Many-body expansion of errors of theoretical binding energies

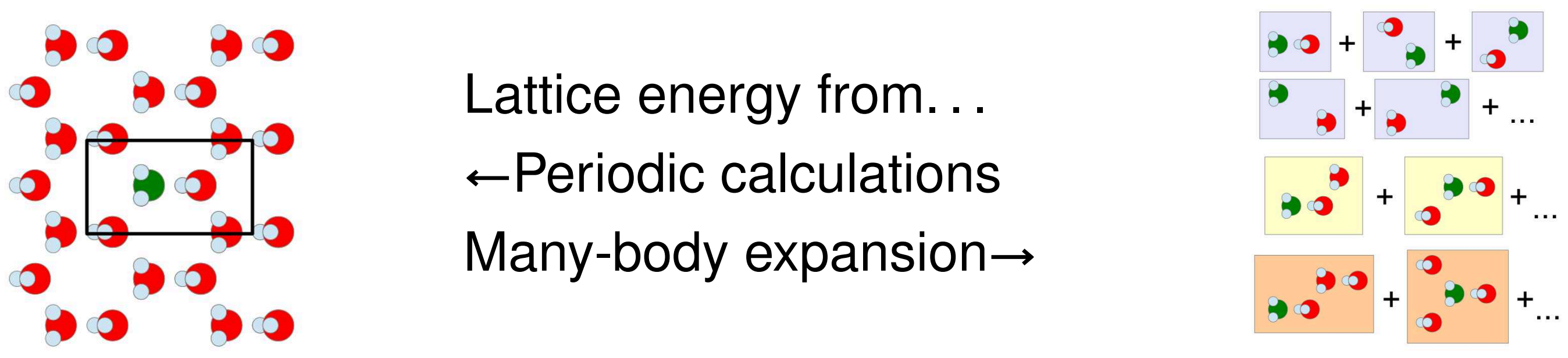
J. Klimeš, K. N. Pham, M. Modrzejewski, and S. Yourdkhani
Department of Chemical Physics and Optics
Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Introduction

- To describe reliably small energy differences occurring for polymorphs, accurate theoretical methods and precise set-up need to be used. We show that many-body expansion is a very useful tool to understand the different errors of methods used to obtain properties of molecular solids.
- By **accuracy** we denote errors due to approximations of theoretical method, e.g., by using density functional theory or Hartree-Fock instead of Full CI.
- **Precision** gives the error due to approximations in the computational set-up, such as basis-set, *k*-point sampling, . . .

Periodic calculations vs. many-body expansion [1]

- Binding energies of molecular solids can be obtained by employing periodic boundary conditions (PBC) or from many-body expansion (MBE).
- If the same structure and method are used, both approaches should yield identical results. Testing if this is actually true provides independent verification of the implementations and of the numerical set-up.



Lattice energy from. . .
←Periodic calculations
Many-body expansion→

E [kJ/mol]		2b	2b & 3b	2b, 3b, & 4b	PBC
Ethane	PBE	−5.55	1.31	−0.50	−0.43
	HF	12.95	12.33	12.36	12.42
Ethylene	PBE	−8.57	−1.71	−3.57	−3.52
	HF	9.38	9.00	9.02	8.96

Precision of pseudopotentials [2]

- There is often an 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.
- 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 kJ/mol can be observed.

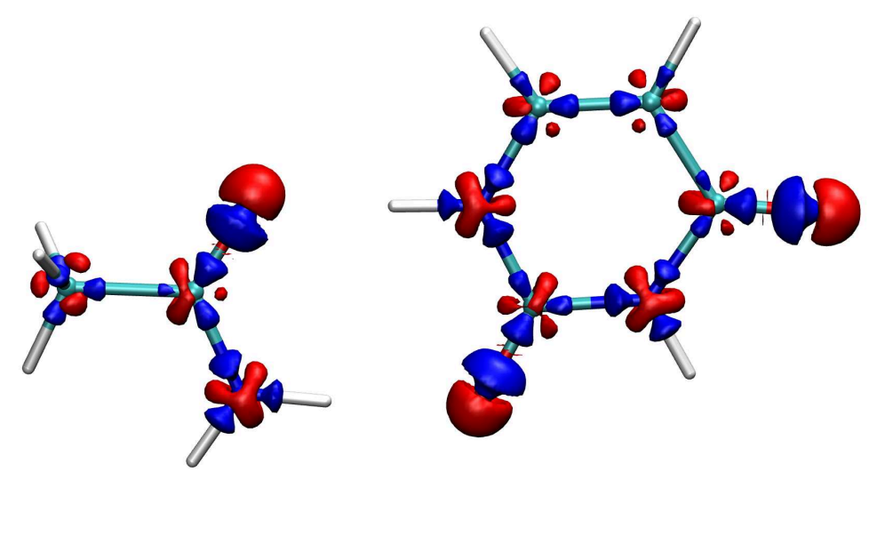
↓PBE-D3^{BJ} binding energies and their differences obtained with different PAWs. Default D3^{BJ} settings were used in either VASP or QuantumEspresso. Data in kJ/mol.

Δ*E* [kJ/mol]	VASP hard	VASP standard	QE precision
MALIAC13	−135.2	−136.8	−132.4
MALIAC14	−135.7	−137.3	−133.2
Δ	−0.5	−0.5	−0.8
PYRZIN15	−114.0	−114.7	−109.2
PYRZIN18	−116.5	−117.2	−111.7
PYRZIN19	−113.6	−114.0	−108.5
Δ_{18-15}	−2.5	−2.6	−2.5
QQQAXG02	−120.9	−121.3	−114.4
QQQAXG05	−120.5	−120.9	−114.7
QQQAXG15	−117.1	−117.1	−108.9
Δ_{5-2}	0.4	0.4	−0.4

↓PBE binding energies and their differences obtained with different PAWs. Data in kJ/mol.

Δ*E* [kJ/mol]	VASP hard	VASP standard	QE precision
MALIAC13	−78.1	−79.6	−79.7
MALIAC14	−82.0	−83.6	−83.6
Δ	−3.9	−4.0	−3.9

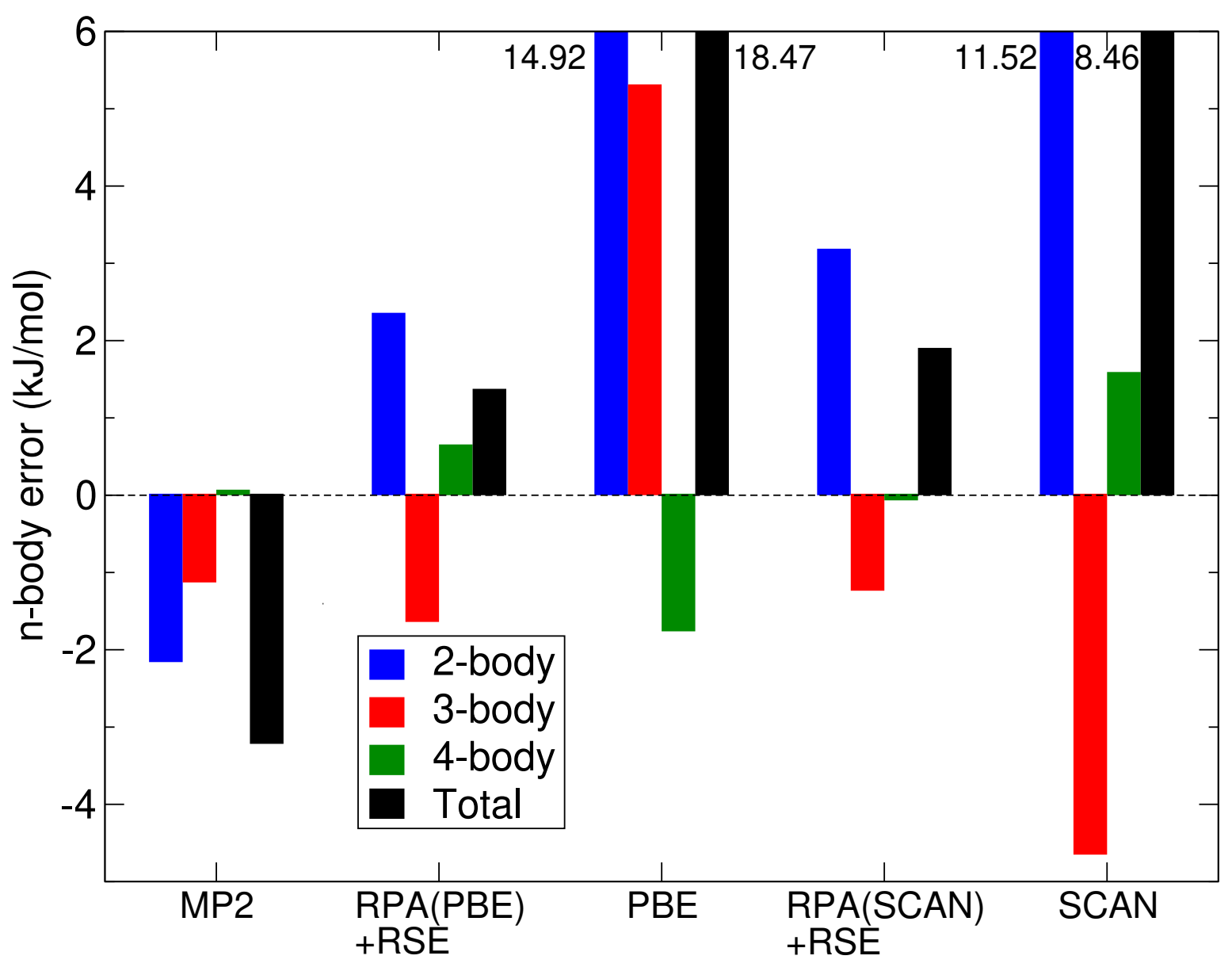
- We tested PAWs provided by the VASP code using interaction energies of molecular dimers. We found that the problem is due to incorrect description of the electron density.
- Cheap ‘soft‘ PPs or PAWs are likely suitable for energy screening with reduced computational cost in CSP. Moreover, the error can be reduced with a correction presented in [2].



←Density error of acetamide-uracil dimer caused by the use of Standard PAW datasets in VASP. The density obtained with Hard PAWs was used as a reference.

Reference MBE data [3]

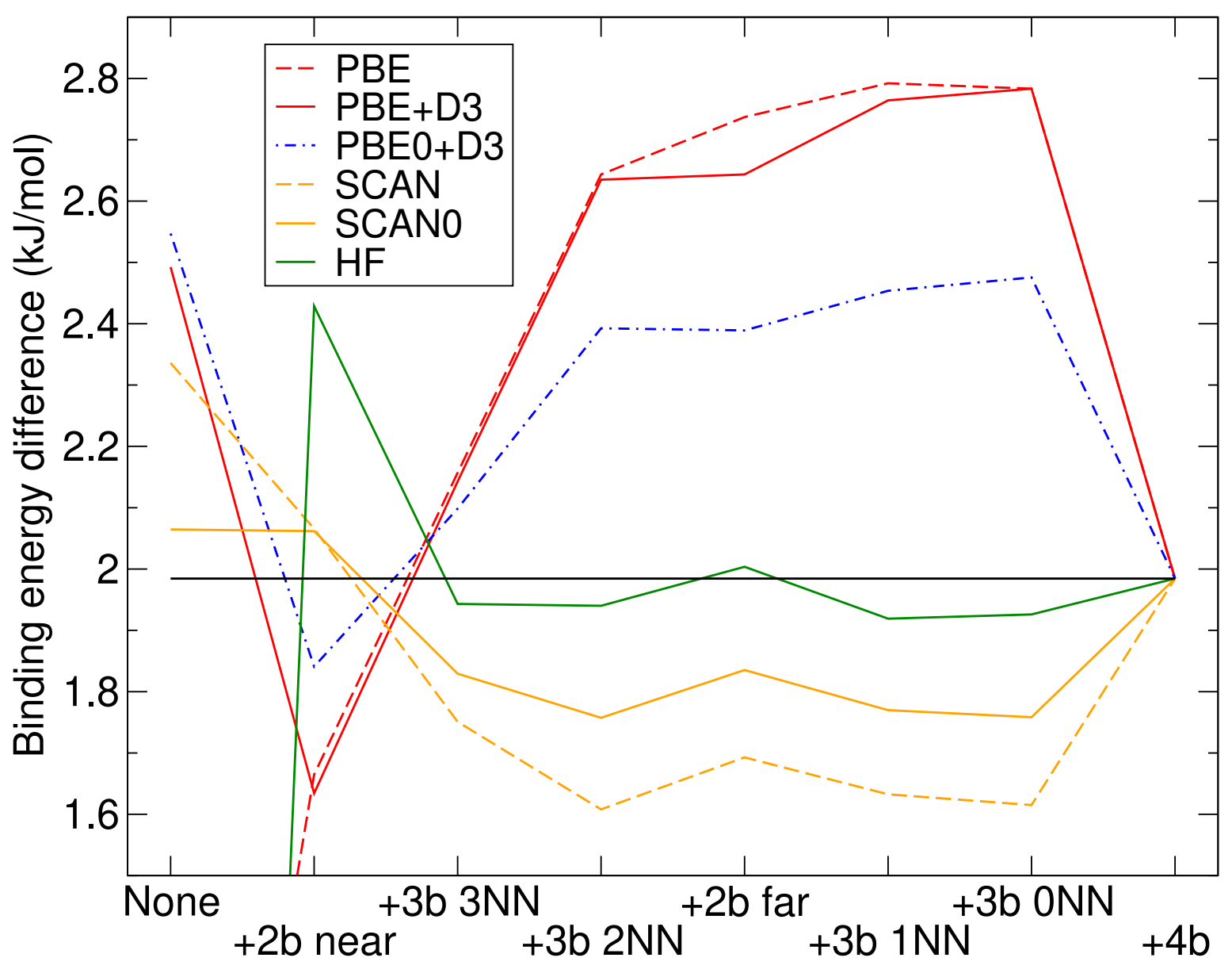
- We use MBE to obtain reference energies at CCSD(T) level.
- We then use them to test the accuracy of different methods, from DFT approximations to perturbation theory (MP2, MP3, . . .) or the random-phase approximation (RPA).



←Error of many-body energies obtained for ethylene. CCSD(T) was used as a reference. DFT errors are too large and reduce the quality of RPA energies based on the DFT states.

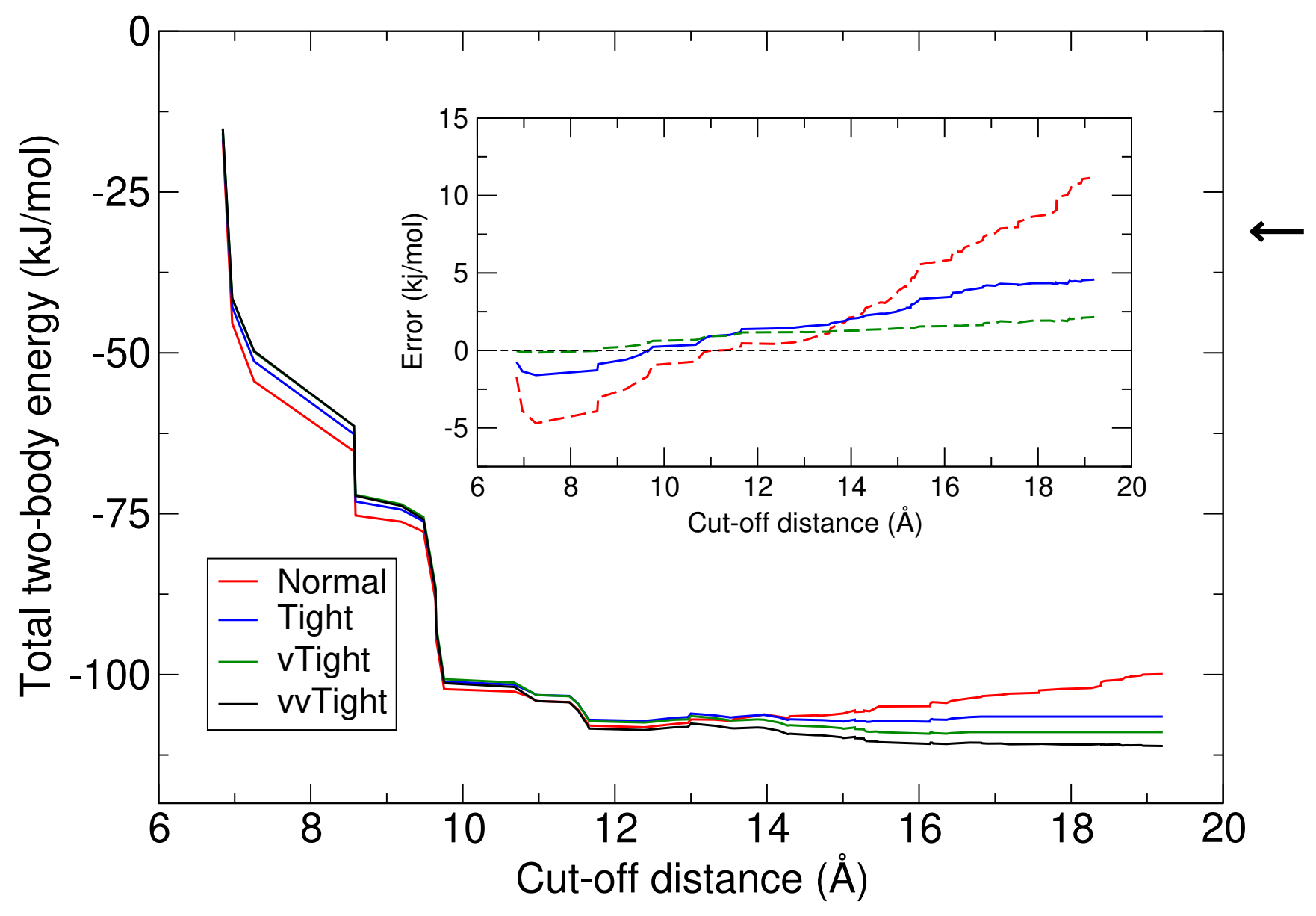
Reference energy differences for polymorphs

- Calculating CCSD(T) is costly, we test several ways to reduce the computational cost.
- **Correction scheme** (subtractive embedding): Use computationally cheaper method to obtain first guess of binding energy and then use MBE to improve the value.



←Energy difference between two structures of acetylene. From left to right more and more MBE contributions at the CCSD(T) level are used to correct the initial difference, shown at the "None" mark.

- **Low scaling CCSD(T) methods**: Approximate approaches that exploit the locality of the largest contributions to the CCSD(T) energy. They reduce computational time and allow calculations of energies of molecules with tens of heavy atoms.



←Two-body energy of benzophenone BPHENO11 structure obtained with LNO-CCSD(T) implemented in the `mrcc` programme. Different precision settings were used. The inset shows the error of the more approximate settings with respect to the `vvTight`.

Summary

- Binding energies of molecular solids can be substantially affected by the pseudopotential/PAW error. For systems with hydrogen bonds, hard pseudopotentials or PAWs are needed.
- Large many-body errors of simple DFT functionals reduce their suitability for correction scheme.
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References

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