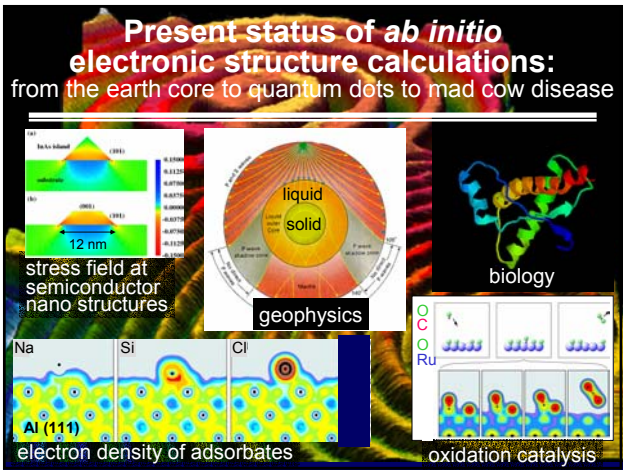
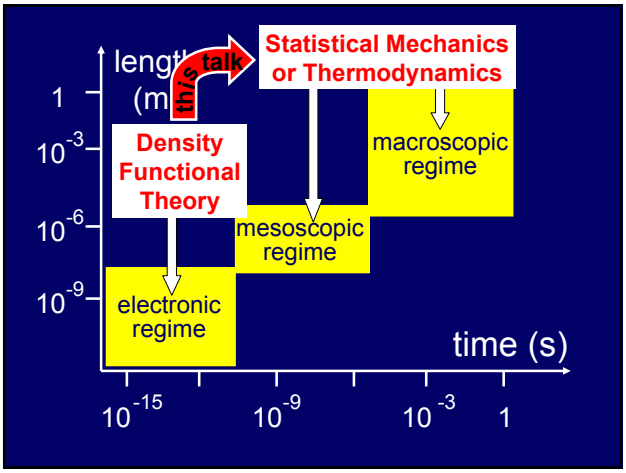
Present status of *ab initio* electronic structure calculations:

from the earth core to quantum dots to mad cow disease





Density functional theory

The energy of the ground state of a many-electron system : $E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_{\Psi} \langle\Psi|H^e|\Psi\rangle$

Hohenberg and Kohn (1964): The functional

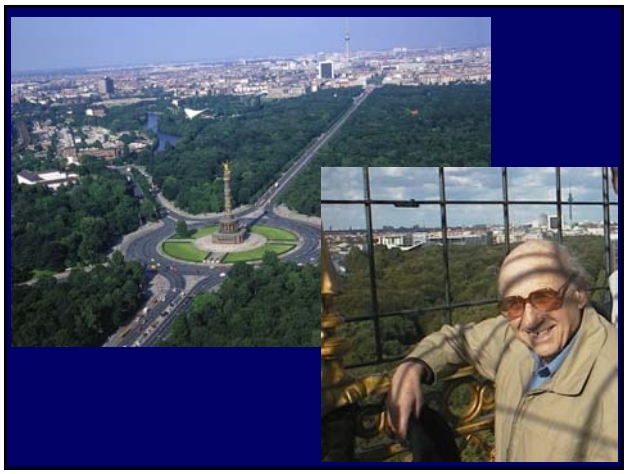
$$n(\mathbf{r}) = n[\Psi] = \langle\Psi| \sum_i \delta(\mathbf{r}-\mathbf{r}_i) |\Psi\rangle$$

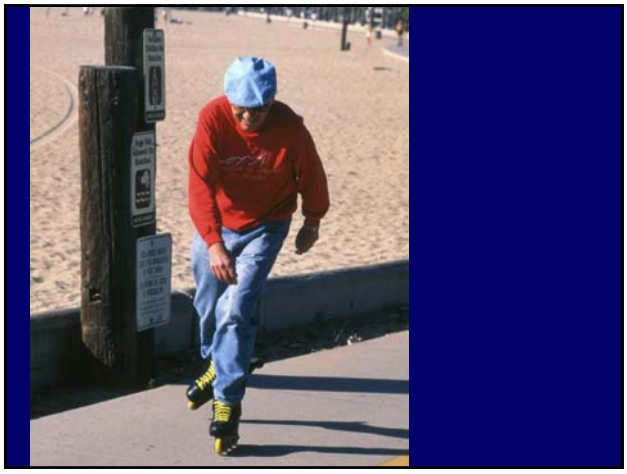
can be inverted, *i.e.*,

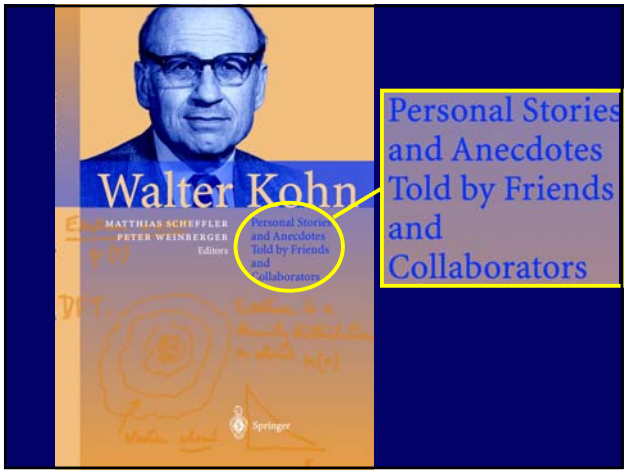
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi[n(\mathbf{r})] \ .$$

This implies:

$$E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_{n(\mathbf{r})} E_{\{\mathbf{R}\}}[n]$$






Walter Kohn
MATTHIAS SCHEFFLER
PETER WEINBERGER
Editors
Personal Stories and Anecdotes Told by Friends and Collaborators
Springer
Personal Stories and Anecdotes Told by Friends and Collaborators

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This implies:

$$E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_{n(\mathbf{r})} E_{\{\mathbf{R}\}}[n]$$

Kohn and Sham (1965):

$$E_{\{\mathbf{R}_I\}}[n] = T_s[n] + \int d^3r \ v^{\mathrm{nuc}}_{\{\mathbf{R}_I\}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2}\int\int d^3r d^3r' \ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E^{\mathrm{xc}}[n]$$

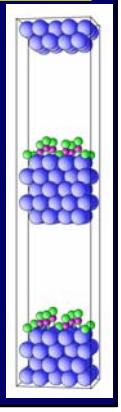
with **local-density approximation**
or **generalized gradient approximation**

Accuracy of geometries is better than 0.1 Å. Accuracy of calculated energies (relative) is better than 0.2 eV [for special cases better than 0.01 eV].

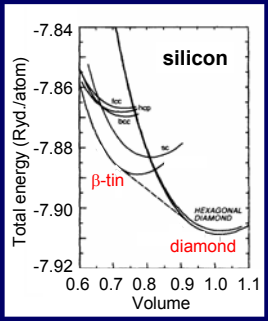
Methods

I
- **Density functional theory**
  - -- ***ab initio* pseudopotentials** (the fhi98md - code --- *www.fhi-berlin.mpg.de/th/th.html*)
  - -- **FP-LAPW** (the WIEN – code by *P. Blaha, K. Schwarz, et al.; M. Petersen et al., CPC **126** (2000)*)
  - -- **All-electron, numerical basis set** (the DMol^3 - code by B. Delley, *et al.*)

II
- ***ab initio* Molecular Dynamics**
- ***ab initio* Lattice Gas Hamiltonian**
- ***ab initio* kinetic Monte Carlo**
- **ab initio Quantum Dynamics**



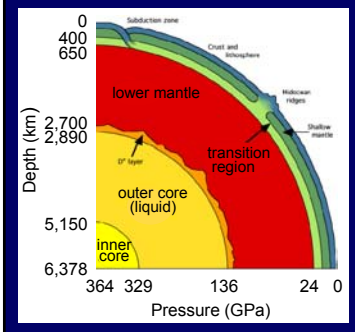
The first (convincing) DFT calculations:
Stability of crystals and crystal phase transitions

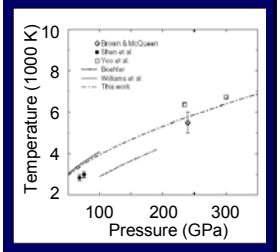


M. T. Yin and M. L. Cohen PRB 26 (1982)

see also: V.L. Moruzzi, J.F. Janak, and A. R. Williams Calculated Electronic Properties of Metals Pergamon Press (1978)

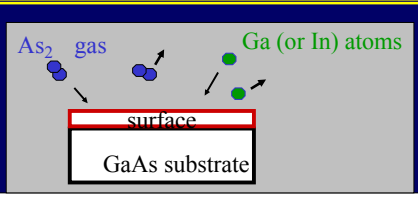
Ab initio melting curve of Fe as function of pressure





D. Alfe, M. J. Gillan, and G. D Price NATURE 401 (1999)

Microscopic processes controlling the growth -- Example: III-V semiconductors

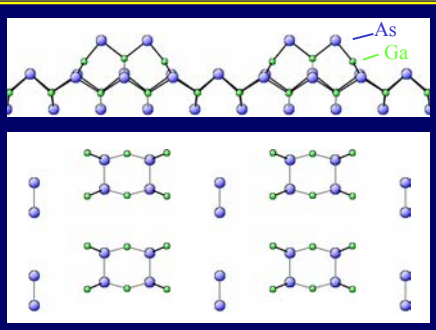


1) deposition of Ga and As
2) adsorption of Ga
3) diffusion of Ga
4) desorption of Ga
5) adsorption of As_2 ?
6) dissociation of As_2 ?
7) diffusion of As
8) desorption of As
9) island nucleation
10) growth

β2 Reconstruction of GaAs (001) (2x4) unit cell

side view

top view

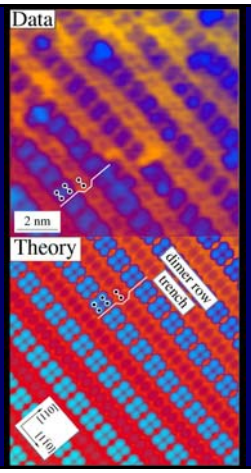


STM Imaging of GaAs(001)

measured filled state image at V_{tip}= - 2.1eV →

simulated image: local density of states integrated to 0.3 eV below the valence band maximum →

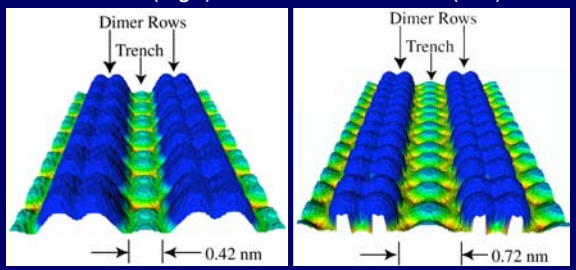
LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL 83, 2989 (1999).



Voltage Dependence of the STM Current

STM Simulation

-3.0 eV (high) -2.1 eV (low)

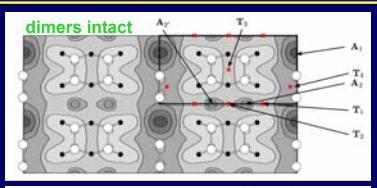


LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL 83, 2989 (1999).

Total Energy of a Diffusing Ga Atom at GaAs (001)

top view

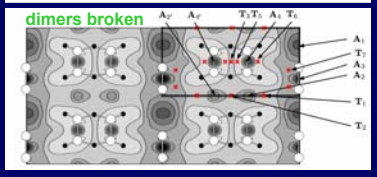
dimers intact



E_{A1} = -1.9 eV
E_{TS} = -1.5 eV

E_{A2} = -1.5 eV
E_{TS} = -1.3 eV

dimers broken



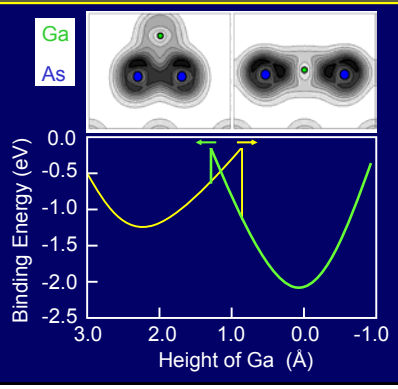
E_{A3} = -2.1 eV
E_{TS} = -1.3 eV

A. Kley, P. Ruggerone, and M.S., PRL 79 (1997)

[$\bar{1}$10]

[110]

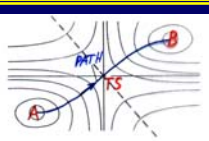
Unusually stable site for Ga adatom inside the trench-site As-dimer



A. Kley, P. Ruggerone, M.S., PRL 79 (1997)

P. Kratzer & M. S., to be published

Transition State Theory



Transition state theory

$$\Gamma = \frac{k_B T}{h} exp\left(\frac{-\Delta F}{k_B T}\right)$$

$$\Delta F = -k_B T \, ln Z_{TS} + k_B T \, ln Z_A$$

$$\Gamma = \Gamma_0 \, exp\left(\frac{-\Delta E}{k_B T}\right)$$

$$\Gamma_0 = \frac{k_B T}{h} \, exp\left(\frac{\Delta S^{vib}}{k_B} - \frac{\Delta U^{vib}}{k_B T}\right)$$

Theory of the kinetics of growth

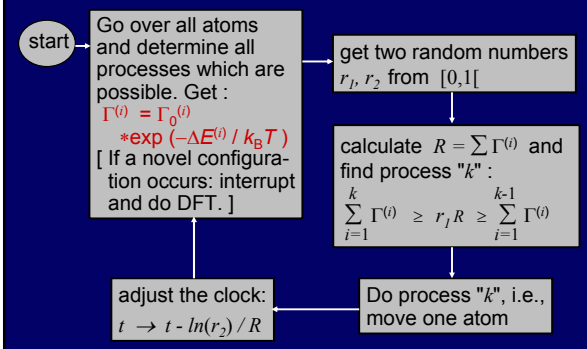
1) Analysis of all possibly relevant processes
2) Calculate the rates of all important processes

$$\Gamma^{(i)} = \Gamma_0^{(i)} \exp\left(-\Delta E^{(i)} / k_B T\right)$$

3) Statistical approach to describe
   - deposition
   - diffusion
   - nucleation
   - growth

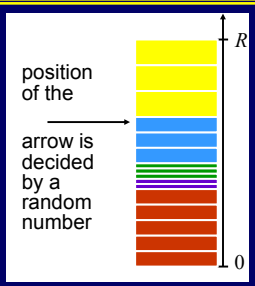
➡ **kinetic Monte Carlo method**

Flowchart of kinetic Monte Carlo Simulation



➡ unsuccessful processes are avoided

Sketch of the kMC Approach



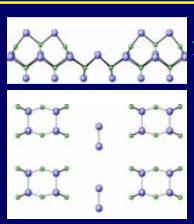
Graphical sketch of the statistics of the process that will be chosen in the kMC approach. Each bar corresponds to a certain atom. The color refers to the type of process, and the thickness to the rate.

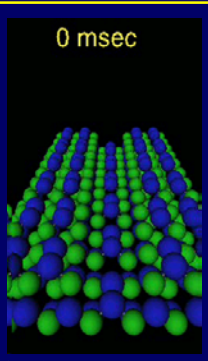
for example: yellow: Ga diffusion in the trench;
light blue: Ga diffusion perpendicular to trench;
green: Ga enters an As dimer;
dark blue: Ga diffusion parallel to steps;
red: As_2 adsorption into the intermediate.

Adsorption, diffusion, island nucleation, and growth of GaAs

side view

top view



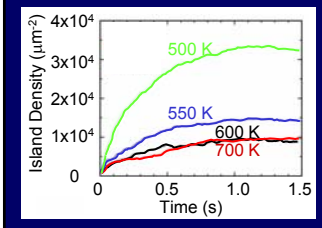


1/60 of the full simulation cell
As_2 pressure ≈ 1.33 x 10^{-8} bar
Ga deposition rate = 0.1 ML/s
T = 700 K

P. Kratzer & M. S., PRL 88, 036102 (2002)

Island density

P. Kratzer & M. S., PRL 88, 036102 (2002)



As_2 pressure
= 1.33 x 10^{-8} bar
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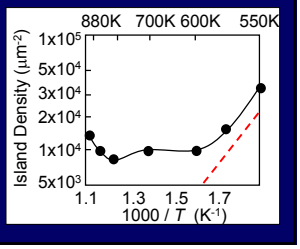
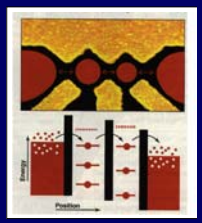


Log_{10} of island density does not increase linearly with $1/T$: Unusual *increase* of island density with increasing T (for T > 800 K).

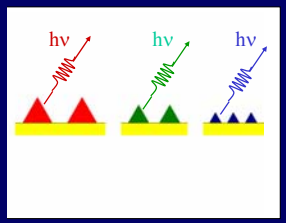
Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

Motivation:

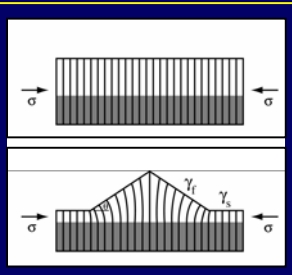
Single-electron transistor



LEDs and laser diodes



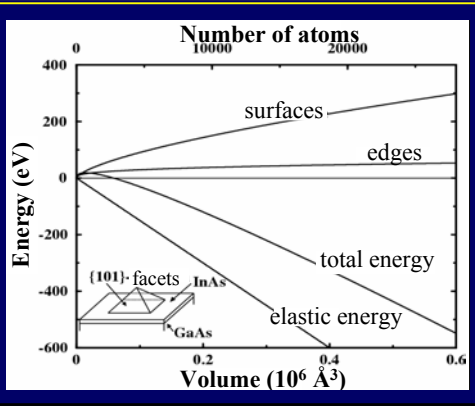
Stranski-Krastanow morphology
as one way to reduce misfit strain energy



e.g. InAs on GaAs

For InAs/GaAs the SK model describes only a part of the full picture

Equilibrium shape of quantum dots

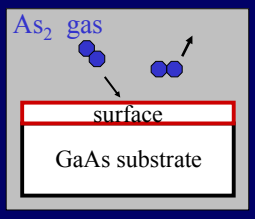


L. Wang, P. Kratzer, and M.S., PRL 82 (1999)

Stoichiometry and structure of the surface depend on the environment

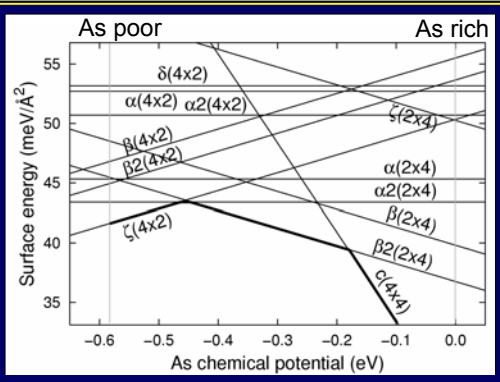
(atomic chemical potentials)

surface energy: $\gamma_0 A_0 = E_{total} - N_{Ga}\,\mu_{Ga} - N_{In}\,\mu_{In} - N_{As}\,\mu_{As}$



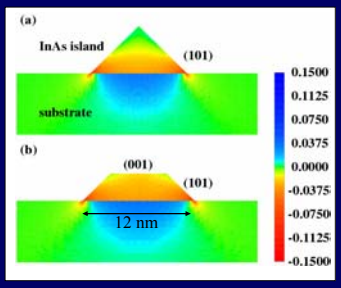
surface stress: $\tau_0 = \gamma_0 + (\partial\gamma/\partial\varepsilon)_{\varepsilon=0}$

Surface energies of clean GaAs (001)

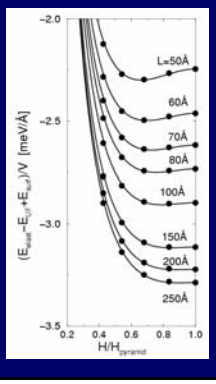


Sung-Hoon Lee, W. Moritz, & M.S., PRL 85, 3890 (2000)

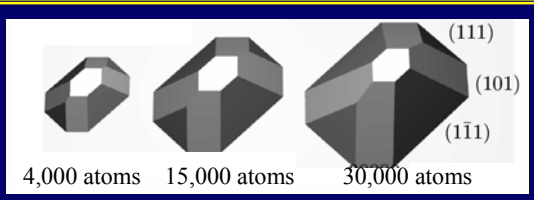
Stress tensor at strained InAs islands on GaAs



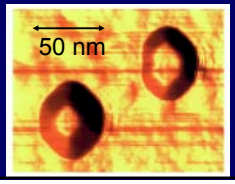
N. Moll, M.S., and E. Pehlke, PRB 58, 4566 (1998)



InP quantum dots on GaP(001)



Q. Liu, E. Pehlke, N. Moll, and M.S., PRB 60 (1999)



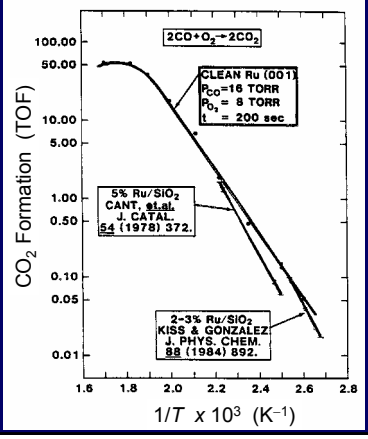
InP islands on GaInP grown by MOVPE

Samuelson et al. (1996)

Oxidation catalysis, e.g.:

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2$$

A "simple", prototypical surface chemical reaction

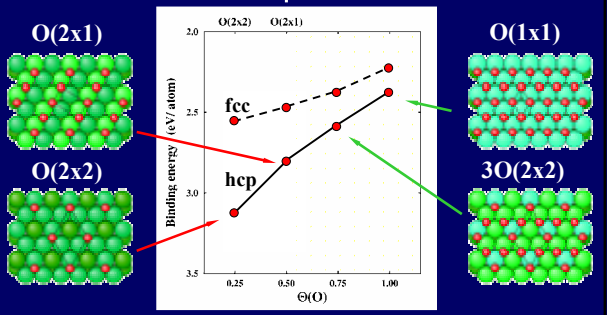


CO_2 formation at Ru supported catalysts and Ru single crystals.

At UHV conditions Ru is least active for CO oxidation. At high-pressure conditions it is best.

Oxygen adsorption on Ru(0001)

UHV ▪▪▪► | High pressure



C. Stampfl and M. Scheffler, PRB 54, 2868 (1996)

Temperature programmed desorption (TPD)

1) Prepare the adsorbate layer, coverage Θ_{init} at temperature T_{init}
2) Change T with time, e.g. $T = T_{init} + \alpha t$ and measure $\Delta\Theta(t)$

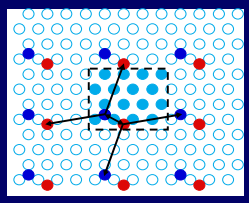
typically α = 0.1 - 10 K/s

Problem: Often important adatom-adatom distances are too big to be tractable *directly* by DFT (this also refers to disorder)

➡ **Lattice-Gas Hamiltonian**

$$\Delta E = \frac{1}{2}\sum_i\sum_j V^{(2)}(d_{ij})\sigma_i\sigma_j + \frac{1}{3}\sum_i\sum_j\sum_k V^{(3)}(d_{ij},d_{ik},d_{jk})\sigma_i\sigma_j\sigma_k + \ldots$$

(pairs) (trios)



ΔE Total Interaction Energy

s_n (n=i,j,k) Site Occupancy

$d_{n,m}$ (n,m=i,j,k) Distance

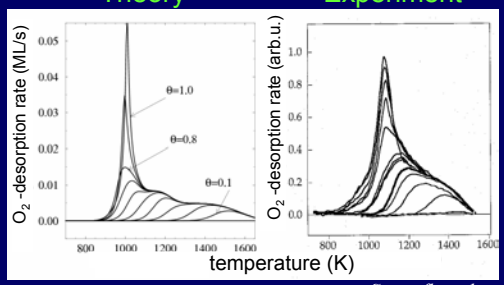
$V^{(2)}$ Pair Interaction

$V^{(3)}$ Trio Interaction

Distances up to 30-th nearest neighbor

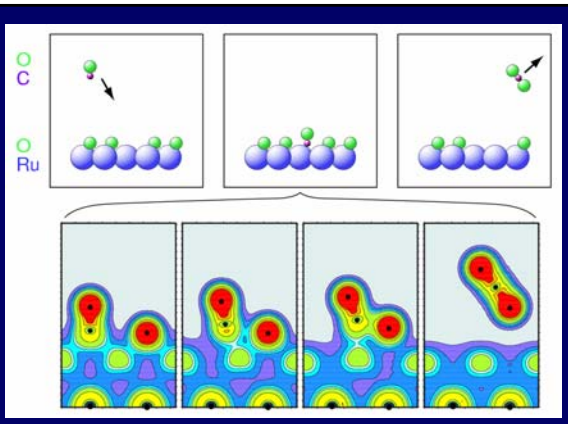
Temperature programmed desorption spectra: O/Ru(0001)

Theory Experiment



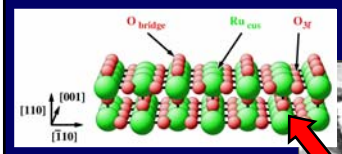
Heating rate: 6 K/s

*Stampfl et al., PRL **83** (1999)*

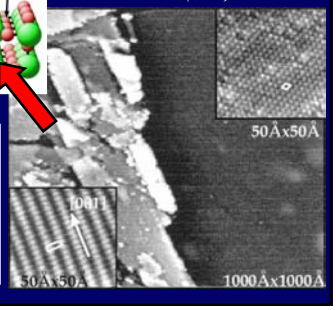


M. Scheffler and C. Stampfl, in Handbook of Surface Science (2000)

Transition-Metals Oxides as Oxidation Catalysts ? !



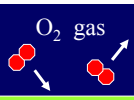
H. Over et al., Science 287, 1474 (2000)



Catalytic activity of Ru(0001) is due to RuO_2(110) domains, that form in the reactive environment

Influence of the environment on surface structure and stoichiometry

$$\gamma_{surface} = \gamma(T, p) = E_{total} - N_O \mu_O - N_{Ru} \mu_{Ru}$$



surface

RuO_2 substrate

$$\mu_{Ru} + 2\,\mu_O = \mu_{RuO_2}$$

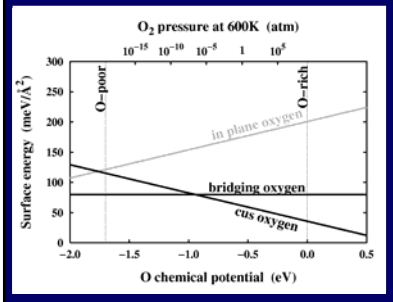
Only one independent variable:

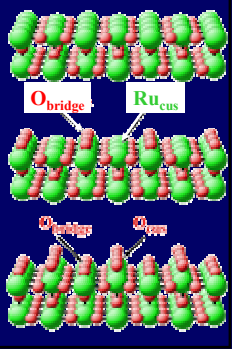
$$\mu_O(T, p) =$$

$$= \tfrac{1}{2}\,\mu_{O_2}(T, p^0) + \tfrac{1}{2}\,kT \ln(p/p^0)$$

C.M. Weinert and M. S., Mater. Sci. Forum 10-12, 25 (1986)
K. Reuter and M.S., PRB 65, 035406 (2002)

RuO_2(110) surface terminations

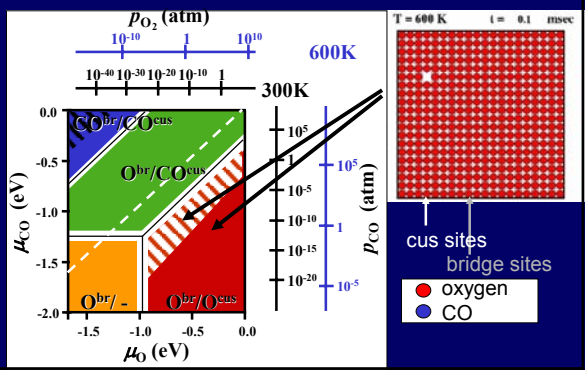




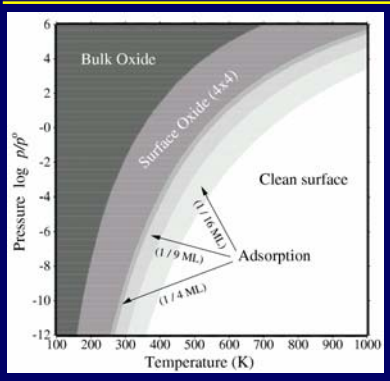
high pressure termination

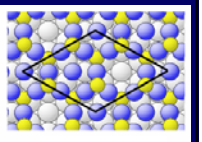
K. Reuter et al., PRB 65 (2001)

RuO_2 (110) stability regions in (*T*, *p*) space

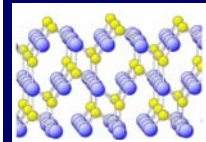


O on Ag(111)





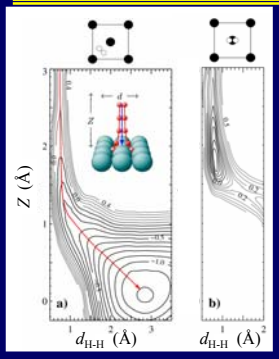
(4x4)



oxide: Ag_2O

W.X. Li, C. Stampfl, and M.S., Phys. Rev. Lett. 90, 256102 (2003); and PRB in print.

"Divide-and-conquer" strategy to determine the reaction dynamics



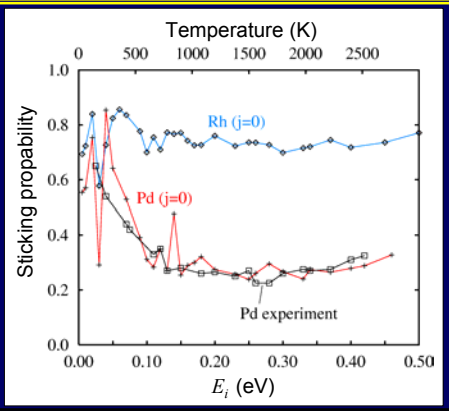
Three independent steps

1) Determine potential energy surface (**PES**) by DFT calculations (GGA for xc)
2) Analytical or numerical representation of this PES
3) Dynamics
   a) Solve time-dependent or time-independent Schrödinger equation
   b) solve Newton's equation of motion

PES for H_2 -- Pd(100)

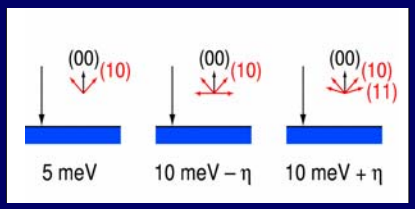
*A. Gross and M.S., PRB **57** (1998)*

Dissociative adsorption of H_2



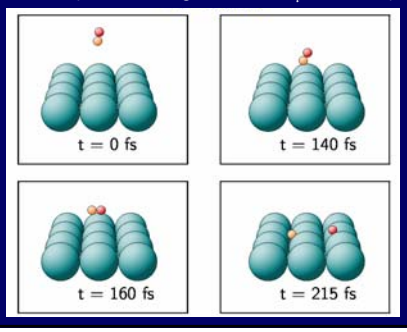
*A. Eichler et al., PRB **59** (1999)*

Oscillations reflect the threshold, e.g., exit conditions of reflected beams



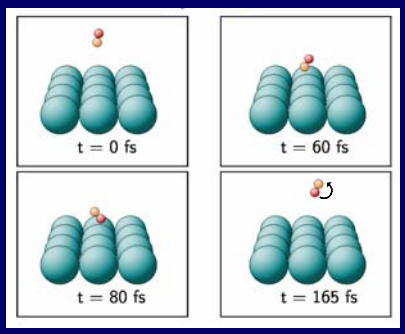
Molecular Dynamics Snapshots of H_2 → Pd(100)

Steering effect: aligning the incoming molecule (at low energies; here: $E_i = 0.01$ eV)



*A. Gross and M.S., PRB **57**, (1998)*

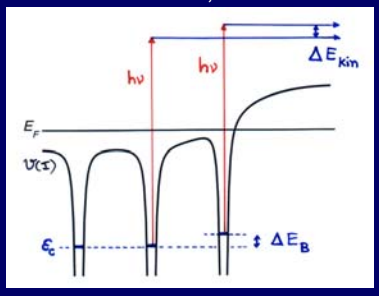
No steering at higher energies; here: $E_i = 0.12$ eV



*A. Gross and M.S., PRB **57** (1998)*

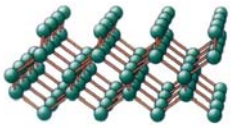
Surface core level shifts (SCLS or ESCA)

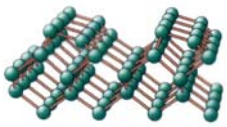
Important tool for surface analysis (identification of atoms, electronic structure, nature of bonding).

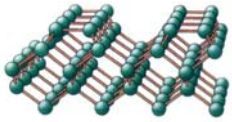


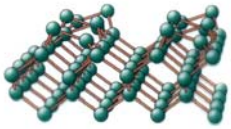
Often surface core-level shifts are interpreted as an initial-state effect.

Dimerization and dimer buckling at Si(001)


truncated bulk geometry


dimer buckling

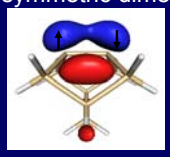

formation of dimers


alternating buckling

Buckling at the clean Si(001) surface is sensitive to electron correlation and electron-lattice coupling

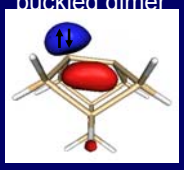
"A negative U system" ?

HOMO of symmetric dimer



Which configuration is the ground state ?

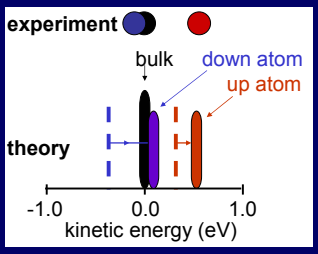
HOMO of buckled dimer



favored by MCSCF (clusters)

favored by DFT (slabs)

Si 2*p* SCLS for Si(001) p(2x2)



Theory
dashed: initial-state effect only

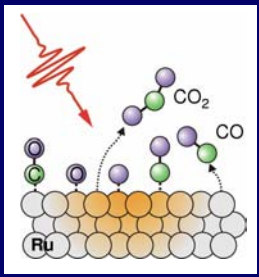
bars: including also final-state screening (*by total-energy differences or transition-state theory*)

E. Pehlke and M.S., PRL ***71****, 2338 (1993).*

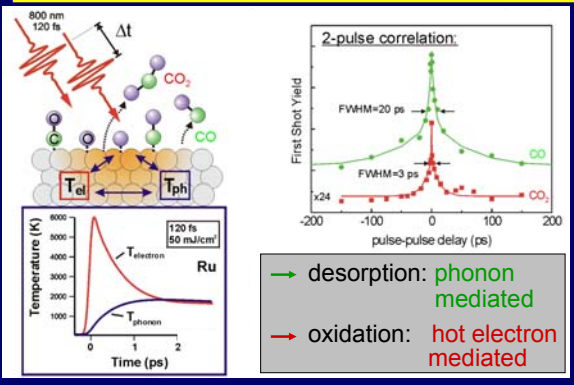
For this system: screening at the surface is better than in the bulk

Two peaks = clear proof for the buckling

Photochemistry: Phonon- versus electron-mediated surface reactions: Laser-induced desorption and oxidation of CO on Ru(0001)



Femtosecond photooxidation of CO on Ru

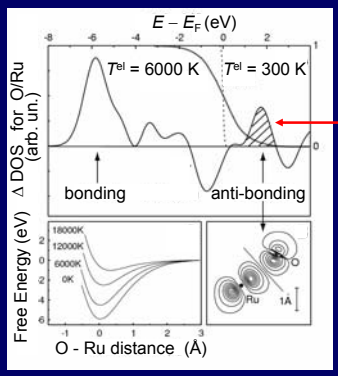


→ desorption: phonon mediated

→ oxidation: hot electron mediated

M. Bonn et al., SCIENCE 285 (1999)

DFT calculations at finite temperature



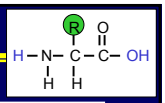
O on Ru(0001)

unoccupied anti-bonding orbital above E_F

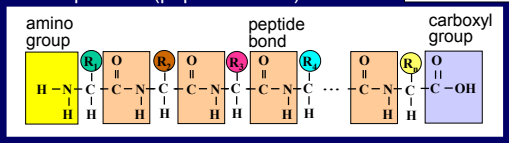
increasing the electronic temperature leads to a weakening of the O-Ru bond

M. Bonn et al., SCIENCE 285 (1999)

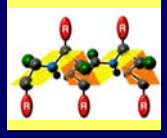
Stability of the α-helix



structure of proteins (peptide chains):

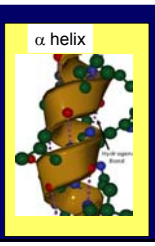


β sheet



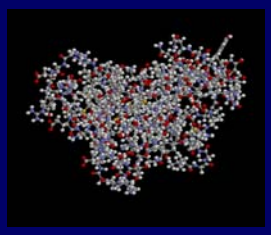
secondary structure

α helix



Folding of the peptide chain

peptide chain in the bovine prion protein

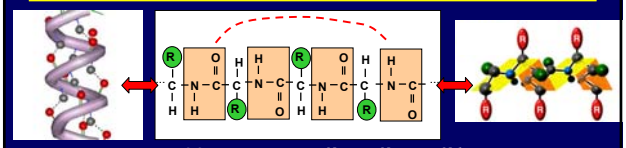


atomic structure

secondary and tertiary structure

http://www.rcsb.org/ -- pdb-id: 1QM0

Enthalpy of formation of a hydrogen Bond



Enthalpy of formation: $\Delta H^N = E_\sigma^N - E_\sigma^{N-1} - \mu_{\text{peptide}}$

poly alanine (R = methyl group = CH_3)

sheet (extended structure) as "reservoir"

α-helix:

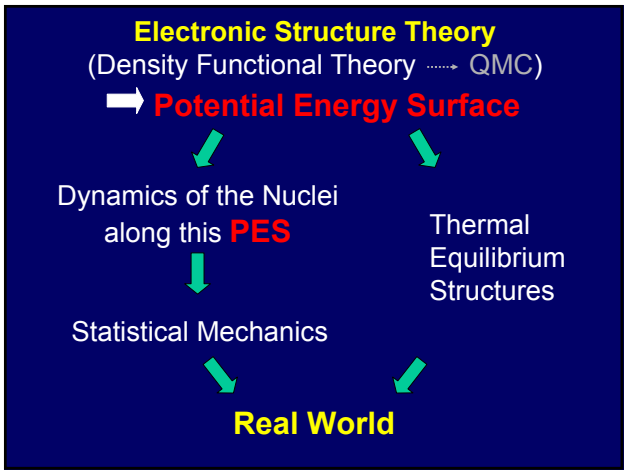
"back bone" costs : $\Delta H^N_{\text{bb}} \approx 6.5$ *kcal/mol* for all N

H-bond gain : $\Delta H^N_{\text{H-bond}} = -2.7$ *kcal/mol* for $N = 4$

$= -9.5$ *kcal/mol* for $N = \infty$

→ **hydrogen bond is strongly cooperative**

J. Ireta et al., J. Phys. Chem. B, in print.


Electronic Structure Theory
(Density Functional Theory ⇢ QMC)
Potential Energy Surface
Dynamics of the Nuclei along this PES
Thermal Equilibrium Structures
Statistical Mechanics
Real World