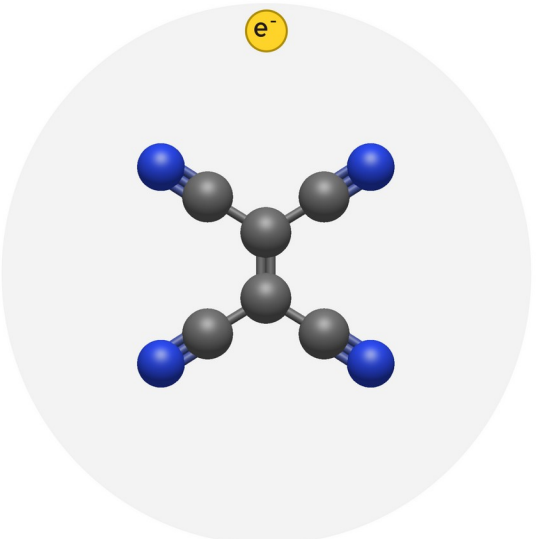
Towards treating the non-valence correlation-bound anion of TCNE with Quantum Monte Carlo



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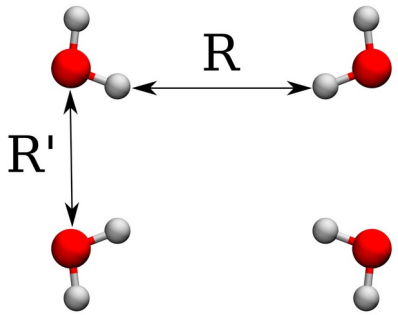
Motivation



Previous work:
- QMC methods can recover from poor trial wavefuncions
- rSDCI offers a balance between accuracy and computational cost

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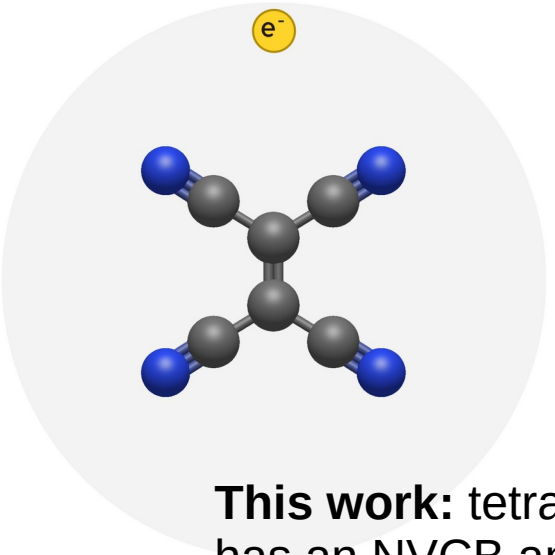
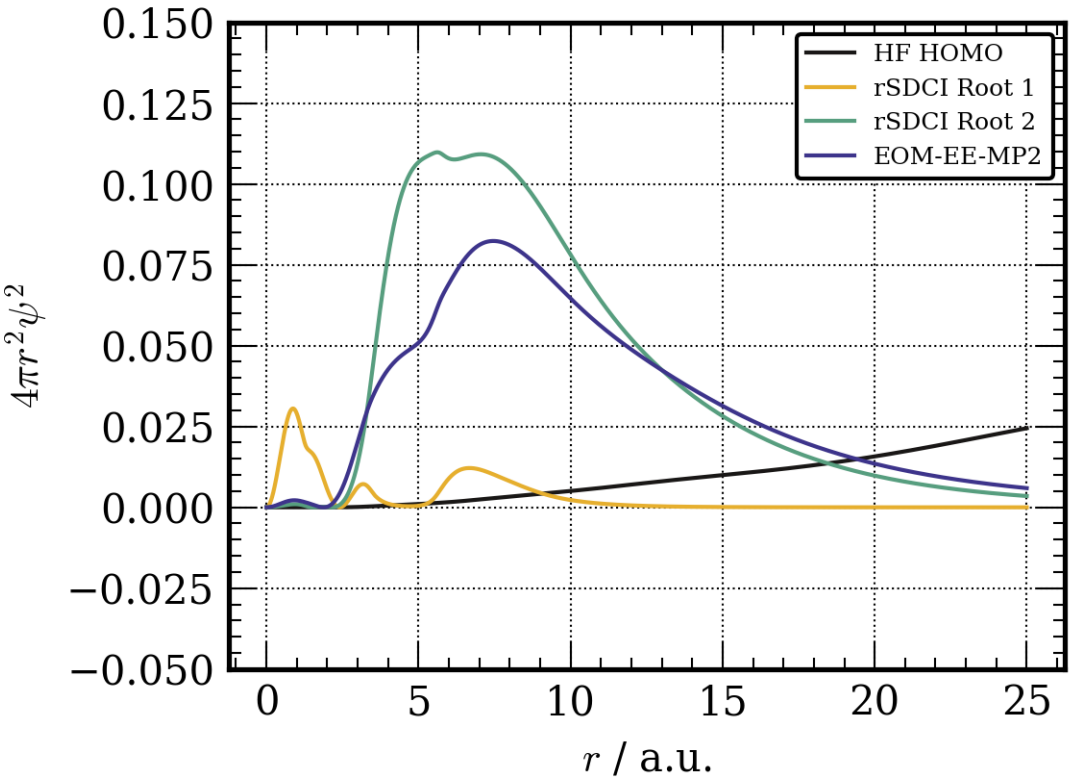
Method (basis: aug-cc-pVTZ+3s1p)	EBE (Ha)
HF	-0.4
EOM-CCSDT(est)	197.5
DMC (HF)	183 +/- 10
AFQMC (rSDCI)	194 +/- 10

$$E_{corr} = E_{true} - E_{Hartree\text{-}Fock}$$



This work: tetracyanoethylene has an NVCB anion but has an additional challenge of low lying valence states.
DOI: 10.1063/1.4991497

Current Findings



Method Basis: aug-cc pvtz+4s2p	EBE (Ha)
HF	-211.4
AFQMC (rSDCI) Root 1	-1034.0
AFQMC (rSDCI) Root 2	3.8
EOM-EE-MP2	89.8

Finding: rSDCI stabalizes a low lying valence state, thus is **not** a suitable trial wave function
Possible solution: EOM-EE-MP2 locates correct state with correct diffuse shape

Conclusion

- rSDCI wave function for this system runs into trouble due to valence states of the same symmetry, making this an even more interesting case.
- Trial wave function based on EOM-EE-MP2 results may offer alternative with more realistic charge distribution of correct state.

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Avogadro2, matplotlib