

International Summer School on Basic Concepts and First-Principles Computations for Surface Science:

Applications in Chemical Energy Conversion and Storage
Norderney, Germany, July 21-26, 2013

Treating surfaces:
(embedded) clusters, supercells, and thermodynamics



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Part I: from xc functionals to total energies calculations in practice

- basis sets
- convergence

Part II: system size

- isolated clusters and molecules
- cluster extrapolation for bulk properties
- supercell approach
- embedded clusters

Part III: extending the scale

- surfaces in thermodynamic equilibrium with a reactive environment
- constrained equilibrium

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Representing solutions to KS equations on a discrete machine

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})$$

Pick a basis set: $\{|\varphi_i\rangle\}$

Achieve self-consistency

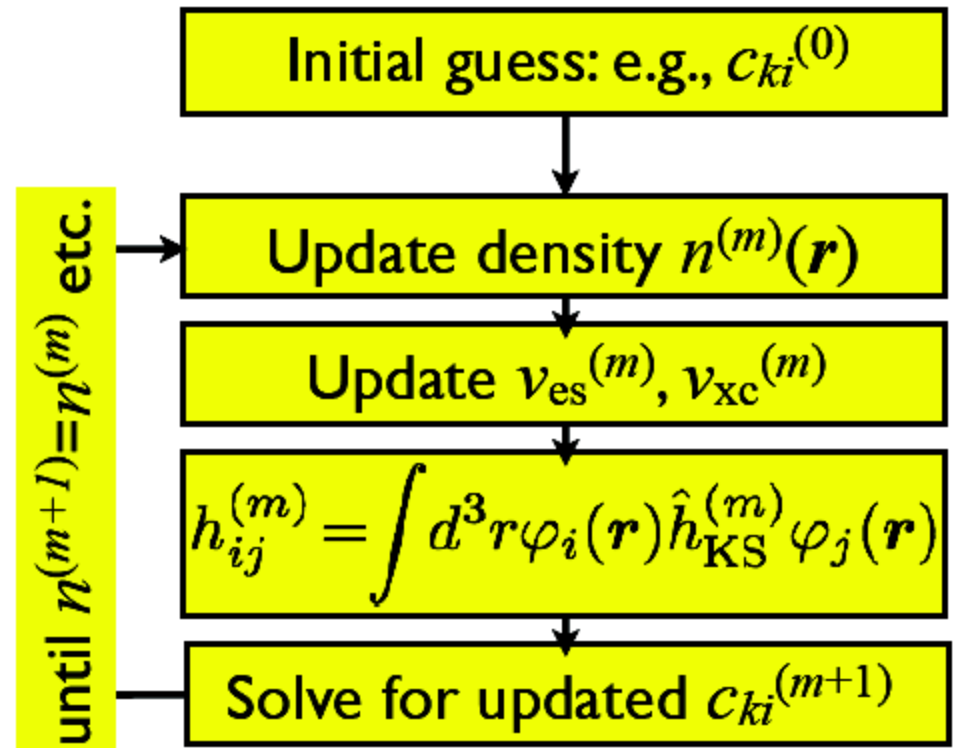
$$\psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})$$

Solve generalized eigenvalue problem:

$$\underline{\underline{h}} \underline{\underline{c}}_k = \epsilon_k \underline{\underline{s}} \underline{\underline{c}}_k$$

$$h_{ij} = \langle \varphi_i | \hat{h}_{\text{KS}} | \varphi_j \rangle$$

$$s_{ij} = \langle \varphi_i | \varphi_j \rangle$$



Basis sets for electronic structure

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})$$

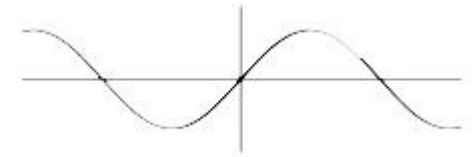
The choice of the basis set determines all further algorithms (hence accuracy and efficiency)

Basis set market:

- Plane waves

- efficient FFT (density, electrostatics)
- inherently periodic
- not all-electron (Slater 1937): pseudoization

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{N} e^{i\mathbf{k}\mathbf{r}}$$



- Augmented plane waves (Slater 1937; Andersen 1975)

- Gaussian type orbitals

$$\varphi_i(\mathbf{r}) = \frac{1}{N} r^l e^{-\alpha r^2}$$



- (Linear) Muffin-tin orbitals

- Numeric atom-centered functions (next slides)

In depth: Numeric atom-centered basis functions

$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)$$

Many popular implementations:
 DMol3 (Delley), FPLO (Koepernik et al.), PLATO (Horsfield et al.),
 Pseudo Atomic Orbitals (Siesta, Conquest, OpenMX2, Fireball, ...)

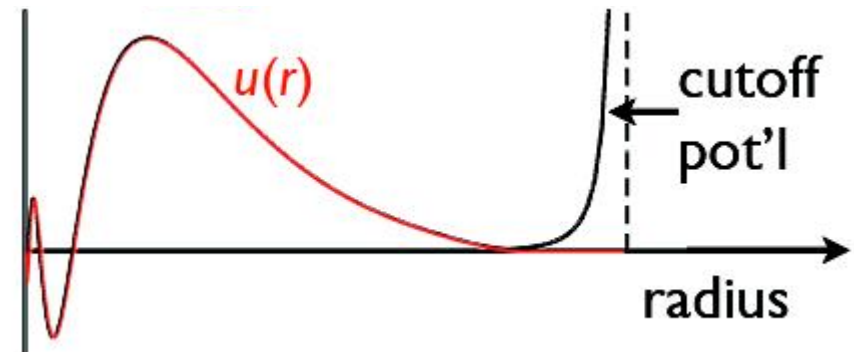
$u_i(r)$ Flexible choice (anything you like)

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}}(r) \right] u_i(r) = \epsilon_i u_i(r)$$

free-atom like: $v_i(r) = v_{\text{free atom}}^{\text{DFT}}(r)$

Hydrogen-like: $v_i(r) = z/r$

free ions, harmonic oscillators (Gaussians), ...



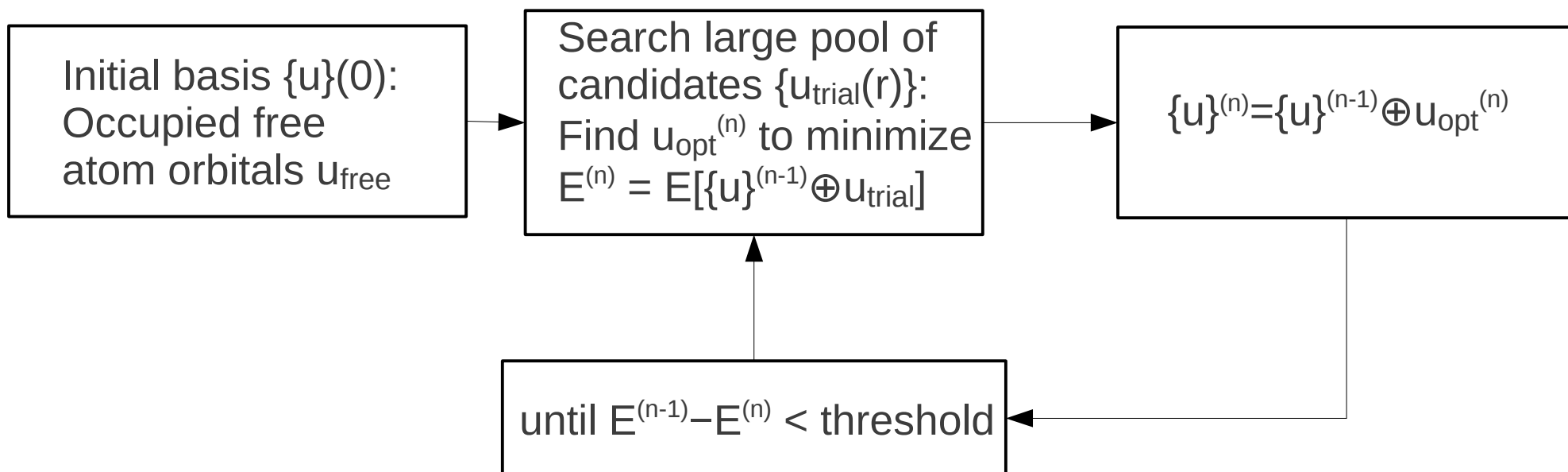
But, in practice? How to find radial functions systematically convergeable?

Search for accurate and transferable NAO basis sets



Goal: Element-dependent, transferable basis sets
from fast qualitative to meV-converged total energy accuracy (ground-state DFT)

Robust iterative selection strategy:
(e.g., Delley 1990)



Hierarchical Basis Set Library for All Elements



	H	C	O	Au
minimal	1s	[He]+2s2p	[He]+2s2p	[Xe]+6s5d4f
Tier 1	H(2s,2.1)	H(2p,1.7)	H(2p,1.8)	Au ²⁺ (6p)
	H(2p,3.5)	H(3d,6.0)	H(3d,7.6)	H(4f,7.4)
		H(2s,4.9)	H(3s,6.4)	Au ²⁺ (6s)
				H(5g,10)
				H(6h,12.8)
			H(3d,2.5)	
Tier 2	H(1s,0.85)	H(4f,9.8)	H(4f,11.6)	H(5f,14.8)
	H(2p,3.7)	H(3p,5.2)	H(3p,6.2)	H(4d,3.9)
	H(2s,1.2)	H(3s,4.3)	H(3d,5.6)	H(3p,3.3)
	H(3d,7.0)	H(5g,14.4)	H(5g,17.6)	H(1s,0.45)
		H(3d,6.2)	H(1s,0.75)	H(5g,16.4)
			H(6h,13.6)	
Tier 3	H(4f,11.2)	H(2p,5.6)	O ²⁺ (2p)	H(4f,5.2)*
	H(3p,4.8)	H(2s,1.4)	H(4f,10.8)	H(4d,5.0)

Systematic hierarchy of basis (sub)sets, iterative *automated* construction based on *dimers*

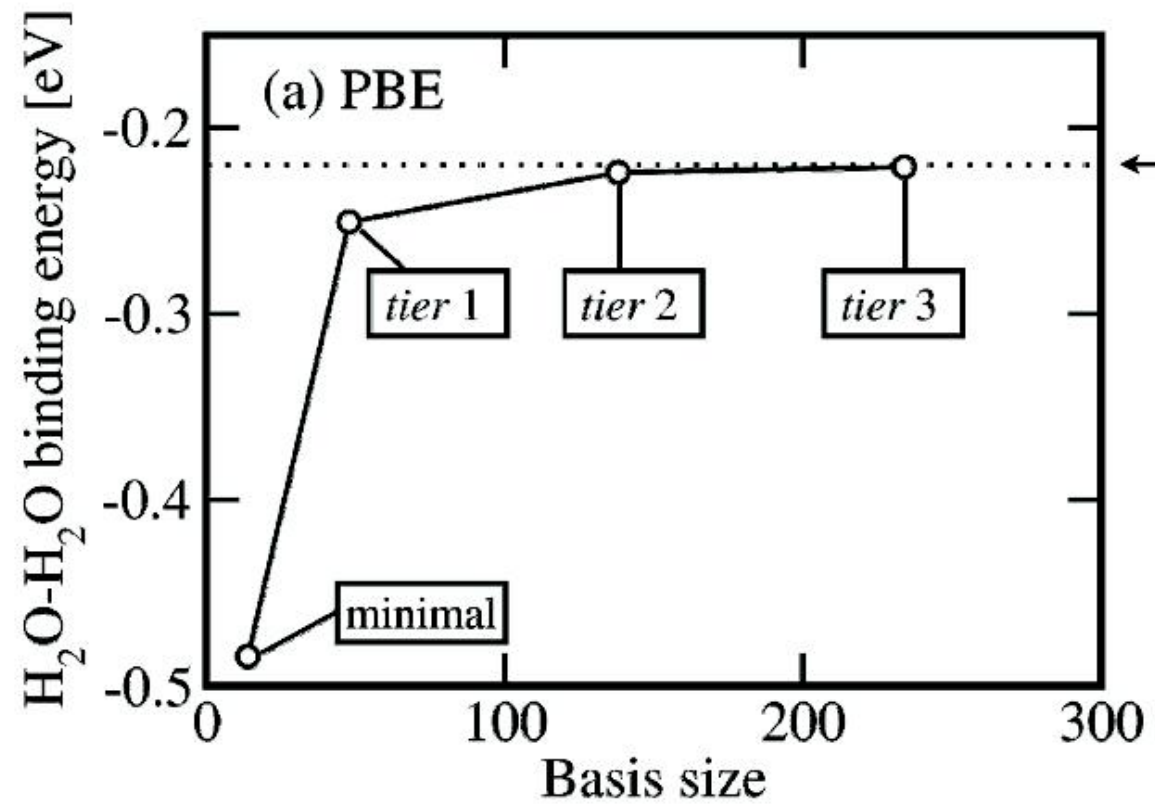
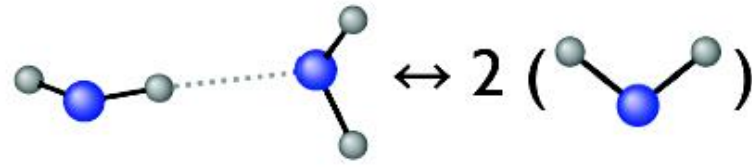
“First *tier* (level)”

“Second *tier*”

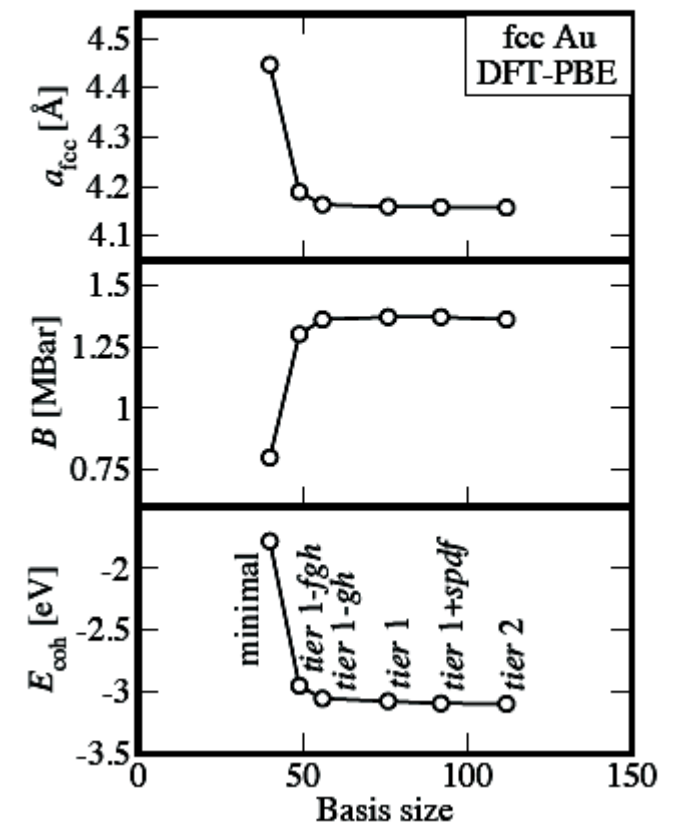
“Third *tier*”

...

Basis set convergence: hydrogen bond



Bulk Au: Cohesive properties



Basis set superposition error

Binding energy $E_b = E(\text{●—●}) - 2E(\text{●})$

Problem:

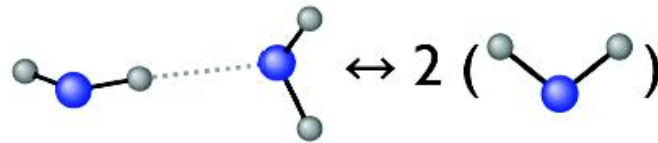
●—● has larger basis set than ●
Distance dependent overbinding!

Remedy:

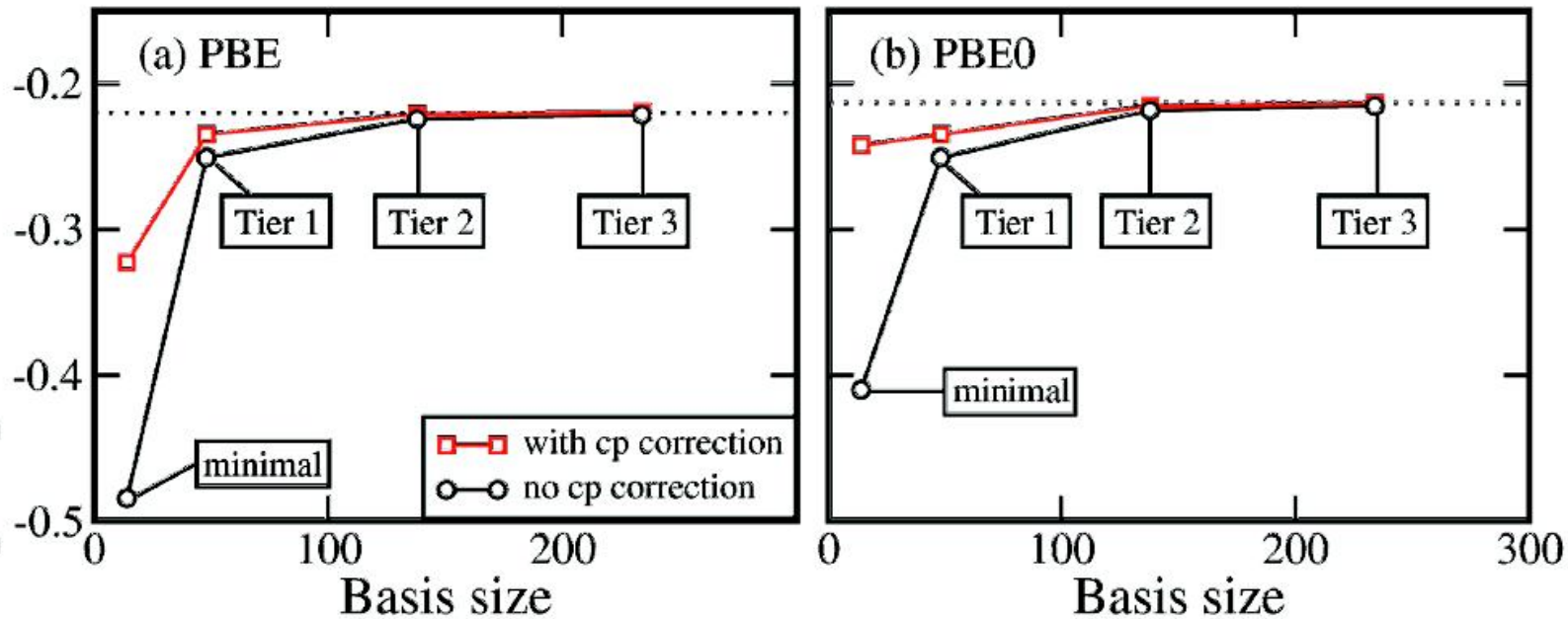
Counterpoise correction:

$$\Delta E_{\text{BSSE}} = E(\text{●—●}) - E(\text{●})$$

“ghost”: no nucleus, basis functions only



H₂O-H₂O binding energy [eV]



- Numerical Integration

$$h_{ij} = \int d^3r \varphi_i(\mathbf{r}) \hat{h}_{\text{KS}} \varphi_j(\mathbf{r})$$

- Electron density update

$$n(\mathbf{r}) = \sum_k f_k |\psi_k(\mathbf{r})|^2$$

- All-electron electrostatics

$$v_{\text{es}}(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Eigenvalue solver

$$\underline{\underline{h}} \underline{\underline{c}}_k = \epsilon_k \underline{\underline{s}} \underline{\underline{c}}_k$$

- Relativity?

needed for heavy elements

- Periodic systems?

need suitable basis, electrostatics

Relativity

Non-relativistic QM: Schrödinger equation

$$V\phi + \frac{\mathbf{p}^2}{2m}\phi = \epsilon\phi$$

One (two with spin) component
One Hamiltonian for all states

Relativistic QM: Dirac equation

$$\begin{pmatrix} V & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & -2c^2 + V \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = \epsilon \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

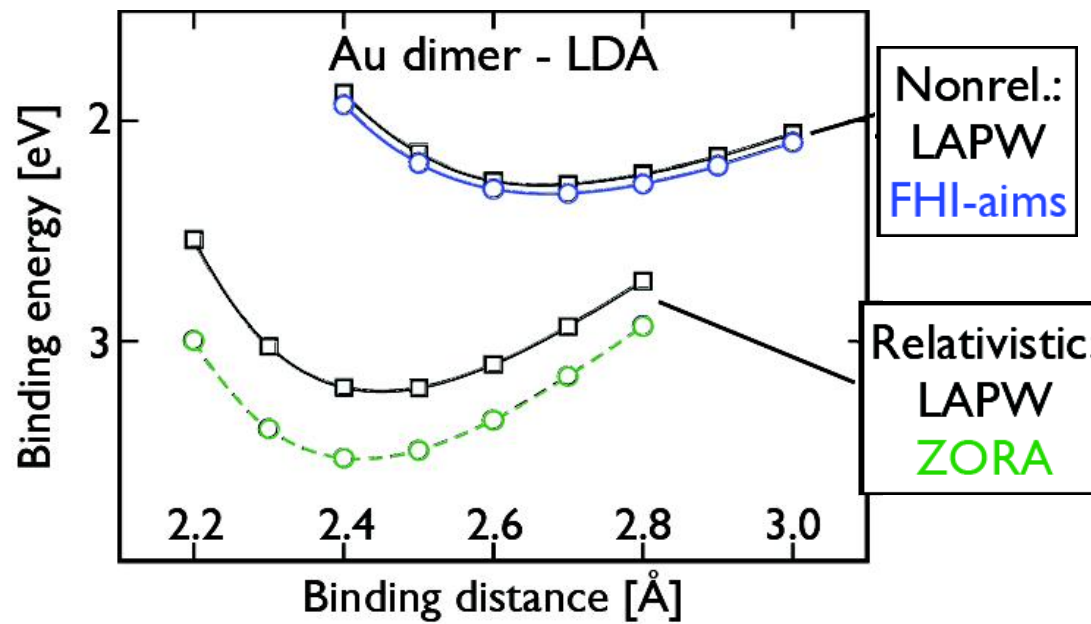
$$V\phi + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \boldsymbol{\sigma} \cdot \mathbf{p} \phi = \epsilon\phi$$

- ▶ ϵ -dependent Hamiltonian
- ▶ Not negligible for
 $\epsilon - v(\mathbf{r}) \approx 2c^2$
⇔ affects near-nuclear part
of *any* wave function

Implementing scalar relativity: ZORA

$$V\phi + \mathbf{p} \frac{c^2}{2c^2 + \cancel{V}} \mathbf{p} \phi = \epsilon \phi$$

ZORA



$$V\phi + \mathbf{p} \frac{c^2}{2c^2 + \cancel{V} - V} \mathbf{p} \phi = \epsilon \phi$$

ZORA

1. "Atomic ZORA"

2. Scaled ZORA

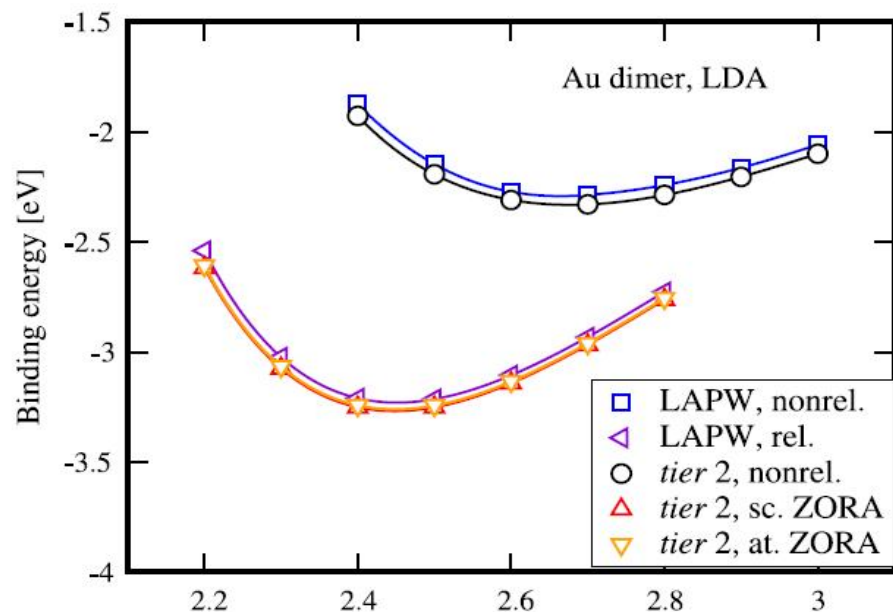
$$V\phi + \mathbf{p} \frac{c^2}{2c^2 - V_{\text{free atom}}} \mathbf{p} \phi = \epsilon \phi$$

- No gauge-invariance problem
- Simple total-energy gradients

$$\epsilon_{\text{ZORA}}^{\text{scaled}} = \frac{\epsilon_{\text{ZORA}}}{1 + \langle \Phi | \mathbf{p} \frac{c^2}{(2c^2 - V)^2} \mathbf{p} | \Phi \rangle}$$

$$E_{\text{tot}}^{\text{SZ}} = E_{\text{tot}}^{\text{ZORA}} - \sum (\epsilon_{\text{ZORA}} - \epsilon_{\text{ZORA}}^{\text{scaled}})$$

- Formally exact for H-like systems
- Perturbative, based on ZORA



1. "Atomic ZORA"

2. Scaled ZORA

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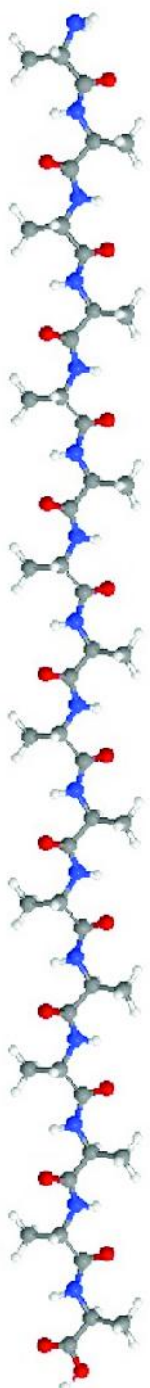
Part III: extending the scale

- surfaces in thermodynamic equilibrium with a reactive environment
- constrained equilibrium

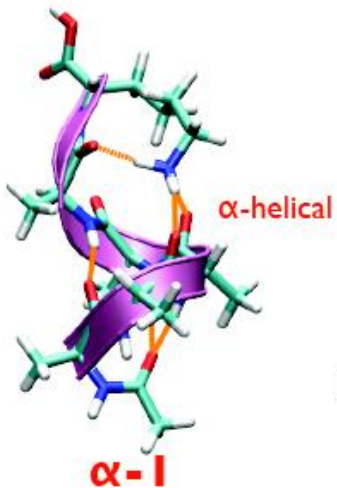
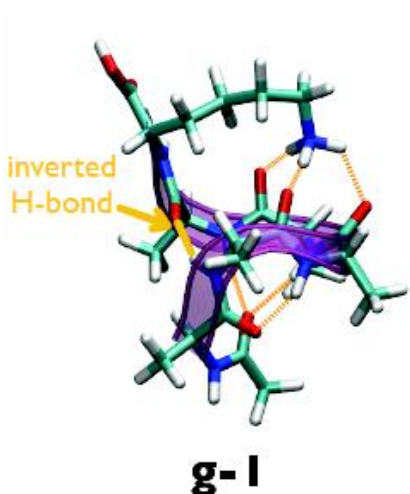
System size

- We may be interested in **isolated** (gas phase) **clusters**, then we just look at the cluster (rigid body motion?)
- In all other cases, we would like to observe (calculate properties of) few particles and “extrapolate” the behavior at macroscopic size.
- E.g., liquids, solid/liquid interface, bulk solid, solid/solid interface, surfaces.
- Using a (large) **cluster as model for a bulk**? What about the spurious surface? In a cube of length L , one particle per unit length : $[L^3(L-2)^3]/L^3 \sim 6L^2/L^3$
- Repeat infinitely the cluster: tile the (half)space. The **supercell** approach
- **Embed the cluster** in an environment that resembles the bulk?

Isolated organic molecules



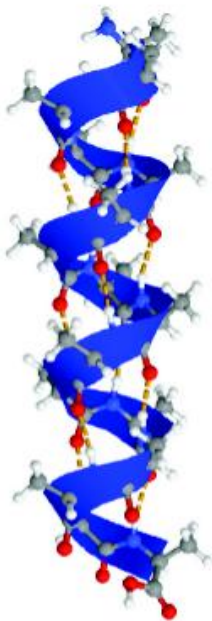
Two lowest energy structure candidates



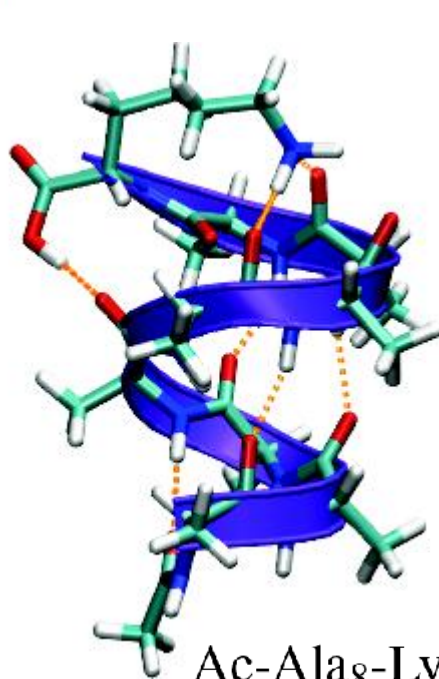
Ac-Ala₅-LysH⁺

Details in: *M. Rossi, et al. J. Phys. Chem. Lett. 1, 3465 (2010)*

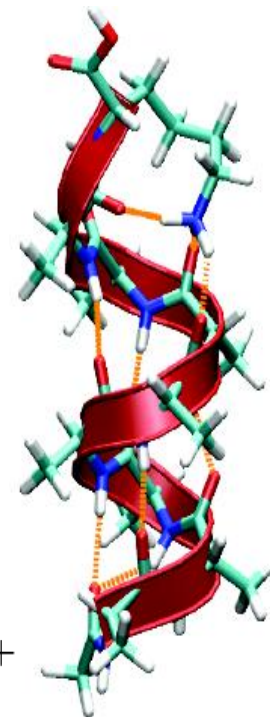
Ala₂₀



Havu *et al.* J Comp Phys (2009)

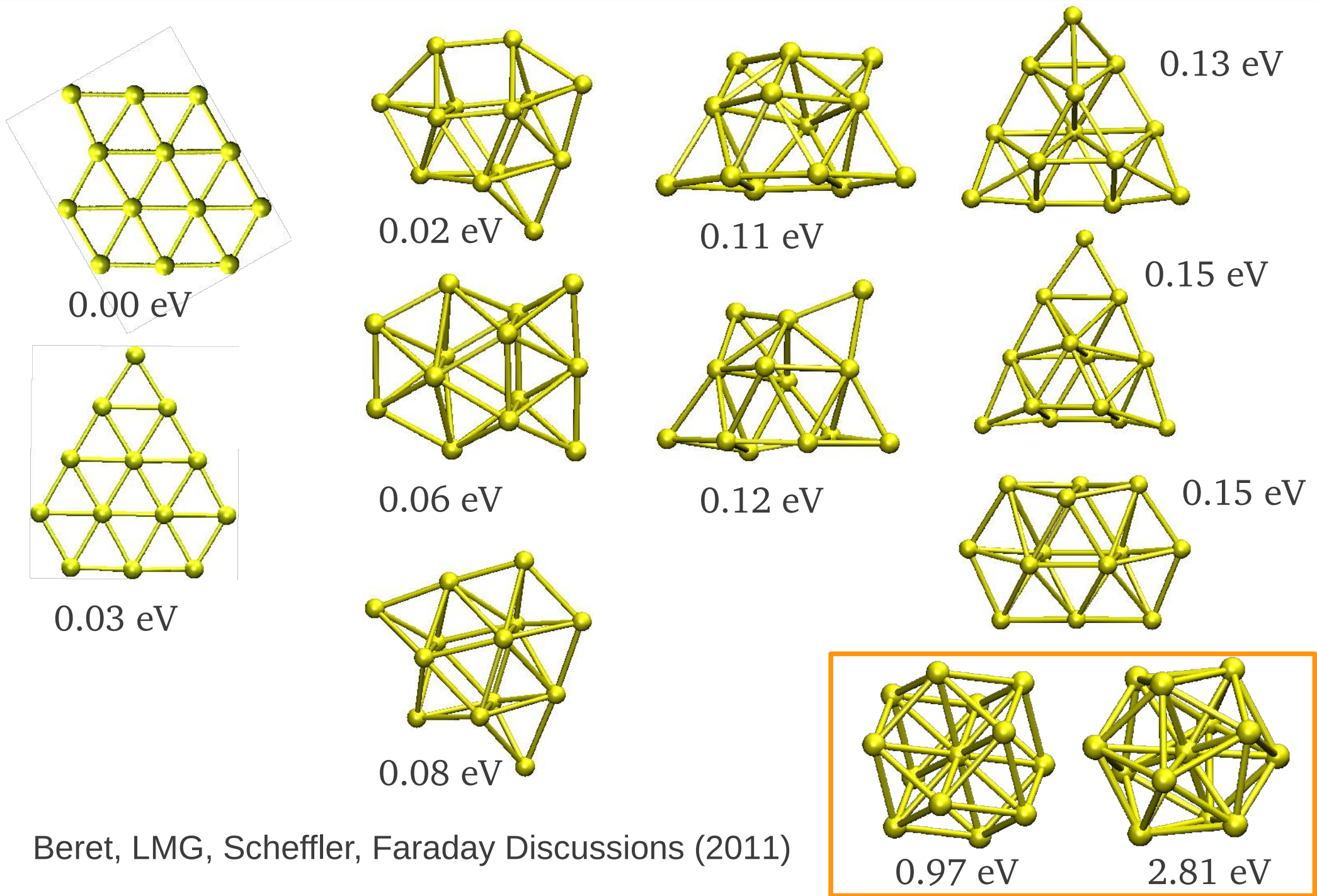


Ac-Ala₈-LysH⁺



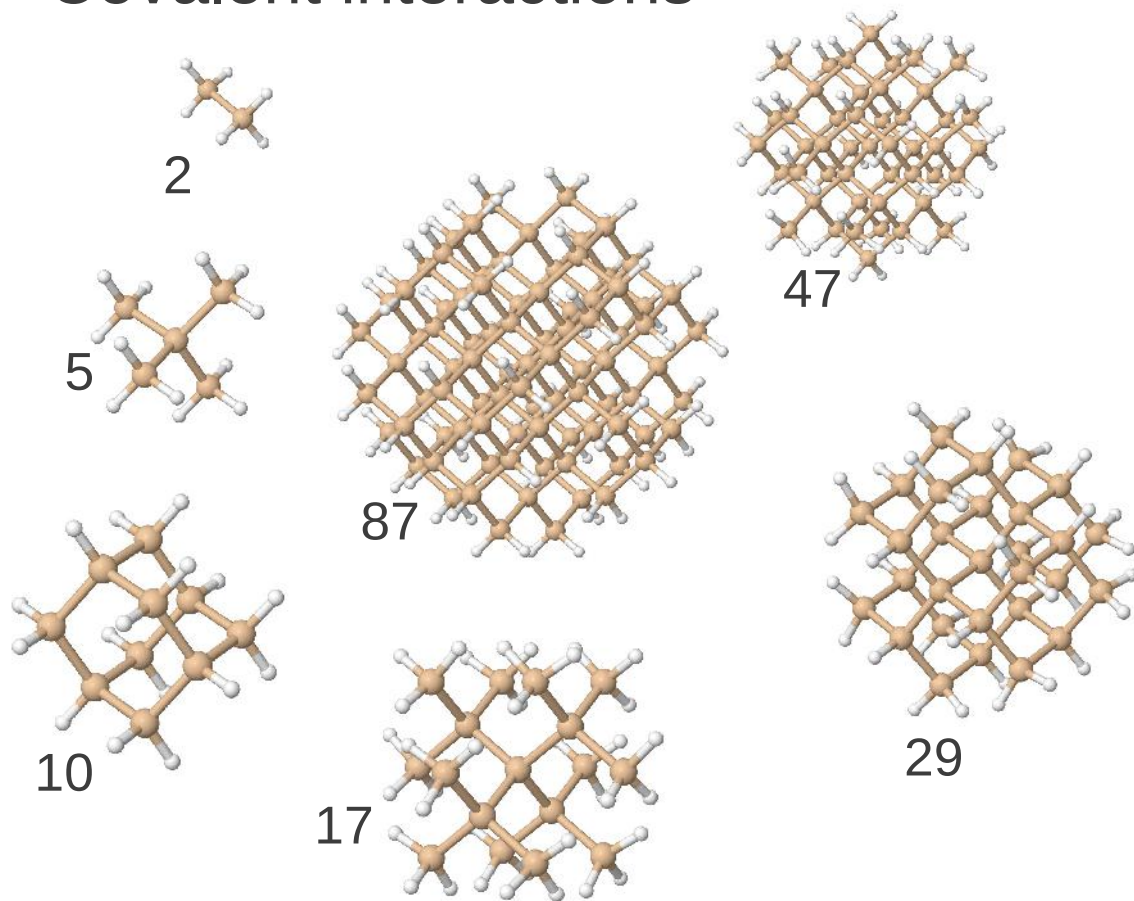
Rossi, Scheffler, Blum JPC B (2013)

Gas phase (gold) clusters



Cluster extrapolated to bulk

Covalent interactions

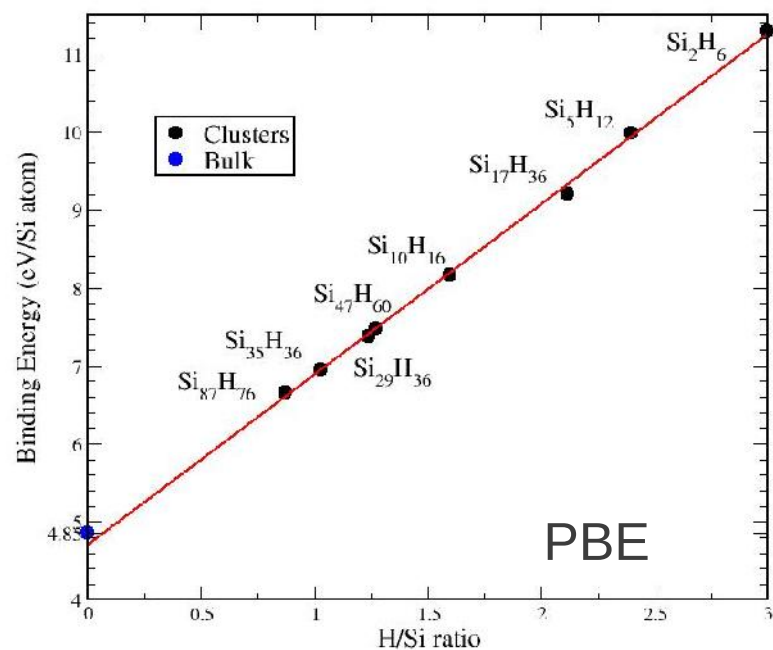
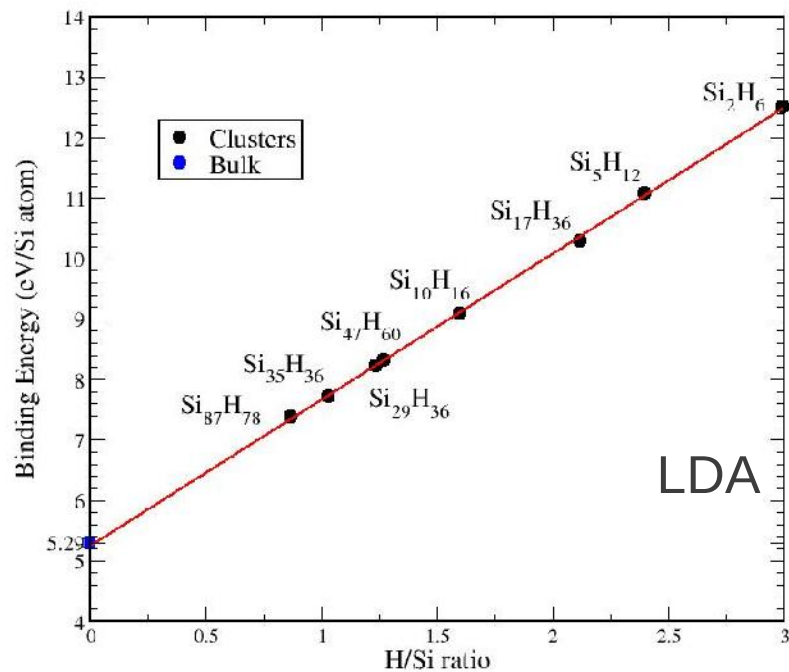


$$n_{\text{Si}} E_{\text{coh}} = 2n_{\text{Si}}^i E_{\text{Si-Si}} + g(n_{\text{Si}}^s) E_{\text{Si-Si}} + n_{\text{H}} E_{\text{Si-H}}$$

$$E_{\text{coh}} = 2E_{\text{Si-Si}} - (0.5E_{\text{Si-Si}} - E_{\text{Si-H}})\alpha$$

Xu, Yang, Guo, Zhang APL (2009)
Keshavarz, Levchenko, LMG, in progress

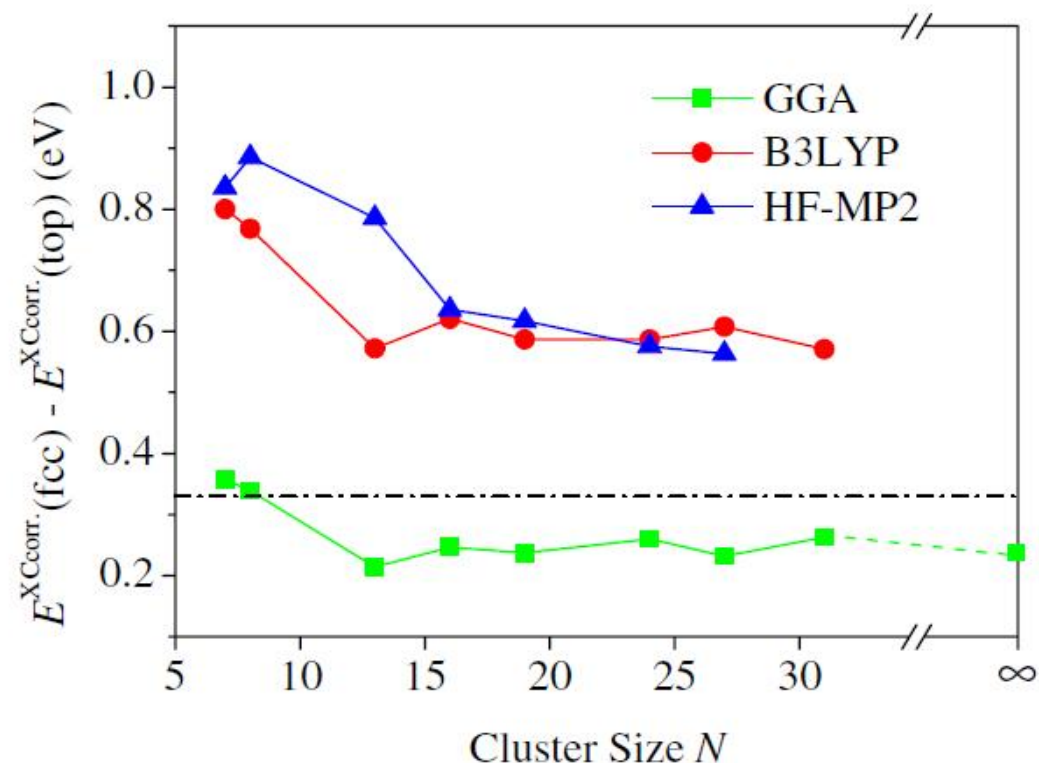
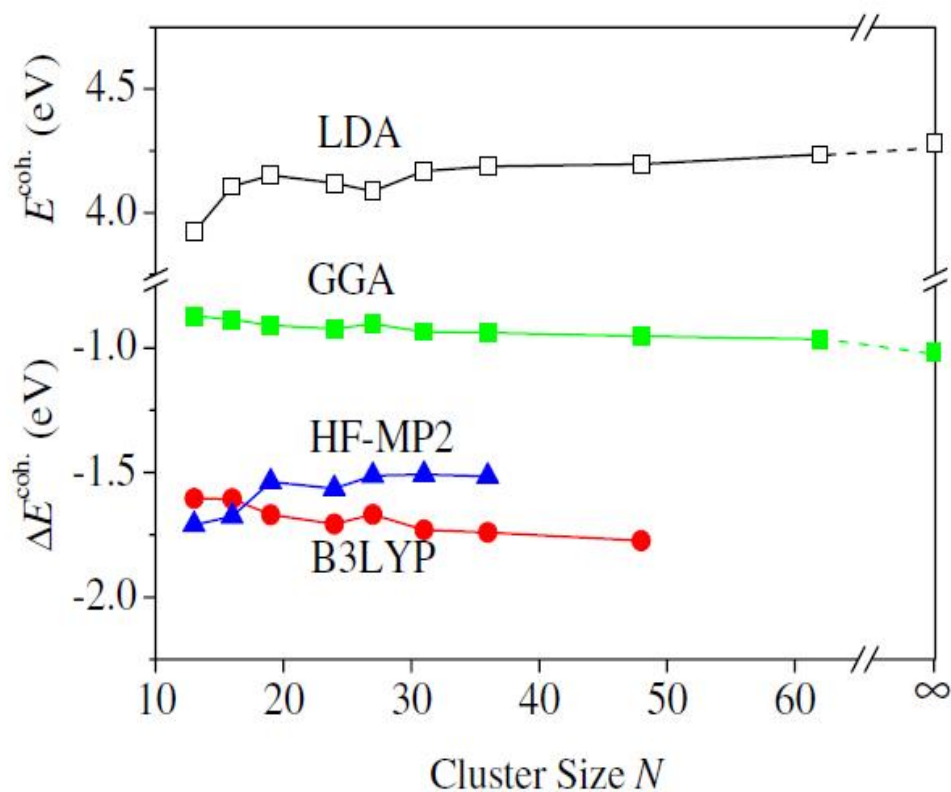
H/Si ratio



Cluster extrapolated to bulk

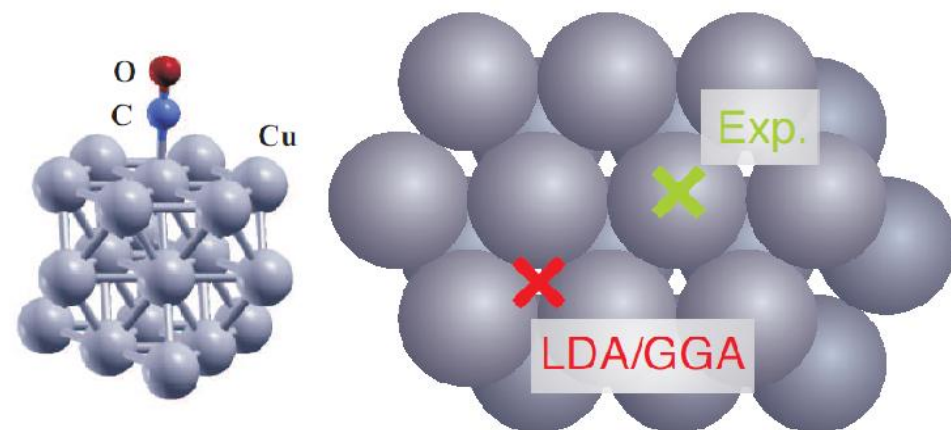
Metals

Cu clusters for bulk and surface

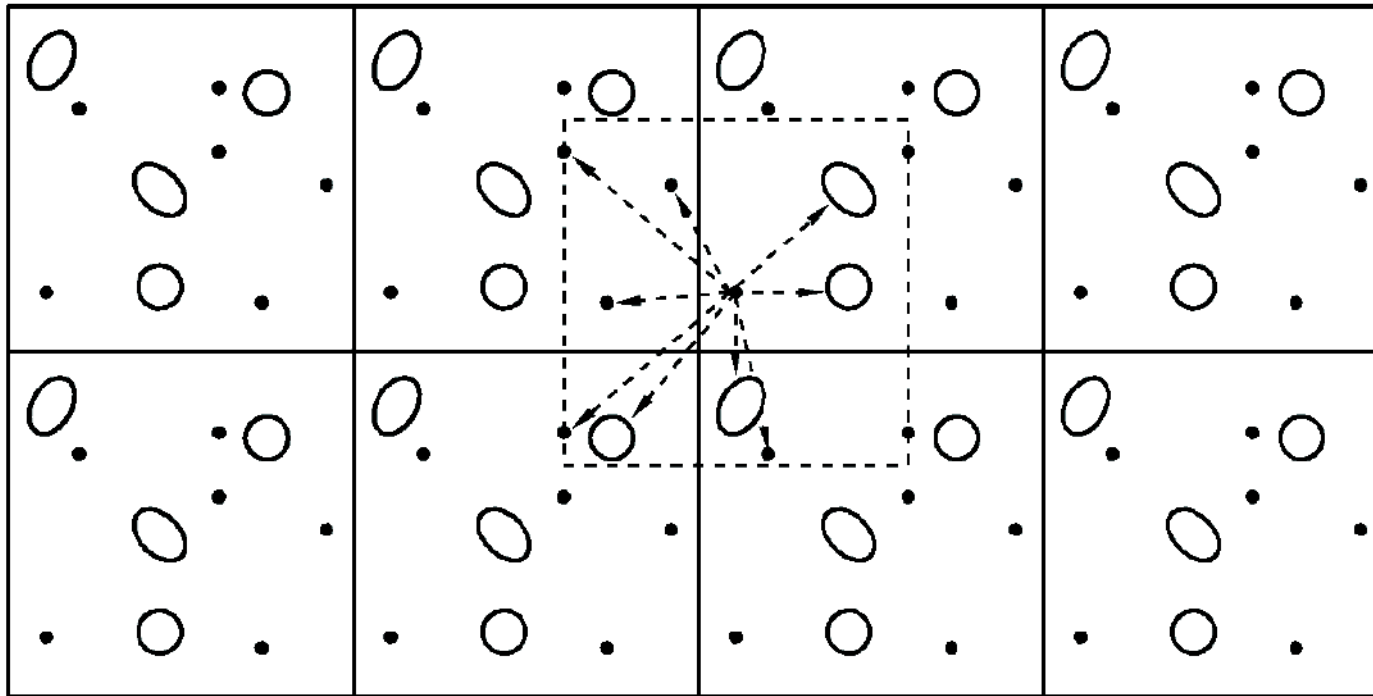


$$E = N * E^{\text{atom}} + (E^{\text{coh.}} / \sqrt{12}) \sum_{c=1}^{12} \sqrt{c} * N_c$$

Hu, Reuter, Scheffler, PRL (2007)

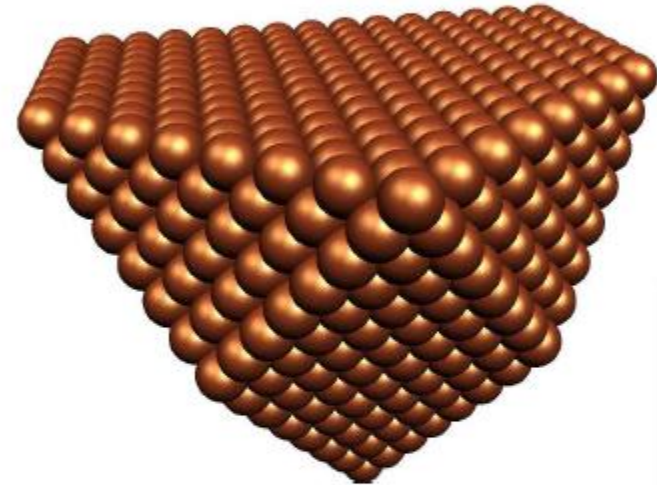
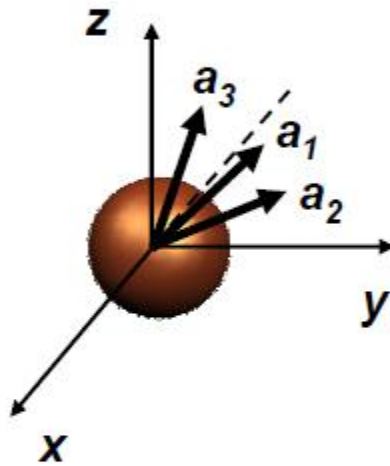


Periodic boundary conditions



Extended periodic systems

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



Position of every atom in the crystal (Bravais lattice):

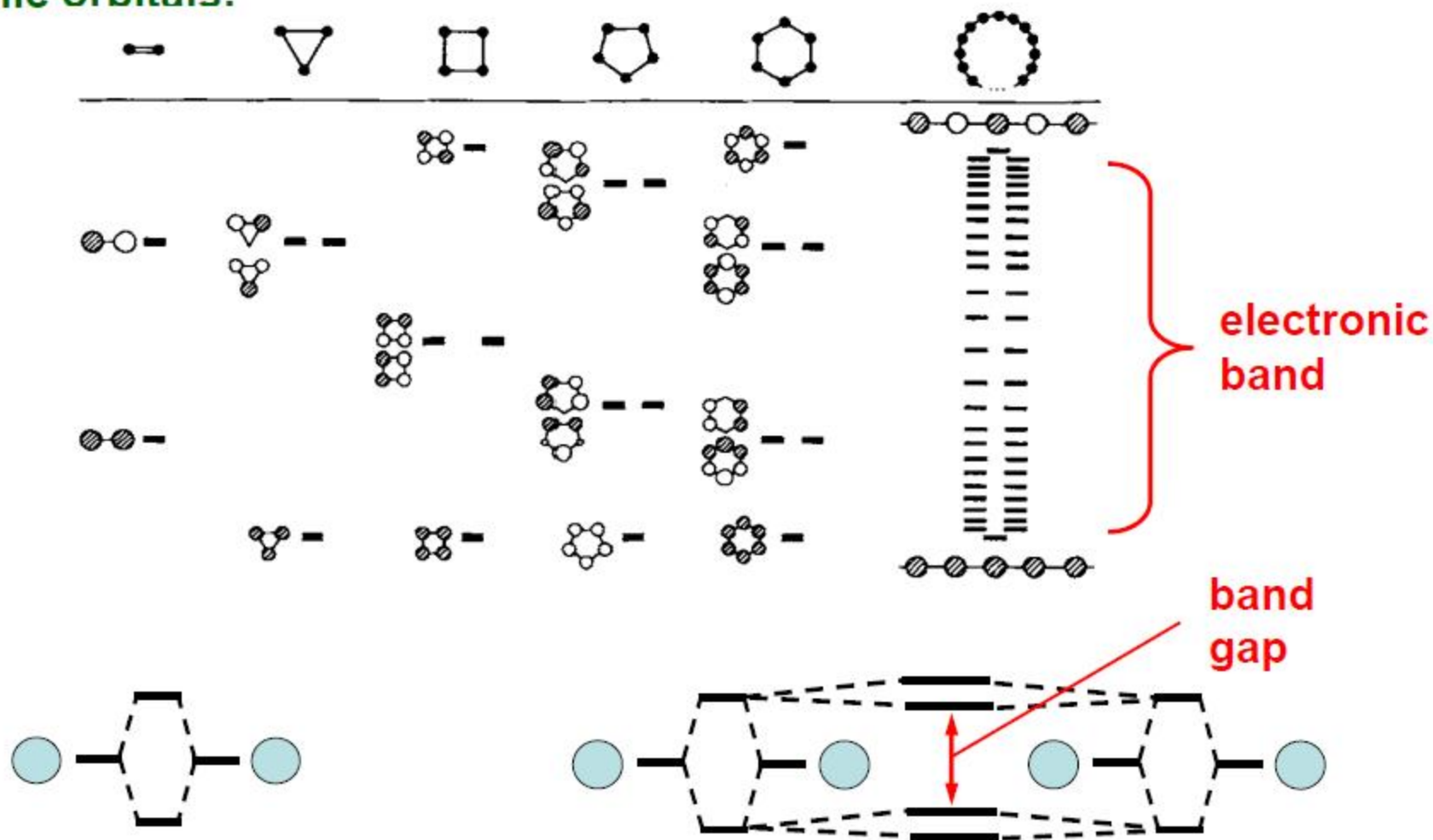
$$\mathbf{r}(n_1, n_2, n_3) = \mathbf{r}(0, 0, 0) + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

lattice vector: $\mathbf{R}(n_1, n_2, n_3) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$

$$n_1, n_2, n_3 = 0, \pm 1, \pm 2, \dots$$

From molecules to solids

Electronic bands as limit of bonding and anti-bonding combinations of atomic orbitals:



Adapted from: Roald Hoffmann, *Angew. Chem. Int. Ed. Engl.* **26**, 846 (1987)

Bloch's theorem

Periodic potential $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$
(translational symmetry)

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

In an infinite periodic solid, the solutions of the one-particle Schrödinger equations must behave like

$$\psi(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k}\mathbf{R})\psi(\mathbf{r})$$

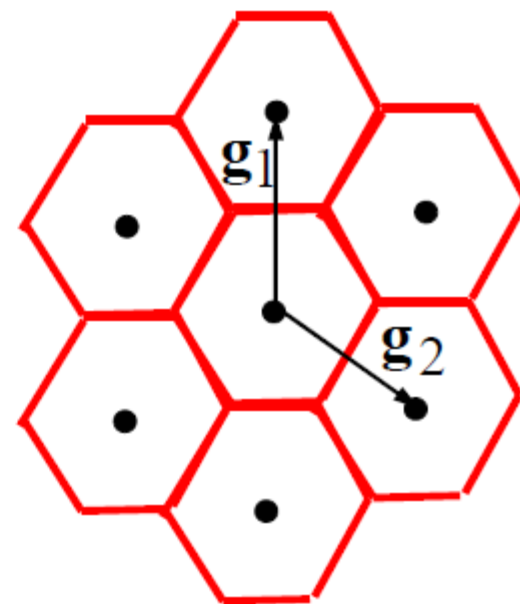
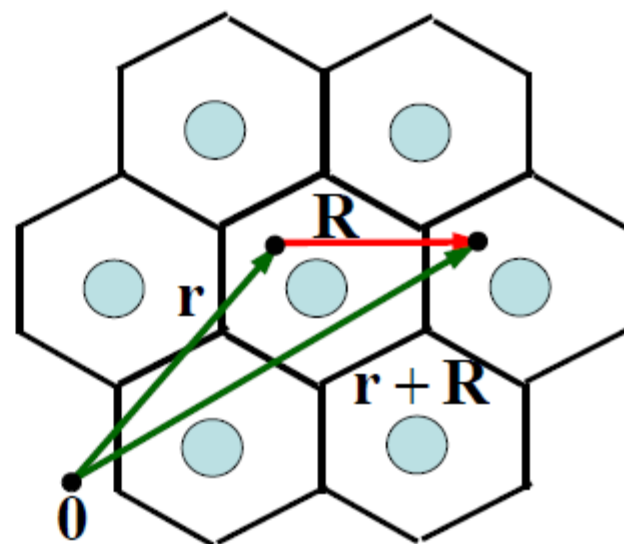
Index \mathbf{k} is a vector in *reciprocal space*

$$\mathbf{k} = x_1 \mathbf{g}_1 + x_2 \mathbf{g}_2 + x_3 \mathbf{g}_3 \quad \mathbf{g}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}$$

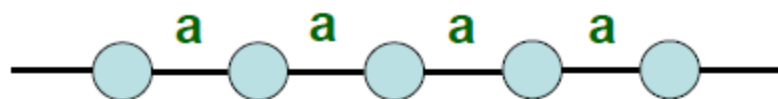
$$\mathbf{g}_l = 2\pi \frac{\mathbf{a}_m \times \mathbf{a}_n}{\Omega} \quad \text{-- reciprocal lattice vectors}$$

Consequently:

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})u(\mathbf{r}), \quad u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r})$$



The meaning of k



chain of hydrogen atoms

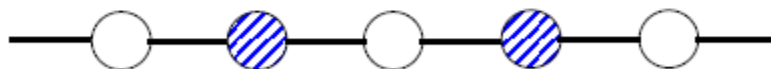
$$\psi_k = \sum_j \exp(ikx_j) \chi_{1s}(j \cdot a)$$

k shows the phase with which the orbitals are combined:

$k = 0$: $\psi_0 = \sum_j \exp(0) \chi_{1s}(j \cdot a) = \chi_{1s}(a) + \chi_{1s}(2a) + \dots$



$k = \frac{\pi}{a}$: $\psi_0 = \sum_j \exp(i\pi \cdot j) \chi_{1s}(j \cdot a) = -\chi_{1s}(a) + \chi_{1s}(2a) - \chi_{1s}(3a) + \dots$



k is a symmetry label and a node counter, and also represents electron momentum

Consequences of Bloch's theorem

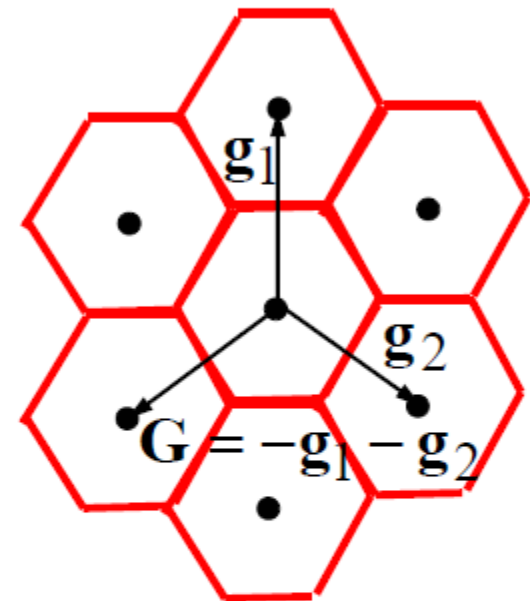
In a periodic system, the solutions of the Schrödinger equations are characterized by an integer number n (called *band index*) and a vector \mathbf{k} :

$$\hat{h}\psi_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}), \quad u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

For any reciprocal lattice vector

$$\mathbf{G} = n_1\mathbf{g}_1 + n_2\mathbf{g}_2 + n_3\mathbf{g}_3$$



$$\psi_{n\mathbf{k}+\mathbf{G}} = \exp(i\mathbf{k}\mathbf{r}) \underbrace{[u_{\mathbf{k}+\mathbf{G}} \exp(i\mathbf{G}\mathbf{r})]}_{\text{a lattice-periodic function } \tilde{u}} = \exp(i\mathbf{k}\mathbf{r})\tilde{u} = \psi_{n'\mathbf{k}}$$

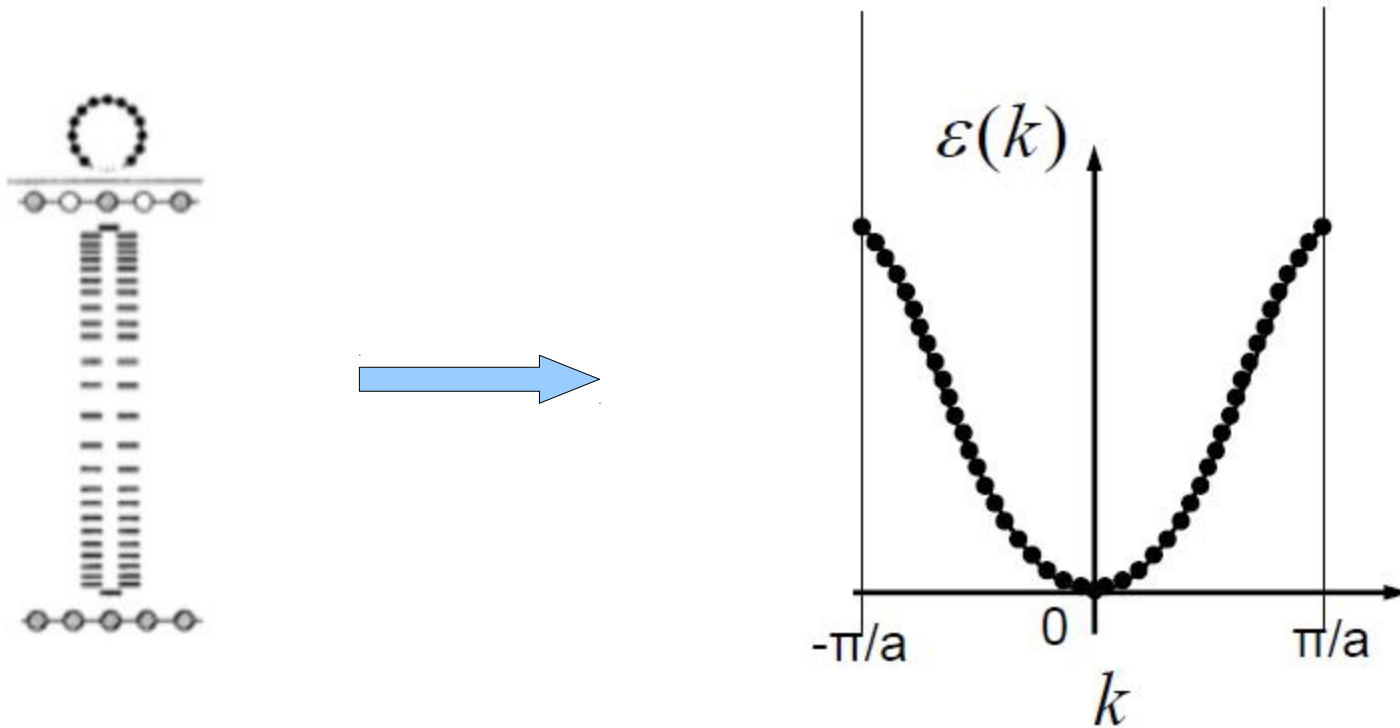
a Bloch state at $\mathbf{k}+\mathbf{G}$ with index n

a lattice-periodic function \tilde{u}

a Bloch state at \mathbf{k} with a different index n'

Can choose to consider only \mathbf{k} within single primitive unit cell in reciprocal space

Electronic band structure (1D)

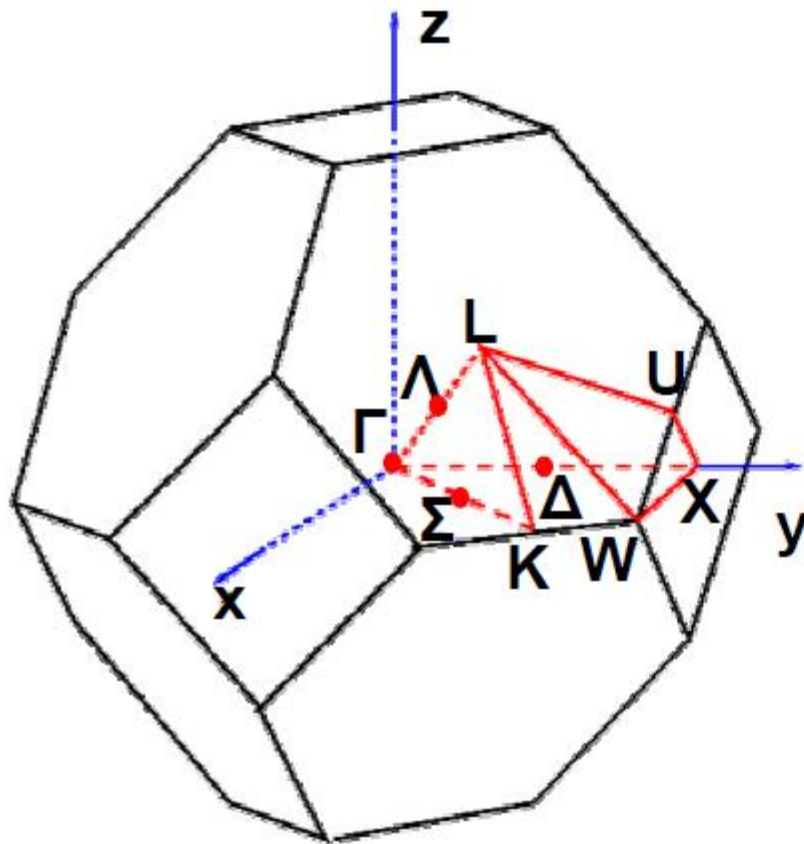


Band structure represents dependence of $\epsilon_{n\mathbf{k}}$ on \mathbf{k}

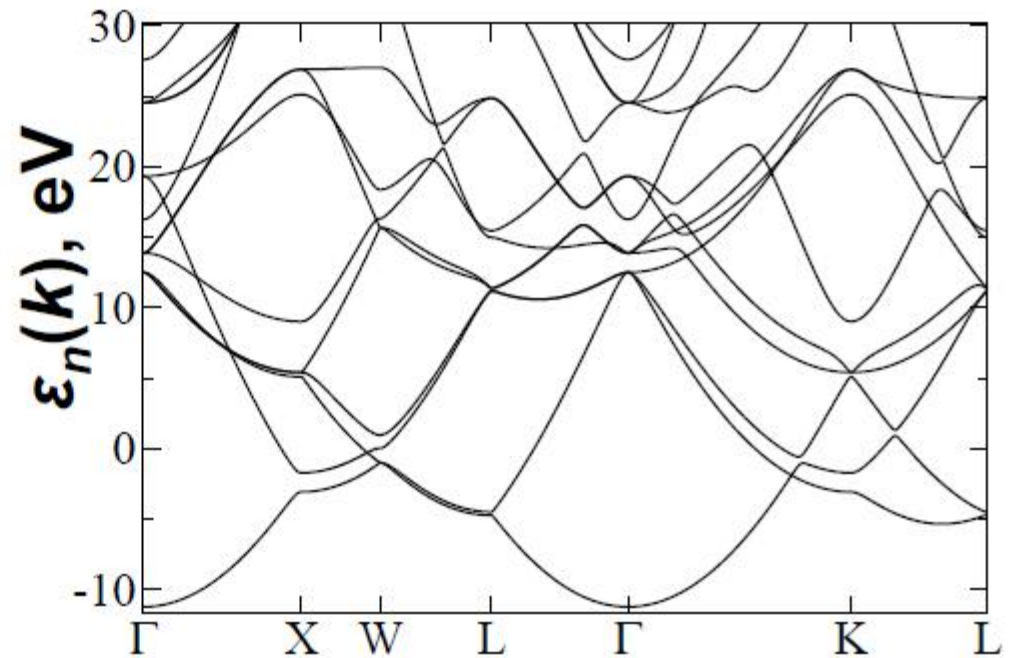
For a periodic (infinite) crystal, there is an infinite number of states for each band index n , differing by the value of \mathbf{k}

Electronic band structure in 3D

Brillouin zone of the fcc lattice

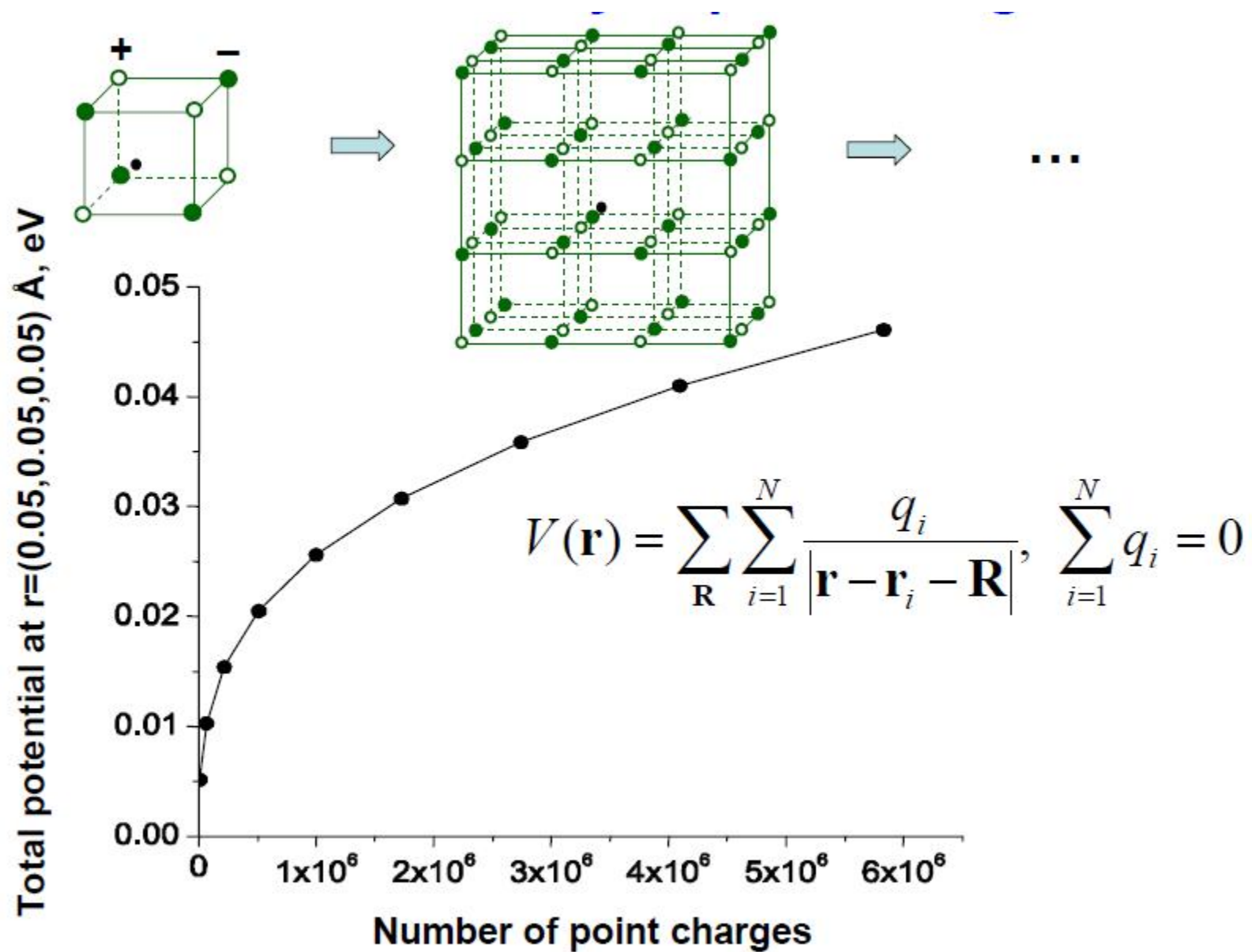


Al band structure (DFT-PBE)



By convention, $\epsilon_{n\mathbf{k}}$ are measured (angular-resolved photoemission spectroscopy, ARPES) and calculated along lines in k -space connecting points of high symmetry

Potential of an array of point charges



Convergence of the potential with number of charges is extremely slow

Ewald summation

$$V(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{i=1}^N \frac{q_i}{|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|}$$

+ $\frac{1}{\eta\sqrt{\pi}} \exp(-(\mathbf{r} - \mathbf{r}_i)^2 / \eta^2)$ \equiv ●

screening gaussian charge distribution

$\nabla^2 V(\mathbf{r}) = -4\pi\rho(\mathbf{r})$
(Poisson's equation)

$$V_1(\mathbf{r}) = \sum_{i,\mathbf{R}} q_i \left(\frac{\text{erfc}(|\mathbf{r} - \mathbf{r}_i - \mathbf{R}| / \eta)}{|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|} \right)$$

Decays fast with $|\mathbf{R}|$

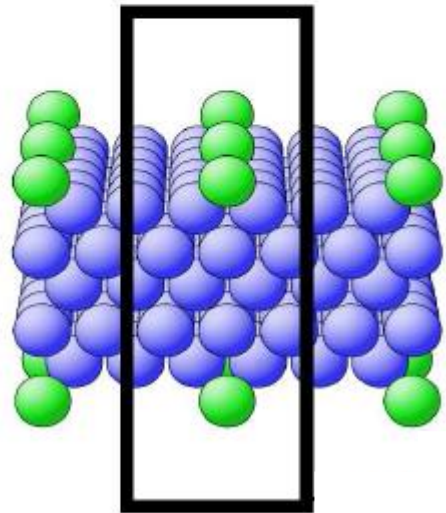
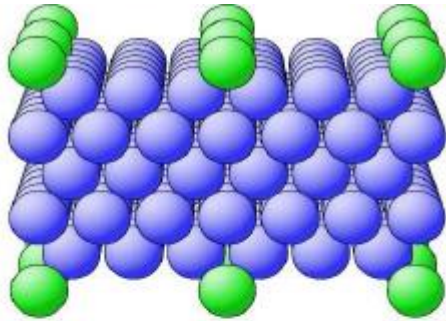
$$V_2(\mathbf{r}) = \sum_{i,\mathbf{G} \neq 0} q_i \frac{4\pi}{\mathbf{G}^2 \Omega} \exp\left(-\frac{\eta^2 \mathbf{G}^2}{4} + i\mathbf{G} \cdot (\mathbf{r} - \mathbf{r}_i)\right)$$

Decays fast with $|\mathbf{G}|$

Diverges at $\mathbf{G} = 0$, but divergence
is cancelled for $\sum_i q_i = 0$

There is no universal potential energy reference (like vacuum level) for periodic systems – important when comparing different systems

Supercell approach



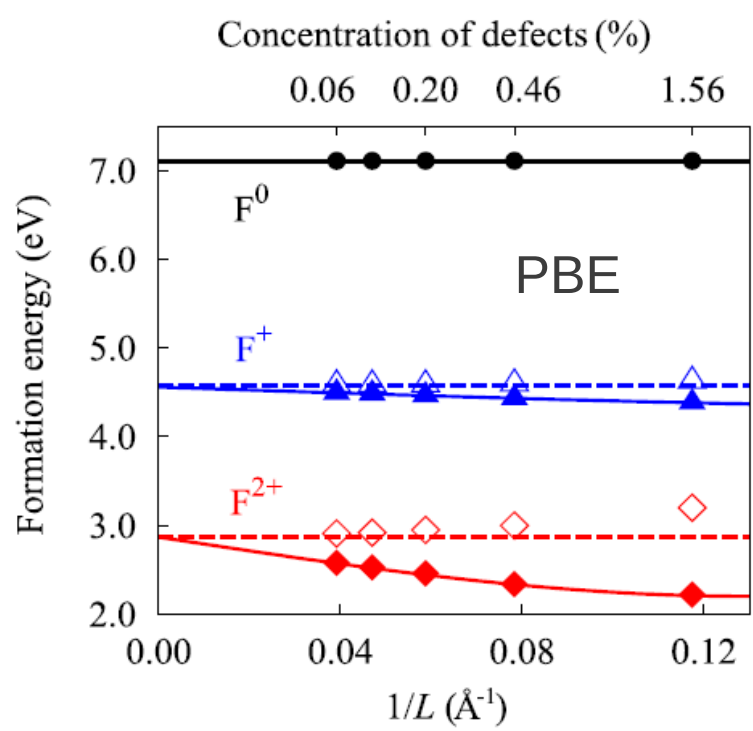
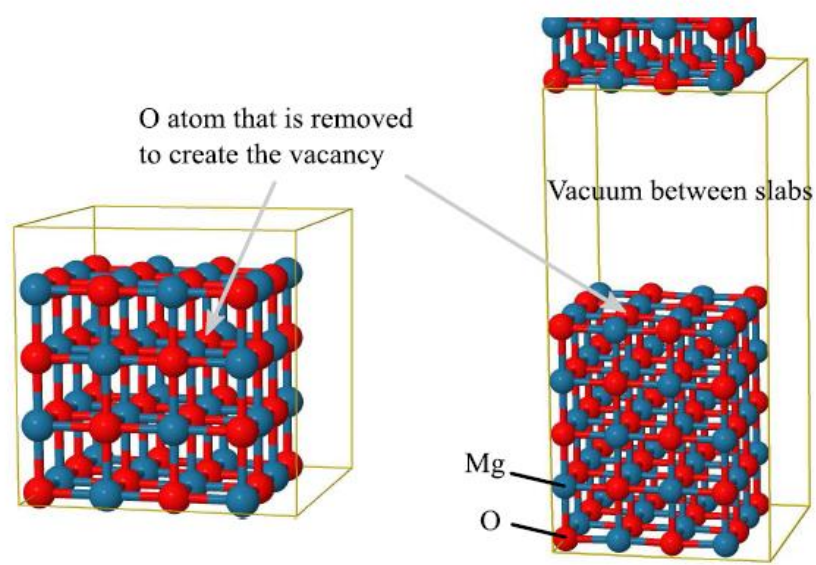
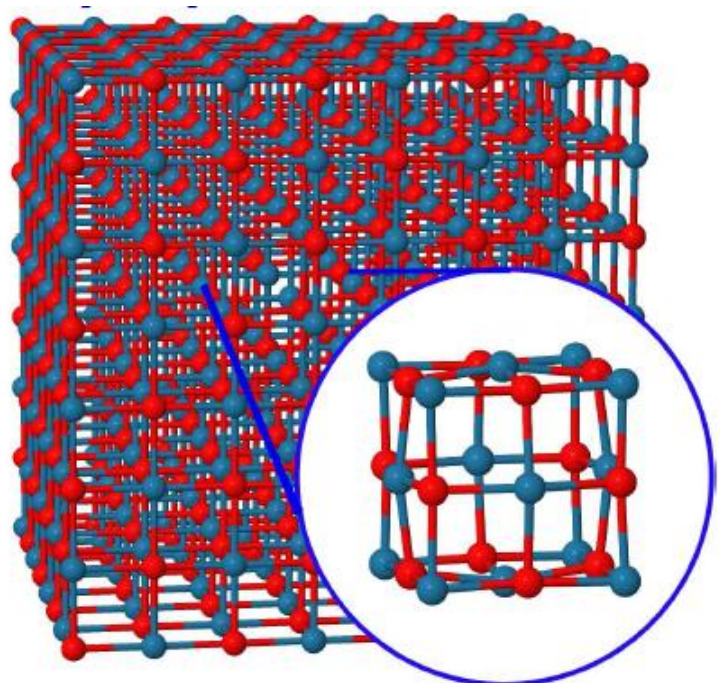
The supercell approach

For periodic bulk (obvious), but also for ...

interfaces (surfaces) and wires (also with adsorbates), and defects (especially for concentration or coverage dependences)

- Approach accounts for the lateral periodicity
- Sufficiently broad vacuum region to decouple the slabs
- Sufficient slab thickness to mimic semi-infinite crystal
- Semiconductors: saturate dangling bonds on the “back” surface
- Non-equivalent surfaces: use dipole correction
- Alternative: cluster models (for defects and adsorbates)

Supercell approach



Makov-Payne correction

$$G_f^{\text{bulk},q}(L, \epsilon_F, \mu_O) = G_f^{\text{bulk},q}(L \rightarrow \infty, \epsilon_F, \mu_O) + \frac{a_1^q}{L} + \frac{a_3^q}{L^3}$$

Supercell approach

Modeling charged defects:

- Neutralizing background charge density
 - - only bulk
 - - problem: level alignment
- Compensating impurities: virtual crystal for doped material

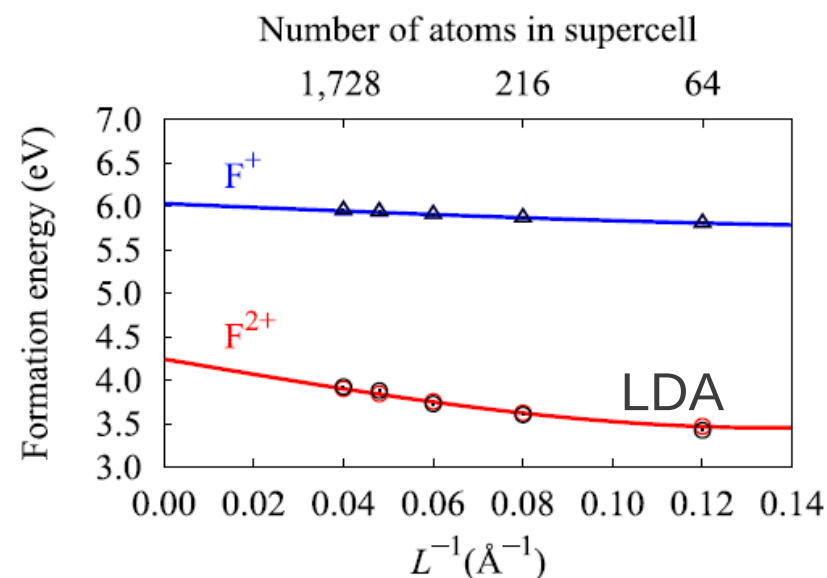
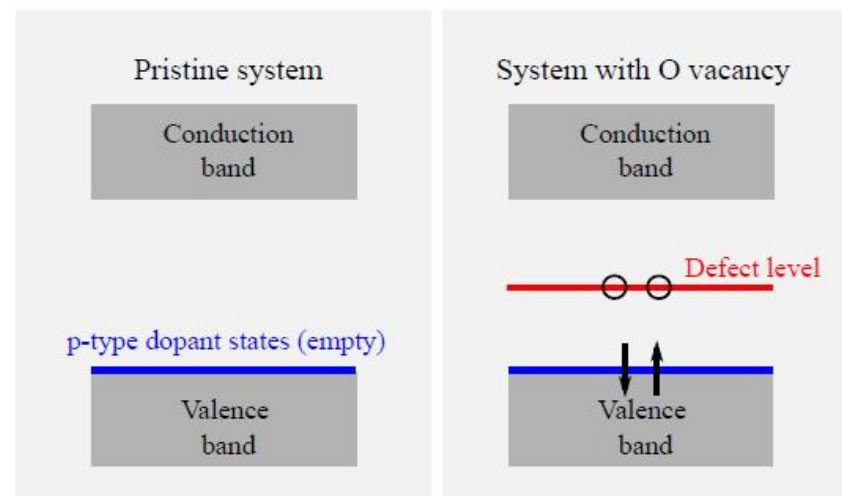
$$V_{\text{VCA}}(\mathbf{r}) = (1 - x)V_{\text{A}}(\mathbf{r}) + xV_{\text{B}}(\mathbf{r})$$

$$Z_{\text{M}} \rightarrow Z_{\text{M}} + \Delta Z_{\text{M}}$$

p-type doping:

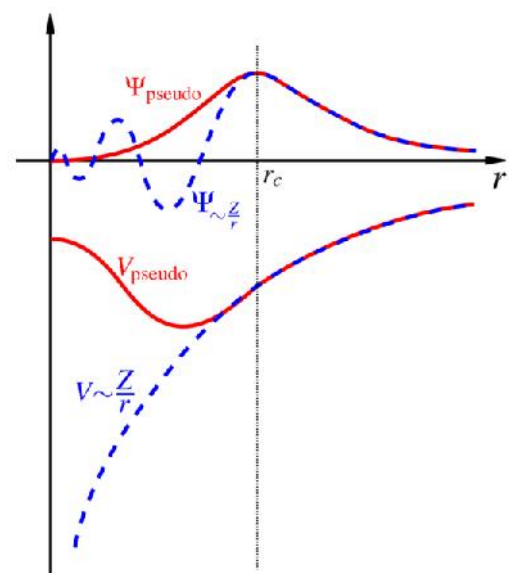
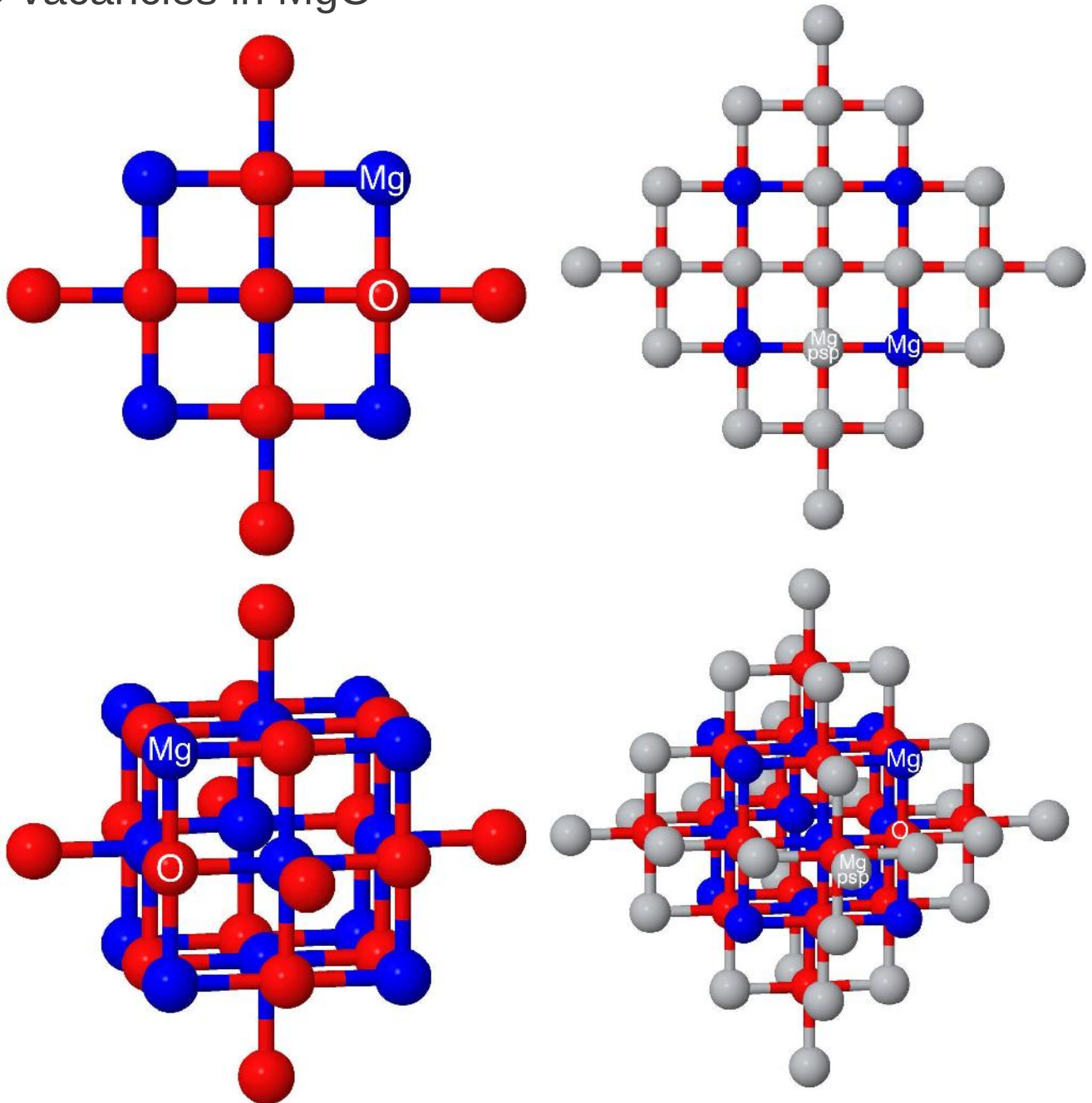
$$\Delta Z_{\text{M}} = -N_{\text{holes}}/N_{\text{M}}$$

$$\begin{aligned} E_{\text{el-nuc}}^{\text{VC}} &\approx \sum_i \int \frac{(Z_i + \Delta Z_i)n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_i|} d^3r \\ &= E_{\text{el-nuc}}^{\text{ref}} + \sum_i \Delta Z_i \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_i|} d^3r \end{aligned}$$



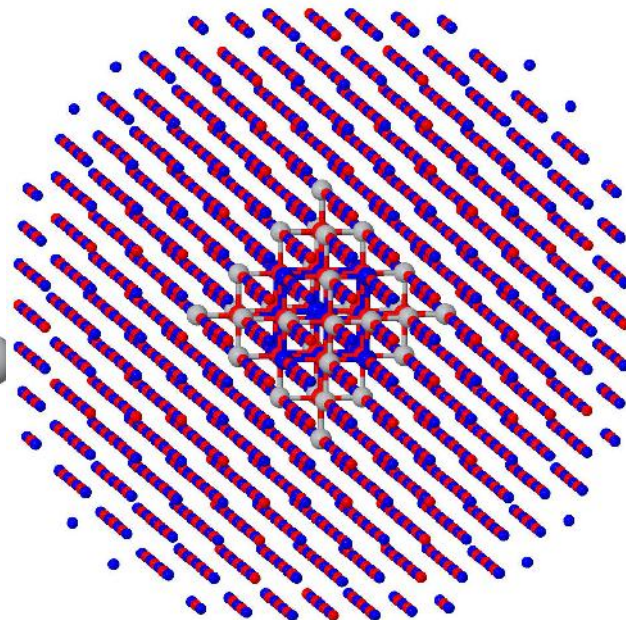
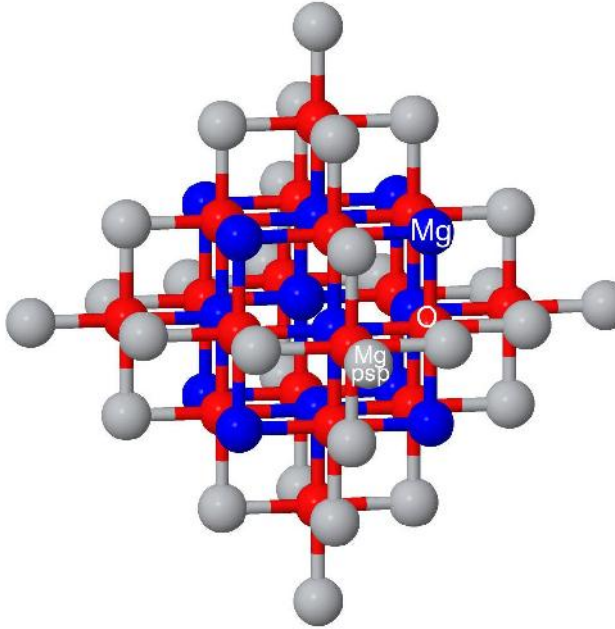
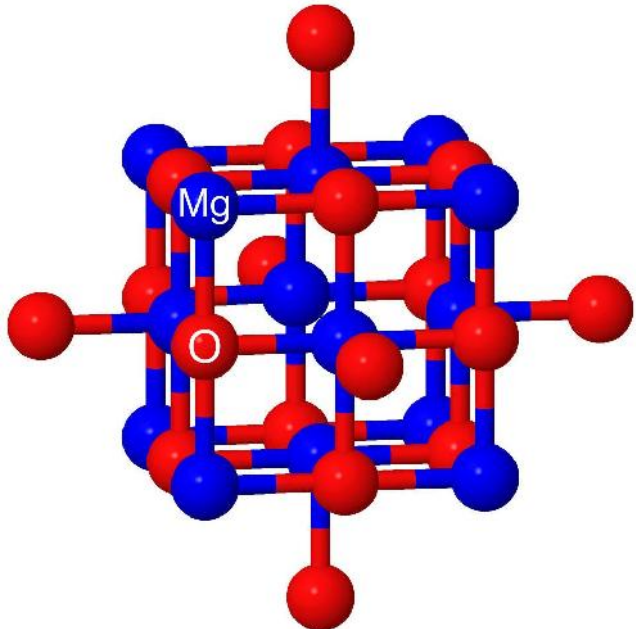
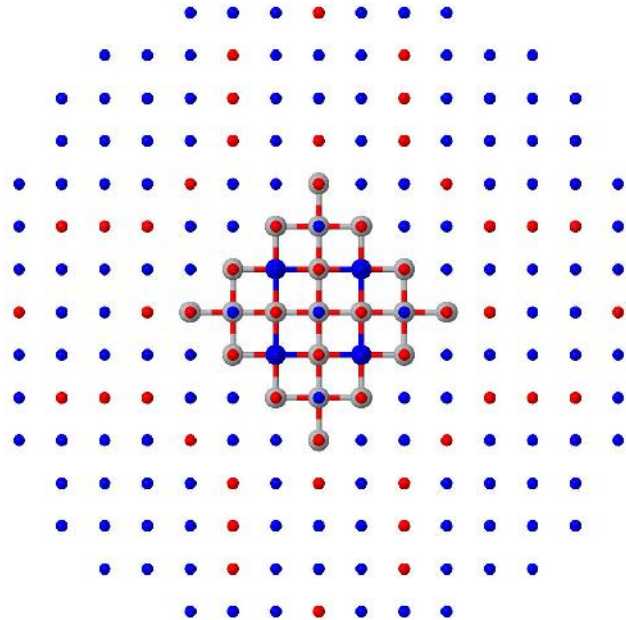
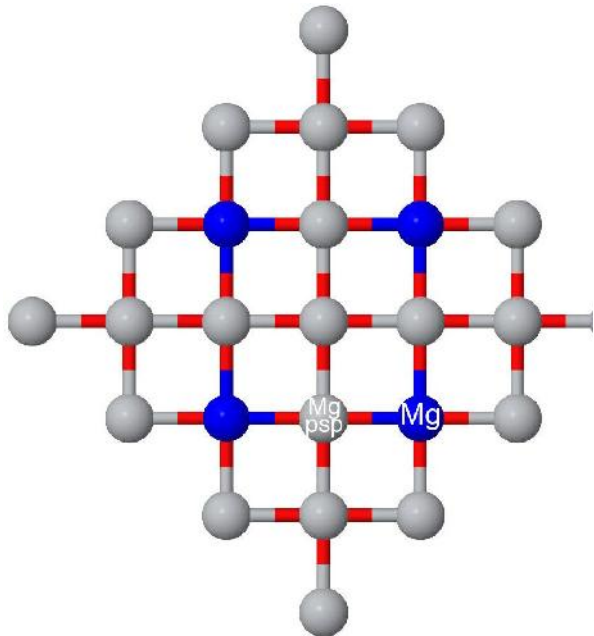
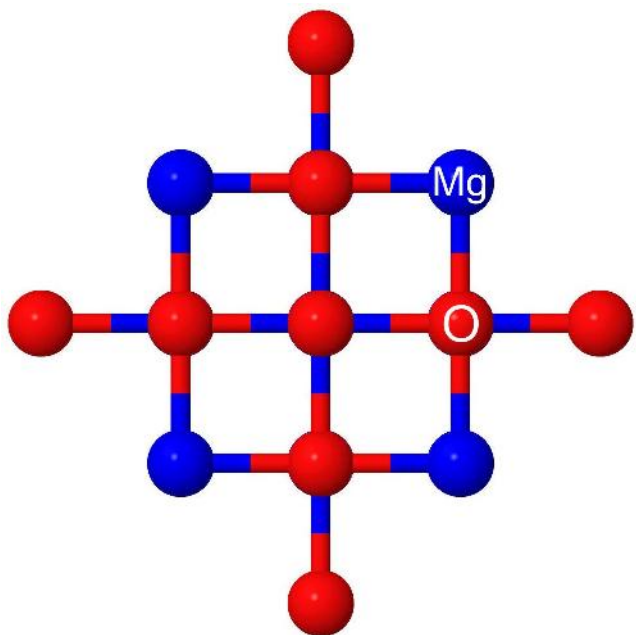
Embedded clusters

O vacancies in MgO

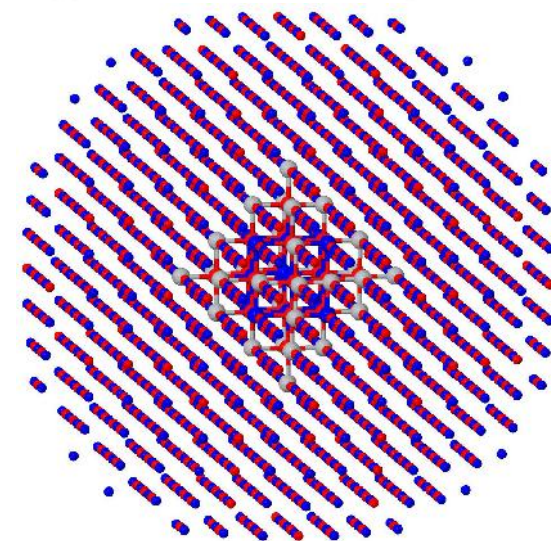
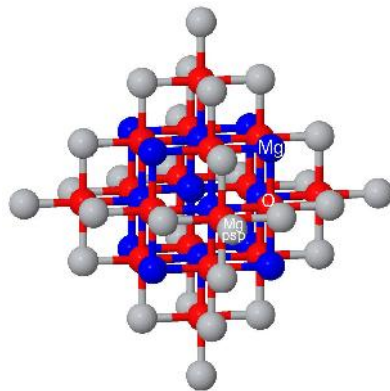
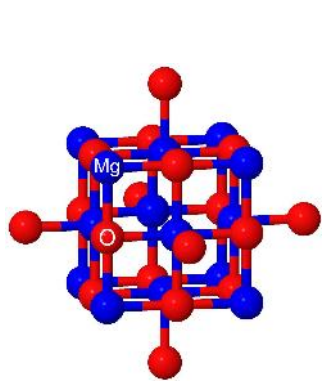
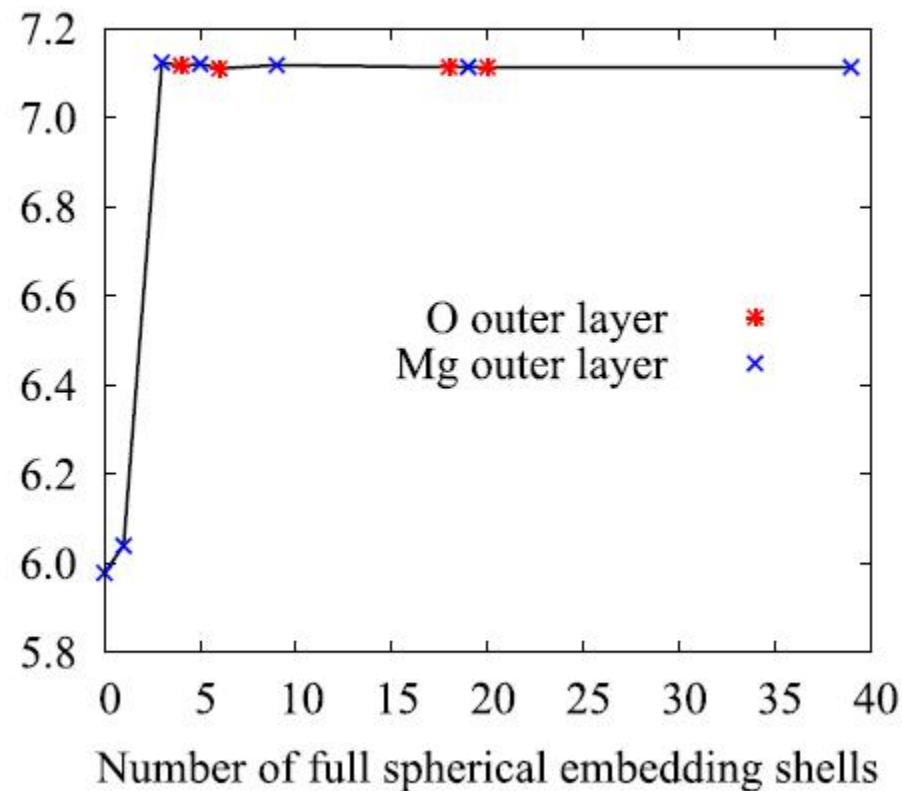
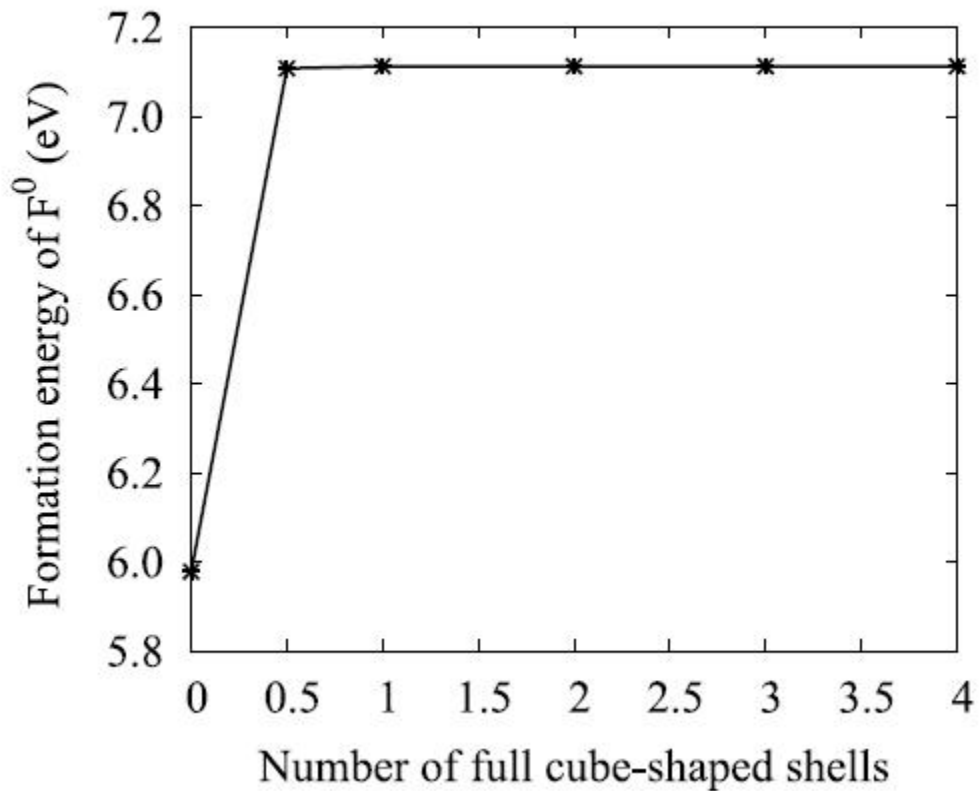


Embedded clusters

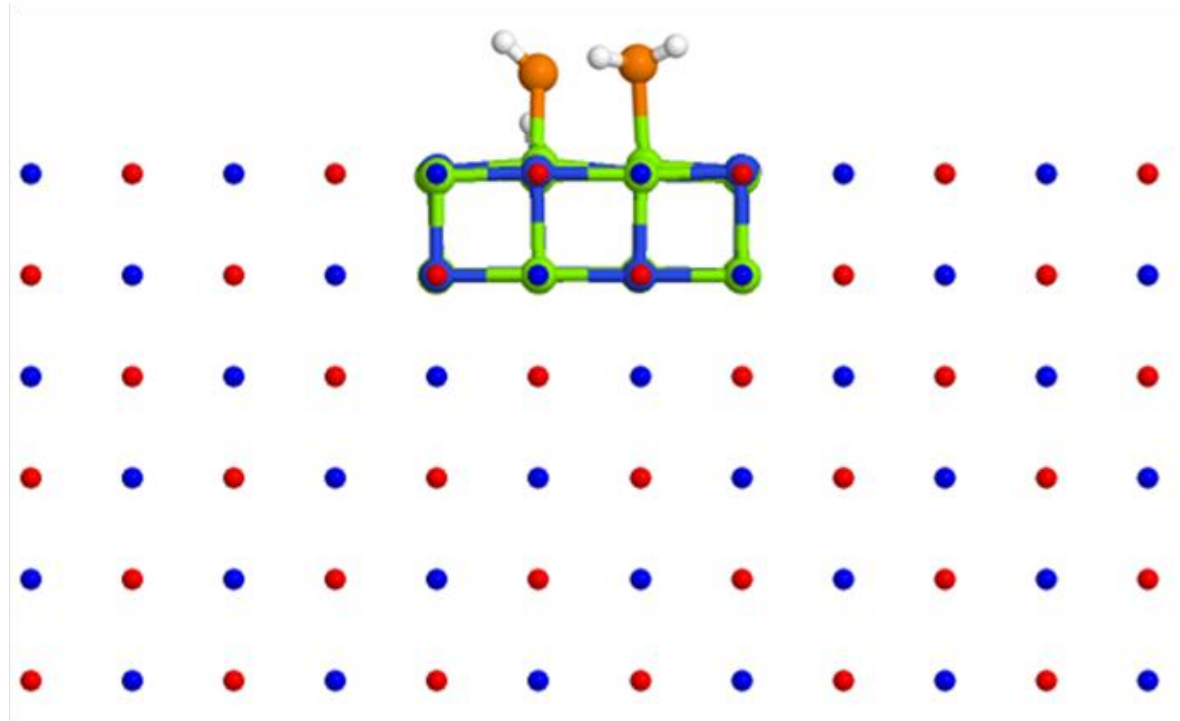
O vacancies in MgO



Embedded clusters, convergence



Embedded clusters



$2\text{H}_2\text{O}/\text{MgO}$ (embedded in point charges)

Part I: from xc functionals to total energies calculations in practice

- basis sets
- convergence

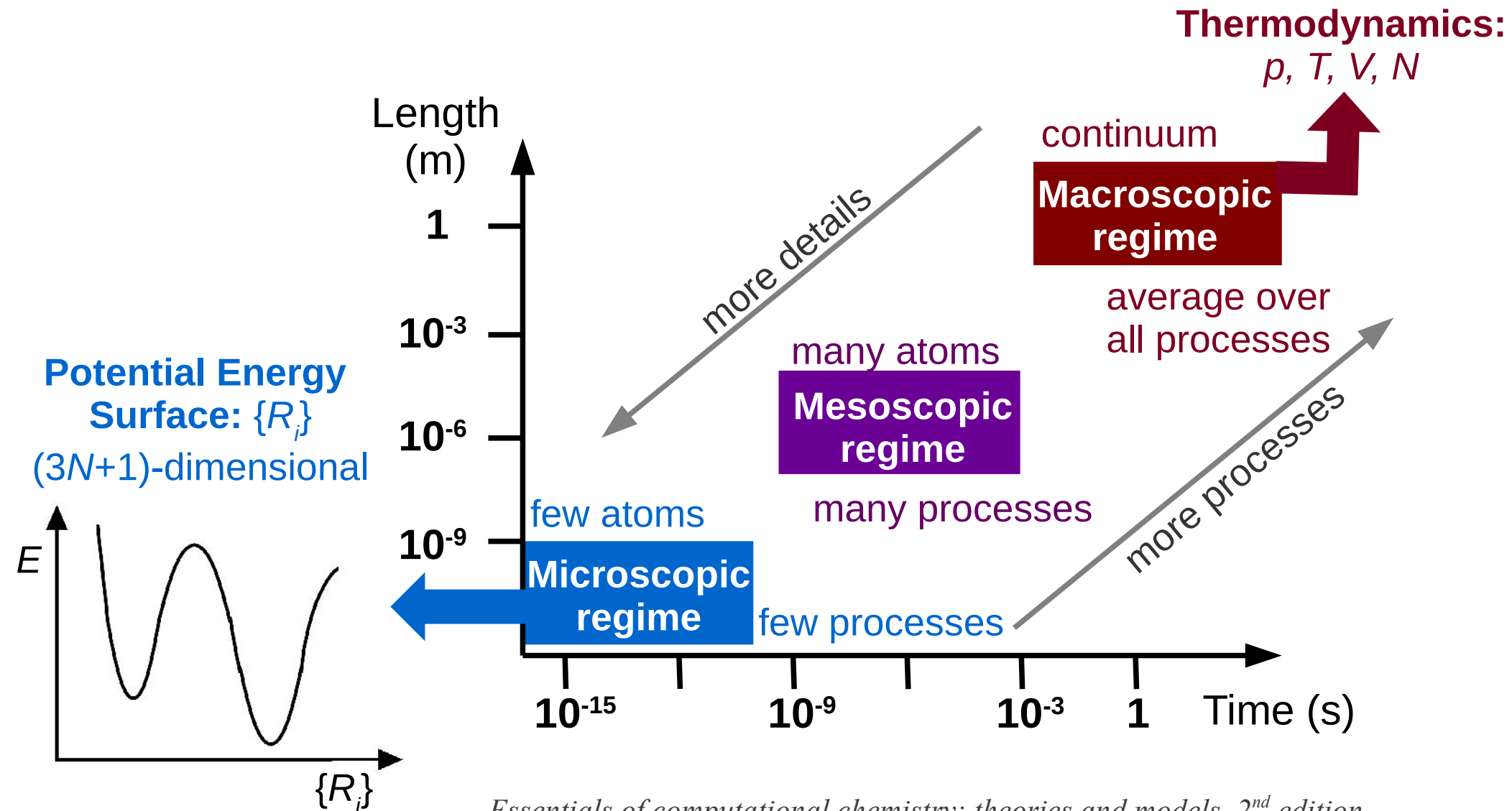
Part II: system size

- isolated clusters and molecules
- cluster extrapolation for bulk properties
- supercell approach
- embedded clusters

Part III: extending the scale

- surfaces in thermodynamic equilibrium with a reactive environment
- constrained equilibrium

Extending the scale



Essentials of computational chemistry: theories and models. 2nd edition.
C. J. Cramer, John Wiley and Sons Ltd (West Sussex, 2004).

*Ab initio atomistic thermodynamics and statistical mechanics
of surface properties and functions*

K. Reuter, C. Stampfl, and M. Scheffler, in: *Handbook of Materials Modeling Vol. 1,*
(Ed.) S. Yip, Springer (Berlin, 2005). <http://www.fhi-berlin.mpg.de/th/paper.html>

Ab initio atomistic thermodynamics: General concepts

Oxide formation on a metal surface

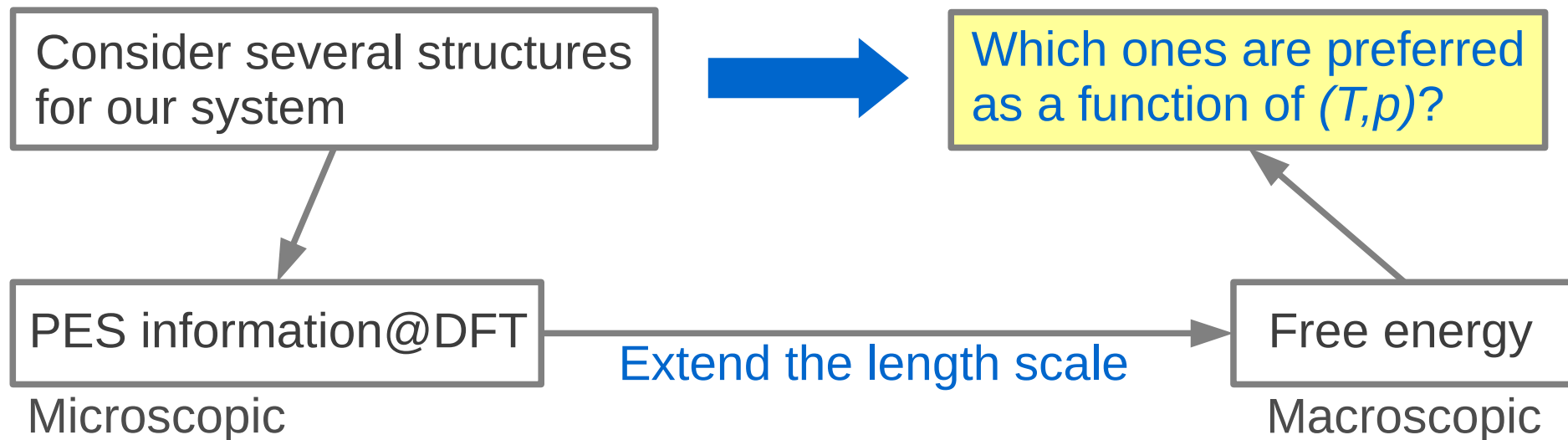
Adsorption of O₂ and CO on a metal oxide

Ab initio atomistic thermodynamics: General concepts

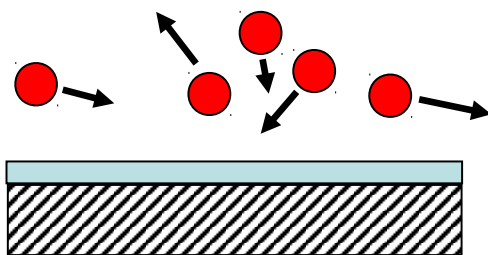
Oxide formation on a metal surface

Adsorption of O₂ and CO on a metal oxide

Ab initio atomistic thermodynamics



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
 $\Rightarrow \nu \sim 10^8 \text{ site}^{-1} \text{ s}^{-1}$

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, not internal energy U

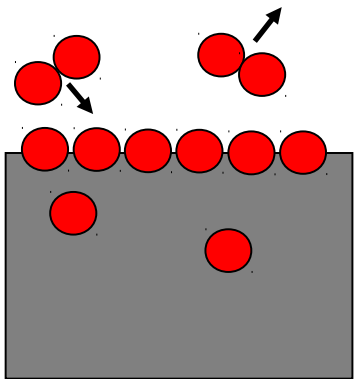
If also volume V is constant, the energy minimized is Helmholtz free energy F

$$F = U - TS$$

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 μ_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 one



In thermodynamic equilibrium, μ_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

$$Q = \frac{1}{N!} q^N$$

$$q = q^{trans} q^{rot} q^{vib} q^{el} q^{conf} \cancel{q^{nucl}}$$

Translational: $q^{trans} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} V$

➔ Need: particle mass m

Use the ideal gas law to relate V and p

Rotational:
$$\left\{ \begin{array}{l} q^{rot} = \frac{8\pi^2 I_A k T}{h^2} \\ q^{rot} = 8\pi^2 \left(\frac{2\pi k T}{h^2} \right)^{\frac{3}{2}} (I_A I_B I_C)^{\frac{1}{2}} \end{array} \right.$$

Linear molecules

Non-linear molecules

Rigid rotor

➔ Need: moments of inertia
 I_A, I_B, I_C

$$Q = \frac{1}{N!} q^N$$

$$q = q^{trans} q^{rot} q^{vib} q^{el} q^{conf} \cancel{q^{nucl}}$$

Vibrational: $q^{vib} = \prod \left[\exp\left(-\frac{h\nu_i}{2kT}\right) \left(1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right)^{-1} \right]$ → Need: vibrational modes

Harmonic oscillator

Electronic: $q^{el} = \sum v_i e^{-\frac{E_i}{kT}} \approx v_0 e^{-\frac{E_0}{kT}}$ → Need: total (DFT) energy of the ground state and its degeneration

$$v_i = 2S_i + 1$$

Assuming that the first excited state is energetically inaccessible

Conformational: $q^{conf} = \frac{1}{\sigma}$ → Need: symmetry number (N. equivalent orientations)

Diatomic molecules:

$$\sigma = 1 \text{ (heteroatomic)}$$

$$\sigma = 2 \text{ (homoatomic)}$$

Polyatomic molecules:

$$\sigma = N. \text{ symmetry operations according to the symmetry point group}$$

From the partition function Q :

Helmholtz free energy: $F = -kT \ln Q$ Canonical ensemble (NVT)

Gibbs free energy: $G = -kT \ln Q + pV$ Isothermal-isobaric ensemble (NpT)

Chemical potential: $\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} = \left(\frac{\partial G}{\partial N} \right)_{p,T} \left\{ \begin{array}{l} \mu = kT \ln N - kT \ln q \quad (NVT) \\ \mu = kT [\ln N + 1 - \ln q] \quad (NpT) \end{array} \right.$

Computation of free energies: solids

$$G(T, p) = E^{tot} + F^{trans} + F^{rot} + F^{vib} + F^{conf} + pV$$

E^{tot} Total electronic energy → DFT

F^{trans} Translational free energy }
 F^{rot} Rotational free energy } → Discarded (consider fixed solids)

F^{vib} Vibrational free energy

$$\left\{ \begin{array}{l} F^{vib} = \int d\omega F^{vib}(T, \omega) \sigma(\omega) \\ F^{vib}(T, \omega) \approx \frac{\hbar\omega}{2} + kT \ln \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right] \end{array} \right.$$

F^{conf} Conformational free energy → Needs more advanced methods (Ex: cluster expansion)

pV Expansion term → Usually small, often neglected

$$G(T, p) \approx E^{tot} + F^{vib}$$

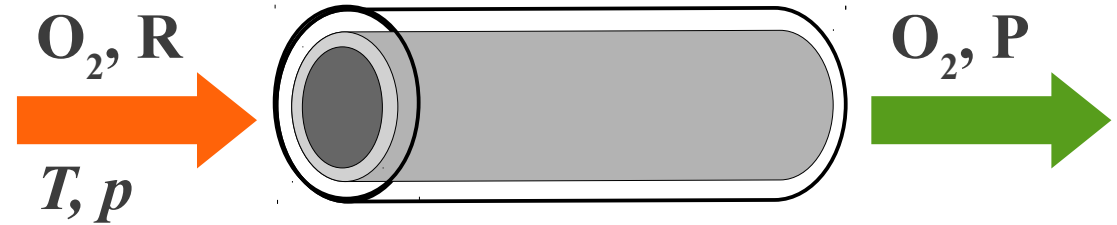
Ab initio atomistic thermodynamics: General concepts

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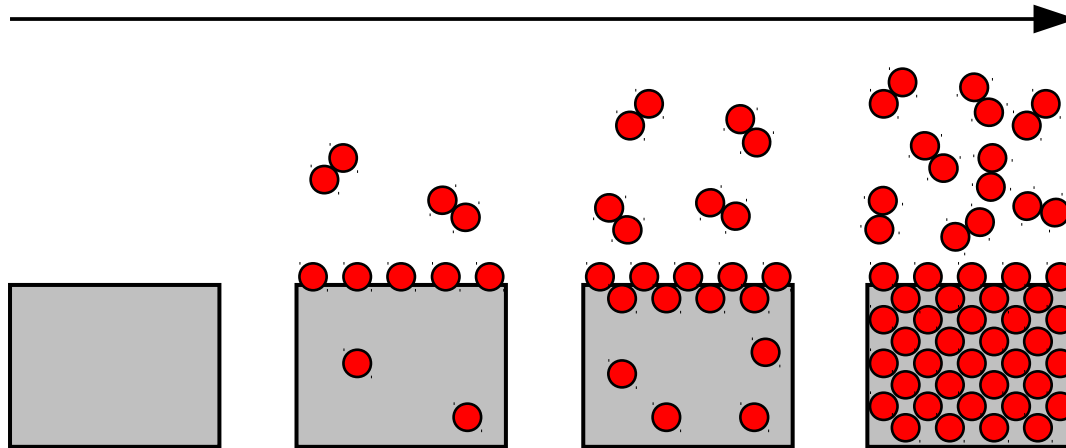
Adsorption of O₂ and CO on a metal oxide

Oxide formation on Pd(100)

Heterogeneous catalysis:



$p(O_2)$



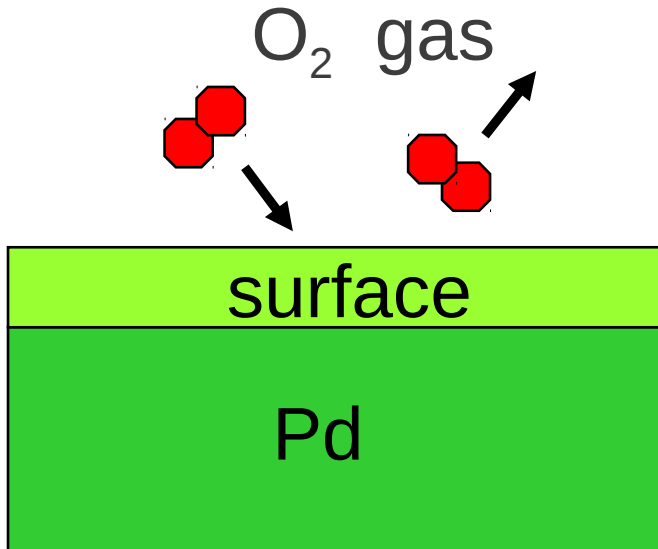
Which oxide forms at given experimental conditions (T, p)?

Reuter and Scheffler, Appl. Phys. A, 78, 793-798, 2004

J. Rogal and K. Reuter, Ab initio atomistic thermodynamics for surfaces: A primer.

In: Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Hypersonic Flights. Educational Notes RTO-EN-AVT-142, Neuilly-sur-Seine (2007)

Oxide formation on Pd(100)



$$\Delta G^{ad} = \frac{1}{A} (G_{\text{Pd} \cdot \text{O}_x} - G_{\text{Pd}(100)} - x \mu_{\text{O}})$$

$$G(T, p) \approx E^{total} + F^{vib} \approx E^{total}$$

$$\Delta F^{vib} \approx \pm 5 \text{ meV/\AA}^2 \quad \text{up to } T = 600 \text{ K}$$

$$\mu_{\text{O}}(T, p) = \frac{1}{2} \mu_{\text{O}_2}(T, p)$$

$$\mu_{\text{O}_2}(T, p) = E_{\text{O}_2}^{DFT} + E_{\text{O}_2}^{ZPE} + \Delta \mu_{\text{O}_2}(T, p)$$

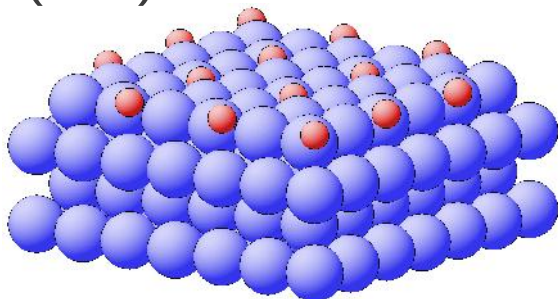
$$\mu_{\text{O}}(T, p) = \frac{1}{2} E_{\text{O}_2}^{DFT} + \frac{1}{2} E_{\text{O}_2}^{ZPE} + \Delta \mu_{\text{O}}(T, p)$$

$$\Delta G^{ad} \approx \frac{1}{A} \left[E_{\text{Pd} \cdot \text{O}_x} - E_{\text{Pd}(100)} - x \left(\frac{1}{2} E_{\text{O}_2}^{DFT} + \frac{1}{2} E_{\text{O}_2}^{ZPE} + \Delta \mu_{\text{O}}(T, p) \right) \right]$$

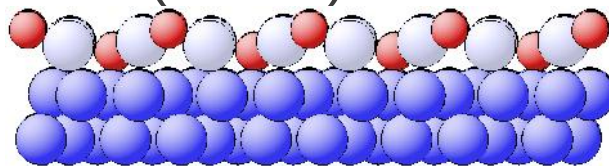
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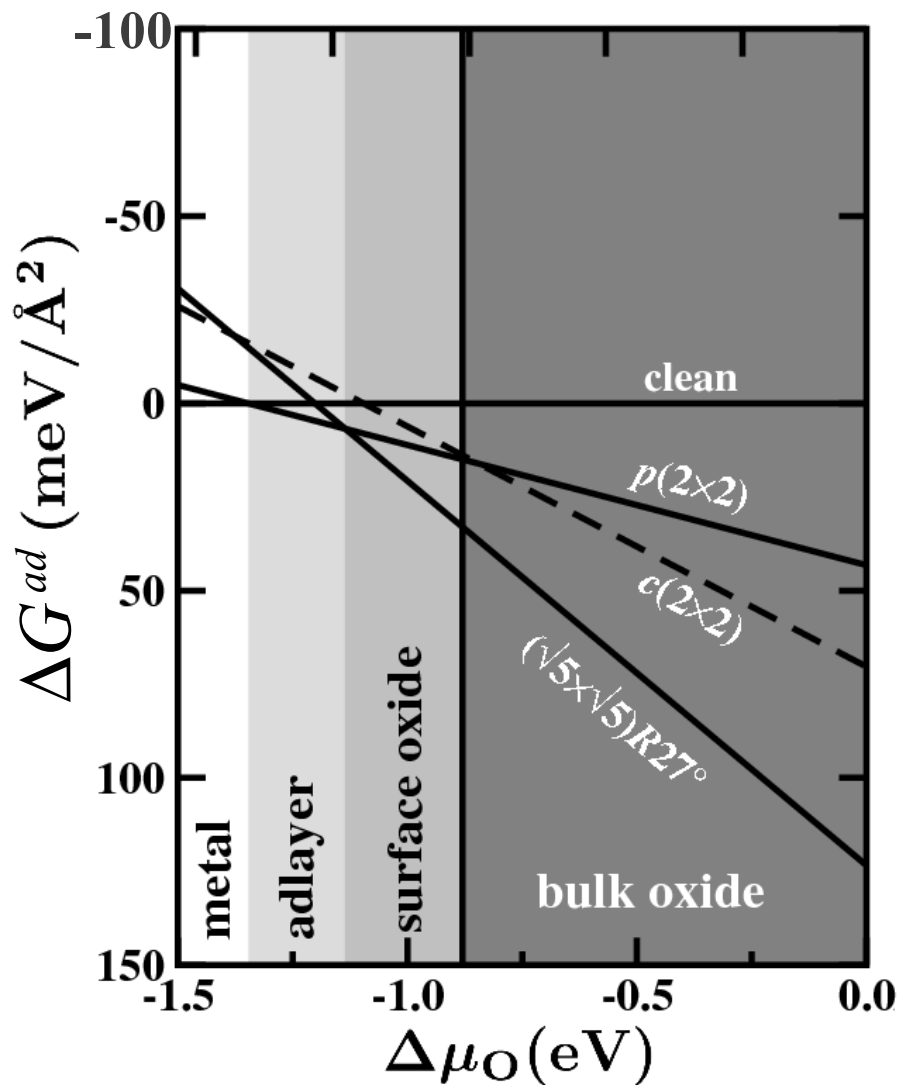
- Clean Pd(100) surface
- O/Pd(100) adlayers:
 $p(2 \times 2)$: 0.25 ML
 $c(2 \times 2)$: 0.50 ML



- PdO(101)/Pd(100) surface oxide:
 $(\sqrt{5} \times \sqrt{5})R27^\circ$: 0.80 ML



- Bulk PdO



Relation between chemical potential and (T, p)

$$\mu_{O_2}(T, p) = E_{O_2}^{DFT} + E_{O_2}^{ZPE} + \Delta \mu_{O_2}(T, p)$$

From the O_2 partition function:

$$\mu(T, p) = -kT \ln \left[\left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} (kT)^{\frac{5}{2}} \right] + kT \ln p - kT \ln \left(\frac{8\pi^2 I_A kT}{\sigma h^2} \right) + \frac{1}{2} h\nu + kT \ln \left(1 - e^{-\frac{h\nu}{kT}} \right) + E^{DFT} - kT \ln v_0$$

$\Delta \mu(T, p)$

From thermochemical tables:

$$\Delta \mu(T, p) = \mu(T, p^\circ) - \mu(T^\circ, p^\circ) + kT \ln(p/p^\circ)$$

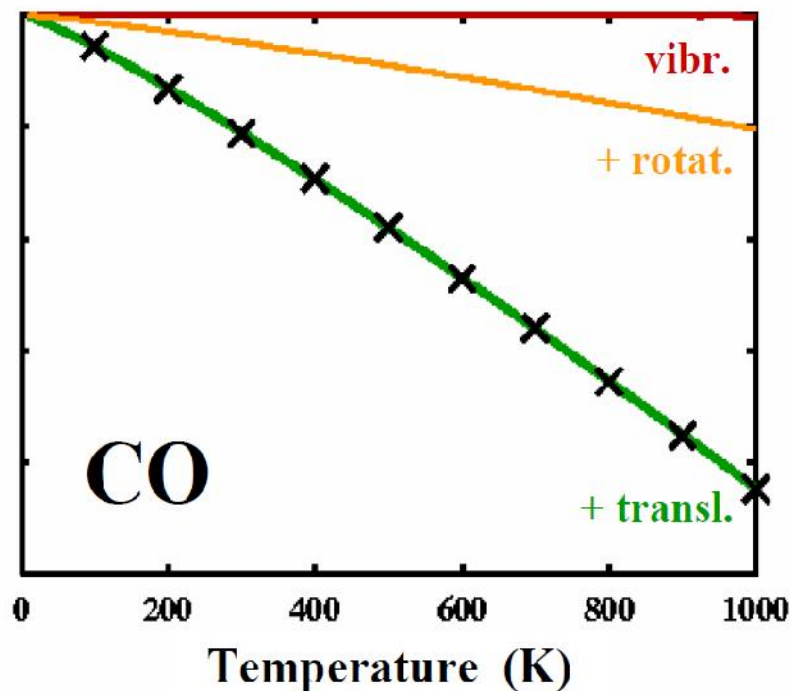
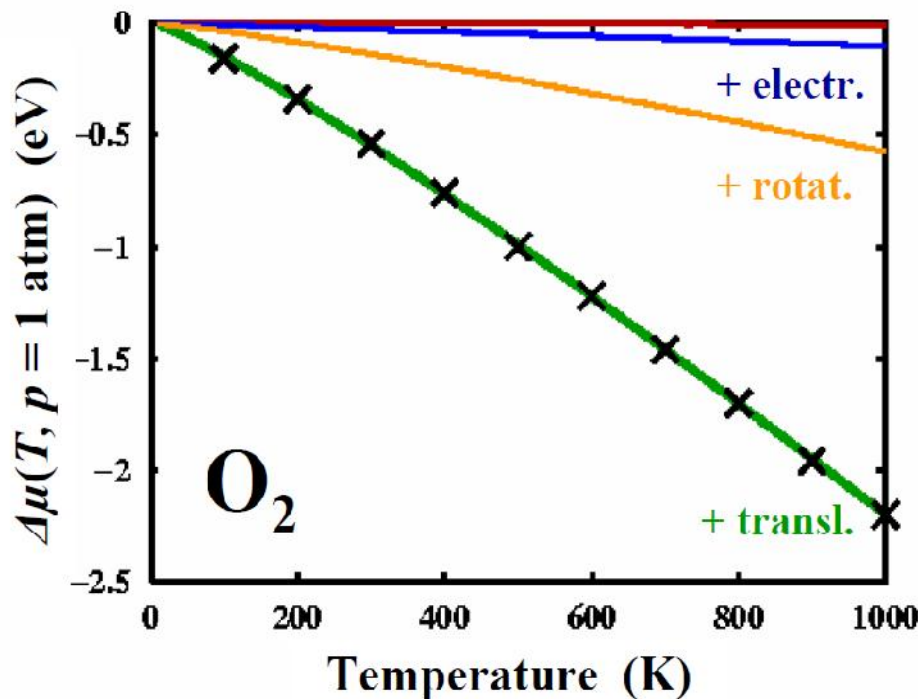
↑ ↑
Tables

Example: JANAF Thermochemical tables, D.R. Stull, H. Prophet.
US National Bureau of Standards, Washington DC, 1971

→ $S^\circ(T), H^\circ(T)$

Relation between chemical potential and (T, p)

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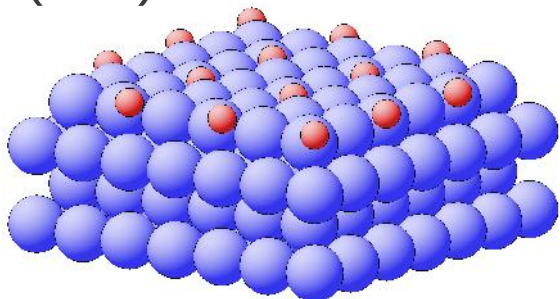
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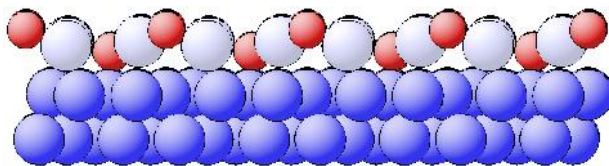
Oxide formation on Pd(100)

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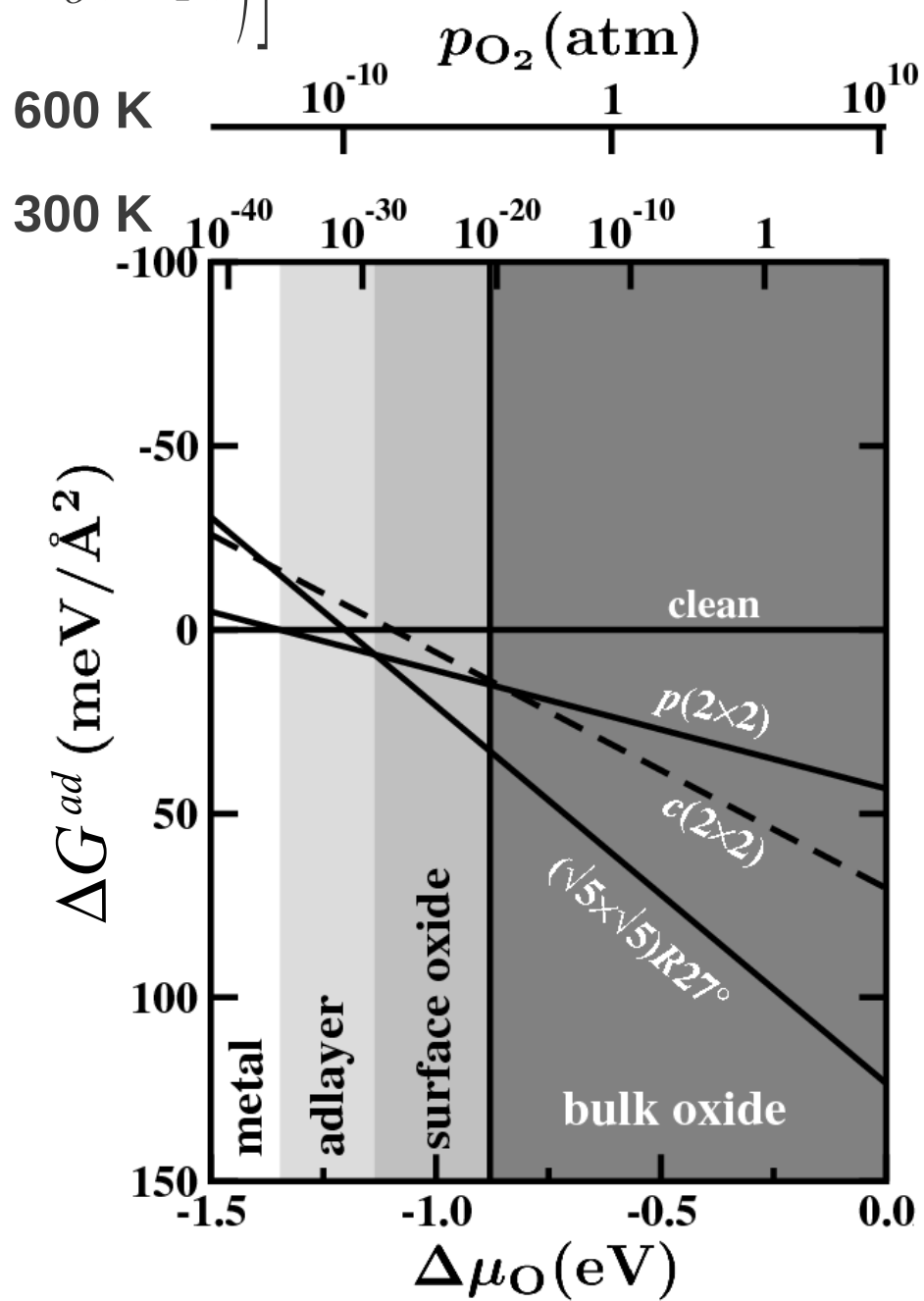
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 $(\sqrt{5} \times \sqrt{5})R27^\circ$: 0.80 ML

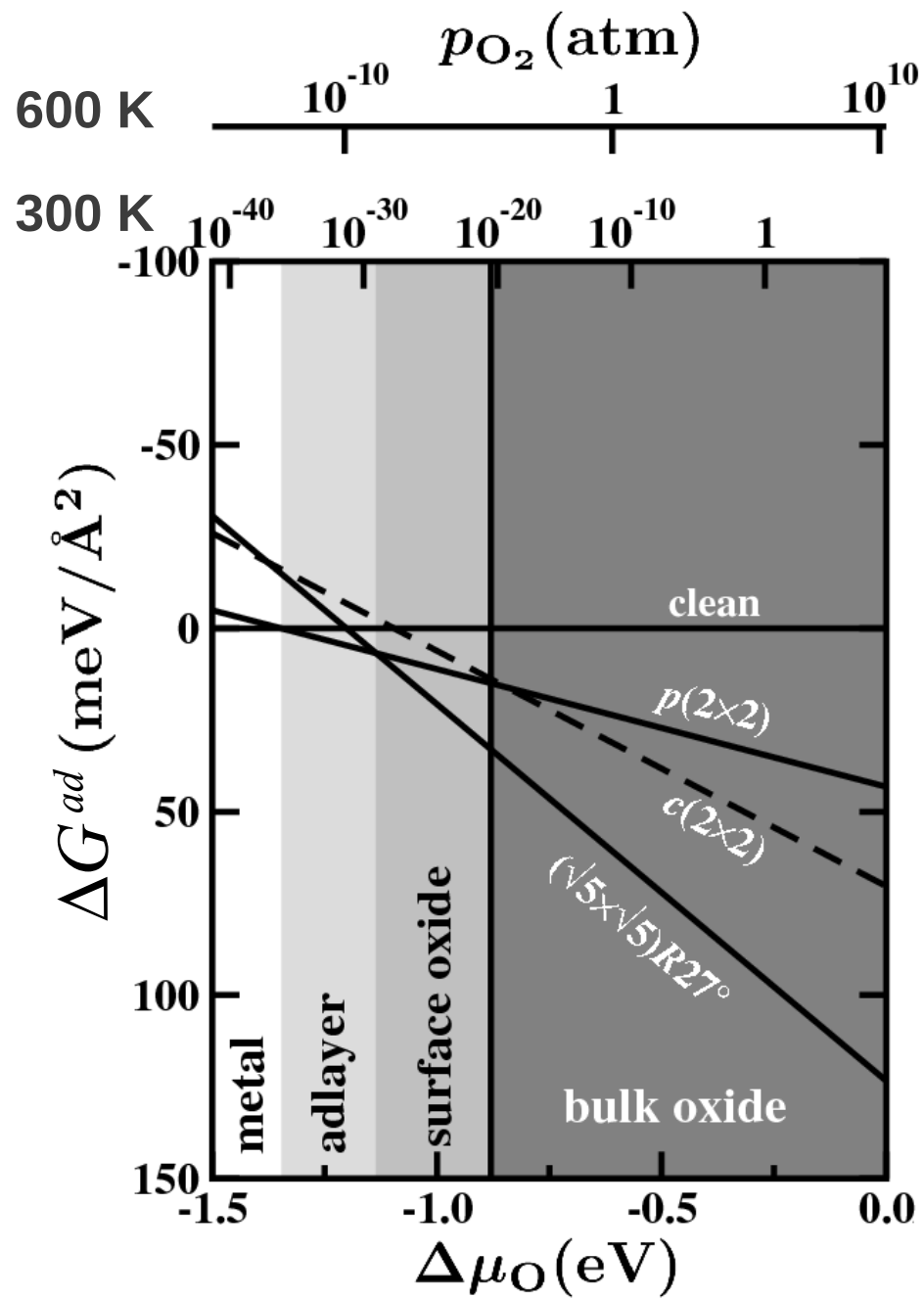


- Bulk PdO

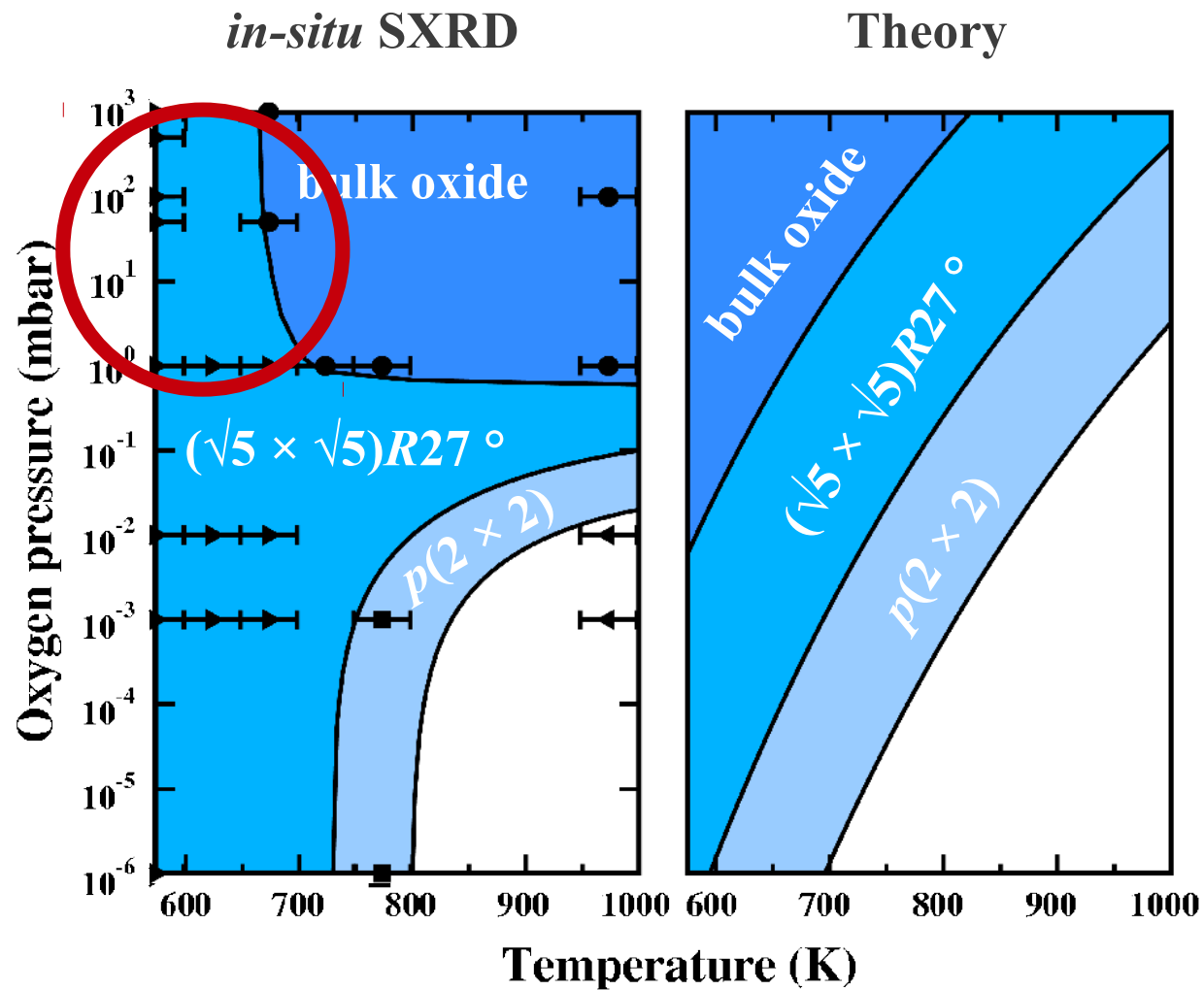


Limitations

- Number of screened structures: structures not considered cannot be predicted
- Neglecting F^{vib} : (slight) horizontal shift of lines
- Neglecting F^{conf} : smearing of phase transitions
- Systems in equilibrium: possible kinetic effects in experiment



Comparing with experiment: kinetic effect



Ab initio atomistic thermodynamics: Outline

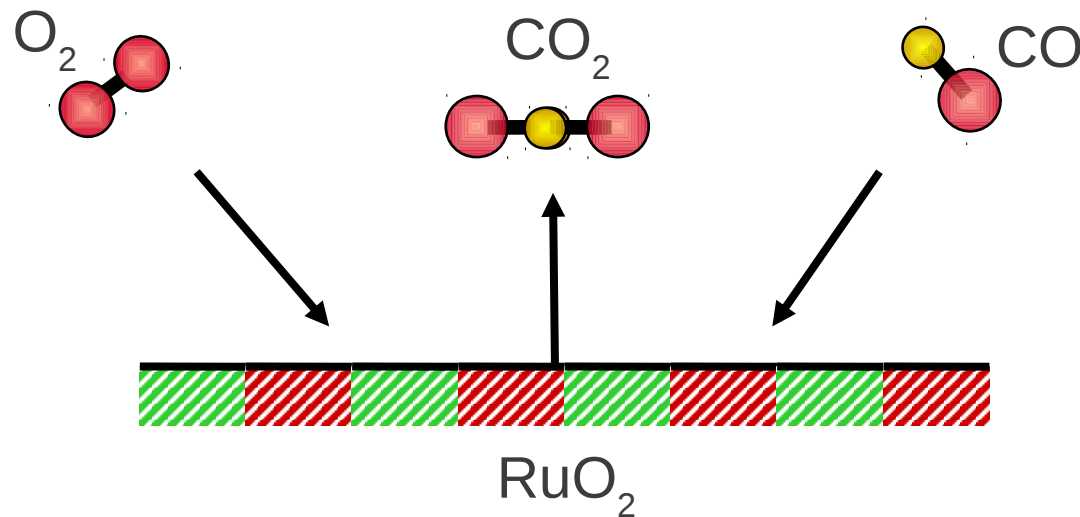
Ab initio atomistic thermodynamics: General concepts

Oxide formation on a metal surface

Adsorption of O₂ and CO on a metal oxide

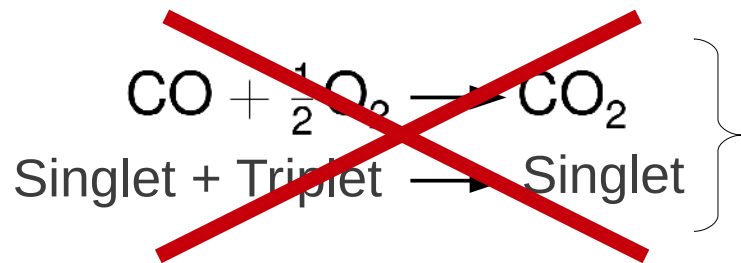
Adsorption of O₂ and CO on RuO₂(110)

CO oxidation over a Ru catalyst:



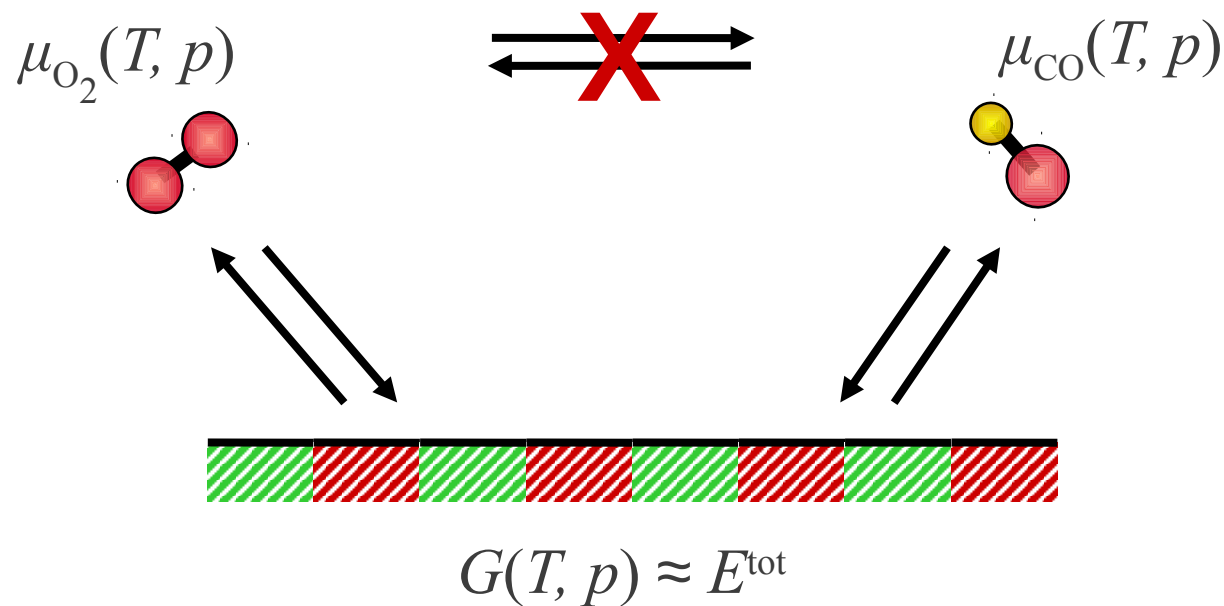
What are the preferred structures for RuO₂·(O)_x·(CO)_y?

This reaction does not take place in the gas phase:



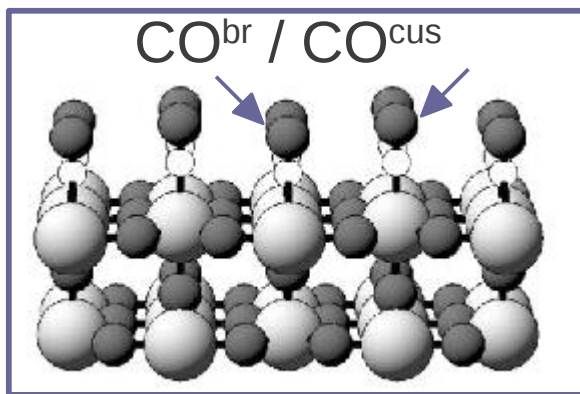
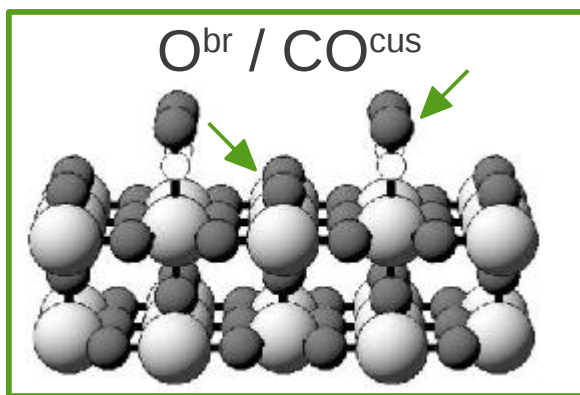
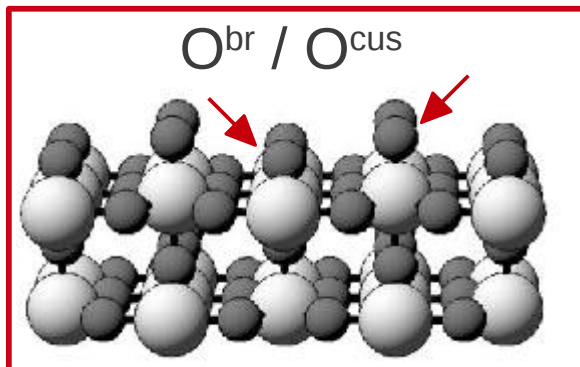
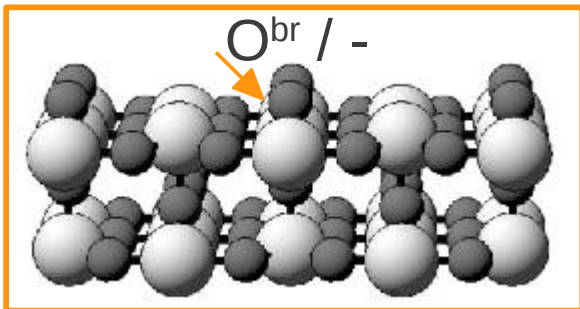
$\Delta E = -3.27$ eV (DFT-PBE+vdW)
Spin forbidden!

Constrained equilibrium

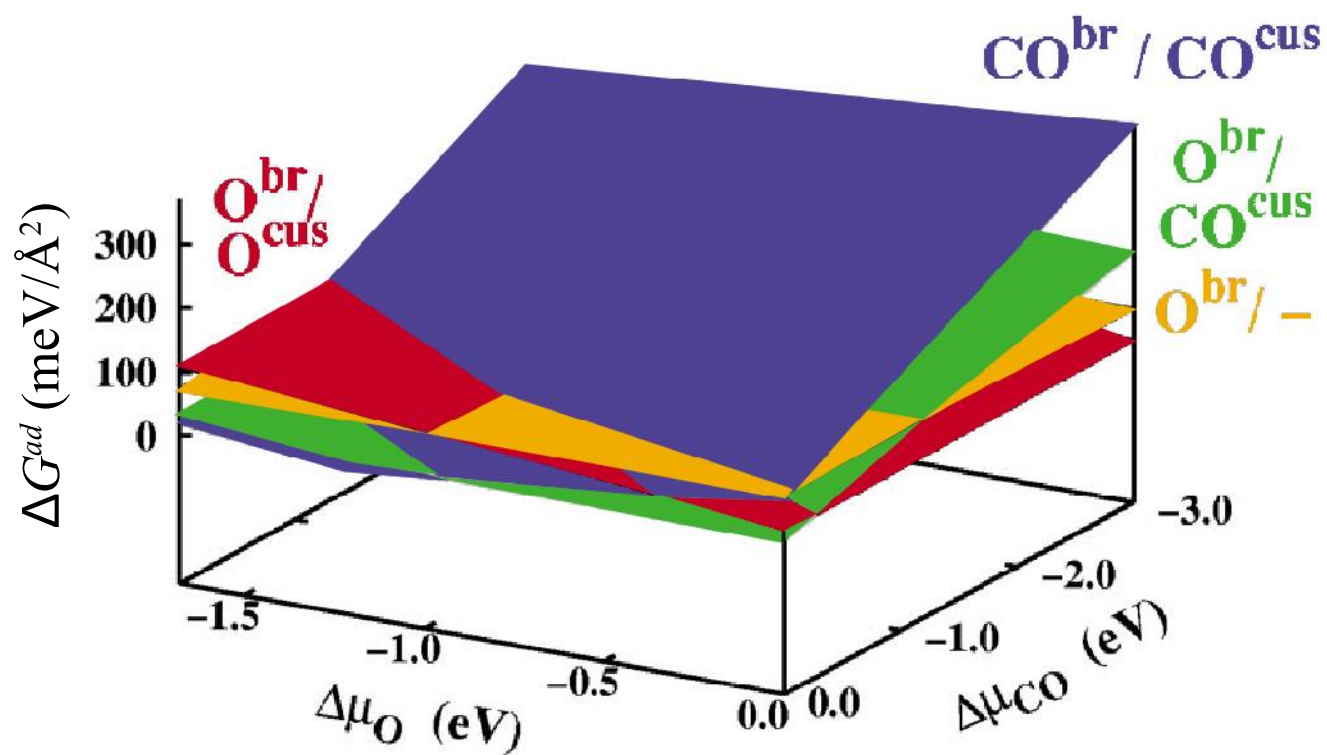


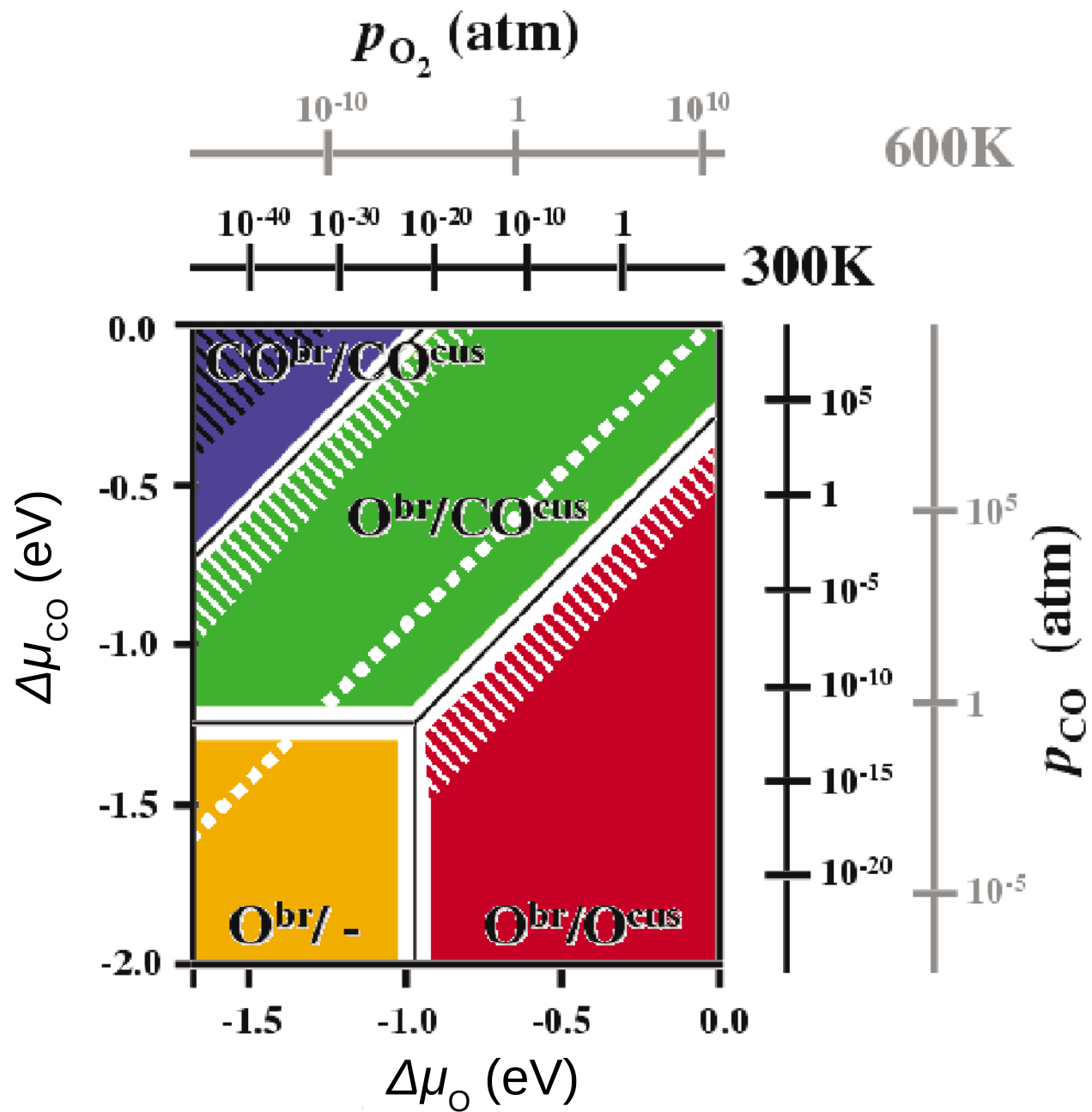
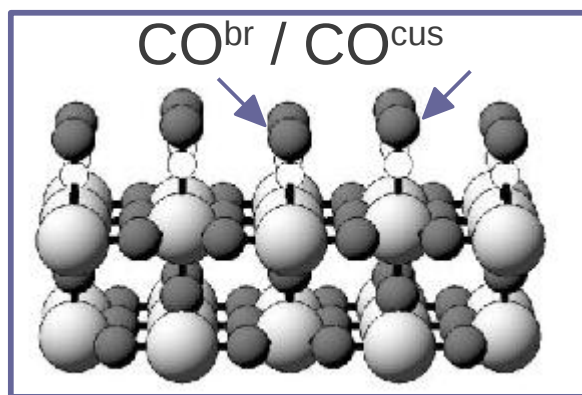
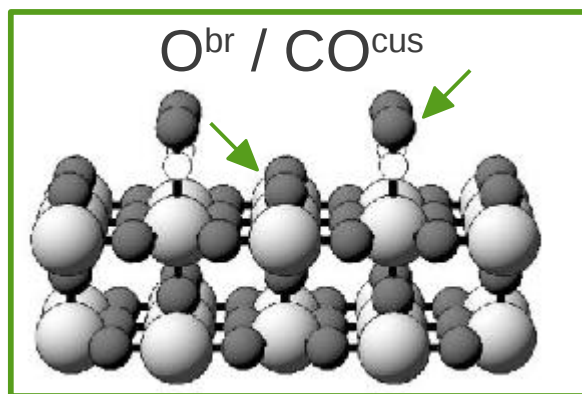
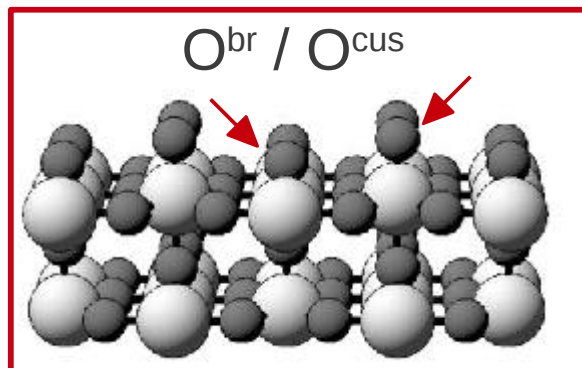
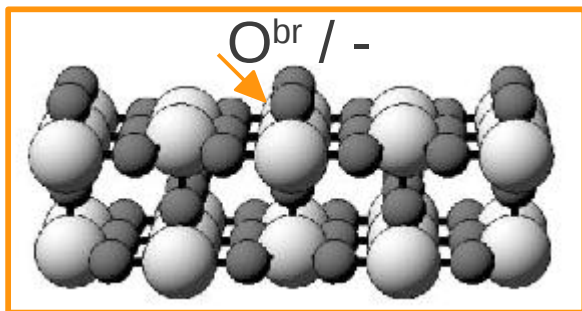
$$\Delta G^{\text{ad}} = \frac{1}{A} \left[G_{\text{RuO}_2 \cdot \text{O}_x \cdot (\text{CO})_y} - G_{\text{RuO}_2(110)} - x \mu_{\text{O}} - y \mu_{\text{CO}} \right]$$

$$\Delta G^{\text{ad}} \approx \frac{1}{A} \left[E_{\text{RuO}_2 \cdot \text{O}_x \cdot (\text{CO})_y} - E_{\text{RuO}_2(110)} - x \left(\frac{1}{2} E_{\text{O}_2}^{\text{DFT}} + \frac{1}{2} E_{\text{O}_2}^{\text{ZPE}} + \Delta \mu_{\text{O}} \right) - y \left(E_{\text{CO}}^{\text{DFT}} + E_{\text{CO}}^{\text{ZPE}} + \Delta \mu_{\text{CO}} \right) \right]$$

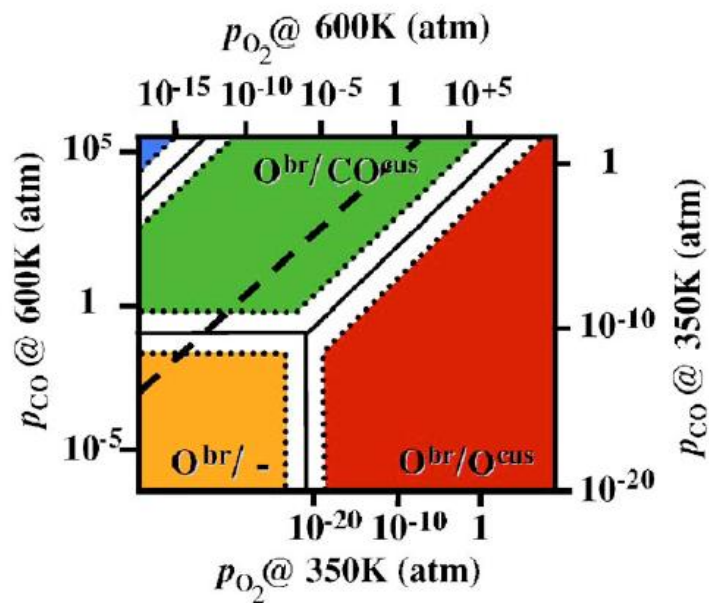


$$\Delta G^{ad} \approx \frac{1}{A} \left[E_{RuO_2 \cdot O_x \cdot (CO)_y} - E_{RuO_2(110)} - x \left(\frac{1}{2} E_{O_2}^{DFT} + \frac{1}{2} E_{O_2}^{ZPE} + \Delta \mu_{O} \right) - y \left(E_{CO}^{DFT} + E_{CO}^{ZPE} + \Delta \mu_{CO} \right) \right]$$

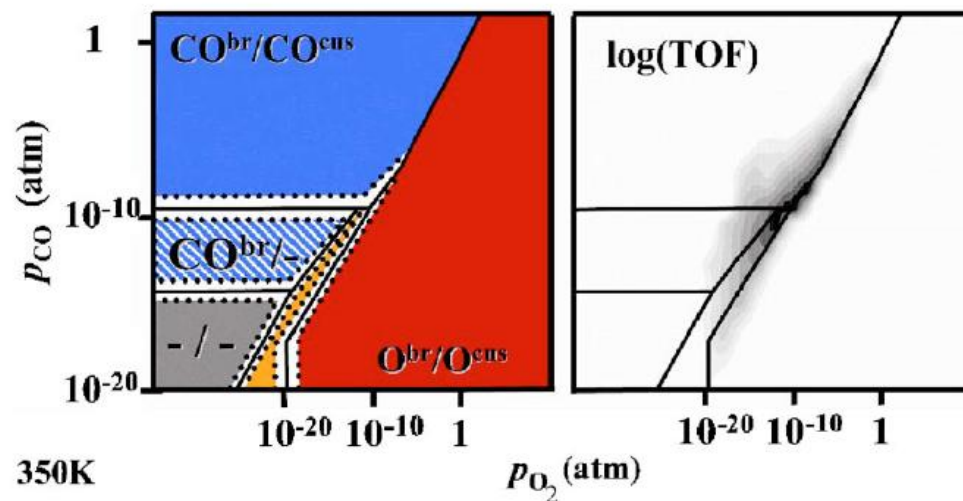
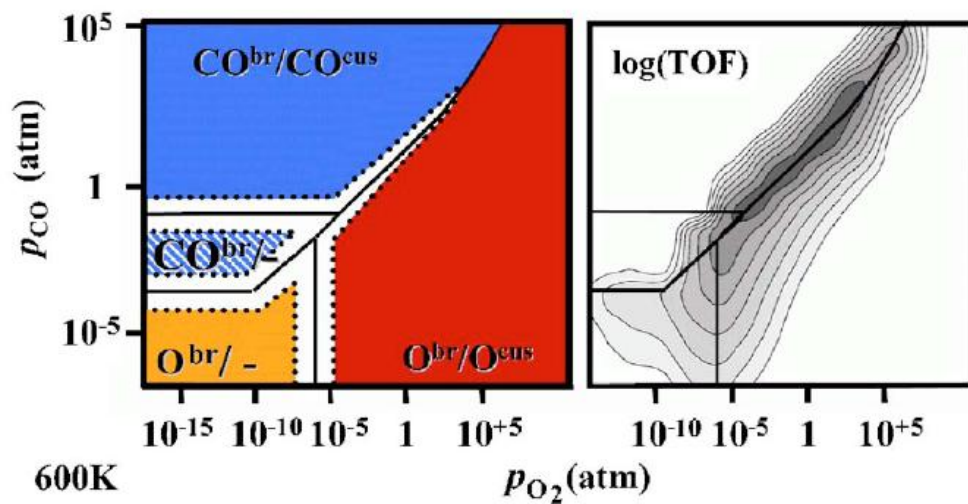




Including kinetics: steady state



No reaction: Same as thermodynamics, but with time evolution information: From fully O-covered surface (red), induction time is 0.1 s (!)



Summary of *ab initio* atomistic thermodynamics

Ab initio atomistic thermodynamics provides a connection between the microscopic and macroscopic regimes

With *ab initio* atomistic thermodynamics one can predict

- the preferred structure of a material as a function of environmental conditions
- the regions of enhanced catalytic activity

Limitations:

- Only actually sampled structures enter the free energy contest:
- Need for an exhaustive structural sampling
- Equilibrium assumption: possible kinetic hindrance in experiment

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