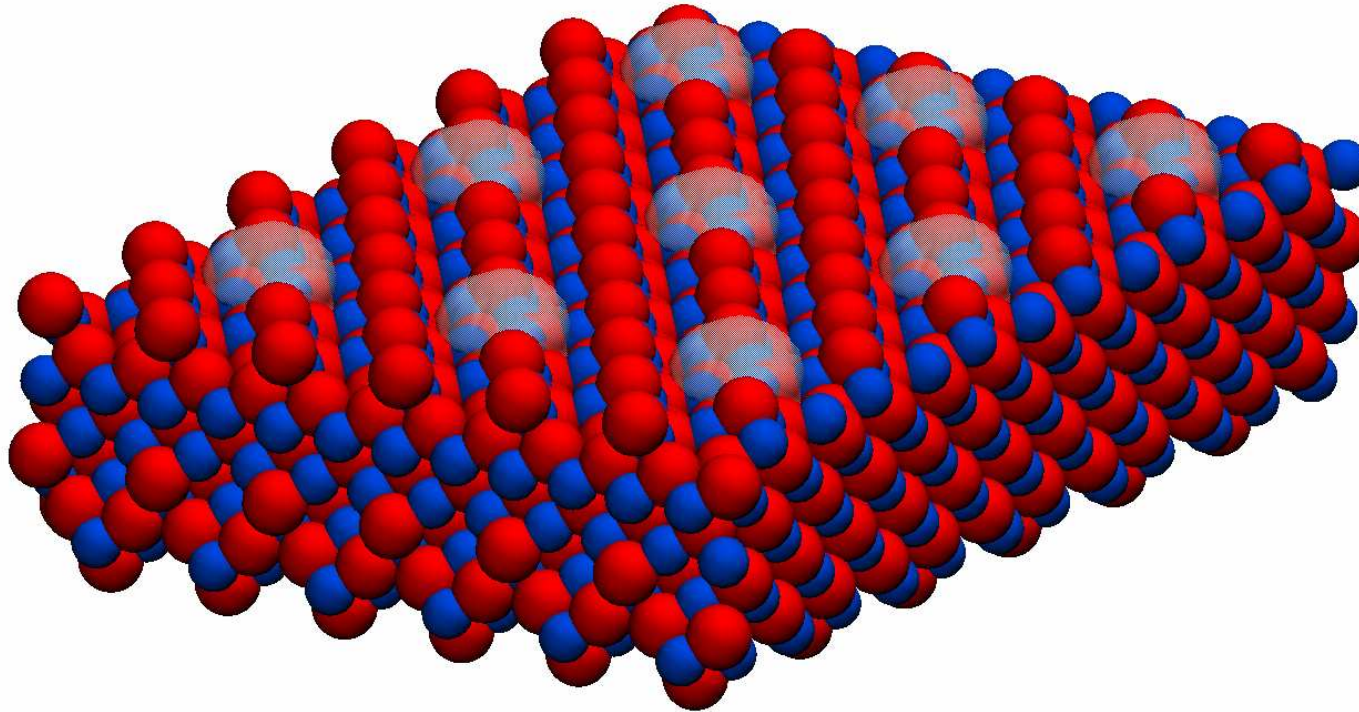# Basics of periodic systems calculations

(Electronic structure theory for materials)
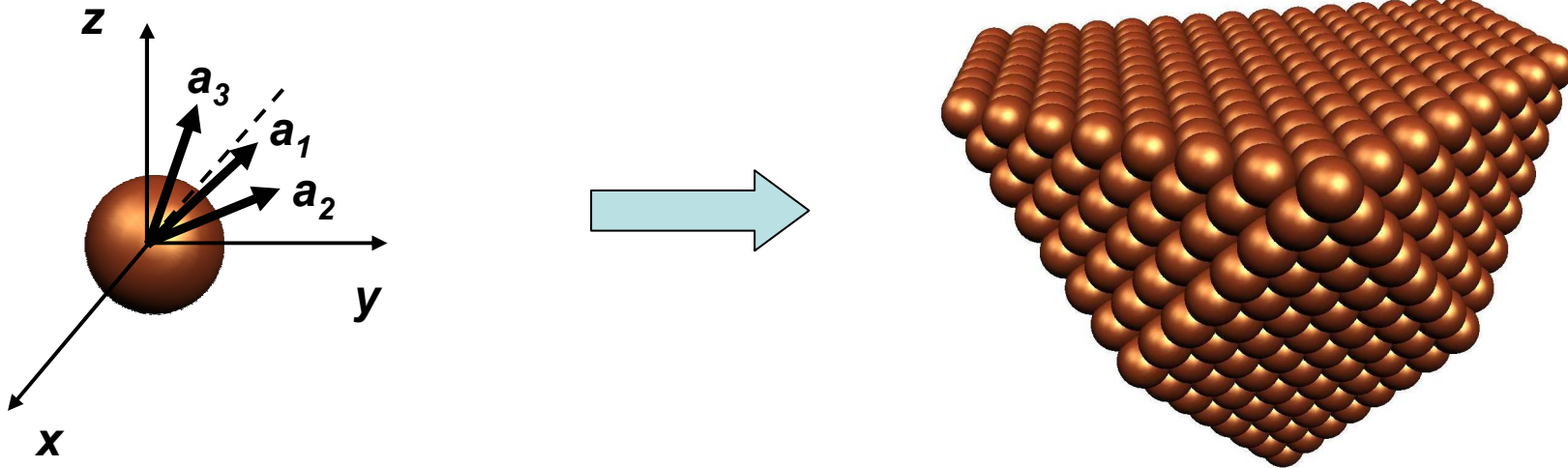
Sergey V. Levchenko

FHI Theory department

Extended (periodic) systems

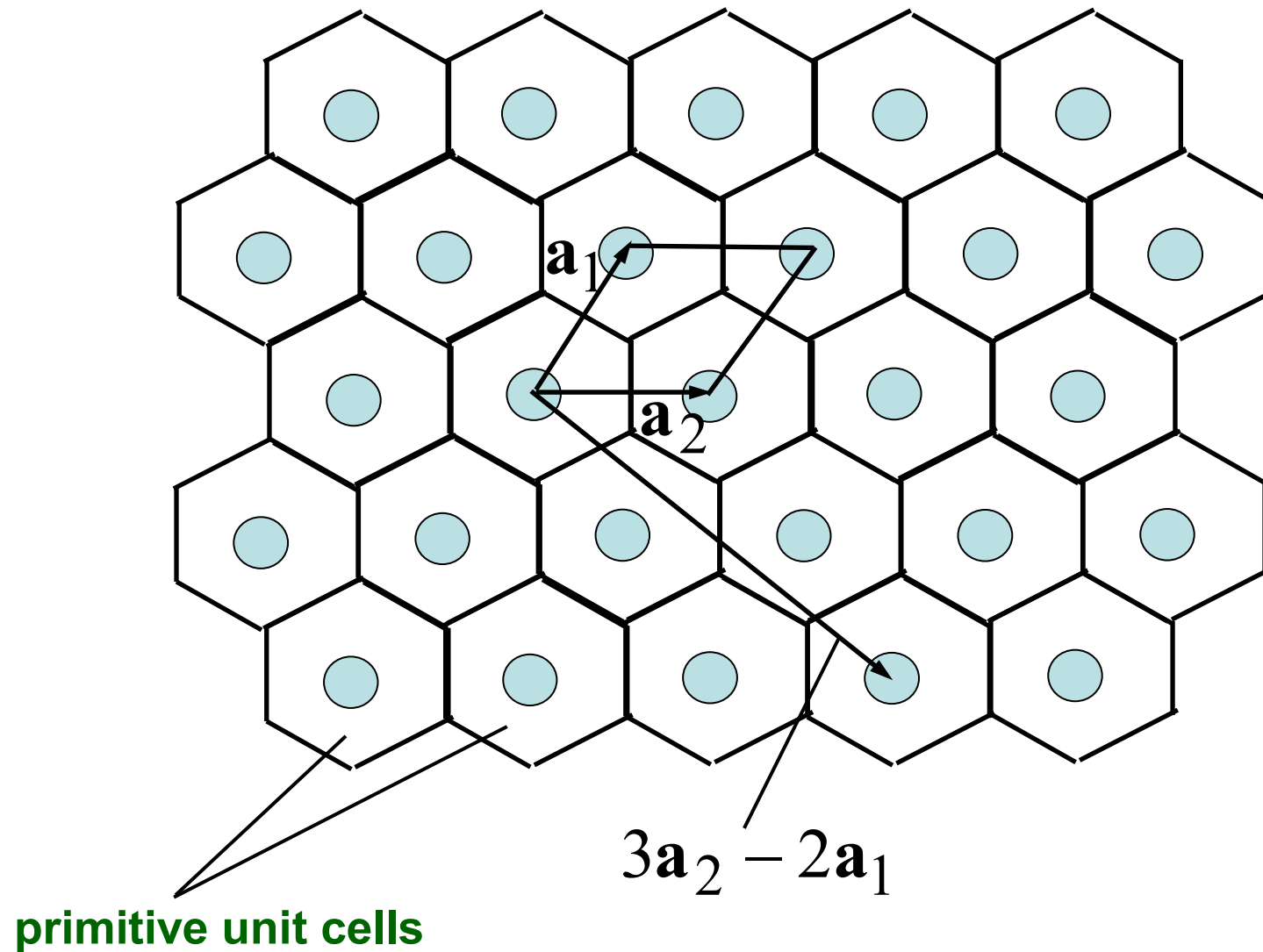**There are 10^{20} electrons per 1 mm^3 of bulk Cu**

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: $\quad \mathbf{R}(n_1, n_2, n_3) = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$
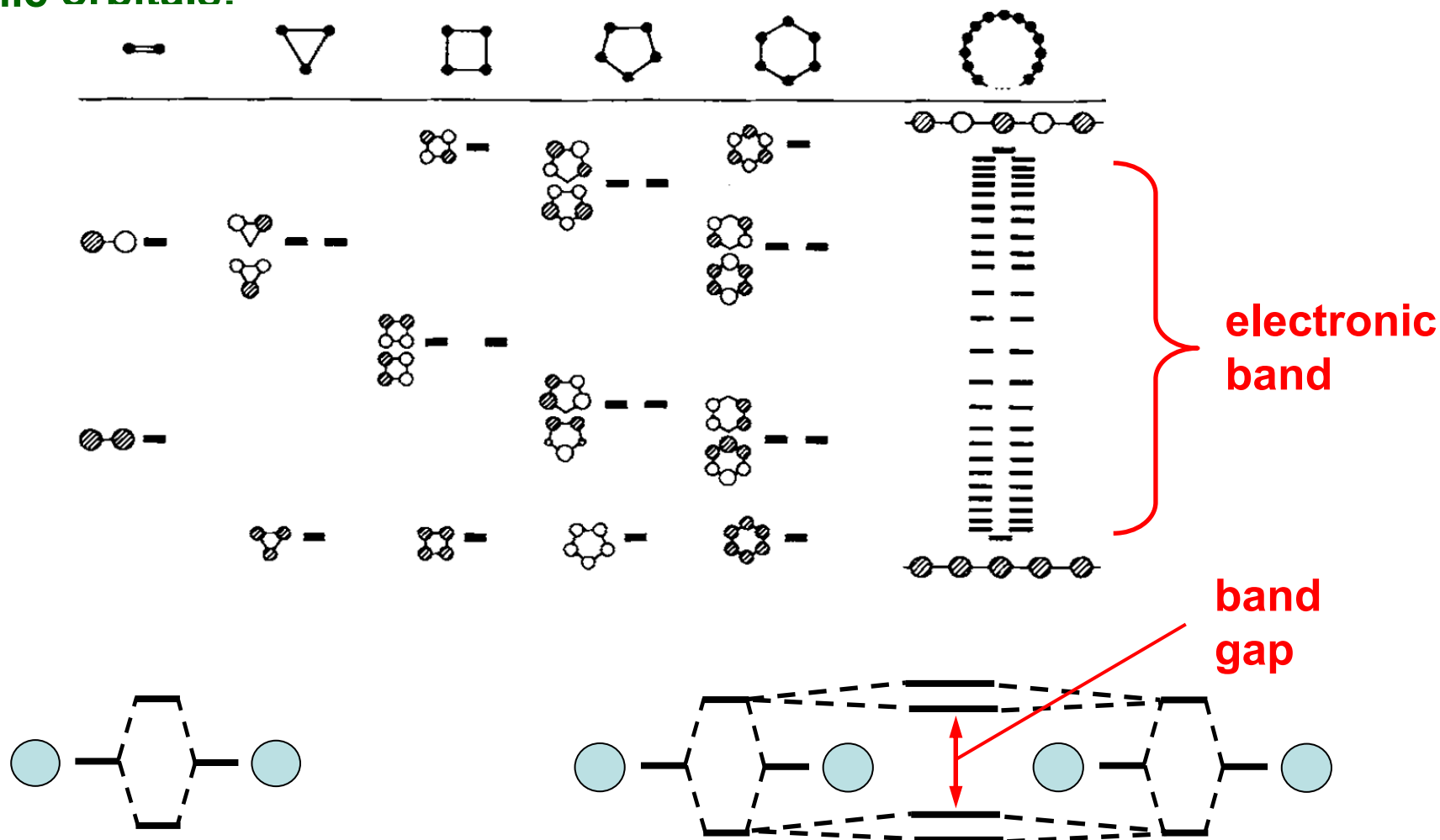
$$n_1, n_2, n_3 = 0, \pm 1, \pm 2, \ldots$$

Example: two-dimensional Bravais lattice

$$3\mathbf{a}_2 - 2\mathbf{a}_1$$

primitive unit cells

The form of the primitive unit cell is not unique

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

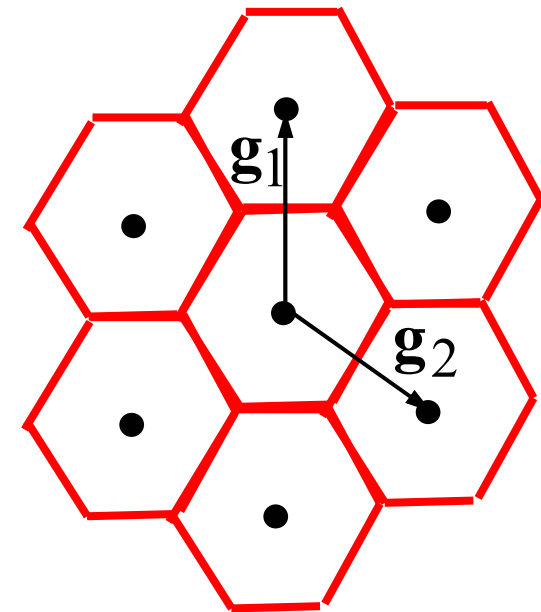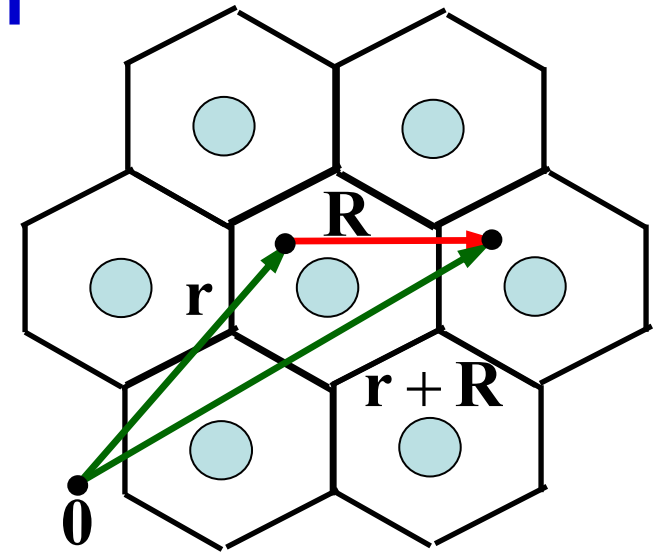$$\psi(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\mathbf{R})\psi(\mathbf{r})$$

Index **k** is a vector in *reciprocal space*

$$\mathbf{k} = x_1\mathbf{g}_1 + x_2\mathbf{g}_2 + x_3\mathbf{g}_3 \qquad \mathbf{g}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$
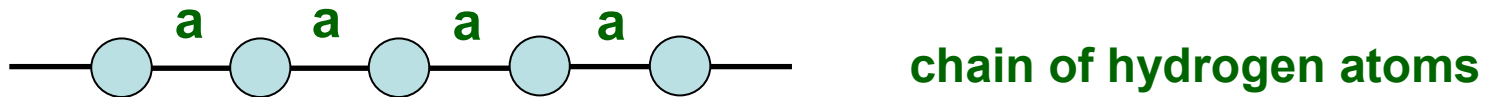
$$\mathbf{g}_l = 2\pi\frac{\mathbf{a}_m \times \mathbf{a}_n}{\Omega}$$ – *reciprocal lattice vectors*

Consequently:

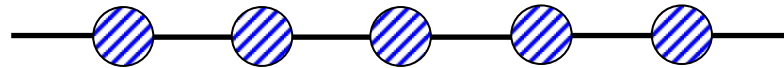$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})u(\mathbf{r}), \;\; u(\mathbf{r}+\mathbf{R}) = u(\mathbf{r})$$
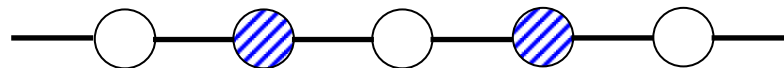
The meaning of k

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

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

k is a symmetry label and a node counter, and also represents electron momentum
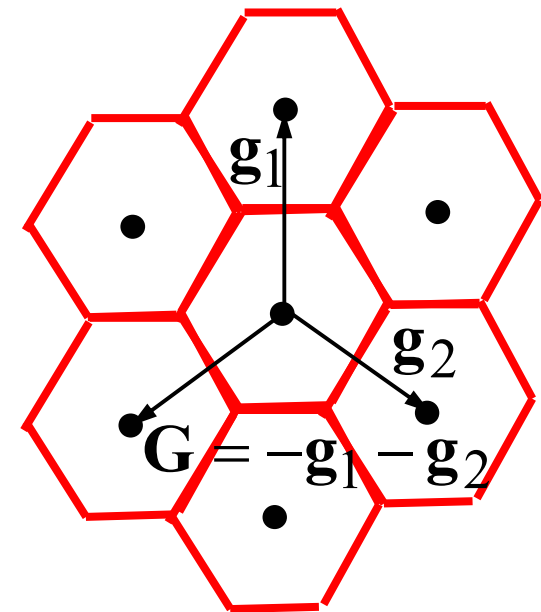
Bloch's theorem: consequences

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

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

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

For any reciprocal lattice vector

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

$$\mathbf{g}_1$$
$$\mathbf{g}_2$$
$$\mathbf{G} = -\mathbf{g}_1 - \mathbf{g}_2$$

$$\psi_{n\mathbf{k}+\mathbf{G}} = \exp(i\mathbf{k}\mathbf{r})[u_{\mathbf{k}+\mathbf{G}}\,\exp(i\mathbf{G}\mathbf{r})] = \exp(i\mathbf{k}\mathbf{r})\widetilde{u} = \psi_{n'\mathbf{k}}$$

a Bloch state at k+G with index *n*

a lattice-periodic function $\widetilde{u}$
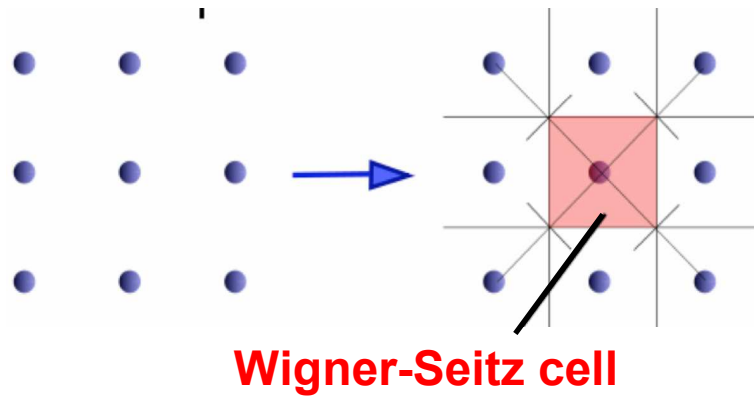
a Bloch state at k with a different index *n'*

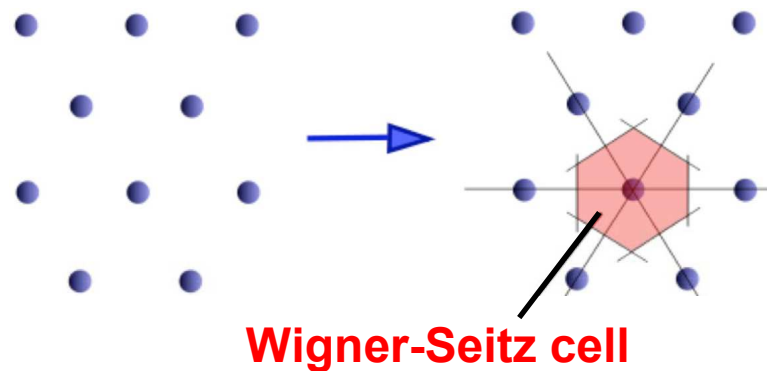**Can choose to consider only k within single primitive unit cell in reciprocal space**

Brillouin zones

A conventional choice for the reciprocal lattice unit cell
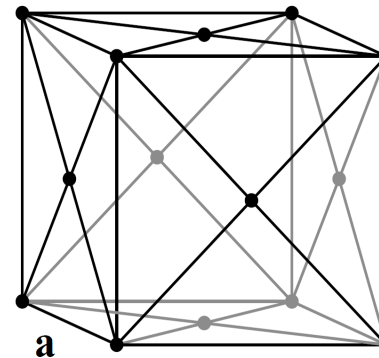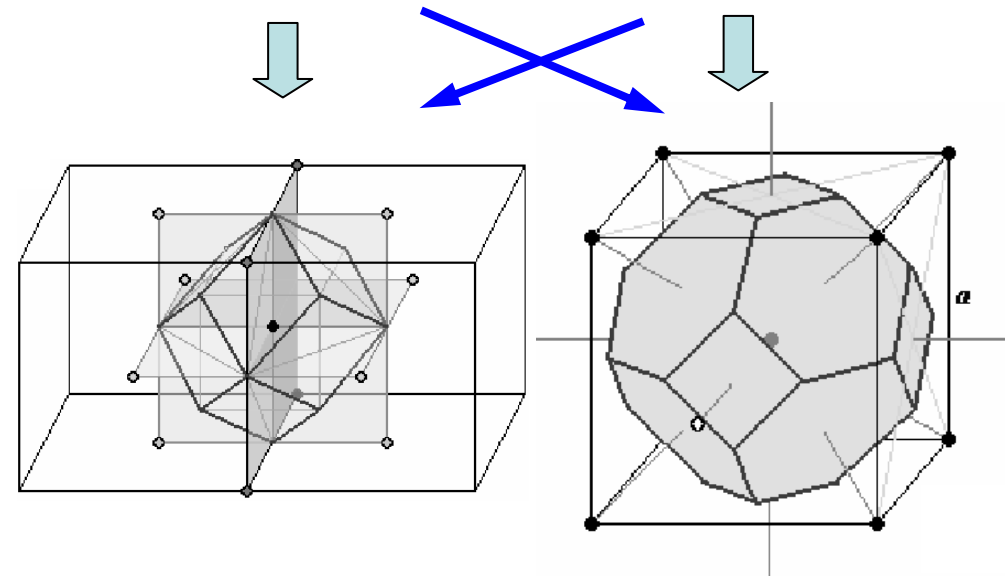
For a square lattice

Wigner-Seitz cell

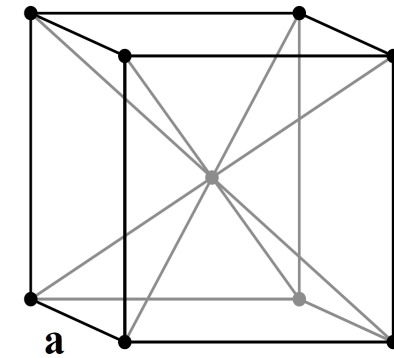**For a hexagonal lattice**

Wigner-Seitz cell

In three dimensions:

Face-centered cubic (fcc) lattice

Body-centered cubic (bcc) lattice

a

a

Time-reversal symmetry

For Hermitian $\hat{h}$, $\varepsilon_{n\mathbf{k}}$ can be chosen to be *real*

$$\hat{h}\psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}) \Rightarrow \hat{h}\psi^{*}_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\psi^{*}_{n\mathbf{k}}(\mathbf{r})$$
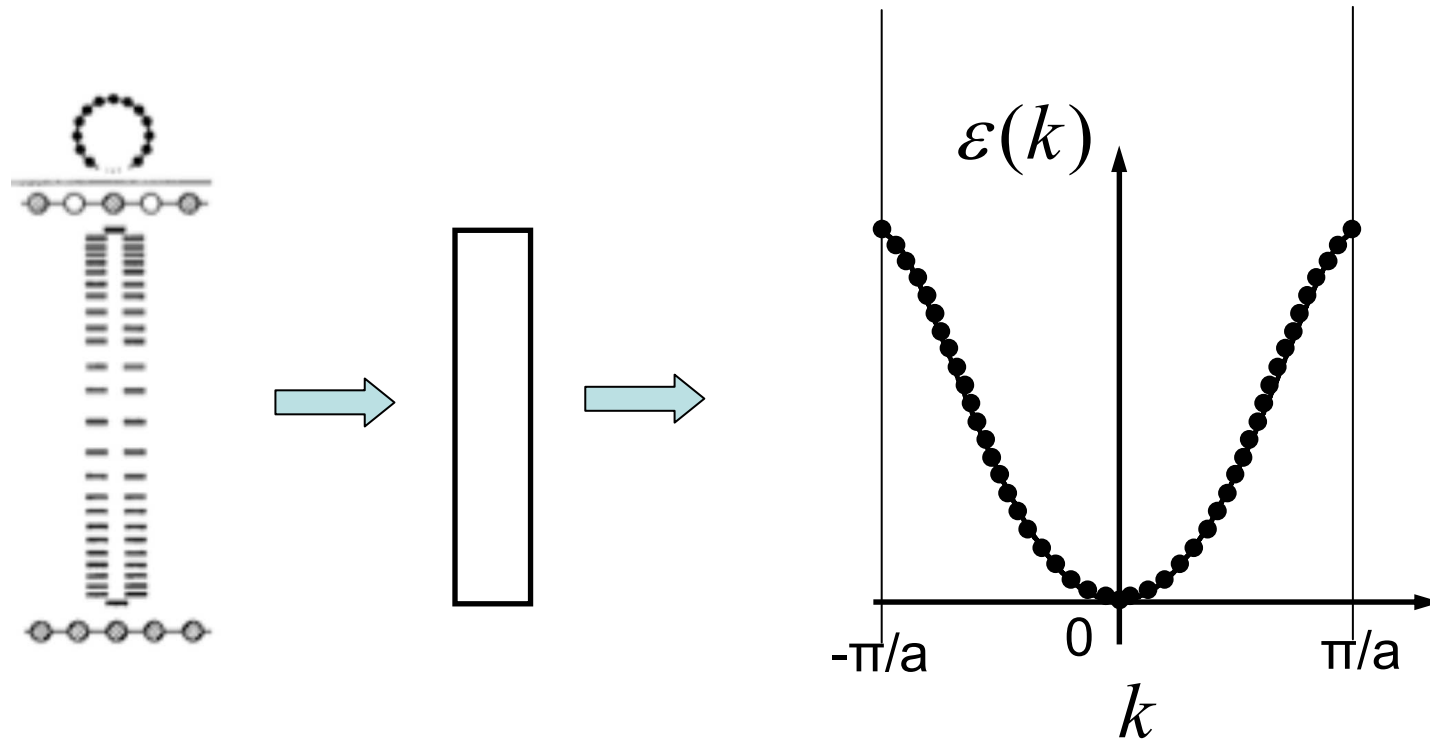
From Bloch's theorem:

$$\psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\mathbf{R})\psi_{n\mathbf{k}}(\mathbf{r}) \Rightarrow \psi^{*}_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \exp(-i\mathbf{k}\mathbf{R})\psi^{*}_{n\mathbf{k}}(\mathbf{r})$$

$$\psi^{*}_{n\mathbf{k}} = \psi_{n(-\mathbf{k})} \qquad \varepsilon_{n(-\mathbf{k})} = \varepsilon_{n\mathbf{k}}$$

Electronic states at k and –k are at least doubly degenerate

(in the absence of magnetic field)
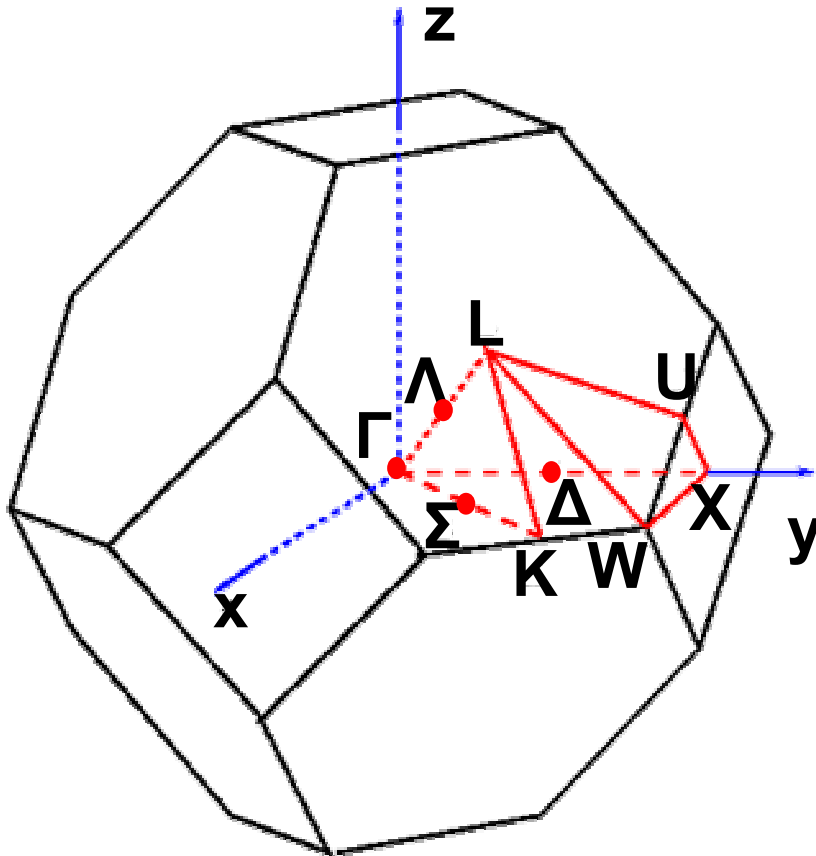
Electronic band structure

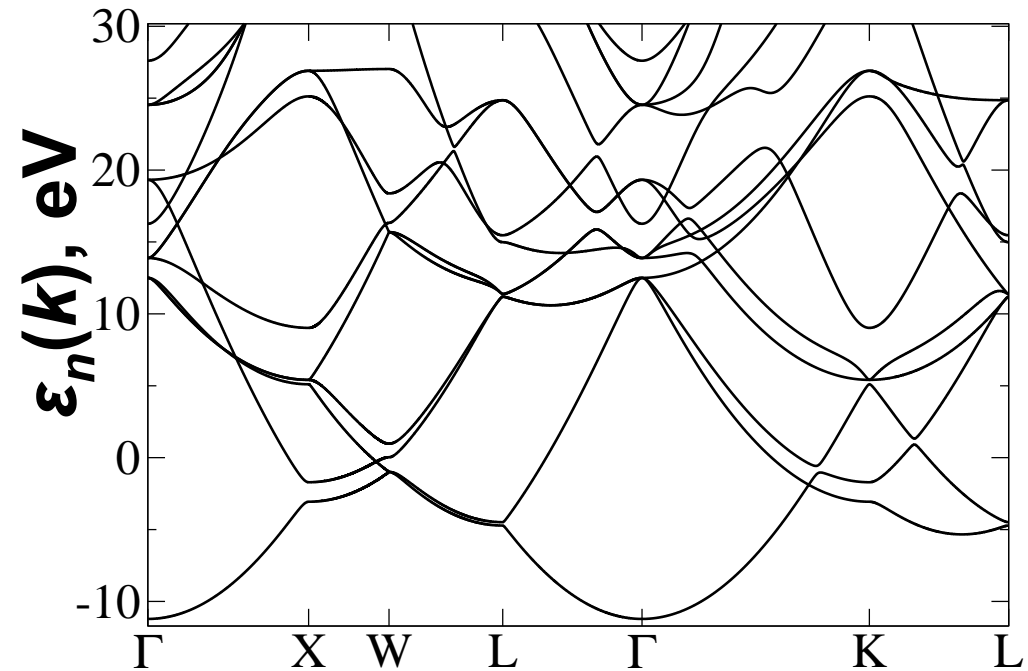Band structure represents dependence of $\varepsilon_{n\mathbf{k}}$ on $\mathbf{k}$

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 three dimensions

Brillouin zone of the fcc lattice

Al band structure (DFT-PBE)

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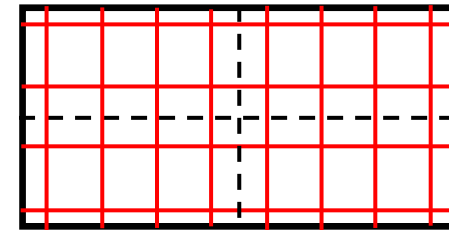
Finite k-point mesh

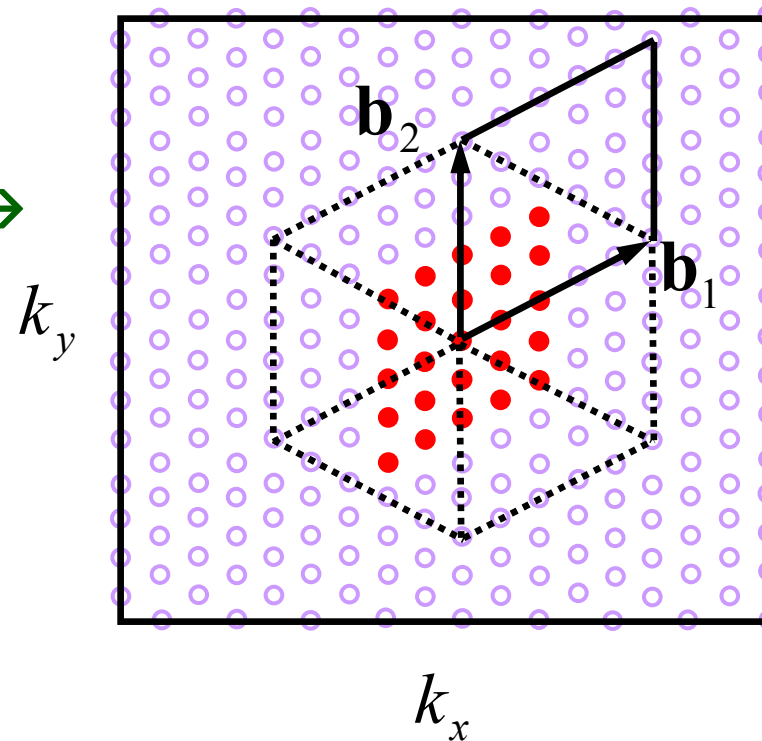**Charge densities and other quantities are represented by Brillouin zone integrals:**

$$n(\mathbf{r}) = \sum_j^{\text{occ}} \int_{\Omega_{\text{BZ}}} \left| \psi_{j\mathbf{k}}(\mathbf{r}) \right|^2 \frac{d^3k}{\Omega_{\text{BZ}}}$$

8x4 Monkhorst-Pack grid

$\psi_{n\mathbf{k}}$, $\varepsilon_{n\mathbf{k}}$ – *smooth* functions of k → **can use a finite mesh, and then** *interpolate* **and/or use perturbation theory to calculate integrals**
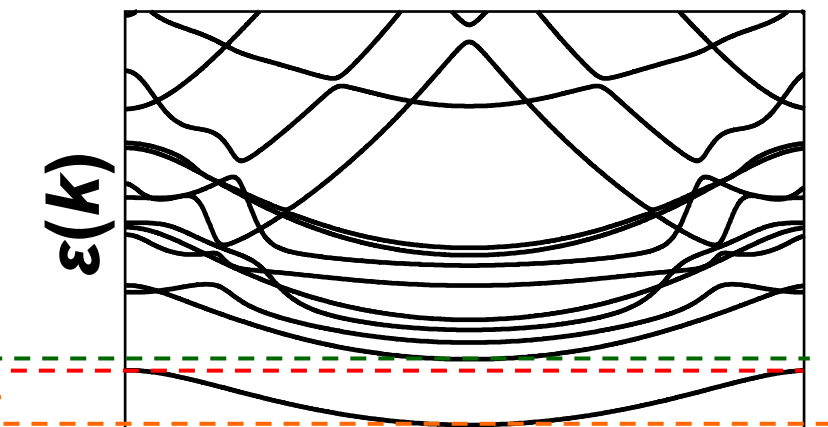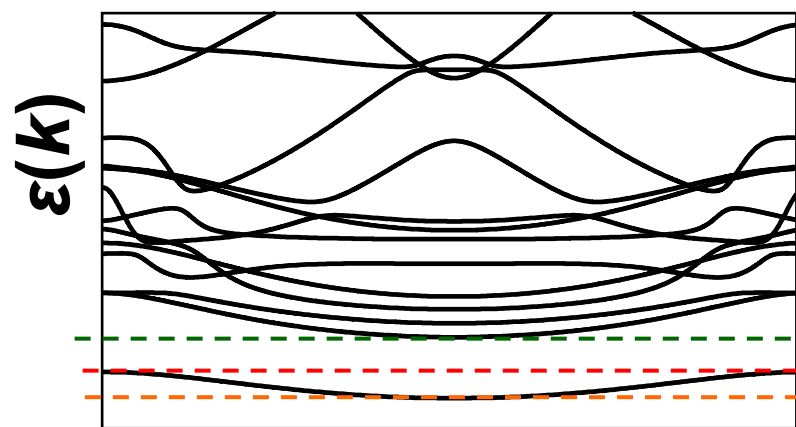
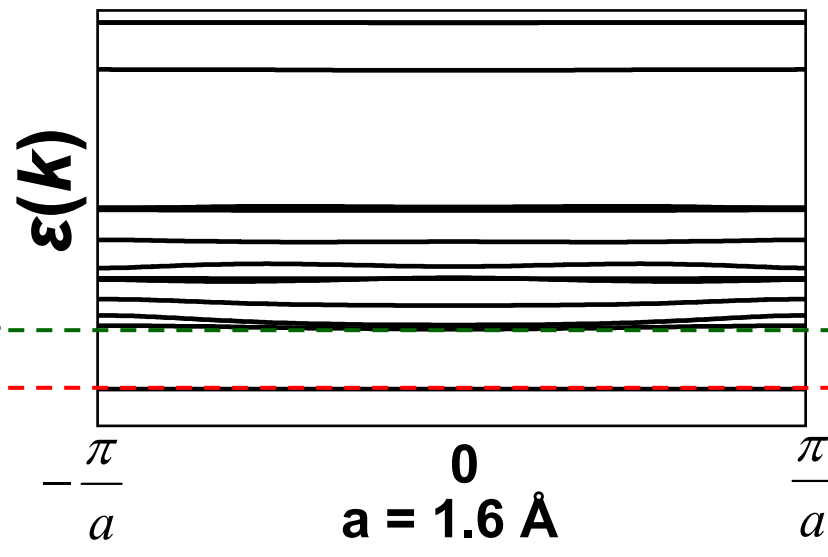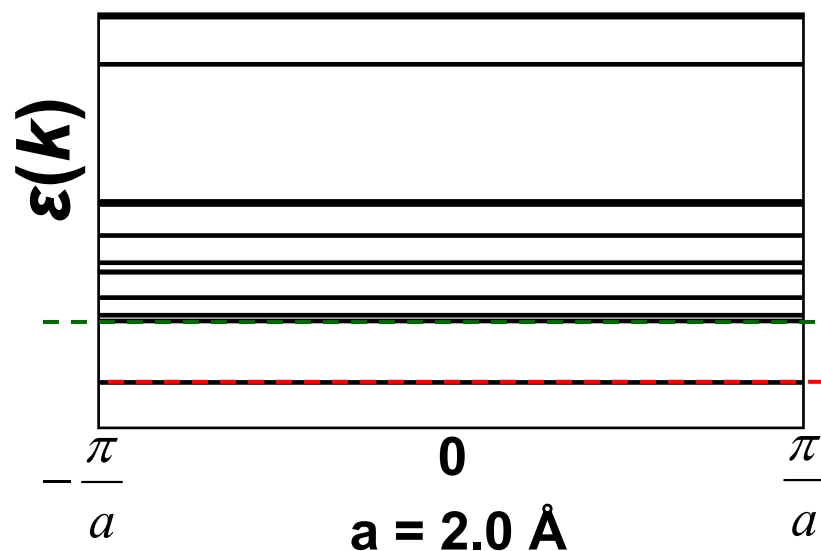$$n(\mathbf{r}) \approx \sum_j^{\text{occ}} \sum_{m=1}^{N_{\text{kpt}}} w_m \left| \psi_{j\mathbf{k}_m}(\mathbf{r}) \right|^2$$

k_y

$\mathbf{b}_2$

$\mathbf{b}_1$

k_x

H.J. Monkhorst and J.D. Pack, Phys. Rev.B **13**, 5188 (1976); Phys. Rev. B **16**, 1748 (1977)

Band gap and band width (dispersion)

0.8 Å — hydrogen molecule chain (DFT-PBE)

a ... a ... a ...

a = 10.0 Å

$\varepsilon(k)$

$-\frac{\pi}{a}$ 0 $\frac{\pi}{a}$

a = 5.0 Å

$\varepsilon(k)$

$-\frac{\pi}{a}$ 0 $\frac{\pi}{a}$

a = 2.0 Å
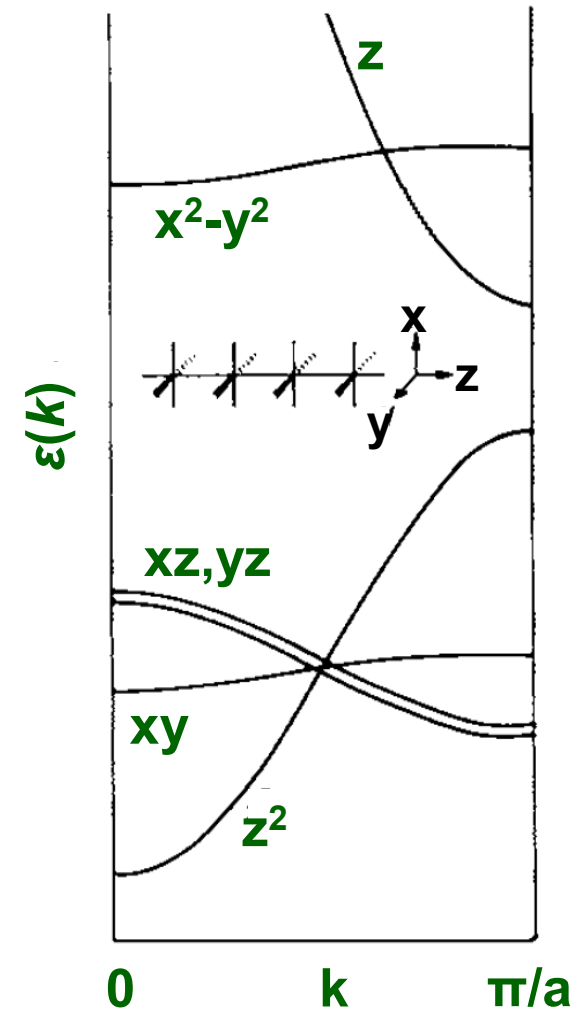
$\varepsilon(k)$
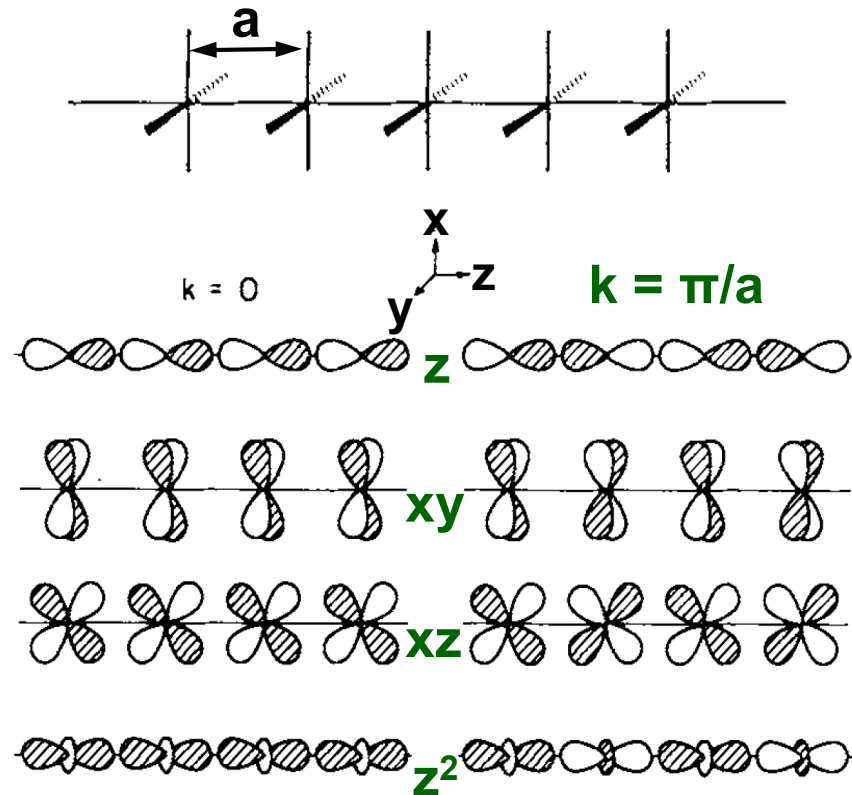
a = 1.6 Å

$\varepsilon(k)$
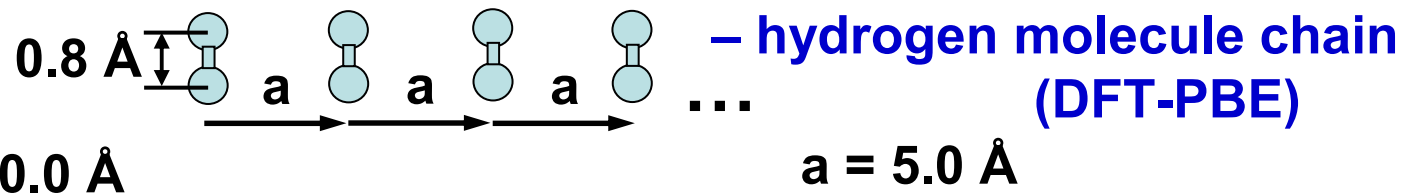
Overlap between interacting orbitals determines band gap and band width

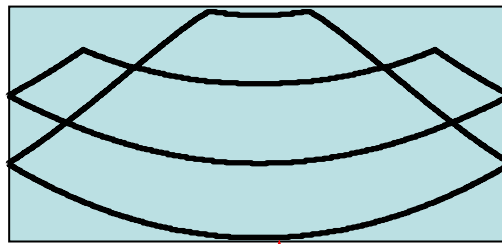# Band structure – test example

Orbital energies are smooth functions of k

Example: chain of Pt-L_4 complexes ($K_2[Pt(CN)_4]$)

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

Insulators, semiconductors, and metals

$E_g \gg k_B T$

$E_g \sim k_B T$

$E_g = 0$

ε_F

k
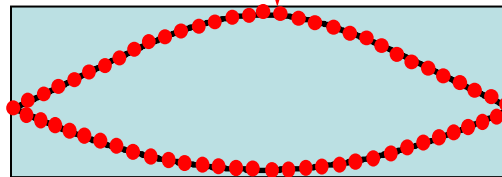
k

Insulators (MgO, NaCl, ZnO,…)
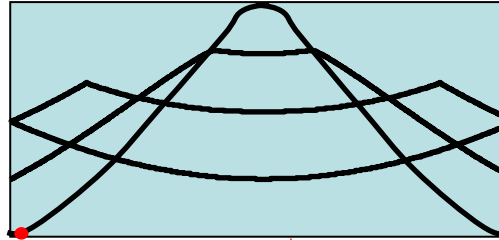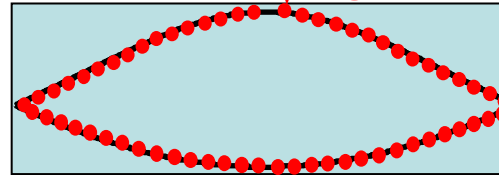
Semiconductors (Si, Ge,…)
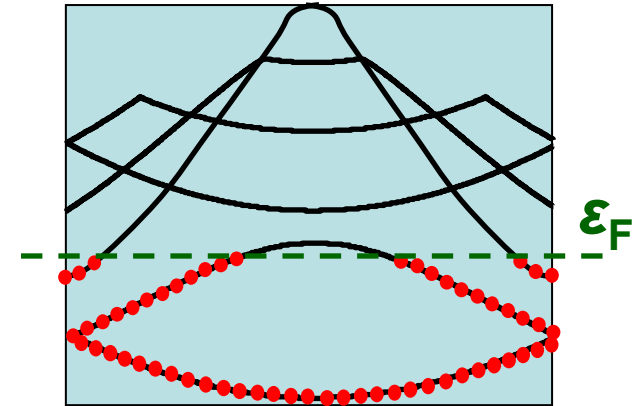
Metals (Cu, Al, Fe,…)

In a metal, some (at least one) energy bands are only partially occupied

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

Fermi surface

Plotting the relation

$$\varepsilon_n(\mathbf{k}) = \varepsilon_F$$

in reciprocal space for different *n* yields different parts of the Fermi surface

For free electrons, Fermi surface is a sphere
$$\frac{\hbar^2 \mathbf{k}^2}{2m_e} = \varepsilon_F$$

K
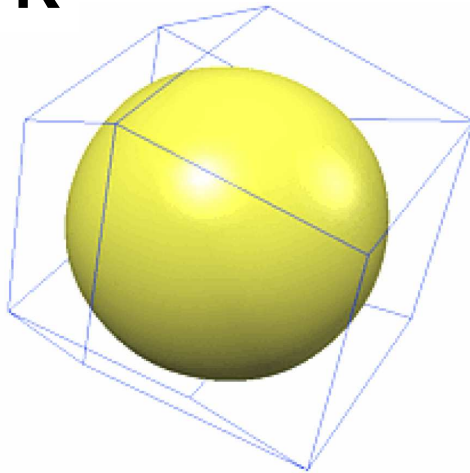
Cu
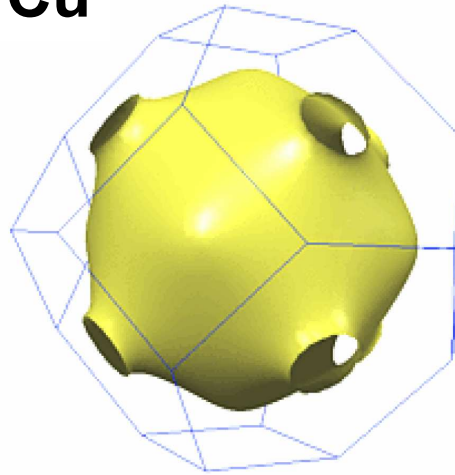
Al
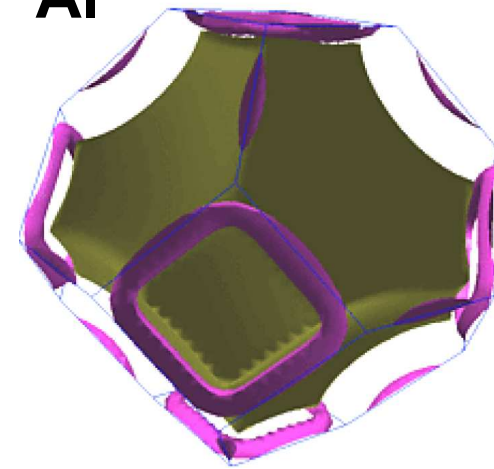
Periodic table of Fermi surfaces: http://www.phys.ufl.edu/fermisurface/

The grid used in k-space must be sufficiently fine to accurately sample the Fermi surface

Density Of States (DOS)

Number of states in energy interval *dε* per unit volume, $\frac{1}{\Omega d\varepsilon}\sum_{\varepsilon}^{\varepsilon+d\varepsilon}1$

$$g(\varepsilon) = \sum_{n}\int_{\Omega_{BZ}}\delta(\varepsilon - \varepsilon_n(\mathbf{k}))d^3k \approx \sum_{n}\sum_{j=1}^{N_{kpt}}w_j\delta(\varepsilon - \varepsilon_n(\mathbf{k}_j))$$
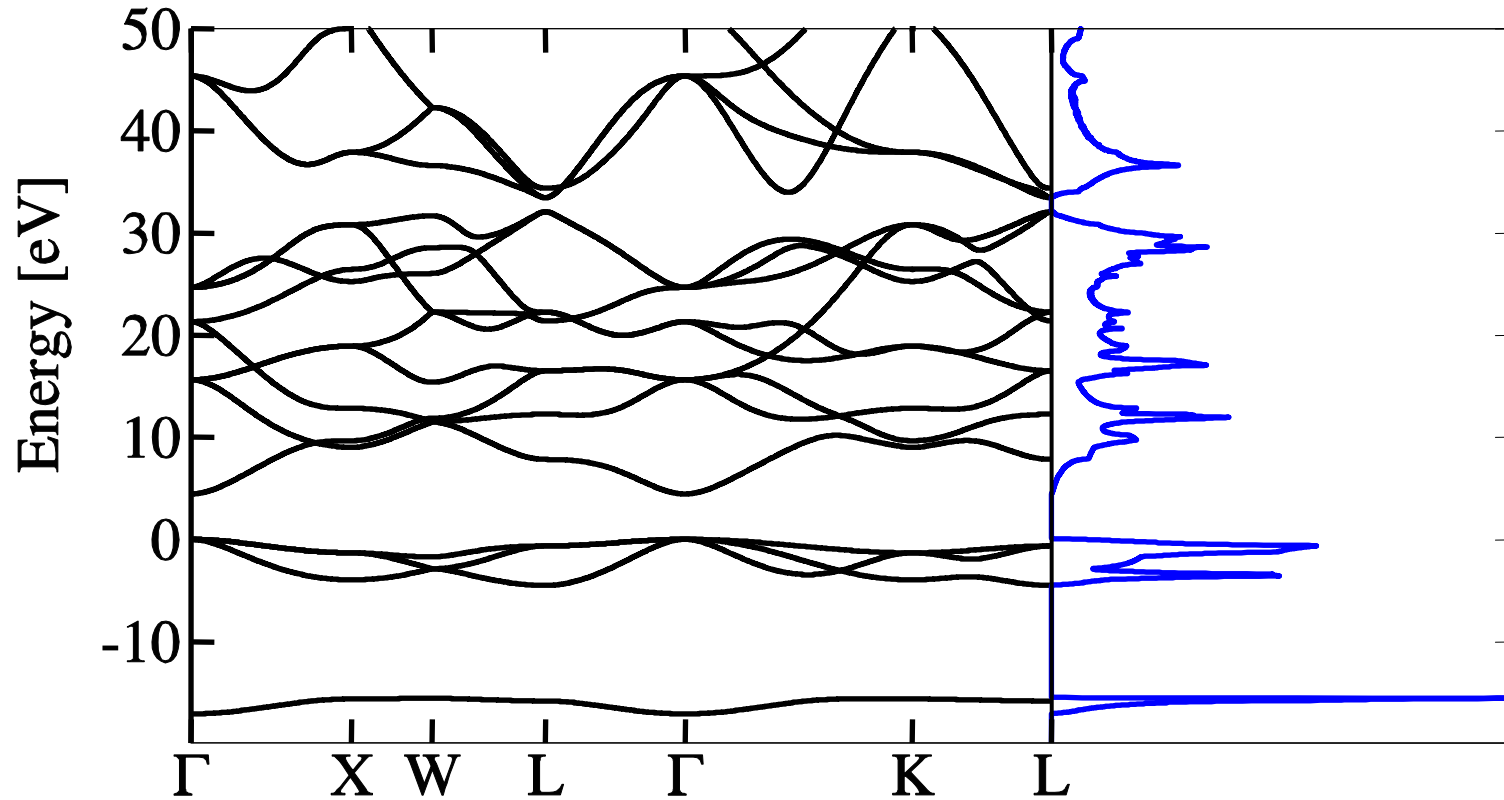
Atom-Projected Density Of States (APDOS)

Decomposition of DOS into contributions from different atomic functions φ_i :

$$g_i(\varepsilon) = \sum_n \int_{\Omega_{BZ}} \left| \int \varphi_i(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) d^3 r \right|^2 \delta(\varepsilon - \varepsilon_n(\mathbf{k})) d^3 k$$
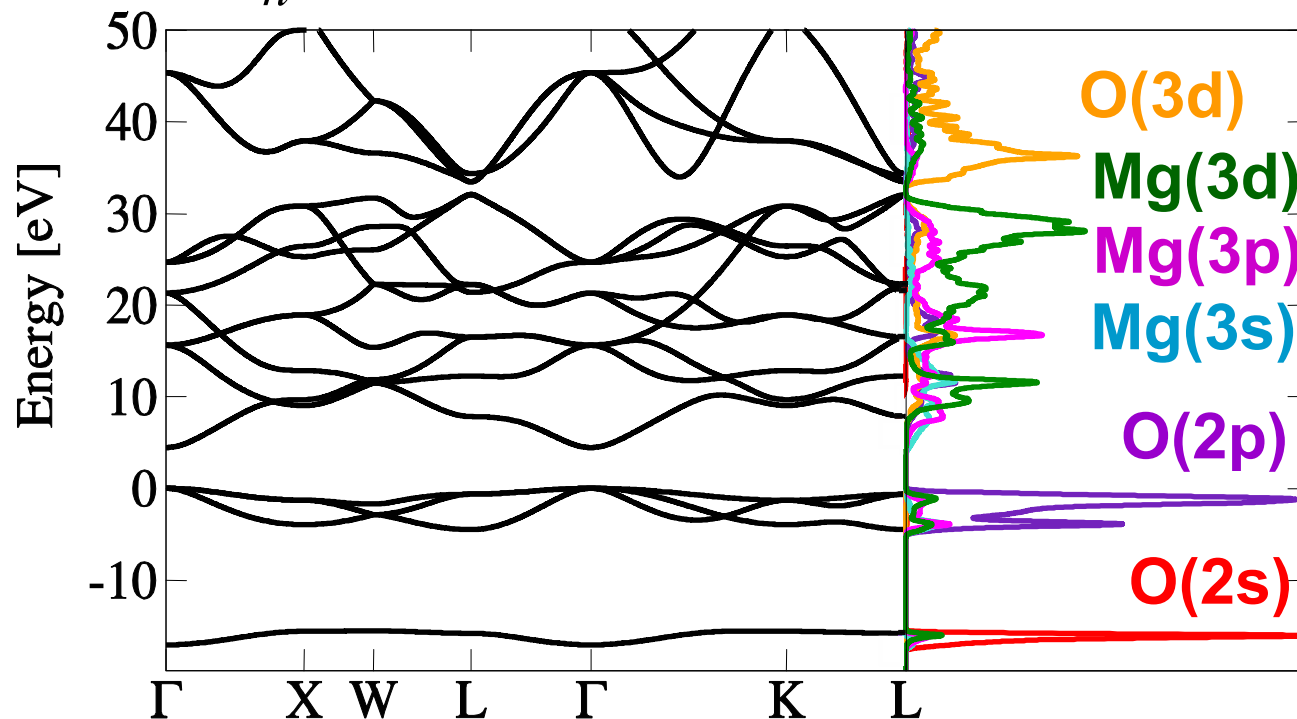
Recovery of the chemical interpretation in terms of orbitals

Qualitative analysis tool; ambiguities must be resolved by truncating the r-integral *or* by Löwdin orthogonalization of φ_i

Potential of an array of point charges

$$V(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{i=1}^{N} \frac{q_i}{|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|}, \quad \sum_{i=1}^{N} q_i = 0$$

Total potential at r=(0.05,0.05,0.05) Å, eV

Number of point charges
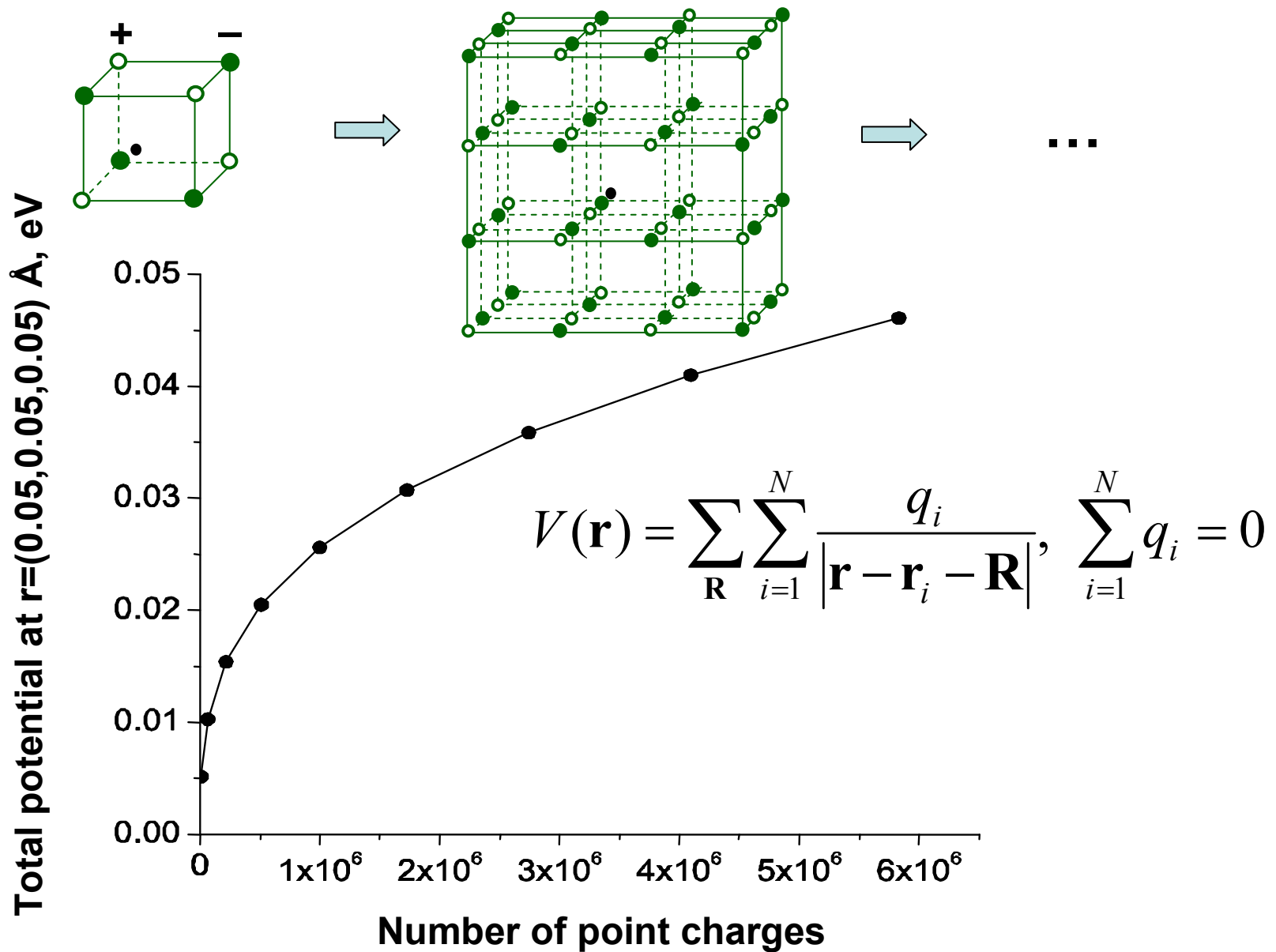
Convergence of the potential with number of charges is extremely slow

Ewald summation

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

$$\frac{1}{\eta\sqrt{\pi}} \exp\left(-(\mathbf{r} - \mathbf{r}_i)^2 / \eta^2\right)$$

+ $\equiv$

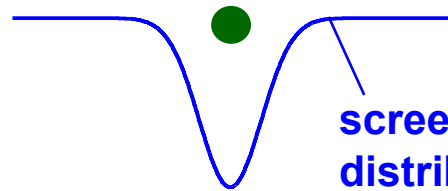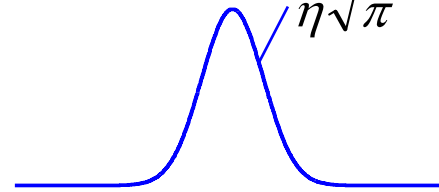**screening gaussian charge distribution**

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

(Poisson's equation)

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

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

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

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

Diverges at $\mathbf{G} = \mathbf{0}$**, but divergence**

is cancelled for $\displaystyle\sum_i q_i = 0$

There is no universal potential energy reference (like vacuum level) for periodic systems – important when comparing different systems
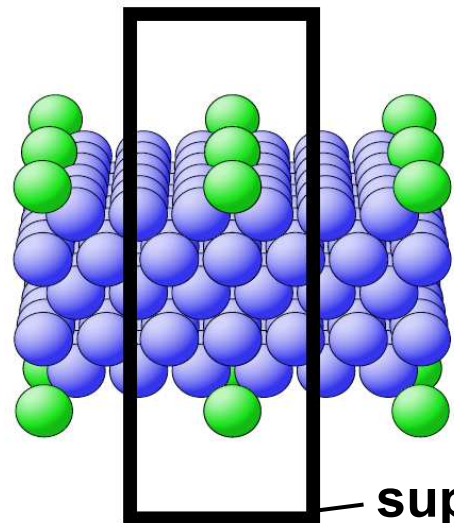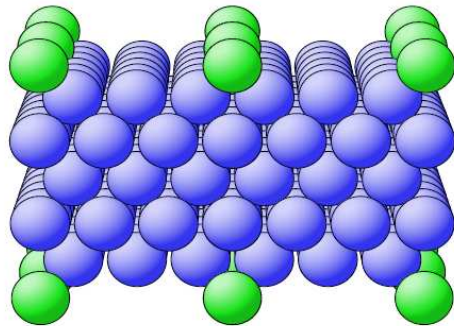
Modeling surfaces, interfaces, and point defects – the supercell approach

The supercell approach

Can we benefit from periodic modeling of non-periodic systems?

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

Supercell approach to surfaces (slab model)

- **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

Surface band structure

Example: fcc crystal, (111) surface

surface Brillouin zone
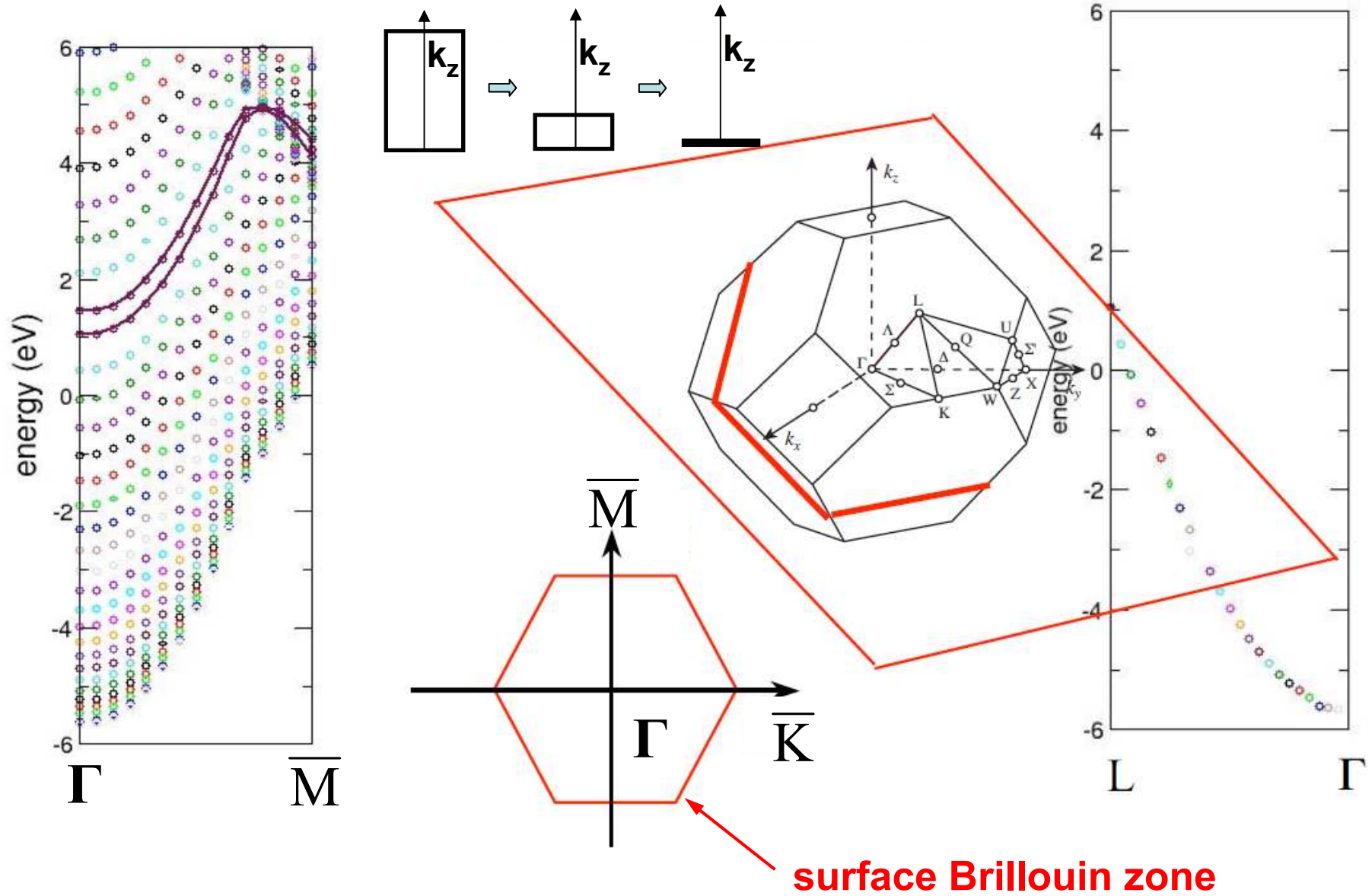
Surface band structure of Cu(111)

Shockley surface state

Tamm surface state

ε_F

Energy, eV

Cu(111)

$\overline{M}$ Γ $\overline{M}$
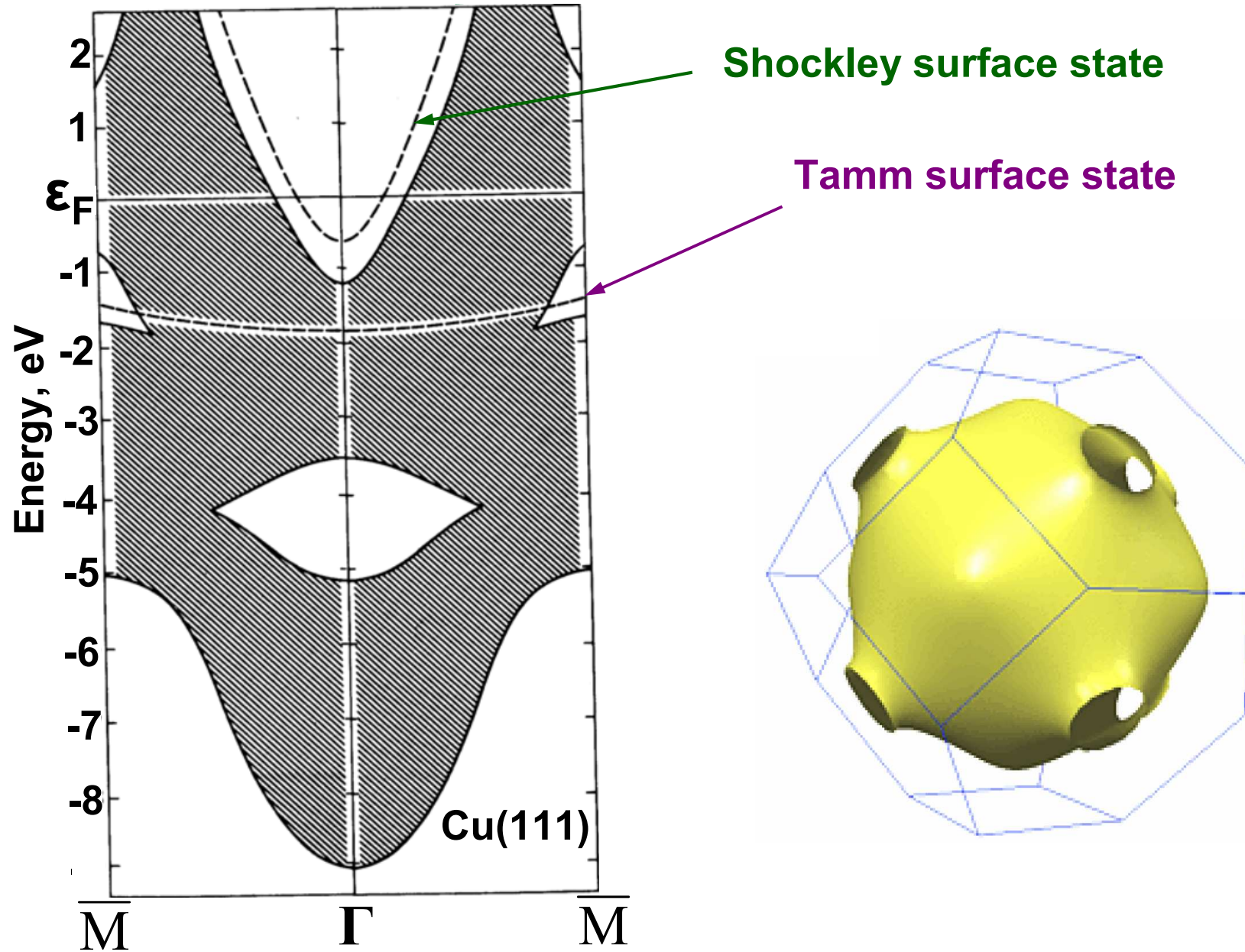
Shockley surface states
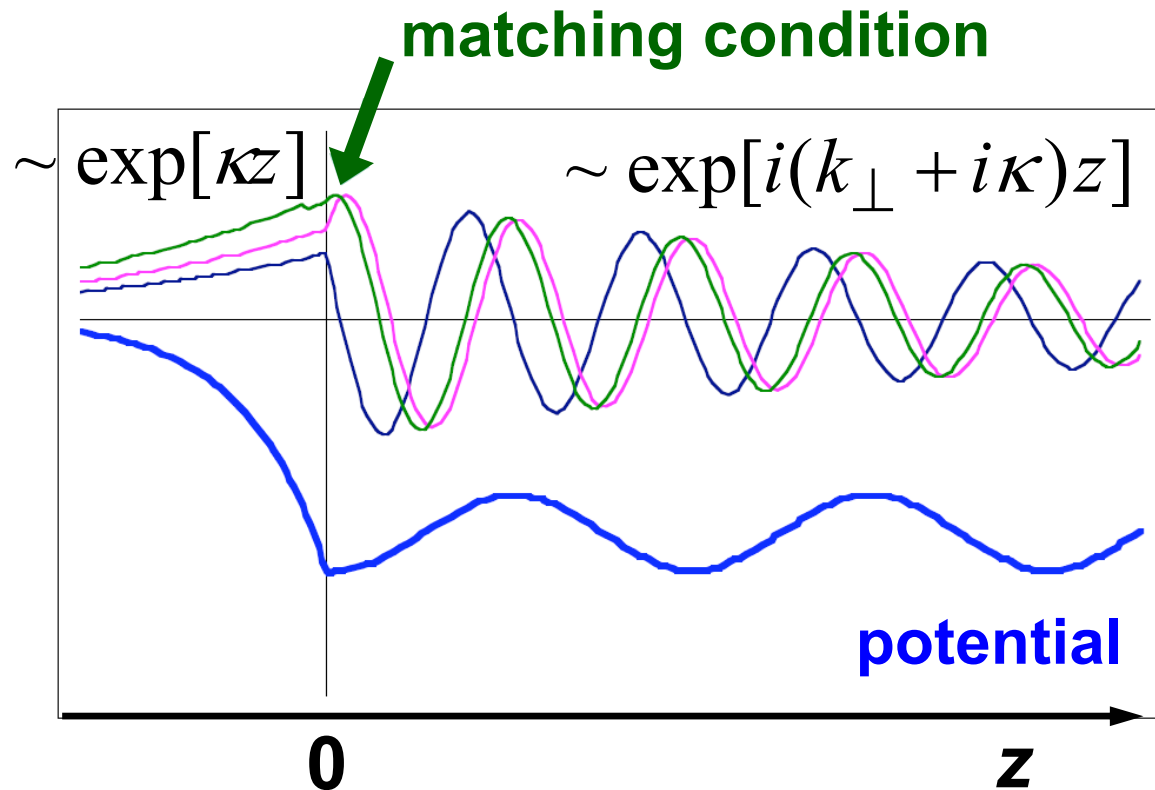
For near-free electrons: $\psi_{\mathbf{k}}(\mathbf{r}) \sim \exp(i\mathbf{k} \cdot \mathbf{r})$

matching condition

$\sim \exp[\kappa z]$ $\sim \exp[i(k_{\perp} + i\kappa)z]$

potential

0   **z**

Decaying states can be treated as Bloch states with complex k (W. Kohn, Phys. Rev., 115, 809 (1959))

Complex band structures can give useful information about conductance through interfaces and molecular junctions

Tamm surface states
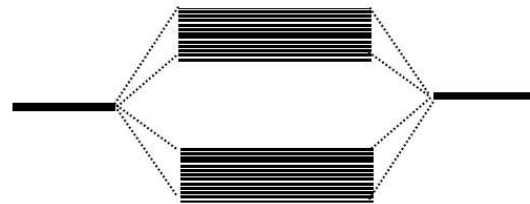
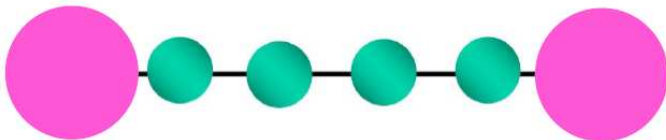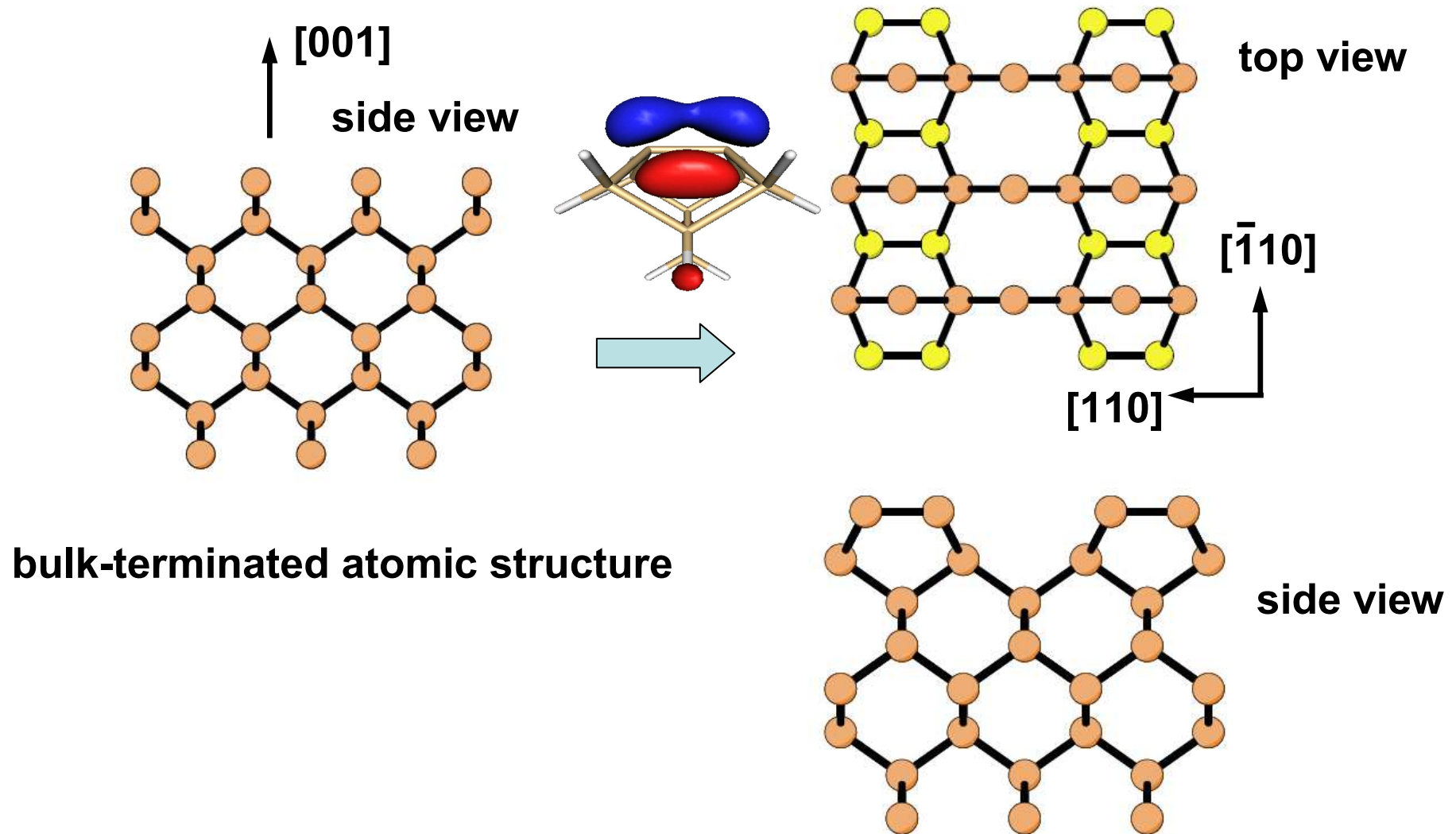In the tight-binding (localized orbital) picture, surface states may appear due to 'dangling orbitals' split off from the band edge

Surface reconstruction and band structure

Dimerization at (001)-surface of group IV-elements

[001]

side view

bulk-terminated atomic structure

top view

[$\bar{1}$10]

[110]

side view

Surface reconstruction and band structure

Buckling of dimers at Si (100) surface
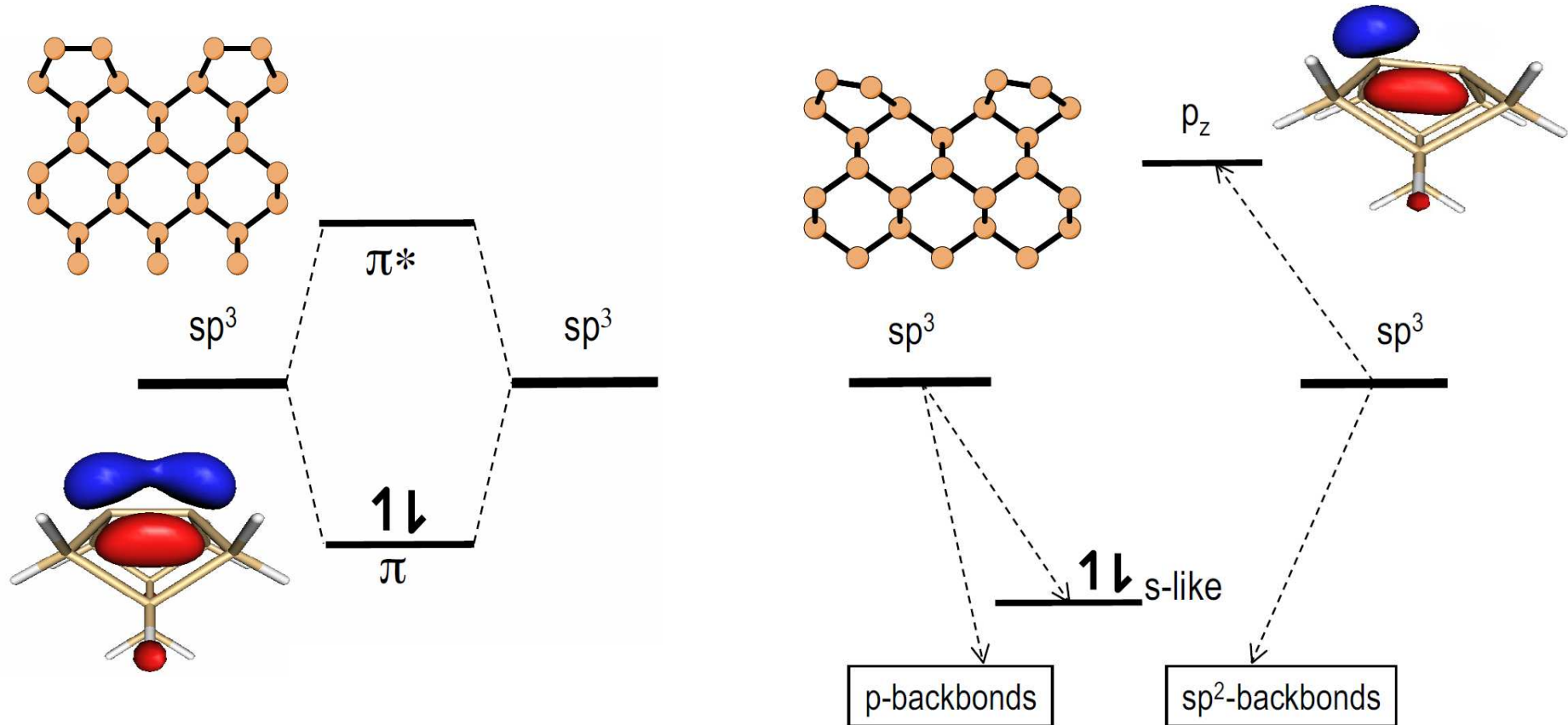
π-bond

re-hybridization and charge transfer (from down to up)

see, e.g., J. Dabrowski and M. Scheffler, Appl. Surf. Sci. **56-58,** 15 (1992)

Surface reconstruction and band structure

Si(001)-(2×1)

symmetric dimer model (SDM)

asymmetric dimer model (ADM)
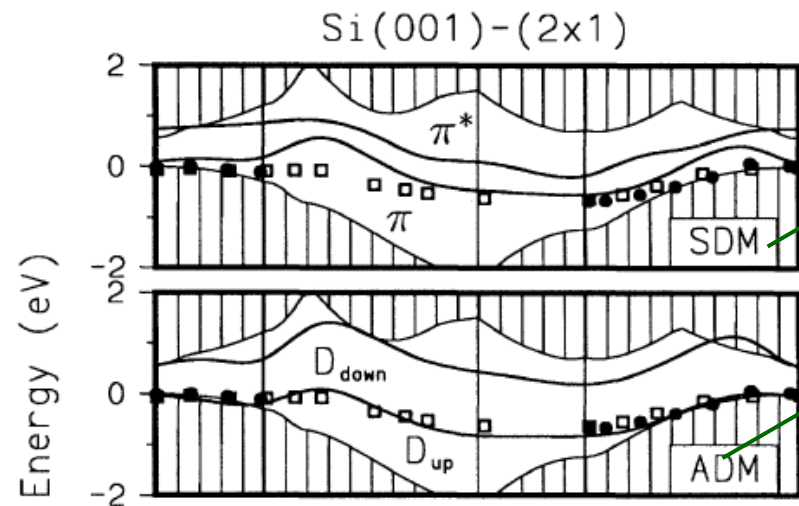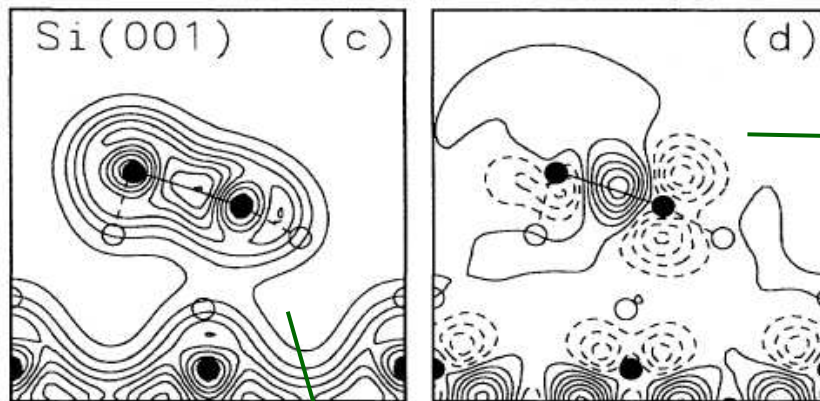
Experimental results from angular-resolved photo-emission spectroscopy

contour plot of electron density difference with respect to free Si atoms (dashed = decrease)

total density contour plot

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

Modeling charged defects in semiconductors

Defects and material properties

• Defects can transform insulator into a semiconductor or a metal (doping)

• Defects can determine optical properties (color)

• At surfaces, defects have unique chemical properties

• Defects can have different number of electrons associated with them (charge), and each charge state can have very different chemical properties

• Measuring concentration of defects, especially at temperatures and pressures relevant for practical applications, is very difficult


Mg   O
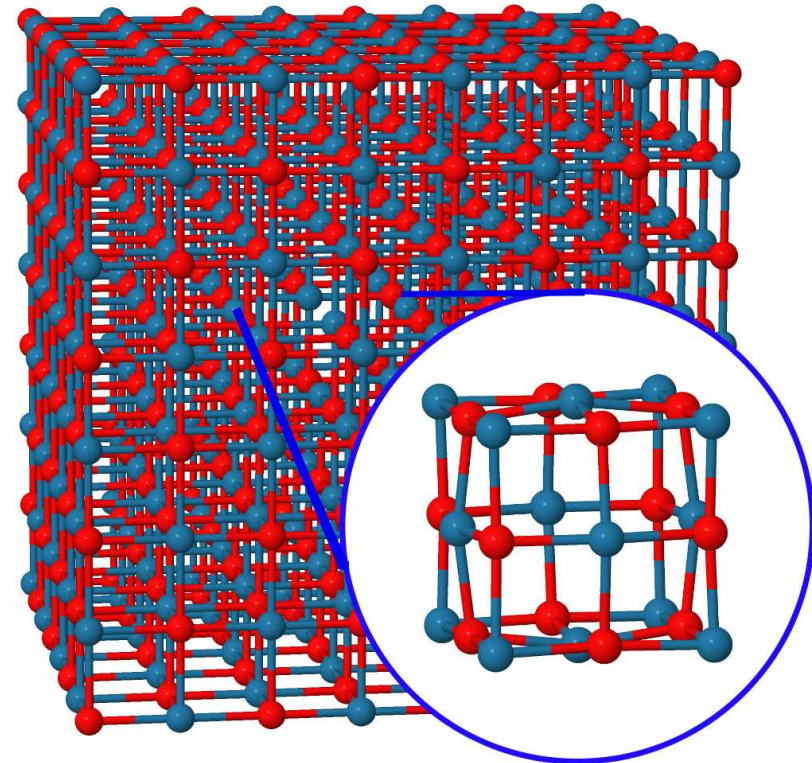
Charged periodic systems

The electrostatic energy of a charged periodic system diverges

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

For charged systems, removing $\mathbf{G}=0$ term $\leftrightarrow$ *uniform compensating background charge*

- **Can model *isolated* charged defects in the *bulk***

- **Interaction of charged defects with each other and with the background can be removed using a correction scheme**

- **Special care must be taken to align potential reference in systems with different charge per unit cell**

background in vacuum

- **Cannot be applied to surfaces**
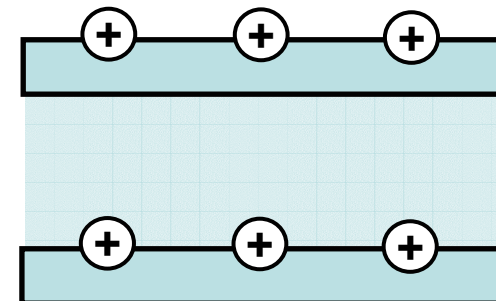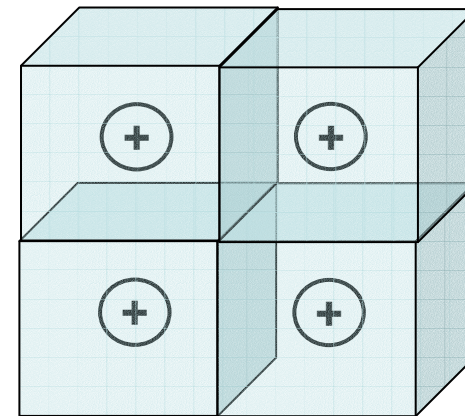
Example: Oxygen vacancies on MgO (100) surface
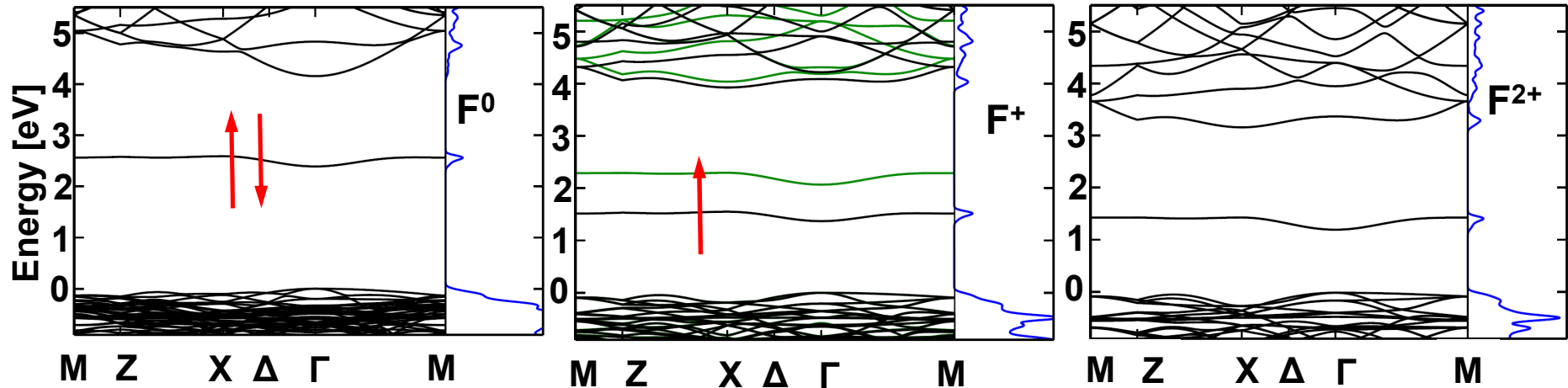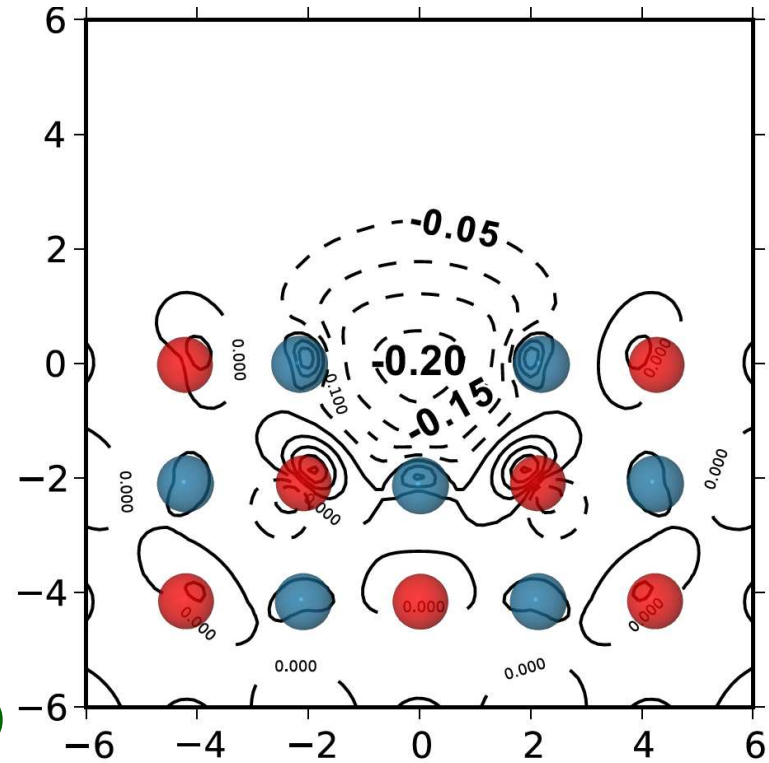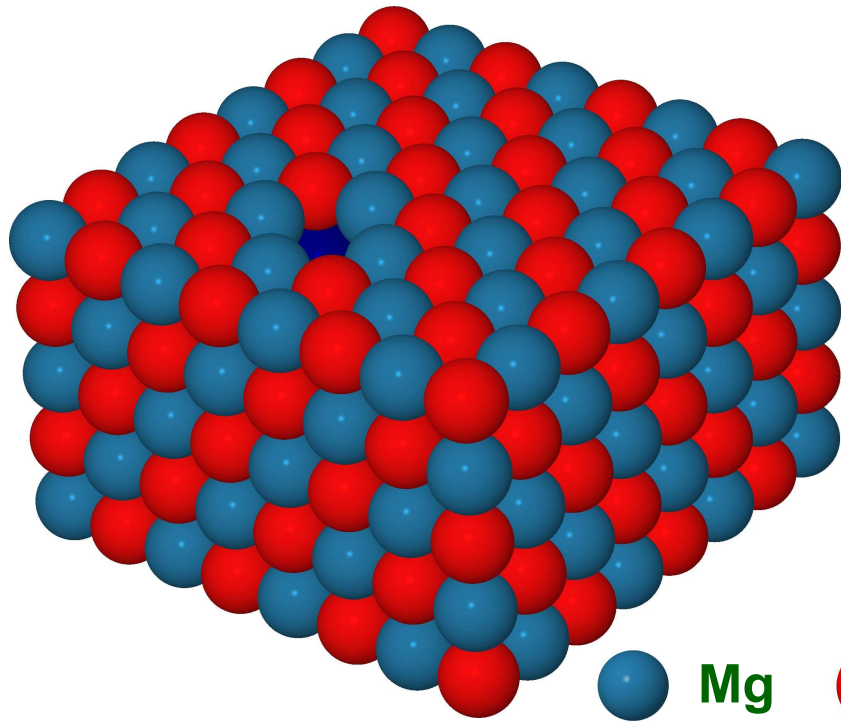
Contributions to the vacancy formation energy

$$\Delta E_{\text{DFT}}^{\text{f}} \approx E_{\text{def}}^{\text{total}} + \frac{1}{2} E_{\text{O}_2}^{\text{total}} - E_{\text{perf}}^{\text{total}}$$

1) Local bonding (ionic or covalent)

2) Atomic and electronic relaxation (change in local bonding, screening)

top view

F^{2+}

0.18 Å

0.25 Å

0.25Å

0.18 Å

side view

Mg   O
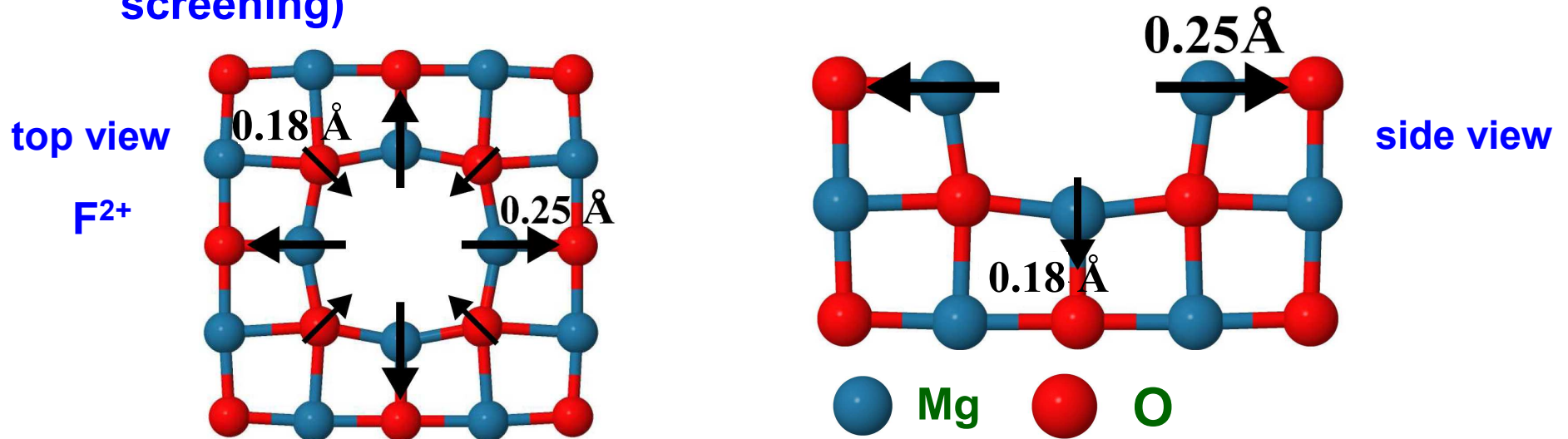
3) Electron transfer (charging)

conduction band

The Fermi level can be tuned by doping, electric field, excitations

ε_F ────────────────── defect level

Doping can occur intentionally and unintentionally

valence band
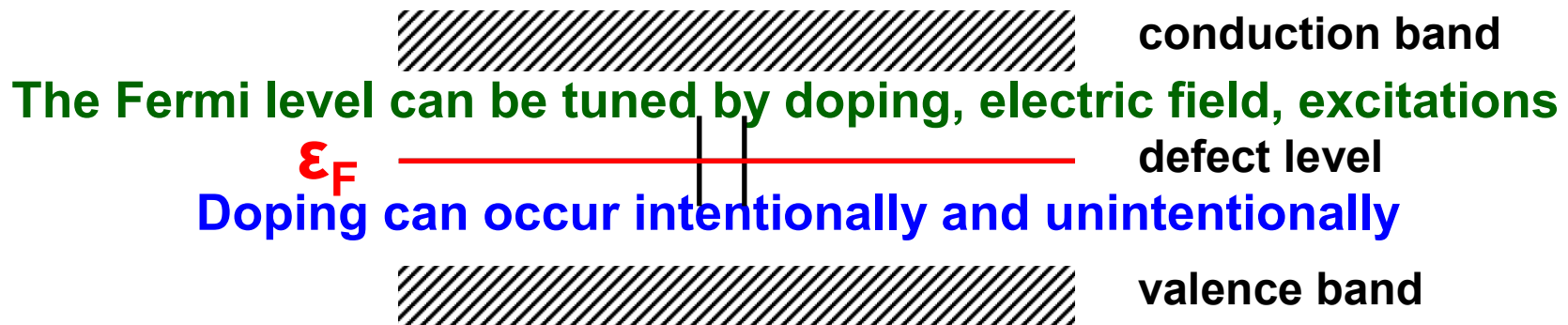
Alternative approaches: Virtual Crystal Approximation (VCA)

Simulate distributed doping via VCA (L. Vegard, Z. Phys. 5, 17 (1921); M. Scheffler, Physica 146B, 176 (1987))

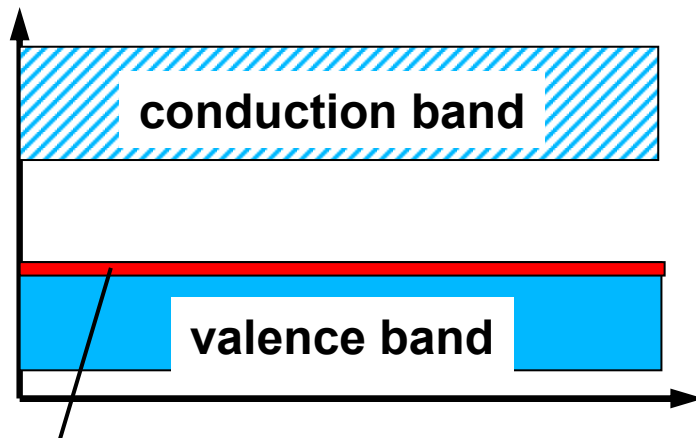$$q_{Mg} = 12 - q_{defect}/N_{Mg}$$ — modified Mg nuclear charge

p-type doping:

pristine surface band structure

surface O vacancy band structure

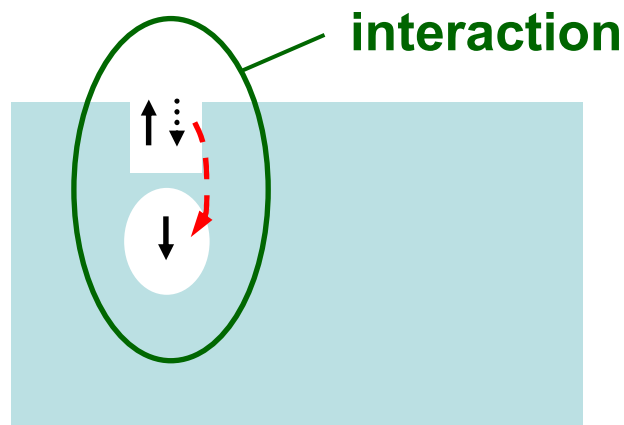empty states (O 2*p*) at the top of the valence band
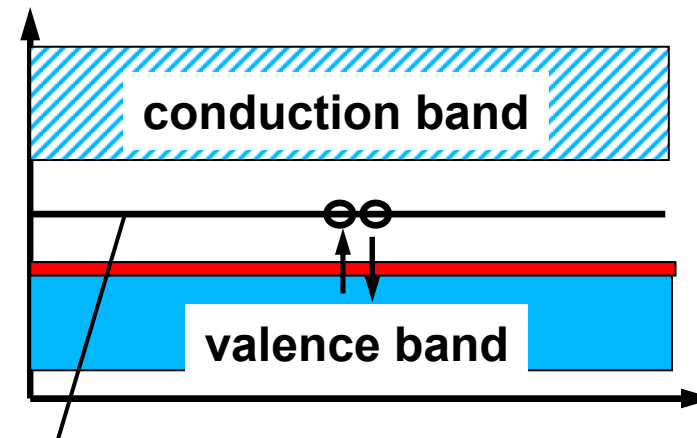
defect level

1) can be applied to surfaces

2) reference energy is well defined (VBM)

Alternative approaches: Introducing explicit dopants

May require larger supercell due to geometric constraints

**Two different effects of doping must be distinguished:
local (interaction between the defect and the dopant site) and global
(electron transfer to/from distant isolated dopant sites)**

Local effect of doping

Global effect of doping

A. Schindlmayr and M. Scheffler, In *Theory of Defects in Semiconductors*; D. A. Drabold, S. E. Estreicher, Eds. Springer Verlag: Berlin, Germany, 2007, p. 165; Bo Li and Horia Metiu, J. Phys. Chem. C **114**, 12234 (2010)
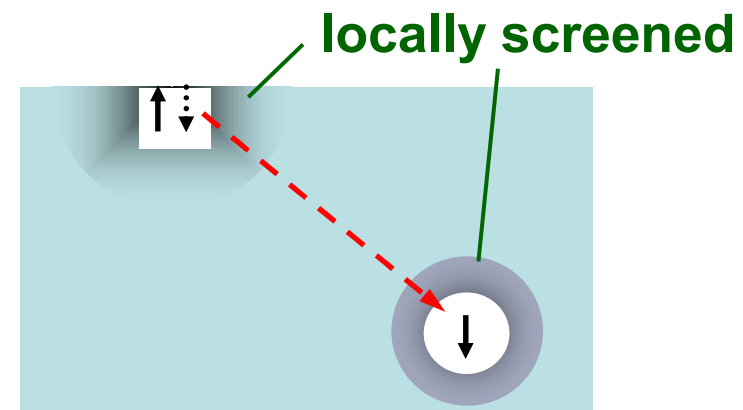
Formation energies of charged O vacancies on MgO (100)

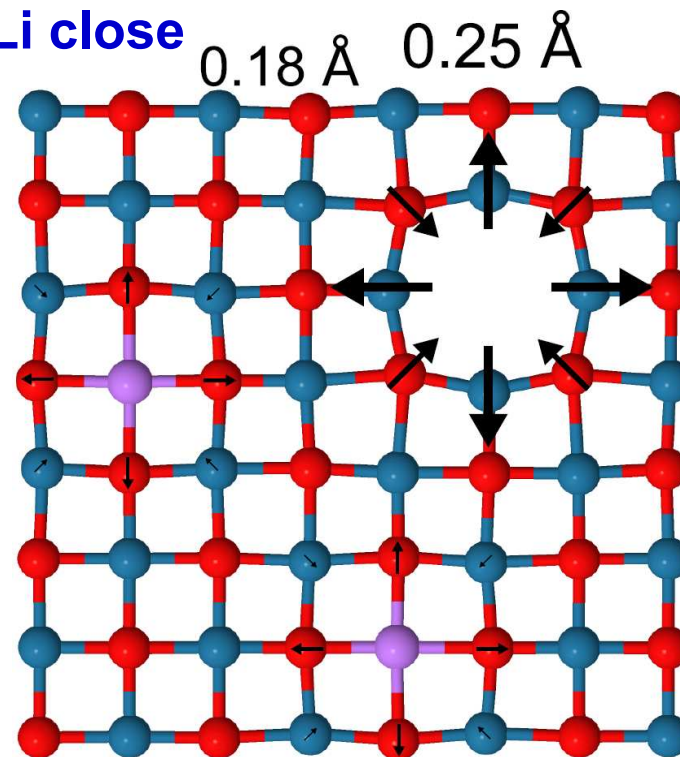$$\Delta E_{\text{DFT}}^{\text{f}} \approx E_{\text{def}}^{\text{total}} + \frac{1}{2} E_{O_2}^{\text{total}} - E_{\text{perf}}^{\text{total}}$$
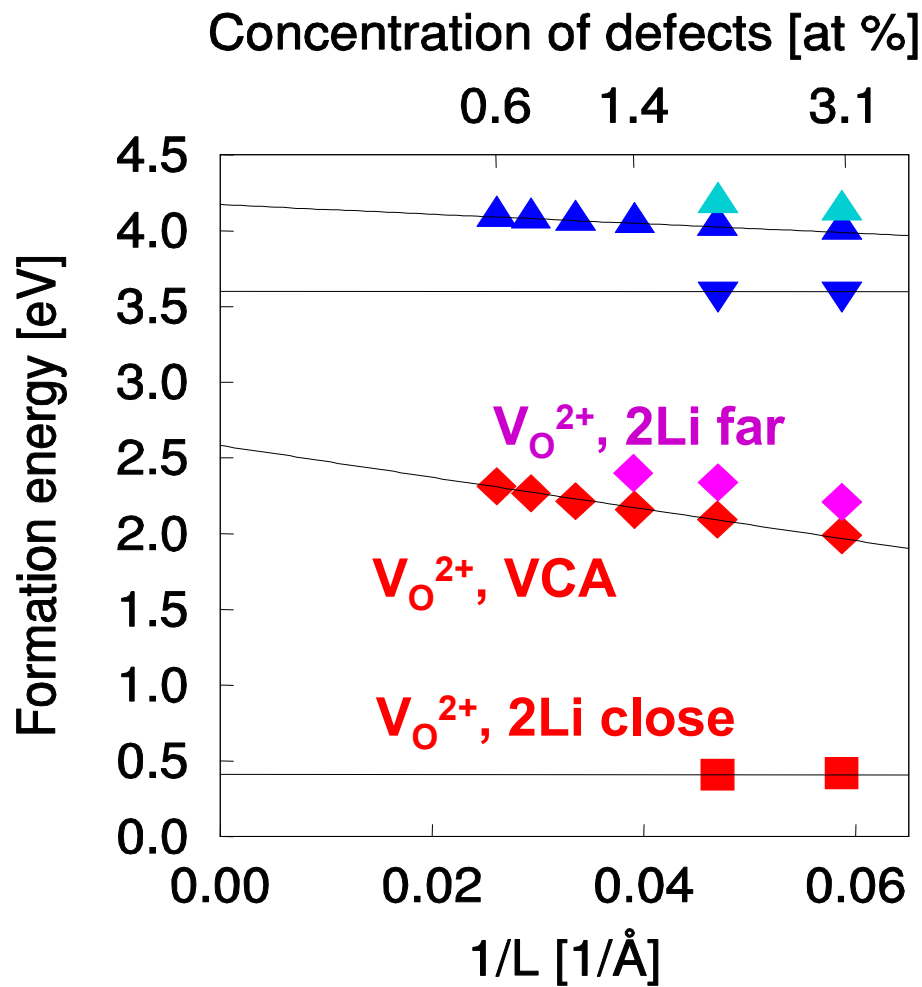
Concluding remarks

1) Periodic models can be efficiently used to study concentration/coverage dependence, including infinitely dilute limit (low-dimensional systems, defects, etc.)

2) A lot of useful and experimentally testable information on material's properties can be obtained from the analysis of its electronic structure (band structure, DOS, APDOS, etc.)

3) A lot of development (in both computational methods and code efficiency) is still necessary to go beyond standard DFT for periodic systems, and to approach accuracy that can be achieved nowadays for molecules

Recommended literature

Neil W. Ashcroft and N. David Mermin, "*Solid state physics*"

Axel Groß, "*Theoretical surface science: A microscopic perspective*"

Roald Hoffmann (1981 Noble Prize in Chemistry (shared with Kenichi Fukui)):

1) "*How Chemistry and Physics Meet in the Solid State*", Angew. Chem. Int. Ed. Engl. 26, 846-878 (1987)
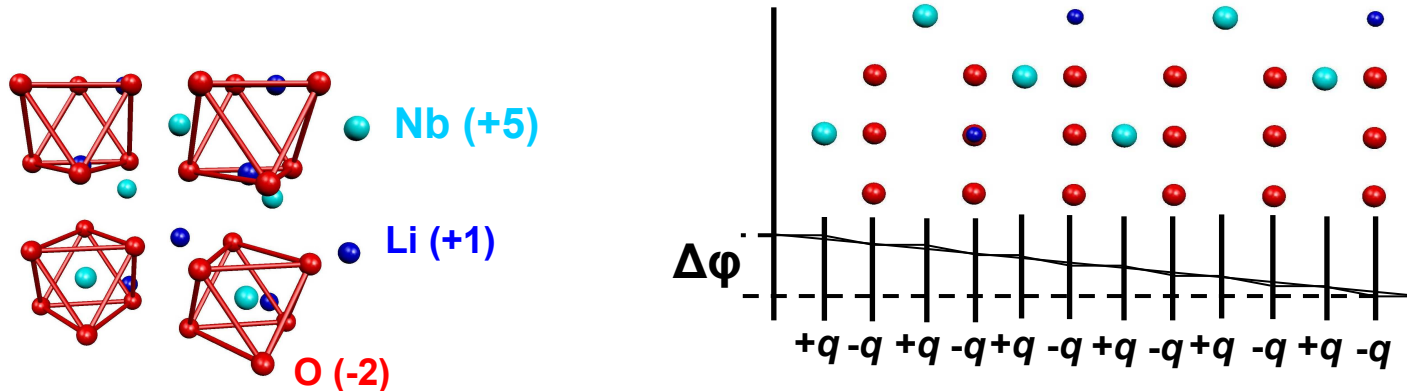
2) "*A chemical and theoretical way to look at bonding on surfaces*", Reviews of modern physics, 60, 601-628 (1988)

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)

periodic boundary conditions

artificial electric field
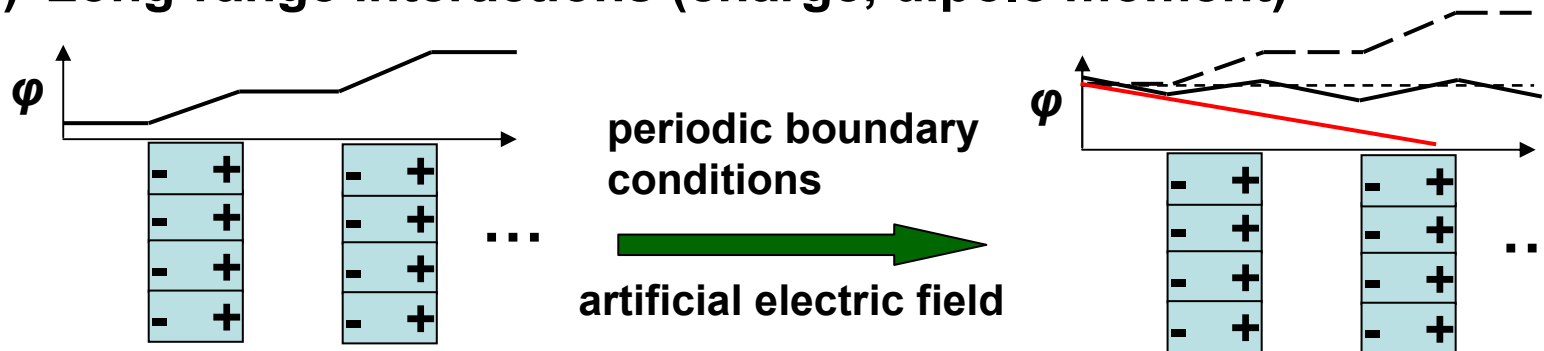
4) Surface polarity

Nb (+5)

Li (+1)

O (-2)

$\Delta\varphi$

$+q$ $-q$ $+q$ $-q$ $+q$ $-q$ $+q$ $-q$ $+q$ $-q$ $+q$ $-q$

Shockley surface states

For nearly-free electrons:

$\varepsilon(k_\perp)$

gap

$2|V_G|$

$i\kappa$

0

$\dfrac{\pi}{a}$

$k_\perp$

$\sim \exp[\kappa z]$

$\sim \exp[i(k_\perp + i\kappa)z]$

potential

0

z