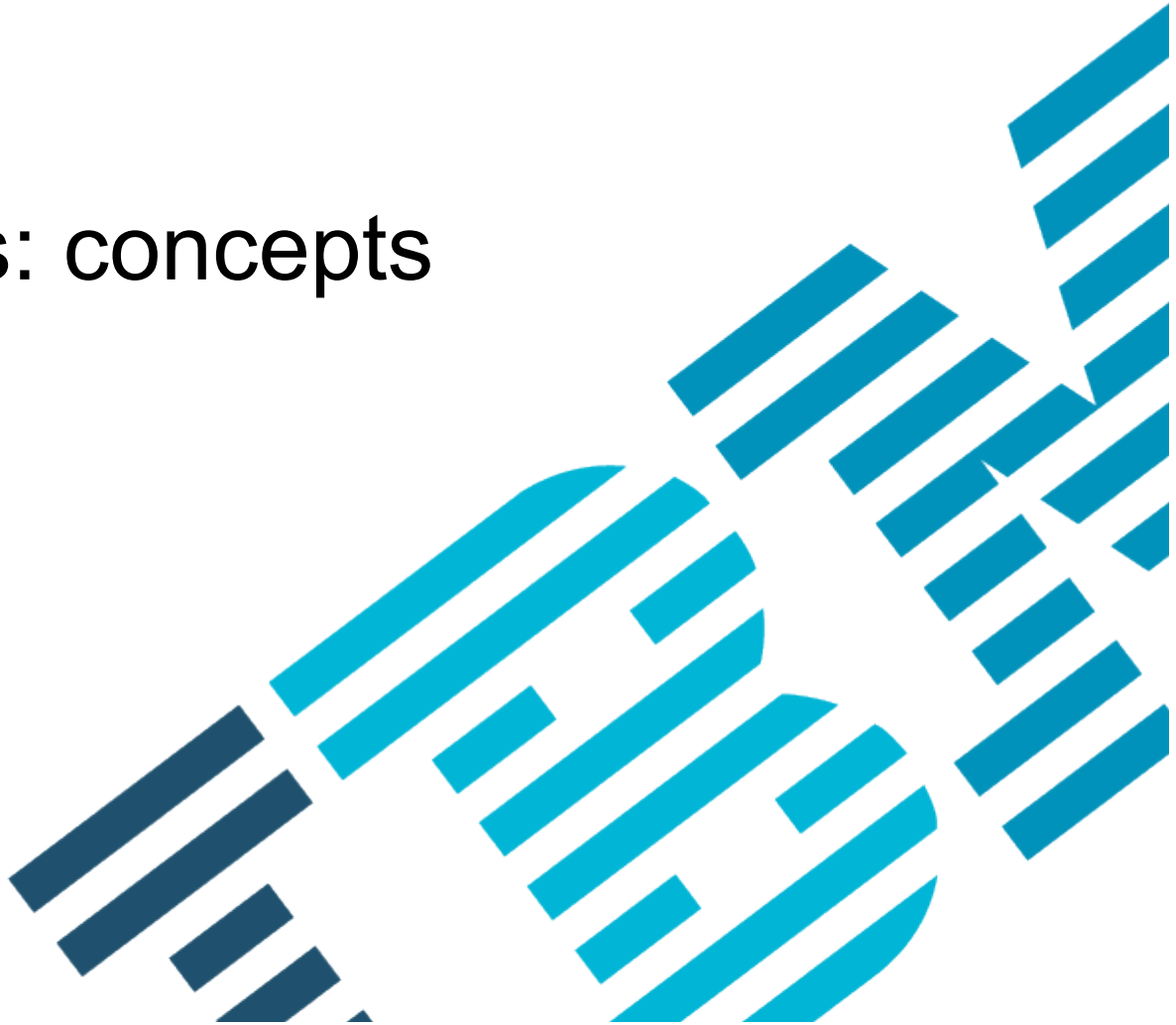
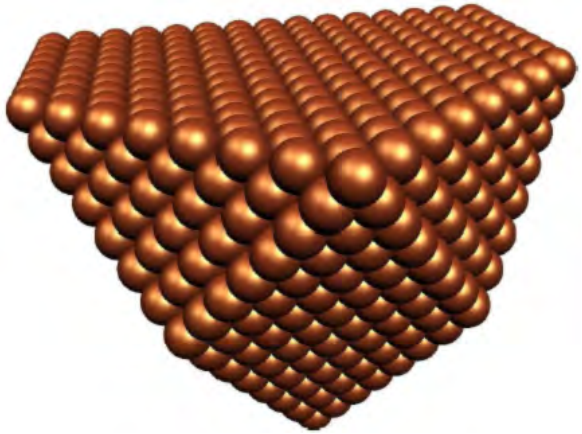
Nikolaj Moll

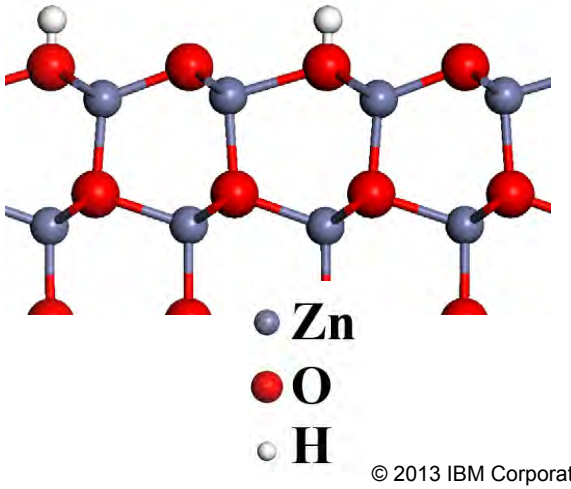


Periodic systems: concepts

Outline



- Periodic systems: concepts
  - Crystal structure
    - Periodicity in real space
  - Electronic structure
    - Periodicity in reciprocal space
    - Bloch theorem and band structures
  - Calculation of defects and surfaces using periodic supercells
- Stabilization of semiconductor surfaces through bulk dopants
  - Ab-initio thermodynamics
    - Adding electrons to surfaces
  - Surface energies of the H-terminated ZnO (000-1)
    - As a function of the electron chemical potential
    - As a function of the H chemical potential
  - Applying a hybrid exchange correlation functional



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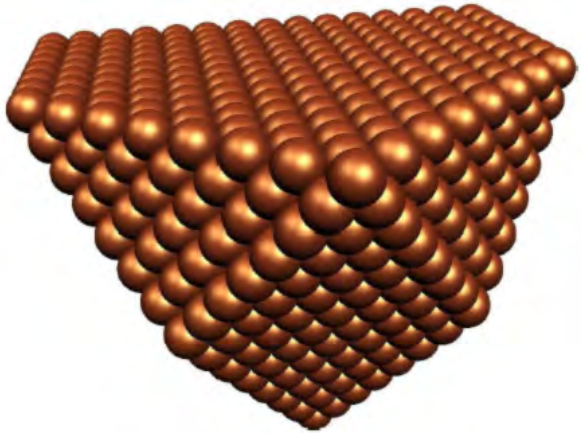

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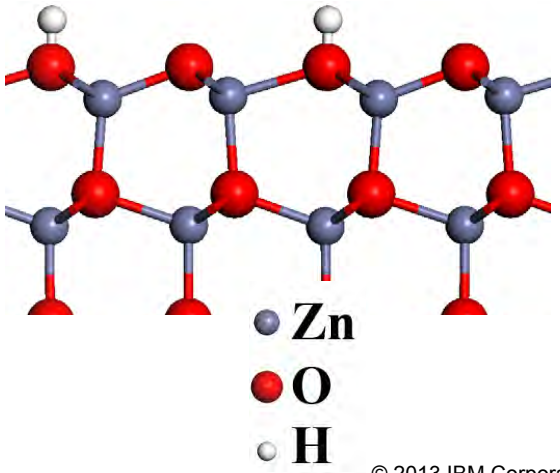
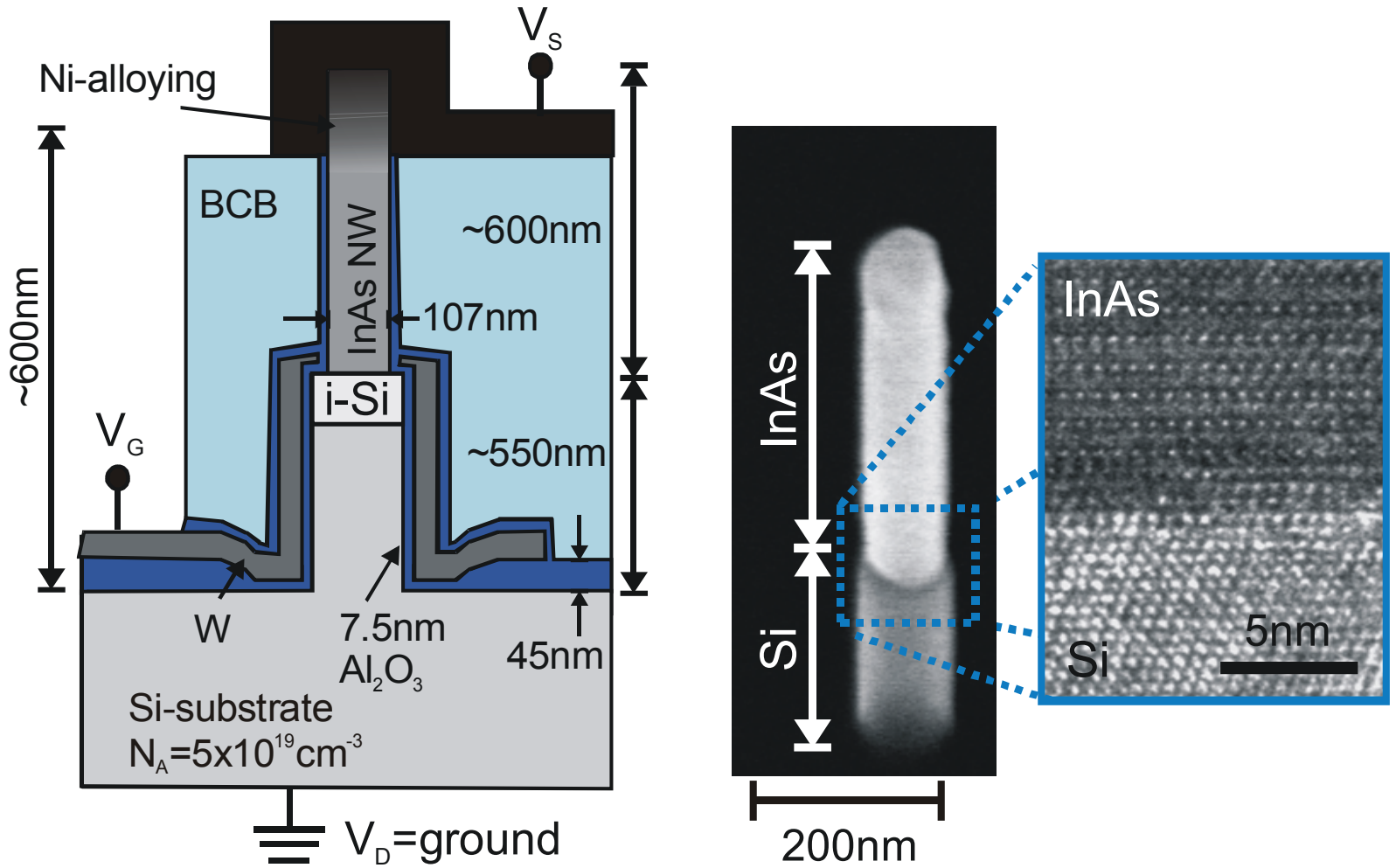


Silicon

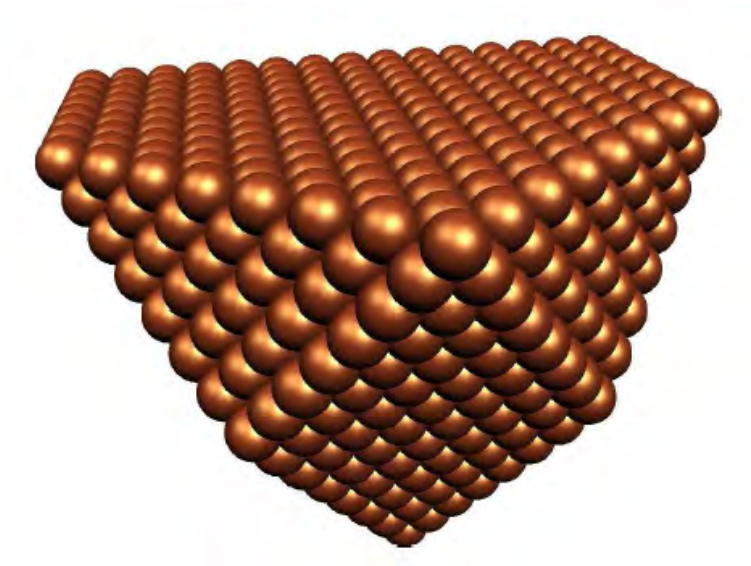
Nanowire Tunnel Diodes

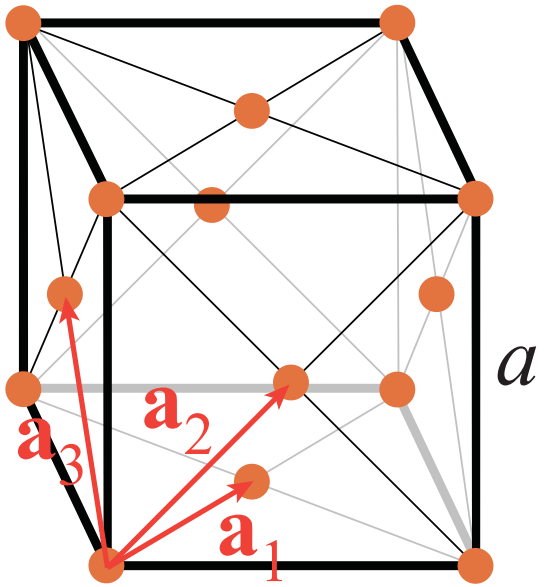


*K.E. Moselund, H. Schmid, C. Bessire, M.T. Bjork, H. Ghoneim, and H. Riel, IEEE Electron Device Letters **33**, 1453 (2012).*

Periodic systems

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





lattice vectors:

$$\mathbf{R} = N_1\mathbf{a}_1 + N_2\mathbf{a}_2 + N_2\mathbf{a}_2$$

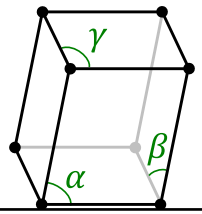
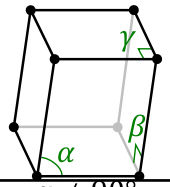
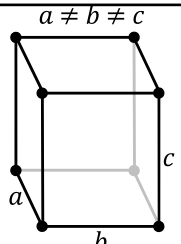
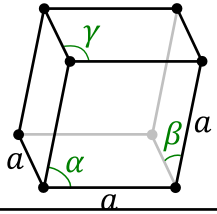
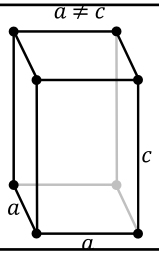
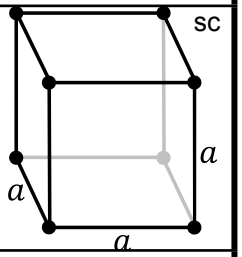
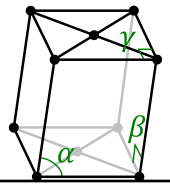
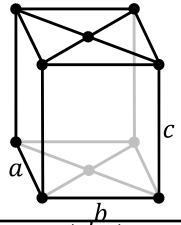
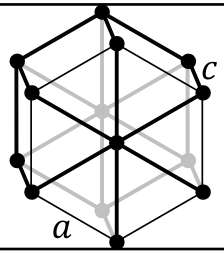
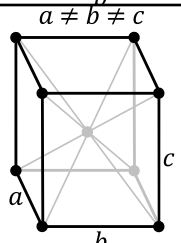
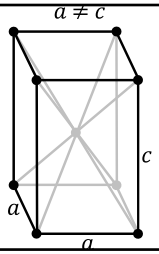
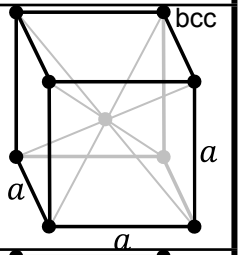
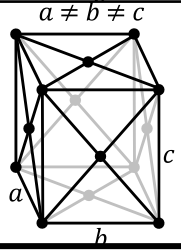
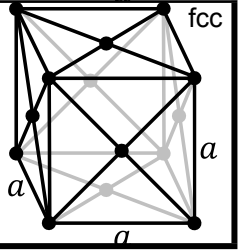
with

$$N_1, N_2, N_2 \in \mathbb{Z}$$

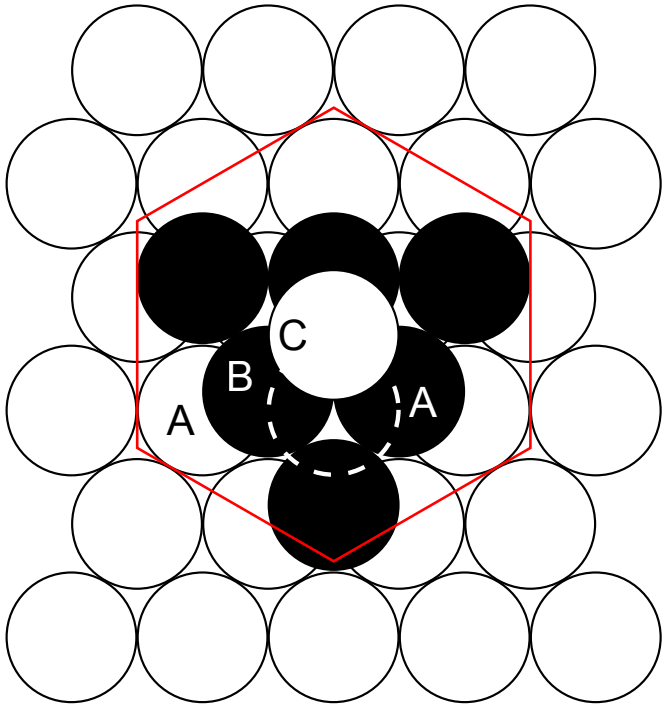
fcc unit cell with unit cell vectors:

$$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$$

Lattice systems (Bravais lattices)

	triclinic	monoclinic	orthorhombic	rhombohedral	tetragonal	hexagonal	cubic
Primitive	$\alpha, \beta, \gamma \neq 90°$ 	$\alpha \neq 90°$ $\beta, \gamma = 90°$ 	$a \neq b \neq c$ 	$\alpha=\beta=\gamma \neq 90°$ 	$a \neq c$ 		sc 
Base-centered		$\alpha \neq 90°$ $\beta, \gamma = 90°$ 	$a \neq b \neq c$ 				
Body-centered			$a \neq b \neq c$ 		$a \neq c$ 		bcc 
Face-centered			$a \neq b \neq c$ 				fcc 

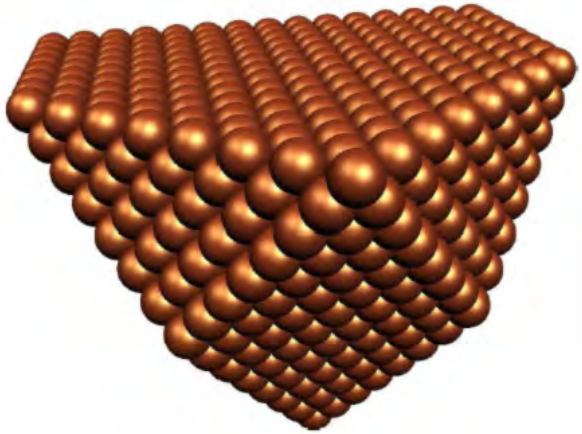
Close packing



hexangonal close packing ...ABABAB...

cubic close packing ...ABCABC... fcc lattice

Outline



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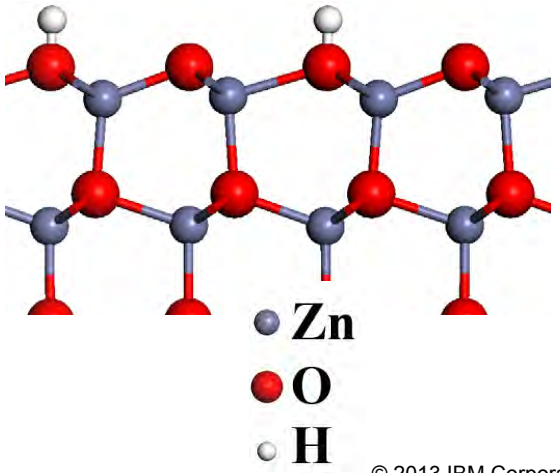
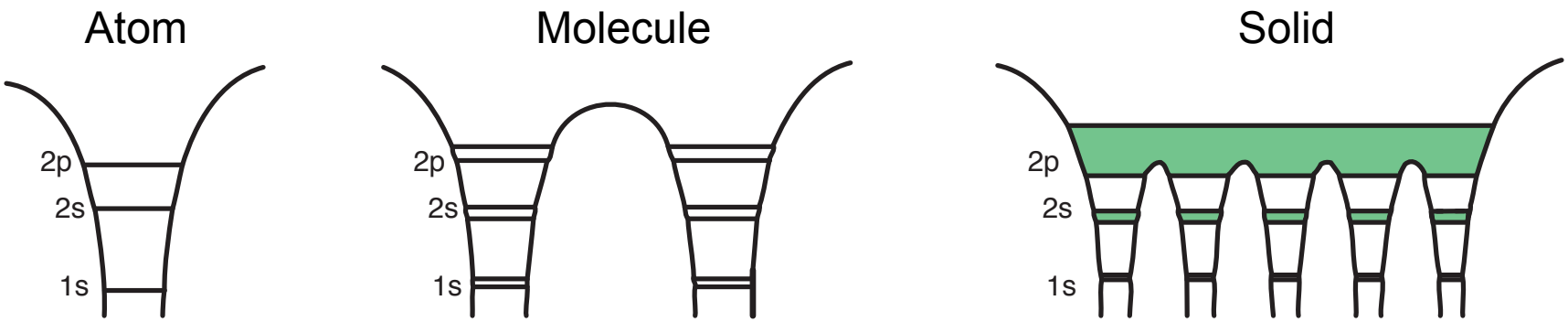
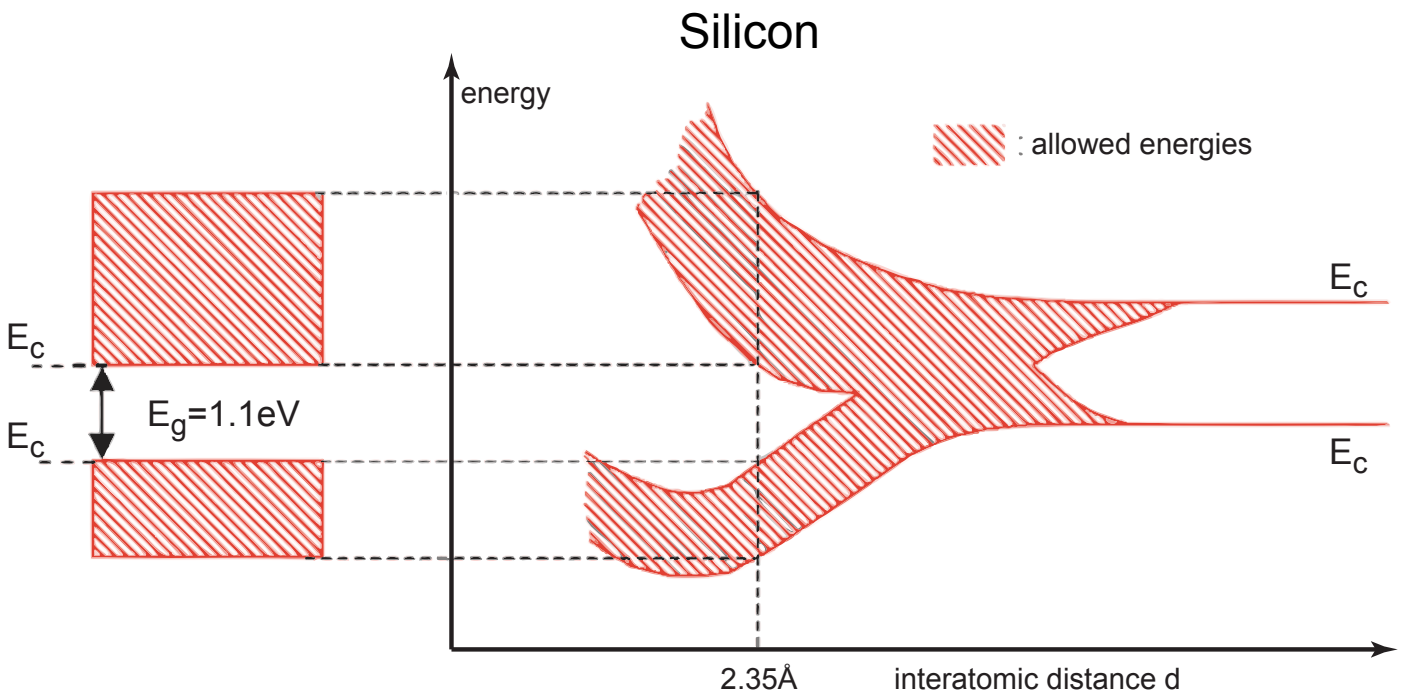
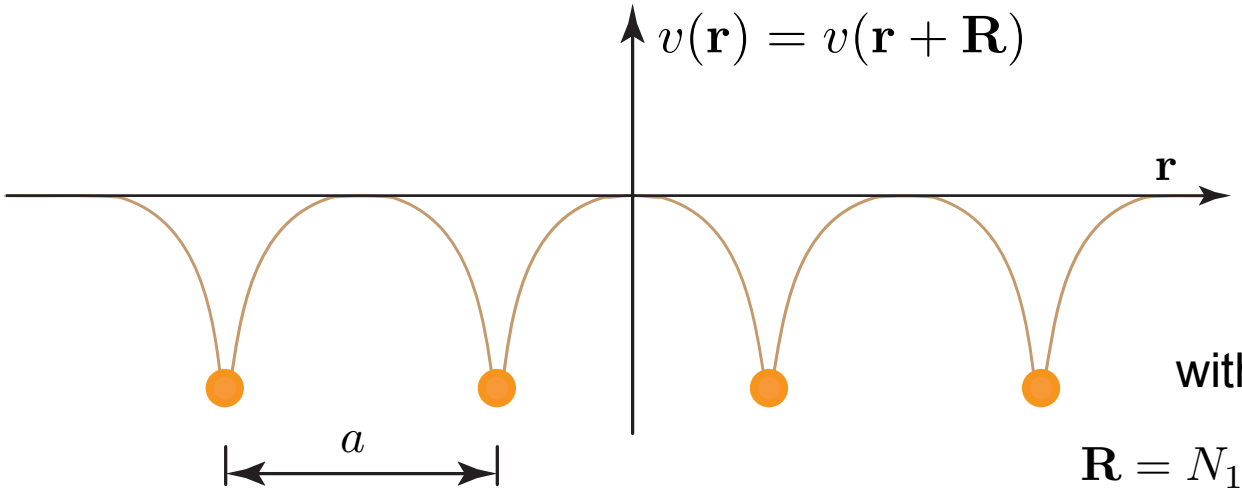


Electronic structure of solids





Periodic Potentials



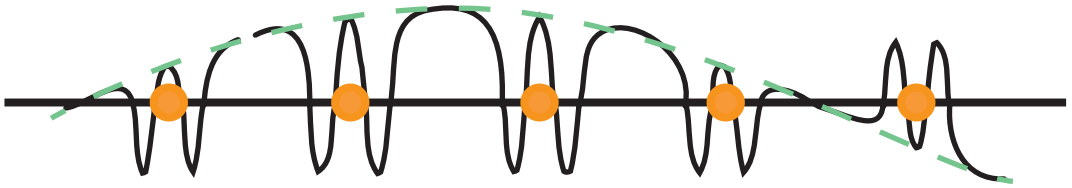
with lattice vectors:

$$\mathbf{R} = N_1\mathbf{a}_1 + N_2\mathbf{a}_2 + N_2\mathbf{a}_2$$

Bloch theorem for the wavefunction:

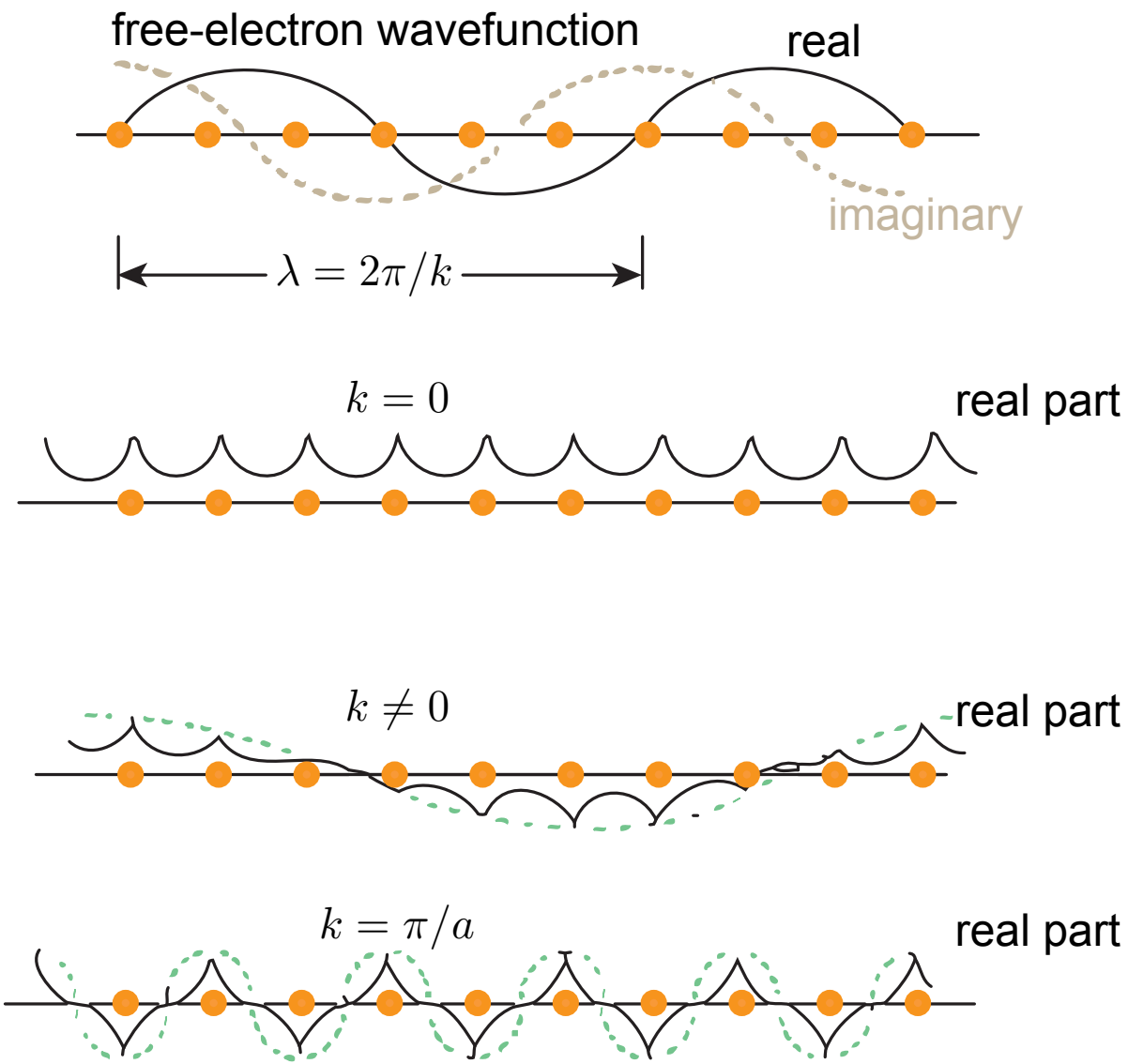
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R})$$

having the same periodicity as the potential



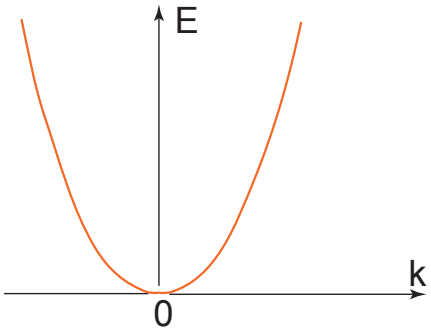
Felix Bloch (1928)

Meaning of different k

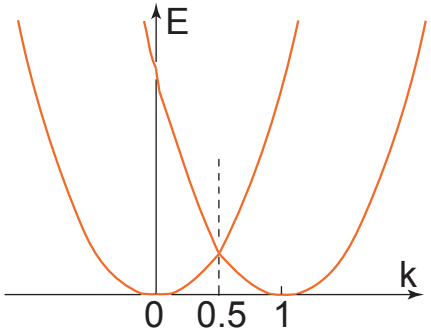


Nearly free-electron model

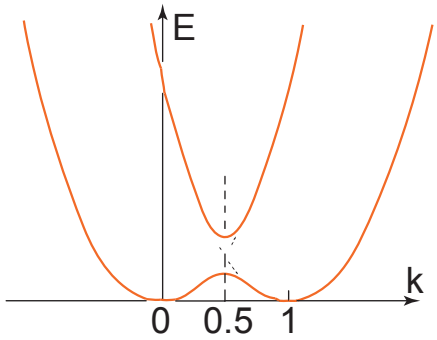
1 dimensional potential

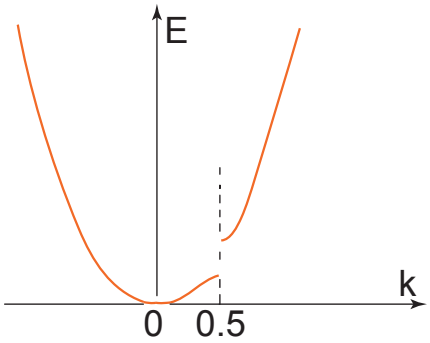


periodic potential

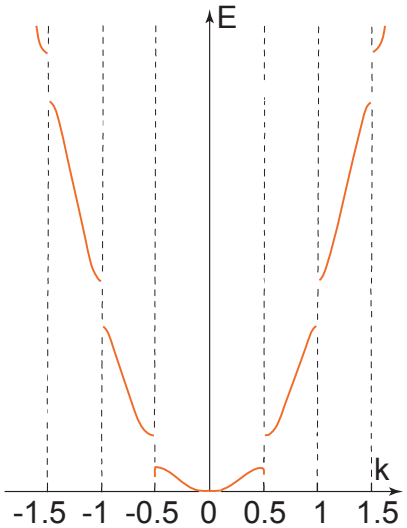


weak interaction

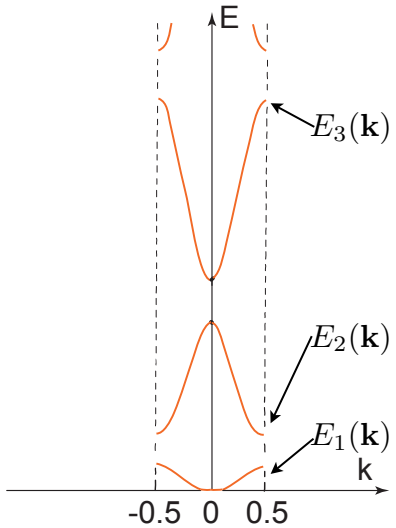




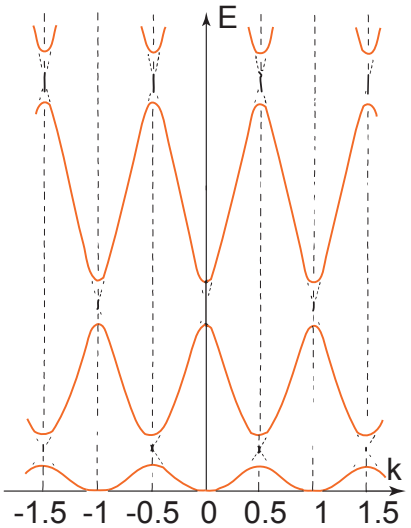
extended zone scheme



reduced zone scheme



repeated zone scheme



two quantum numbers

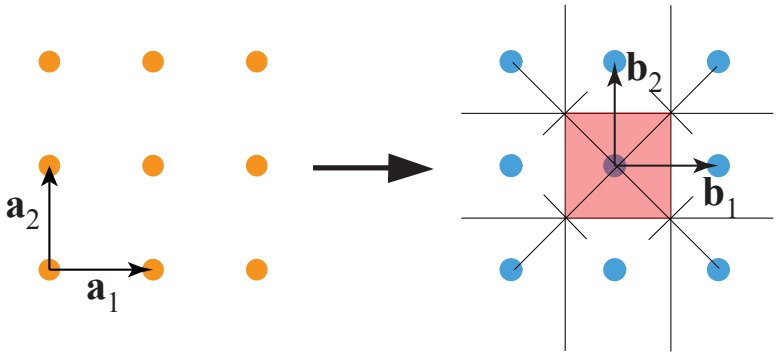
$\mathbf{k}, n$

eigenvalues

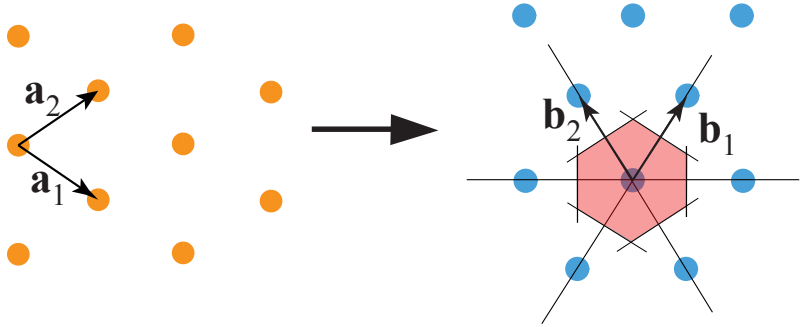
$E_n(\mathbf{k})$

Brillouin zone for reciprocal space

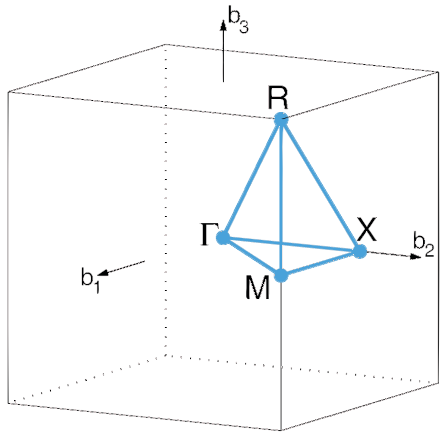
square lattice



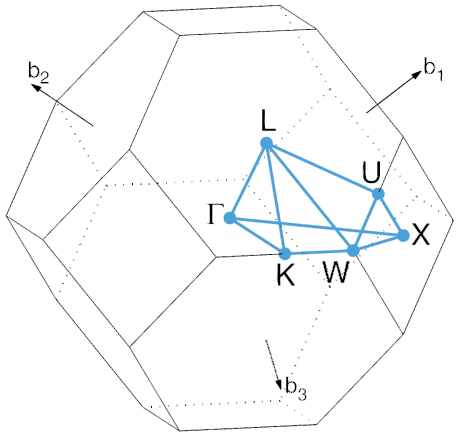
hexagonal lattice



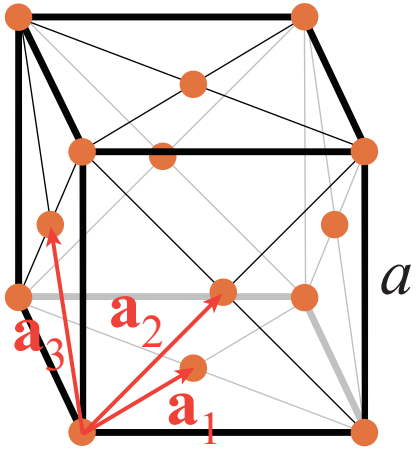
cubic

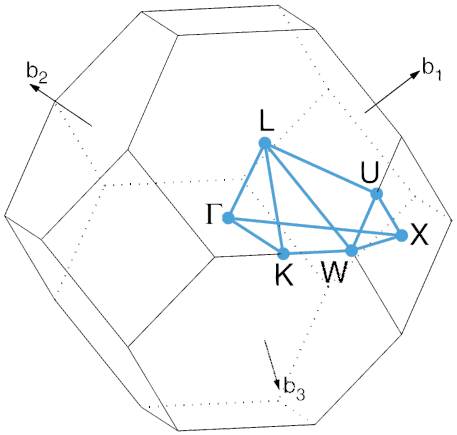


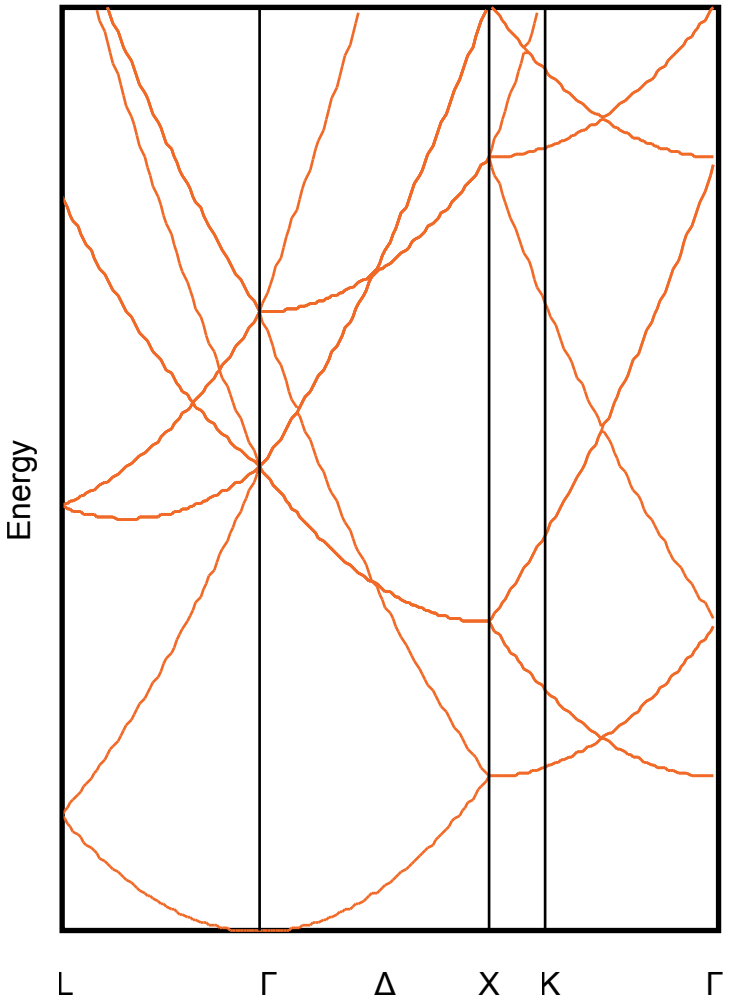
FCC



Nearly free-electron model for FCC lattice







fcc band structure

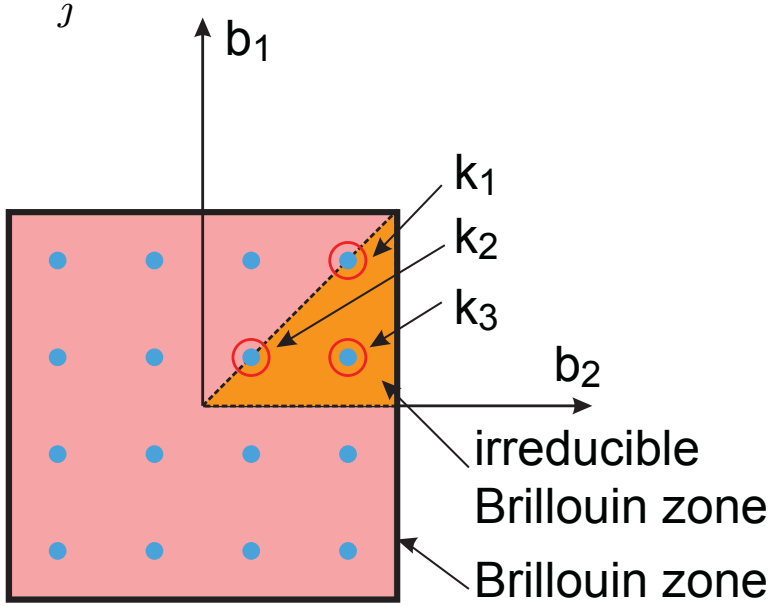
In calculations: finite k-point mesh

Example: charge density

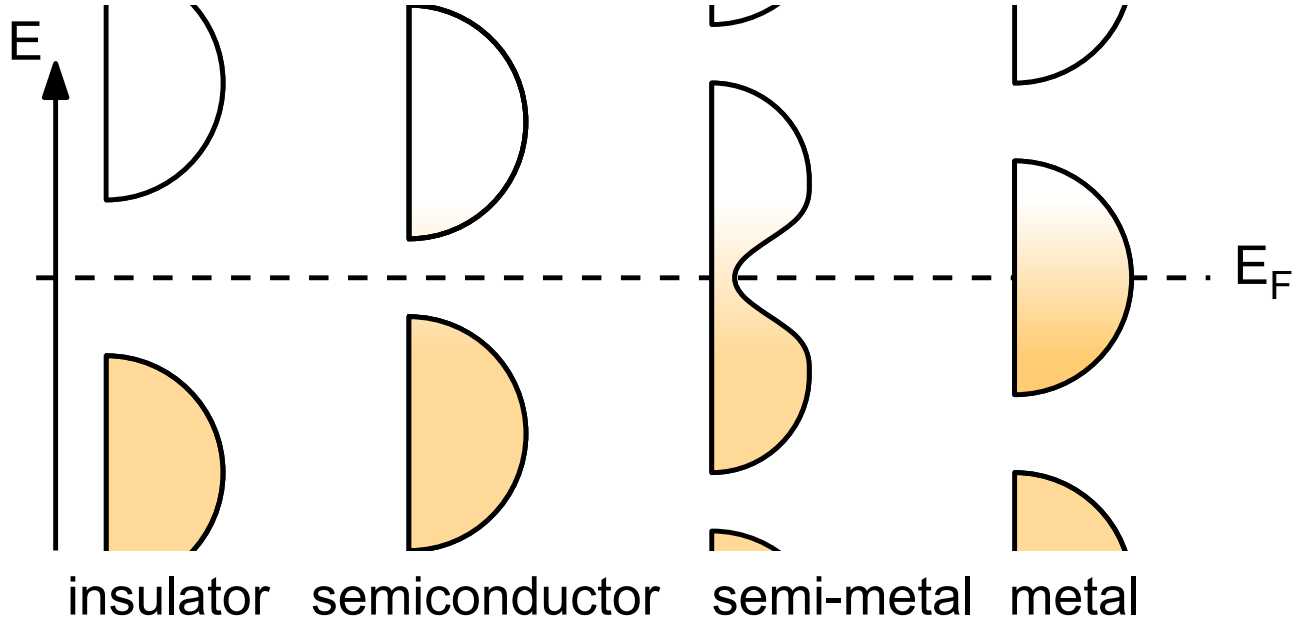
$$n(r) = \frac{1}{\Omega_{\mathbf{BZ}}} \sum_{n}^{\mathrm{occ}} \int_{\Omega_{\mathbf{BZ}}} |\psi_n(\mathbf{k}, \mathbf{r})|^2 \, d^3\mathbf{k} \longrightarrow n(r) = \sum_{n}^{\mathrm{occ}} \sum_{j} w_j \, |\psi_n(\mathbf{k_j}, \mathbf{r})|^2$$

$$\frac{1}{\Omega_{\mathbf{BZ}}} \int_{\Omega_{\mathbf{BZ}}} d^3\mathbf{k} \longrightarrow \sum_{n}^{\mathrm{occ}} \sum_{j} w_j$$

Use a uniform finite k-point mesh to approximate the integrals



Insulators, semiconductors, and metals



diamond, NaCl Si, Ge, GaAs graphite, Sn Cu, Al, Fe

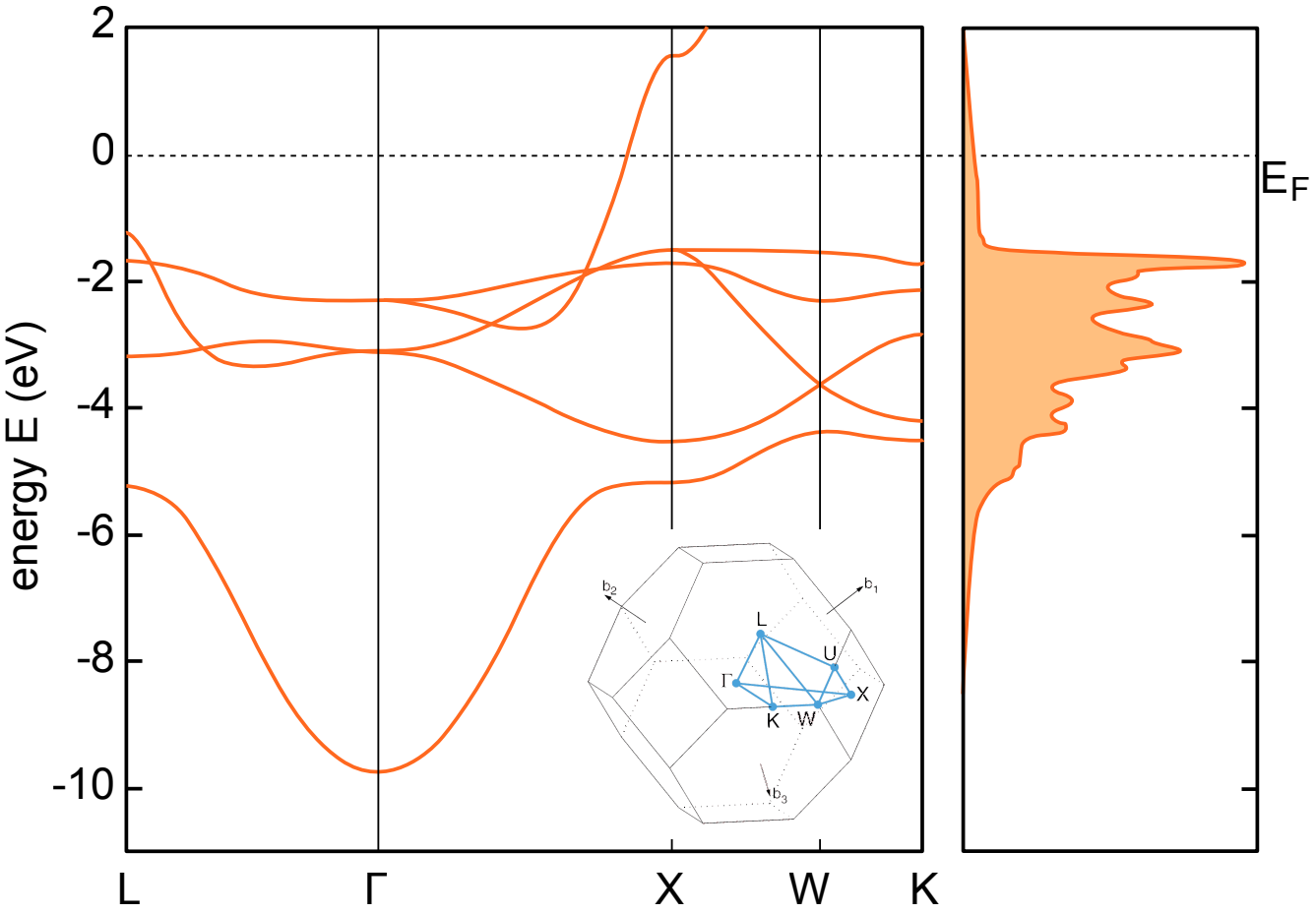
The Fermi energy E_F separates the highest occupied states from lowest unoccupied

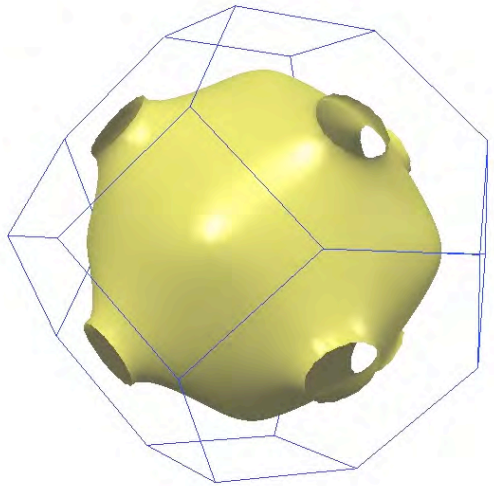
Copper

band structure

density of states

Fermi surface:

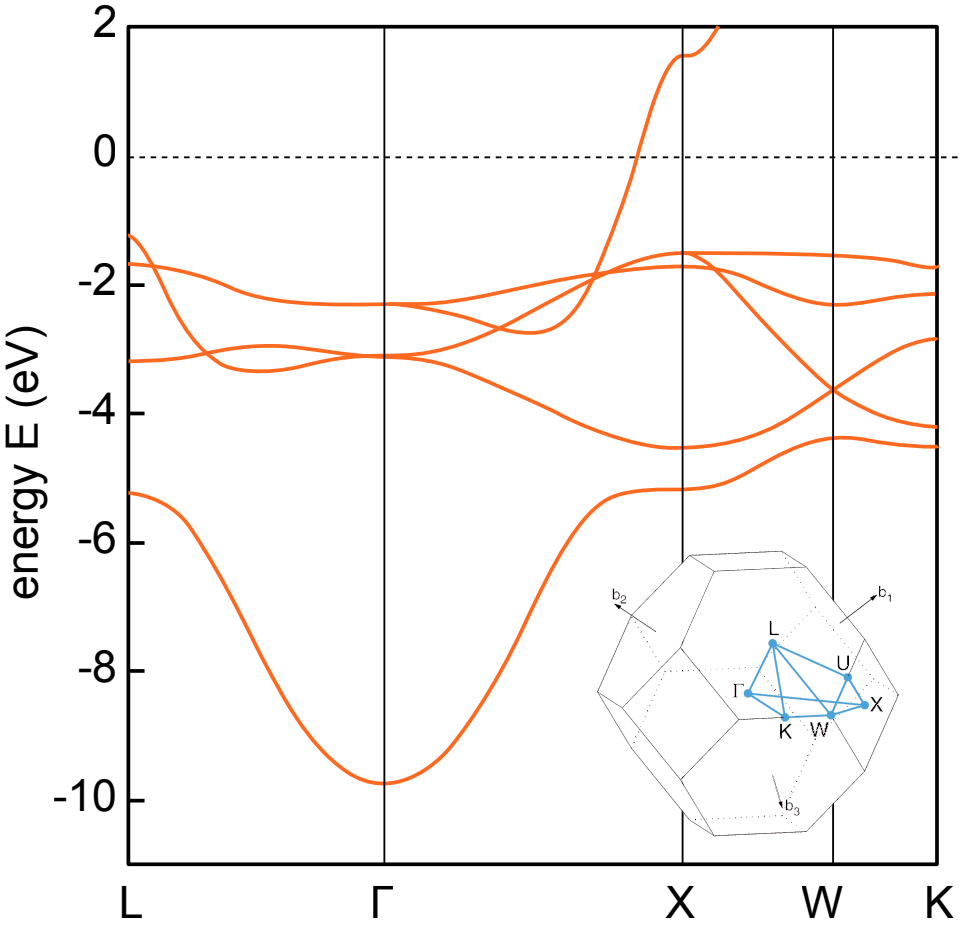




find $\mathbf{k}$ with:

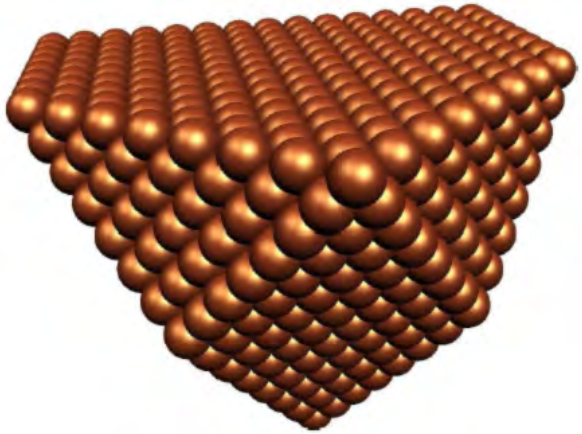
$$E_n(\mathbf{k}) = E_F$$

How to treat metals



- Fermi distribution function enters Brillouin zone integral
- Dense k-point meshes are mandatory
- *Smearing* of the Fermi function reduces the k-point mesh
  - artificially increased electron temperature ~ 0.2 eV
  - extrapolation of the total energy to zero electron temperature
- Tetrahedron method for density of states
  - Fermi surface is approximated by a polyhedron consisting of small tetrahedra in

Outline



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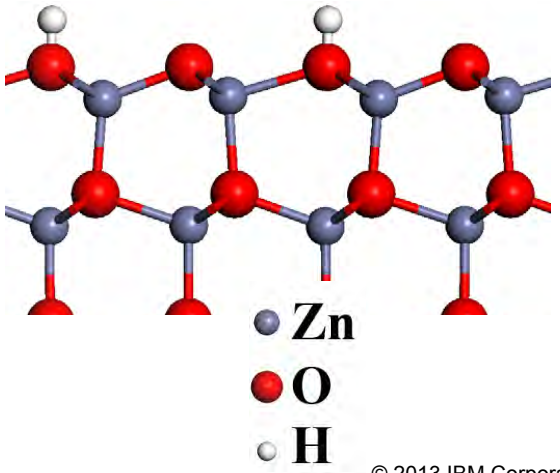
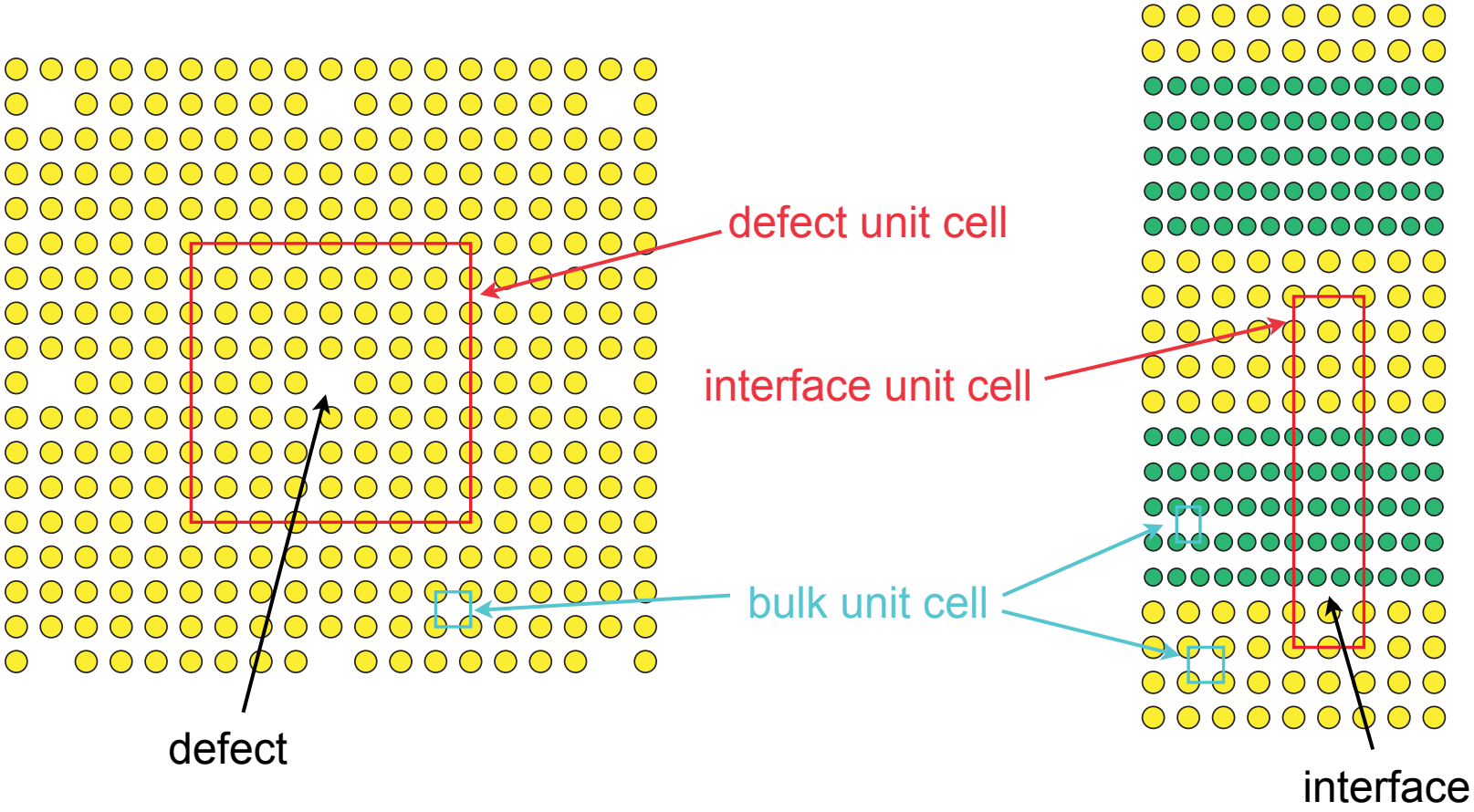
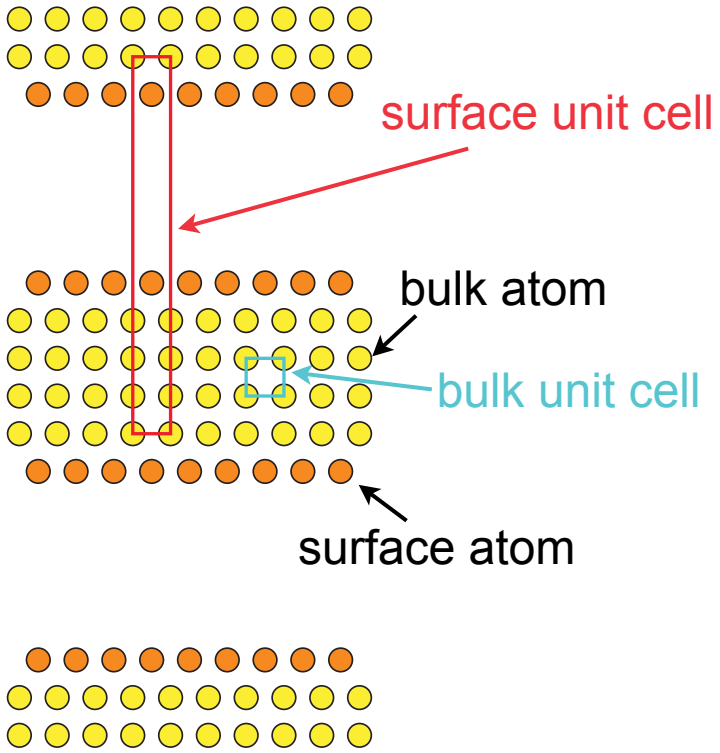


Supercells for defects, interfaces and surfaces

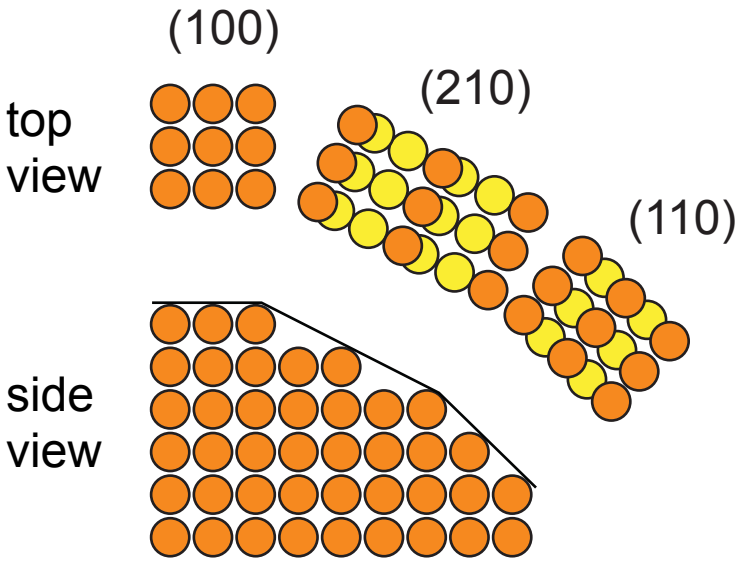


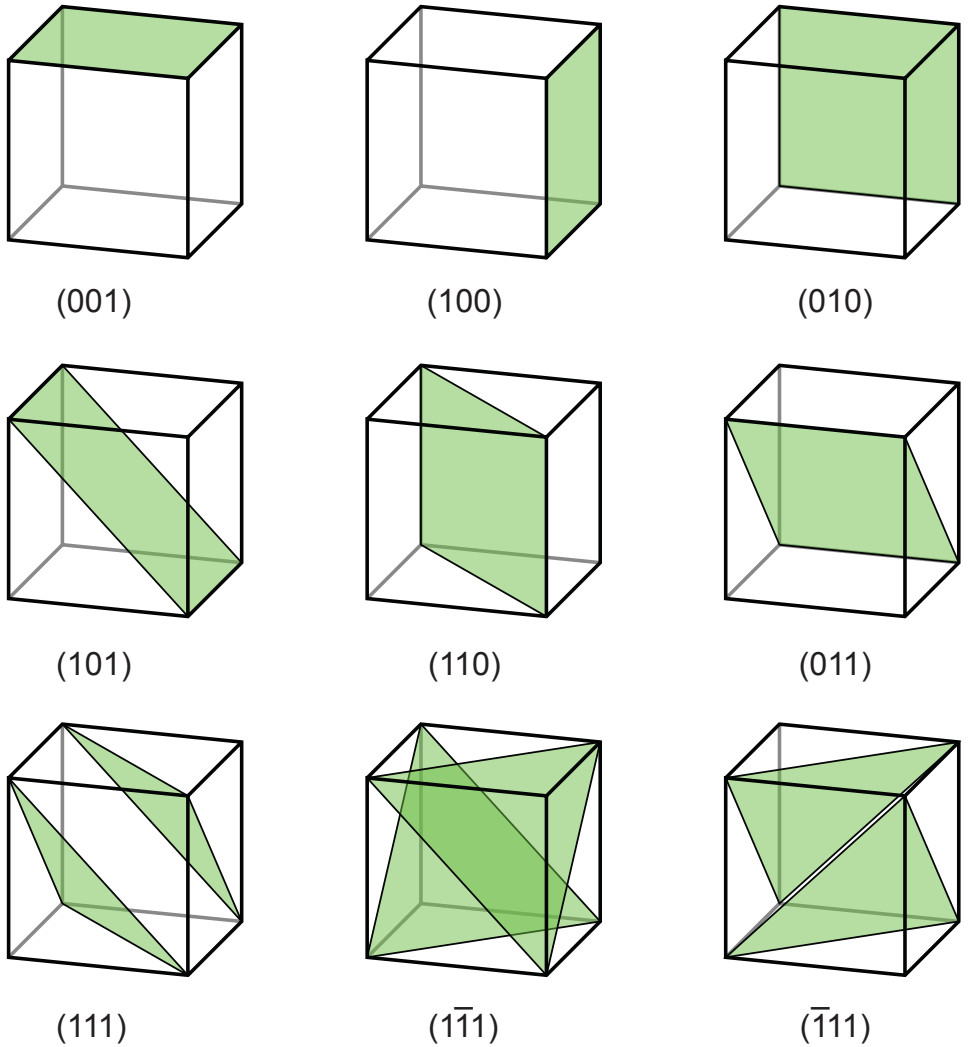
Supercells for defects, interfaces and surfaces



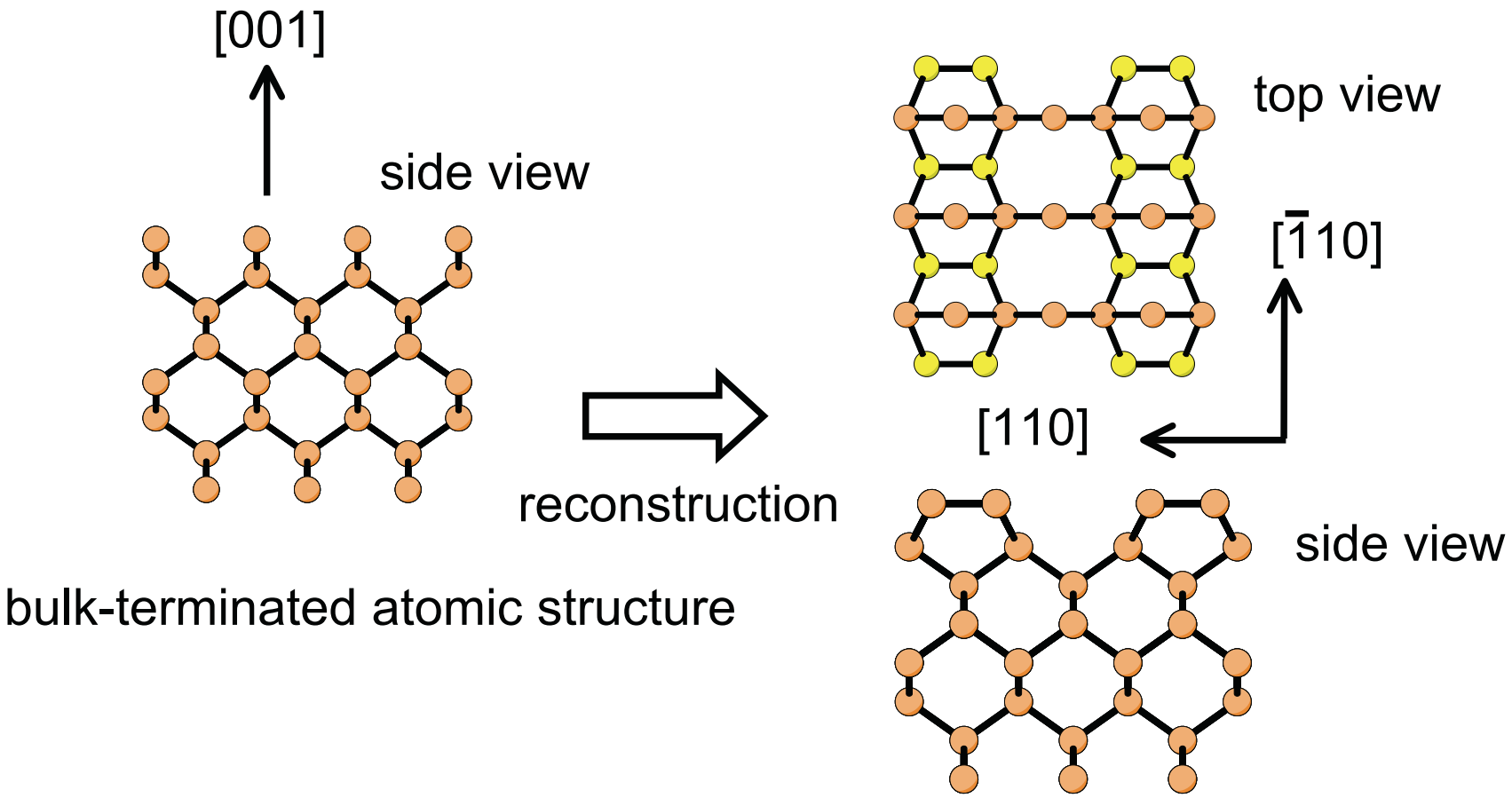
- Approach accounts for the lateral periodicity
- Sufficiently broad vacuum region to decouple the slabs
- Sufficient slab thickness to mimic semi-infinite crystal
- Semiconductors: saturate dangling bonds on the back surface
- Inequivalent surfaces: use dipole correction
- Alternative: cluster model

Miller indices for surfaces



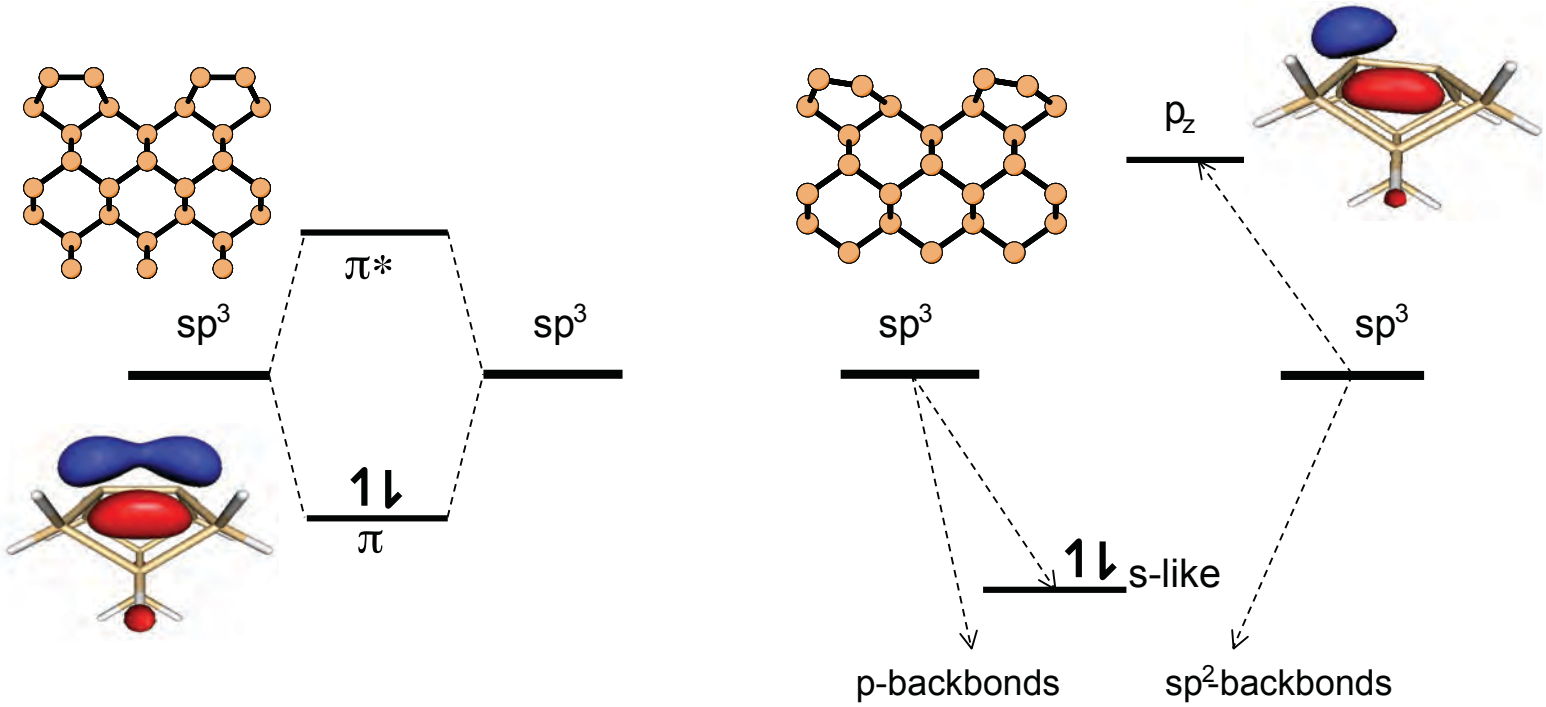


Example: silicon (001) surface

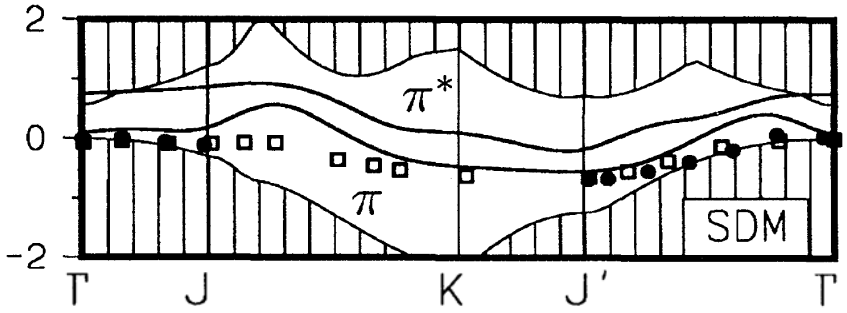


bulk-terminated atomic structure

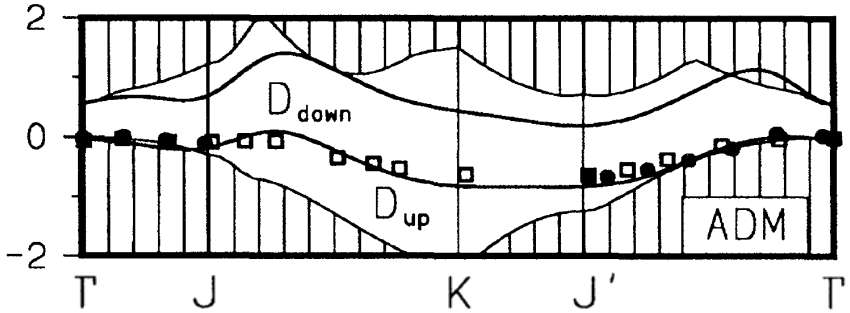
Example: silicon (001) surface



π-bond



re-hybridisation and charge transfer



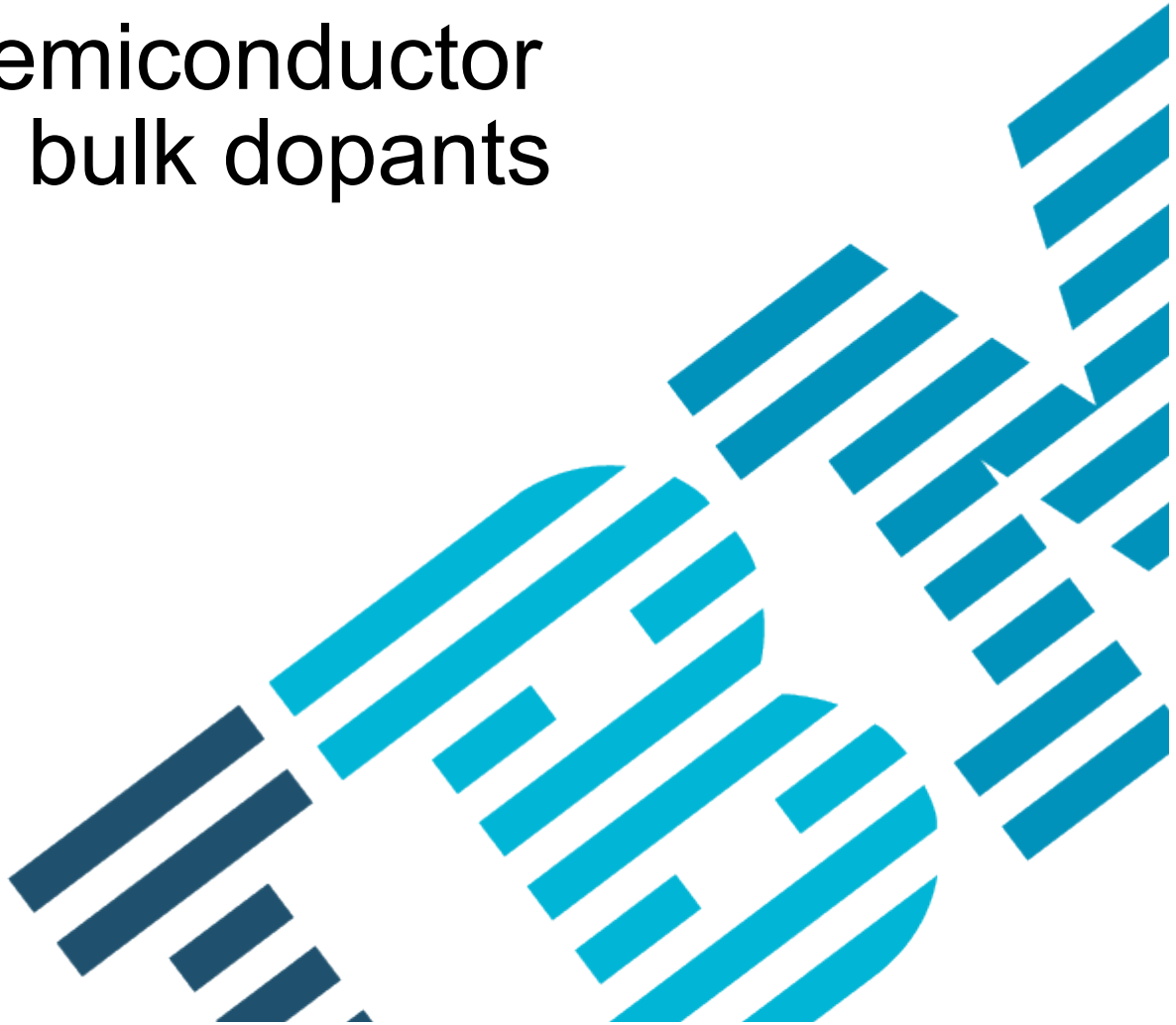
P. Krüger and J. Pollmann, Phys. Rev. Lett. ***74****, 1155 (1995)*

Nikolaj Moll, Yong Xu[1], Oliver T. Hofmann[1], Patrick Rinke[1]

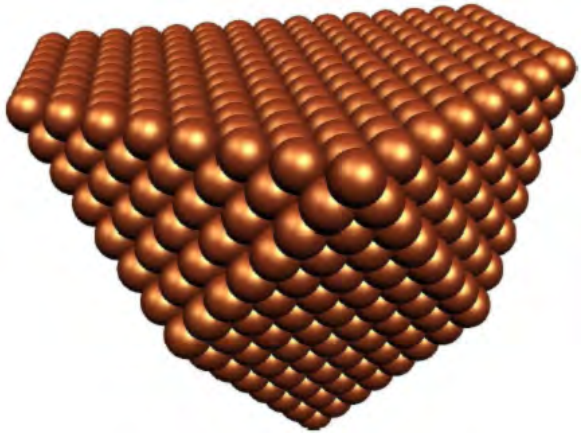
Stabilization of semiconductor surfaces through bulk dopants

New J. Phys. ***15*** *(2013) 083009.*

[1]Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany



Outline



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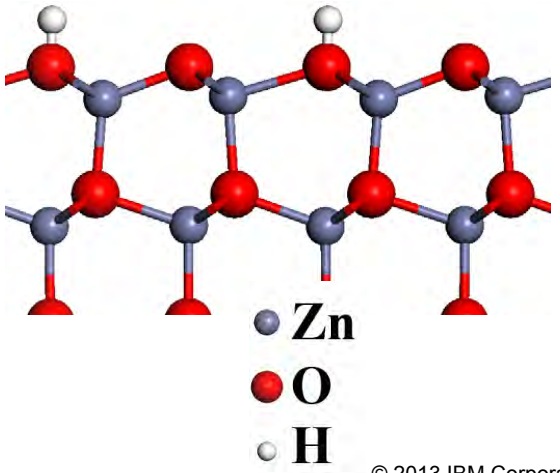


Ab-initio thermodynamics

surface free energy:

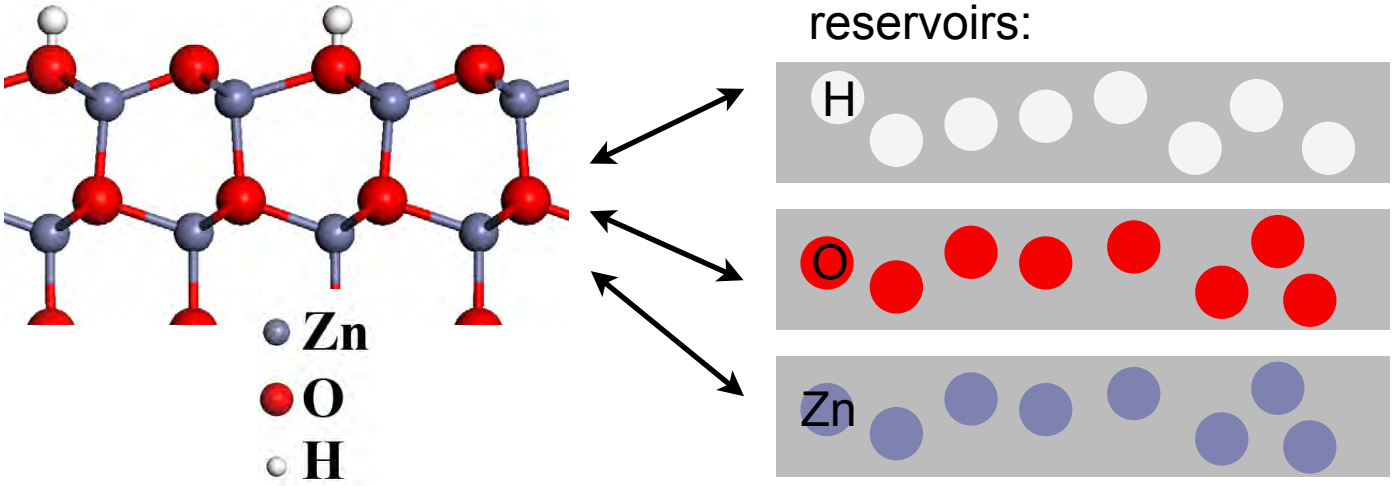
number of species i

$$\gamma(T,p) = \frac{1}{A}\left(G(T,p,\{N_i\}) - \sum_i N_i \mu_i(T,p)\right)$$

chemical potential of species i

Gibb's free energy:

$$G(T,V,\{N_i\}) = E^{\mathrm{DFT}}(T=0,V,\{N_i\}) + F^{\mathrm{vib}}(T,V,\{N_i\}) + pV$$



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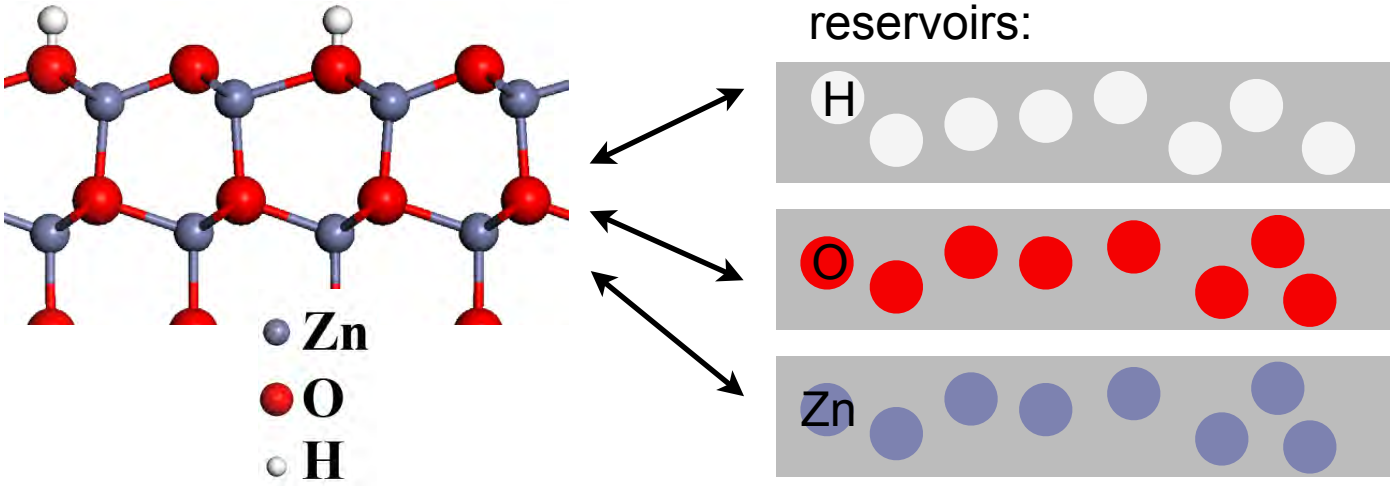

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T/p dependence introduced through chemical potentials:

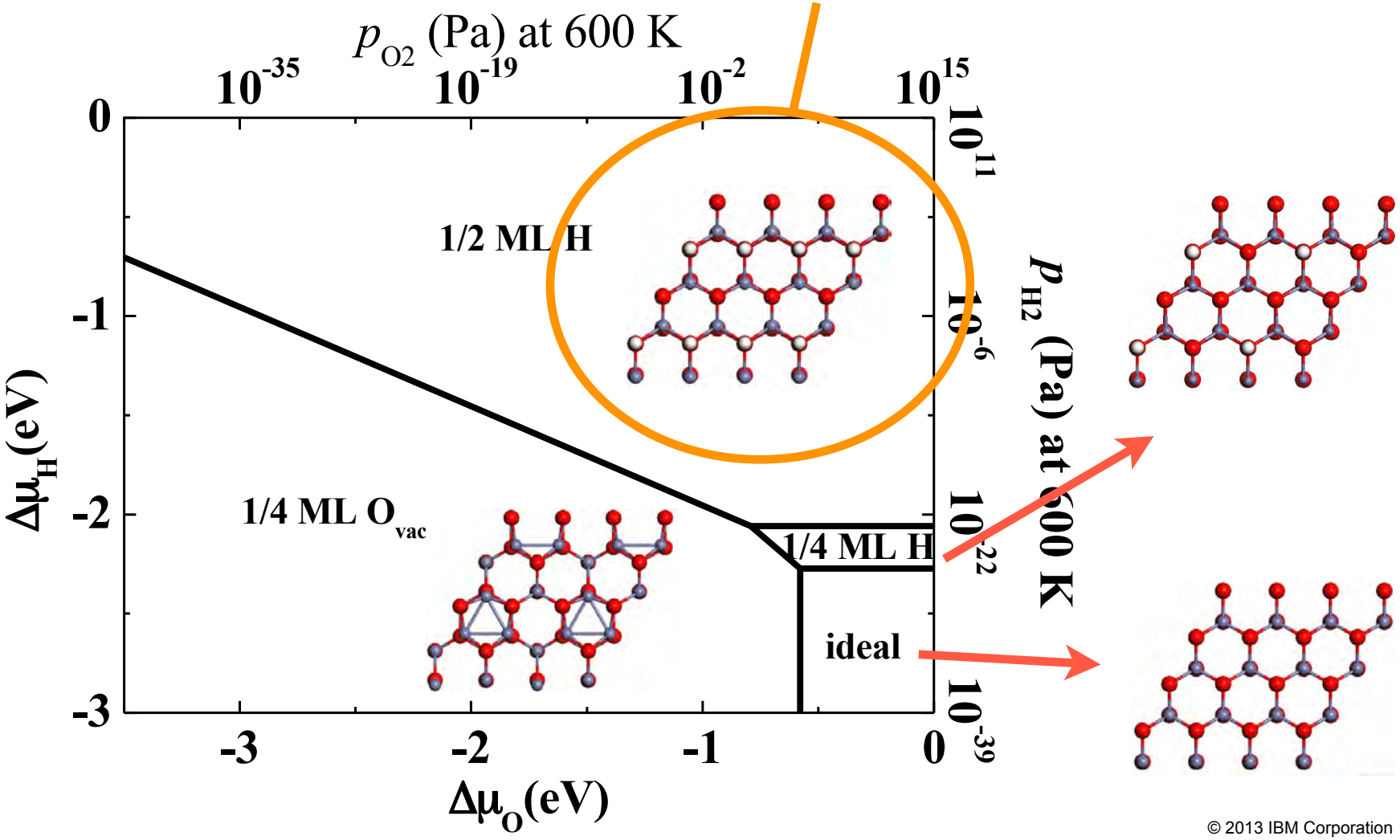
$$\mu_i(T,p_i) = E_i + \mu_i(T,p^0) + k_B T \ln\left(\frac{p_i}{p^0}\right)$$

taken from thermochemical reference data

O-terminated ZnO(000-1) surface

surface in equilibrium with O_2 and H_2, but no gas phase reactions

most stable under relevant conditions

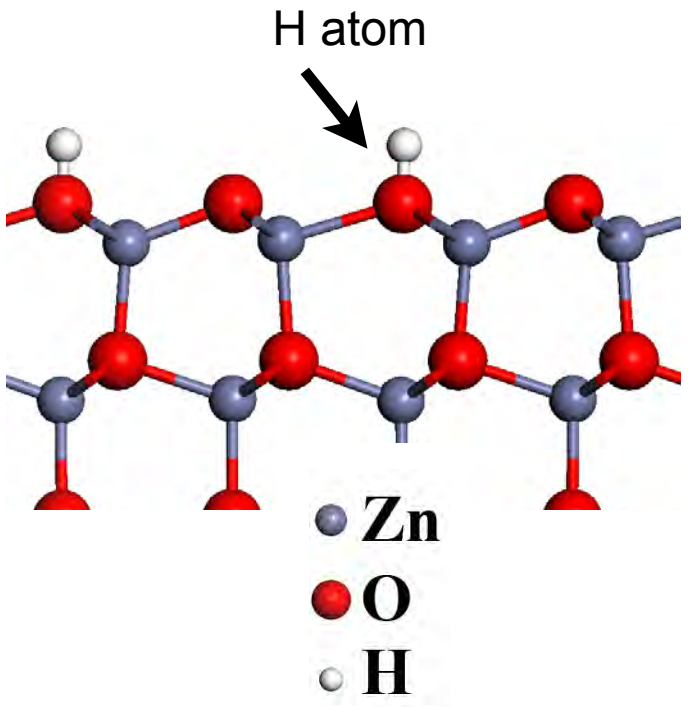


What about other factors?

conduction band

Fermi level

valence band



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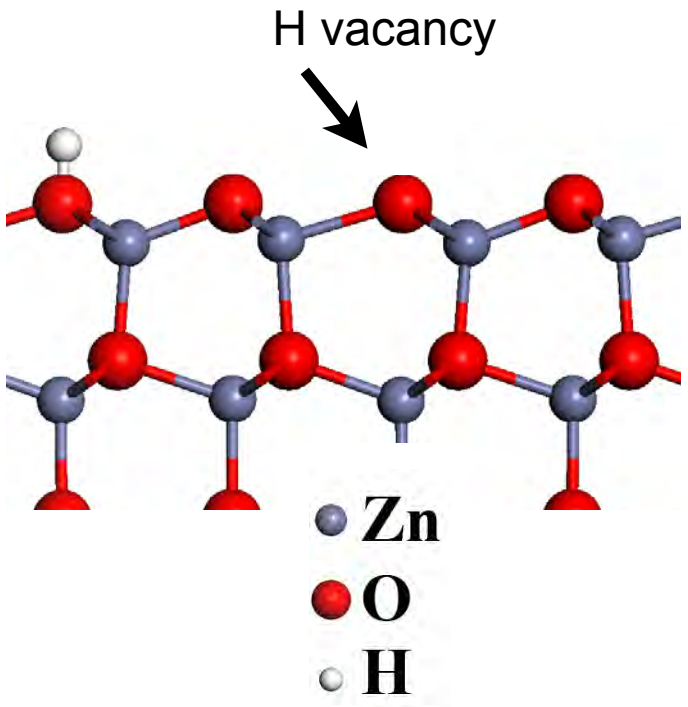

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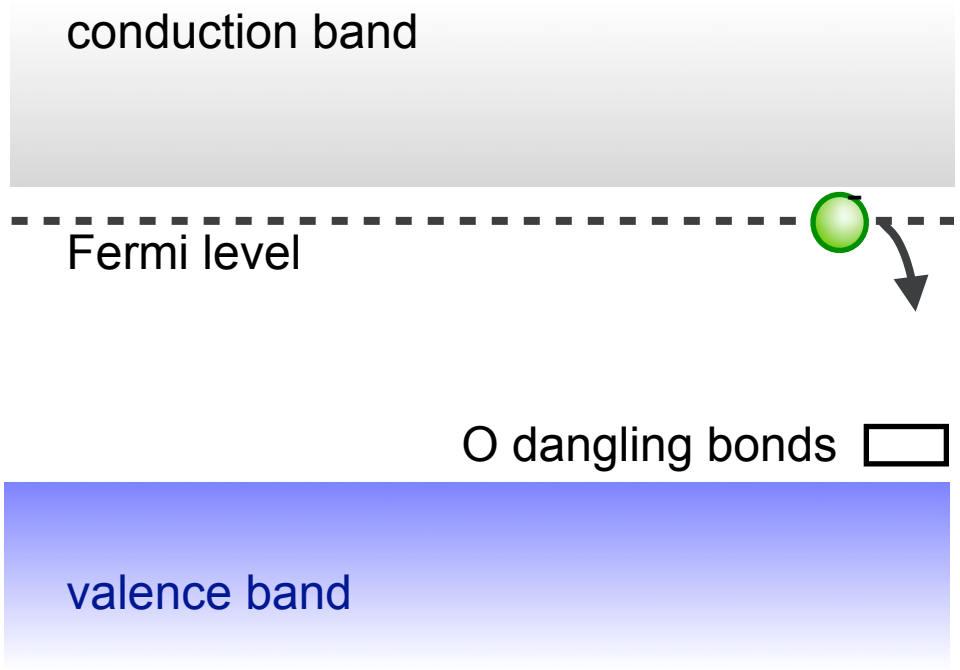
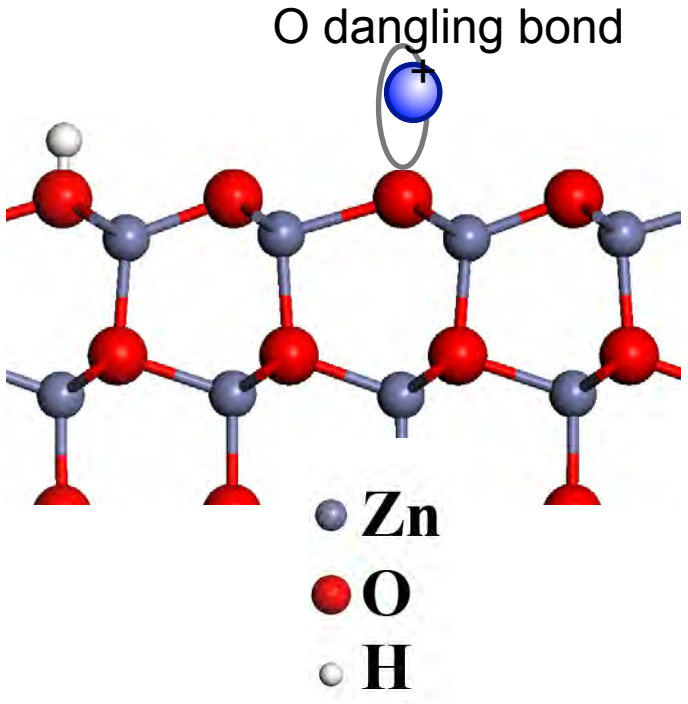




- Can doping stabilize otherwise unstable surfaces?
- And what about band bending?

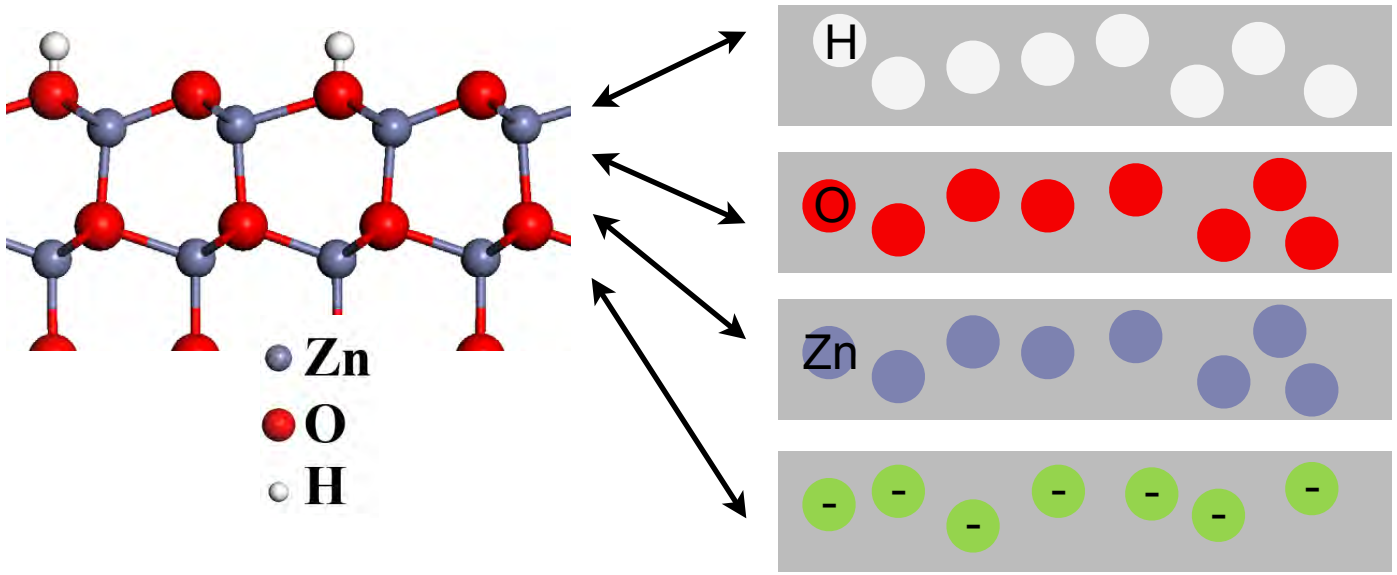
Ab initio thermodynamics - adding electrons

surface free energy:

chemical potential of species i

$$\gamma(T,p) = \frac{1}{A}\left(G(T,p,\{N_i\}) - \sum_i N_i\mu_i(T,p) + q\mu_e\right)$$

chemical potential of electrons



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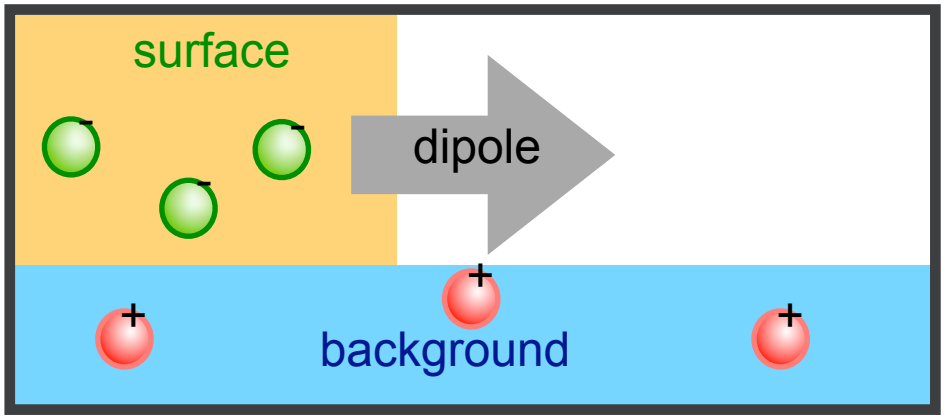
Adding electrons to supercells:

- requires compensating charge background



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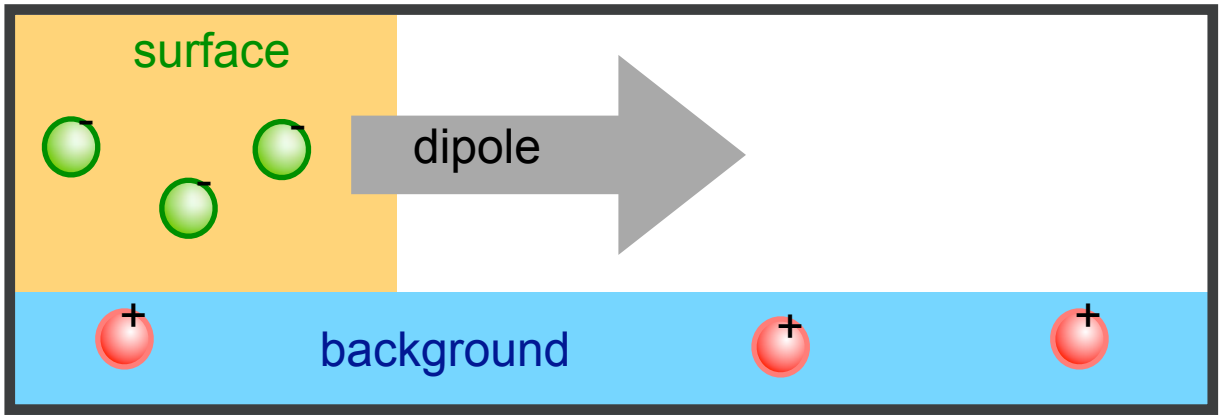

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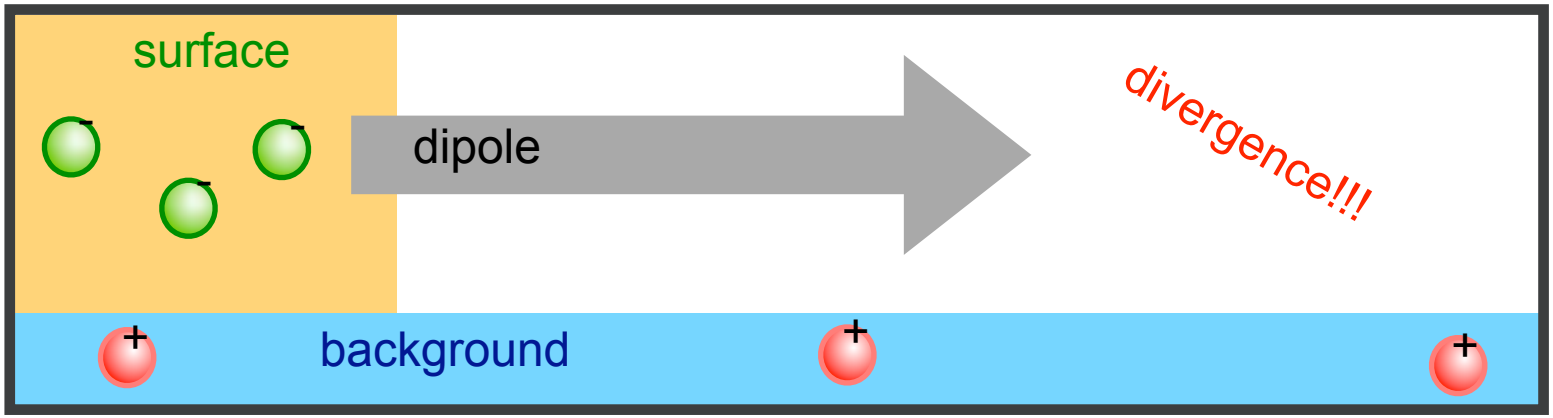

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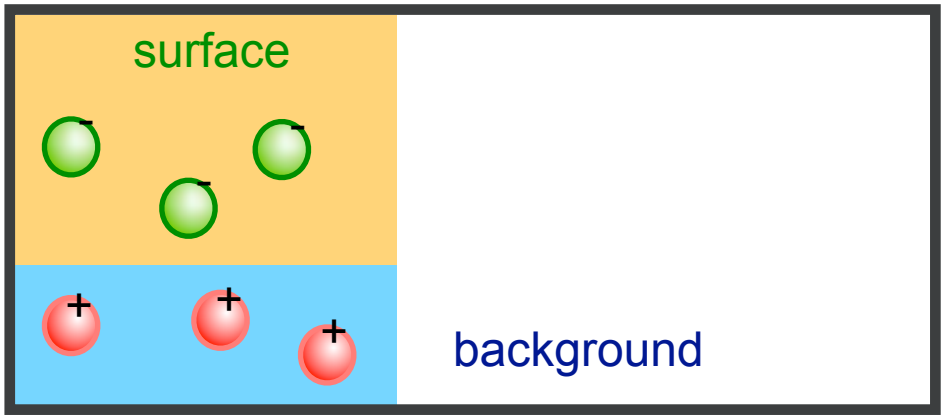
chemical potential of electrons

Adding electrons to supercells:

we confine charge background to slab



supercell

In our all-electron code:

we change nuclear charge:

$Z \longrightarrow Z+\delta \quad (\delta \sim 10^{-2})$

Ab initio thermodynamics - adding electrons

surface free energy:

chemical potential of electrons

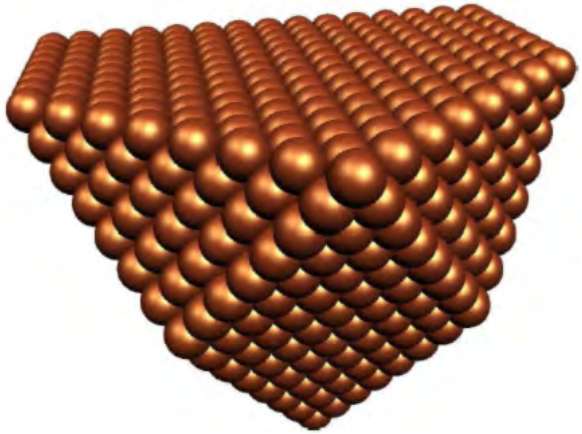
$$\gamma(\Delta\mu_{\mathrm{H}}, \Delta\mu_{\mathrm{e}}) = E_q^{\mathrm{slab}} - E_q^{\mathrm{bulk}} - N_{\mathrm{H}}\Delta\mu_{\mathrm{H}} + q\Delta\mu_{\mathrm{e}} + q(\epsilon_q^{\mathrm{VBM}'} - \mu_{\mathrm{e},q}^{\mathrm{bulk}})$$

chemical potential of hydrogen

correction term
(for filling of conduction band)

N. Moll, Y. Xu, O. T. Hofmann, P. Rinke, New J. Phys. ***15*** *(2013) 083009.*

Outline



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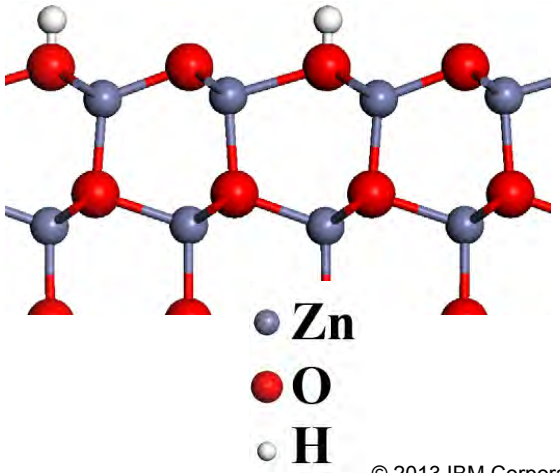
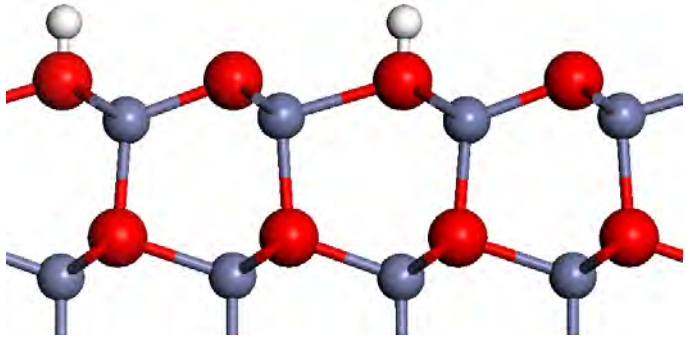


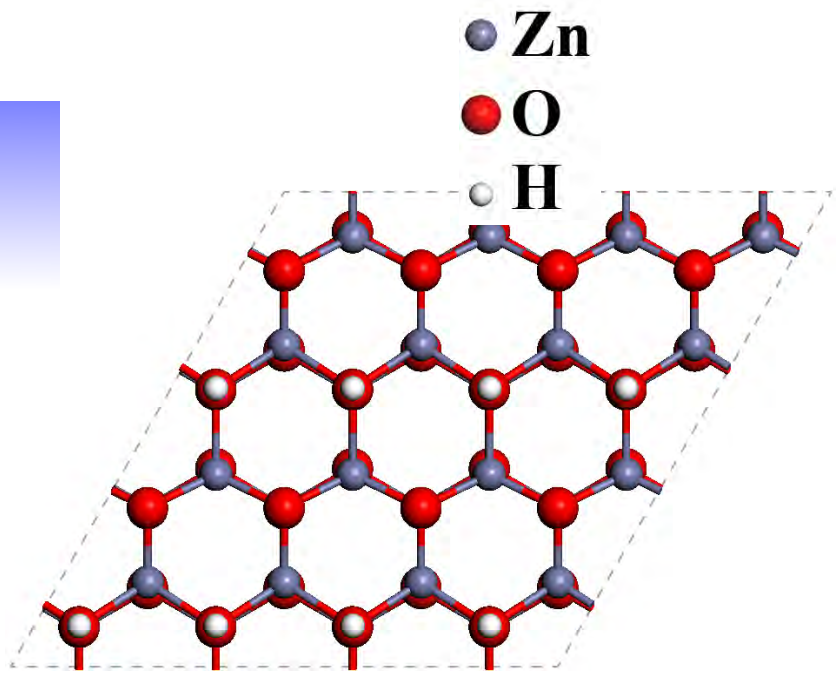
Pristine ZnO-O 2x1-H surface

conduction band

Fermi level

valence band





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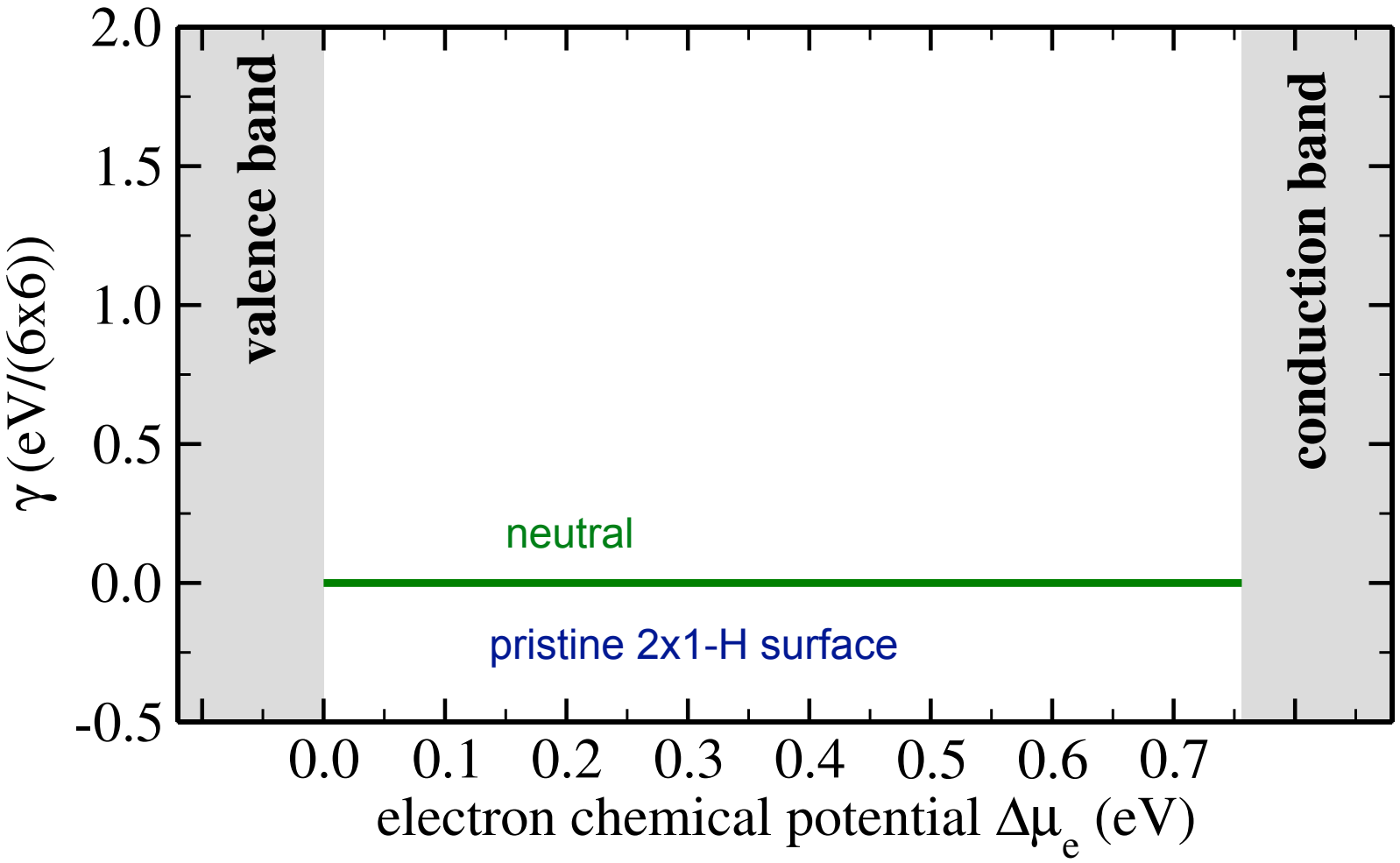
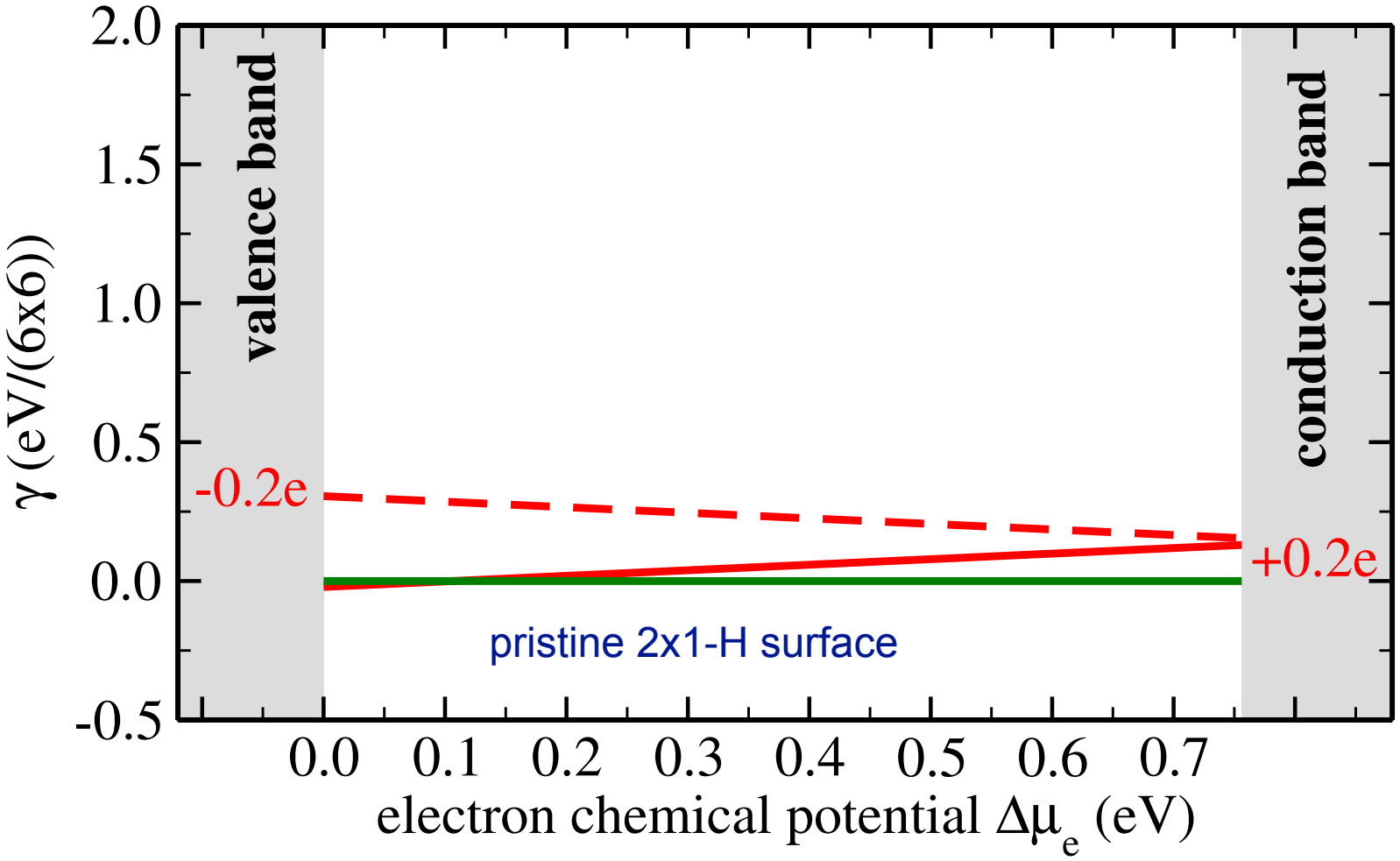


Pristine ZnO-O 2x1-H surface

- extra charge increases surface energy



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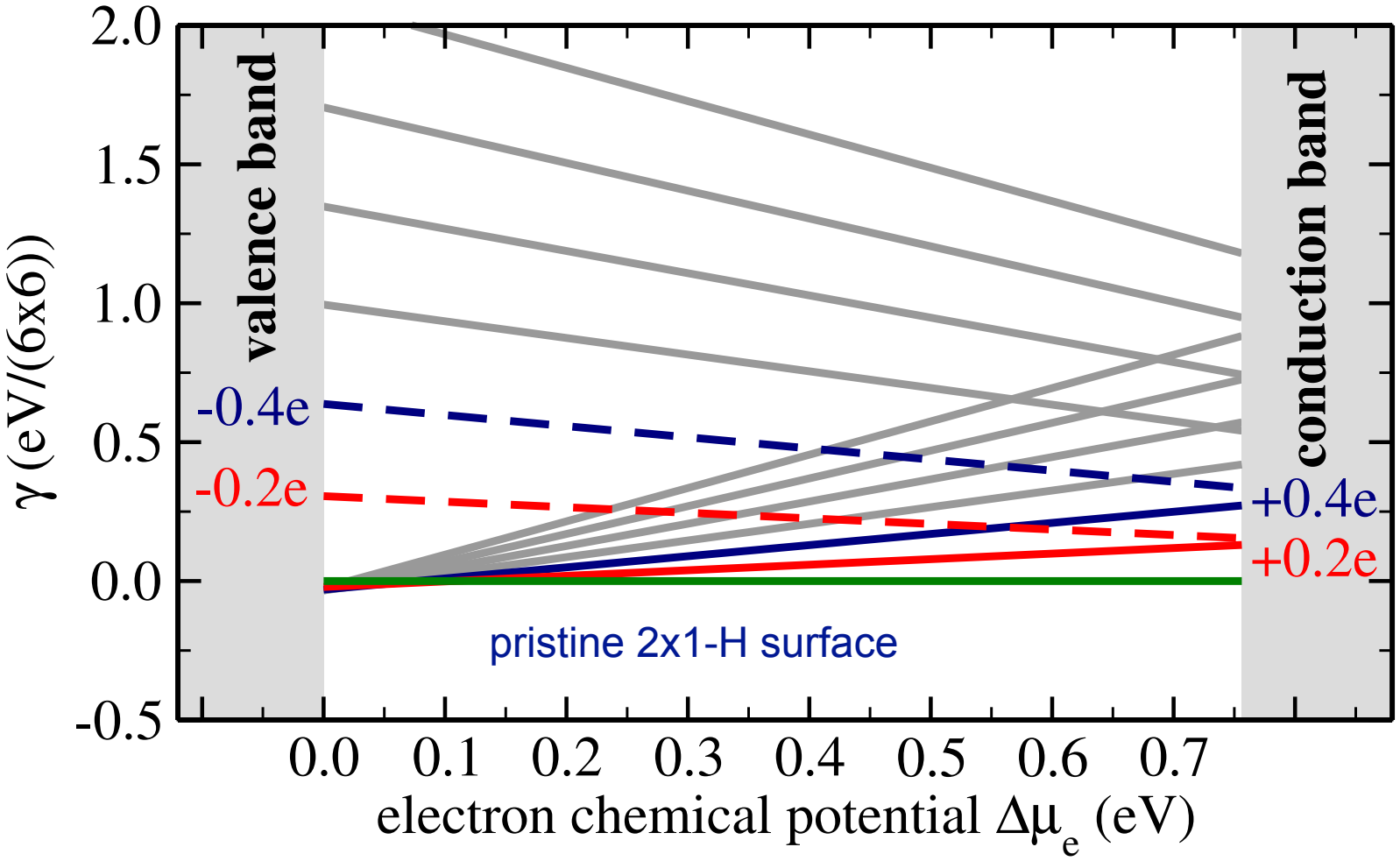
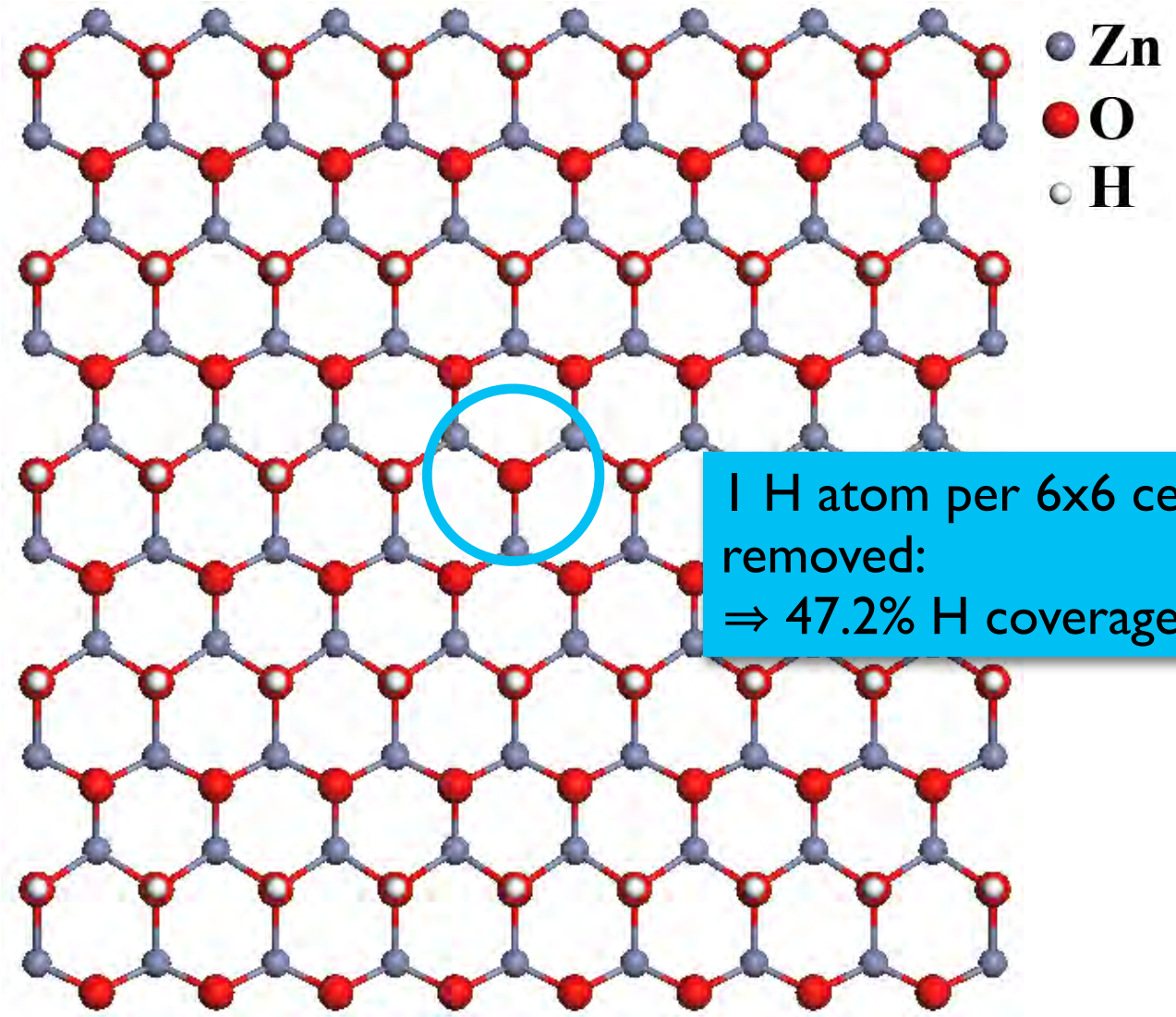
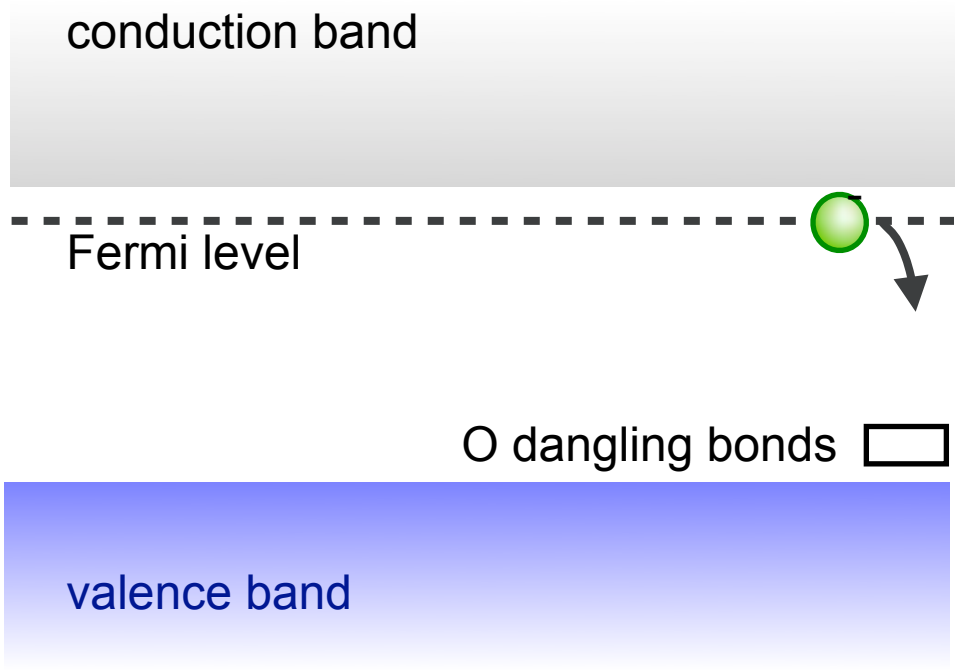


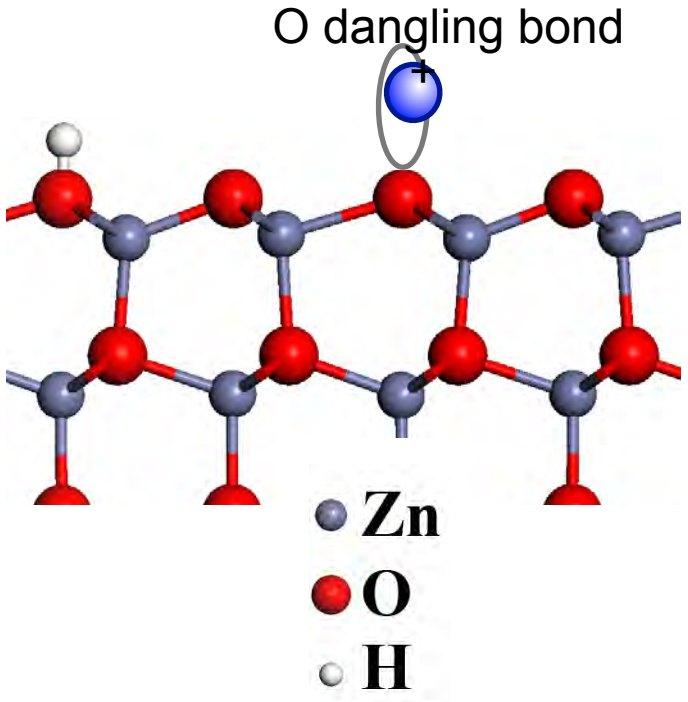
H-deficient ZnO-O 2x1-H surface



1 H atom per 6x6 cell removed:
⇒ 47.2% H coverage

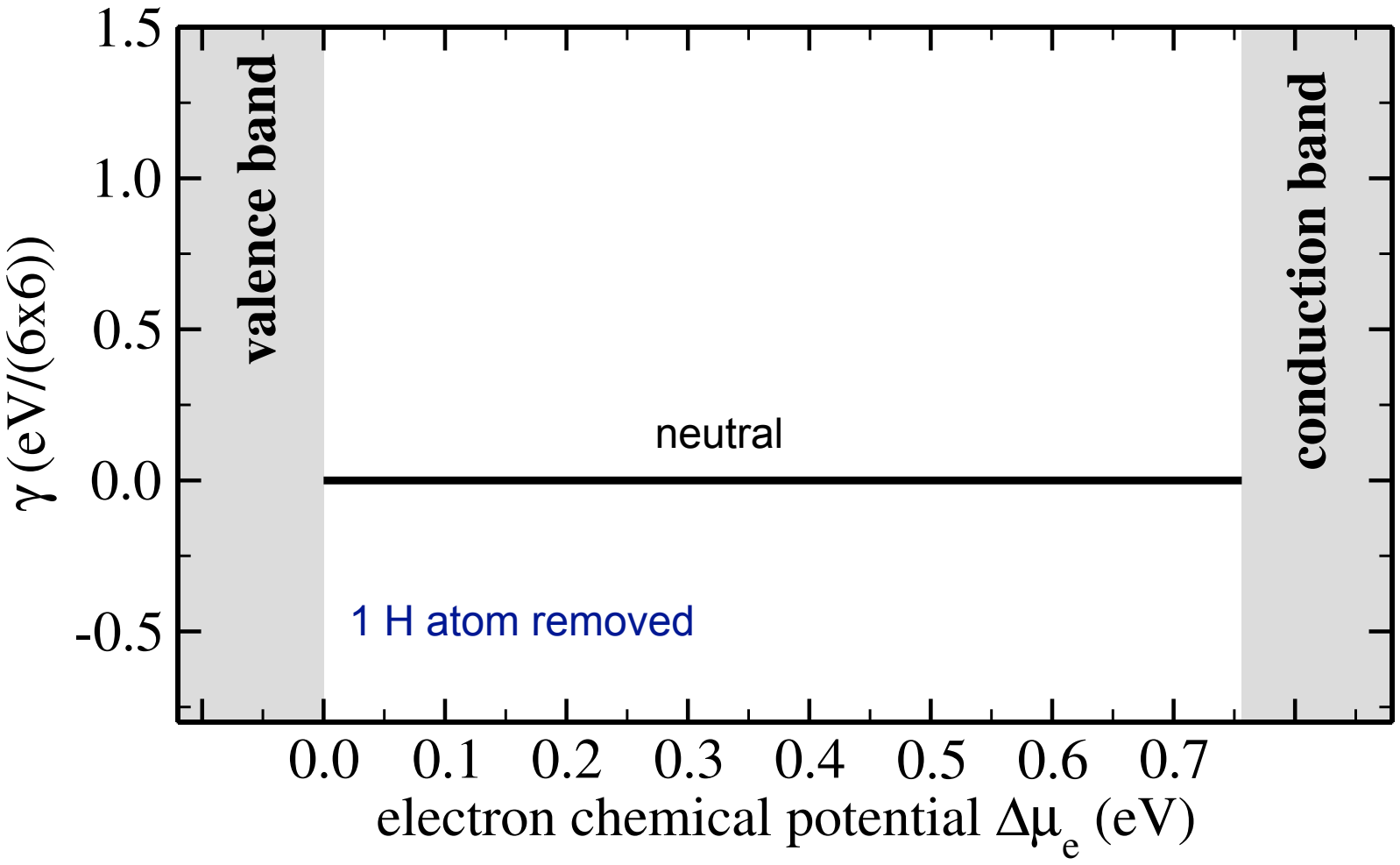
H-deficient ZnO-O 2x1-H surface





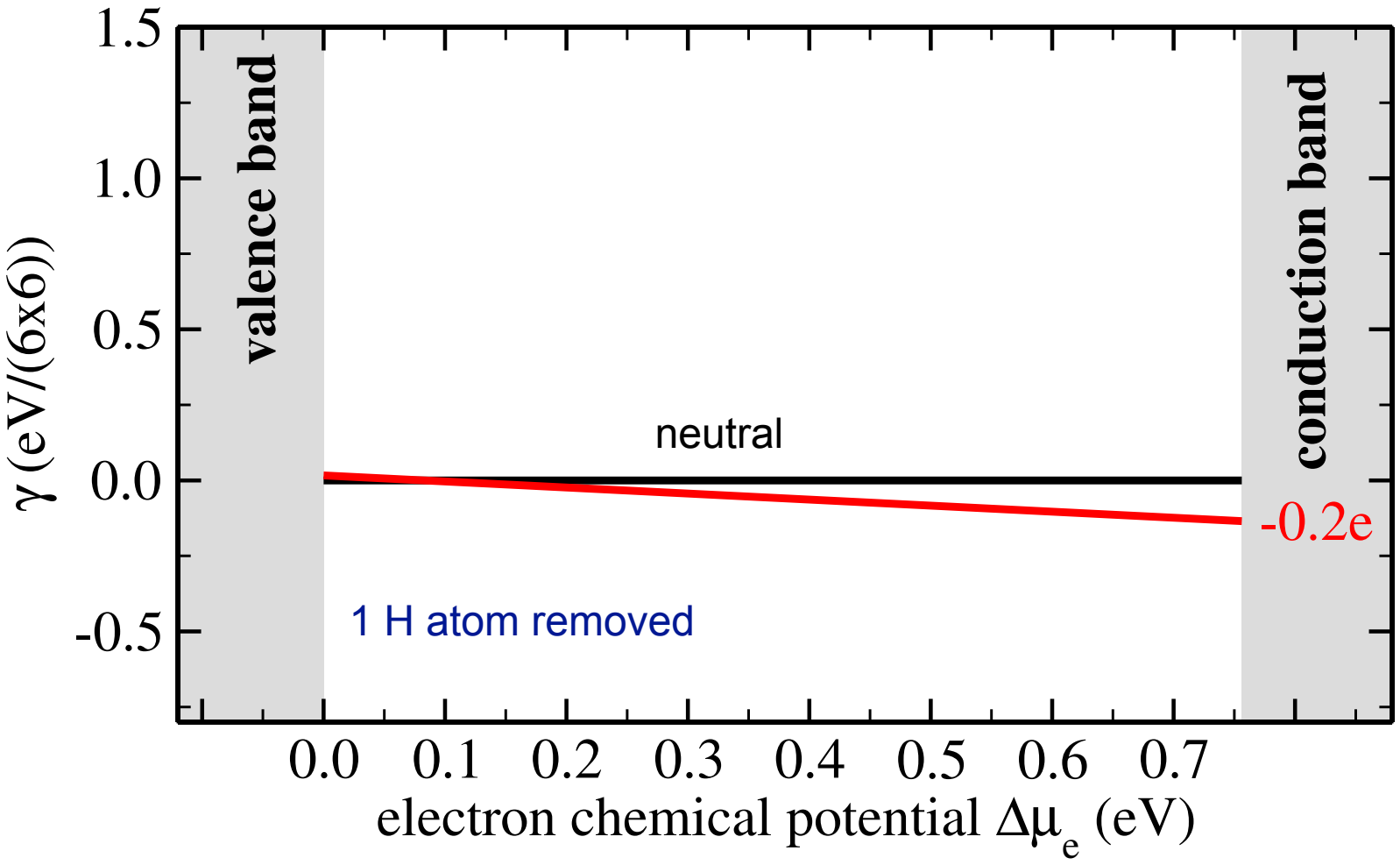
- Can doping stabilize otherwise unstable surfaces?
- And what about band bending?

H-deficient ZnO-O 2x1-H surface



H-deficient ZnO-O 2x1-H surface

- extra negative charge stabilizes surface



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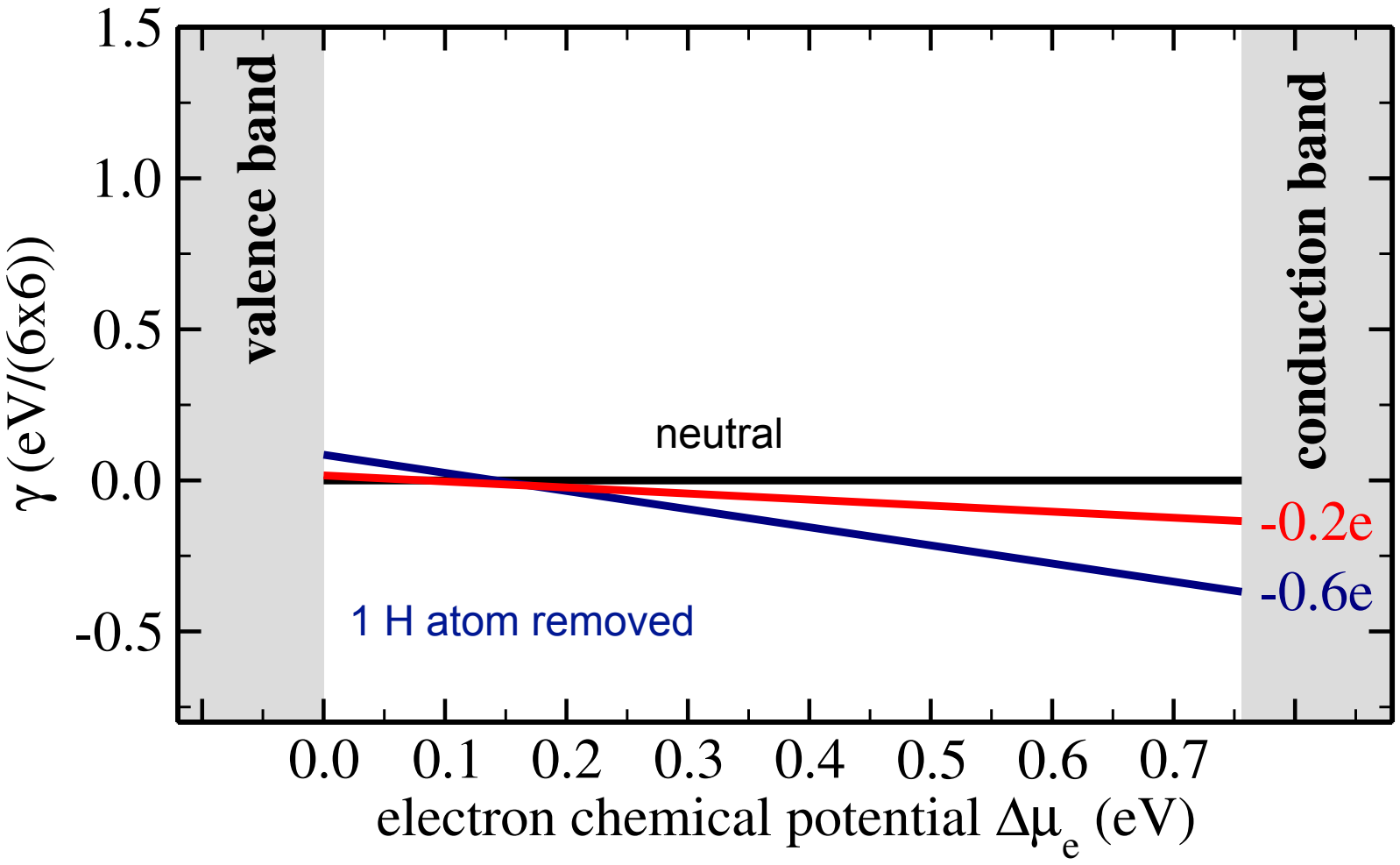

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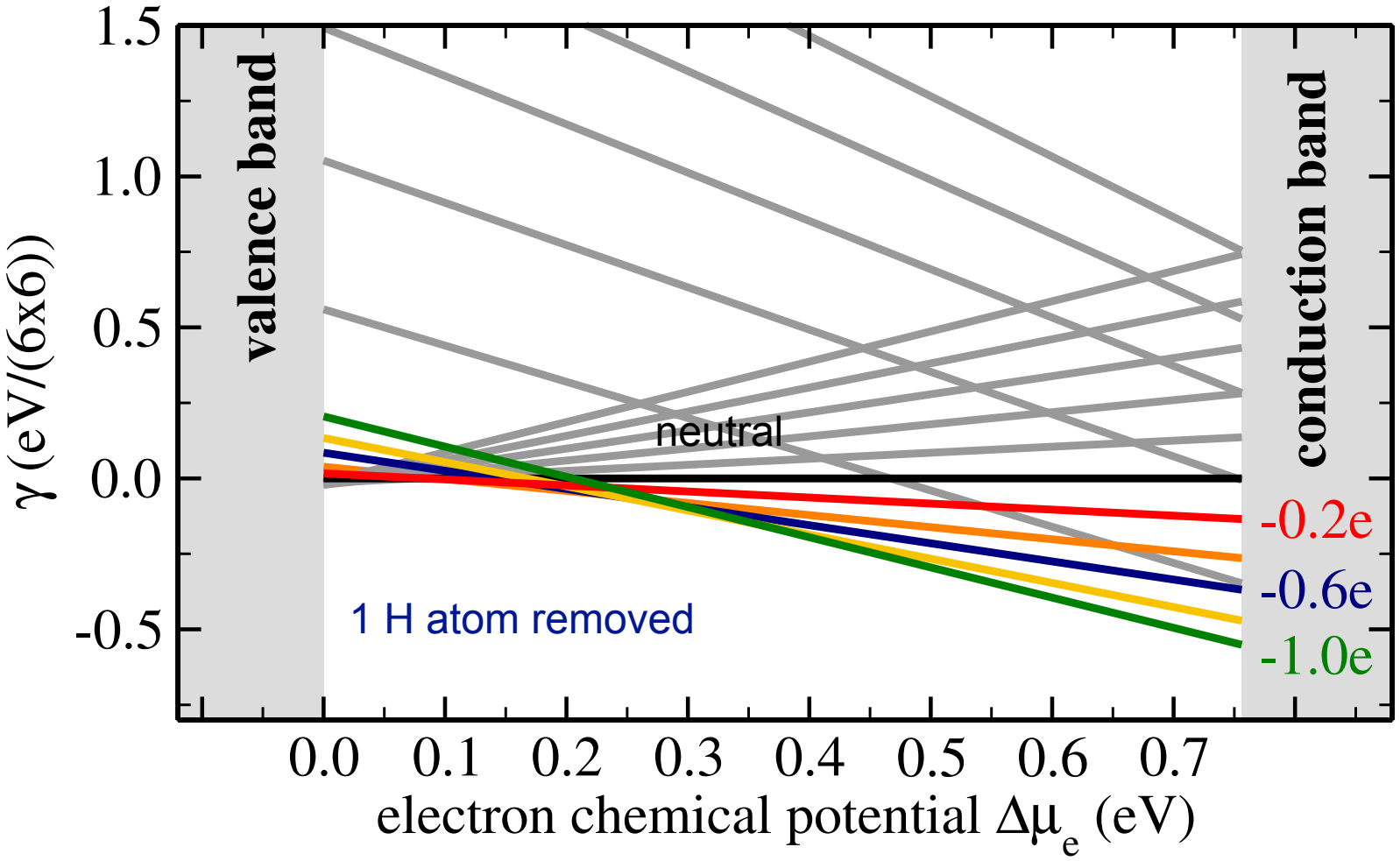

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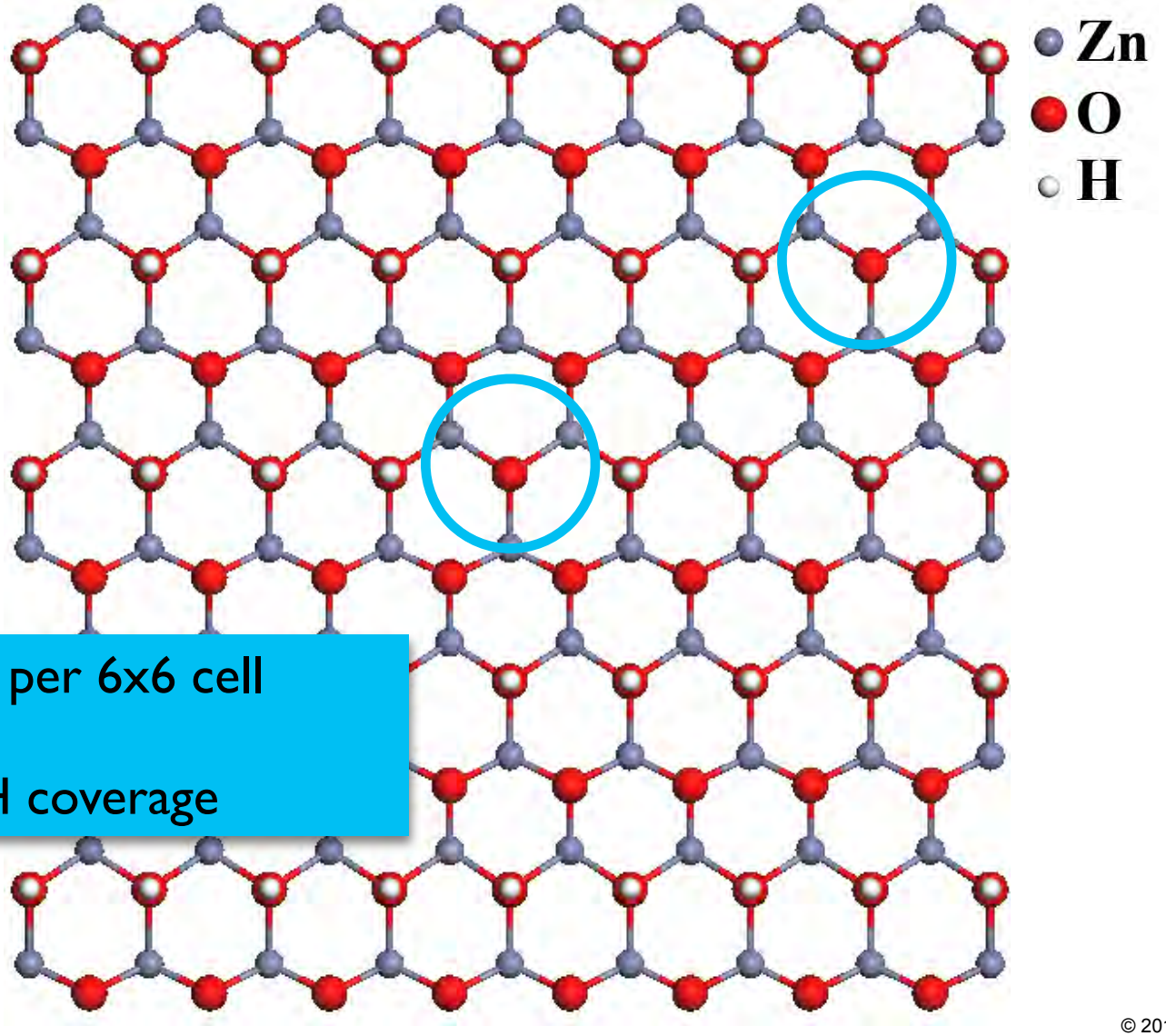
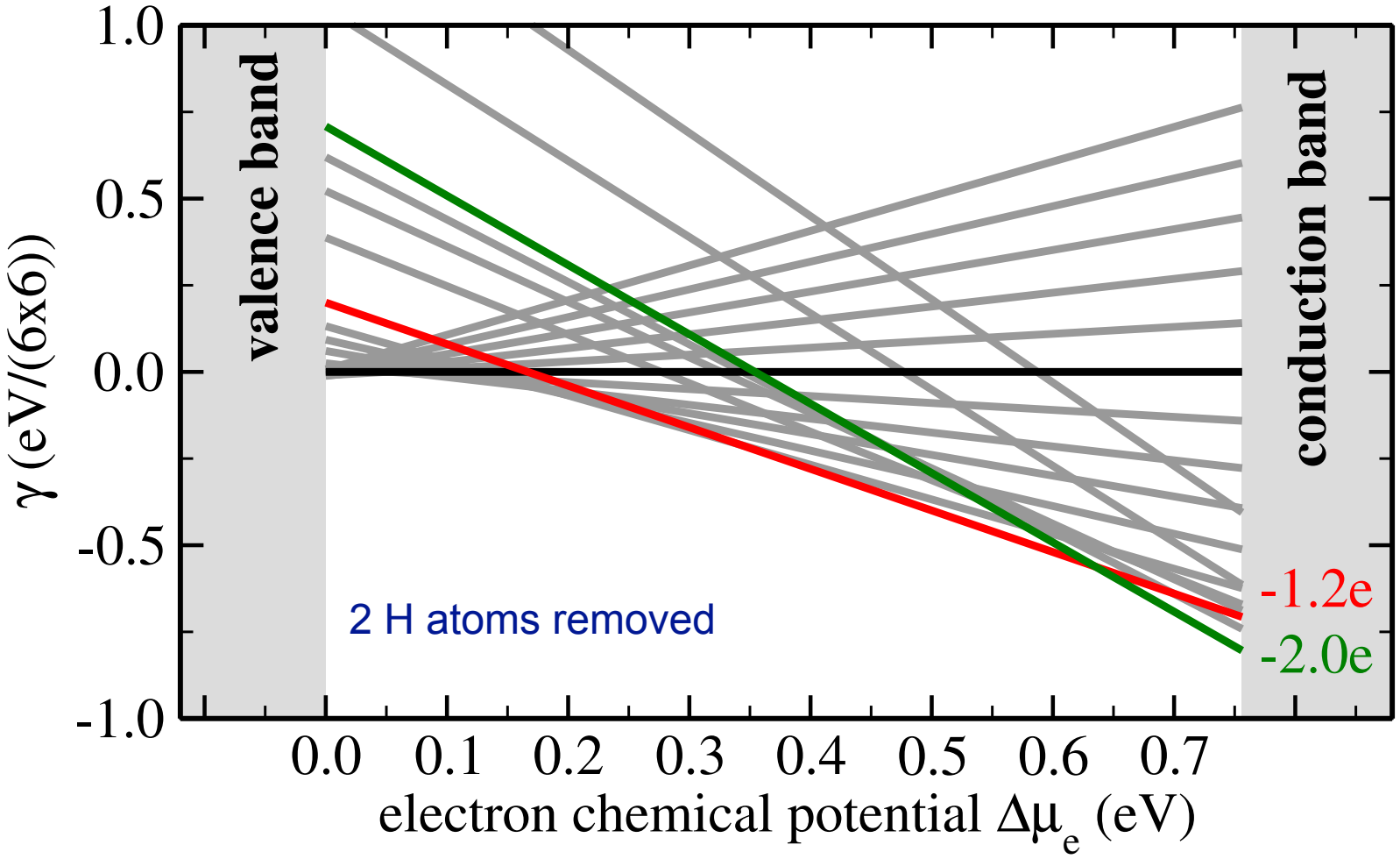


2 H atoms per 6x6 cell removed:
⇒ 44.4% H coverage

H-deficient ZnO-O 2x1-H surface

- highest stability when all dangling bonds are compensated



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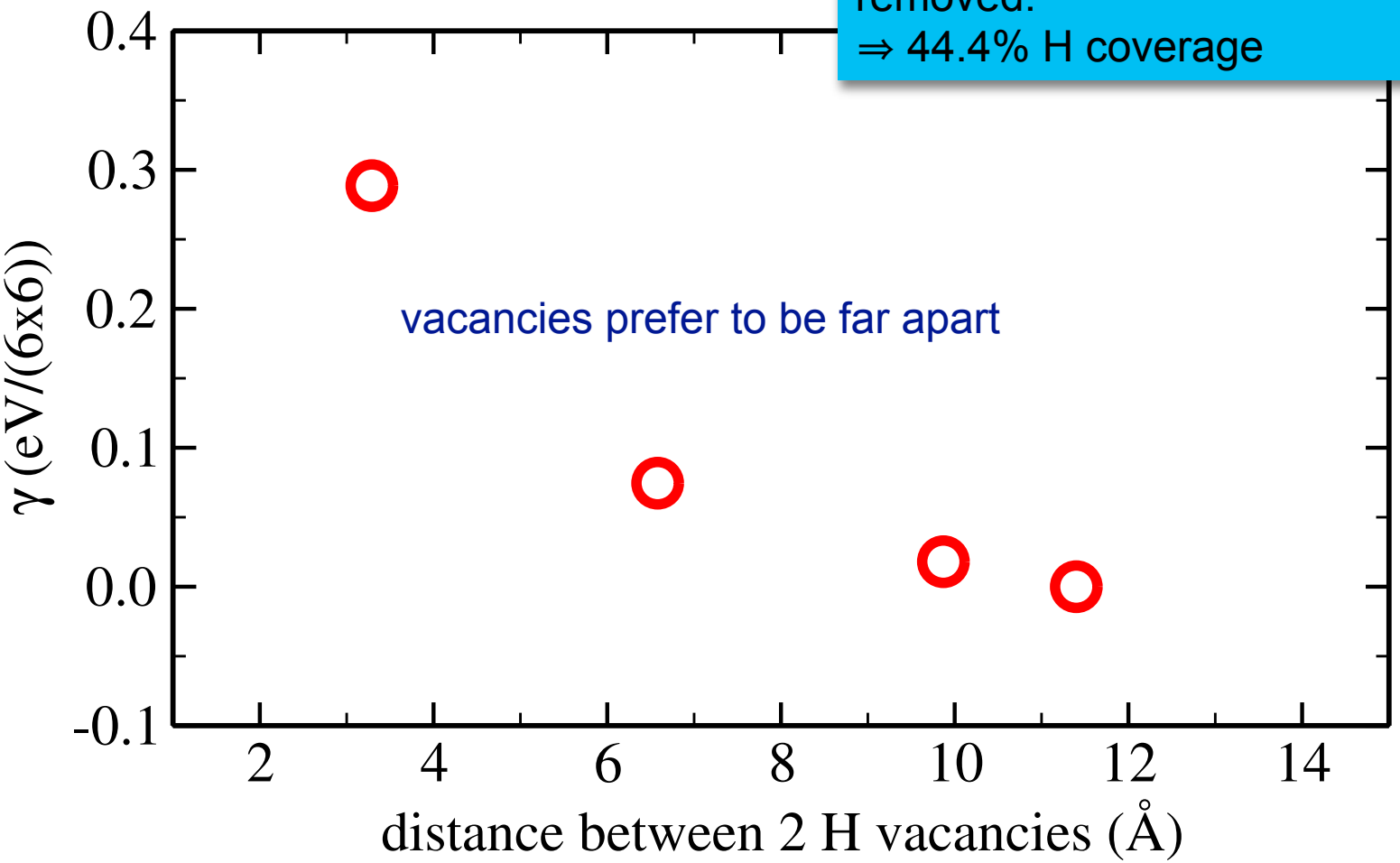

Ab initio thermodynamics - adding electrons

surface free energy:

fix chemical potential of electrons to conduction band minimum

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vary chemical potential of hydrogen

correction term
(for filling of conduction band)

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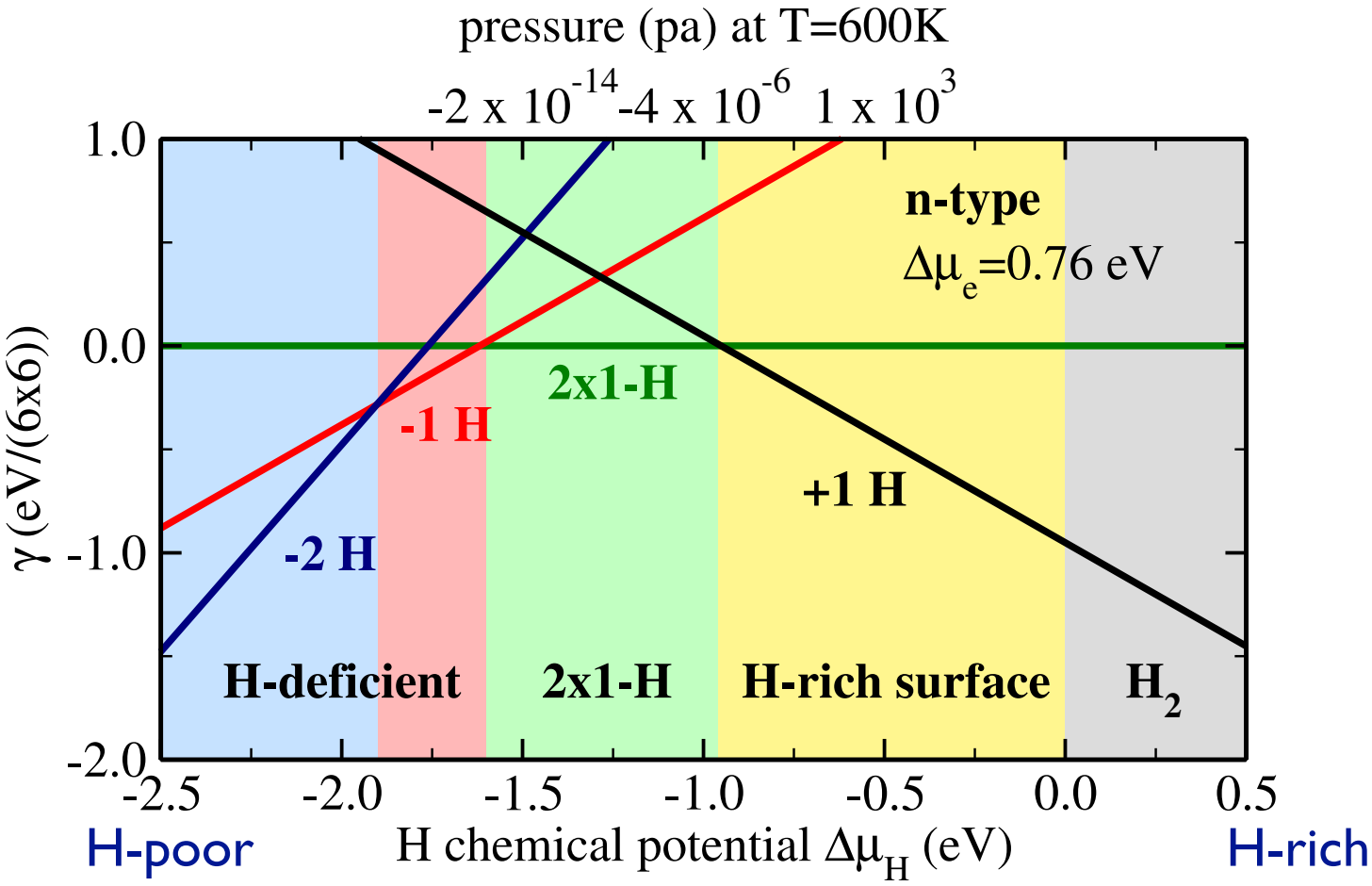
ZnO-O in contact with H-reservoir

- different H-terminations are stable



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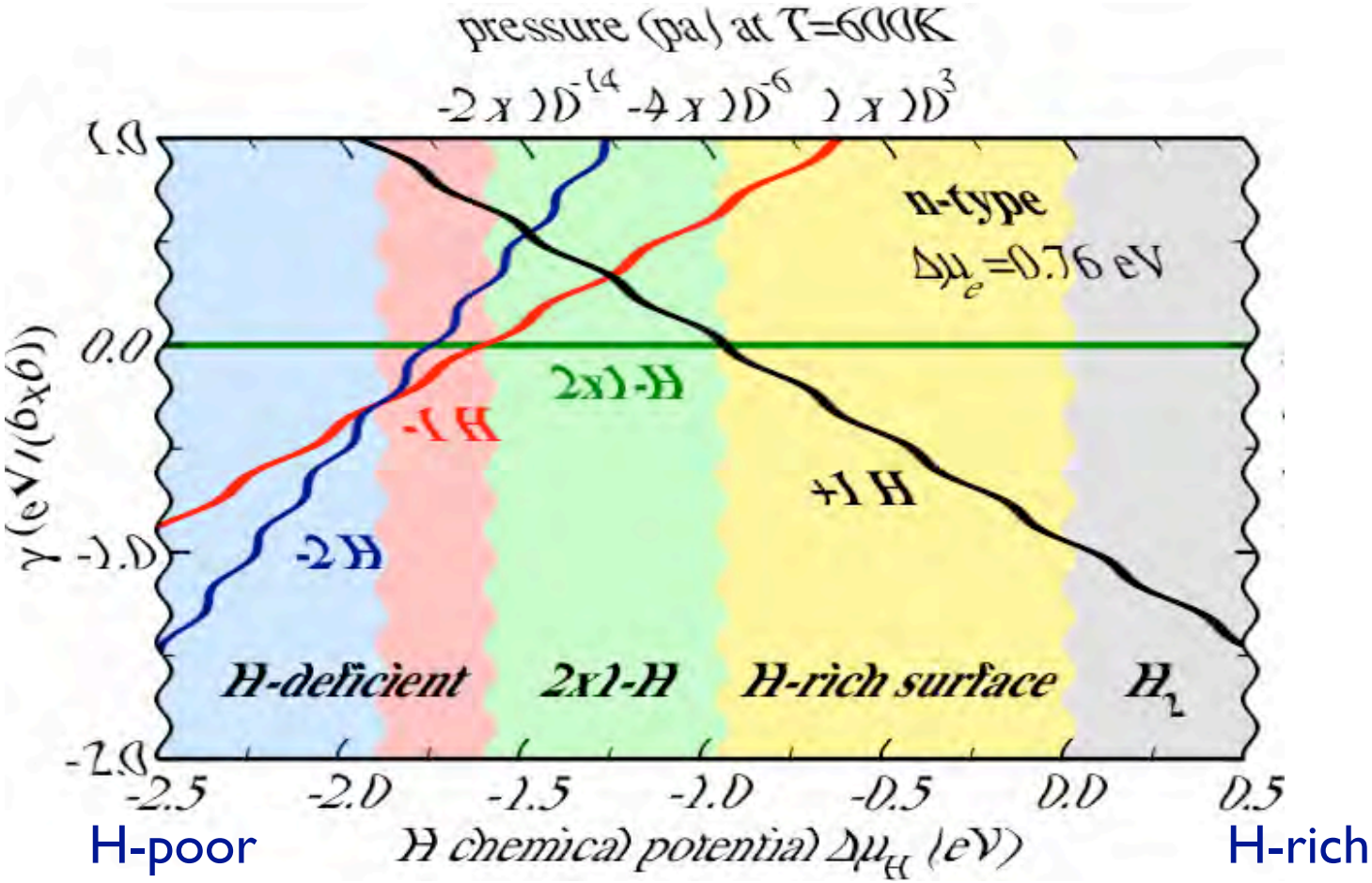
ZnO-O in contact with H-reservoir

- different H-terminations are stable



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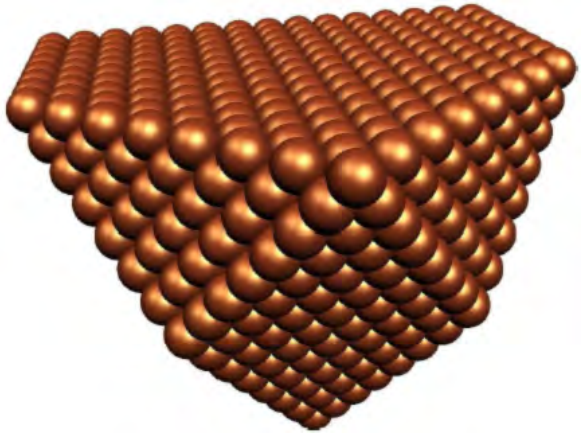
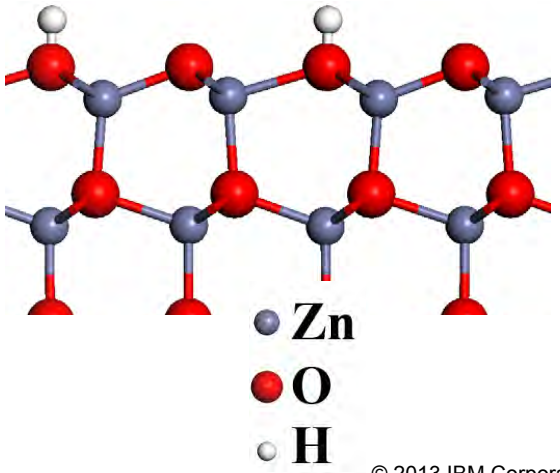
Outline



- Periodic systems: concepts
  - Crystal structure
    - Periodicity in real space
  - Electronic structure
    - Periodicity in reciprocal space
    - Bloch theorem and band structures
  - Calculation of defects and surfaces using periodic supercells
- Stabilization of semiconductor surfaces through bulk dopants
  - Ab-initio thermodynamics
    - Adding electrons to surfaces
  - Surface energies of the H-terminated ZnO (000-1)
    - As a function of the electron chemical potential
    - As a function of the H chemical potential
  - Applying a hybrid exchange correlation functional



How much can we trust the PBE functional?

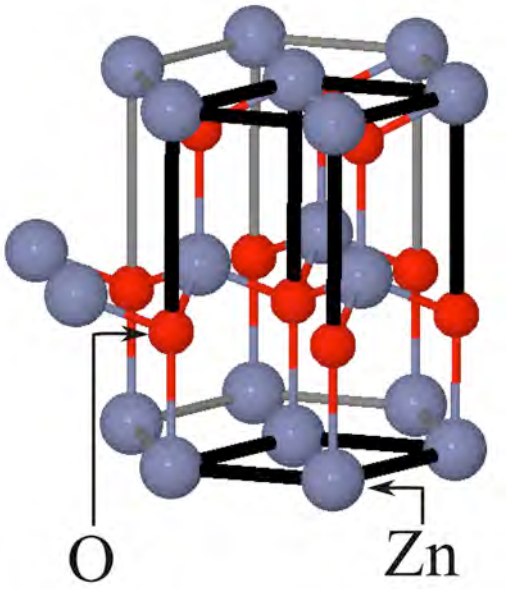
PBE suffers from:

- self-interaction error
- absence of derivative discontinuity

E_{bind} (eV)	H_2	O_2	OH
PBE	4.54	6.23	4.76
W4	4.75	5.24	4.65

accurate quantum chemical reference

*Karton et al. J. Phys. Chem. A **112**, 12868 (2008)*



band gap:

- PBE: 0.76 eV
- Exp: 3.30 eV

Hybrid Functionals

DFT total energy

$$E[n] = T + E_{\mathrm{ext}} + E_{\mathrm{H}} + E_{\mathrm{xc}}$$

exchange-correlation

Hybrid functionals

$$E_{\mathrm{xc}} = \alpha E_{\mathrm{x}}^{\mathrm{HF}} + (1-\alpha) E_{\mathrm{x}}^{\mathrm{PBE}} + E_{\mathrm{c}}^{\mathrm{PBE}}$$

mixing parameter

exact exchange (Hartree-Fock exchange)

- self-interaction free
- non-local

HSE (Heyd-Scuseria-Ernzerhof)

E_x^{HF} is screened (i.e. short ranged)

Hybrid Functionals

DFT total energy

lation

Hybrid

How to determine mixing parameter?

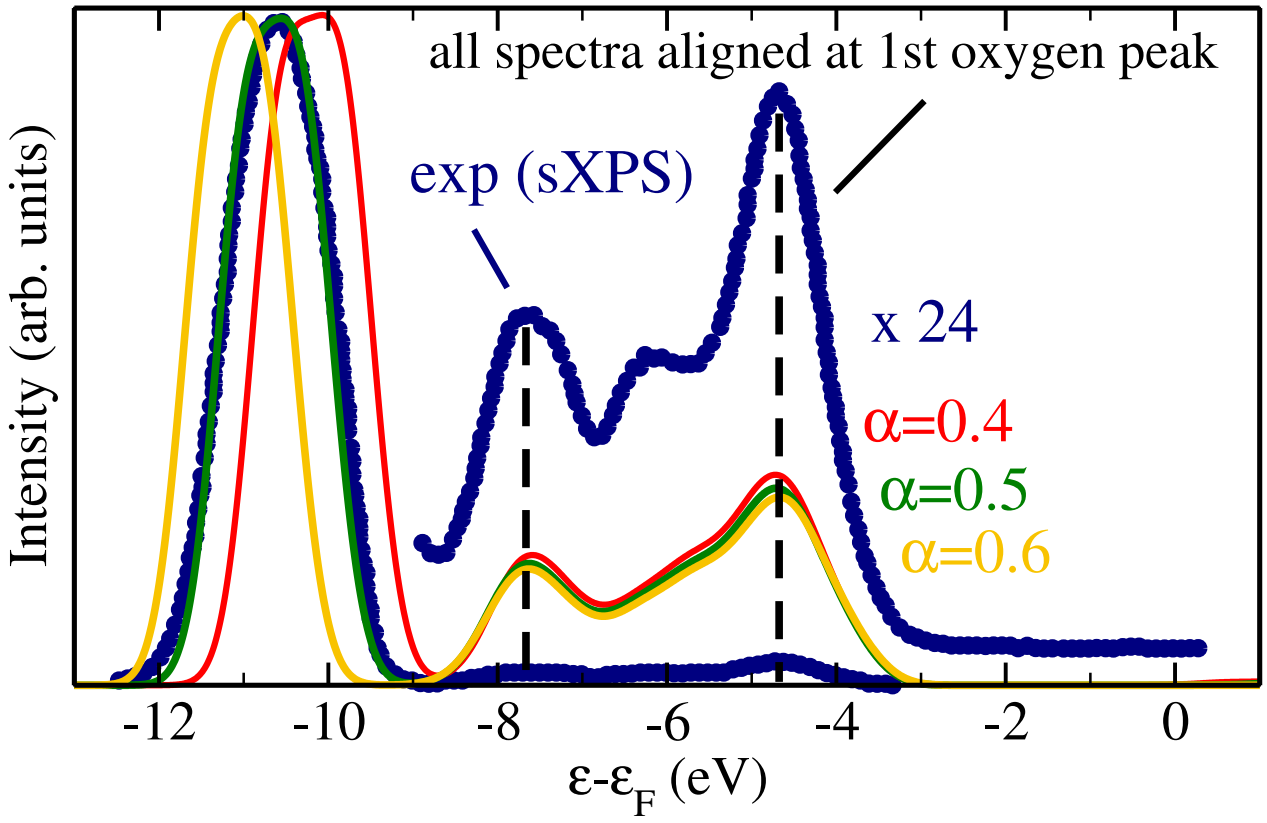
- theoretical grounds:
  - α=0.25: PBE0 functional (material independent)
- judicial choice:
  - reproduce certain materials property (material specific)

HSE (

E_x^{HF} is screened (i.e. short ranged)

Pinning down the HSE functional

sXPS data courtesy of M. Kobayashi



	E_{gap}
Exp.	3.3 eV
α=0.4	3.4 eV
α=0.5	4.1 eV
α=0.6	4.9 eV

- band width (as measure of cohesion[1]) reproduced by all
- α=0.4 gives overall good performance ⇒ HSE*=HSE(0.4)

[1] *Ramprasad et al., Phys. Rev. Lett.* ***108****, 066404 (2012)*

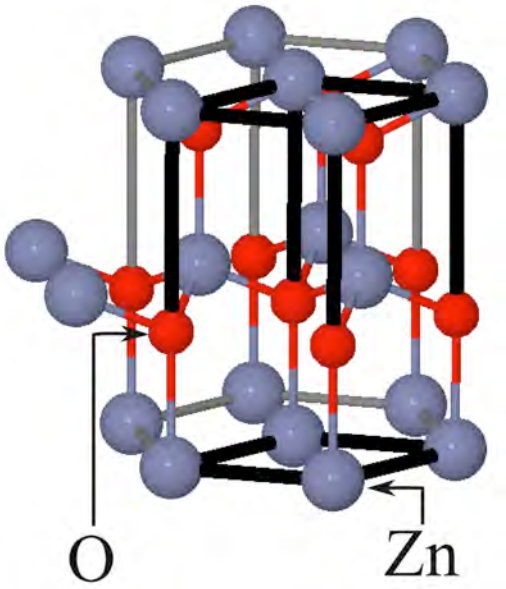
Performance of HSE*

HSE*:

- reduces self-interaction error
- includes derivative discontinuity

E_{bind} (eV)	H_2	O_2	OH
PBE	4.54	6.23	4.76
HSE*	4.52	4.89	4.47
W4	4.75	5.24	4.65

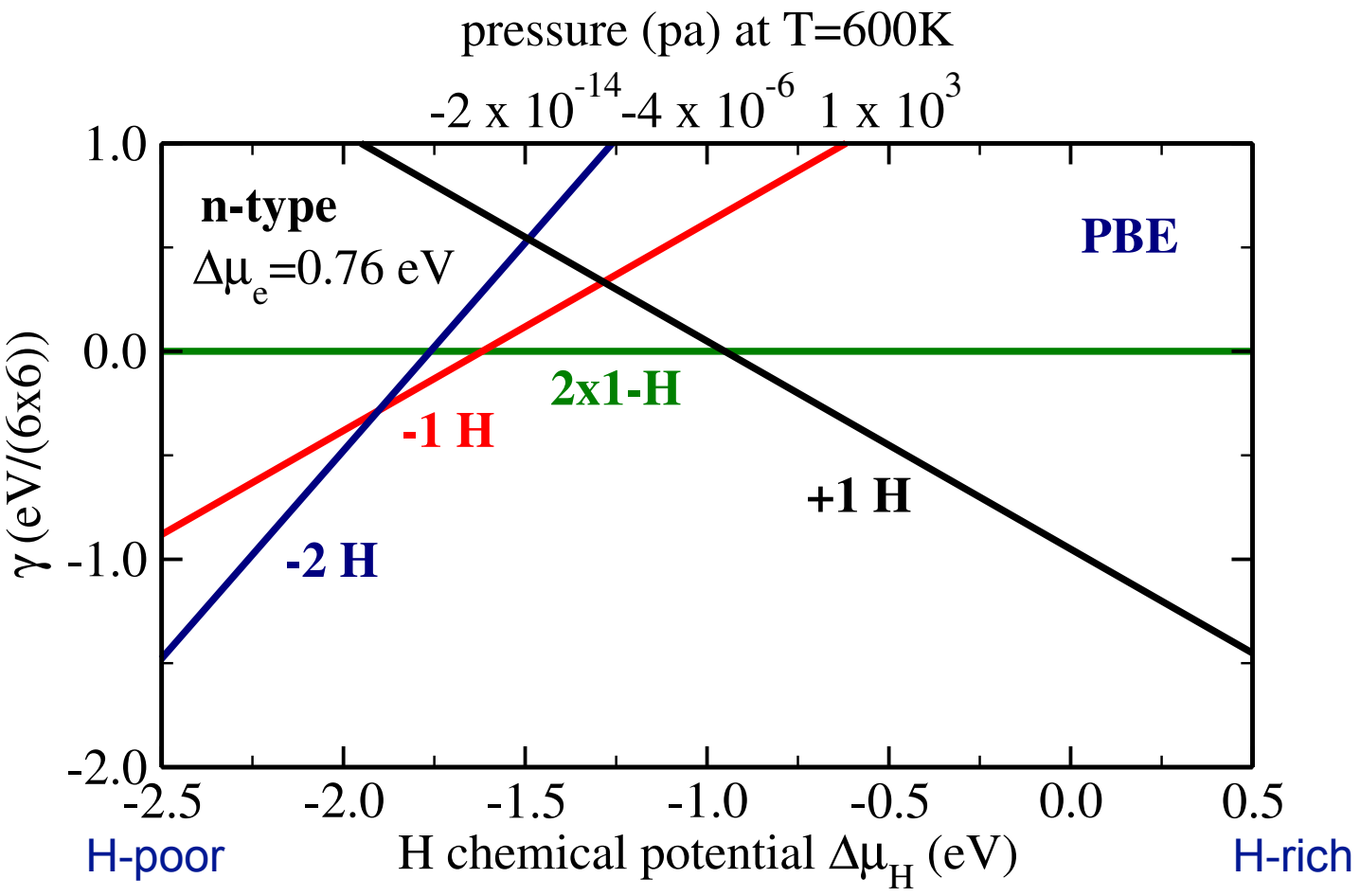
accurate quantum chemical reference
Karton *et al.* J. Phys. Chem. A **112**, 12868 (2008)



band gap:

- PBE: 0.76 eV
- HSE*: 3.40 eV
- Exp: 3.30 eV

ZnO-O in contact with H-reservoir



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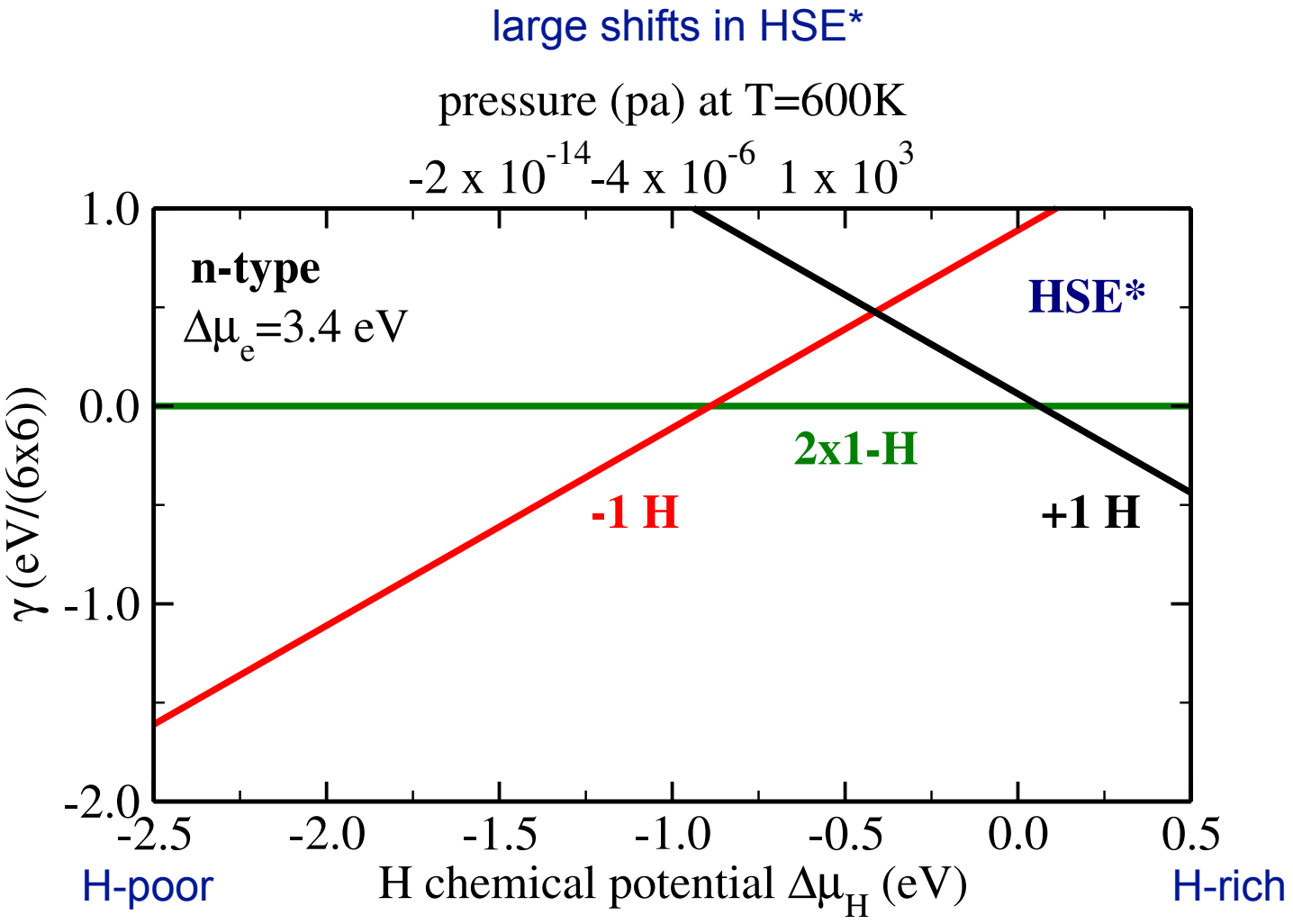
ZnO-O in contact with H-reservoir



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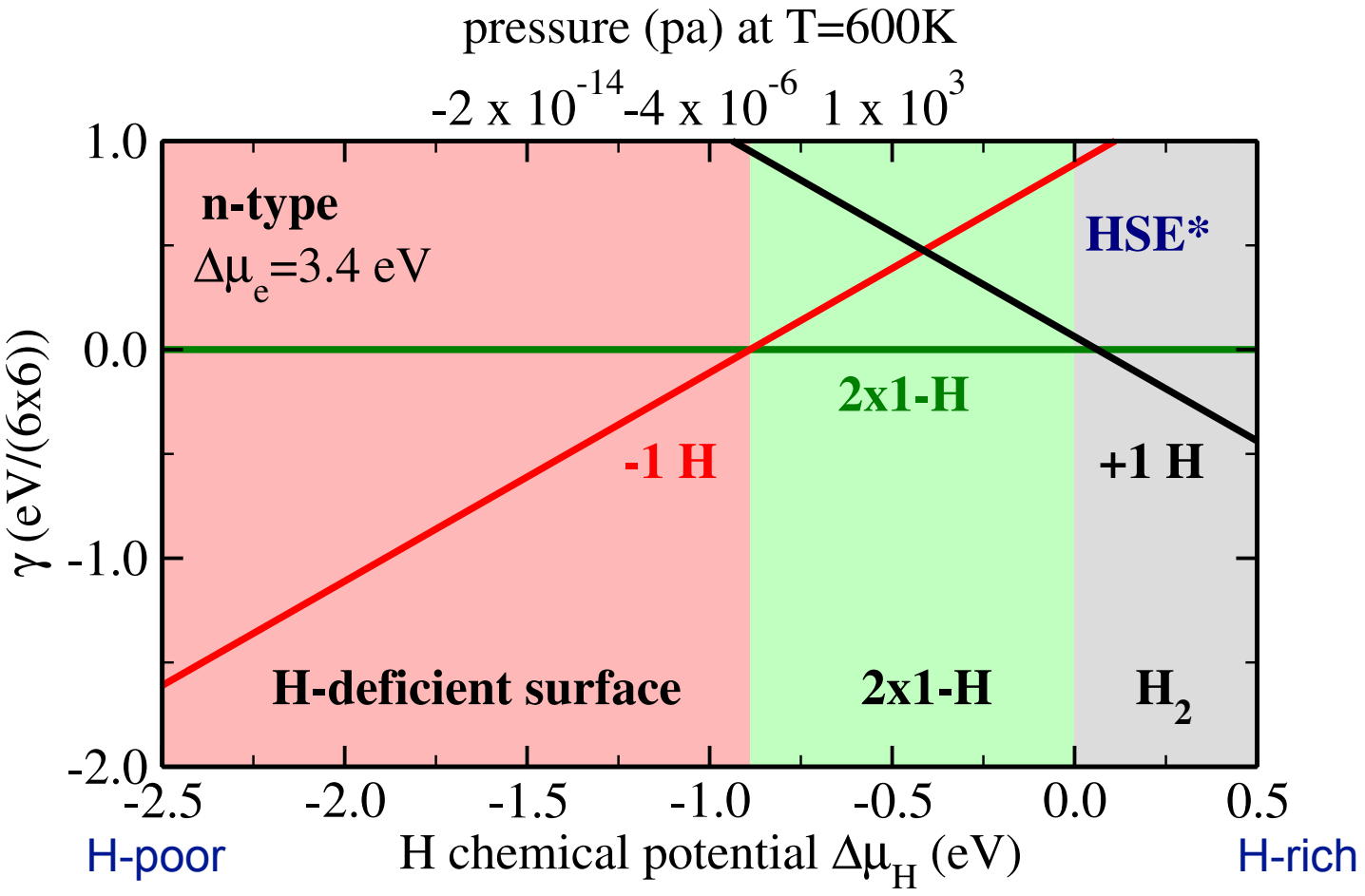
ZnO-O in contact with H-reservoir

- H-deficient surfaces stable at low pressures



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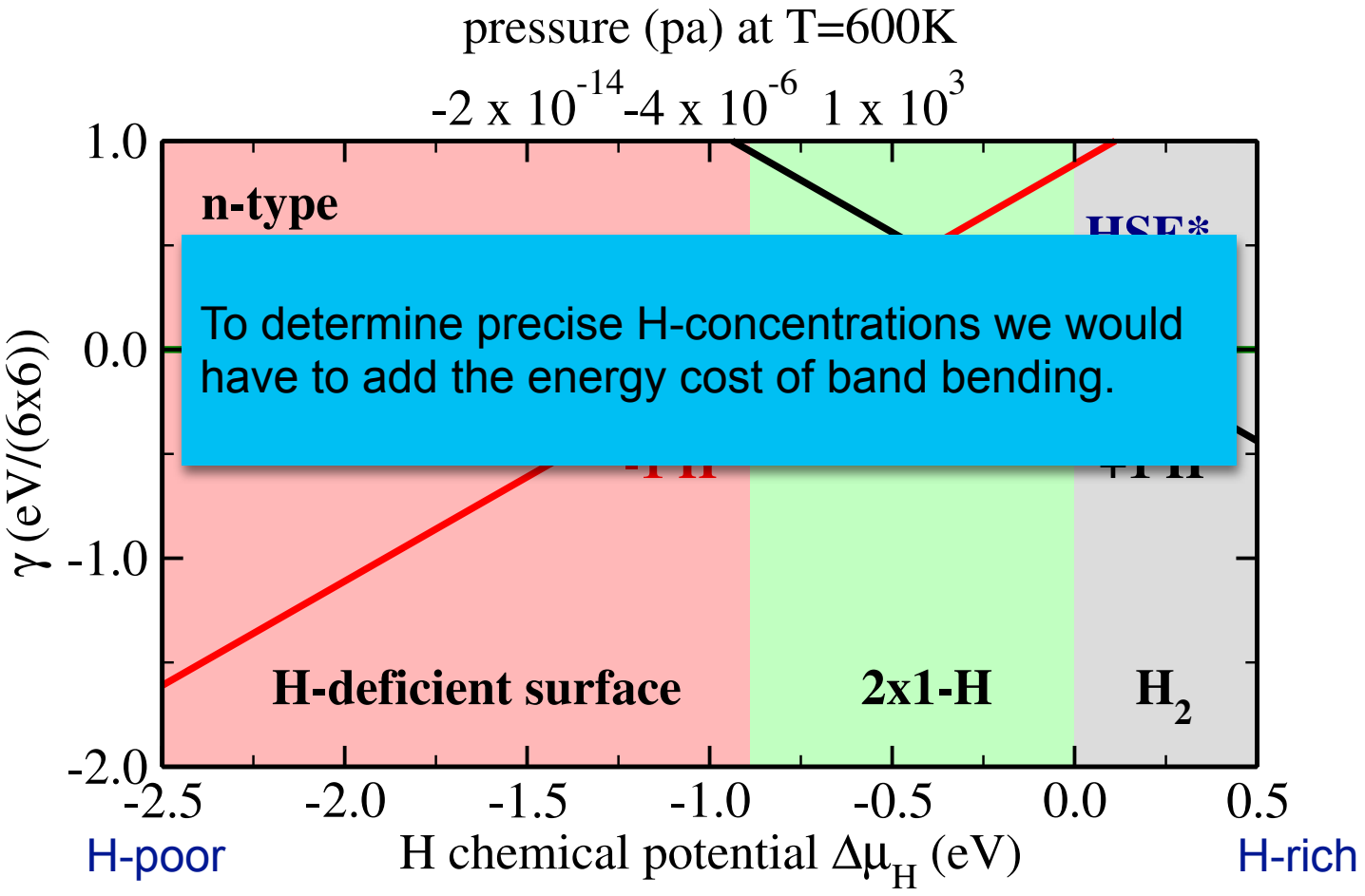
ZnO-O in contact with H-reservoir

- H-deficient surfaces stable at low pressures



To determine precise H-concentrations we would have to add the energy cost of band bending.

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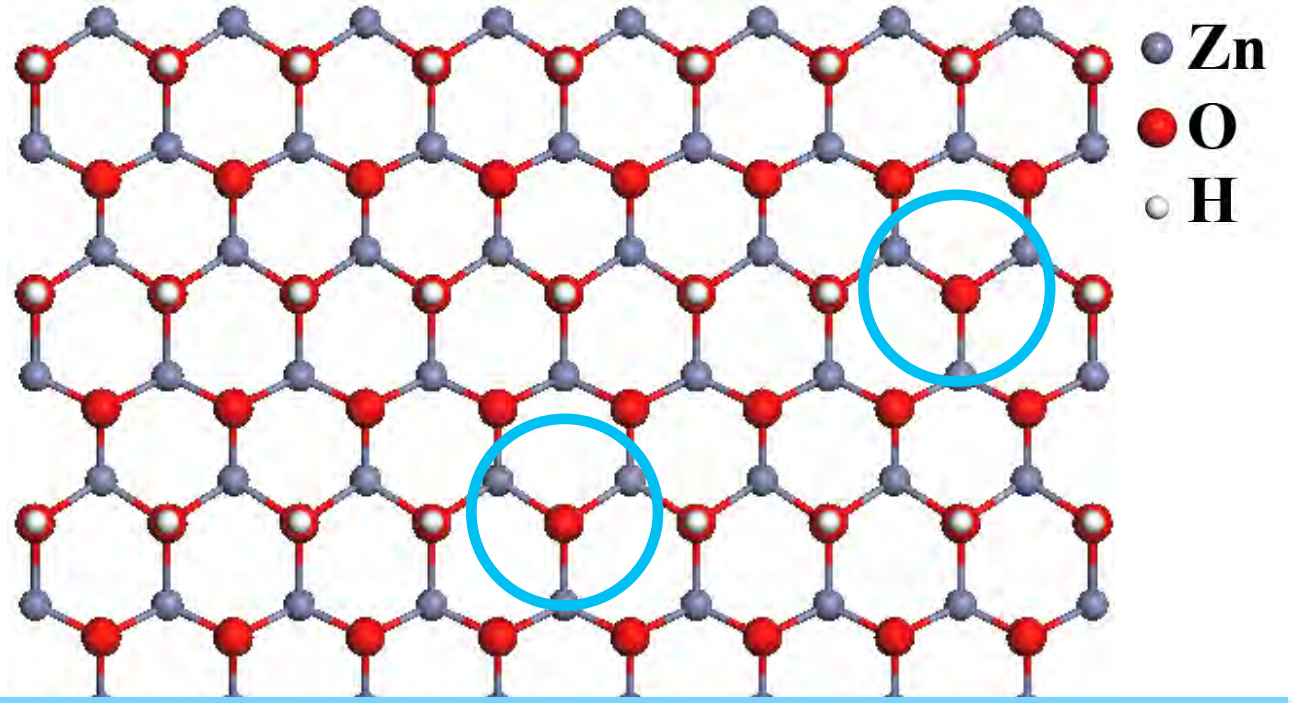
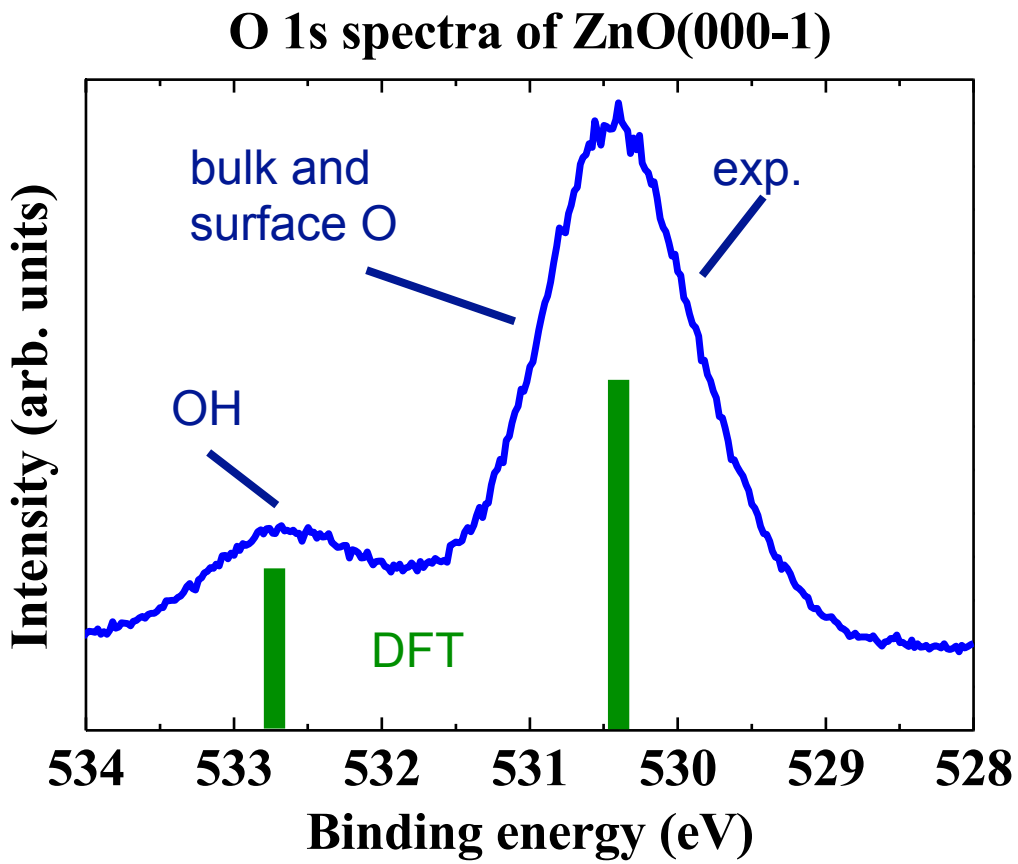
Conclusions



- Bulk doping creates H-deficient surfaces
- H-rich environments ⇒ well ordered surfaces

Ab-initio thermodynamics



	surface core level shift
exp.	2.0 eV
DFT	2.3 eV

from peak weights:
H-coverage ~30-40%