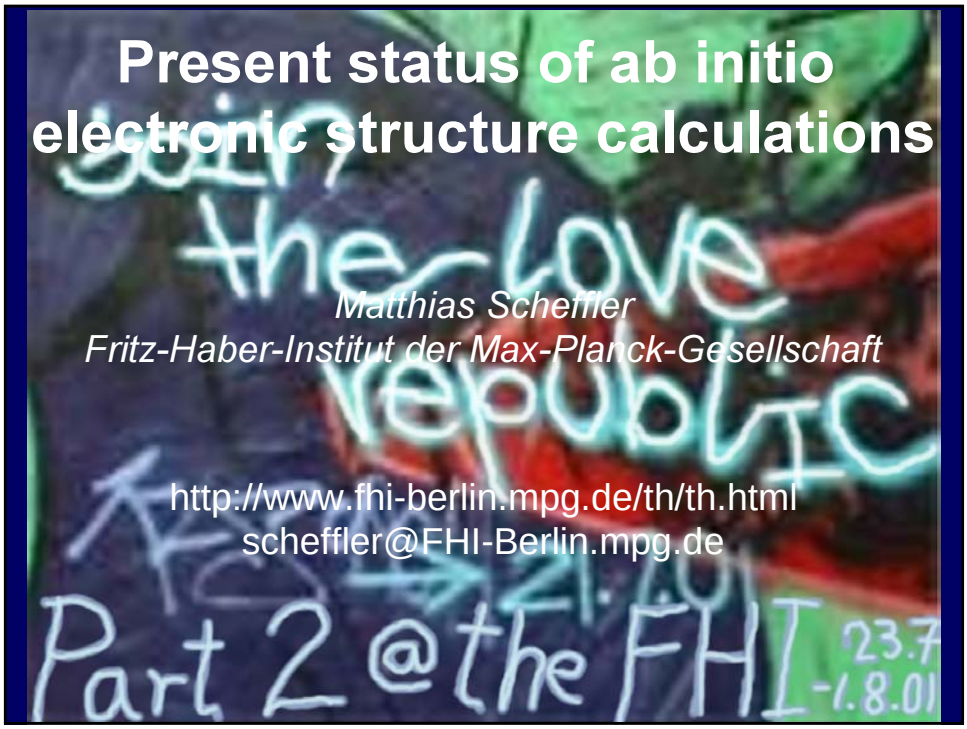


Abstract

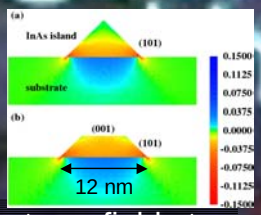
In this talk I will sketch the "ab initio line" of the field often called "Computational Sciences and Engineering", that at present is significantly increasing in importance and impact. To predict materials properties starting from the electronic structure and going all the way to technically relevant time and length scales, is a desire that has existed for many years in particular in condensed-matter physics, materials science, chemistry, and bio-chemistry. However, only recent, spectacular developments in methodology, and the availability of fast computers, enable us now to approach this goal.

I will emphasize how density-functional theory calculations can and should be combined with methods from statistical mechanics, meso-/macroscopic continuum mechanics, and thermo-dynamics, and I will demonstrate the value of such studies using selected examples. These examples include:

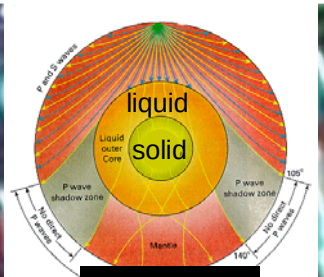
- phase transitions of crystals with relevance to mineralogy and geophysics,
- predictions and description of the function of materials surfaces (e.g., atomic structure, chemical activity),
- excited states, core-level spectroscopy (many-electron effects), etc.,
- crystal growth and self-assembly of nano structures,
- insights into the nature of interactions in biological molecules.

Emphasis will be placed on methodology, simple physical models, concepts, and the development of understanding.

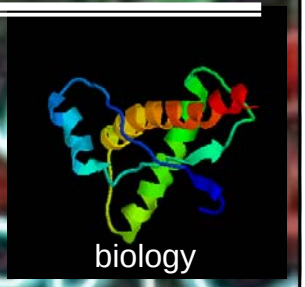
Present status of *ab initio* electronic structure calculations



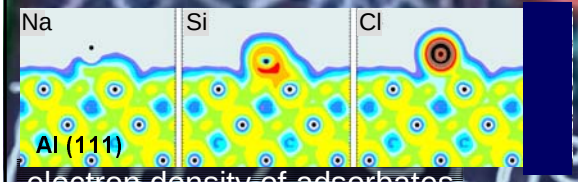
stress field at semiconductor nano structures



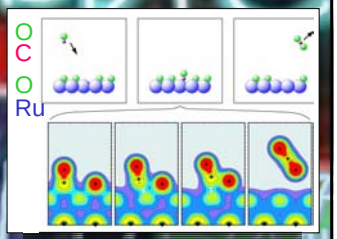
geophysics



biology



electron density of adsorbates

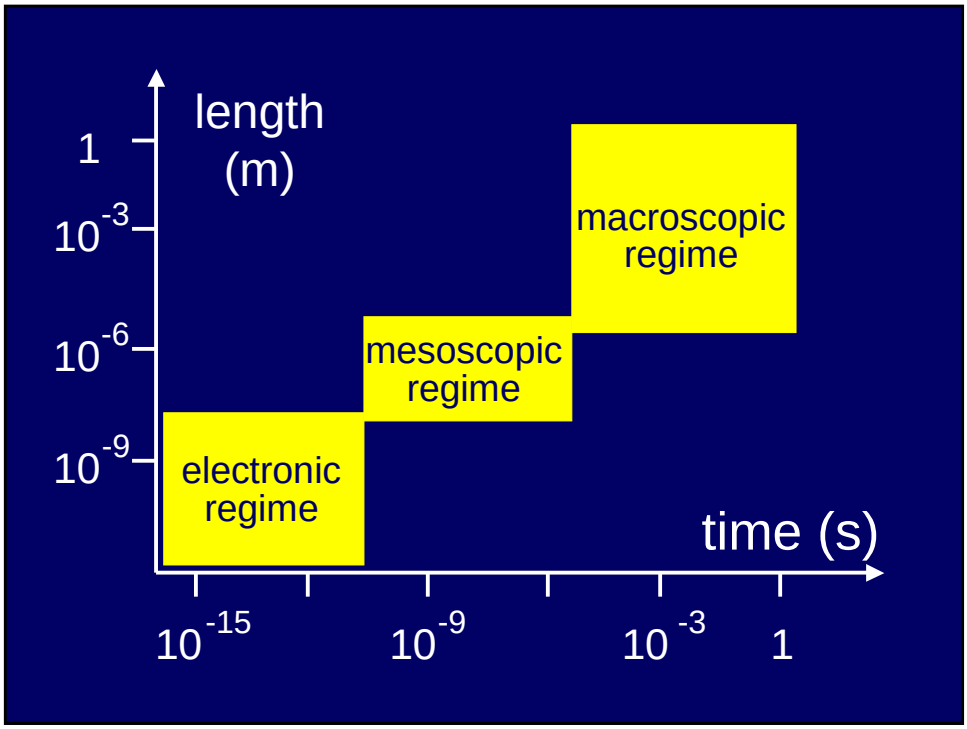


oxidation catalysis

Methods: schematic summary

Results, for example:

- crystal phase transitions and examples from mineralogy/geology
- thermal expansion of crystals in the bulk and at surfaces,
- crystal growth and self-organization of nano-scale structures.
- surface structure, chemical reactions, catalysis, thermal desorption,
- excited states, core-level spectroscopy (many-body effects), photo-chemistry, etc.
- nature of the interactions in bio-molecules



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:

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

Kohn and Sham (1965):

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

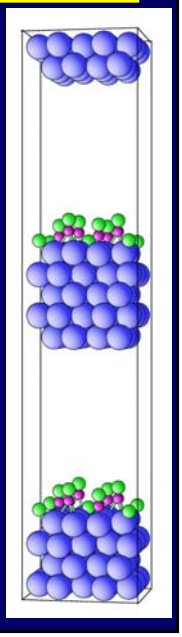
with **local-density approximation**
or **generalized gradient approximation**

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)* **)**

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



Methods: schematic summary

Results, for example:

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- surface structure, chemical reactions, catalysis, thermal desorption,
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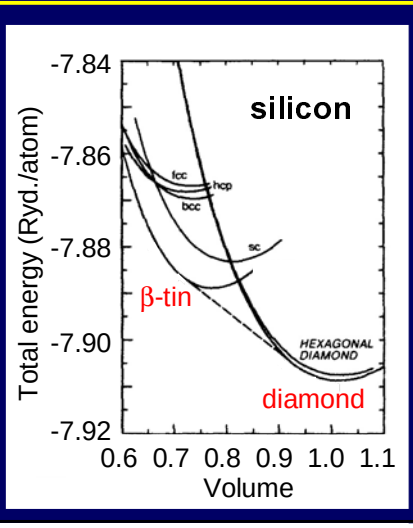
- excited states, core-level spectroscopy (many-body effects), photo-chemistry, etc.
- nature of the interactions in bio-molecules

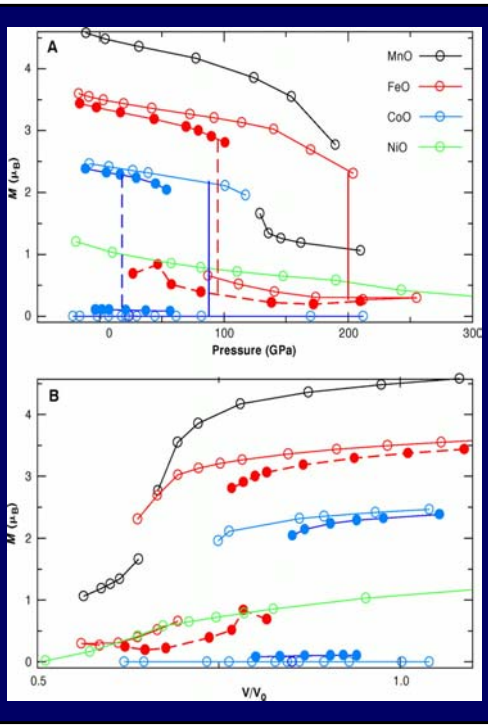
The First (Convincing) DFT Calculations: Stability of Crystals and Crystal Phase Transitions



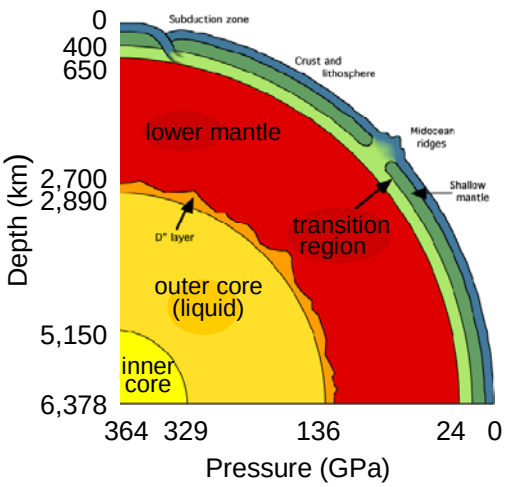
M. T. Yin and M. L. Cohen PRB **26** *(1982)*

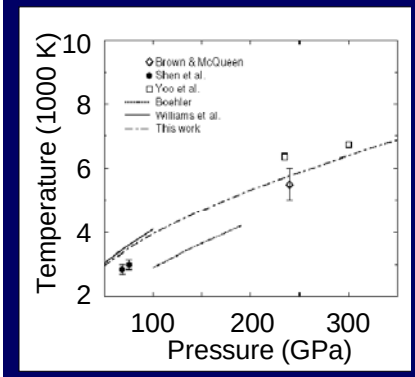
Magnetic Collapse in Transition Metal Oxides at High Pressure: Implications for the Earth

R. Cohen, Mazin, Isaak, Science 1997



Ab Initio Melting Curve of Fe as Function of Pressure





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

Methods: schematic summary

Results, for example:

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- excited states, core-level spectroscopy (many-body effects), photo-chemistry, etc.,
- nature of the interactions in bio-molecules.

Thermal Expansion of Crystals

S. Biernacki, S. and M. Scheffler: Negative thermal expansion of diamond and zinc-blende semiconductors.
Phys. Rev. Lett. **63**, *290 (1989).*

J. Xie, S. de Gironcoli, S. Baroni, and M. Scheffler,
First-principles calculation of the thermal properties of silver.
Phys. Rev. B **59**, *965 (1999)*

and at Surfaces

J. Xie, S. de Gironcoli, S. Baroni, and M. Scheffler,
Temperature dependent surface relaxations of Ag(111).
Phys. Rev. B **59**, *970 (1999).*

Methods: schematic summary

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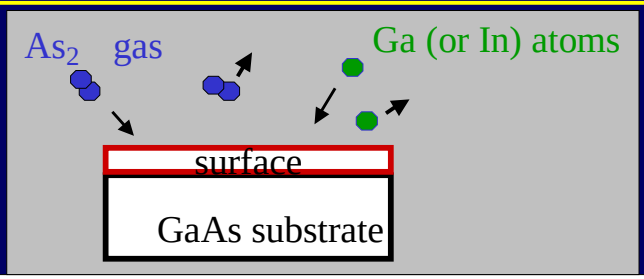
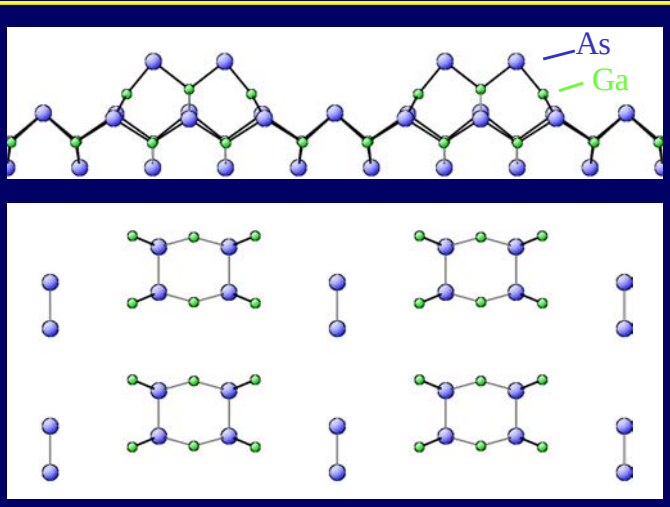
- nature of the interactions in bio-molecules.

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

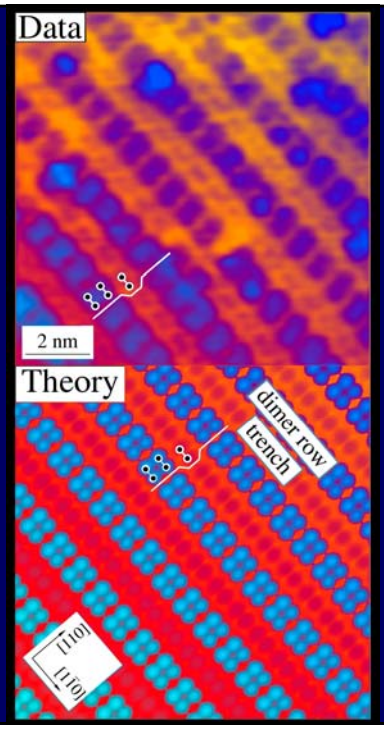


STM Imaging of GaAs(001)

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 →

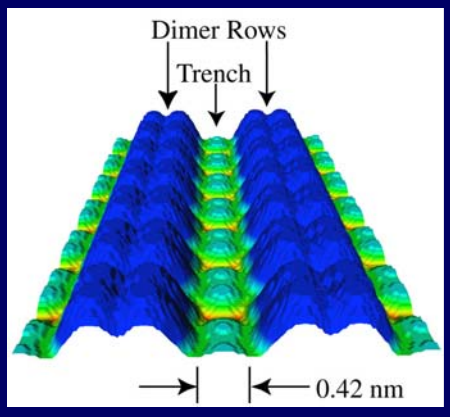
*LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL **83**, 2989 (1999).*



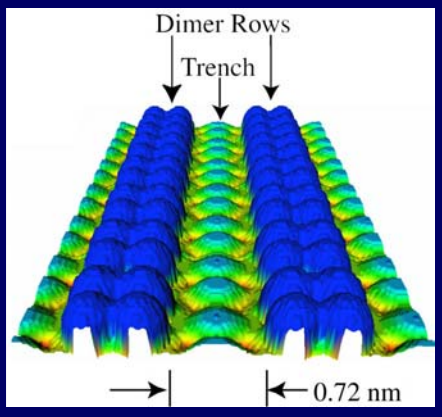
Voltage Dependence of the STM Current

STM Simulation

-3.0 eV (high)



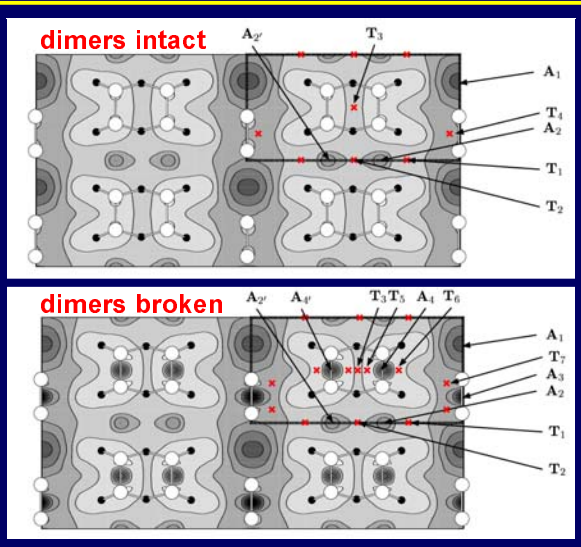
-2.1 eV (low)



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

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

top view



$[\bar{1}10]$

$[110]$

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

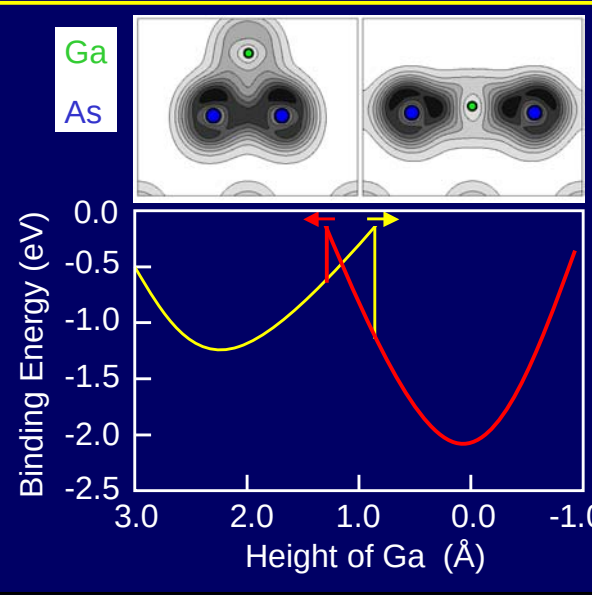
E_{A2} = -1.5 eV
E_{TS} = -1.3 eV

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

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

Calculating such potential-energy surfaces is a significant part of modern *ab initio* electronic struture theory.

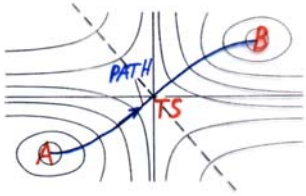
Unusually Stable Site for Ga Adatom Inside The Trench-Site As-Dimer



*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

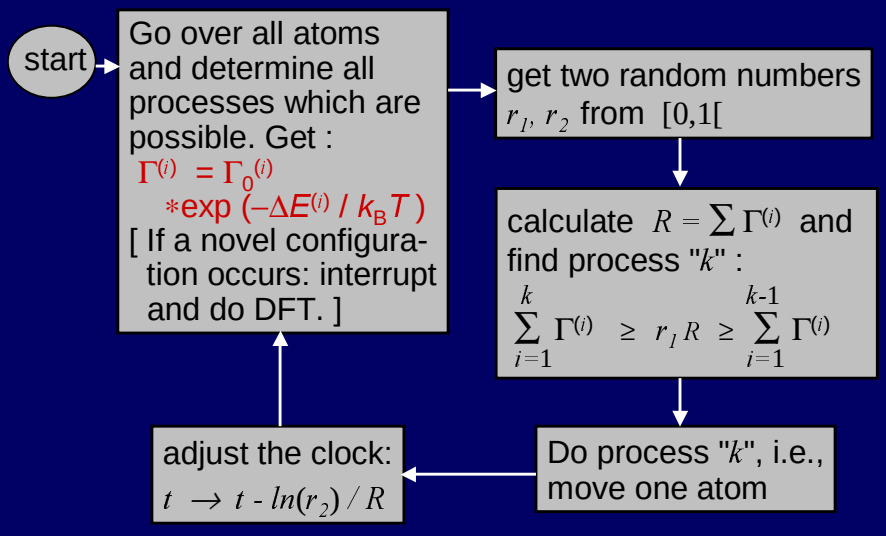
1) Analysis of all possibly relevant processes
2) Calculate the rates of all important processes

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

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

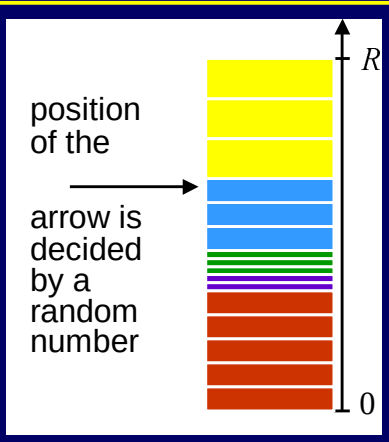
➡ **kinetic Monte Carlo method**

Flowchart of kinetic Monte Carlo Simulation



➡ unsuccessful processes are avoided

Sketch of the kMC Approach

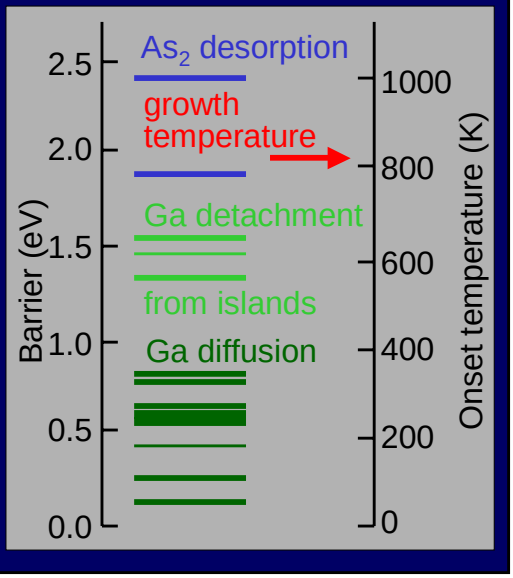


Graphical sketch of the statistics of the process that will be chosen in the kMC approach. Each bar corresponds to a certain atom. The color refers to the type of process, and the thickness to the rate.

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.

Kinetic Monte Carlo Simulations

- Reconstruction of surface considered
- 32 microscopically different Ga diffusion processes, and As_2 adsorption/desorption are included explicitly
- Computational challenge: very different time scales (10^{-12} sec to 10 sec)



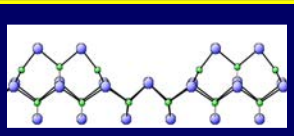
Kinetic Monte Carlo calculations are a very important add-on to modern *ab initio* electronic-struture theory.

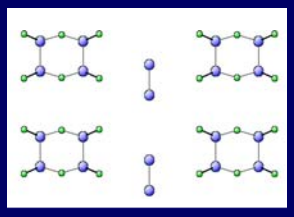
Likely, this is the way to go in the future.

Adsorption, Diffusion, Island Nucleation, and Growth of GaAs

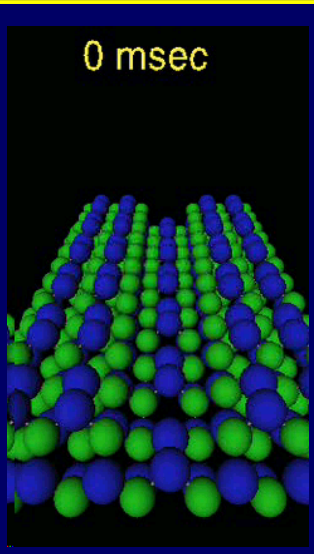
side view

top view





Ga
As

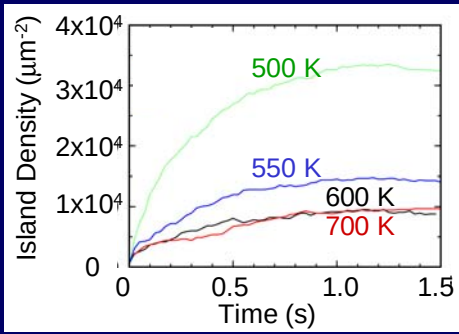


1/60 of the full simulation cell
As_2 pressure ≈ 1.33 x 10^{-8} bar
Ga deposition rate = 0.1 ML/s
T = 700 K

P. Kratzer & M. S., submitted to PRL

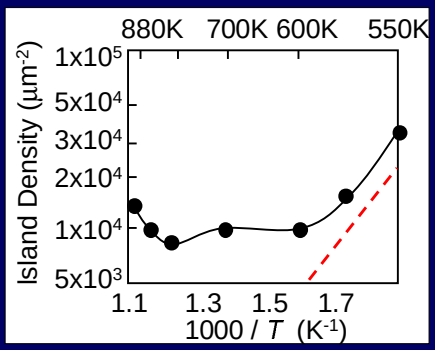
Island Density

P. Kratzer & M. S., submitted to PRL



As_2 pressure
≈ 1.33 x 10^{-8} bar

Ga deposition rate
= 0.1 ML/s

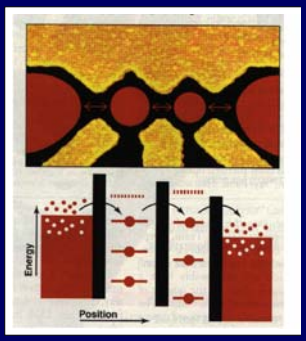


Log_{10} of island density does not increase linearly with $1/T$.

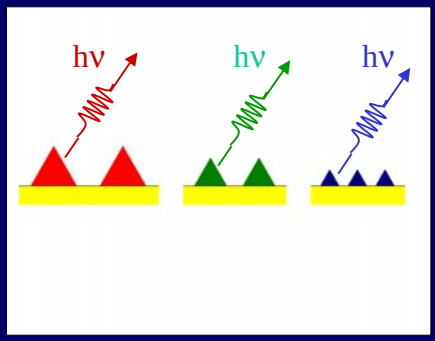
Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

Motivation:

Single-electron transistor

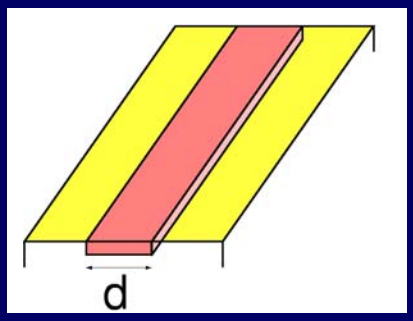


LEDs and laser diodes



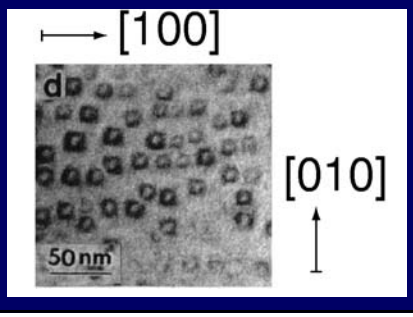
Required dimensions: 50 - 200 Å

Lithography ends at $d > 200$ Å, and has rough edges

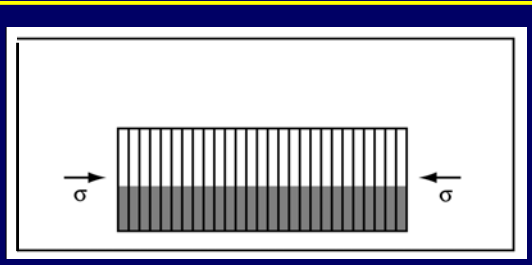


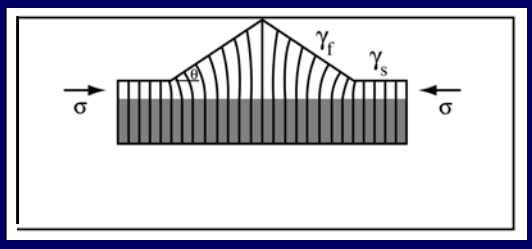
Self-assembly of InAs quantum-dots on GaAs (100)

Ruvimov et al., PRB ***51*** *(1995)*



Stranski-Krastanow Morphology
as one Way to reduce Misfit Strain Energy

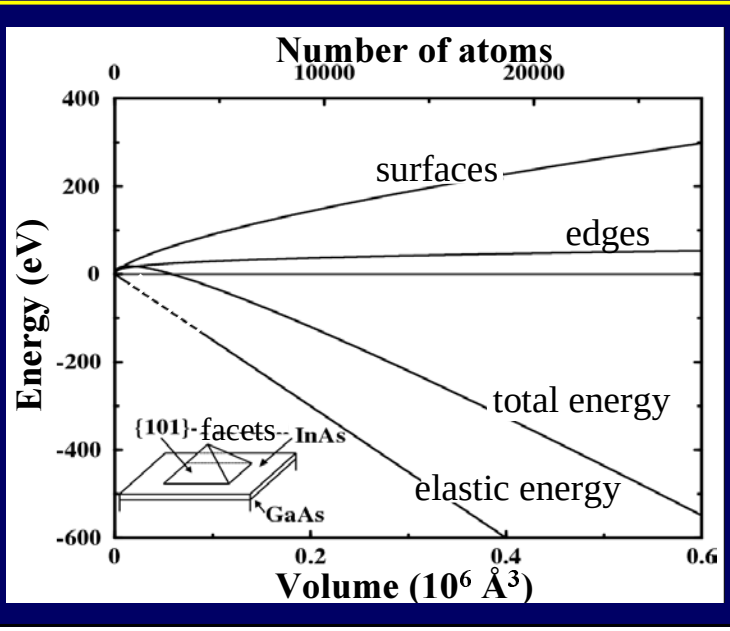




e.g. InAs on GaAs

or InP on GaP

Equilibrium Shape of Quantum Dots

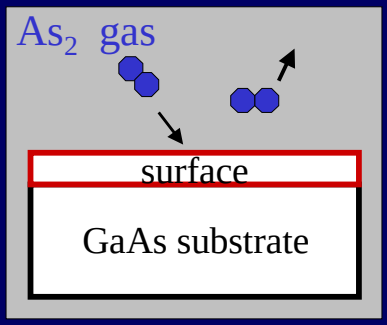


L. Wang, P. Kratzer, and M.S., PRL **82** *(1999)*

Stoichiometry and Structure of the Surface depend on the Environment

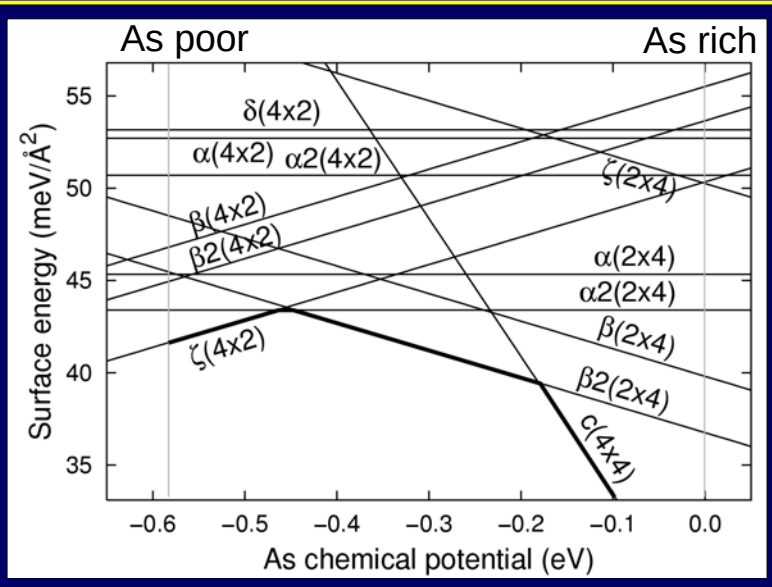
(atomic chemical potentials)

$$E_{surface} = \Delta E_{tot} - N_{Ga}\,\mu_{Ga} - N_{As}\,\mu_{As}$$



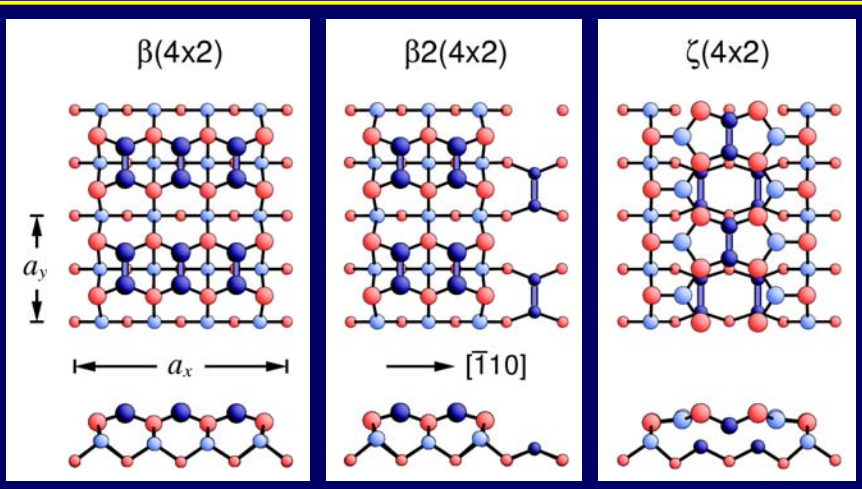
$$\mu_{Ga} + \mu_{As} = E^{bulk}(GaAs)$$

Surface Energies of GaAs (001)



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

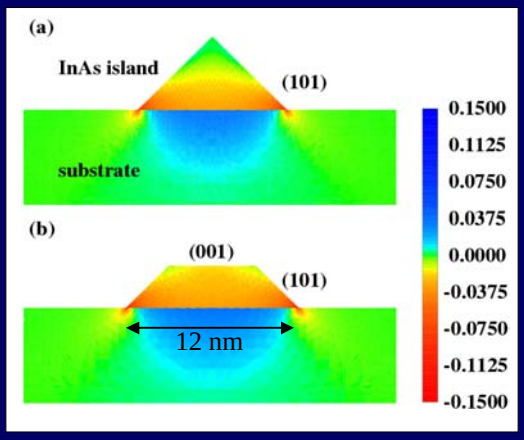
Surface Structures of GaAs (001)



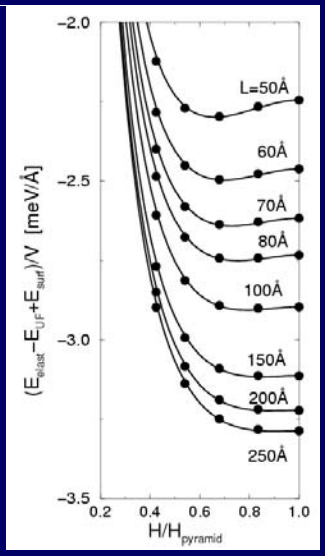
all these structures fulfill the electron counting rule

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

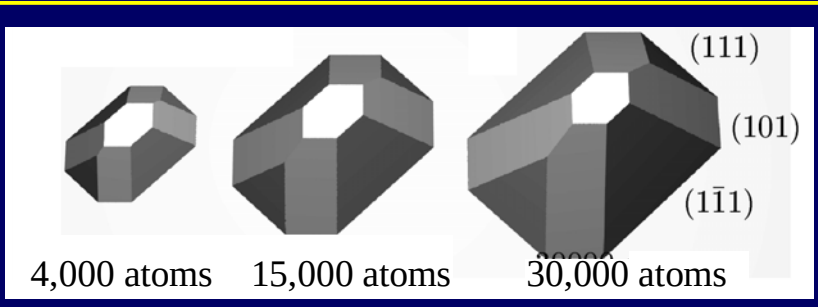
Stress Tensor at strained InAs Islands on GaAs

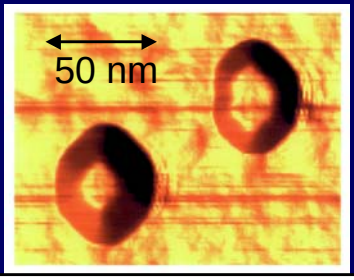


N. Moll, M.S., and E. Pehlke, PRB **58,** *4566 (1998)*



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

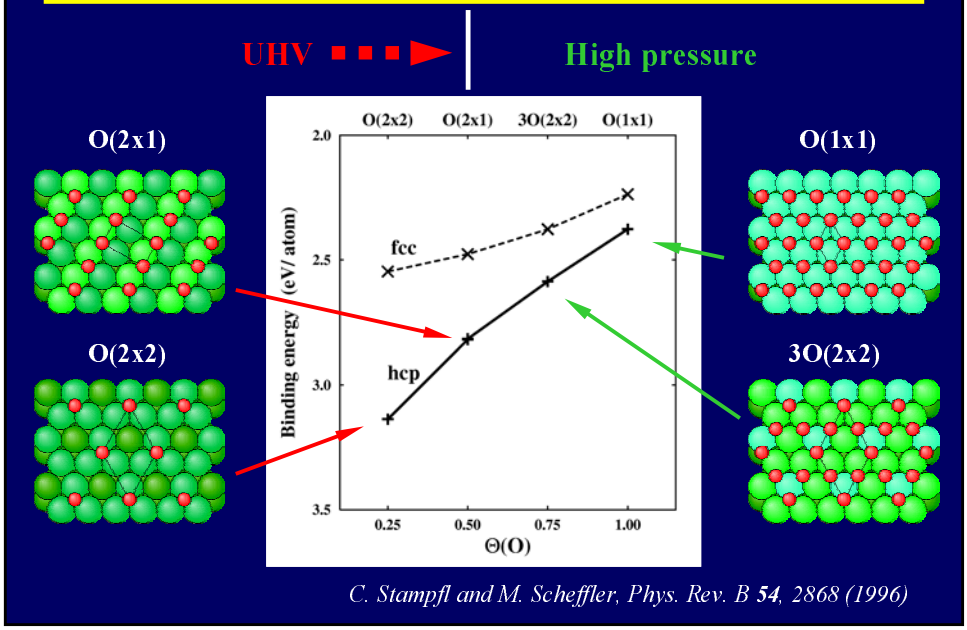
Samuelson et al. (1996)

Oxidation Catalysis, e.g.:

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

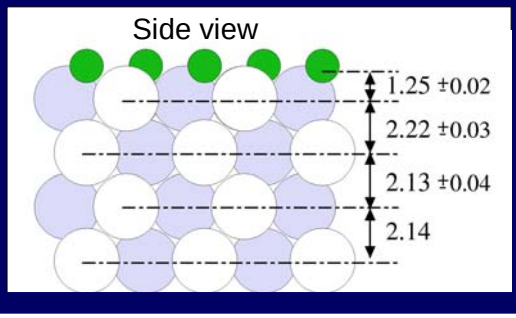
A "simple", prototypical surface chemical reaction

Oxygen Adsorption on Ru(0001)



C. Stampfl and M. Scheffler, Phys. Rev. B ***54****, 2868 (1996)*

Prediction of new (unexpected) structures. Example: (1x1)-O/Ru(0001)



Prepared by O_2 adsorption up to 1/2ML, (2x1) phase, then NO_2 exposure at 600K to form 1ML (1x1) phase.

PARAMETER	DFT-GGA	LEED
Ru-O spacing (A)	1.26	1.25± 0.02
Ru-O bond length (A)	2.03	2.00± 0.03
Ru_1-Ru_2 spacing (%)	+2.7	+3.7± 1.4
Ru_2-Ru_3 spacing (%)	-0.9	-0.5±1.8

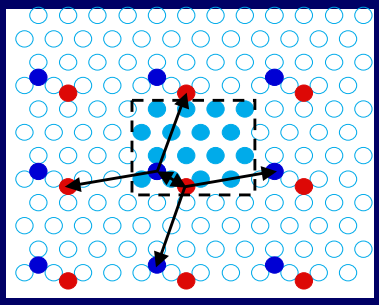
C. Stampfl et al., PRL 77 (1996)

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

σ_n $(n=i,j,k)$ Site Occupancy

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

$V^{(2)}$ Pair Interaction

$V^{(3)}$ Trio Interaction

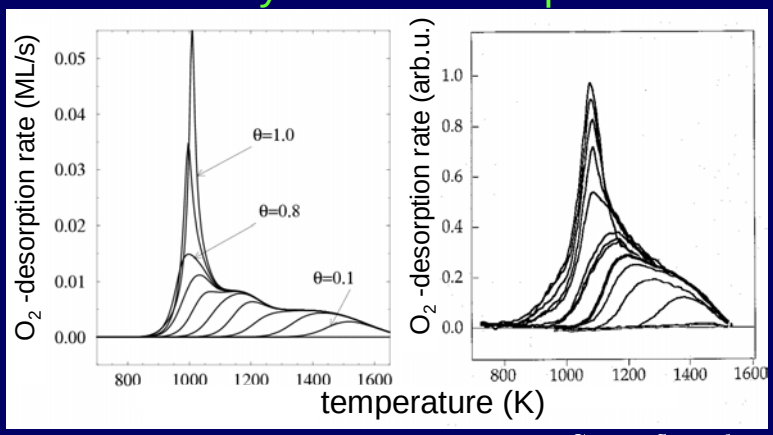
Distances up to 20-th nearest neighbor

Building lattice-gas Hamiltonians from DFT calculations and evaluating the partition function is most helpful.

Also this is an important way to go in the future.

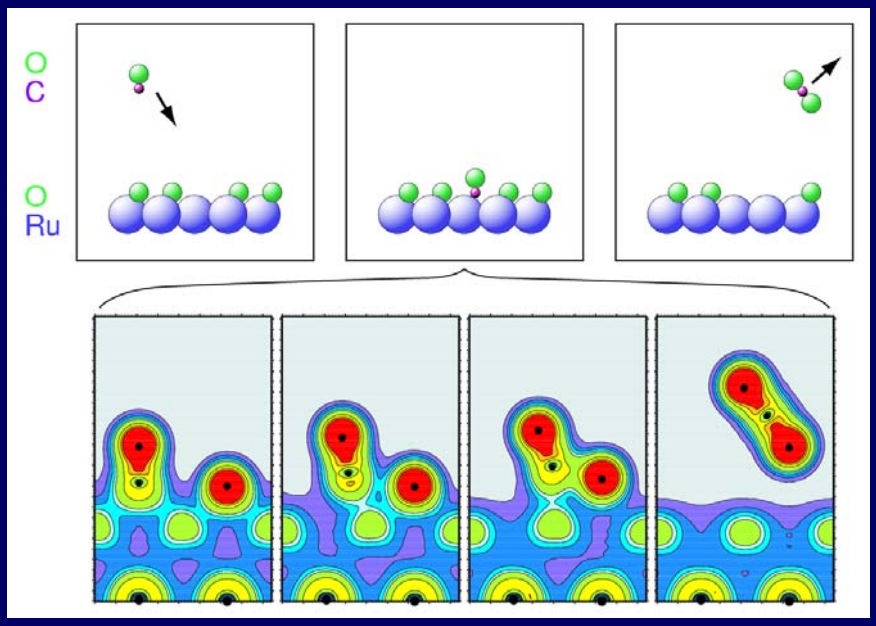
Temperature Programmed Desorption Spectra: O/Ru(0001)

Theory Experiment



Heating rate: 6 K/s

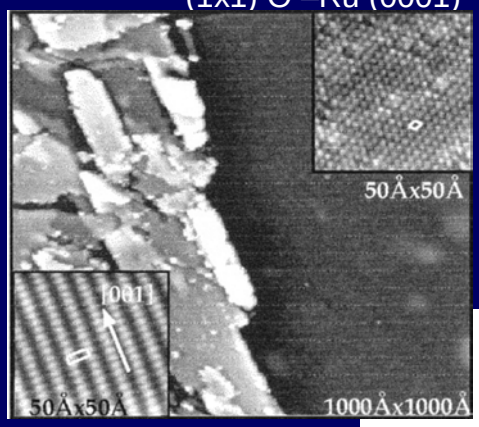
Stampfl et al., PRL ***83*** *(1999)*



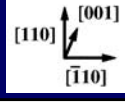
M. Scheffler and C. Stampfl, in Handbook of Surface Science (2000)

Ru(0001) after Exposure to Oxygen: Atomic scale structure

(1x1) O –Ru (0001)

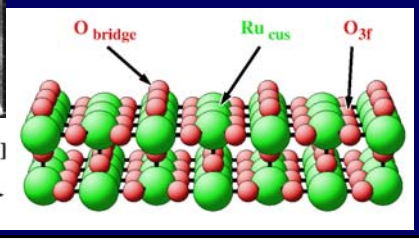


RuO_2 (110)

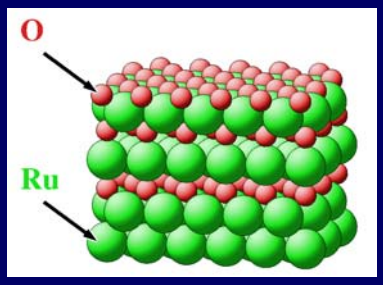


STM

*H. Over, Y.D. Kim, A.P. Seitsonen, S. Wendt, A. Morgante, E. Lundgren, M. Schmid, P. Varga, and G. Ertl, Science **287** (2000)*

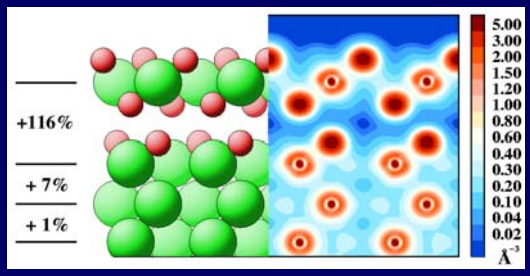


Increasing the Coverage Above Two Oxygen Layers



K. Reuter et al., to be published

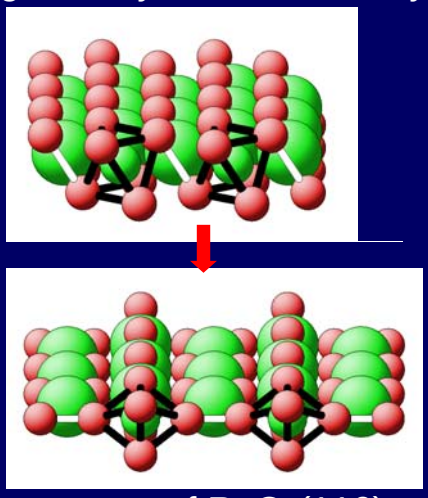
Test all 18 possible combinations



Additional O layer saturates the underlying Ru(0001) substrate and decouples the O-Ru-O trilayer.

Accordion Mechanism of Surface-Oxide Formation

geometry of O-Ru-O trilayer



geometry of $RuO_2(110)$

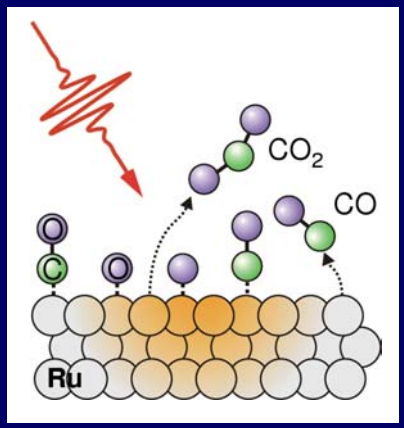
K. Reuter et al., to be published

Methods: schematic summary

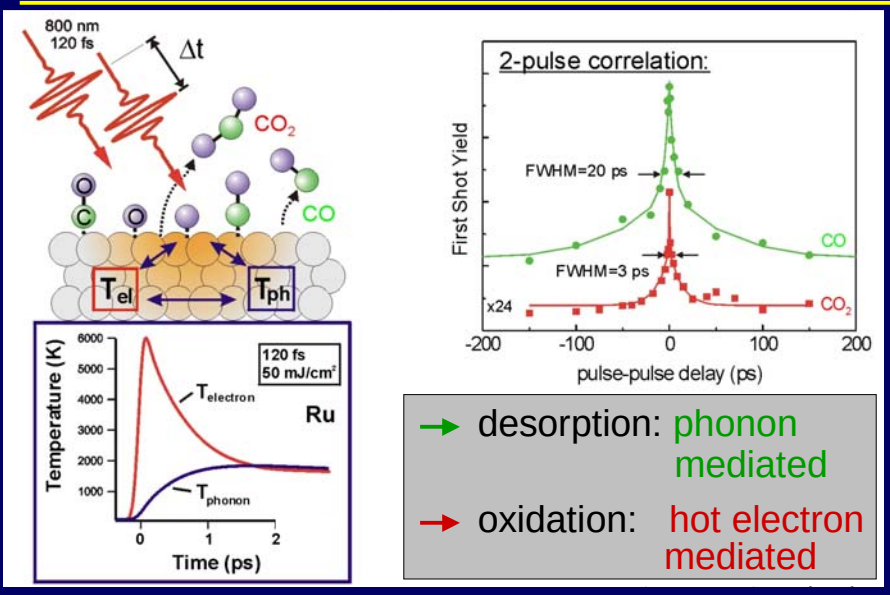
Results, for example:

- crystal phase transitions and examples from mineralogy/geology,
- thermal expansion of crystals in the bulk and at surfaces,
- crystal growth and self-organization of nano-scale structures,
- surface structure, chemical reactions, catalysis, thermal desorption,
- excited states, core-level spectroscopy (many-body effects), photo-chemistry, etc.,
- nature of the interactions in bio-molecules.

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



Femtosecond photooxidation of CO on Ru

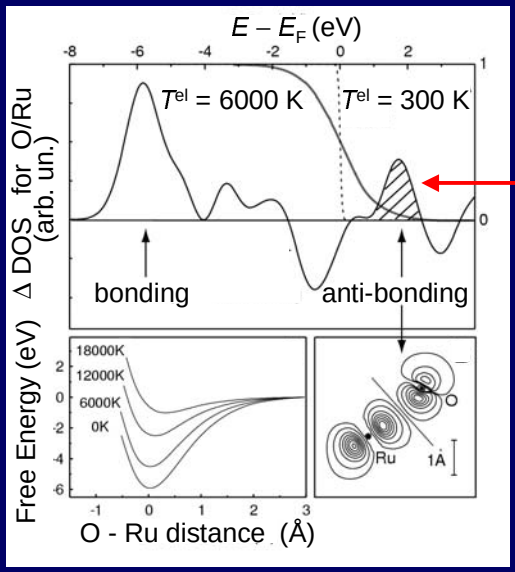


→ desorption: phonon mediated

→ oxidation: hot electron mediated

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

DFT calculations at finite temperature



O on Ru(0001)

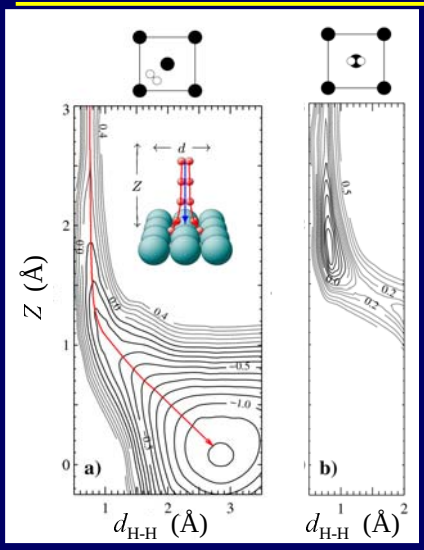
unoccupied anti-bonding orbital above E_F

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

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

Quantum-dynamics (and molecular dynamics) of H2 dissociation at metal surfaces

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



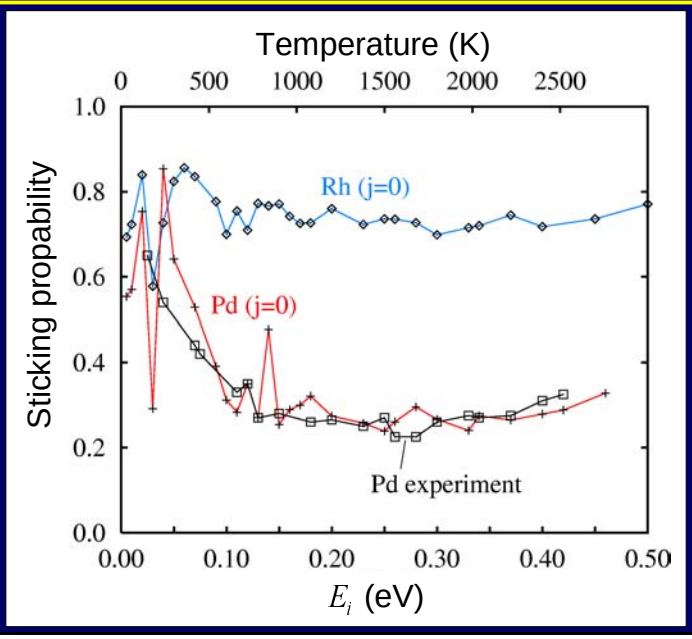
PES for H_2 -- Pd(100)

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

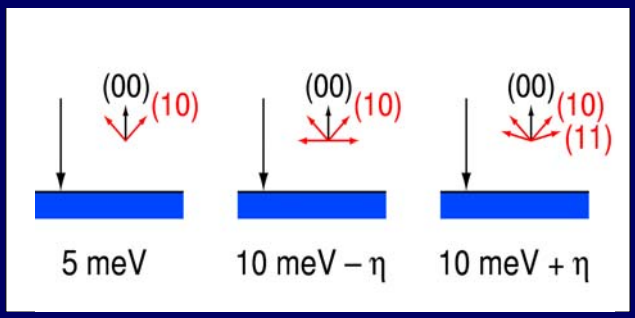
*A. Gross and M.S., PRB **57** (1998)*

Dissociative adsorption of H_2



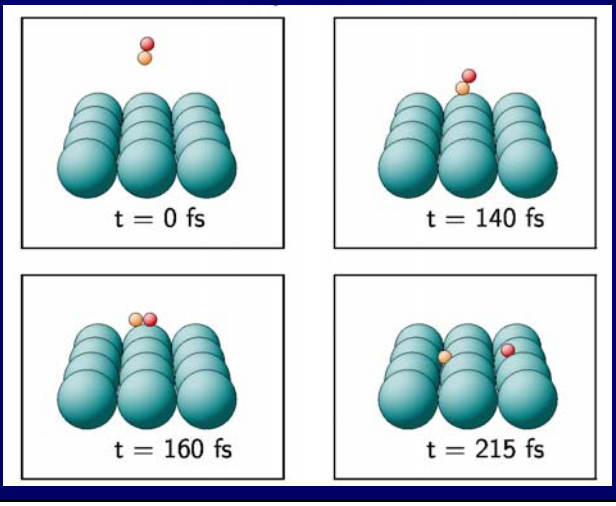
*A. Eichler et al., PRB **59** (1999)*

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



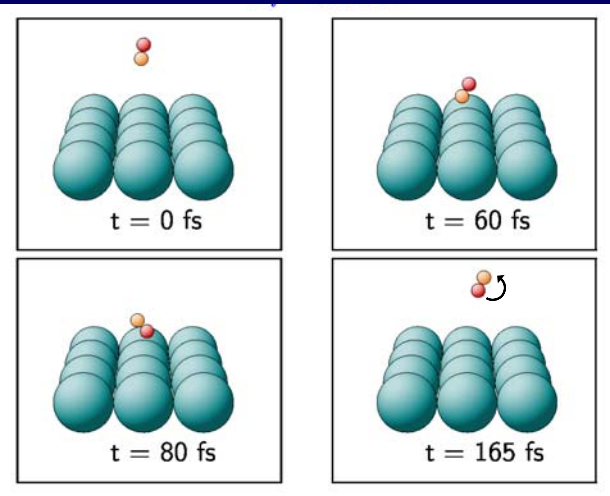
Molecular Dynamics Snapshots of H_2 → Pd(100)

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)*

Often the statistics of chemical reactions is very involved. Then a "divide and conquer" approach, as the one described here, is crucial for DFT-based molecular dynamics.

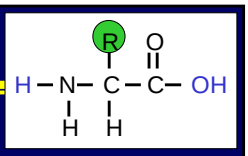
The difficult step is the representation (and interpolation) of the DFT total energies to represent the full potential-energy surface.

Methods: schematic summary

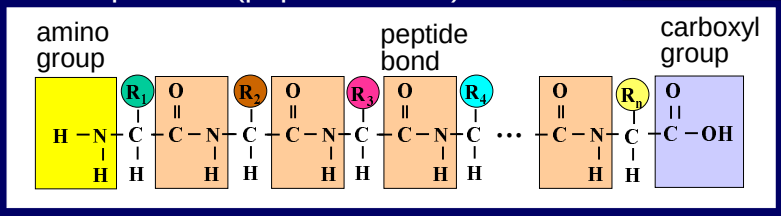
Results, for example:

- crystal phase transitions and examples from mineralogy/geology,
- thermal expansion of crystals in the bulk and at surfaces,
- crystal growth and self-organization of nano-scale structures,
- surface structure, chemical reactions, catalysis, thermal desorption,
- excited states, core-level spectroscopy (many-body effects), photo-chemistry, etc.,
- nature of the interactions in bio-molecules.

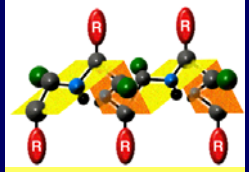
Stability of The α-Helix



structure of proteins (peptide chains):

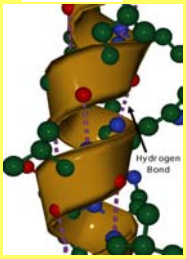


β sheet



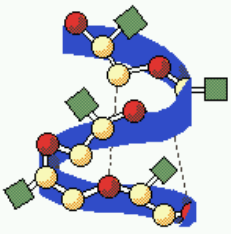
secondary structure

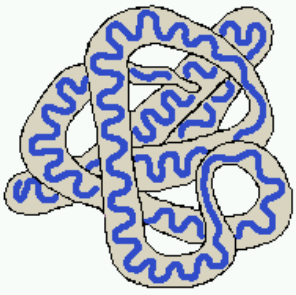
α helix

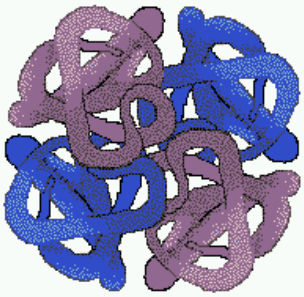


Structure of Proteins

amino acid

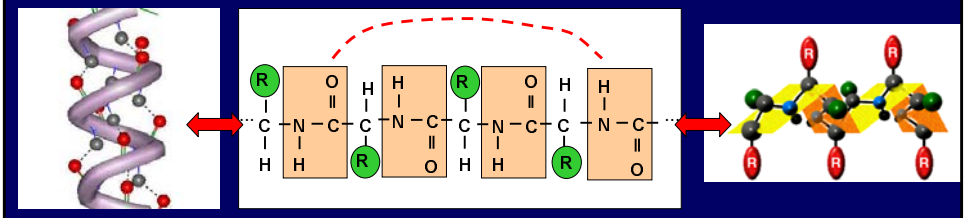






secondary structure | tertiary structure | quaternary structure

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 $N = 4$

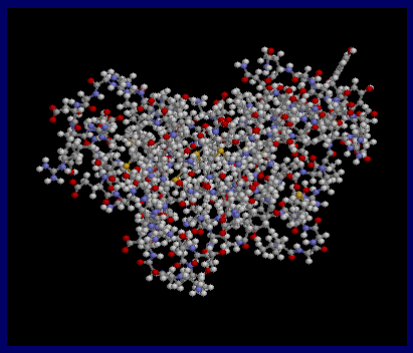
$= -9{,}5$ *kcal/mol* for $N = \infty$

➡ **hydrogen bond is strongly cooperative**

J. Ireta, et al., submitted to PRL

Folding of the peptide chain

peptide chain in the bovine prion protein

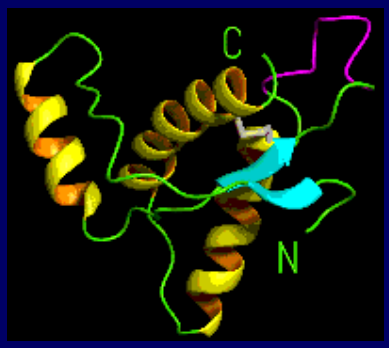


atomic structure

secondary and tertiary structure

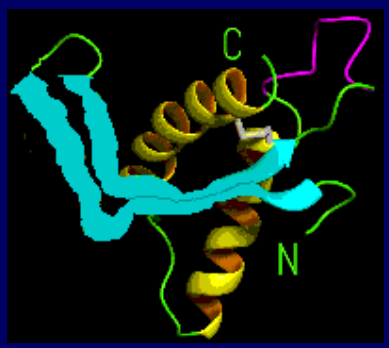
http://www.rcsb.org/ -- pdb-id: 1QM0

peptide chain in the bovine prion protein



http://cyber-dyne.com/~tom/reverse_chron.html

peptide chain in the bovine prion protein



http://cyber-dyne.com/~tom/reverse_chron.html

Electronic Structure Theory
(Density Functional Theory)

➡ **Potential Energy Surface**

Dynamics of the Nuclei along this **PES**

Statistical Mechanics

Thermal Equilibrium Structures

Real World

The people behind the work:

Peter Kratzer

Cathy Stampfl

Karsten Reuter

Jörg Neugebauer

Joel Ireta

et al. …