Towards reliable theoretical description of molecular solids

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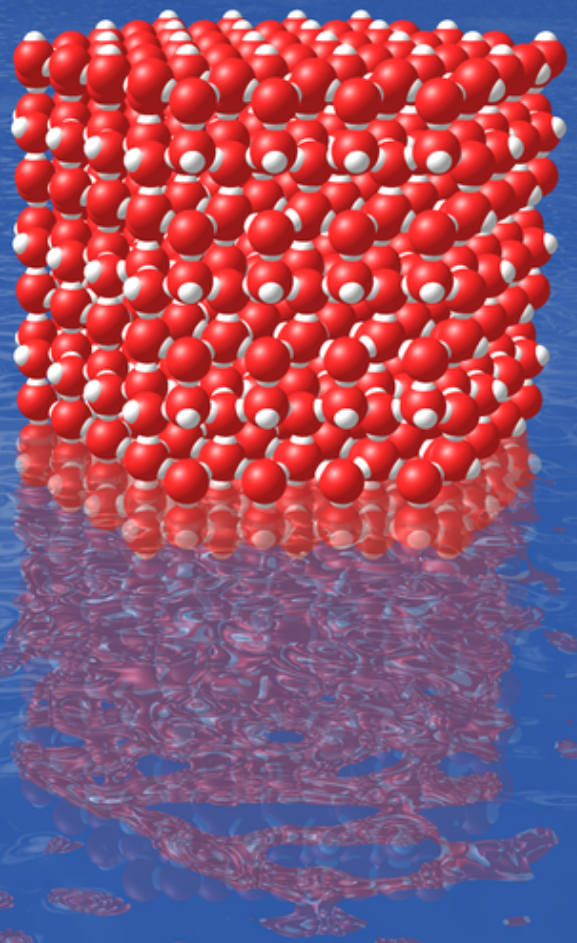
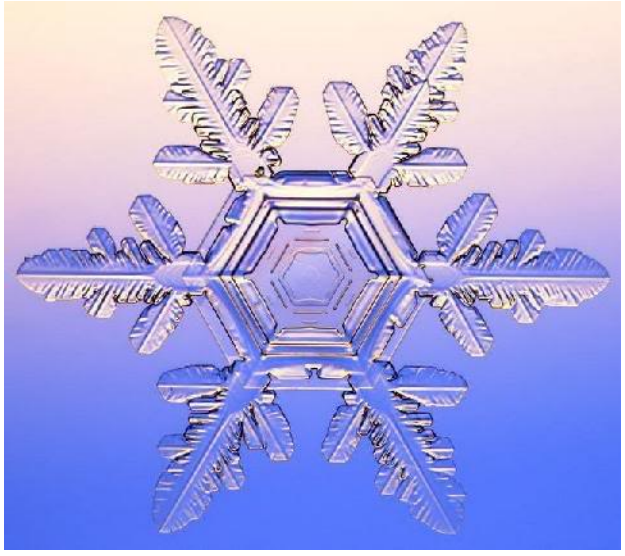
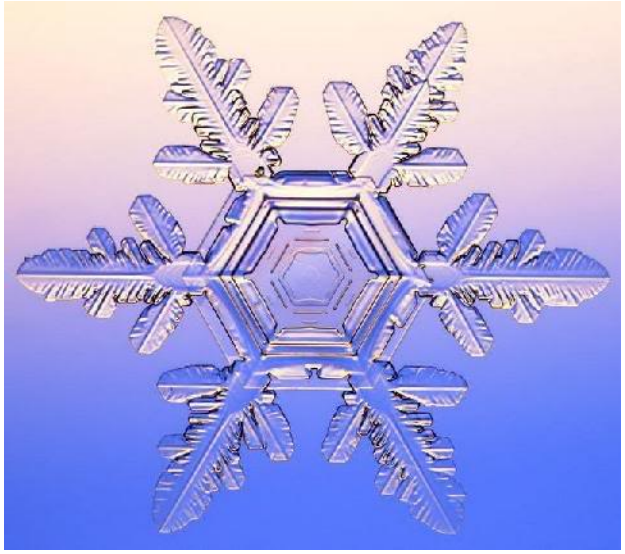
Jaroslav Hofierka

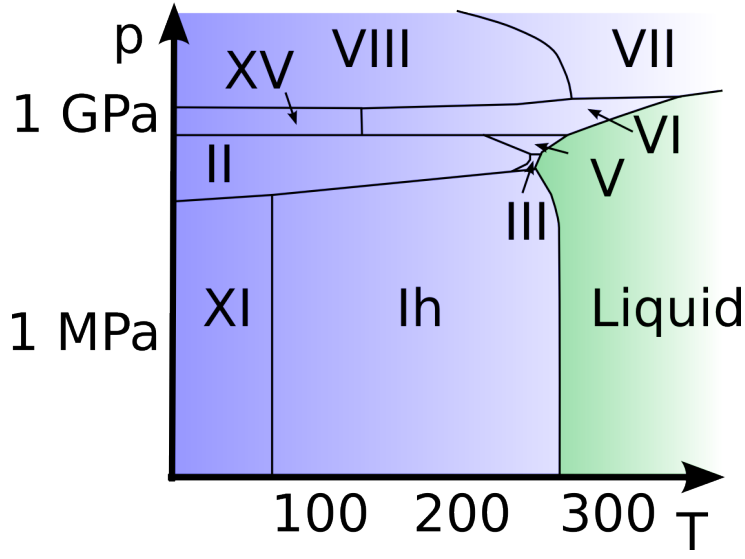
Charles University
Prague

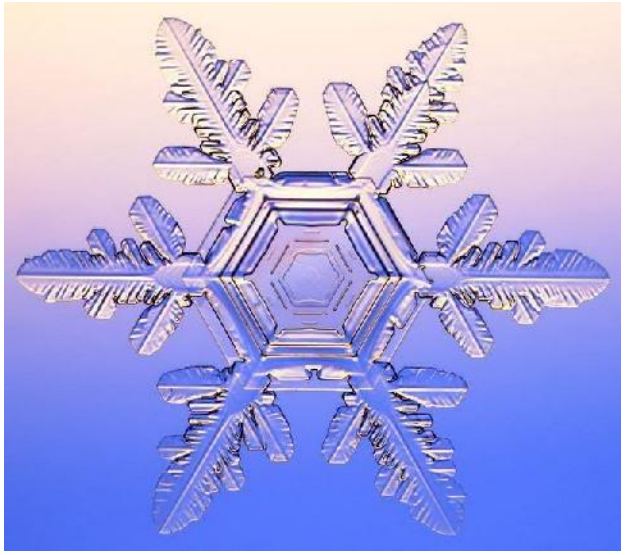
31. 10. 2018

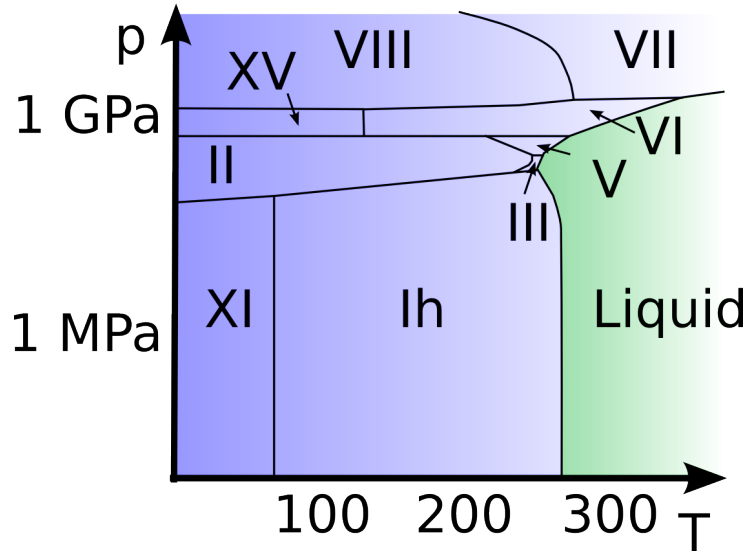


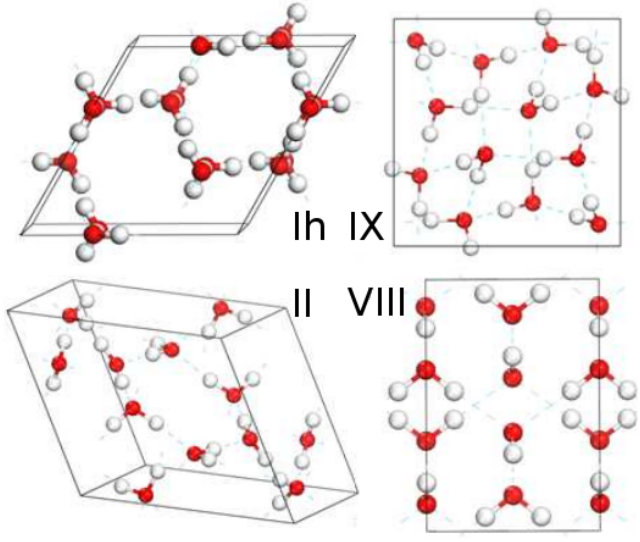





p
1 GPa
1 MPa
XV
VIII
VII
VI
V
II
III
XI
Ih
Liquid
100
200
300
T



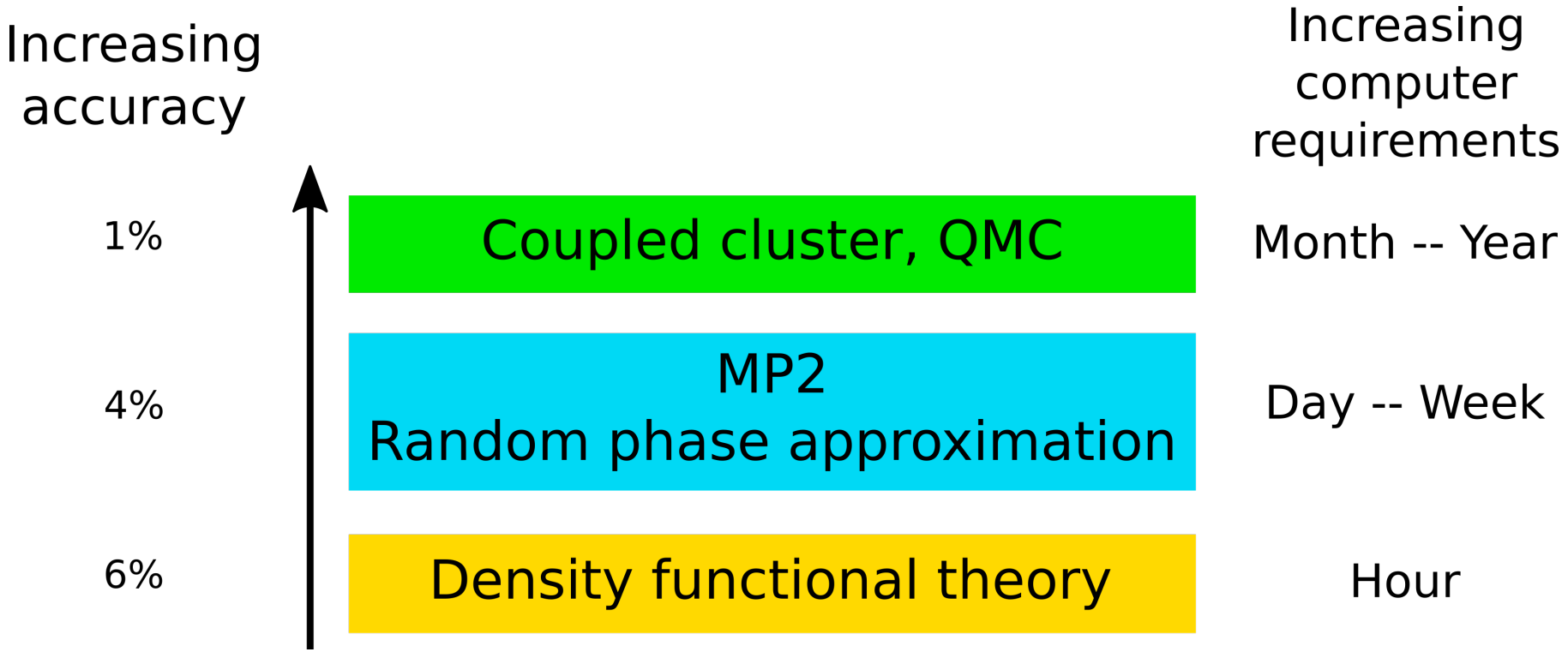




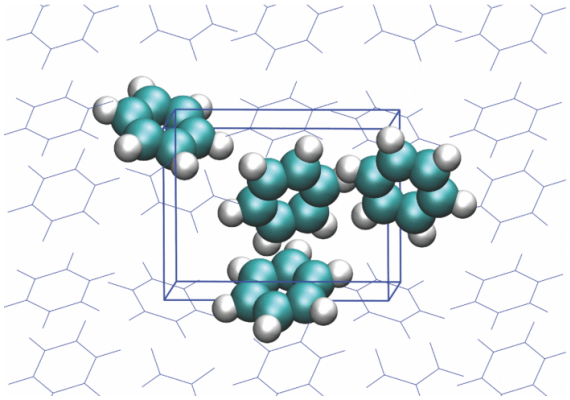
Water ice phases

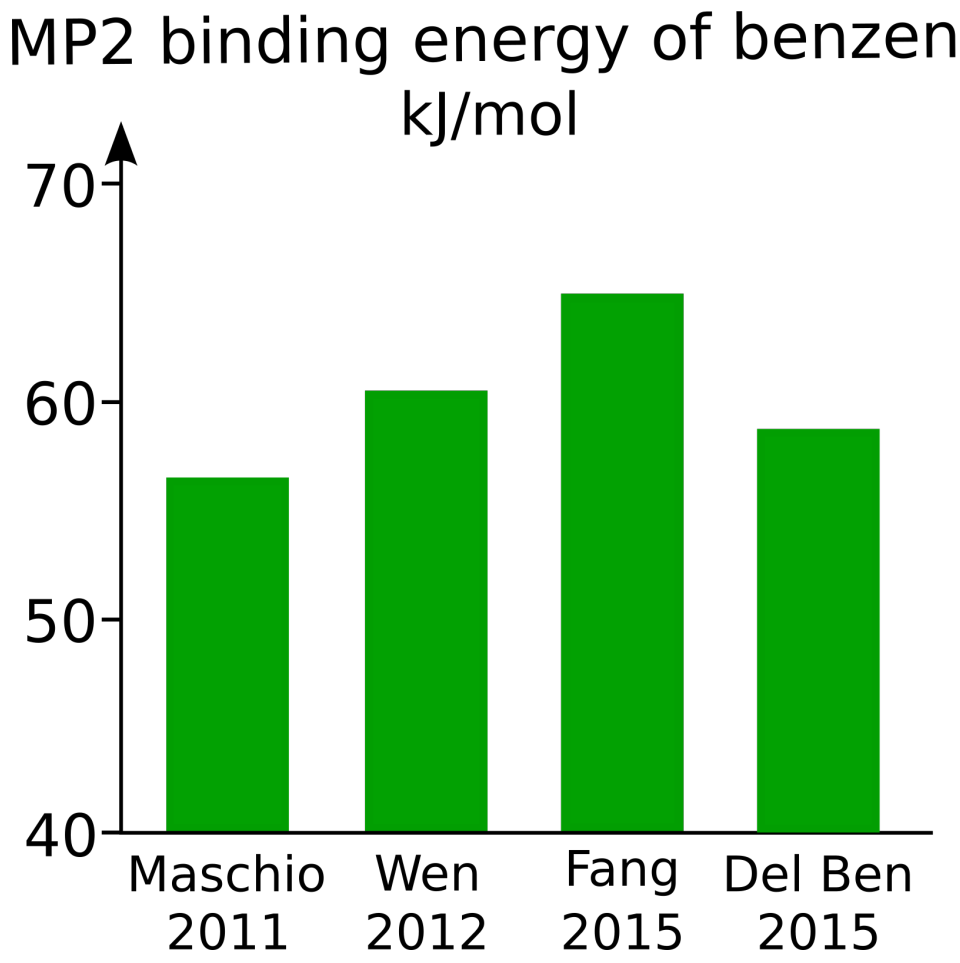
(kJ/mol)	E_{coh} (Exp.)
I*h*	−58.9
IX	−58.5
II	−58.8
VIII	−55.7

Approximations in quantum chemistry



Benzene example





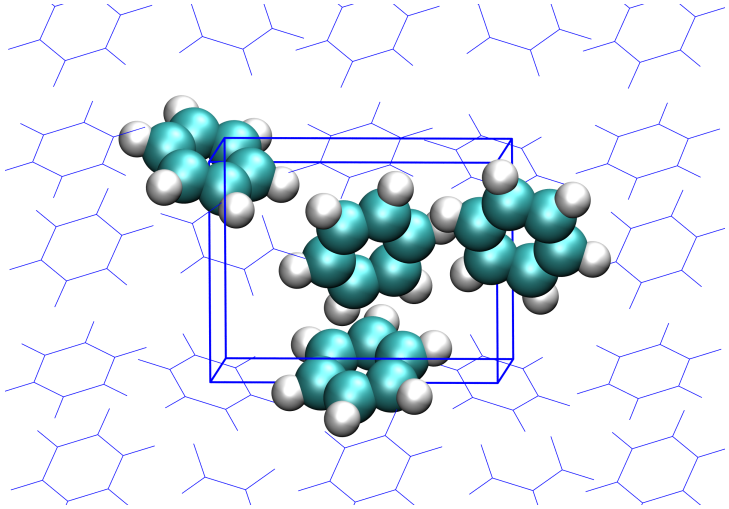
Data from G. J. O. Beran, Chem. Rev. **116**, 5567 (2016).

Problems with convergence of parameters

Molecular solids – Precision

Lattice energy

$$E_{\text{latt}} = E_{\text{solid}}/Z - E_{\text{molecule}}$$



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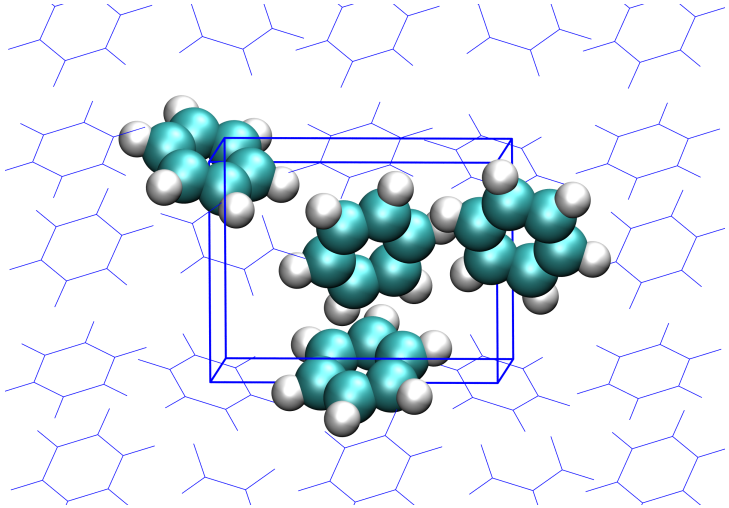

- Periodic calculations.

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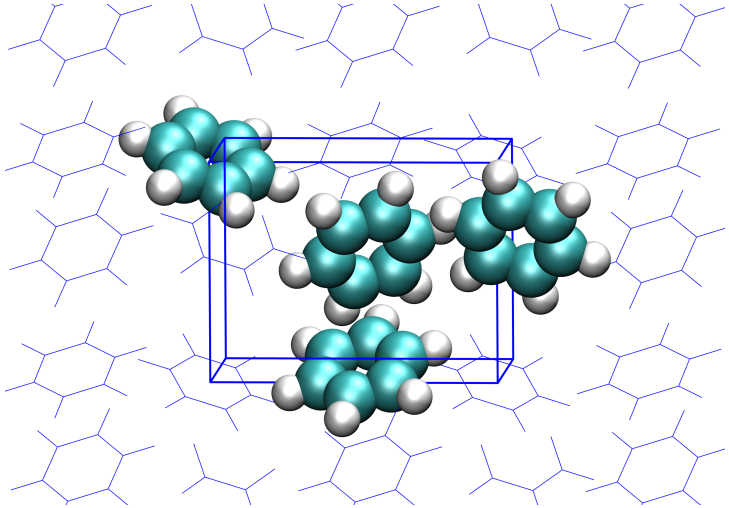

- Periodic calculations.
- Many-body expansion:

$$E_{\mathrm{solid}} = E_1 + \frac{1}{2}\sum_{i>1} \Delta E_{1i} + \frac{1}{3}\sum_{k>j>1} \Delta E_{1jk} + \ldots.$$

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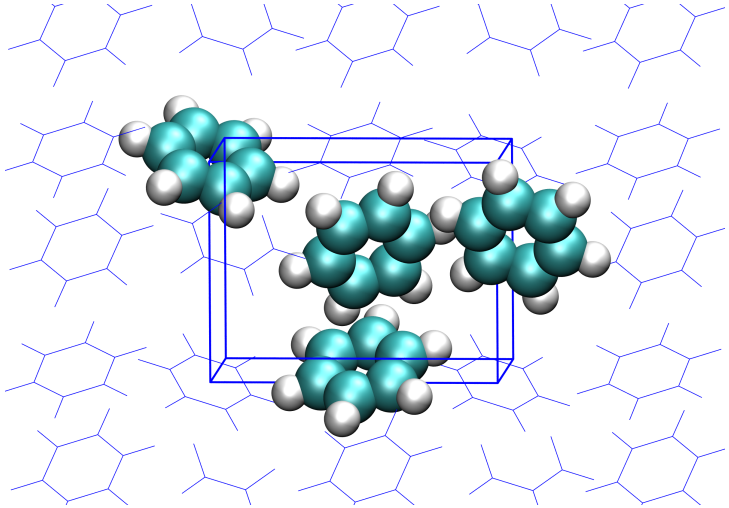

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In both cases, it is often difficult to know that you are converged.

Periodic calculations vs. many-body expansion

- We directly compared lattice energies obtained with many-body expansion using Molpro with periodic calculations done with VASP.
- We used methane, methanol, ammonia, and CO_2.
- HF with CABS corrections, MP2 with F12 corrections $\rightarrow$ AVTZ basis within 0.1% of AVQZ.
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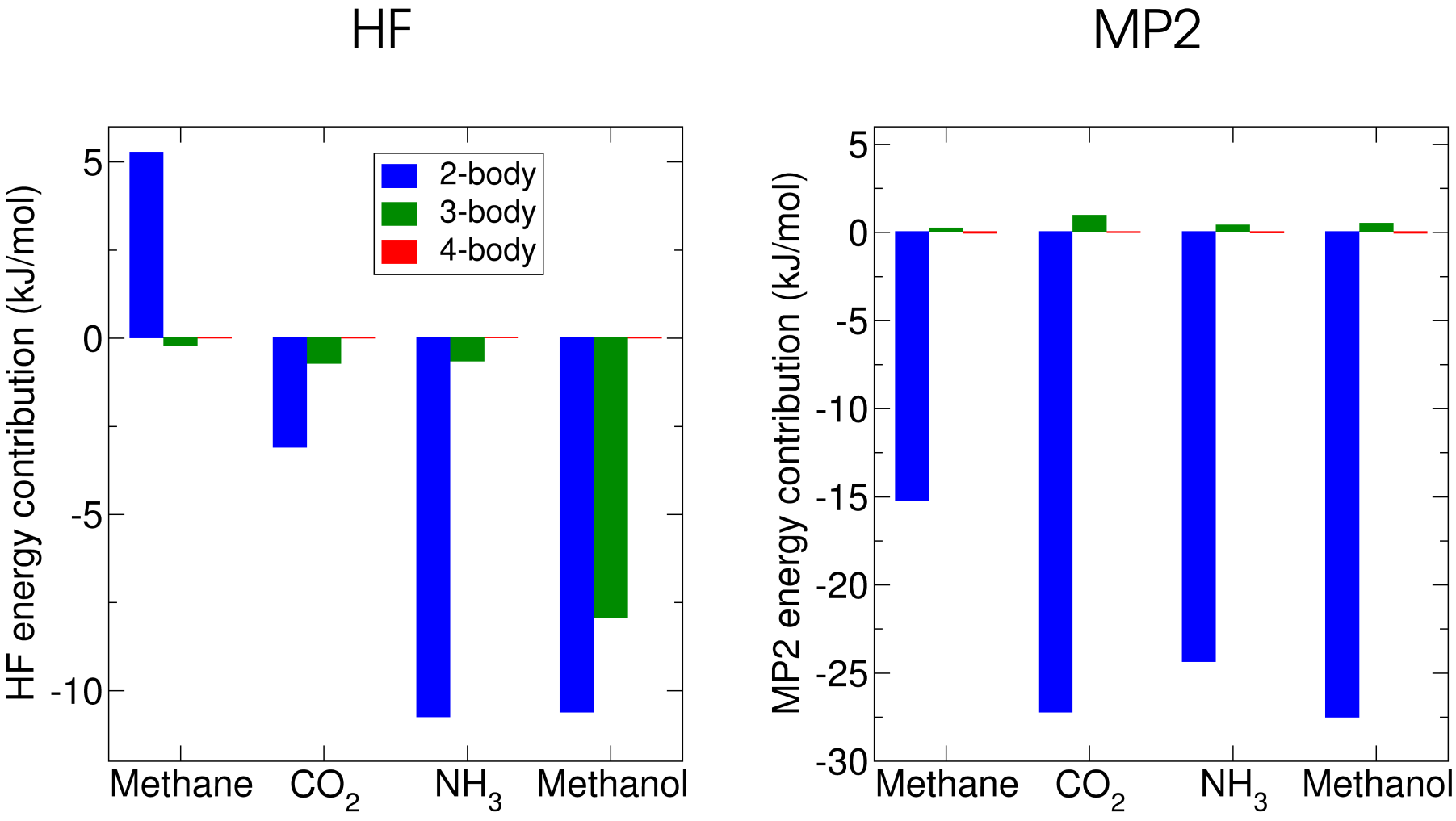
- Typically $10^3 - 10^4$ dimers and $10^4 - 10^5$ trimers.
- Automatic generation of dimers and trimers, input files, summing energies, ...
- Automatic job submition, recognition of failure, ...

Periodic calculations vs. many-body expansion

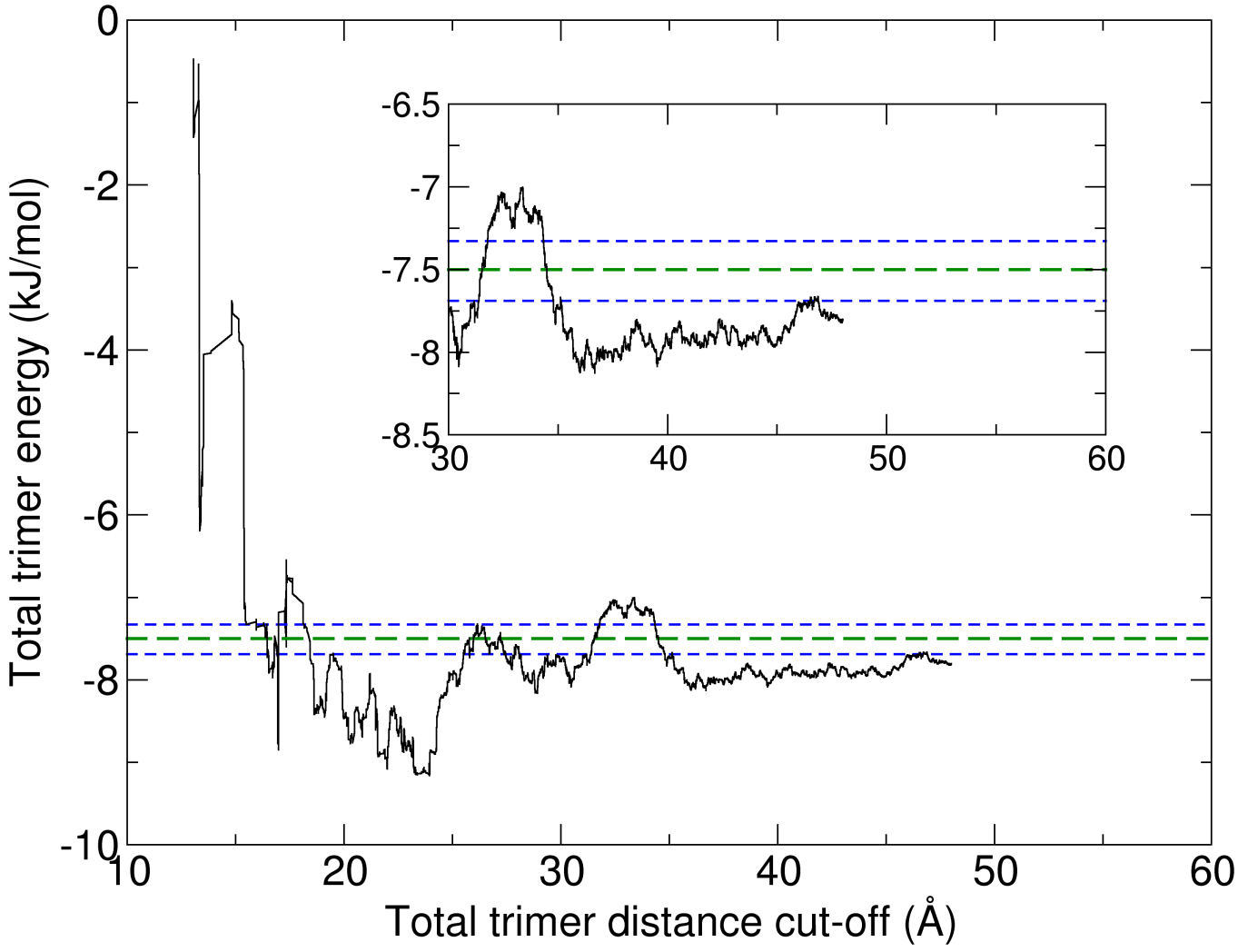
	HF (MBE)	HF (PBC)	MP2 (MBE)	MP2 (PBC)
Methane	5.07	5.06	−15.0	−15.1
CO_2	−3.8	−3.8	−26.2	−26.3
Ammonia	−11.4	−11.1	−23.9	−24.2
Methanol	−18.4	−18.1	−37.0	−36.8

Data in kJ/mol

MBE components

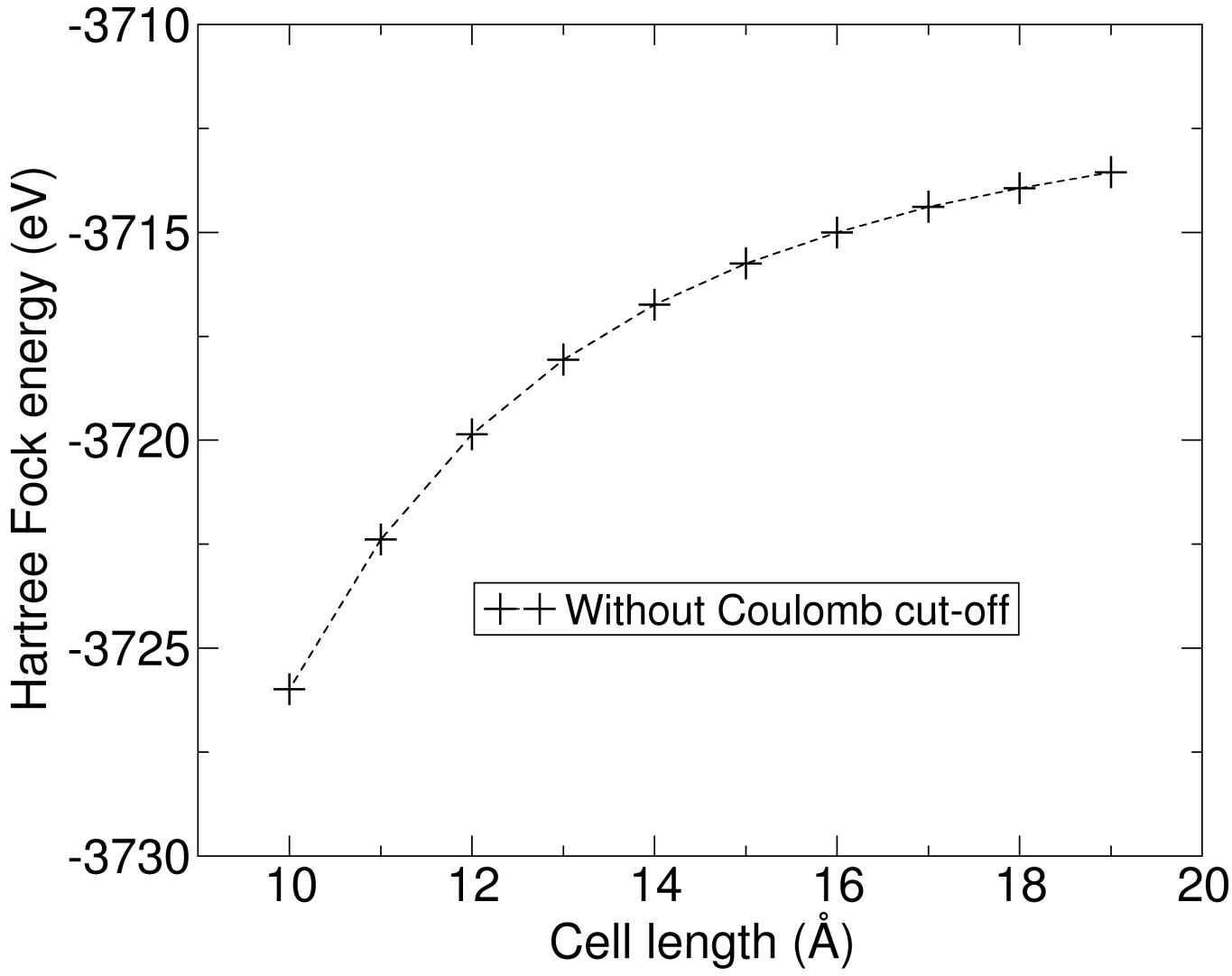


Methanol Hartree-Fock



Periodic Hartree-Fock – Methane molecule

- Slow convergence due to singular interaction with periodic images.



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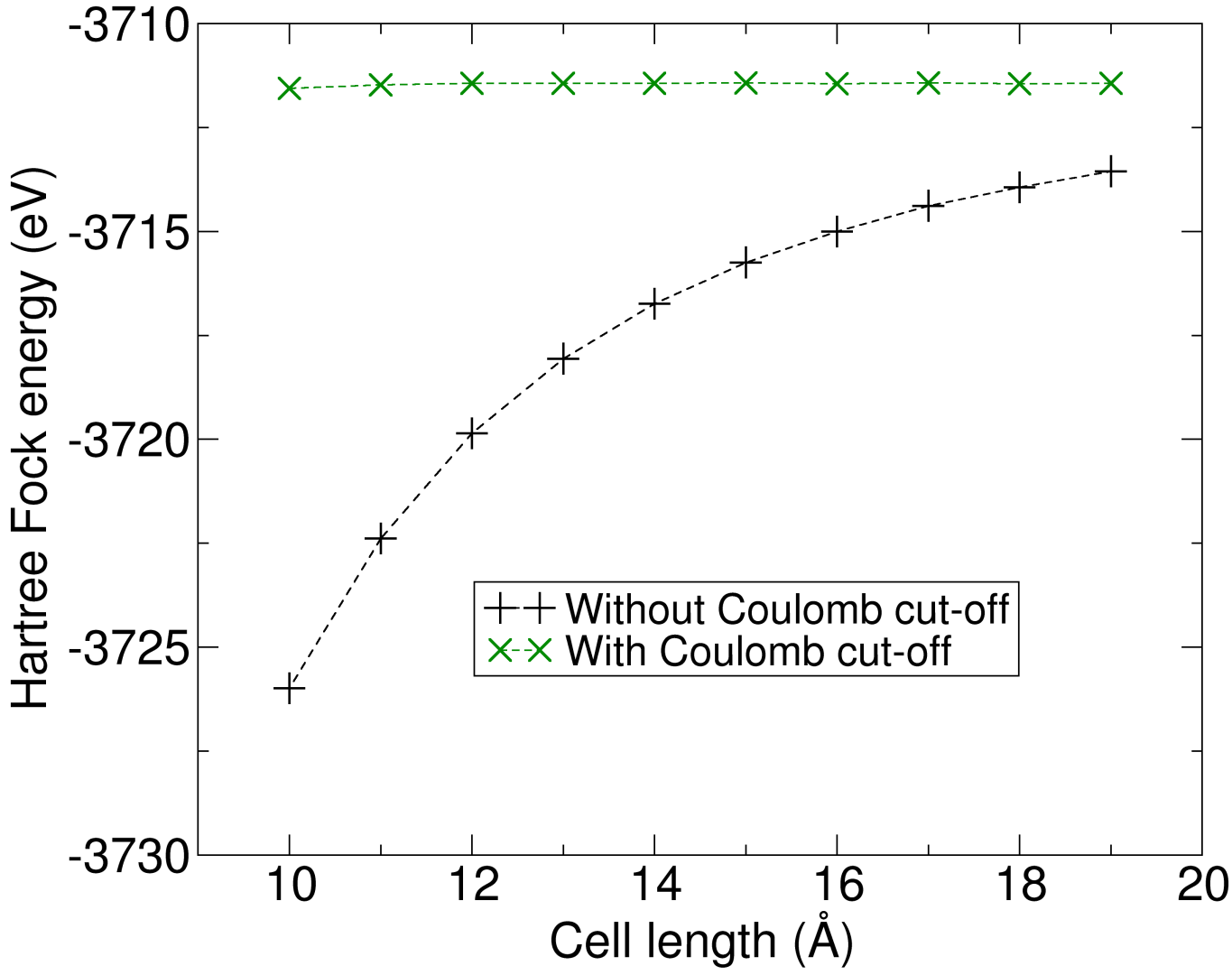
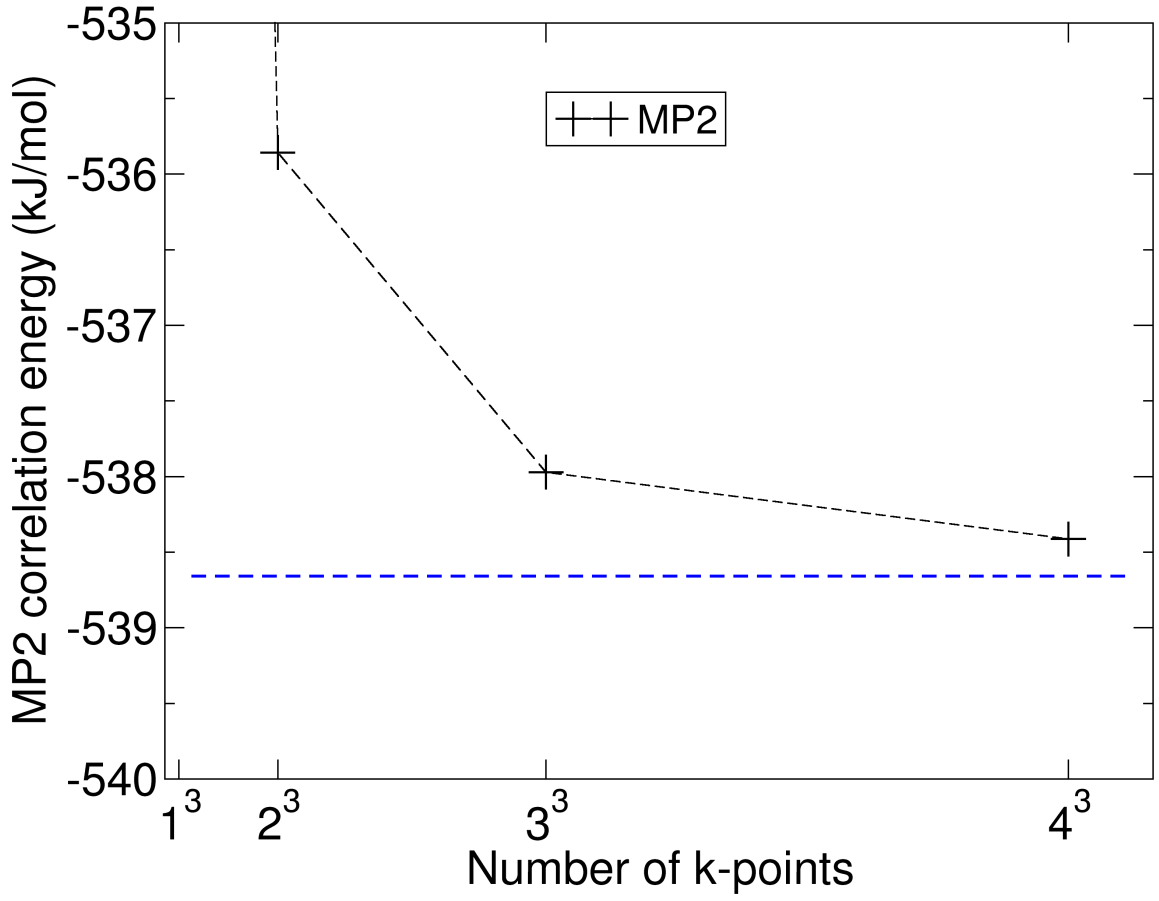
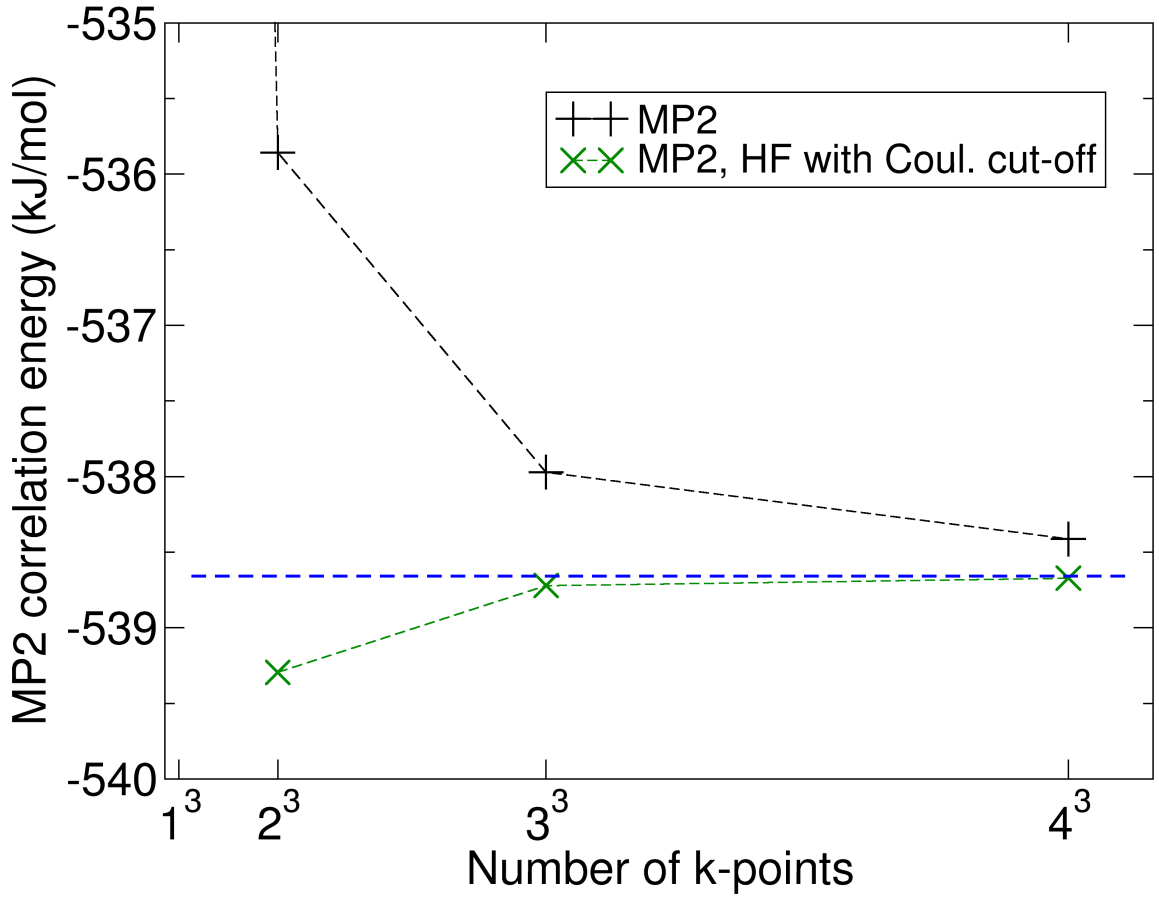


Periodic MP2 – Methane solid



k-points	CPU hours	RAM (GB)
2×2×2	0.01	2
3×3×3	8	27
4×4×4	210	160

Periodic MP2 – Methane solid



k-points	CPU hours	RAM (GB)
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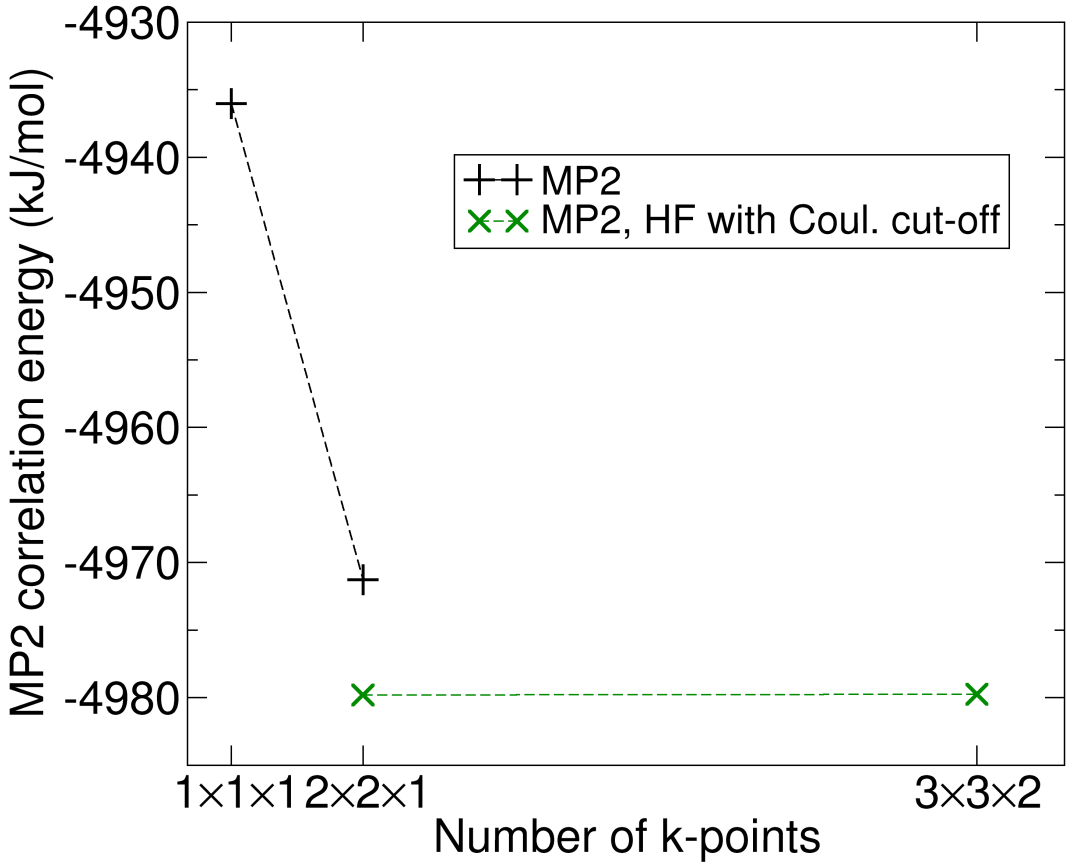
Periodic MP2 – Methanol solid



k-points	CPU hours	RAM (GB)
1×1×1	4	8
2×2×1	1600	220
3×3×2	60000	4300

Conclusions

- To understand the accuracy of a method, we need precise data (converged with parameters).
- Much more difficult to attain for correlated methods.
- MBE and periodic calculations agree well for methane and CO_2, less for hydrogen-bonded systems.
- Avoiding HF singularity improves also the k-point convergence MP2 energies.

Thank you for your attention.

MSC grant No. 658705

PRIMUS grant

ERC grant APES

CPU time:

cesnet metacentrum

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