This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 890300.

UNIVERSITÄT GRAZ
UNIVERSITY OF GRAZ

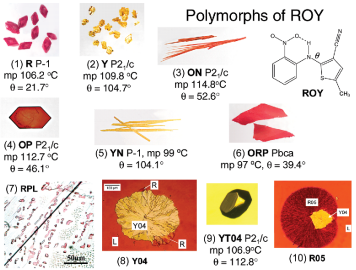
Improving the Description of Molecular Crystals via Multimer Embedding

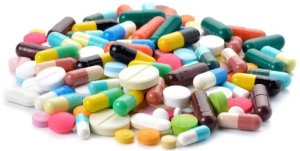
Alexander List, Johannes Hoja, A. Daniel Boese

University of Graz, Austria

Molecular Crystals

- Solids composed of molecules
- Non-covalent interactions
- Can exhibit polymorphism
- Small energy differences
- Properties differ between polymorphs



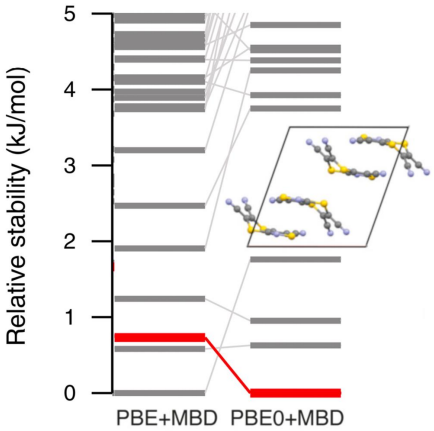


Polymorphs can exhibit different

- Solubilities
- Kinetic stabilities
- Melting points
- THz spectra
- NMR chemical shifts
- Elastic constants
- Heat capacities
- Conductivities
- Colors

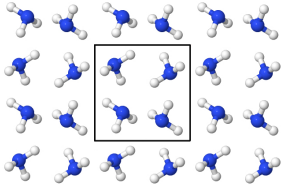
L. Yu, *Acc. Chem. Res.* 43, 1257 (2010).

- Small lattice energy differences between polymorphs require accurate methods
- Vibrational free energies often needed for correct polymorph stabilities
- Hybrid DFT desirable
- Converged periodic calculations using hybrid functionals are often computationally too expensive



J. Hoja, H. Y. Ko, M. A. Neumann, R. Car, R. A. DiStasio, A. Tkatchenko, *Sci. Adv.* 5, eaau3338 (2019).

$$E(\textbf{high}) \approx$$



only low

$$+ \sum_{\text{Mon.}}$$

high − low

ME1

$$+ \sum_{\text{Dimers}}$$

high − low

ME2(*n*Å)

$$+ \sum_{\text{Trimers}}$$

ME3(*n*Å)

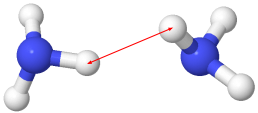
$$E_{\text{per}}^{\text{high}} \approx E_{\text{per}}^{\text{low}} + \sum_i n_i \Delta E_i + \sum_{i>j} \frac{n_{ij}}{2} \Delta E_{ij}^{\text{int}} + \sum_{i>j>k} \frac{n_{ijk}}{3} \Delta E_{ijk}^{\text{int}}$$

$$E_{\text{latt}}^{\text{high}} = \frac{E_{\text{per}}^{\text{high}}}{Z} - E_{\text{mon}}^{\text{high}}$$

$$\Delta E = E_{\text{high}} - E_{\text{low}} \qquad E_{ij}^{\text{int}} = E_{ij} - E_i - E_j$$

$$E_{ijk}^{\text{int}} = E_{ijk} - E_{ij}^{\text{int}} - E_{ik}^{\text{int}} - E_{kj}^{\text{int}} - E_i - E_j - E_k$$

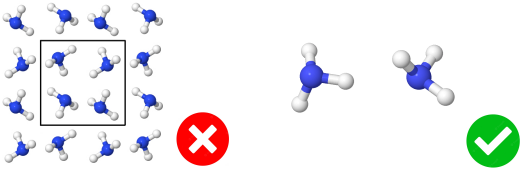
Multimers within cutoff distance:



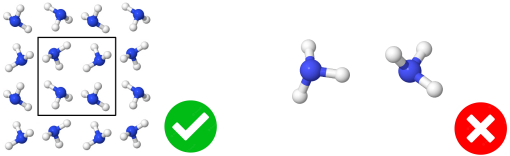
A. D. Boese, J. Sauer, *Cryst. Growth Des.* 17, 1636 (2017).
J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).
A. List, J. Hoja, A. D. Boese, in preparation.

Which Kind of Basis Set for Multimer Embedding?

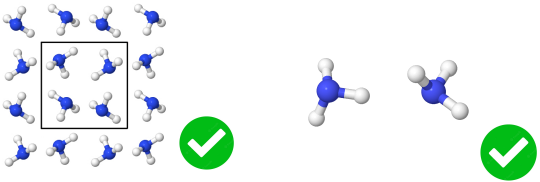
Gaussian basis set:



Plane waves:



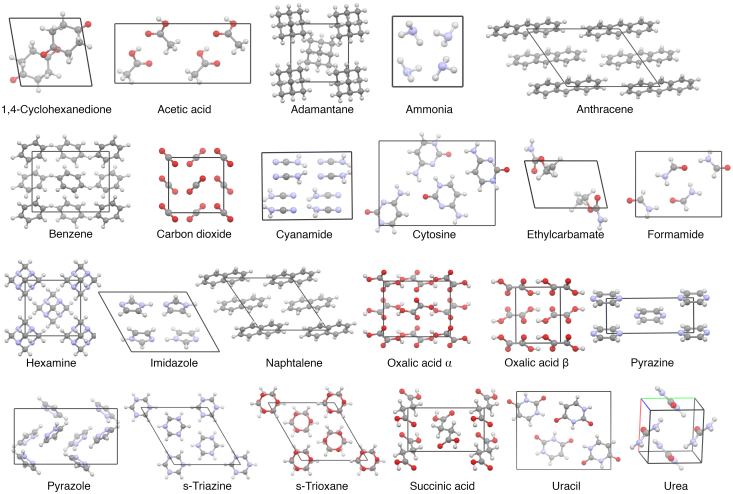
Numeric atom-centered basis set:



FHI-aims

The ab initio materials simulation package

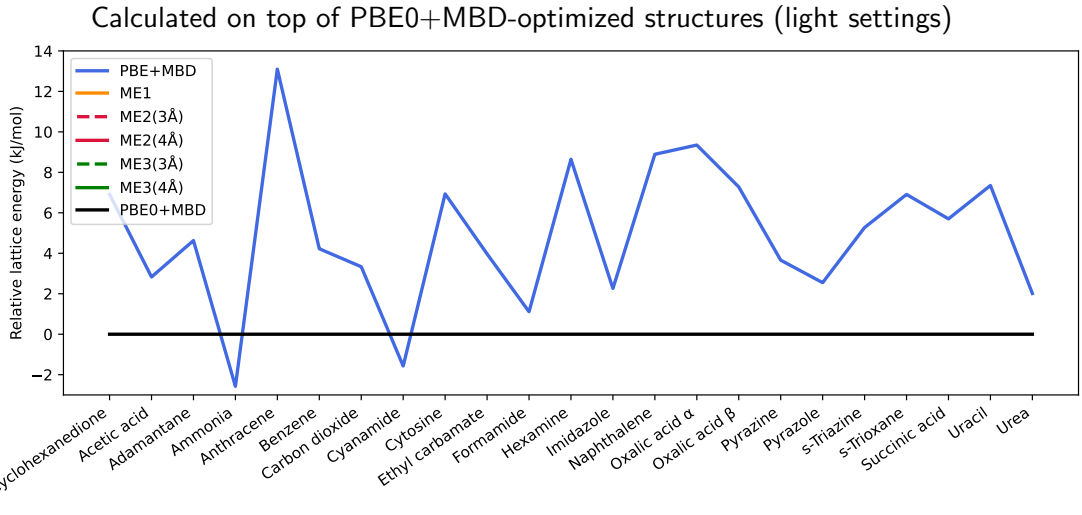
X23 Benchmark Set for Molecular Crystals



- High: PBE0+MBD
- Low: PBE+MBD
- Light basis set

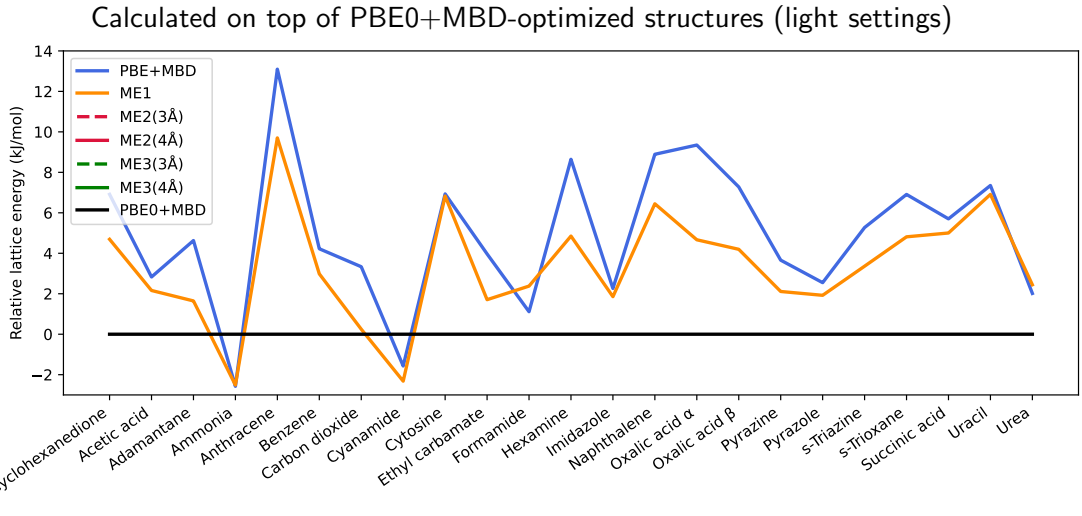
A.M. Reilly and A. Tkatchenko, *J. Chem. Phys.* 139, 024705 (2013).

Multimer Embedding for Lattice Energies



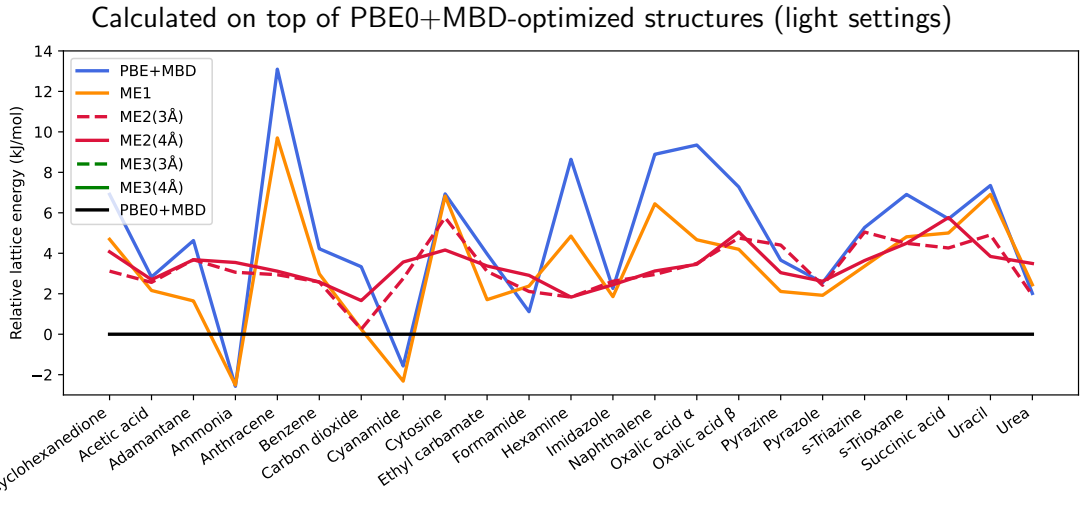
J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).

Multimer Embedding for Lattice Energies



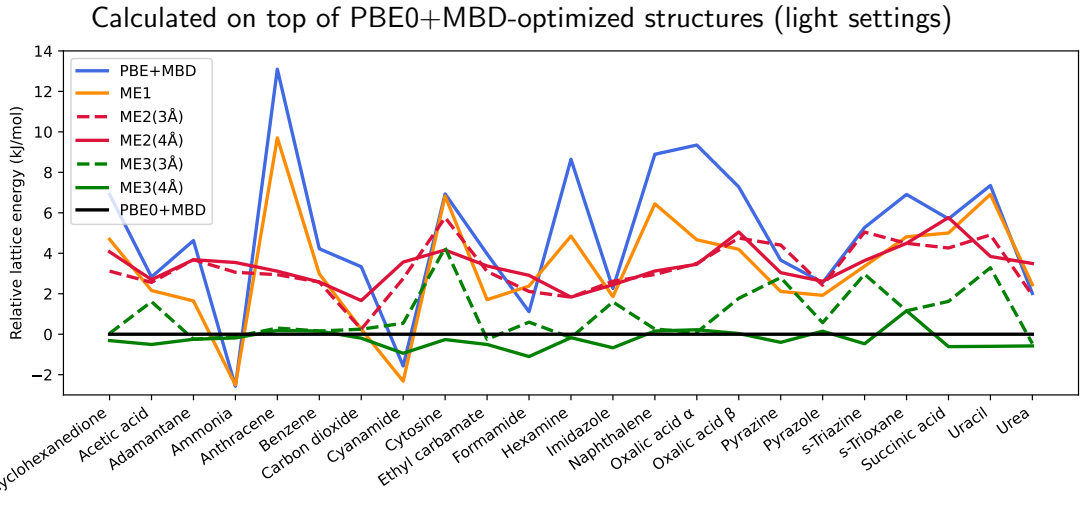
J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).

Multimer Embedding for Lattice Energies



J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).

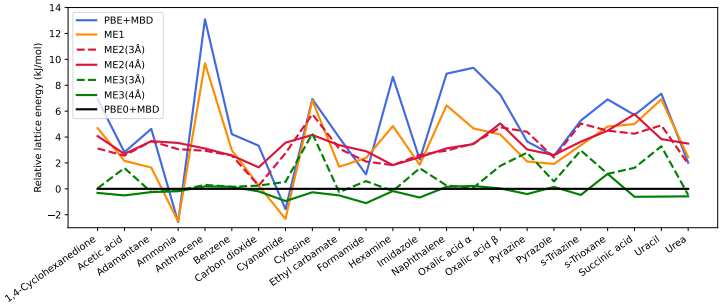
Multimer Embedding for Lattice Energies



J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).

Errors of lattice energies in kJ/mol:

Method	ME	MAE	MAX
PBE+MBD	4.9	5.3	13.1
ME1	3.3	3.7	9.7
ME2(3Å)	3.3	3.3	5.8
ME2(4Å)	3.4	3.4	5.8
ME3(3Å)	1.0	1.1	4.3
ME3(4Å)	-0.2	0.4	1.2



Trimers needed for convergence to 1 kJ/mol

J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).

Embedding forces on atom a:

$$\mathbf{f}_{\mathrm{per}}^{\mathrm{high}}(a) \approx \mathbf{f}_{\mathrm{per}}^{\mathrm{low}}(a) + \Delta\mathbf{f}_i(a) + \sum_j \Delta\mathbf{f}_{ij}^{\mathrm{int}}(a) + \sum_{j>k} \Delta\mathbf{f}_{ijk}^{\mathrm{int}}(a)$$

$$\mathbf{f}_{ij}^{\mathrm{int}}(a) = \mathbf{f}_{ij}(a) - \mathbf{f}_i(a)$$

$$\mathbf{f}_{ijk}^{\mathrm{int}}(a) = \mathbf{f}_{ijk}(a) - \mathbf{f}_{ij}^{\mathrm{int}}(a) - \mathbf{f}_{ik}^{\mathrm{int}}(a) - \mathbf{f}_i(a)$$

Errors compared to PBE0+MBD results calculated at PBE+MBD-optimized structures:

	Forces (eV/Å)	
Method	**MAE**	**MAX**
PBE+MBD	0.226	1.422
ME1	0.023	0.216
ME2(3Å)	0.008	0.120
ME2(4Å)	0.006	0.055
ME3(3Å)	0.006	0.107
ME3(4Å)	0.004	0.043

J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).
A. List, J. Hoja, A. D. Boese, in preparation.

Embedding stress tensor components:

$$\sigma_{pq}^{\text{high}} \approx \sigma_{pq}^{\text{low}} - \frac{1}{V}\sum_{i}\sum_{a} n_i r_{i,p}(a)\,\Delta f_{i,q}(a) - \frac{1}{V}\sum_{i>j}\sum_{a} \frac{n_{ij}}{2} r_{ij,p}(a)\,\Delta f_{ij,q}^{\text{int}}(a) - \frac{1}{V}\sum_{i>j>k}\sum_{a} \frac{n_{ijk}}{3} r_{ijk,p}(a)\,\Delta f_{ijk,q}^{\text{int}}(a)$$

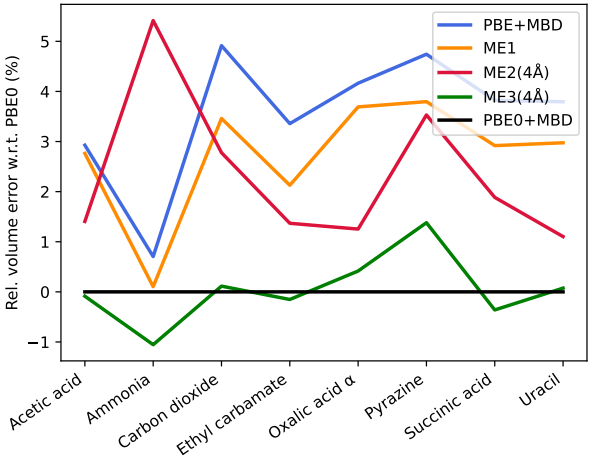
Errors compared to PBE0+MBD results calculated at PBE+MBD-optimized structures:

	Stress (eV/Å^3)	
Method	**MAE**	**MAX**
PBE+MBD	0.0190	0.0496
ME1	0.0009	0.0034
ME2(3Å)	0.0007	0.0039
ME2(4Å)	0.0007	0.0039
ME3(3Å)	0.0003	0.0032
ME3(4Å)	0.0002	0.0032

J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).
A. List, J. Hoja, A. D. Boese, in preparation.

Errors of cell volumes in % compared to PBE0+MBD results (reduced X23 set):

Method	ME	MAE	MAX
PBE+MBD	3.55	3.55	4.91
ME1	2.73	2.73	3.80
ME2(4Å)	2.34	2.34	5.41
ME3(4Å)	0.04	0.45	1.38



J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).
A. List, J. Hoja, A. D. Boese, in preparation.

- Finite displacements within sufficiently large super cells
- Number of multimers to calculate increases significantly

Multimers to calculate for Ammonia:

Multimer	SP	VIB
Monomers	1	8
Dimers (3Å)	2	96
Dimers (4Å)	3	144
Trimers (3Å)	7	192
Trimers (4Å)	11	480

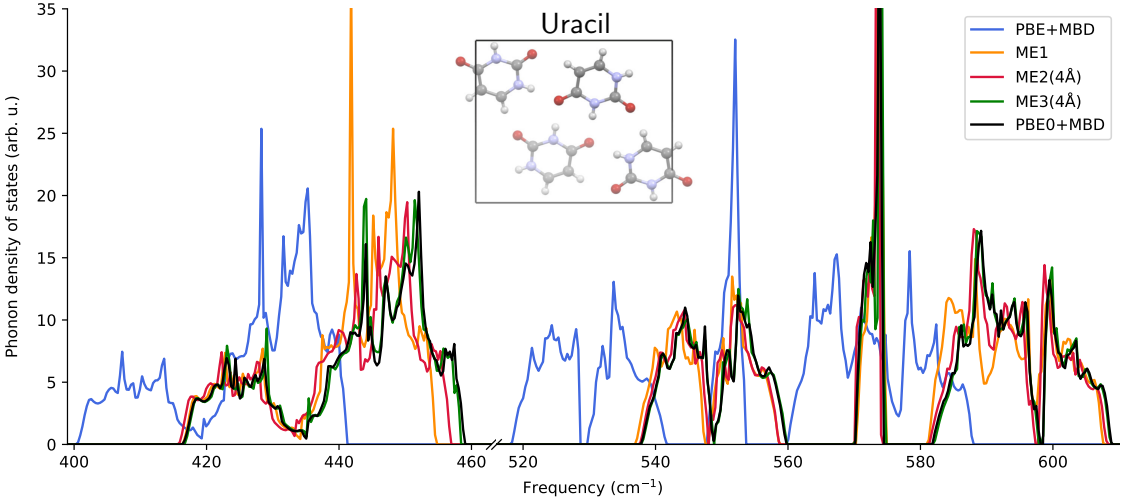
Errors compared to PBE0+MBD results:

Quantity	Method	ME	MAE
	PBE+MBD	-48.2	49.0
$\nu(\Gamma)$	ME1	-1.2	4.2
(cm^{-1})	ME2(3Å)	-1.1	2.5
	ME2(4Å)	-1.0	2.7
	PBE+MBD	-10.9	10.9
F_{vib}	ME1	-1.2	1.2
(kJ/mol)	ME2(3Å)	-0.8	0.8
	ME2(4Å)	-0.8	0.8

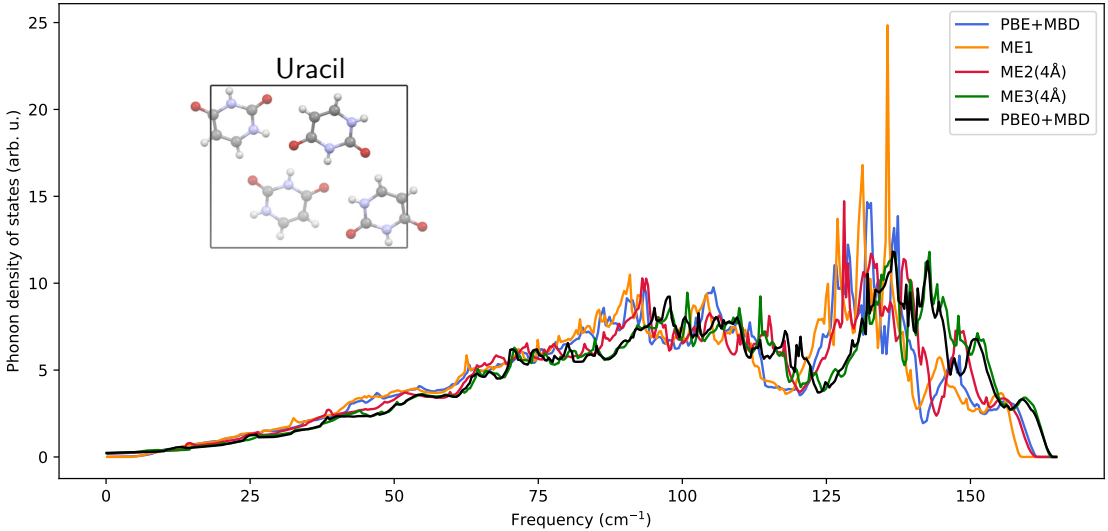
Harmonic vibrational free energies (per molecule) at 300 K

J. Hoja, A. List, A. D. Boese, submitted, arXiv:2209.02687 (2022).

Multimer Embedding for Harmonic Vibrational Properties – Trimers



Multimer Embedding for Harmonic Vibrational Properties – Trimers



Timings for Multimer Embedding in FHI-aims

Relative timings (light basis set):

Method	Ammonia	Succinic acid
PBE+MBD	1.0	2.7
ME1	1.0	2.9
ME2(3Å)	1.2	7.9
ME2(4Å)	1.2	9.6
ME3(3Å)	2.0	16.4
ME3(4Å)	2.6	34.1
PBE0+MBD	3.4	15.3

calculated on 4 cores

Relative timings (tight basis set):

Method	Ammonia	Succinic acid
PBE+MBD	1.0	2.7
ME1	1.0	3.6
ME2(3Å)	1.2	24.8
ME2(4Å)	1.3	33.2
ME3(3Å)	2.8	64.1
ME3(4Å)	3.8	151.3
PBE0+MBD	93.3	258.6

calculated on 24 cores

MEmbed: Multimer Embedding Code for Molecular Crystals

- Python package available at https://gitlab.com/membed/membed
- Dependencies: ASE, Phonopy, Spglib
- Input files: geometry.in, membed.in
- Results of all individual calculations saved to an ASE database
- single points, lattice relaxations, phonon calculations

multimer_order	3	
multimer_cutoff	4	
atoms_per_molecule	3	
identify_fragments	automatic	
calculation_type	opt	
f_max	0.005	
symmetrize	True	
calculator	aims	
xc	PBE	lo
xc	PBE0	hi
many_body_dispersion	""	
species_dir	/species_dir/light	
aims_command	"srun aims.x"	
k_grid	"4 4 4"	per
many_body_dispersion	k_grid=5:5:5	per

Conclusions

- Multimer embedding scheme to approximate high-level methods
- Lattice energies can be converged to 1 kJ/mol with trimers
- Trimers needed for cell volumes within 1 % of PBE0 cell volumes
- Harmonic vib. free energies well described at monomer/dimer level

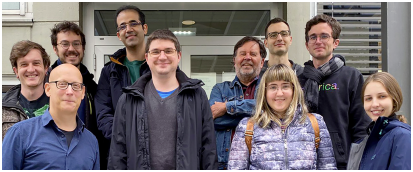
MSCA-IF VibMolCryst

Outlook:

Lattice optimizations/phonons with trimer interactions
Anharmonic vibrational effects
Multimer selection

Embedding code: MEmbed

https://gitlab.com/membed/membed



Boese Group at the University of Graz

Thank you for your attention!