

# Understanding precision of binding energies of molecules and molecular solids

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## Introduction

- Many molecular solids exhibit polymorphs or have different phases. Their energies can differ by less than 1 kJ/mol. To describe this difference accurate methods need to be used and the set-up has to be tightly converged – precise.
- The quality of the set-up can be assessed by comparing interaction energies of molecular dimers to reference data. The reference data can be obtained using quantum chemistry programmes.
- This allows for assessment of projector-augmented wave potentials (PAWs) or pseudopotentials (PPs) or of basis-set convergence.

## Quality of PAWs and PPs

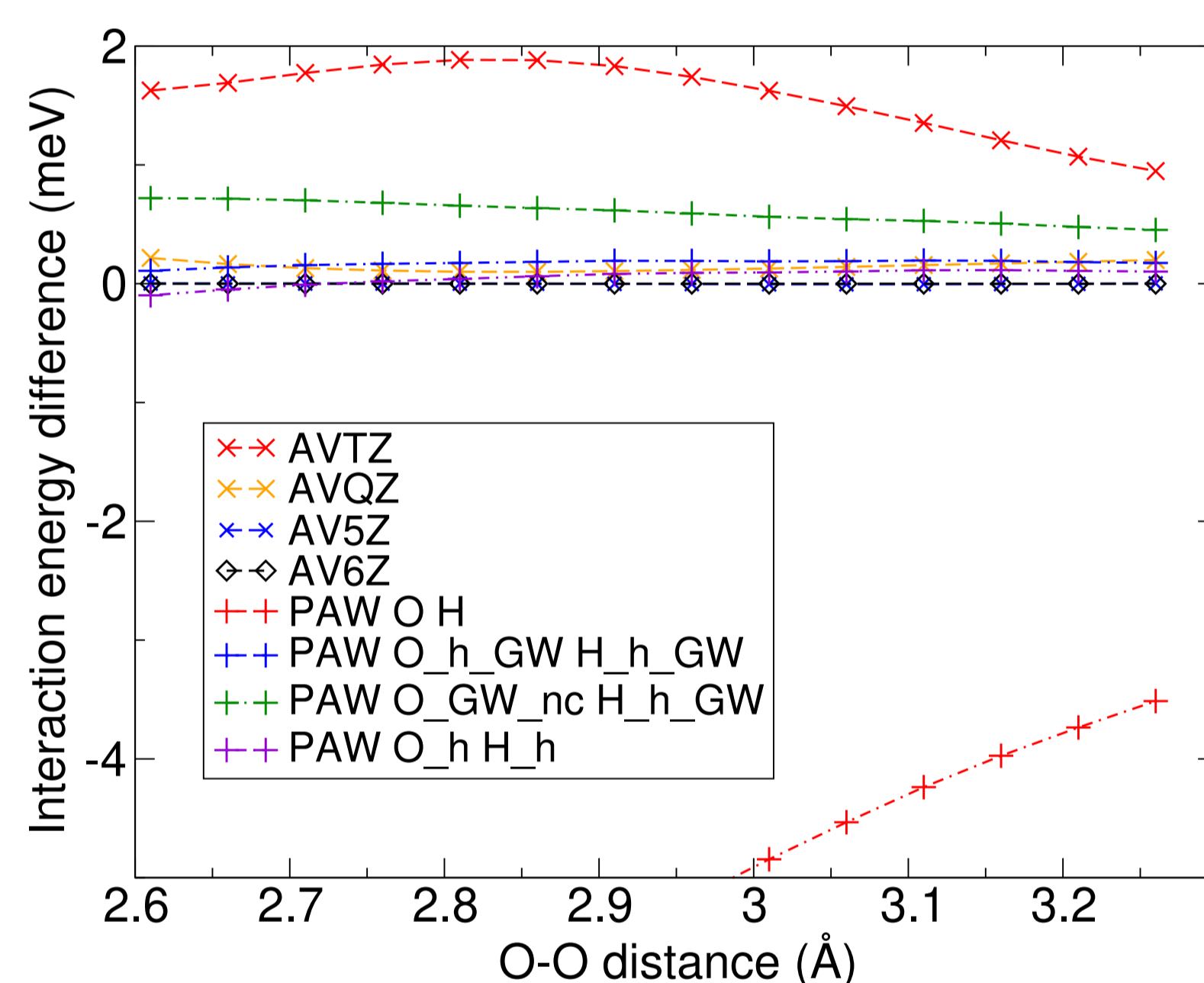
- There is unsatisfactory agreement between binding energies of molecular solids published in the literature. The differences can be caused by different k-points sets, geometries, (pseudo)potentials, and basis sets.
- It turns out that in many cases the (pseudo)potentials used for oxygen are the cause of the problem. When too soft PAWs or PPs are used, errors of several tens of meV can be observed.

PBE+vdW(TS) results from different publications

$E_{\text{coh}}$ [meV]	Ref. 3	Ref. 4	VASP hard	VASP normal
Acetic acid	-867	-856	-845	-867
Ammonia	-456	-471	-459	-463
Oxalic acid $\alpha^a$	-1298	-	-1249	-1289
Oxalic acid $\alpha^b$	-	-1044	-1023	-1064

<sup>a</sup> monomer with no intra hydrogen bond

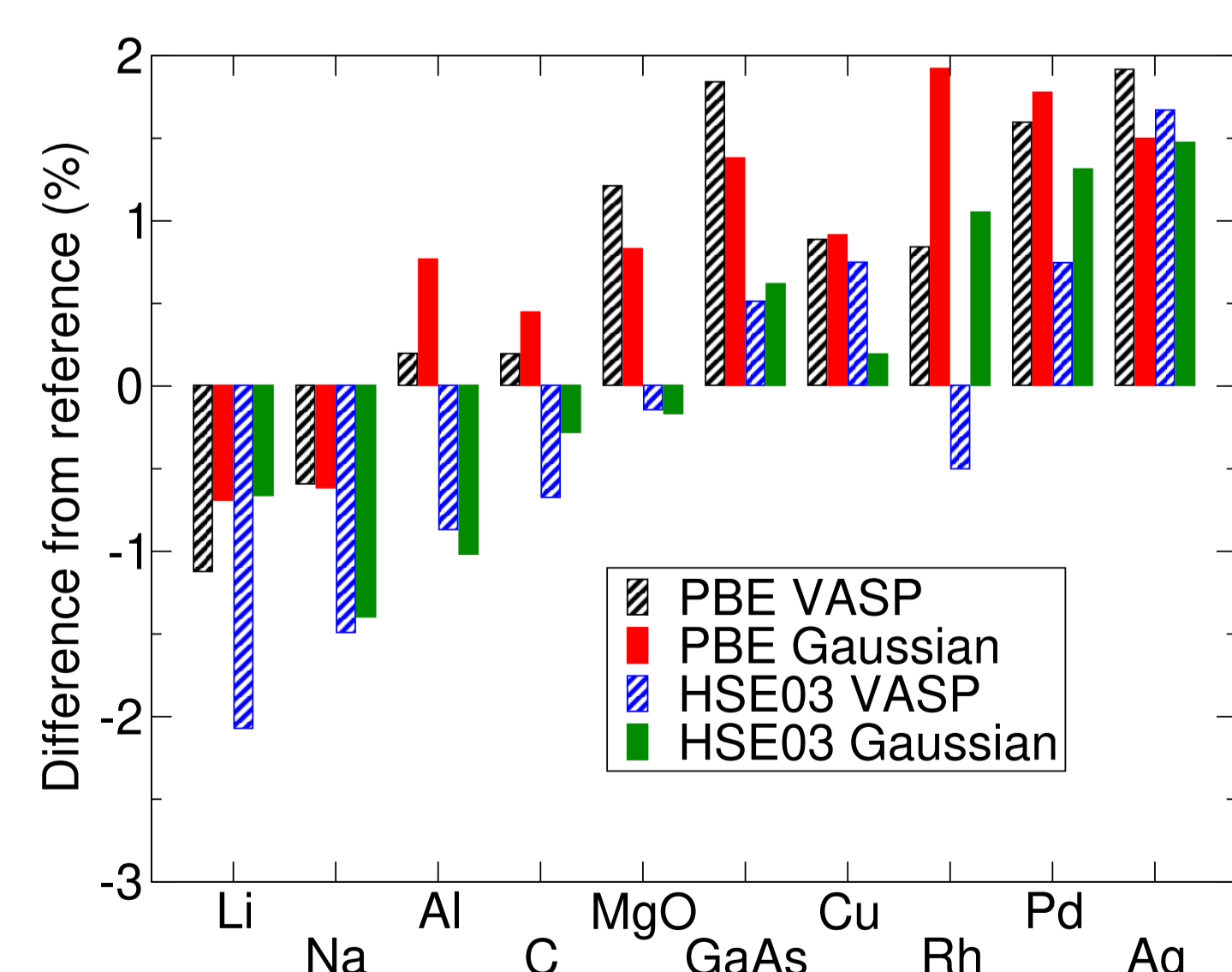
<sup>b</sup> monomer with intra hydrogen bond



← Differences of water dimer interaction energies for the PBE functional. Different gaussian basis sets and VASP PAW potentials are compared to the reference data obtained with the AV6Z basis set.

## Validation of method implementation

- Interaction energies of molecules can be used to cross-validate implementations of methods.
- Comparison of interaction energies for the HSE functional identified a previously unnoticed disagreement. This was caused by a simplification of the expression for the xc energy in VASP.
- Using the Ernzerhof-Perdew xc hole in VASP gives data in agreement with the reference. The Henderson-Janesco-Scuseria xc hole is, however, more physically sound and should be used instead.



← The original validation used lattice constants which were difficult to converge using the gaussian basis sets used in the reference code [5].

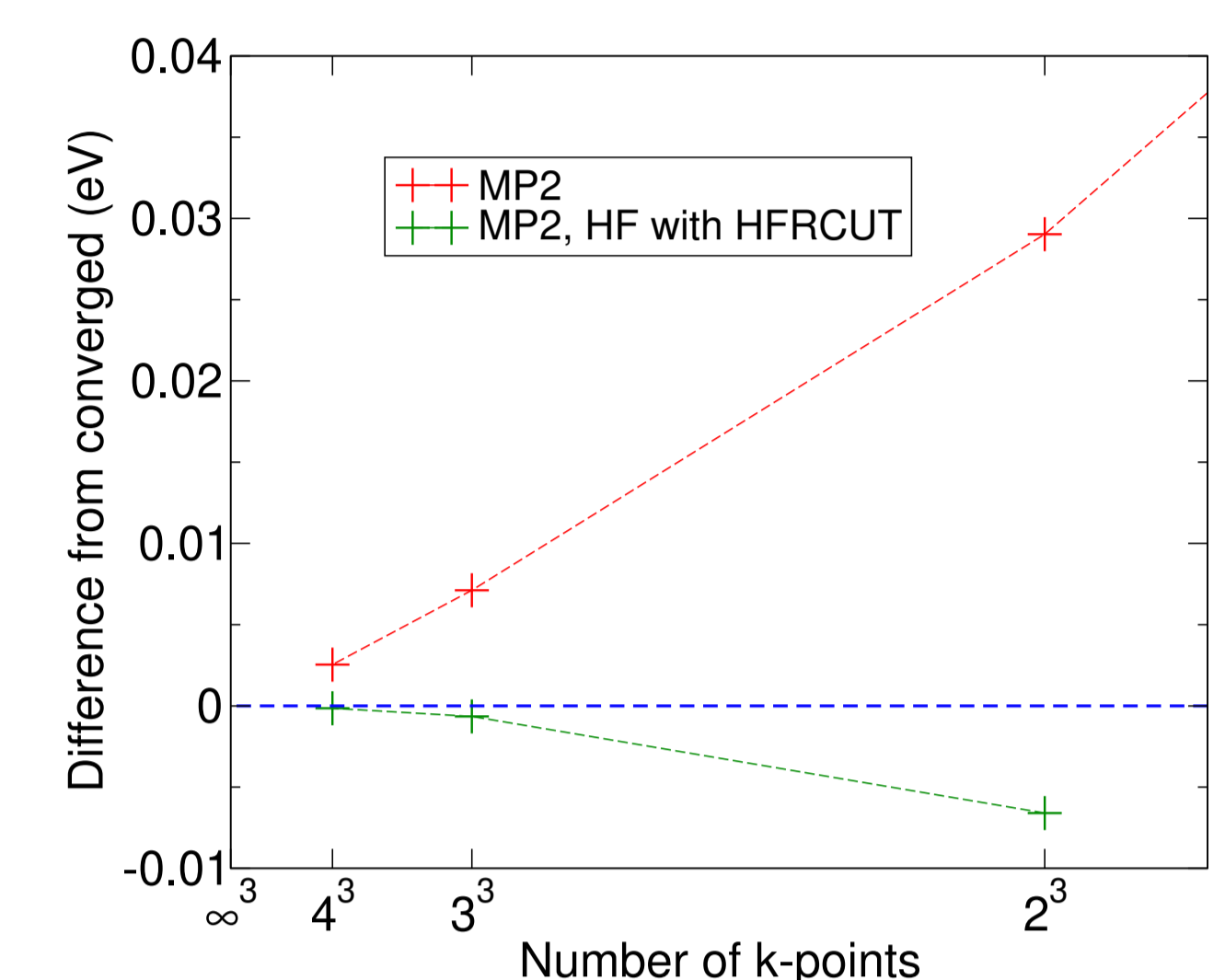
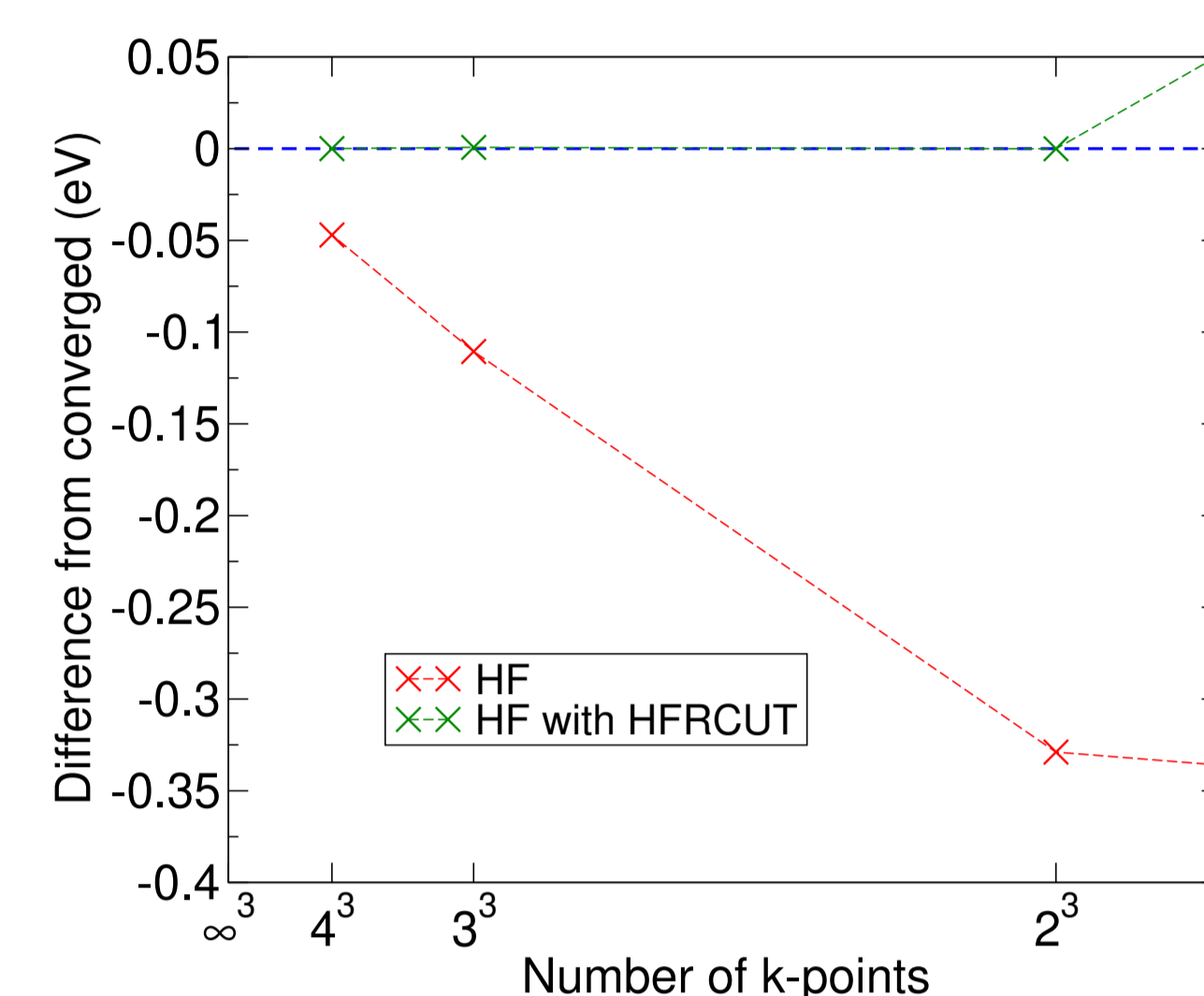
↓ Comparison of interaction energies shows clear differences.

Interaction energies of water dimer

	G09/CP2K	VASP	Note
PBE	-214.8	-214.5	
PBE0	-214.7	-214.4	
HSE06	-219.6	-215.2	Results with default settings
HSE-EP	-219.6	-219.1	Using Ernzerhof-Perdew xc hole
HSE-HJS	-215.4	-215.2	Using Henderson-Janesco-Scuseria xc hole

## Hartree-Fock and post-Hartree-Fock methods

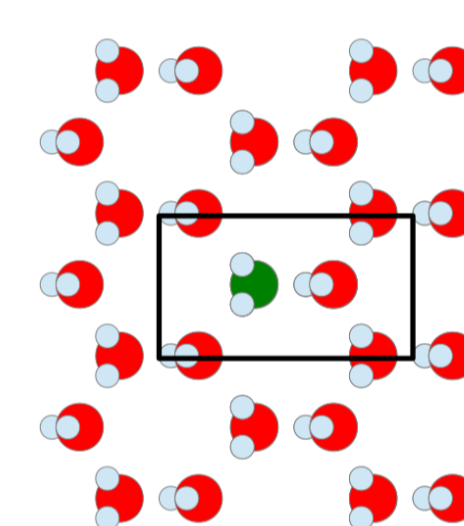
- For periodic systems, convergence with k-points is typically slower already for Hartree-Fock due to the Coulomb singularity at the  $\Gamma$  point. Moreover, correlated methods have stronger dependence on basis-set size.
- Obtaining converged results is thus more demanding. This leads to a lack of agreement between published data.



↑ Convergence of HF and MP2 energies of methane solid. Calculations used Hartree-Fock with and without the Coulomb cut-off technique.

## Periodic calculations vs. many-body expansion

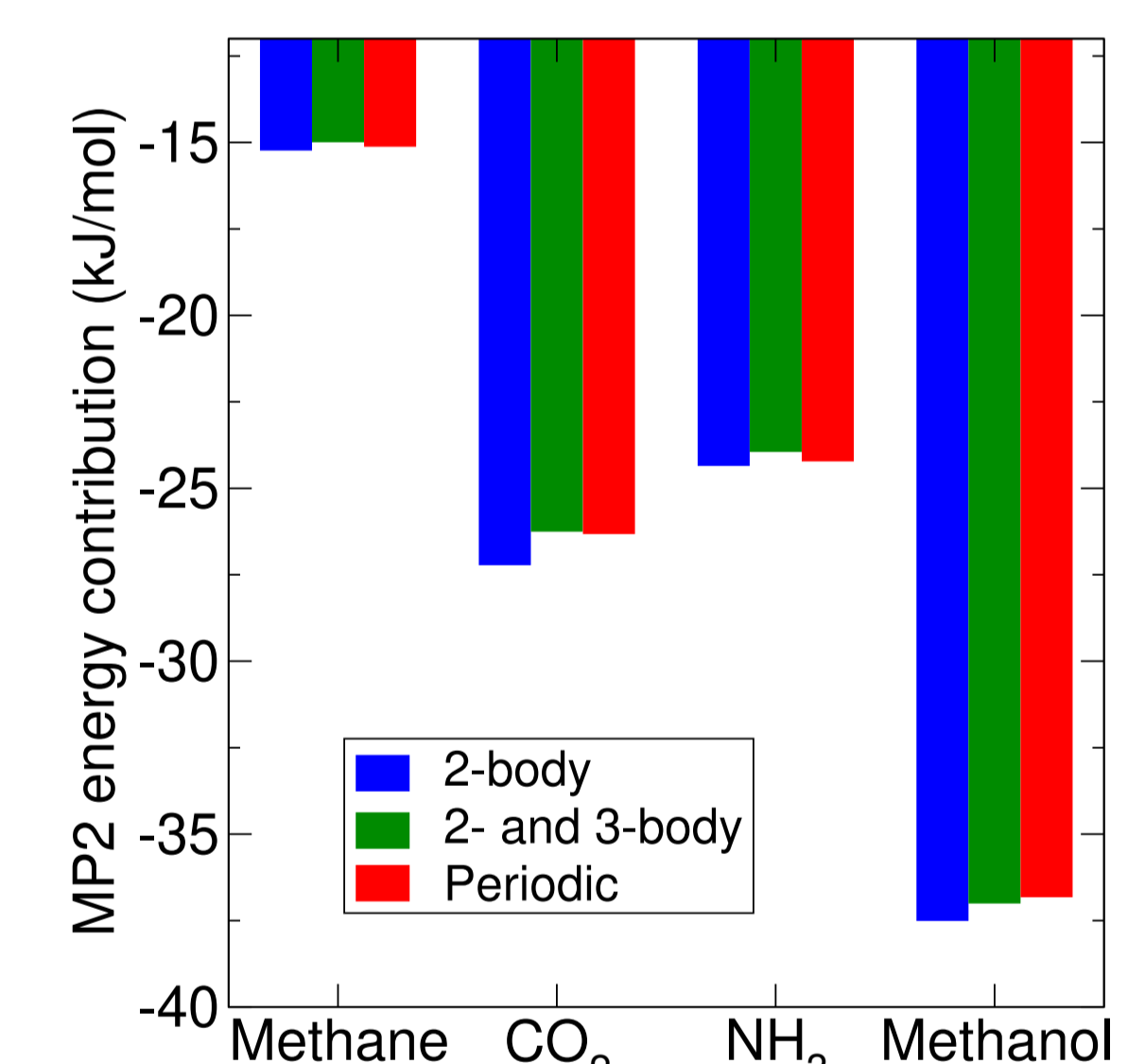
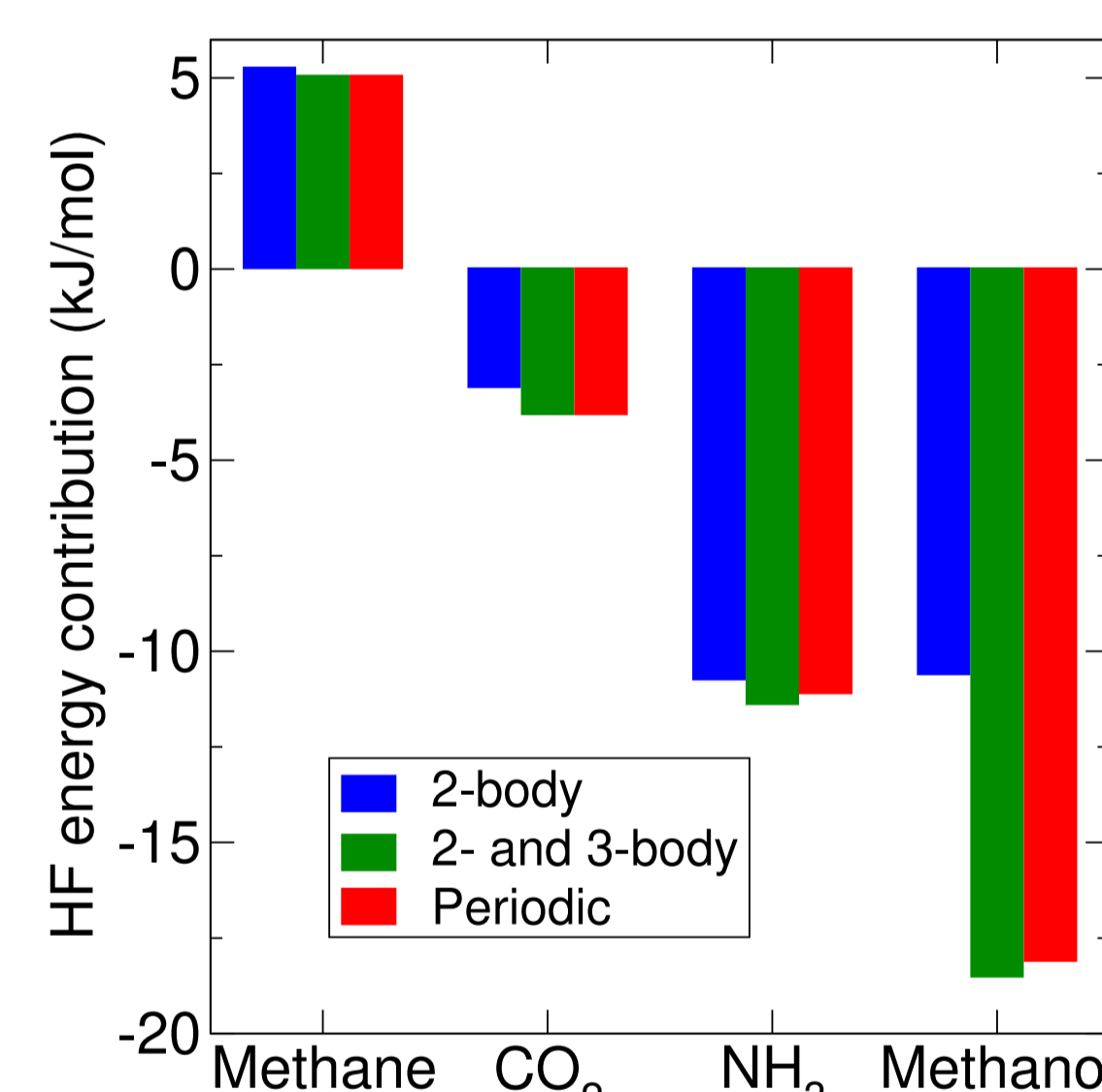
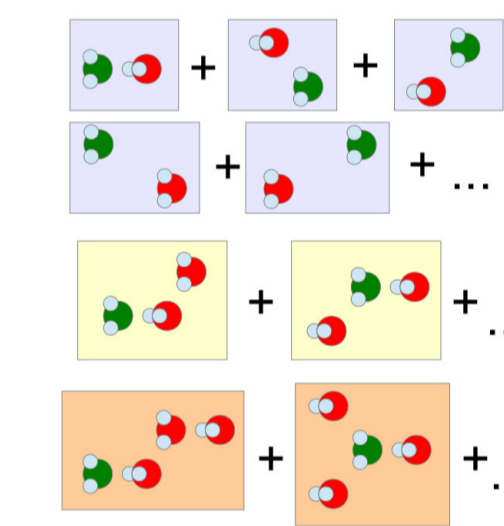
- Binding energies of molecular solids can be obtained by employing periodic boundary conditions or from many-body expansion.
- If the same structure and method are used, both approaches should yield identical results. We tested this for HF and MP2 and four solids.
- We find a nice agreement for methane and  $\text{CO}_2$ , for systems with hydrogen bonds, the contribution of tetramers (few meV) can't be neglected.



Lattice energy from...

← Periodic calculations

Many-body expansion →



↑ Comparison of many-body expansion with periodic calculations for Hartree-Fock (left) and MP2 (right).

## Summary

- Interaction energies of molecular dimers are a suitable tool for checking the quality of PAWs and PPs. For systems with hydrogen bonds, hard (pseudo)potentials are needed.
- The convergence of Hartree-Fock and post-Hartree-Fock methods with the number of k-points is much faster with the Coulomb cut-off technique.
- The binding energies obtained by periodic calculations and many-body expansion agree for methane and  $\text{CO}_2$ . For systems with hydrogen bonds, the contribution of tetramers needs to be included.

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## References

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