



MAX-PLANCK-GESELLSCHAFT



Van der Waals Effects in HIOS

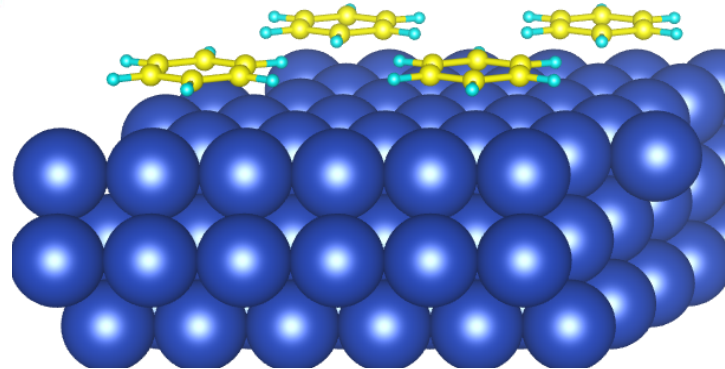
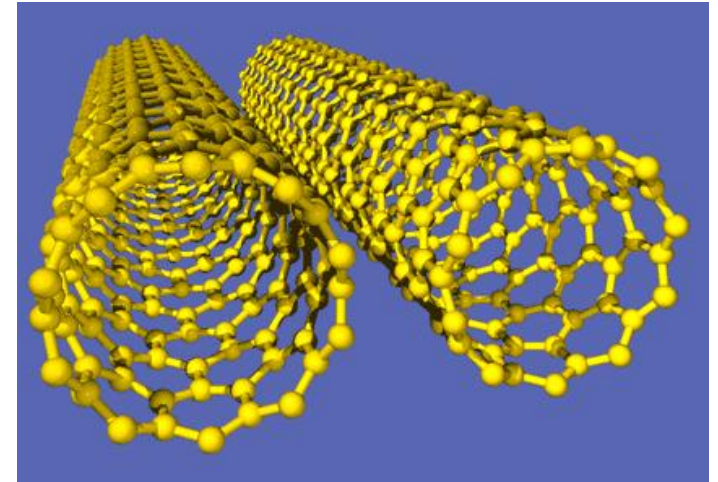
Alexandre Tkatchenko and Matthias Scheffler

Presented by Wei Liu

(Project A10)

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Intermolecular (Non-Covalent) Interactions in Physics, Chemistry, and Materials Science



- Ubiquitous in nature
- Play a major role in defining the structure, stability, and function for molecules and materials

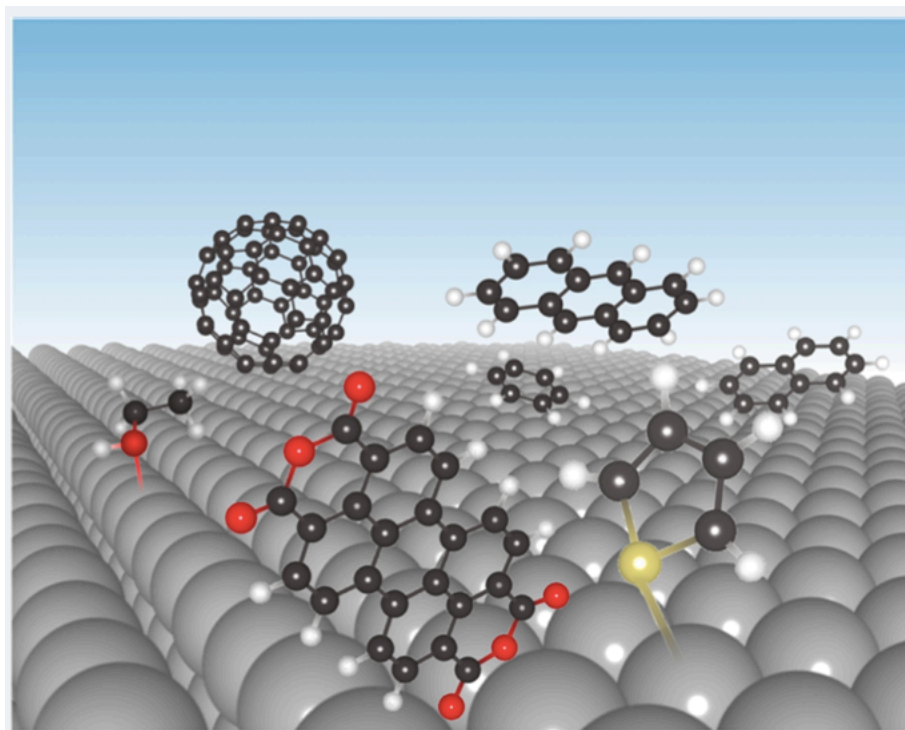


Organic/**metal** interfaces: Accurate description of vdW interactions is the key

DFT+vdW^{surf} method

General accuracy
within **0.1 Å** in
adsorption height
and **0.1 eV** in
binding energy *wrt.*
experiments for **25**
adsorption systems

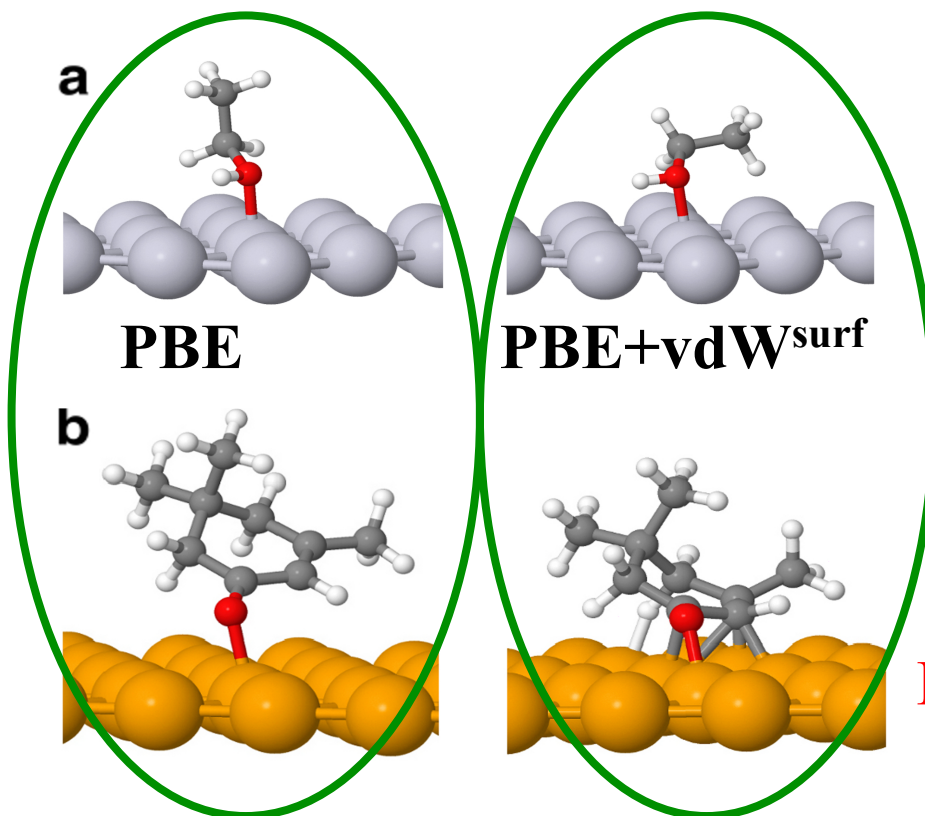
V. G. Ruiz et al. *PRL*
108 (2012) 146103.



VdW interactions can significantly affect the orientation of functional groups

DFT+vdW^{surf} method

General accuracy within **0.1 Å** in adsorption height and **0.1 eV** in binding energy wrt. experiments for **25 adsorption systems**



Ethanol@Pt(111)

W. Liu,
A. Tkatchenko,
M. Scheffler,
Acc. Chem. Res.
(2014).

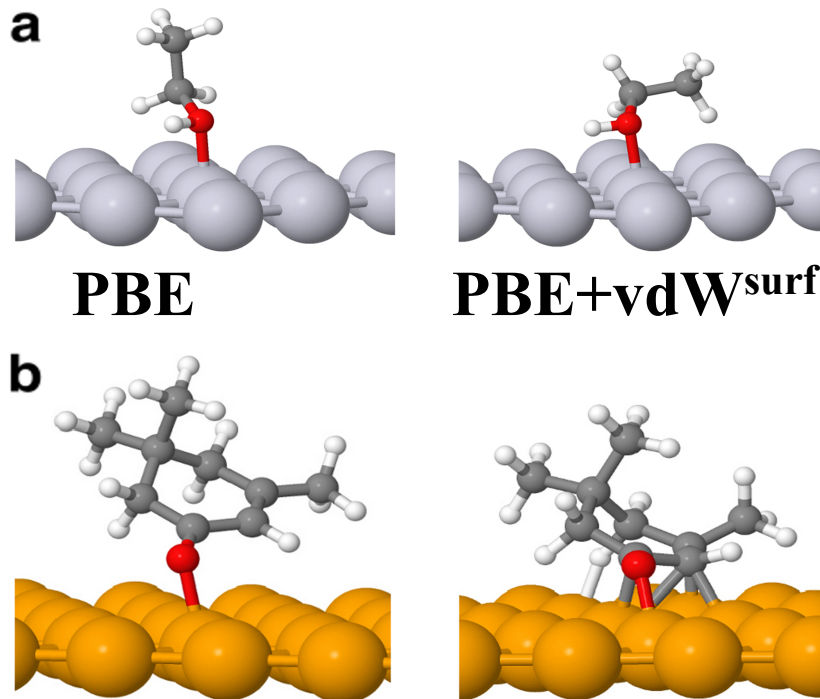
Isophorone@Pd(111)

Change the activation barriers
and reaction pathways in
catalytic applications

Organic/**semiconductor** interfaces: vdW Interactions also play a big role

DFT+vdW^{surf} method

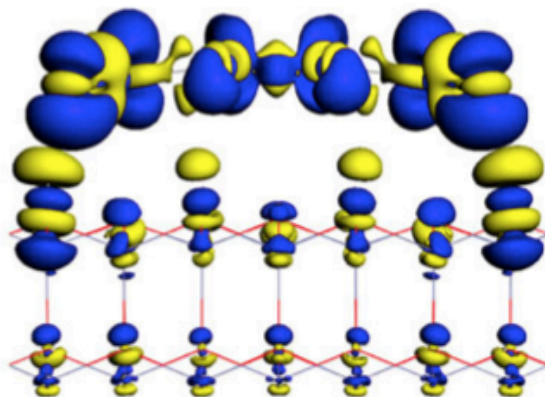
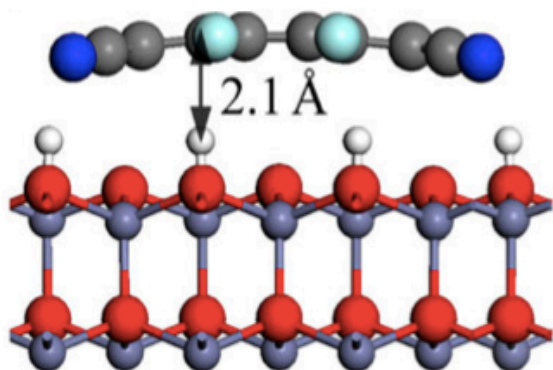
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(2014).

Isophorone@Pd(111)



F4TCNQ@ZnO(000-1)

Y. Xu et al. *PRL* 111 (2013) 226802.

(Collaboration FHI/HU)

VdW effects beyond total energies: *There is plenty of room at the bottom*

VdW correlations are “weak”, but ubiquitous, and of increasing importance in larger (heterogeneous) systems

Long list of important properties beyond energies:

- **Electronic** (dipole, multipoles, charge transfer, ...)
- **Optical** (absorption/reflection spectra, excitons, ...)
 - **Vibrational** (THz and IR phonons, polarons, ...)
- **Mechanical** (bulk modulus, elastic constants, ...)
 - **Novel coupling mechanisms in HIOS?**

VdW effects beyond total energies

Self-consistent DFT+vdW^{surf}:

The DFT exchange-correlation potential includes the **long-range vdW correlation potential (unpublished work)**

$$v'_{xc}[n](\mathbf{r}) = v_{xc}[n](\mathbf{r}) + v_{vdW}[n](\mathbf{r})$$

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VdW can directly
change work functions

Work function values in eV

	Exp.	PBE	PBE+vdW ^{surf}
Cu(111)	4.94	4.79	4.86
Ag(111)	4.74	4.41	4.73
Au(111)	5.32	5.16	5.11

Note: Same geometry!

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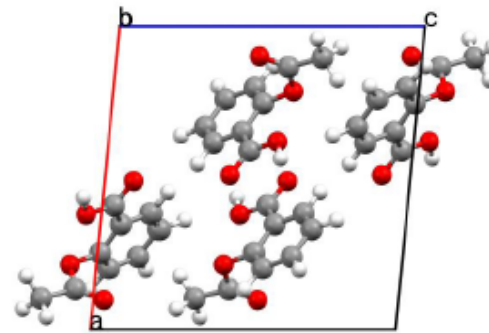
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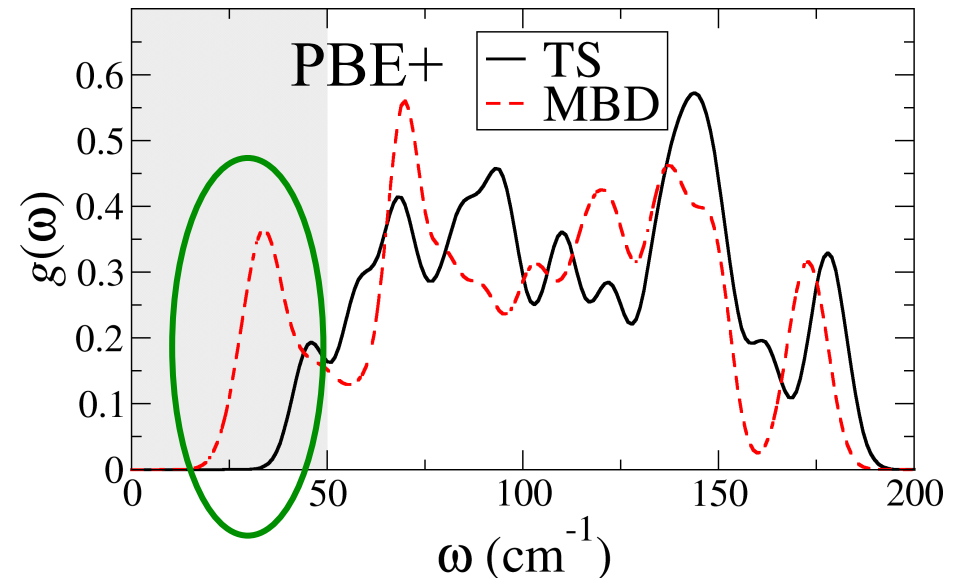
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Aspirin crystal



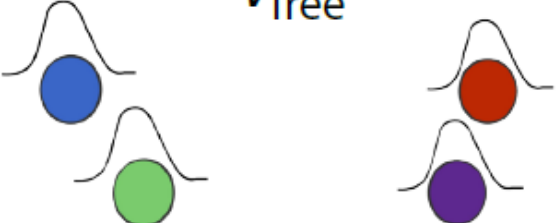
“Plasmon-Phonon”
coupling in Aspirin

A.M. Reilly and A. Tkatchenko, *PRL* 113 (2014) 055701.

DFT+MBD method in a nutshell

A. Tkatchenko and
M. Scheffler,
Phys. Rev. Lett. (2009)


1
$$\alpha_0 = \frac{V[n]}{V_{\text{free}}} \alpha_{0,\text{free}}$$



Valence electrons
projected to oscillators

A. Tkatchenko,
R. A. DiStasio Jr.,
R. Car, M. Scheffler,
Phys. Rev. Lett. (2012)

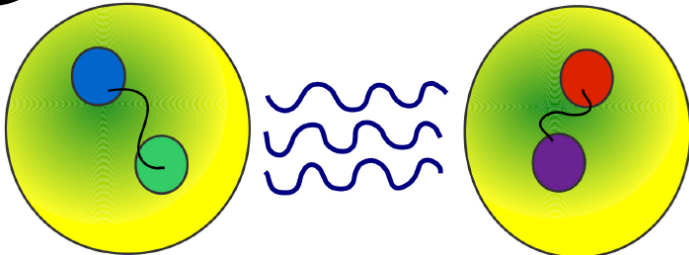
2
$$\tilde{\alpha} = \alpha - \alpha T_{<R} \tilde{\alpha}$$



Dyson-like
short-range
electrodynamic
screening

A. Ambrosetti,
R. A. DiStasio Jr.,
A. M. Reilly,
A. Tkatchenko,
J. Chem. Phys. (2014)

3
$$\hat{\mathcal{H}}_{>R} \Psi = E \Psi$$




Long-range
correlation
energy
calculated
using ACFD

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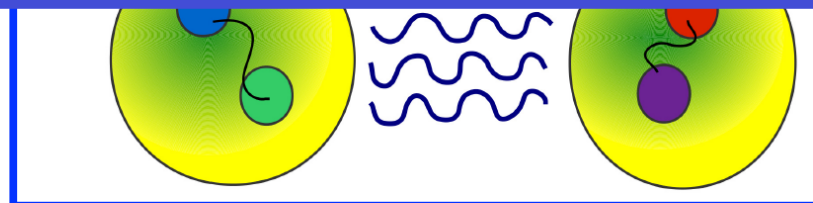
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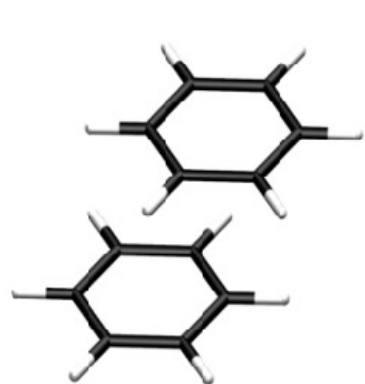
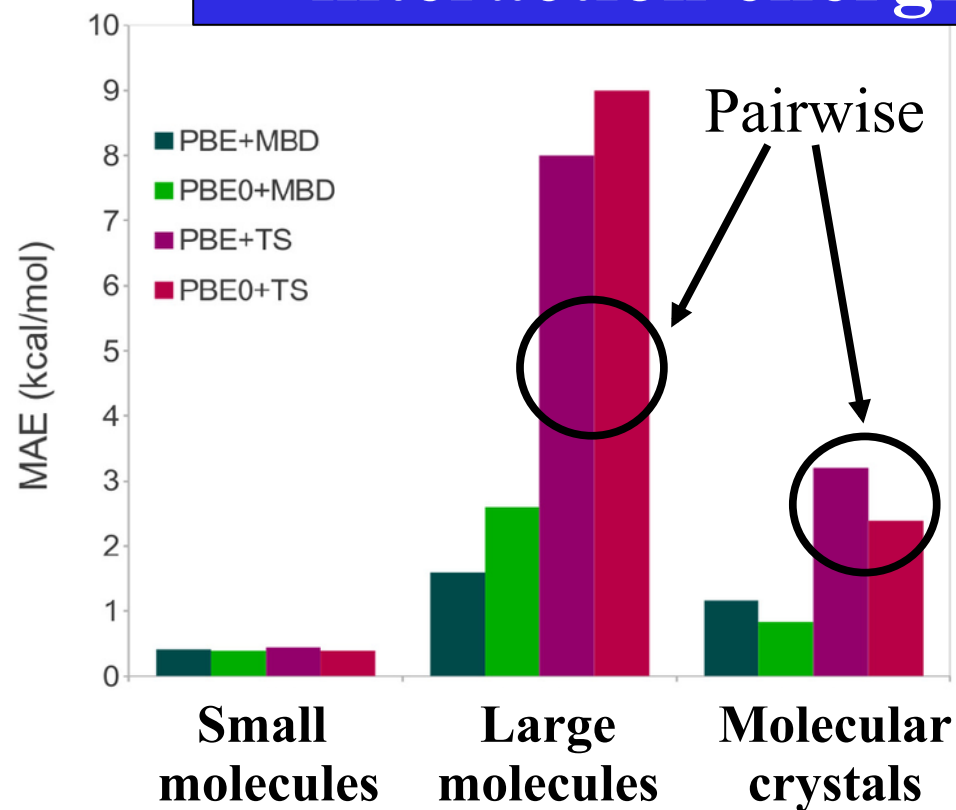
The many-body vdW energy is from the solution of the Schrödinger equation for a system of coupled oscillators

*A. Tkatchenko,
J. Chem. Phys. (2014)*

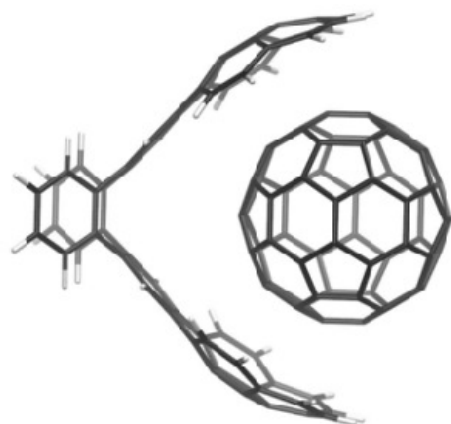


calculated
using ACFD

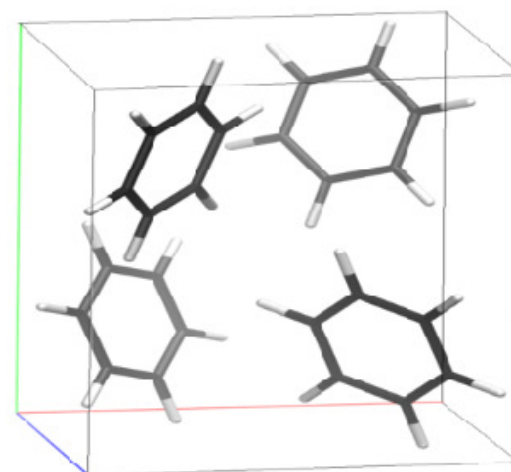
Performance of DFT+MBD for interaction energies in molecular systems



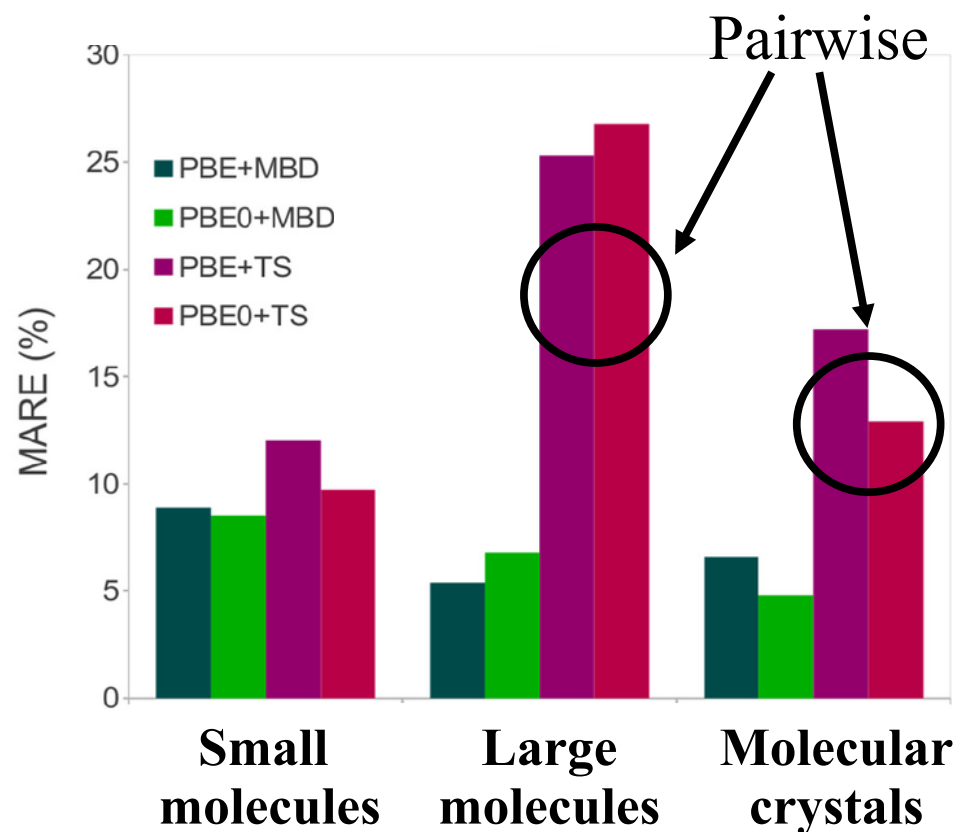
528 dimers



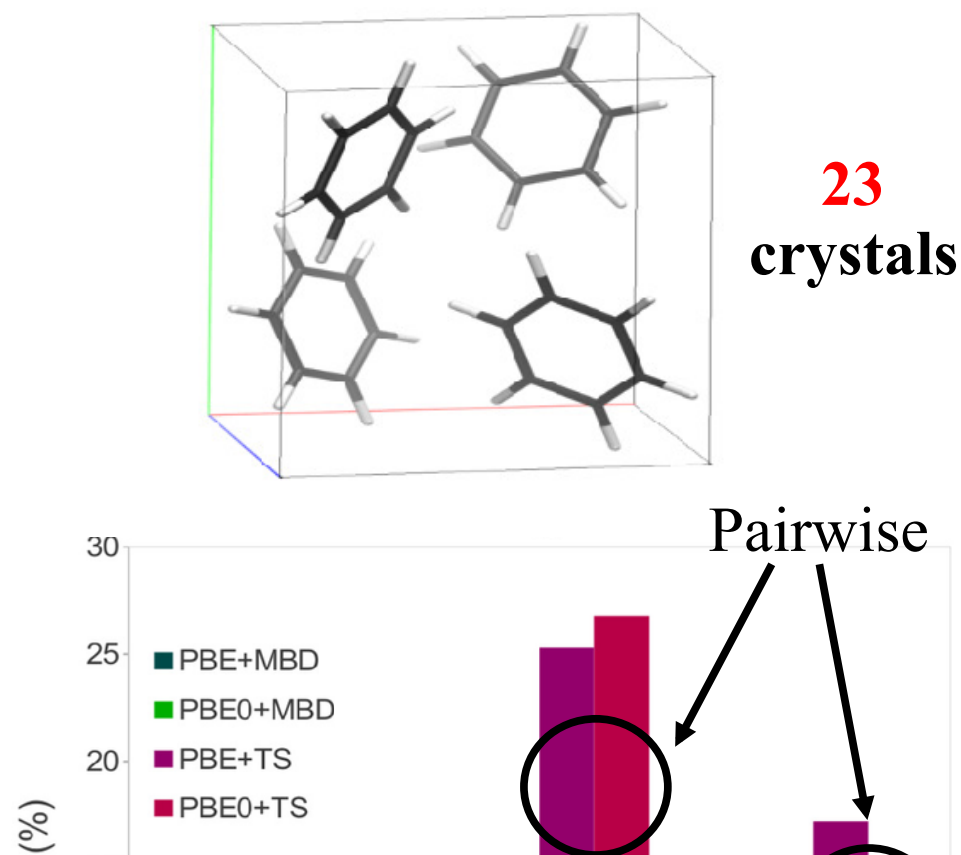
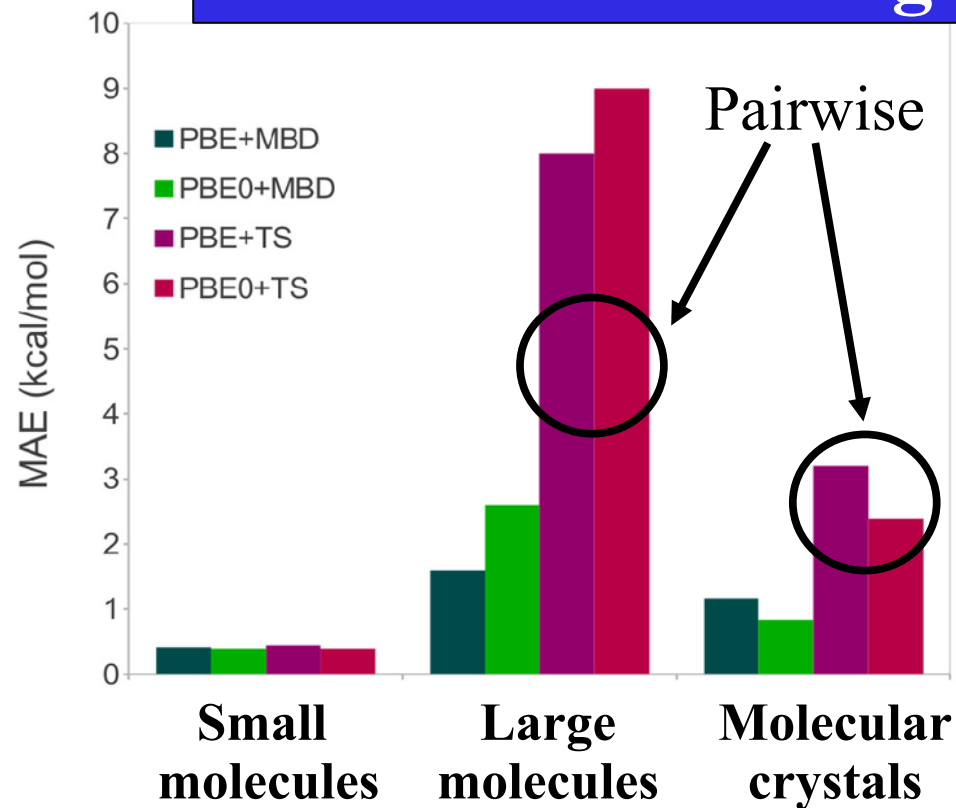
12 dimers



23
crystals



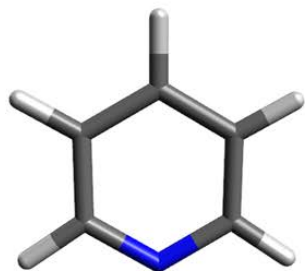
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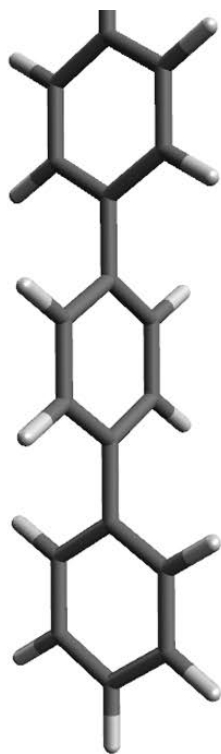
Less is known the performance of DFT+MBD for HIOS, although very recently encouraging results have been achieved for benzene on coinage metal surfaces

HIOSs to be studied with DFT+MBD

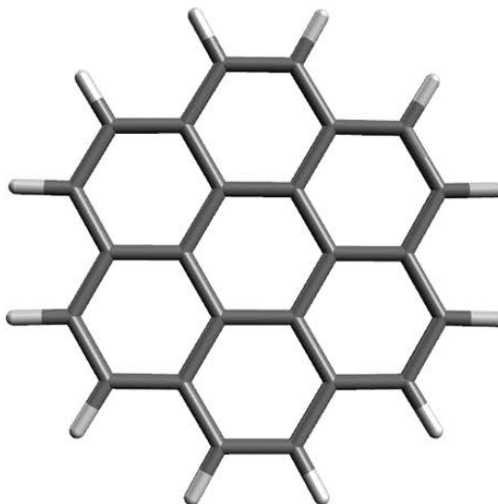
pyridine



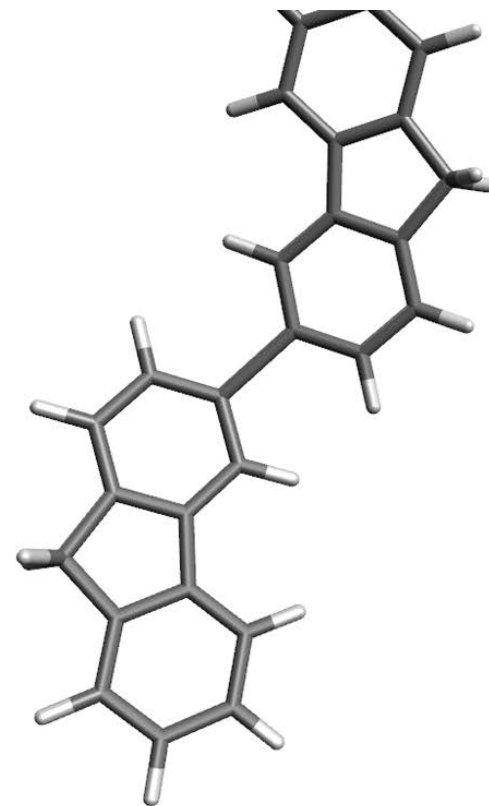
oligophenyls



coronene



oligofluorenes



Substrates: pristine and doped ZnO, Si, Ge ...

Self-consistent DFT+MBD interactions



1 $\alpha_0 = \frac{V[n]}{V_{\text{free}}} \alpha_{0,\text{free}}$

2 $\tilde{\alpha} = \alpha - \alpha T_{<R} \tilde{\alpha}$

3 $\hat{\mathcal{H}}_{>R} \Psi = E \Psi$



Potential: $\frac{\delta E_{\text{MBD}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$

Kernel: $\frac{\delta^2 E_{\text{MBD}}[n(\mathbf{r})]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}$

- Many-body dispersion effects influence electronic properties!

- Study static and time-dependent electronic and vibrational properties for a hierarchy of HIOS

Collaborations



Wörner/Elsässer (B5)
Linear and non-linear THz spectroscopy



Henneberger (A5)
Molecules on doped ZnO



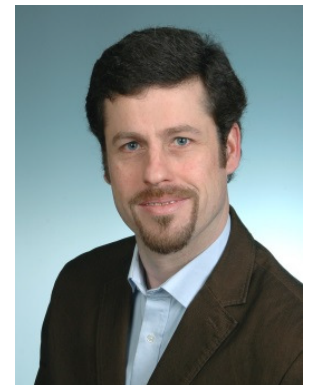
Stähler (B9)
Electronic properties with vdW interactions



Körzdörfer/Scheffler/Rinke (B4)



Dzubiella/Klapp (A7)



Heimel (A4)