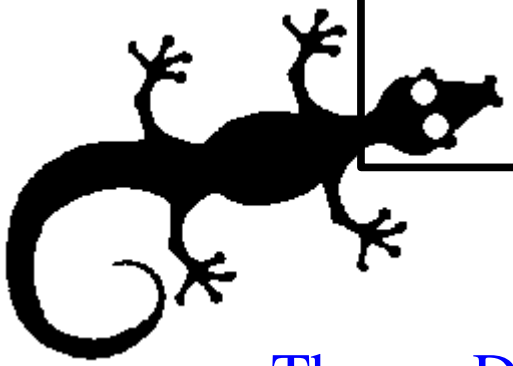
Methods for van der Waals Interactions



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FHI "*DFT and Beyond*" Workshop, Jul. 15, 2011

http://johnbokma.com/

Van der Waals (dispersion) energy

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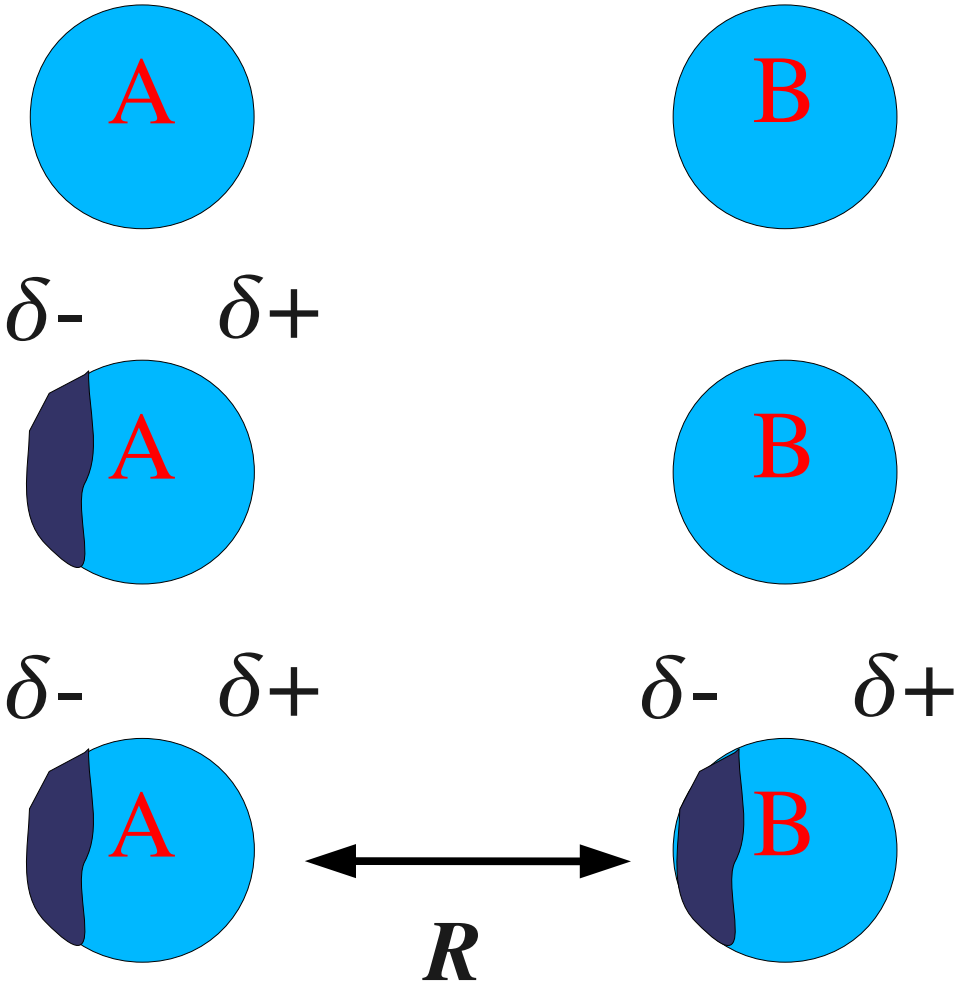
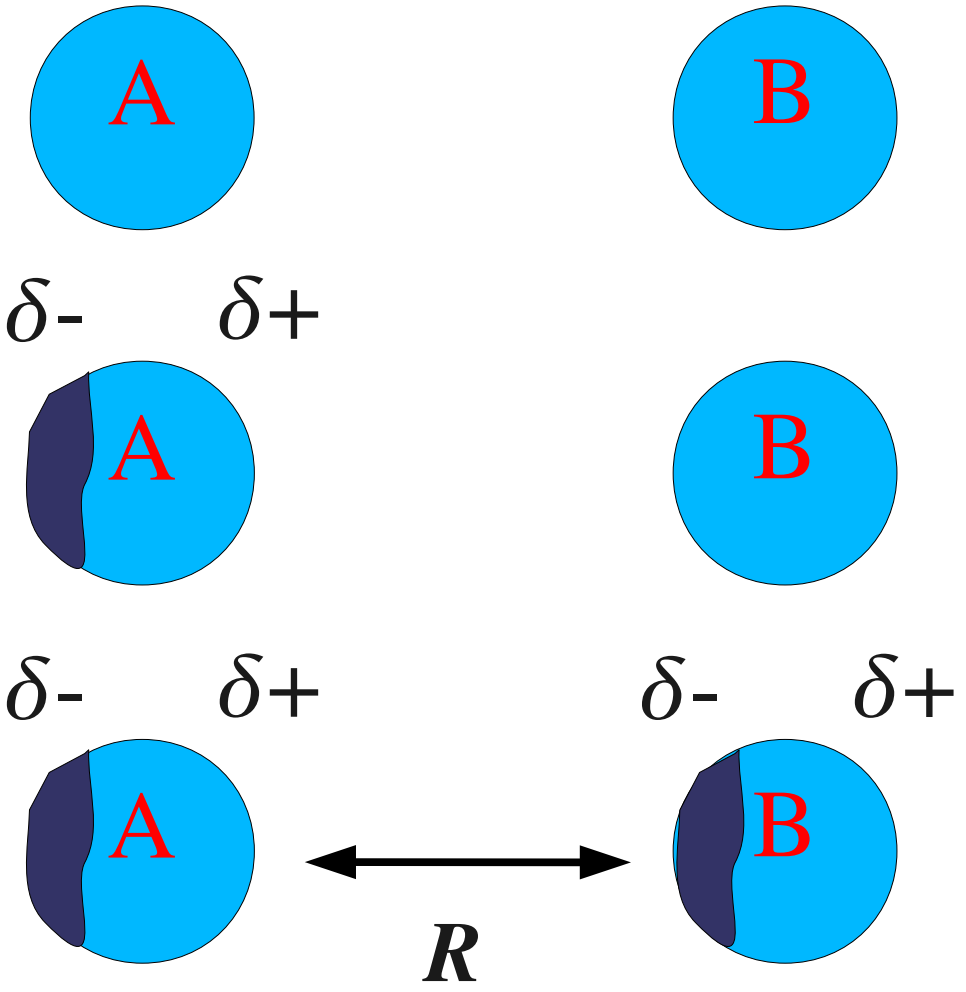


Van der Waals (dispersion) energy

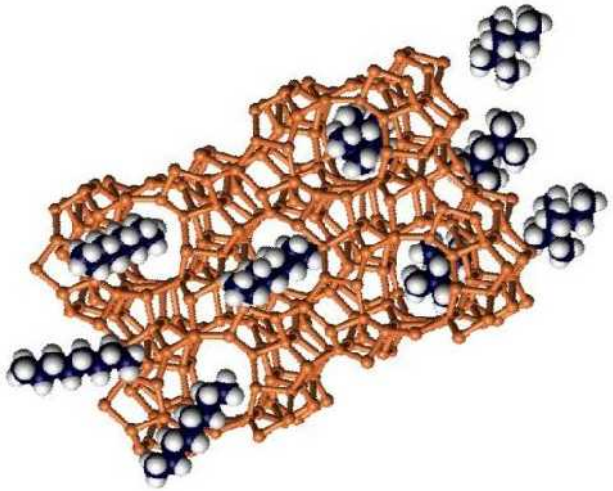


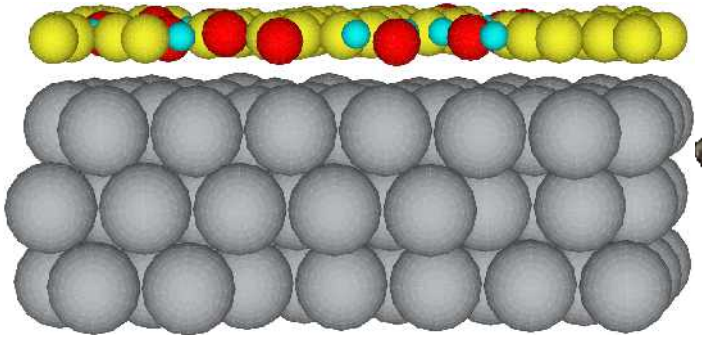
- Ubiquitous interatomic and intermolecular interaction
- Scales linearly with system size
- Weak compared to hydrogen or covalent bonds

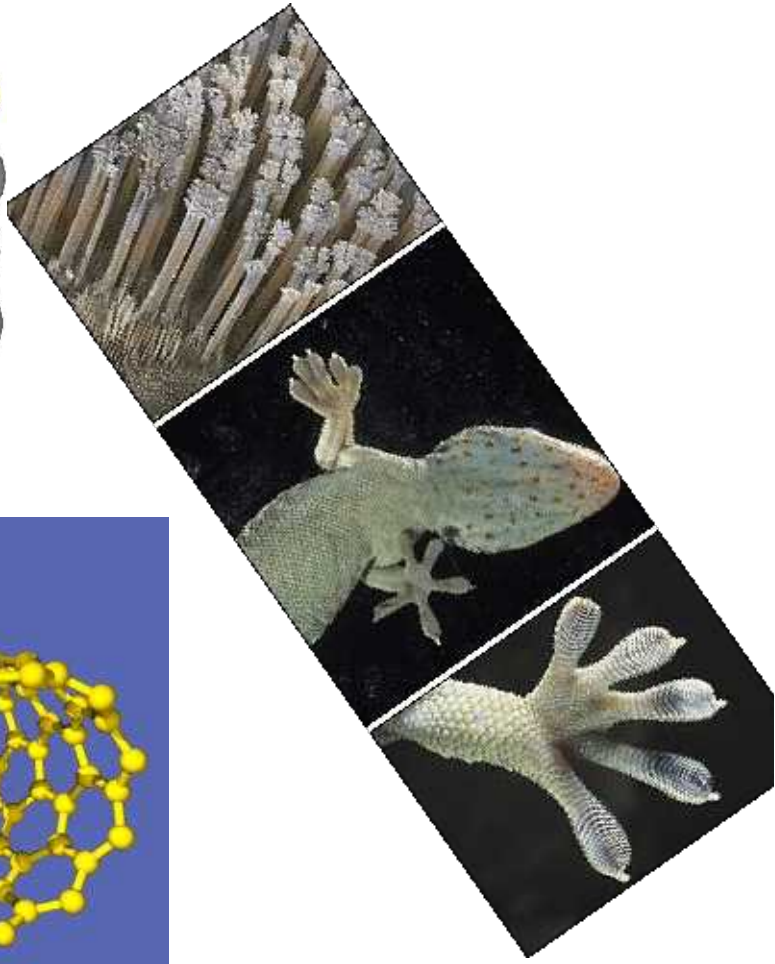
... **but** is a significant component of *intermolecular binding energies* !

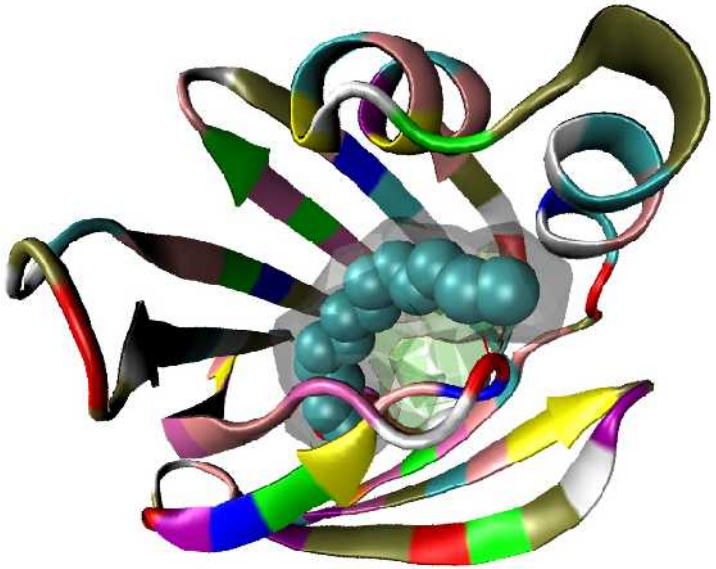
$$E^{disp}(R) = -\left(f_6(R)\frac{C_6}{R^6} + f_8(R)\frac{C_8}{R^8} + f_{10}(R)\frac{C_{10}}{R^{10}} + \ldots \right)$$

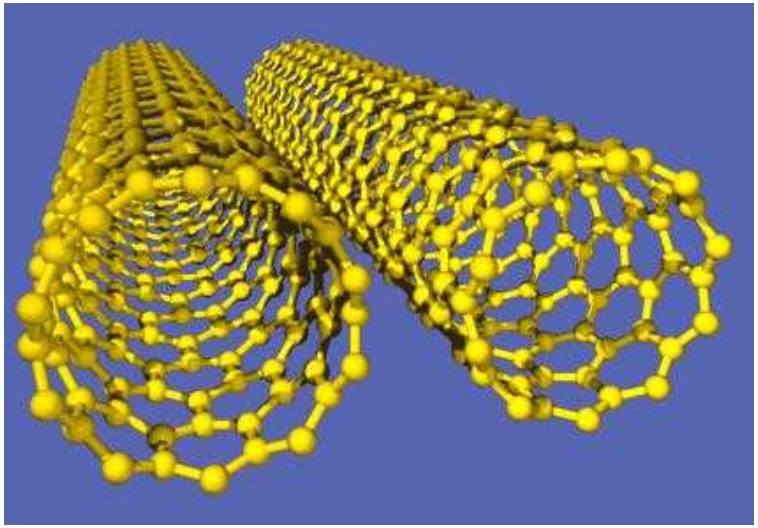
VdW Interactions Are Ubiquitous ...





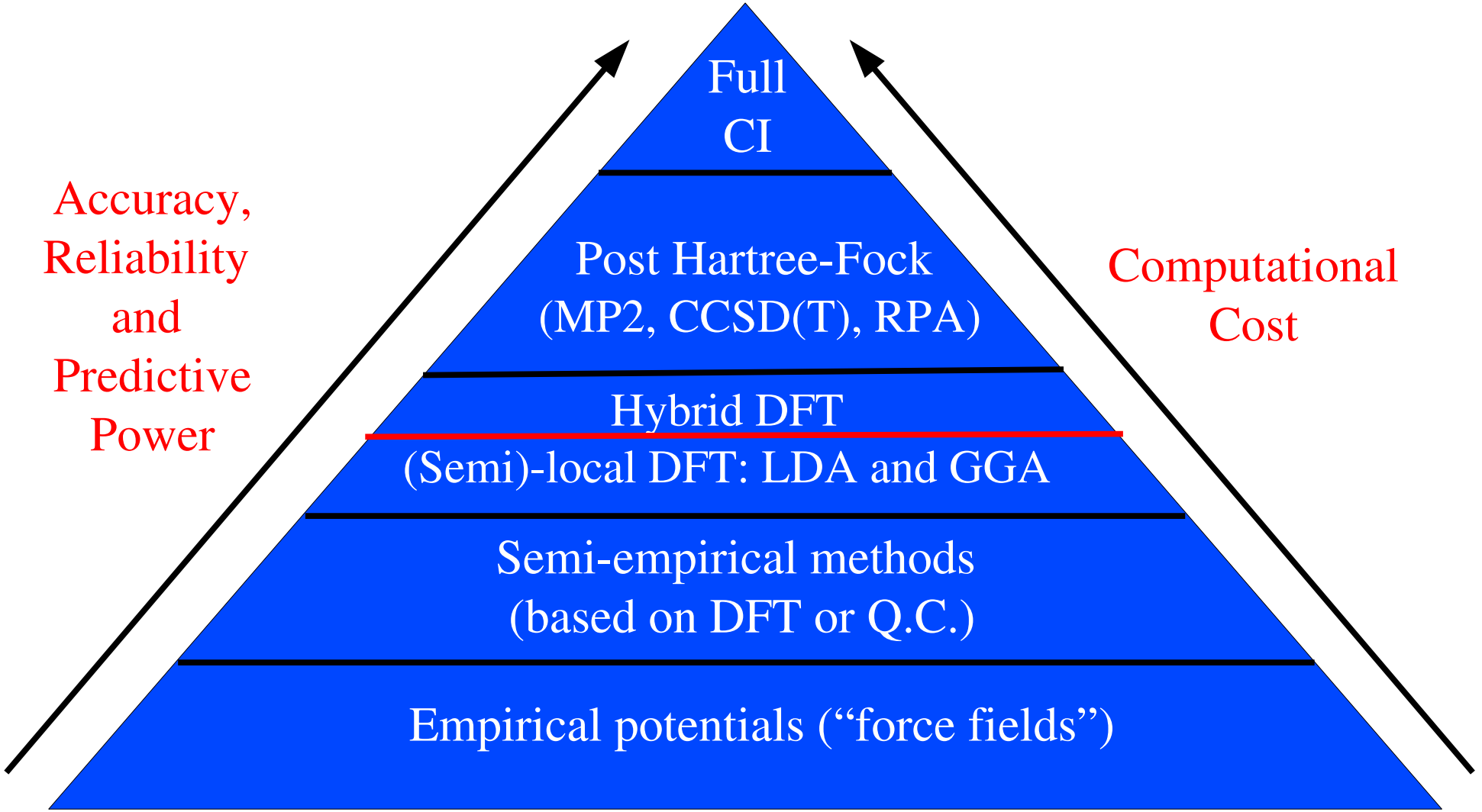






Current state-of-the-art of modeling

$$H\Psi = E\Psi$$



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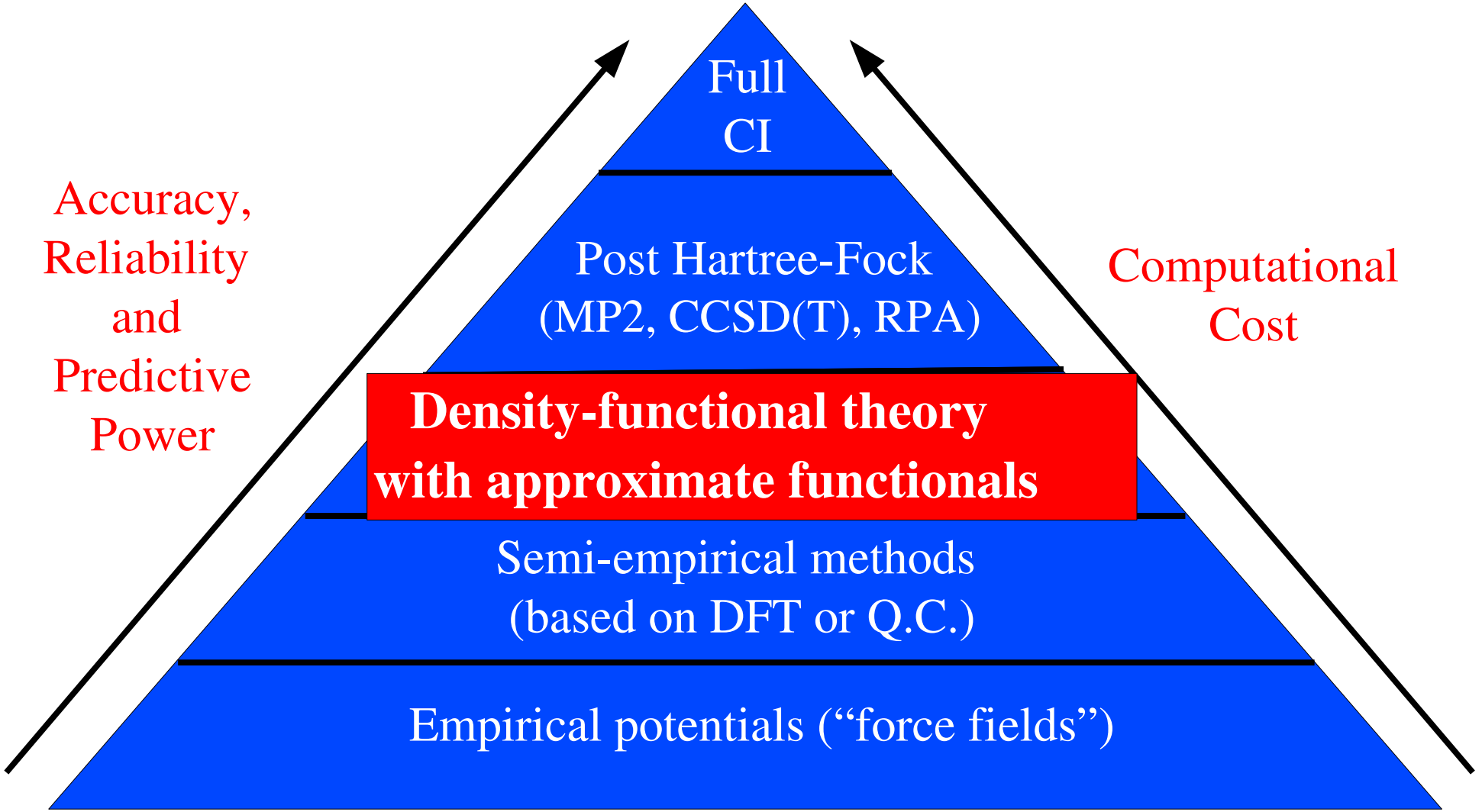


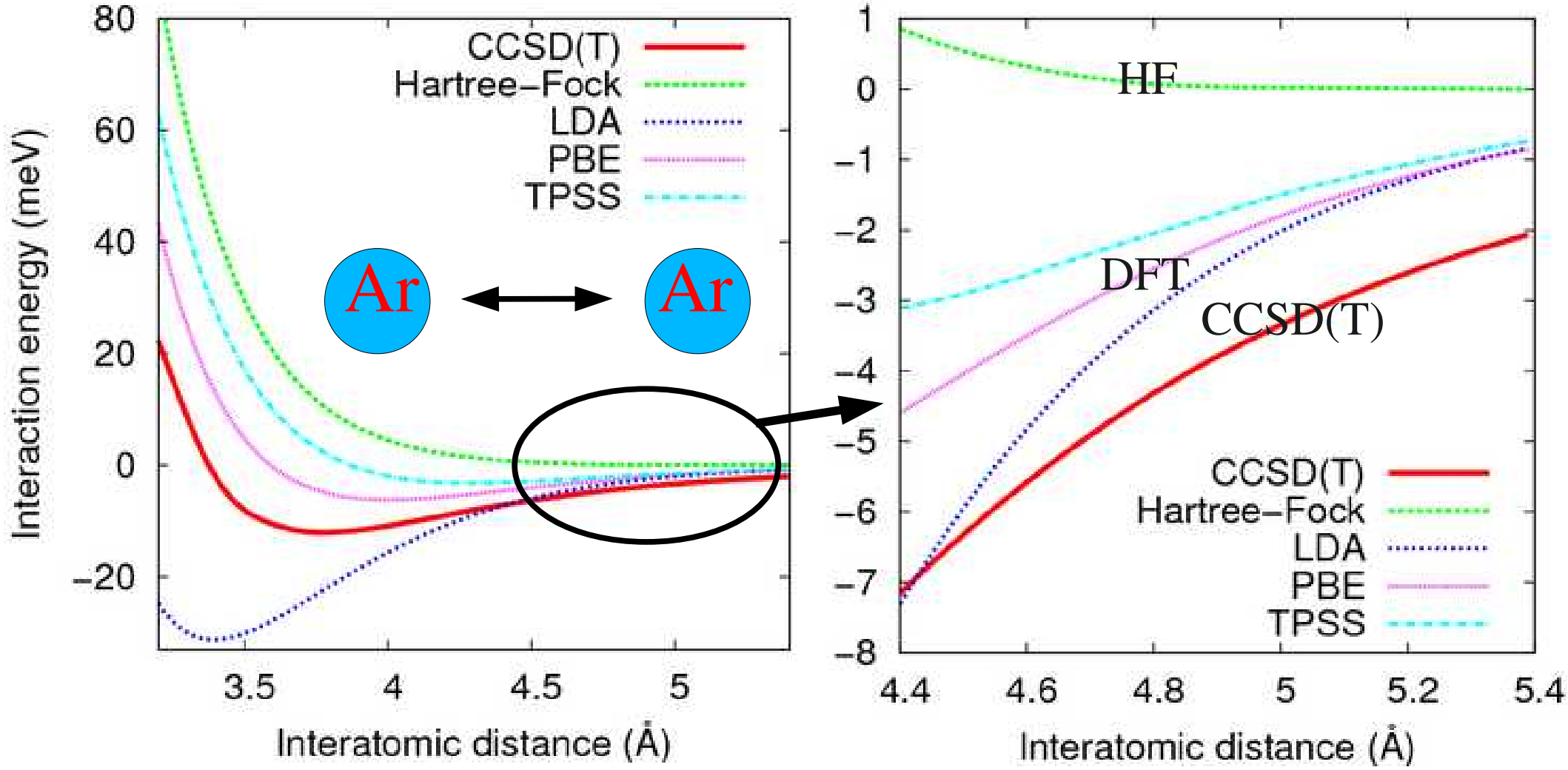
Correlated methods: MP2, RPA, CCSD(T)

- Compute the correlation energy based on a Hartree-Fock or DFT wavefunction
- Include different many-body diagrams for the correlation energy

- MP2: Minimal level for correlation energy
- RPA: Doubles to infinite order, no singles
- CCSD(T): Quantum chemisty “gold standard”

DFT and vdW interaction: Rare-gas dimers

$$E^{disp}(R) = -\left(f_6(R)\frac{C_6}{R^6} + f_8(R)\frac{C_8}{R^8} + f_{10}(R)\frac{C_{10}}{R^{10}} + \ldots \right)$$

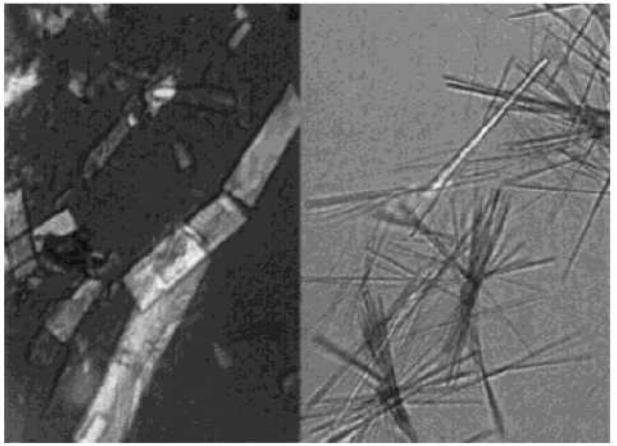


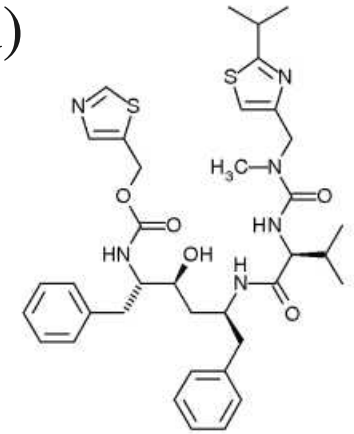
Why existing methods are not sufficient ?

Polymorphism in drugs

Ritonavir (HIV protease inhibitor)

1996 (launch) 1998 (recall)
2001 (*trans* form found)





Polymorph energies
are typically within
1 kcal/mol per molecule

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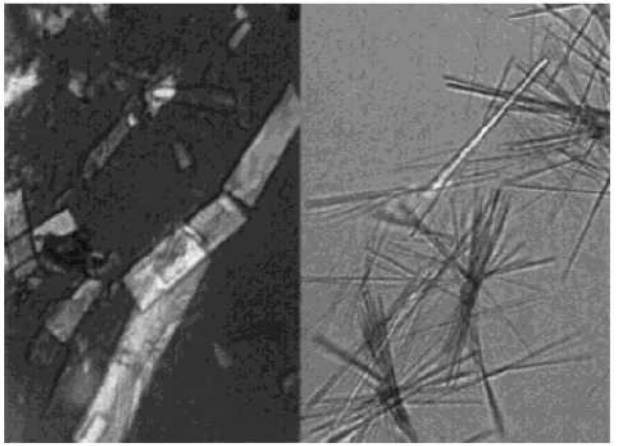
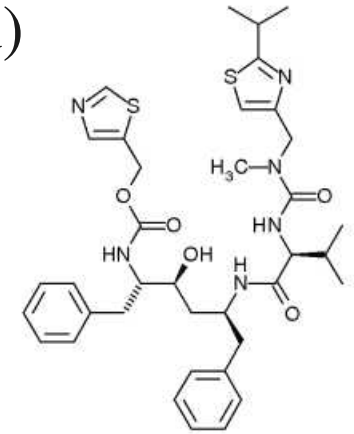
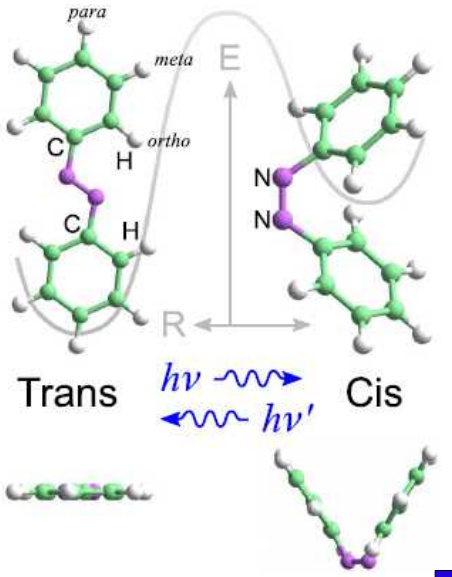
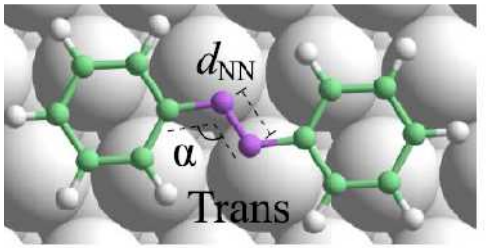


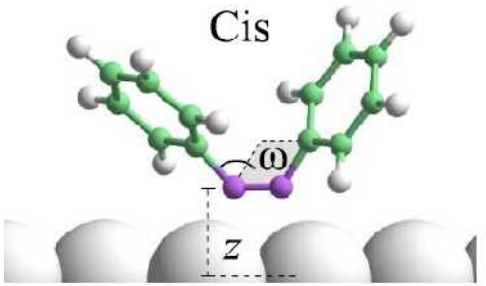


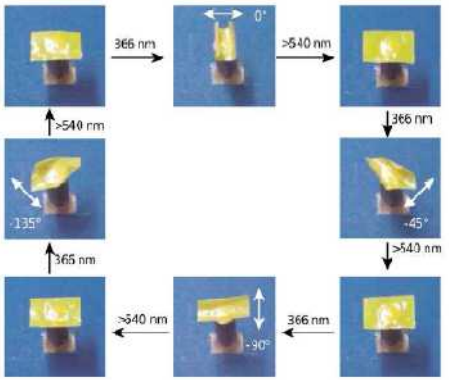
Polymorph energies are typically within 1 kcal/mol per molecule

Molecular switches at surfaces







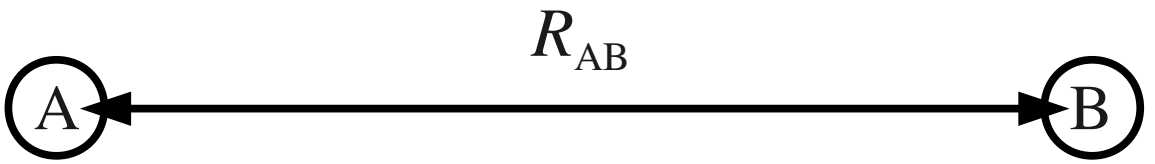


Standard DFT yields wrong adsorption structure.

No available method gives quantitative energetics!

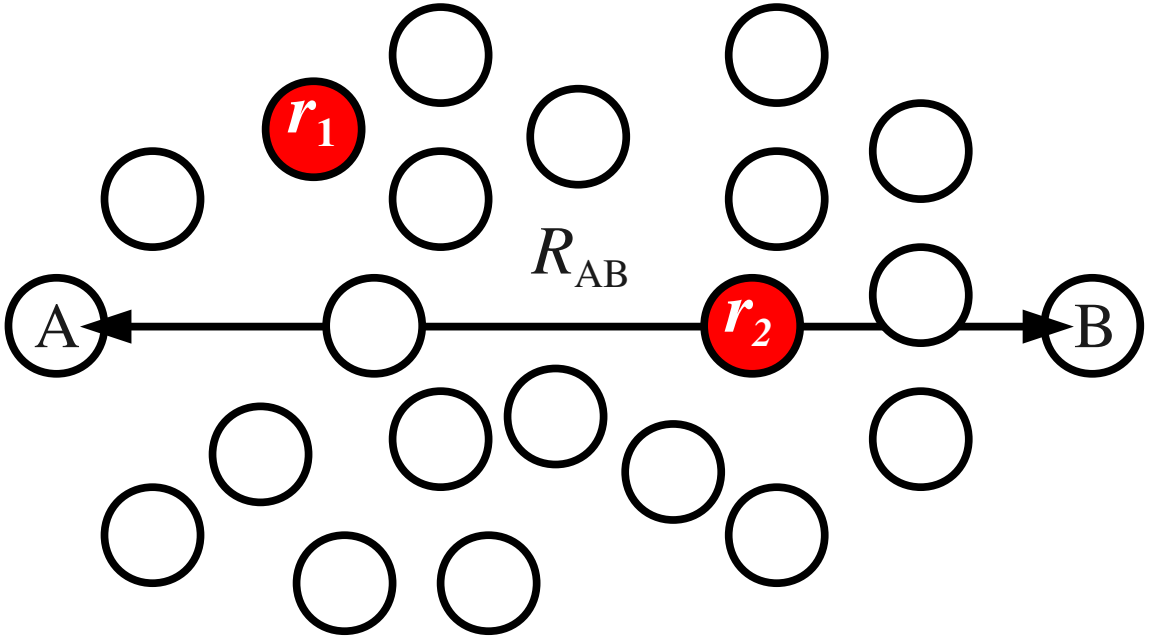
Yu, Nakano, Ikeda, ***Nature*** (2003).

Accurate *First-Principles* Modeling of vdW Interactions is Challenging



$$E_{\mathrm{vdW}}^{(2)} = -\frac{C_6^{\mathrm{AB}}}{R_{\mathrm{AB}}^6} \rightarrow C_6^{\mathrm{AB}} = \frac{3}{\pi}\int \alpha_{\mathrm{A}}(i\omega)\alpha_{\mathrm{B}}(i\omega)d\omega$$

Accurate *First-Principles* Modeling of vdW Interactions is Challenging



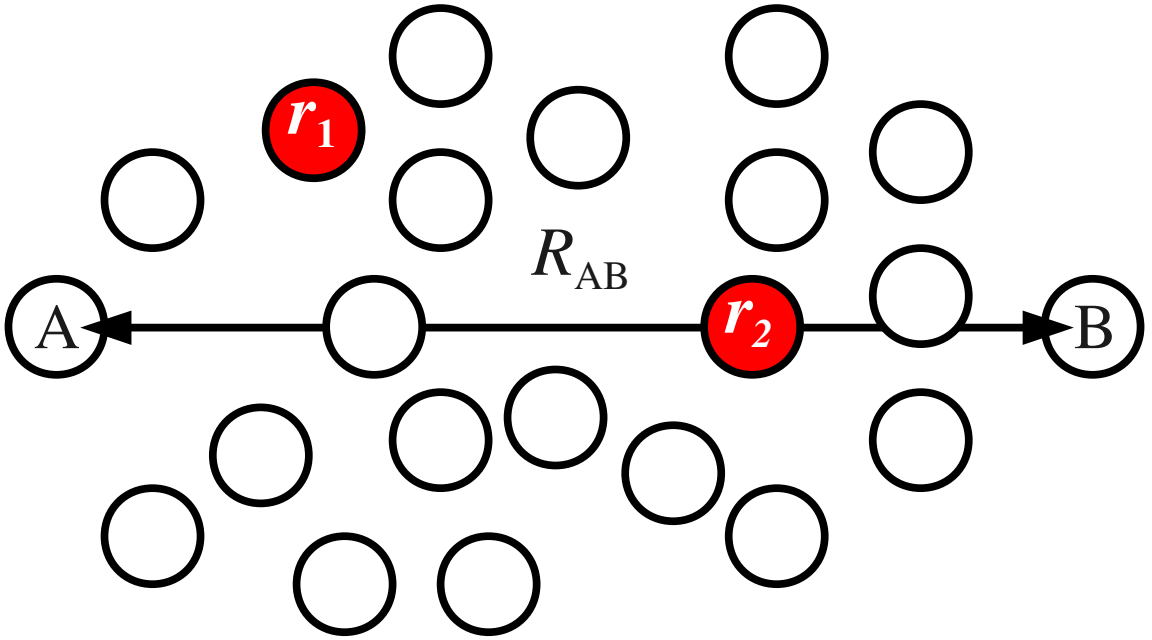
$$E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1}, \mathbf{r_2}; i\omega) - \chi_0(\mathbf{r_1}, \mathbf{r_2}; i\omega)) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \right)$$

Extremely expensive !

Accurate *First-Principles* Modeling of vdW Interactions is Challenging

1

Accurate Microscopic Modeling of Coulomb Screening



2

Full (All-Order) Many-Body van der Waals Energy

$$E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1}, \mathbf{r_2}; i\omega) - \chi_0(\mathbf{r_1}, \mathbf{r_2}; i\omega)) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \right)$$

VdW-corrected DFT methods

Concepts and methods for dispersion in DFT

$$E_{\mathrm{xc}} = E_{ex}^{\mathrm{GGA\ or\ EX}} + E_{\mathrm{corr}}^{\mathrm{LDA,GGA}} + E_{\mathrm{corr}}^{\mathrm{non-local}}$$

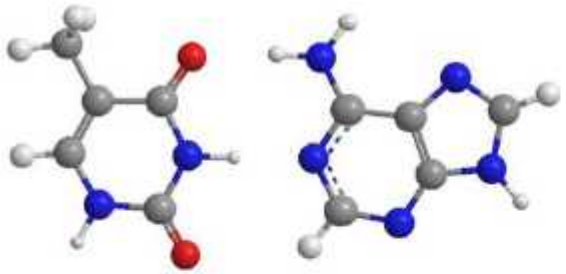
Concepts and methods for dispersion in DFT

$$E_{\rm xc} = E_{ex}^{\rm GGA\ or\ EX} + E_{\rm corr}^{\rm LDA,GGA} + E_{\rm corr}^{\rm non-local}$$

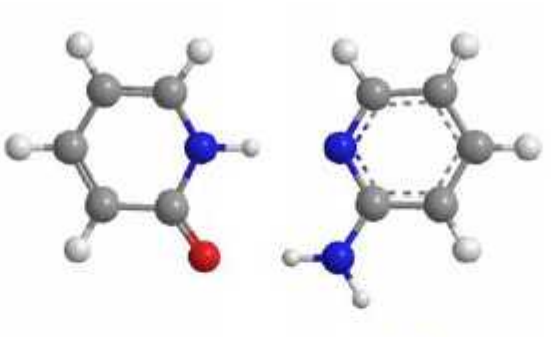
- Non-local functionals (depend explicitly on ***r*** and ***r'***) (*Langreth, Lundqvist et al.*).
- Modified pseudopotentials (*von Lilienfeld et al.*)
- Highly empirical (hybrid) meta-GGA functionals (*Truhlar et al.*)
- Interatomic (pairwise or beyond) dispersion corrections (Many people)

Wu and Yang ***JCP*** *(2002);* *Grimme* ***J. Comp. Chem.*** (2004,2006); *Dion et al.* ***PRL*** (2004); *Zhao and Truhlar* ***JCP*** (2006); *von Lilienfeld et al.* ***PRL*** (2004); *Johnson and Becke* ***JCP*** (2005-2007); *Tkatchenko and Scheffler* ***PRL*** (2009); and many others ...

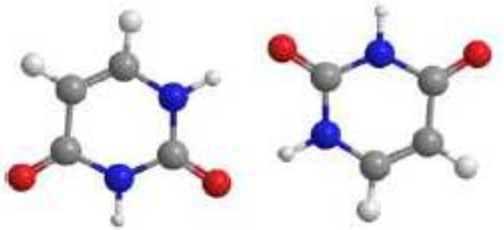
S22 benchmark database



A···T WC



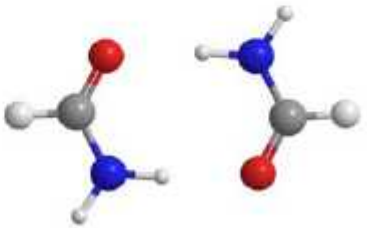
2-pyridoxine···2-aminopyridine



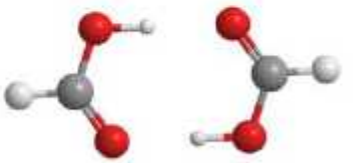
Hydrogen bonded uracil dimer

$(NH_3)_2$

$(H_2O)_2$



$(HCONH_2)_2$

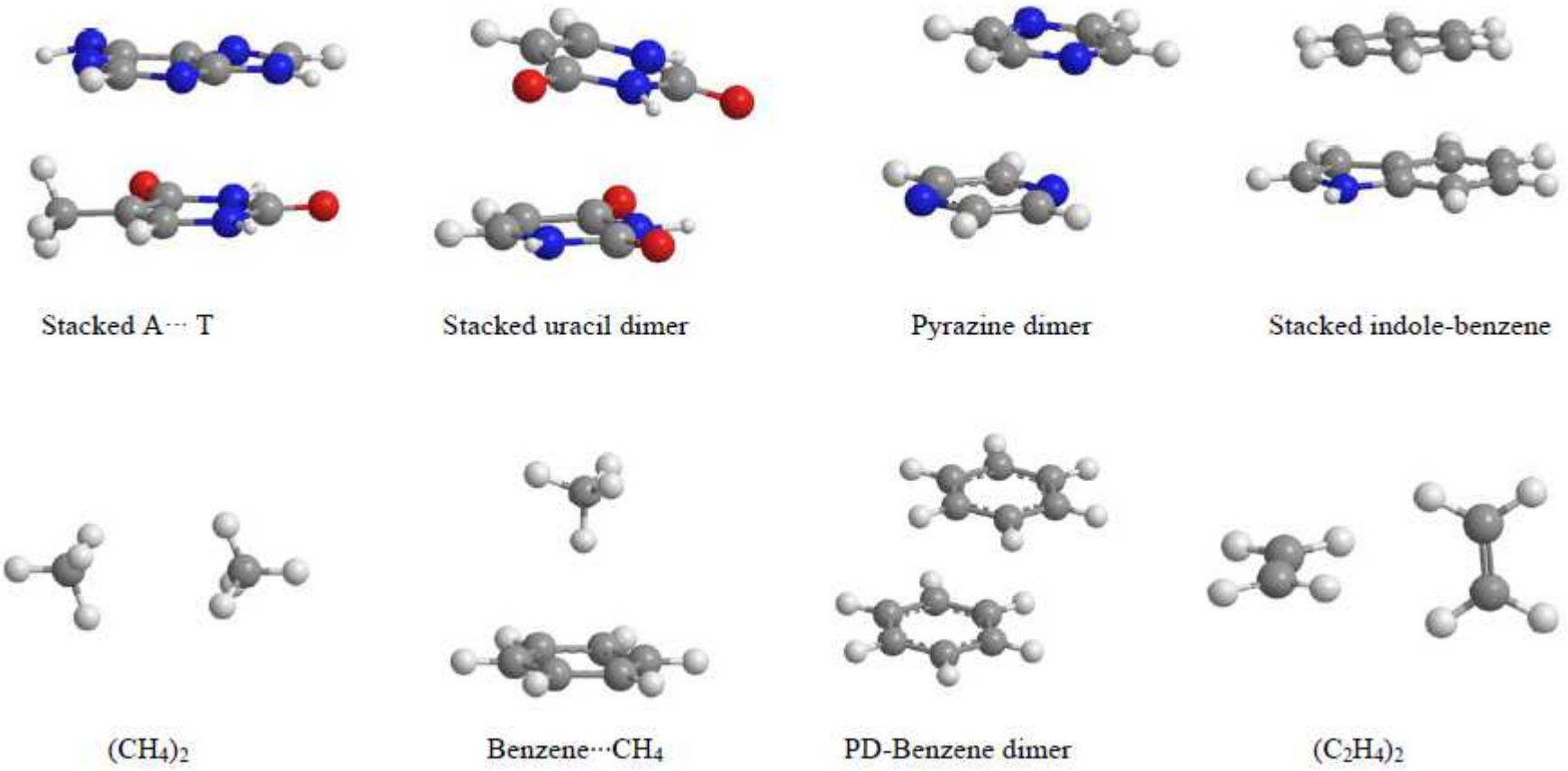


$(HCOOH)_2$

Hydrogen bonding

P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, ***Phys. Chem. Chem. Phys.*** (2006)

S22 benchmark database



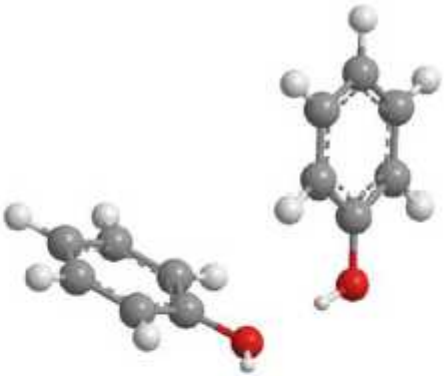
VdW bonding

P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, ***Phys. Chem. Chem. Phys.*** (2006)

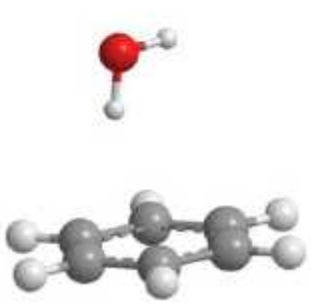
S22 benchmark database

T-shaped indole···benzene

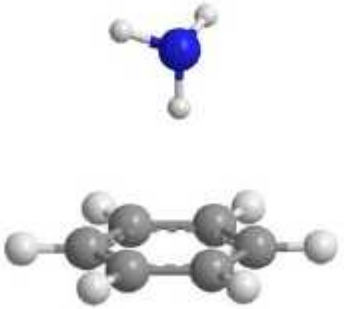
T-shaped benzene dimer



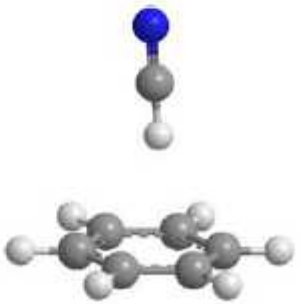
Phenol dimer



Benzene···H2O



Benzene···NH_3



Benzene···HCN

Ethene···ethyne

Mixed bonding

P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, ***Phys. Chem. Chem. Phys.*** (2006)

Langreth-Lundqvist functional (vdW-DF-04 and vdW-DF-10)

Langreth-Lundqvist functional

$$E_{\rm xc} = E_{\rm ex}^{\rm GGA}[n(\mathbf{r})] + E_{\rm corr}^{\rm LDA}[n(\mathbf{r})] + E_{\rm corr}^{\rm non-local}[n(\mathbf{r})]$$

$$E_{\rm corr}^{\rm non-local}[n(\mathbf{r})] = \frac{1}{2}\int d^3r d^3r' n(\mathbf{r}) K(\mathbf{r},\mathbf{r}') n(\mathbf{r}')$$

Dion, Rydberg, Schroeder, Langreth, Lundqvist, ***PRL*** (2004).
Lee, Murray, Kong, Lundqvist, Langreth, ***PRB*** (2010).

Langreth-Lundqvist functional (vdW-DF-04 and vdW-DF-10)

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$$E_{\rm corr}^{\rm non-local}[n(\mathbf{r})] = \frac{1}{2}\int d^3r d^3r' n(\mathbf{r}) K(\mathbf{r},\mathbf{r}') n(\mathbf{r}')$$

vdW-DF-04

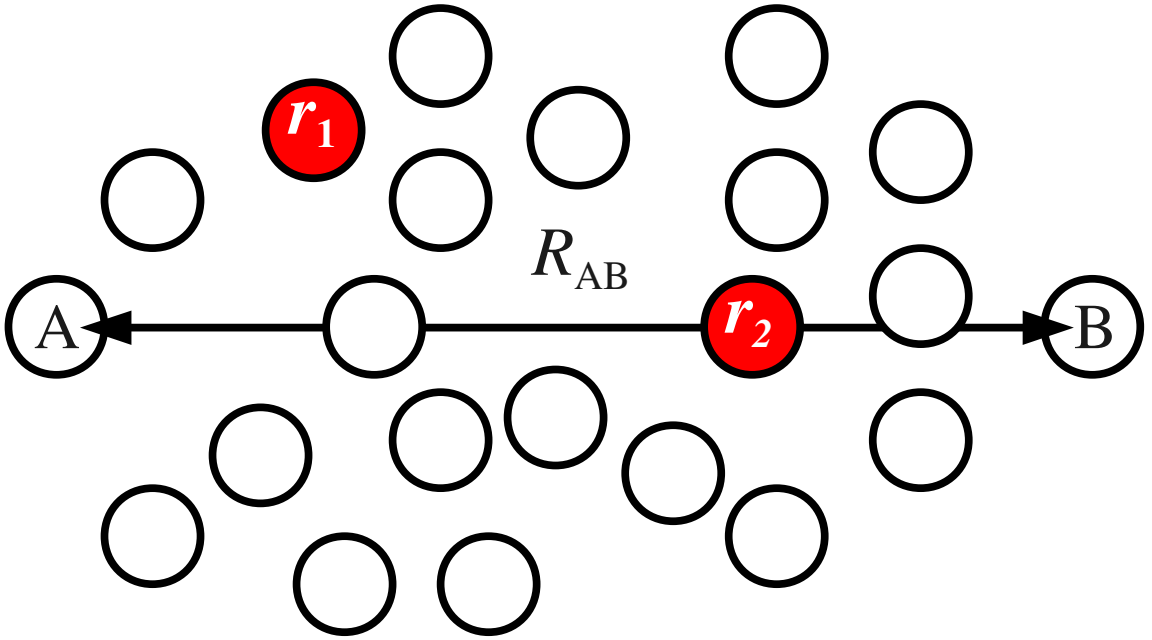
- Exchange: revPBE
- Local corr.: LDA
- No free parameters
- C_6 error: ~ 20%

vdW-DF-10

- Exchange: PW86
- Local corr.: LDA
- 2 parameters
- C_6 error: ~ 60%(*)

(*) *Vydrov and van Voorhis*, ***PRA*** (2010).

Approximations for $E_{\mathrm{corr}}^{\mathrm{non-local}}$ in vdW-DF

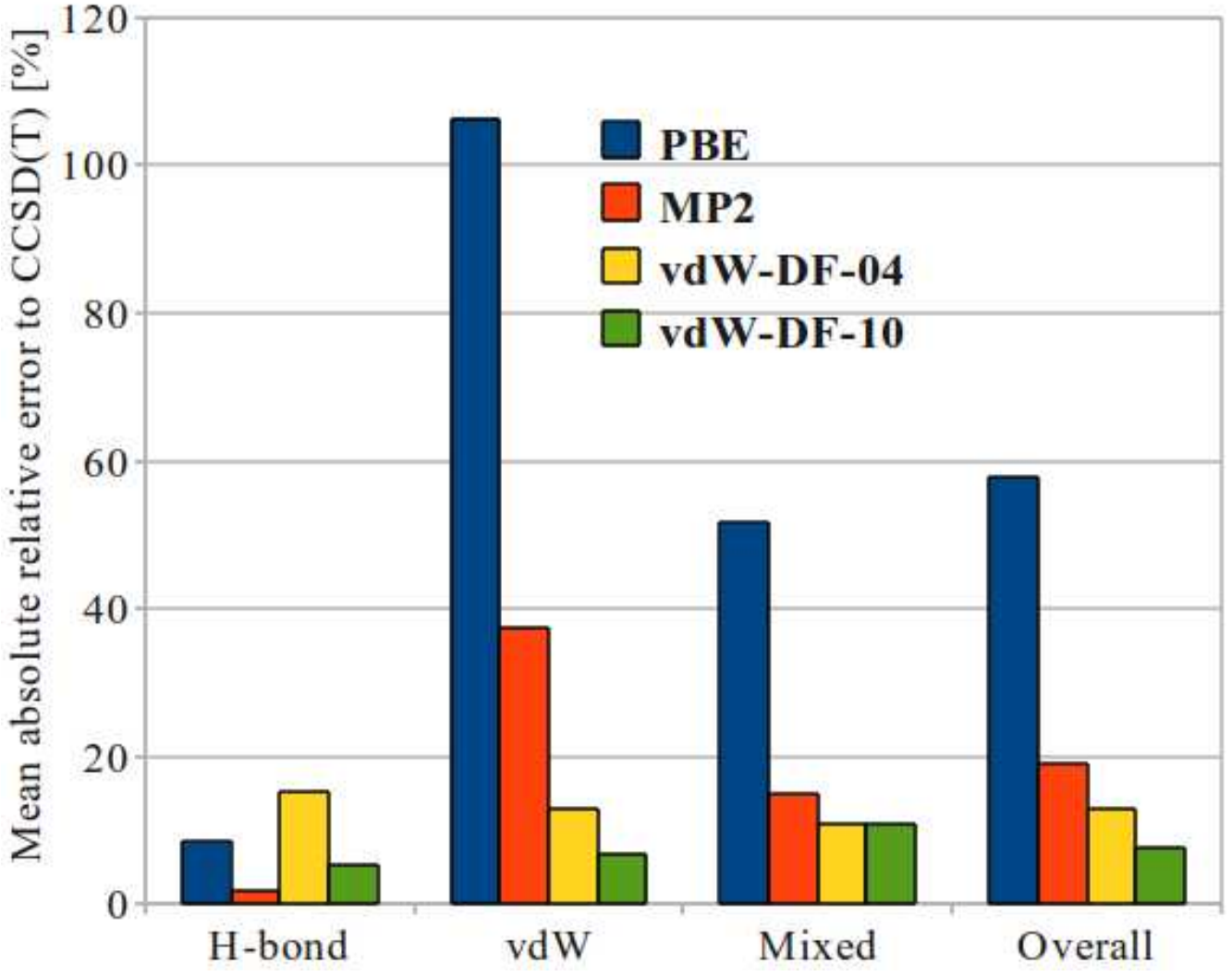


$$E_c = -\int_0^\infty \frac{d\omega}{2\pi}\int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1},\mathbf{r_2};i\omega)-\chi_0(\mathbf{r_1},\mathbf{r_2};i\omega))\frac{1}{|\mathbf{r_1}-\mathbf{r_2}|}\right)$$

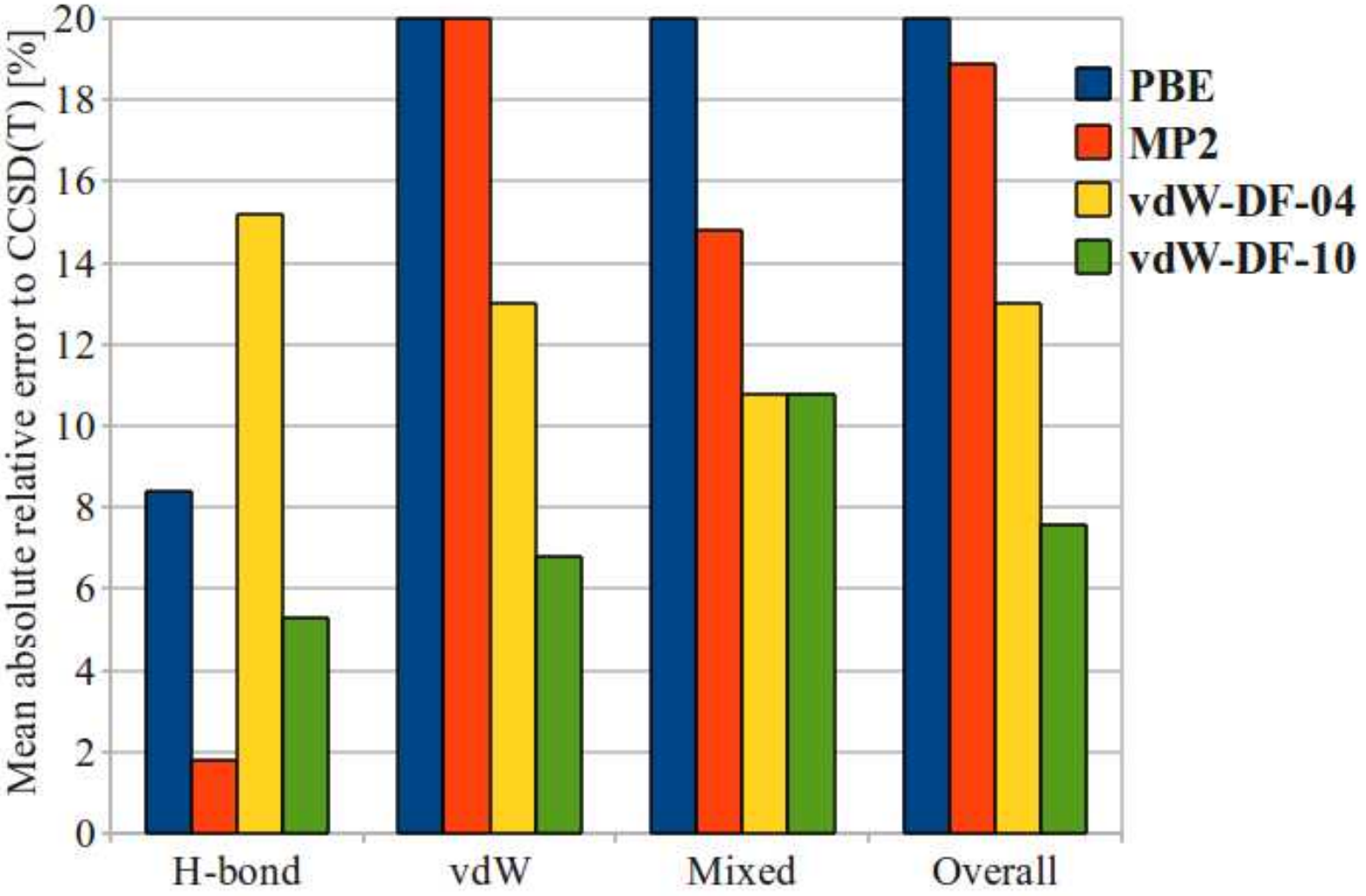
1) Local approximation for the response function

2) Only pairwise point-point interaction, ignoring non-additive many-body energy

Performance of vdW-DF on the S22 database



Performance of vdW-DF on the S22 database



Limitations of the Langreth-Lundqvist functional

- vdW-DF-04 is a general purpose functional, however its performance is not optimal (errors significantly larger than chemical accuracy)
- vdW-DF-10 is a special purpose functional with good performance for molecules. Asymptotic vdW interactions are significantly underestimated (~60%), so no good performance should be expected for larger systems
- The vdW-DF concept does not have flexibility for the coupling to semi-local DFT functional. This is being improved by Vydrov and van Voorhis (***PRL*** 2009, ***JCP*** 2010)

Empirical Minnesota functionals (Zhao-Truhlar, M06 family)

Empirical Minnesota functionals (Zhao-Truhlar, M06 family)

- Highly flexible (and empirical) form for a functional (**20-40** parameters) trained on a broad set of benchmark (theory and experiment) data
- A *family* of functionals:
  - M06: Hybrid meta-GGA functional
  - M06-L: GGA (non-hybrid) version of M06
  - M06-2X: M06 with twice the amount of HF exchange
  - M06-HF: M06 with 100% HF exchange

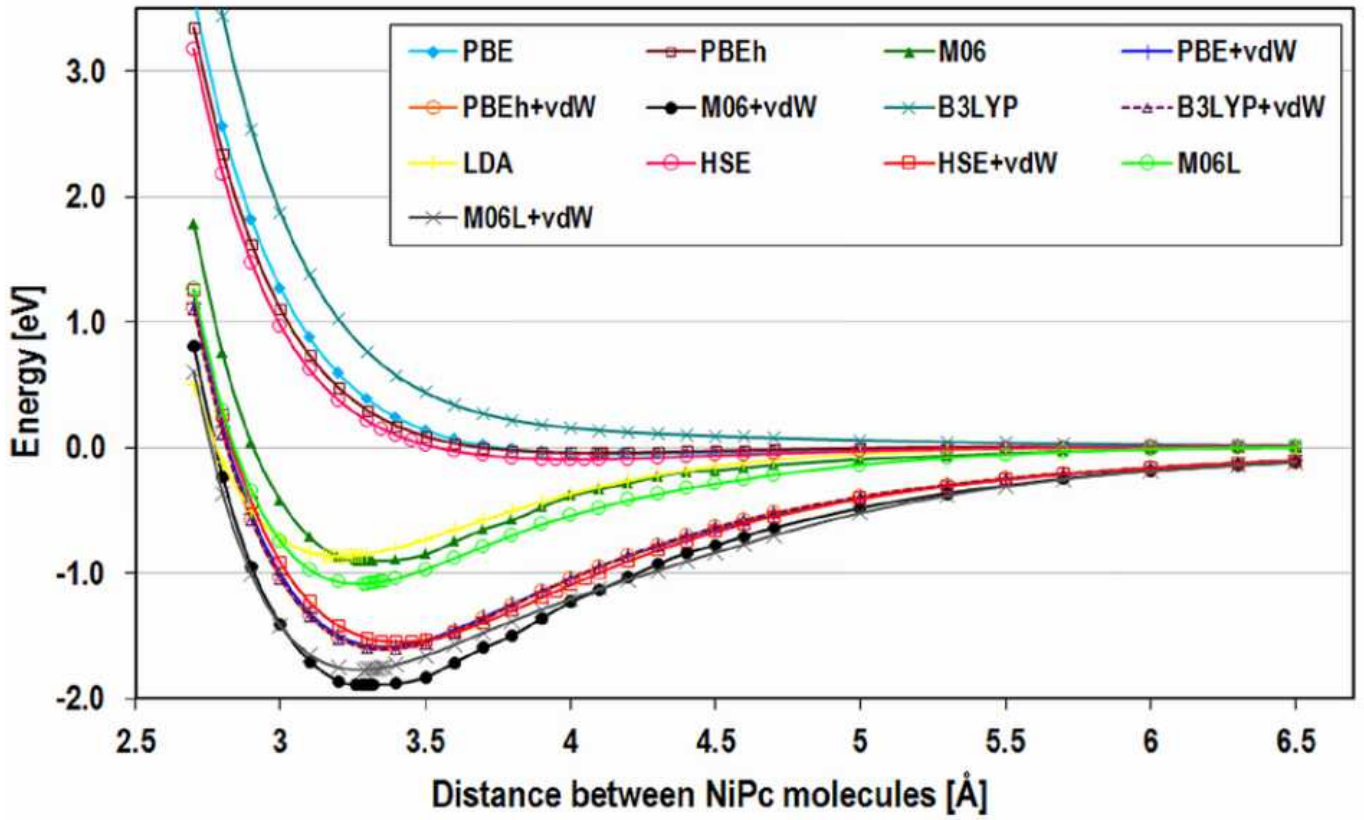
The description of vdW in M06

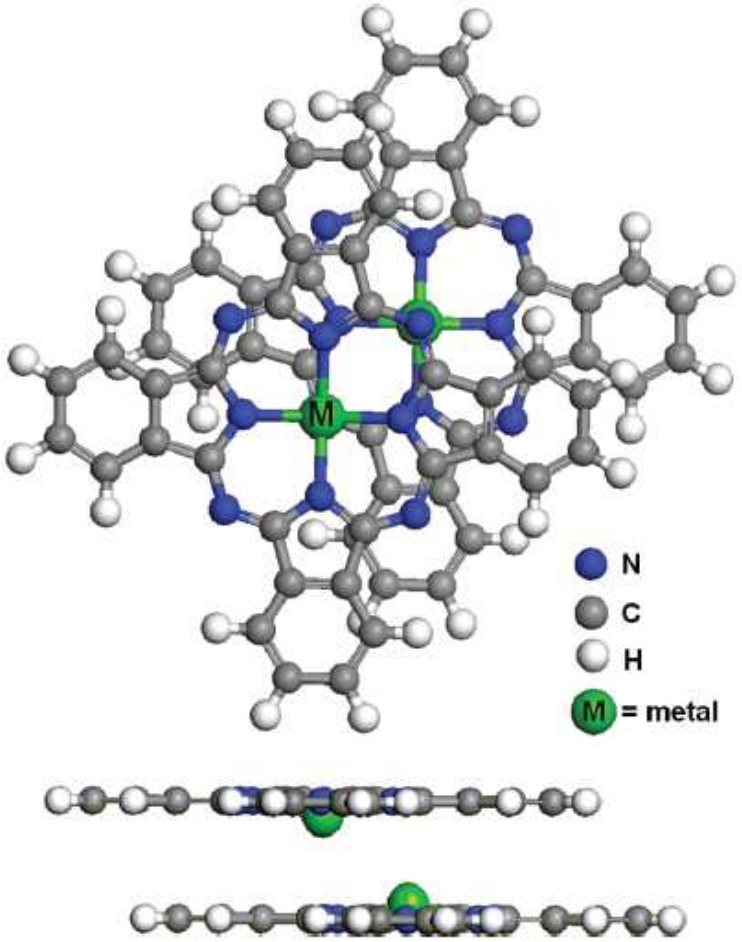
Flexible meta-GGA form allows for an approximate modeling of vdW interactions at short-range whenever there is a non-negligible electron density overlap

M06 converges to zero interaction at ~ 5 Å separation between atoms, in the same way as LDA and GGA

Thus, M06 does not include the correct physics of vdW interactions, typically leading to underbinding of vdW-bound systems

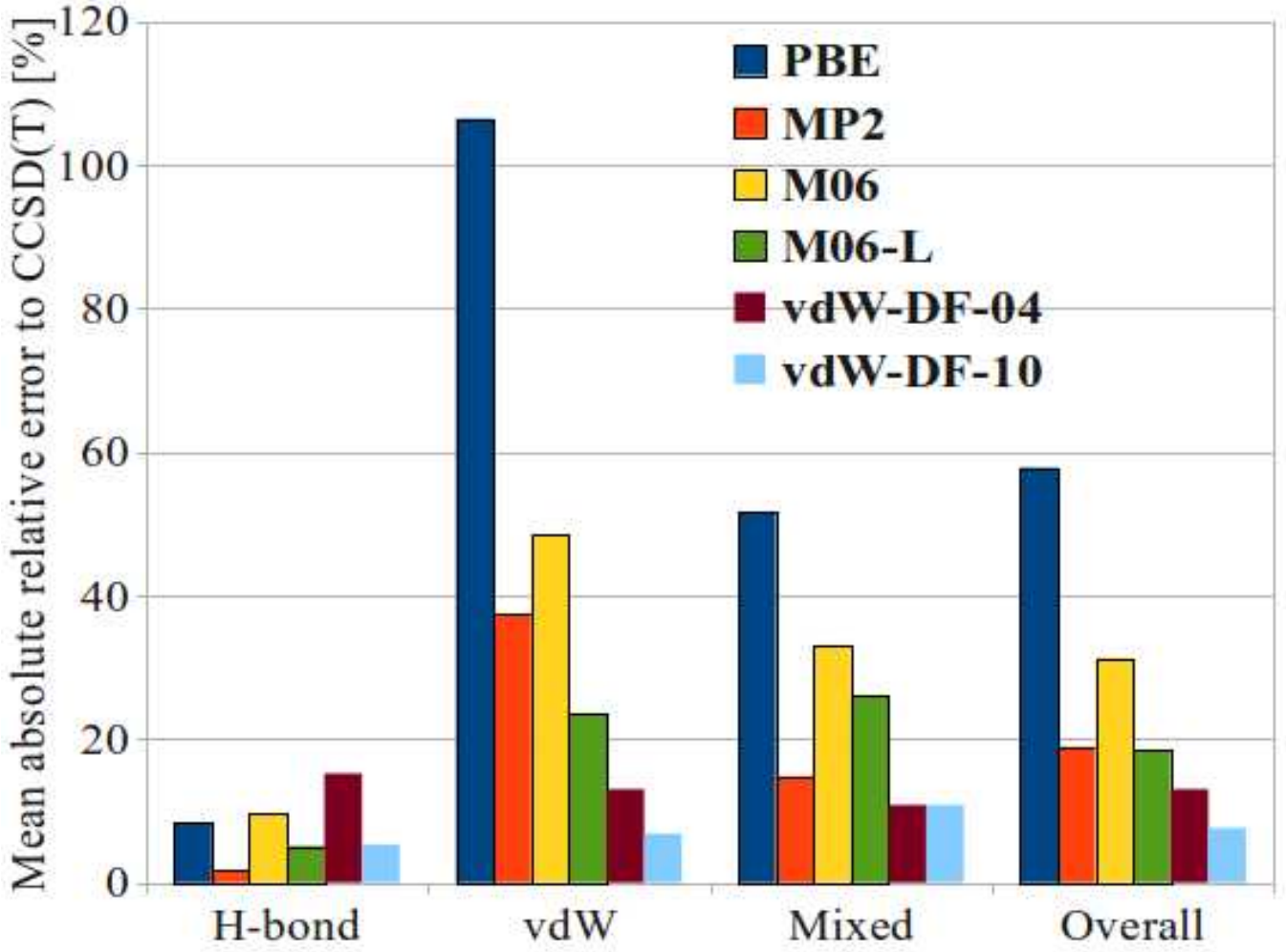
The description of vdW in M06





Marom, Tkatchenko, Gobre, Rossi, Hod, Scheffler, Kronik, to be submitted.

Performance of M06(-L) for S22



Interatomic vdW correction methods

Interatomic vdW methods

$$E_{\rm xc} = E_{ex}^{\rm GGA\ or\ EX} + E_{\rm corr}^{\rm LDA,GGA} + E_{\rm corr}^{\rm non-local}$$

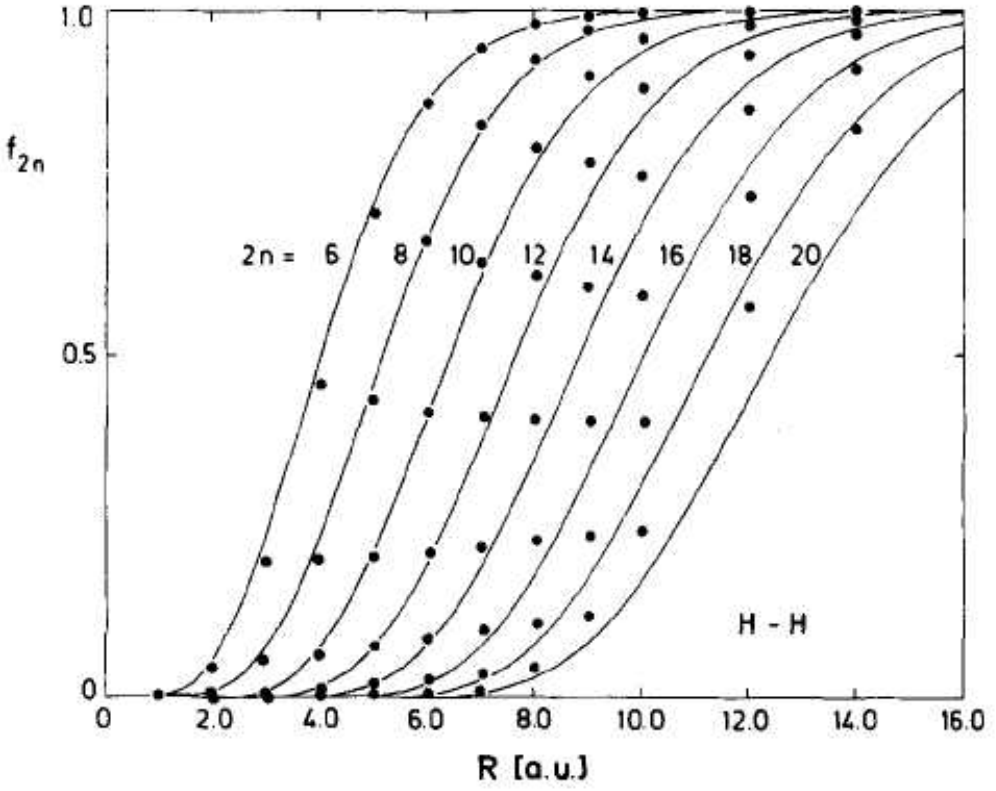
$$E^{vdW}(R) = -\left(f_6(R)\frac{C_6}{R^6} + f_8(R)\frac{C_8}{R^8} + f_{10}(R)\frac{C_{10}}{R^{10}} + \ldots \right)$$

- Two parameters per atomic pair: (1) VdW C_6 interaction coefficient and (2) vdW radius.
- Clearly, if (1) and (2) are empirical, this leads to many fitting parameters. This was frequently the case before 2008.

Damping function for vdW-corrected DFT

$$f_{damp}(R_{AB}, R^0_{AB}) = [1 + \exp(-d(\frac{R_{AB}}{s_R R^0_{AB}} - 1))]^{-1}$$

- Steep damping function required to separate the short range from vdW energy
- About 5 different functional forms proposed
- Fermi function (above) among the most popular ones
- Works for molecules, but the functional form is arbitrary !



Evolution of interatomic vdW methods

- Grimme's D1,D2 (2004-2006): Parameterization for many elements in the periodic table
  - Highly empirical, some approximations unfounded
- Jurečka *et al.* (2007): Accurate parameterization for organic molecules
  - Better theoretical ground, but still very empirical
- Johnson and Becke (2005-2008), Silvestrelli (2008): C_6 and vdW radii from HF or DFT orbitals
  - Reduced empiricism, errors of ~ 20%-40% in C_6 coefficients
- Tkatchenko and Scheffler (2009): C_6 coefficients and vdW radii from ground-state electron density
  - First-principles C_6 accurate to **5%**
- ....

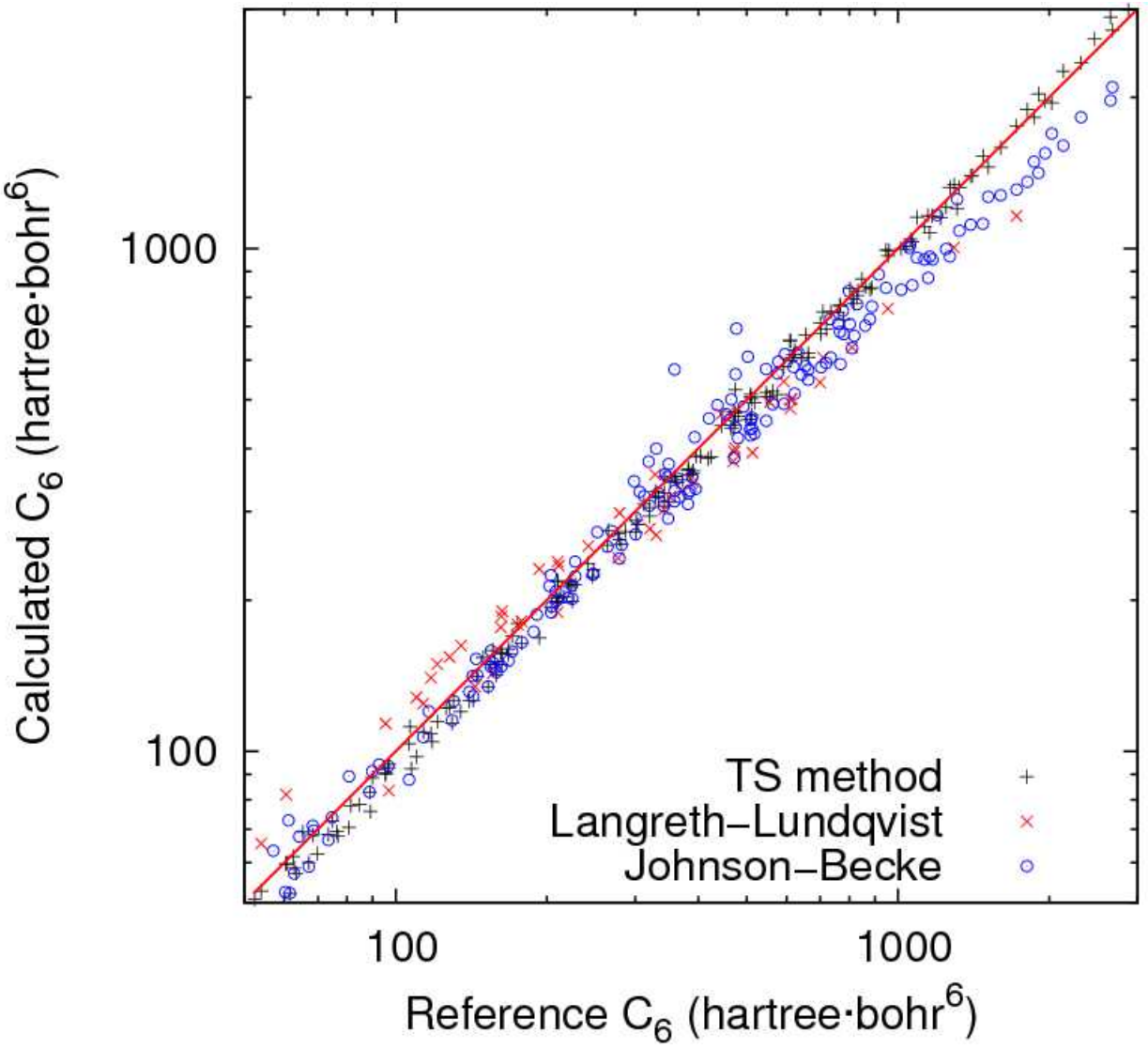
Highlights of TS-vdW method

- VdW asymptotics with an accuracy of 5%
- Transparent partitioning of vdW coefficients over atoms
- Reduced empiricism (1 parameter in the damping function)
- Polarizability is directly proportional to volume
- Computationally efficient
- Valid for the whole periodic table

$$C_{6AA}[n(\mathbf{r})] = \left(\frac{V_A[n(\mathbf{r})]}{V_A^{free}[n^{free}(\mathbf{r})]} \right)^2 C_{6AA}^{free}$$

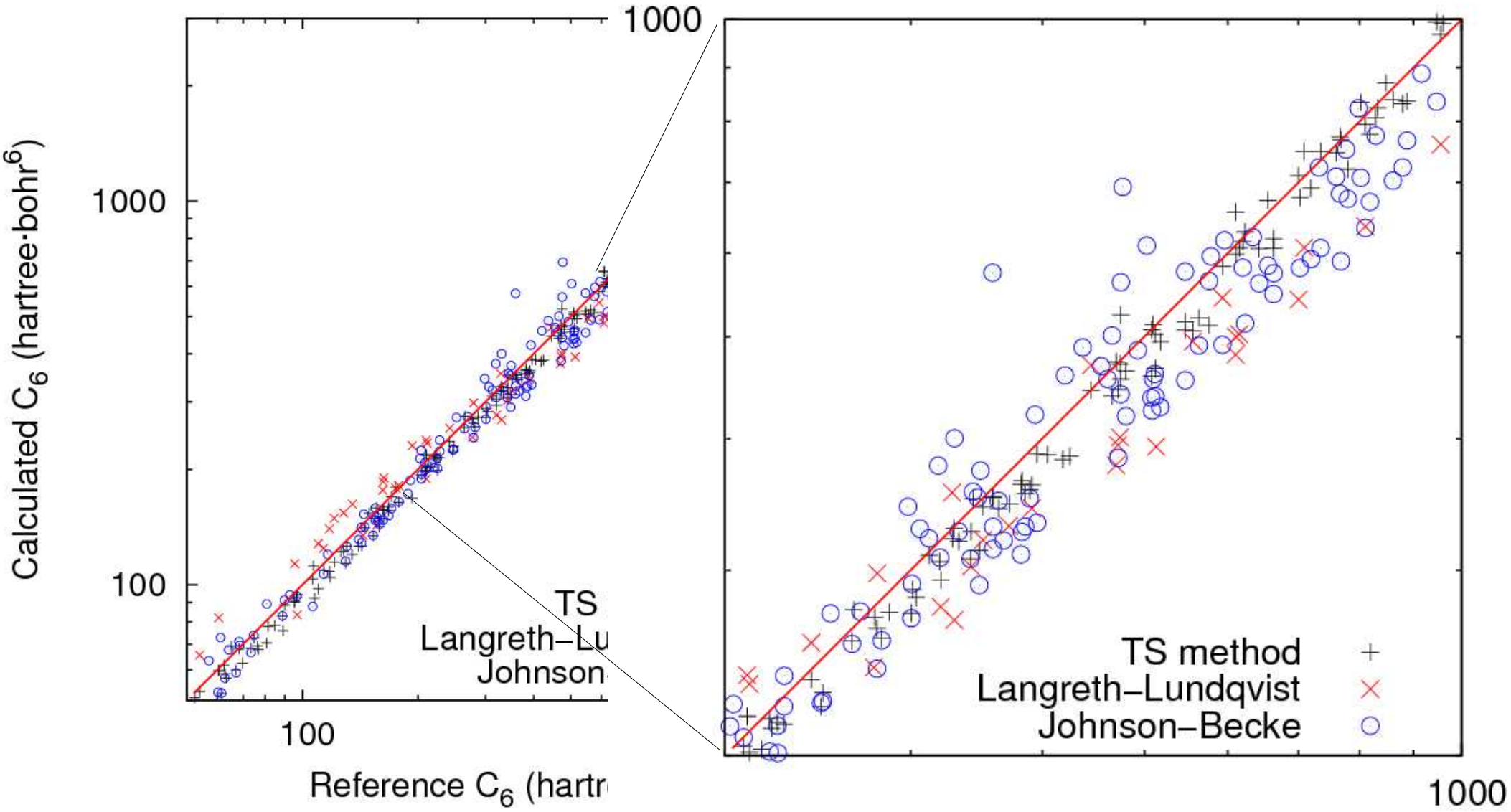
Tkatchenko and Scheffler, ***PRL*** (2009)

Performance of TS-vdW method for molecules



Mean absolute error of 5.5% for 1225 molecular C_6 from reference DOSD data of *W. J. Meath et al.*

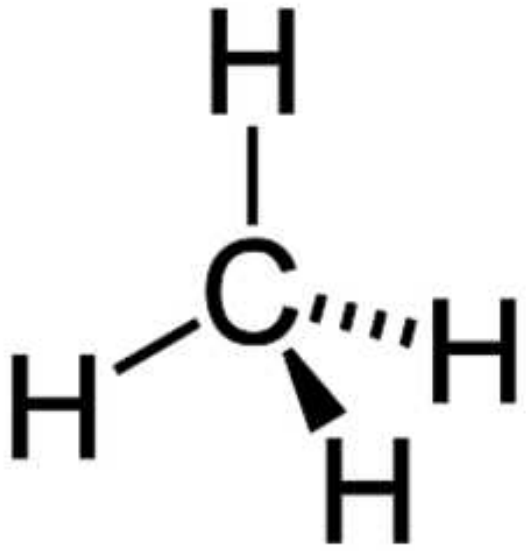
Performance of TS-vdW method for molecules



Results depend negligibly (1% deviation) on the employed *xc* functional

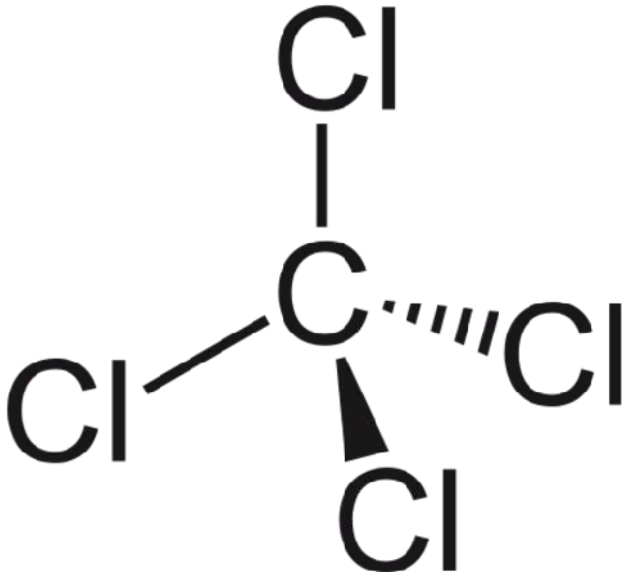
C_6 is a functional of the density

(Carbon-Carbon C_6 coefficient / Hartree Bohr^6)



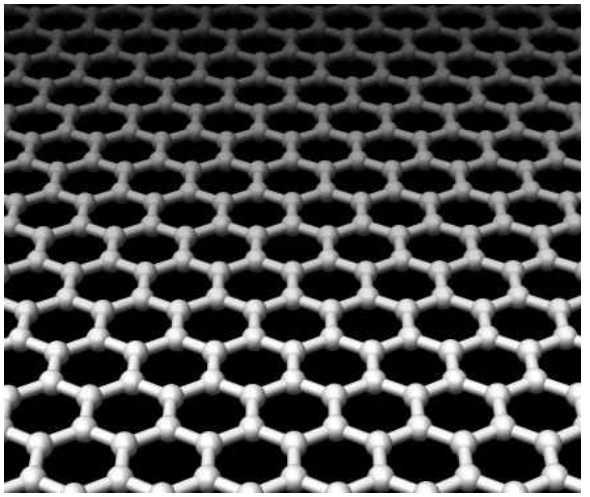
24.1

sp^3



43.1

sp^3



33.0

sp^2

DFT+vdW

Leading dispersion term is added to DFT total energy, damped at short interatomic distance,

$$E_{vdW} = -\sum_{A}\sum_{B>A} f_{damp}(R_{AB}, R^0_A, R^0_B) C_{6AB} R^{-6}_{AB}$$

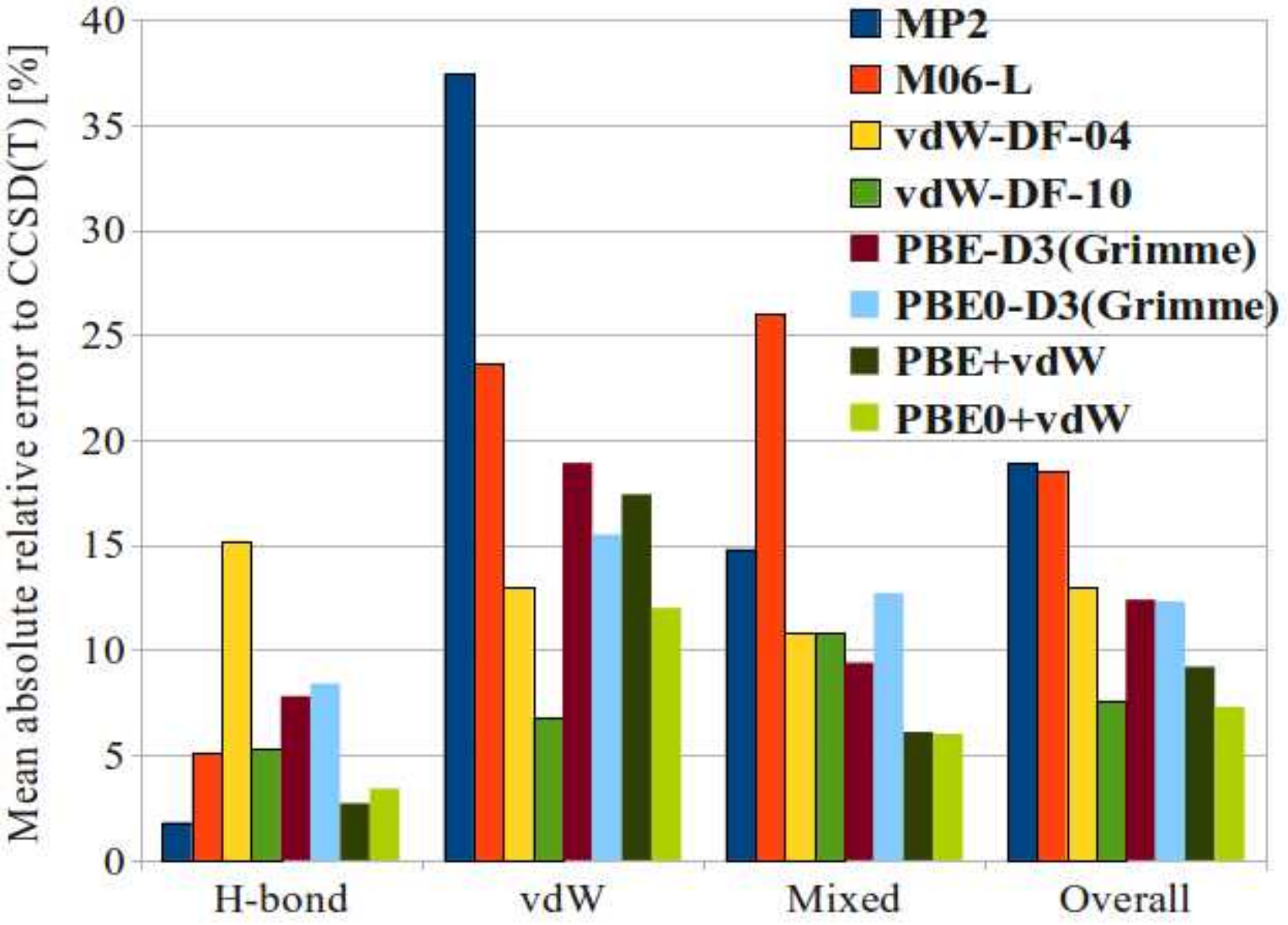
$$R^0_{eff} = \left(\frac{V^{eff}}{V^{free}}\right)^{1/3} R^0_{free}$$

- Effective vdW parameters are functionals of the electron density:

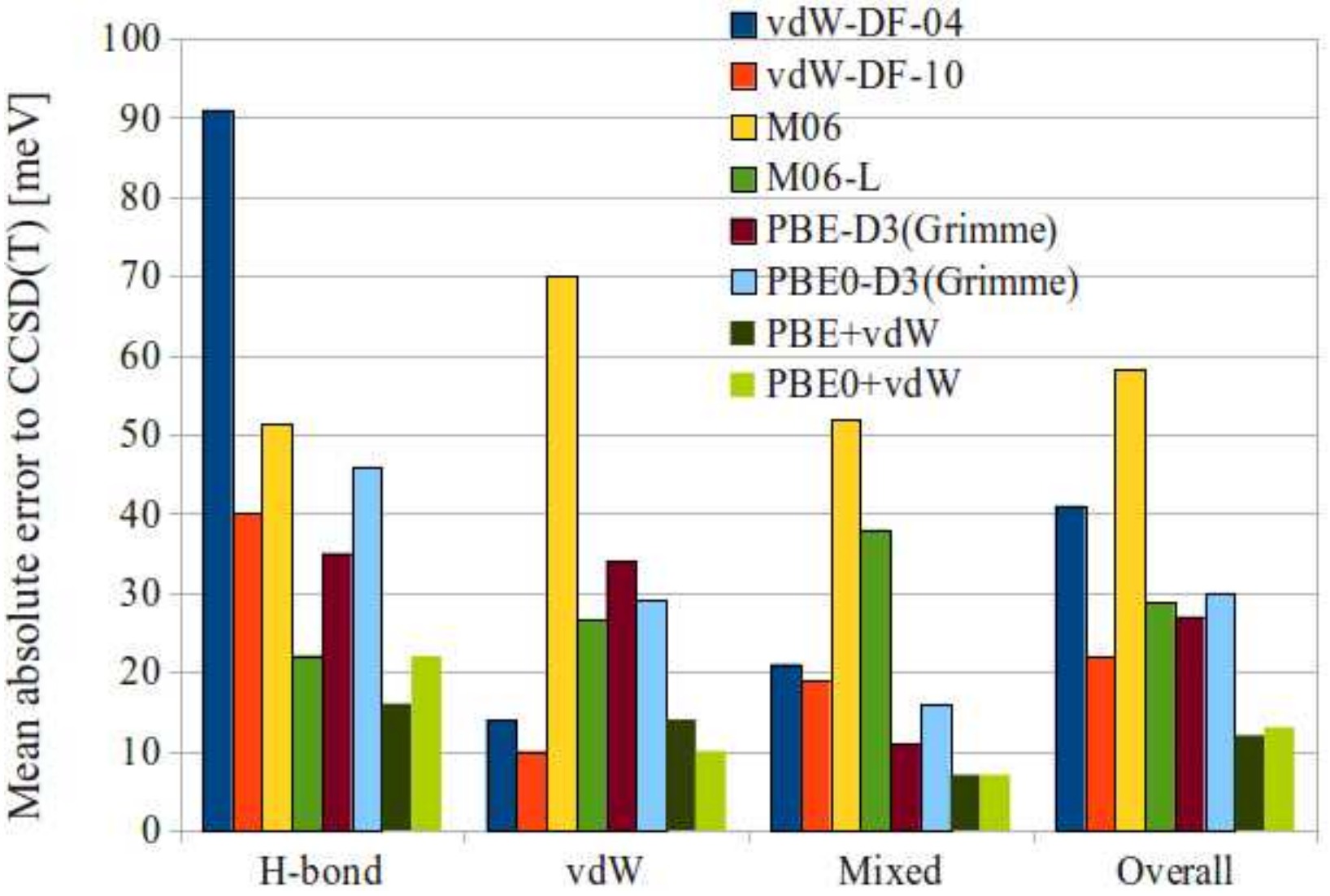
$$C_6 = C_6[n(\boldsymbol{r})], \quad R_{\mathrm{vdW}} = R_{\mathrm{vdW}}[n(\boldsymbol{r})]$$

DFT+vdW: *Tkatchenko and Scheffler*, ***PRL*** (2009)

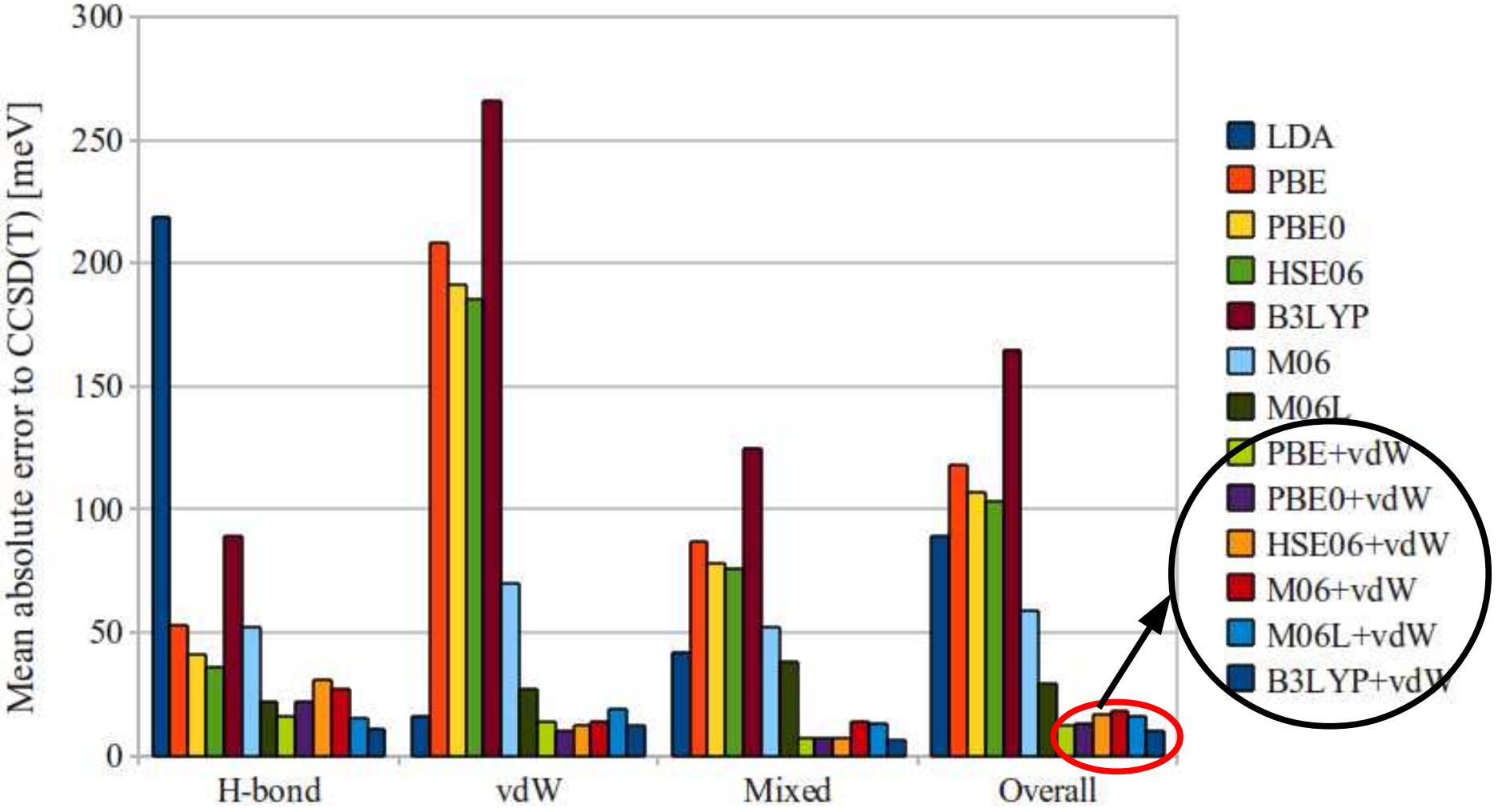
Performance of DFT+vdW for S22



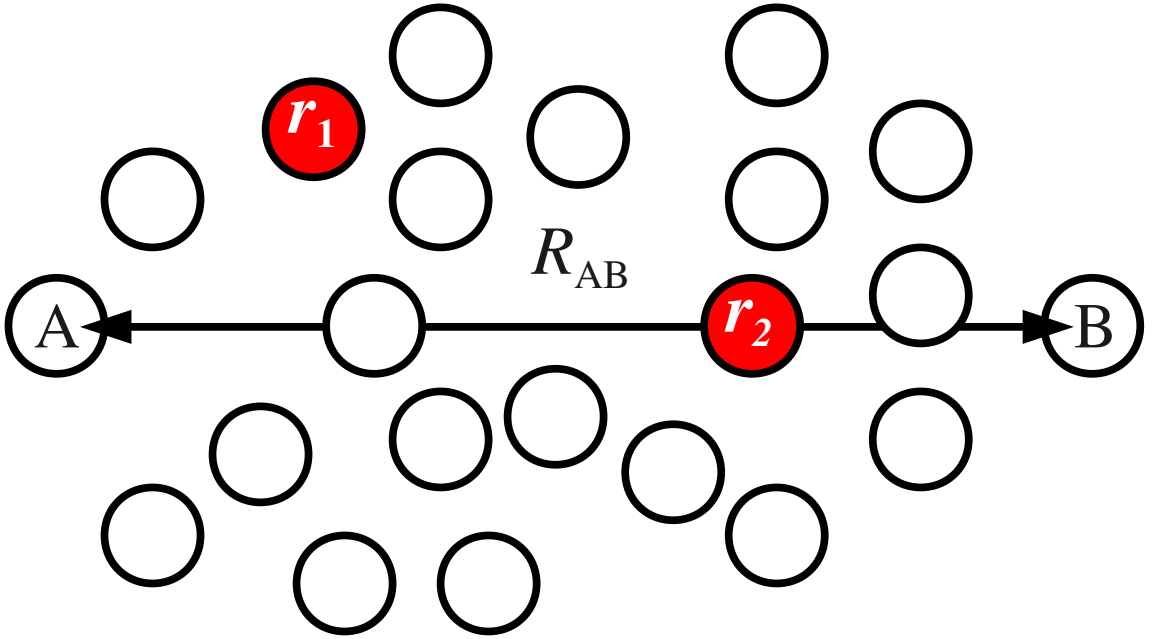
Performance of DFT+vdW for S22 (Mean Absolute Error)



Performance of DFT+vdW for S22: Different functionals



What is missing in DFT+vdW?

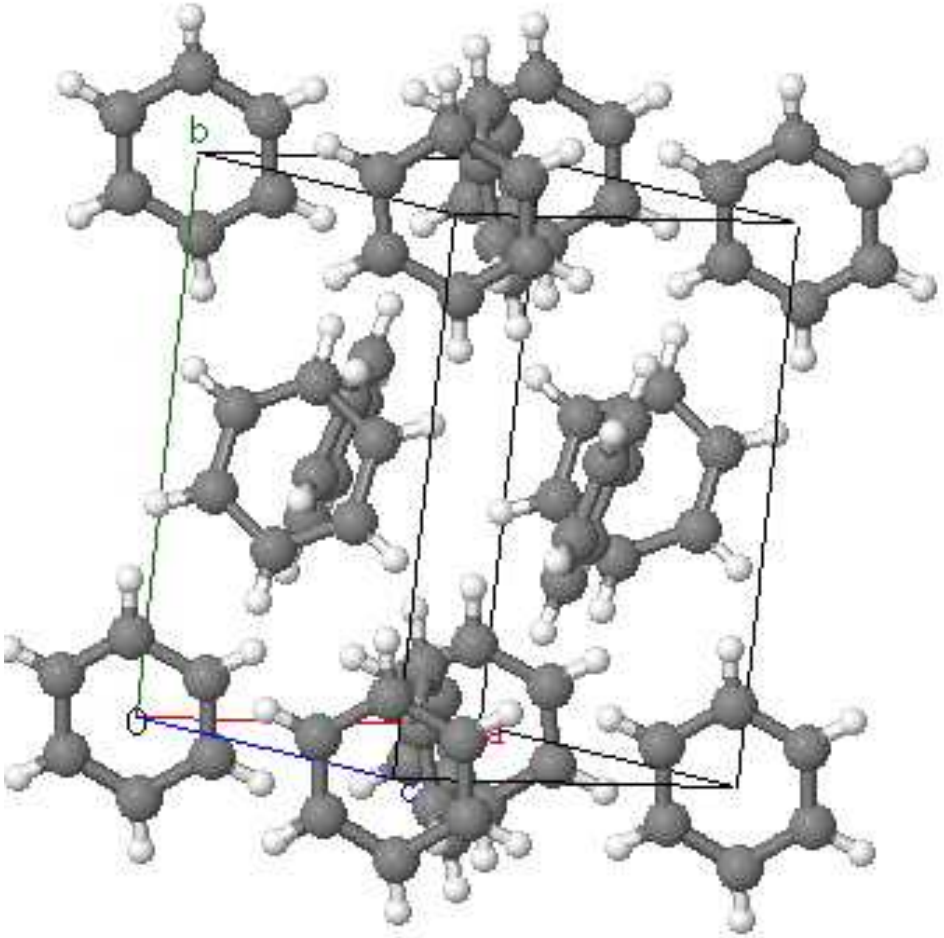


$$E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1}, \mathbf{r_2}; i\omega) - \chi_0(\mathbf{r_1}, \mathbf{r_2}; i\omega)) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \right)$$

1) Long-range electrostatic screening among fluctuating dipoles

2) Non-additive many-body vdW energy beyond two-body

DFT+vdW^{SCS+MB}: Screening and Many-Body vdW Energy



Benzene crystal

PBE+vdW
690 meV/molecule

PBE+vdW^{SCS+MB}
565 meV/molecule

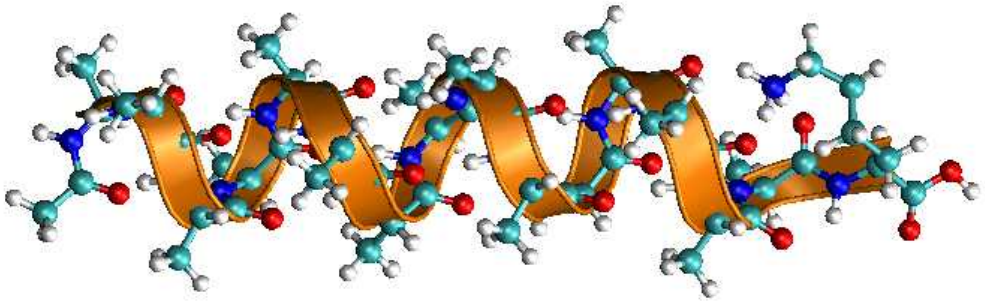
2.9 kcal/mol
due to screening
and many-body
VdW effects

Experiment
518-560 meV/molecule

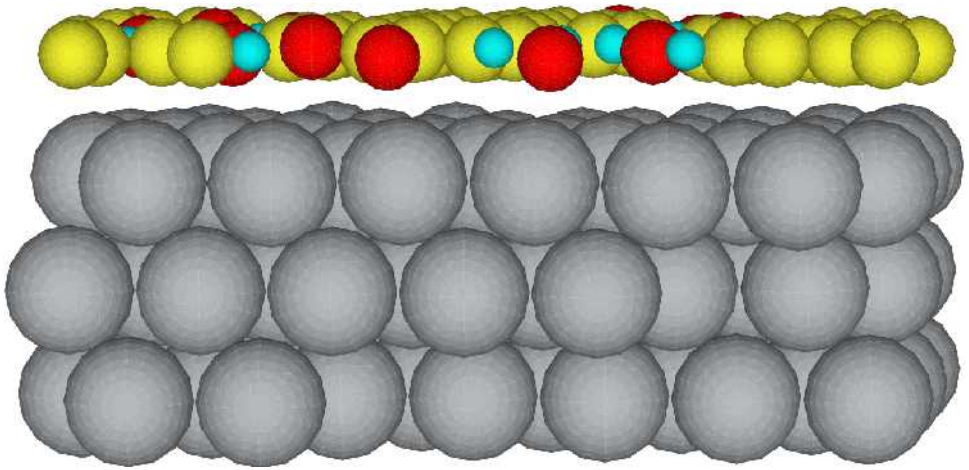
Tkatchenko, DiStasio Jr., Car, Scheffler, to be submitted.

DFT+vdW: Challenges

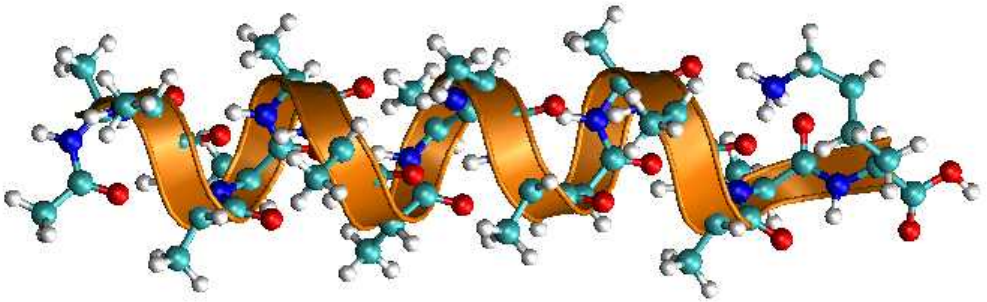
- DFT+vdW treats intra- and intermolecular interactions accurately. Recent extension permits the treatment of insulators, ionic, and semiconductor solids
- Coupling of (short-range) DFT and (long-range) vdW remains empirical, and one of the biggest issues to address
- No satisfactory model for metallic bulk systems yet
- Interatomic potentials may not work for highly anisotropic low-dimensional systems (*Dobson, Rubio, et al.*)



Applications



Unraveling the Role of vdW Interactions for Peptide Secondary Structure

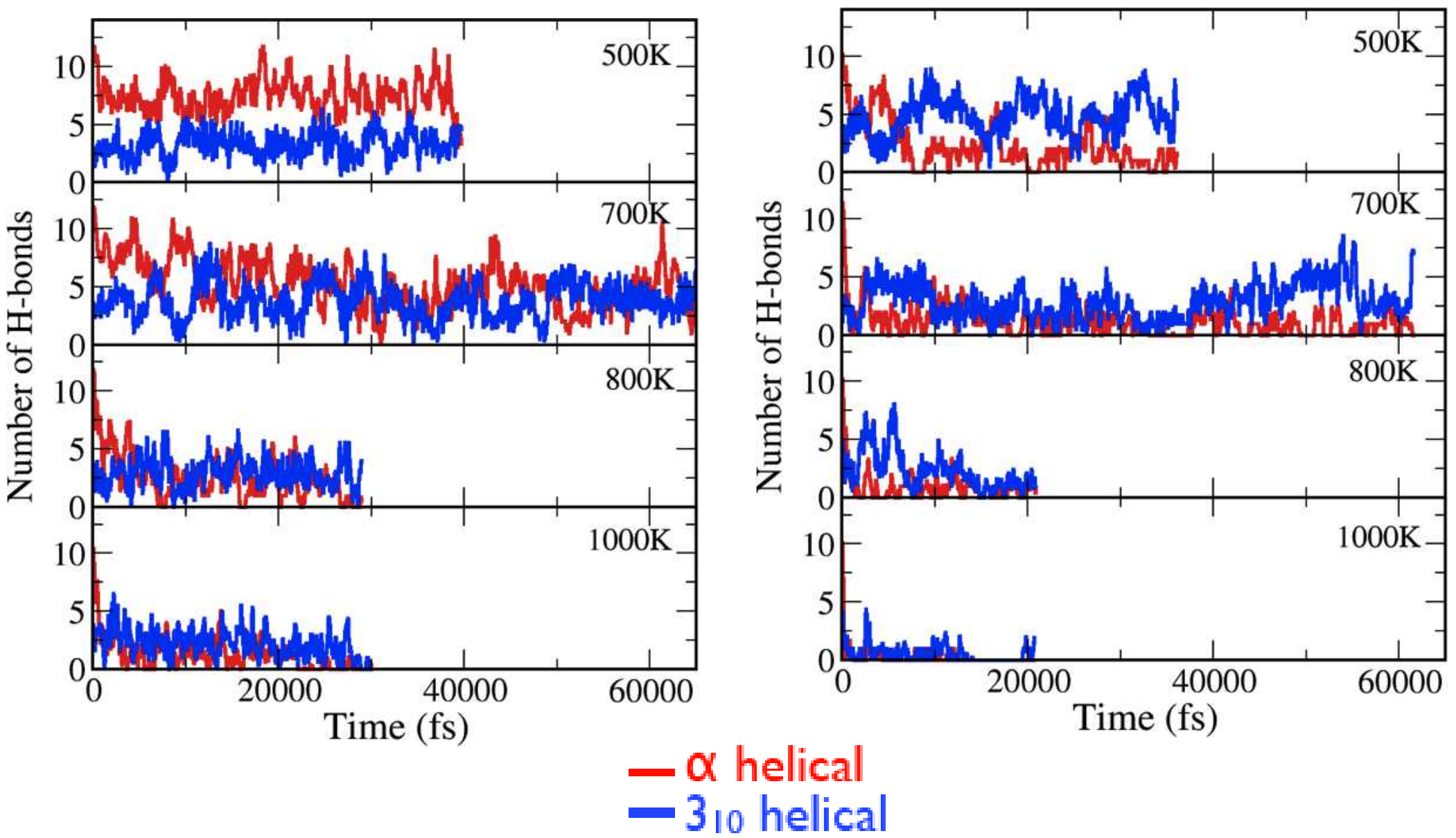


- $Ala_{15}LysH^{+}$ forms stable helices *in vacuo* up to ~ 700 *K* (in solution only up to ~ 340 *K*)
- Direct first-principles folding simulations are not feasible, but unfolding dynamics could provide similar insight !

Experiments: *Kohtani, Jones, Schneider, Jarrold,* ***JACS*** (2004)

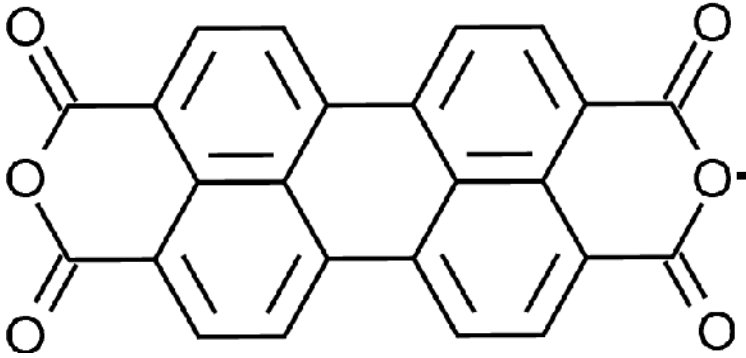
DFT-PBE+vdW

DFT-PBE



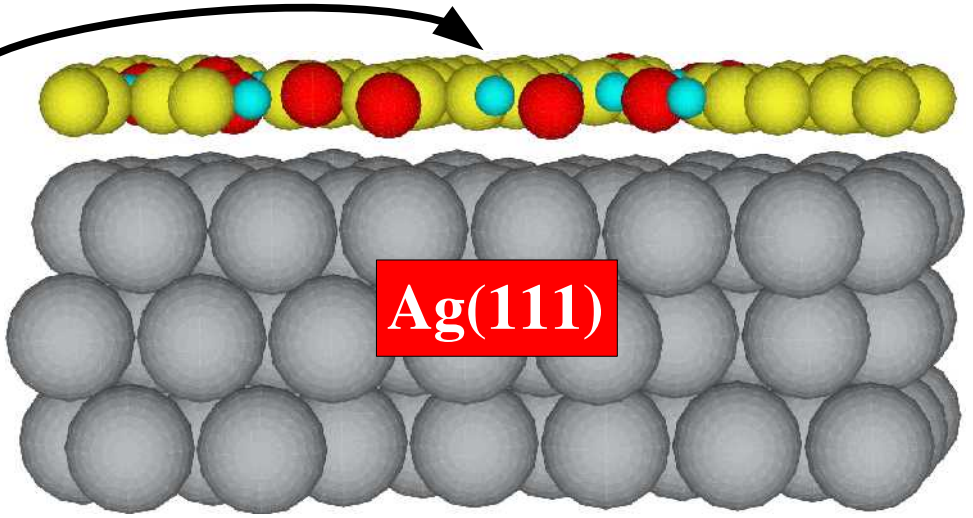
Tkatchenko, Rossi, Blum, Ireta, Scheffler, ***PRL*** (2011)

Van der Waals and Inorganic/Organic Interfaces

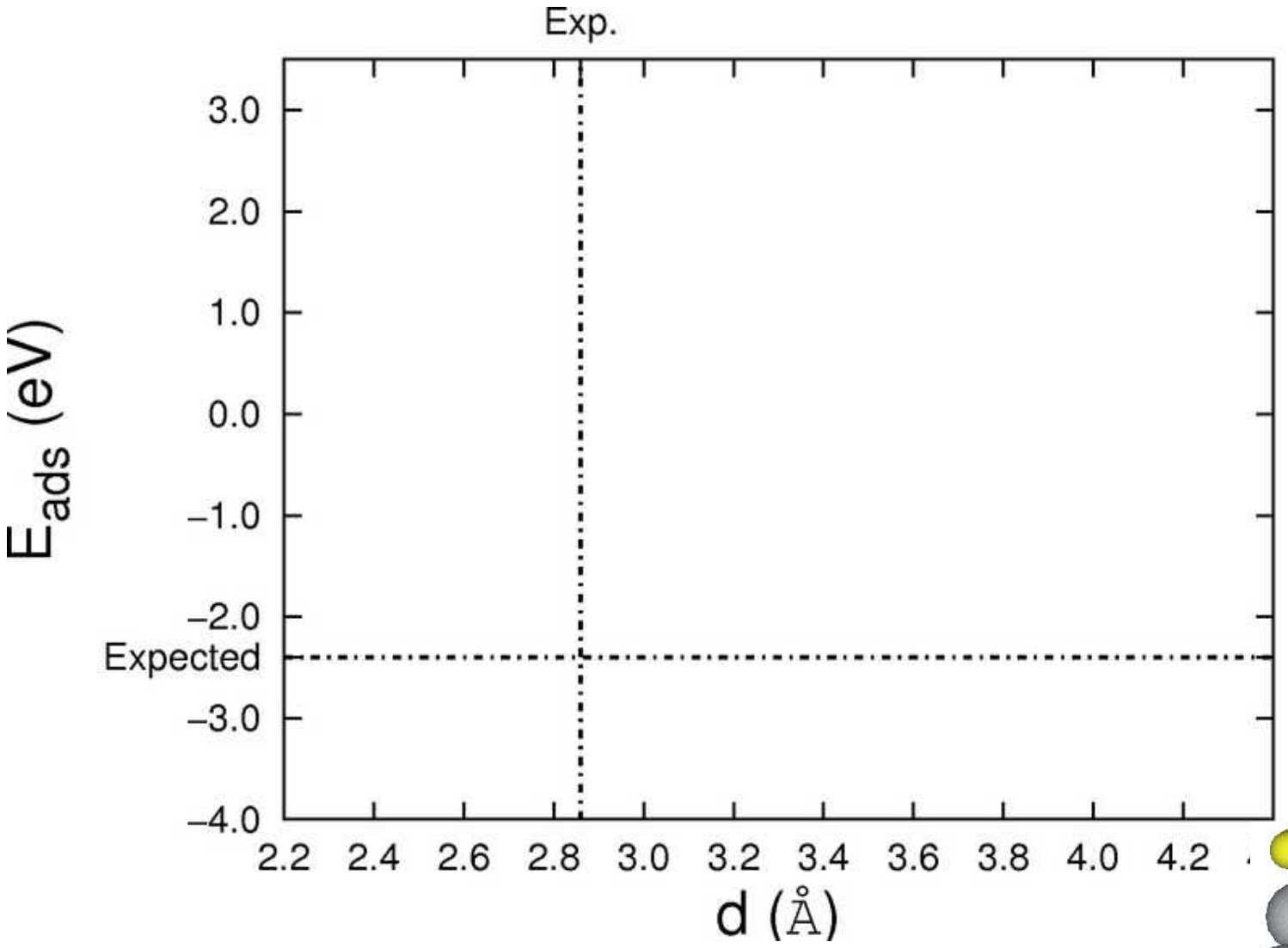


perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride

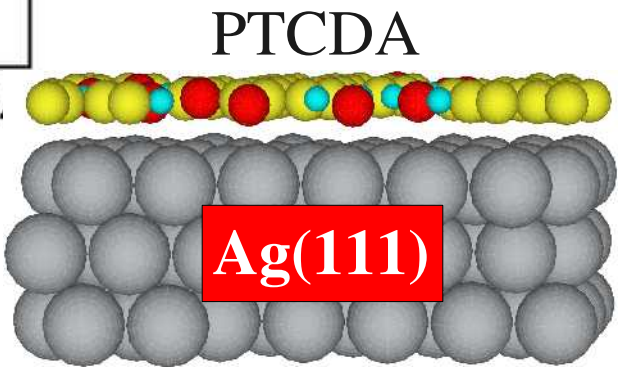
(PTCDA)



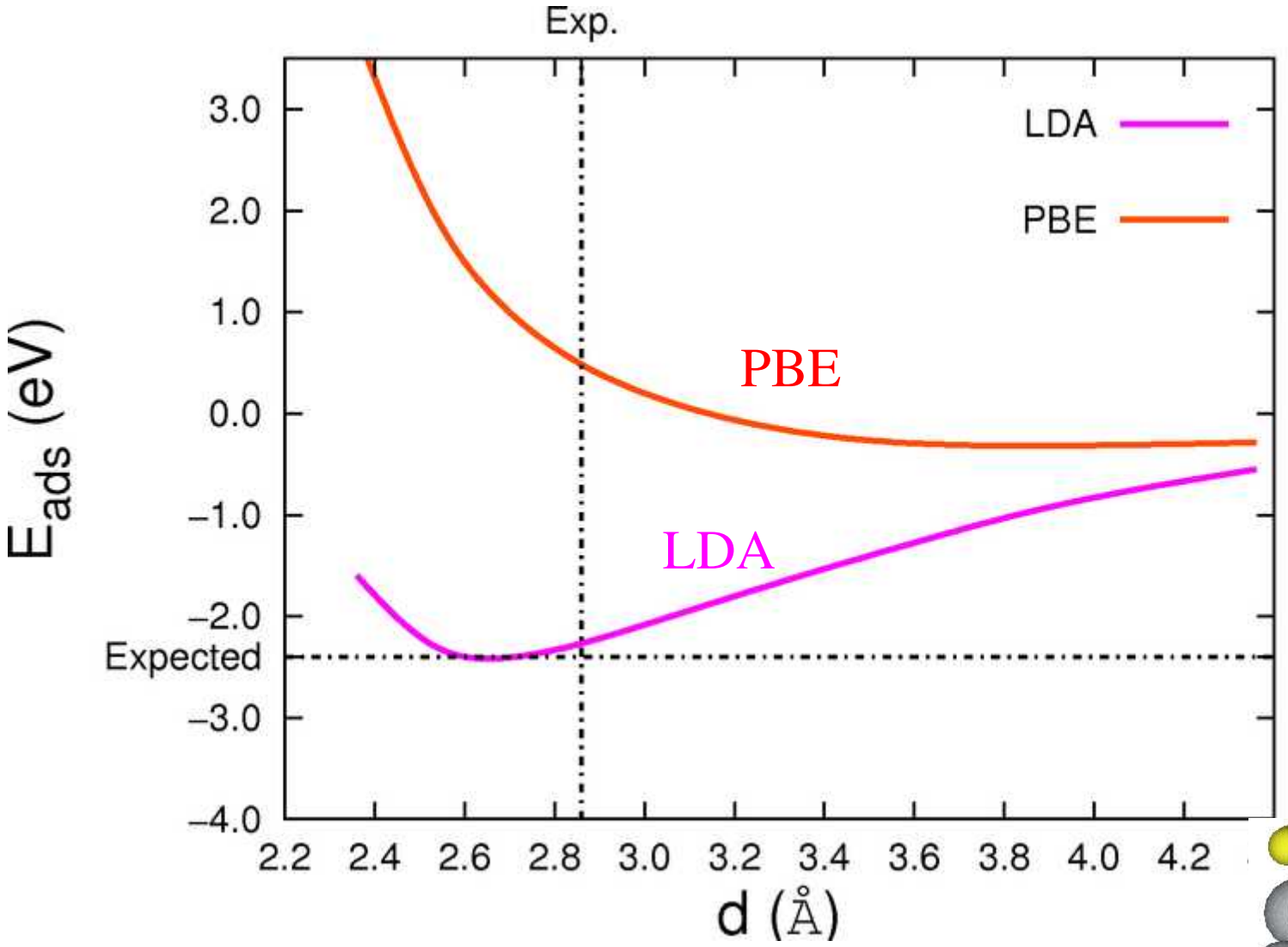
Van der Waals and Interfaces: Which theoretical method ?



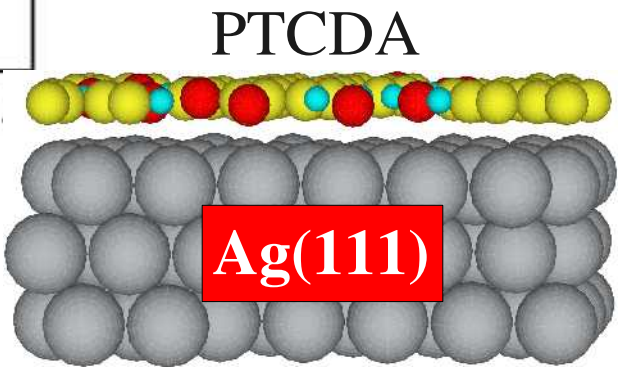
Experiment: *A. Hauschild et al.*, ***PRL*** (2007)



Van der Waals and Interfaces: Which theoretical method ?



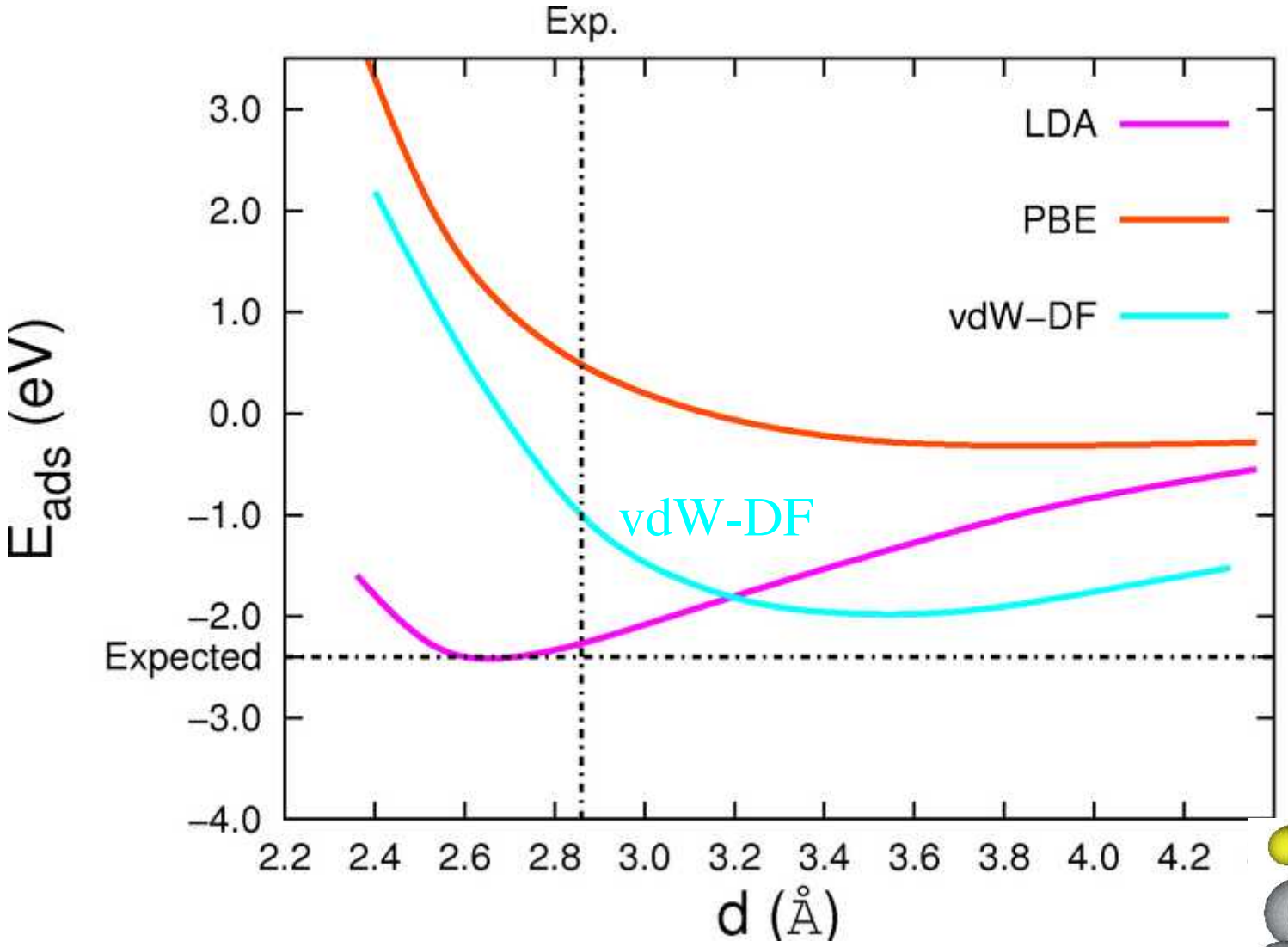
LDA/PBE:
(semi-)local DFT.
Can be applied to
> 1000 atoms



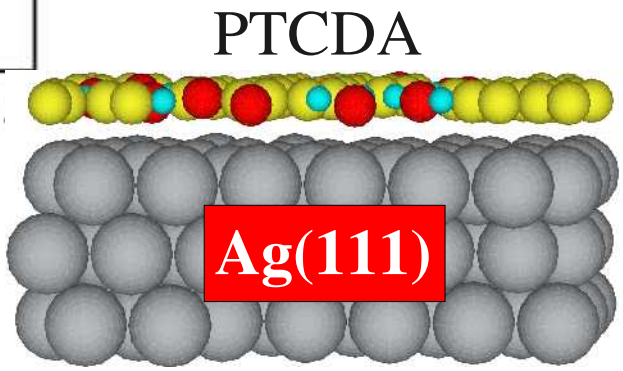
Experiment: *A. Hauschild et al.*, ***PRL*** (2007)

Theory review: *A. Tkatchenko et al.*, ***MRS Bulletin*** (2010)

Van der Waals and Interfaces: Which theoretical method ?

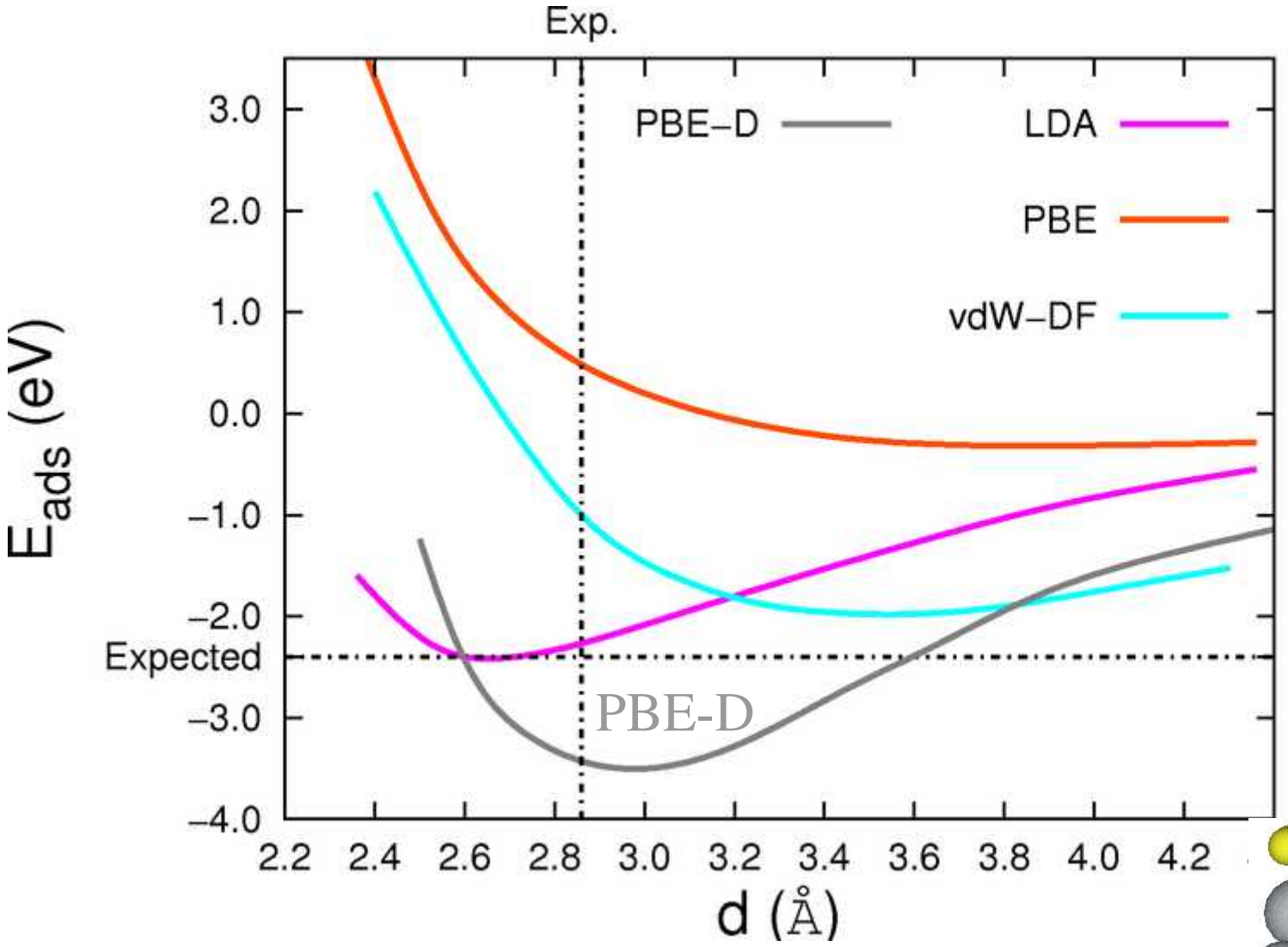


vdW-DF:
Non-local Langreth-Lundqvist functional.
Can be applied to > 1000 atoms

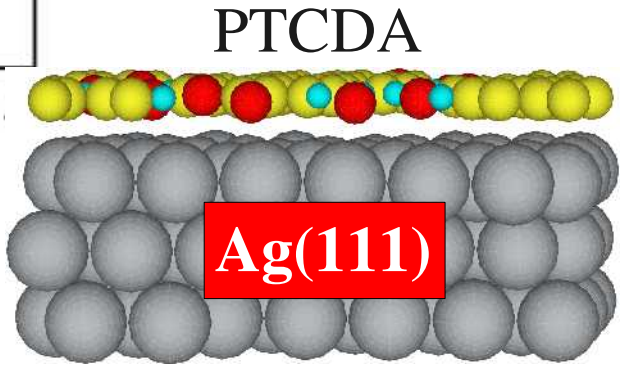


Experiment: *A. Hauschild et al.*, ***PRL*** (2007)
vdW-DF: *L. Romaner et al.*, ***New J. Phys.*** (2009)

Van der Waals and Interfaces: Which theoretical method ?

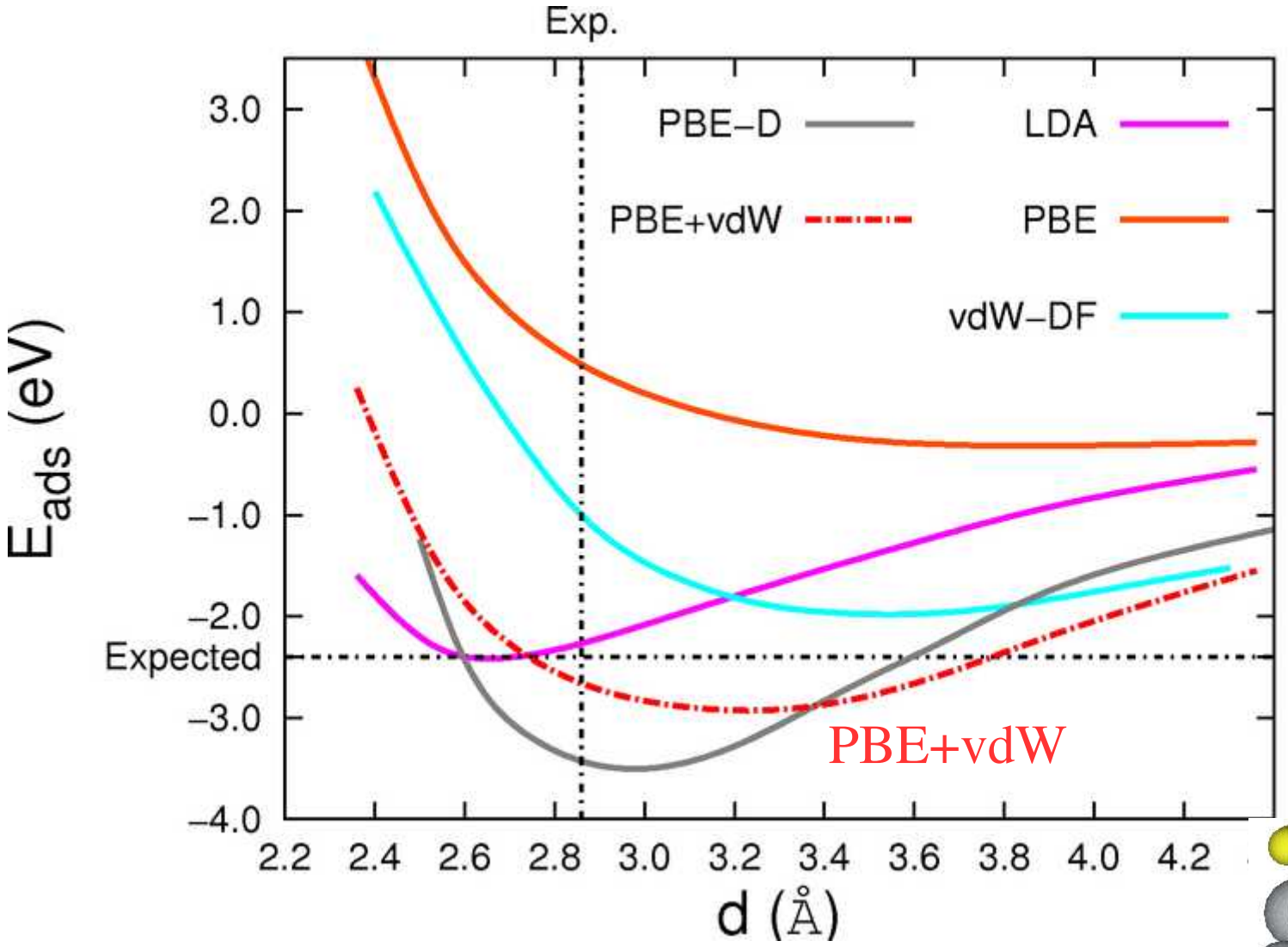


PBE-D:
PBE+Pairwise correction by Grimme.
Can be applied to > 1000 atoms

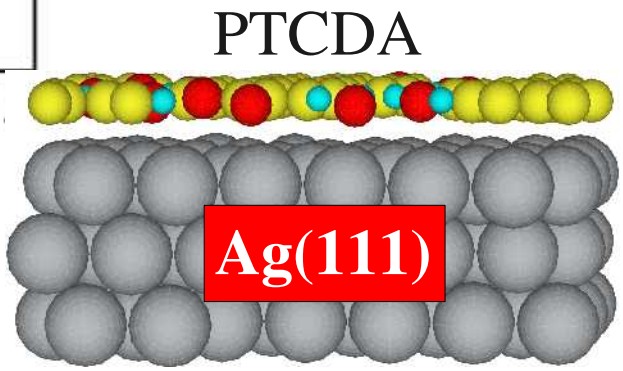


Experiment: *A. Hauschild et al.*, ***PRL*** (2007)
PBE-D: *E. McNellis,* PhD thesis (2010)

Van der Waals and Interfaces: Which theoretical method ?

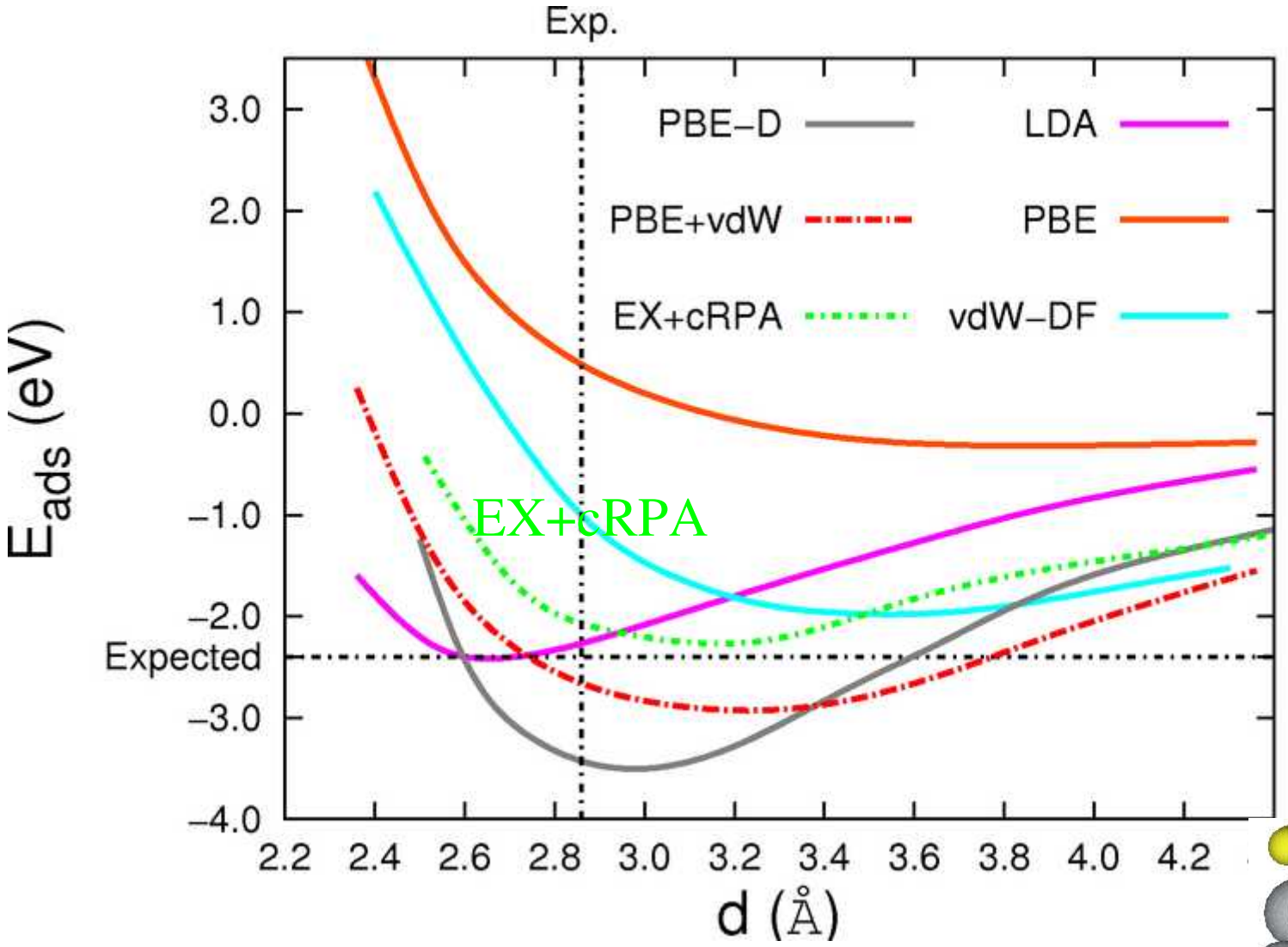


PBE+vdW:
PBE+Pairwise correction by Tkatchenko-Scheffler.
Can be applied to > 1000 atoms



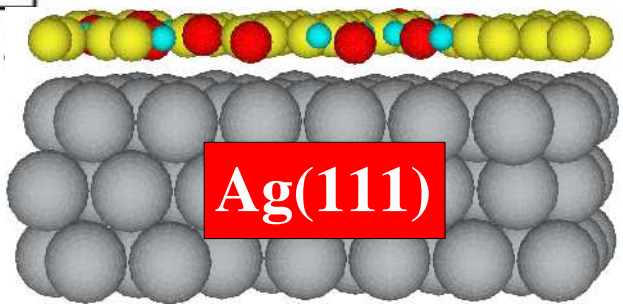
Experiment: *A. Hauschild et al.*, ***PRL*** (2007)
PBE+vdW: *E. McNellis*, PhD thesis (2010)

Van der Waals and Interfaces: Which theoretical method ?



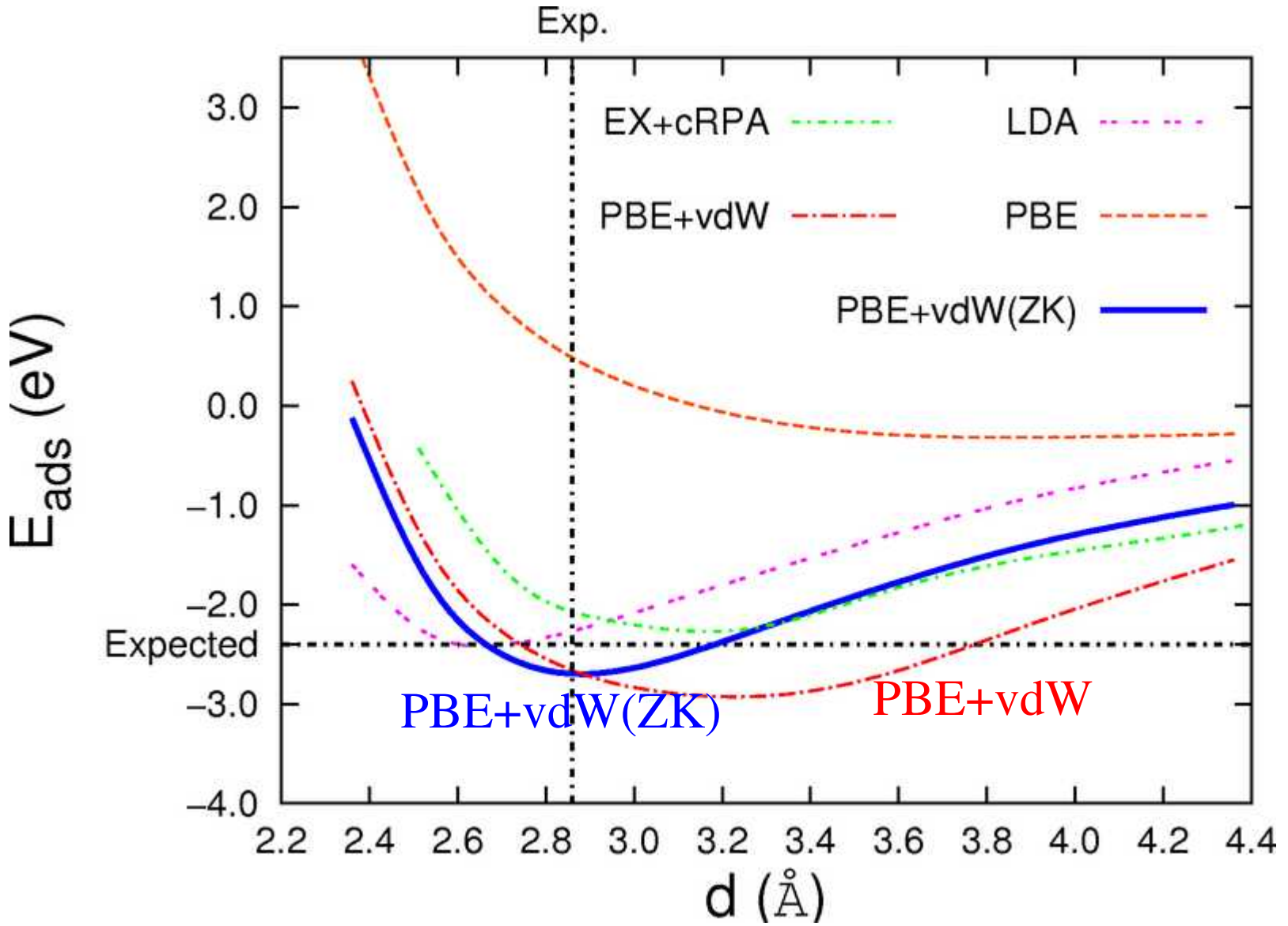
EX+cRPA:
Exact exchange + approximate many-body correlation energy.
Can be applied to < 200 atoms

PTCDA

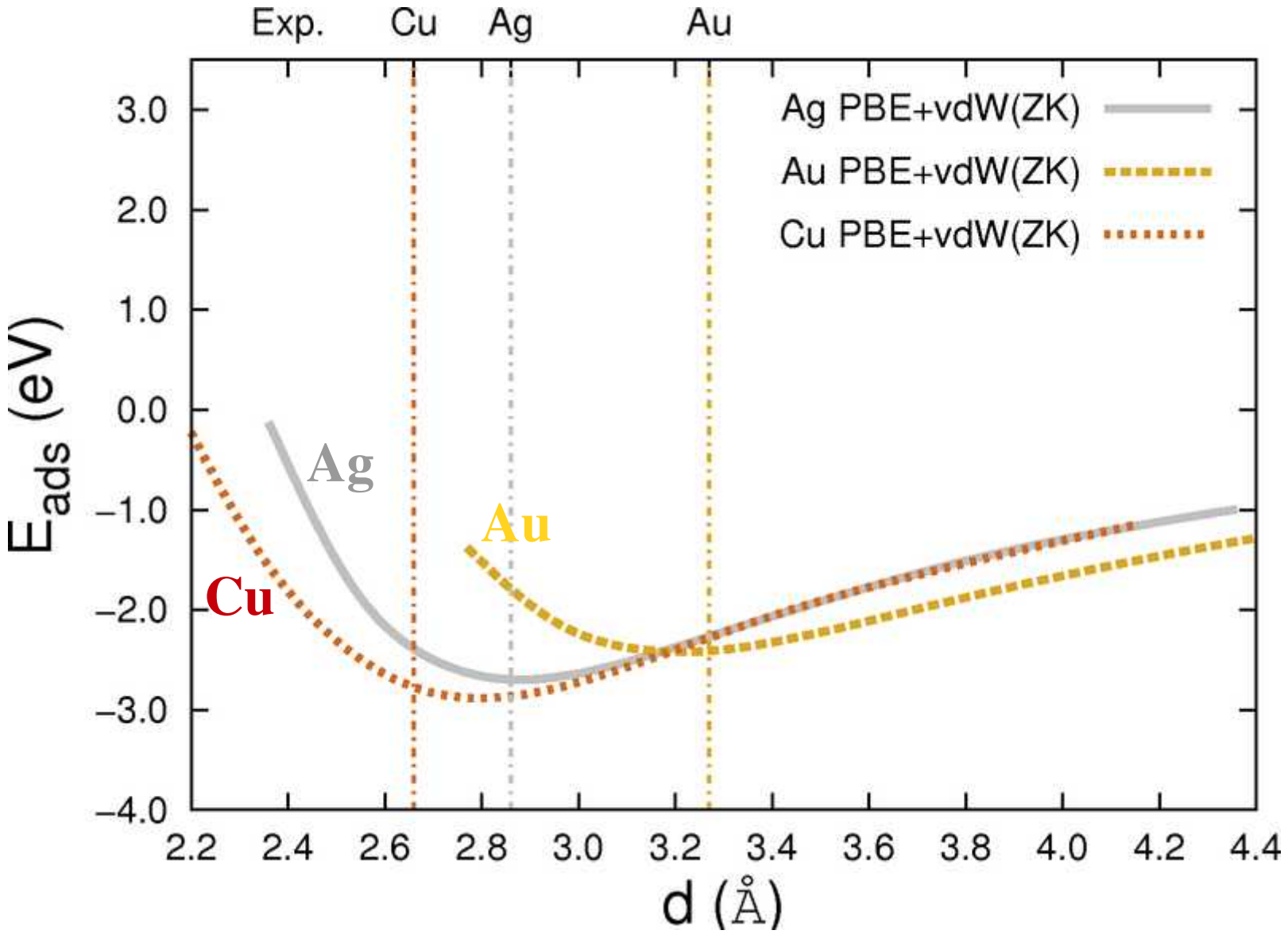


Experiment: *A. Hauschild et al.*, ***PRL*** (2007)
EX+cRPA: *M. Rohlfing and T. Bredow*, ***PRL*** (2008)

PTCDA@Ag(111): PBE+vdW(ZK)

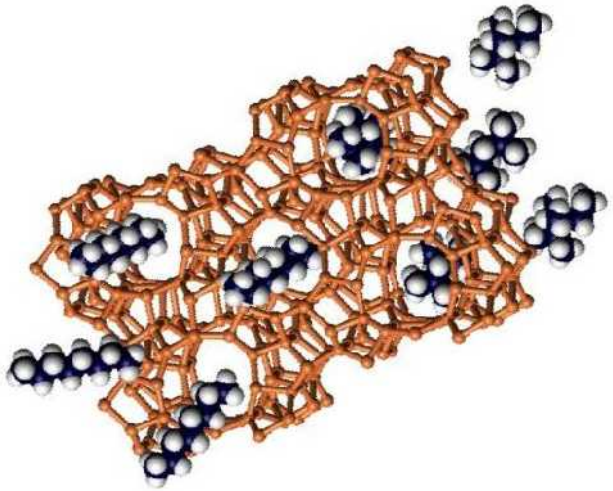


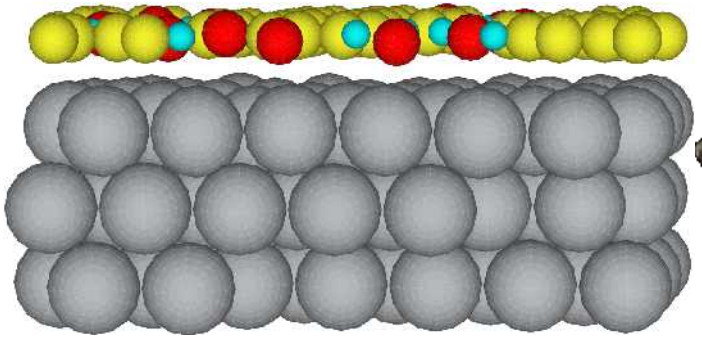
PTCDA@Cu/Ag/Au: PBE+vdW(ZK)

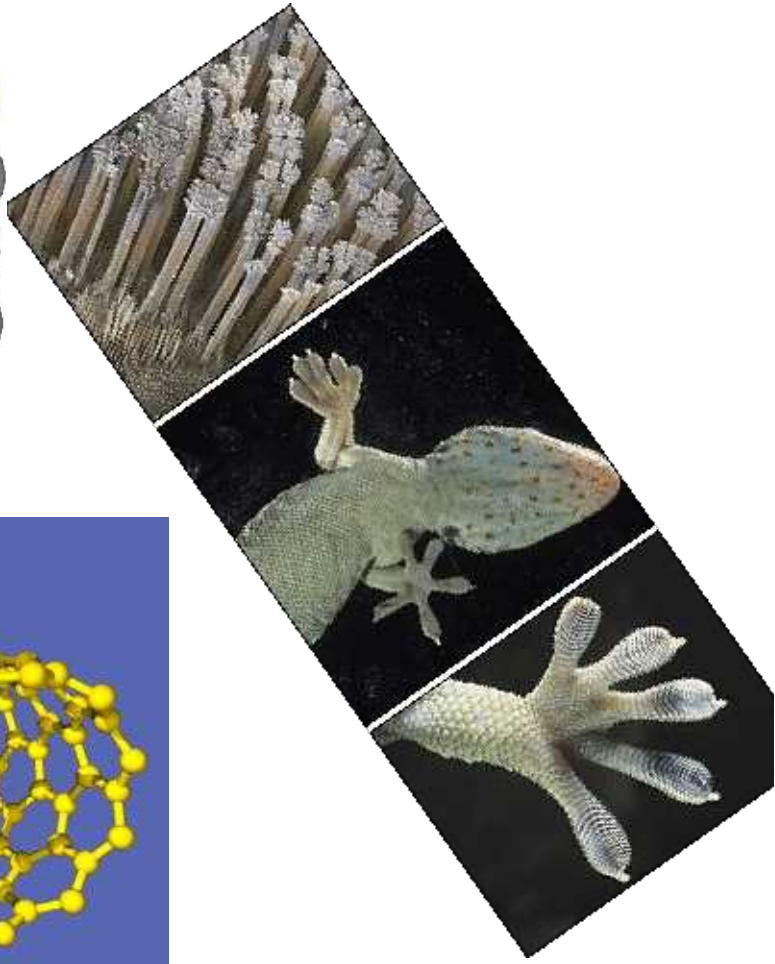


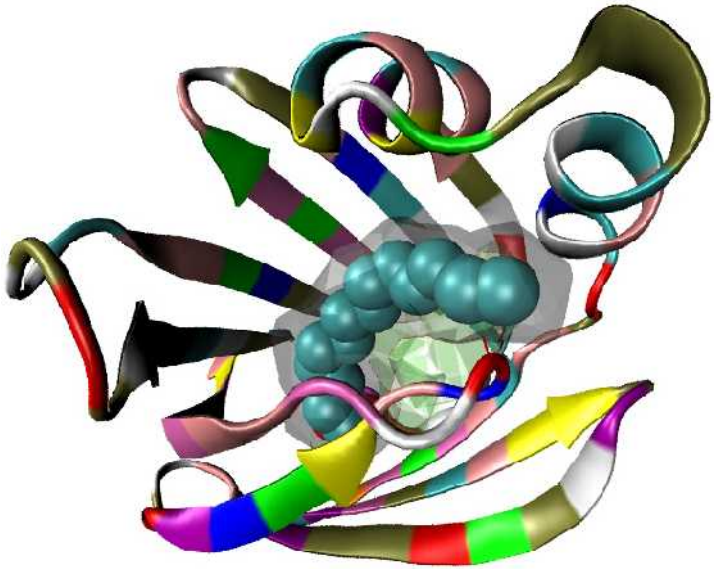
Joint work with *V. Ruiz, E. Zojer, M. Scheffler.*

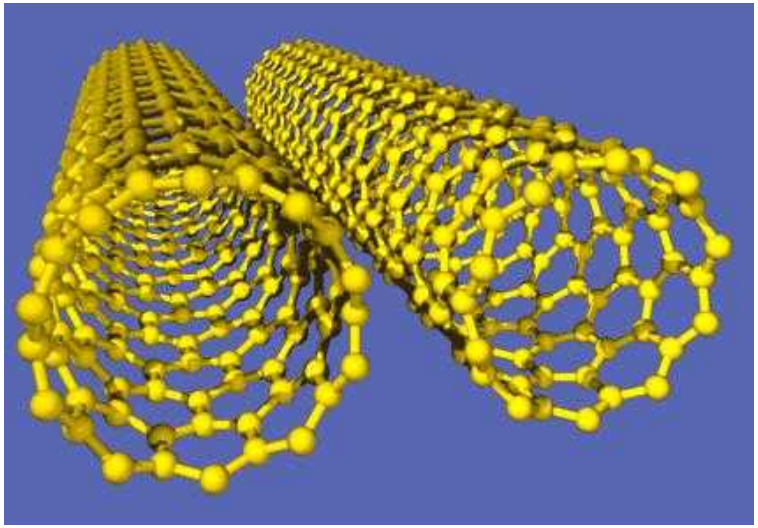
VdW Interactions Are Ubiquitous ...







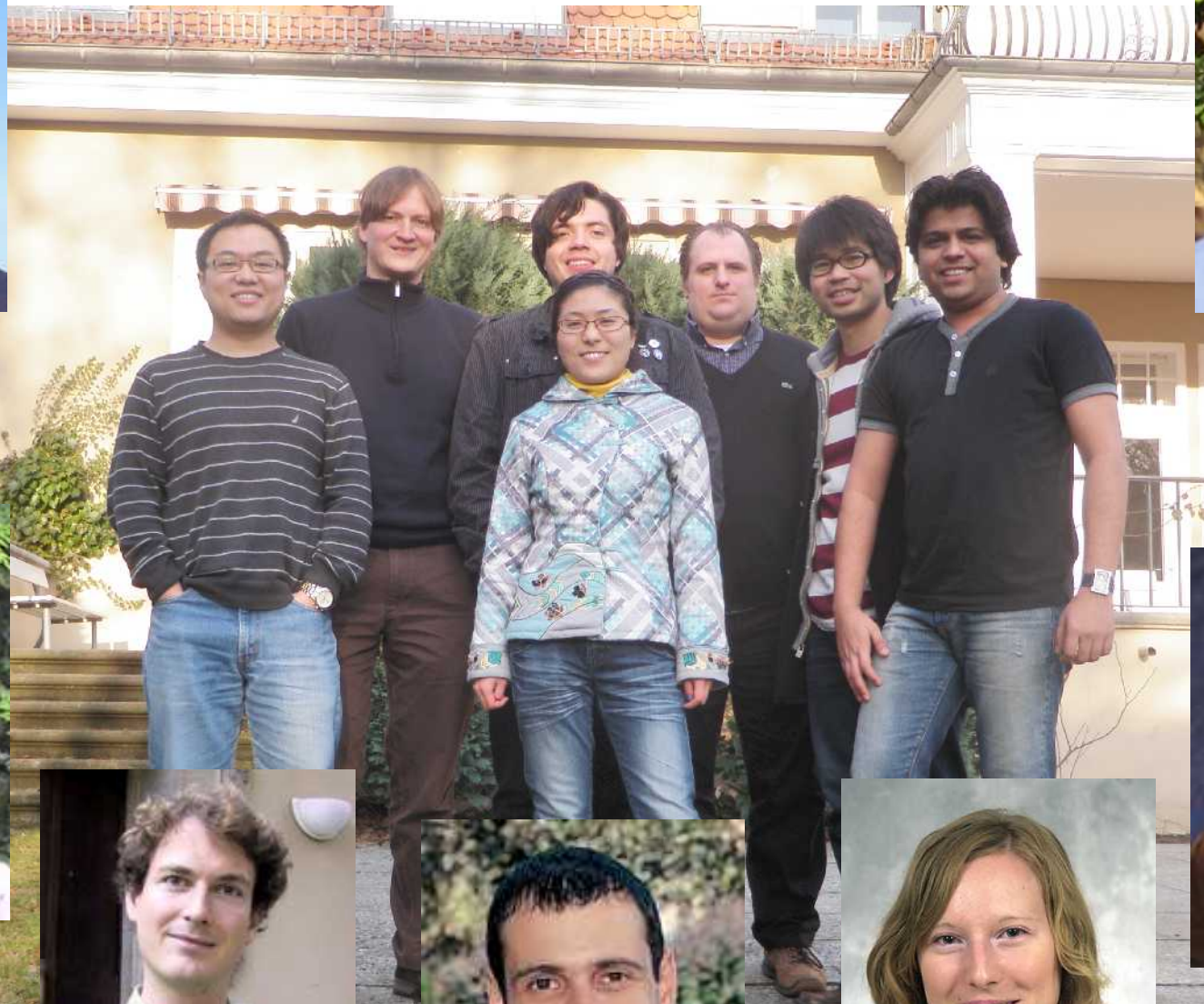




Thank you!


M. Scheffler


R. Car




M. Rossi

V. Blum


L. Kronik

N. Marom


O. A. von Lilienfeld