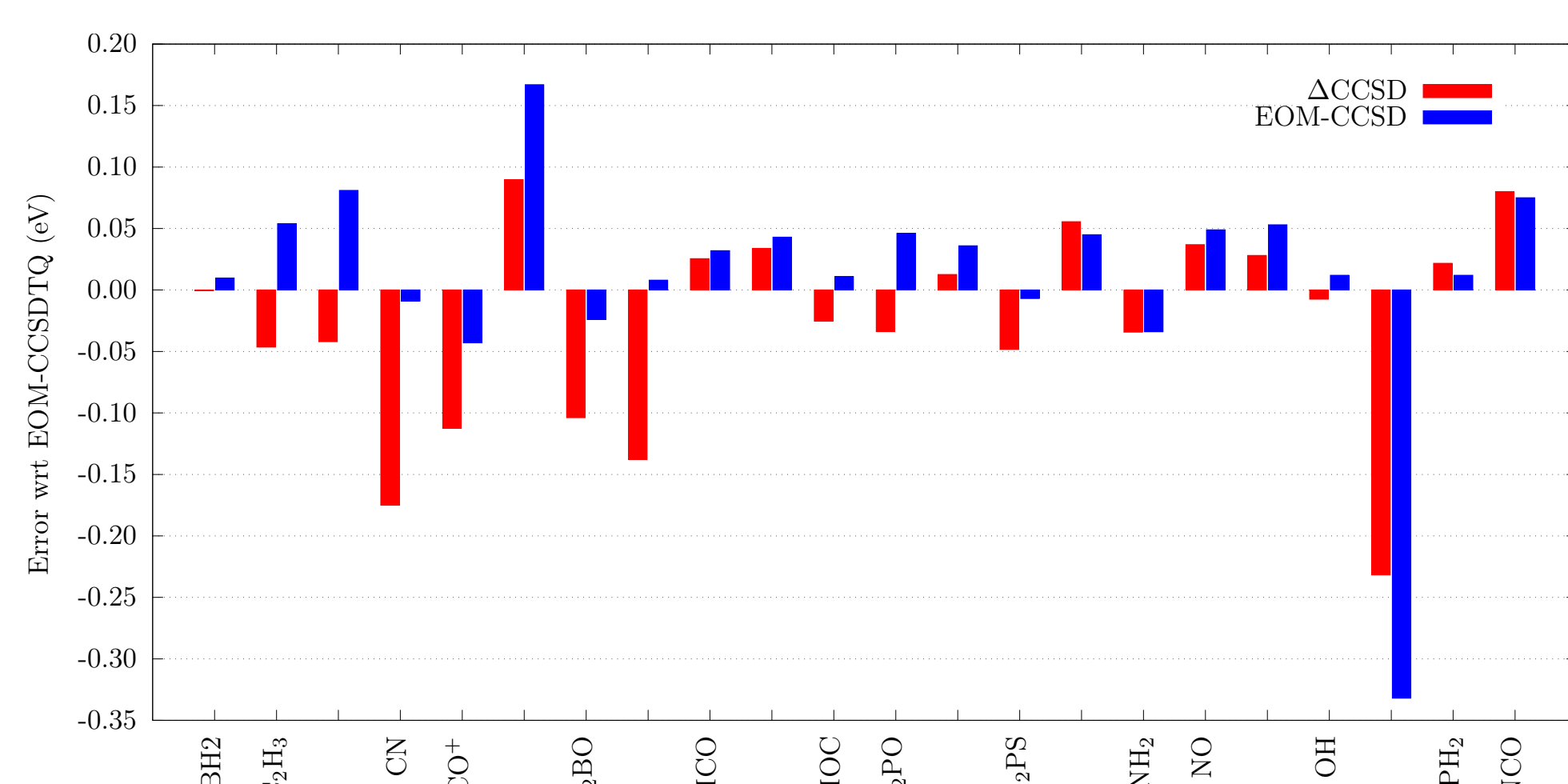


Figure 4. Error in excitation energy for doublet-doublet transitions computed at the Δ CCSD and EOM-CCSD levels (aug-cc-pVDZ) using ground-state ROHF orbitals.

Multi-reference coupled cluster

Multi-reference coupled cluster (MRCC) seeks to find a wave operator $\hat{\Omega}$ such that

$$|\Psi\rangle = \hat{\Omega} |\Psi_0\rangle \quad (2)$$

with $|\Psi_0\rangle = \sum_I c_I |\Phi_I\rangle$. The simplest MRCC scheme is TD-CC that considers an incomplete active space with two open-shell determinants. [4, 5, 6]

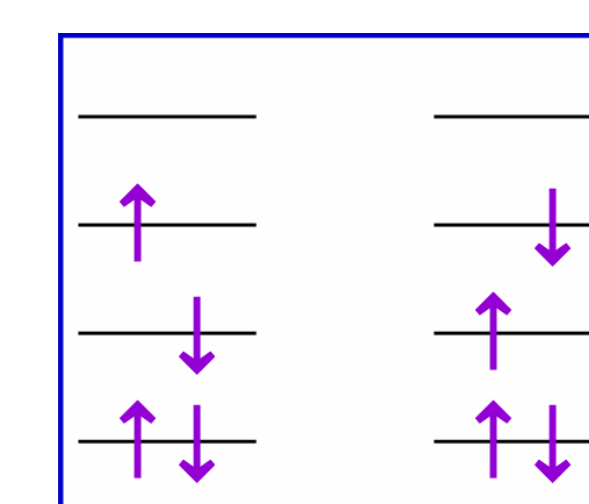


Figure 5. Determinants in TD-CC model wave function, $|\Psi_0\rangle = \frac{1}{\sqrt{2}} (|\Phi_A\rangle \pm |\Phi_B\rangle)$

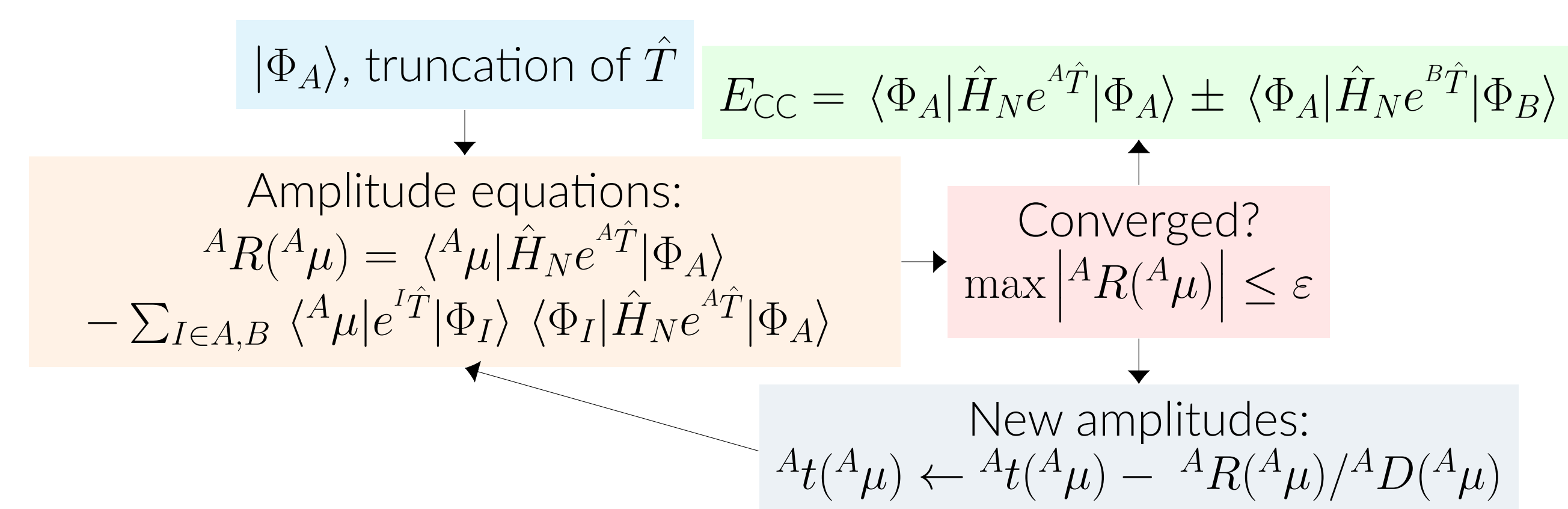
In this case, one can use the wave operator proposed by Jeziorski and Monkhorst

$$\hat{\Omega} = \sum_I e^{I\hat{T}} |\Phi_I\rangle \langle \Phi_I| \quad (3)$$

with reference-dependent amplitudes $I\hat{T}$. [7] The resulting wave functions have the form

$$|\Psi\rangle = \frac{1}{\sqrt{2}} (e^{A\hat{T}} |\Phi_A\rangle \pm e^{B\hat{T}} |\Phi_B\rangle) \quad (4)$$

and can be used to describe the singlet and triplet states. Note that $|\Phi_B\rangle = \text{spin-flip}(|\Phi_A\rangle) \Rightarrow B\hat{T} = \text{spin-flip}(A\hat{T})$.



Singly-excited states

Thence, TD-CC can be used to compute transitions between ground and singly-excited states (singlets or triplets).[8]

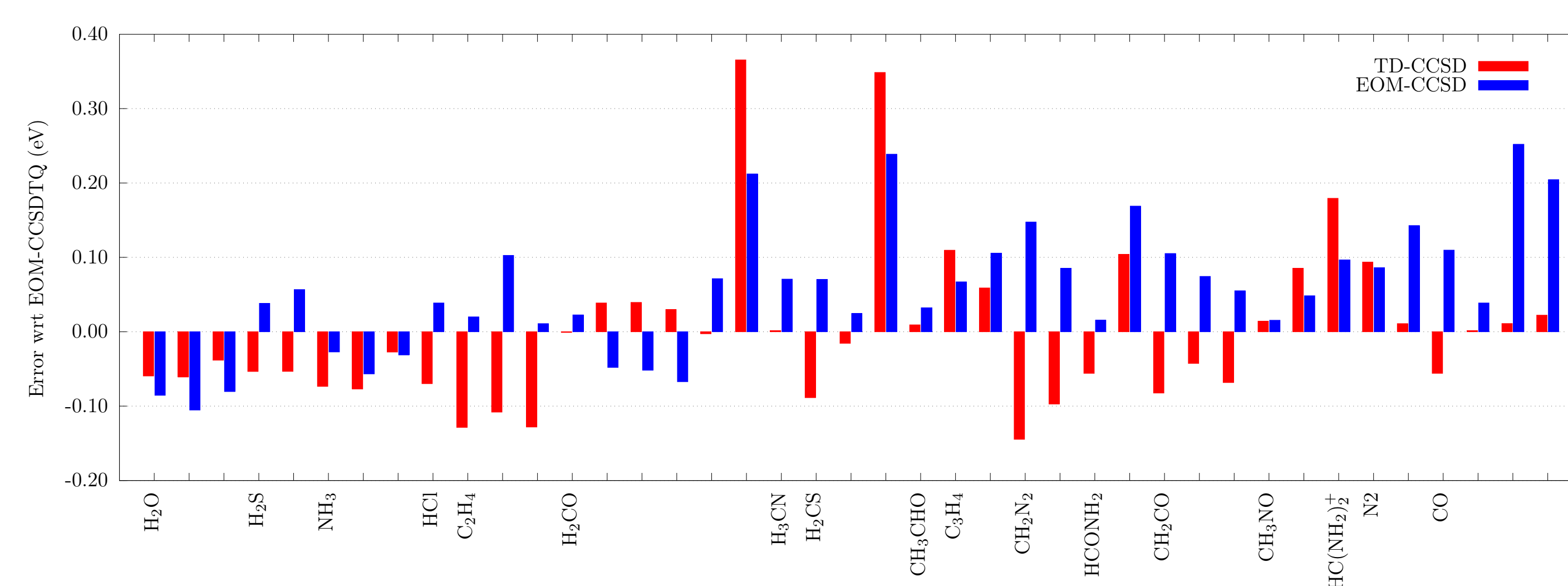


Figure 6. Error in excitation energy for singlet-singlet transitions computed at the TD-CCSD and EOM-CCSD levels (aug-cc-pVDZ) using ground-state RHF orbitals.

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References

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