

# Modern theoretical methods in heterogeneous catalysis

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# Outline

- 1) Solution of Schrödinger equation: Born-Oppenheimer approximation
- 2) Approximate solutions of electronic problem: Wave-function and DFT methods
- 3) First-principles statistical methods: *Ab initio* atomistic thermodynamics
- 4) Molecular dynamics: reaction barriers and configurational sampling
- 5) First-principles statistical methods: kinetic Monte Carlo simulations
- 6) Concluding remarks

# Non-relativistic Schrödinger equation (atomic units)

$$i \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

$\Psi(\{\mathbf{r}_i\}, \{\sigma_i\}, t)$  – wave function, depends on spatial ( $\mathbf{r}_i$ ) and spin ( $\sigma_i$ ) coordinates of particles, and time  $t$

**Hamiltonian operator** 
$$\hat{H} = \underbrace{-\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2}}_{\text{kinetic energy}} + \underbrace{U(\mathbf{r}_i, \sigma_i, t)}_{\text{potential energy}}$$

$$U(\{\mathbf{r}_i\}, \{\sigma_i\}, t) = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j|} + V^{ext}(\{\mathbf{r}_i\}, t) + \sum_i C(\mathbf{r}_i, t) (\hat{\mathbf{L}} \cdot \sigma_i)$$

# Stationary Schrödinger equation

If  $\hat{H}$  is independent on  $t$  :

$$\Psi(\mathbf{r}_i, \sigma_i, t) = \Phi(\mathbf{r}_i, \sigma_i) f(t)$$

$$i \frac{\partial f(t)}{\partial t} \Phi(\mathbf{r}_i, \sigma_i) = f(t) \hat{H} \Phi(\mathbf{r}_i, \sigma_i)$$

$$i \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = \frac{\hat{H} \Phi(\mathbf{r}_i, \sigma_i)}{\Phi(\mathbf{r}_i, \sigma_i)} \quad \text{– left- and right-hand sides depend on different variables}$$

$$f(t) = A \exp(-iEt)$$

$$\hat{H} \Phi(\mathbf{r}_i, \sigma_i) = E \Phi(\mathbf{r}_i, \sigma_i)$$

with constant  $E$

# Born-Oppenheimer (adiabatic) approximation

$\frac{m_e}{M_{H^+}} \approx 0.0005$  – electrons see frozen nuclei most of the time

$$\hat{H}\Phi(\mathbf{r}_i, \sigma_i) = E\Phi(\mathbf{r}_i, \sigma_i)$$

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_J\}) = \sum_n \chi_n(\{\mathbf{R}_J\}) \underbrace{\Psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_J\})}_{\text{electronic wave function at fixed nuclei}} \text{ – exact!}$$

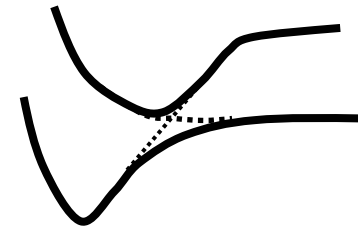
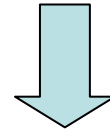
electronic wave  
function at fixed nuclei

Substitute into the Schrödinger equation, integrate over  $\mathbf{r}_i$

$$\left[ -\frac{1}{2} \sum_J \frac{1}{M_J} \frac{\partial^2}{\partial \mathbf{R}_J^2} + E_n(\{\mathbf{R}_J\}) - E \right] \chi_{vn}(\{\mathbf{R}_J\}) = -\sum_m C_{nm} \chi_{vm}(\{\mathbf{R}_J\})$$

# Born-Oppenheimer (adiabatic) approximation

The approximation: electrons remain in a given state  $n$  as the nuclei move  $\leftrightarrow$  neglect off-diagonal  $C_{nm}$



Equation for nuclei:

$$\left[ -\frac{1}{2} \sum_J \frac{1}{M_J} \frac{\partial^2}{\partial \mathbf{R}_J^2} + E_n(\{\mathbf{R}_J\}) \right] \chi_{vn}(\{\mathbf{R}_J\}) = E_{vn}^{\text{nuc}} \chi_{vn}(\{\mathbf{R}_J\})$$

Equation for electrons:

$$\left[ -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V^{\text{ext}}(\{\mathbf{r}_i\}) \right] \Psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_J\}) = E_n(\{\mathbf{R}_J\}) \Psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_J\})$$

# Approximations to the electronic problem

$\Psi_n(\{\mathbf{r}_i\})$  –  $3N_e$ -dimensional function, second-order differential equation  $\rightarrow$  cannot solve analytically for  $N_e > 1$ , hard to interpret

## 1) Wave-function methods: Hartree-Fock approximation

$$\Psi(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det|\psi_1(\vec{r}_1, \sigma_1), \dots, \psi_N(\vec{r}_N, \sigma_N)|$$

**one-particle states**

$$E_{\text{tot}} = \sum_{i=1}^N \langle \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} \sum_{I=1}^M \sum_{J=1}^M \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' - \frac{1}{2} \int \frac{\psi_i^*(\vec{r}, \sigma)\psi_j^*(\vec{r}', \sigma')\psi_j(\vec{r}, \sigma)\psi_i(\vec{r}', \sigma')}{|\vec{r} - \vec{r}'|} d^3r d^3r' d\sigma d\sigma'$$

# Approximations to the electronic problem

## 2) Density functional theory: Hohenberg-Kohn theorem

$$\rho(\vec{r}) \begin{cases} \hat{H} & \text{-- many-body Hamiltonian} \\ \Psi(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) & \text{-- many-body wave function} \\ E_{\text{tot}} & \text{-- total energy} \end{cases}$$

$$E_{\text{tot}} = T[\rho] - \sum_{I=1}^M Z_I \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{R}_I|} d^3r + \frac{1}{2} \sum_{I=1}^M \sum_{J=1}^M \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + E_{\text{xc}}[\rho]$$

**Approximations to  $E_{\text{XC}}[\rho]$  : Local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA, hybrid functionals**

**LDA and GGA are widely used due to balance between accuracy and computational cost**



# Approximations to the electronic problem: Basis set

Idea: represent all unknown functions (  $\rho(\vec{r})$  ,  $\psi_i(\vec{r}_1)$  )  
as a linear combination of known functions with well-  
defined properties:  $\psi_i(\mathbf{r}) = \sum_p C_{ip} \varphi_p(\mathbf{r})$

**Widely used basis sets:**

**gaussians**  $x^i y^j z^k \exp(-\alpha r^2)$  (localized, analytic integrals)

**plane waves**  $\exp(i\mathbf{k} \cdot \mathbf{r})$  (delocalized, analytic integrals)

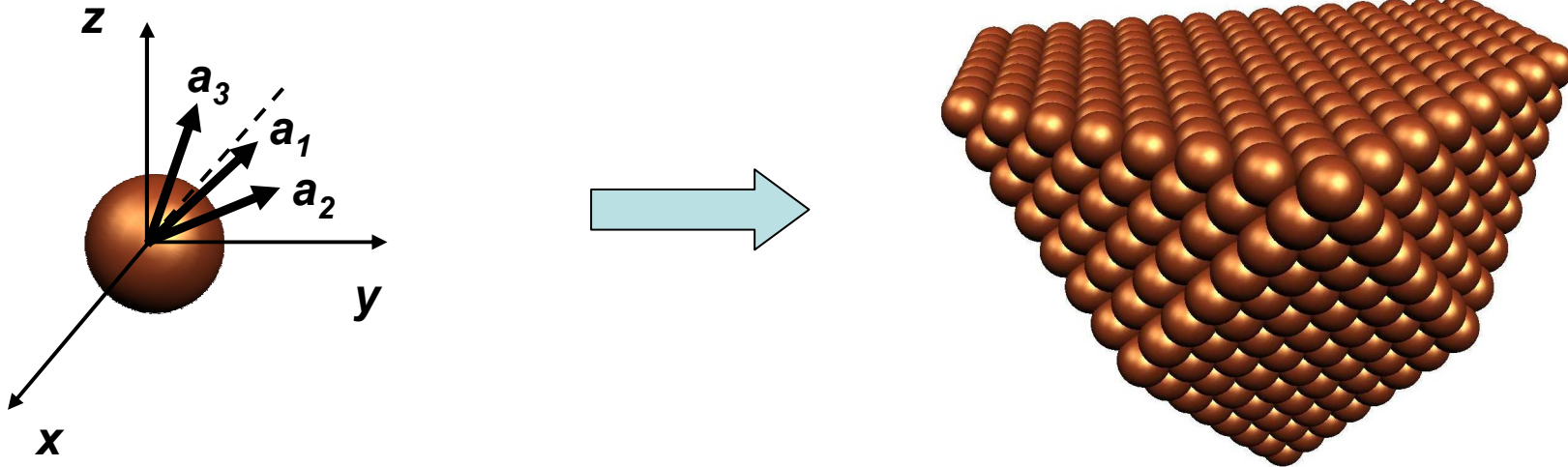
**Slater-type**  $x^i y^j z^k \exp(-\alpha r)$  (localized, nuclear cusp)

**grid-based**  $\delta(\mathbf{r} - \mathbf{r}_i)$  (localized, analytic integrals)

**Core electrons are often treated separately**  
(pseudopotentials, plane-wave + localized basis)

# Extended (periodic) systems

There are  $10^{20}$  electrons per  $1 \text{ mm}^3$  of bulk Cu



**Bloch's theorem:**

$$U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \rightarrow \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

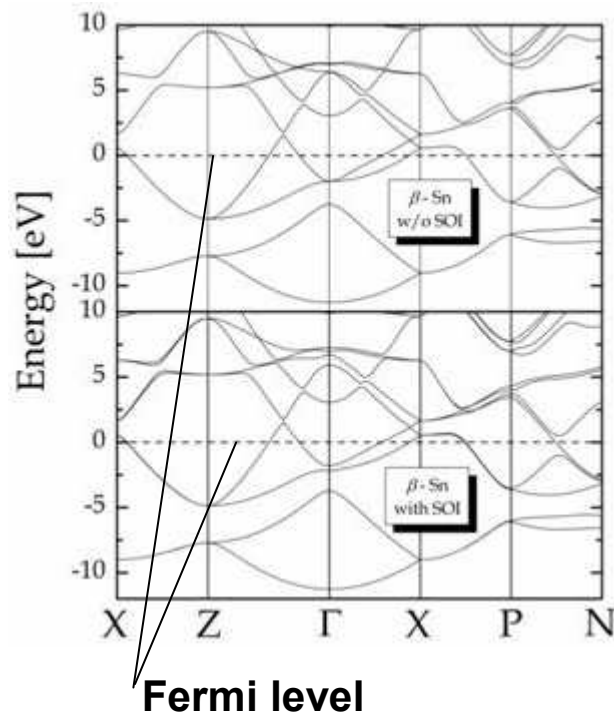
band index

**Periodic model  $\rightarrow$  finite number of electrons at infinite number of k-points...**

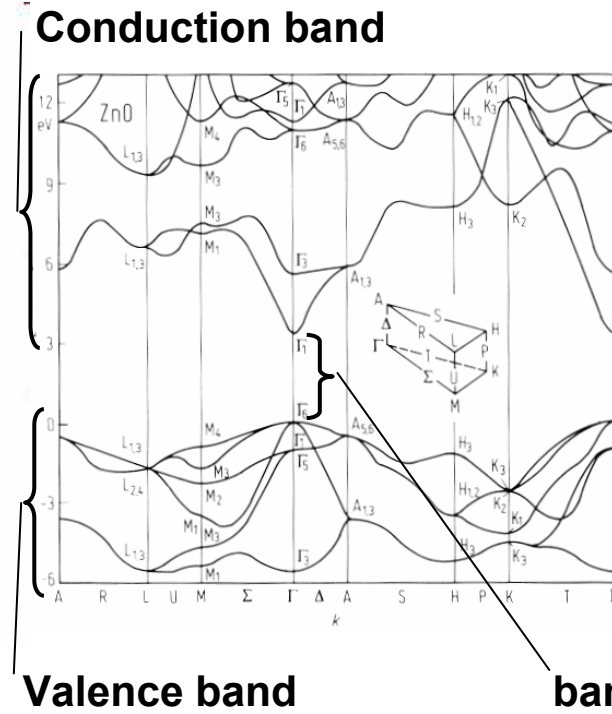
**But can be solved by interpolation on a finite mesh of k**

# Insulators, metals, and semiconductors

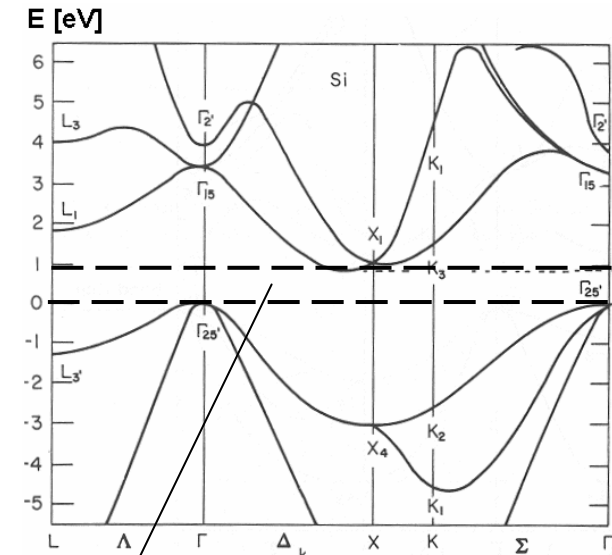
Metal (Sn)



Insulator (ZnO)



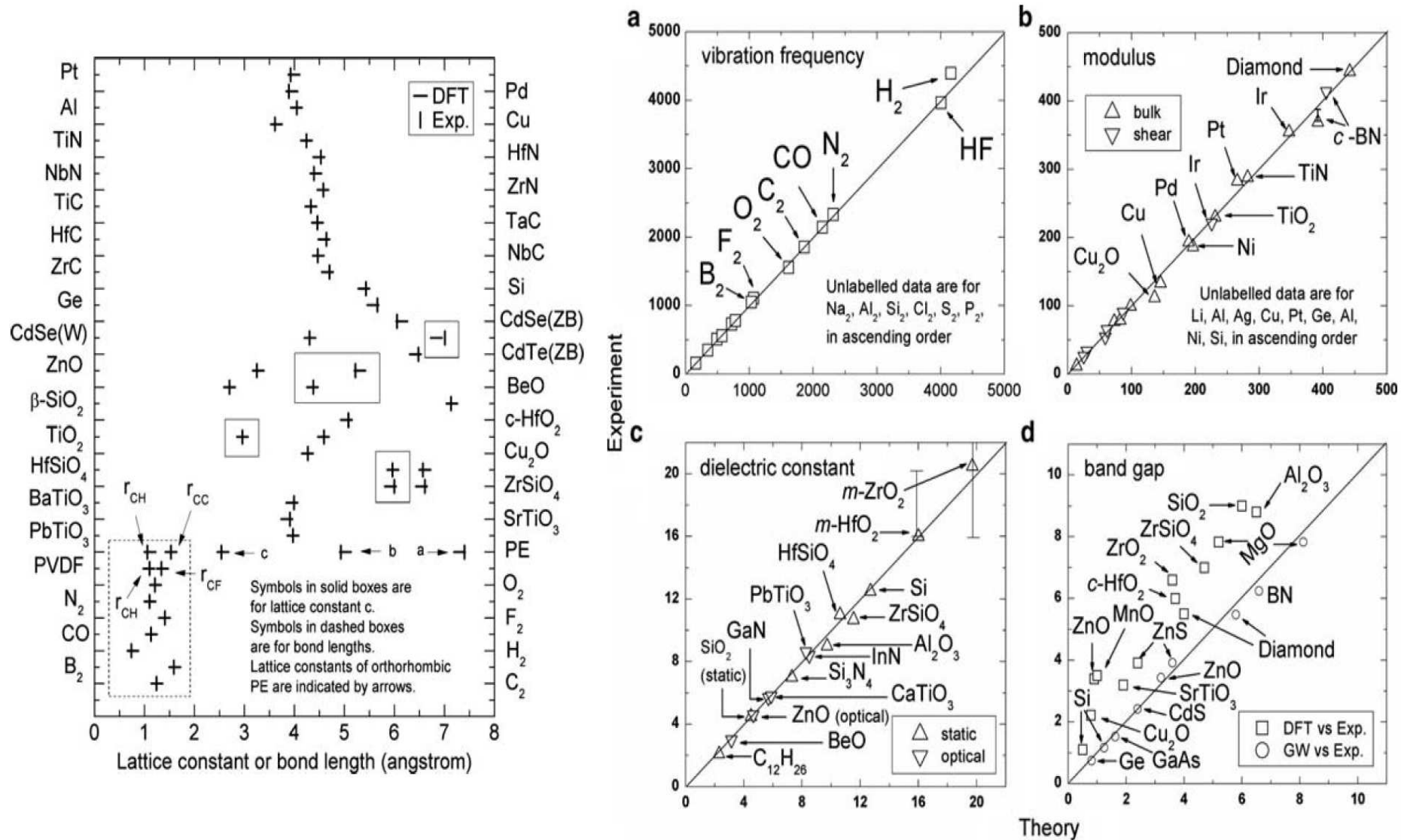
Semiconductor (Si)



**Semiconductors have a smaller band gap, so that electron and/or hole states can be thermally populated**

**An insulator can be made a semiconductor by creating defects (doping)**

# Is standard DFT (LDA, GGA) accurate?



**Lattice constants, cohesive energies (metals), reaction energies – OK; band gaps, reaction barriers, magnetic properties – not good; no systematic way to improve**

Taken from “Dielectric polymer nanocomposites”, Editor J. K. Nelson, Springer (2010)

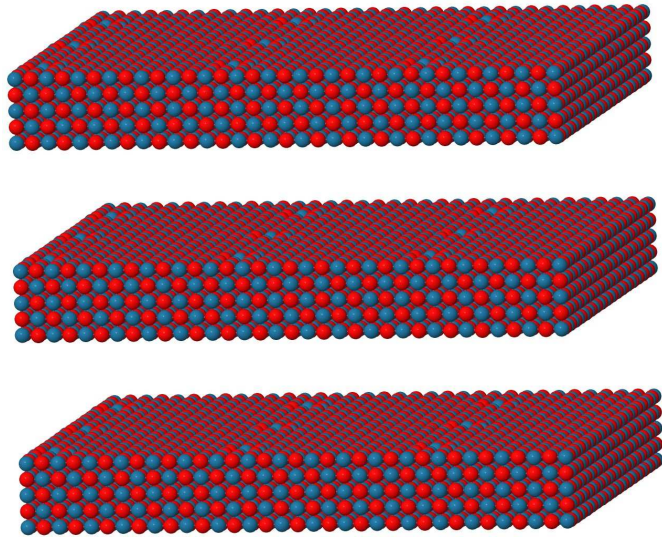
# What can we calculate with DFT

- 1) Total energy (bulk, surface, wire, cluster)
- 2) Geometry (relative atomic positions, unit cell parameters)
- 3) Electron density (bonding, hybridization)
- 4) Bulk modulus (materials under pressure)
- 5) Vibrational frequencies (molecules, solids)
- 6) Dielectric constant (polarization, charge screening)
- 7) Cohesive energy
- 8) Adsorption energy
- 9) Reaction energy
- 10) One-particle wave functions
- 11) Density of states (total, projected, local)
- 12) NMR shifts, XPS, STM, ...

**Nowadays can do: ~3000 atoms, 50000 electrons per u. c.**

# Surface modeling

## 1) Slab model (supercell approach)

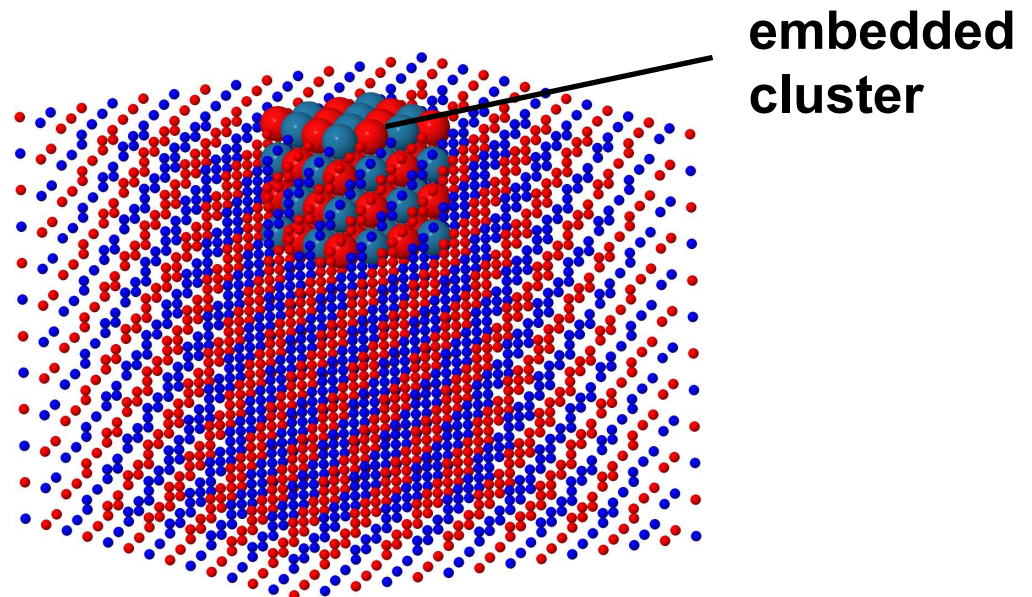


- + regular surfaces
- + coverage dependence
- defect-defect interaction

## 2) Cluster model:

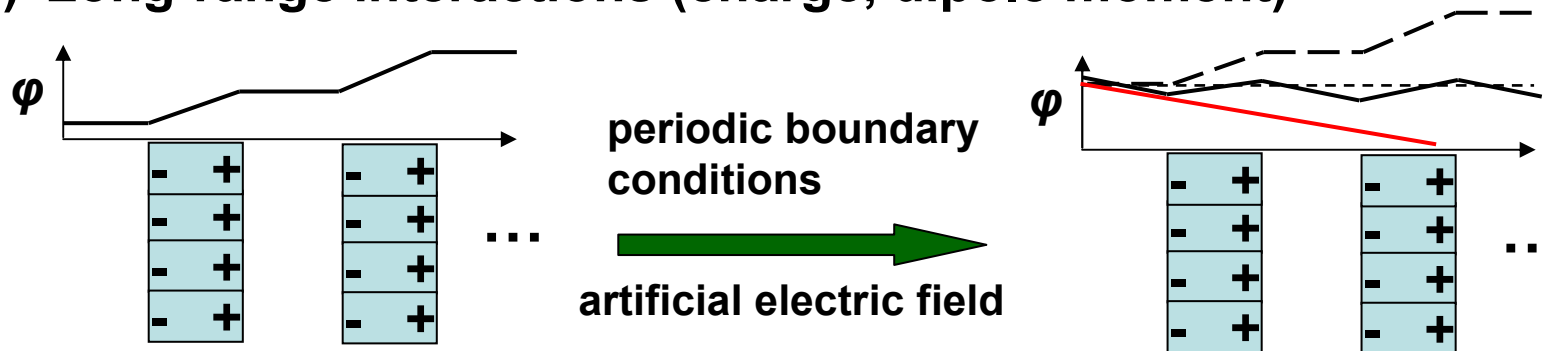
- + isolated defect
- border effects

Embedding: point charges (ionic systems), dangling bond saturation (covalently-bound systems),...

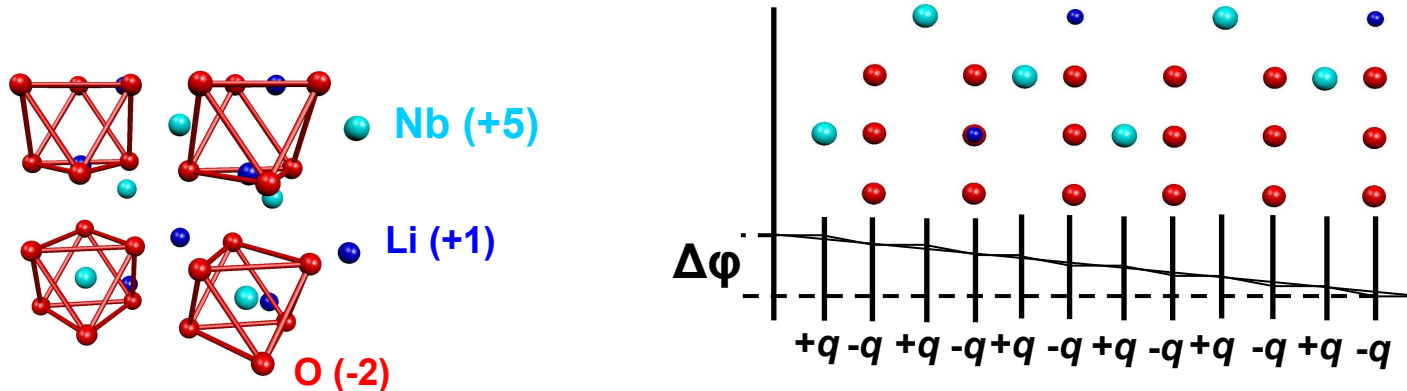


# Surface modeling: important issues

- 1) Finite slab thickness (surface-surface interaction)
- 2) Finite vacuum layer thickness (image-image interactions)
- 3) Long-range interactions (charge, dipole moment)



## 4) Surface polarity

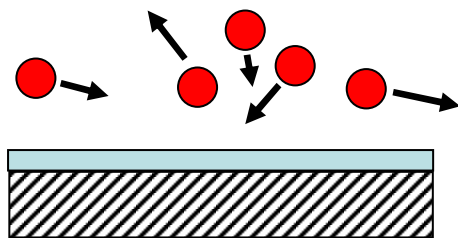


# Real versus model surfaces (materials and pressure gaps)

- 1) A straightforward DFT calculation corresponds to  $T = 0$  K
- 2) In literature, 1-5000 Å is called a “surface”, depending on experimental technique
- 3) Real surfaces are full of defects (vacancies, steps, dislocations,...)
- 4) Surface structure and composition can strongly depend on preparation
- 5) Impurities and adsorbates can influence the surface morphology

Special care must be taken in experiment to produce a defect-free pure surface of known termination. But even then...

- 6) A surface cannot be separated from a gas (or liquid) above it



$$\nu = \frac{p}{\sqrt{2\pi mkT}}$$

For  $T = 300$  K,  $p = 1$  atm  $\rightarrow \nu \sim 10^8$  site $^{-1}$  s $^{-1}$

Requires  $p \leq 10^{-12}$  atm to keep a “clean” surface clean; surface can also lose atoms



# DFT (internal) versus free energy

At constant  $T$  a system minimizes its free energy ( $-TS$ ), not internal energy  $U$

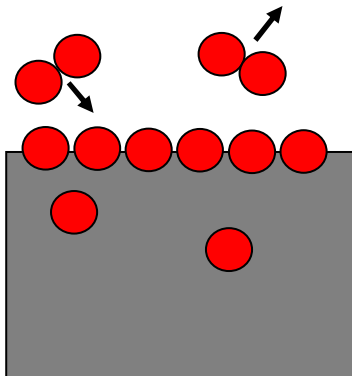
If also volume  $V$  is constant, the energy minimized is Helmholtz free energy  $F$

$$F = U - TS$$

If  $(T,p)$  are constant, the energy minimized is Gibbs free energy  $G$

$$G = U + pV - TS = \sum_i \mu_i N_i$$

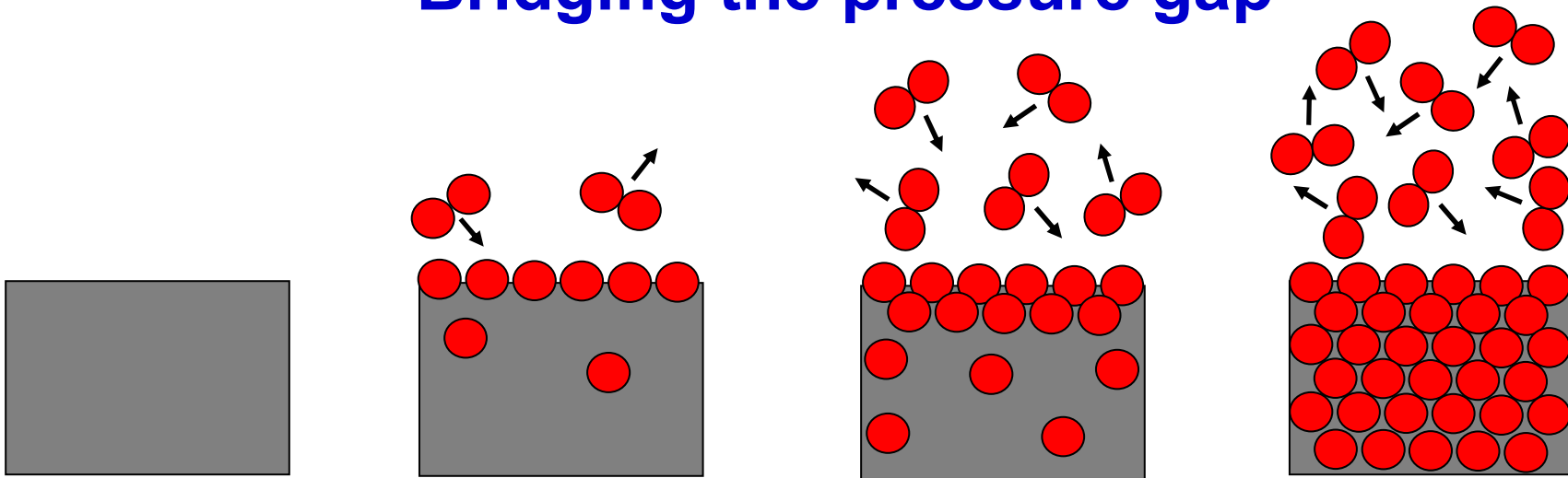
Chemical potential  $\mu_i$  of the  $i$ -th atom type is the change in free energy as the number of atoms of that type in the system increases by 1



In thermodynamic equilibrium,  $\mu_i$  is the same in the whole system (surface, bulk, gas)

Statistics plays a crucial role due to a macroscopically large number of particles in the system

## Bridging the pressure gap

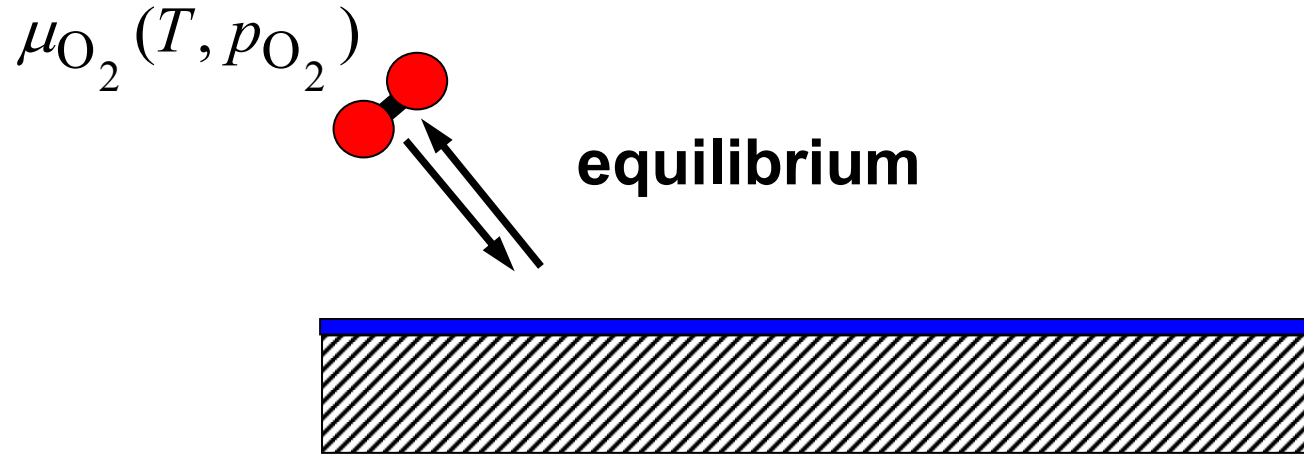


**Theory:** Development and use of first-principle statistical mechanics approaches

**Experiment:** Awareness and diligent experiments...  
Development and use of „*in situ*“ techniques

*Nanometer and sub-nanometer thin oxide films at surfaces of late transition metals,*  
K. Reuter, in: *Nanocatalysis: Principles, Methods, Case Studies,*  
(Eds.) U. Heiz, H. Hakkinen, and U. Landman, Springer (Berlin, 2006)  
<http://www.fhi-berlin.mpg.de/th/paper.html>

# First-principles atomistic thermodynamics



$$G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV$$

DFT

**Surface free formation energy:**  $\gamma_{\text{surf}}(T, p) = \frac{1}{A} \left[ G_{\text{sufr}}(\{N_i\}) - \sum_i N_i \mu_i \right]$

**Defect free formation energy:**  $\Delta G(T, p) = \frac{1}{A} \left[ G_{\text{def}}(\{N_i + \Delta N_i\}) - \sum_i \mu_i \Delta N_i - G_{\text{perf}}(\{N_i\}) \right]$

# Computation of free energies: Ideal gas

For an ideal gas of  $N$  particles in a box:

$$Z = \frac{1}{N!} (Z_{\text{nucl}} Z_{\text{el}} Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}})^N \quad - \quad \text{partition function (canonical)}$$

$$\mu(T, p) = G / N = (-k_B T \ln Z + pV) / N \quad - \quad \text{chemical potential}$$

1) **Electronic free energy:**  $Z_{\text{el}} = \sum_i \exp(-E_i^{\text{el}} / k_B T)$

Typical excitation energies  $\text{eV} \gg k_B T$ ,  
only (possibly degenerate) ground state  
contributes significantly  $\implies \mu_{\text{el}}(T, p) \approx E_0 - k_B T \ln(2I + 1)$

Required input:  $E_0, I$

2) **Translational free energy (particle in a box):**  $Z_{\text{transl}} = \sum_{\mathbf{k}} \exp(-\hbar^2 \mathbf{k}^2 / 2mk_B T)$

Box length of length  $L \rightarrow \infty \implies Z_{\text{transl}} \approx V (2\pi mk_B T / \hbar^2)^{3/2}$

Required input: particle mass  $m$

# Computation of free energies: Ideal gas

3) Rotational energy (rigid rotator):  $Z_{\text{rot}} = \sum_J (2J + 1) \exp(-J(J + 1)B_0 / k_B T)$

Diatomic molecule:  $\mu_{\text{rot}} \approx -k_B T \ln(k_B T / \sigma B_0)$   $\sigma = 2$  (homonucl.),  $= 1$  (heteronucl.)  
 $B_0 \sim md^2$  ( $d$  – bond length)

Required input: rotational constant  $B_0$  (calculations, microwave spectroscopy)

4) Vibrational free energy (harmonic approx.):  $Z_{\text{vib}} = \sum_{i=1}^M \sum_n \exp(-(n + \frac{1}{2})\hbar\omega_i / k_B T)$

$\longrightarrow \mu_{\text{vib}}(T, p) = \sum_{i=1}^M \left( \frac{1}{2} \hbar\omega_i + k_B T \ln(1 - \exp(-\hbar\omega_i / k_B T)) \right)$

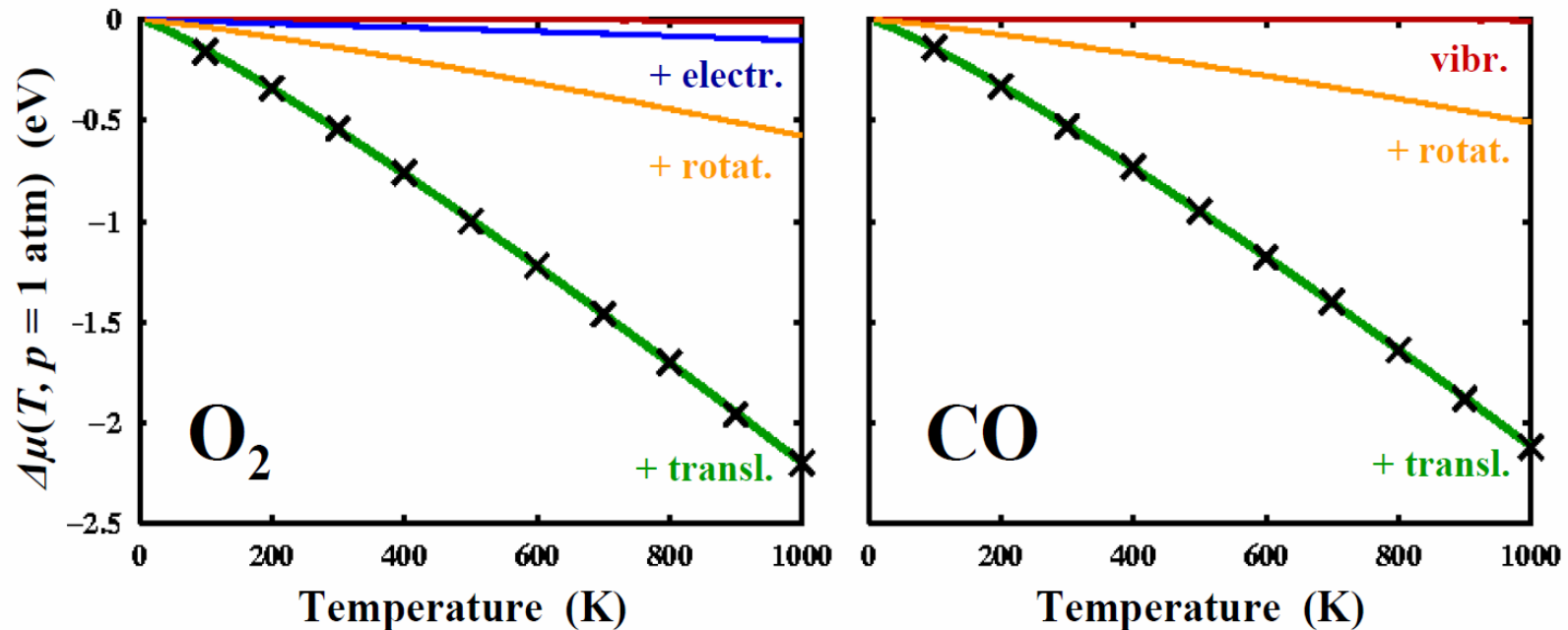
Required input:  $M$  fundamental vibrational modes  $\omega_i$

Calculate dynamic matrix  $D_{ij} = (m_i m_j)^{-1/2} (\partial^2 E_0 / \partial r_i \partial r_j)_{\text{req}}$ ,

solve eigenvalue problem  $\det(\mathbf{D} - \mathbf{1}\omega^2) = 0$

# Computation of free energies: Ideal gas

It is convenient to define a reference for  $\mu(T, p)$  :  $\mu(T, p) = E_0 + \Delta\mu(T, p)$

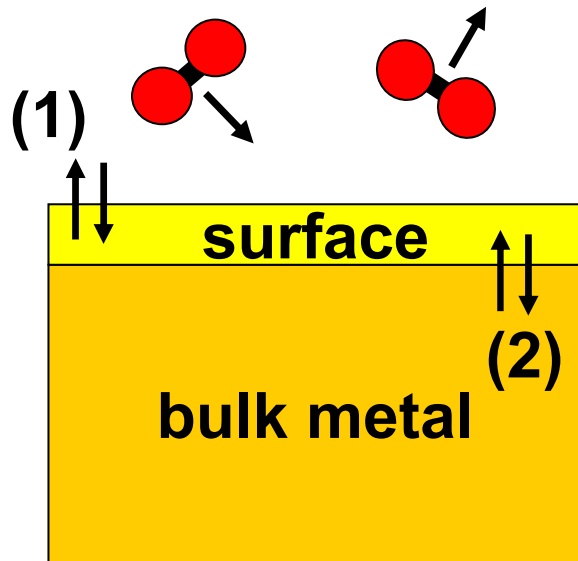


Alternatively:  $\Delta\mu(T, p) = \Delta\mu(T, p^\circ) + k_B T \ln(p / p^\circ)$

and  $\Delta\mu(T, p^\circ = 1 \text{ atm})$  from thermochemical tables (e.g., JANAF)

## Example I: Metal surface in contact with O<sub>2</sub> gas

$$\gamma_{\text{surf}}(T, p) = \frac{1}{A} [G_{\text{surf}}(N_{\text{O}}, N_{\text{M}}) - N_{\text{O}}\mu_{\text{O}} - N_{\text{M}}\mu_{\text{M}}]$$



**Reservoirs:**

1)  $\mu_{\text{O}}(T, p_{\text{O}_2})$  from ideal gas

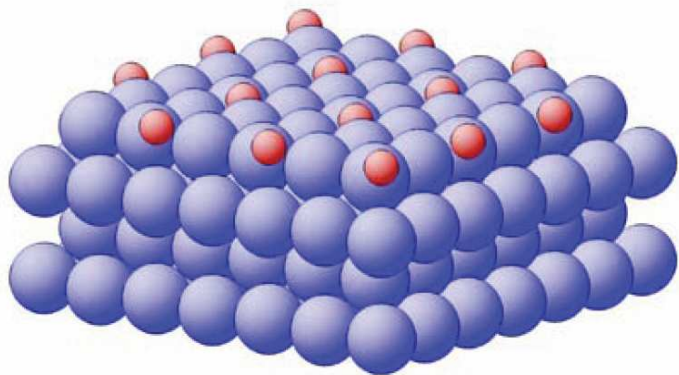
2)  $\mu_{\text{M}} = g_{\text{M}}^{\text{bulk}}$

**Neglect for now  $F^{\text{vib}}$  and  $TS^{\text{conf}}$ :**

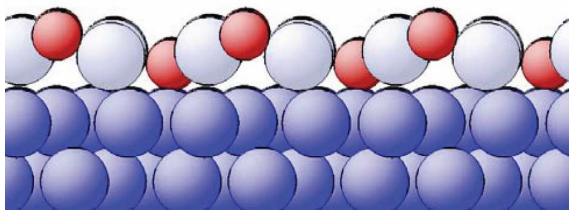
$$\gamma(T, p) \approx \left( E_{\text{surf}}^{\text{slab}} - N_{\text{M}}E_{\text{M}}^{\text{bulk}} - N_{\text{O}} \frac{1}{2} E_{\text{O}_2} \right) / A - N_{\text{O}}\Delta\mu_{\text{O}}(T, p) / A$$

# Example I: Metal surface in contact with O<sub>2</sub> gas

$$\gamma \approx \left( E_{\text{surf}}^{\text{slab}} - N_{\text{Pd}} E_{\text{Pd}}^{\text{bulk}} - N_{\text{O}} \frac{1}{2} E_{\text{O}_2} \right) / A - N_{\text{O}} \Delta \mu_{\text{O}} / A$$

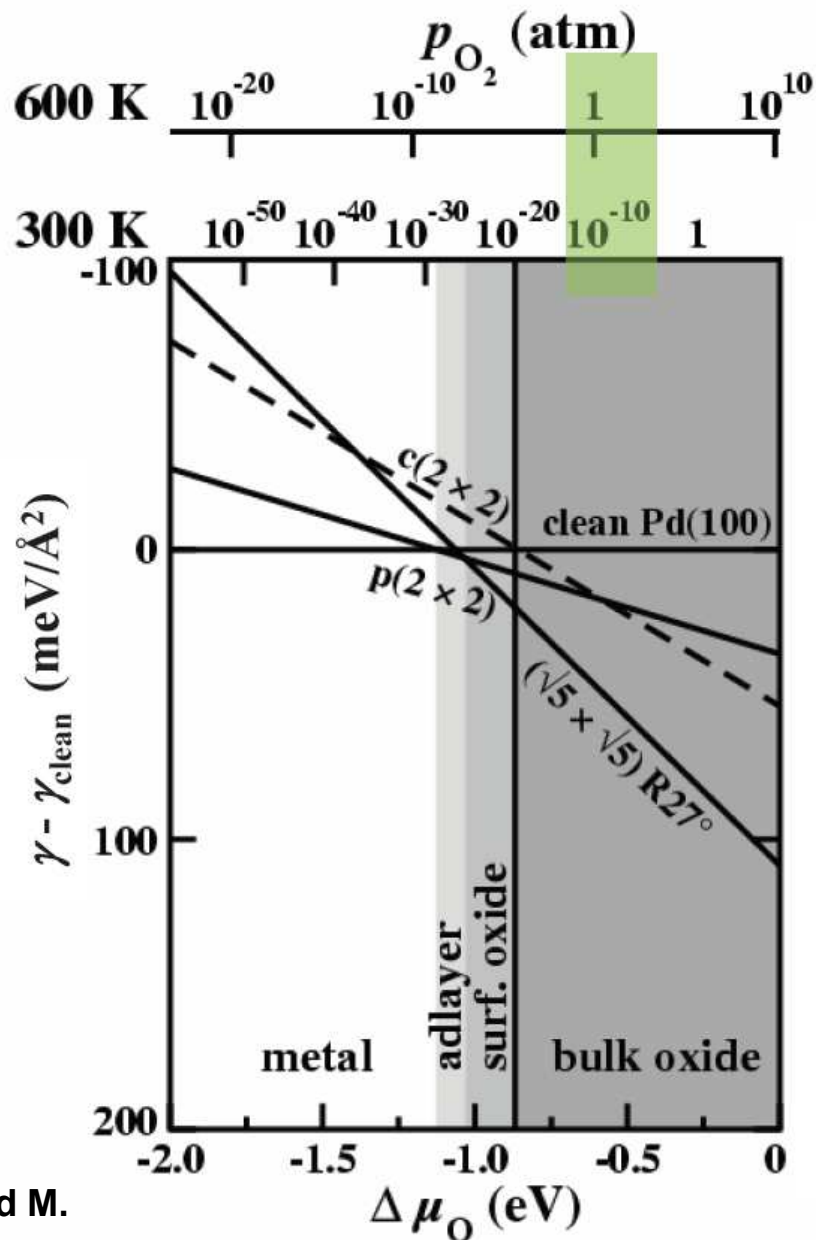


**p(2x2) O/Pd(100)**



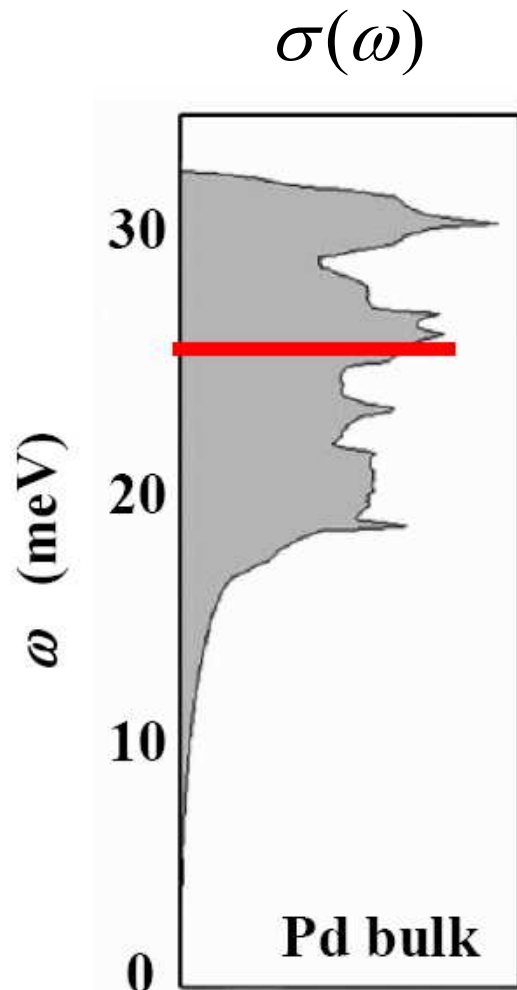
**( $\sqrt{5} \times \sqrt{5}$ )R27° PdO(101)/Pd(100)**

M. Todorova *et al.*, Surf. Sci. 541, 101 (2003); K. Reuter and M. Scheffler, Appl. Phys. A 78, 793 (2004)





# Vibrational contributions to the surface free energy



$$F^{\text{vib}}(T, V) = \int F^{\text{vib}}(T, \omega) \sigma(\omega) d\omega$$

$$\gamma^{\text{vib}} = \Delta F^{\text{vib}} / A =$$

$$\frac{1}{A} \int F^{\text{vib}}(T, \omega) [\sigma_{\text{surf}}(\omega) - N_{\text{Pd}} \sigma_{\text{bulk}}(\omega)] d\omega$$

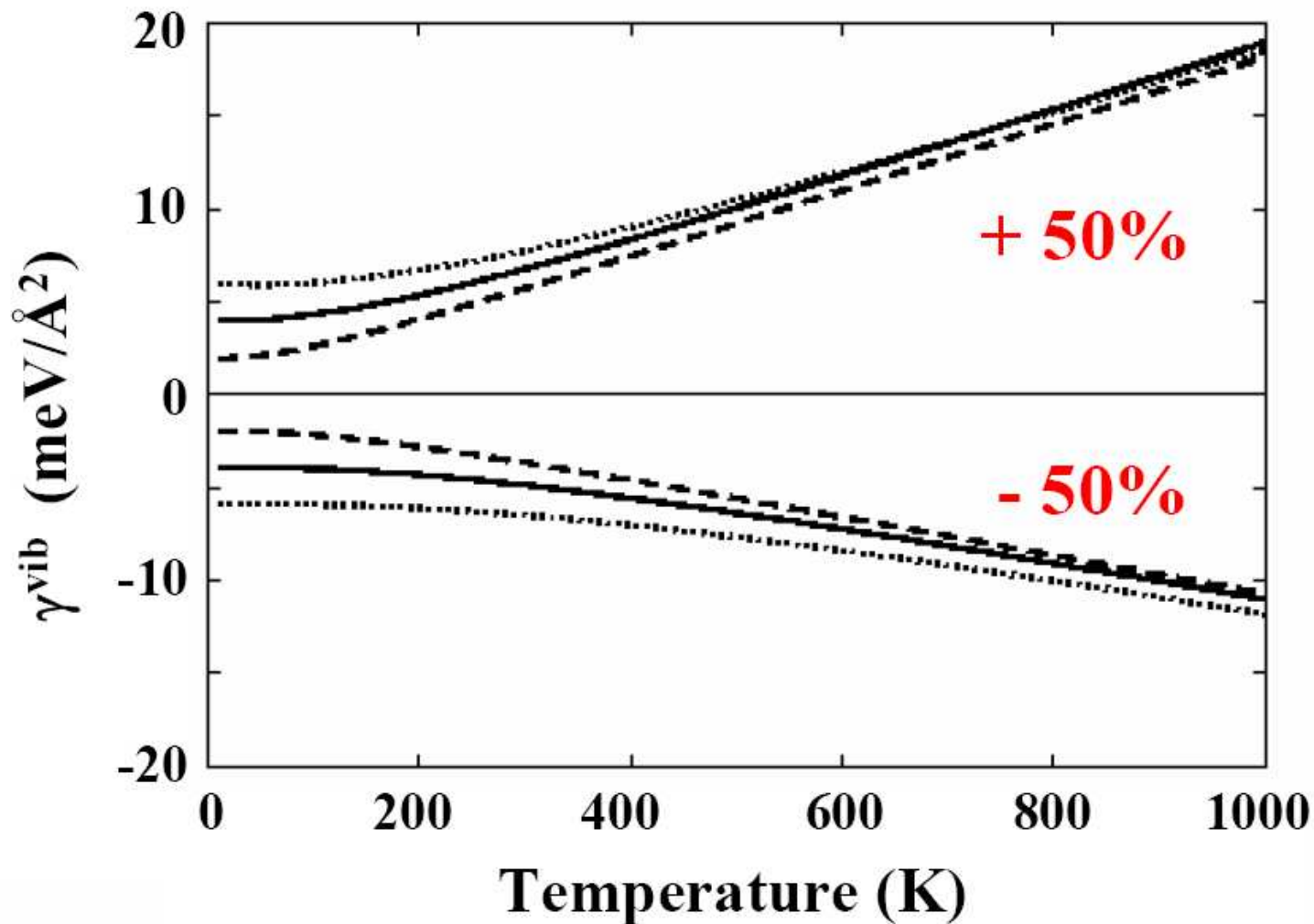
Only changes in vibrational free energy contribute to the surface free energy

Make estimate from simple models

e.g., Einstein model:  $\sigma(\omega) = \delta(\omega - \langle \omega \rangle)$

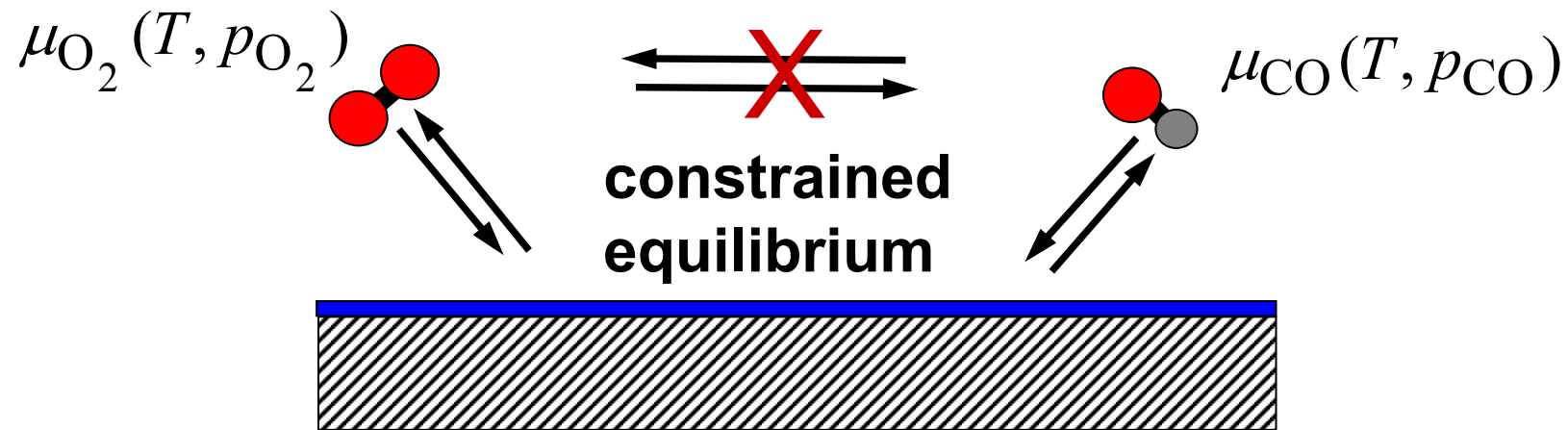
$$\langle \omega \rangle_{\text{Pd}}(\text{bulk}) \sim 25 \text{ meV}$$

# Surface-induced variations of substrate modes



**< 10 meV/Å<sup>2</sup> for T = 600 K – in this case!!!**

# First-principles atomistic thermodynamics: constrained equilibria



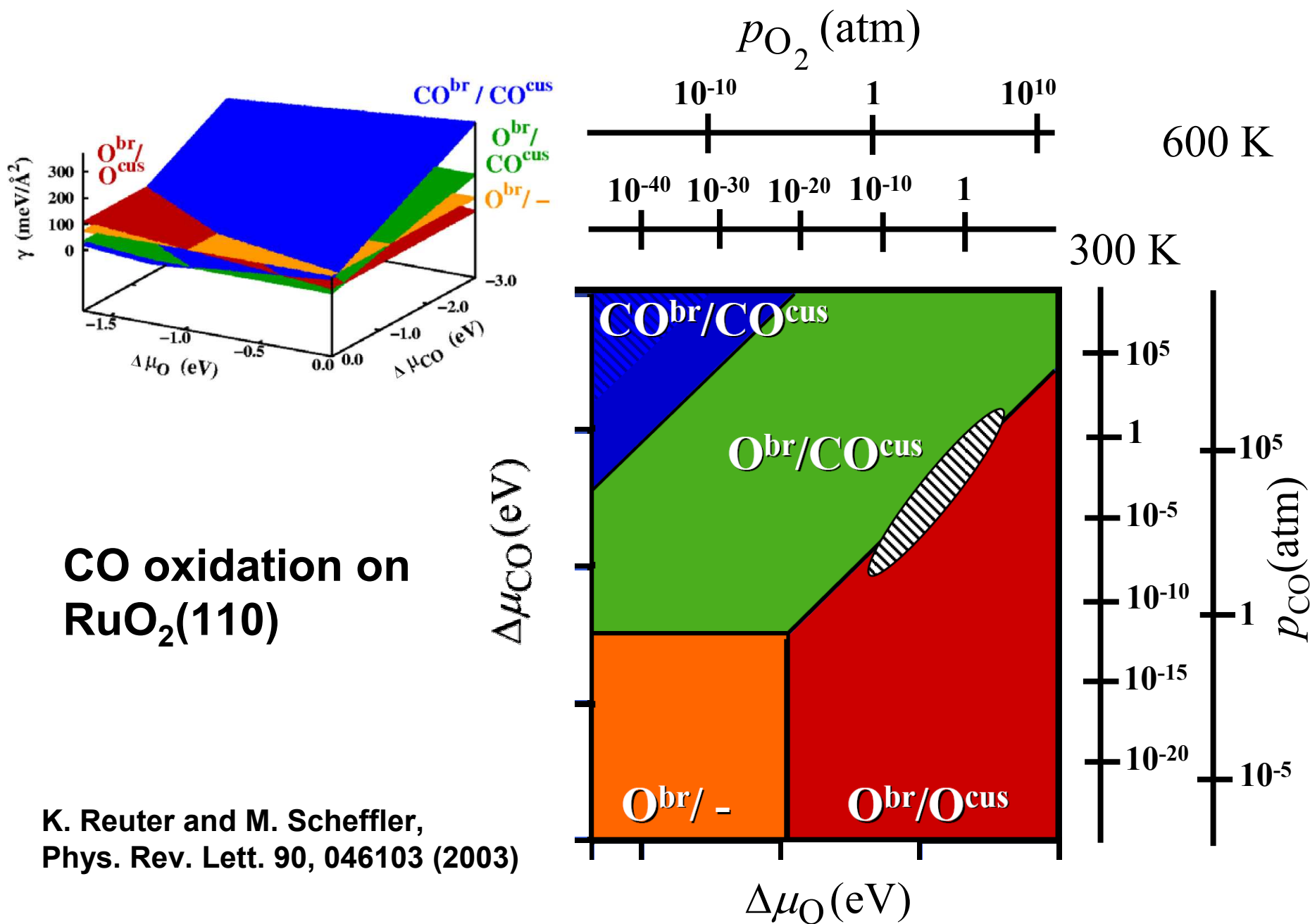
$$G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV$$

DFT

C.M. Weinert and M. Scheffler, *Mater. Sci. Forum* 10-12, 25 (1986); E. Kaxiras *et al.*, *Phys. Rev. B* 35, 9625 (1987);

K. Reuter and M. Scheffler, *Phys. Rev. B* 65, 035406 (2001); *Phys. Rev. B* 68, 045407 (2003)

# Surface phase diagrams

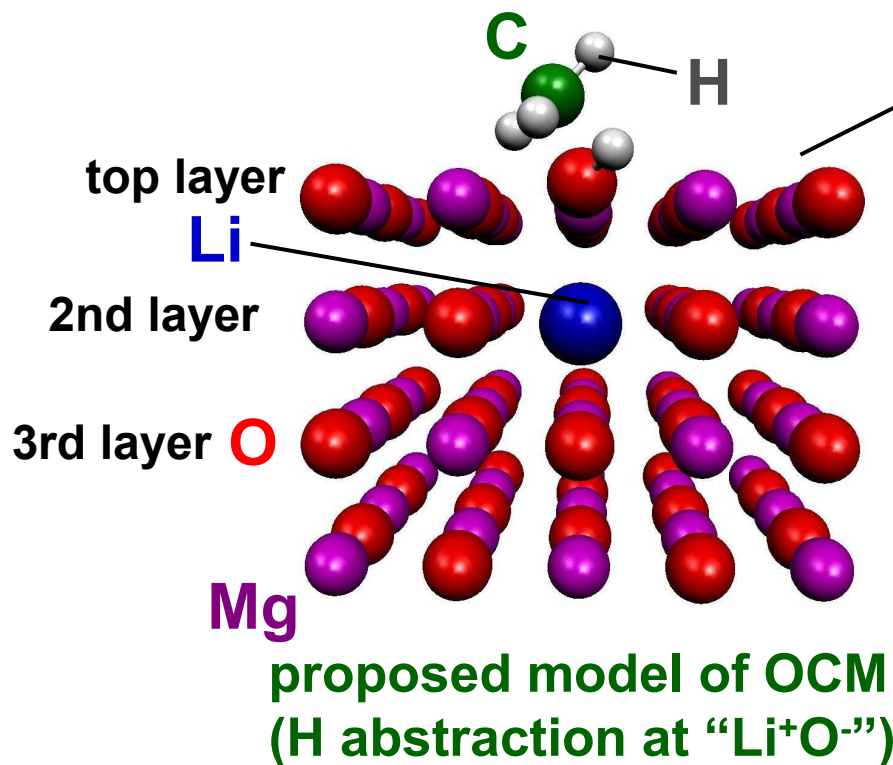
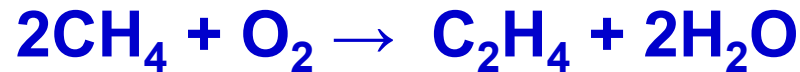


**CO oxidation on RuO<sub>2</sub>(110)**

K. Reuter and M. Scheffler,  
Phys. Rev. Lett. 90, 046103 (2003)

# Example II: defects on oxide surfaces

Li-induced defects at MgO (001) surface  
(for oxidative coupling of methane)



MgO (001) surface with  
subsurface Li<sub>Mg</sub> defects

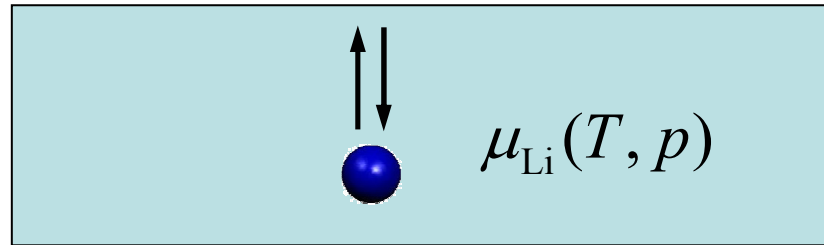
- 1) Li<sub>Mg</sub>: Li substitutional defects  
( $r_{\text{Li}^+} \approx r_{\text{Mg}^{2+}}$ )
- 2) Li<sub>Mg</sub> with adjacent O or Mg  
vacancies or interstitials
- 3) Li<sub>Mg</sub> with adjacent O or Mg  
ad-atoms

Electronic structure, total energies + *ab initio* atomistic  
thermodynamics

# Defect formation energies: methodology

## *Ab initio* atomistic thermodynamics

$$\mu_{\text{O}_2}(T, p)$$



fixed concentration  $\delta$   
of  $\text{Li}_{\text{Mg}}$  in the bulk

$$\Delta G(T, p) = \Delta E^{\text{tot}} + \cancel{\Delta F^{\text{vib}}} - \underline{\underline{TS^{\text{conf}}}} + p\cancel{\Delta V} - \sum_i \mu_i \Delta N_i$$

$\swarrow$   
**DFT**

$$\Delta \mu_{\text{O}}(T, p) = \frac{1}{2} \Delta \mu_{\text{O}_2}(T, p^\circ) + \frac{1}{2} k_{\text{B}} T \ln(p / p^\circ)$$

$$\mu_{\text{Li}}(T, p) = \frac{1}{2} k_{\text{B}} T \ln(p / p^\circ) + \underbrace{E}_{\text{constant from DFT}} - \mu_{\text{O}}(T, p)$$

constant from DFT

# Configurational entropy and defect concentration

$$S^{\text{conf}} = k_B \ln(N! / [(N - N_{\text{def}})! N_{\text{def}}!])$$

For a very large supercell, when  $N \gg 1$ ,  $N_{\text{def}} \gg 1$ , and  $(N - N_{\text{def}}) \gg 1$  (Stirling formula):

$$S^{\text{conf}} \approx k_B [N \ln N - (N - N_{\text{def}}) \ln(N - N_{\text{def}}) - N_{\text{def}} \ln(N_{\text{def}})]$$

In equilibrium:

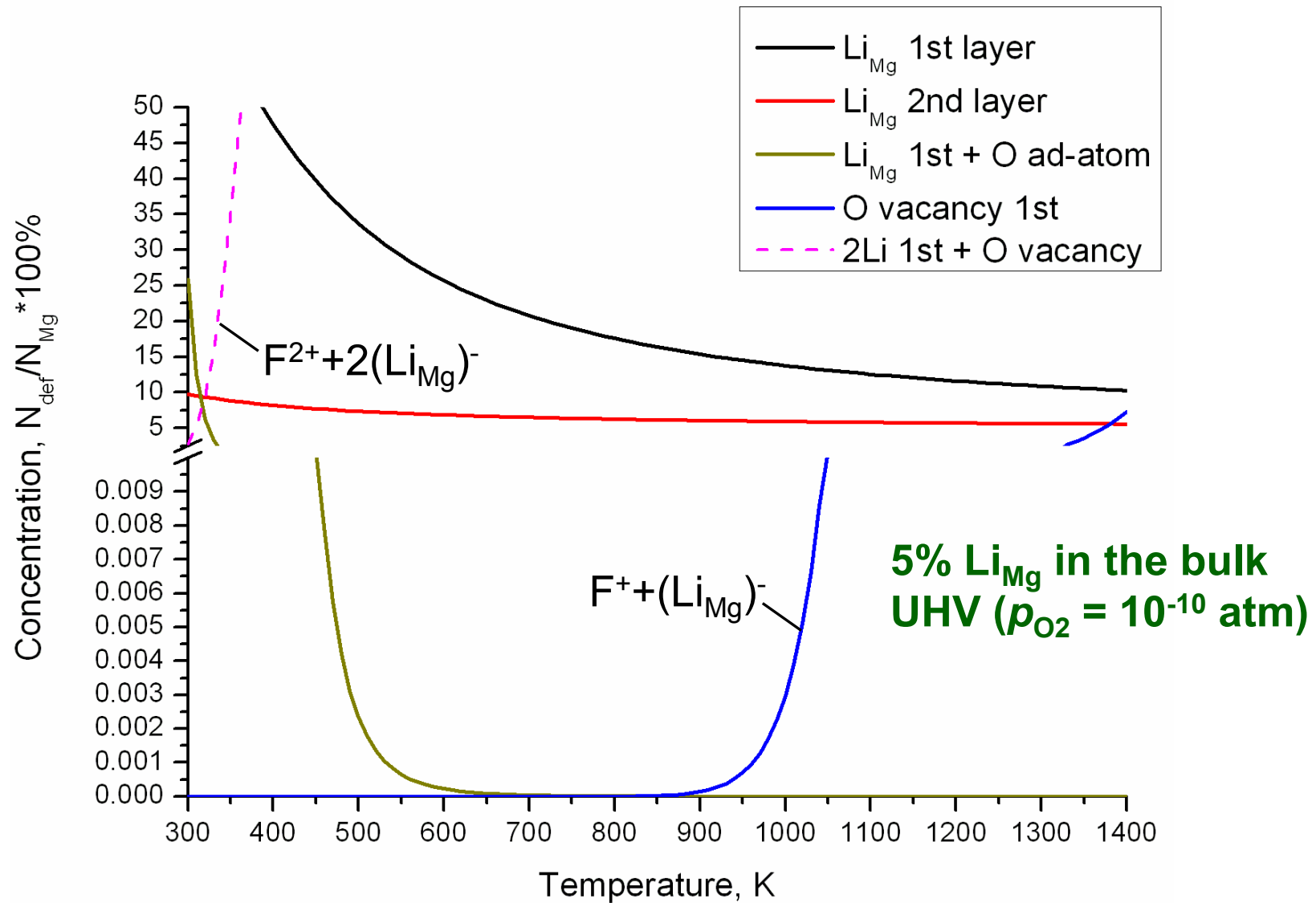
(assumes no interaction between defects)

$$\frac{dG^{\text{def}}}{dN_{\text{def}}} = \frac{d}{dN_{\text{def}}} \left[ G^{\text{perf}} + \overbrace{N_{\text{def}} \Delta G_{+TS}^{\text{def}}} - TS^{\text{conf}} \right] = 0$$



$$\frac{N_{\text{def}}}{N} = \frac{1}{\exp(\Delta G_{+TS}^{\text{def}} / k_B T) + 1}$$

# Equilibrium defect concentrations in Li/MgO



Concentration of  $\text{Li}_{\text{Mg}}$  and  $\text{V}_{\text{O}}$  at the surface increases under reducing conditions



# Explicit atom motion: Molecular dynamics

Goal: Integrate equations of motion, add heat bath; input – forces

$$\frac{dp}{dt} = -\frac{\partial H(p, q)}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H(p, q)}{\partial p} \quad \text{Not trivial to integrate!}$$

Hamiltonian  $H$  is by construction energy conserving

How to model a system at constant temperature?

$$H = H^{\text{sys}} + H^{\text{bath}}$$

conserves energy ← yields Maxwell-Boltzmann distribution of velocities for given  $T$

Nosé-Hoover thermostat (fictitious degrees of freedom):

$$H(\{\mathbf{p}_i\}, \{\mathbf{r}_i\}, \pi, \eta) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U(\{\mathbf{r}_i\}) + \frac{1}{2Q} \pi^2 + 3N \frac{\eta}{\beta}$$

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial U}{\partial \mathbf{r}_i} - \frac{\mathbf{p}_i \pi}{Q} \quad \frac{d\eta}{dt} = \frac{\pi}{Q} \quad \frac{d\pi}{dt} = \sum_i \frac{\mathbf{p}_i}{m_i} - \frac{3N}{\beta}$$

Thermostat takes and gives energy to the atomic subsystem

# Explicit atom motion: Molecular dynamics

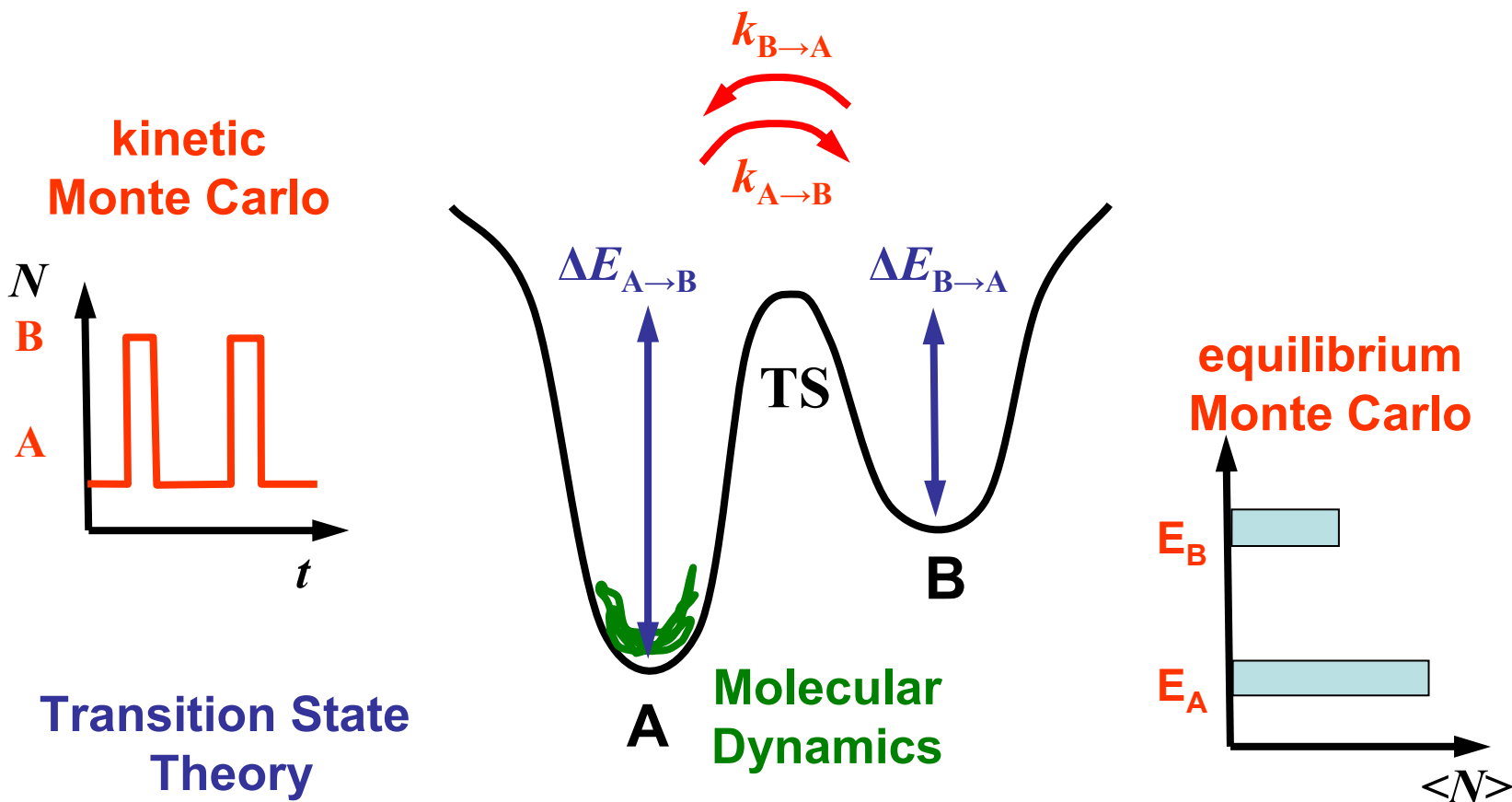
## What can we use it for?

- *T*-dependent rotational-vibrational spectra with anharmonic contributions
- Rates of reactions (or conformational changes, or phase transformations)
- Out-of-equilibrium quantities, e.g. reaction of the system to a time dependent external field

## Including electronic degrees of freedom

- Car-Parrinello MD: coupled equations of motion for both ions and electrons (versus Born-Oppenheimer dynamics)
- Wave function extrapolation (Kühne-Parrinello, Niklasson)

# First-principles kinetic Monte Carlo simulations



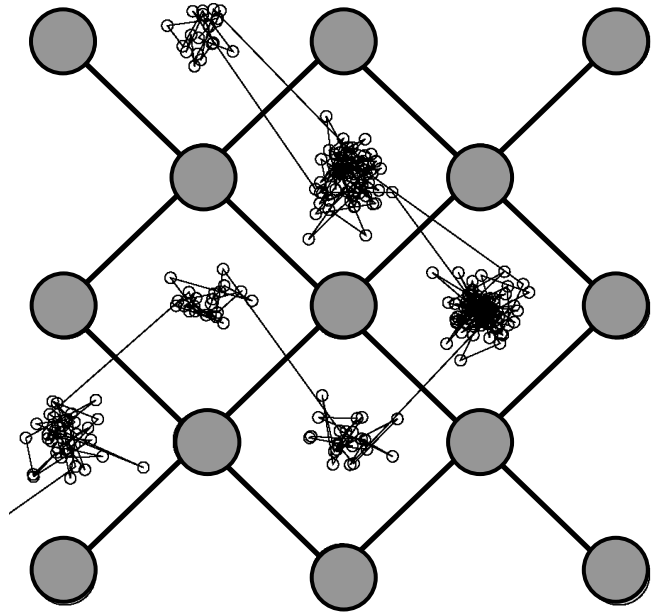
$$k_{i \rightarrow j} = \left( \frac{k_B T}{h} \right) \frac{Z_{\text{TS}(i \rightarrow j)}}{Z_i}$$

$$= \Gamma_0 \exp \left( \frac{-\Delta E_{i \rightarrow j}}{k_B T} \right)$$

**Master equation**

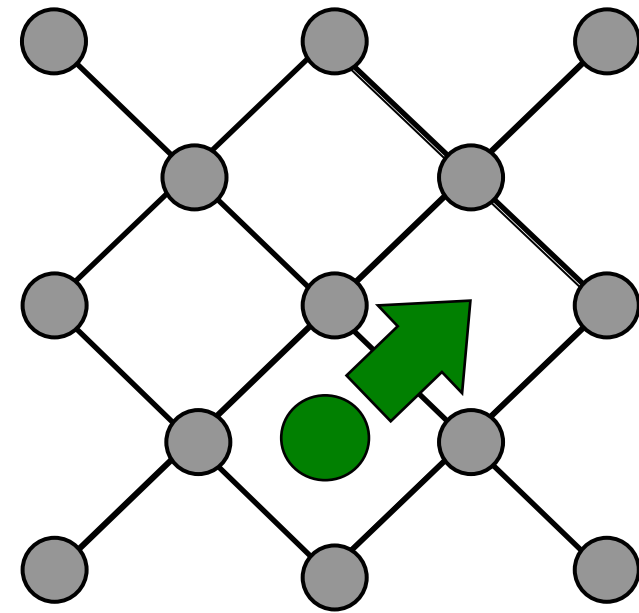
$$\frac{dP_i(t)}{dt} = -\sum_j k_{i \rightarrow j} P_i(t) + \sum_j k_{j \rightarrow i} P_j(t)$$

# Kinetic Monte Carlo – essentially coarse-grained MD



**Molecular Dynamics:  
the whole trajectory**

***ab initio* MD:  
up to 50 ps**

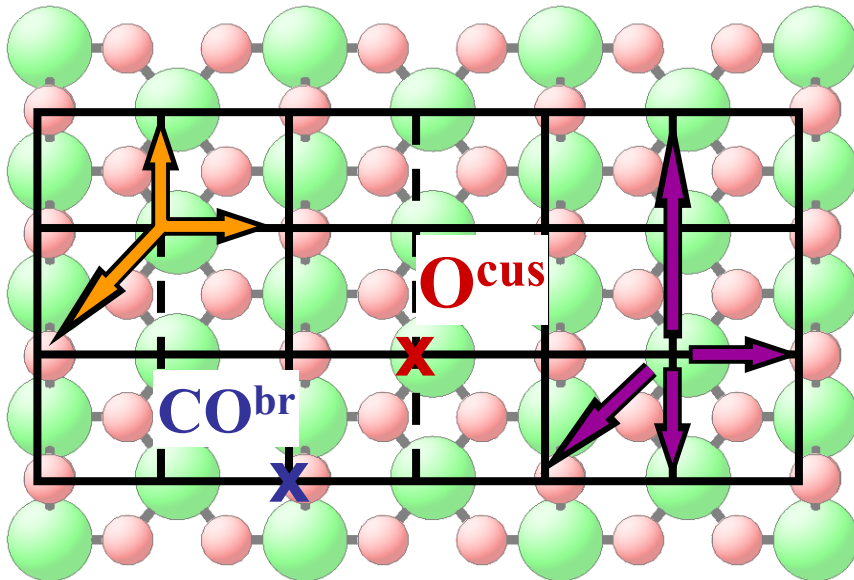


**Kinetic Monte Carlo:  
coarse-grained hops**

***ab initio* kMC:  
up to minutes**

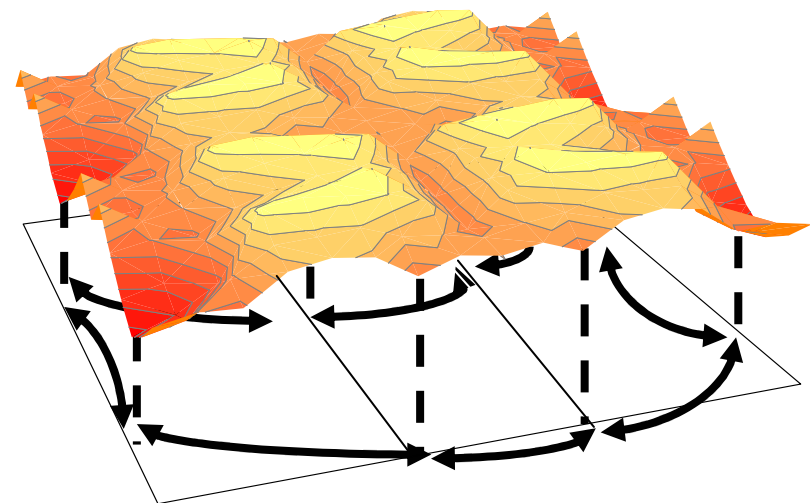
# Crucial ingredients of a kMC simulation

$$\frac{dP_i(t)}{dt} = -\sum_j k_{i \rightarrow j} P_i(t) + \sum_j k_{j \rightarrow i} P_j(t)$$



## 1) Elementary processes

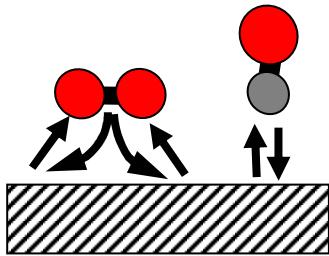
Fixed process list vs. „on-the-fly“ kMC  
Lattice vs. off-lattice kMC



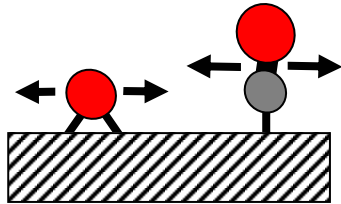
## 2) Process rates

PES accuracy  
Reaction rate theory

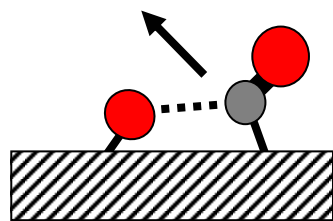
# kMC events for CO oxidation over RuO<sub>2</sub>(110)



**Adsorption:** CO - unimolecular, O<sub>2</sub> – dissociative  
no barrier  
rate given by impingement  $k \approx S_0 p / (2\pi m k_B T)$



**Desorption:** CO – 1st order, O<sub>2</sub> – 2nd order  
out of DFT adsorption well (= barrier)  
prefactor from detailed balance



**Diffusion:** hops to nearest neighbor sites  
site and element specific  
barrier from DFT (TST)  
prefactor from DFT (hTST)

**Reaction:** site specific  
immediate desorption, no readsorption  
barrier from DFT (TST)  
prefactor from detailed balance

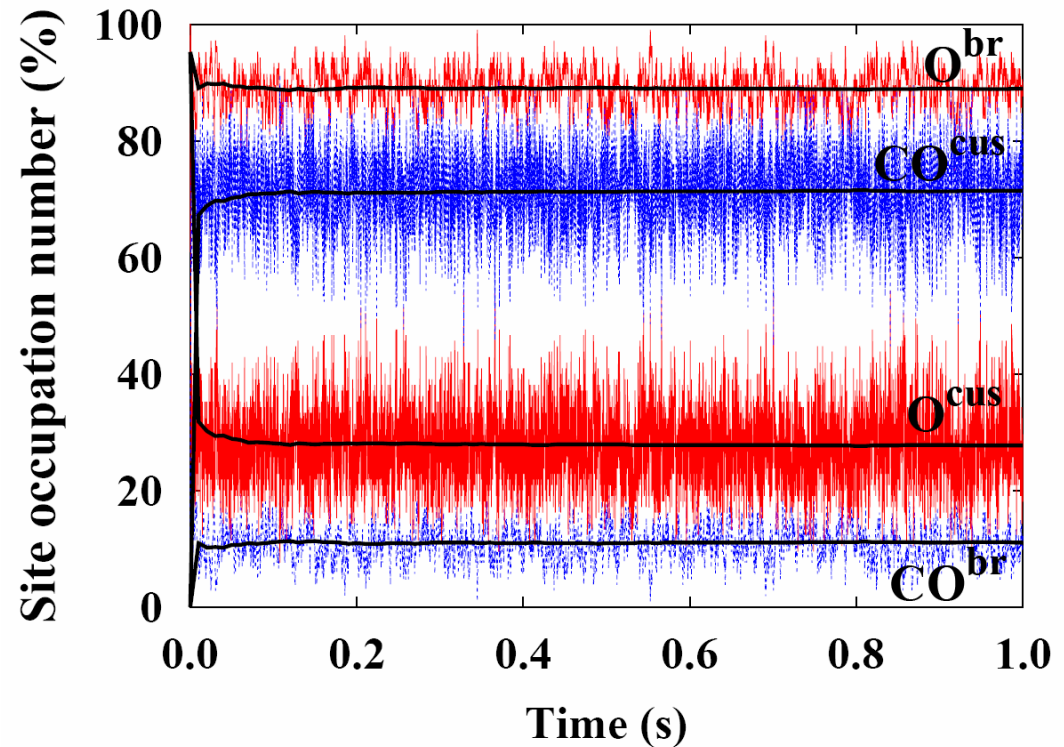
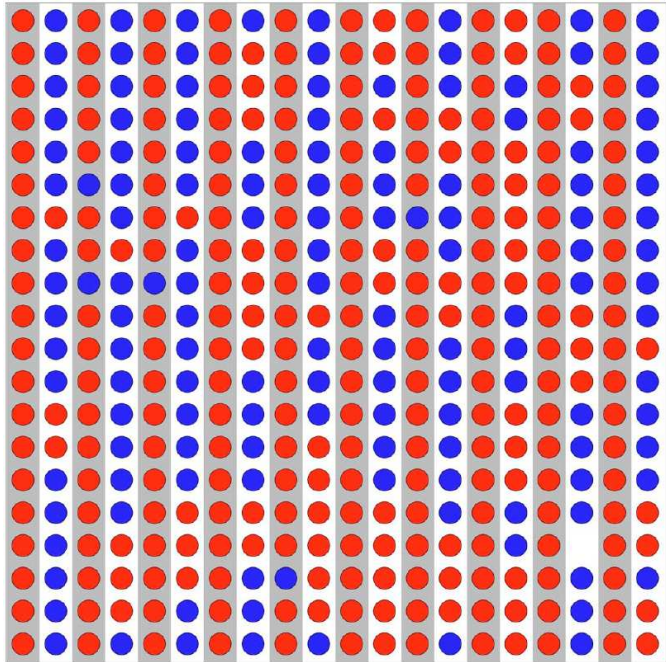
**26 elementary processes  
considered**

# The steady state of heterogeneous catalysis

$T = 600 \text{ K}$

$p_{\text{O}_2} = 1 \text{ atm}$

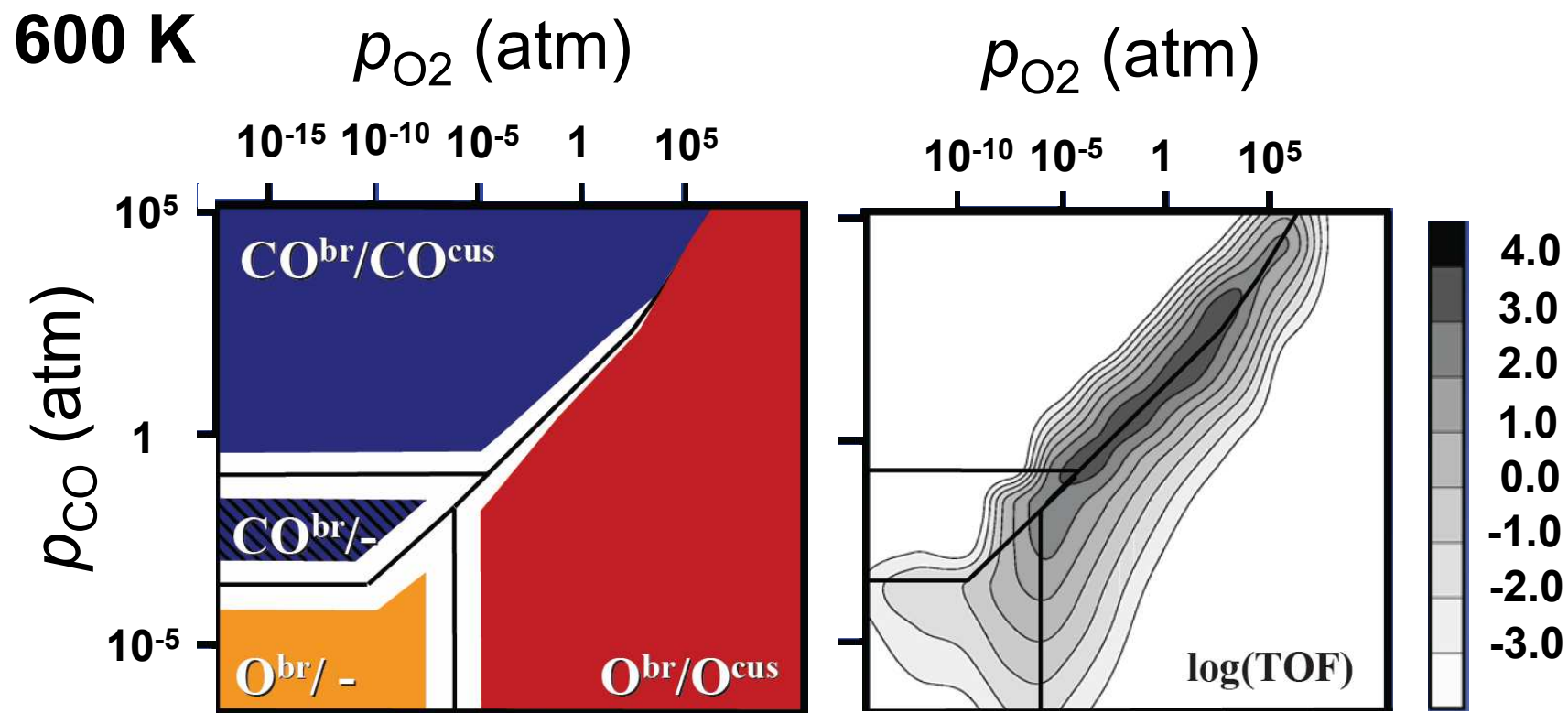
$p_{\text{CO}} = 7 \text{ atm}$



K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

K. Reuter, C. Stampfl, and M. Scheffler, Handbook of materials modeling, part A. Methods, p. 149, Springer, Berlin (2005)

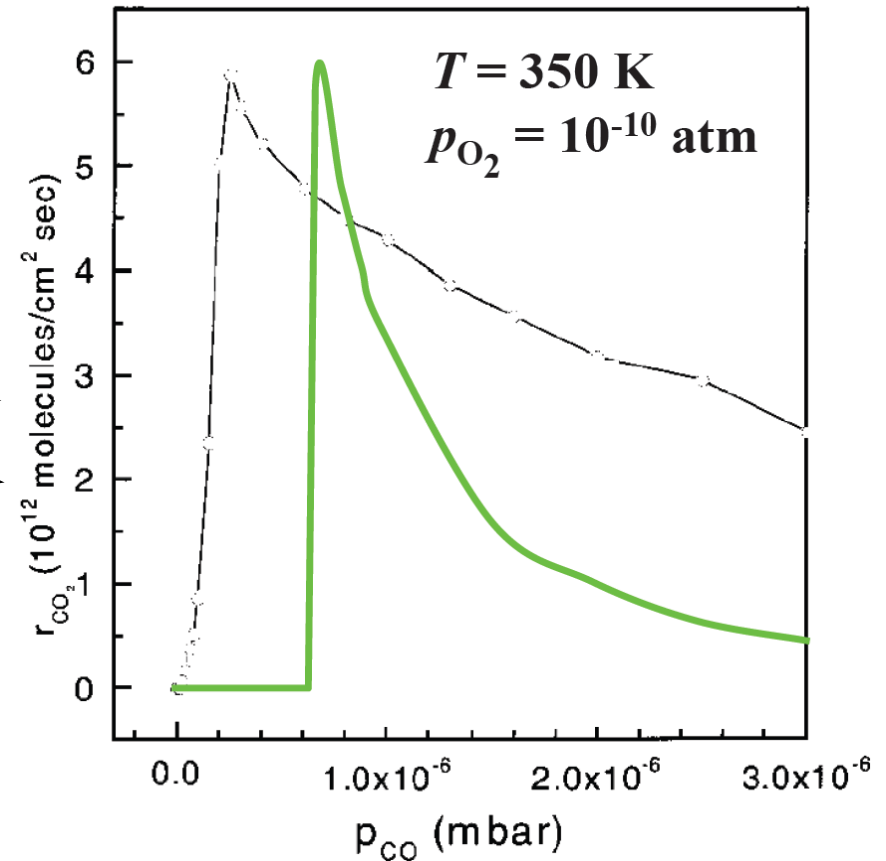
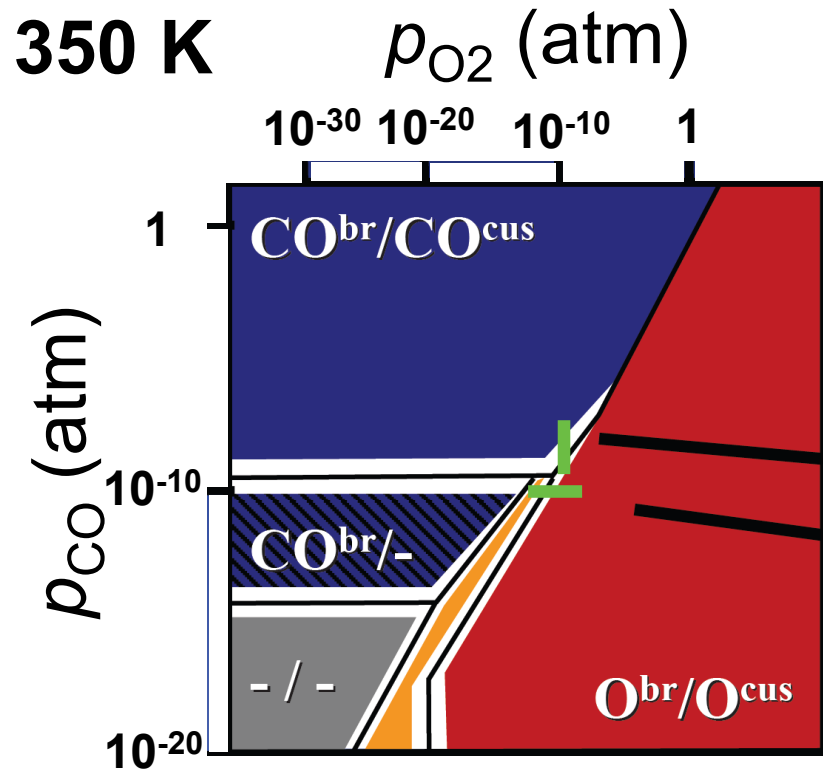
# $(p_{O_2}, p_{CO})$ -map of catalytic activity



K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

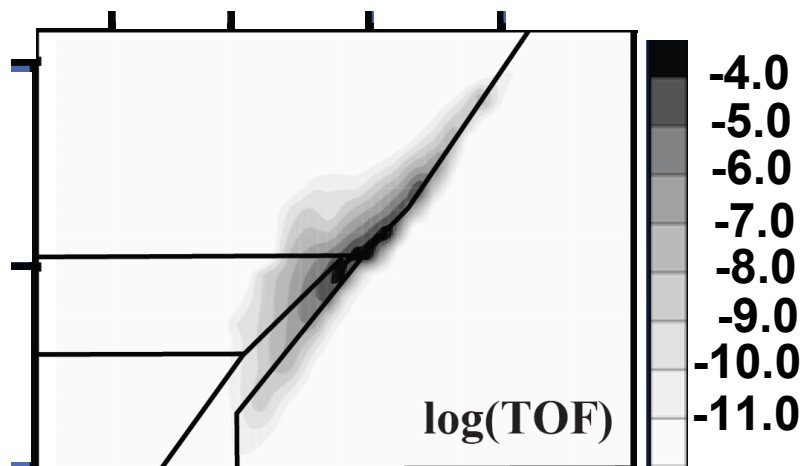


# Comparison to experiment



J. Wang *et al.*, J. Phys. Chem. B  
106, 3422 (2002)

→ cf. NH<sub>3</sub>/Ru(0001):  
K. Honkala *et al.*, Science 307, 555 (2005)



## **Concluding remarks**

- 1) DFT is only the beginning**
- 2) Standard DFT accuracy may be enough for rough estimate of reaction energies, but going beyond is necessary for predictive calculations**
- 3) To predict catalytic activity, statistical effects must be taken into account**

# Is there anything left to do in methodology?

**1) Beyond DFT (electronic correlation)**

**2) Heat and mass transfer in catalytic systems**

**3) Excited states (photocatalysis)**