Surface Structure and Chemisorption

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Topics:

(i) interplay between the geometric and electronic structure of solid surfaces,

(ii) physical properties of surfaces: surface energy, surface stress and their relevance for surface morphology

(iii) adsorption and desorption energy barriers, chemical reactivity of surfaces -> heterogeneous catalysis

Technological Importance of Surfaces

Solid surfaces are intriguing objects for basic research,

and they are also of high technological utility:

- substrates for homo- or hetero-epitaxial growth of semiconductor thin films used in device technology

- surfaces can act as heterogeneous catalysts, used to induce and steer the desired chemical reactions

# The Geometric and
the Electronic Structure
of Crystal Surfaces

Surface Crystallography

	2D	3D
number of space groups:	17	230
number of point groups:	10	32
number of Bravais lattices:	5	14

2D-crystal system	symbol	lattice parameters	2D Bravais lattice	space group	point groups
oblique	m (mono-clin)	a, b, γ	mp	2	1 (2)
rectangular	o (ortho-rhom-bic)	a, b γ = 90°	op oc	7	m 2mm
square	t (tetra-gonal)	a = b γ = 90°	tp	3	4 4mm
hexagonal	h (hexa-gonal)	a = b γ = 120°	hp	5	3 6 3m 6mm
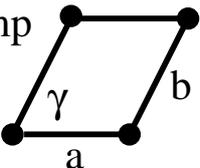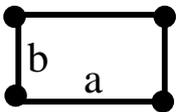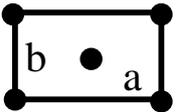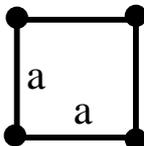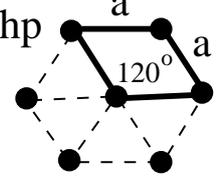
Bulk Terminated fcc Crystal Surfaces

fcc

(010)

c

$a = c/\sqrt{2}$
square lattice (tp)

fcc **(110)**

a

c

$[1\bar{1}0]$

rectangular lattice (op)

(111) **fcc**

$[0\bar{1}1]$

$[\bar{1}10]$

a

hexagonal lattice (hp)
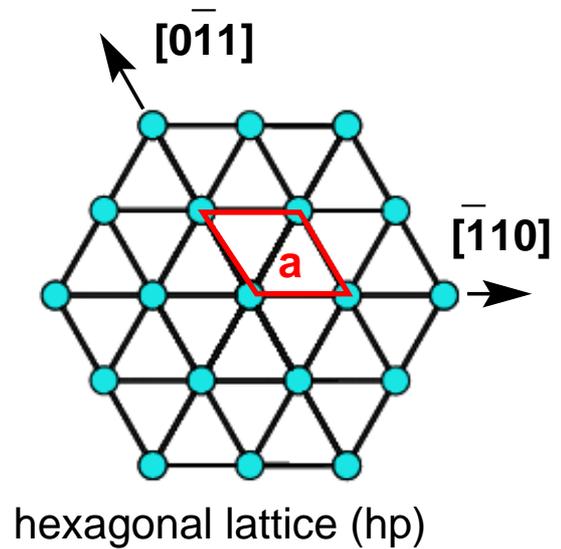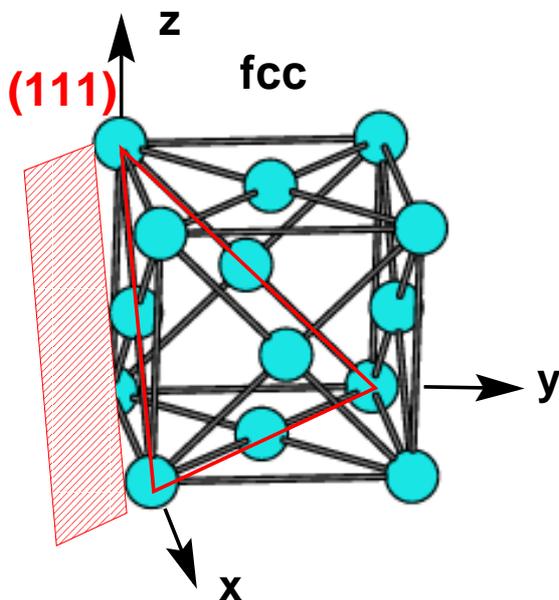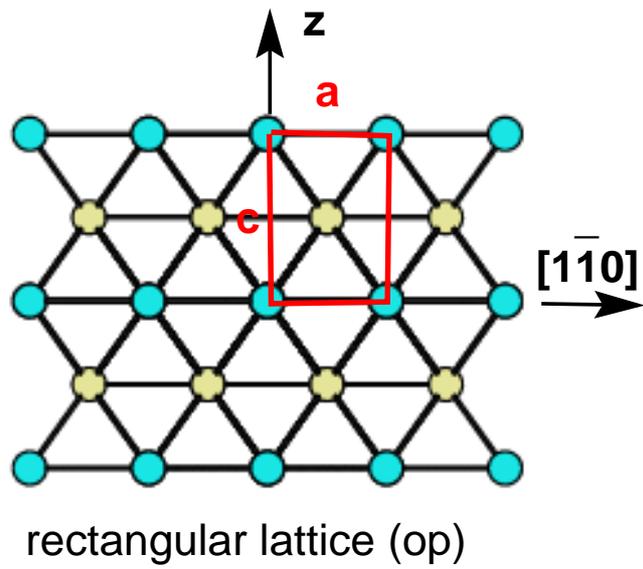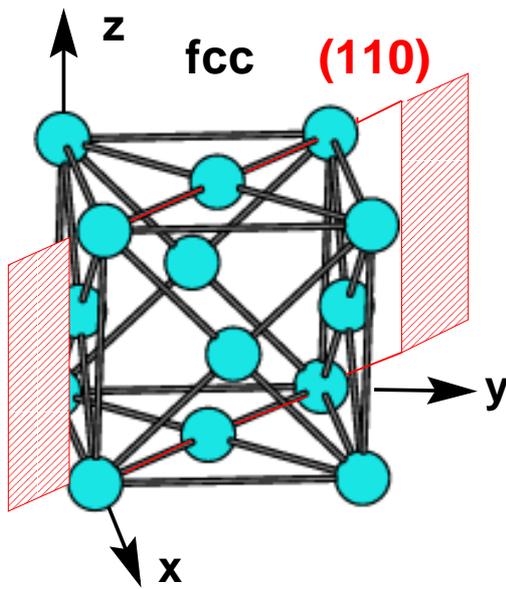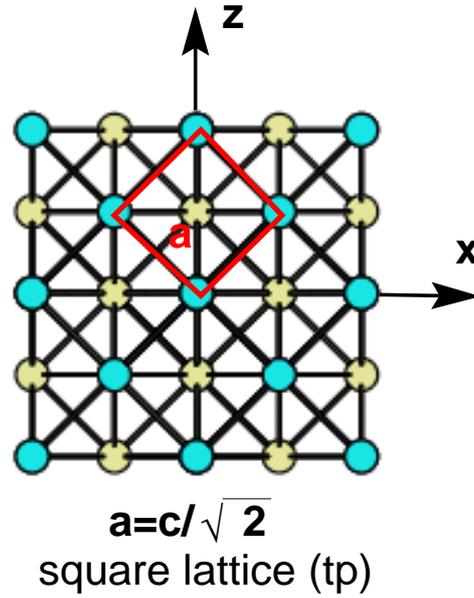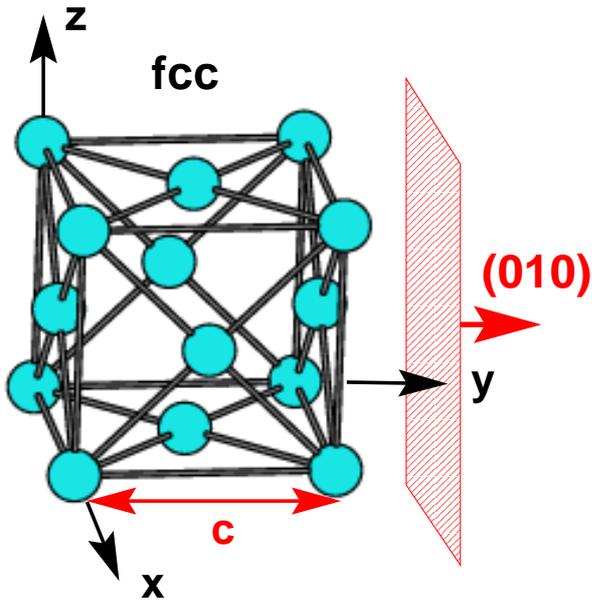
Surface Atomic Geometry

a

reduced inter-layer separation

normal relaxation

2a

(2x1) reconstruction
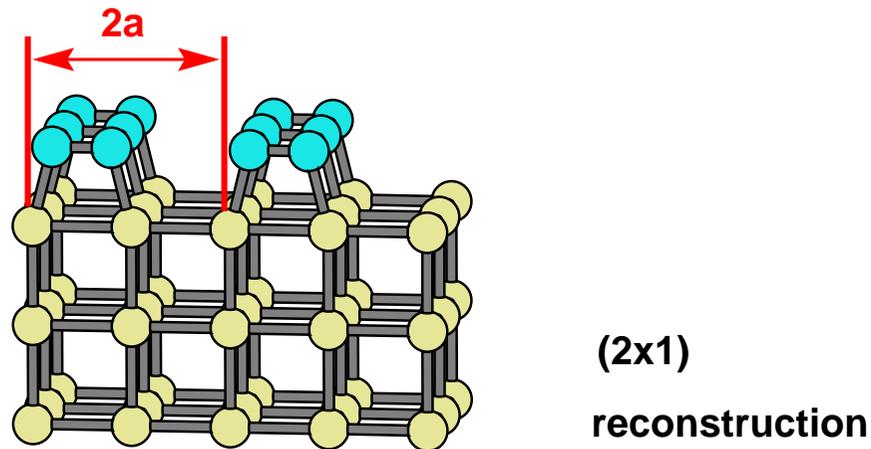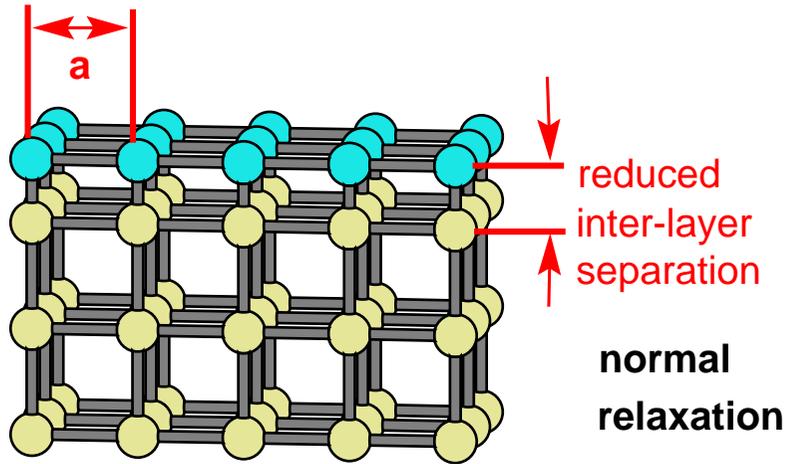
Examples:

H/Si(111)

Si(111) (7x7)

(a)

(b)
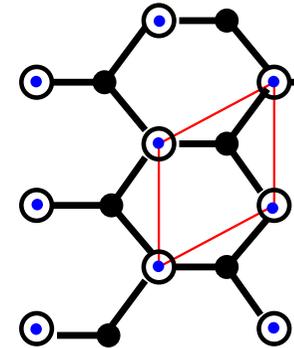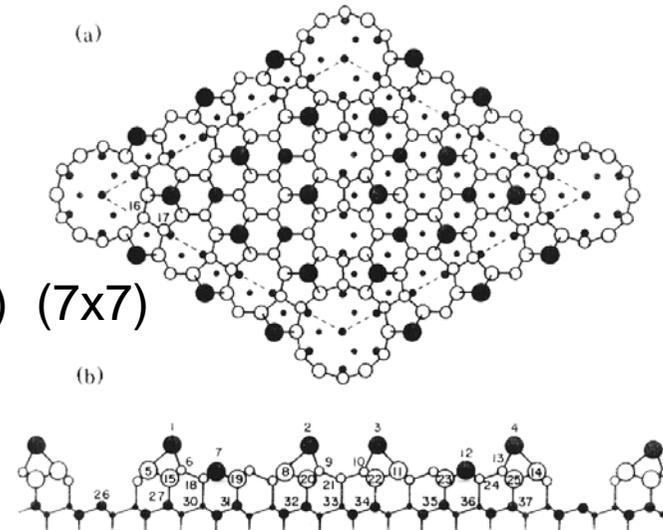
K. Brommer et al., Phys. Rev. Lett. 68, 1355 (1992)

Electronic Structure of Surfaces:
Shockley States in the Projected Band Structure

wave function matching at the surface

virtual induced gap states bridge the band gap

$\sim e^{\kappa z}$ ψ

cusp — no surface state

ε

gap $2|V_G|$

κ

$k_\perp$

π/a

V $V_G > 0$ z

ψ

surface state

V $V_G < 0$ z
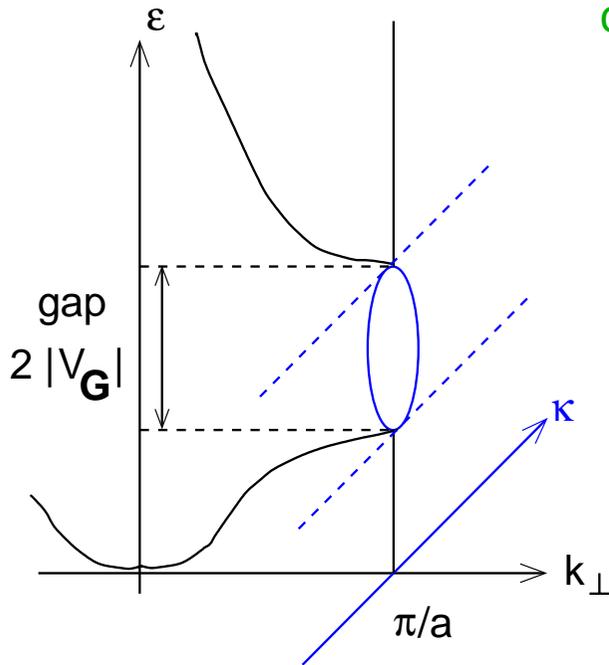
real energy, complex Bloch vector

$e^{i(k_\perp + i\kappa)z}$
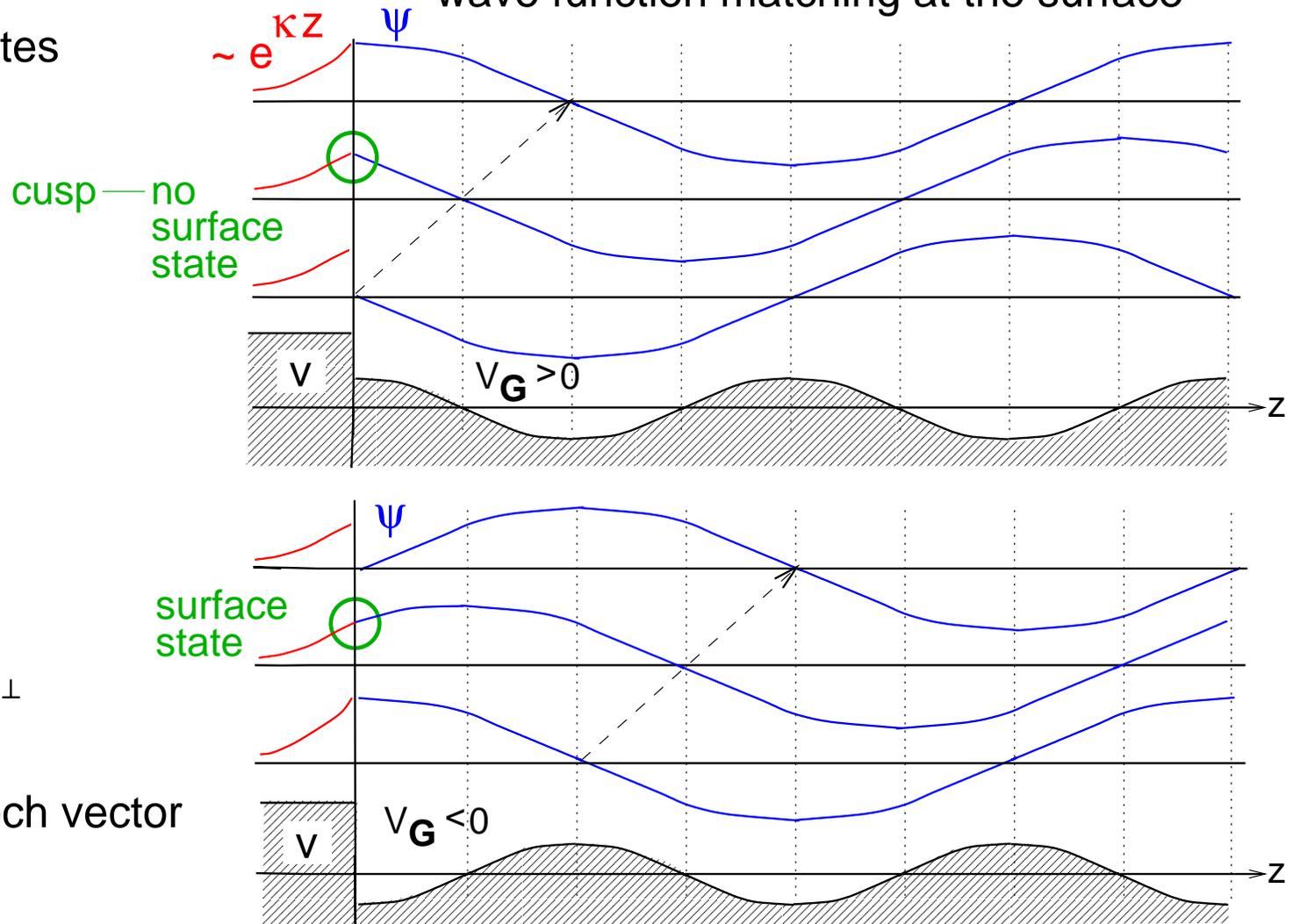
The Al(100) Surface State
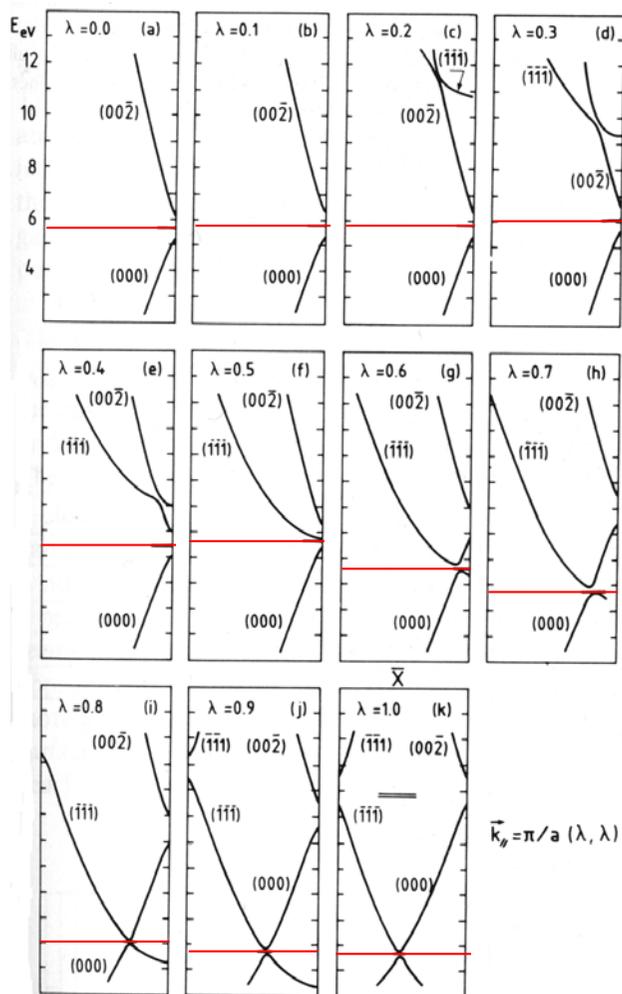
BZ of fcc lattice

bulk band structure for wave-vector perpendicular to the surface

D. Spanjaard et al., Phys. Rev. B 19, 642 (1979).
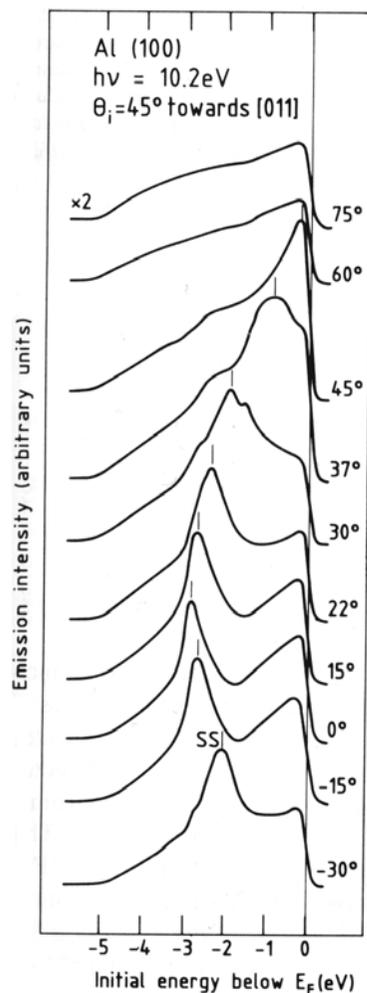
ARUPS spectra exit angle in (01̄1)

Al(100) surface state in the projected band structure

G.V. Hansson, S.A. Flodström, Phys. Rev. B 18, 1562 (1978).

Figures taken from: M.C. Desjonqueres, D. Spanjaard, "Concepts in Surface Physics", Springer (Berlin, 1993).

Electronic Structure of Semiconductor Surfaces: Dangling Bonds on Si (001)


surface dimer

$\sigma*$ $\varepsilon_o + |\beta|$

empty

empty conduction band

(CB)

(CB)

$+$

$-$

Si

db (down) empty

band gap

E_F

ε_p

3

ε_o

db state ε_o

sp^3 hybrid-orbital

db (up) (occupied)

σ $\varepsilon_o - |\beta|$

fully occupied valence band

2 x 4 el occupied

(VB)

(VB)

1

ε_s

Si

atom

molecular orbital picture

fictitious surface with almost non-interacting dbs

after reconstruction and relaxation

$sp^3 \longrightarrow sp^2 + p$
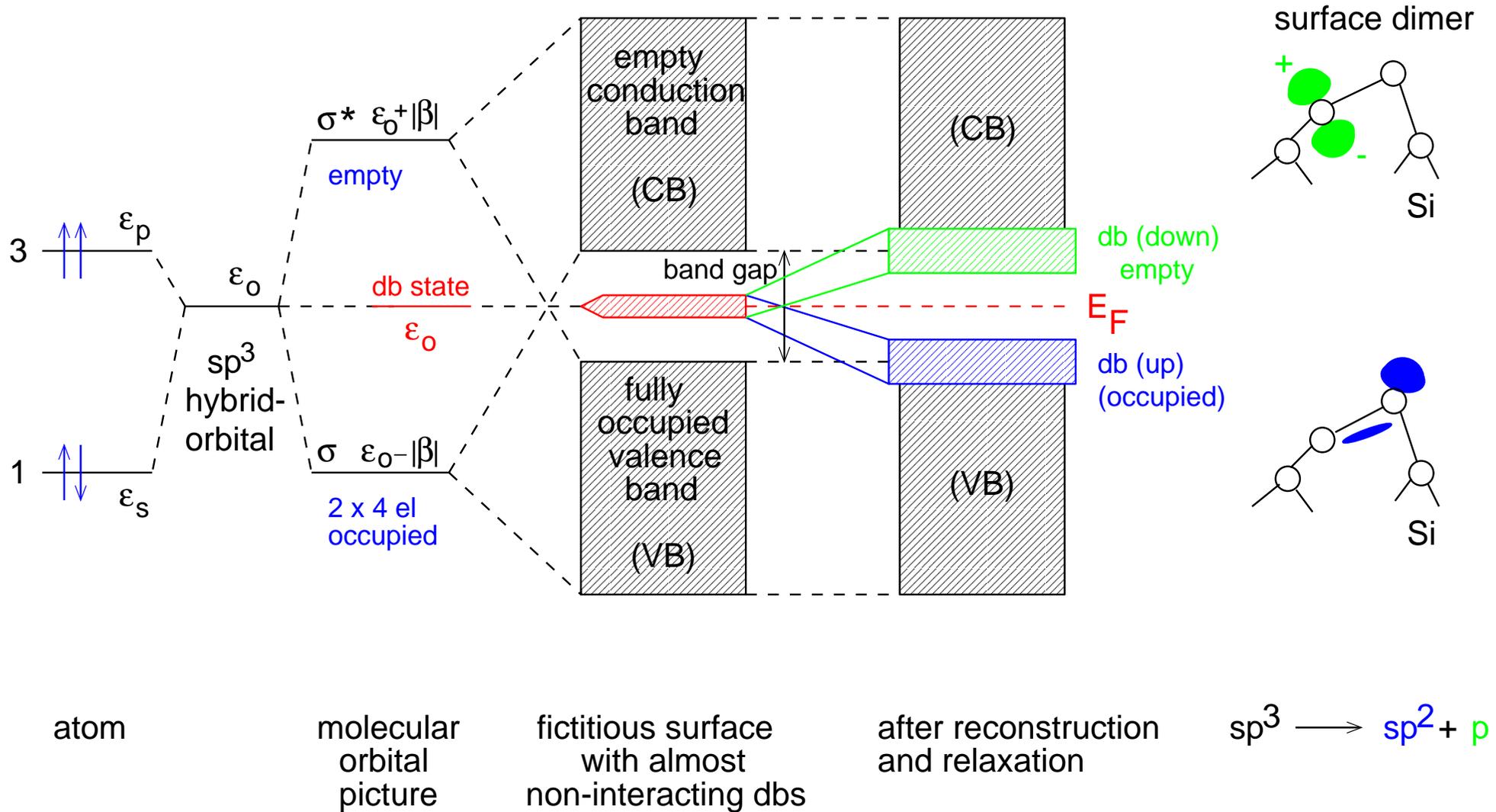
Interplay of the Atomic and Electronic Structure of Si(001)

p(2x2)

Si(001)(1x2)

lowest unoccupied
surface state (LUMO)

π^*

π

highest occupied
surface state (HOMO)
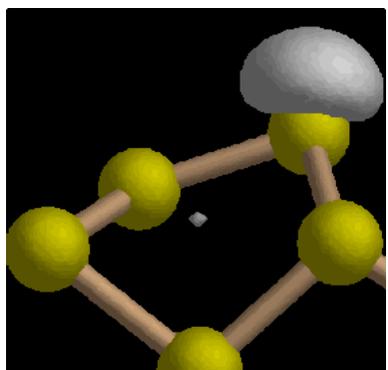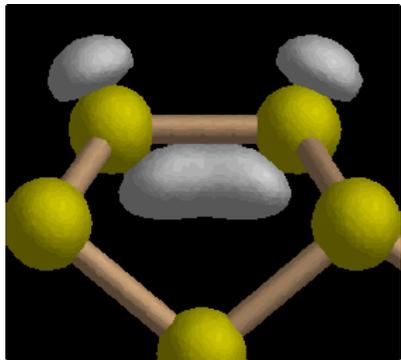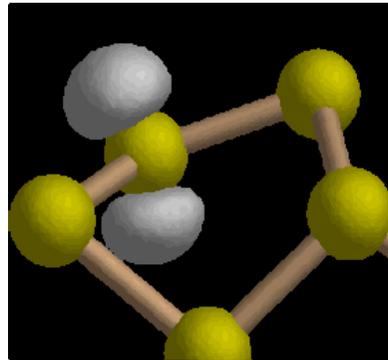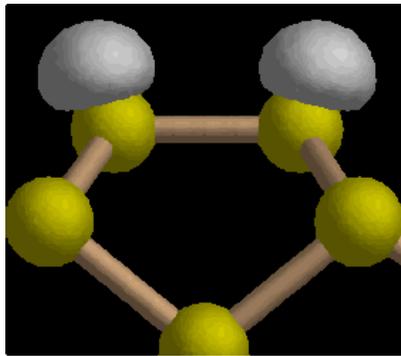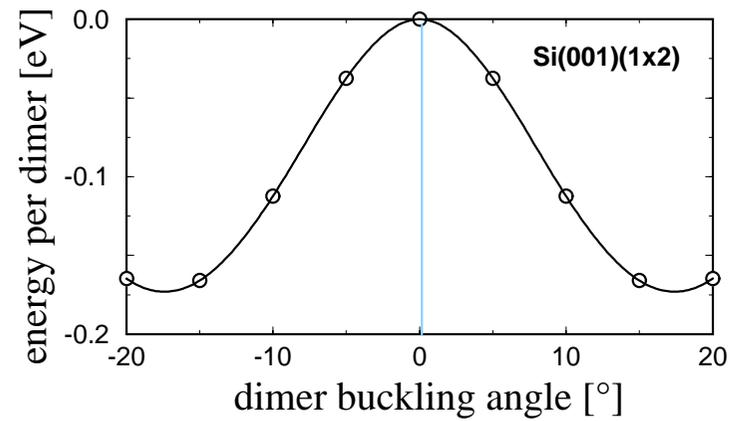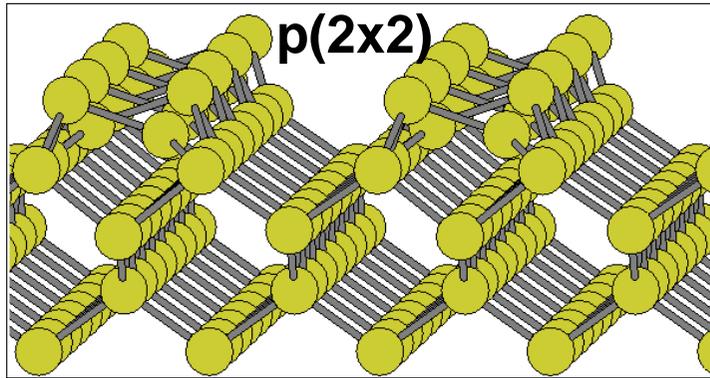
symmetric dimers

buckled dimers

Mechanisms for Lowering the Surface Energy

- reduce density of dangling bonds
  -> by dimerization (Si(100), ~1 eV/db)
  -> ad-atoms (Si(111), rebonded steps on Si(100) vicinals)

- formation of π bonds between dangling bonds
  -> Pandey's model of Si(111) (2x1)

- Jahn-Teller-like distortions: relaxation and re-hybridization
  -> dimer buckling on Si(100)

- minimization of elastic strain

- unusual atomic configurations
  -> subsurface interstitial on Si(113)

and other mechanisms (e.g. for compound semiconductors)

Sect. II:

Material Properties of Crystal Surfaces:

Surface Energy

Surface Stress Tensor

Surface Energy and the Thermo-dynamic Stability of Facets

(1) **Definition:** $\gamma =$ excess free energy of a surface per surface area

(2) **Calculation:** total-energy DFT calculations for slab geometries

(i) slab with equivalent surfaces:

$$\gamma = \frac{1}{2A}\{E(N_1, \ldots) - \sum_{\text{all species } i} N_i\,\mu_i\}$$

(ii) slab with inequivalent surfaces: derive individual surface energies from an energy density

(N. Chetty, R. Martin, Phys. Rev. B 45, 6074 (1992).)

(3) **equilibrium crystal shape (ECS)**

$$\min_{V=\text{const.}} \oint_{\partial V} \gamma(\mathbf{n})\,dA \longrightarrow r(\mathbf{h}) = \min_{\mathbf{n}} \frac{\gamma(\mathbf{n})}{\mathbf{n}\cdot\mathbf{h}}$$

polar plot of the surface energy

$\gamma(\mathbf{n})$

$r(\mathbf{h})=\gamma(\mathbf{n})/\mathbf{n}\cdot\mathbf{h}$

equilibrium crystal shape (ECS)

Wulff-construction
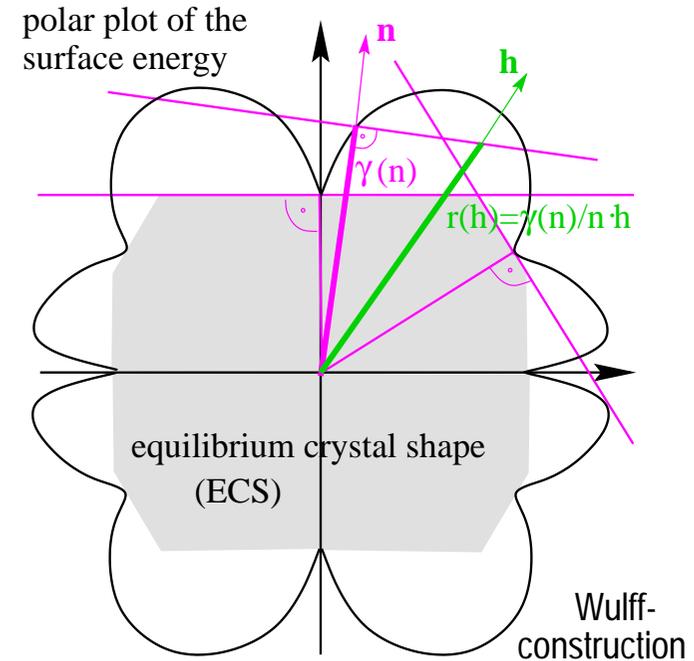
(4) **Application: facet formation**

thermodynamic stable surface orientations

A_1 n_1 A_2 n_2 n A

(a) side view

n_1 n_2 A_1 A_2 n_3 A_3
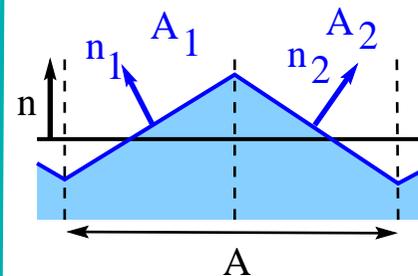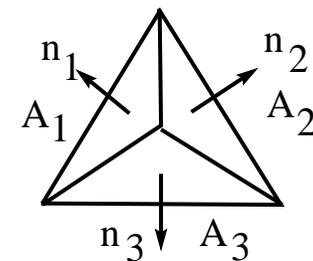
(b) top view

Surface Stress Tensor

Definition: surface stress = linear coefficient σ describing the change of surface energy with an applied strain ε :

$$\Delta E_{\mathrm{surf}} = \int_A \sum_{i,j=1,2} \sigma_{ij}\varepsilon_{ij} \;\; d^2\mathbf{x}$$

$$\Delta E_{Vol} \sim \varepsilon^2$$
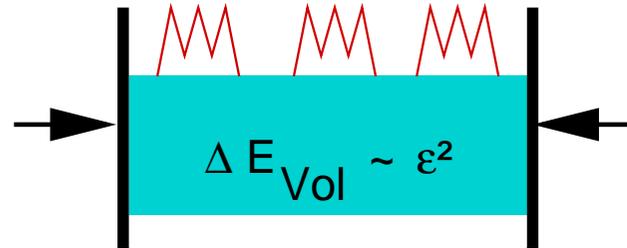
($\sigma_{xx} > 0$ <u>tensile</u>: $\varepsilon_{xx} < 0$ => $\Delta E_{surf} < 0$, preference for contraction,

 $\sigma_{xx} < 0$ <u>compressive</u>: $\varepsilon_{xx} > 0$ => $\Delta E_{surf} < 0$, preference for expansion)

Relation to surface energy: $$\sigma_{ij} = \gamma\delta_{ij} + \frac{\partial\gamma}{\partial\varepsilon_{ij}}$$ (different from liquids!)

Application:
Force density on a surface: $$\mathbf{f}(\mathbf{x}) = \mathrm{div}\ \sigma(\mathbf{x})$$

Consequence: forces acting at stress domain boundaries -> elastic relaxation -> structure formation on mesoscopic length scales.

Surface Stress Anisotropy: Si(100)

Measurement of surface stress anisotropy: strain surface (by bending the wafer) and determine the relative area of (1x2) and (2x1) dimerized terraces.
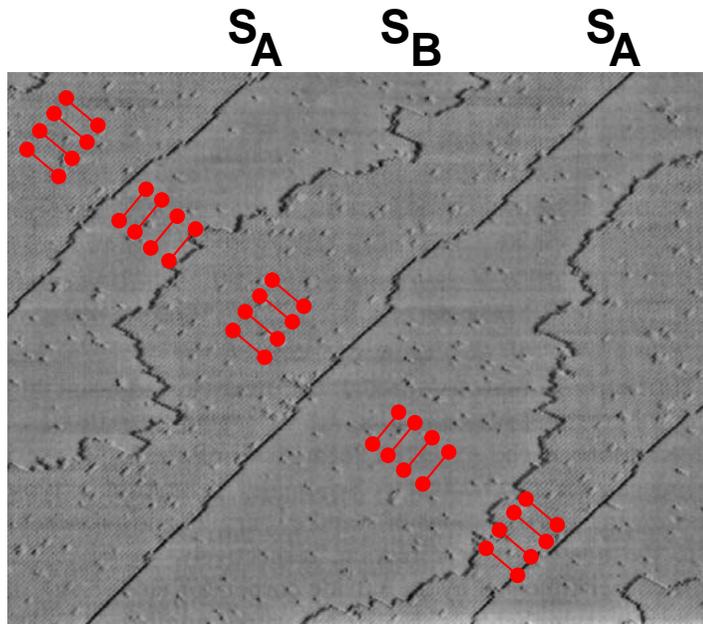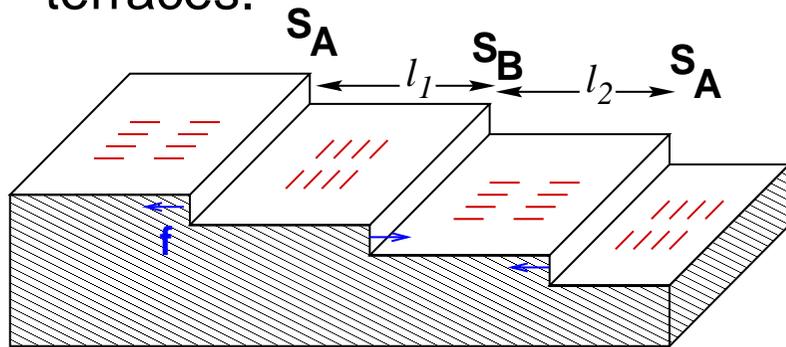
$$\Delta E_{\mathrm{surf}} = \int_A \sum_{i,j=1,2} \sigma_{ij}\varepsilon_{ij} \quad d^2\mathbf{x}$$
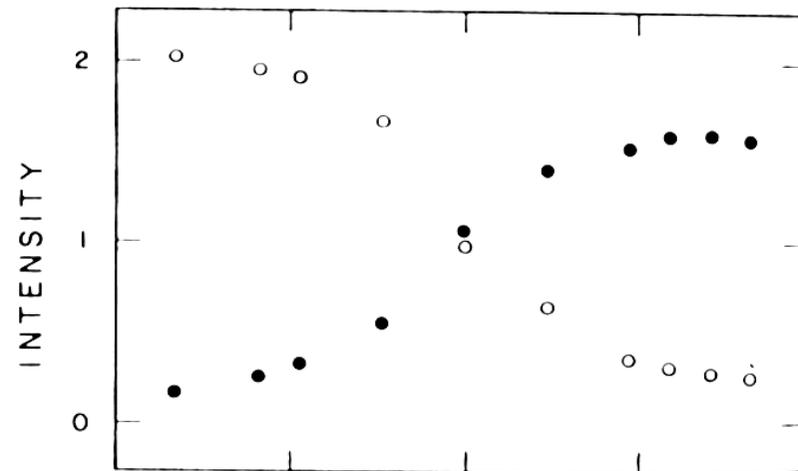
F.K. Men, W.E. Packard, M.B. Webb, Phys. Rev. Lett. 61, 2469 (1988). O.L. Alerhand, D. Vanderbilt, R.D. Meade, J.D. Joannopoulos, Phys. Rev. Lett. 61, 1973 (1988).

tunneling microscope image, single atomic-height steps

miscut angle $\Theta = 0.3°$ (S_A step separation ~ 500 Å)

From Swartzentruber et al., Phys. Rev. Lett. 65, 1913 (1990).

Influence of the Reconstruction on Surface Stress Anisotropy

Stress anisotropy calculated from total energy differences: $\Delta E_{\mathrm{surf}} = \int_A \sum_{i,j=1,2} \sigma_{ij} \varepsilon_{ij} \ d^2\mathbf{x}$

| reconstruction	$\sigma^s_{\parallel} - \sigma^s_{\perp}$	$\sigma^b_{\parallel} - \sigma^b_{\perp}$	$\sigma^b_{\parallel} - \sigma^s_{\parallel}$	$\sigma^b_{\perp} - \sigma^s_{\perp}$
SW (1x2) (Poon et al.)	77 meV/Å^2	-	-	-
DFT-LDA (1x2)	150 meV/Å^2	105 meV/Å^2	30 meV/Å^2	75 meV/Å^2
DFT-LDA p(2x2)	150 meV/Å^2	55 meV/Å^2	30 meV/Å^2	125 meV/Å^2
expt. (Webb et al.)	-	60 − 80 meV/Å^2	-	-
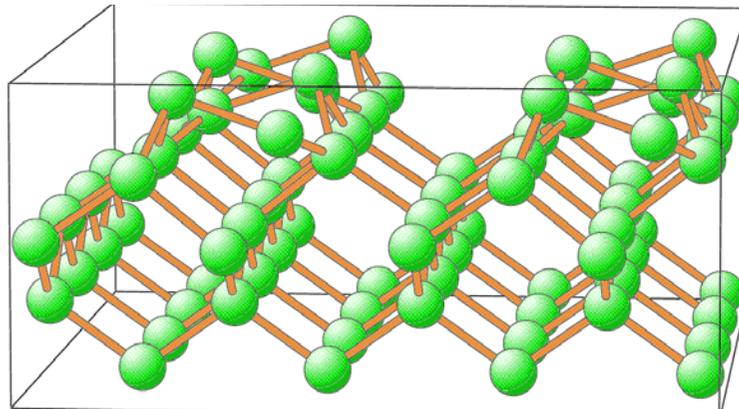
Si(001) p(2x2)
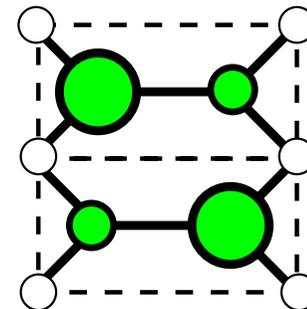
J. Dabrowski, E. P., M. Scheffler, Phys. Rev. B 49, 4790 (1994).
T.W. Poon, S. Yip, P.S. Ho, F.F. Abraham, Phys. Rev. B 45, 3521 (1992).
M.B. Webb, F.K. Men, B.S. Swartzentruber, R. Kariotis, M.G. Lagally, Surf. Sci. 242, 23 (1991).

Calculation of Surface Stress from Total-Energy Differences: The "Reference Surface" Si(111) (1x1) - H

DFT total-energy calculations with fhi96md
slab geometry with up to 12 Si layers, H-termination on both sides
PW91 GGA for the XC functional
Hamann pseudopotentials for Si, 1/r Coulomb potential for H
kinetic-energy cut-off for plane-wave basis-set: 50 Ry
9 special k-points in the irreducible part of the Brillouin zone
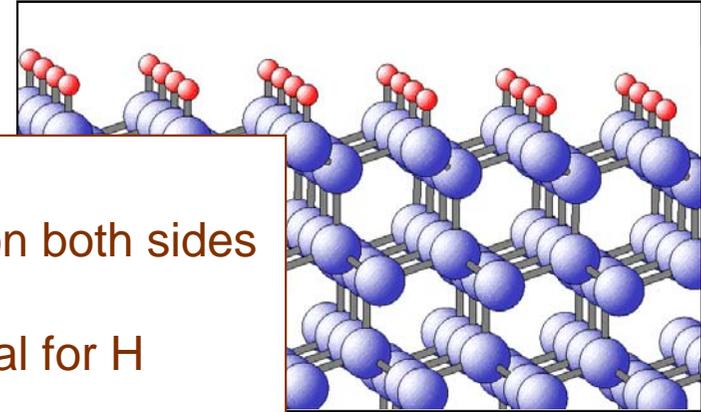
◄ Method
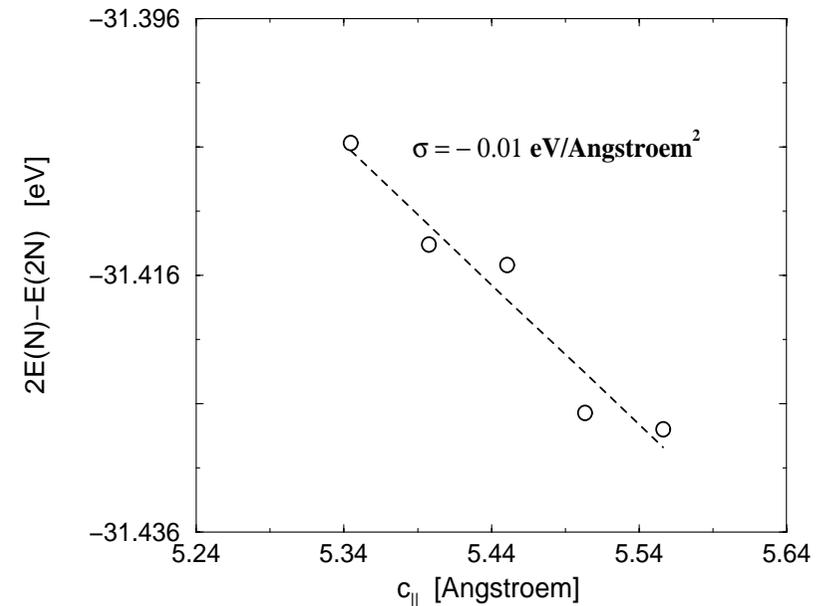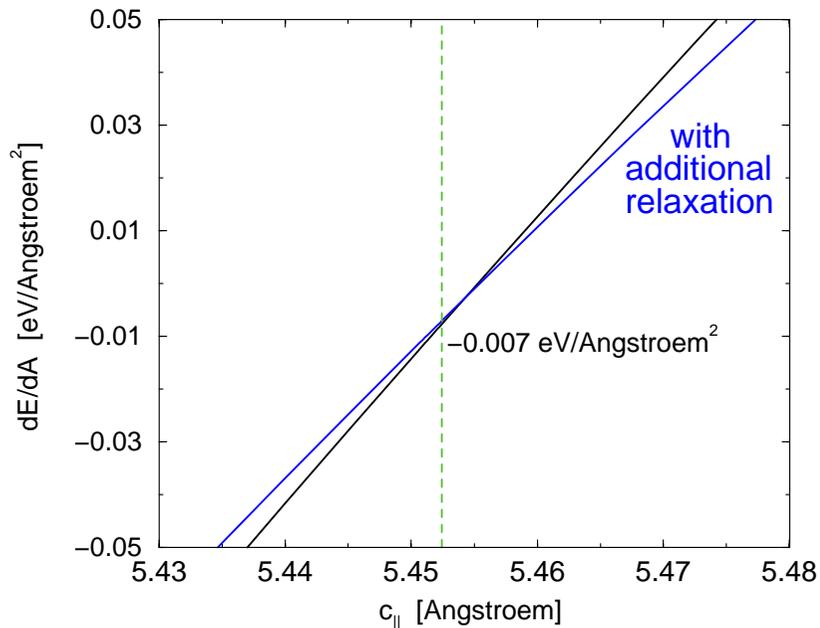
Sect. III:

Chemisorption on Semiconductor Surfaces

Model System:

## Dissociative Adsorption and Recombinative Desorption of Hydrogen Molecules on/from a Si(100) Surface

Surface Reactivity and Heterogeneous Catalysis

The rate of chemical reactions depends on the reaction energy-barriers along the reaction path:
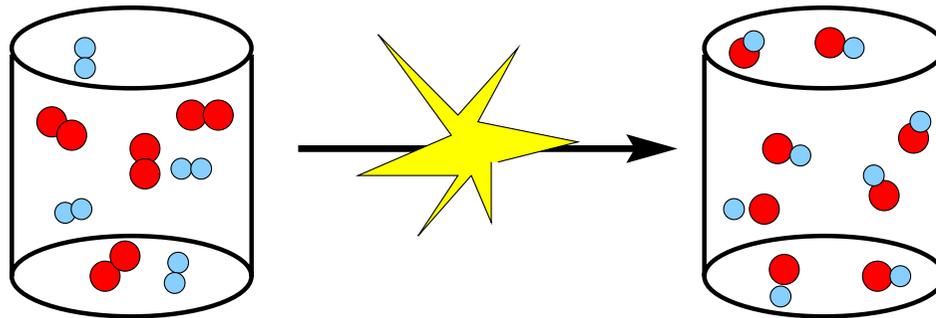
Dissociative adsorption and recombinative desorption of molecules on a solid surface are an essential step of heterogeneous catalysis:
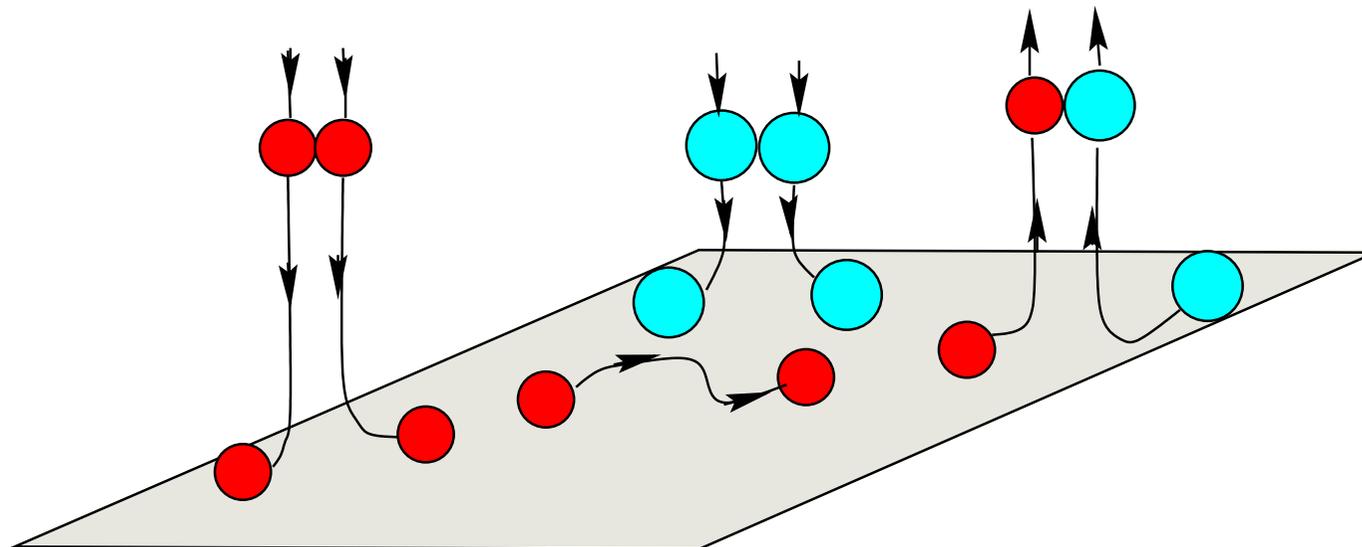
Langmuir-Hinshelwood mechanism

Dissociative Adsorption of a Molecule on a Solid Surface
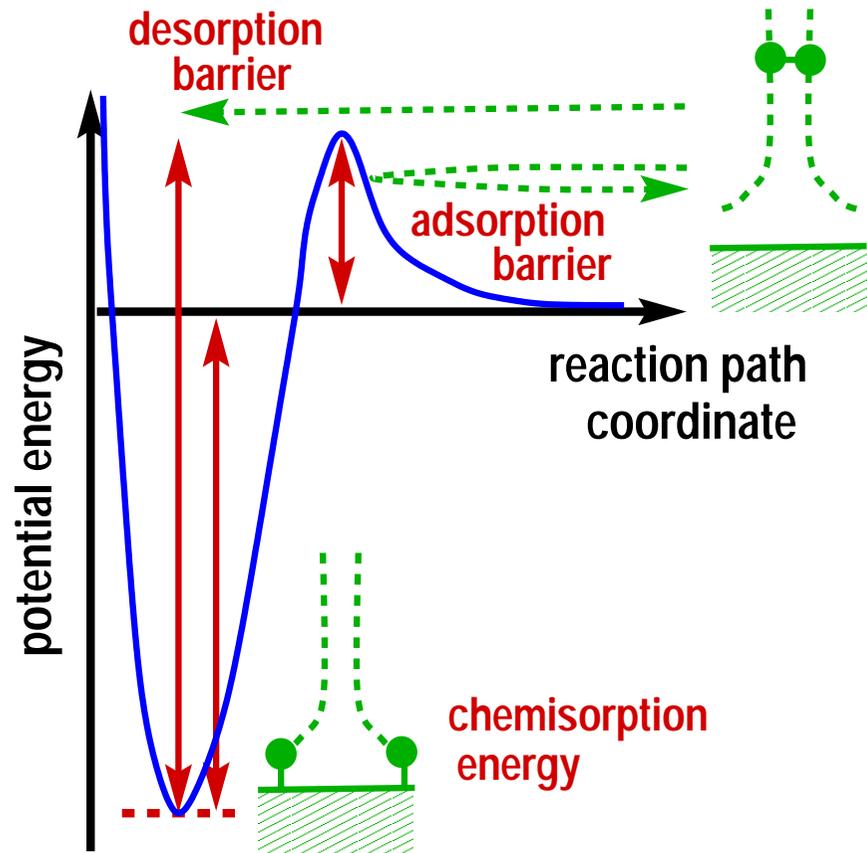
potential energy
along the reaction path
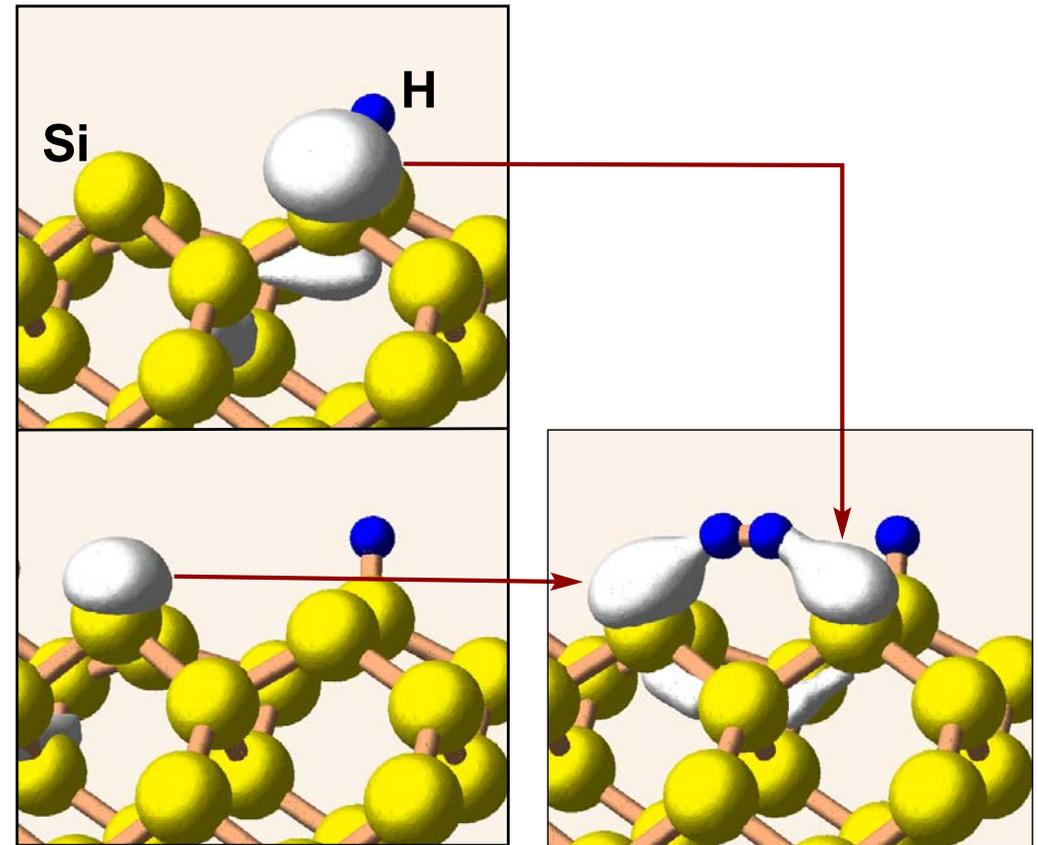
electronic mechanism of bond
formation and breaking

What makes H$_2$/Si a fascinating system?

**Apparently contradictory experimental observations:**

small sticking coefficient -> large adsorption energy barrier

desorbing hydrogen molecules do not have large (> thermal) kinetic energies

Microreversibility?

K.W. Kolasinski et al., Phys. Rev. Lett. 72, 1356 (1994).

The (most intensely studied) intra-dimer reaction path:
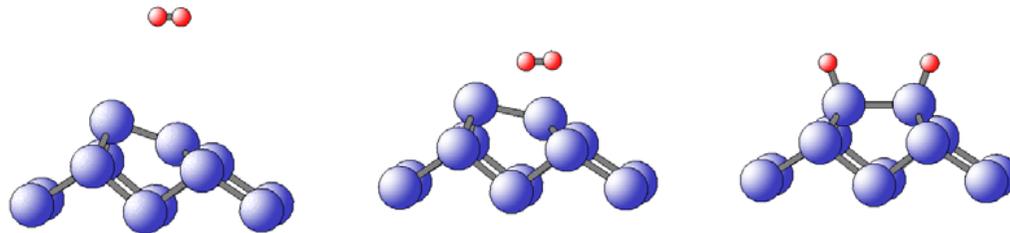
It is essential to include the "mechanical" surface degree of freedom in the adsorption/desorption dynamics.

W. Brenig, A. Groß, R. Russ (see e.g. Phys. Rev. B 54, 5978 (1996)).

z separation of hydrogen molecule from surface

d surface degree of freedom

(model-potential)

V

z [Å]

d [Å]
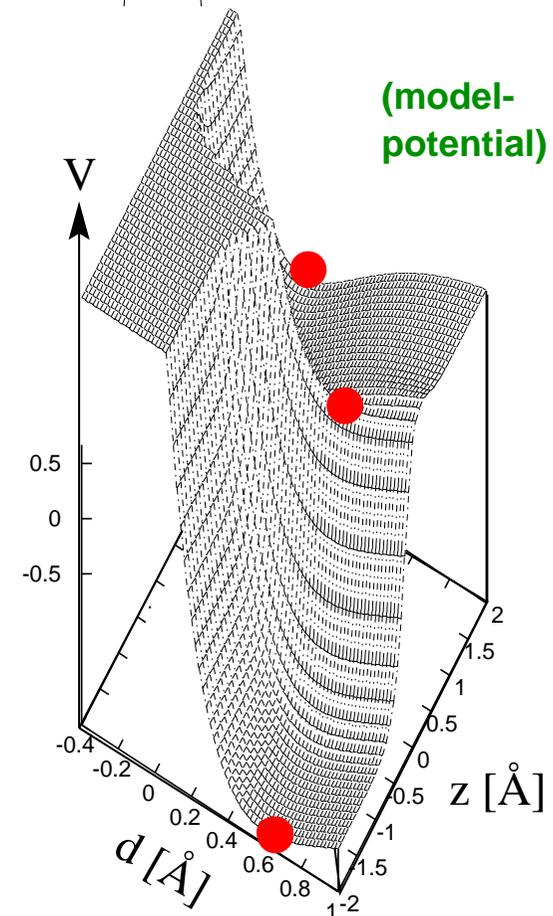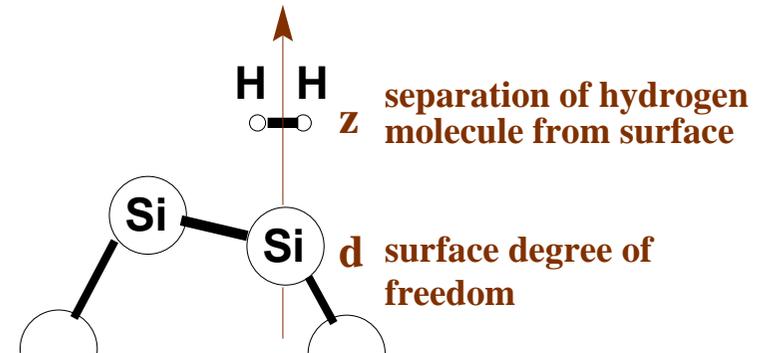
DFT for Chemisorption: Reaction Path, PES, ...

- **chemisorption geometries and energies**
  (equilibrium geometries, reaction energy)

- **locate transition state**
  (automated search for special saddle
 points in the potential energy surface)

- **adsorption and desorption
  energy barrier**

- **reaction path**
  (steepest descent from transition state)

- **PES, vibrational frequencies**
 P. Kratzer, B. Hammer, J.K. Norskov,
  Phys. Rev. B 51, 13432 (1995).

- **strain energy of substrate at the
  transition geometry, etc.**
  ("computer experiments")

PES (schematic)
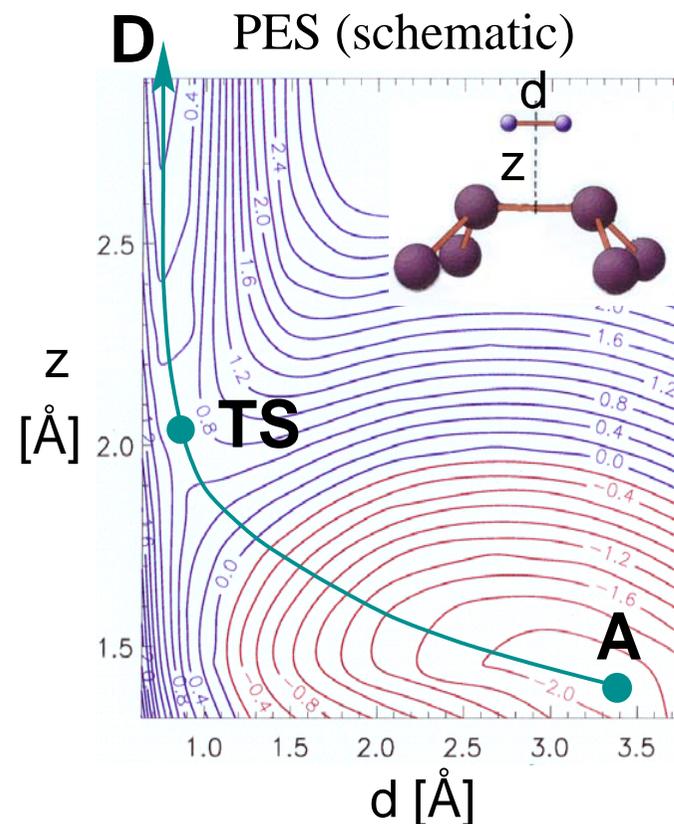
- **analyse electronic structure**
  (learn about bond breaking
  and forming mechanism)

- **molecular dynamics,
  quantum-mech. sticking calc.**
  (high-dimensional PES!)
  A. Groß, Surf. Sci. Rep. 32, 291 (1998).

Highly Reactive Sites for the Dissociative Adsorption of Hydrogen Molecules on Partially H-Precovered Si(001)
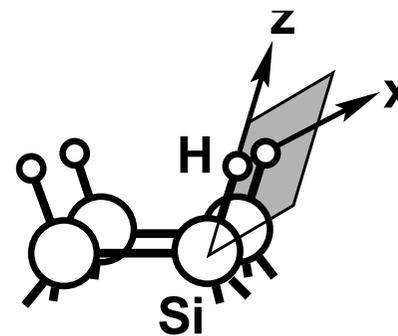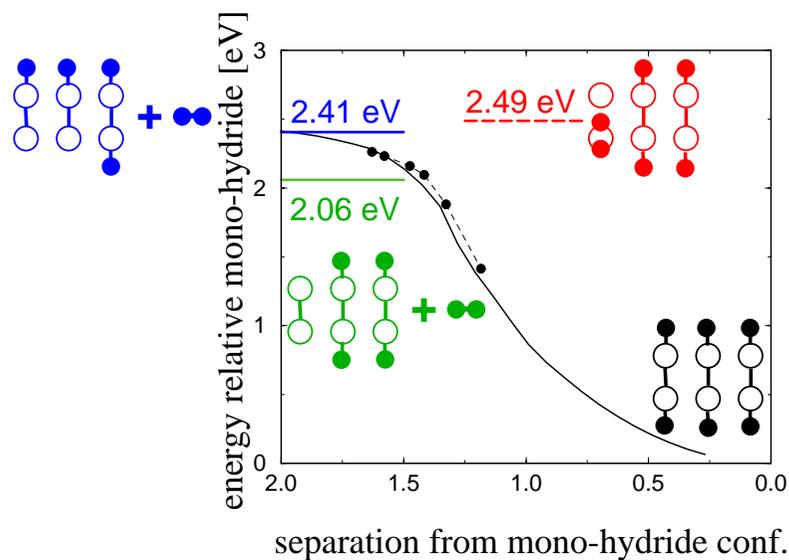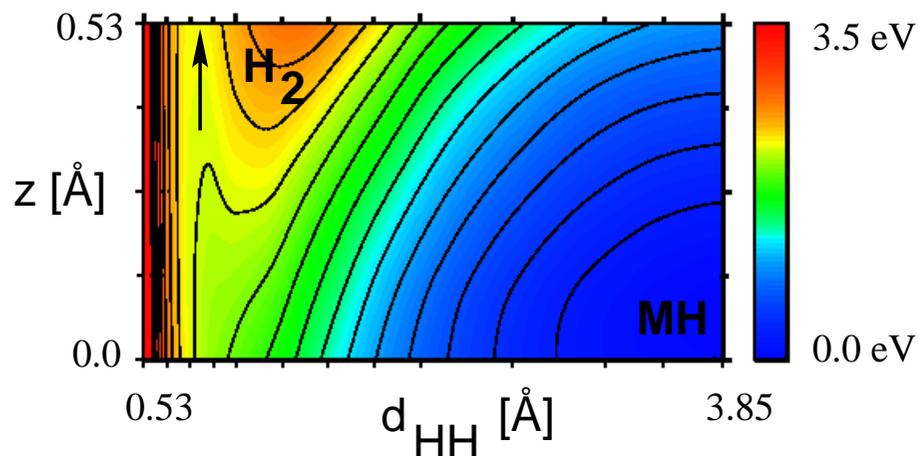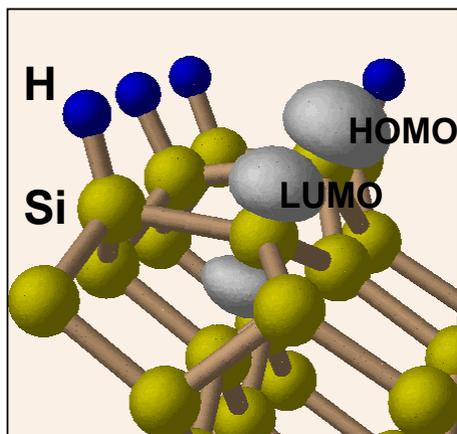
- **Reaction path without adsorption energy-barrier for H4 site.**

- **Comparative study of adsorption sites with fewer pre-adsobed H atoms:**
  Existence of small adsorption energy barriers for H3 and H2 sites (inter-dimer paths).

Things to Keep in Mind ...

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

J.A. Steckel, T. Phung, K.D. Jordan, P. Nachtigall, J. Phys. Chem. B 105, 4031 (2001).

(1) Cluster size convergence:

Si clusters with >= 3 surface dimers should be used.

(2) Semi-local approximation to XC functional (PW91) is not sufficiently accurate for H$_2$/Si reaction barriers.

Current QMC calculations by S. Healy, C. Filippi for the inter-dimer TS (with PW91 geometries):

QMC: E(rxn) ~ 2.4 eV,   E(TS) ~ 3.0 eV, E(ads) ~ 0.6 eV

PW91: E(rxn) = 1.95 eV, E(TS) = 2.15 eV, E(ads) = 0.2 eV

PW91 calculations are nevertheless usefull to compare between various reaction paths!

H$_2$/Si(001) intra-dimer path

Legend:
- E_{des}, PW91 (Penev et al.)
- E_{des}, PW91 (Steckel et al.)
- E_{des}, B3LYP (")
- E_{rxn}, PW91 (")
- E_{rxn}, B3LYP (")

energy [eV]: 3.30, 2.80, 2.30, 1.80

desorption barrier

reaction energy

cluster size: Si9, Si15, Si21, slab

(3) Correct reaction energies and barriers for zero-point vibrations.

E.g., decrease reaction energy by 0.2 eV (Steckel et al.).

(4) Be aware of different reaction paths.

Different reaction paths for dissociative adsorption of hydrogen molecules on Si surfaces.
Reaction barriers influenced by electronic and geometric effects!
Dramatic increase of reactivity at steps and on partially H-precovered surfaces.