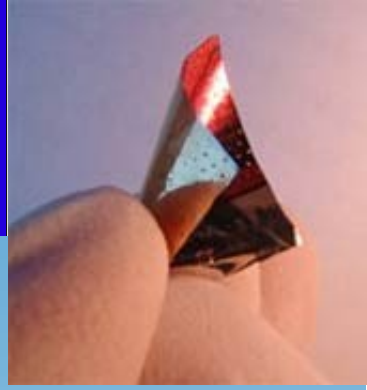
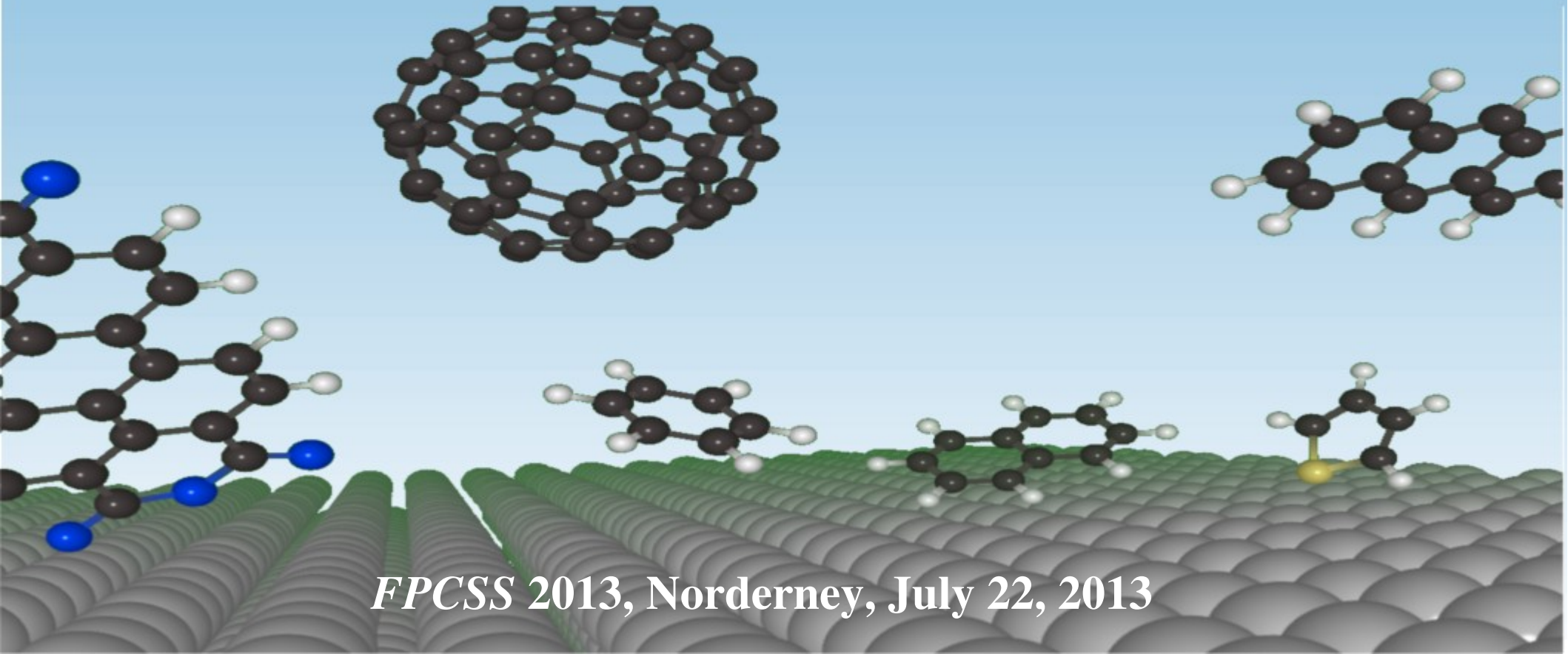
Bonding at Surfaces



Alexandre Tkatchenko

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

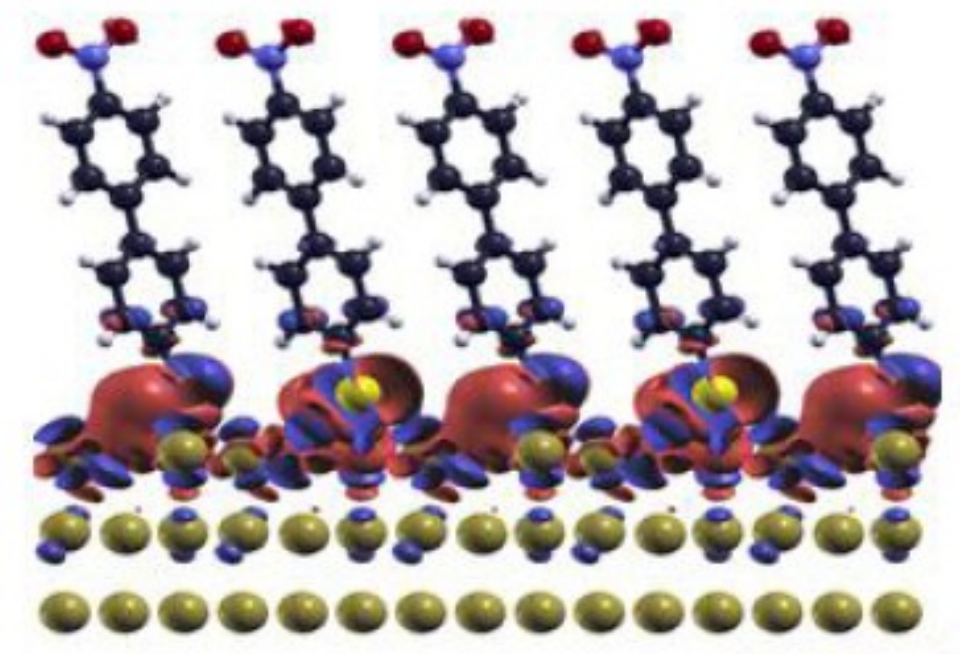
Berlin, Germany



FPCSS 2013, Norderney, July 22, 2013

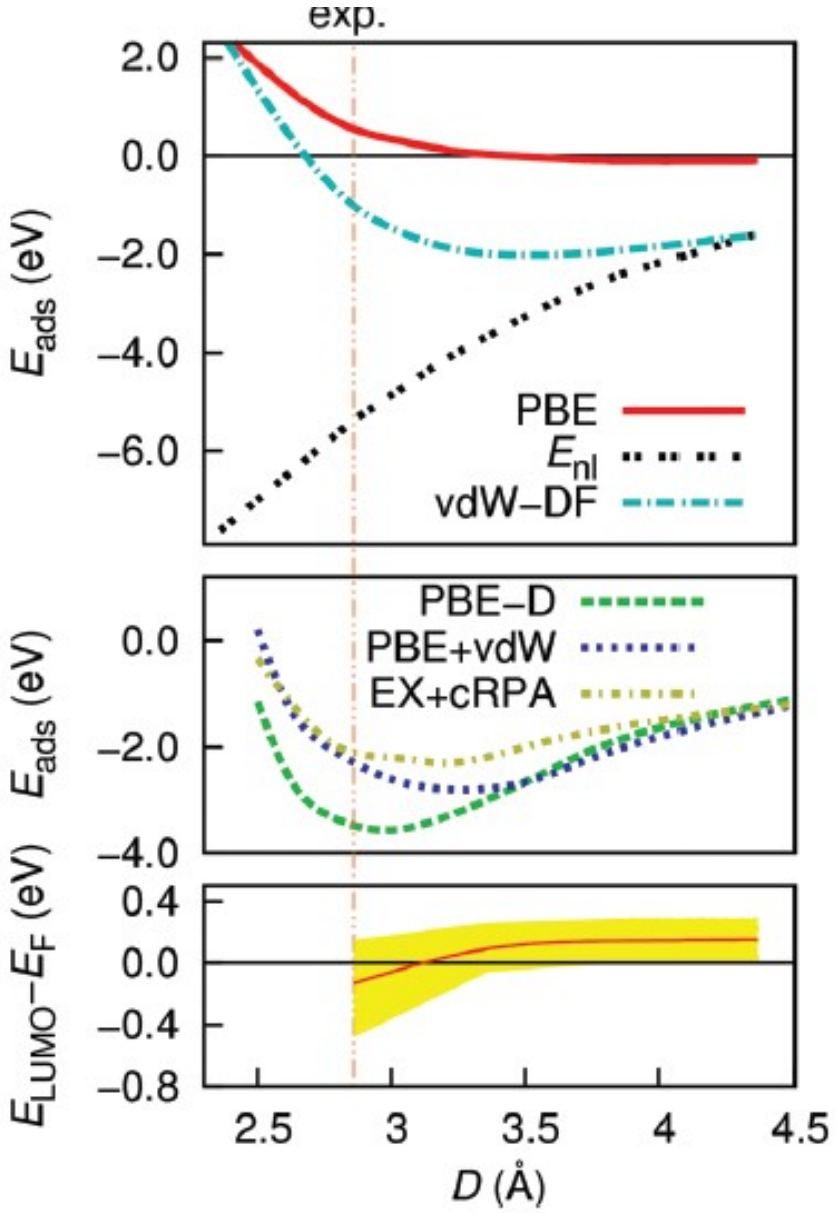
HIOS (Hybrid Inorganic/Organic Systems)

"*Combine the best of both worlds*": High carrier mobilities of inorganic materials with tunable electronic properties of organic molecules / polymers.

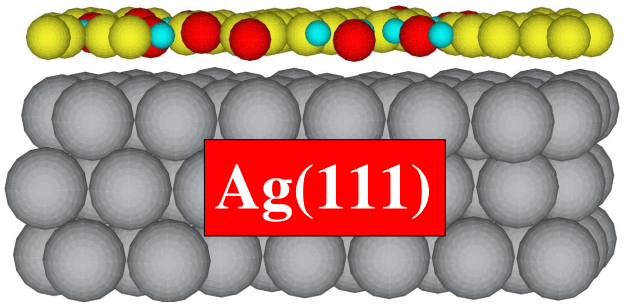


Interface electronic states

HIOS electronic states are highly sensitive to structure

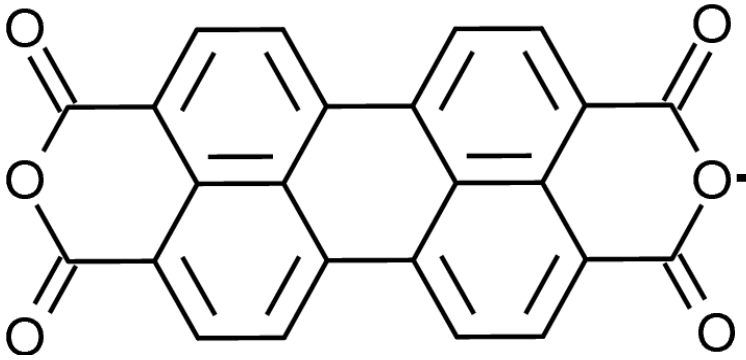


PTCDA



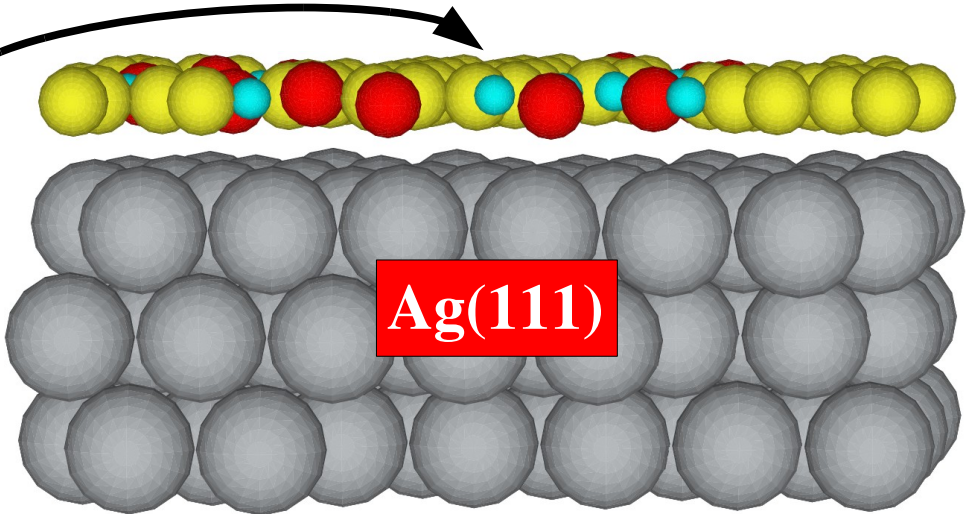
A. Tkatchenko, L. Romaner, O. T. Hofmann, E. Zojer, C. Ambrosch-Draxl, and M. Scheffler, ***MRS Bulletin*** 35, 435 (2010).

Structure and bonding of HIOS: In DFT we trust ?



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

(PTCDA)



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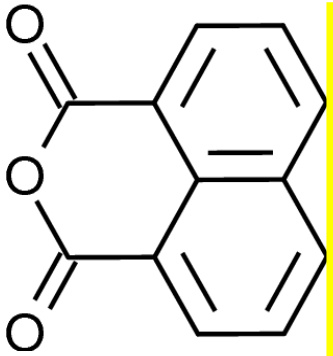


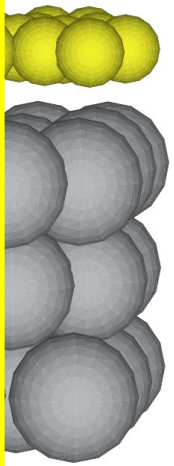
perylene-
tetracarboxylic-
3,4,9,10-dianhydride
(PTCDA)

Experiment

A. Gerlach *et al.*, Phys. Rev. B **75**, 045401 (2007).
S. K. M. Henze *et al.*, Surf. Sci. **601**, 1566 (2007).
A. Hauschild *et al.*, Phys. Rev. B **81**, 125432 (2010).

Theory

M. Rohlfing, R. Temirov, and F. Tautz, Phys. Rev. B **76**, 115421 (2007).
M. Rohlfing and T. Bredow, Phys. Rev. Lett. **102**, 073005 (2009).
L. Romaner *et al.*, New J. Phys. **11**, 053010 (2009).
E. McNellis, Ph.D. thesis, Fritz-Haber-Institut der MPG (2010).
A. Tkatchenko *et al.*, MRS Bulletin **35**, 435 (2010).



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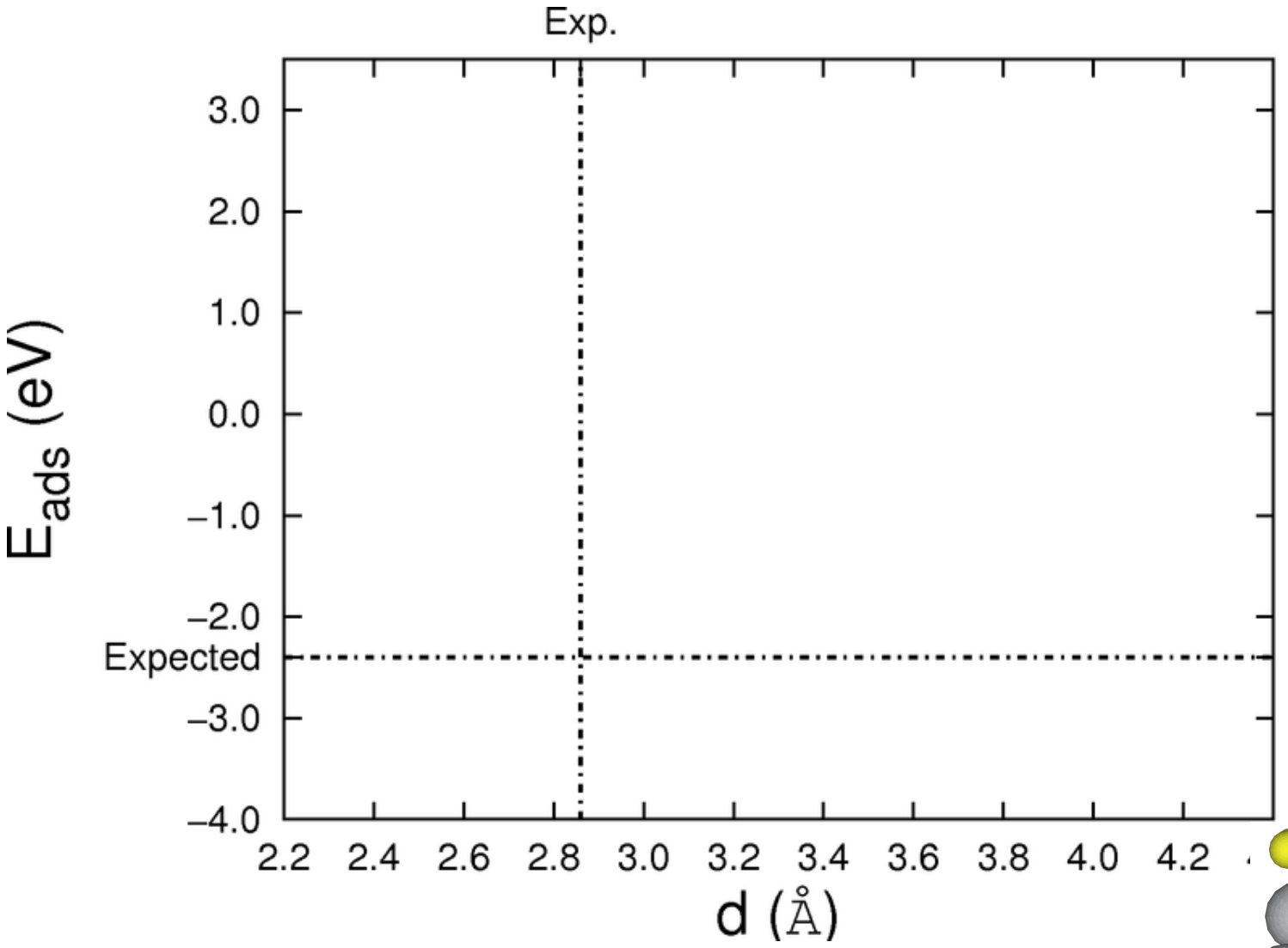
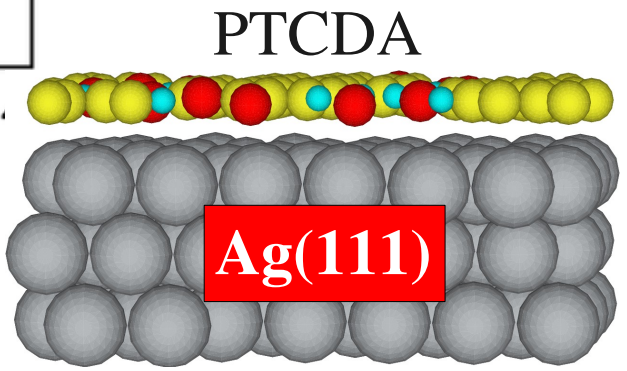
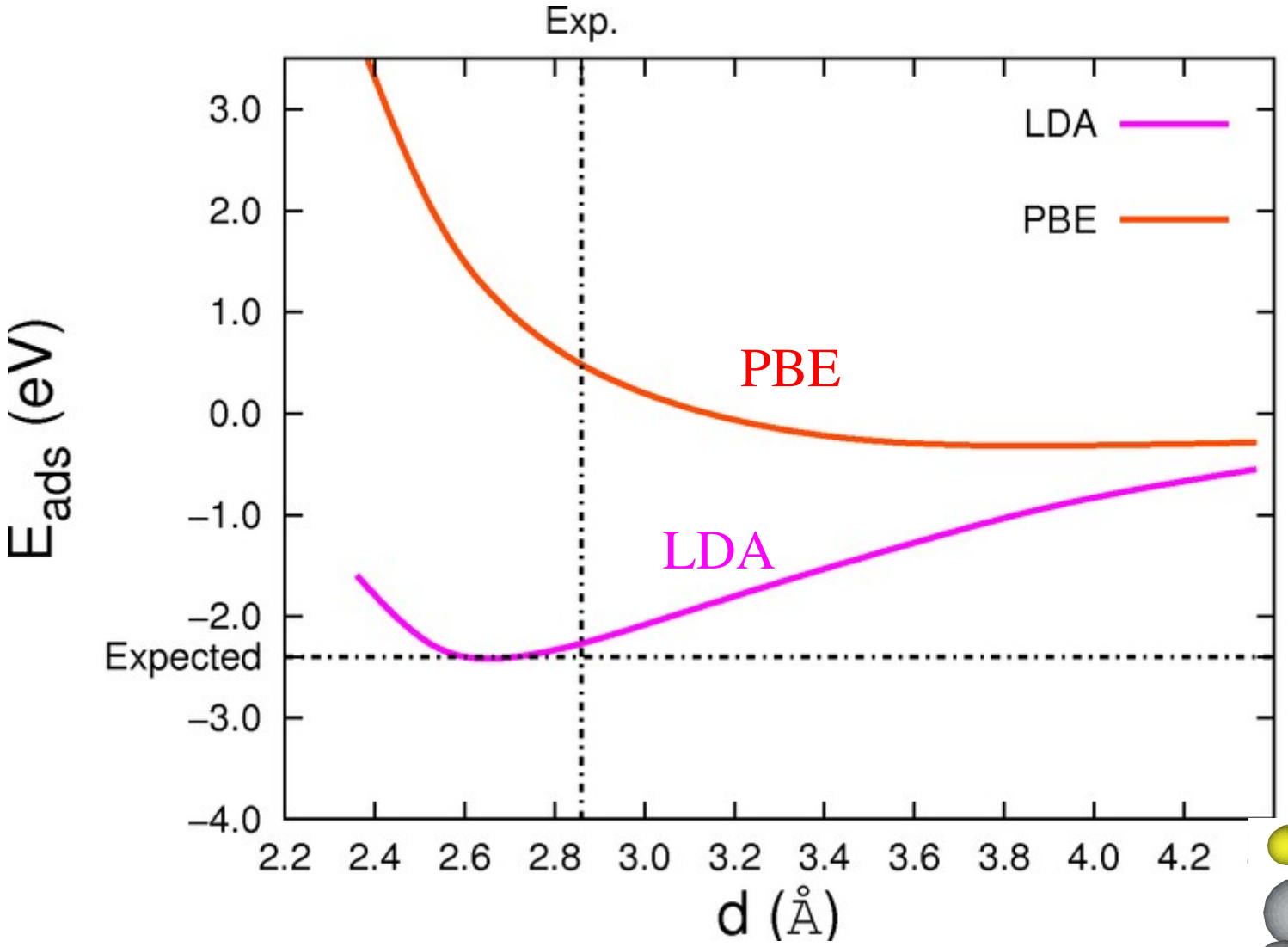


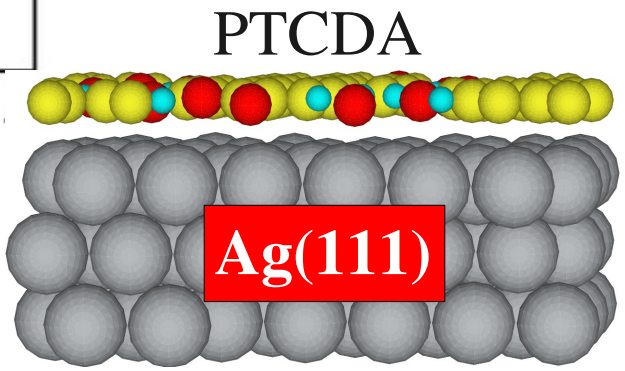
Experiment: *A. Hauschild et al.*, ***PRL*** (2007)



Structure and bonding of HIOS: LDA & PBE



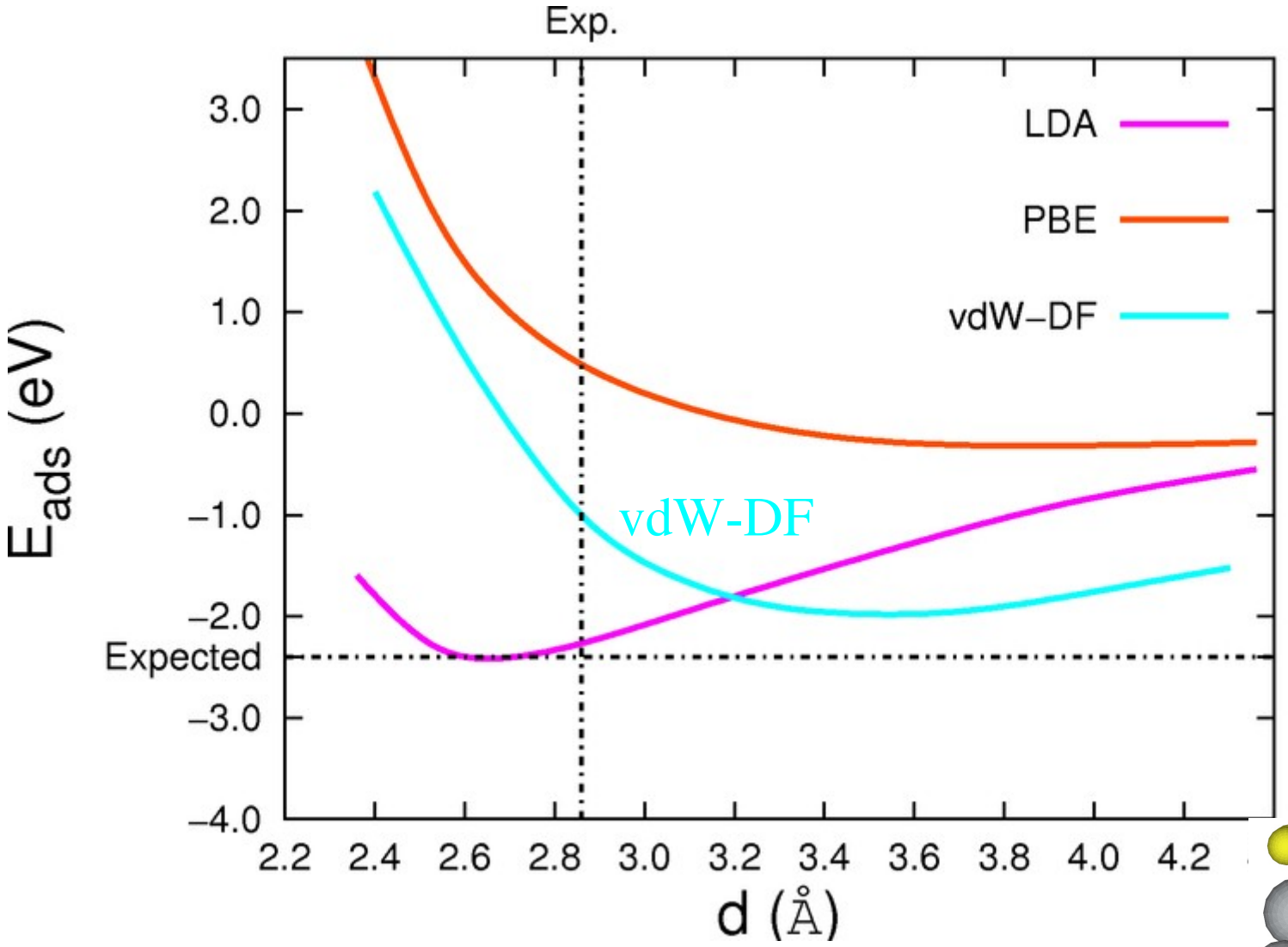
LDA/PBE:
(semi-)local DFT.
Can be applied to
> 1000 atoms



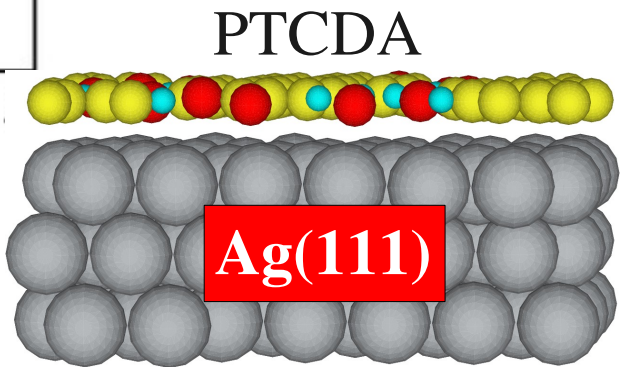
Experiment: *A. Hauschild et al.*, ***PRL*** (2007)

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

Structure and bonding of HIOS: Langreth-Lundqvist vdW-DF

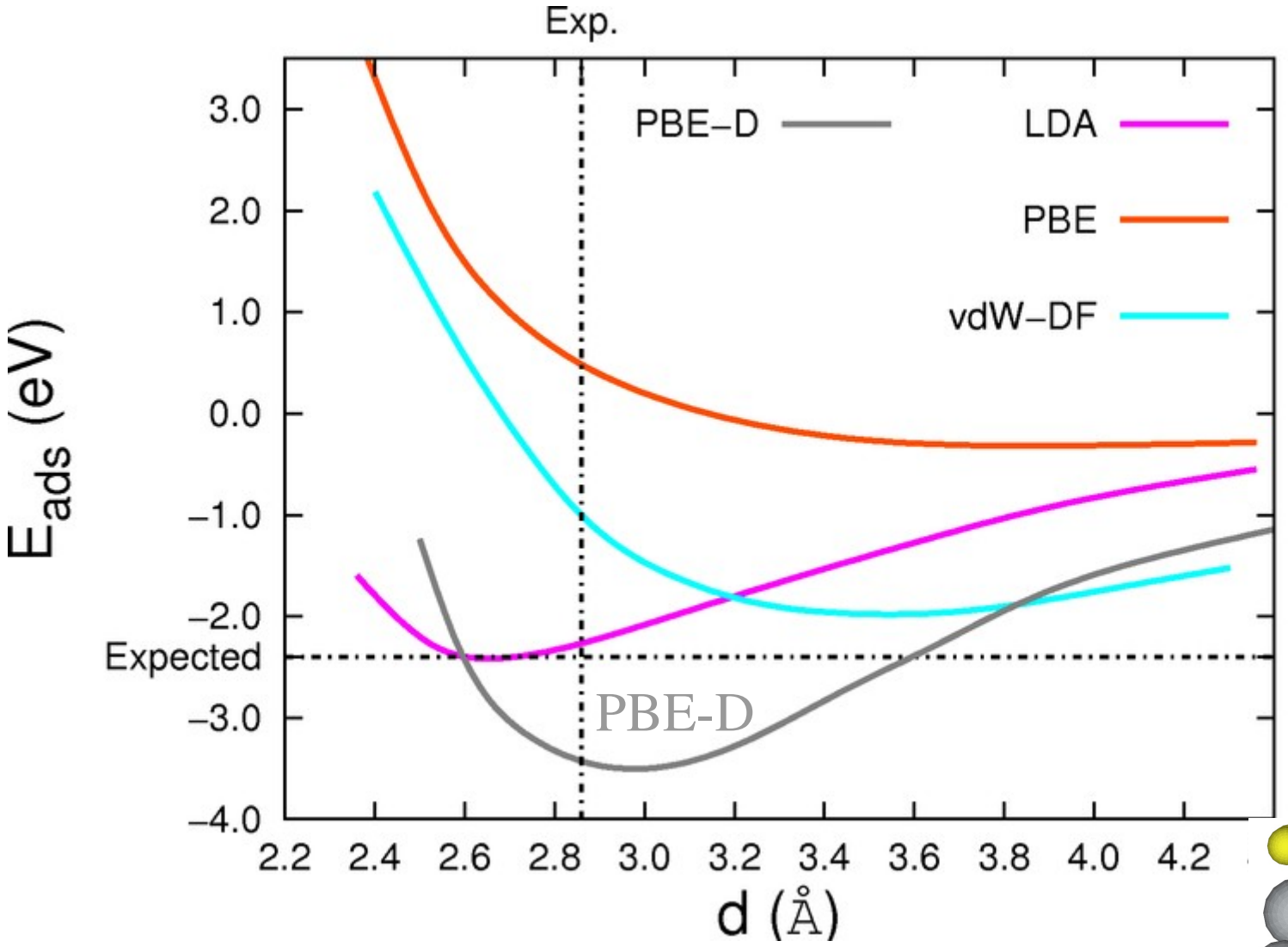


vdW-DF:
Non-local Langreth-Lundqvist functional.
Can be applied to > 1000 atoms

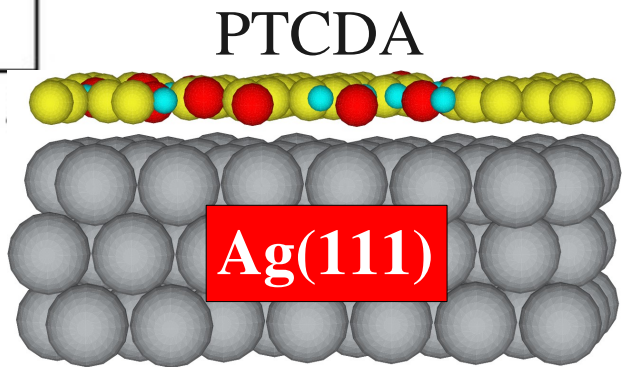


Experiment: *A. Hauschild et al.*, ***PRL*** (2007)
vdW-DF: *L. Romaner et al.*, ***New J. Phys.*** (2009)

Structure and bonding of HIOS: PBE + Grimme D

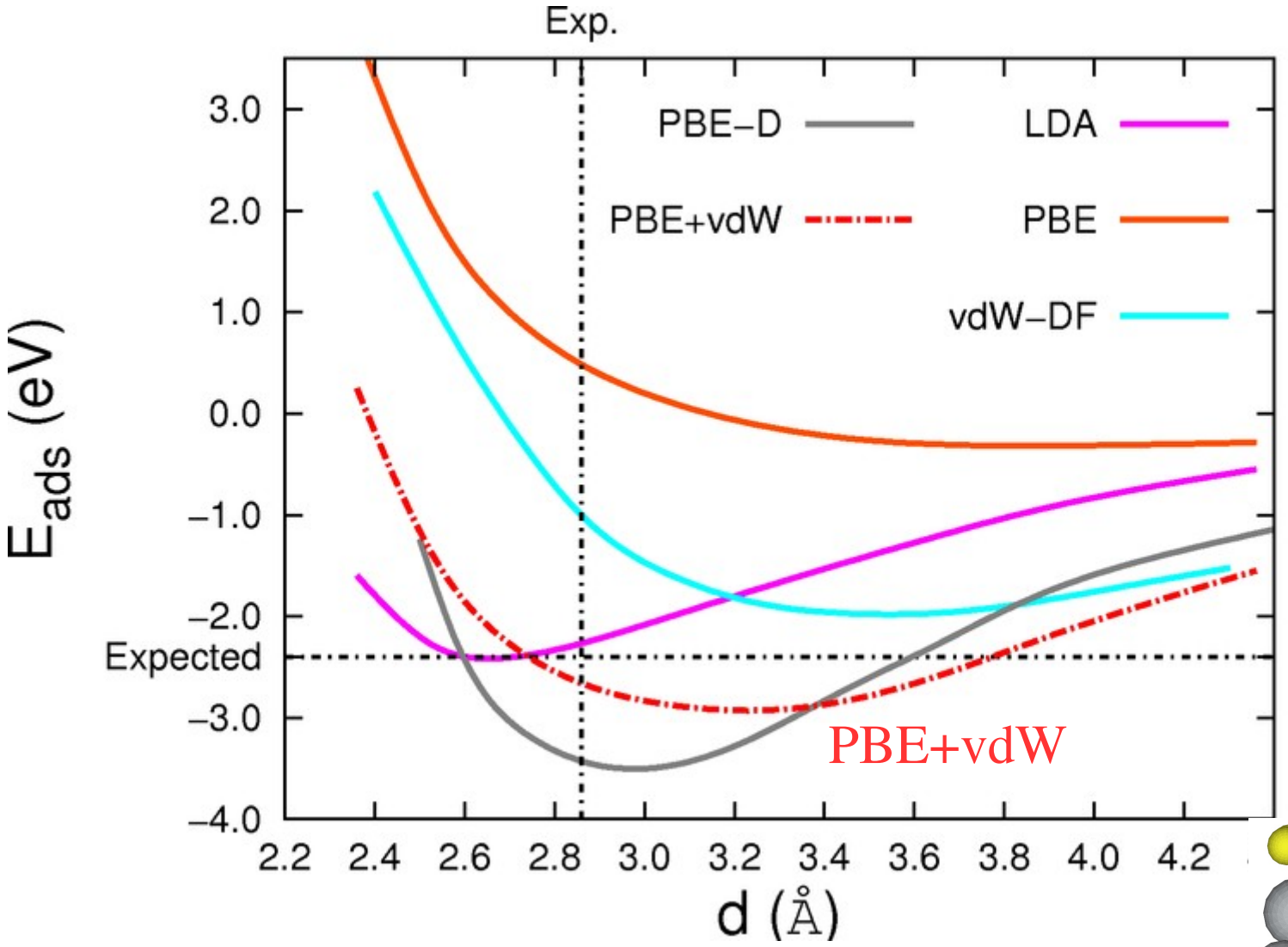


PBE-D:
PBE+Pairwise correction by Grimme.
Can be applied to > 1000 atoms

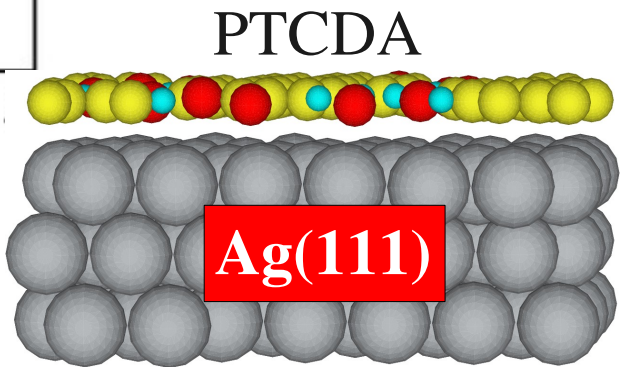


Experiment: *A. Hauschild et al.*, ***PRL*** (2007)
PBE-D: *E. McNellis,* PhD thesis (2010)

Structure and bonding of HIOS: PBE+vdW

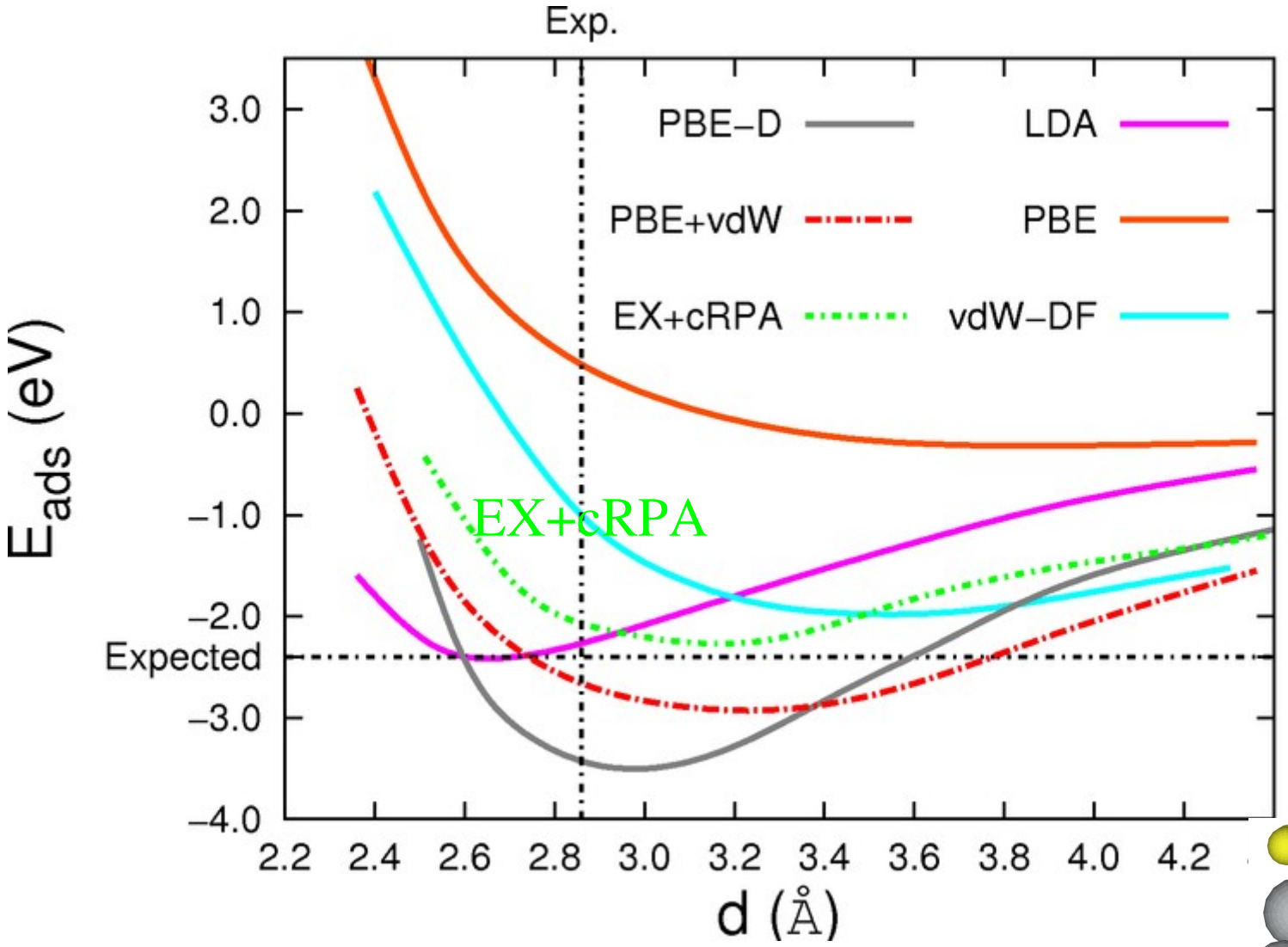


PBE+vdW:
PBE+Pairwise correction by Tkatchenko-Scheffler.
Can be applied to > 1000 atoms

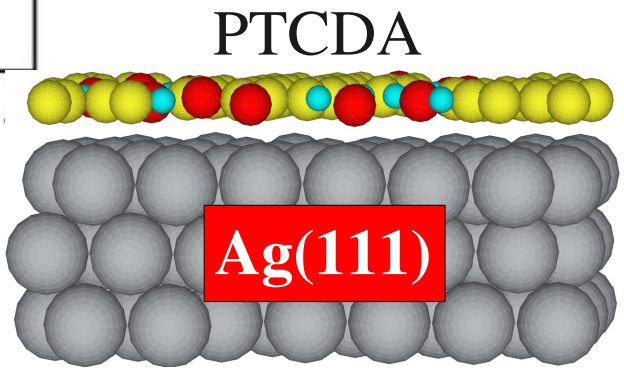


Experiment: *A. Hauschild et al.*, ***PRL*** (2007)
PBE+vdW: *E. McNellis*, PhD thesis (2010)

Structure and bonding of HIOS: EX+cRPA



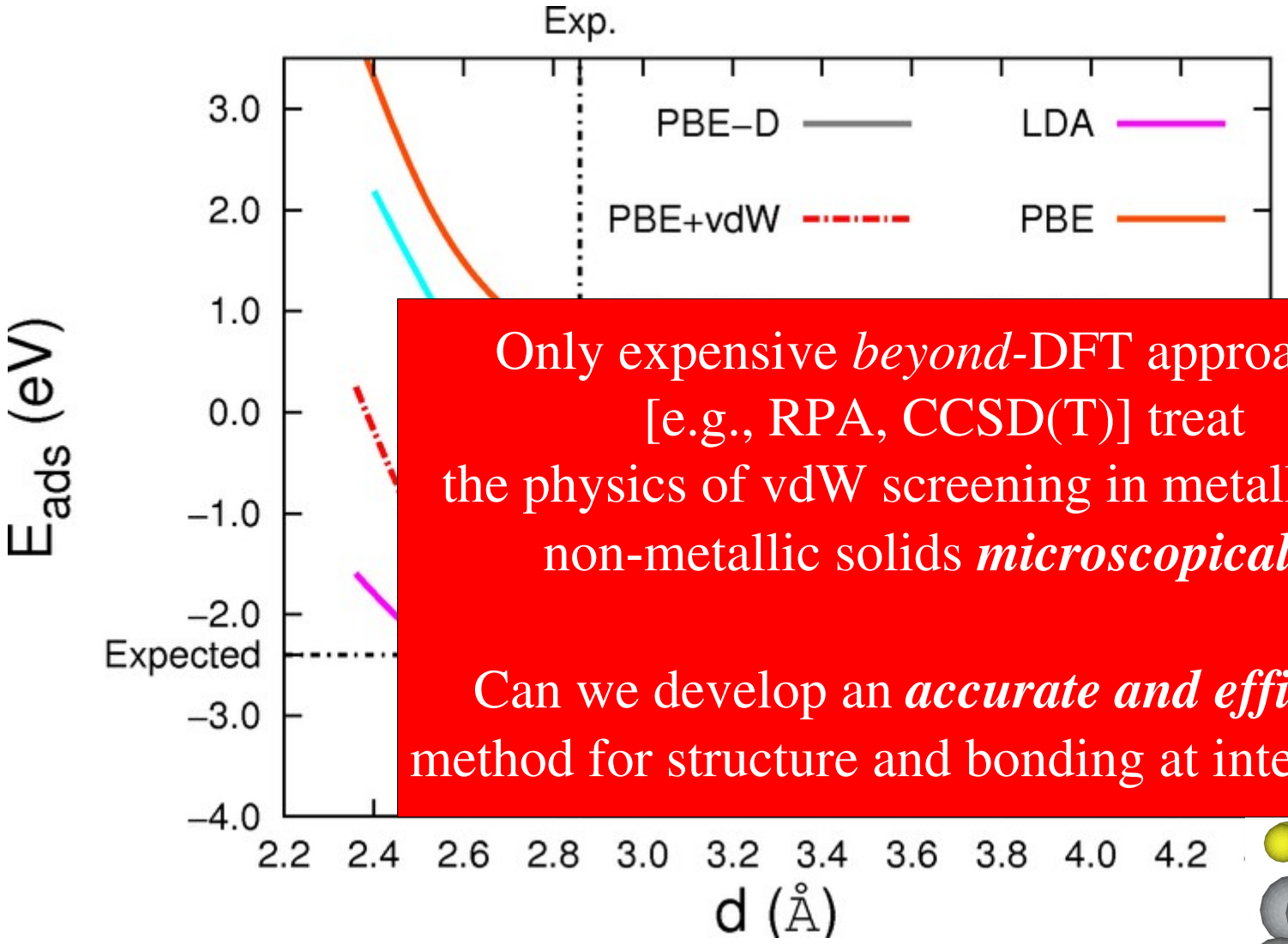
EX+cRPA:
Exact exchange + approximate many-body correlation energy.
Can be applied to < 100 atoms



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

EX+cRPA: *M. Rohlfing and T. Bredow*, ***PRL*** (2008)

Structure and bonding of HIOS: In RPA we trust?

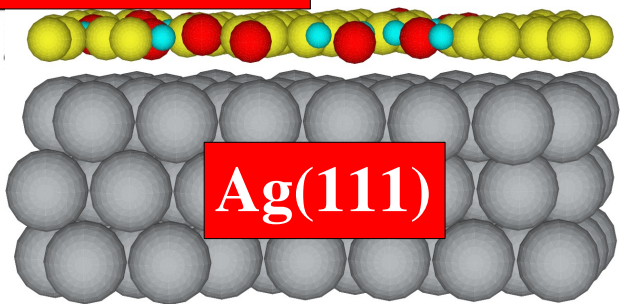


EX+cRPA:
Exact exchange + approximate many-body
on energy.
applied to
oms

Only expensive *beyond*-DFT approaches [e.g., RPA, CCSD(T)] treat the physics of vdW screening in metallic and non-metallic solids ***microscopically***.

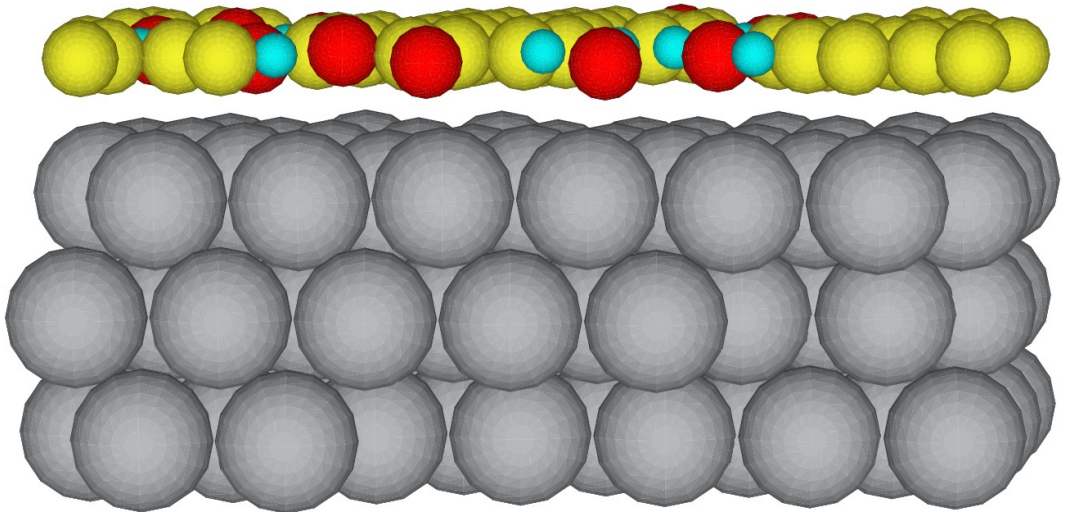
Can we develop an ***accurate and efficient*** method for structure and bonding at interfaces ?

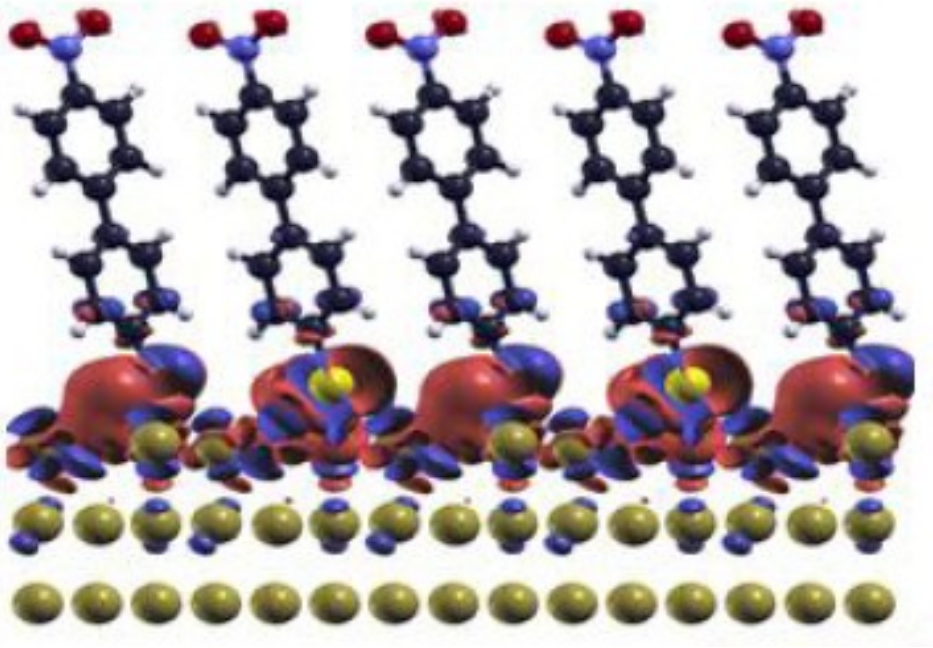
CDA



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

Bonding = Key to understand structure and electronic properties





Outline

- **Bonding types for molecules on surfaces**
- The good and the bad things about DFT
- Van der Waals interactions in DFT
- Understanding bonding of real molecules on surfaces: Benzene on metals
- Reconciling experiment and theory at a single-molecule level
- An example of “unusual” bonding
- Summary and outlook

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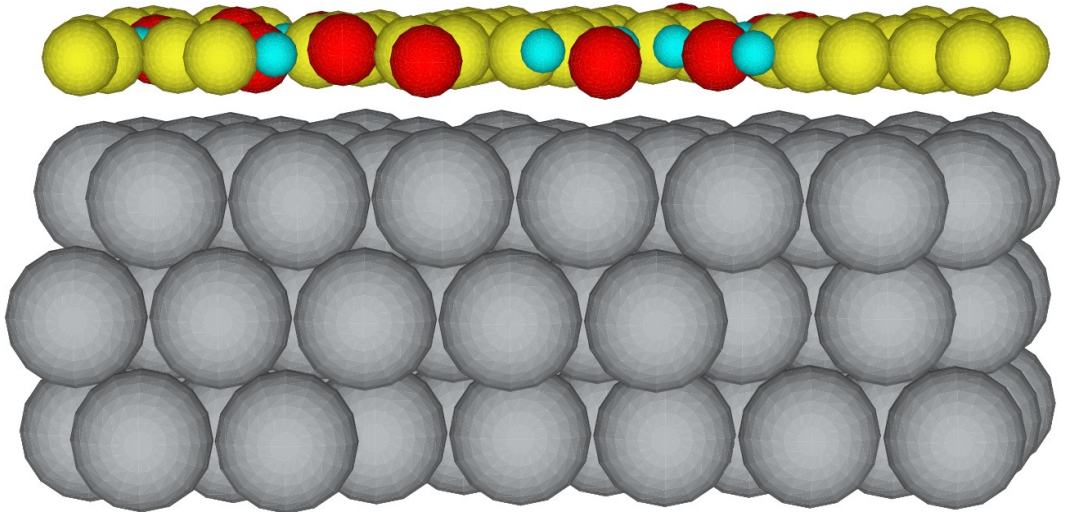
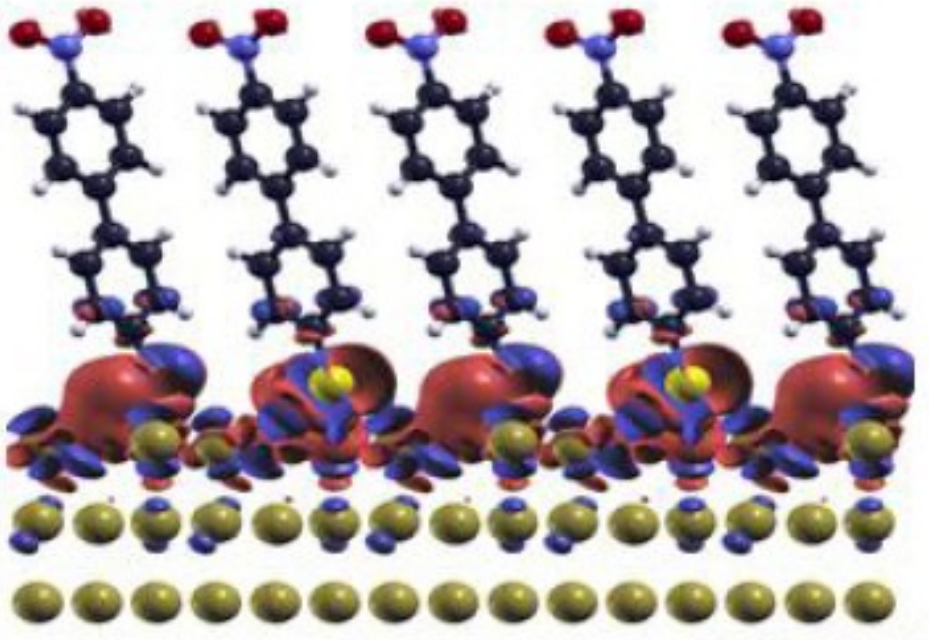
Bonding = Key to understand structure and electronic properties

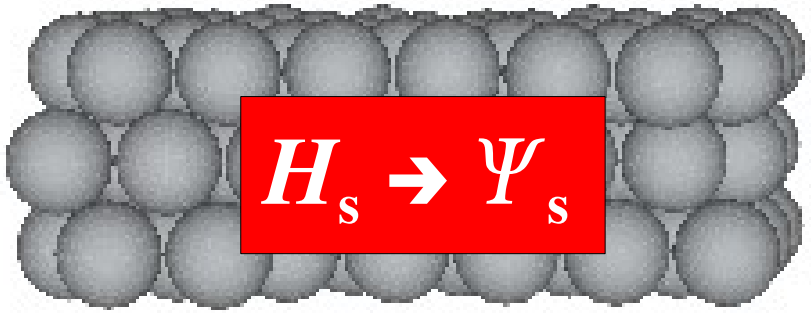
- Covalent bonding
- Ionic bonding (charge transfer)
- Pauli repulsion
- Van der Waals



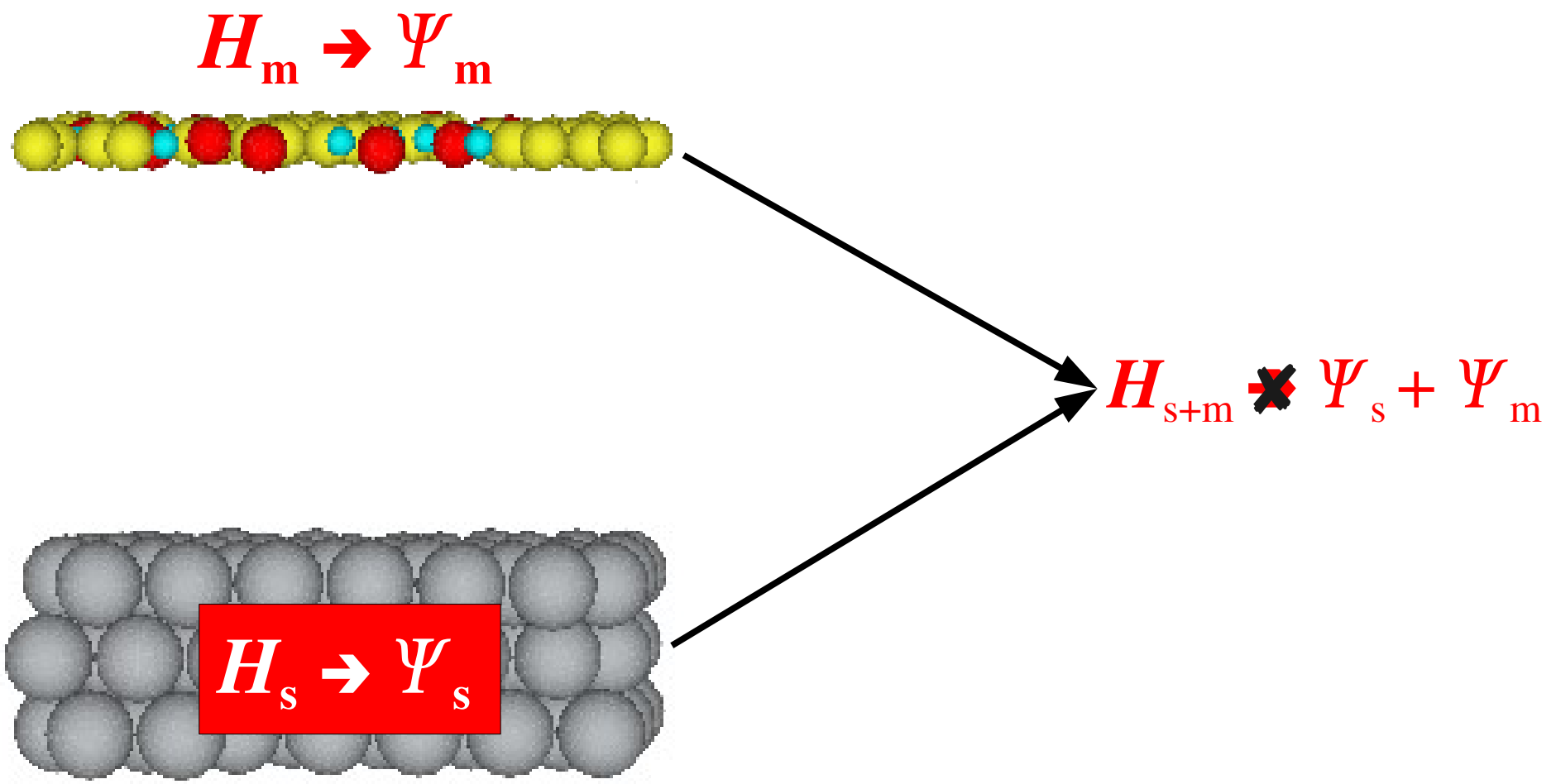


Pauli repulsion

$H_m \rightarrow \Psi_m$



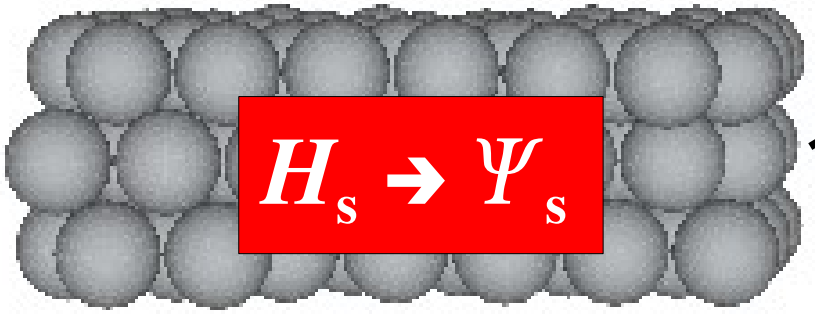
Pauli repulsion



Pauli repulsion

$H_m \rightarrow \Psi_m$

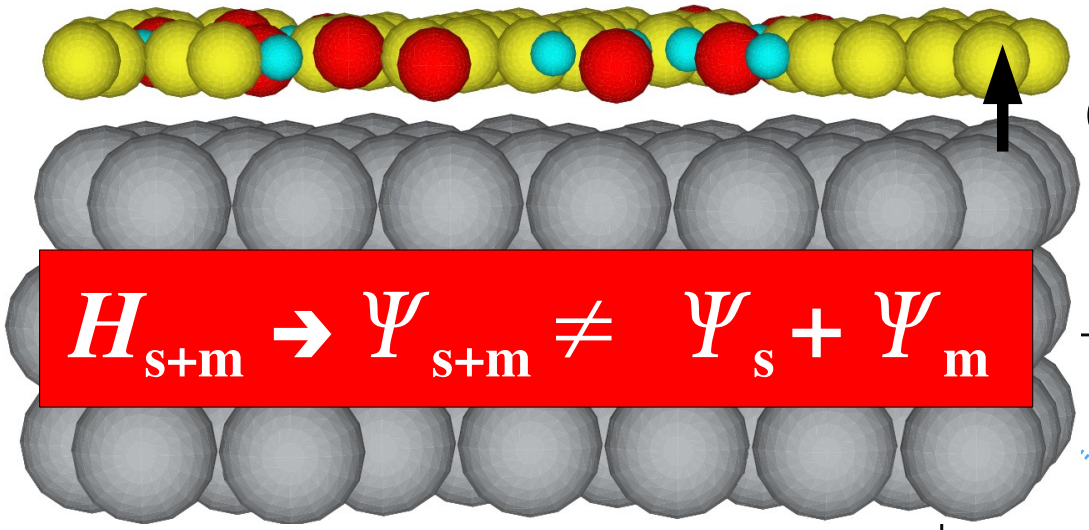
$H_{s+m} \rightarrow \Psi_s + \Psi_m$



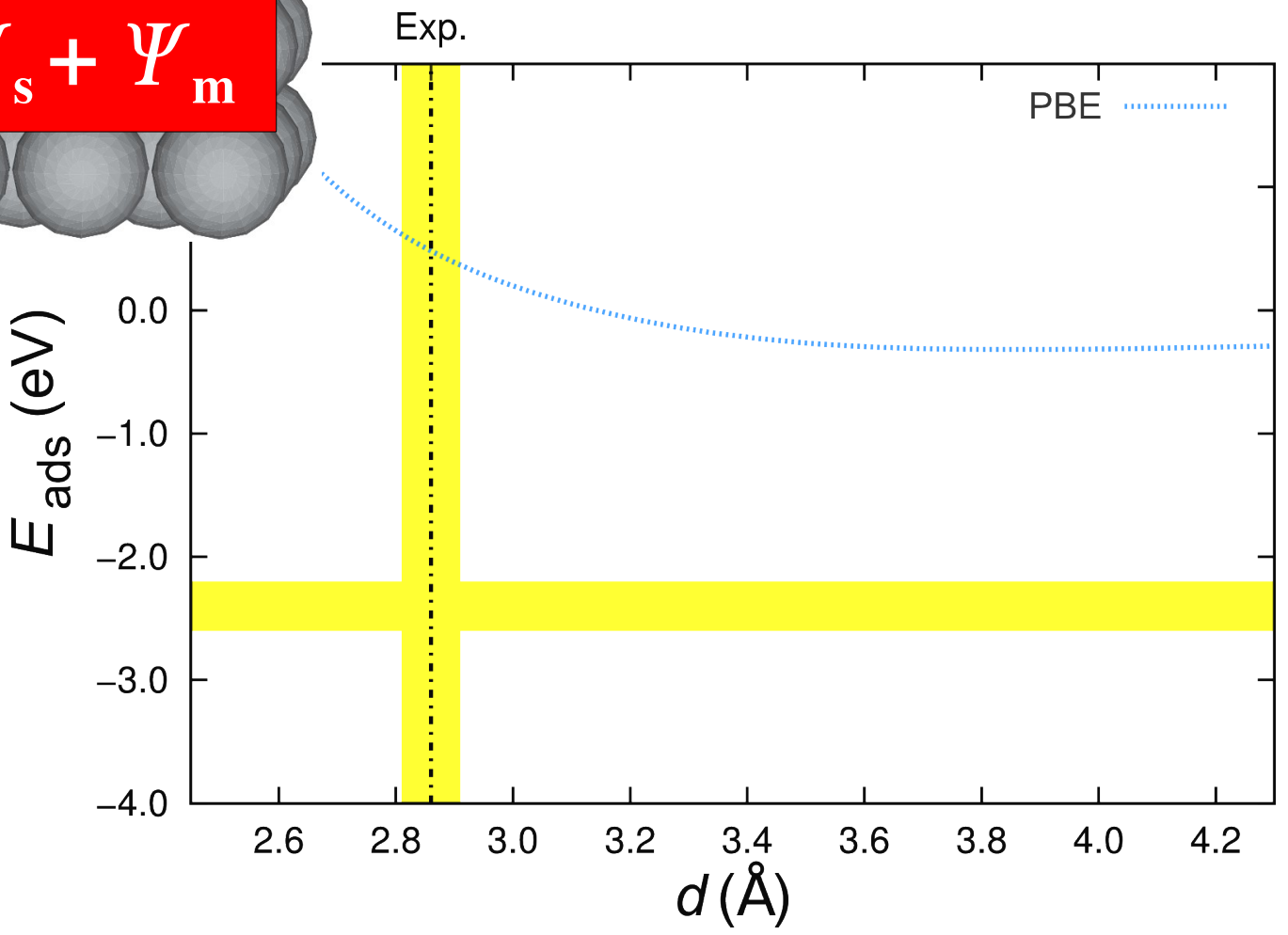
OK at large M / S distance

Exact in 1st order perturbation theory

Pauli repulsion



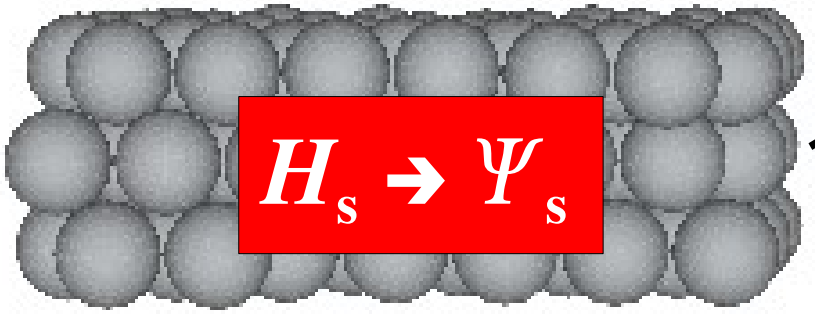
$$H_{s+m} \rightarrow \Psi_{s+m} \neq \Psi_s + \Psi_m$$



Van der Waals interactions

$H_m \rightarrow \Psi_m$

$H_{s+m} \rightarrow \Psi_s + \Psi_m$



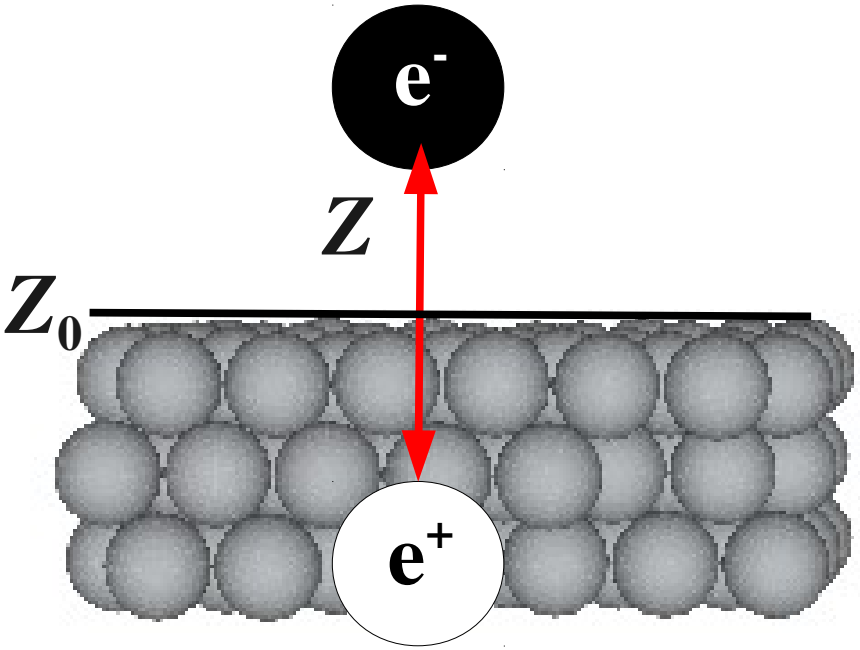
$H_s \rightarrow \Psi_s$

OK at large M / S distance

Exact in 1st order perturbation theory

What happens at 2nd order PT?

Van der Waals interactions

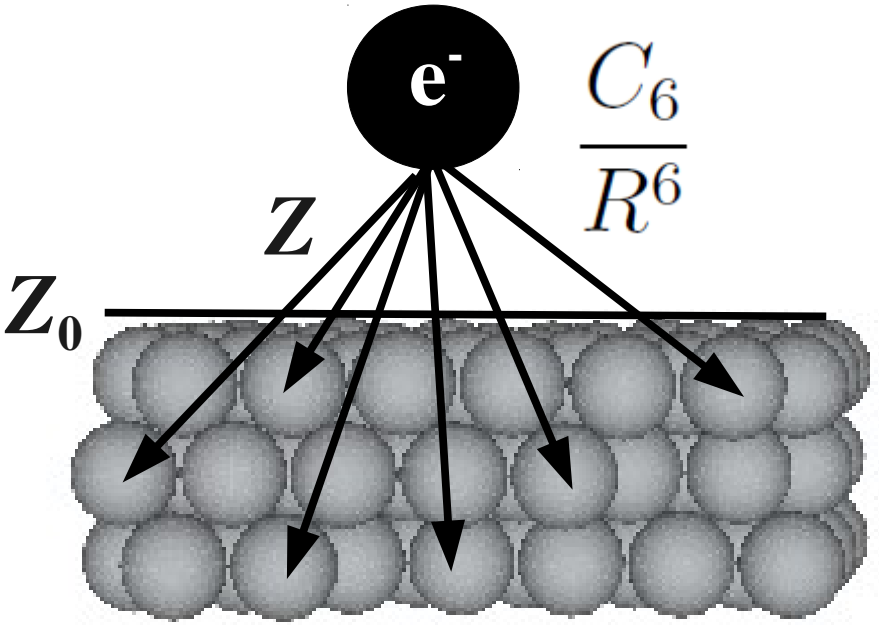


$$E_{\mathrm{vdW}}(Z) = -\frac{C_3}{(Z - Z_0)^3}$$

$$C_3 = \frac{1}{4\pi}\int d\omega \alpha(i\omega)\frac{\varepsilon(i\omega) - 1}{\varepsilon(i\omega) + 1}$$

L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Dover, New York, 2009).

Van der Waals interactions

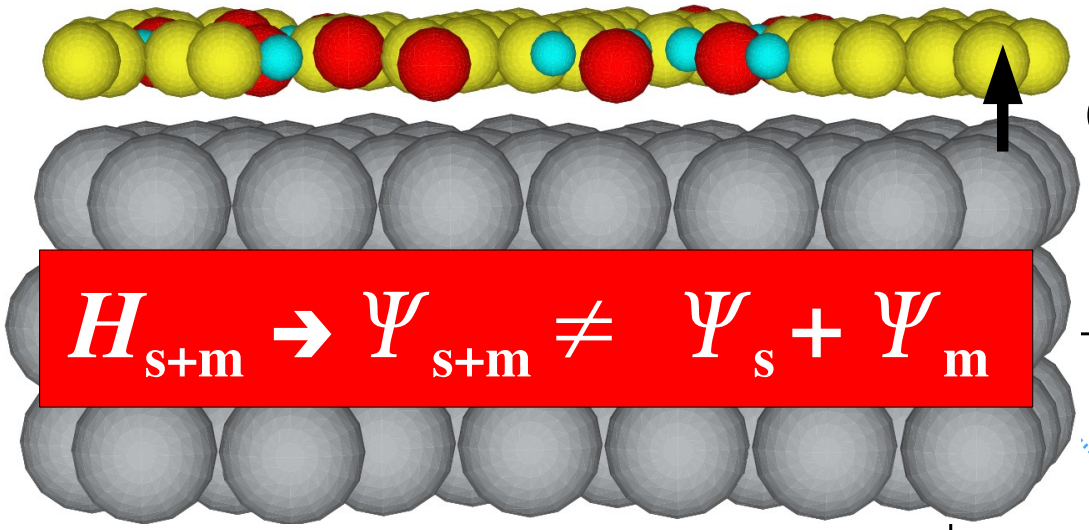


$$E_{\mathrm{vdW}}(Z) = -\frac{C_3}{(Z - Z_0)^3}$$

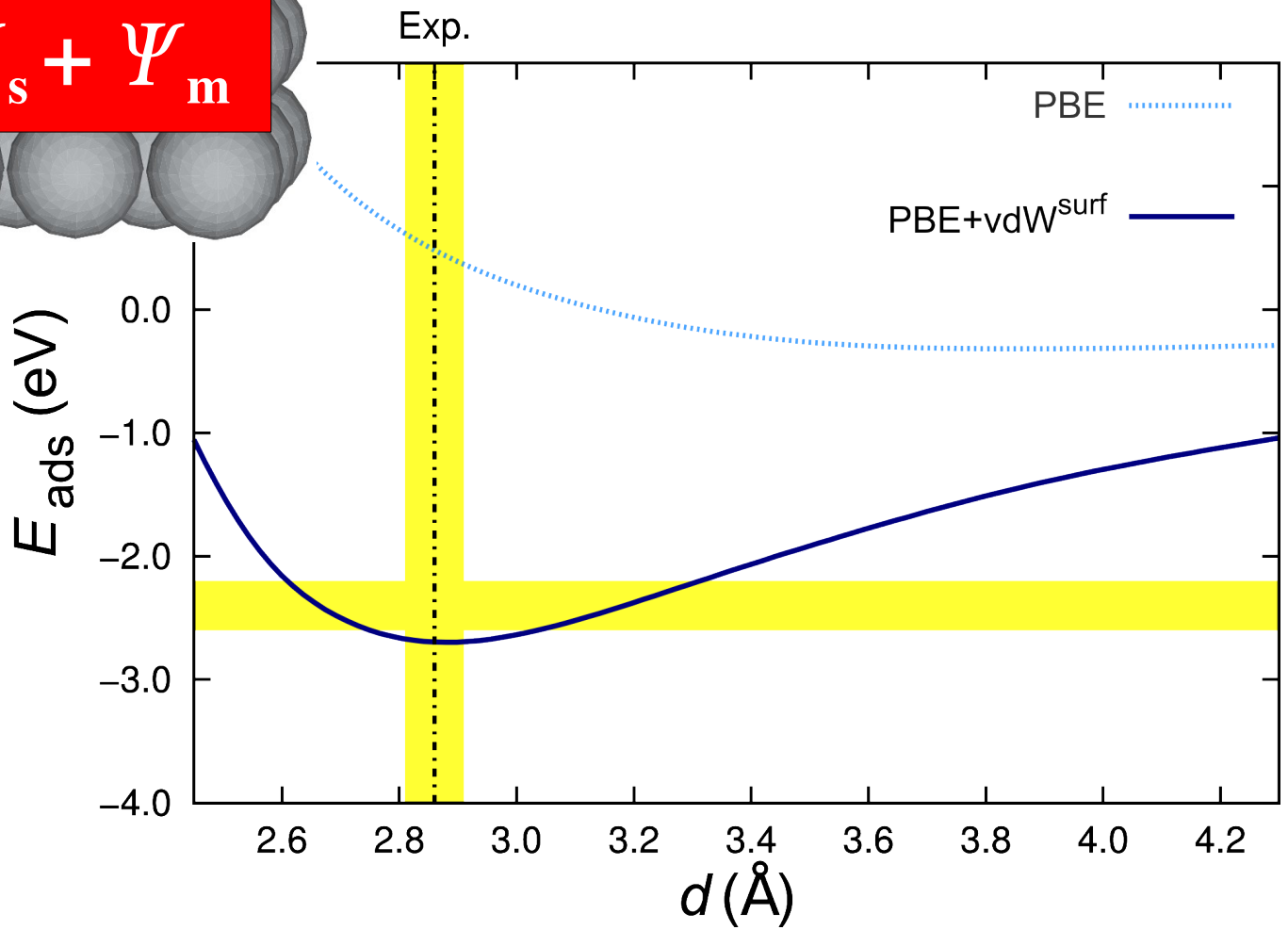
$$C_3 = \frac{\pi}{6} n_s C_6$$

L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Dover, New York, 2009).

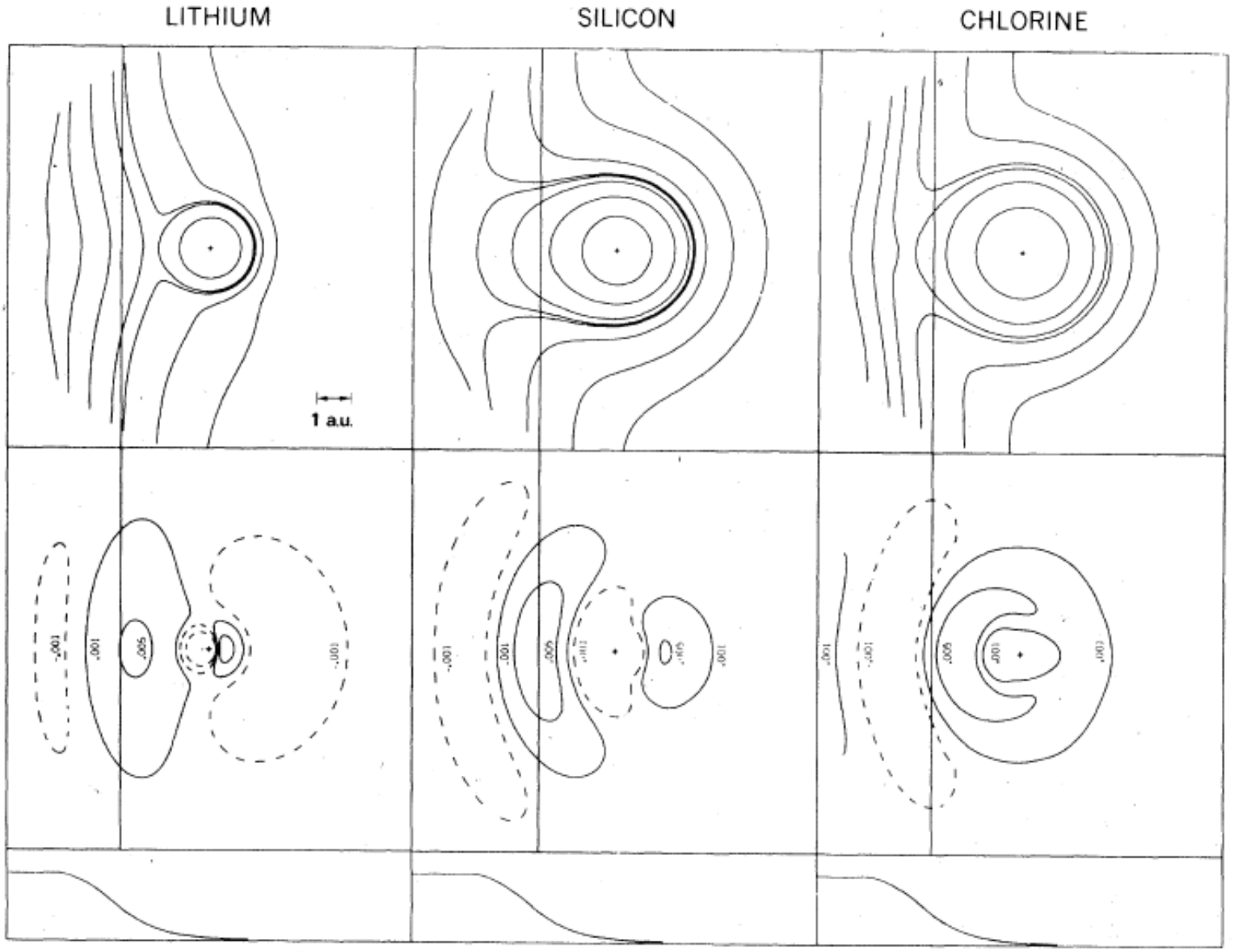
Van der Waals interactions

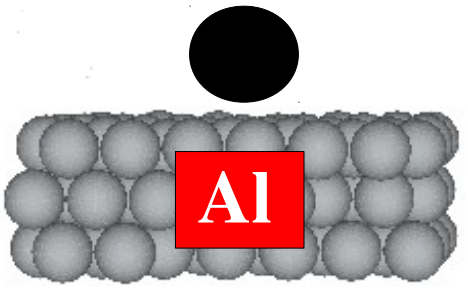


$$H_{s+m} \rightarrow \Psi_{s+m} \neq \Psi_s + \Psi_m$$



Covalent/Ionic bonding

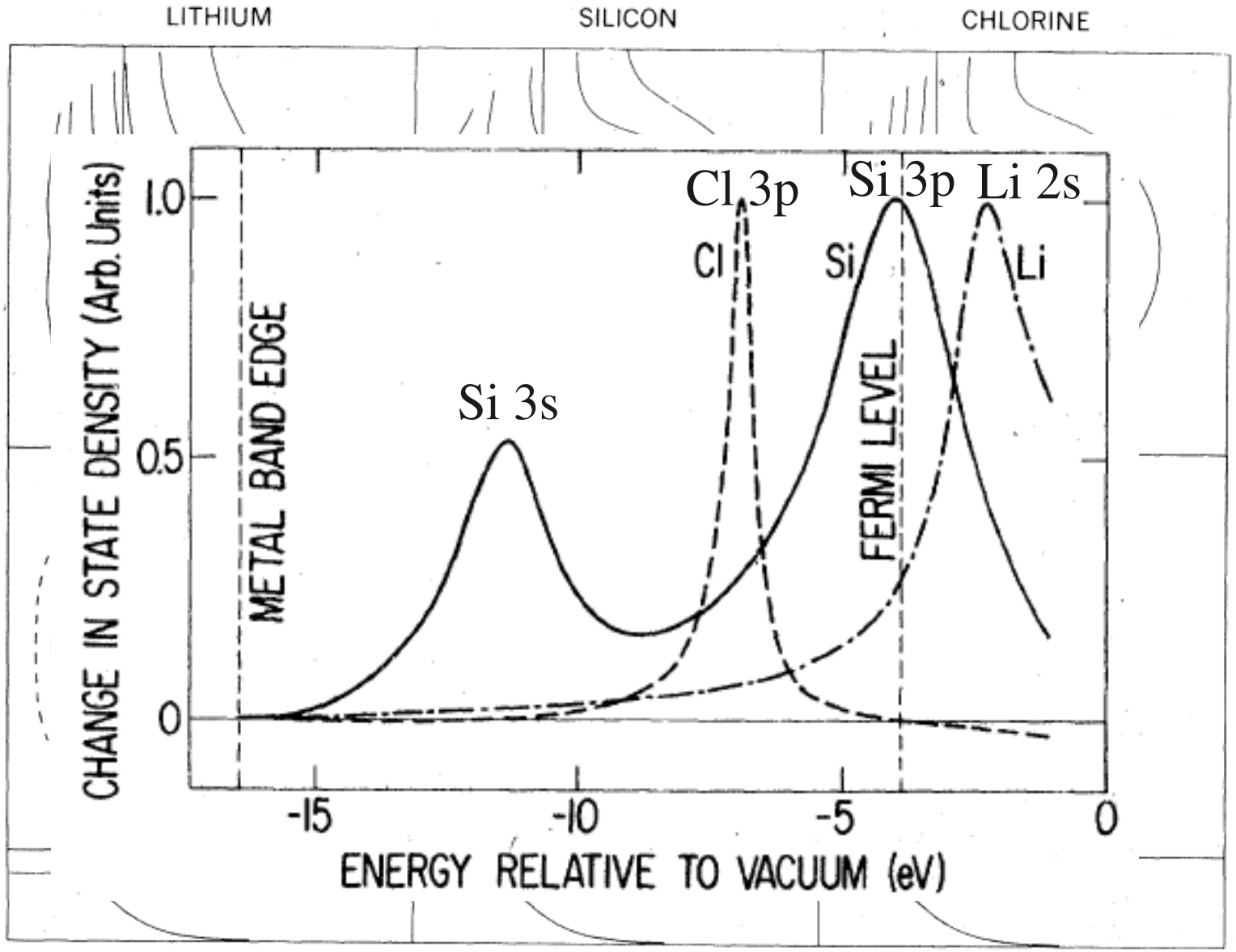


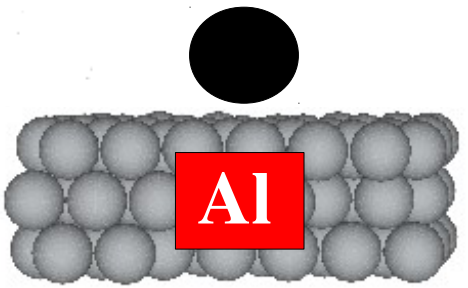


N. D. Lang and A. R. Williams, *Phys. Rev. B* 18, 616 (1978).

A. Gross, *Theoretical Surface Science: A Microscopic Perspective* (Springer, 2003).

Covalent/Ionic bonding

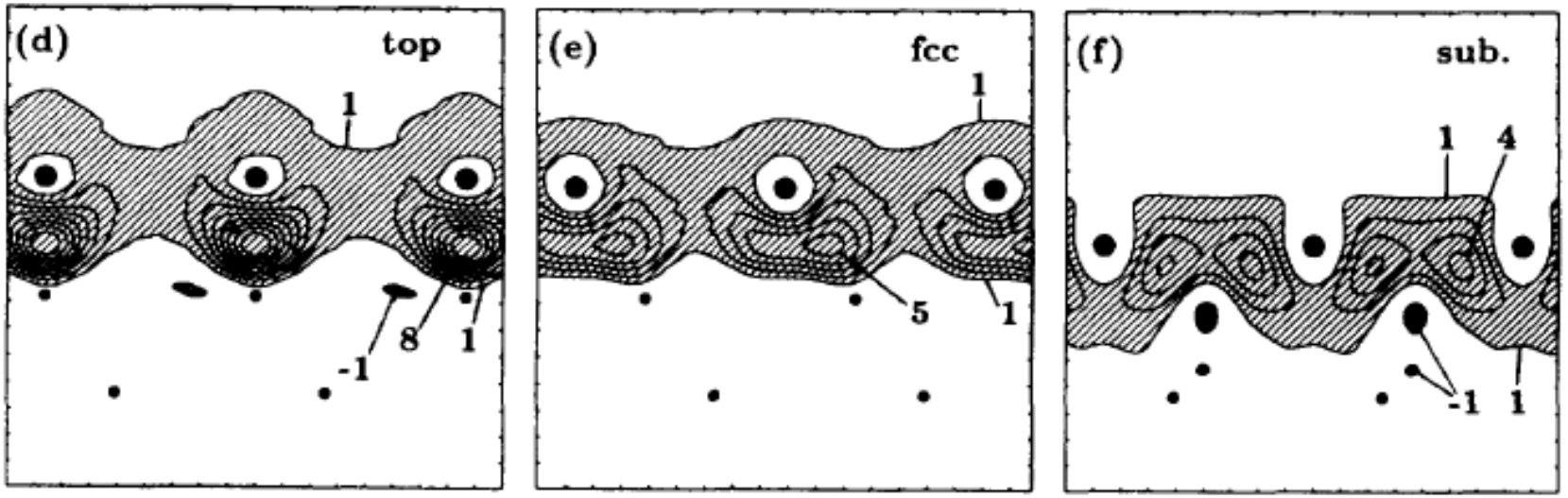


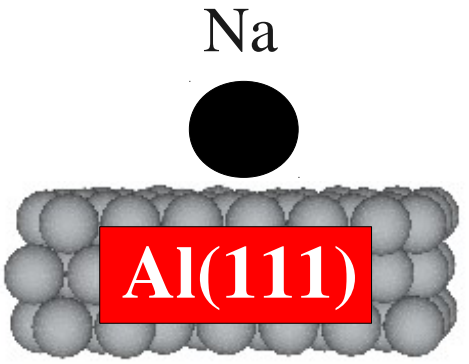


N. D. Lang and A. R. Williams, *Phys. Rev. B* 18, 616 (1978).

A. Gross, *Theoretical Surface Science: A Microscopic Perspective* (Springer, 2003).

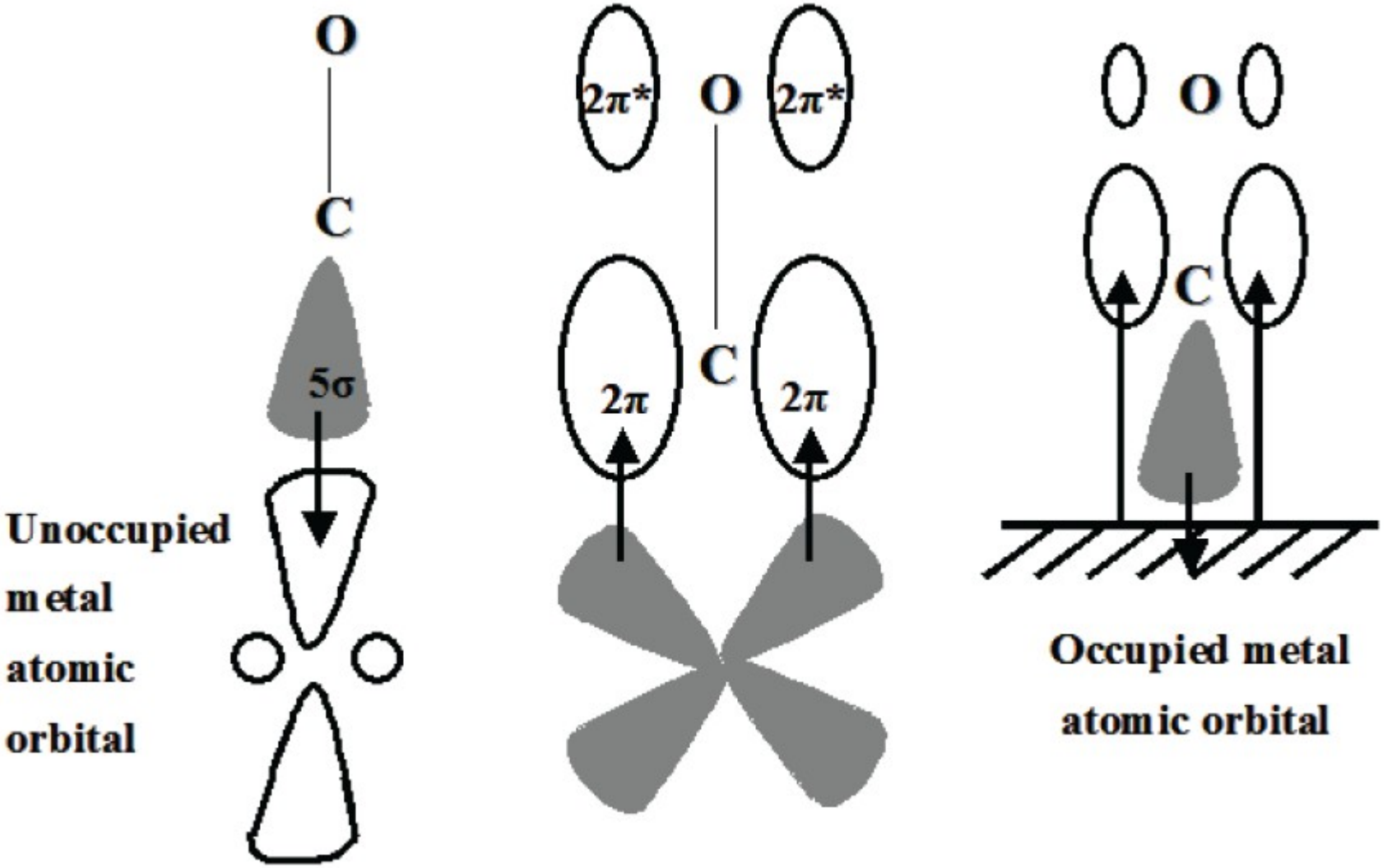
Getting real: Covalent/Ionic bonding in Na/Al(111)





J. Neugebauer and M. Scheffler, *Phys. Rev. B* 46, 16067 (1992).

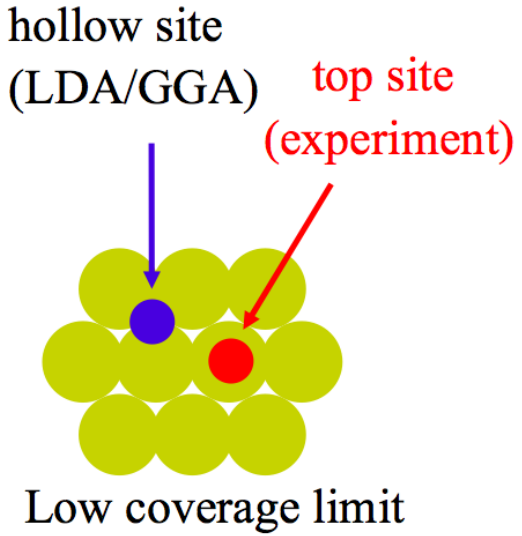
(Synergic) Donation / backdonation bonding mechanism



E. M. McCash, *Surface Chemistry* (Oxford University Press, 2002).

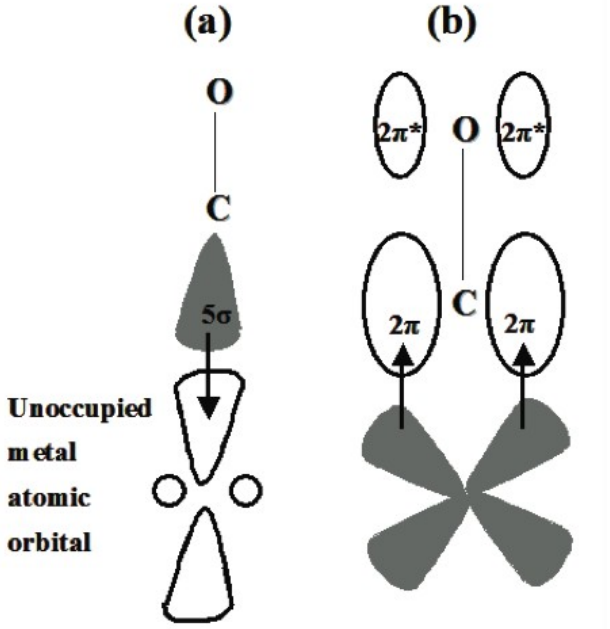
Semi-local DFT can lead to qualitatively wrong predictions

The commonly used DFT functionals (e.g. LDA and GGA) predict wrong adsorption site for CO on Cu(111), Pt(111), and Rh(111) [1]



Blyholder's model for CO/metal [2]

*- **Donation** of electrons from the CO-5σ orbital to the empty metal d orbital (plot a below);*
*- **Back-donation** of electrons from the occupied metal d orbitals to the empty CO-2π* orbitals (plot b).*



Present understanding of the puzzle

Incorrect description of the relative position of HOMO and LUMO with respect to the Fermi energy of the metal leads to the "CO adsorption puzzle"

2π is **too low** in LDA/GGA*
=> hollow site is incorrectly favored

[1] Feibelman *et al.*, *J. Phys. Chem. B* 105 (2001) 4018.
[2] Blyholder, *J. Chem. Phys.* 68 (1964) 2772.

How good is present-day DFT for bonding at surfaces?

✔ GGA and hybrid functionals often (but not always) yield good results for Pauli repulsion, covalent, and ionic bonding

✘ Completely fail for long-range van der Waals interactions

(addressed in this talk)

✘ Substantial problems with electronic level alignment (self-interaction, delocalization)

(See next talk by *N. Marzari)*

Van der Waals in DFT

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

Van der Waals 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 ...

Interatomic vdW methods

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

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

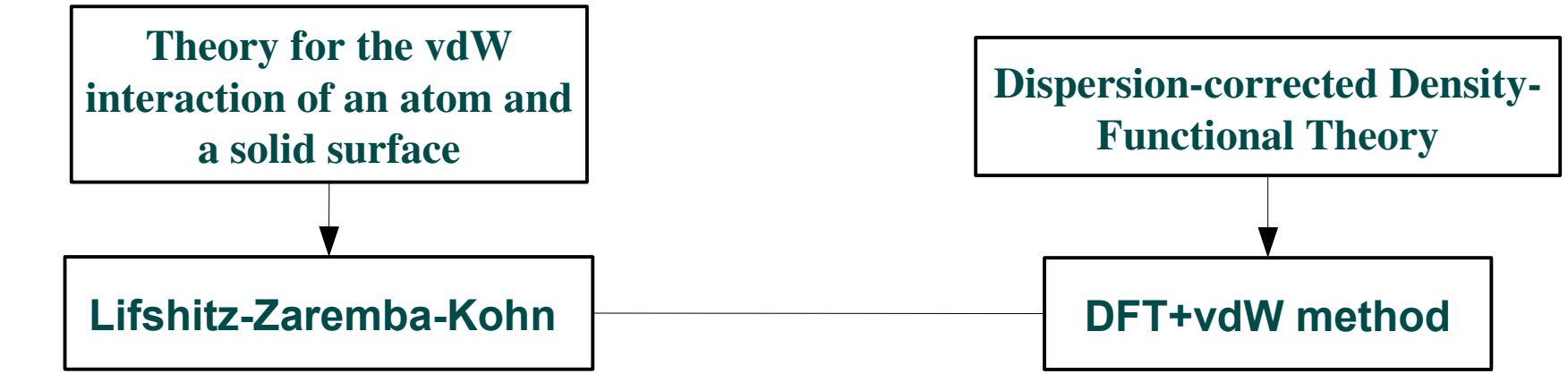
- Two parameters per atomic pair: (1) VdW C_6 interaction coefficient and (2) vdW radius.
- Clearly, if (1) and (2) are empirical, this leads to many fitting parameters. This was frequently the case before 2008.

R. Ahlrichs, G. Scoles, W. Yang, S. Grimme, A. Becke, P. Hobza, et al.

Evolution of interatomic vdW methods

- Grimme's D1,D2 (2004-2006): Parameterization for many elements in the periodic table
  - Highly empirical, some very *ad hoc* approximations
- 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 $C_6[n(\mathbf{r})]$ accurate to **5%** for **1225** molecular pairs
- ....

Van der Waals for bonding at surfaces: DFT+vdW^{surf}



Lifshitz, Sov. Phys. JETP 2, 73, 1956

Zaremba and Kohn, PRB 13, 2270, 1976

Tkatchenko and Scheffler, PRL 102, 073005, 2009

$$C_6 = C_6[n(r)]$$

Van der Waals for bonding at surfaces: DFT+vdW^{surf}

Theory for the vdW interaction of an atom and a solid surface

Lifshitz-Zaremba-Kohn

Lifshitz, Sov. Phys. JETP 2, 73, 1956

Zaremba and Kohn, PRB 13, 2270, 1976

$$C_3^{aB} = \frac{\hbar}{4\pi}\int_0^\infty d\omega\ \alpha(i\omega)\frac{\varepsilon_B(i\omega)-1}{\varepsilon_B(i\omega)+1}$$

Dispersion-corrected Density-Functional Theory

DFT+vdW method

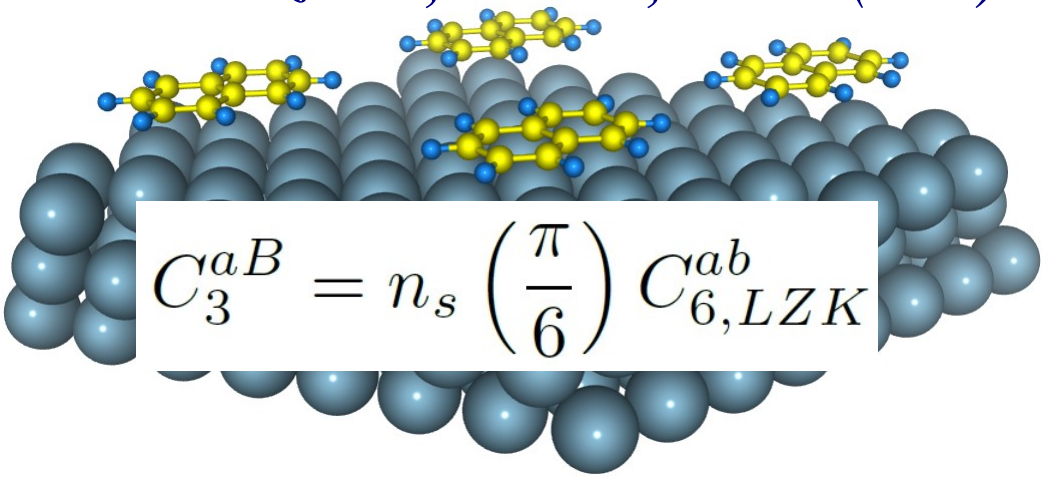
Tkatchenko and Scheffler, PRL 102, 073005, 2009

$$C_6 = C_6[n(r)]$$

DFT+vdW^{surf} method

Ruiz et al., PRL 108, 146103 (2012)

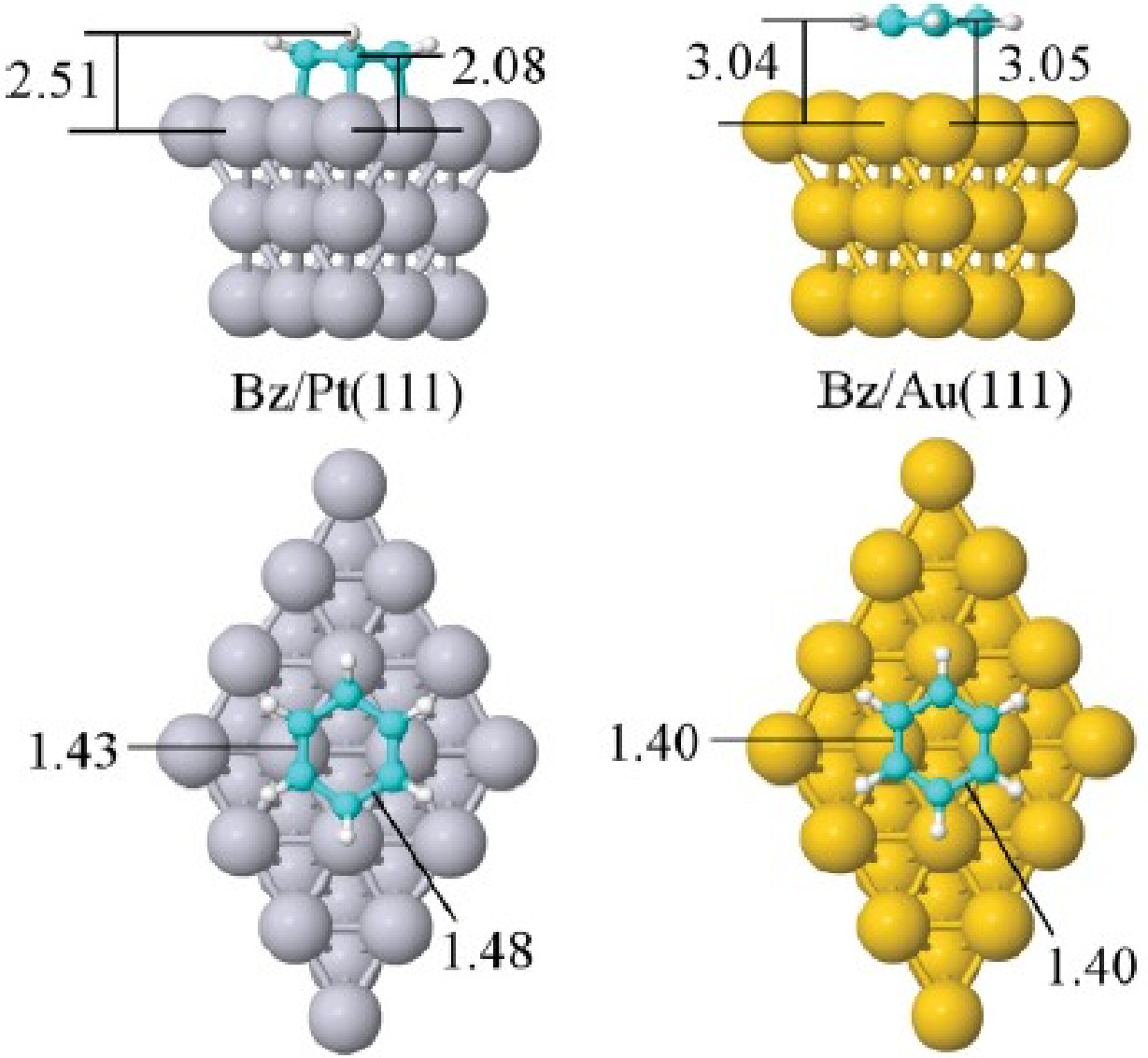
Collective substrate response (screening)



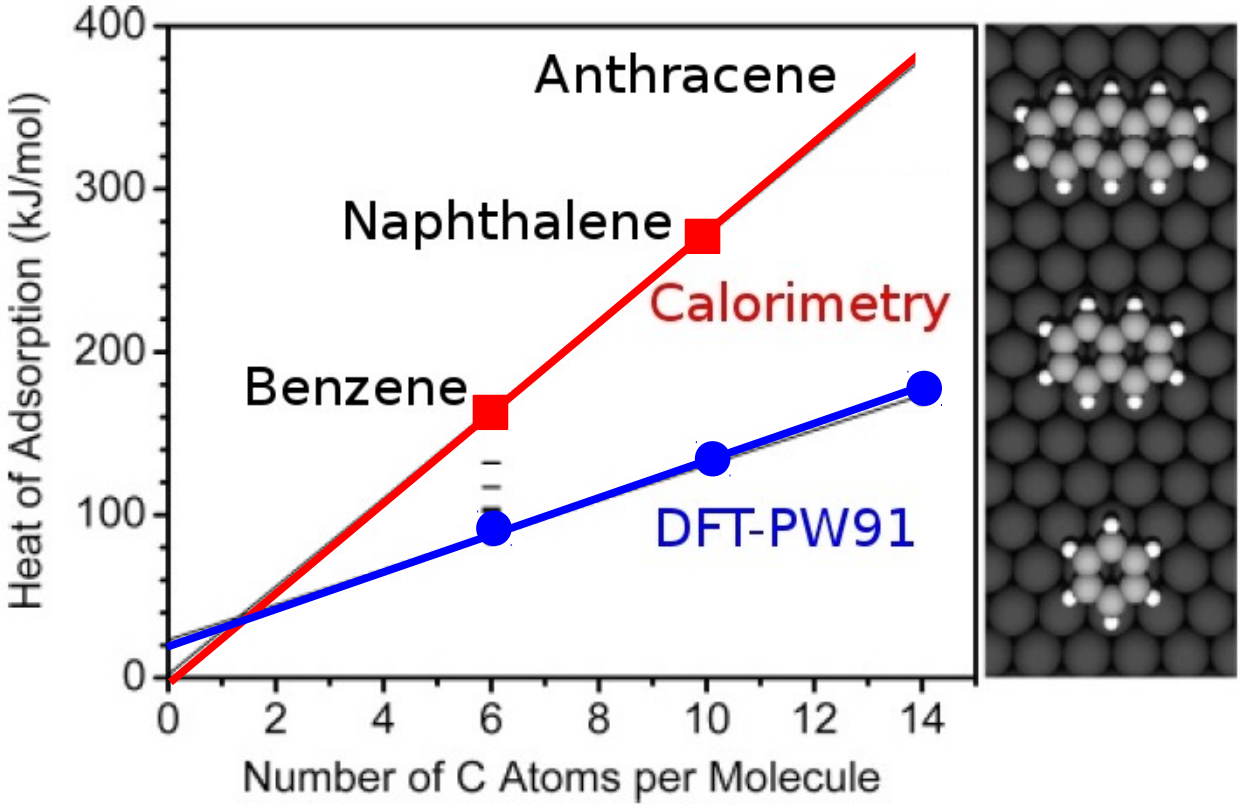
$$C_3^{aB} = n_s\left(\frac{\pi}{6}\right)C_{6,LZK}^{ab}$$

Molecular interactions

Understanding molecule/surface bonds: Benzene on Au(111) and Pt(111)

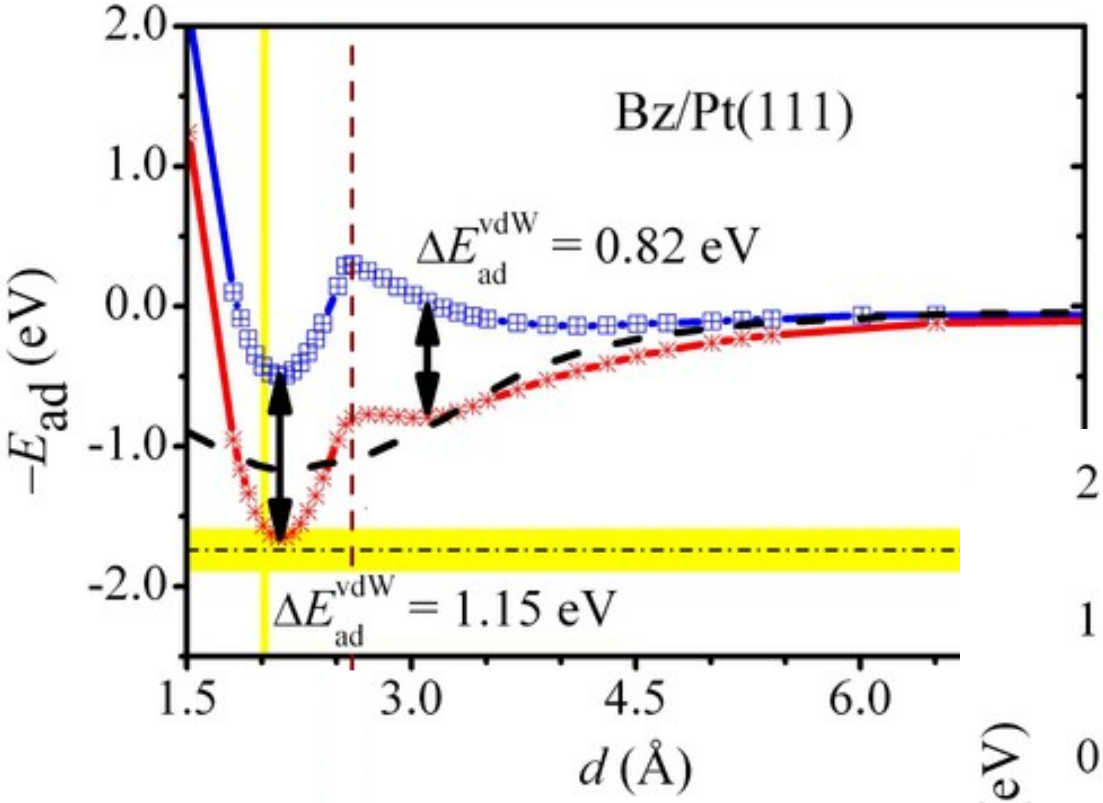


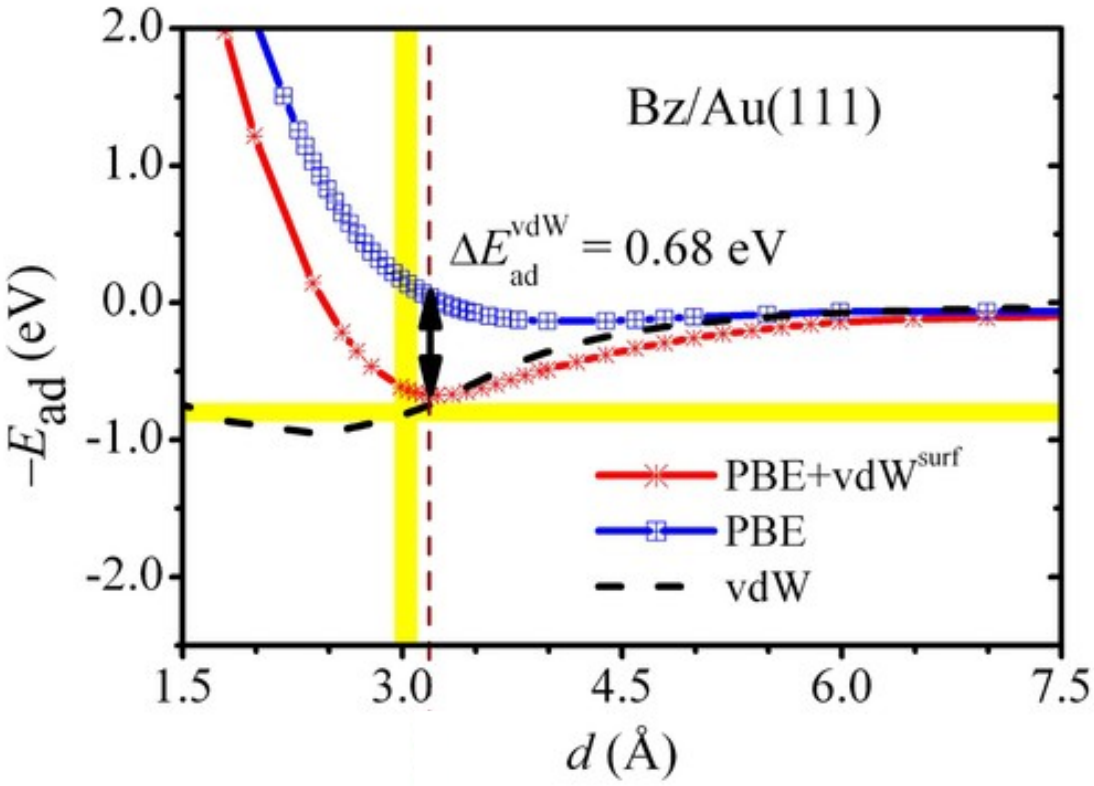
Understanding molecule/surface bonds: Benzene on Au(111) and Pt(111)



Gottfried *et al. J. Phys. Chem. B* 110, 17539 (**2006**).

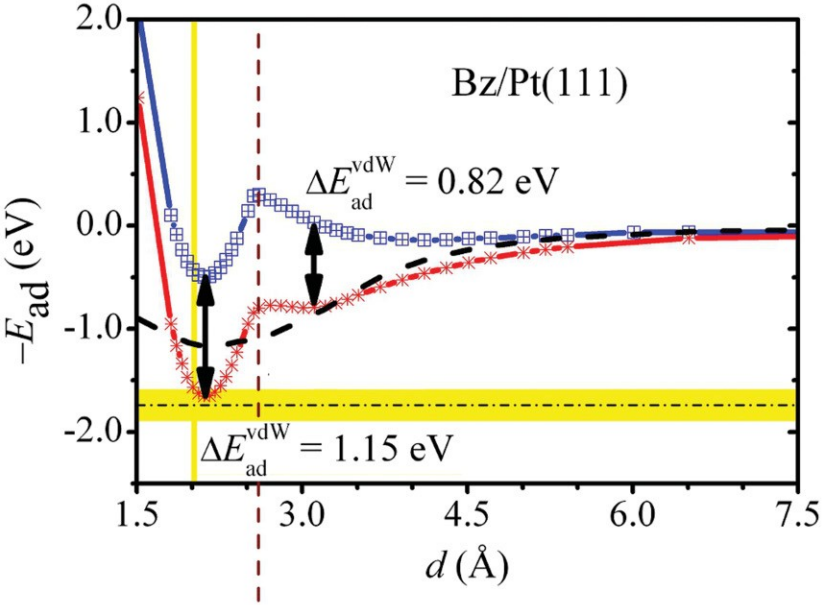
Understanding molecule/surface bonds: Benzene on Au(111) and Pt(111)

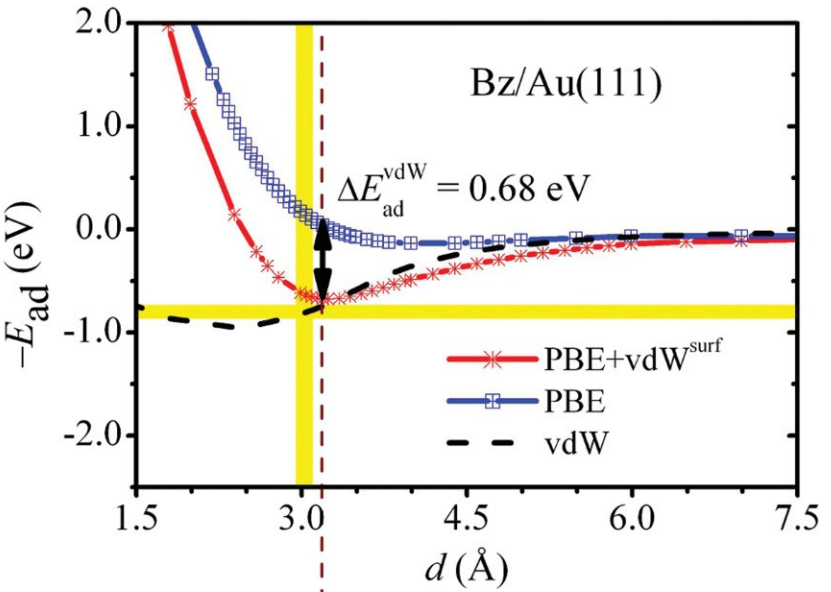


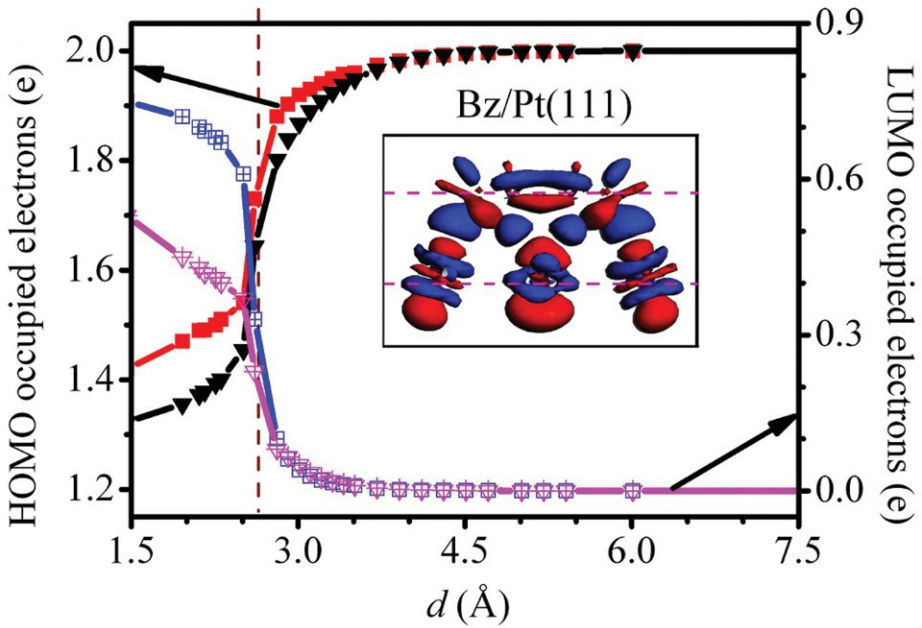


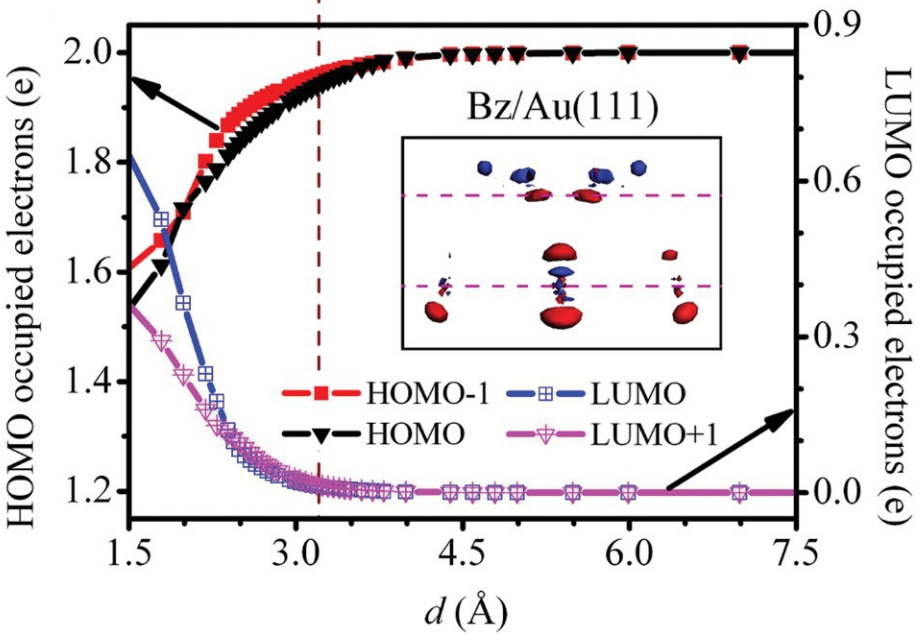
W. Liu, J. Carrasco, B. Santra, A. Michaelides, M. Scheffler, and A. Tkatchenko, *Phys. Rev. B* 86, 245405 (2012).

Understanding molecule/surface bonds: Benzene on Au(111) and Pt(111)

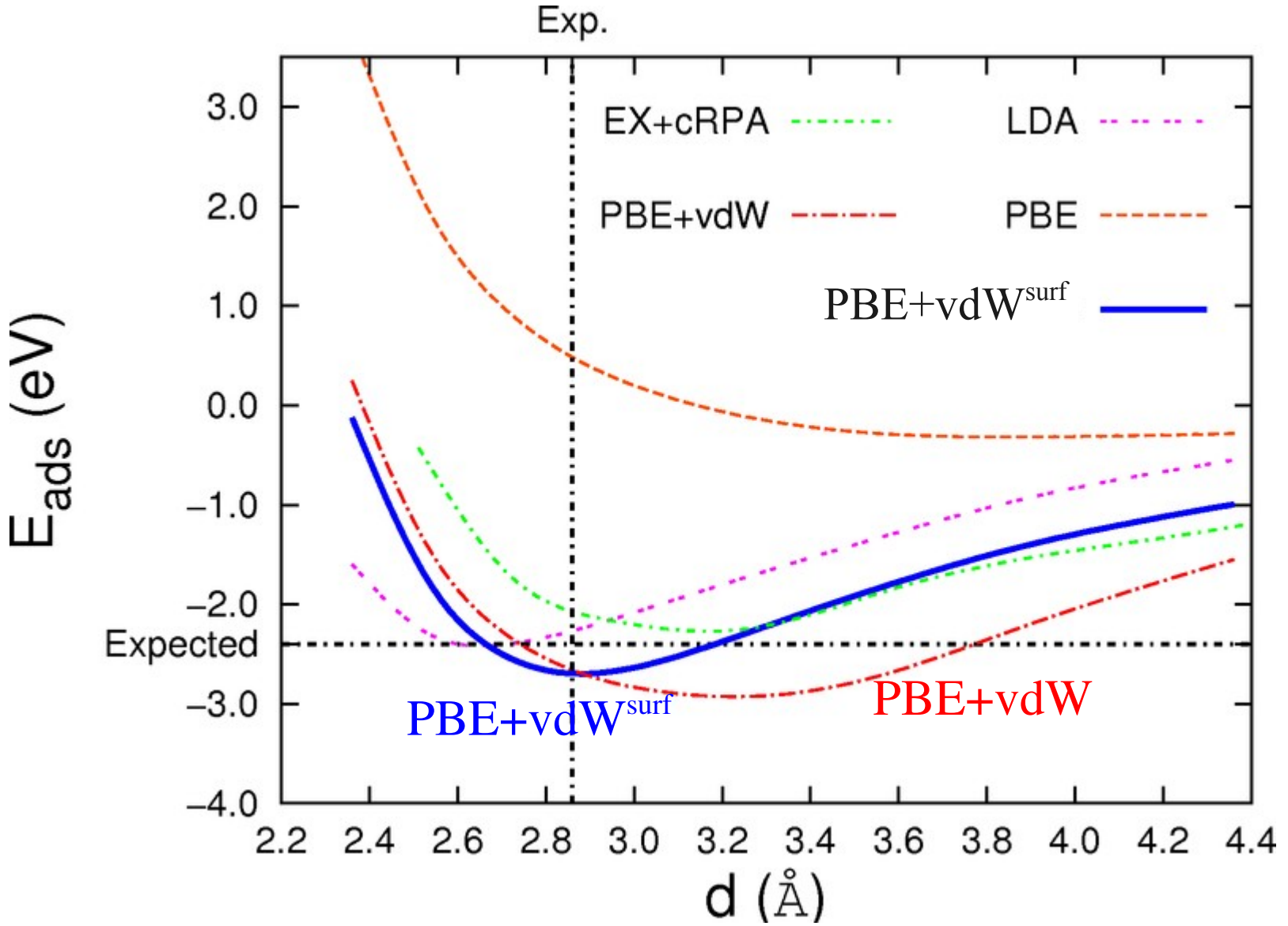




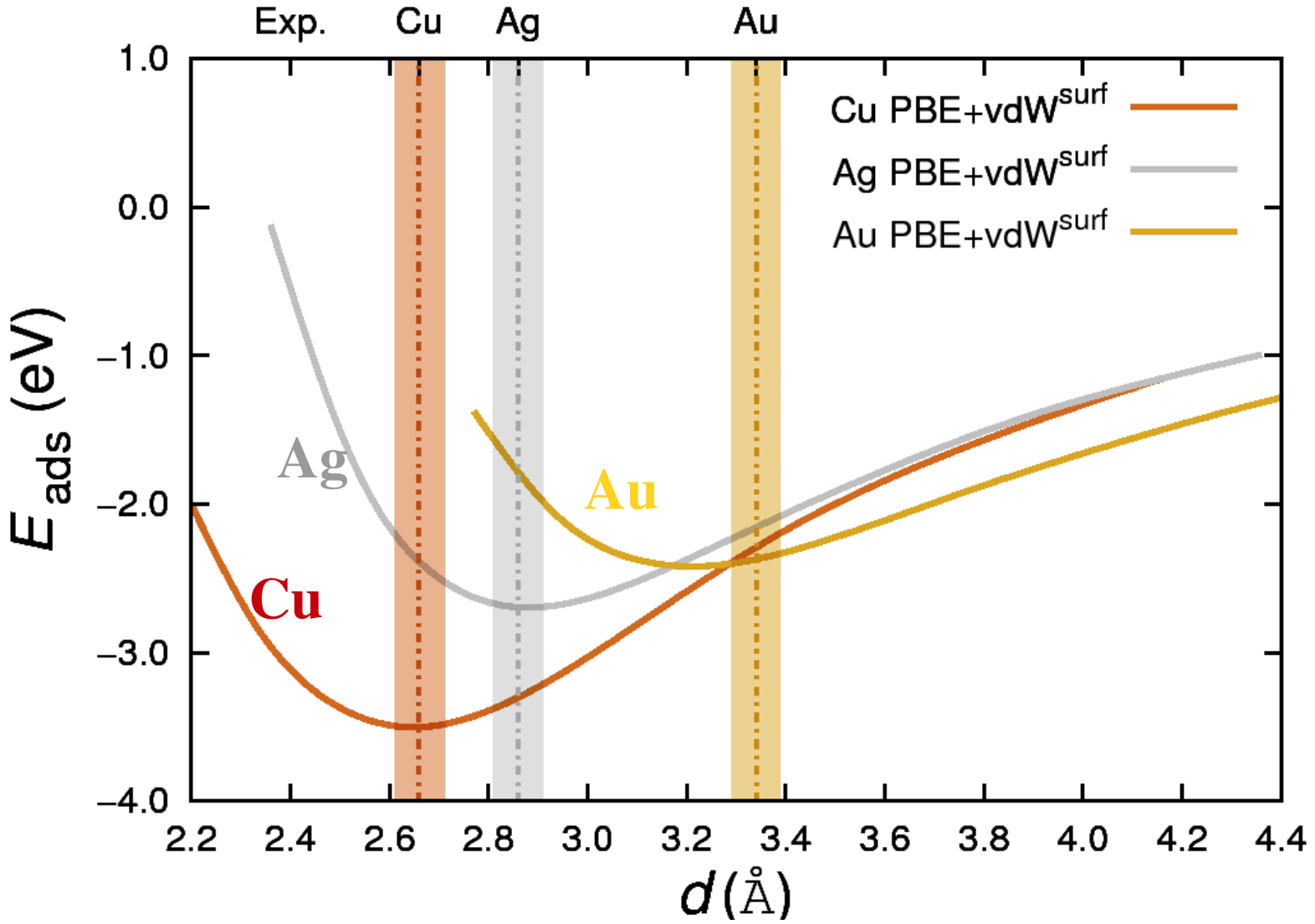




Reliability of DFT+vdW^{surf}: PTCDA/Ag(111)

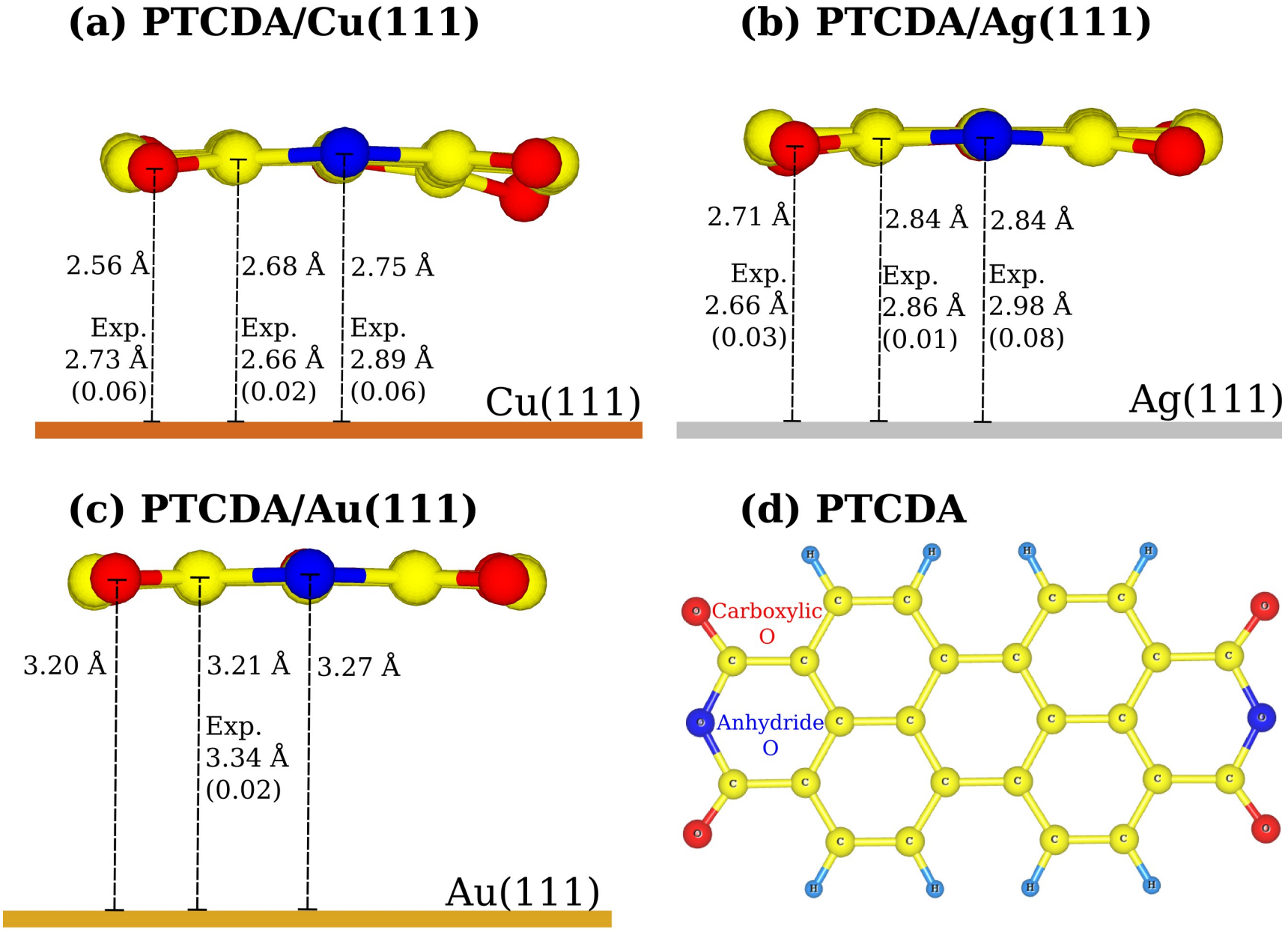


Reliability of DFT+vdW^{surf}: PTCDA@metals



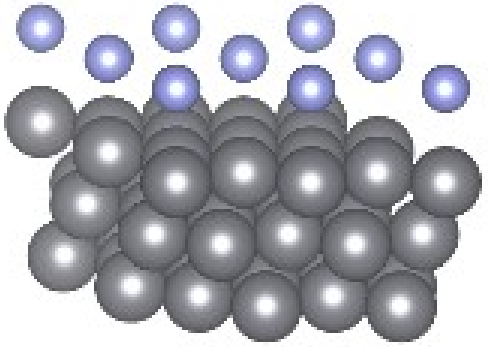
Experiments: *Hauschild et al.*, ***PRL*** (2007); ***PRB*** (2010).

Reliability of DFT+vdW^{surf}: PTCDA@metals

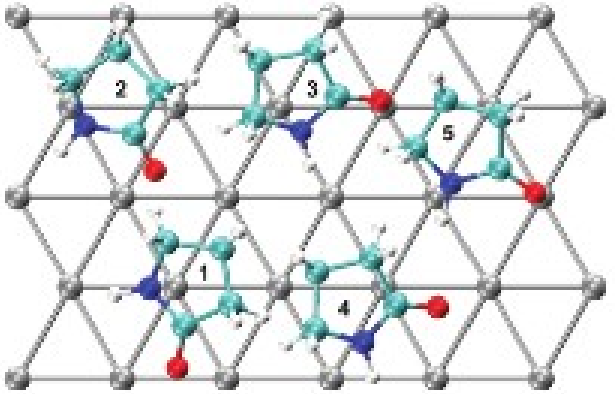


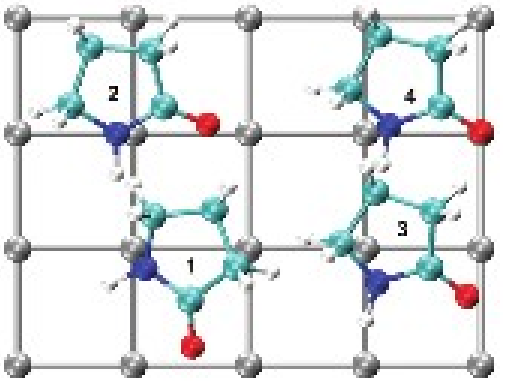
Experiments: *Hauschild et al.*, ***PRL*** (2007); ***PRB*** (2010).

Reliability of DFT+vdW^{surf}: More examples

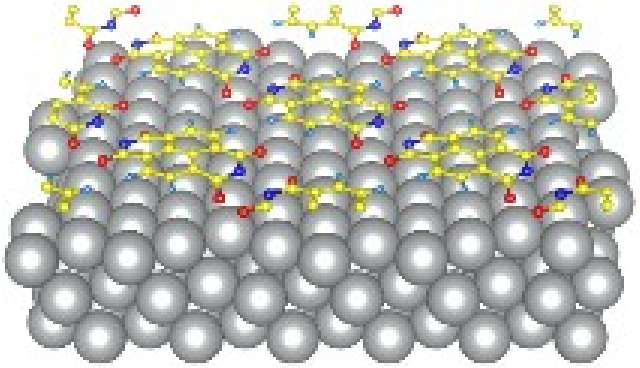


Xe on Me(111)
W. Liu, FHI





2-Pyrrolidone on Ag(111) and Ag(100)
W. A. Al-Saidi, H. Feng and K. A. Fichthorn,
Nano Lett. **12**, 997, (2012).

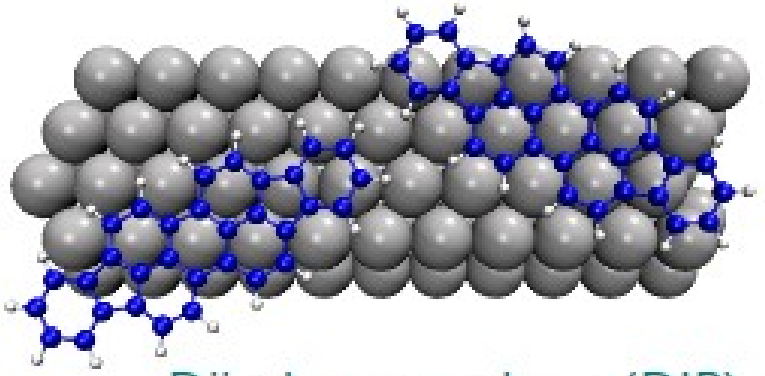


NTCDA on Ag(111)

Typical accuracy within
0.1 Å and 0.1eV
with respect to experiment

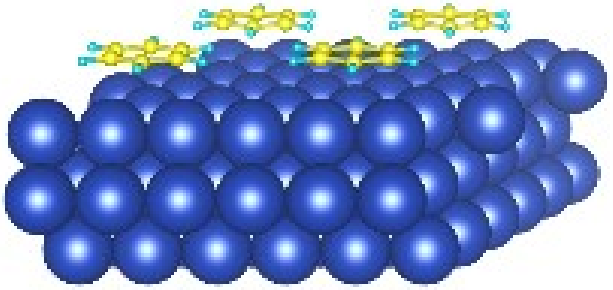
Naphthalene and Anthracene on Pt(111)
W. Liu, FHI

Reliability of DFT+vdW^{surf}: More examples



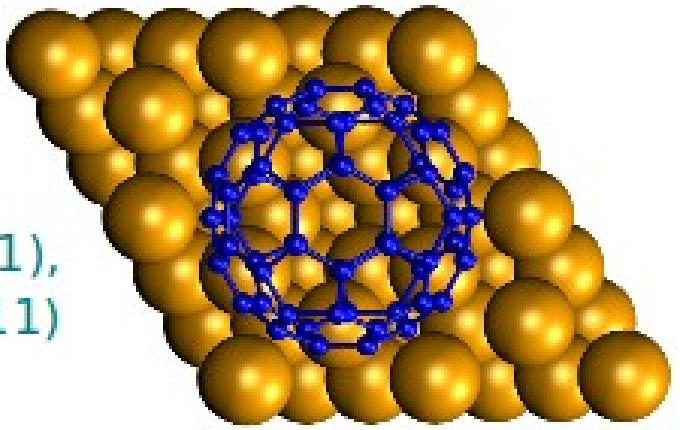
Diindenoperylene (DIP)
on Cu(111), Ag(111), and Au(111)

Nicola Ferri, FHI



Benzene on Me(111)
Wei Liu, FHI

Typical accuracy within
0.1 Å and 0.1eV
with respect to experiment



C_{60} on Ag(111),
and Au(111)

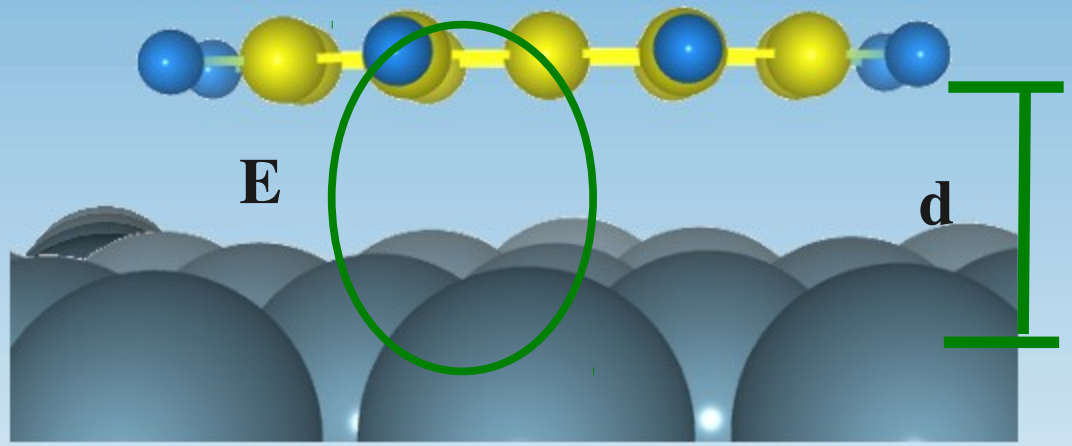
Revealing bonds on surfaces: "Collective" measurements

Spectroscopies

- NEXAFS
- NIXSW
- IRAS; SERS
- ARUPS
- XPS
- LEED
- TDS/TPD

Scanning Probe

STM/AFM



Calorimetry

Micro Calorimetry

Tautz, Prog. Surf. Sci. 82, 479, 2007.

Rong et al., Langmuir 17, 1582, 2001.

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Crowe and Campbell, Annu. Rev. Anal. Chem. 4, 41, 2011.

Avouris and Demuth, Annu. Rev. Phys. Chem. 35, 49, 1984.

Willets and Van Duyne, Annu. Rev. Phys. Chem. 58, 267, 2007.

Reconciling bonding in theory and experiment: Towards single-molecule measurements

PRL **109,** 076102 (2012) PHYSICAL REVIEW LETTERS week ending 17 AUGUST 2012

Measurement of the Binding Energies of the Organic-Metal Perylene-Teracarboxylic-Dianhydride/Au(111) Bonds by Molecular Manipulation Using an Atomic Force Microscope

C. Wagner,[1,2,*] N. Fournier,[1,2] F. S. Tautz,[1,2] and R. Temirov[1,2]

[1]*Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany*

[2]*Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany*

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to be published, *Phys. Rev. Lett.* (2013)

Adsorption geometry determination of single molecules by atomic force microscopy

Bruno Schuler,[1,*] Wei Liu,[2] Alexandre Tkatchenko,[2] Nikolaj Moll,[1]
Gerhard Meyer,[1] Anish Mistry,[3] David Fox,[3] and Leo Gross[1]

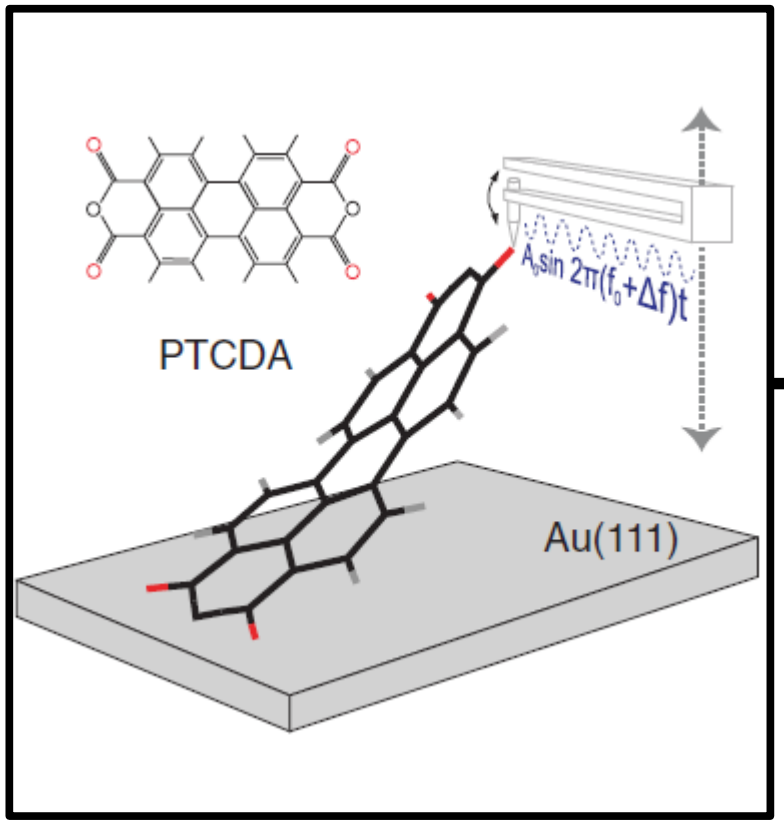
[1]*IBM Research – Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland*

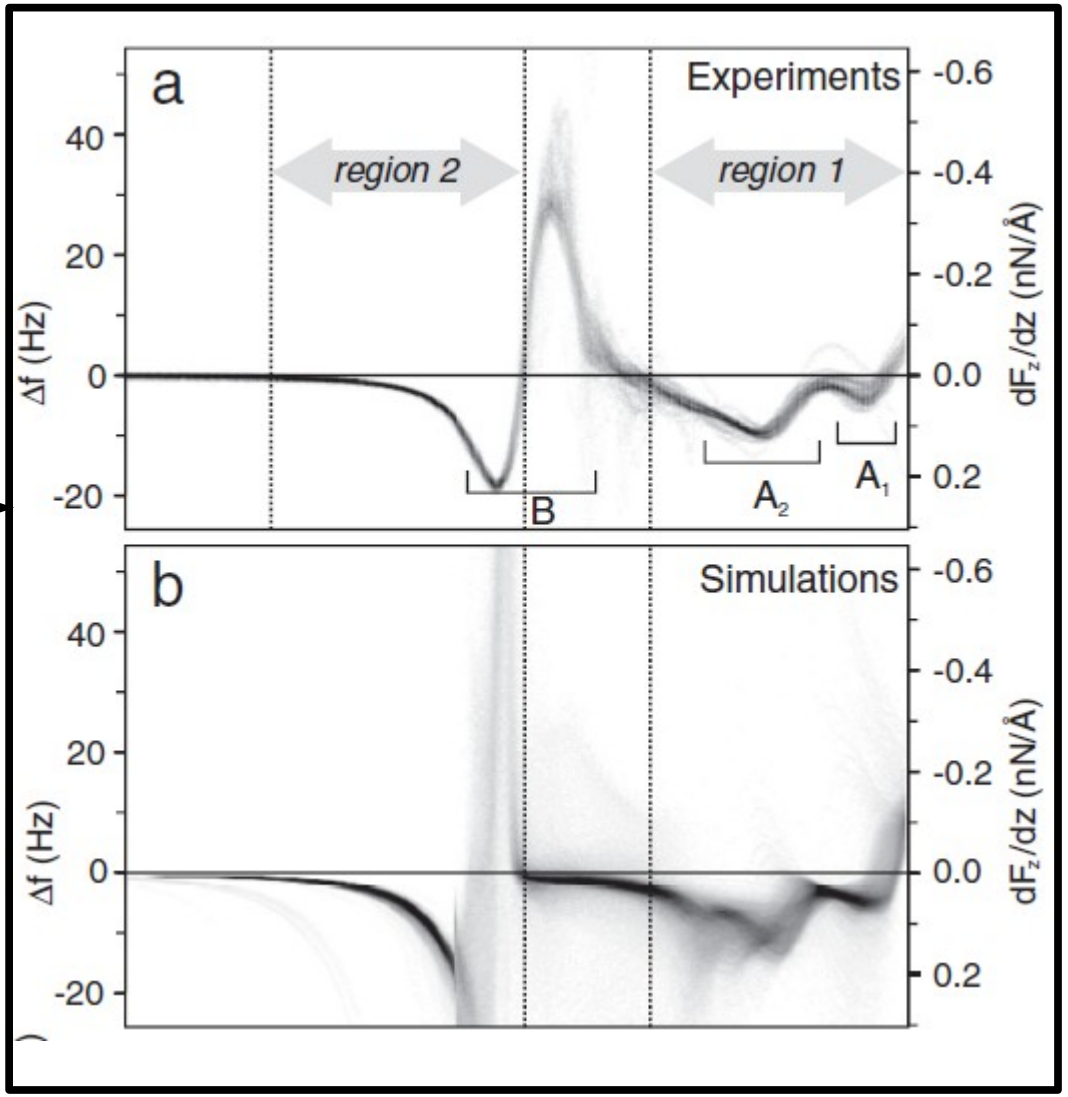
[2]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

[3]*University of Warwick, Gibbet Hill, CV34 Warwick, UK*

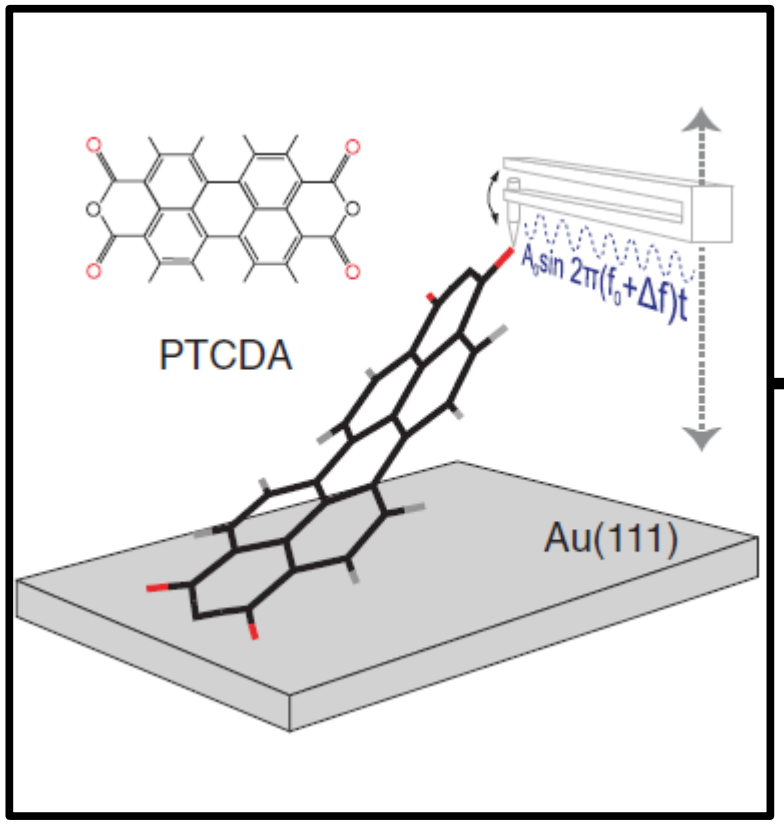
(Dated: July 2, 2013)

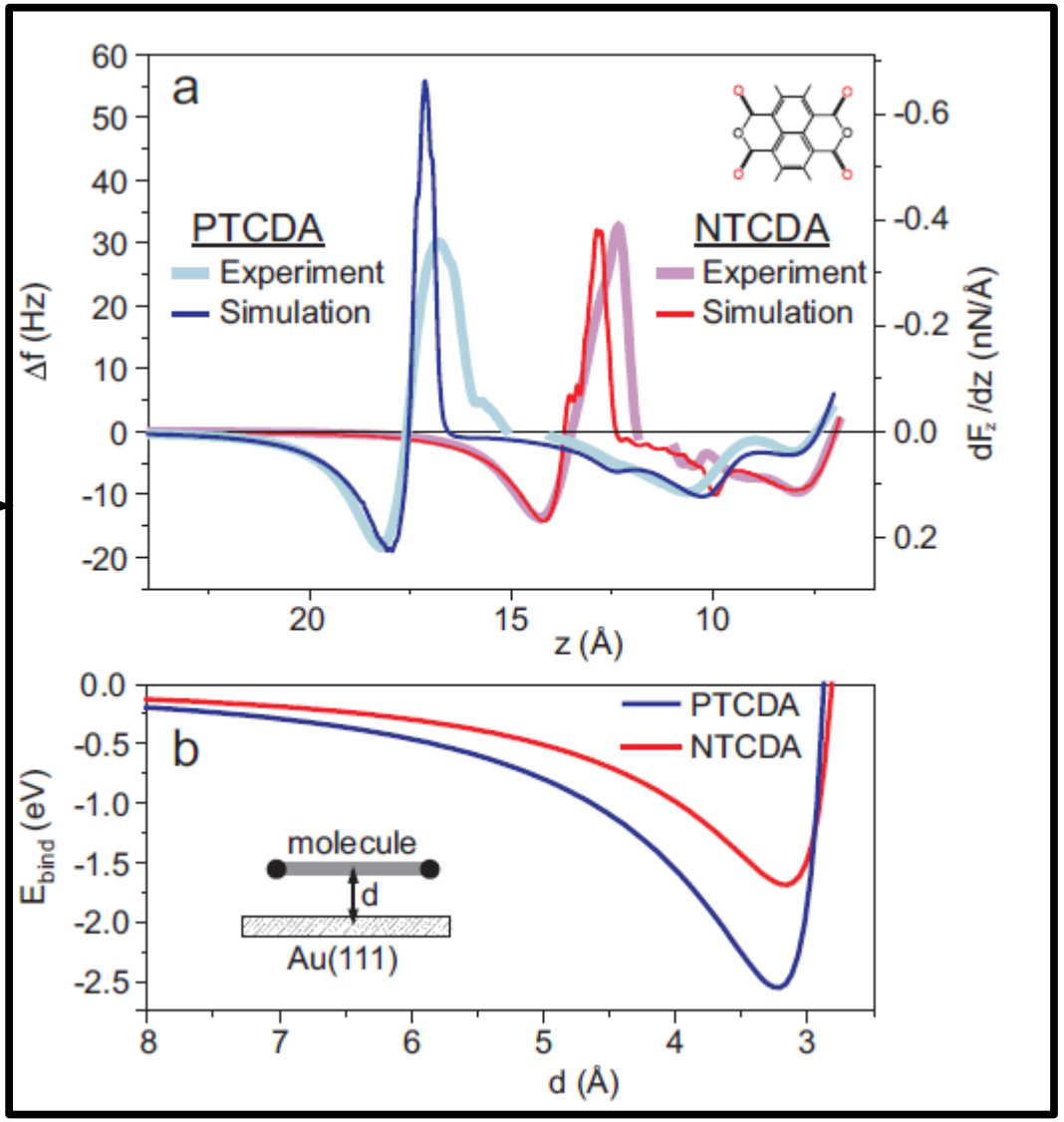
Single-molecule measurement of adsorption energy by AFM



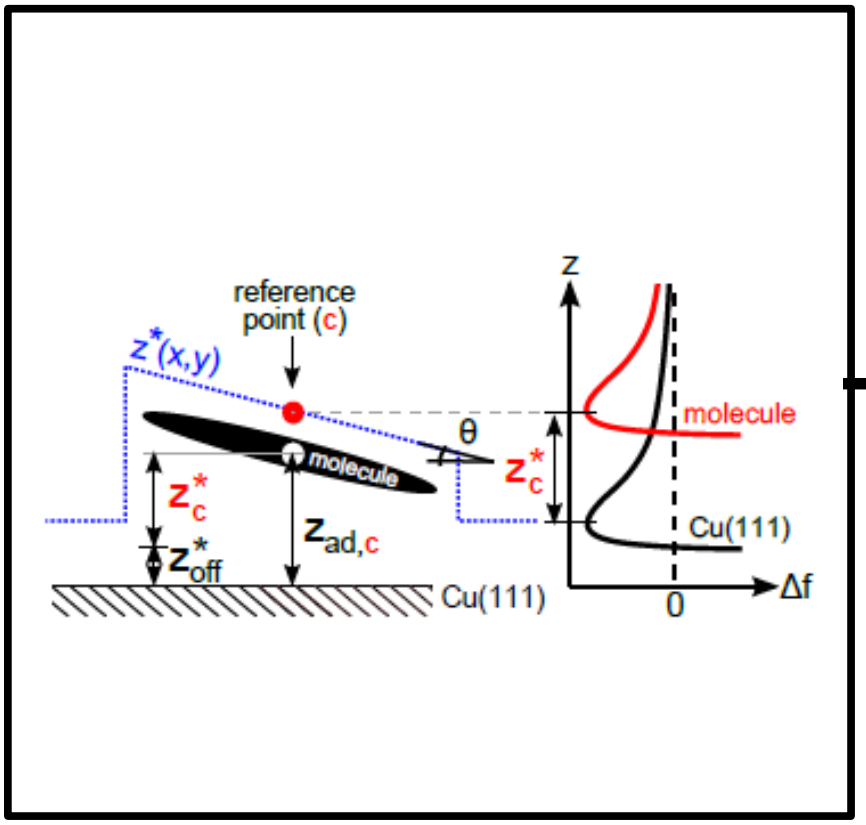


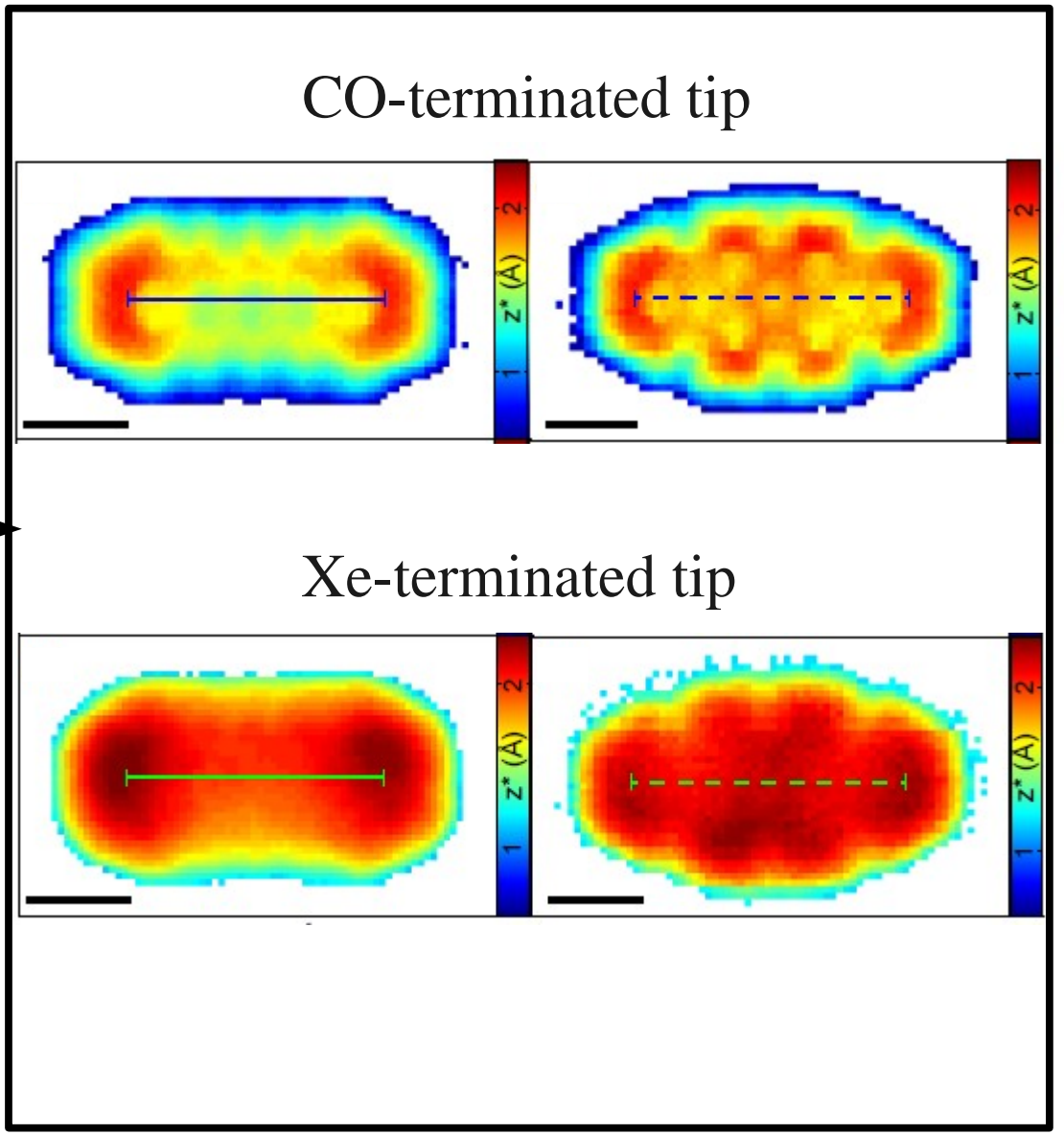
Single-molecule measurement of adsorption energy by AFM





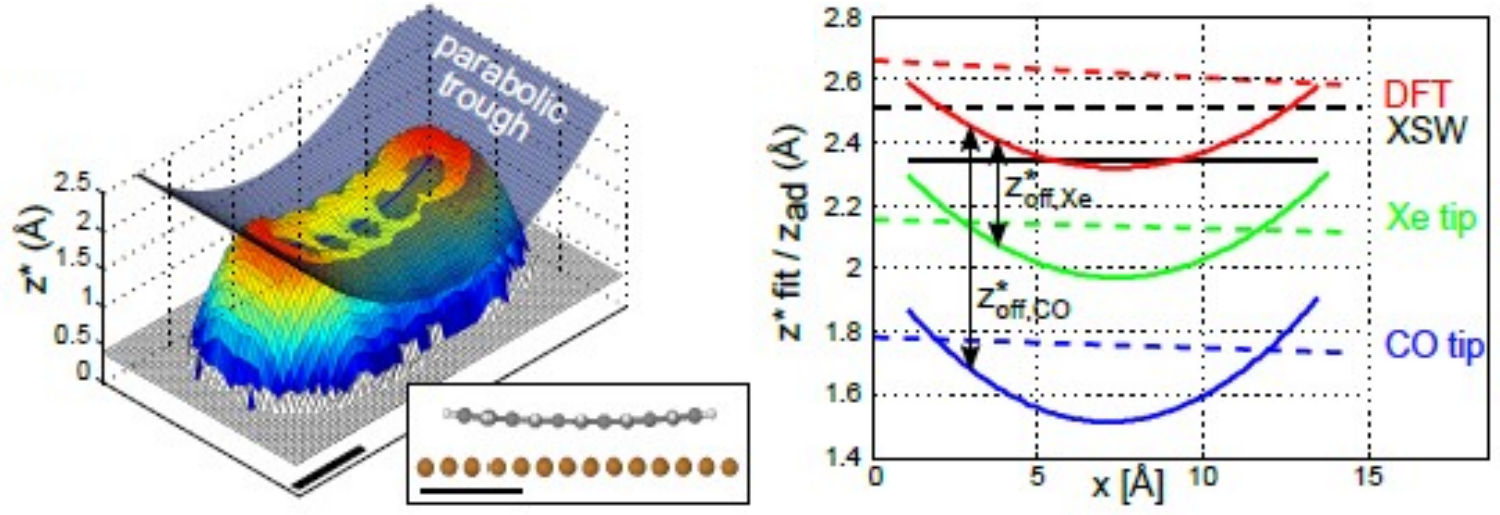
Single-molecule measurement of adsorption height by AFM

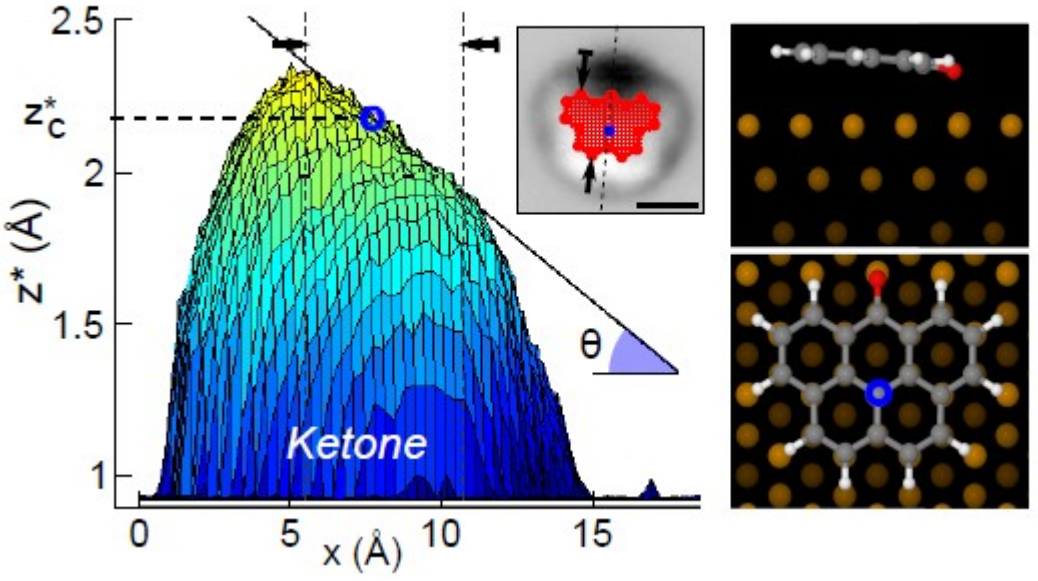




B. Schuler *et al.*,
Phys. Rev. Lett. (2013).

Single-molecule measurement of adsorption height by AFM

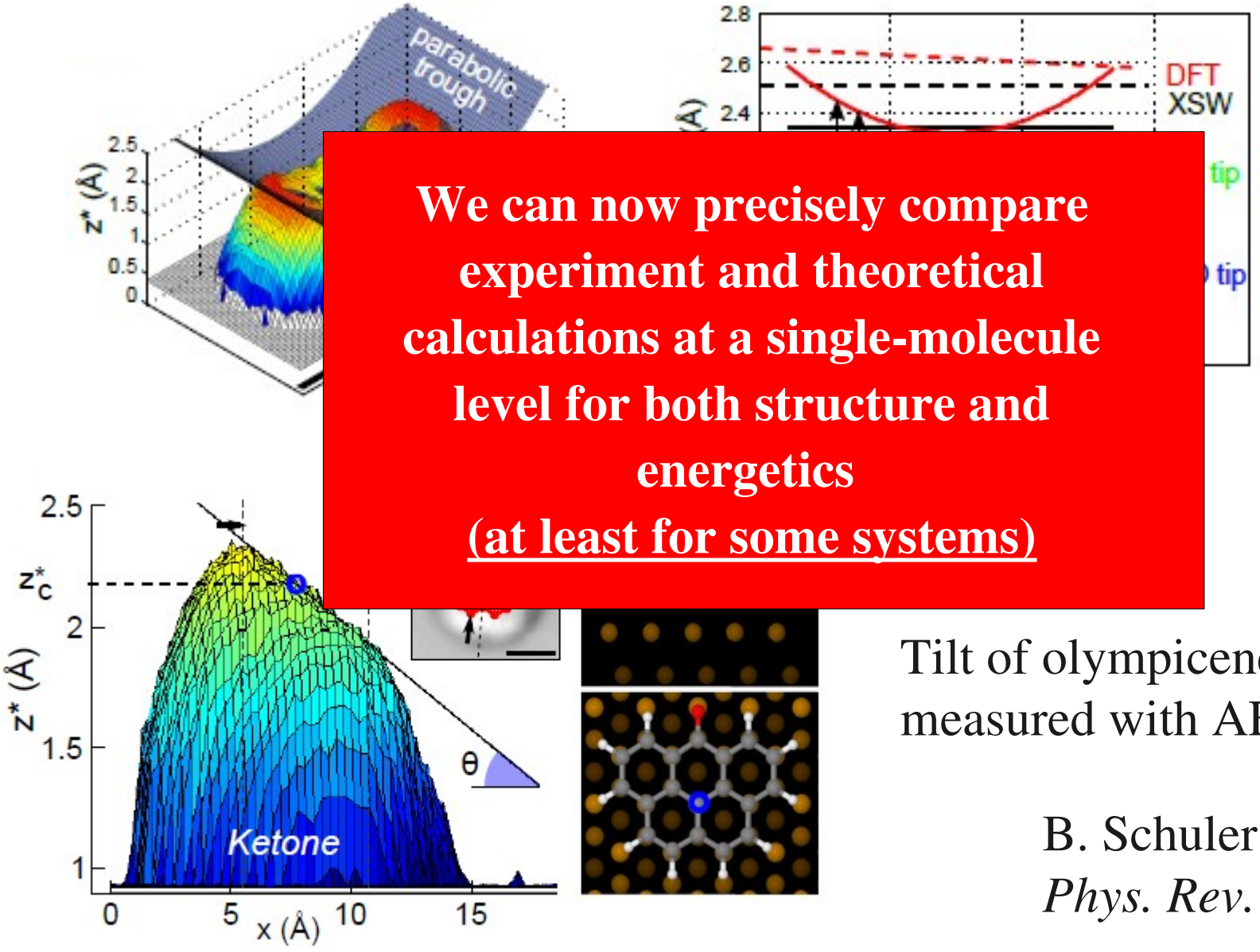




Tilt of olympicene ketone measured with AFM

B. Schuler *et al.*,
Phys. Rev. Lett. (2013).

Single-molecule measurement of adsorption height by AFM



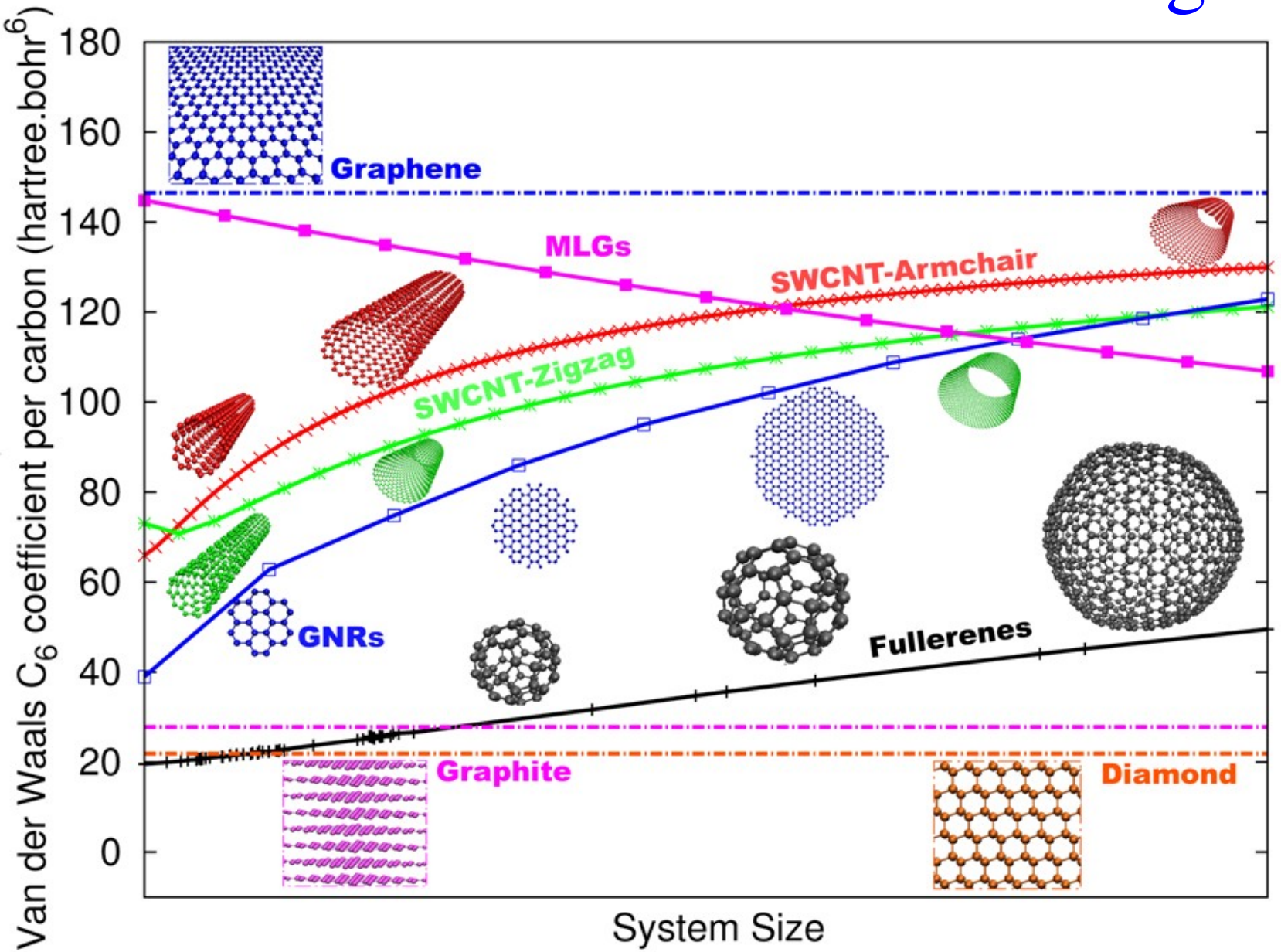
We can now precisely compare experiment and theoretical calculations at a single-molecule level for both structure and energetics

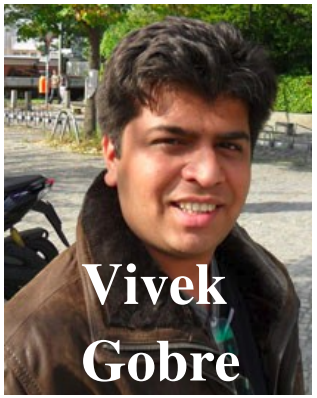
(at least for some systems)

Tilt of olympicene ketone measured with AFM

B. Schuler *et al.*, *Phys. Rev. Lett.* (2013).

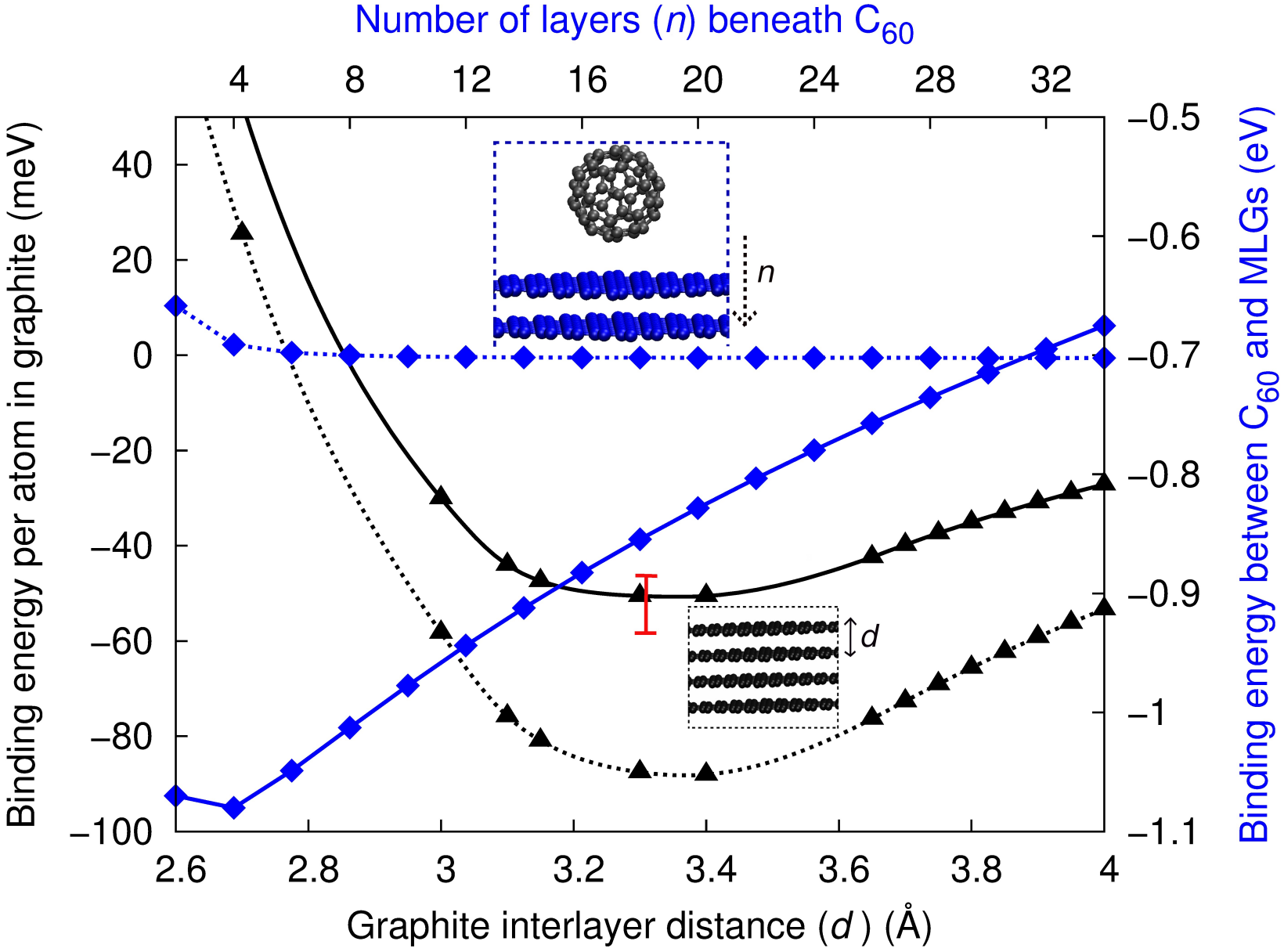
An example of unconventional molecule/surface bonding

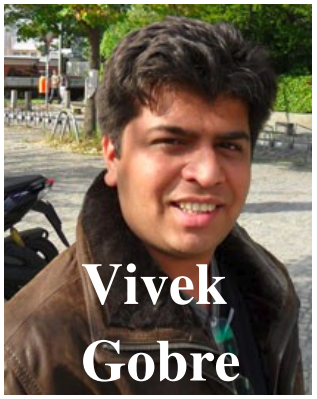




V.V. Gobre and A. Tkatchenko, *Nature Comms.* (2013).

An example of unconventional molecule/surface bonding





V.V. Gobre and A. Tkatchenko, *Nature Comms.* (2013).

Bonding at Surfaces: Summary

- Useful classification: Covalent/ionic bonding, Pauli repulsion, van der Waals interactions.
- Real systems = synergy of different bonding contributions.
- Van der Waals interactions can be very substantial (1 eV per benzene ring).
- DFT+vdW works well, but not always reliable. Comparison with experiment is crucial.
- Many surprises for bonding of molecules on surfaces, making it an exciting field!

Bonding at Surfaces: Outlook

Towards reliable and predictive modeling of bonding, structure, and electronic properties of hybrid inorganic/organic interfaces.
Understand **and** ***control*** **their functionality!**