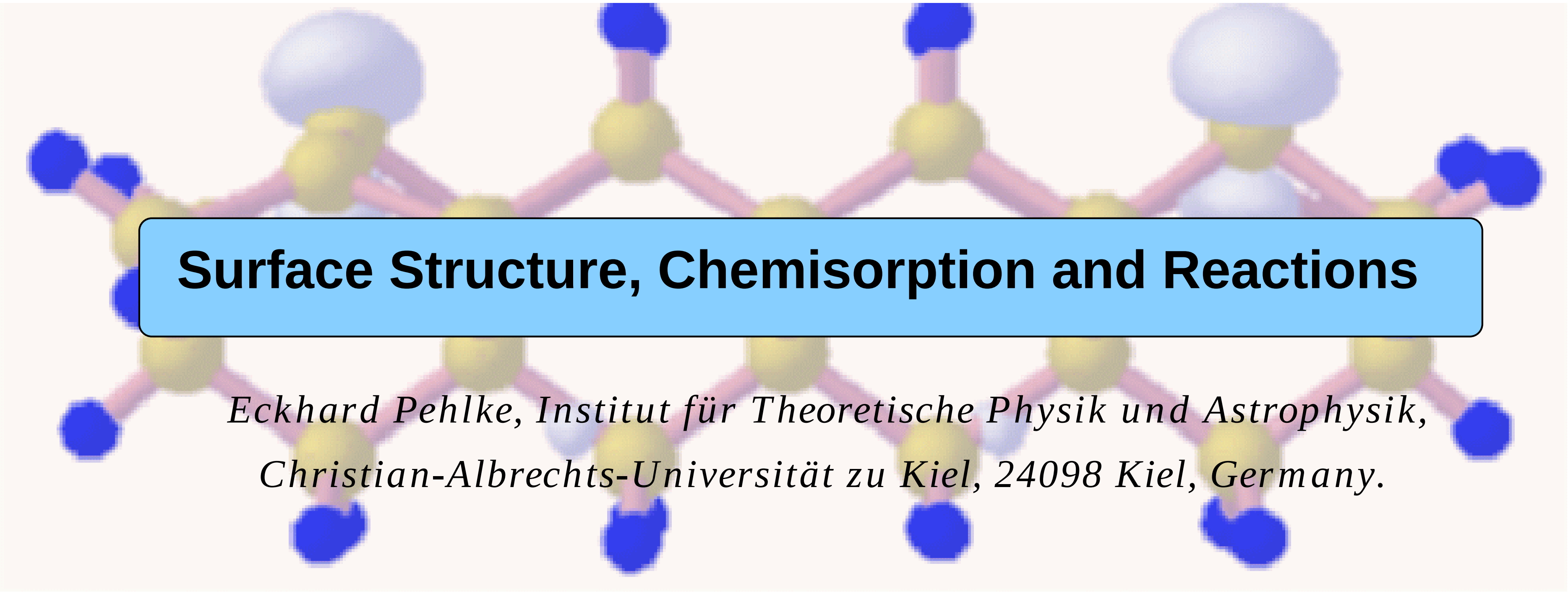


Surface Structure, Chemisorption and Reactions

Eckhard Pehlke, Institut für Theoretische Physik und Astrophysik,
Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany.

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
- (iv) chemisorption dynamics and energy dissipation: electronically non-adiabatic processes

Technological Importance of Surfaces

Solid surfaces are intriguing objects for basic research,

and they are also of high technological utility:

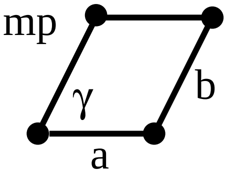
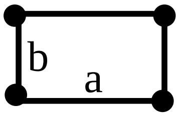
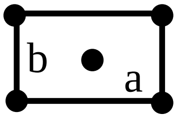
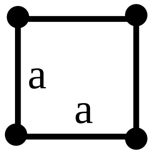
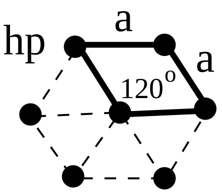
- substrates for homo- or hetero-epitaxial growth of semiconductor thin films used in device technology
- surfaces can act as heterogeneous catalysts, used to induce and steer the desired chemical reactions

Sect. I:

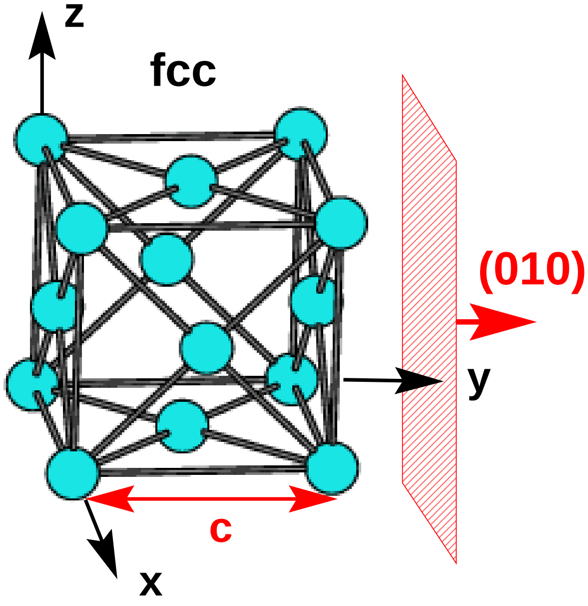
The Geometric and the Electronic Structure of Crystal Surfaces

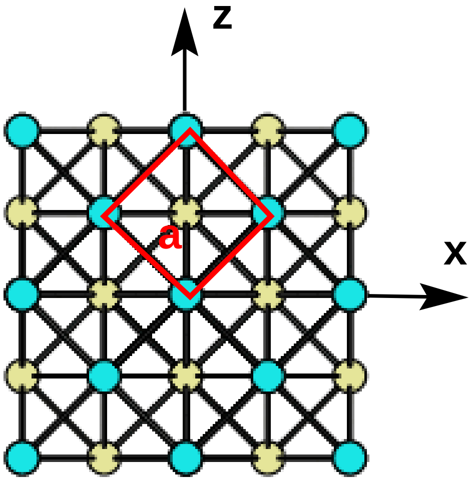
Surface Crystallography

	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 (monoclin)	a, b, γ	mp 	2	1 $\boxed{2}$
rectangular	o (orthorhombic)	a, b $\gamma = 90^\circ$	op  oc 	7	m $\boxed{2mm}$
square	t (tetragonal)	a = b $\gamma = 90^\circ$	tp 	3	4 $\boxed{4mm}$
hexagonal	h (hexagonal)	a = b $\gamma = 120^\circ$	hp 	5	3 6 3m $\boxed{6mm}$

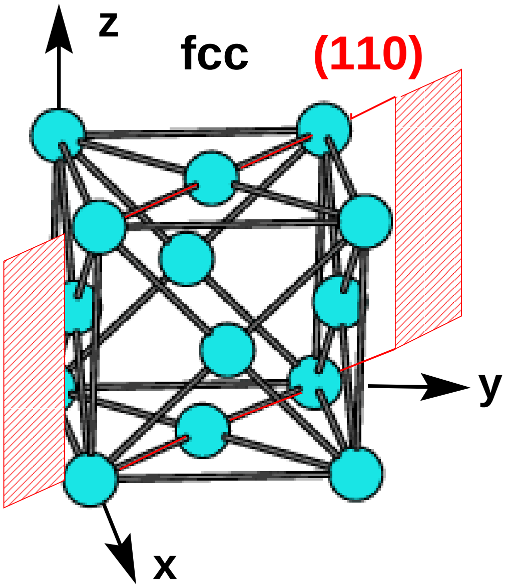
Bulk Terminated fcc Crystal Surfaces

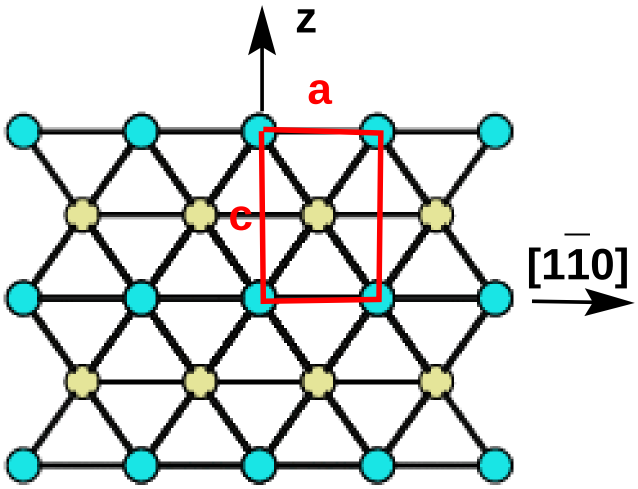




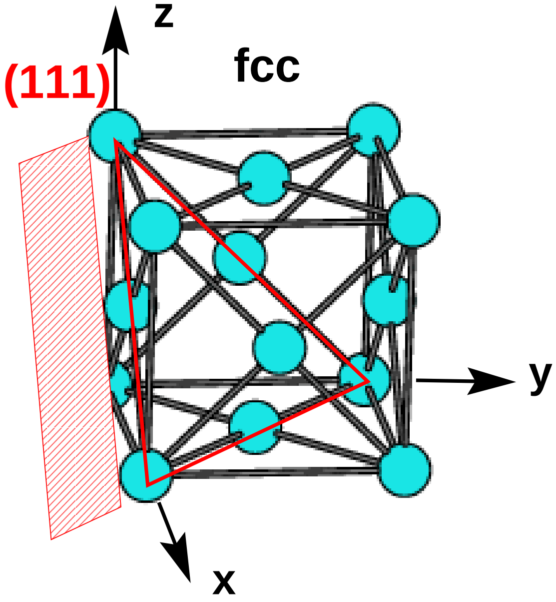
$a=c/\sqrt{2}$

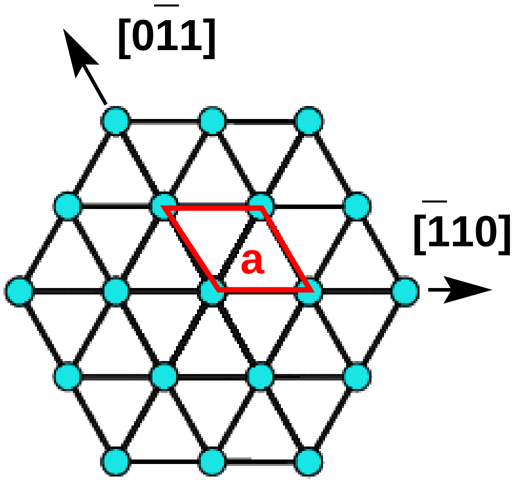
square lattice (tp)





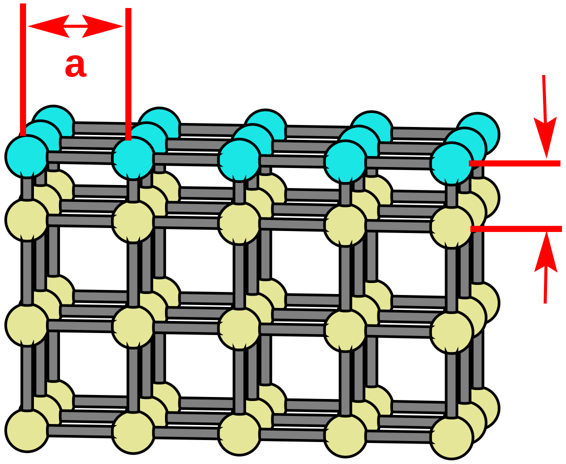
rectangular lattice (op)





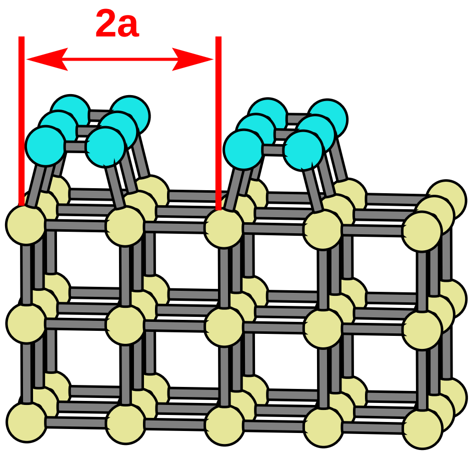
hexagonal lattice (hp)

Surface Atomic Geometry



normal

relaxation

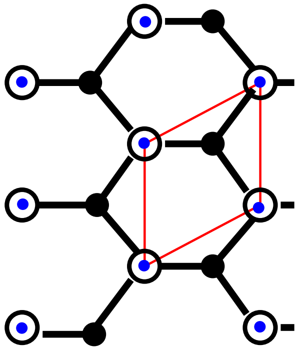


(2x1)

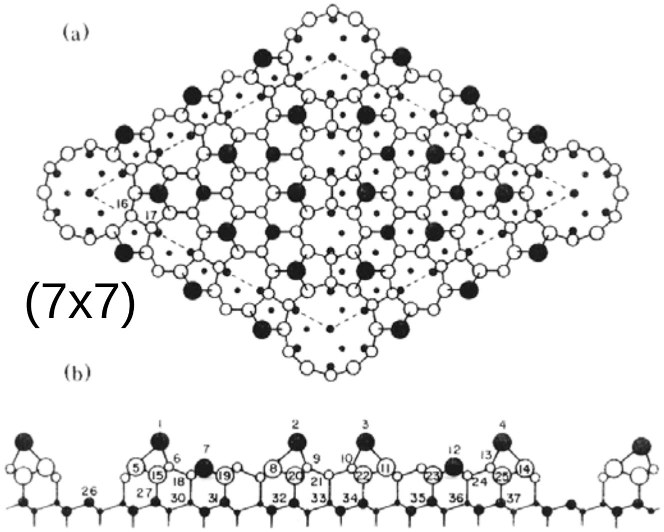
reconstruction

Examples:

H/Si(111)



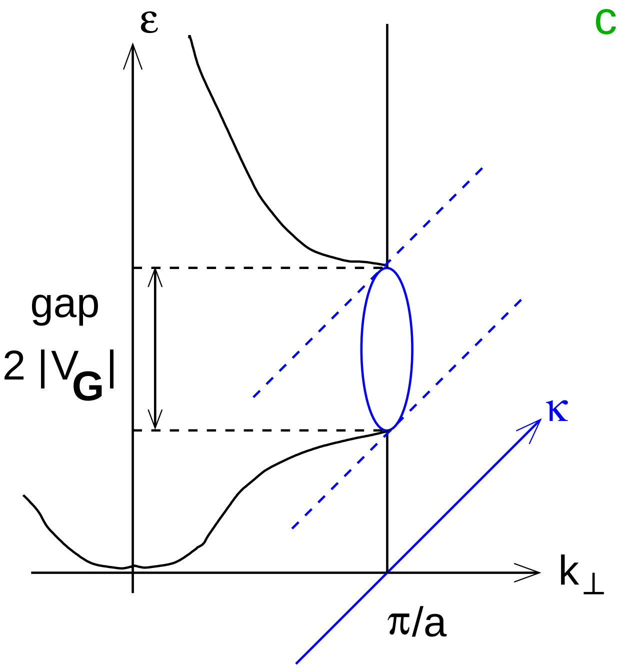
Si(111) (7x7)



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

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

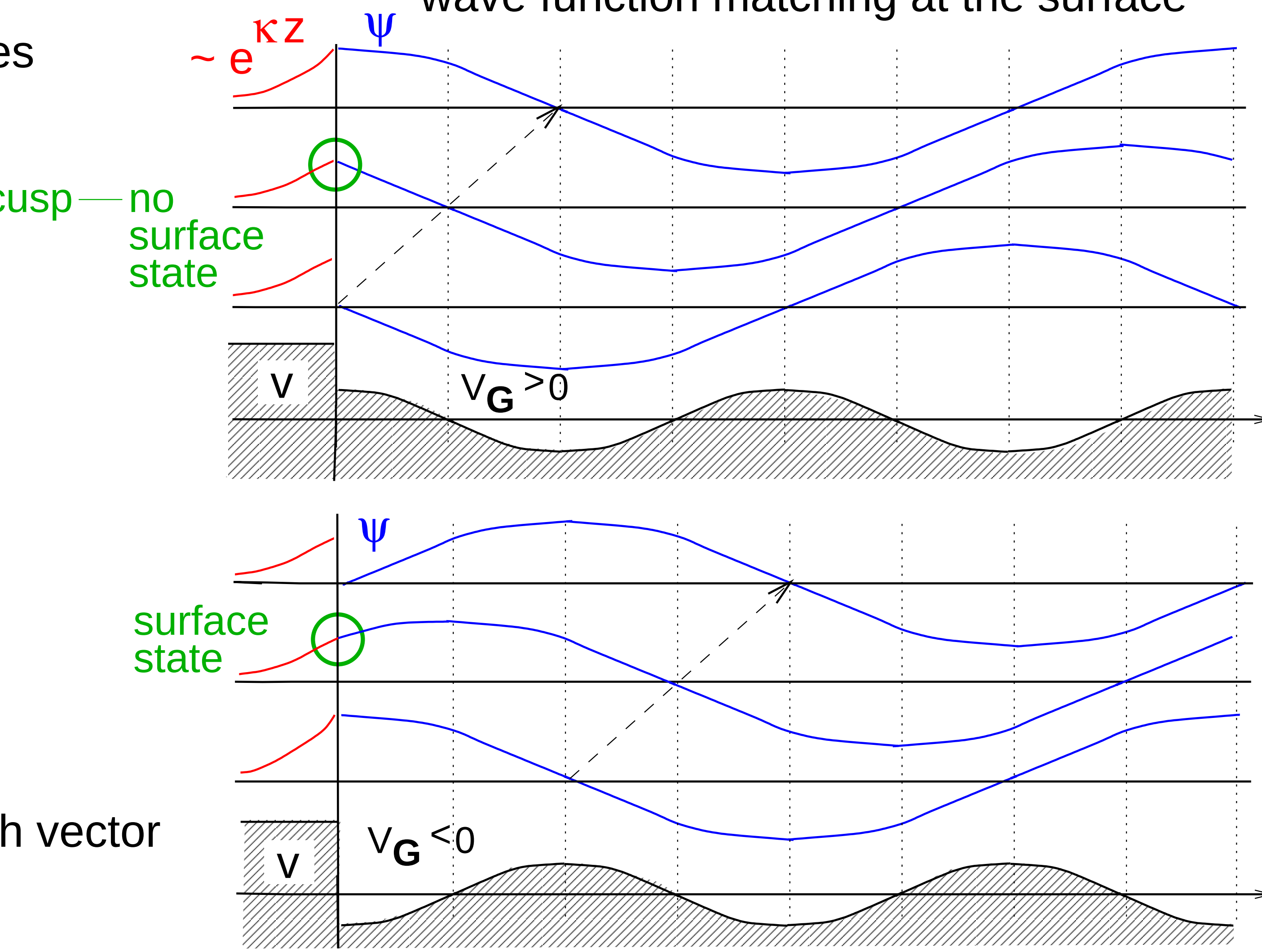
virtual induced gap states
bridge the band gap



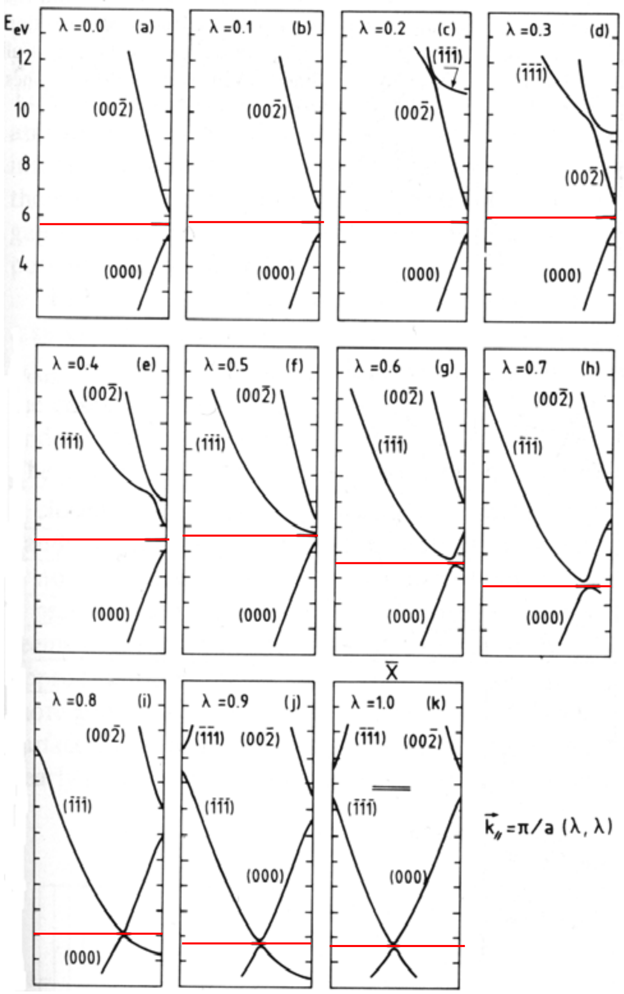
real energy,complex Bloch vector

$$e^{i(k_\perp + i\kappa)z}$$

wave function matching at the surface

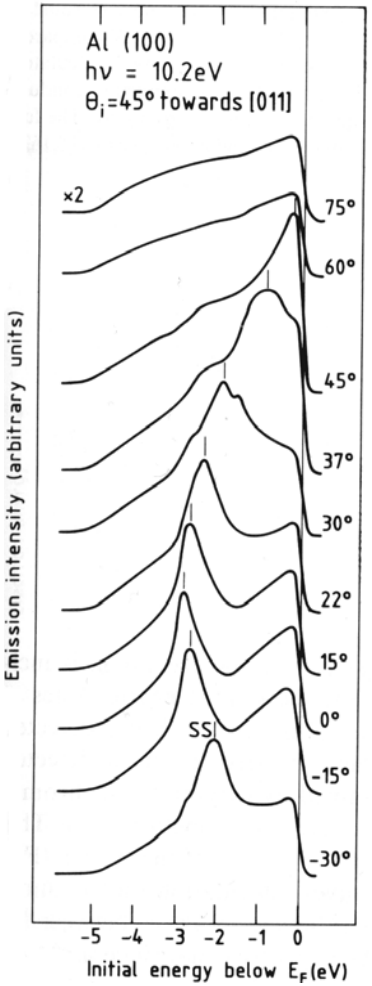


The Al(100) Surface State

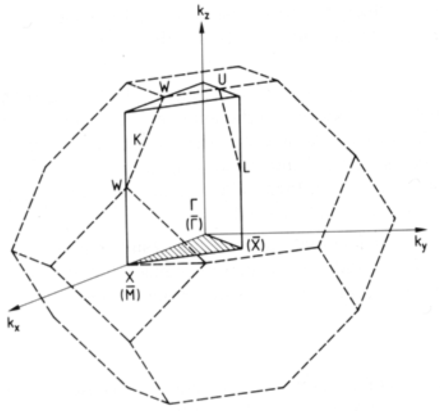


bulk band structure for wave-vector perpendicular to the surface

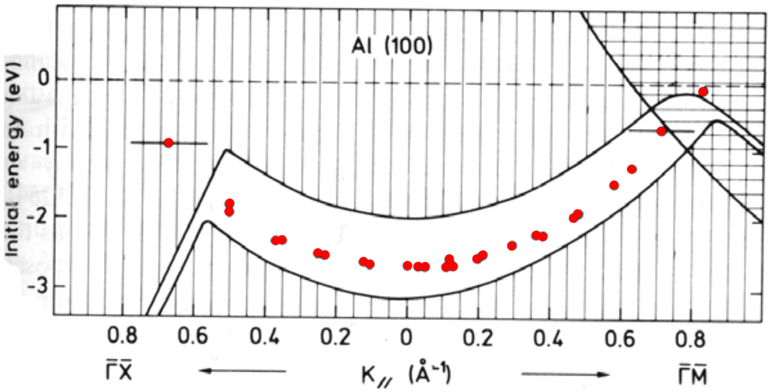
D. Spanjaard et al., Phys. Rev. B 19, 642 (1979).



ARUPS spectra exit angle in (01$\bar{1}$)



BZ of fcc lattice

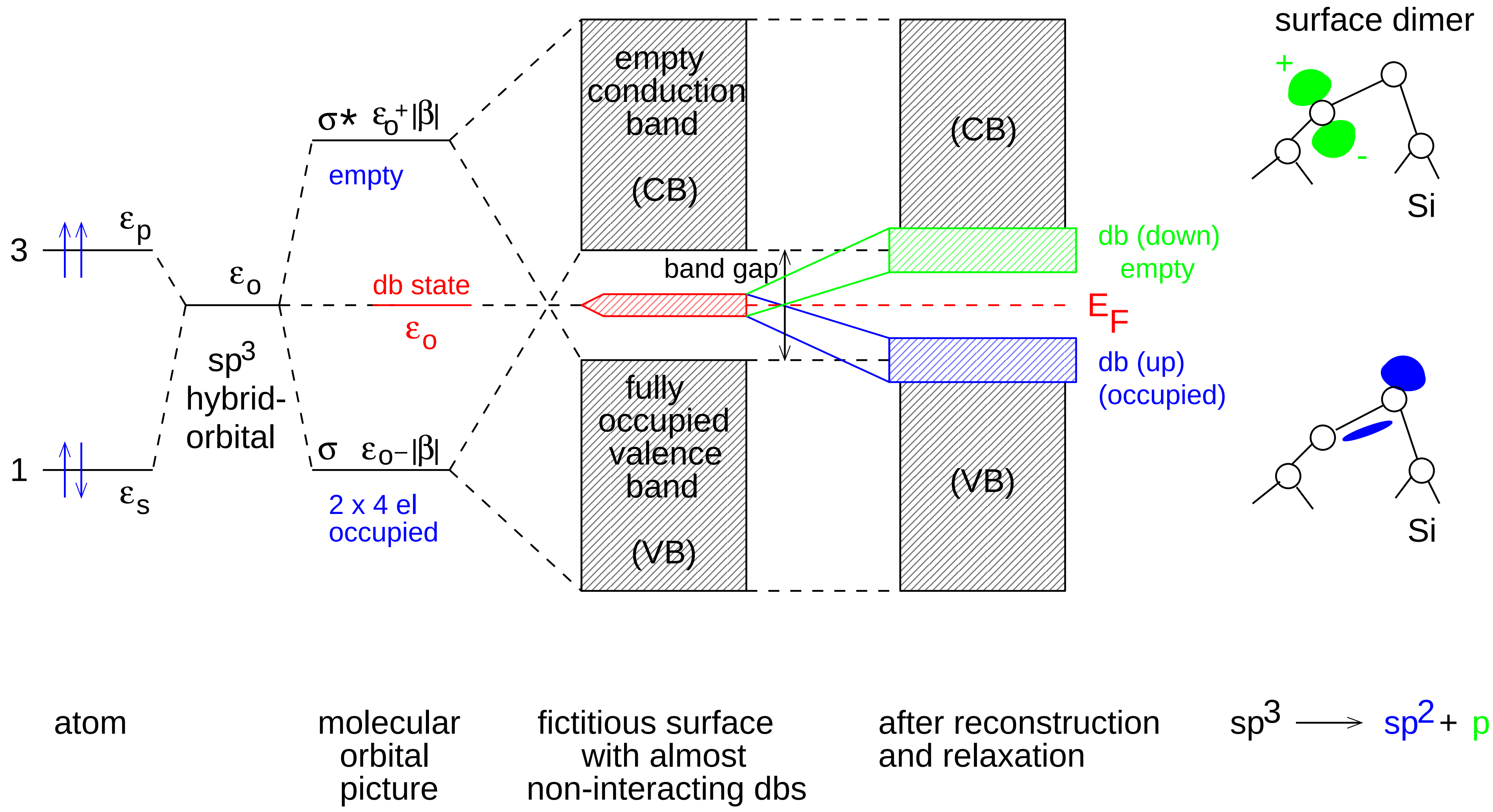


Al(100) surface state in the projected band structure

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)



3 ε_p

1 ε_s

ε_o

sp^3 hybrid-orbital

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

empty

db state

ε_o

σ $\varepsilon_o-|\beta|$

2 x 4 el occupied

empty conduction band

(CB)

band gap

fully occupied valence band

(VB)

(CB)

(VB)

db (down) empty

E_F

db (up) (occupied)

surface dimer

+

-

Si

Si

atom

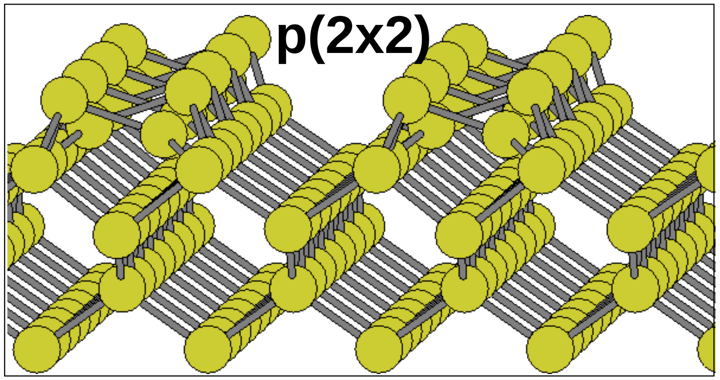
molecular orbital picture

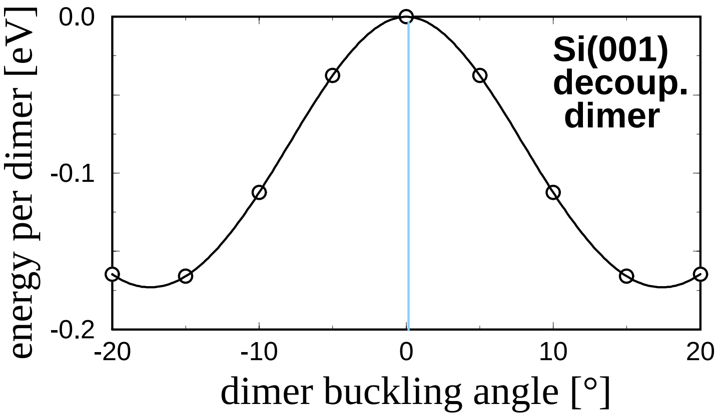
fictitious surface with almost non-interacting dbs

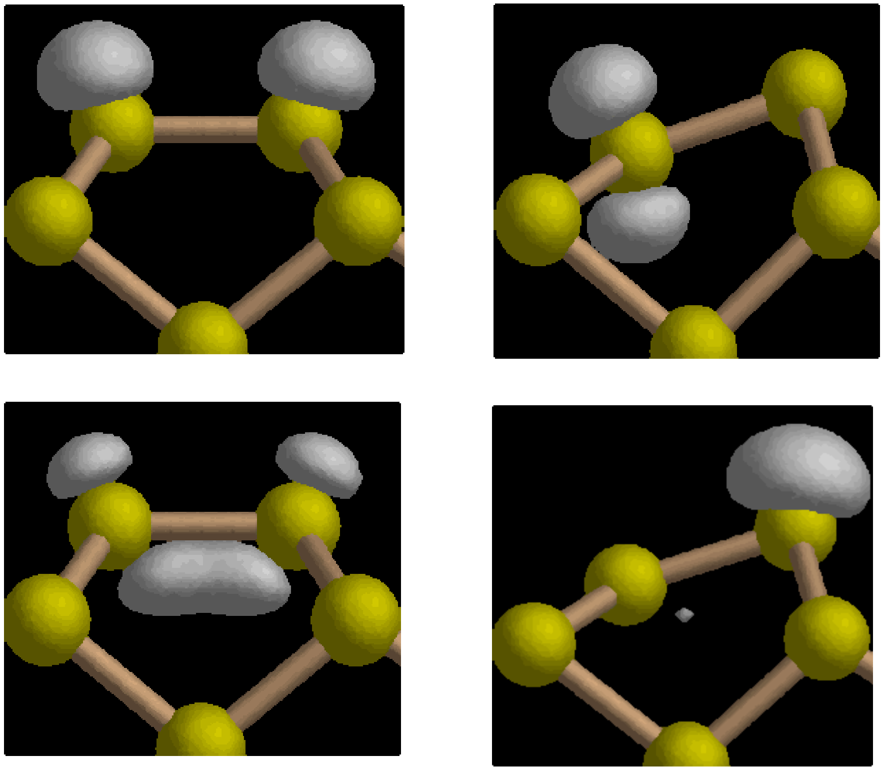
after reconstruction and relaxation

$sp^3 \longrightarrow sp^2 + p$

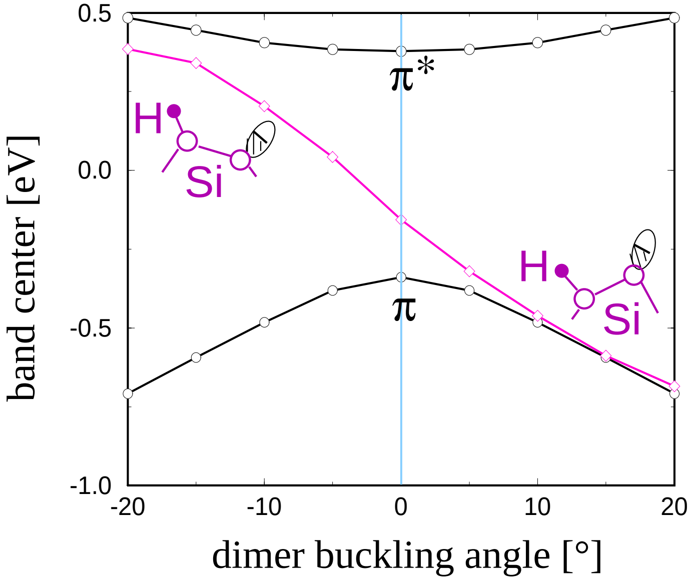
Interplay of the Atomic and Electronic Structure of Si(001)







lowest unoccupied surface state (LUMO)



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 Thermodynamic Stability of Facets

(1) **Definition:** γ = excess free energy of a surface per surface area

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

(i) slab with equivalent surfaces:

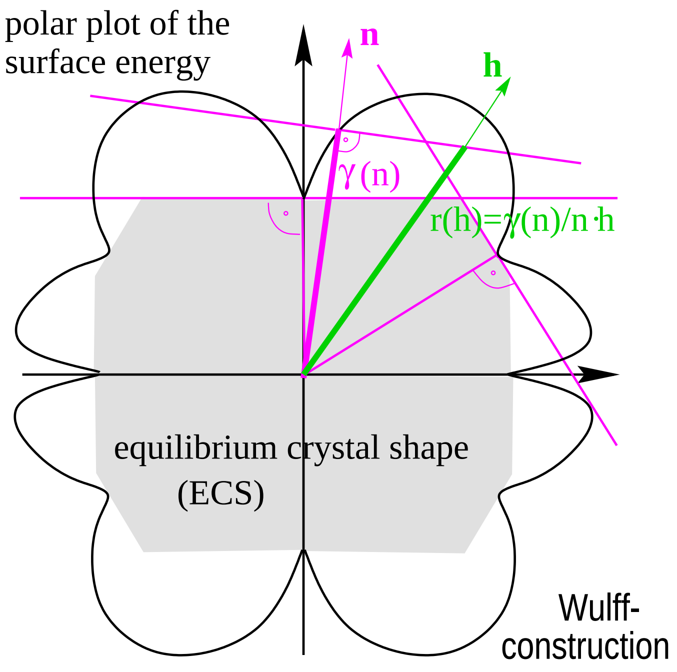
$$\gamma = \frac{1}{2A}\{E(N_1,\ldots) - \sum_{\text{all species } i} N_i\,\mu_i\}$$

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

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

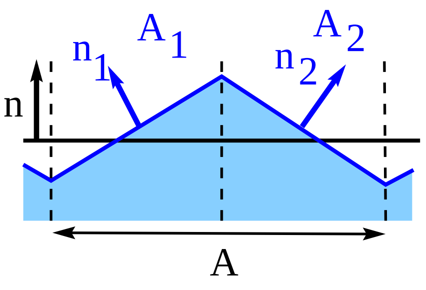
(3) **equilibrium crystal shape (ECS)**

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

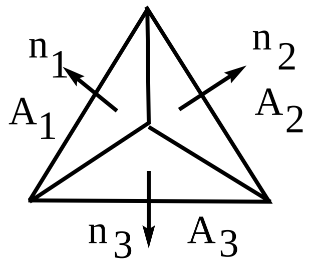


(4) **Application: facet formation**

thermodynamic stable surface orientations



(a) side view

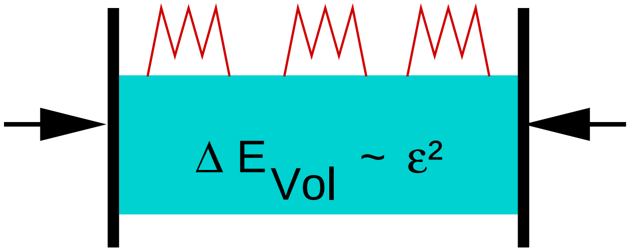


(b) top view

Surface Stress Tensor

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

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



($\sigma_{xx} > 0$ tensile: $\varepsilon_{xx} < 0$ => $\Delta E_{\mathrm{surf}} < 0$, preference for contraction,

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

Relation to surface energy:

$$\sigma_{ij} = \gamma\delta_{ij} + \frac{\partial\gamma}{\partial\varepsilon_{ij}}$$

(different from liquids!)

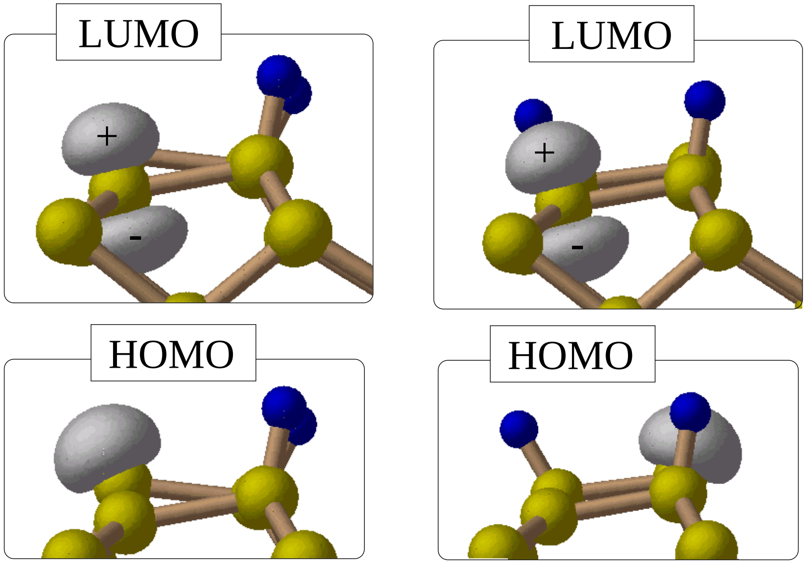
Application:

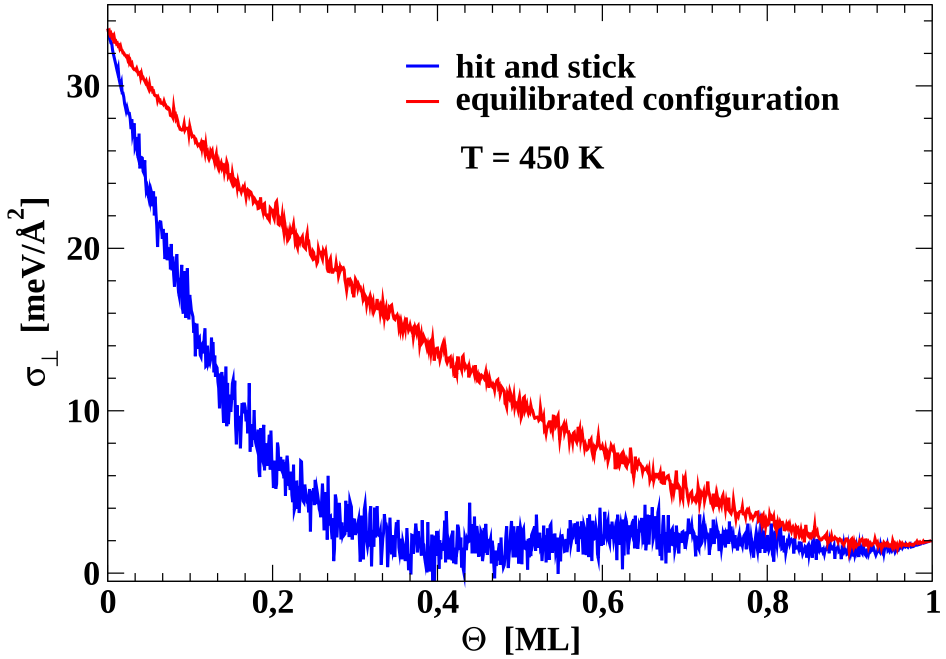
Force density on a surface:

$$\mathbf{f}(\mathbf{x}) = \mathrm{div}\ \sigma(\mathbf{x})$$

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

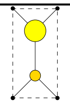
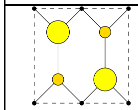
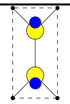
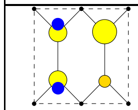
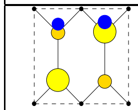
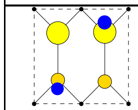
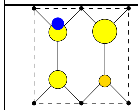
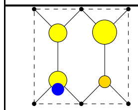
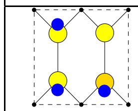
Surface Stress Variation Induced by Surface Reactions





J. van Heys, E.P., unpublished.

partially H-covered Si(001)

surface	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\Delta\sigma$	$\frac{(\sigma_{\parallel}+\sigma_{\perp})}{2}$	ΔE
	meV/Å²				meV/p(2x2)
	$84_{\pm 7}$	$-12_{\pm 7}$	$97_{\pm 4}$	36	2×90
	$77_{\pm 7}$	$38_{\pm 7}$	$37_{\pm 4}$	58	Ref.
	$72_{\pm 7}$	$2_{\pm 7}$	$70_{\pm 4}$	37	Ref.
	$70_{\pm 7}$	$-4_{\pm 7}$	$78_{\pm 4}$	33	60
	$60_{\pm 7}$	$29_{\pm 7}$	$31_{\pm 4}$	45	260
	$58_{\pm 7}$	$22_{\pm 7}$	$39_{\pm 4}$	40	460
	$60_{\pm 7}$	$1_{\pm 7}$	$57_{\pm 4}$	31	280
	$59_{\pm 7}$	$-50_{\pm 7}$	$107_{\pm 4}$	5	290
	$66_{\pm 7}$	$-2_{\pm 7}$	$75_{\pm 4}$	32	310

Sect. III:

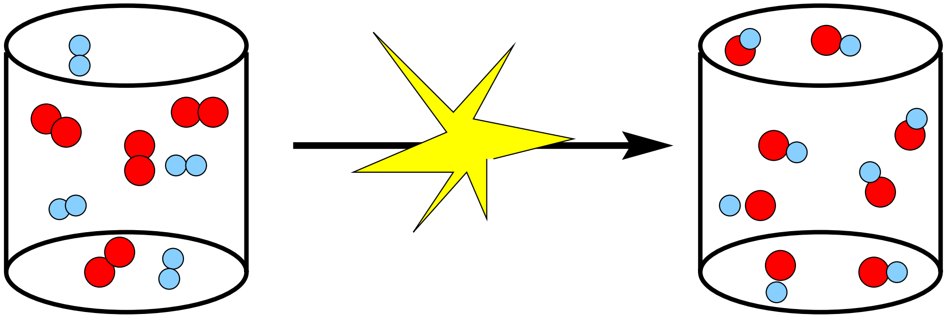
Chemisorption on Semiconductor Surfaces

Model System:

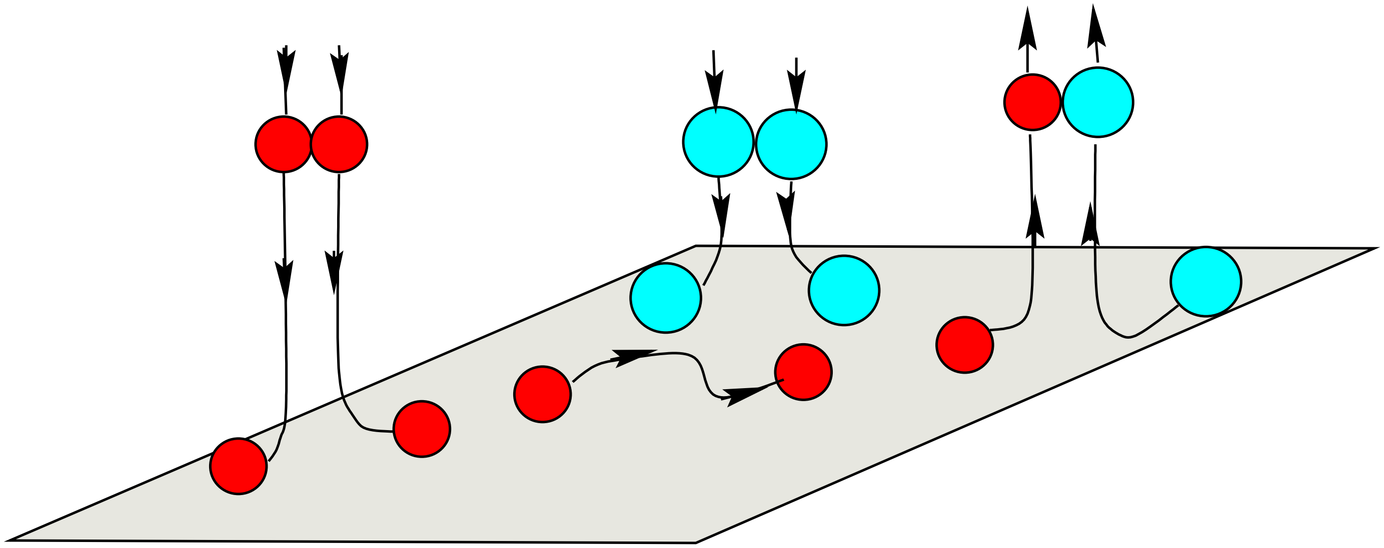
Dissociative Adsorption and Recombinative Desorption of Hydrogen Molecules on/from a Si(100) Surface

Surface Reactivity and Heterogeneous Catalysis

The rate of chemical reactions depends on the reaction energy-barriers along the reaction path:

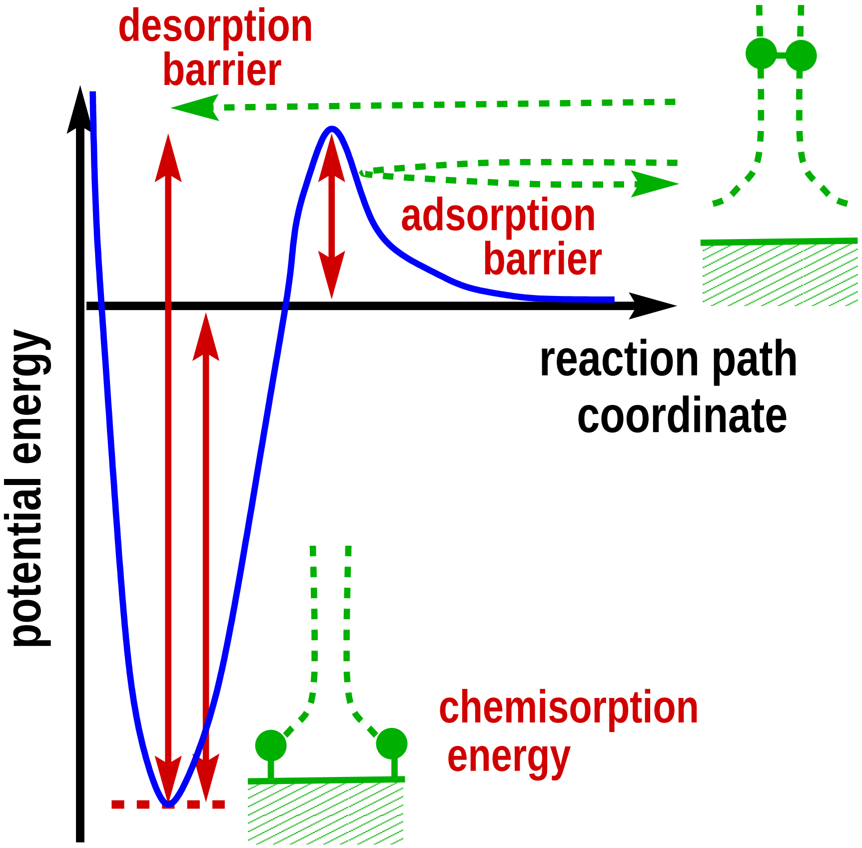


Dissociative adsorption and recombinative desorption of molecules on a solid surface are an essential step of heterogeneous catalysis:



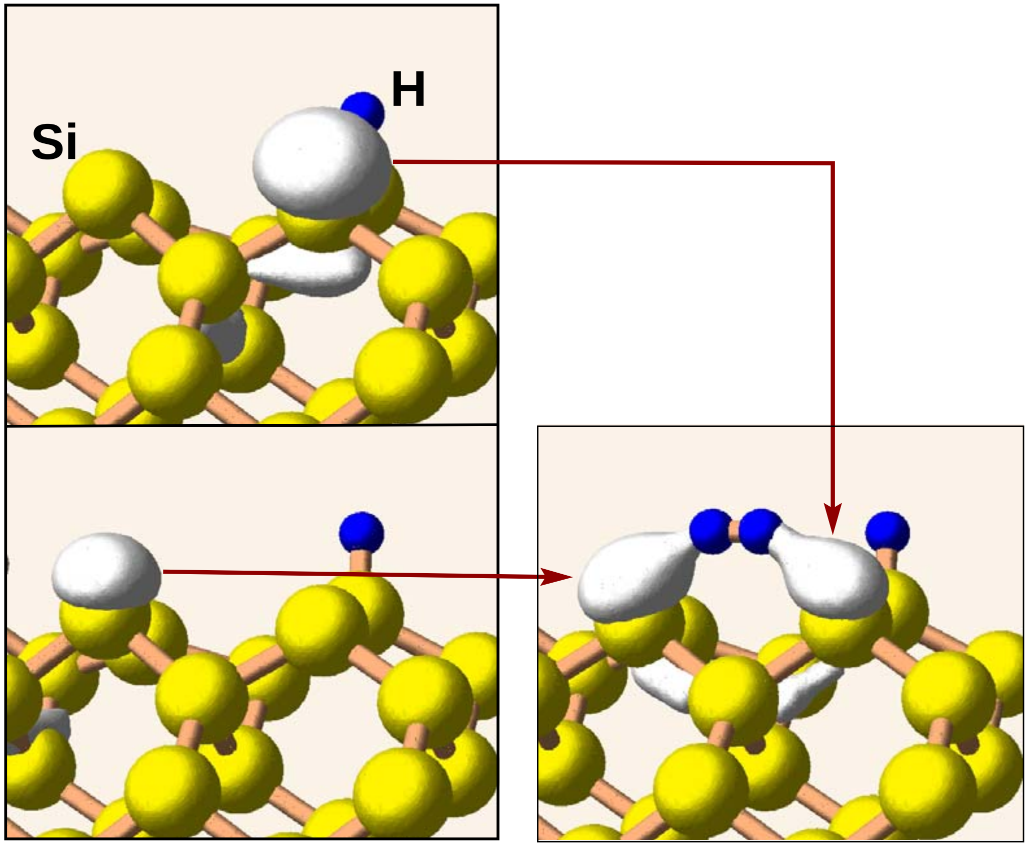
Langmuir-Hinshelwood mechanism

Dissociative Adsorption of a Molecule on a Solid Surface



potential energy
along the reaction path

hydrogen molecule / H-precovered Si(100)(2x2



electronic mechanism of bond
formation and breaking

DFT for Chemisorption: Reaction Path, PES, ...

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

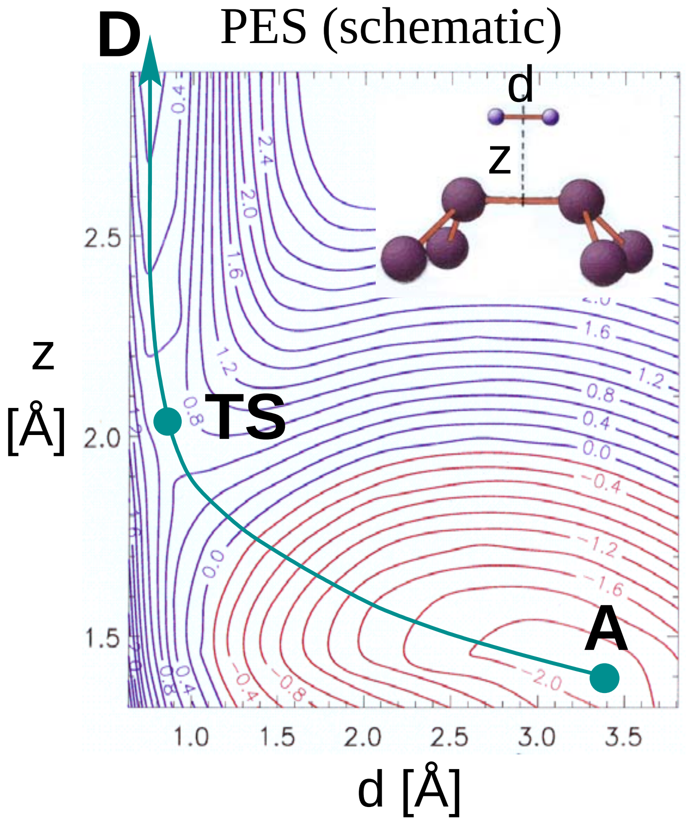
- **locate transition state**
  (automated search for special saddle points in the potential energy surface)

- **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")



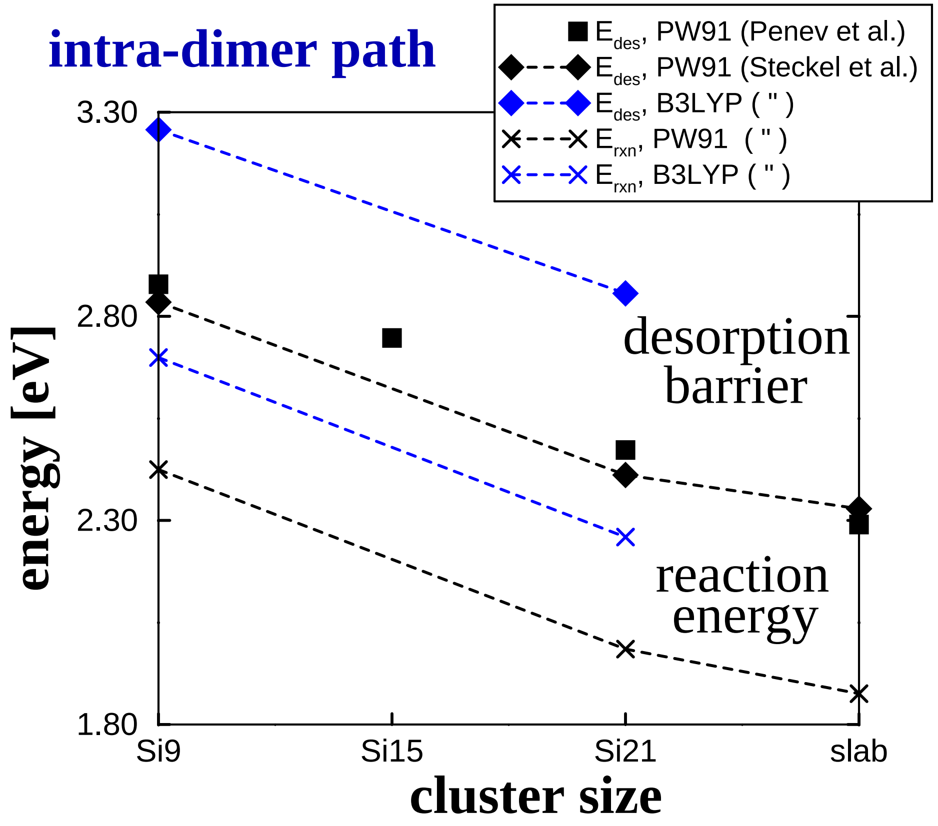
PES (schematic)

- **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).

Calculation of Chemical Reactions: Things to Keep in Mind

(1) Cluster size convergence: at least 3 surface Si-dimers should be used.



H_2/Si(001)

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).

Calculation of Chemical Reactions: Things to Keep in Mind

(2) Quantum Monte-Carlo calculations for H_2/Si(100) clusters:

PW91 not sufficiently accurate.

(but still useful, e.g to compare between various reaction paths!)

C. Filippi, S.B. Healy, P. Kratzer, E.P., M. Scheffler, Phys. Rev. Lett. 89, 166102 (2002).

inter-dimer reaction path (H2),
PW91-geometry, no ZPE:

	chemisorption energy	adsorption energy barrier
PW91 slab	1.95 eV	0.2 eV
PW91 cluster	1.99 eV	0.26 eV
QMC cluster	2.5 eV	0.6 eV

QMC-corrected, incl. approx. ZPE:

	chemisorption energy	adsorption energy barrier
intra-dimer H2*	2.20(5) eV	0.75 eV
inter-dimer H2	= 2.28(9) eV	0.63 eV
expt. (Höfer et al.)	1.95(25) eV	> 0.6 eV

(experimental desorption energy barrier: 2.5 eV)

(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 are influenced by electronic and geometric effects.
Dramatic increase of reactivity at steps and on partially H-precovered Si(001) surfaces.

Sect. IV:

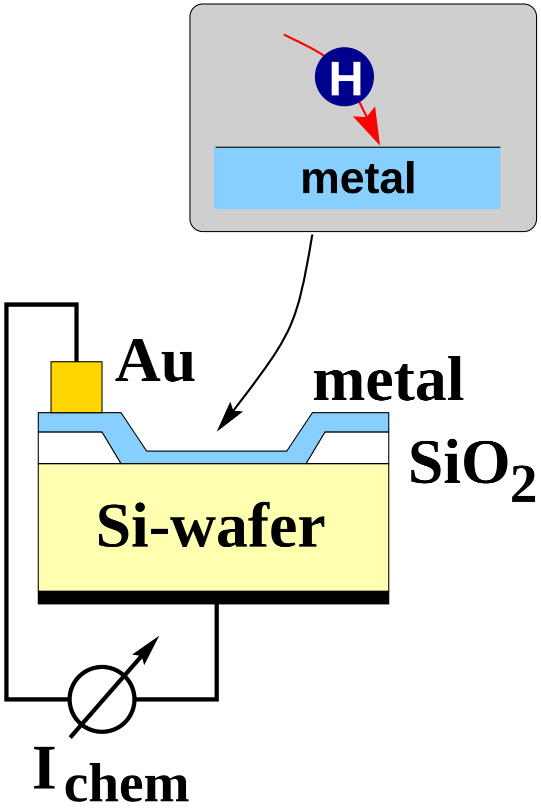
Molecular Dynamics of

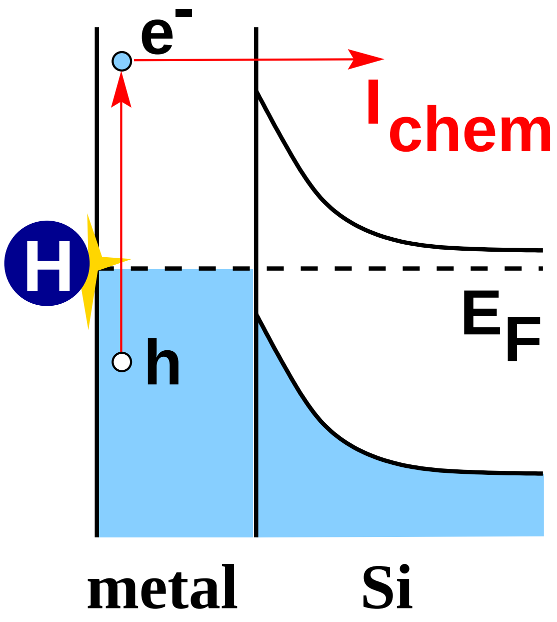
Electronically Non-Adiabatic Processes

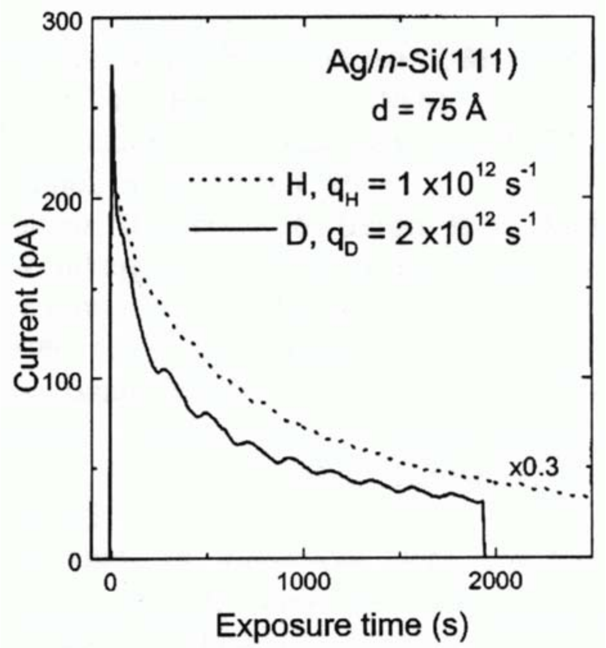
Time-Dependent DFT

Electron-Hole Pair Creation by Chemisorption: Experimental Evidence

- chemo-luminescence
- exo-electron emission
- chemicurrent



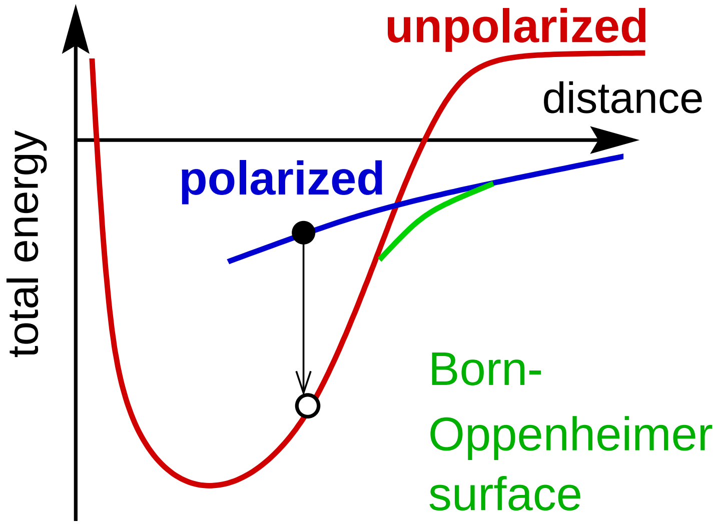


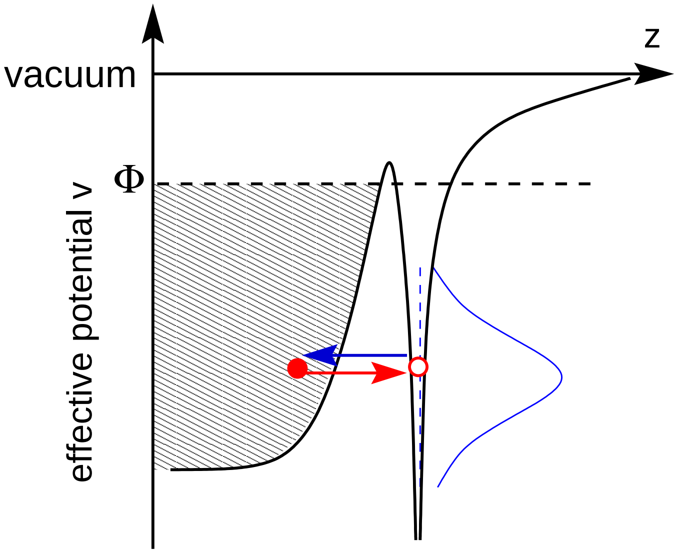


H. Nienhaus et al., PRL 82, 446 (1999).
H. Nienhaus, Surf. Sci. Rep. 45, 1 (2002).

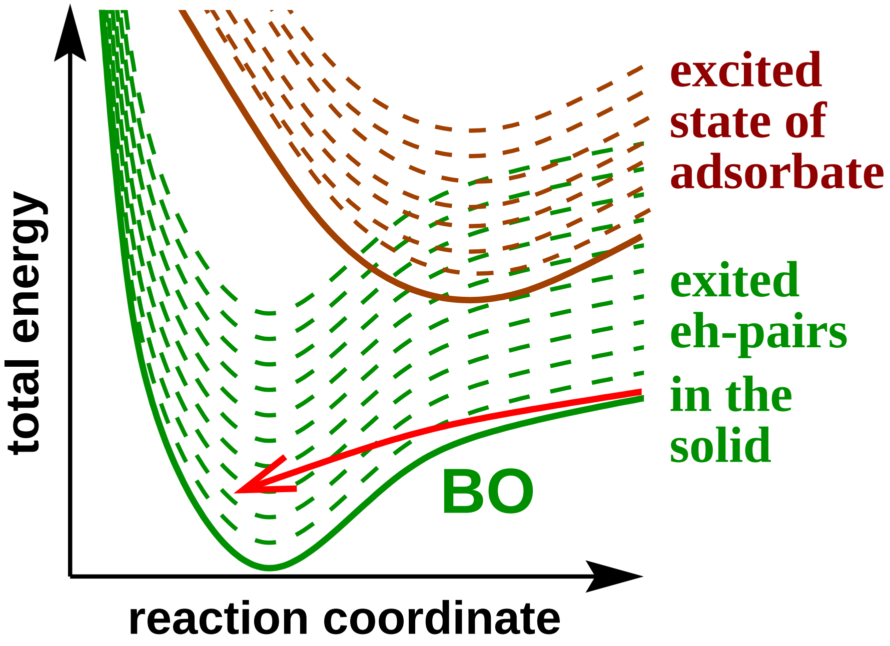
Mechanism of Electron-Hole Pair Excitation

loss of spin polarisation: slow tunneling process





electronic friction



direct molecular dynamics simulation of combined motions of electrons and ions

See also: J.R.Trail et al. PRL 88, 166802 (2002).

Simulation of the Combined Motion of Electrons and Ions

- time-dependent electron density from self-consistent solution for a system of non-interacting fermions (E. Runge, E.K.U. Gross, W. Kohn):

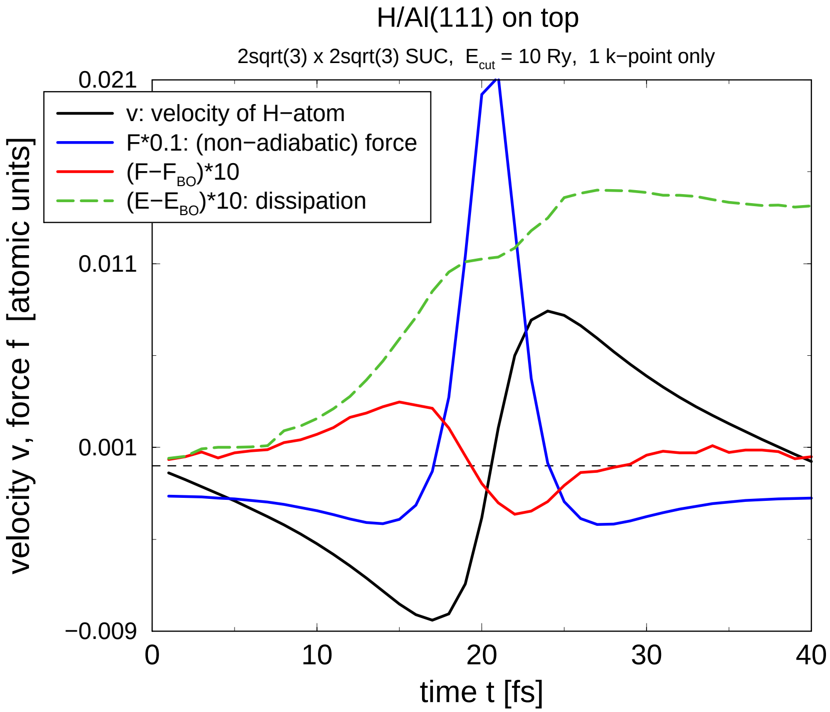
$$\boxed{\begin{aligned} i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) &= -\frac{1}{2}\nabla^2\phi_j(\mathbf{r},t) + v_{\text{eff}}([n];\mathbf{r},t)\phi_j(\mathbf{r},t) \\ n(\mathbf{r},t) &= \sum_{j\ \text{occ.}} |\phi_j(\mathbf{r},t)|^2 \\ v_{\text{eff}}([n];\mathbf{r},t) &= v(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' + \frac{\delta A_{\text{XC}}[n]}{\delta n(\mathbf{r},t)} \end{aligned}}$$

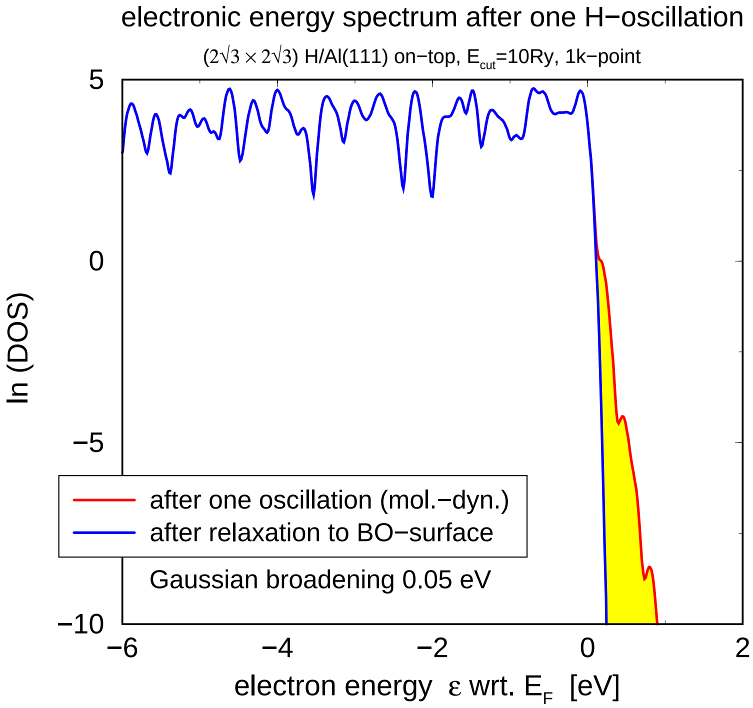
- adiabatic approx. for exchange and correlation (on top of LDA, GGA):

$A_{\text{XC}}^{\text{ALDA}}[n] := \int_{t_0}^{t_1} dt \int d^3\mathbf{r}\ n(\mathbf{r},t)\ \varepsilon_{\text{XC}}^{\text{hom}}(n(\mathbf{r},t))$, thus $\boxed{\frac{\delta A_{\text{XC}}^{\text{hom}}[n]}{\delta n(\mathbf{r},t)} = v_{\text{XC}}^{\text{LDA}}(n(\mathbf{r},t))}$.

- motion of ions treated classically (Newton’s equation of motion) no entangled states

H/Al(111) On-Top Adsorption: Electronic Friction





Dissipate of the order of 36 meV during the first H-oscillation into electron-hole pair excitations.

Simulations computationally rather demanding. Convergence has to be improved.