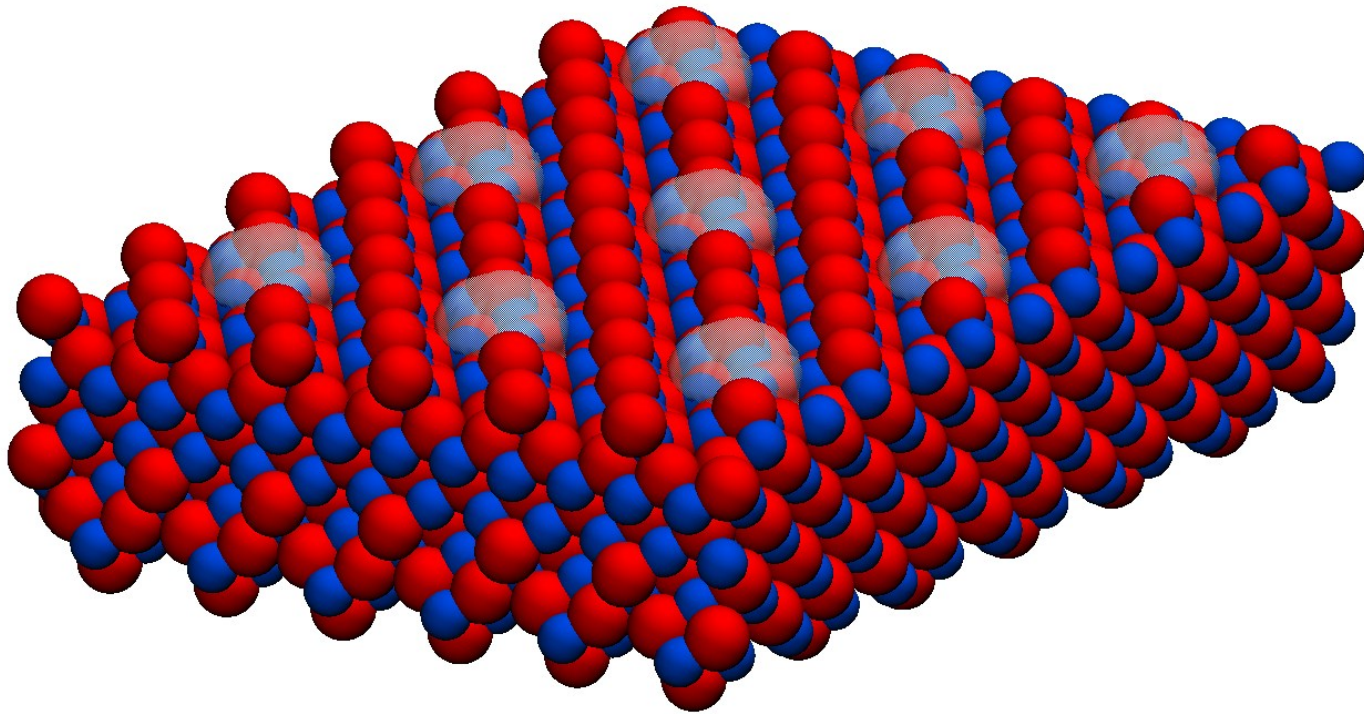


Periodic systems: Concepts



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Skoltech and FHI Theory department

Reminder: electronic-structure problem

$$\hat{h}\psi_i = \varepsilon_i\psi_i$$

$$\hat{h} = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \hat{V}_{XC}$$

ψ_i - unknown functions (one-electron wave functions)

$$\psi_i(\mathbf{r}) = \sum_p C_{ip} \phi_p(\mathbf{r}) \quad \text{- basis set expansion}$$

$\phi_p(\mathbf{r})$ - known functions (basis functions)

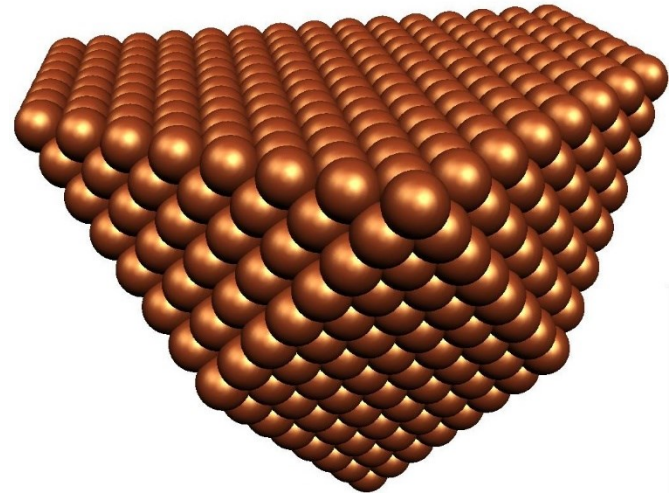
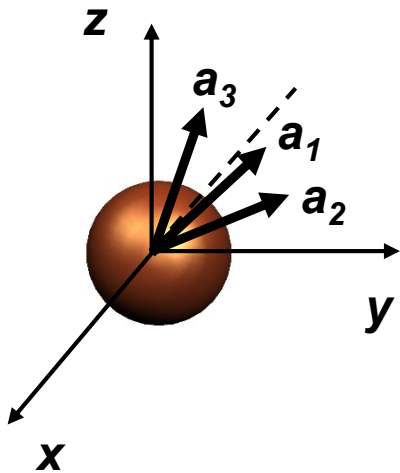


Generalized eigenvalue problem:

$$\sum_q \langle \phi_p | \hat{h}[\mathbf{C}] | \phi_q \rangle C_{iq} = \varepsilon_i \sum_q \langle \phi_p | \phi_q \rangle C_{iq}$$

Extended (periodic) systems

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



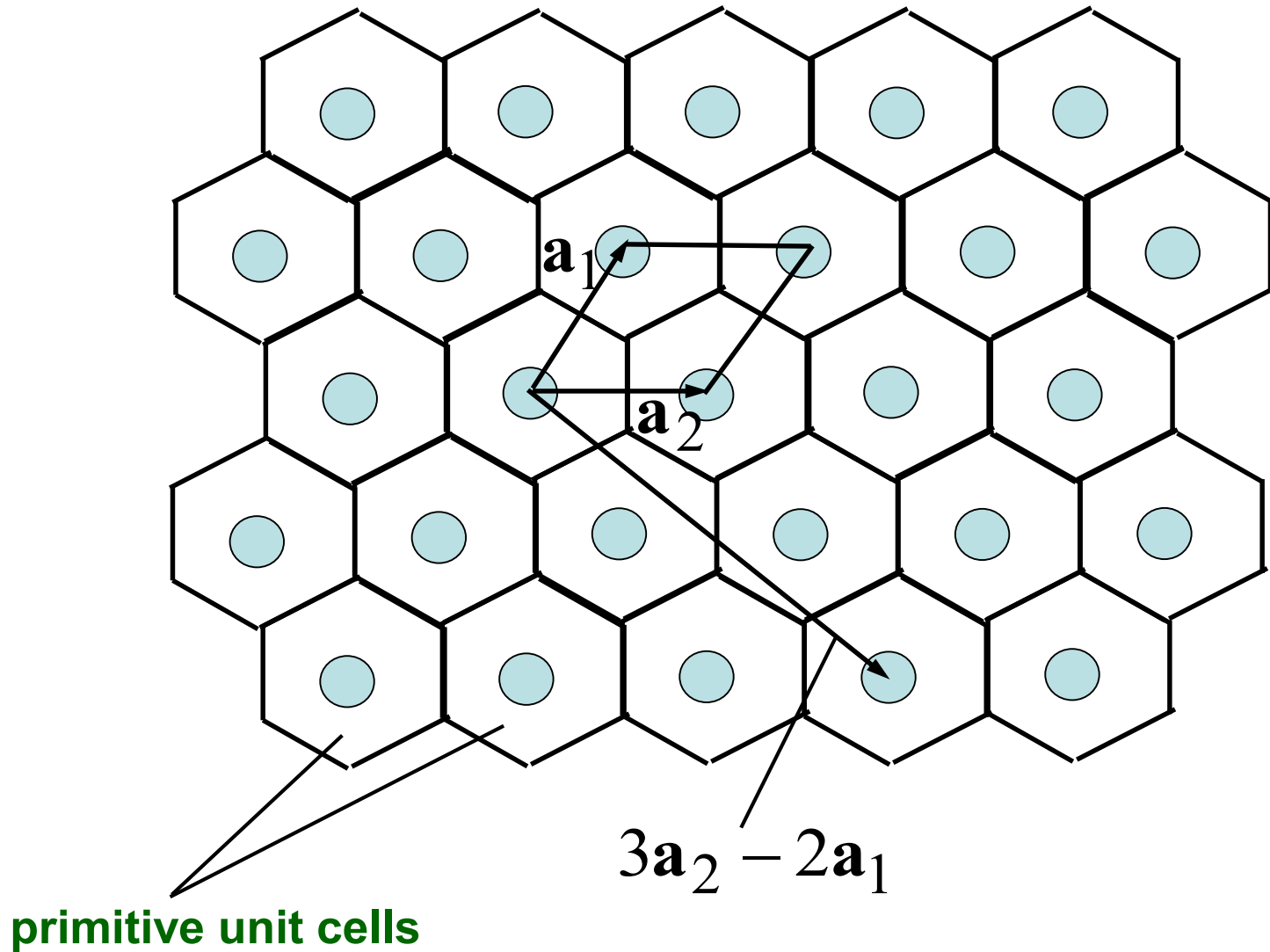
Position of every atom in the crystal (Bravais lattice):

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

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

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

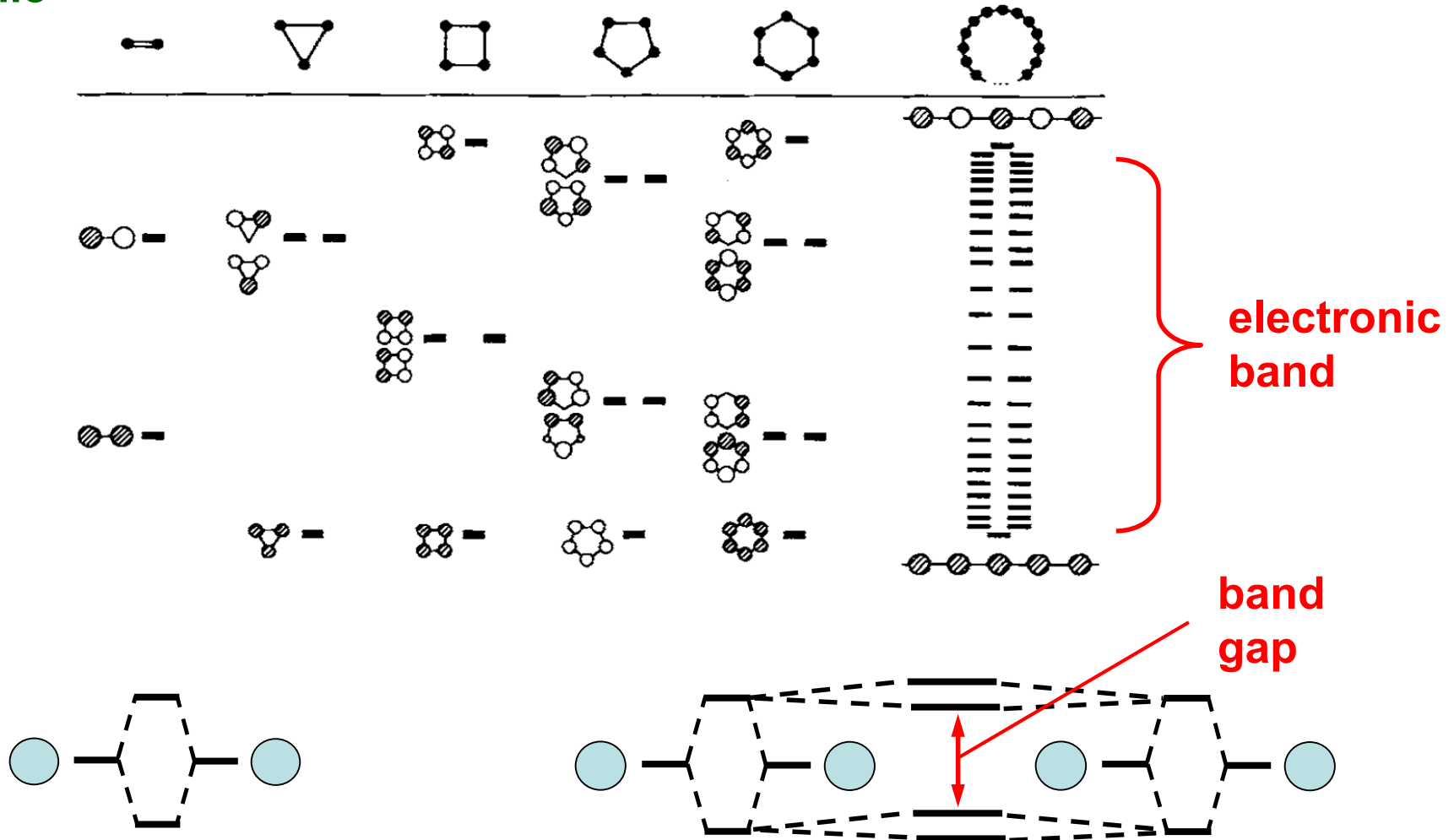
Example: two-dimensional Bravais lattice



The shape 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:



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

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

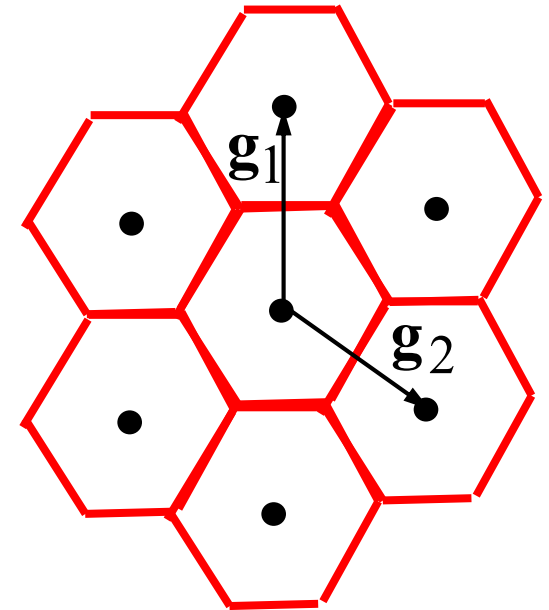
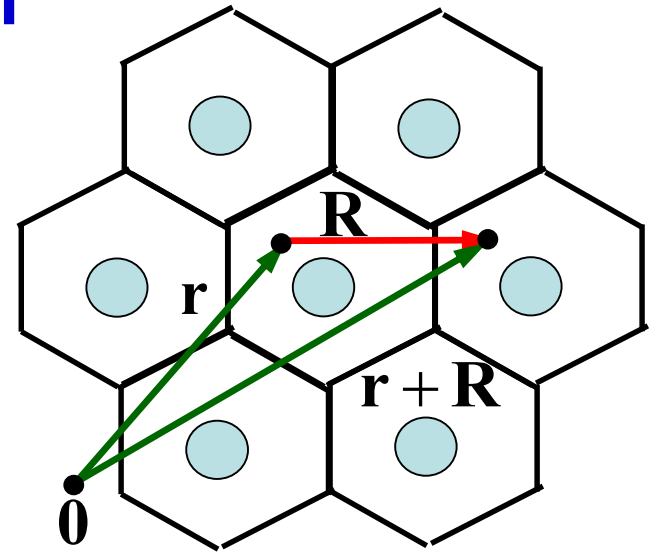
Index \mathbf{k} is a vector in *reciprocal space*

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

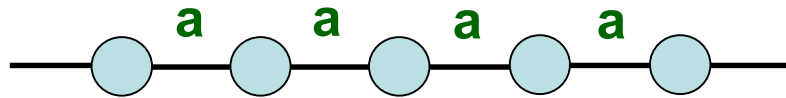
$$\mathbf{g}_l = 2\pi \frac{\mathbf{a}_m \times \mathbf{a}_n}{\Omega} \quad \text{-- reciprocal lattice vectors}$$

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

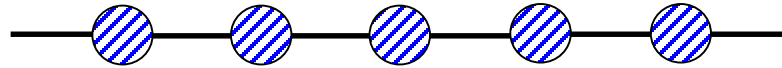


chain of hydrogen atoms

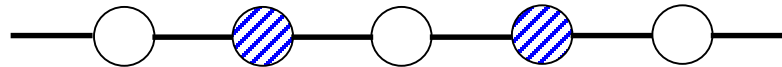
$$\psi_k = \sum_j \exp(ikx_j) \chi_{1s}(j \cdot a)$$

k shows the phase with which the orbitals are combined:

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



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



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

Bloch's theorem: consequences

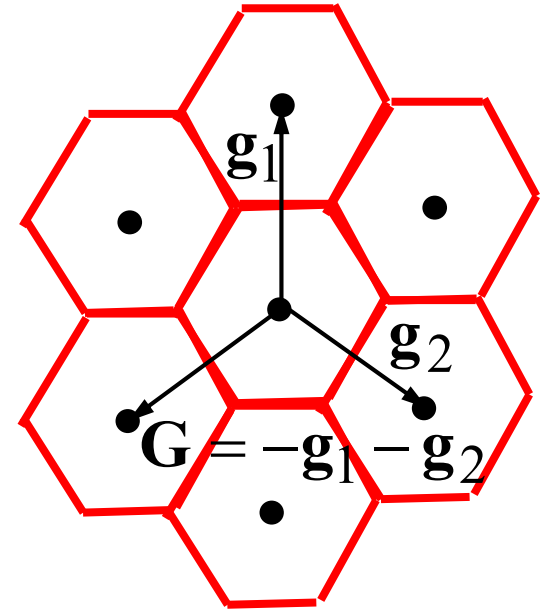
In a periodic system, the solutions of the Schrödinger equations are characterized by an integer number n (called *band index*) and a vector \mathbf{k} :

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

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

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}

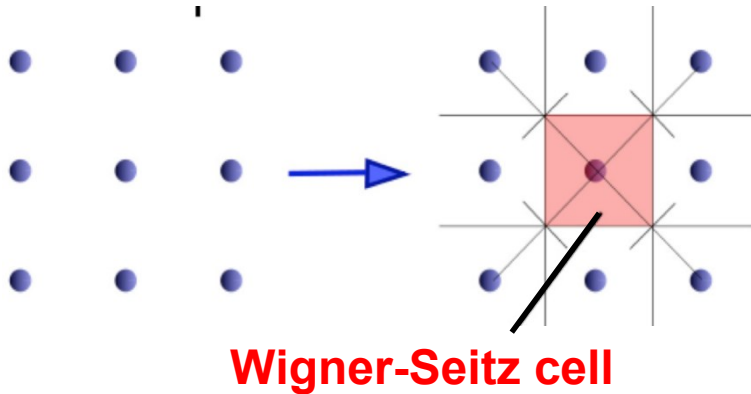
a Bloch state at \mathbf{k} with a different index n'

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

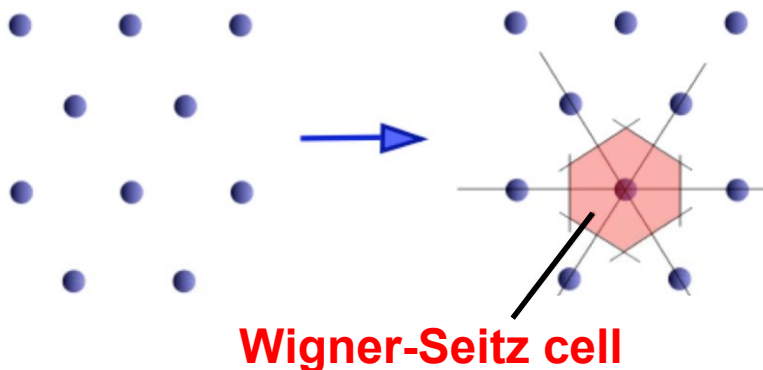
Brillouin zones

A conventional choice for the reciprocal lattice unit cell

For a square lattice

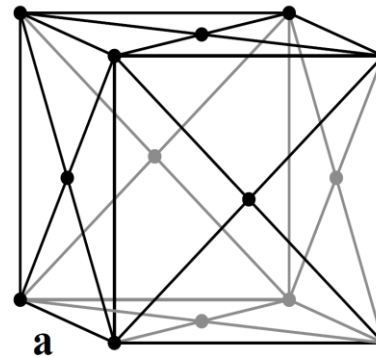


For a hexagonal lattice

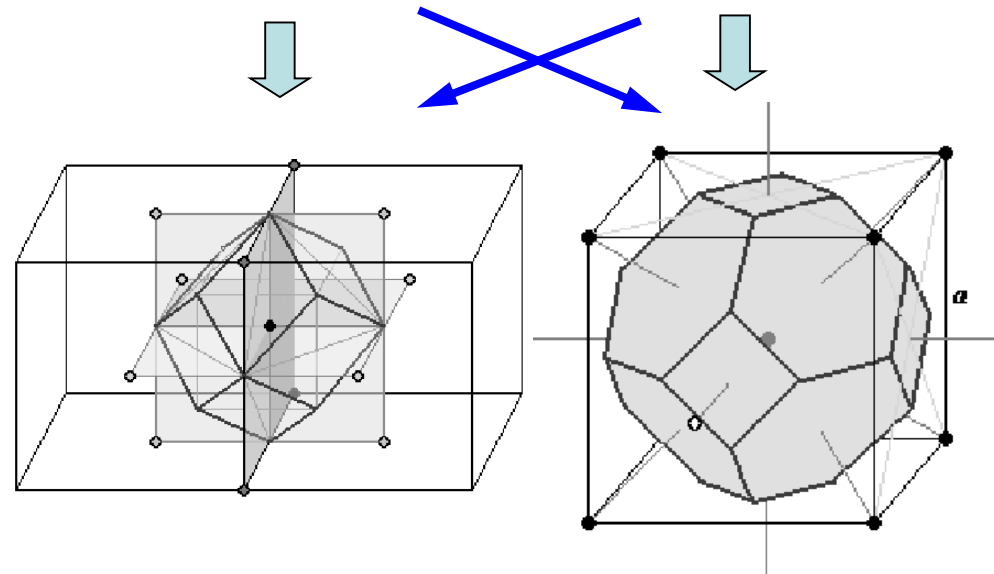
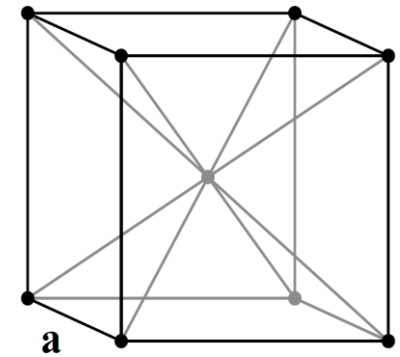


In three dimensions:

Face-centered
cubic (fcc) lattice



Body-centered
cubic (bcc) lattice



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:

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



$$\psi_{n\mathbf{k}}^* = \psi_{n(-\mathbf{k})} \quad \varepsilon_{n(-\mathbf{k})} = \varepsilon_{n\mathbf{k}}$$

**Electronic states at \mathbf{k} and $-\mathbf{k}$ are at least doubly degenerate
(in the absence of magnetic field)**

Basis sets

$$\psi_i(\mathbf{r}) = \sum_p C_{ip} \varphi_p(\mathbf{r})$$

Commonly used basis sets:

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

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

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

Numeric atomic orbitals $\frac{u(r)}{r} Y_{lm}(\theta, \phi)$ (**localized, flexible**)

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

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

Numeric atomic orbitals

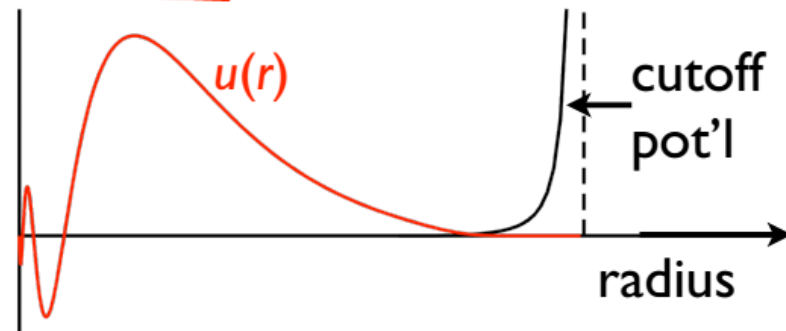
$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)$$

Many popular implementations:
DMol³ (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (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, harm. osc. (Gaussians), ...



Numeric atomic orbitals

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

Many popular implementations:
DMol³ (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX², Fireball, ...)

- $u_i(r)$: Flexible choice - “Anything you like.”

- Localized; “naturally” all-electron

- The choice of efficient and of enough radial functions is obviously important

- We have a basis set library for all elements (1-102), from fast qualitative to meV-converged (total energy, LDA/GGA) calculations - efficient and accurate approach

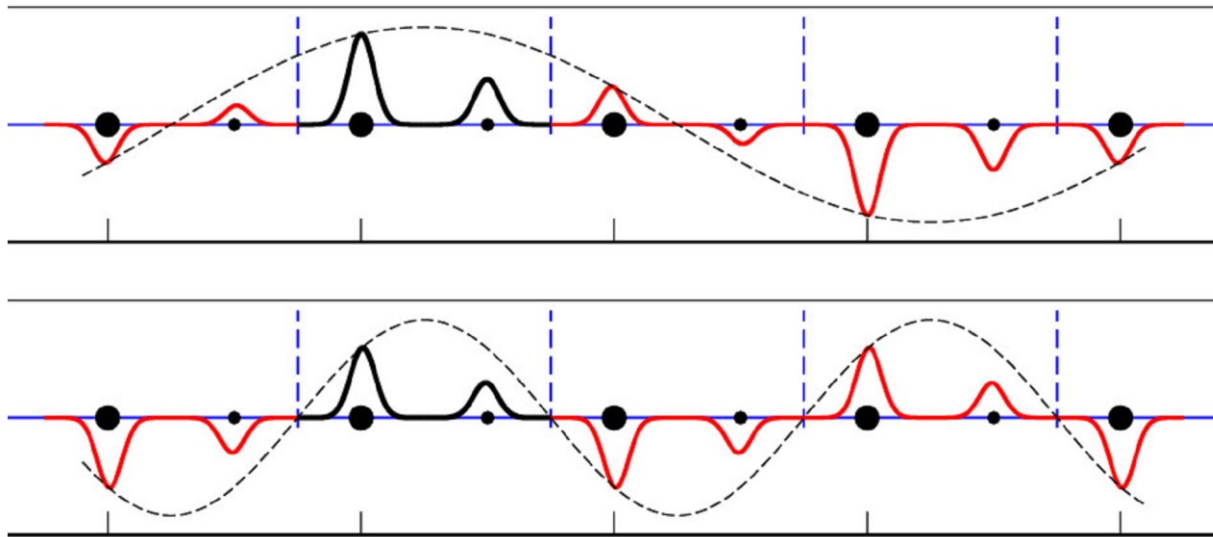
V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
“Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals”,
Computer Physics Communications **180**, 2175-2196 (2009)

Localized basis sets and periodic systems

$$\chi_{pk}(\mathbf{r}) = \sum_{\mathbf{R}} e^{-i\mathbf{k}\mathbf{R}} \phi_p(\mathbf{r} + \mathbf{R})$$

New basis functions satisfying Bloch's theorem:

$$\chi_{pk}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}} \chi_{pk}(\mathbf{r})$$



$$\psi_{ik}(\mathbf{r}) = \sum_p C_{ik,p} \chi_{pk}(\mathbf{r})$$

$$\psi_{ik}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}} \psi_{ik}(\mathbf{r})$$

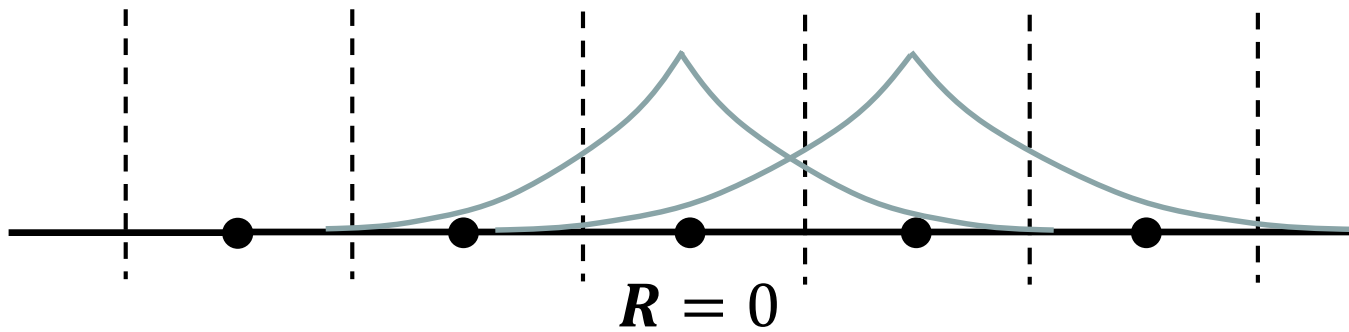
Localized basis sets and periodic systems

$$\hat{h} \left[\sum_p C_{ik}^p \sum_R e^{-ikR} \phi_p(\mathbf{r} + \mathbf{R}) \right] = \varepsilon_{ik} \left[\sum_p C_{ik}^p \sum_R e^{-ikR} \phi_p(\mathbf{r} + \mathbf{R}) \right]$$

Multiply by ϕ_q and integrate over all space:

$$\sum_p C_{ik}^p \underbrace{\sum_R e^{-ikR} \langle \phi_q | \hat{h} | \phi_p(\mathbf{r} + \mathbf{R}) \rangle}_{h_{qp}^k} = \varepsilon_{ik} \sum_p C_{ik}^p \underbrace{\sum_R e^{-ikR} \langle \phi_q | \phi_p(\mathbf{r} + \mathbf{R}) \rangle}_{S_{qp}^k}$$

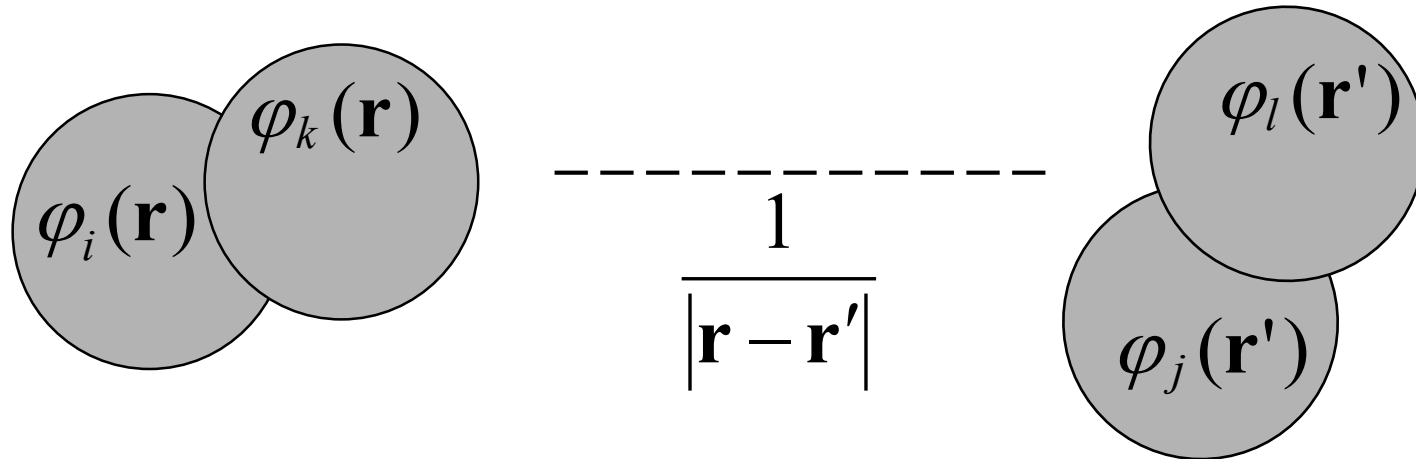
In practice, all integration points and pieces of ϕ_p are mapped back to the original unit cell:



Hartree-Fock exchange – the problem

$$E_X^{\text{HF}} = -\frac{1}{2} \sum_{i,j,k,l} D_{il} D_{jk} \underbrace{\int \frac{\varphi_i(\mathbf{r})\varphi_k(\mathbf{r})\varphi_j(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'}_{\text{electron repulsion integrals}}$$

electron repulsion integrals

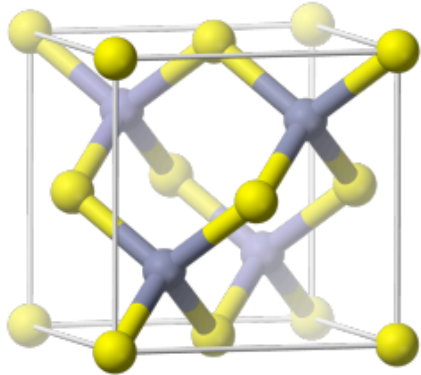


Lots of integrals, naïve implementation $\rightarrow N^4$ scaling
(storage impractical for $N > 500$ basis functions)



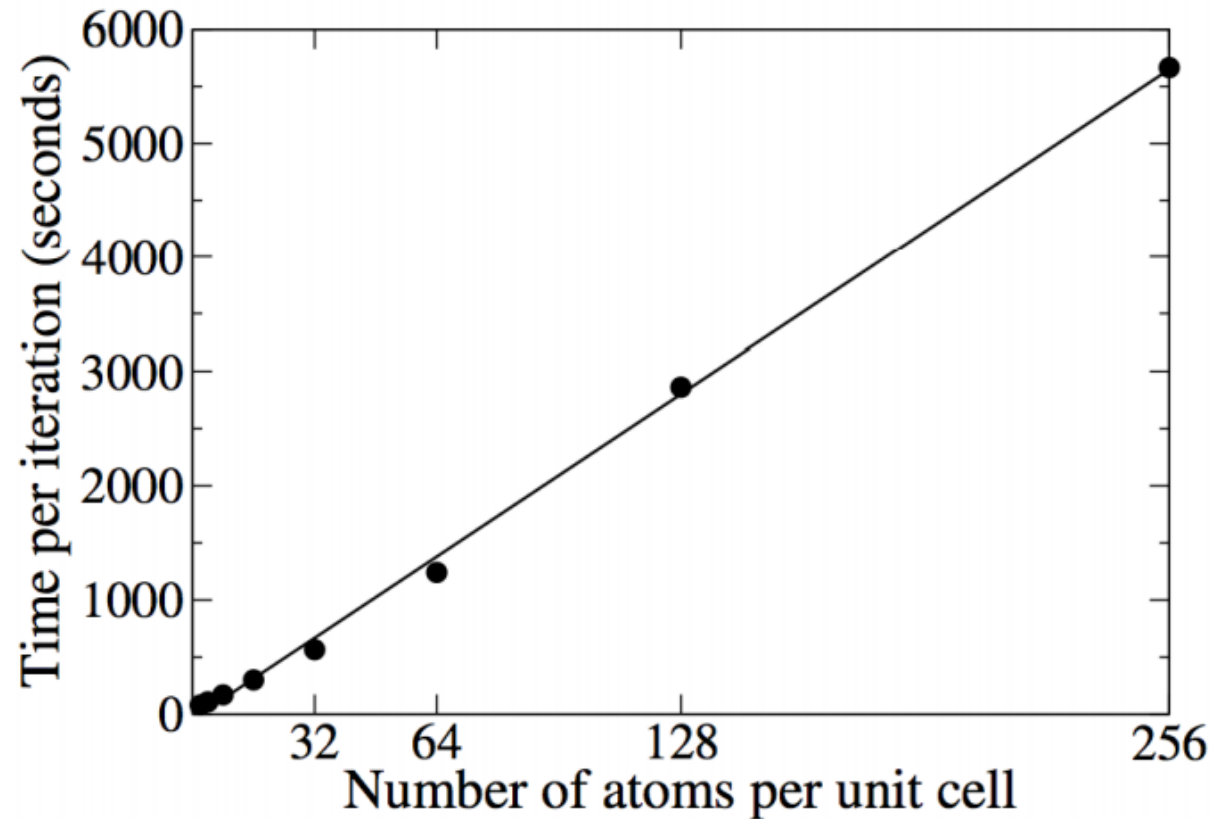
- need fast evaluation
- need efficient use of sparsity (screening)

Hybrid functionals in FHI-aims



Zincblende GaAs

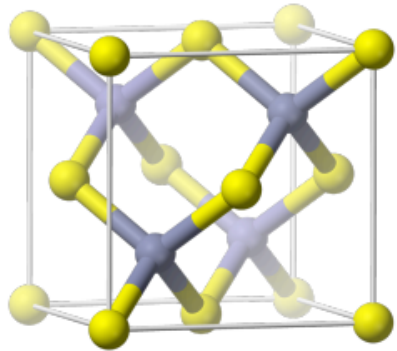
Computational Scaling of Periodic GaAs,
HSE06 Hybrid Functional,
with Increasing System Size



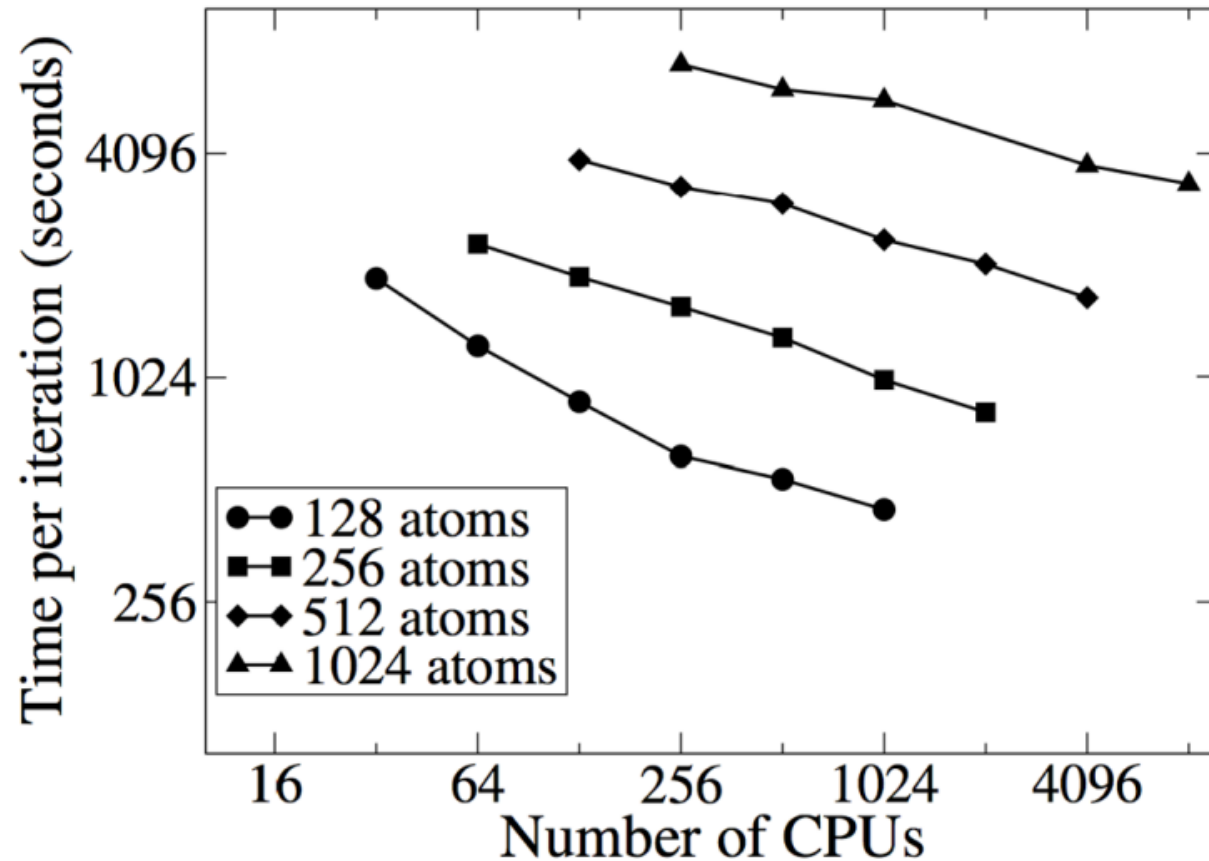
Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler,
Comp. Phys. Commun. **192**, 60-69 (2015).

Hybrid functionals in FHI-aims

Computational Scaling of Periodic GaAs,
HSE06 Hybrid Functional,
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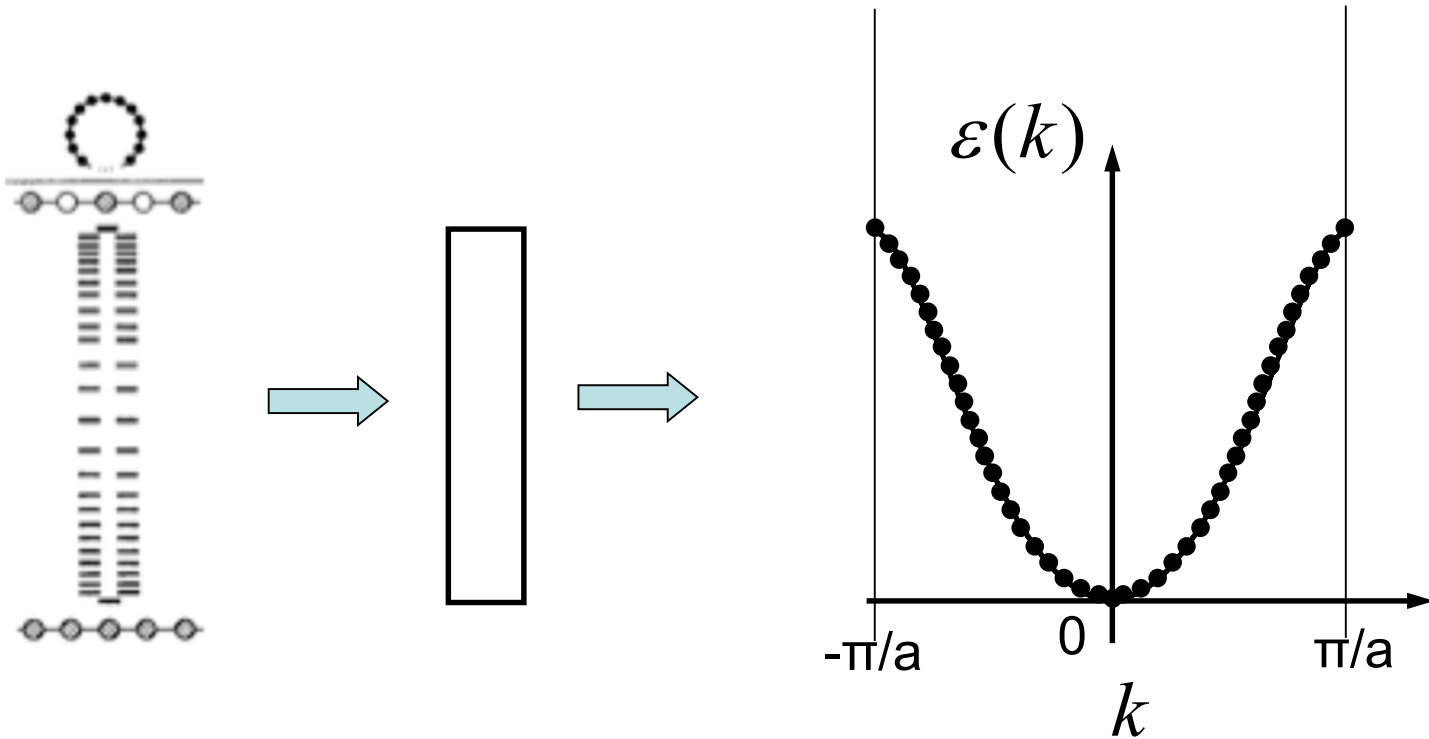


Zincblende GaAs



Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler,
Comp. Phys. Commun. **192**, 60-69 (2015).

Electronic band structure

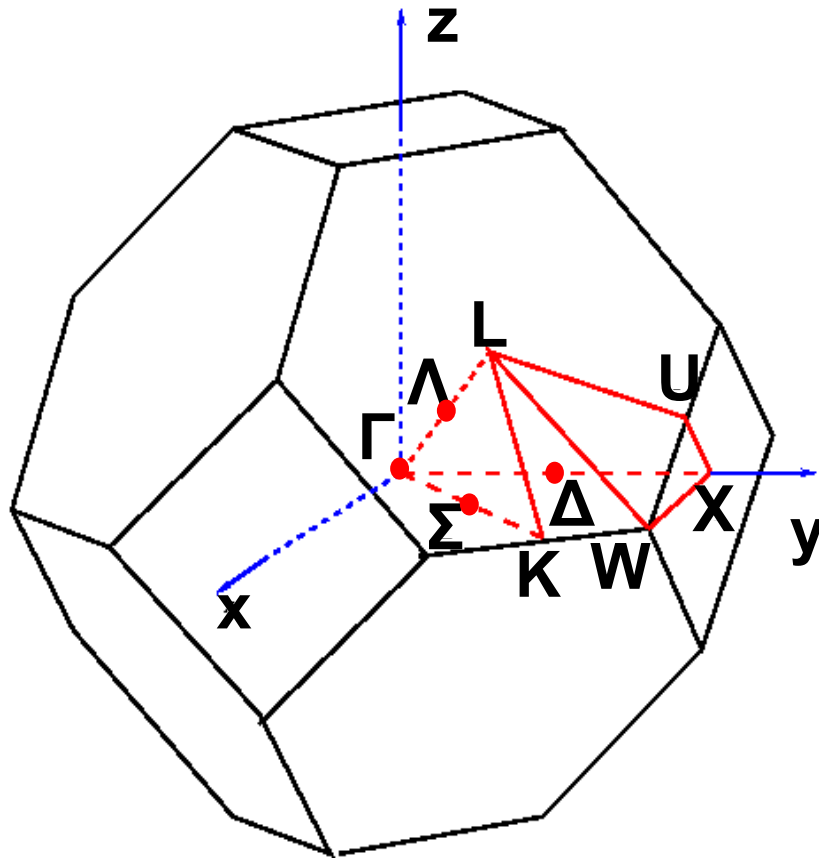


Band structure represents dependence of $\epsilon_{n\mathbf{k}}$ on k

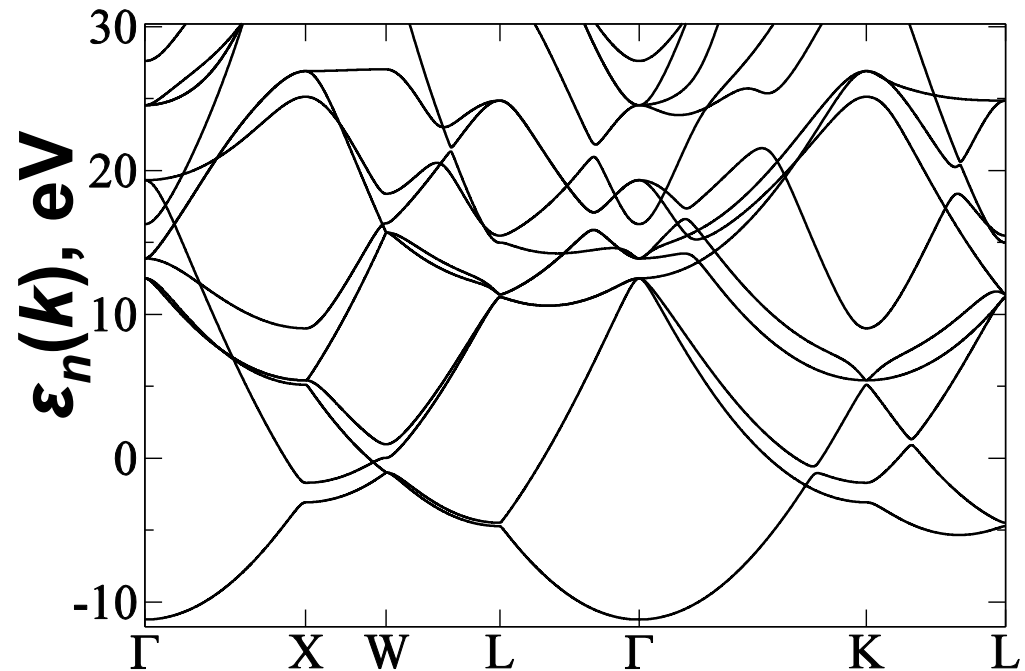
For a periodic (infinite) crystal, there is an infinite number of states for each band index n , differing by the value of k

Electronic band structure in three dimensions

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

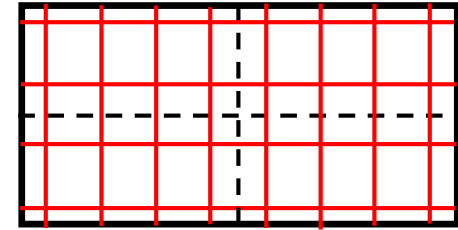
Finite k-point mesh

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

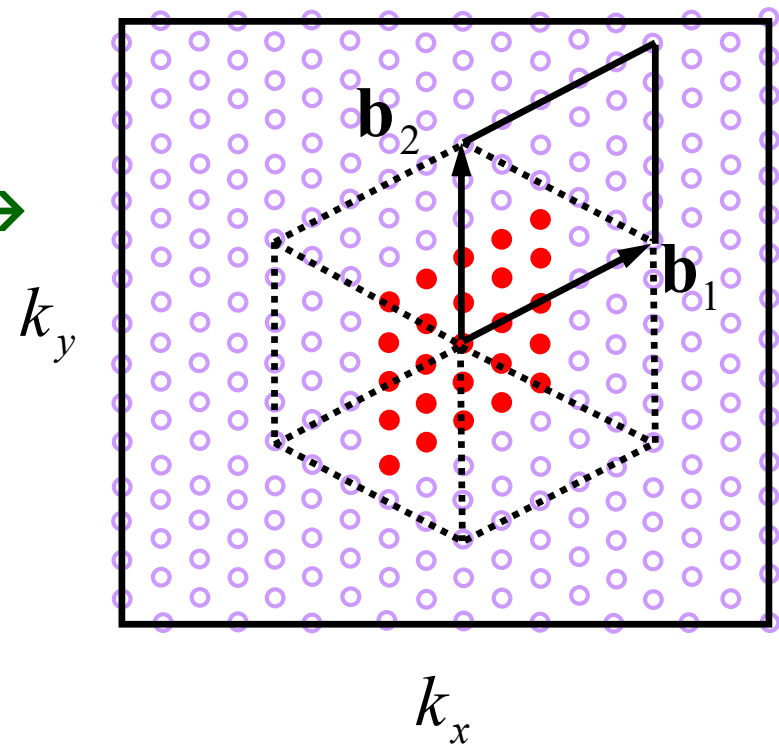
$$n(\mathbf{r}) = \sum_j^{\text{occ}} \int_{\Omega_{\text{BZ}}} |\psi_{j\mathbf{k}}(\mathbf{r})|^2 \frac{d^3k}{\Omega_{\text{BZ}}}$$

$\psi_{n\mathbf{k}}$, $\varepsilon_{n\mathbf{k}}$ – *smooth* functions of $\mathbf{k} \rightarrow$ can use a **finite** mesh, and then *interpolate* and/or use perturbation theory to calculate integrals

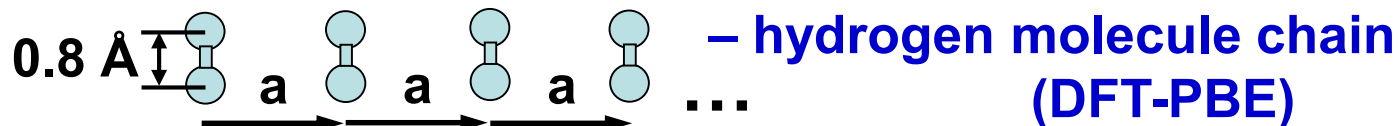
$$n(\mathbf{r}) \approx \sum_j^{\text{occ}} \sum_{m=1}^{N_{\text{kpt}}} w_m |\psi_{j\mathbf{k}_m}(\mathbf{r})|^2$$



8x4 Monkhorst-Pack grid

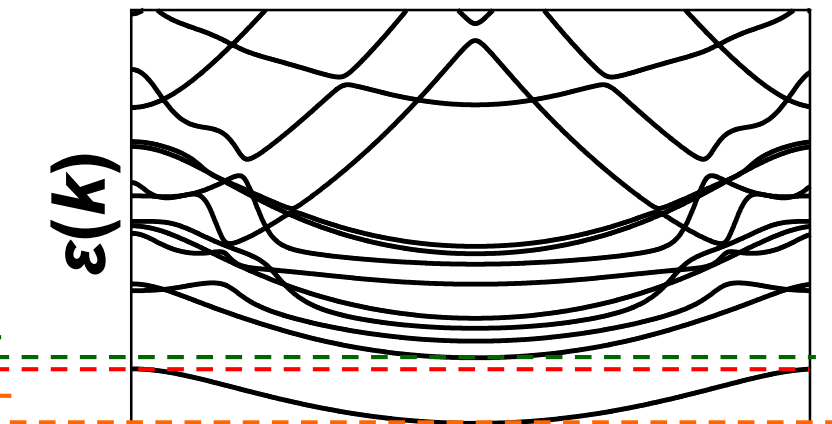
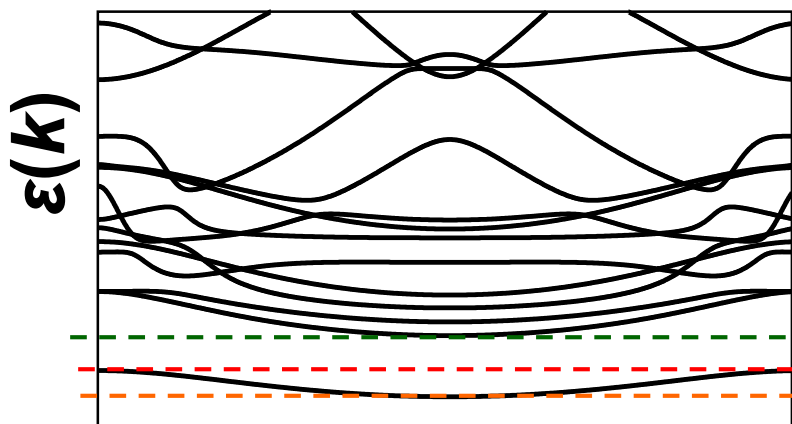
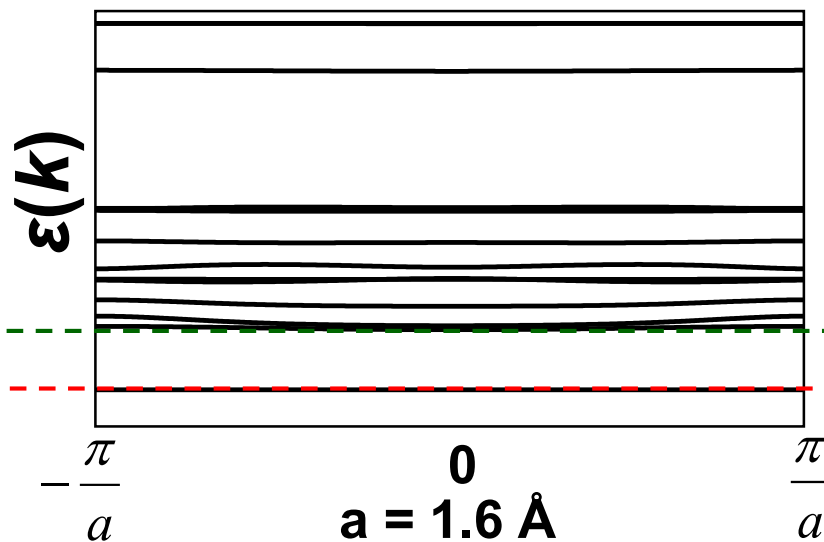
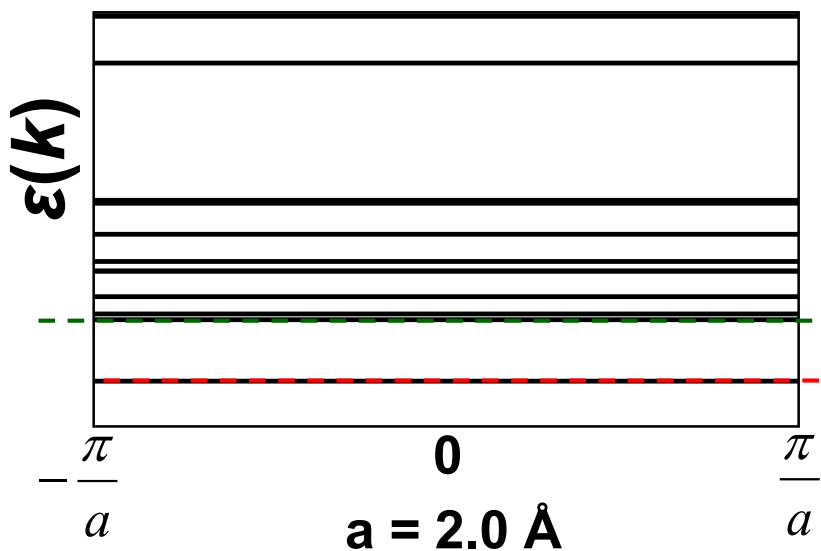


Band gap and band width (dispersion)



$a = 10.0 \text{ \AA}$

$a = 5.0 \text{ \AA}$

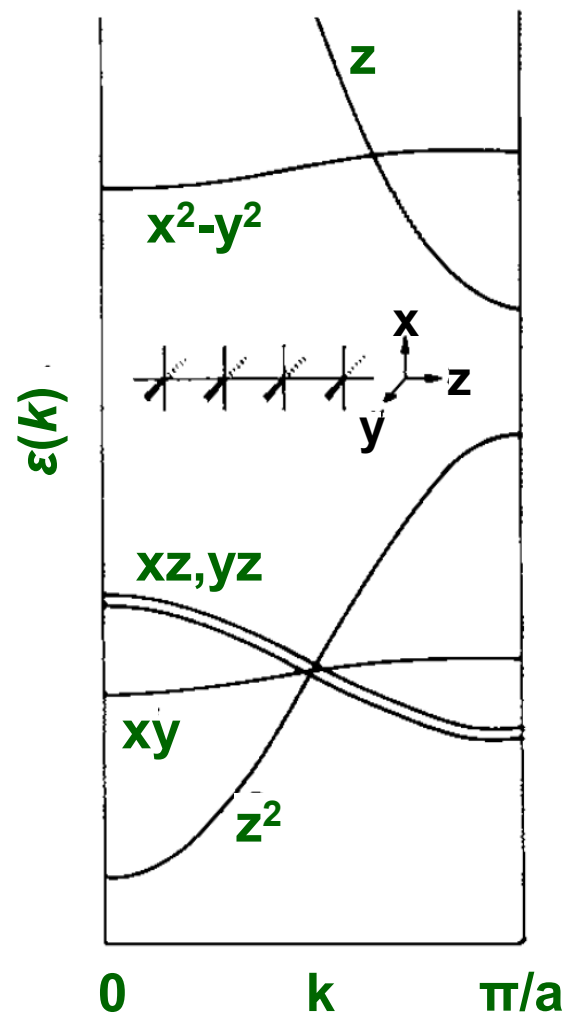
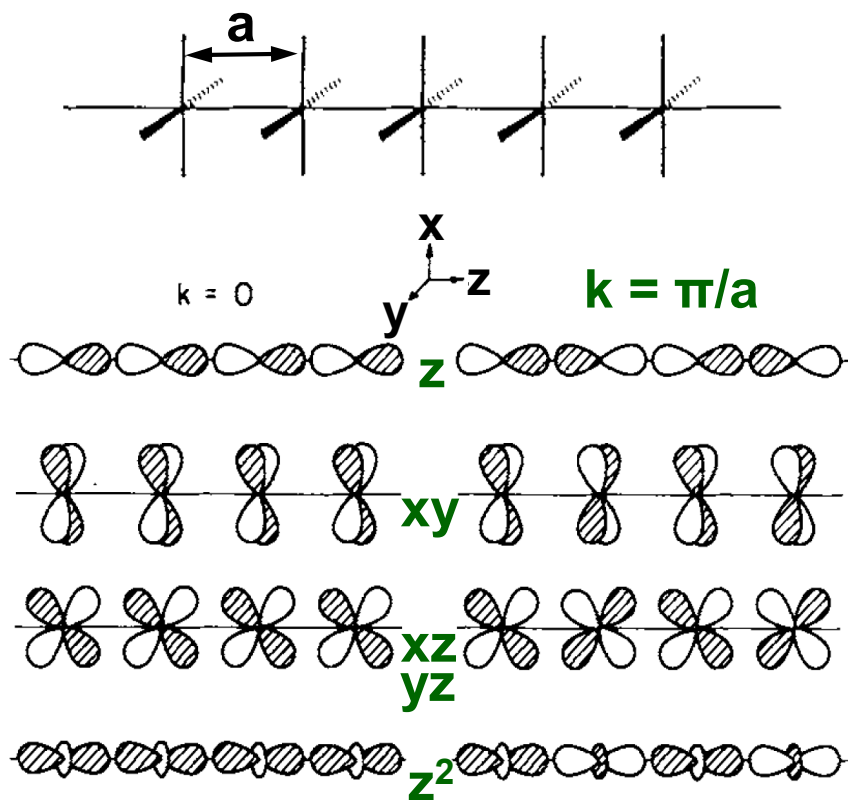


Overlap between interacting orbitals determines band gap and band width

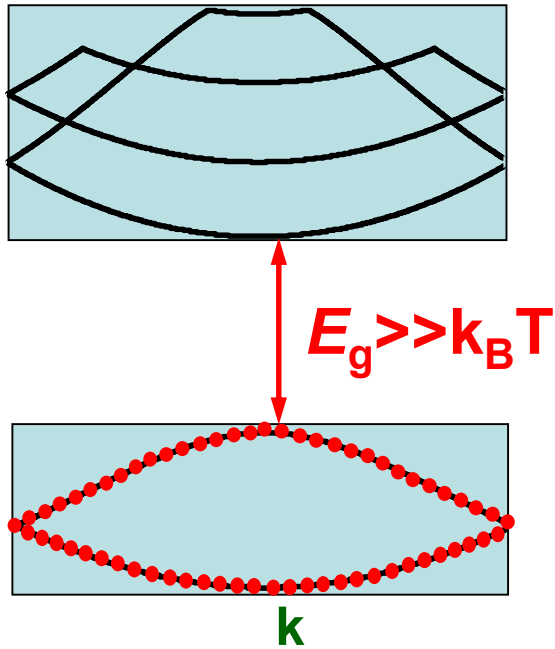
Band structure – test example

Orbital energies are smooth functions of k

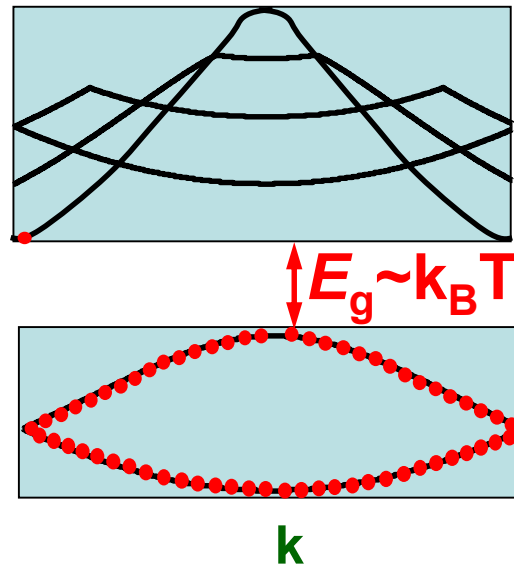
Example: chain of Pt-L₄ complexes (K₂[Pt(CN)₄])



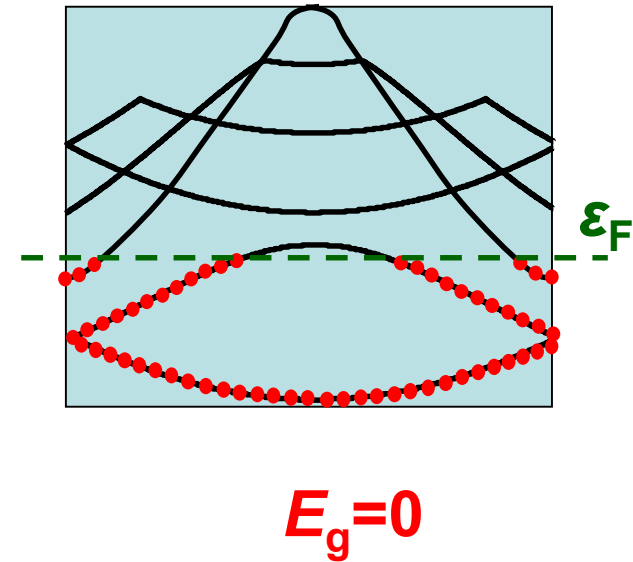
Insulators, semiconductors, and metals



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

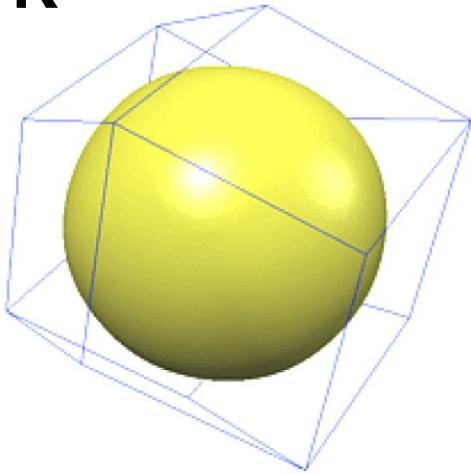
$$\varepsilon_n(\mathbf{k}) = \varepsilon_F$$

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

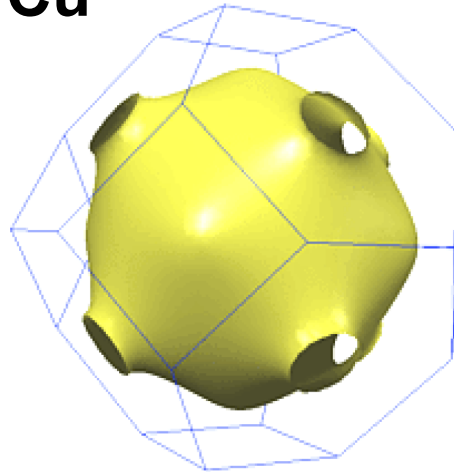
For free electrons, Fermi surface is a sphere

$$\frac{\eta^2 \mathbf{k}^2}{2m_e} = \varepsilon_F$$

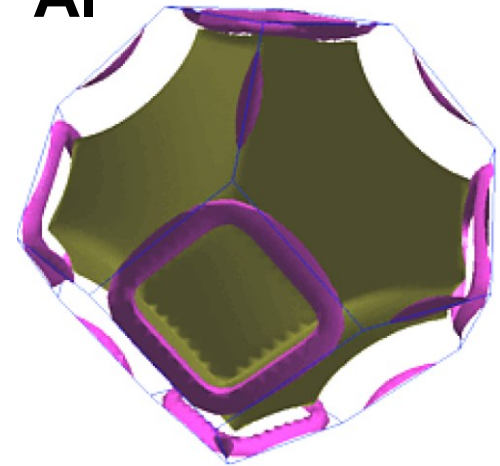
K



Cu



Al



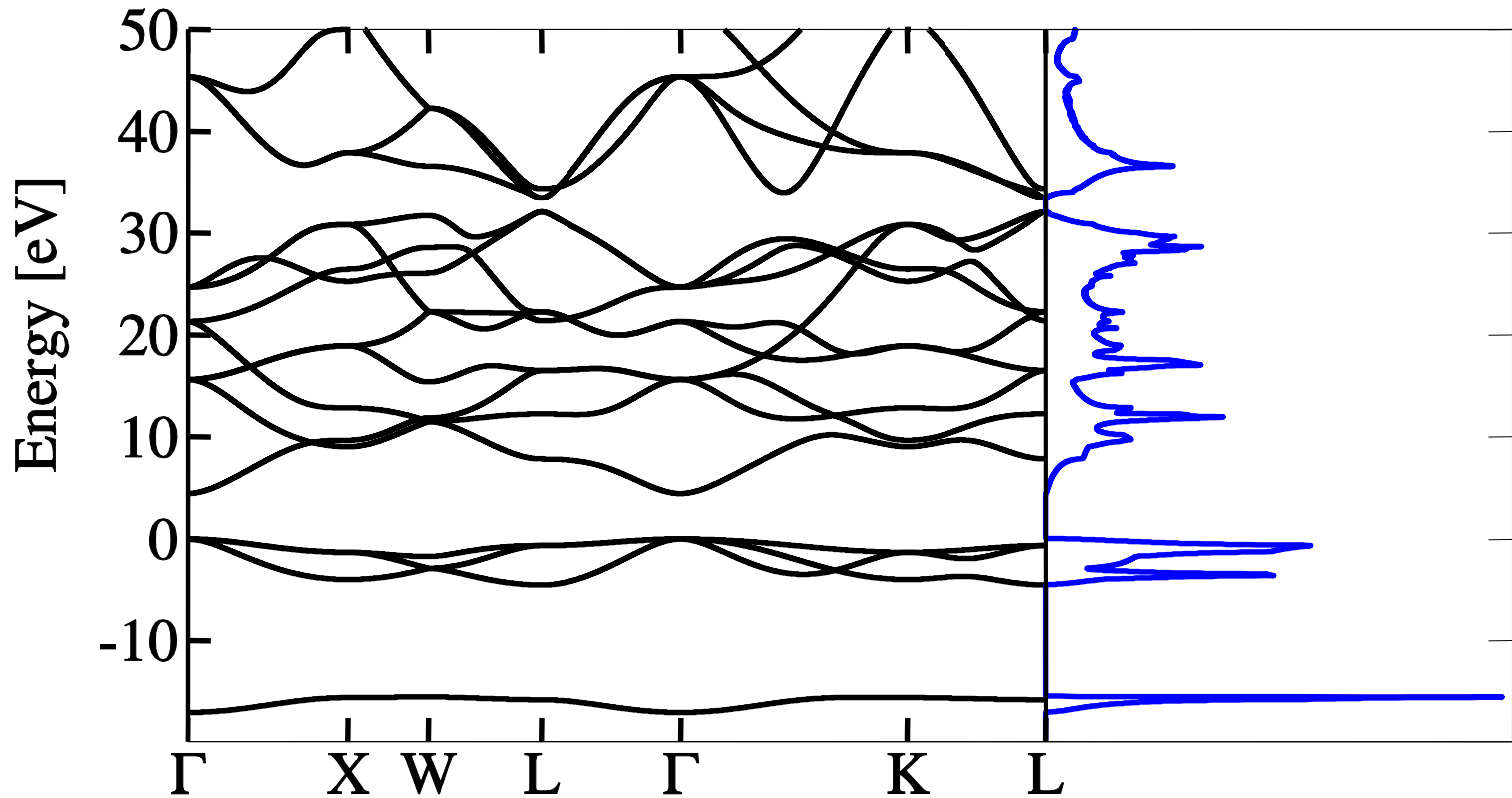
Periodic table of Fermi surfaces: <http://www.phys.ufl.edu/fermisurface/>

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 $d\varepsilon$ per unit volume, $\frac{1}{\Omega d\varepsilon} \sum_{\varepsilon}^{\varepsilon+d\varepsilon} 1$

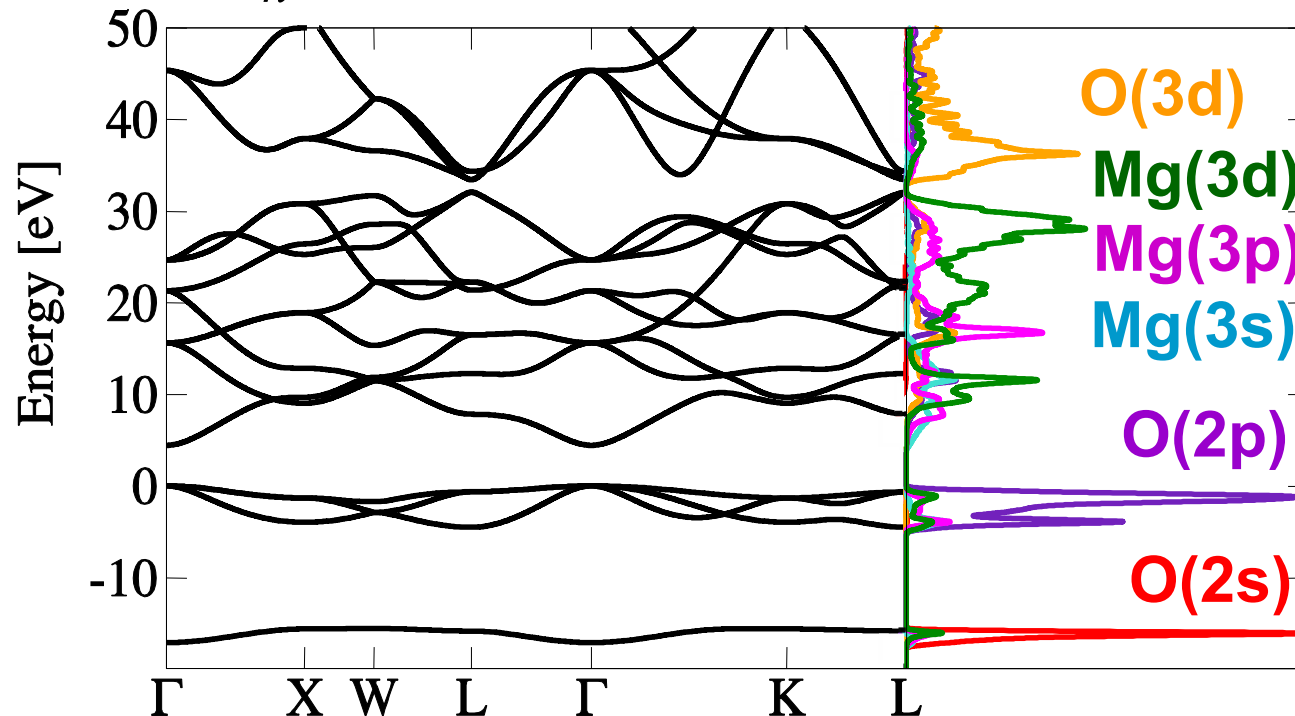
$$g(\varepsilon) = \sum_n \int_{\Omega_{\text{BZ}}} \delta(\varepsilon - \varepsilon_n(\mathbf{k})) d^3k \approx \sum_n \sum_{j=1}^{N_{\text{kpt}}} w_j \delta(\varepsilon - \varepsilon_n(\mathbf{k}_j))$$



Atom-Projected Density Of States (APDOS)

Decomposition of DOS into contributions from different atomic functions φ_i :

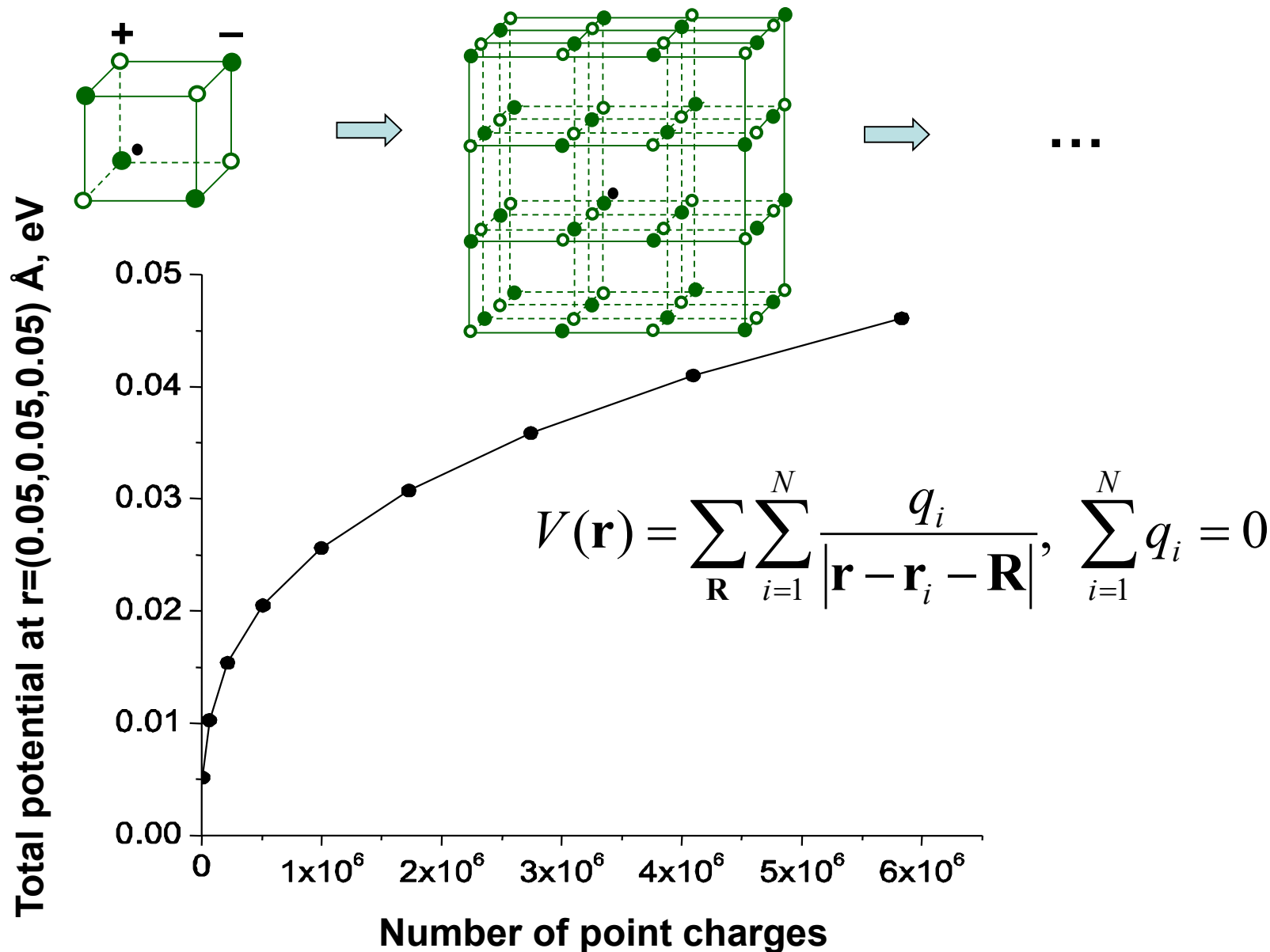
$$g_i(\varepsilon) = \sum_n \int_{\Omega_{\text{BZ}}} \left| \int \varphi_i(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) d^3r \right|^2 \delta(\varepsilon - \varepsilon_n(\mathbf{k})) d^3k$$



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



Convergence of the potential with number of charges is extremely slow

Ewald summation

$$V(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{i=1}^N \frac{q_i}{|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|} + \frac{1}{\eta\sqrt{\pi}} \exp(-(\mathbf{r} - \mathbf{r}_i)^2 / \eta^2)$$



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

(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 $|\mathbf{R}|$

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

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

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

is cancelled for $\sum_i q_i = 0$

There is no universal potential energy reference (like vacuum level) for 3D periodic systems – important when comparing different systems

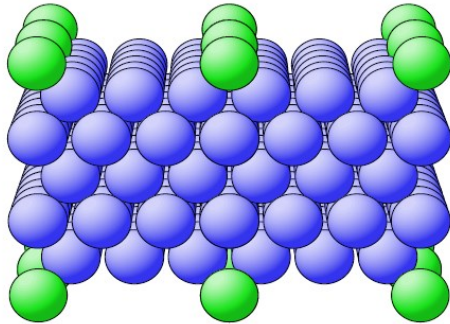
Modeling surfaces, interfaces, and point defects – the supercell approach

The supercell approach

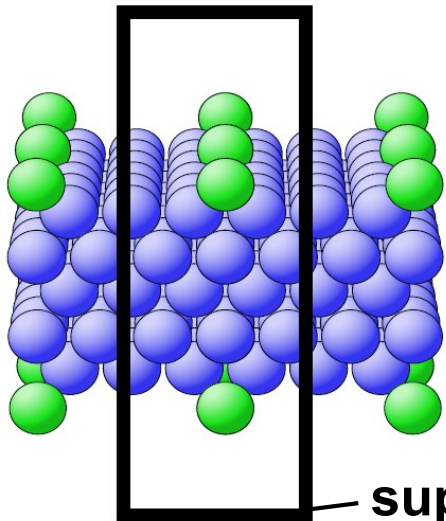
Can we benefit from periodic modeling of non-periodic systems?

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

Supercell approach to surfaces (slab model)



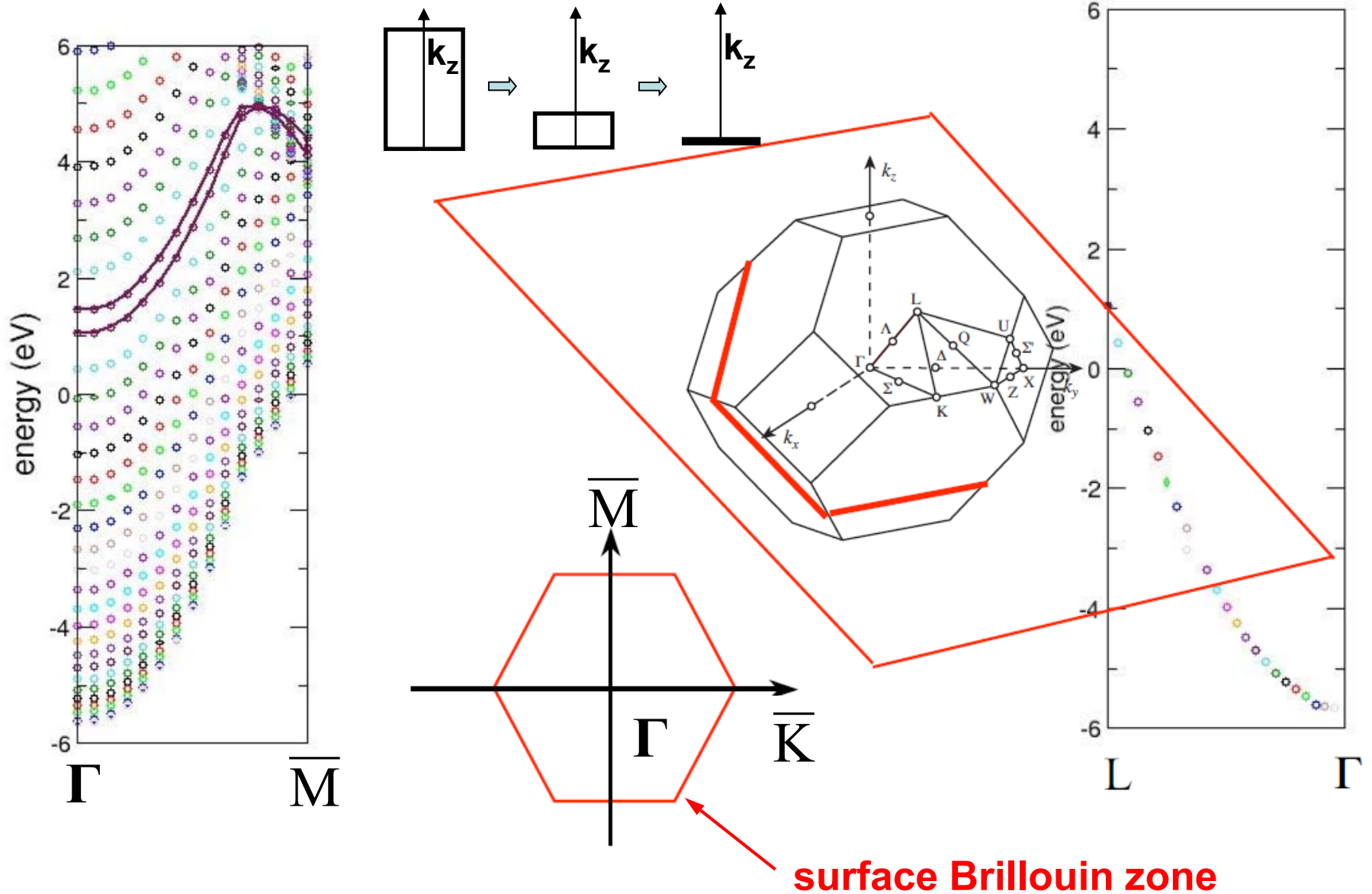
- Approach accounts for the lateral periodicity
- Sufficiently broad vacuum region to decouple the slabs
- Sufficient slab thickness to mimic semi-infinite crystal
- Semiconductors: saturate dangling bonds on the back surface
- Non-equivalent surfaces: use dipole correction
- Alternative: cluster models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



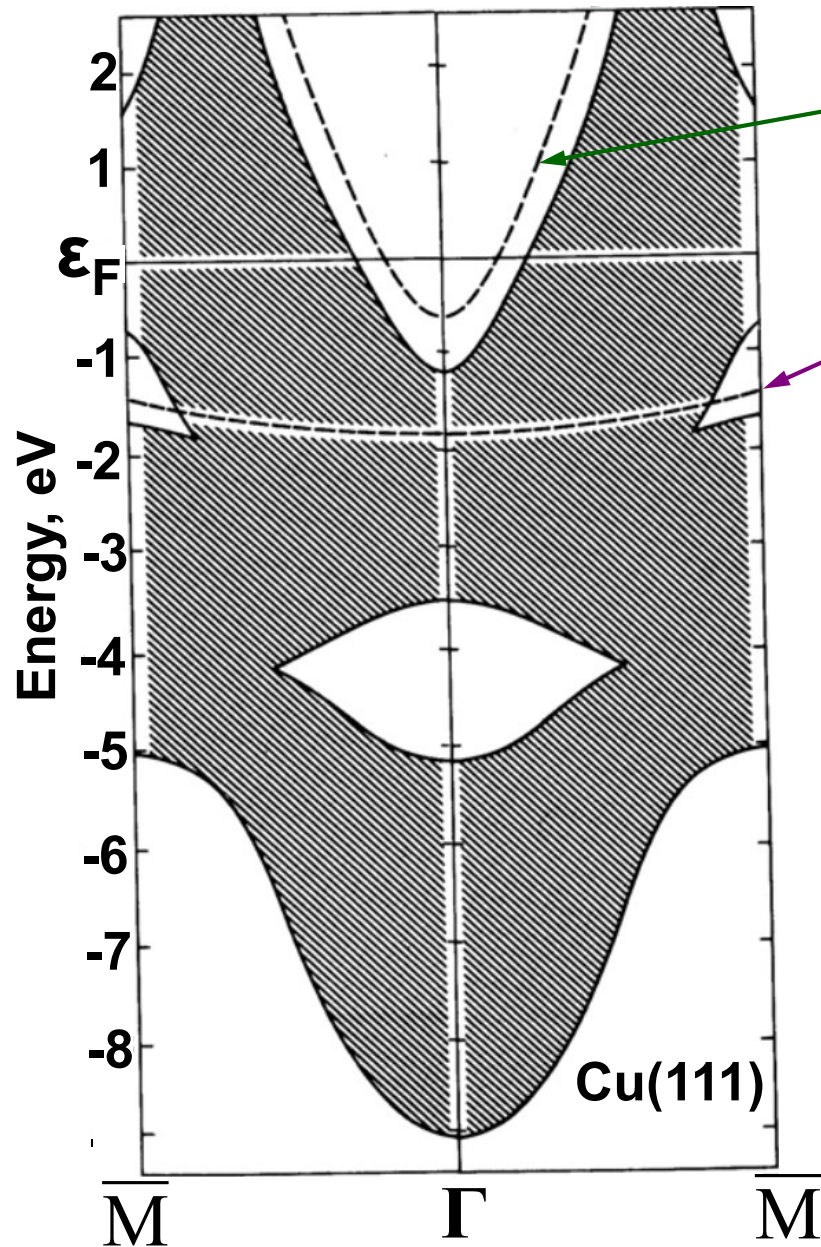
supercell

Surface band structure

Example: fcc crystal, (111) surface

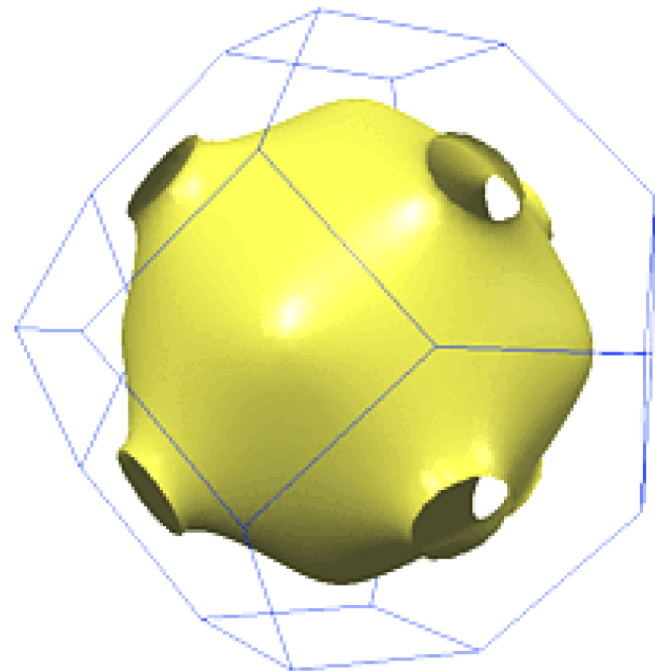


Surface band structure of Cu(111)



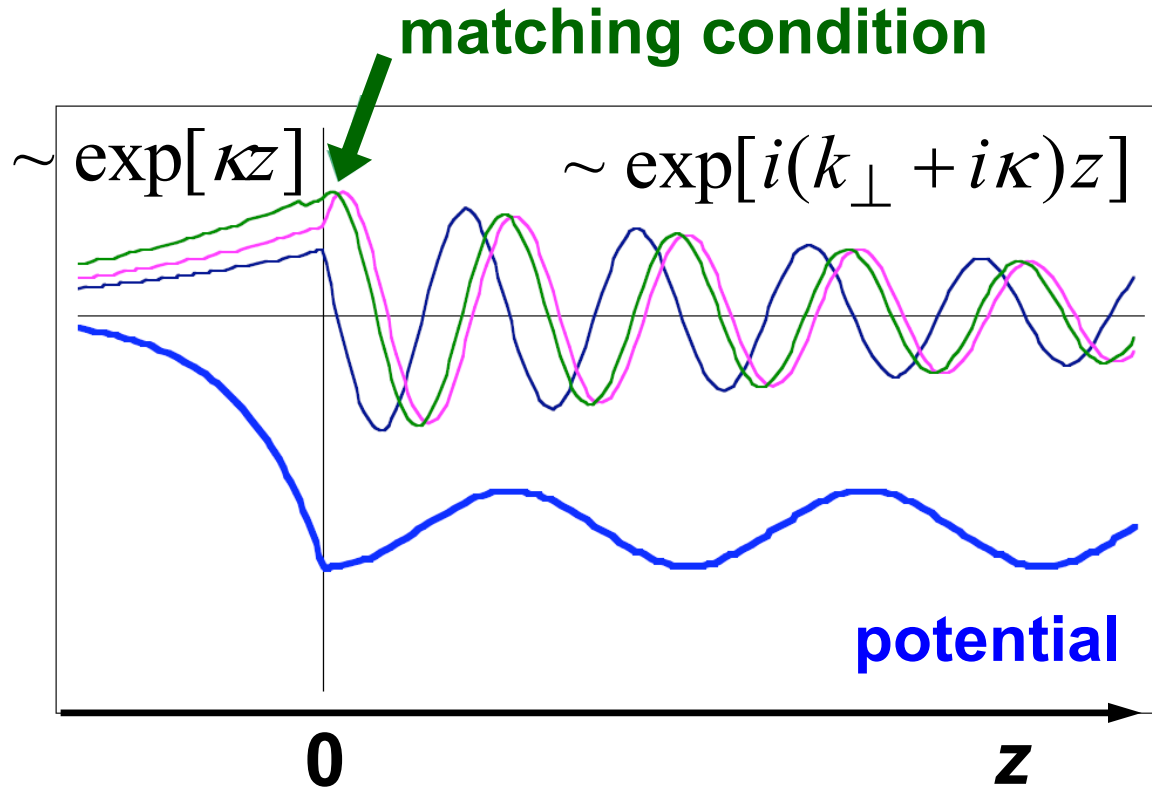
Shockley surface state

Tamm surface state



Shockley surface states

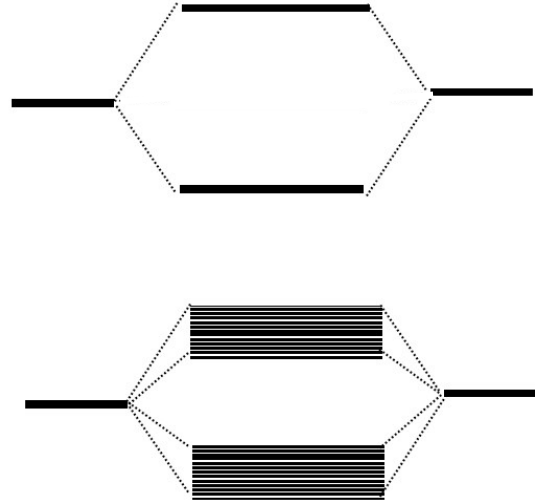
For near-free electrons: $\psi_{\mathbf{k}}(\mathbf{r}) \sim \exp(i\mathbf{k} \cdot \mathbf{r})$



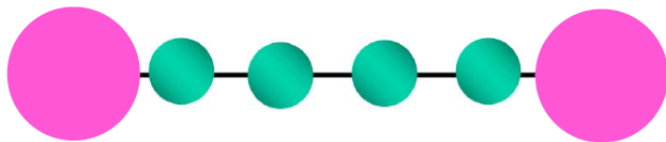
Decaying states can be treated as Bloch states with complex k
(W. Kohn, Phys. Rev., 115, 809 (1959))

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

Tamm surface states

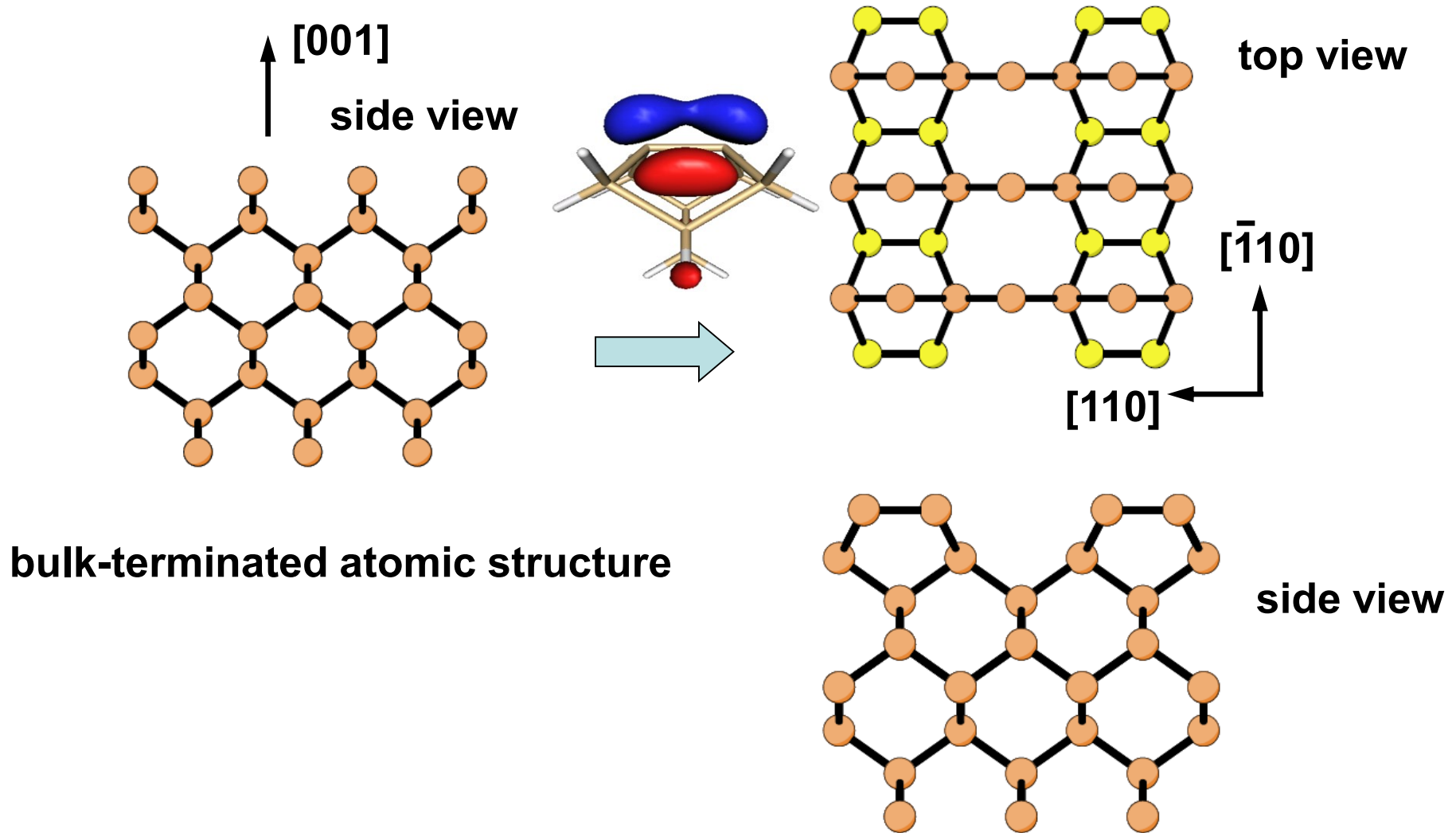


In the tight-binding (localized orbital) picture, surface states may appear due to 'dangling orbitals' split off from the band edge



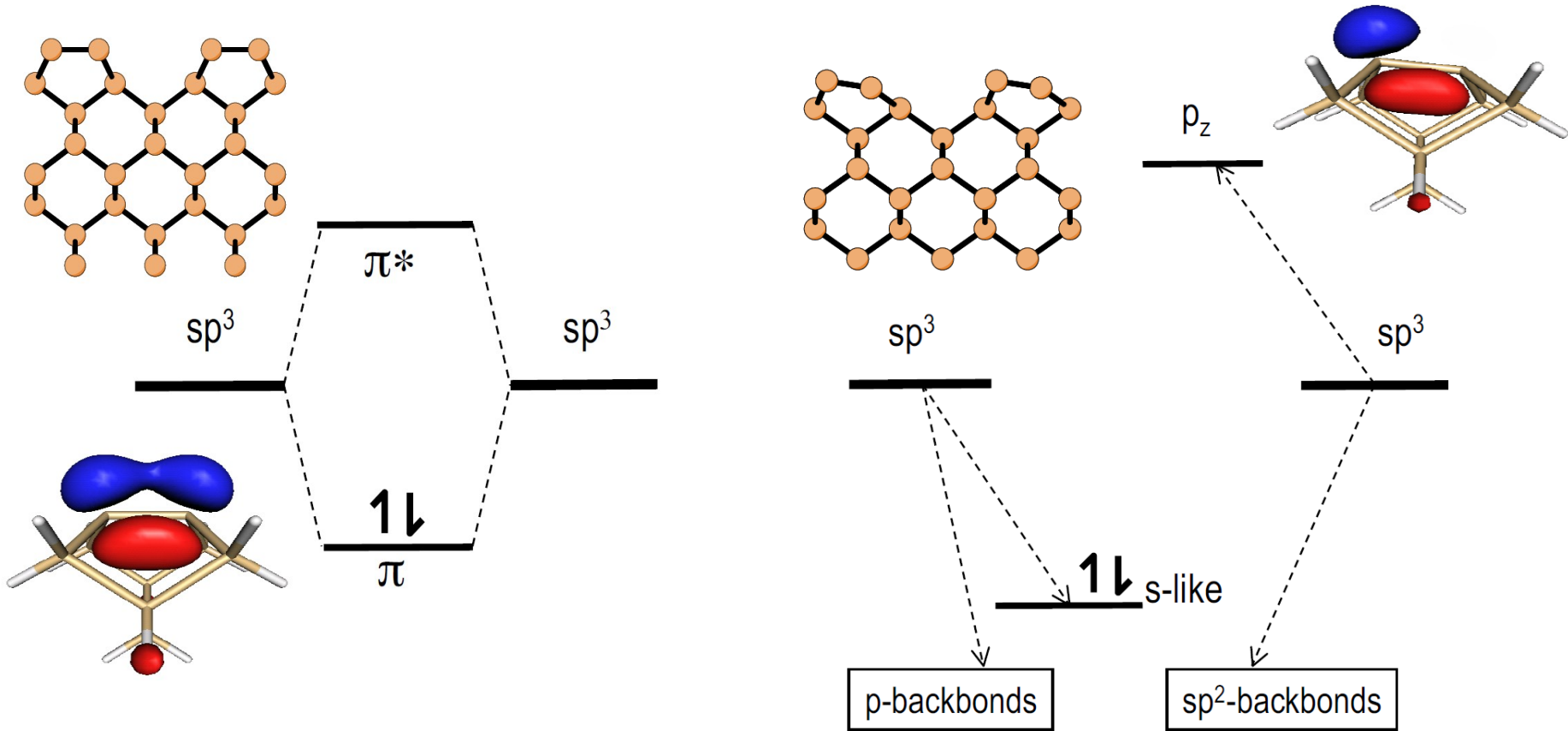
Surface reconstruction and band structure

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



Surface reconstruction and band structure

Buckling of dimers at Si (100) surface

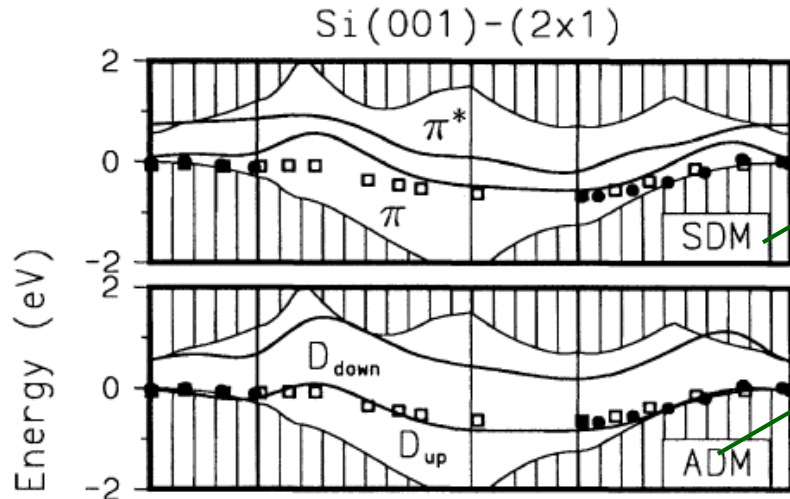


π -bond

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

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

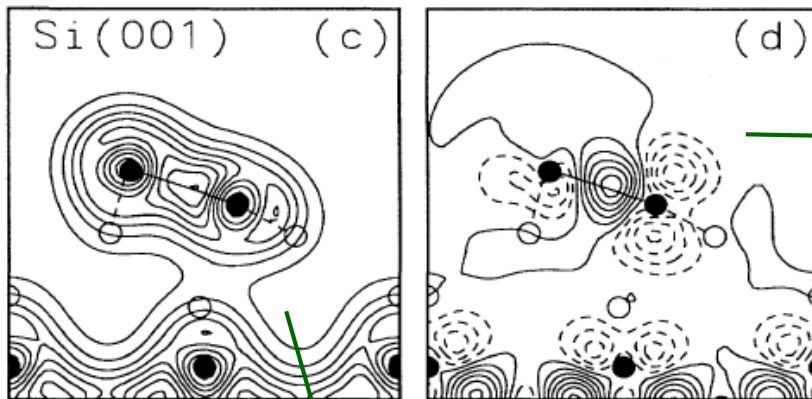
Surface reconstruction and band structure



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)

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*”

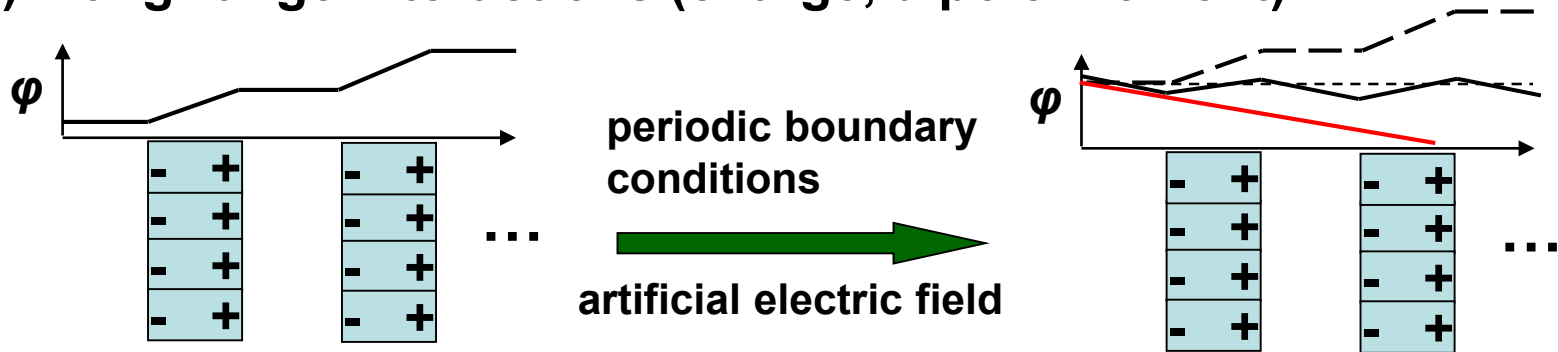
Axel Groß, “*Theoretical surface science: A microscopic perspective*”

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

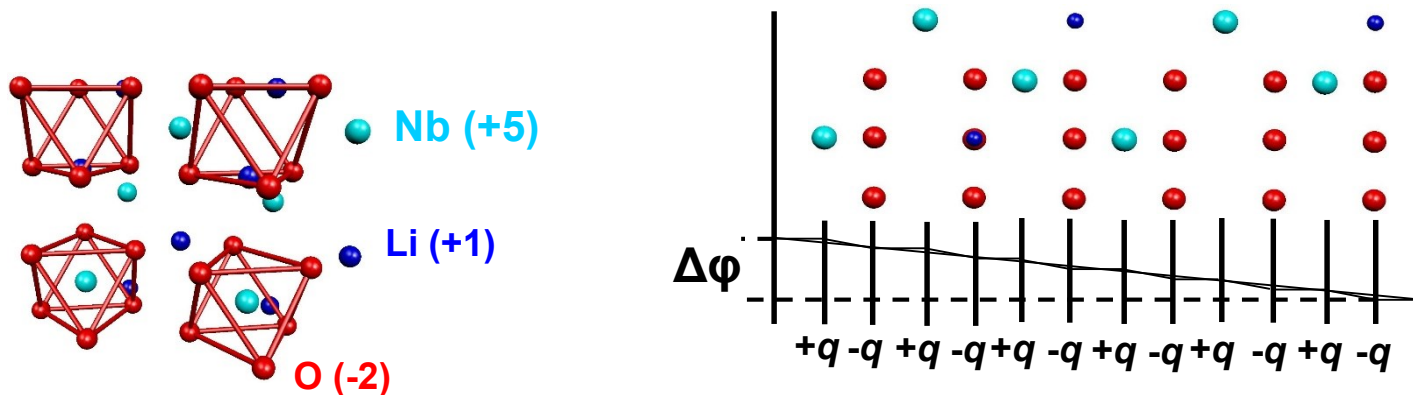
- 1) “*How Chemistry and Physics Meet in the Solid State*”, *Angew. Chem. Int. Ed. Engl.* 26, 846-878 (1987)
- 2) “*A chemical and theoretical way to look at bonding on surfaces*”, *Reviews of modern physics*, 60, 601-628 (1988)

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)

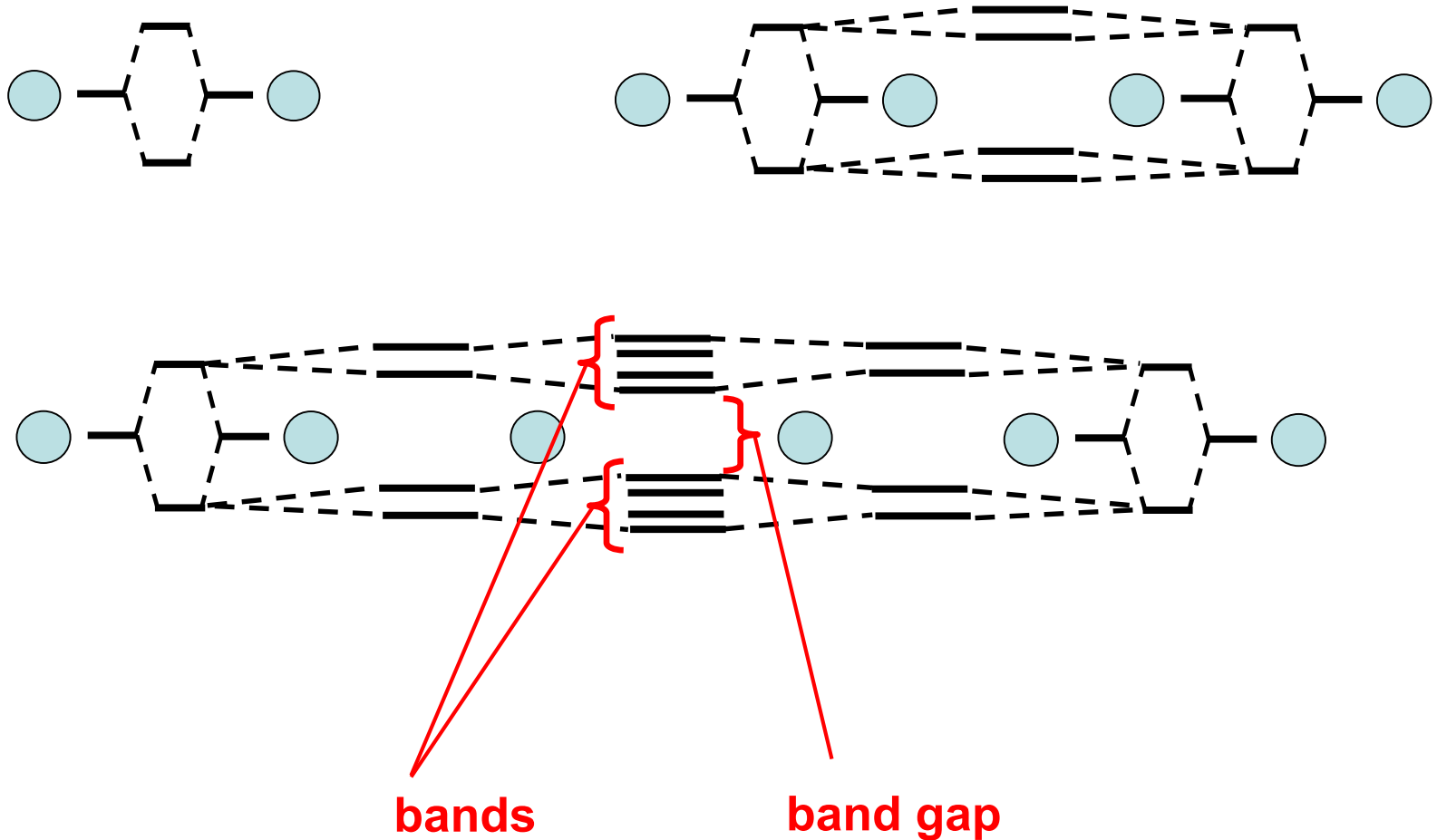


4) Surface polarity



From molecules to solids

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



Shockley surface states

For nearly-free electrons:

