Modelling of surface properties of lamellar zeolites

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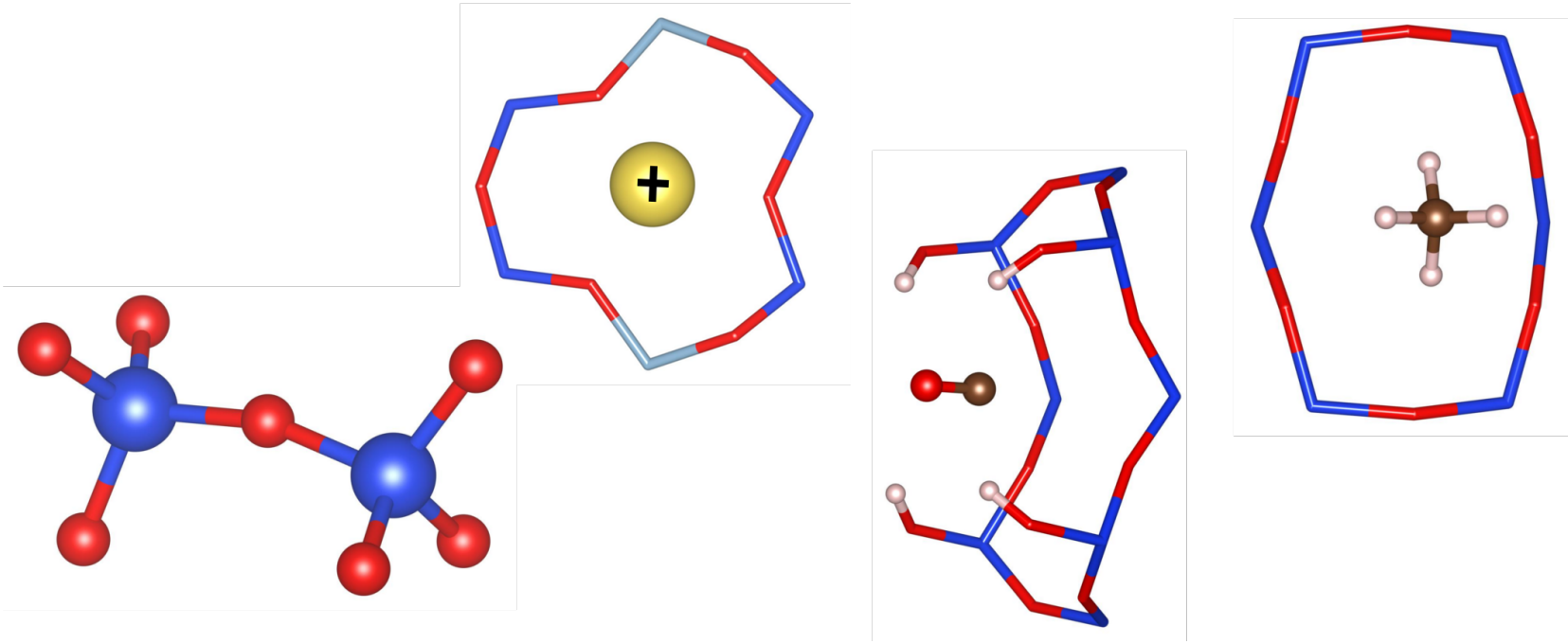
DFT and dispersion

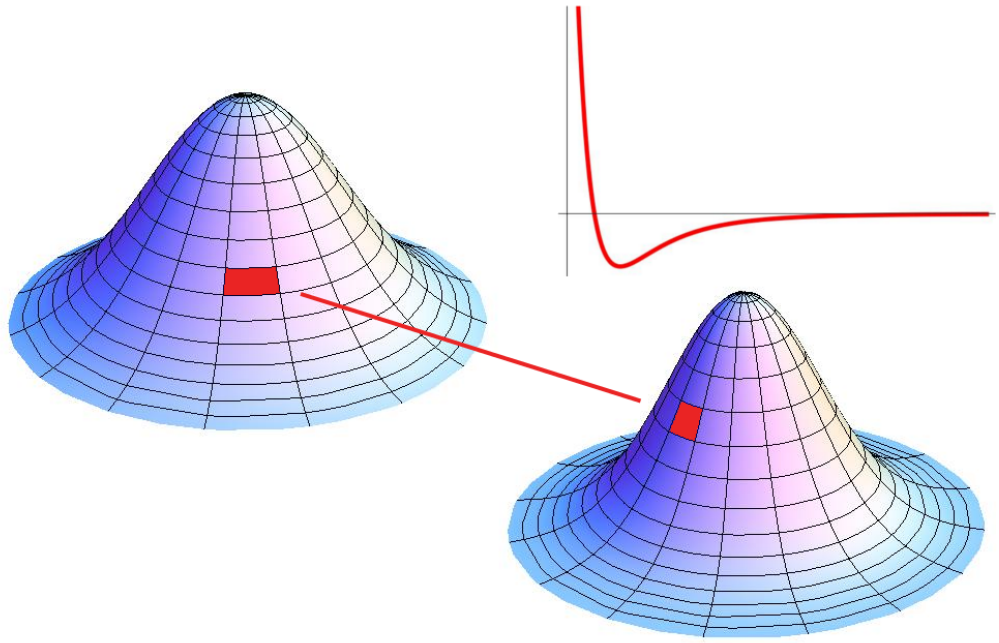
- DFT is a primary tool for modelling zeolites
- Describes covalent bonds and ions very well
- Dipoles interaction or hydrogen bonds might be inaccurate
- Dispersion forces are completely missing in standard DFT



- Standard DFT not suitable for modelling physisorption
- Many competing methods for including dispersion in DFT

vdW-DF[1]

- Non-empirical method for including dispersion in DFT
- Expressed as interaction of electrons

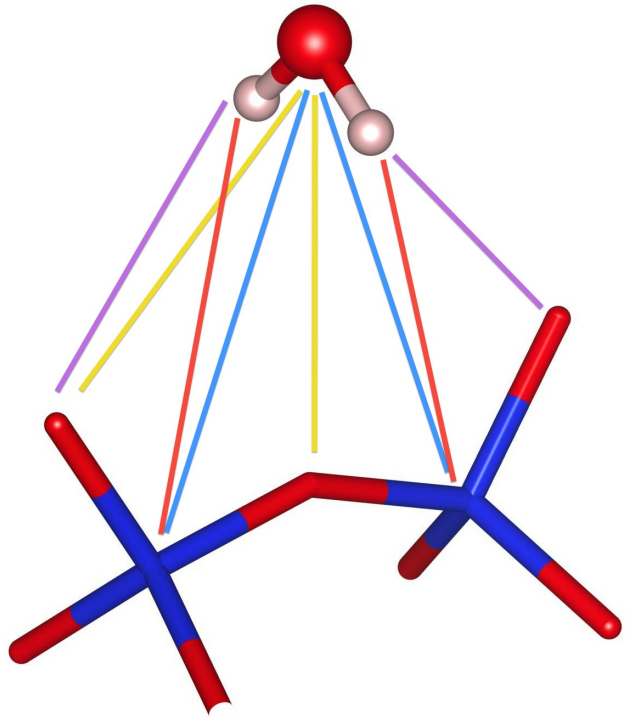


- No need to parametrize ⇒ does not artificially (non-physically) treat errors not related to dispersion
- Slowly becoming a standard method, popular with physicists
- For small models less accurate than empirical methods

[1]Phys. Rev. Lett **92**, 246401 (2004)

DFT/CC[2]

- Empirical correction scheme for DFT
- Expressed as atom–atom pair correction curves (Si–O, O–O,…)

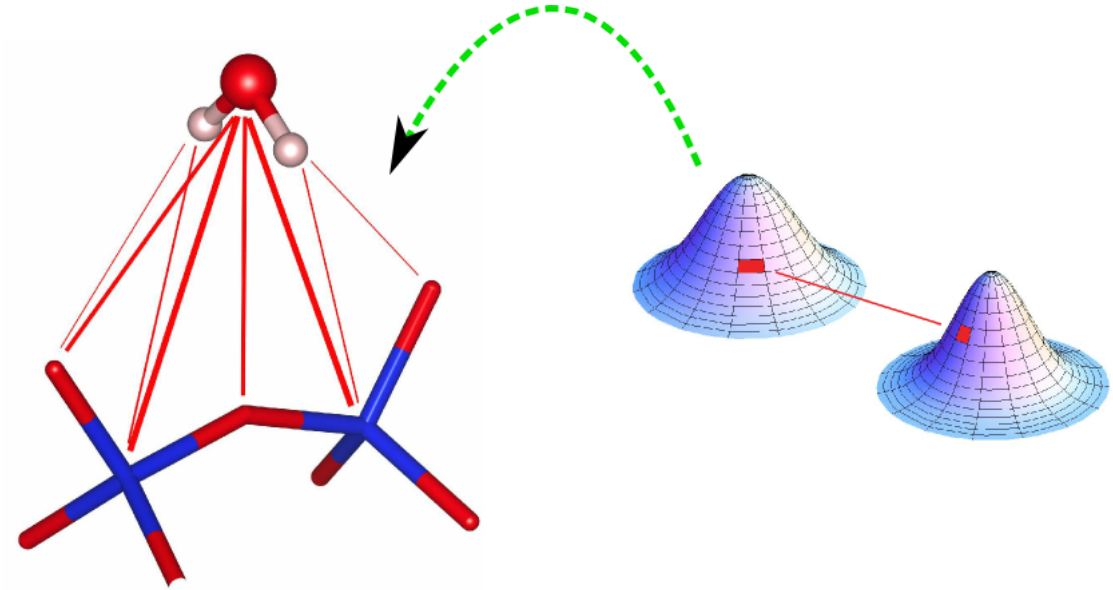


- Trained on accurate energies calculated on small models ⇒ incorporates all kinds of errors (dispersion, electrostatics)
- Very accurate but can be numerically instable
- Alternation of Si and O atoms in zeolites complicates training

[2] J. Chem. Phys **128**, 114102 (2008)

vdW-DF/CC

- “best of both methods”
- Single correction curve for all atom–atom pairs weighed by vdW-DF

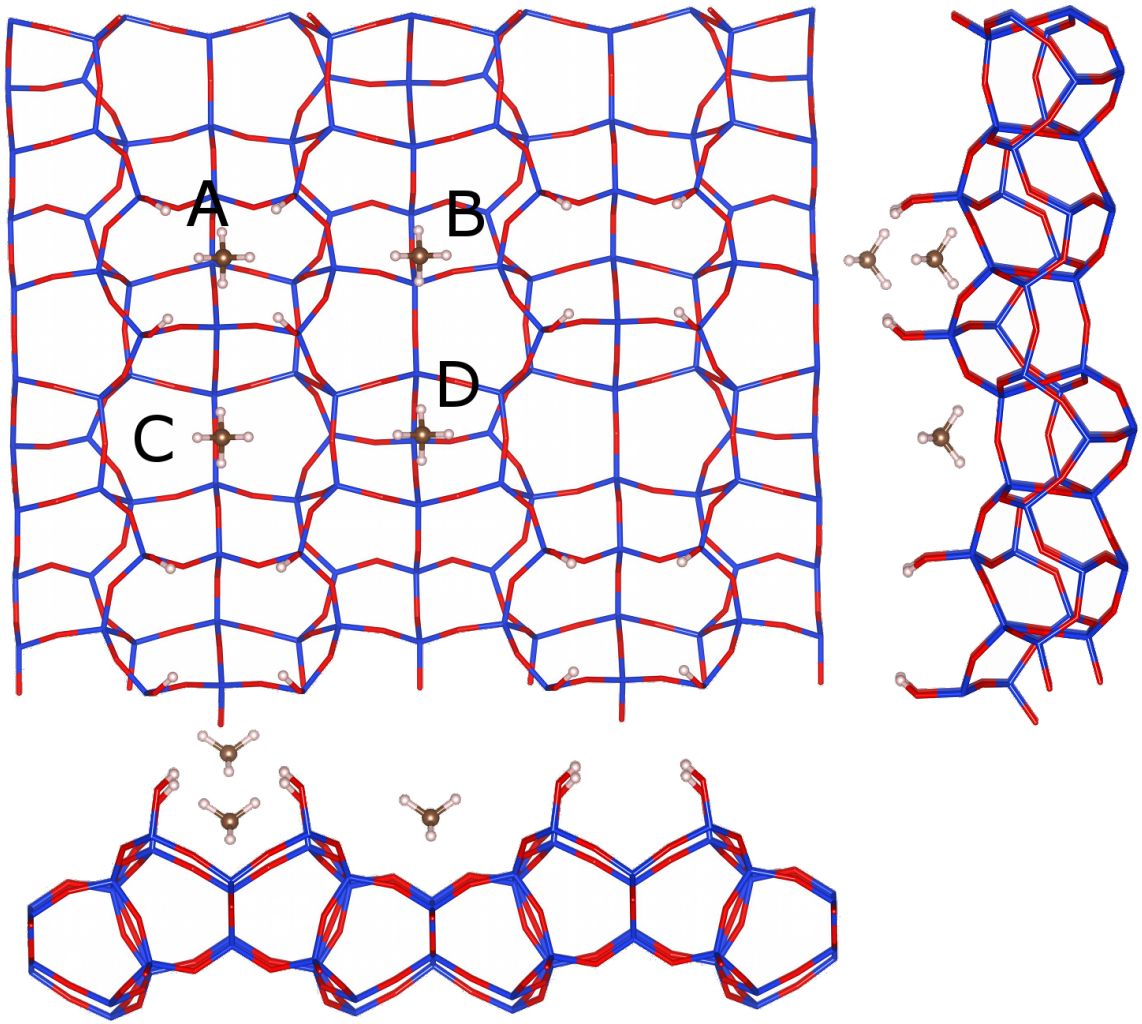


- Uses vdW-DF as a physical constraint to avoid artefacts
- Uses DFT/CC-like training on small models for high accuracy
- Expectations: more accurate than vdW-DF, more robust than DFT/CC

Studied systems

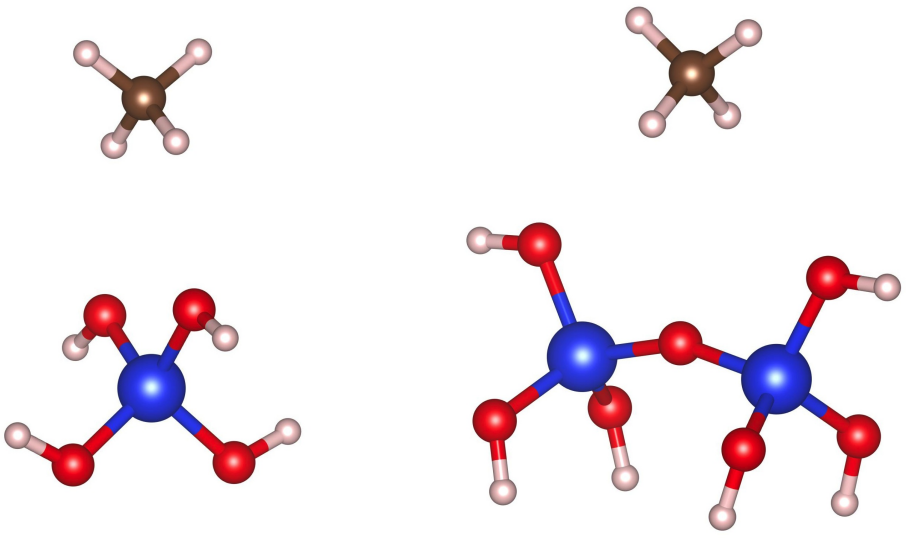
- Interaction of small molecules with zeolitic lamellas
- IWW, IWV, UTL, ITH, IWR, ITR
- CH_4, CO, CO_2, H_2, N_2, H_2O

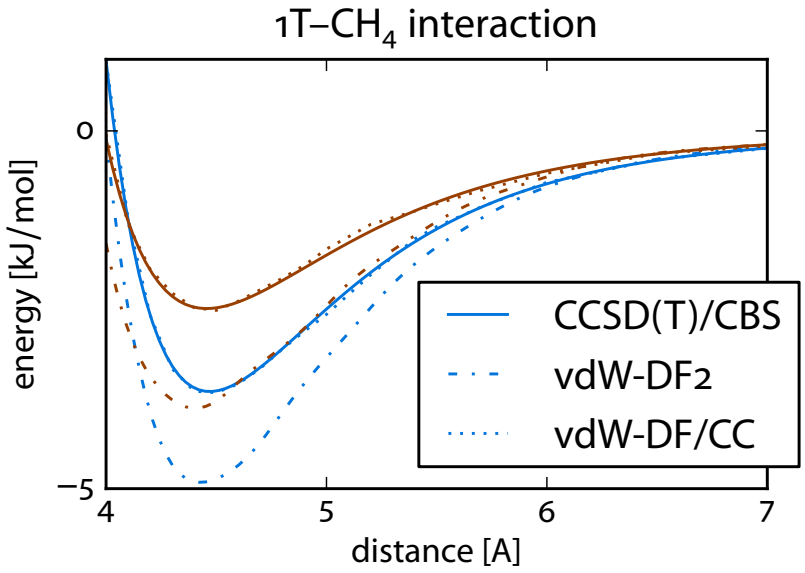
- Example case: UTL
- Valleys between silanol islands
- Four topological sites

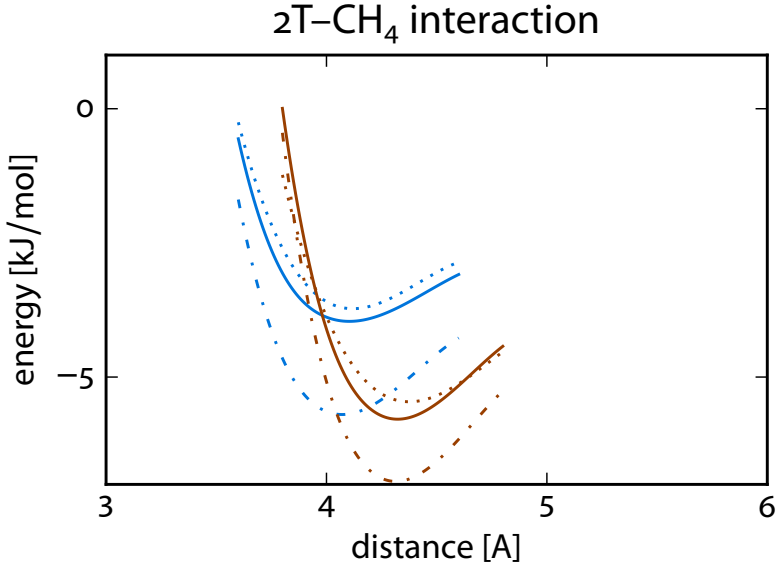


Model systems

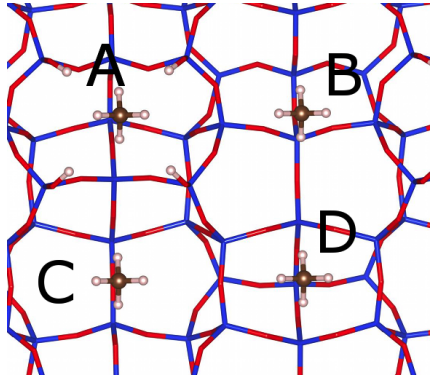
- Highly accurate energies by QM ab-initio methods
- 1T model used for parametrization
- 2T model used for verification







Results



- Geometries optimized at vdW-DF2 level

vdW-DF2 energies [kJ/mol]

	A	B	C	D
CH_4	−24.3	−25.9	−21.6	−16.1
CO	−29.7	−24.4	−24.2	−15.1
CO_2	−47.1	−33.5	−31.2	−26.8
H_2	−12.2	−12.3	−9.6	−8.2
H_2O	−68.1	−47.3	−53.9	−29.3
N_2	−28.0	−23.7	−23.2	−17.4

vdW-DF/CC correction

	A	B	C	D
CH_4	5.7	2.9	3.0	1.3
CO	3.2	−3.2	1.9	1.4
CO_2	−4.0	3.0	−2.0	1.2
H_2	2.4	2.4	2.1	1.5
H_2O	4.9	4.1	3.5	4.5
N_2	2.9	2.2	1.4	2.2

- Mean absolute percentage correction: 12%
- Mean absolute correction: 2.9 kJ/mol

Conclusions

- Standard DFT cannot be used for physisorption
- vdW-DF has not chemical accuracy (errors ~5 kJ/mol)
- We have devised an empirical scheme for correcting vdW-DF
- Estimated accuracy is less than 1 kJ/mol

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