Prerequisites for reliable modeling with first-principles methods

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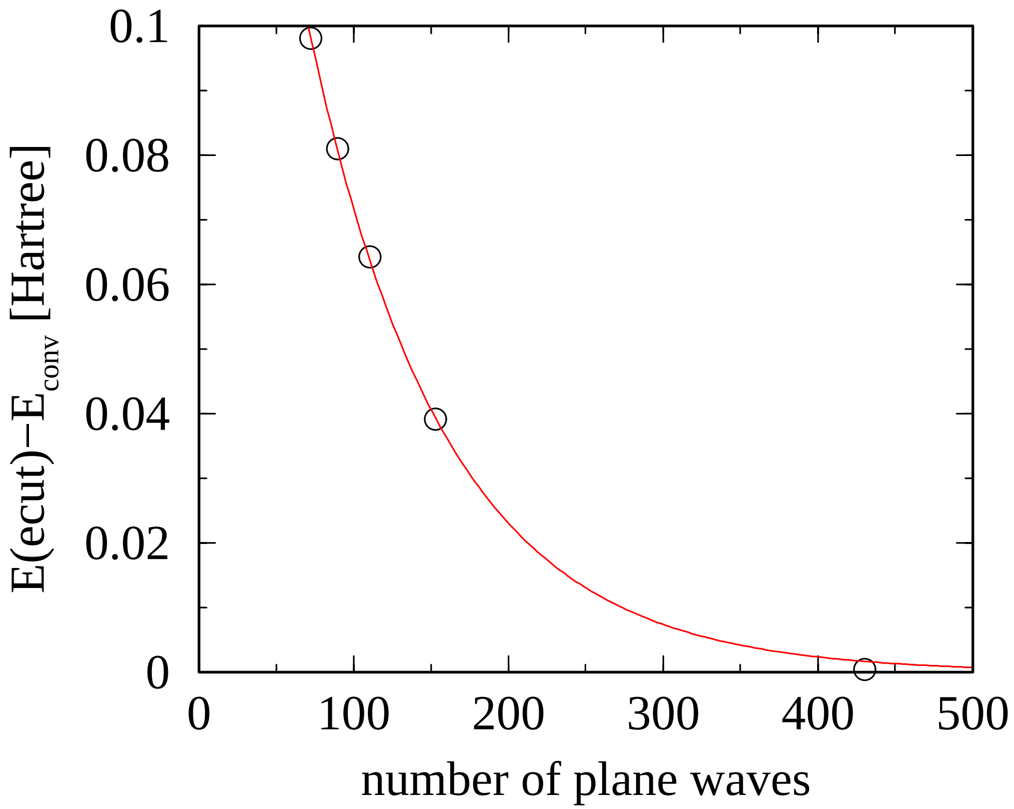
Prerequisites for modeling

Issues to consider when applying the plane wave/supercell method

- How appropriate is the model for your physical system ?
  e.g. cluster versus slab model for surfaces
- Is your model system big enough to avoid spurious interactions ?
  e.g. slab thickness, size of the unit cell
- Are there long-range (electrostatic or elastic) interactions?
  e.g. charge defects
- Is the k-point sampling appropriate to describe the dispersion of the bands and the Fermi surface ?
- Is the calculation converged with respect to technical parameters, like cut-off, T_{el}, … ?

Absolute *versus* relative convergence

Example 1:
absolute convergence
for GaAs, LDA, Hamann
pseudopot.,
data points at
E_{cut} = 7, 8, 10, 20 Ry



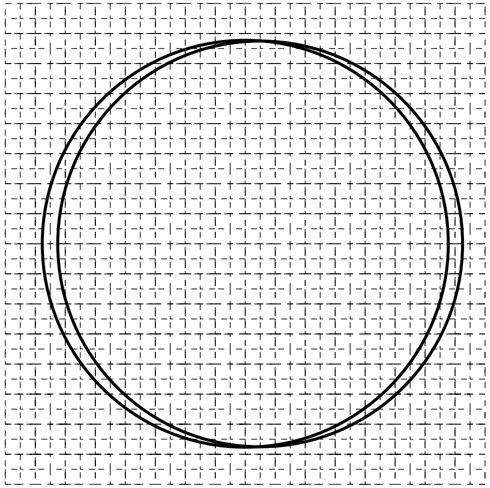
empirical dependence on the
number of plane waves:
$E(N) - E_{conv} \approx a_1 \exp(-a_2 N)$

The *G+k* plane-wave basis set

spheres with radius $(E_{cut})^{1/2}$ with origin in $\vec{k}$: $N_{ideal} = (V/6\pi^{2}) (E_{cut})^{3/2} = 84.941$

$E_{cut} = 7$ Ry

$V = 271.6$ bohr^3

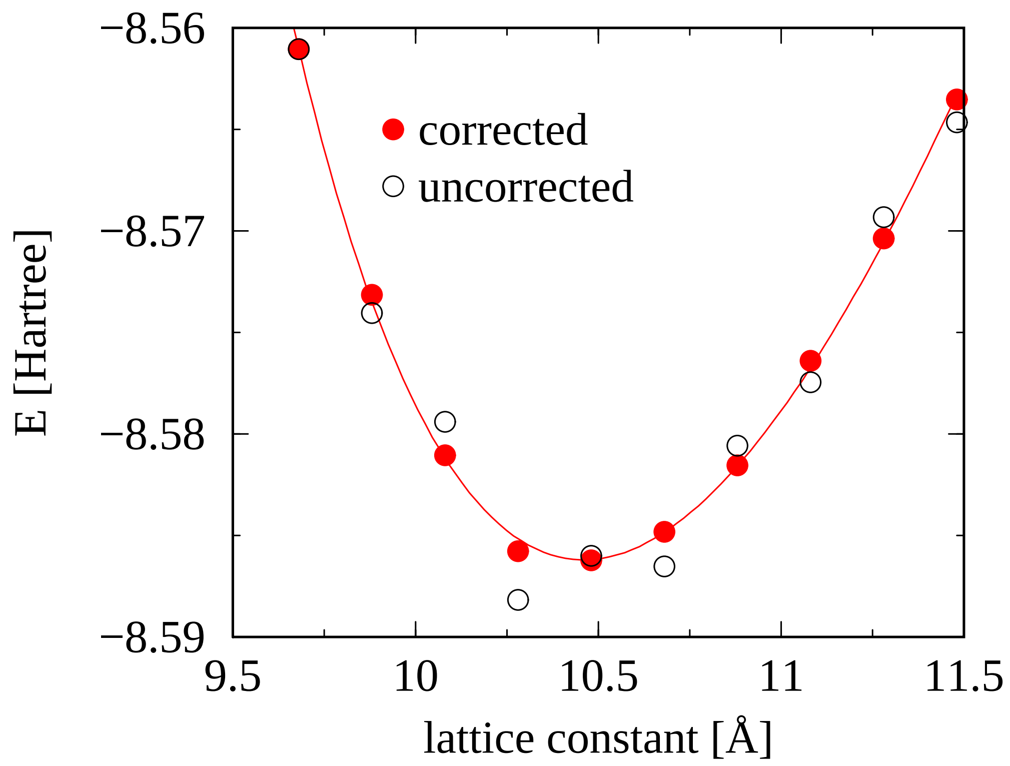


2x2x2	weight	plane waves
1	0.25	83
2	0.75	89
weighted average		87.461

4x4x4	weight	plane waves
1	0.03125	77
2	0.09375	84
3	0.09375	83
4	0.09375	81
5	0.03125	83
6	0.09375	82
7	0.09375	87
8	0.09375	87
9	0.18750	86
10	0.18750	89
weighted average		85.01

Correction for the discreteness of the basis set

The calculated curve must show discontinuities because the N_{av} values are scattered around N_{ideal}.
Correcting for this effect gives much better agreement with the equation-of-state curve.



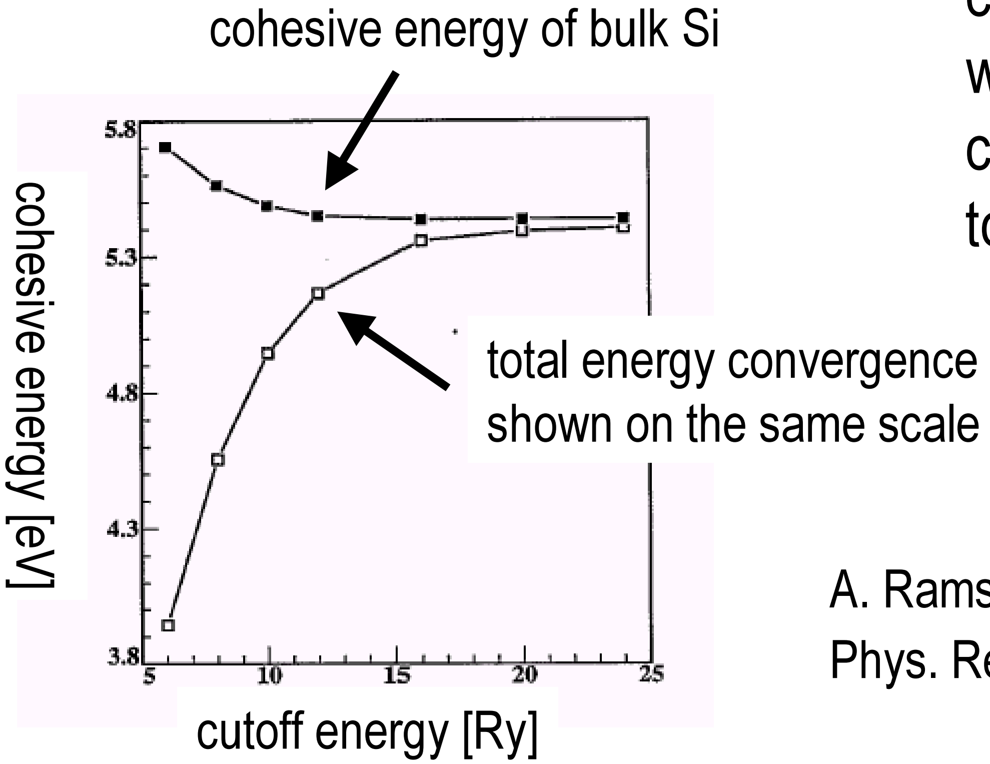
Rignanese *et al.*, Phys. Rev. B **52**, 8160 (1995);
Francis and Payne, J. Phys. Cond. Mat., **17**, 1643 (1990)

$$\Delta E = N_{ideal} \ln(N_{av}/N_{ideal}) \left(\partial E_{tot}(N)/\partial N\right)\Big|_{N_{ideal}}$$
$$\approx N_{ideal} \ln(N_{av}/N_{ideal})\, a_1\ \ a_2 \exp(-a_2 N_{ideal})$$

Example: GaAs bulk,
7 Ry cut-off, 2 x 2 x 2 k-points

Relative *versus* absolute convergence

Example: Si

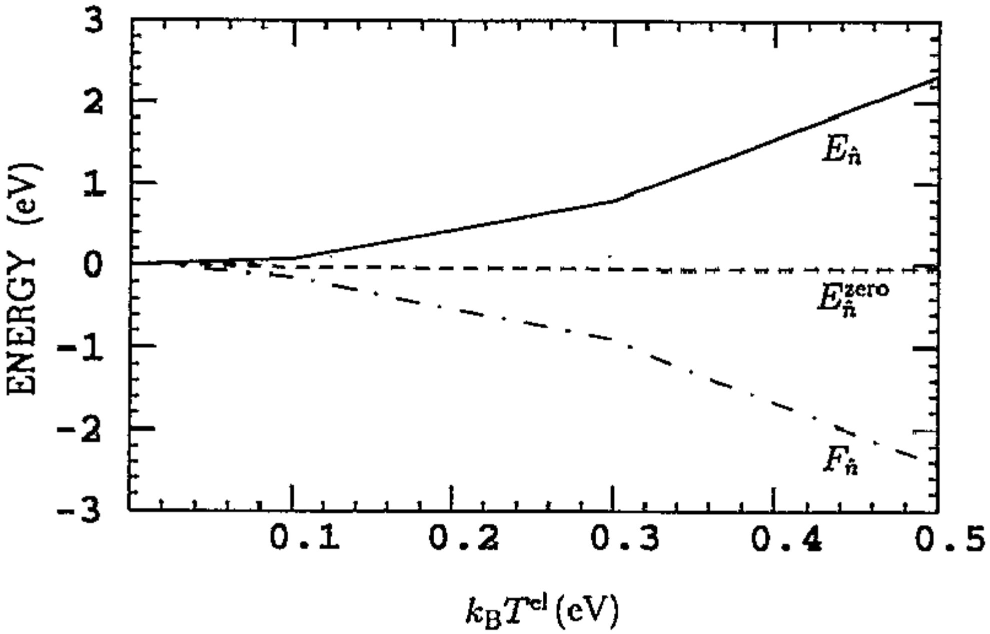


relative energies converge much faster with the plane wave cutoff than the absolute total energy !

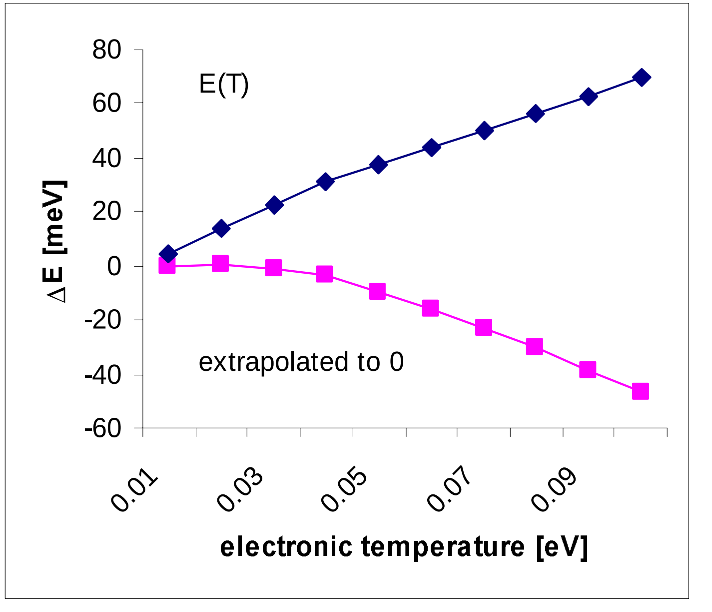
A. Ramstad, G. Brocks, and P. J. Kelly, Phys. Rev. B **51**, 14504 (1995).

Correction for finite T^{el}

$$E^{zero} = \tfrac{1}{2}\,(F(T)+E(T)) + \mathcal{O}(T^3) = F(T) - \tfrac{1}{2}\;T^{el}\,S^{el}(T) + \mathcal{O}(T^3)$$



substitutional adsorption of Na on Al(111)
J. Neugebauer and M. Scheffler,
Phys. Rev. B **46**, 16067 (1992)



Indium adatom on GaAs(001)
c(4x4) surface
E. Penev, unpublished

k-points convergence for metals: Pd

For a good description of a metal, in particular the bulk modulus, it may be necessary to sample the Fermi surface in great detail !

Netscape Hypertext Document

http://www.phy.tu-dresden.de/~fermisur/

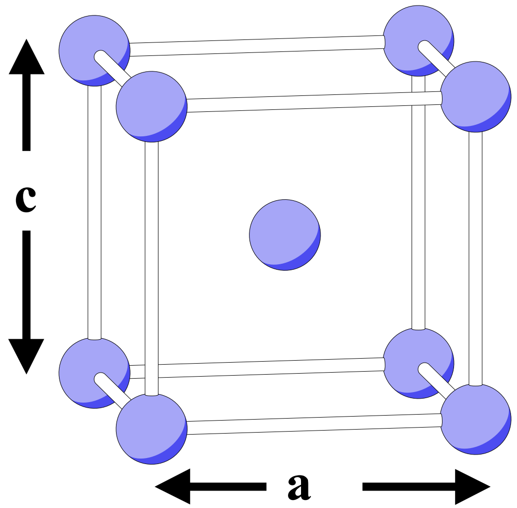
k-point set	6x6x6	10x10x10	14x14x14
lattice constant [Å]	3.83	3.85	3.85
bulk modulus [Mbar]	2.32	2.26	2.23
B'	5.66	5.63	5.62
cohesive energy [eV]	5.09	5.08	5.06

LDA, LAPW calculation, r_{MT}=2.4, ecut=14 Ry, l_{max}=10

Juarez da Silva, unpublished

Convergence with k-points: In bulk

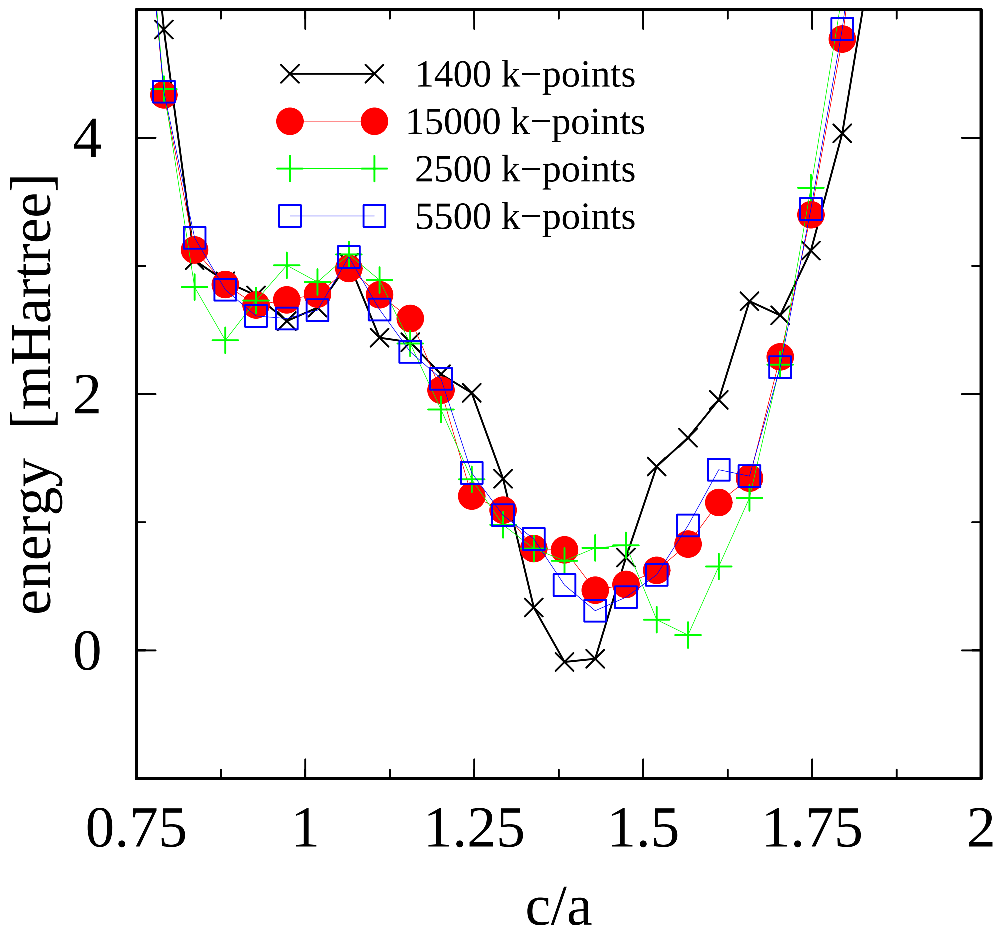
Centered tetragonal, a=3.252 Å



LDA, LAPW calculation

r_{MT}=2.7, ecut=13.7 Ry, l_{max}=9

Juarez da Silva, unpublished



Topic: Surface Chemistry

- How well are (small) molecules described in DFT?

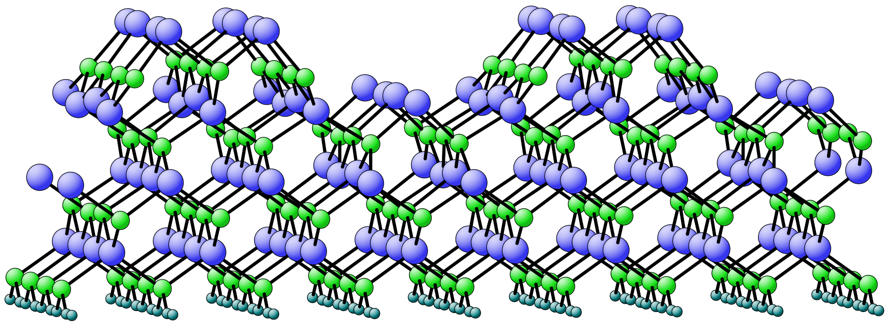
  dissociation energies in eV

	HF	LSD	GGA(PBE)	meta-GGA[1]	exp.
H_2	3.56	4.91	4.53	4.96	4.75
H_20	6.27	11.56	10.16	9.98	10.07
HF	3.80	7.04	6.16	6.01	6.10
CO	7.43	12.96	11.65	11.10	11.24
N_2	4.70	11.60	10.55	9.94	9.91
F_2	<0	3.39	2.32	1.87	1.67
O_2	1.36	7.58	6.23	5.70	5.22

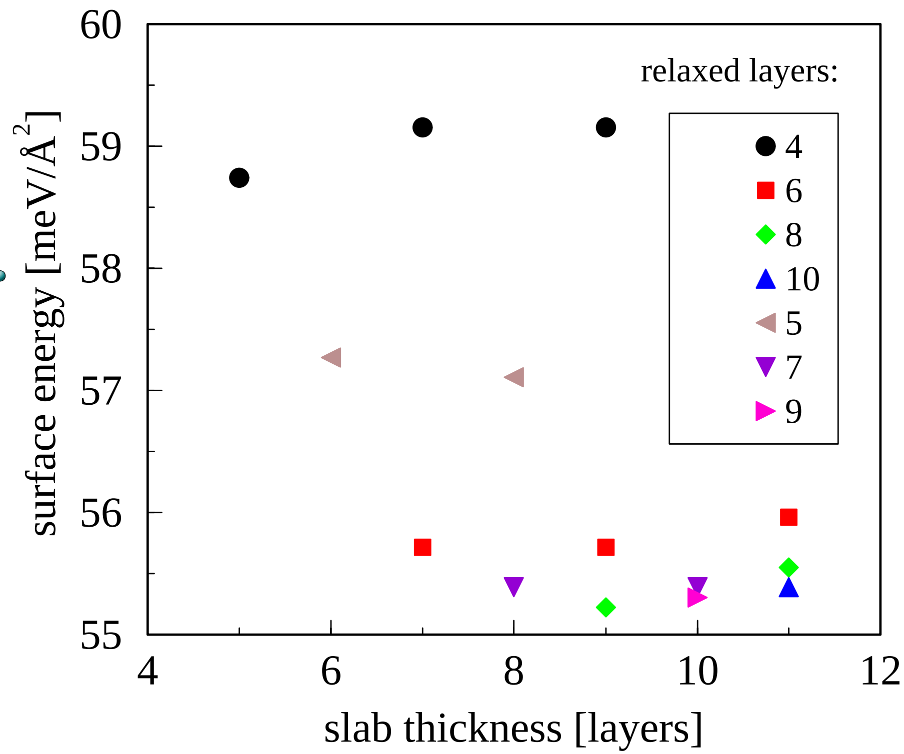
[1] J.Perdew et al, Phys. Rev. Lett. **82** (1999) 2544

- How well do we describe the surface structure?
- Can we identify reaction mechanisms and locate transition states for simple surface reactions (e.g. dissociation of a diatomic molecule) ?

Surface relaxation: GaAs(001)(2x4)



P. Kratzer, unpublished



LDA, 10 Ry plane-wave cut-off,
2x4 k points in BZ

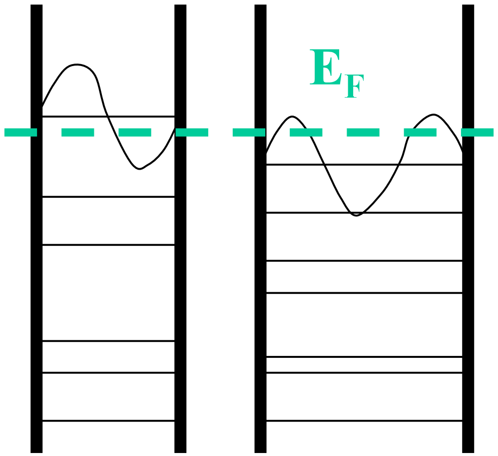
Slabs with n layers

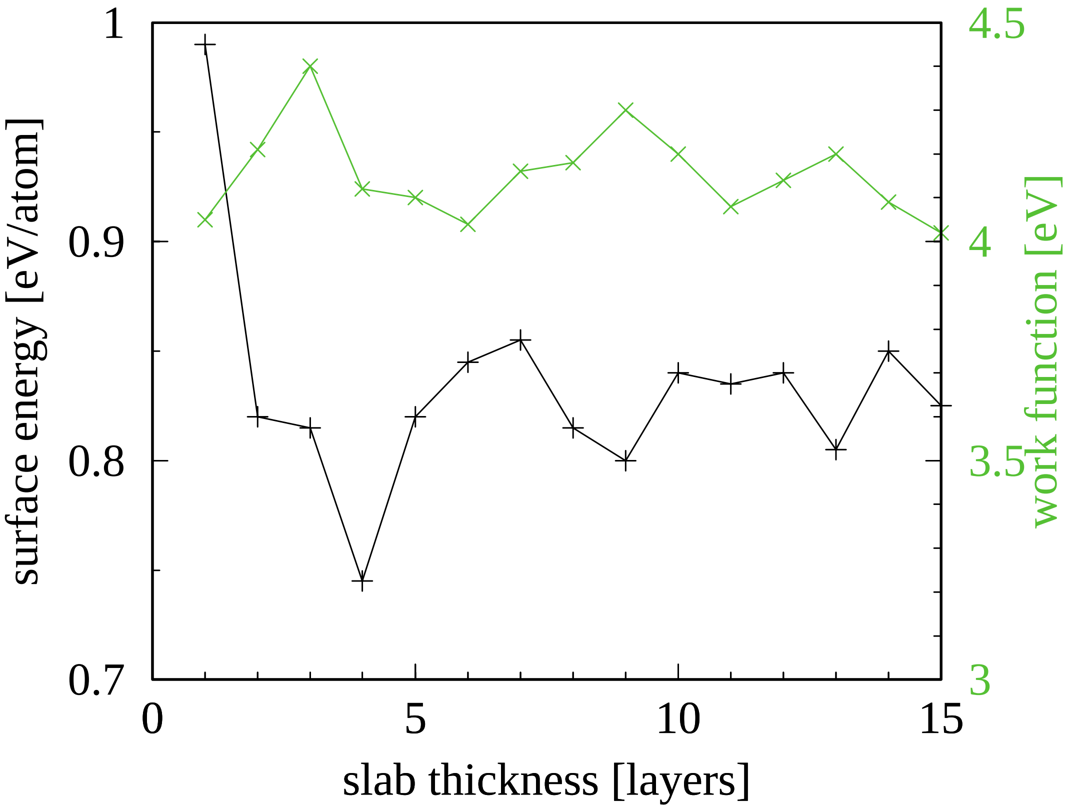
$E_{bulk}(n) := [E_{sl}(n) - E_{sl}(n-2)]/N_{at}$

surface energy

$\gamma(n)A := E_{sl}(n) - (N_{As}+N_{Ga})\ E_{bulk}(n) - (N_{As}-N_{Ga})\mu_{As}$

Quantum size effects: Al(110)



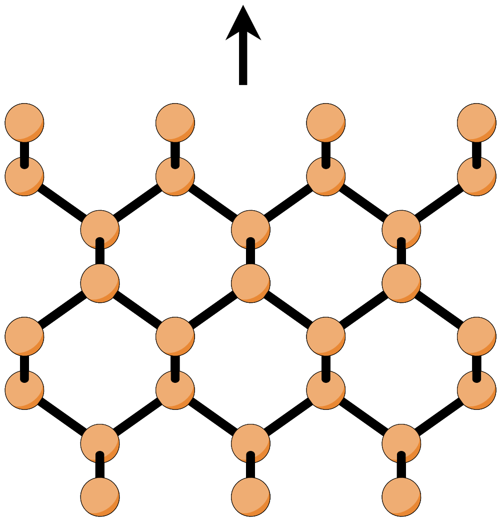


LDA, 20Ry plane wave cut-off, 16 k-points in IBZ

A. Kiejna, J. Peisert and P. Scharoch, Surf. Sci. **432** (1999) 54

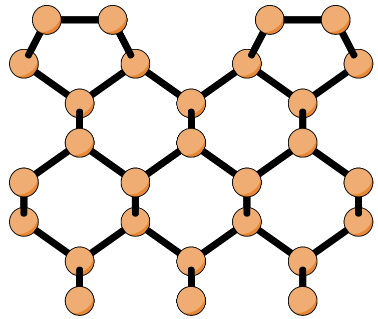
Surface reconstruction of Si(001): (2x1)

[001]



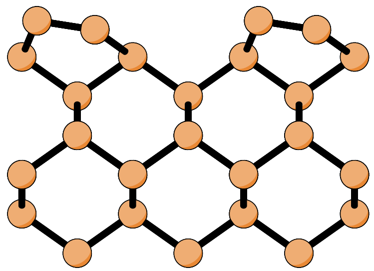
side view

reconstruction by surface dimerization



symmetric dimers

?

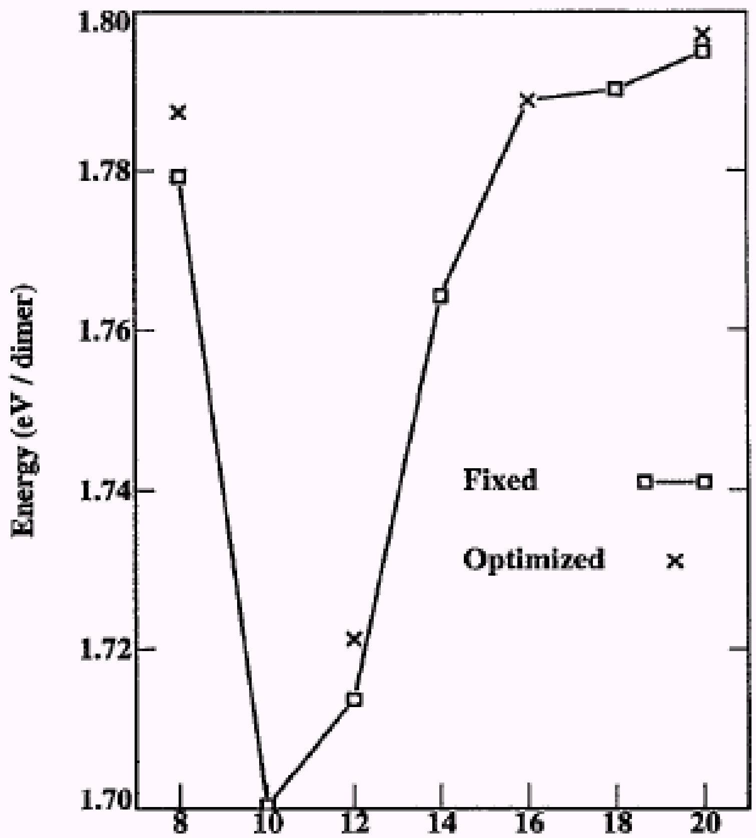


buckled dimers

Jahn-Teller like effect may lift the overlap of surface states.
See: J. Dabrowski and M. Scheffler, Appl. Surf. Sci. **56-58,** 15 (1992)

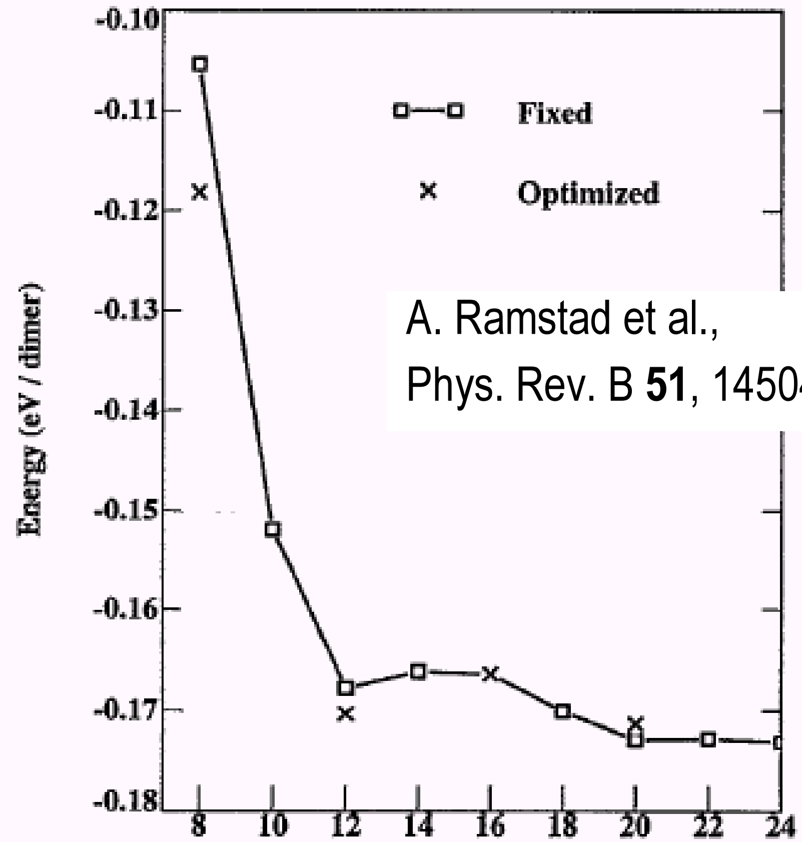
Surface reconstruction: Si(001)

dimerization energy



cutoff energy [Ry]

energy gain from buckling



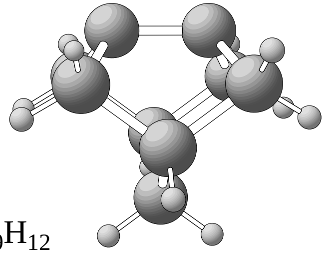
cutoff energy [Ry]

A. Ramstad et al.,
Phys. Rev. B **51**, 14504 (1995).

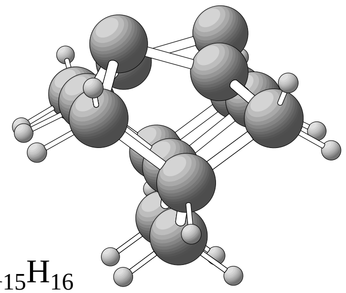
Cluster models for the Si(001) surface

Is it possible to describe the buckling of the surface Si dimers using a cluster models of the Si (001) surface ?

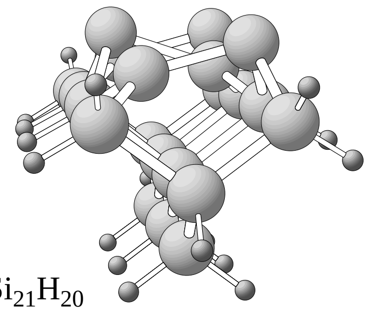
	angle [deg.]	bond length [Å]	ΔE [eV]	HOMO-LUMO gap[eV]
Si_9	6.9	2.21	0.00	1.18
Si_{15}	15.7	2.28	0.12	0.86
Si_{21}	18.6	2.35	0.17	0.70
slab	18.9	2.36	0.20	0.00



Si_9H_{12}



$Si_{15}H_{16}$



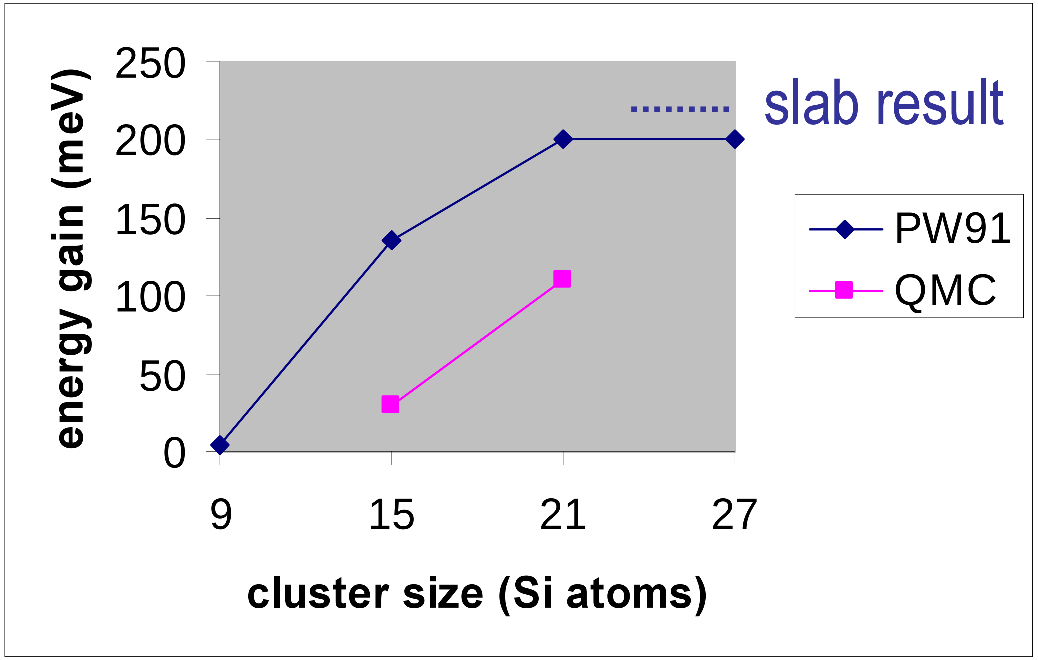
$Si_{21}H_{20}$

The buckling only developes fully in a cluster containing 3 surface Si dimers. The failure to describe the buckling is related to differences in the electronic structure.

E. Penev, P. Kratzer and M. Scheffler, J. Chem. Phys. **110**, 3986 (1999)

Electronic correlation effects at the surface

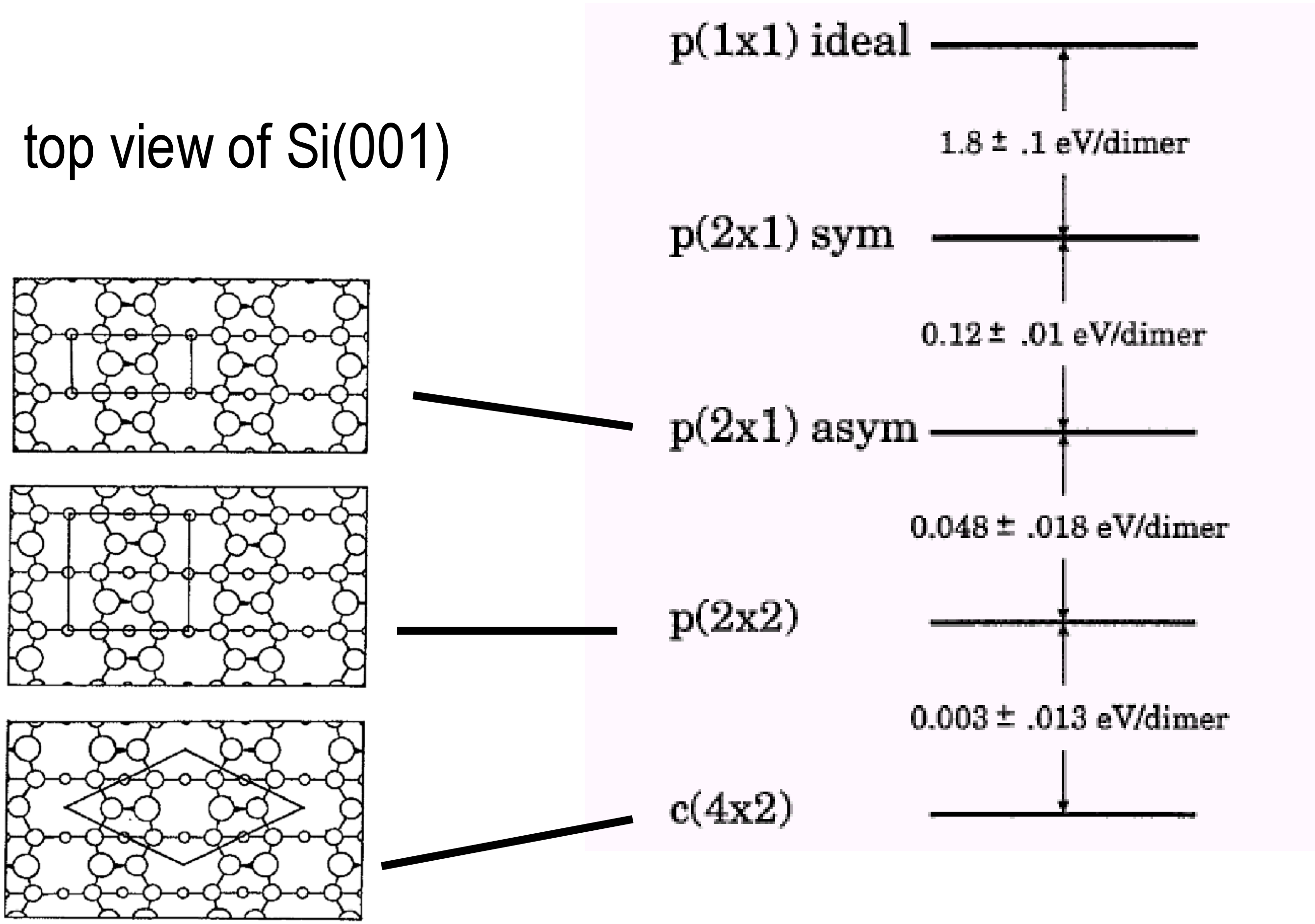
Since the symmetric dimer is a bi-radical, the buckling effect could be sensitive to subtle electronic correlation effects.



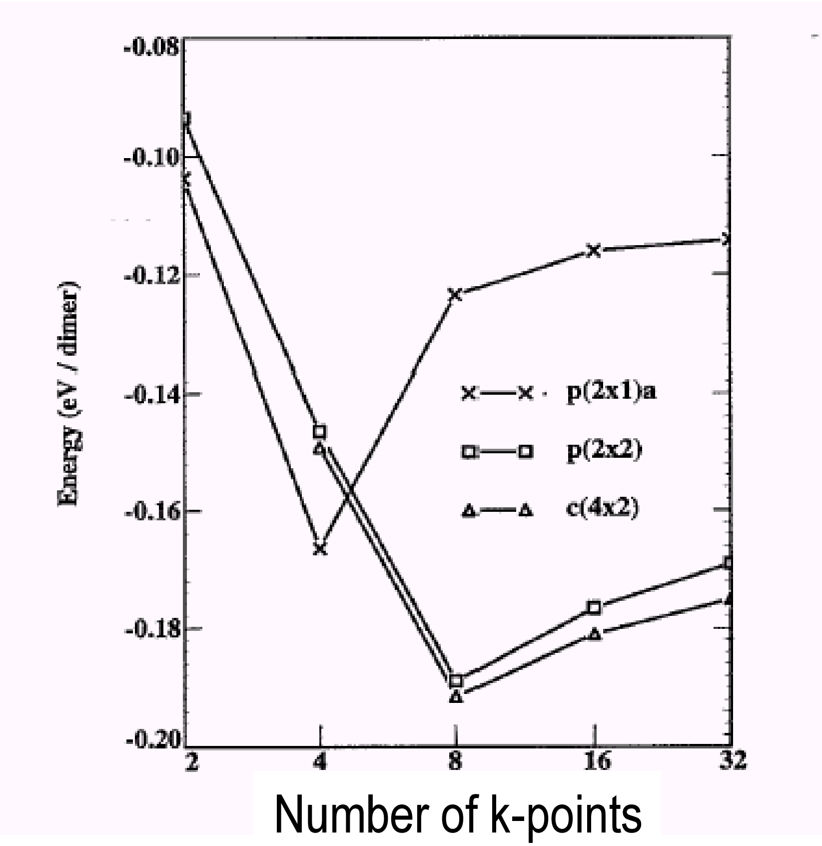
S. B. Healy, C. Filippi, P. Kratzer, E. Penev, M. Scheffler, Phys. Rev. Lett. 016105 (2001)

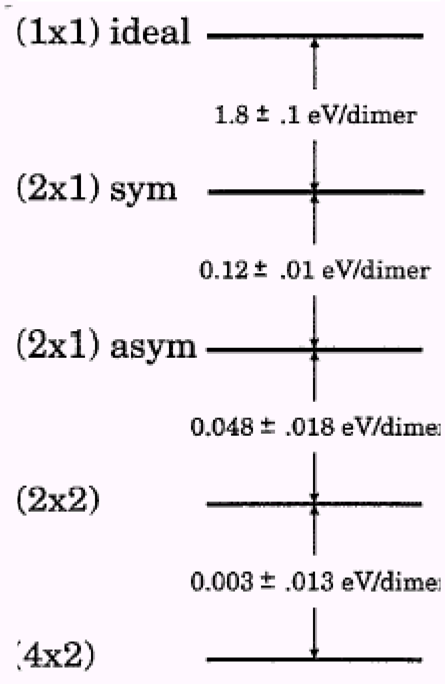
Arrangement of neighboring Si dimers

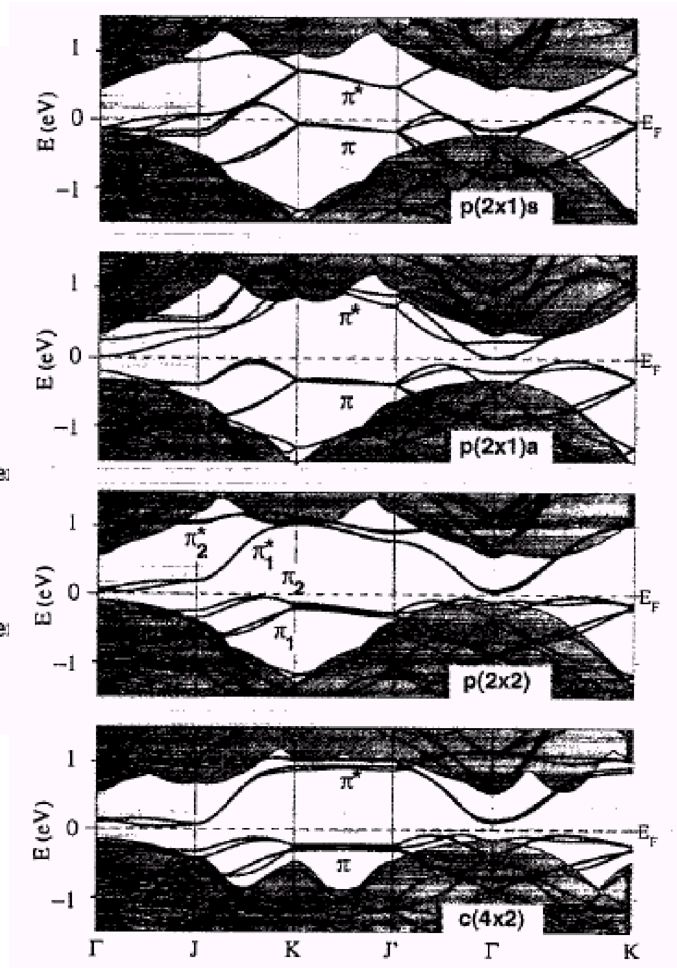
top view of Si(001)



Periodicity of the reconstruction: effects of k-point sampling



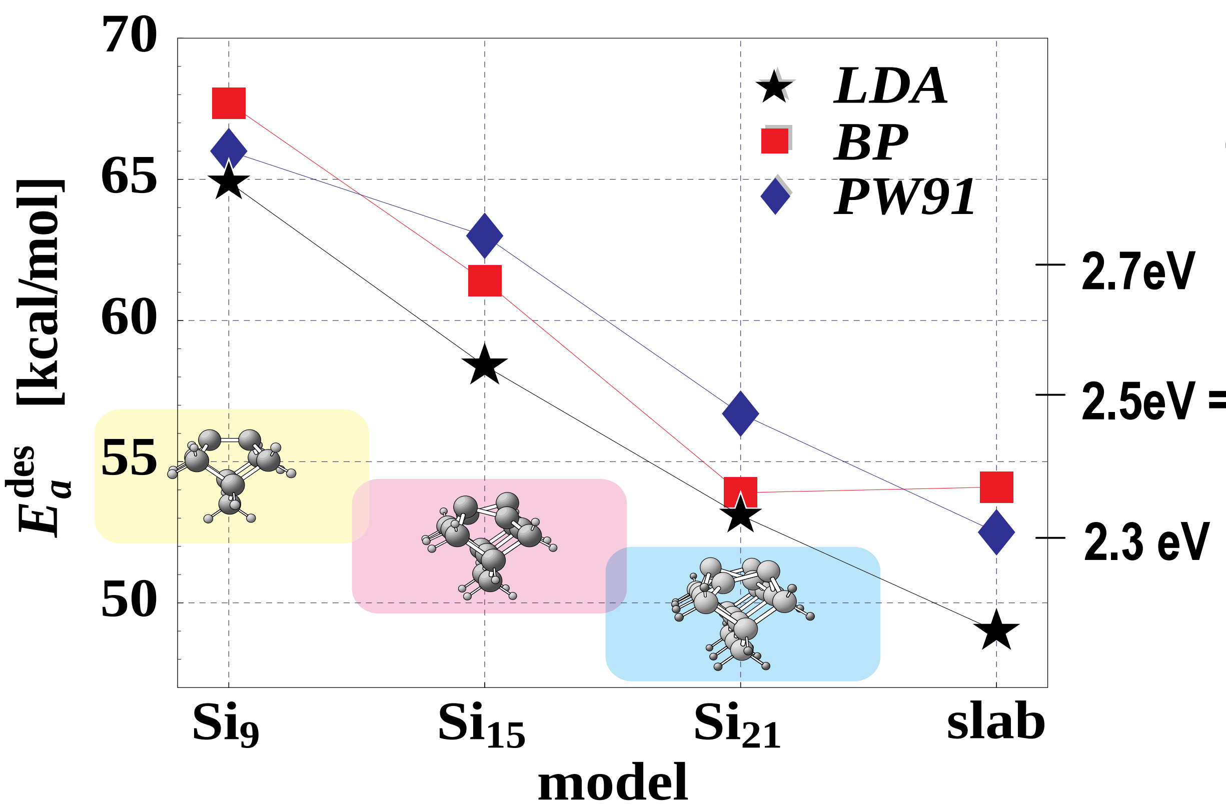




A. Ramstad, G. Brocks, and P. J. Kelly, Phys. Rev. B **51**, 14504 (1995).

Cluster models: H_2 associative desorption

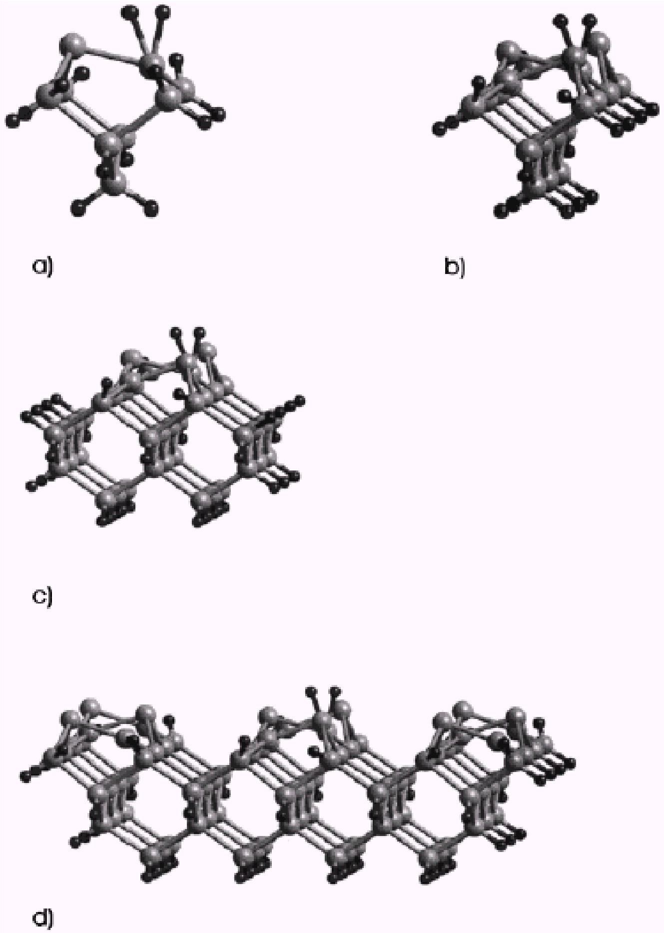
monohydride ↔ Si(001) + H_2

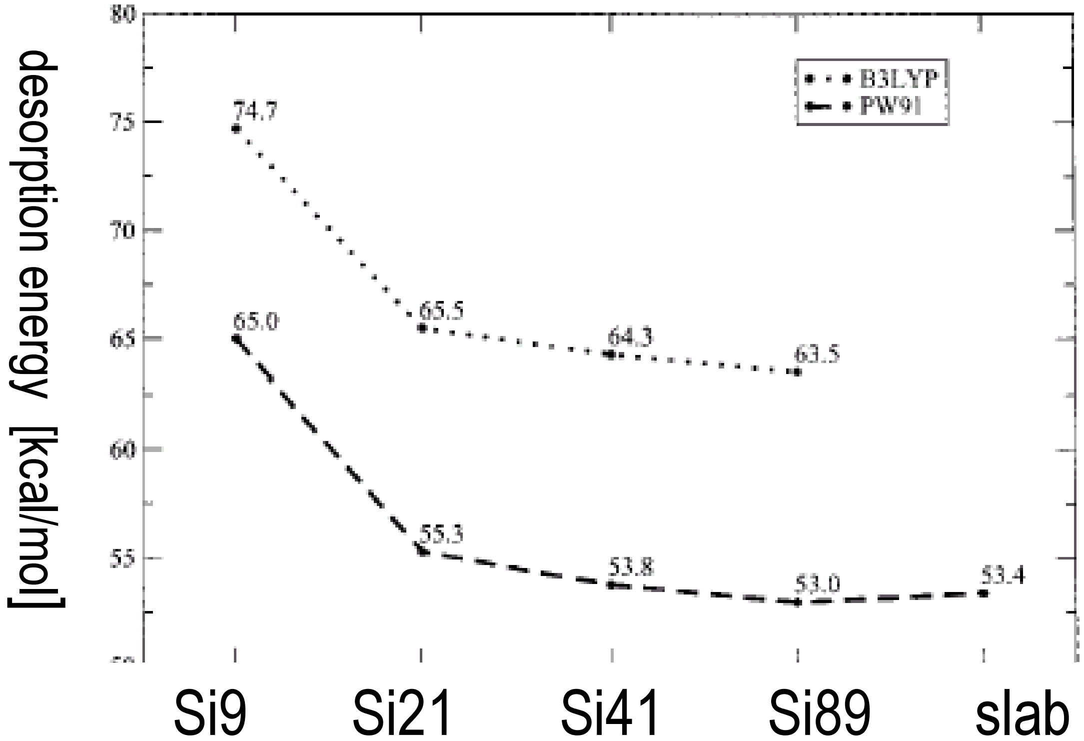


Convergence with cluster size is slow, and may result in misleading conclusions about the reaction mechanism.

E. Penev, P. Kratzer and M. Scheffler, J. Chem. Phys. **110**, 3986 (1999)

Cluster models: size convergence

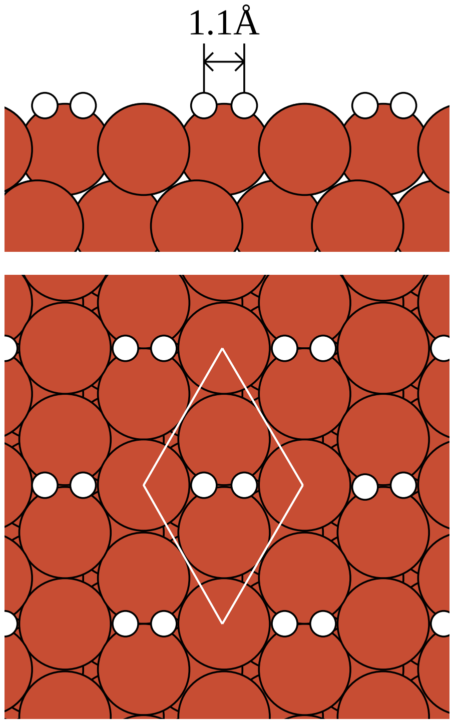




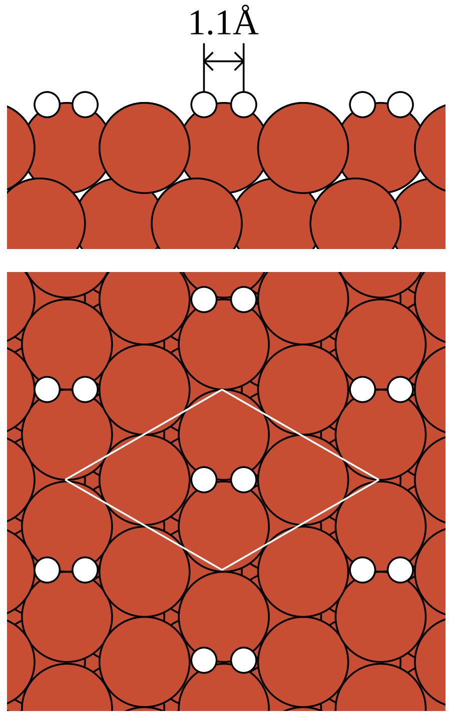
J. A. Stechel, T. Phung, K. D. Jordan, and P. Nachtigall,

J. Phys. Chem. B **105**, 4031 (2001).

Cu(111): H_2 dissociative adsorption



atoms in cell	3	3	4
layers	2	4	6
k-points	dissociation barrier [eV]		
1	5.48		
6	1.41		
18	0.35	0.73	0.48
54	0.62	0.54	0.55
162	0.61	0.60	0.51



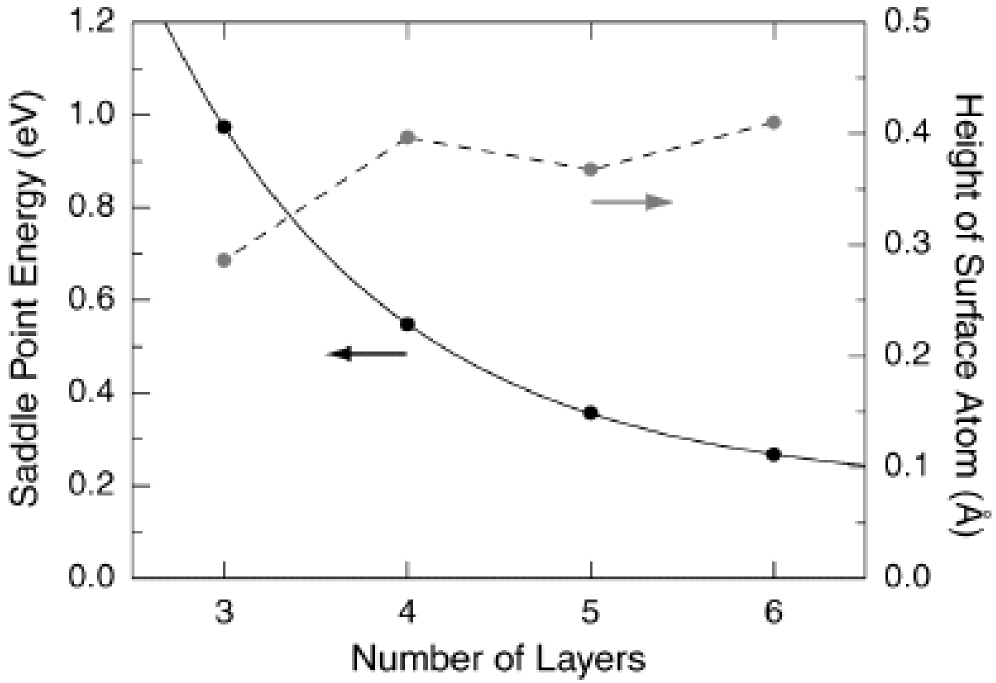
Note: LDA yields zero dissociation barrier

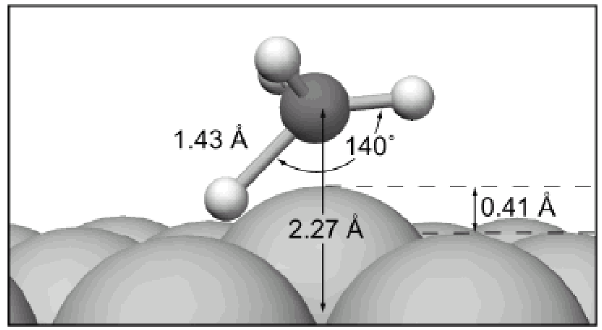
GGA(PW91), 50 Ry plane wave cut-off,

P. Kratzer, B. Hammer and J.K. Nørskov, Surf. Sci. **359**, 45 (1996)

Importance of surface relaxations

Example: CH_4 / Ir(111) slab calculations





Strong outward relaxation of the surface Ir atom at the transition state !

G. Henkelman and H. Jonsson, Phys. Rev. Lett. **86** (2001), 664

Conclusions

- The quality of the Brillouin zone sampling ought to be tested carefully for each system, in particular for metals.
- If long-range effects are to be expected, it can be helpful to explore their size in advance, by using simple (e.g. elastic) models.
- (meta-)GGAs have brought us a good way closer to chemical accuracy for surface reactions.
- In the DFT approach, slabs are usually a more efficient model of the surface then clusters.
- When trying to model single isolated objects (e.g. defects, adsorbates …), one needs to be aware of unwanted substrate-mediated interactions.

A few words of guidance

- When starting a new project, first repeat some bulk calculations for the chemical elements constituting your material under study. Compare to all-electron calculations, if available, to check the performance of the pseudopotentials !
- ‘Design’ your project:
  - For each critical parameter, find out a satisfactory ‘production setting’ and an improved ‘check setting’.
  - Make sure that the checks are feasable with your computer hardware.
  - Complete all checks before going into the production phase.
- When producing thermochemical data, use various functionals to get an idea of the possible spread of results.

Closing remarks

- First-principles DFT calculations have evolved into a very powerful and versatile theoretical tool, useful for analysis and explanation or even prediction of a large variety of phenomena.
- However, one has to be aware of the principal limitations of the DFT approach and of the unavoidable approximations which enable us to do large-scale calculations for the systems of real interest.
- So far, this tool has high credibility. To maintain this high standard, the users ought to perform each individual project with utmost care. Please do all the necessary checks and convergence tests!