Accurate description of the bonding of C_6H_6 at noble metal surfaces, using a local exchange-correlation correction scheme

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Motivation

Adsorption and bonding at metal surfaces

- Hetereogeneous catalysis
- Epitaxy

➔ Need high accuracy PES

- Metallic bandstructure
- Need to model extended surface

➔ Large system sizes

PBC calculations typically restricted to DFT / {LDA,GGA,...}

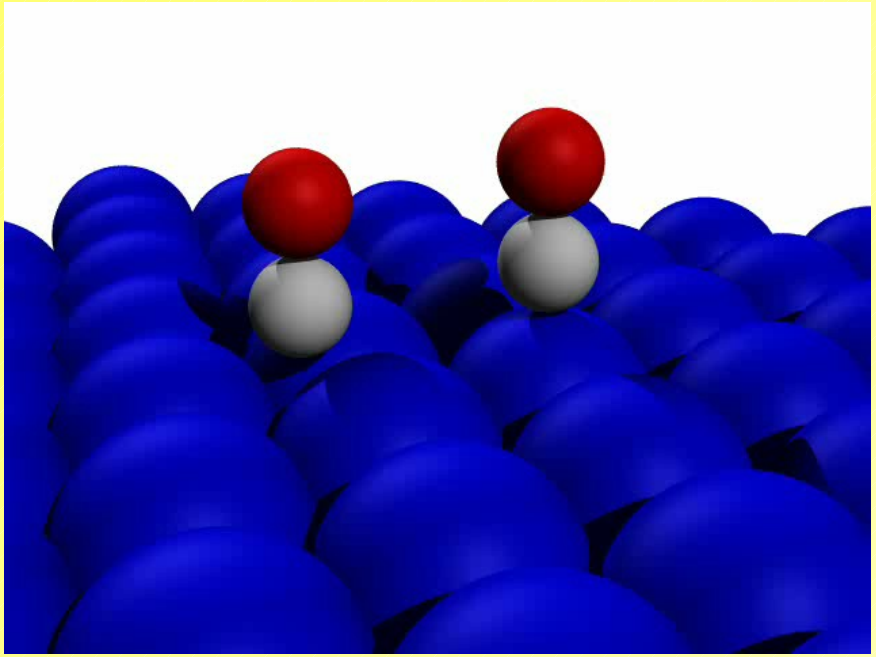
SIE?

van der Waals?

Reliable energy?

Challenge for first-principles modelling!

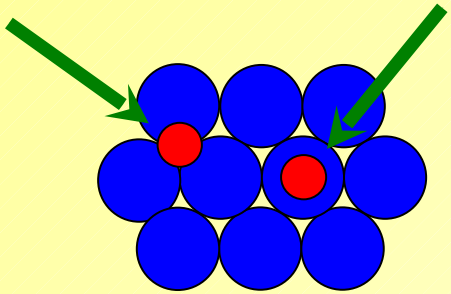
The CO adsorption puzzle



low coverage

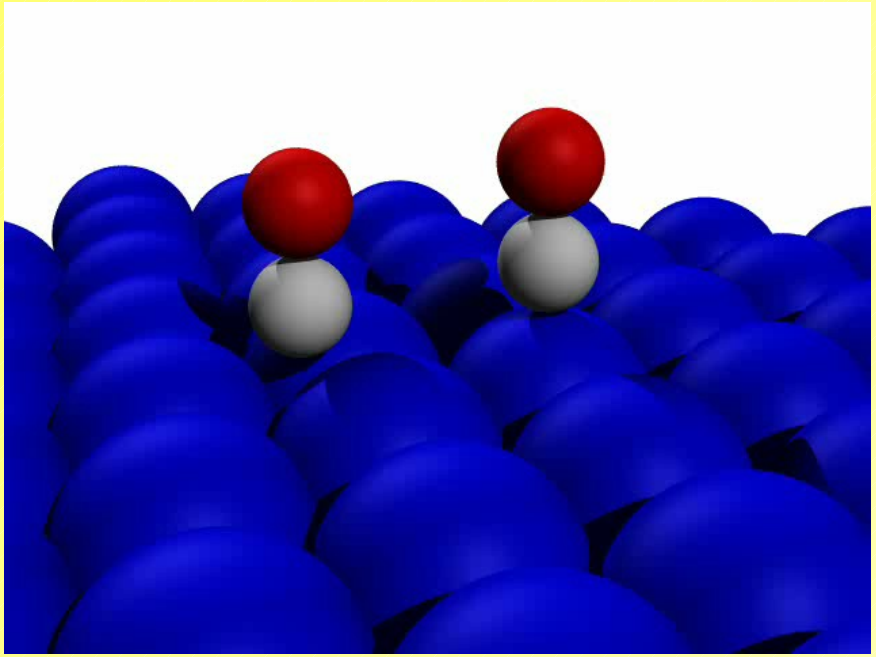
DFT
LDA/GGA

Experiment



P.J. Feibelman *et al*., J. Phys. Chem. B 105, 4018 (2001);
M. Gajdos *et al*., J. Phys.: Cond. Matter 16, 1141 (2004)

The CO adsorption puzzle



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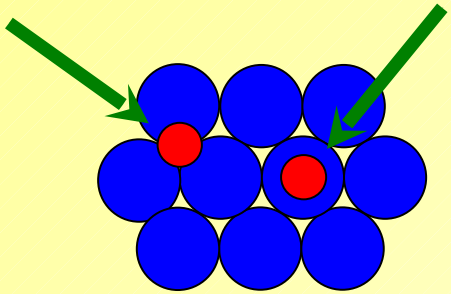

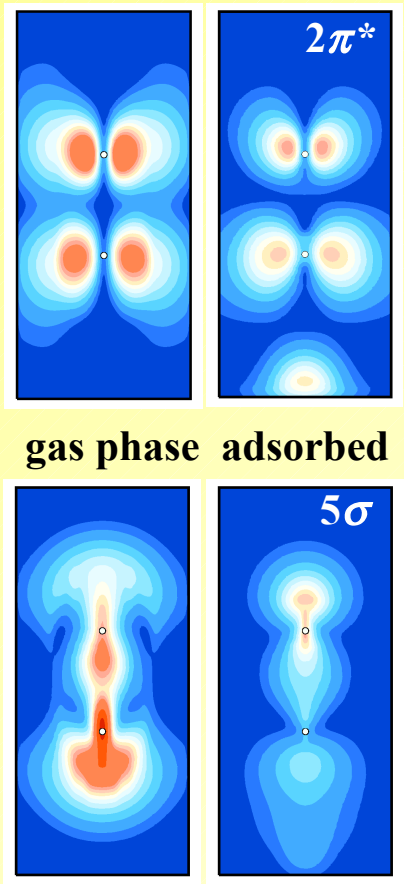

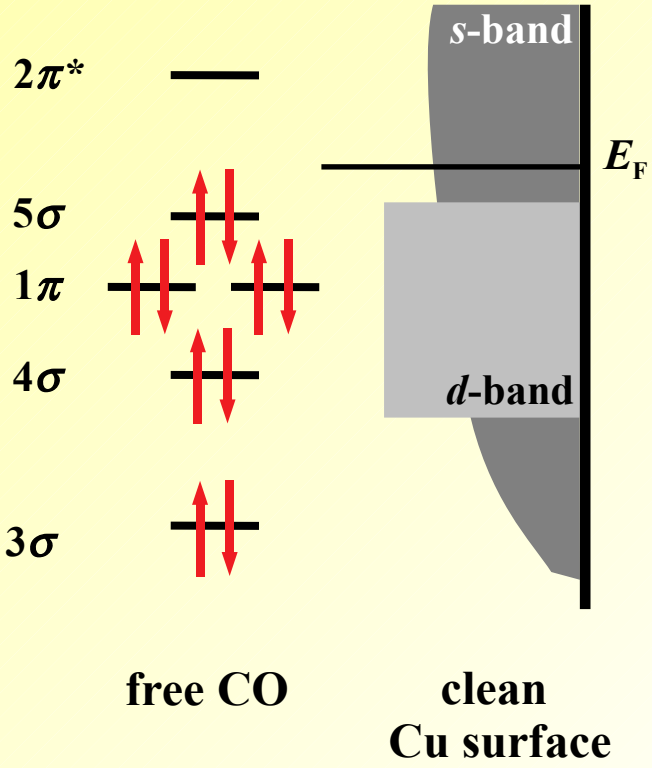

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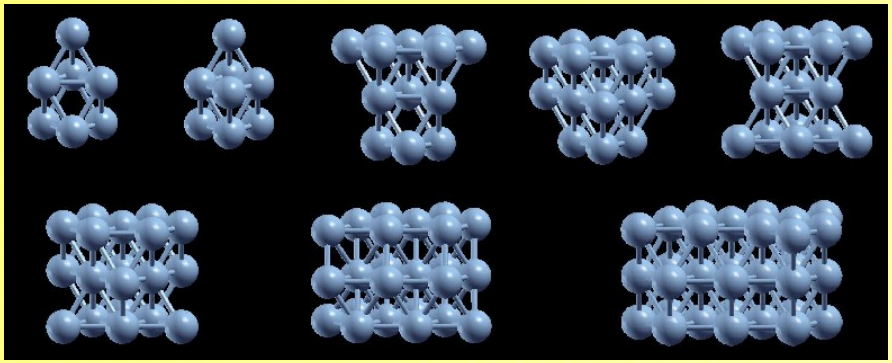
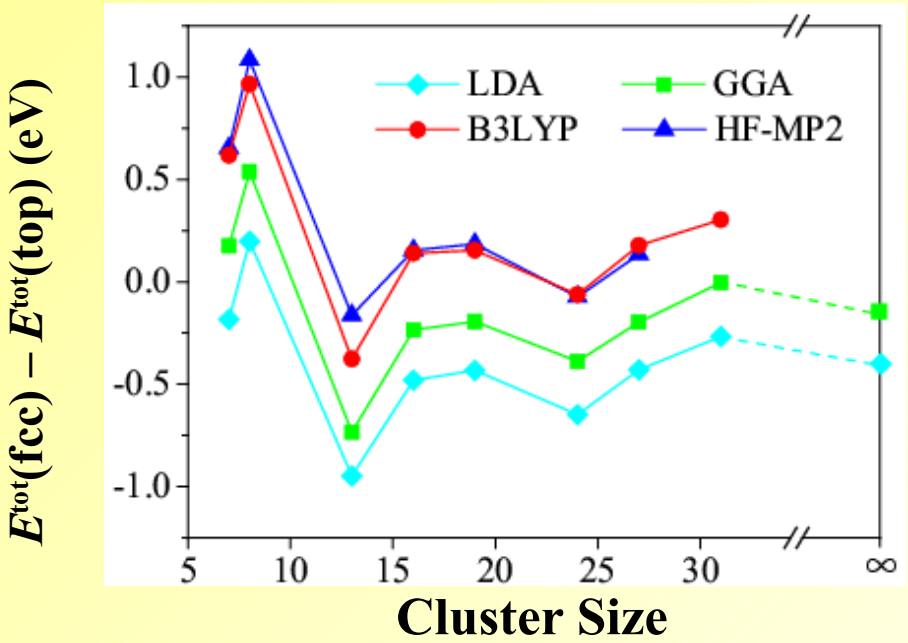
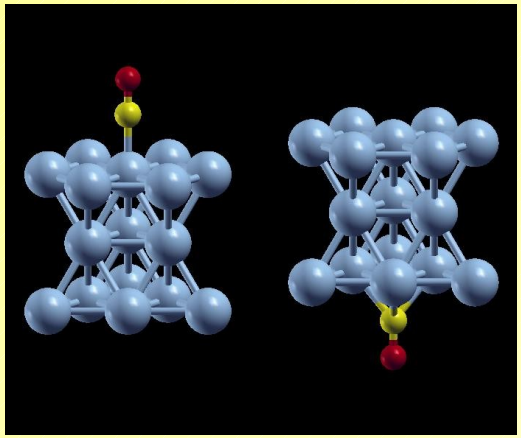
G. Kresse, A. Gil and P. Sautet,
Phys. Rev. B 68, 073401 (2004)

Local xc-correction scheme

Systematic cluster calculations (Gaussian03, TZVP)







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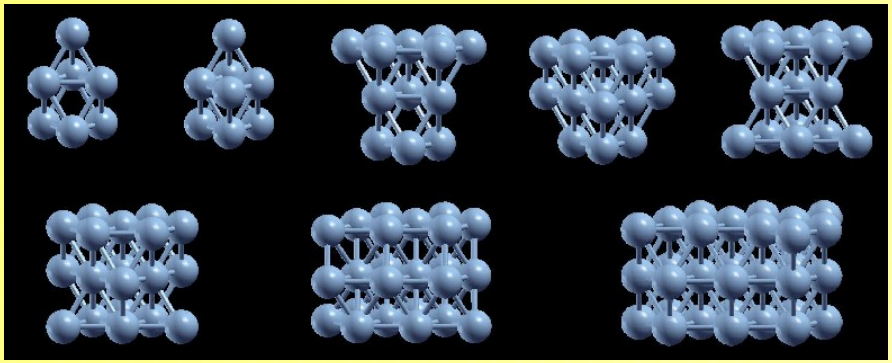
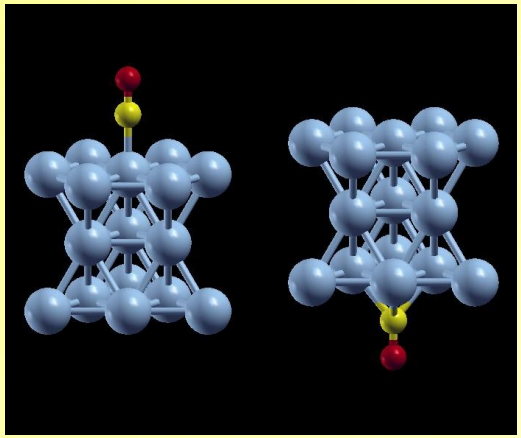
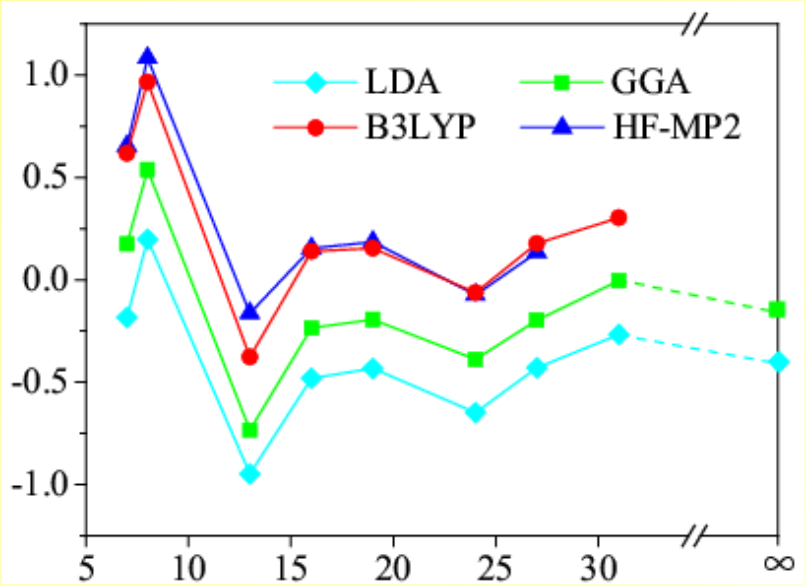
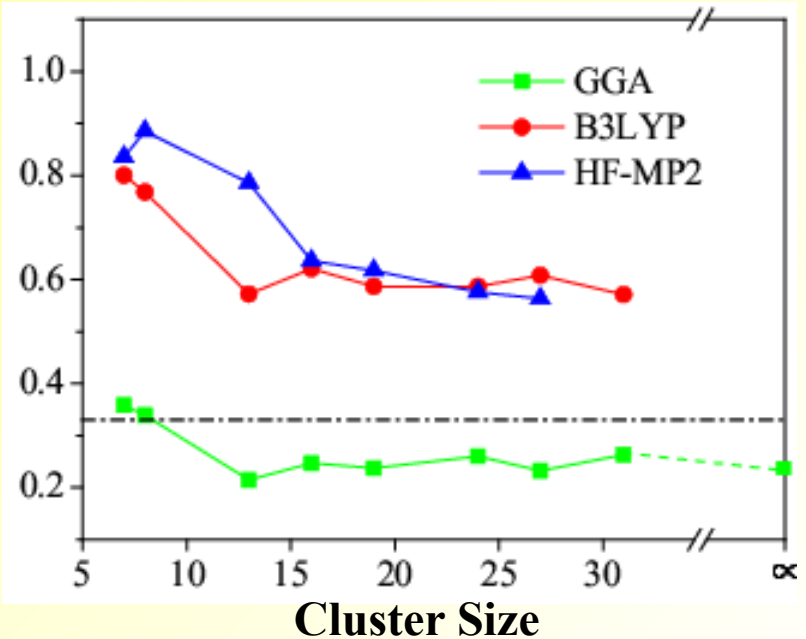


$$E^{xc\ corr.} = \left[E^{tot}(xc) - E^{tot}(LDA) \right]$$





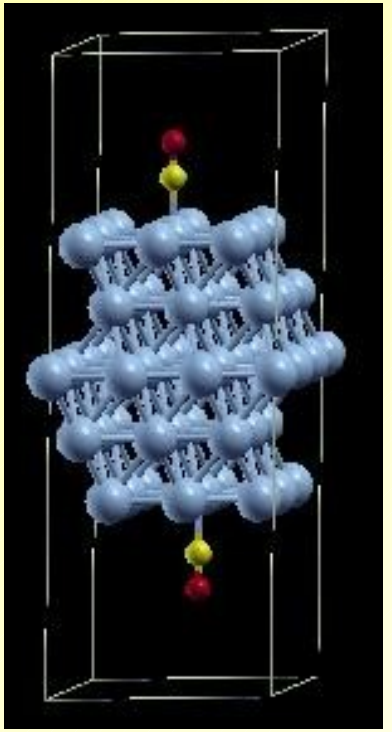


Application I: CO / Cu(111)

$$(\mathrm{E}^{fcc} - \mathrm{E}^{top}) = (\mathrm{E}^{fcc}_{LDA} - \mathrm{E}^{top}_{LDA})|_{slab} + \underbrace{\left[(\mathrm{E}^{fcc}_{xc} - \mathrm{E}^{top}_{xc}) - (\mathrm{E}^{fcc}_{LDA} - \mathrm{E}^{top}_{LDA})\right]}\Big|_{cluster}$$

$$= (\mathrm{E}^{fcc}_{LDA} - \mathrm{E}^{top}_{LDA})|_{slab} + \Delta\mathrm{E}^{xc-LDA}_{corr.}(\mathrm{fcc} - \mathrm{top})$$

Initial slab reference energies:
FP-LAPW/APW+lo (WIEN2k),
1/9 ML in (3x3) cells



Application I: CO / Cu(111)

$$(E^{fcc} - E^{top}) = (E^{fcc}_{LDA} - E^{top}_{LDA})|_{slab} + \underbrace{\left[(E^{fcc}_{xc} - E^{top}_{xc}) - (E^{fcc}_{LDA} - E^{top}_{LDA})\right]}\Big|_{cluster}$$

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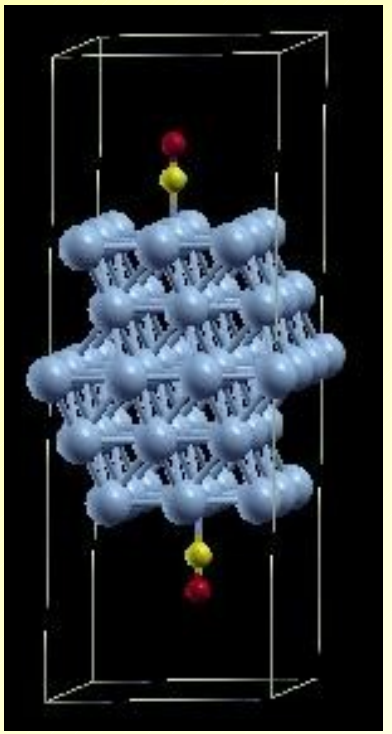


X Wrong fcc site more stable

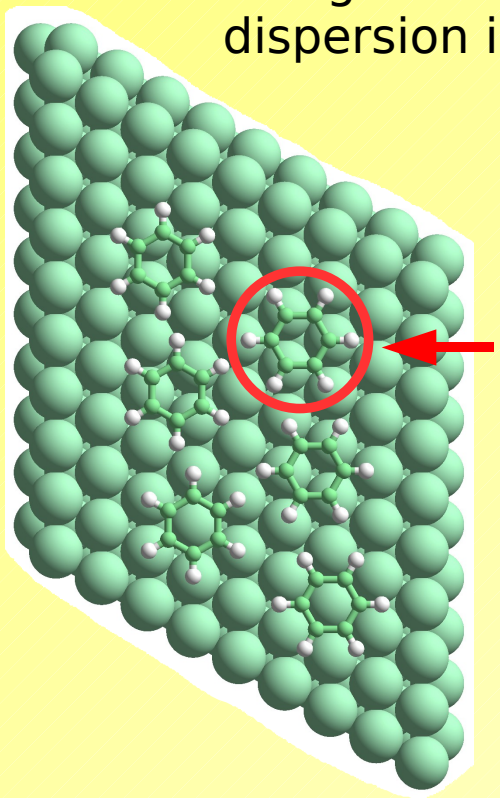
	LDA	GGA	B3LYP	HF-MP2
Site preference energy	**-0.33 eV**	**-0.11 eV**	**+0.27±0.02 eV**	**+0.29±0.03 eV**

Q.-M. Hu, K. Reuter and M. Scheffler,
Phys. Rev. Lett. 98, 176103 (2007)
Same concept: C. Tuma and J. Sauer, Chem. Phys. Lett. 387, 388 (2004)

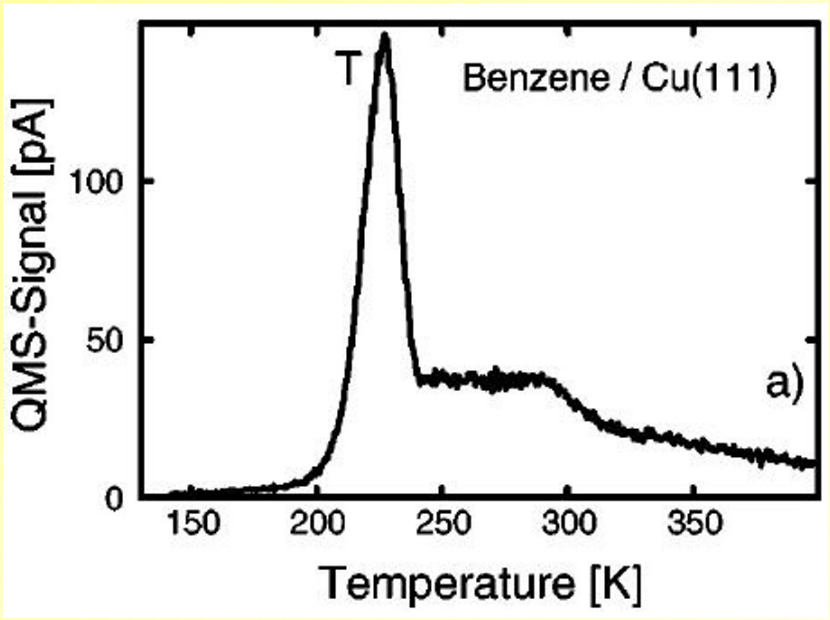
✓ **B3LYP/MP2 yield correct top site more stable**

Application II: Benzene / Cu(111)

- Why benzene on Cu?
- Model system for range of organic molecules adsorbed at coinage metals
- Experiments show definite binding[(1)]
- Bonding assumed van der Waals / dispersion interaction dominated



- Three-fold hollow geometry chosen for testing and method convergence



TPD[(1)]

1) S. Lukas, S. Vollmer, G. Witte and Ch. Wöll, *J. Phys. Chem.* 114, 10123 (2001)

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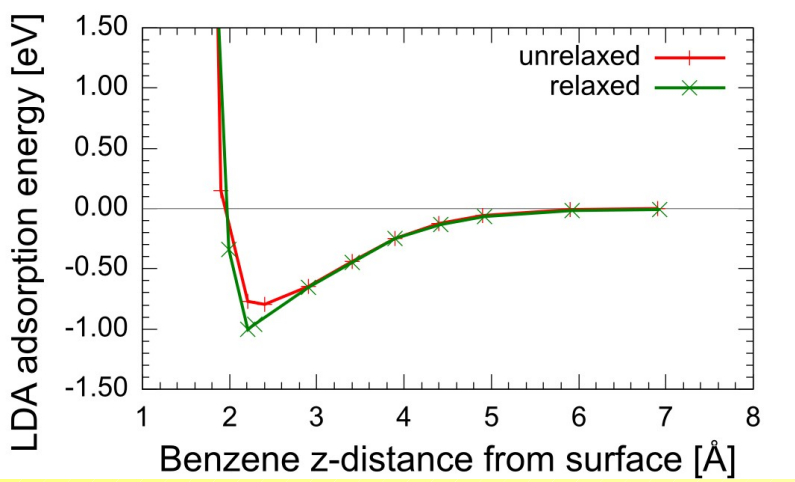
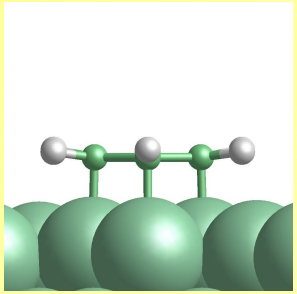
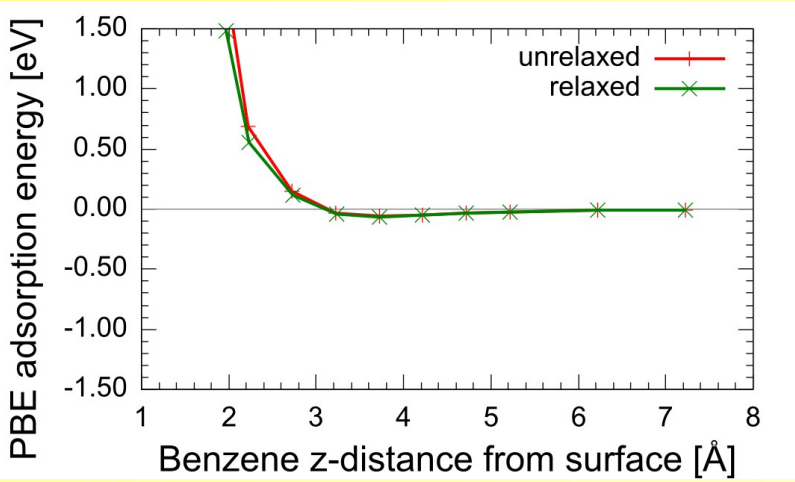
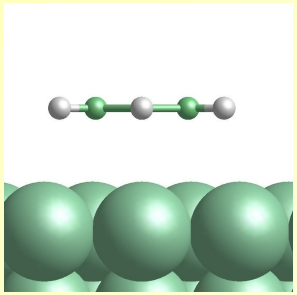




- Relaxed binding curves:
  - Supercell approach / PBC
  - Code: CASTEP[1]
  - PWs / USPPs
  - 3x3 surface cell, 4 slab layers

- LDA binding strong (> 1 eV)
- Structural relaxation significant (molecule buckles)

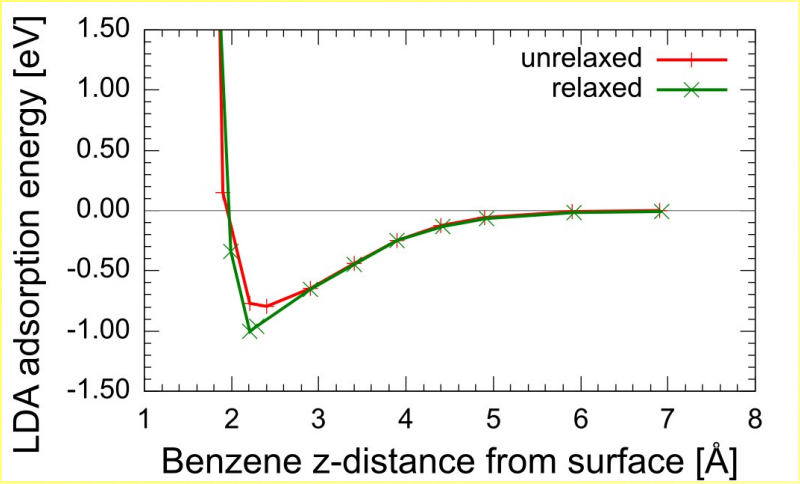


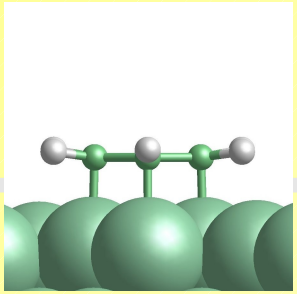


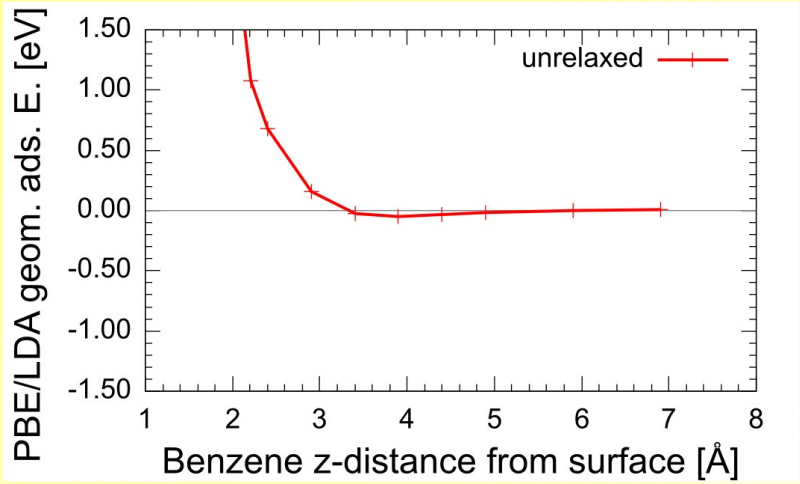
- PBE binding weak (~ 60 meV)
- Structural relaxation insignificant (molecule remains flat)

1) M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne,
***J. Phys.: Cond. Matt.* 14, 2717 (2002)**

Application II: Benzene / Cu(111)



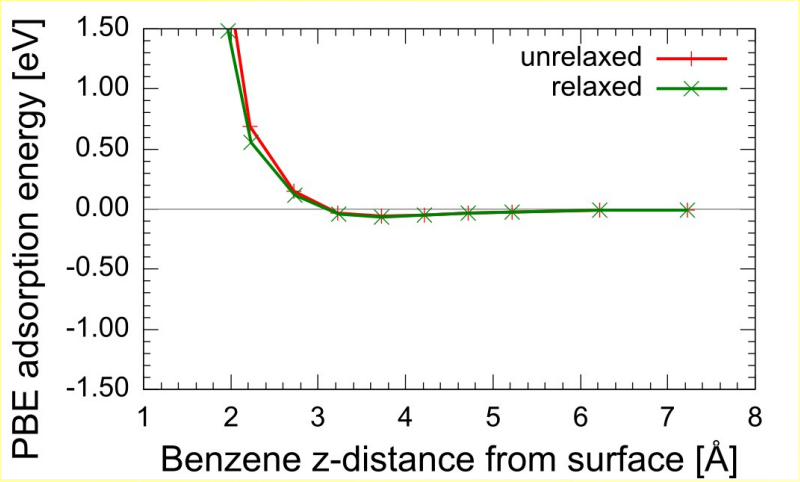


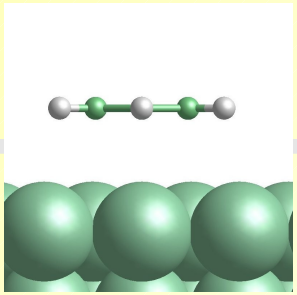


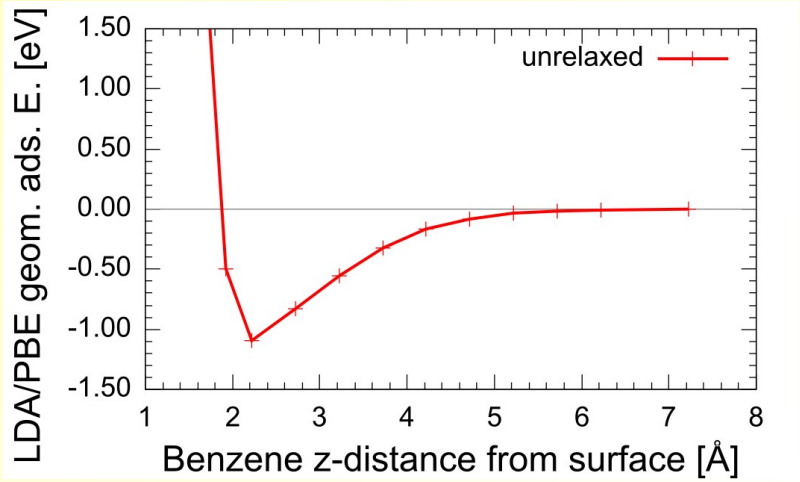
LDA

Switch functionals

PBE







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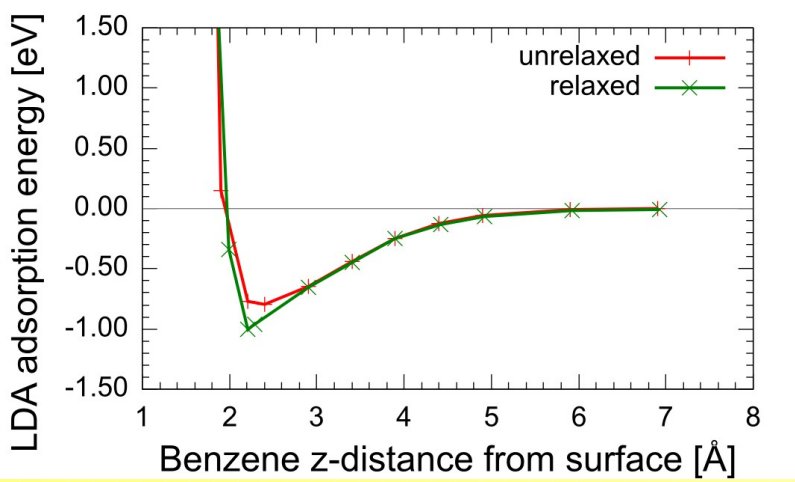
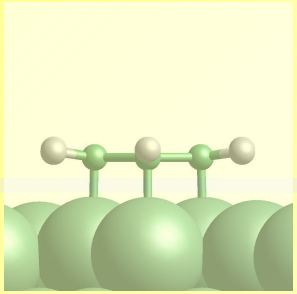
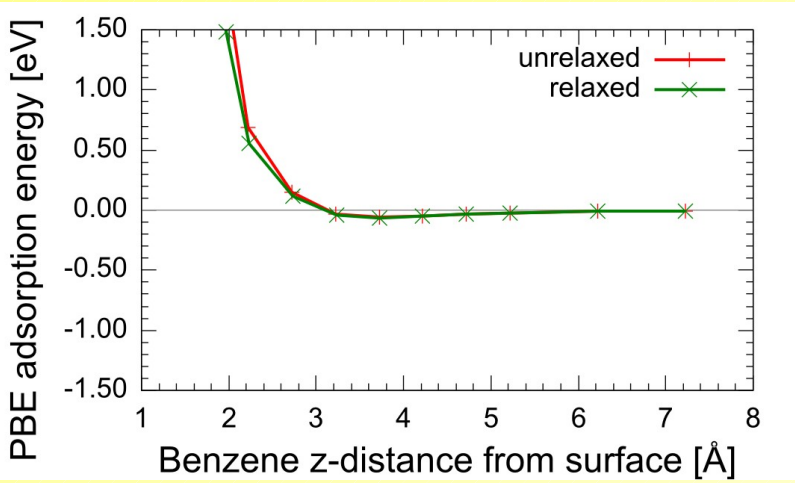
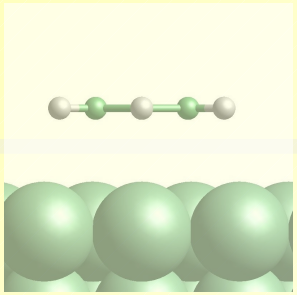
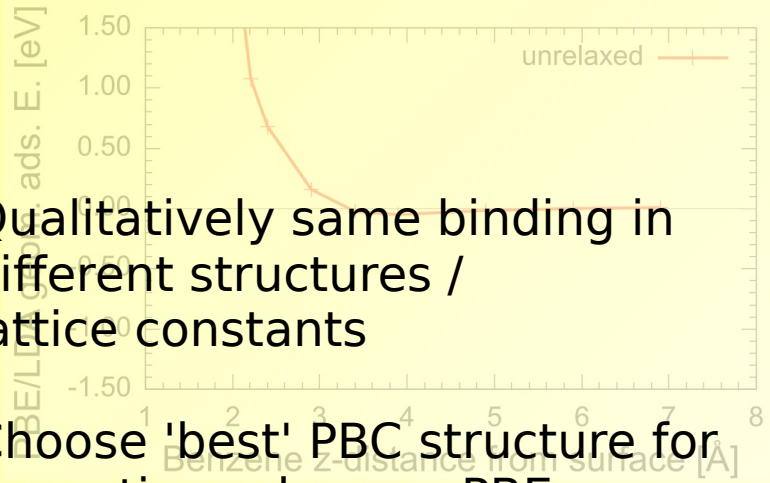


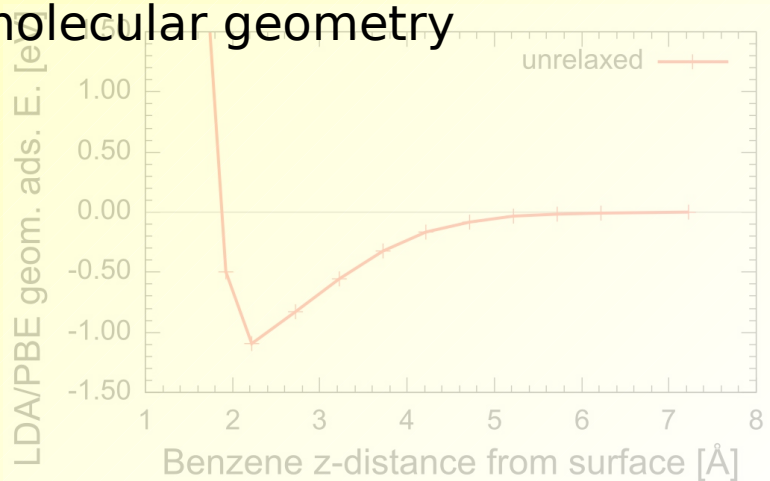






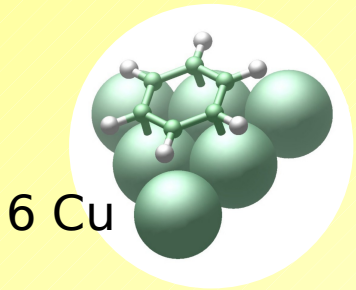
- Qualitatively same binding in different structures / lattice constants
- Choose 'best' PBC structure for correction scheme - PBE
- PBE relaxation negligible - create clusters from truncated bulk / unrelaxed molecular geometry

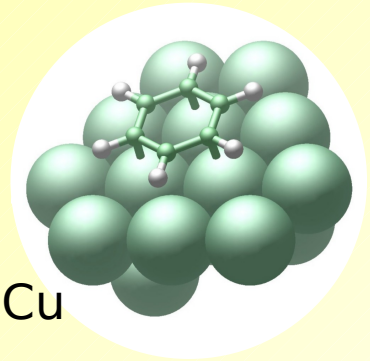


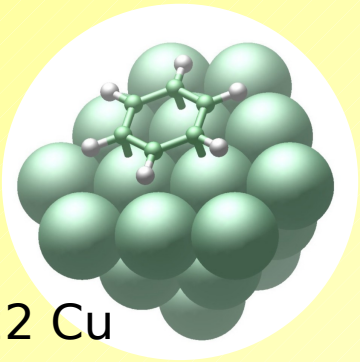


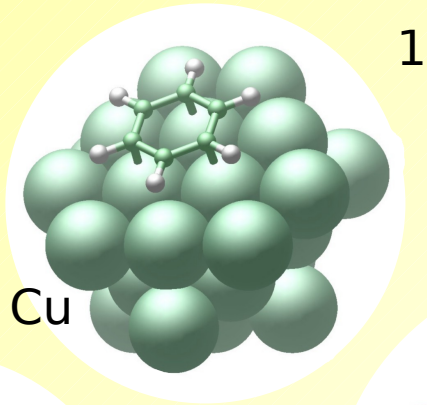
Application II: Benzene / Cu(111)

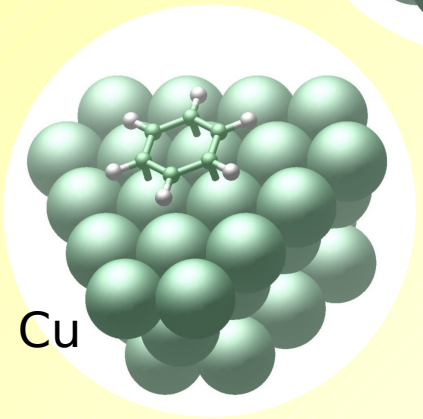
- Larger clusters (> 16 Cu) three layers thick
- Codes: Gaussian 03[(1)] / NWChem[(2)]
- All electron
- Counterpoise BSSE correction
- Closed shell

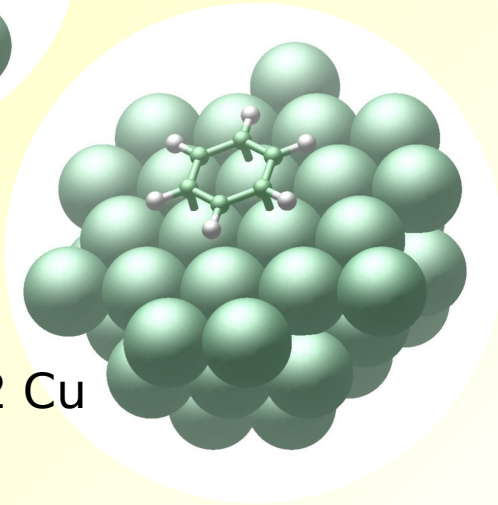








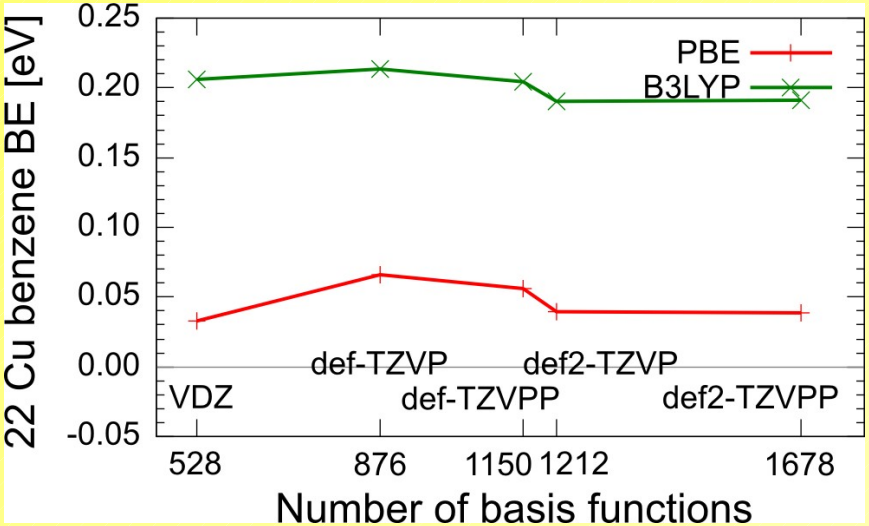




1) Gaussian 03, Revision B.05, M.J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman *et al*, Gaussian Inc., Pittsburgh PA, 2003

2) E. Apra, T.L. Windus, T.P. Straatsma, E.J. Bylaska, W. de Jong, S. Hirata *et al*, "NWChem, A Computational Chemistry Package for Parallel Computers, version 4.7" (2005), Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA

Application II: Benzene / Cu(111)



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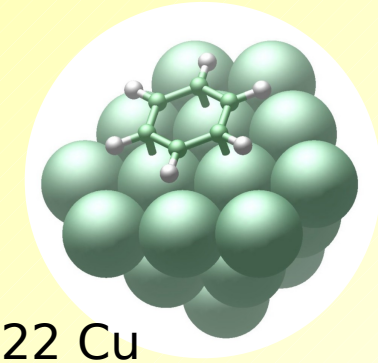
- 22 Cu cluster
- PBC/PBE optimal z-distance geometry



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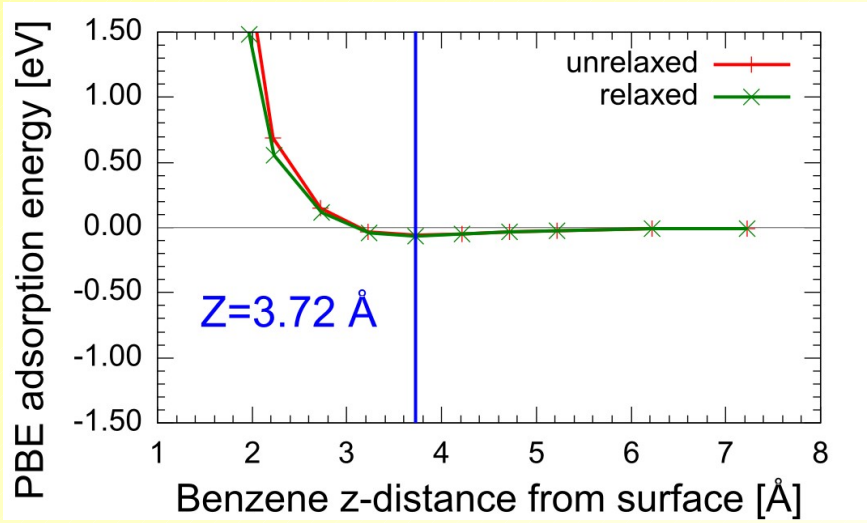

1) A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.* 97, 2571 (1992)
2) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.* 100, 5829 (1994)
3) F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.* 294, 143 (1998)
4) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 7, 3297 (2005)

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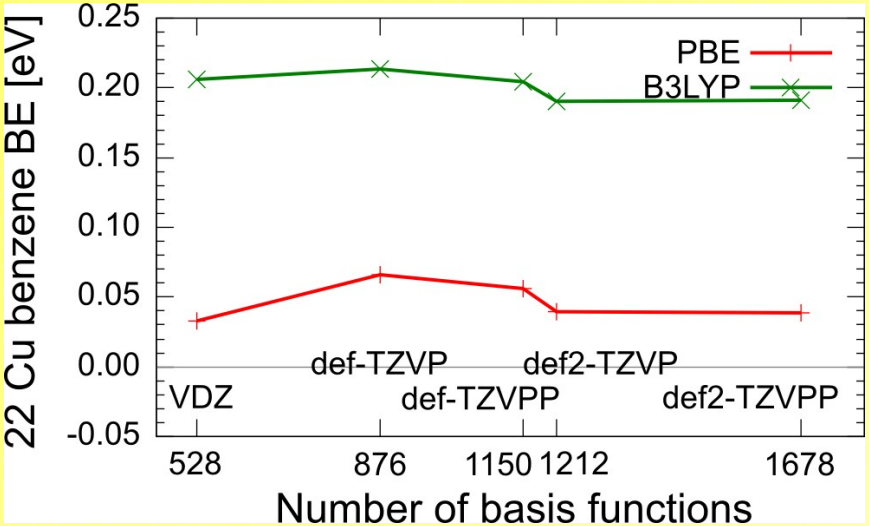

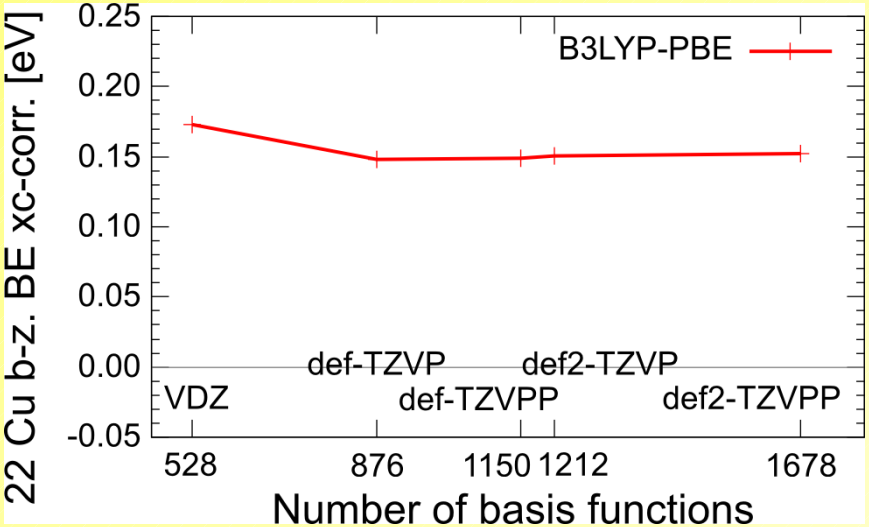

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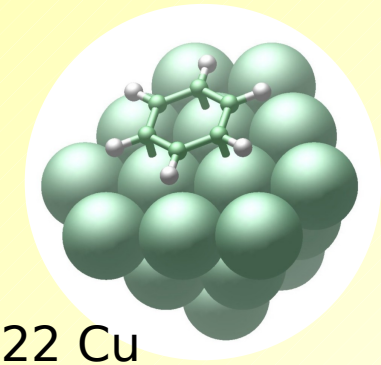
- 22 Cu cluster
- PBC/PBE optimal z-distance geometry
- DFT binding energy xc-correction converged with def-TZVP



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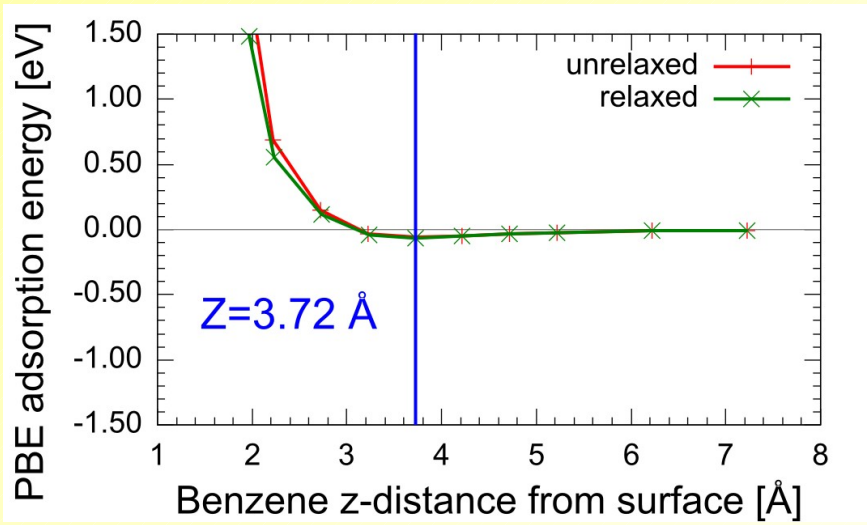

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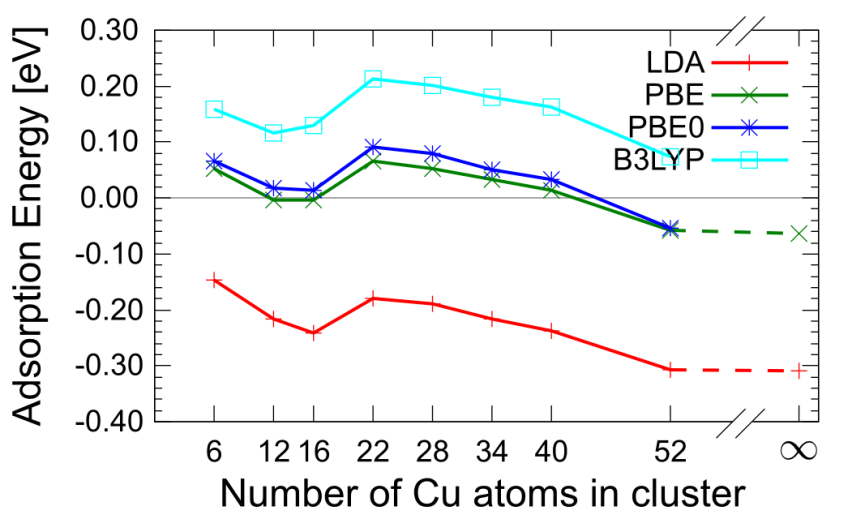
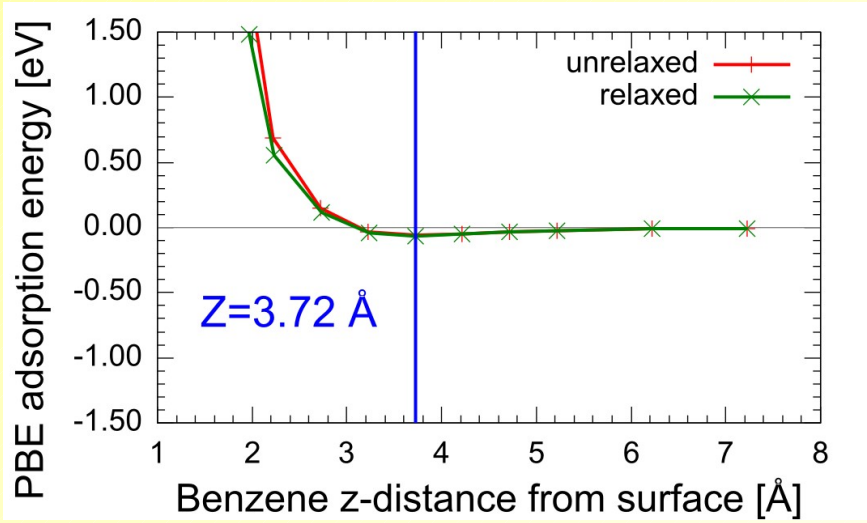
4) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 7, 3297 (2005)

Application II: Benzene / Cu(111)

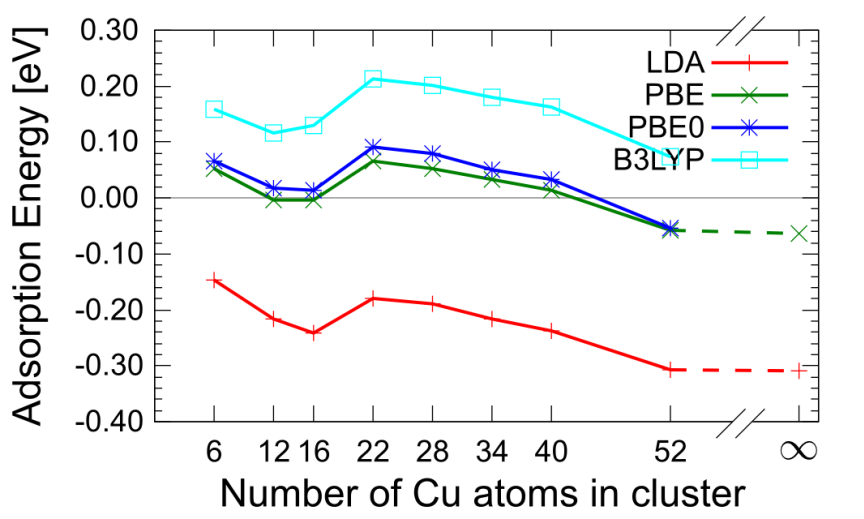


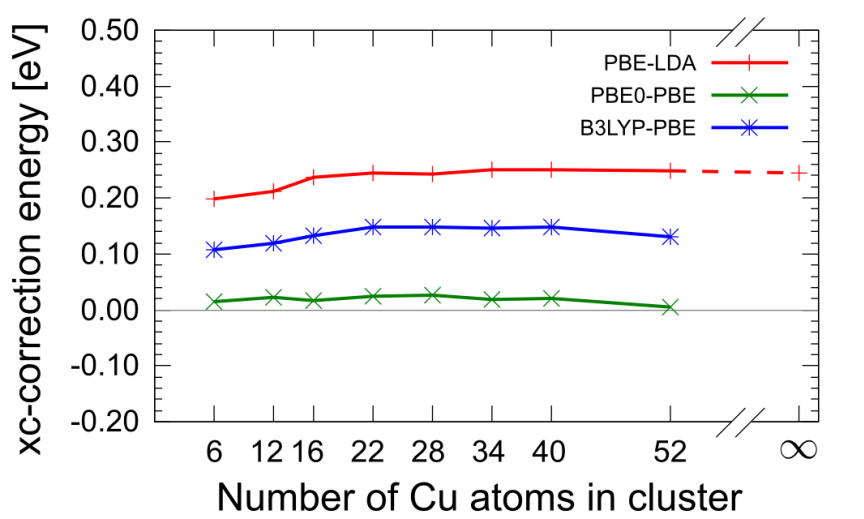
- Size convergence studied at optimal Z
- Cluster properties converge slowly:
  BE with 52 Cu (1550 electrons)
  not converged for *any* functional

- How far must we go in cluster size?



Application II: Benzene / Cu(111)

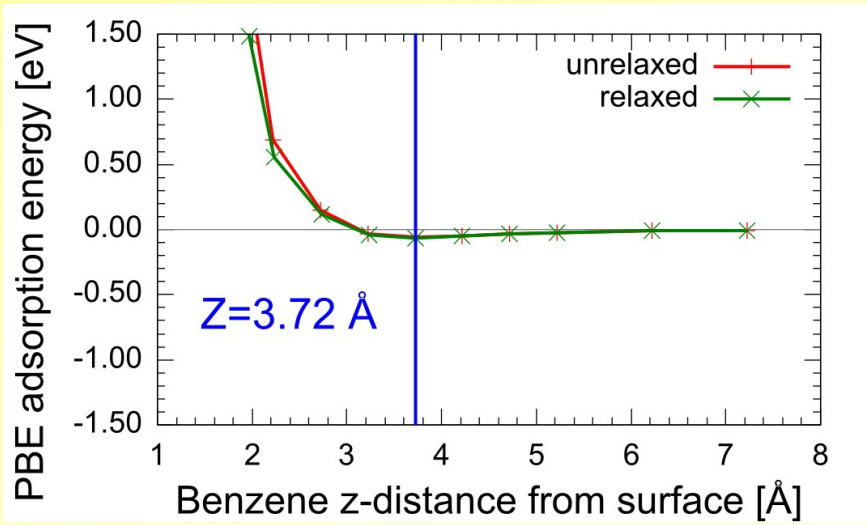




- Size convergence studied at optimal Z
- Cluster properties converge slowly:
  BE with 52 Cu (1550 electrons)
  not converged for *any* functional

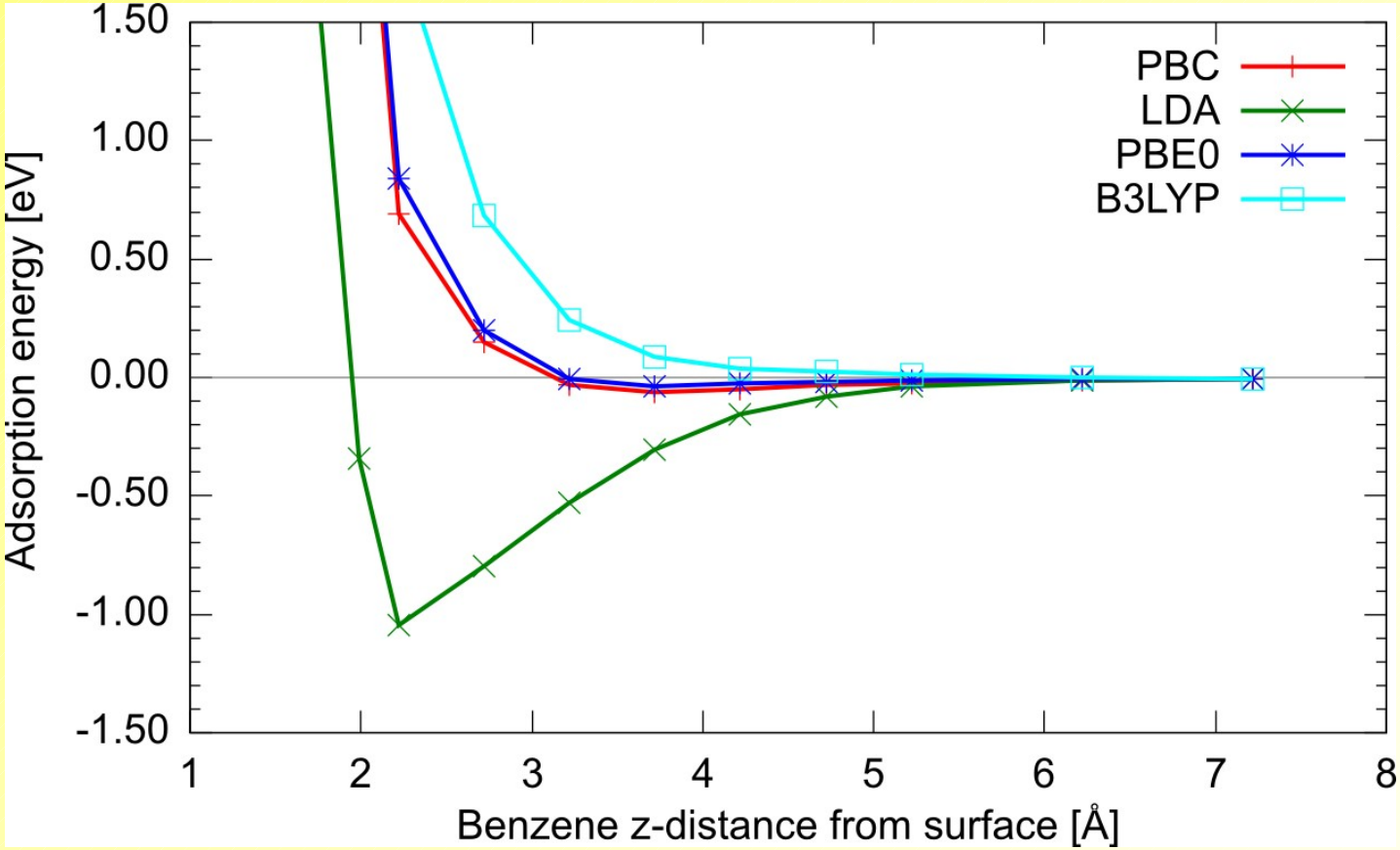
- How far must we go in cluster size?

- *xc-correction* converges much faster



Application II: Benzene / Cu(111)

Now, add converged xc-corrections to PBC/PBE binding energy curve:



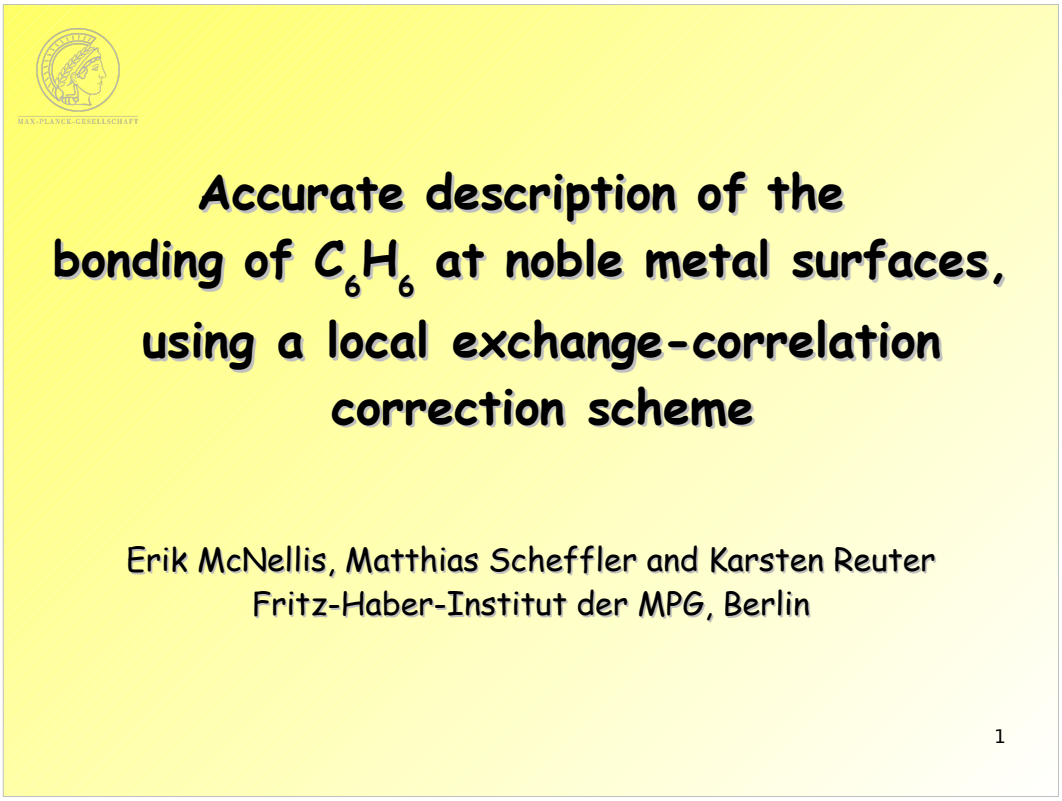
Application II: Outlook

- Finish converging RI-MP2 calculations
- Is a description of electronic correlation above MP2 level feasible?
- Pointers welcome!

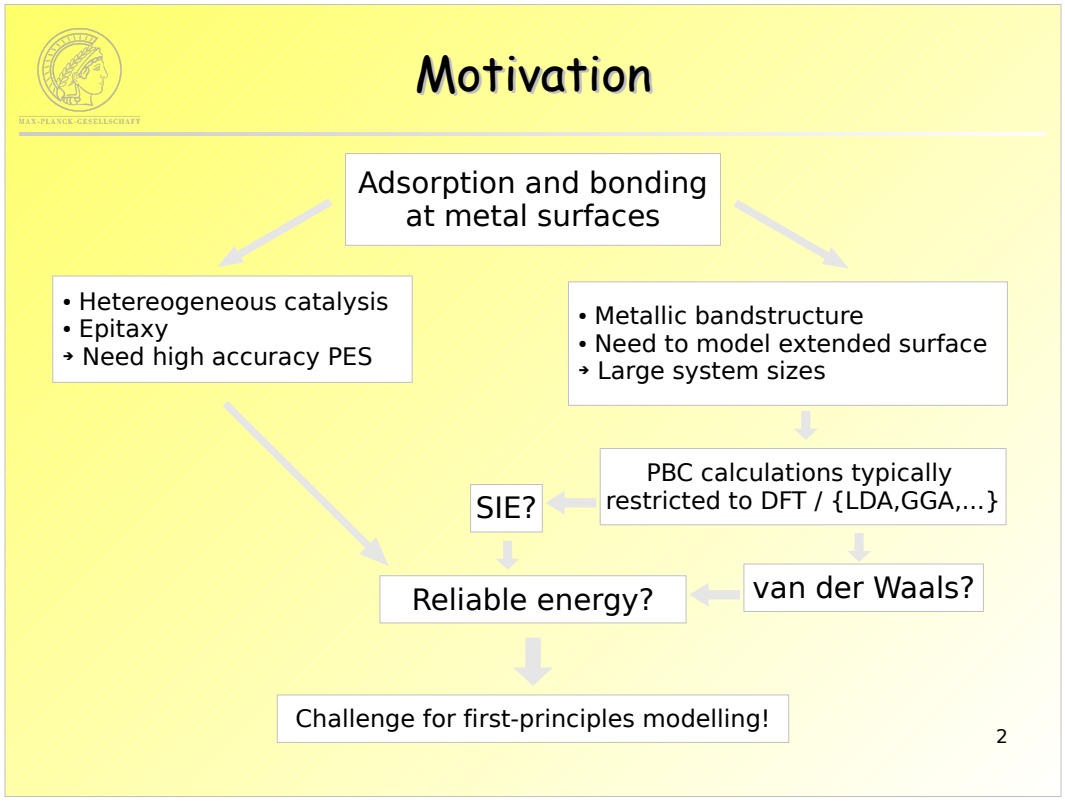
Thank you!

Funding by

gratefully acknowledged

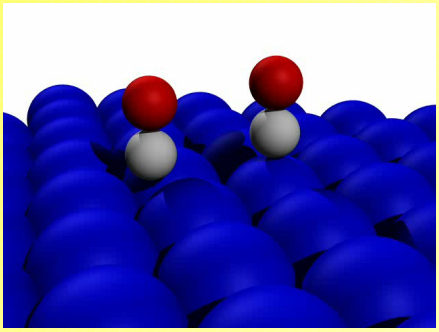

Accurate description of the
bonding of C_6H_6 at noble metal surfaces,
using a local exchange-correlation
correction scheme
Erik McNellis, Matthias Scheffler and Karsten Reuter
Fritz-Haber-Institut der MPG, Berlin
1

Intro:


Motivation
Adsorption and bonding at metal surfaces
• Hetereogeneous catalysis
• Epitaxy
➔ Need high accuracy PES
• Metallic bandstructure
• Need to model extended surface
➔ Large system sizes
PBC calculations typically restricted to DFT / {LDA,GGA,...}
SIE?
van der Waals?
Reliable energy?
Challenge for first-principles modelling!
2

- Motivation

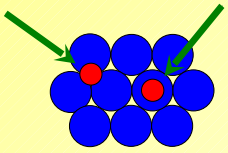
The CO adsorption puzzle



low coverage

DFT
LDA/GGA

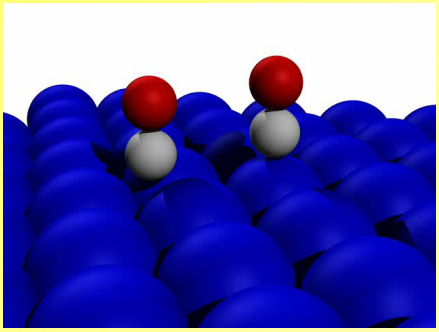
Experiment



P.J. Feibelman *et al*., J. Phys. Chem. B 105, 4018 (2001);
M. Gajdos *et al*., J. Phys.: Cond. Matter 16, 1141 (2004)

- CO ads 1

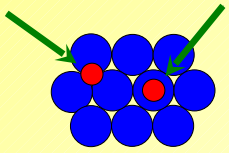
The CO adsorption puzzle

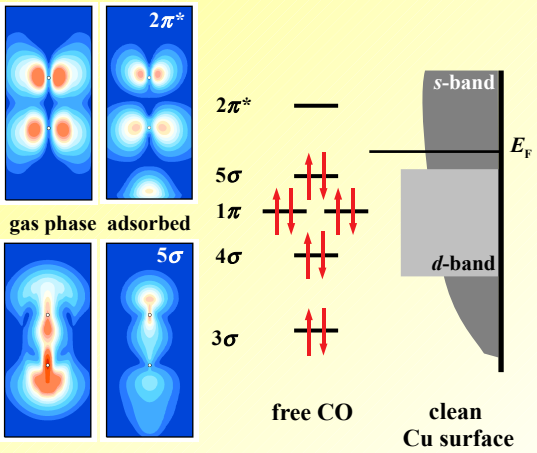


low coverage

DFT
LDA/GGA

Experiment





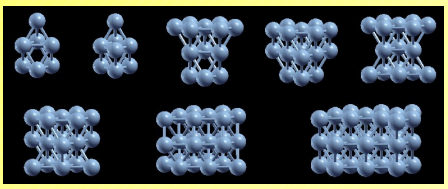
P.J. Feibelman *et al*., J. Phys. Chem. B 105, 4018 (2001);
M. Gajdos *et al*., J. Phys.: Cond. Matter 16, 1141 (2004)

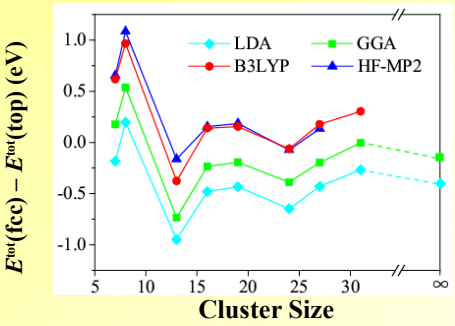
G. Kresse, A. Gil and P. Sautet,
Phys. Rev. B 68, 073401 (2004)

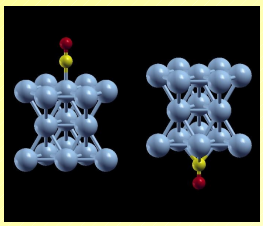
CO ads 2:

Local xc-correction scheme

Systematic cluster calculations
(Gaussian03, TZVP)



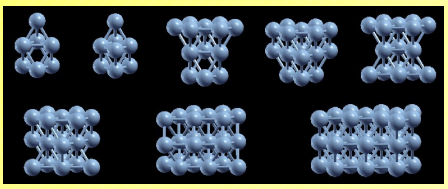




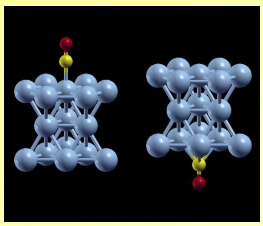
Local xc-corr:

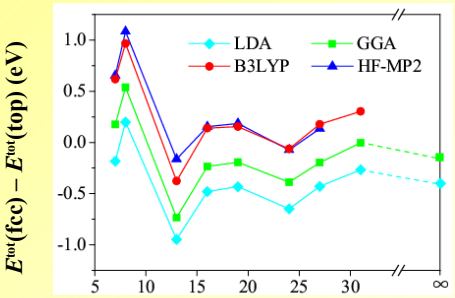
Local xc-correction scheme

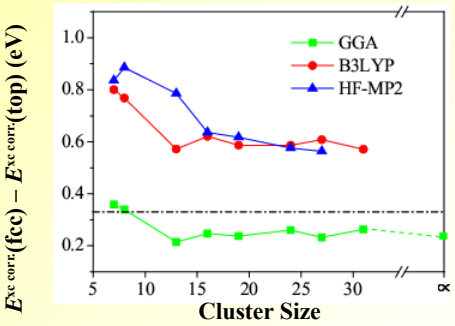
Systematic cluster calculations
(Gaussian03, TZVP)



$$E^{xc\ corr.} = \left[E^{tot}(xc) - E^{tot}(LDA) \right]$$





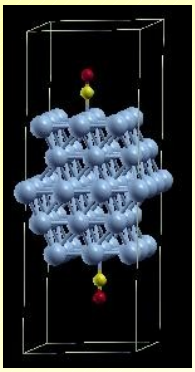


Local xc-corr 2:

Application I: CO / Cu(111)

$$(E^{fcc} - E^{top}) = (E^{fcc}_{LDA} - E^{top}_{LDA})|_{slab} + \underbrace{\left[(E^{fcc}_{xc} - E^{top}_{xc}) - (E^{fcc}_{LDA} - E^{top}_{LDA})\right]}\Big|_{cluster}$$
$$= (E^{fcc}_{LDA} - E^{top}_{LDA})|_{slab} + \Delta E^{xc-LDA}_{corr.}(\mathrm{fcc} - \mathrm{top})$$

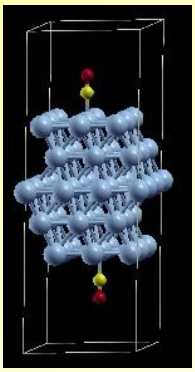
Initial slab reference energies:
FP-LAPW/APW+lo (WIEN2k),
1/9 ML in (3x3) cells



CO / Cu 111:

Application I: CO / Cu(111)

$$(E^{fcc} - E^{top}) = (E^{fcc}_{LDA} - E^{top}_{LDA})|_{slab} + \underbrace{\left[(E^{fcc}_{xc} - E^{top}_{xc}) - (E^{fcc}_{LDA} - E^{top}_{LDA})\right]}_{}\Big|_{cluster}$$
$$= (E^{fcc}_{LDA} - E^{top}_{LDA})|_{slab} + \Delta E^{xc-LDA}_{corr.}(\mathrm{fcc} - \mathrm{top})$$



Initial slab reference energies:
FP-LAPW/APW+lo (WIEN2k),
1/9 ML in (3x3) cells

X **Wrong fcc site more stable**

	LDA	GGA	B3LYP	HF-MP2
Site preference energy	**-0.33 eV**	**-0.11 eV**	**+0.27±0.02 eV**	**+0.29±0.03 eV**

Q.-M. Hu, K. Reuter and M. Scheffler,
Phys. Rev. Lett. 98, 176103 (2007)
Same concept: C. Tuma and J. Sauer, Chem. Phys. Lett. 387, 388 (2004)

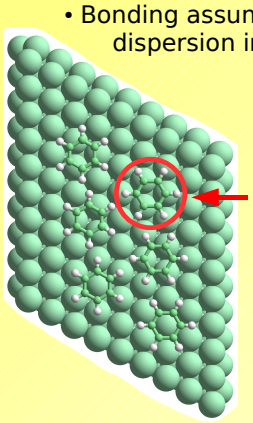
✓ **B3LYP/MP2 yield correct top site more stable**

8

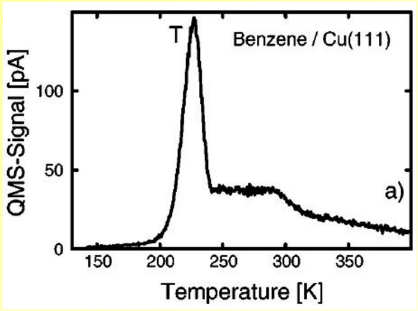
CO / Cu 111:

Application II: Benzene / Cu(111)

- Why benzene on Cu?
- Model system for range of organic molecules adsorbed at coinage metals
- Experiments show definite binding[1]
- Bonding assumed van der Waals / dispersion interaction dominated



- Three-fold hollow geometry chosen for testing and method convergence

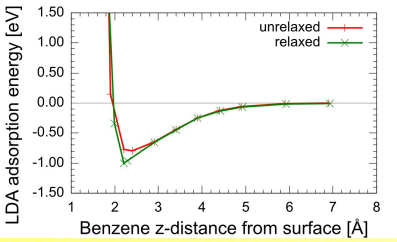


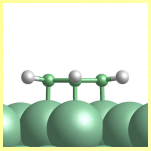
TPD[1]

1) S. Lukas, S. Vollmer, G. Witte and Ch. Wöll, *J. Phys. Chem.* 114, 10123 (2001)

Benzene @ Cu 111

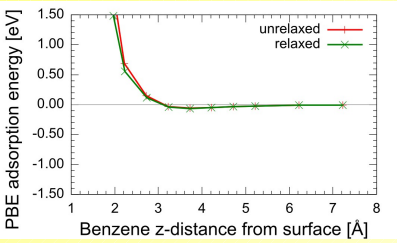
Application II: Benzene / Cu(111)

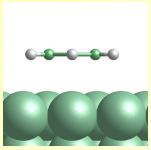




- Relaxed binding curves:
  - Supercell approach / PBC
  - Code: CASTEP[1]
  - PWs / USPPs
  - 3x3 surface cell, 4 slab layers

- LDA binding strong (> 1 eV)
- Structural relaxation significant (molecule buckles)

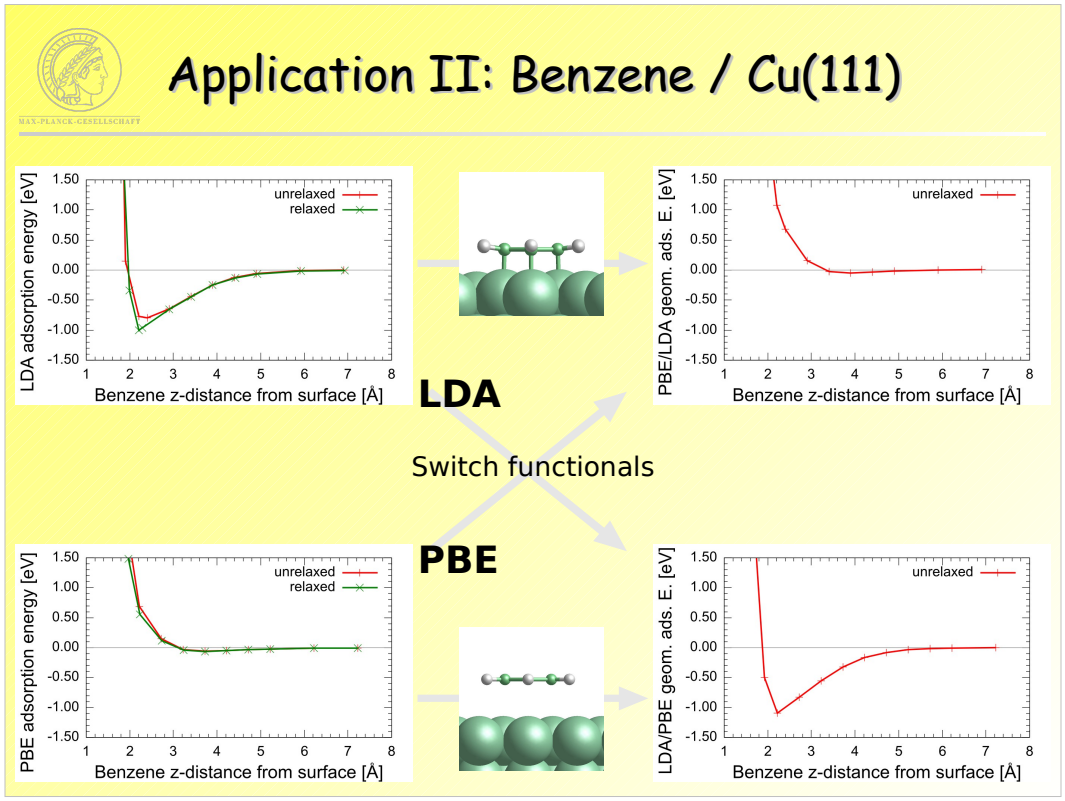




- PBE binding weak (~ 60 meV)
- Structural relaxation insignificant (molecule remains flat)

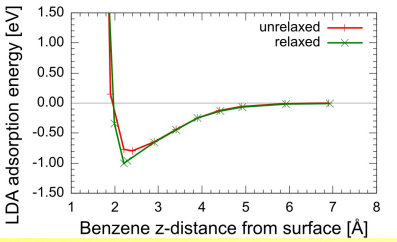
1) M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne,
***J. Phys.: Cond. Matt.* 14, 2717 (2002)**

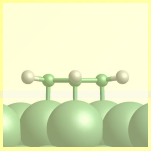
Benzene @ Cu 111

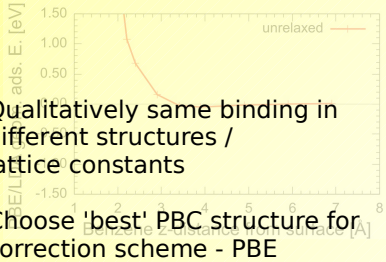


Benzene @ Cu 111

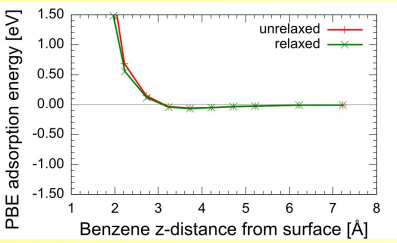
Application II: Benzene / Cu(111)

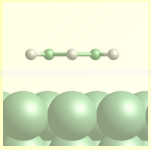


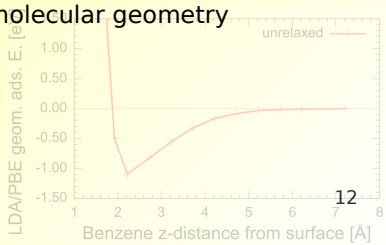




- Qualitatively same binding in different structures / lattice constants
- Choose 'best' PBC structure for correction scheme - PBE
- PBE relaxation negligible - create clusters from truncated bulk / unrelaxed molecular geometry



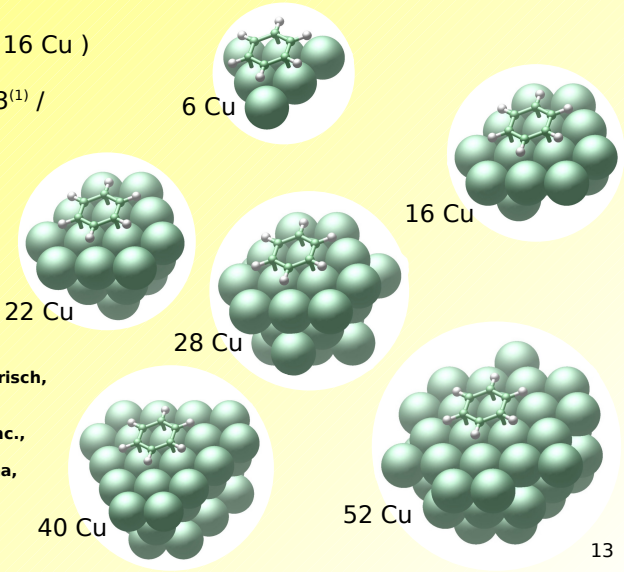




Benzene @ Cu 111

Application II: Benzene / Cu(111)

- Larger clusters (> 16 Cu) three layers thick
- Codes: Gaussian 03[1] / NWChem[2]
- All electron
- Counterpoise BSSE correction
- Closed shell

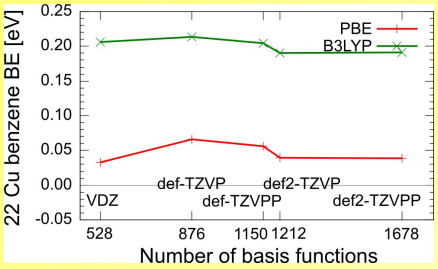


1) Gaussian 03, Revision B.05, M.J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman *et al*, Gaussian Inc., Pittsburgh PA, 2003

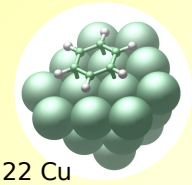
2) E. Apra, T.L. Windus, T.P. Straatsma, E.J. Bylaska, W. de Jong, S. Hirata *et al*, "NWChem, A Computational Chemistry Package for Parallel Computers, version 4.7" (2005), Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA

Benzene @ Cu 111

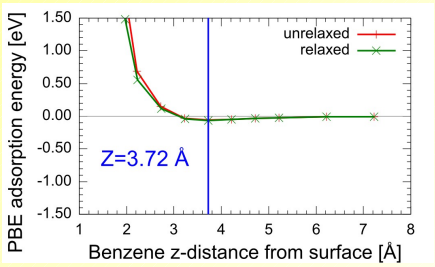
Application II: Benzene / Cu(111)



- Ahlrichs VDZ(1), def{2}-TZVP{P}(2-4) basis set convergence studied
- 22 Cu cluster
- PBC/PBE optimal z-distance geometry



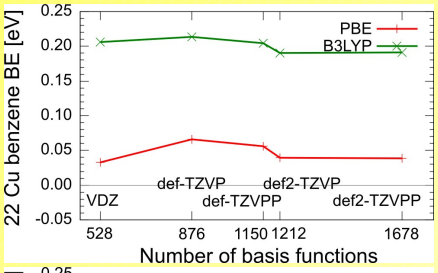
22 Cu

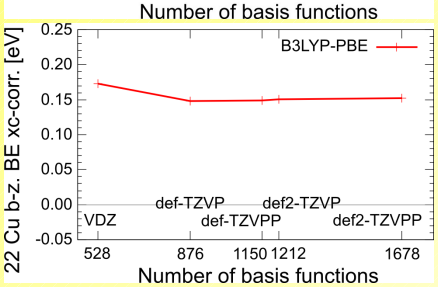


1) A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.* 97, 2571 (1992)
2) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.* 100, 5829 (1994)
3) F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.* 294, 143 (1998)
4) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 7, 3297 (2005)

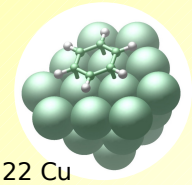
Benzene @ Cu 111

Application II: Benzene / Cu(111)

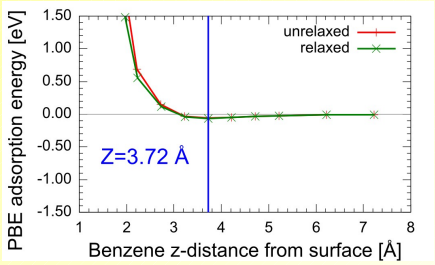




- Ahlrichs VDZ[1], def{2}-TZVP{P}[2-4] basis set convergence studied
- 22 Cu cluster
- PBC/PBE optimal z-distance geometry
- DFT binding energy xc-correction converged with def-TZVP



22 Cu



1) A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.* 97, 2571 (1992)
2) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.* 100, 5829 (1994)
3) F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.* 294, 143 (1998)
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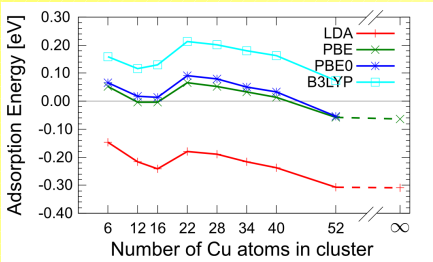
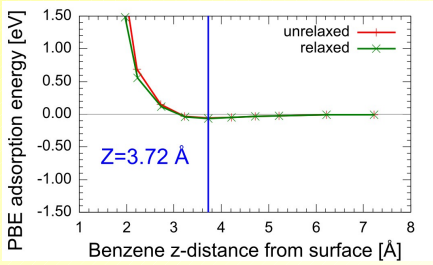
Benzene @ Cu 111

Application II: Benzene / Cu(111)



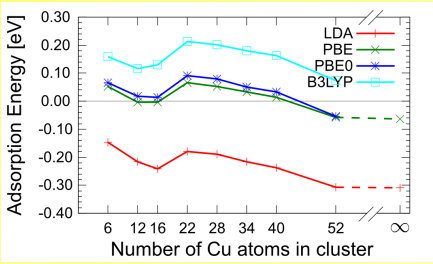
- Size convergence studied at optimal Z
- Cluster properties converge slowly:
  BE with 52 Cu (1550 electrons)
  not converged for *any* functional

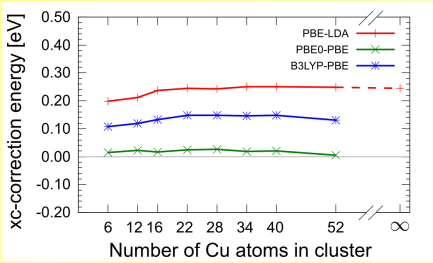
- How far must we go in cluster size?



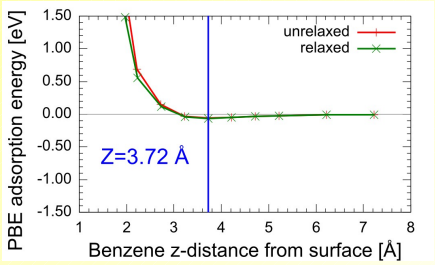
Benzene @ Cu 111

Application II: Benzene / Cu(111)





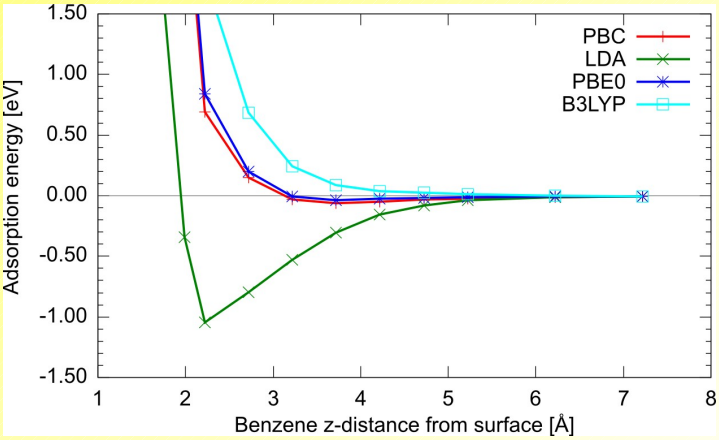
- Size convergence studied at optimal Z
- Cluster properties converge slowly:
  BE with 52 Cu (1550 electrons)
  not converged for *any* functional
- How far must we go in cluster size?
- *xc-correction* converges much faster



Benzene @ Cu 111

Application II: Benzene / Cu(111)

Now, add converged xc-corrections to PBC/PBE binding energy curve:



Benzene @ Cu 111

Application II: Outlook

- Finish converging RI-MP2 calculations
- Is a description of electronic correlation above MP2 level feasible?
- Pointers welcome!

Thank you!

Funding by

IMPRS Complex Surfaces in Materials Science

gratefully acknowledged

Benzene @ Cu 111