Assessment of random phase approximation with different exchange-correlation functionals for description of binding energies of molecular solids

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Introduction

Reliable prediction of the structure and stability of molecular solids is considered one of the important keys to explore the numerous applications of these systems. However, the need to describe reliably electron correlations in solids makes the accurate calculations of their binding energies challenging. In this study, we employ the coupled-cluster with singles, doubles, and perturbative triples (CCSD(T)) method to obtain a reference-quality many-body expansion (MBE) of the binding energy of four crystalline hydrocarbons: ethane, ethene, and cubic and orthorhombic forms of acetylene. We then assess the accuracy of a simpler and computationally cheaper method (random phase approximation (RPA)) based on different exchange-correlation functionals (PBE, SCAN, PBE0, and SCAN0) by comparing with CCSD(T) reference data.

Theoretical and computational details

The binding energy (E_b) of a solid is evaluated within MBE approach by adding two-, three-, and higher-order contributions:

$$E_b = \frac{1}{2}\sum_j \Delta^2 E_{ref,j} + \frac{1}{3}\sum_{j<k} \Delta^3 E_{ref,j,k} + \frac{1}{4}\sum_{j<k<l} \Delta^4 E_{ref,j,k,l} + \cdots$$

where i, j, and k are indices of molecules other than the reference (ref) one.

$$\Delta^2 E_{ref,j} = E_{ref,j} - E_{ref} - E_j$$

$$\Delta^3 E_{ref,j,k} = E_{ref,j,k} - \Delta^2 E_{ref,j} - \Delta^2 E_{ref,k} - \Delta^2 E_{j,k} - E_{ref} - E_j - E_k$$

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- Molpro program was used for CCSD(T) calculations.
- An in-house code [Modrzejewski et al., J. Chem. Theory Comput. 16, 427- 442 (2020)] was used for RPA calculations.
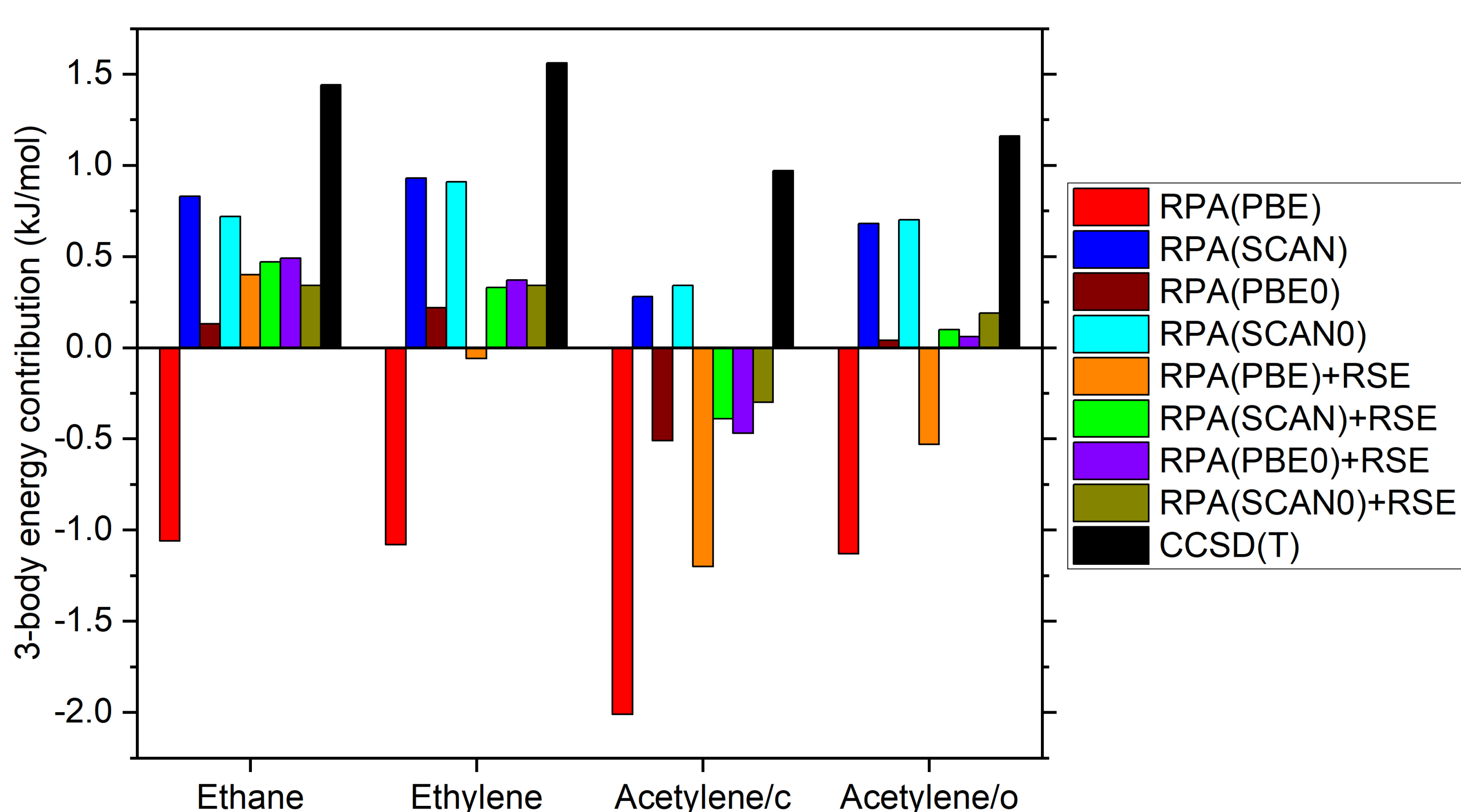
Two-body terms

● The accuracy of the 2-body RPA energies based on all functionals is improved when renormalized singles corrections (RSE) are added.
● The 2-body RPA energies based on PBE and SCAN states are closer to CCSD(T) values than that based PBE0 and SCAN0 states.
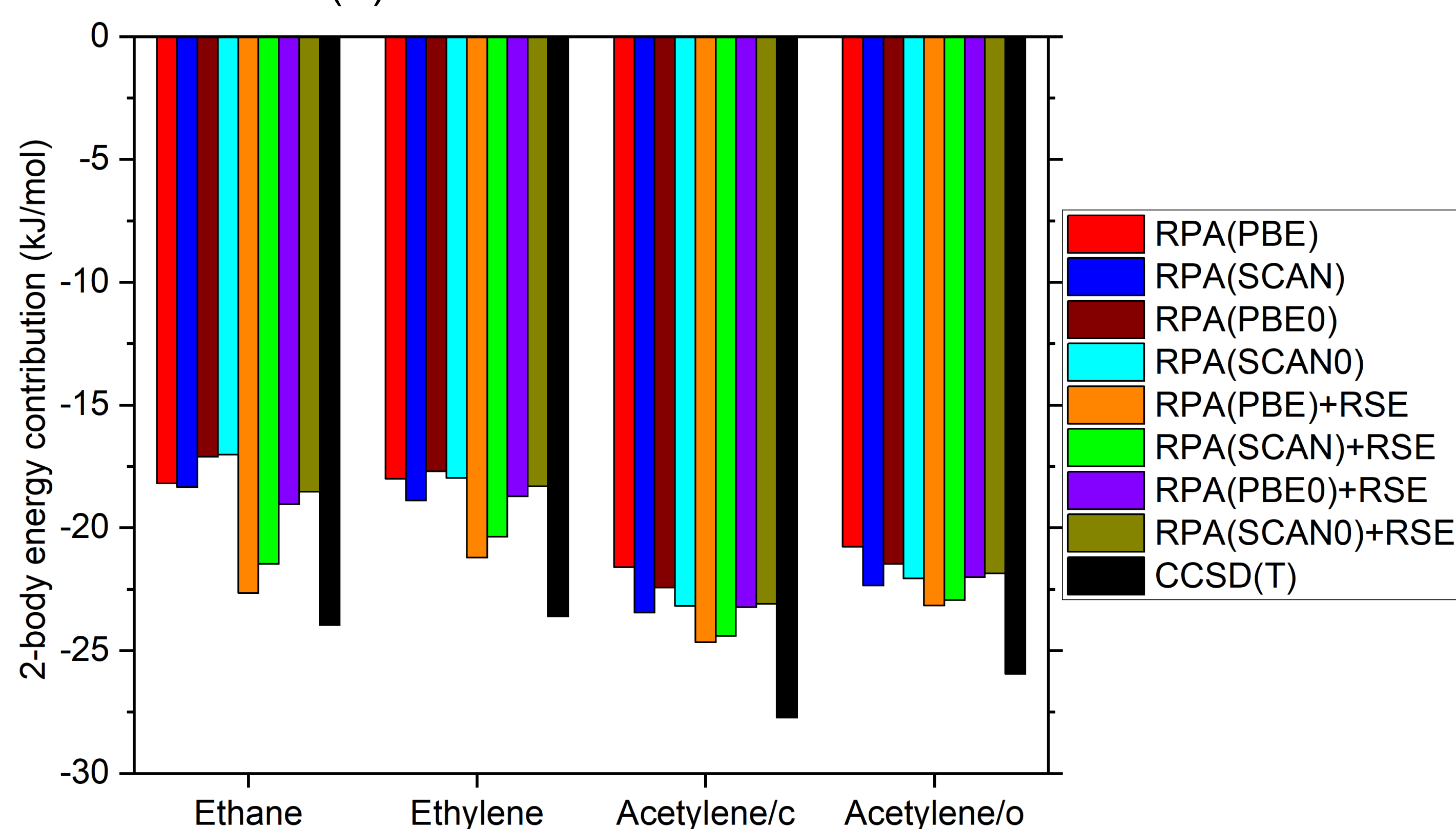
The two-body contributions to the total RPA binding energies compared to the CCSD(T) reference data.

Three-body terms

● The 3-body RPA values without RSE using SCAN and SCAN0 states are closer to the reference than when PBE and PBE0 states are used.
● While RSE corrections improve the accuracy of the PBE- and PBE0-based 3-body RPA, they make the accuracy of the SCAN- and SCAN0-based 3-body RPA poorer.

The three-body contributions to the total RPA binding energies compared to the CCSD(T) reference data.

Four-body terms

● Adding Hatree-Fock (HF) exchange in hybrid functionals leads to an accurate improvement of the 4-body RPA energies.
● The RSE corrections generally improves the 4-body RPA energies upon bare values.
● The 4-body RPA values with and without RSE based on SCAN0 are in better agreement with the reference in comparison with other states.
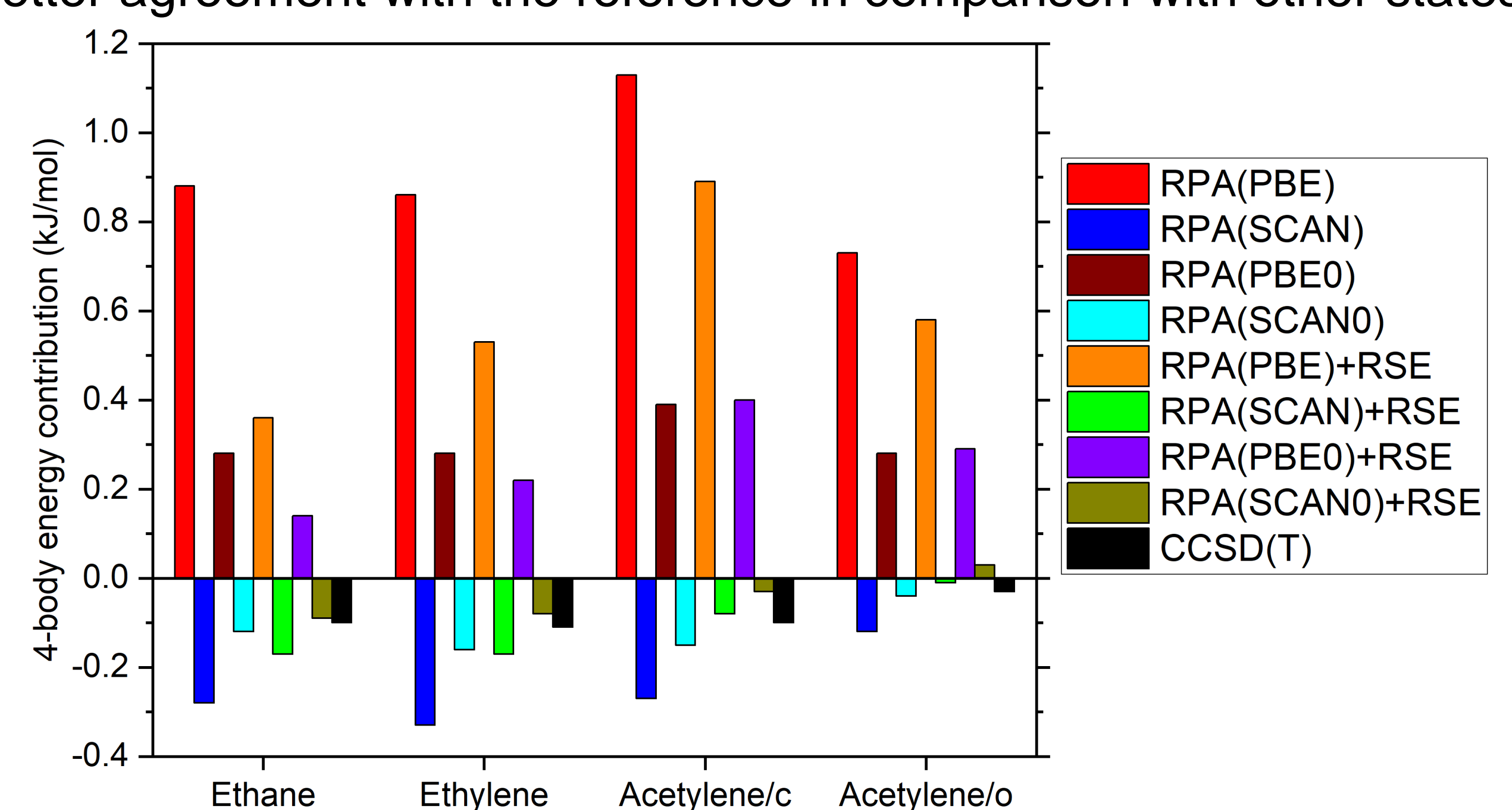
The four-body contributions to the total RPA binding energies compared to the CCSD(T) reference data.

Total RPA energies

● The PBE and SCAN states give smaller errors than PBE0 and SCAN0 states.
● When RSE corrections are added, the accuracy of the RPA method based on pure functionals is improved more significantly than that based on hybrid functionals.
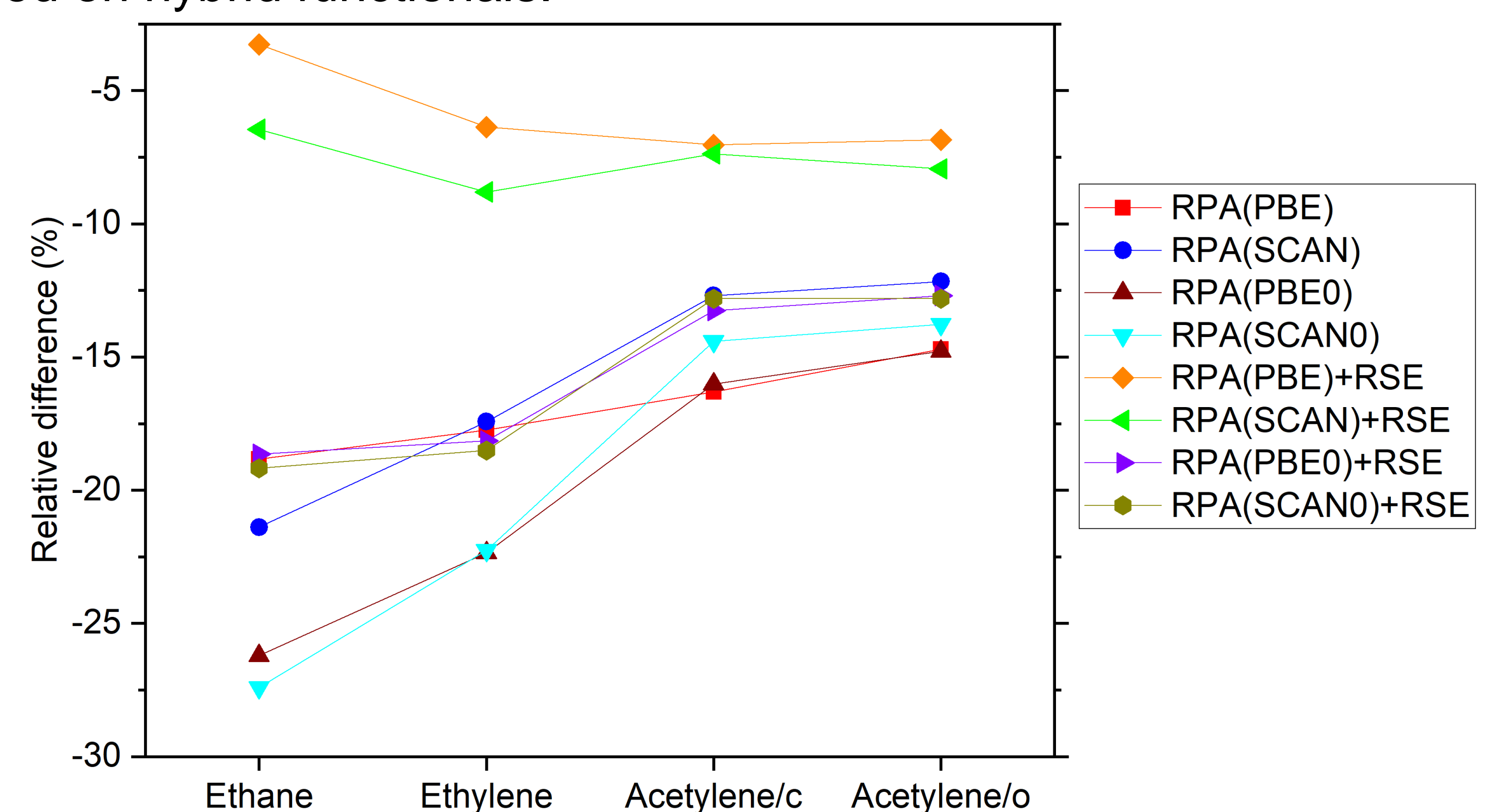
Relative difference of the RPA binding energies with respect to the reference data

Summary

● The choice of the DFT functional affects significantly the results of the many-body contributions, but the total binding energies are found to be similar for PBE and SCAN, and for PBE0 and SCAN0.
● The energy changes of all many-body contributions are larger for PBE than for SCAN when HF exchange is added.
● The RPA method with RSE corrections based on PBE and SCAN performs better than that based on PBE0 and SCAN0.

References

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