Benchmarking VQE
for quantum chemistry

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Outline

- Goals:
  - Assess the accuracy of unitary CCSD based VQE for typical chemical systems: whether there is any advantage compared against classical CCSD?

- Datasets:
  - Diatomic molecules:
    - Single bond dissociation: H2, HF, F2
    - Triple bond dissocaition: N2
    - Open-shell molecule: O2
  - Chemical reactions:
    - Isomerization of HCN <-> HNC
    - Isomerization of H2CO
    - Ethylene rotation (E<->Z)

Diatomic molecules: single bond breaking for H_2
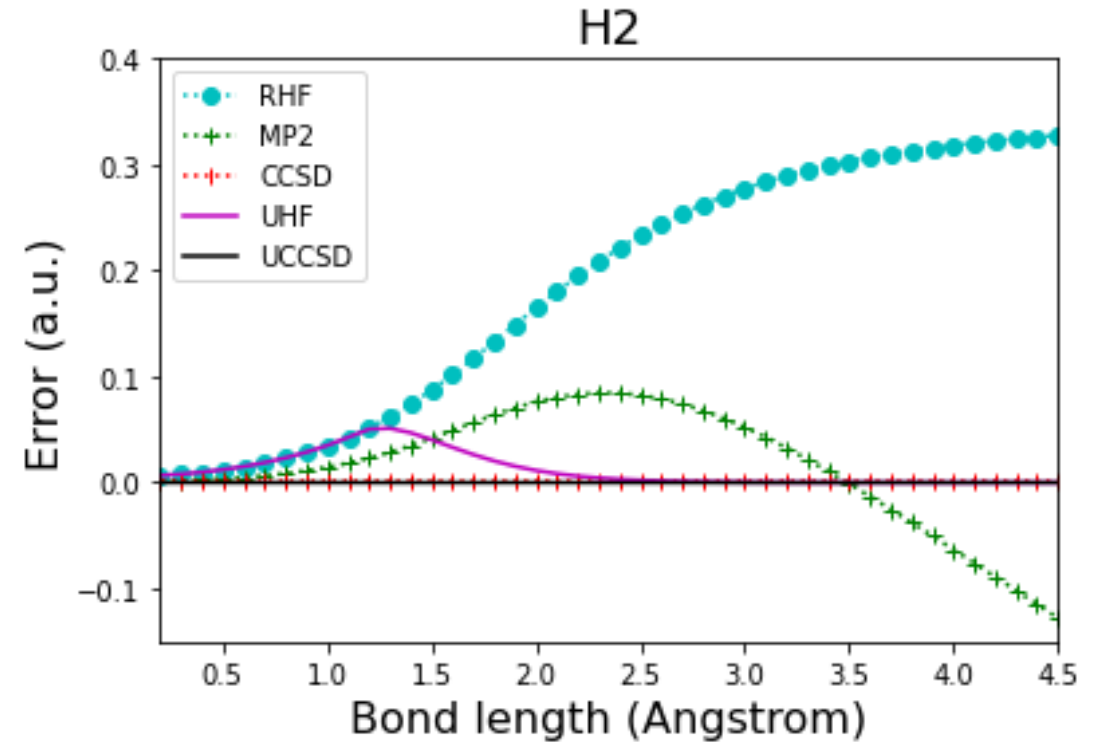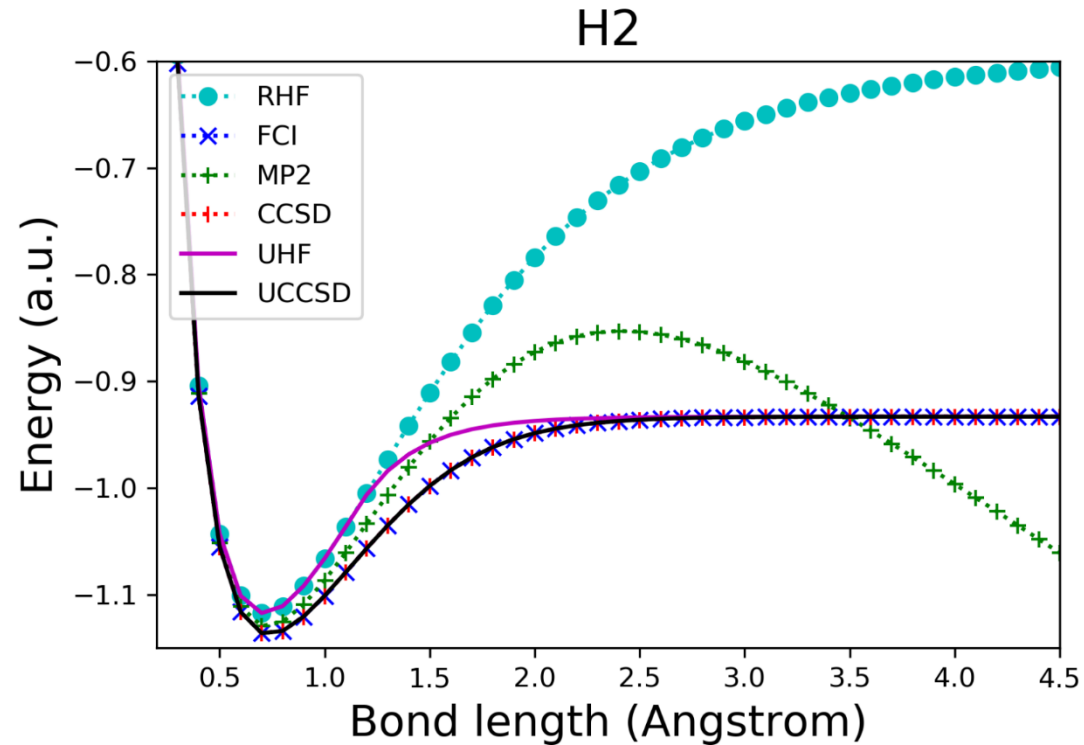
Right: The dissociation curve of H_2 with STO-3G by PySCF.
Left: Energy difference between RHF/MP2/CCSD/UHF/UCCSD and FCI.

Diatomic molecules: single bond breaking for HF
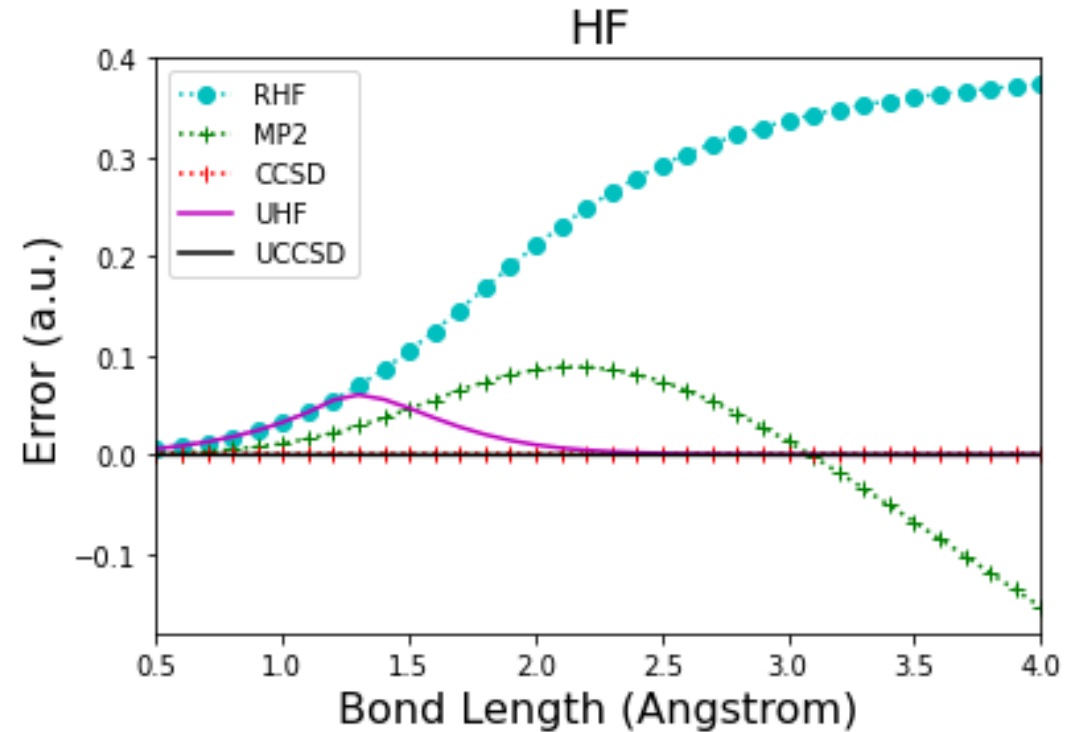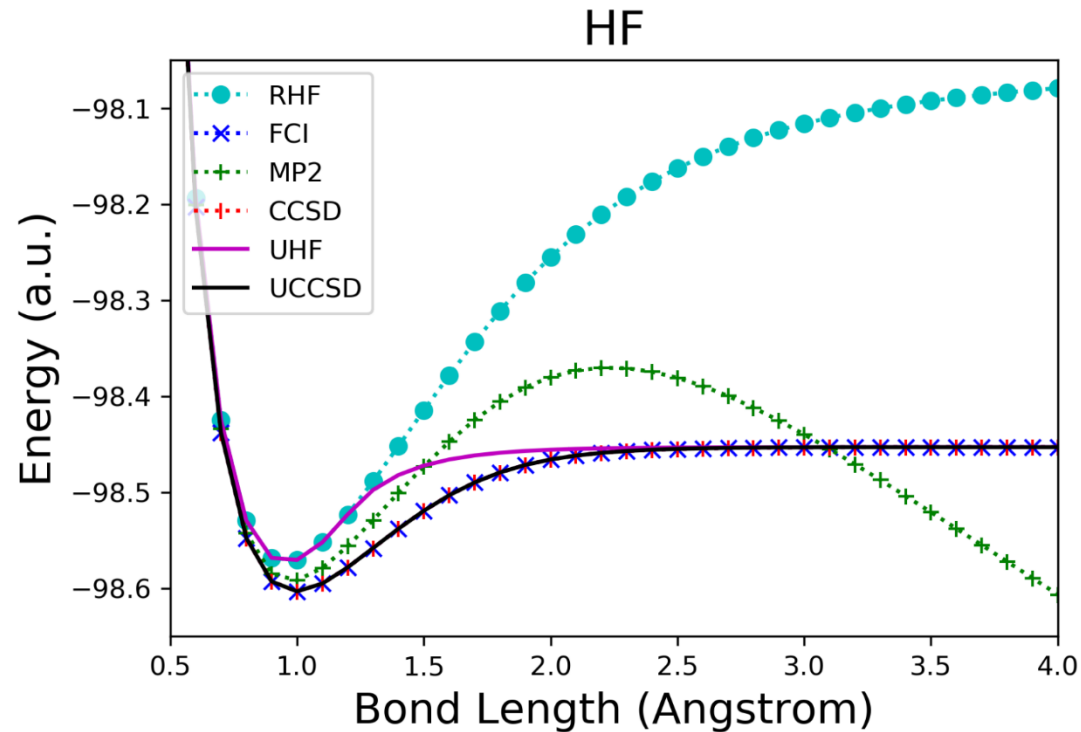
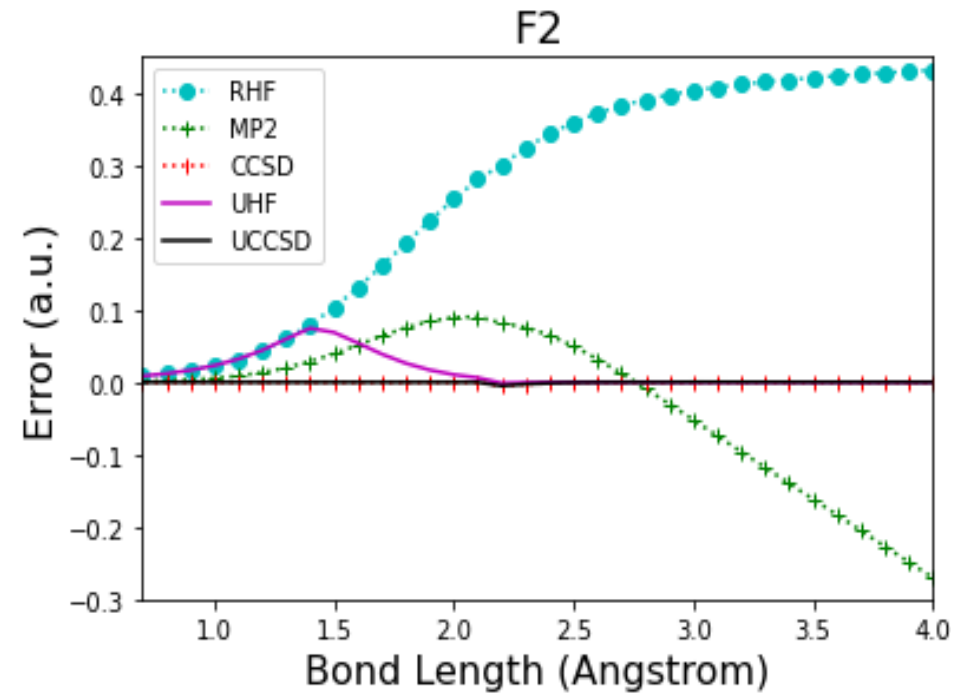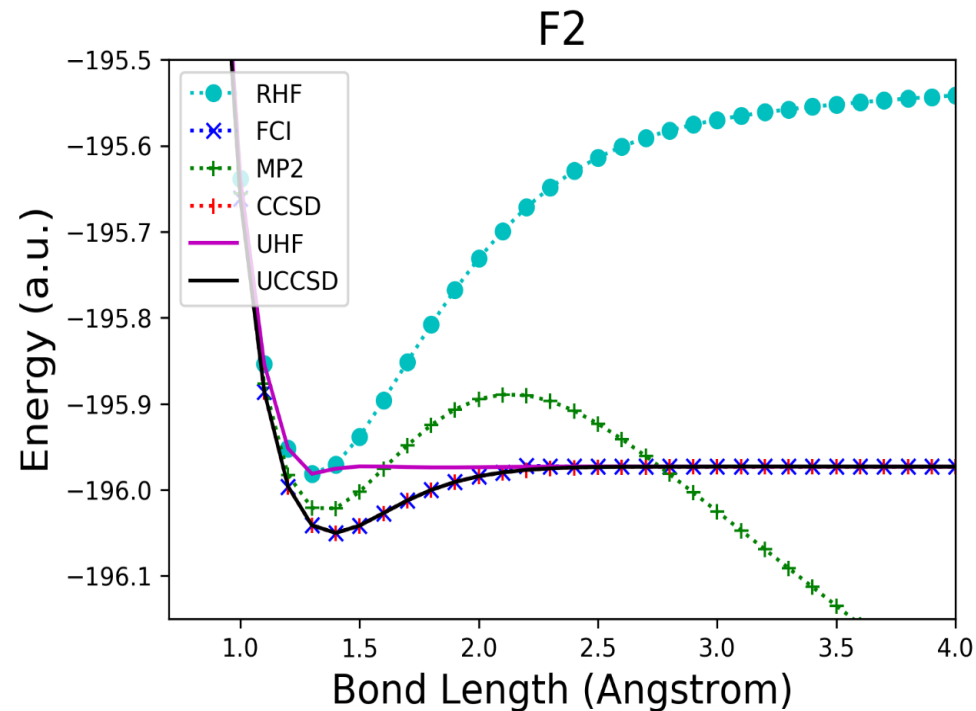

Right: The dissociation curve of HF with STO-3G by PySCF.
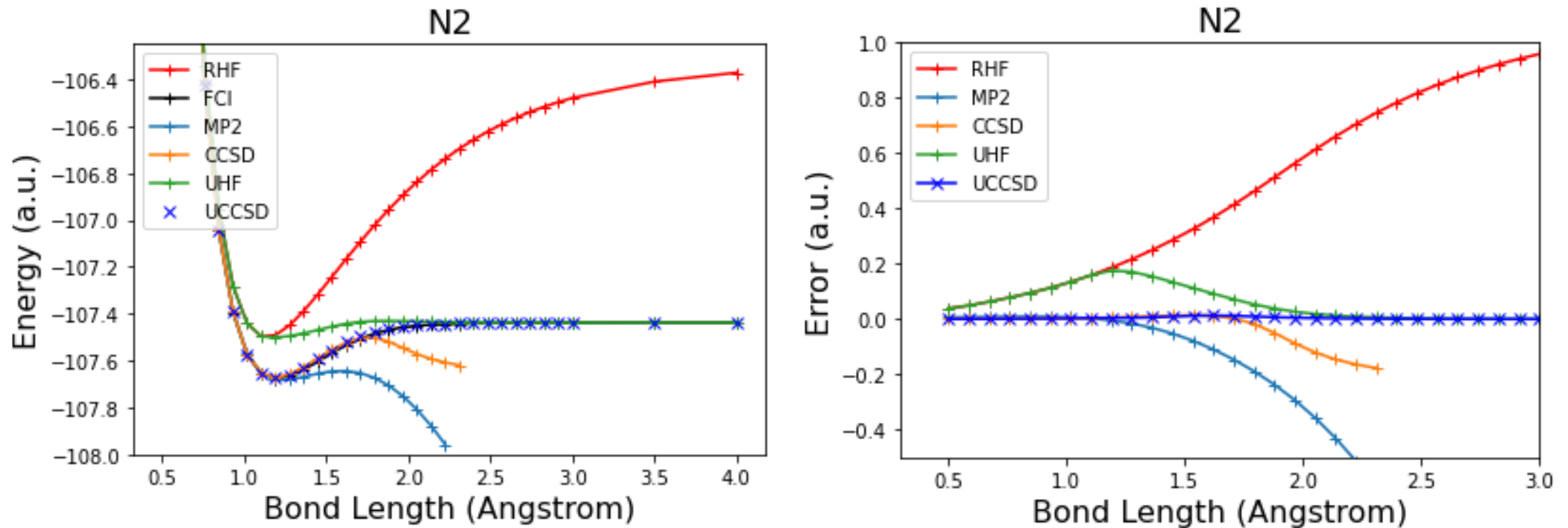Left: Energy difference between RHF/MP2/CCSD/UHF/UCCSD and FCI.

Diatomic molecules: single bond breaking for F_2

Note: For HF and F2 with STO-3G, CCSD happens to be exact as they are problems with at most two holes. This is not true for larger basis sets.

Right: The dissociation curve of F_2 with STO-3G by PySCF.
Left: Energy difference between RHF/MP2/CCSD/UHF/UCCSD and FCI.

Diatomic molecules: triple bond breaking for N_2

Note: (1) RCCSD fails to converge after the bond length exceeds ca. 2.2 Angstrom.
(2) The UHF happens to give the exact energy at the dissociation limit due to the limited basis set.

Right: The dissociation curve of N_2 with STO-3G by PySCF.
Left: Energy difference between RHF/MP2/CCSD/UHF/UCCSD and FCI.

Diatomic molecules: double bond breaking for O_2
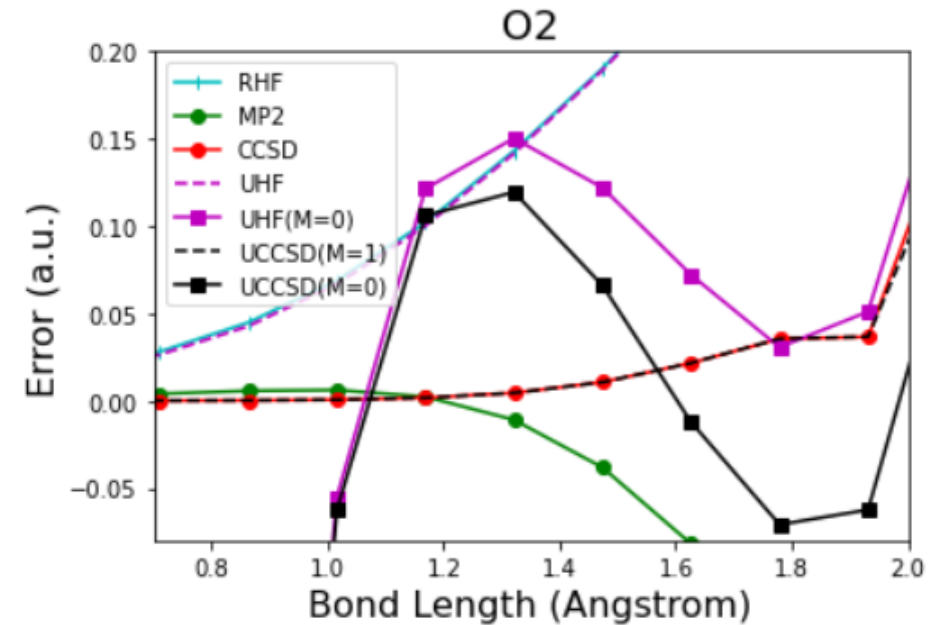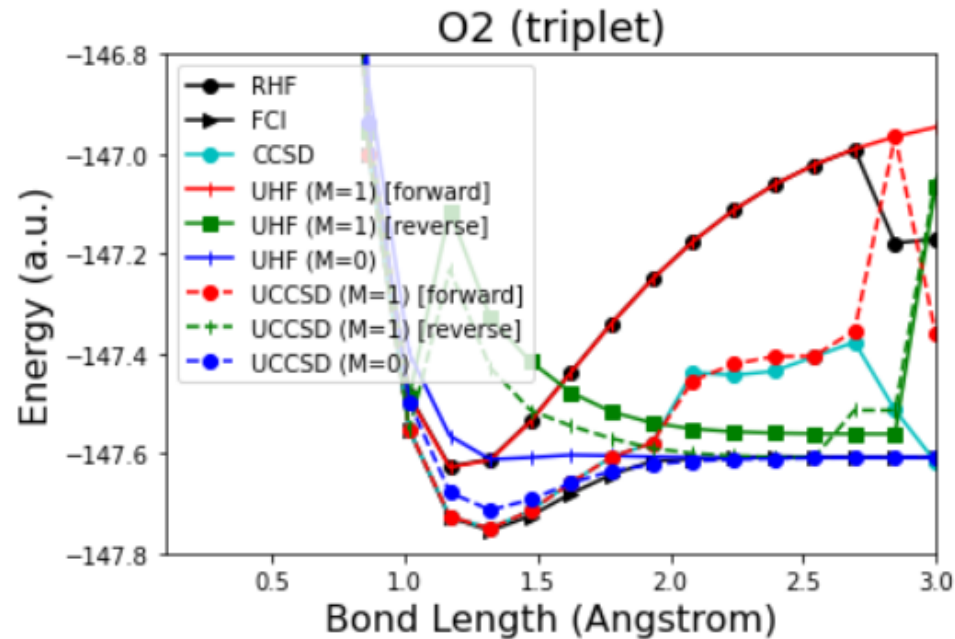
Note: (1) The open-shell molecule O2 is challenging for a mean-field description (both ROHF and UHF) at large bond length. (2) Multiple UHF solutions with M=1 exist. (3) UHF energies obtained with M=1 at the dissociation limit are not exact (!= E[two O atoms] by ROHF=FCI) as limited by the single-determinant framework.

Right: The dissociation curve of O_2 with STO-3G by PySCF.
Left: Energy difference between RHF/MP2/CCSD/UHF/UCCSD and FCI.
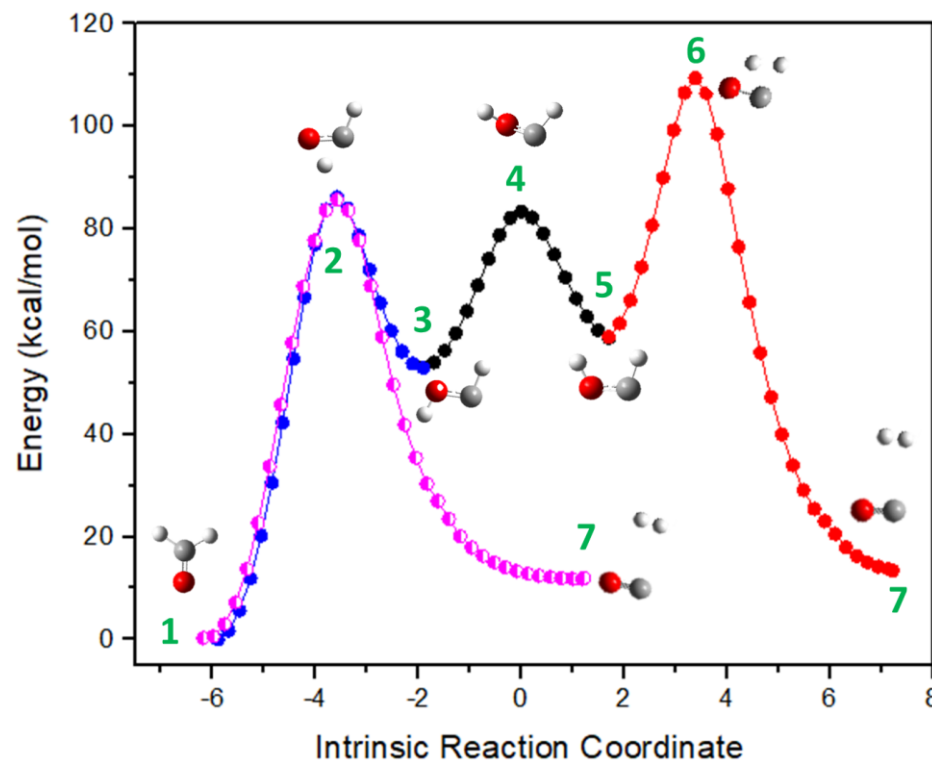
Reactions: isomerization of HCN <-> HNC
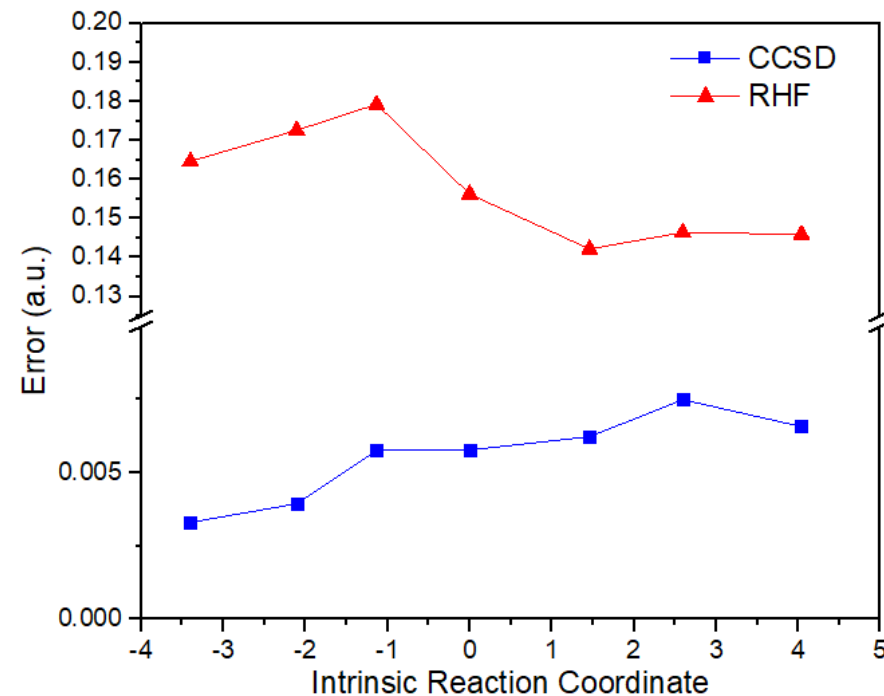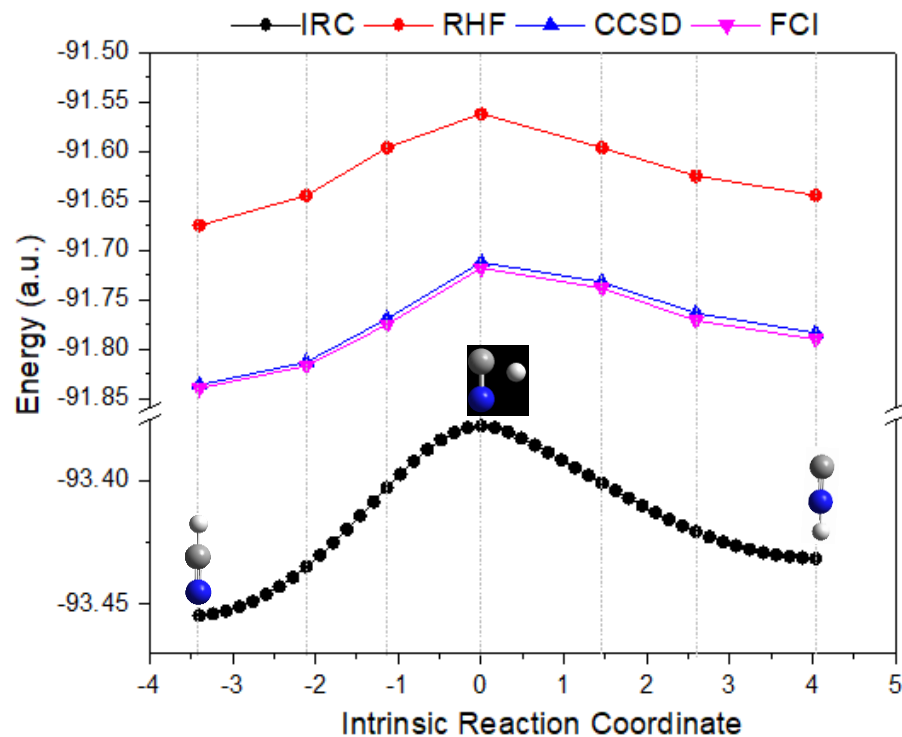
Simulate the isomerization of HCN and HNC by Gaussian 16 program and select seven geometries from the IRC curve.
Key words: # irc=(CalcFC,Recalc=10,maxpoints=200,stepsize=15, LQA) b3lyp/6-311+g(d,p) geom=connectivity
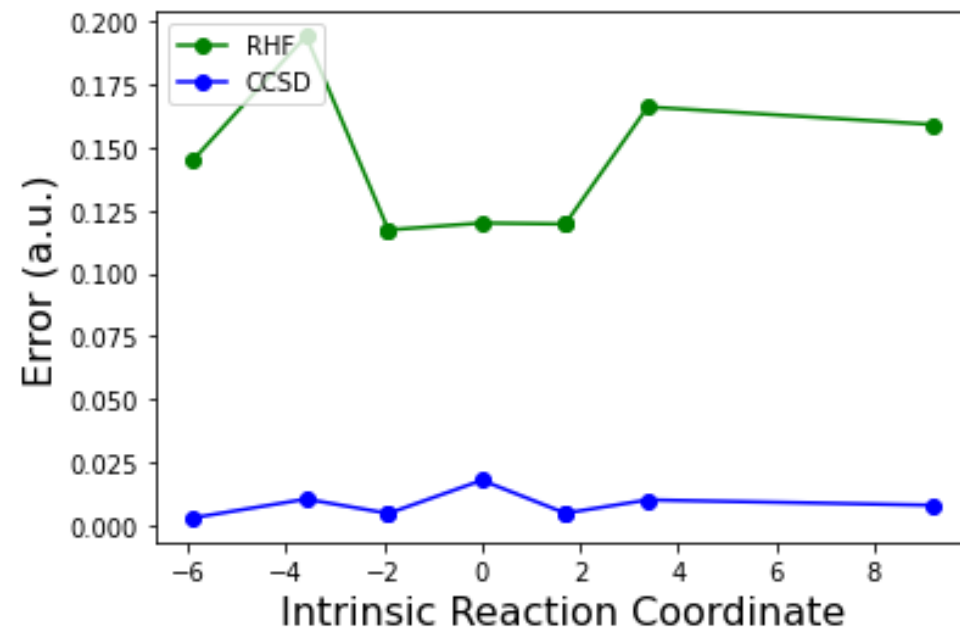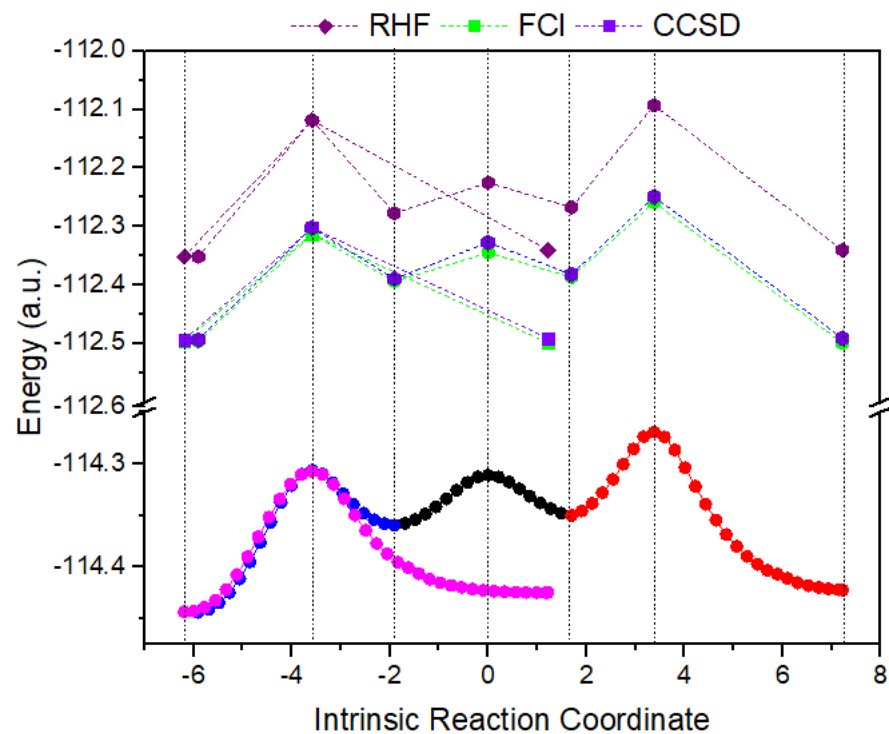The energy of RHF/CCSD/FCI with STO-3G obtained by PySCF.

Reactions: isomerization of H2CO

- As the number of atoms increases, there are several minima on the potential energy surface of H2CO: formaldehyde, hydroxycarbene (HCOH: cis and trans), and H2 + CO.

- Interesting reactions:
  - Dissociation of formaldehyde: 1->7
  - 1,2 hydrogen shift reaction: 1->3/5
  - Trans-cis transition: 3->5 (~4-5kcal/mol, conversion to each other is relatively easy at temperatures not far from room temperature)

- Activation energies for the reactions determine reaction rates
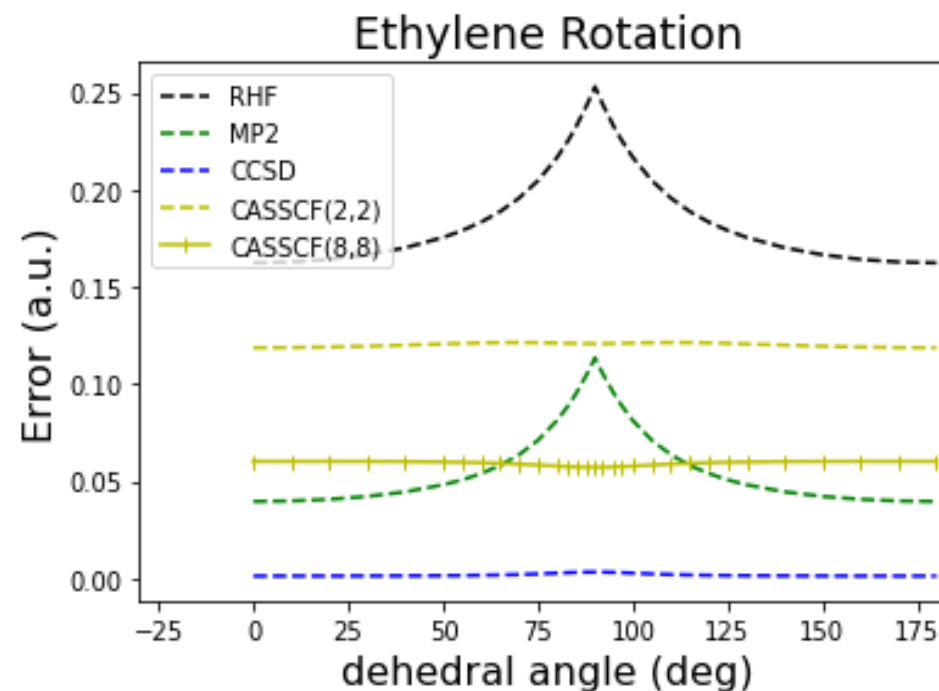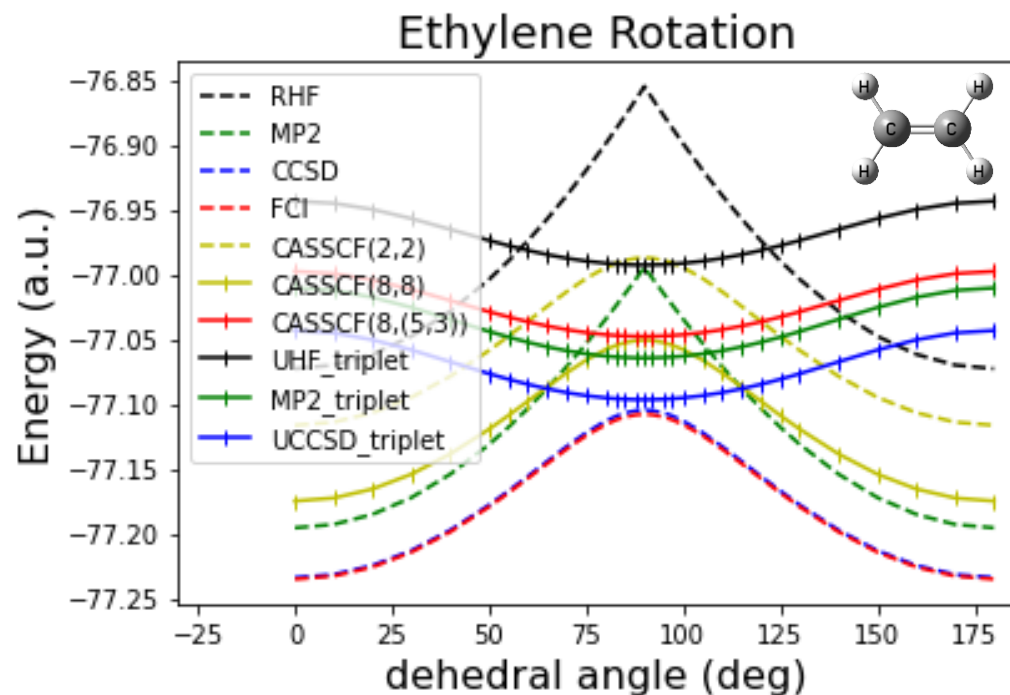
Reactions: isomerization of H2CO

Simulate the isomerization of H_2CO by Gaussian 16 program and select seven geometries from the IRC curve.
Key words: # OPT=QST2 FREQ APFd 6-311+G(2d,p) Geom=Connectivity Int(Ultrafine,Acc2E=12)
The energy of RHF/CCSD/FCI with STO-3G obtained by PySCF.

Reactions: ethylene rotation (E<->Z)

The initial geometry are constructed by GaussView 6.0, opted at B3LYP/6-31G* and then obtain a series of input geometries (no optimization) by adjusting the dihedral angel.
Right: The Ethylene torsional barrier with STO-3G by PySCF.
Left: Energy error between RHF/MP2/CCSD/CASSCF and FCI.

Reactions: ethylene rotation (E<->Z)

Note: CCSD energy looks good at 90 deg, but this is an artifact of the minimal basis. With an increased basis set (e.g., DZP), there should be a cusp. Only multi-configurational methods can recover the correct behavior.
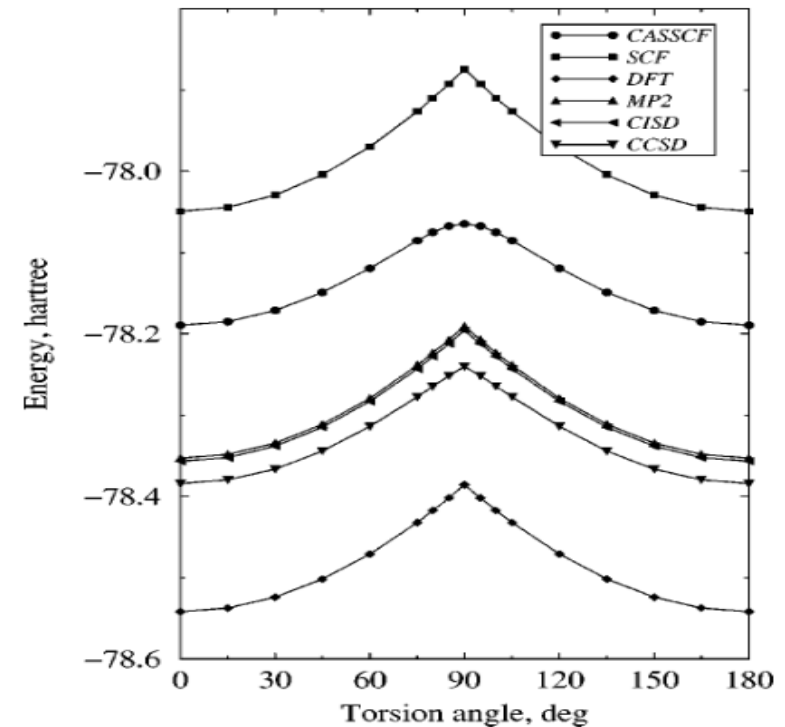

FIG. 9. Ethylene torsional barrier using a DZP basis set. The RHF SCF energy at for the planar structure is −78.049 241 hartree.