

Crystallography and Crystal Chemistry
X International School-Conference of
Young Scientists 2025

***Mini-lecture 1: Modeling of crystals
using density functional theory***

Dr. Anton Boev, PhD Arseniy Burov

PhD Maria Solovieva, PhD Daniil Chernyshov

PhD Nikita Davydov, MSc Ilya Kraev

Skoltech Center for
Energy Science
and Technology
Energy

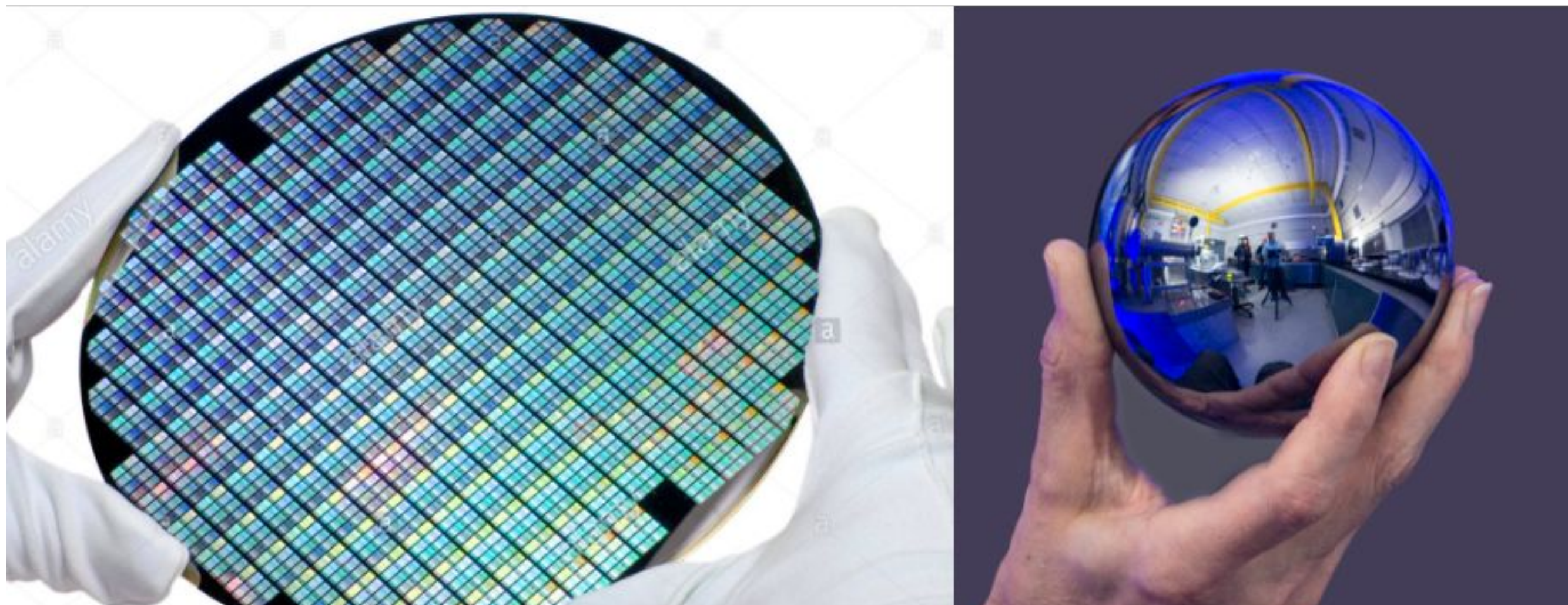
November, 2025

What are the examples of crystals?

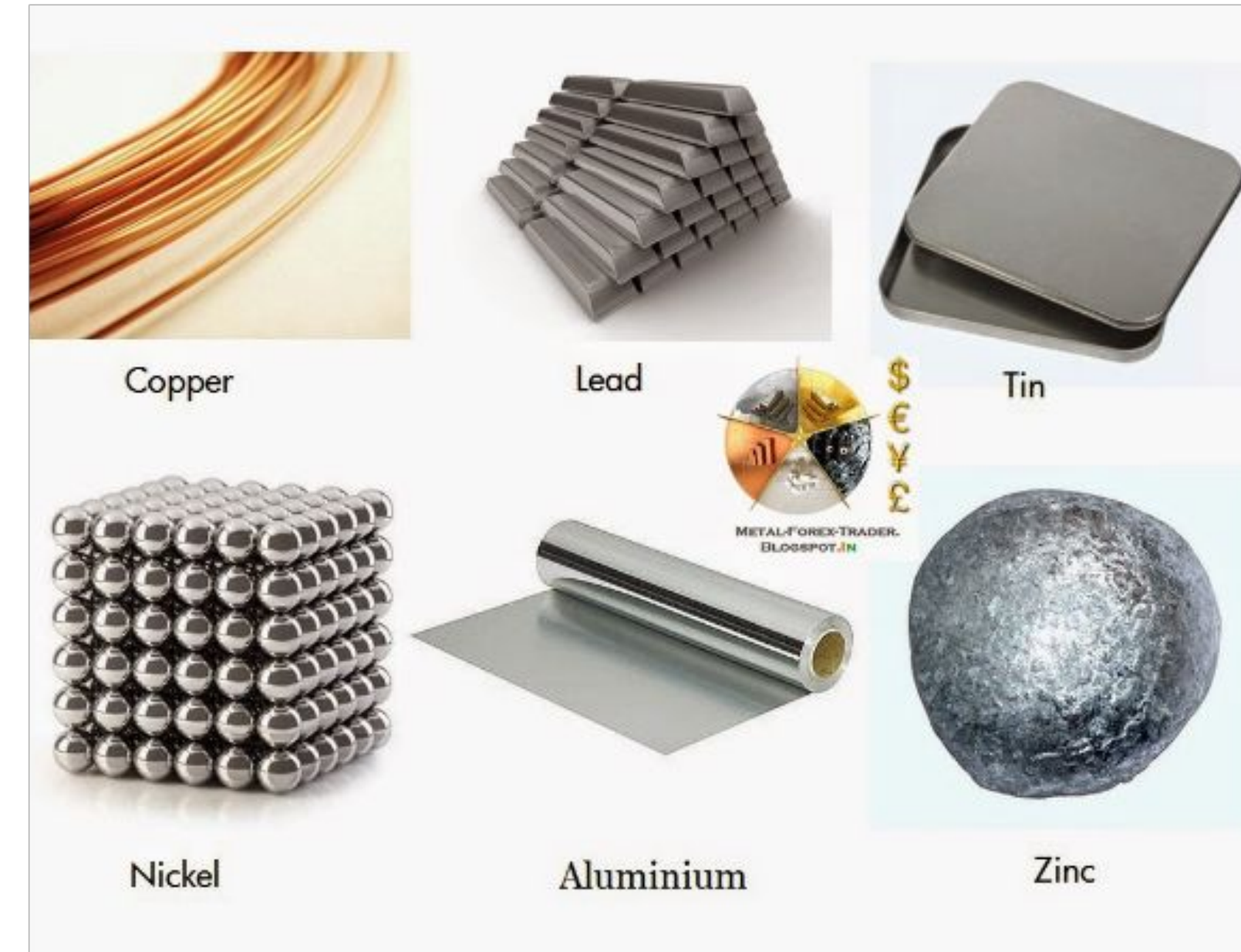
- Minerals (insulating)



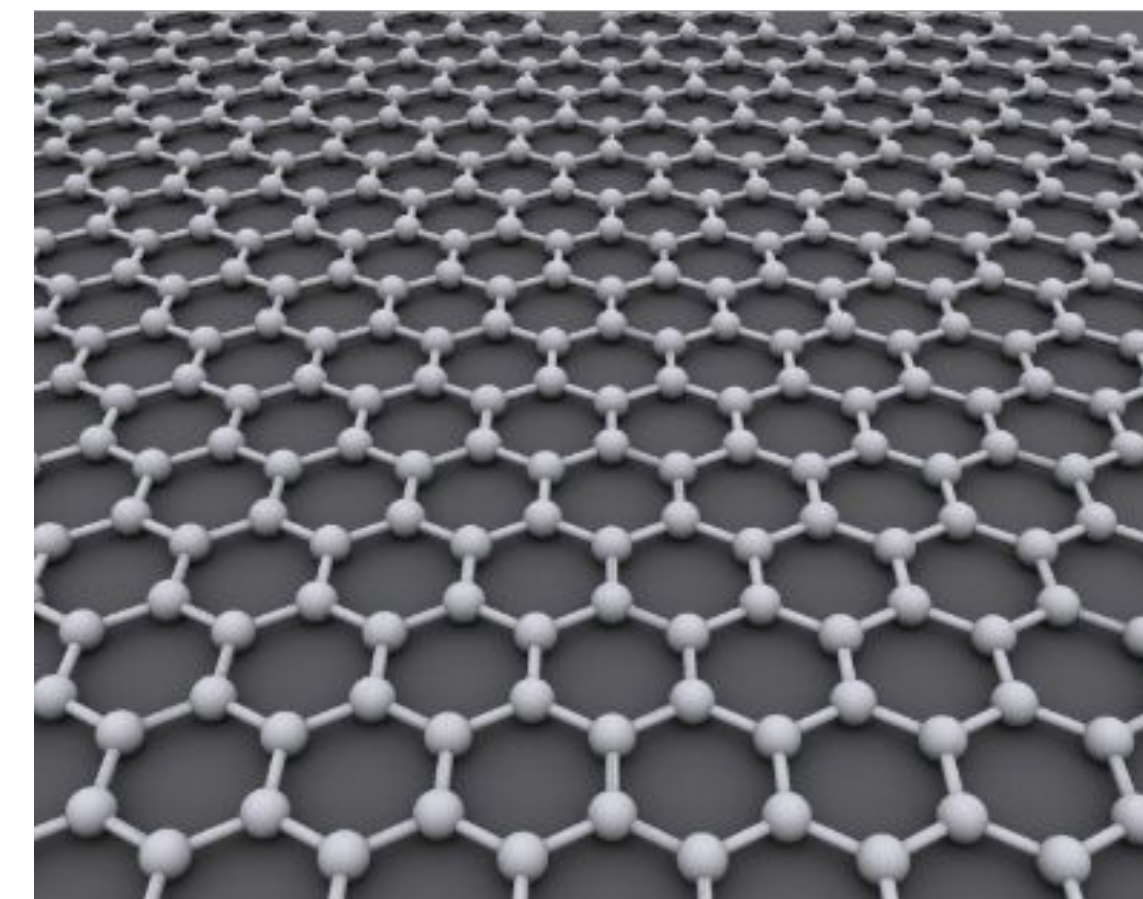
- Semiconductors



- Metals and alloys



- 2D materials



Quantum-mechanics for calculating total energies

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

could be solved only for simplest systems like hydrogen atom!

External potential

$$\begin{aligned}\hat{H} &= \left[\hat{T} + \hat{V} + \hat{V}_{ext} \right] = \\ &= \left[-\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_{i \neq j}^{N,N} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{i,j}^{N,M} \frac{Z_j}{|\vec{R}_j - \vec{r}_i|} \right]\end{aligned}$$

Density Functional Theory

Electron density: $\rho(\vec{r}) = N \langle \Psi | \Psi \rangle$

Hohenberg-Kohn theorems (1964):

$$\rho(\vec{r}) \leftrightarrow V_{ext}$$

$$\begin{aligned} H[\rho] &= \langle \Psi | \hat{T} + \hat{V} | \Psi \rangle + \langle \Psi | V_{ext} | \Psi \rangle \\ &= F_{HK}[\rho] + \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} \end{aligned}$$

Density Functional Theory

Kohn-Sham equations (1965):

- **Replace real electrons with non interacting particles**
- **Account interaction using effective potential (V_{xc})**

$$\hat{H}_{KS} = \left[-\frac{1}{2} \nabla_i^2 + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \hat{V}_{xc} + \hat{V}_{ext} \right]$$

Exchange-Correlation potential

$$\hat{H}_{KS} \phi_i = \epsilon_i \phi_i$$

$$\rho(\vec{r}) = \sum_i^N \phi_i(\vec{r})^* \phi_i(\vec{r})$$

Mendeleev Table $\rightarrow V_{ext} \rightarrow H_{KS}$

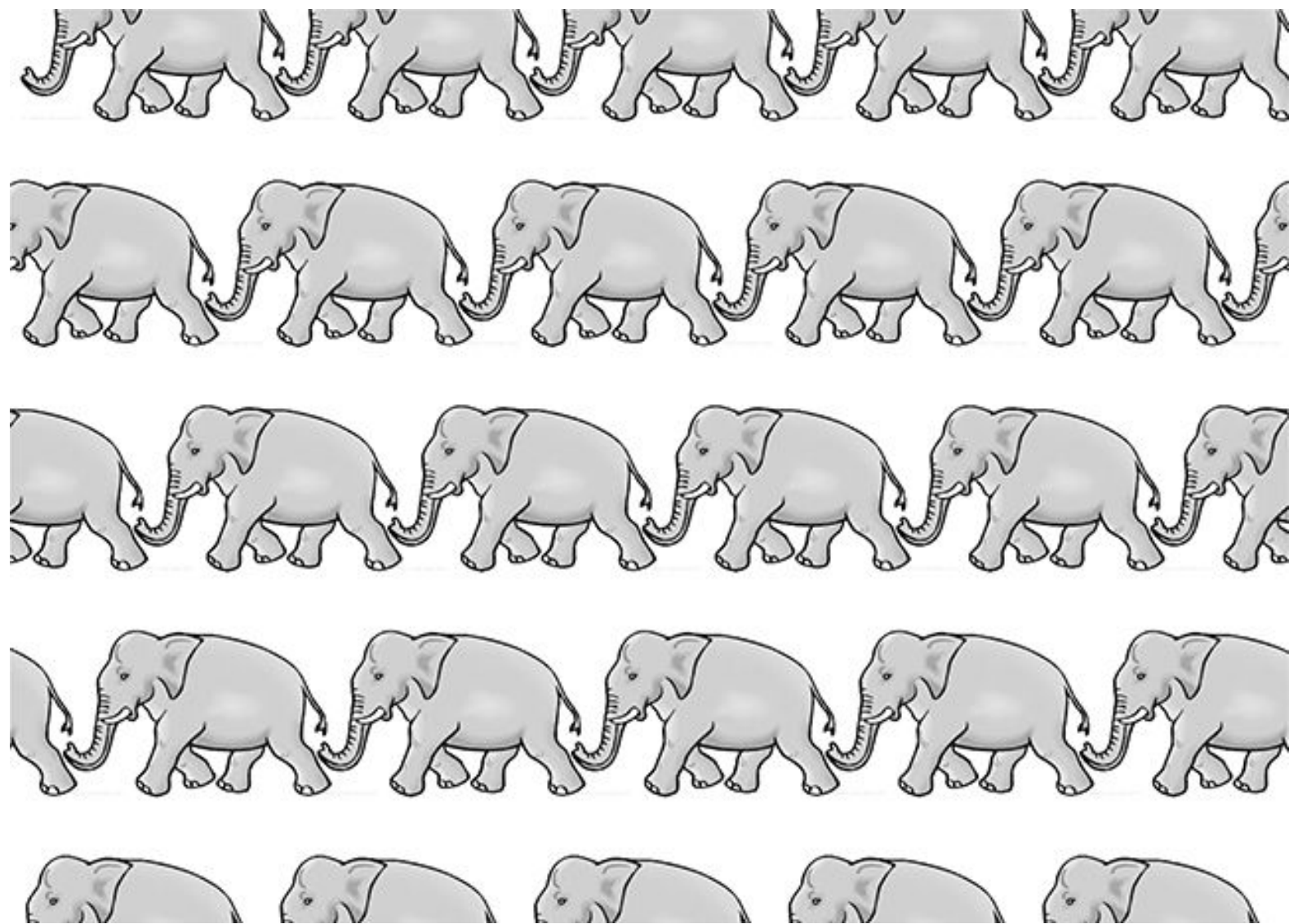
- known as first-principles and handle hundreds of atoms

XC functional

- PBE – the most popular functional for general purposes; averagely good for any properties
 - PBEsol – improves equilibrium properties of densely-packed solids and their surfaces
 - RPBE – improves adsorption description
- PBE+ U – for strongly correlated systems
- Hybrids PBE0, HSE – for strongly correlated systems
 - may be worse than PBE+ U
 - very computationally demanding (by 3 orders in plane-wave codes)
- PBE + dispersion corrections — for layered materials
 - [DFT-D2](#) , [DFT-D3](#), [Tkatchenko-Scheffler method](#), etc

Crystals have translational symmetry

- Translational symmetry - the atomic structure is repeated infinitely in three dimensions
- The number of symmetries is limited



Evgraf Fedorov,
mathematician,
crystallographer and
mineralogist
derived **230**
symmetry space
groups *The Symmetry of
Regular Systems of
Figures*, 1891

Problem: How to represent the infinite system?

Fourier transform: functions of space

The Fourier transform F of a function $f(\mathbf{r})$ is a function $F(\mathbf{g})$ in g space domain:

$$F(\mathbf{g}) = \mathcal{F}\{f\} = \int f(\mathbf{r})e^{-i\mathbf{g}\cdot\mathbf{r}}d\mathbf{r}$$

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

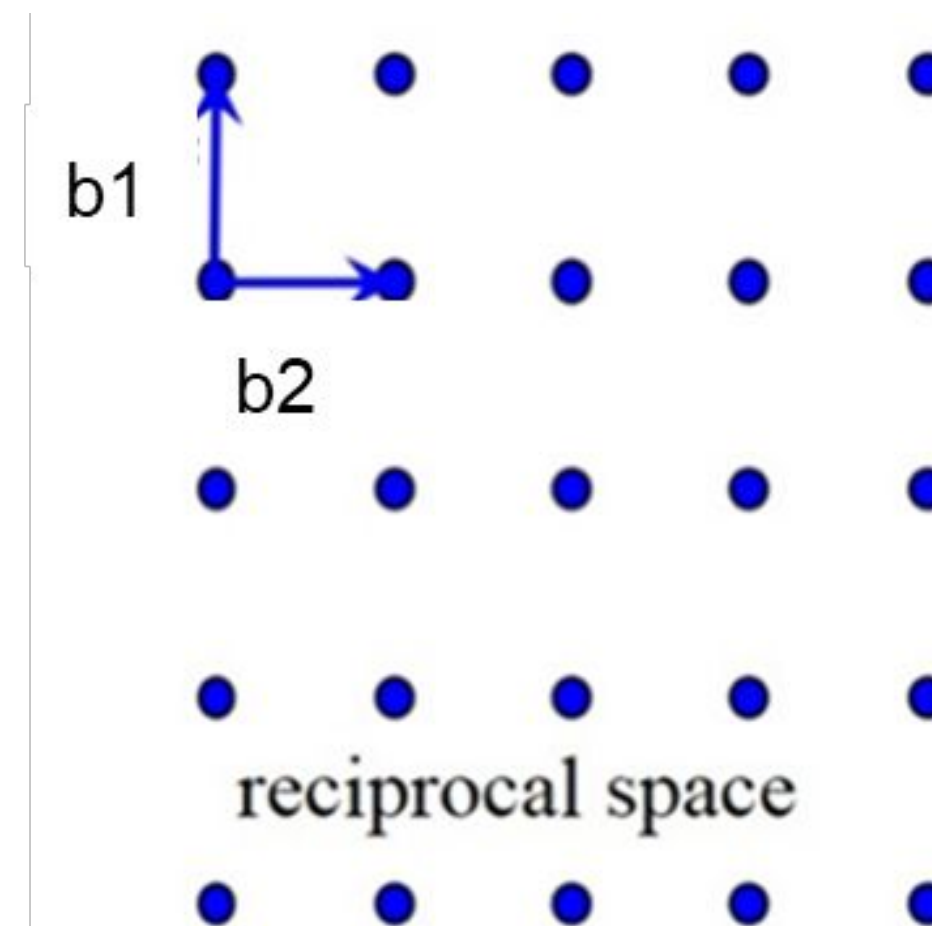
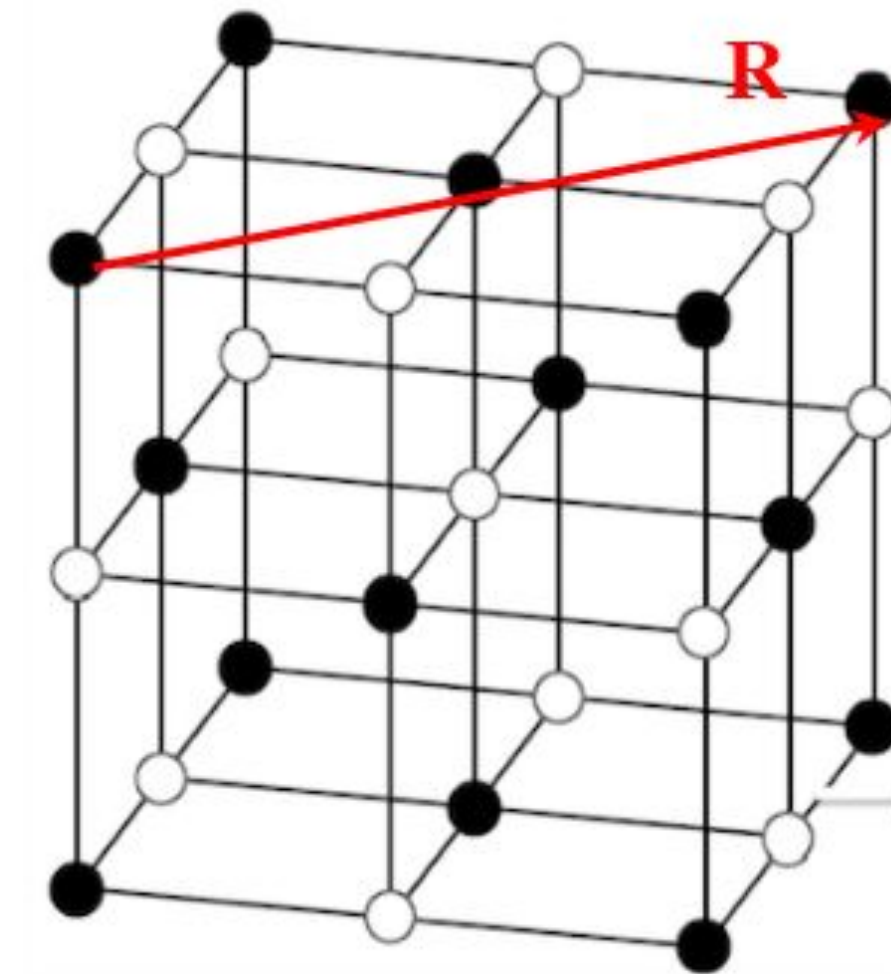
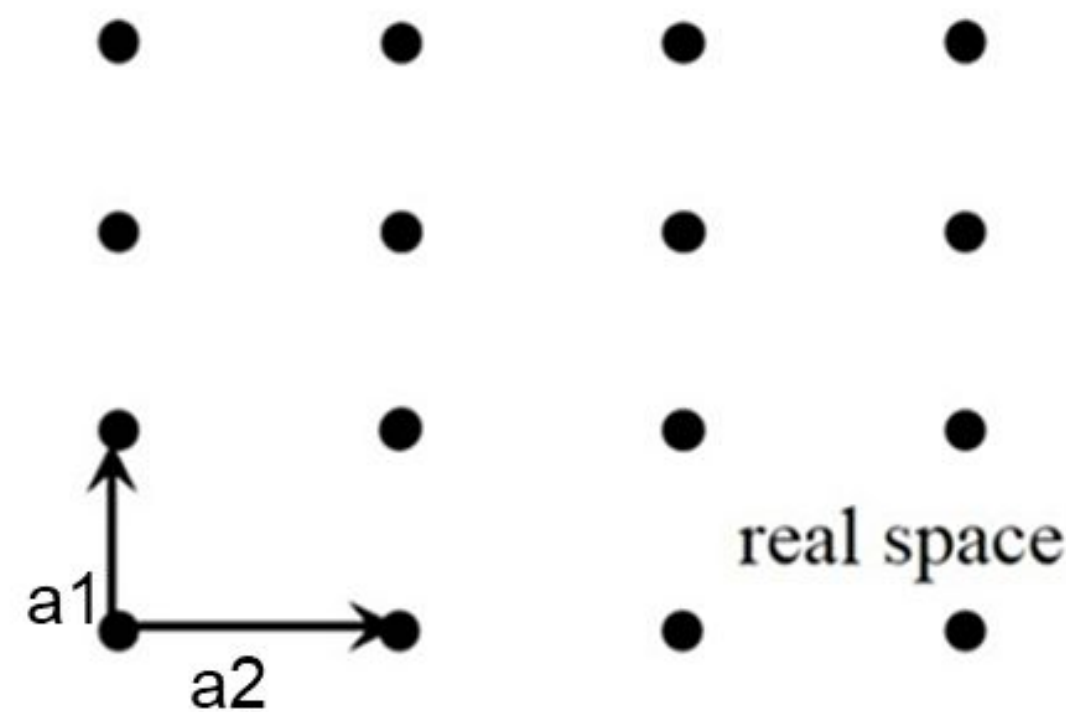
$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$$

$$\mathbf{G}_m \cdot \mathbf{R}_n = 2\pi N$$

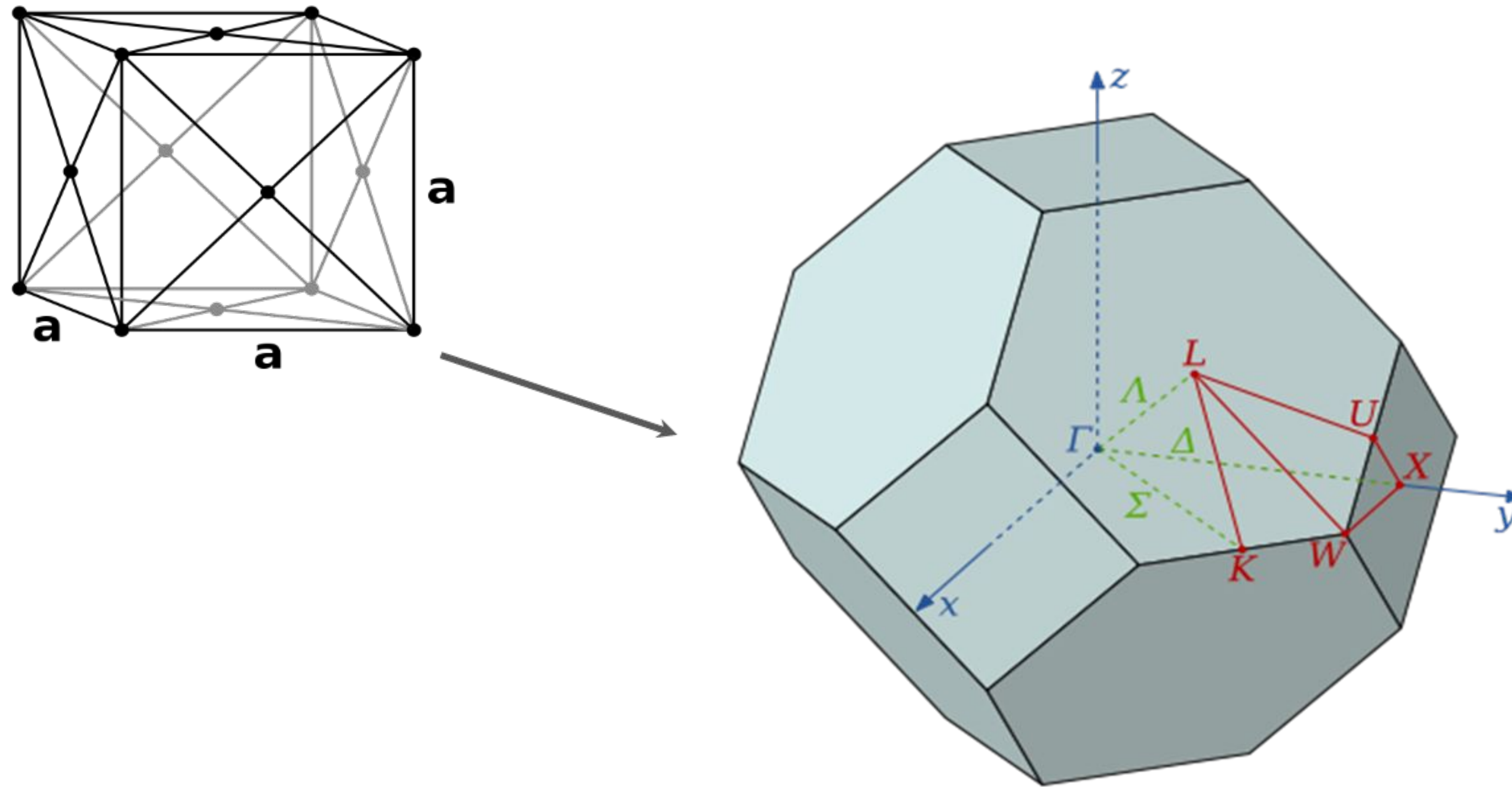
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$



First BZ for FCC lattice



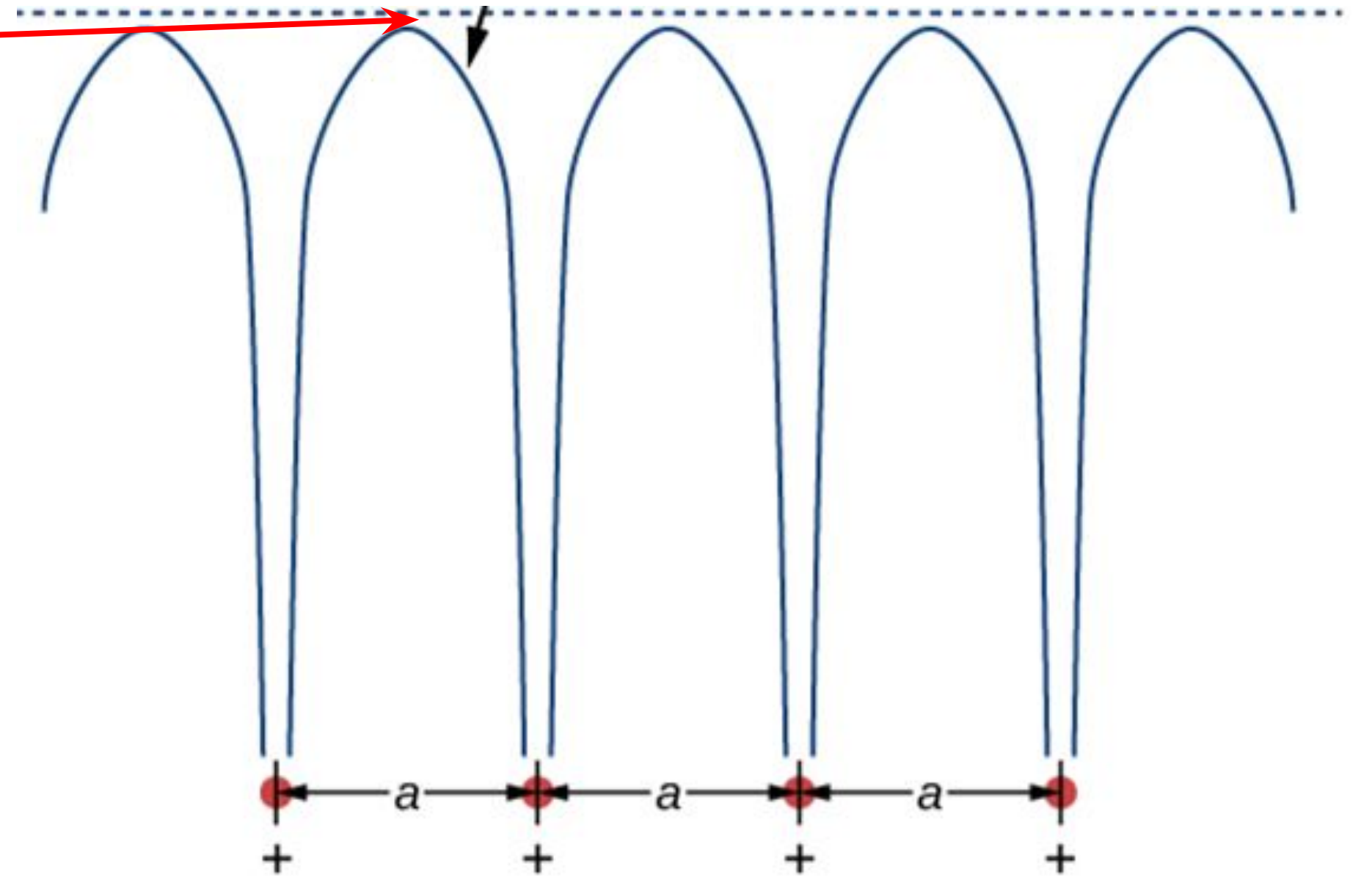
- The reciprocal lattice for FCC lattice is BCC
- Γ is the center of Brillouin zone
- High-symmetry directions are called with Greek letters ([see here](#)), high symmetry points with Latin
- Fundamental domain of BZ is often called **irreducible Brillouin zone (IBZ)**

Electrons in periodic potential of ions

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$$

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}},$$

where \mathbf{G} is a set of vectors and the $V_{\mathbf{G}}$ are Fourier coefficients



Bloch theorem for periodic systems

Theorem: In periodic system, one-electron wavefunction can be chosen to be a plane wave times the periodicity of the Bravais lattice:

$$\phi_{\mathbf{k},n}(\mathbf{r}) = u_{\mathbf{k},n}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$$

- \mathbf{k} - new quantum number, vector in **reciprocal space!**
- n is band number from the solution of reduced spectral problem with PBC
- only one reciprocal cell \rightarrow finite volume problem
- $e^{i\mathbf{k}\mathbf{r}}$ - invariant with respect $k = k+G$, where G is translation vector



Felix Bloch
Nobel prize
in 1952

Plane wave basis set for periodic part, $u_{\mathbf{k}}(\mathbf{r})$

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}],$$

\mathbf{G} is translation vector of reciprocal lattice
The periodic part is a sum of plane waves

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G})\mathbf{r}].$$

$$E = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2. \quad E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2.$$

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| < G_{\text{cut}}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G})\mathbf{r}].$$

Typical E_{cut} of 500 eV corresponds to **0.5 Å** distance in real space.

- In real crystal we do not expect too large energies
- Therefore we can omit plane waves with large G
- In VASP **ENCUT** parameter
- Important to perform all calculations at the same E-cut
- Check convergence!

Bloch theorem for Kohn-Sham equations

$$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + V_{\text{tot}}(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

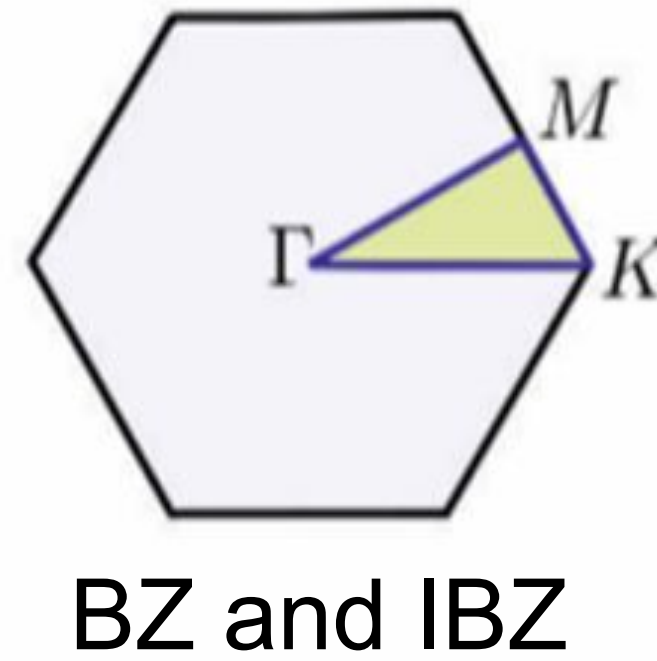
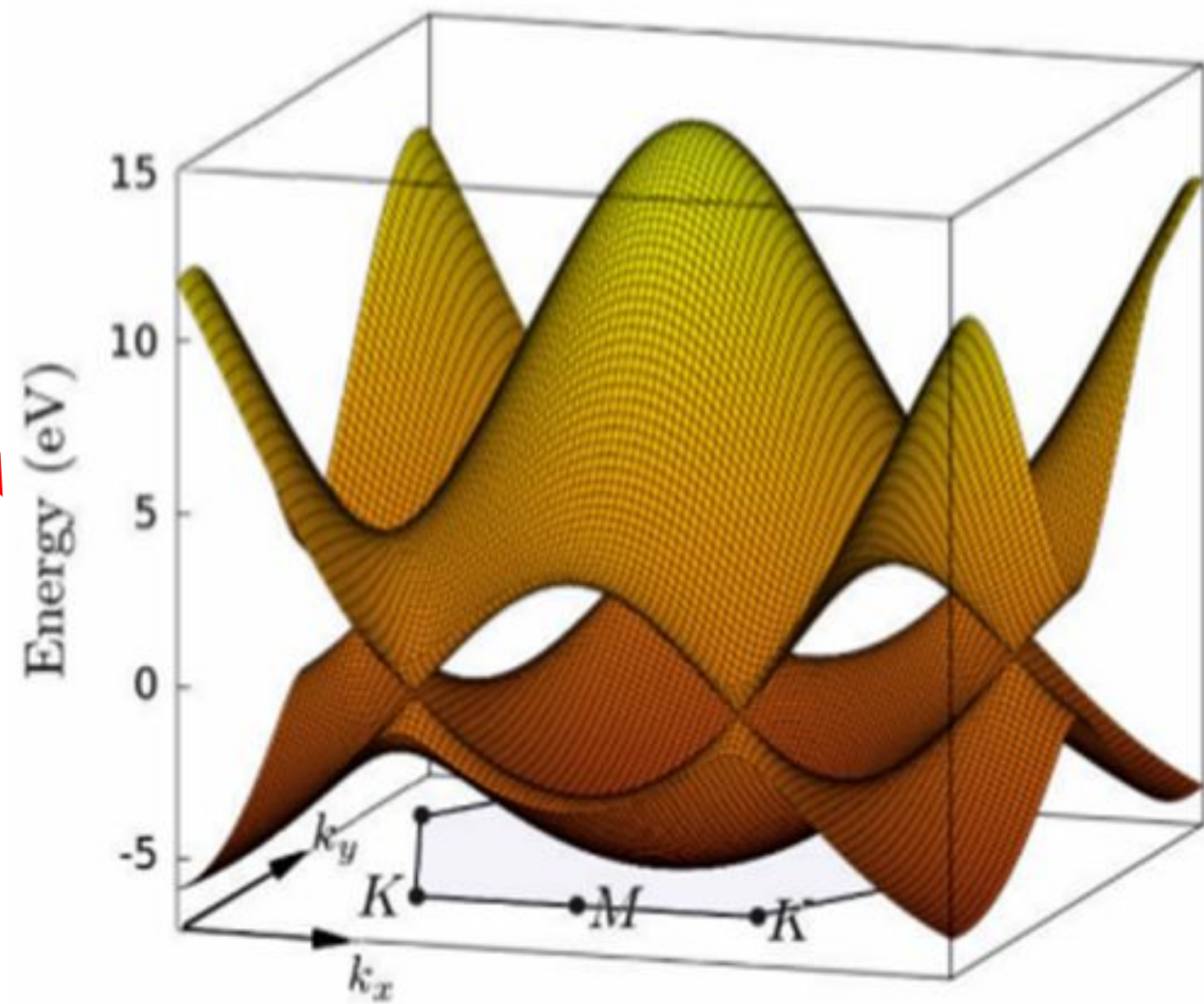
Kohn-Sham equations can be solved separately for each point at k -space

$$\left[-\frac{1}{2}(\nabla + i\mathbf{k})^2 + V_{\text{tot}}(\mathbf{r}) \right] u_{i\mathbf{k}}(\mathbf{r}) = \varepsilon_{i\mathbf{k}}u_{i\mathbf{k}}(\mathbf{r}).$$

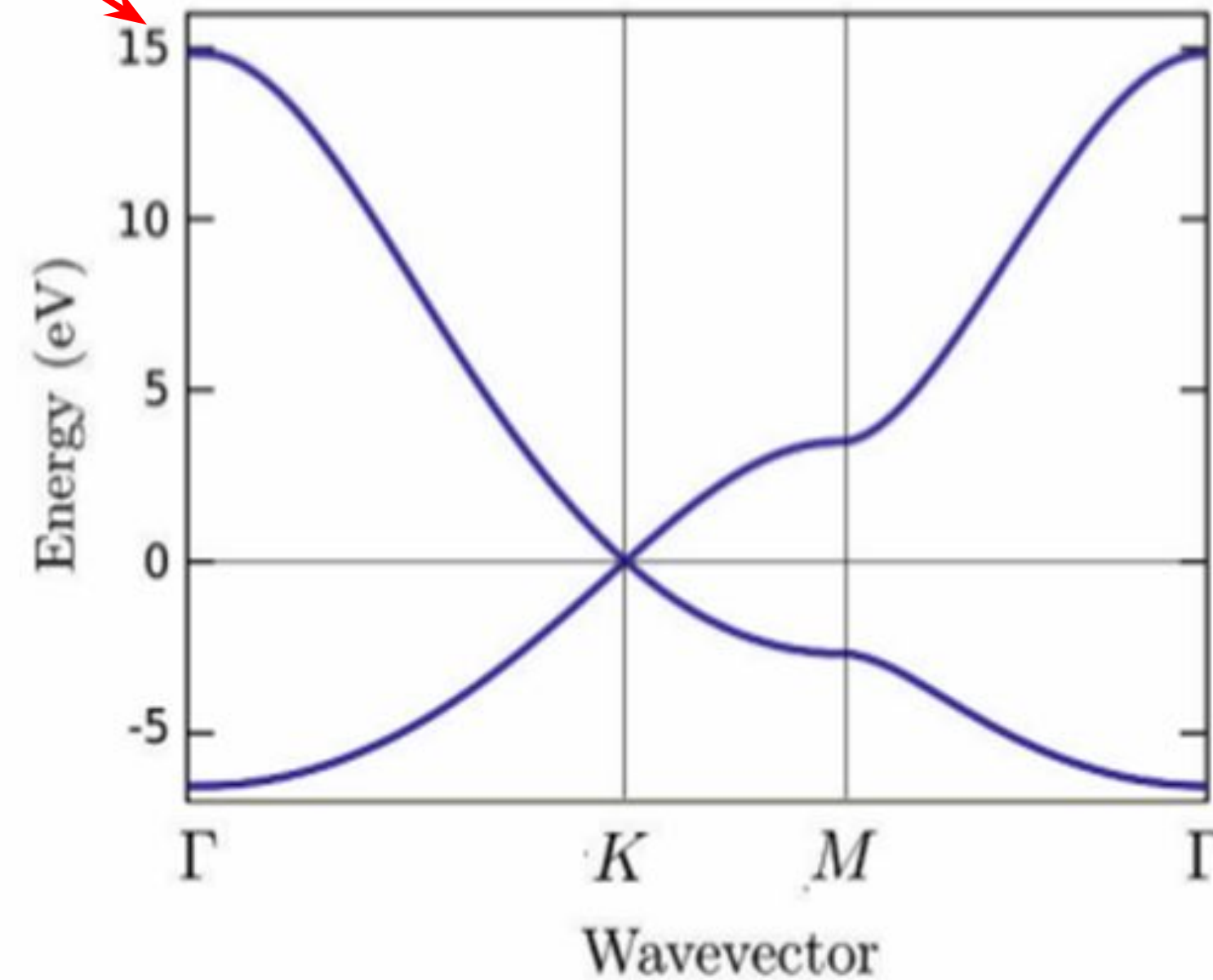
- In analogy to the particle in the box there are infinite number of solutions i , $\phi_{i\mathbf{k}+\mathbf{G}} = \phi_{i\mathbf{k}}$ where i is the number of band
 - but now, number of occupied bands is finite
- The energy of electron now is a function of \mathbf{k} for each $i - E_i(\mathbf{k})$. This is called **band dispersion**.

Example of band structure for graphene

$$\left[-\frac{1}{2}(\nabla + i\mathbf{k})^2 + V_{\text{tot}}(\mathbf{r}) \right] u_{i\mathbf{k}}(\mathbf{r}) = \epsilon_{i\mathbf{k}} u_{i\mathbf{k}}(\mathbf{r}).$$



Glustion Fig D2



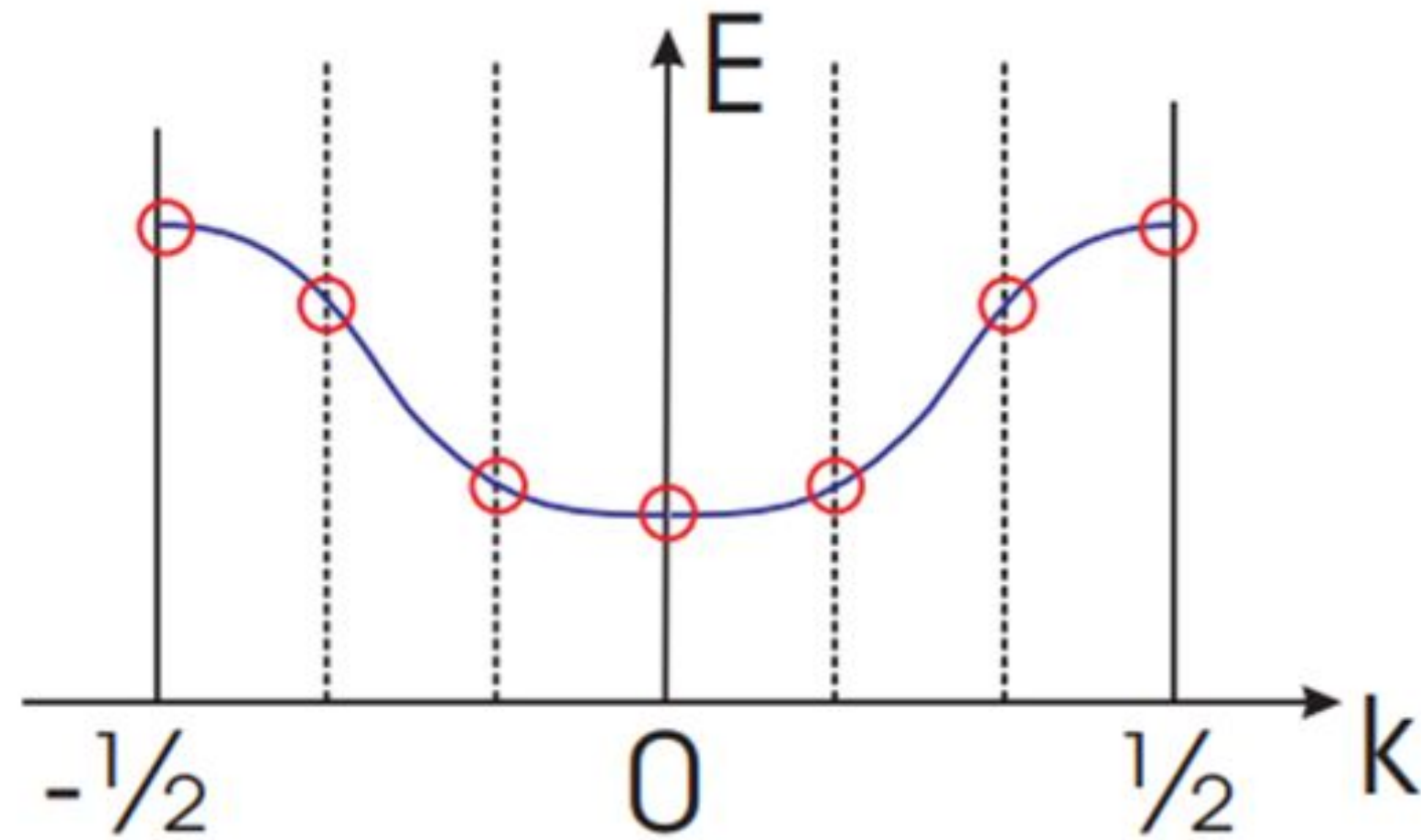
one-dimensional cross-sections is the most common way to visualize bands



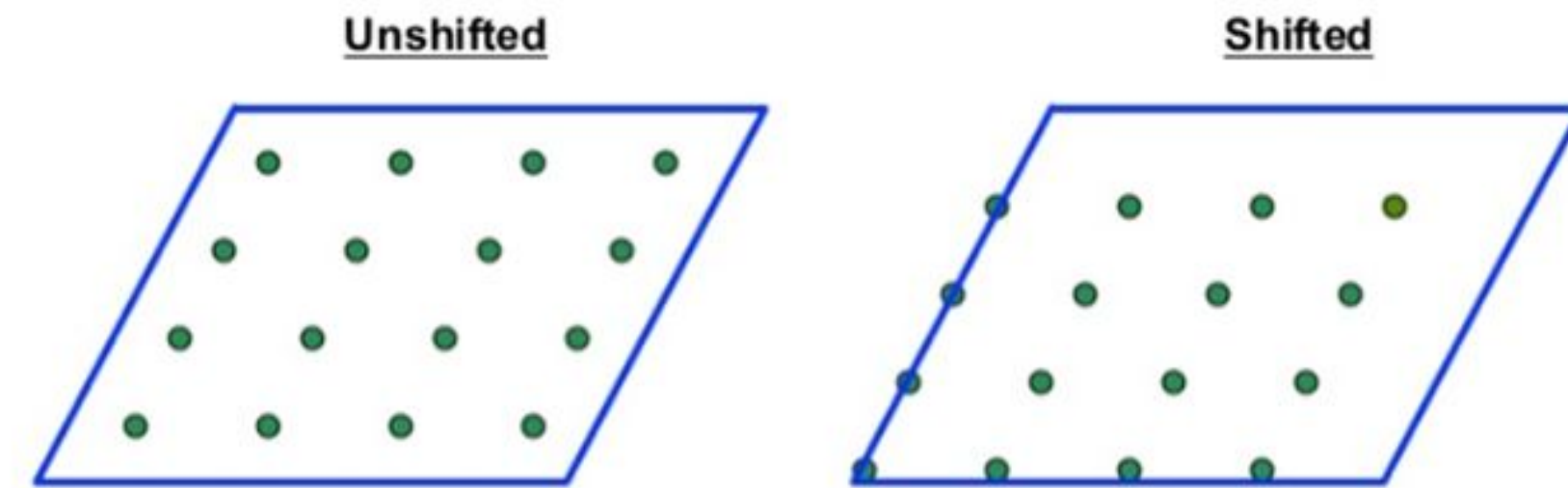
Change of energy along high-symmetry direction

k -point sampling

$$E = \frac{V_c}{8\pi^3} \int d^3k \varepsilon(\mathbf{k})$$



Monkhorst-Pack - regular equispaced mesh



- For continuous function very efficient integration can be done using only several k -points
- k -point grid $N_1 \times N_2 \times N_3$ in 3D

TABLE 3.1 Approximations to the Integral $\int_{-1/2}^1 \frac{\pi x}{2} \sin(\pi x) dx = 1$ Using the Trapezoidal and Legendre Quadrature Methods

N	Trapezoidal Method	Legendre Quadrature Method
2	0.6046	1.7605
3	0.7854	0.8793
4	0.8648	1.0080
5	0.9070	0.9997

Choosing k -points mesh

How to choose N_1, N_2, N_3 ?

Commonly the following rule of thumb applies:

$$N_1:N_2:N_3 = |\mathbf{b}_1|:|\mathbf{b}_2|:|\mathbf{b}_3|$$

where \mathbf{b}_i are the reciprocal lattice vectors.

- for VASP k -points are provided in [KPOINTS](#) file
- For automatic generation use [KSPACING](#) tag
- check convergence up to k -spacing of 0.05 \AA^{-1} !
 - k -spacing 0.5 \AA^{-1} risk of large errors

Advices on choosing k -grid and smearing

K -grids

- Be sure that k -grids are converged
- Use fine grid for DOS
- Use equivalent k -points meshes when comparing different cells

Orbital occupation (smearing)

- **Systems with a band-gap** (semiconductors, insulators, molecules): Use *Gaussian* smearing (robust) with a low broadening, e.g. around **0.05 – 0.2 eV (Smaller is better, but the SCF convergence can be long ...)**.
- **Metals** : Use *Methfessel-Paxton* with as large a broadening as possible as long as the entropy contribution to the free energy remains small. Ensure that you have several empty bands, which is required for convergence
- **DOS**: tetrahedron smearing with Blöchl corrections – accurate interpolation for energies and DOS, but may introduce errors in forces

Smearing at Fermi level

$$E = \sum_i \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} f_{i\mathbf{k}} \epsilon_{i\mathbf{k}} - \left[E_{\text{H}} + \int d\mathbf{r} V_{xc}(\mathbf{r}) n(\mathbf{r}) - E_{xc} \right]$$

$$f_{i\mathbf{k}} = \frac{1}{e^{(\epsilon_{i\mathbf{k}} - \mu)/\sigma} + 1}$$

Discontinuity - very large number of k-points is needed to calculate integrals correctly

Sholl, p. 60

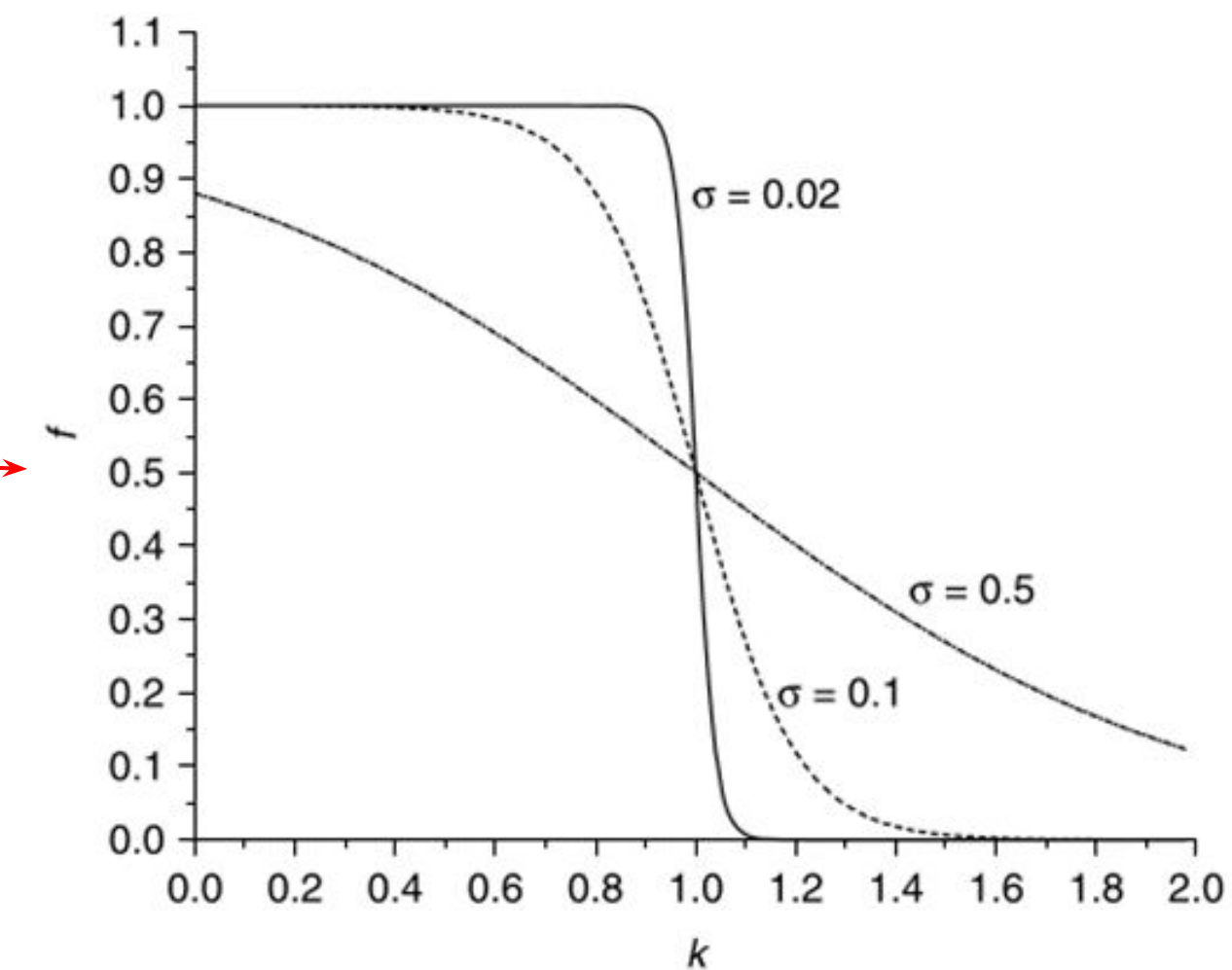
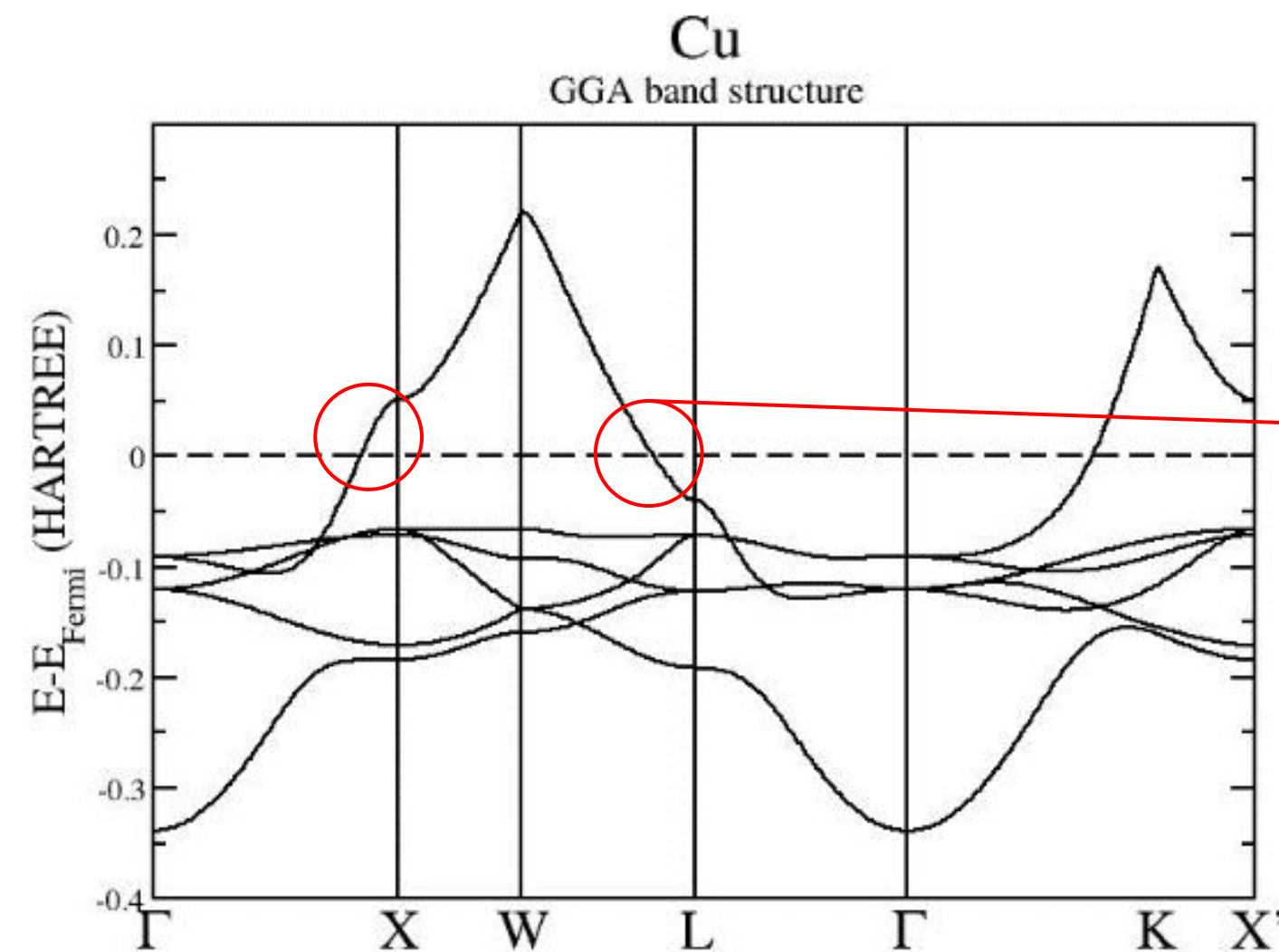


Figure 3.3 Fermi Dirac function [Eq. (3.10)] with $k_0 = 1$ and several values of σ .

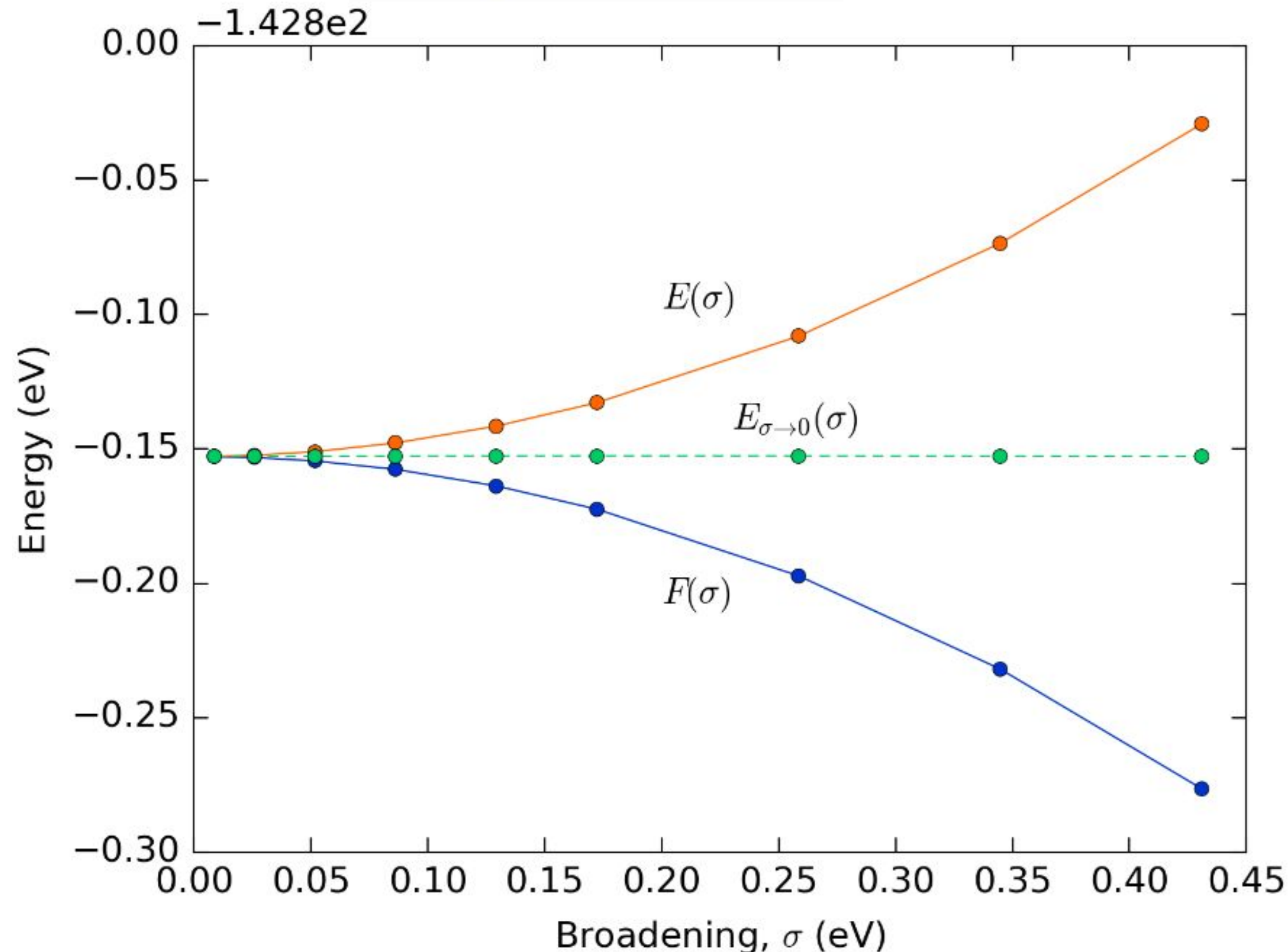
- Smearing is needed to make function continuous, [ISMEAR](#).
- In VASP: **ISMEAR** – choose method for smearing; [SIGMA](#) — the value of smearing
- Check smearing parameter!
- More k -points for metals, density $< 0.15 \text{ \AA}^{-1}$ (**KSPACING**)

(Electronic) free energy functional

When introducing the *Fermi-Dirac* distribution one effectively considers an equivalent system of non-interacting electrons at a temperature T with electronic entropy S .

$$F[n] = E[n] - TS$$

$$E_{\sigma \rightarrow 0}(\sigma) = \frac{1}{2}[E(\sigma) + F(\sigma)].$$

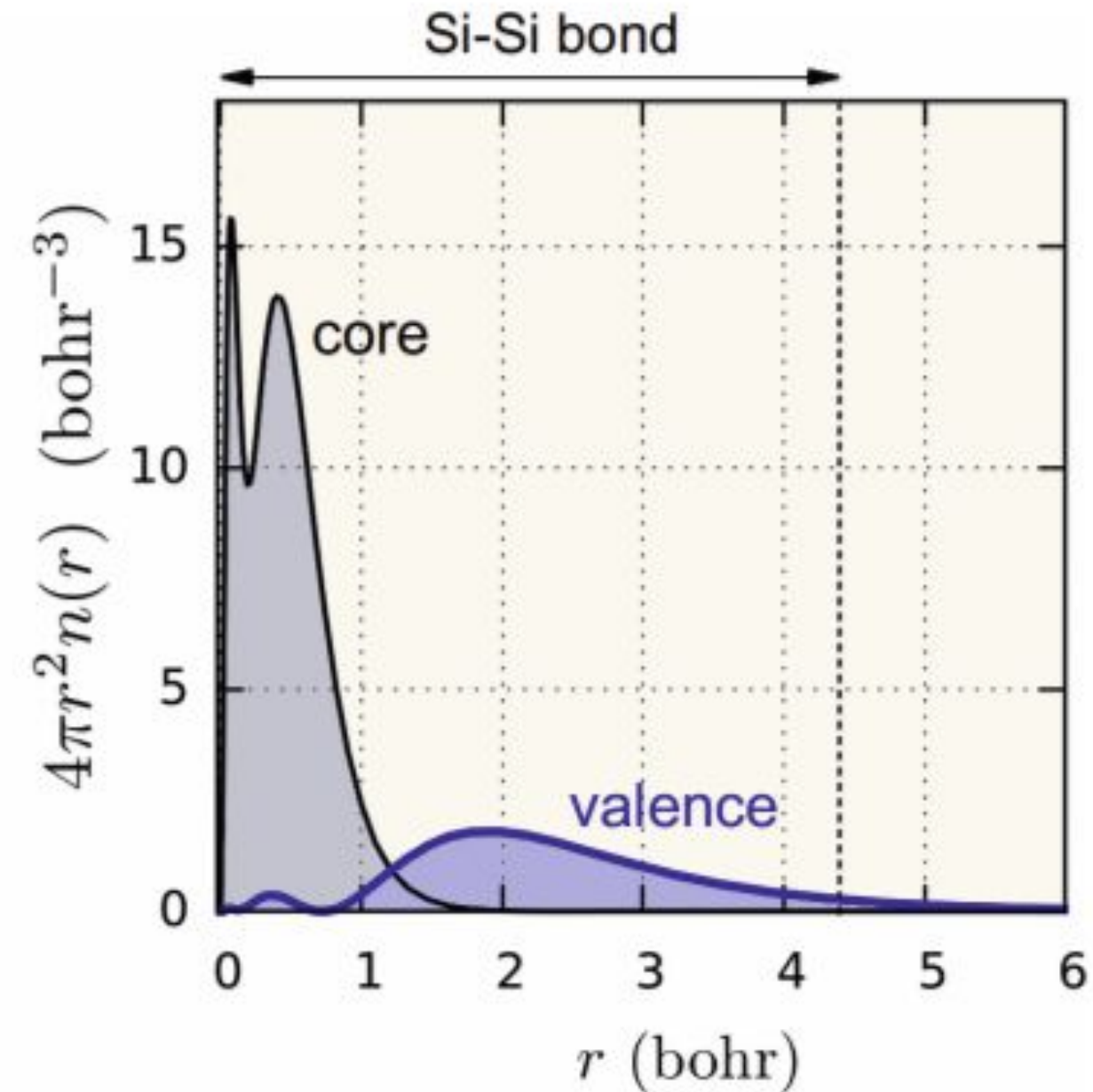
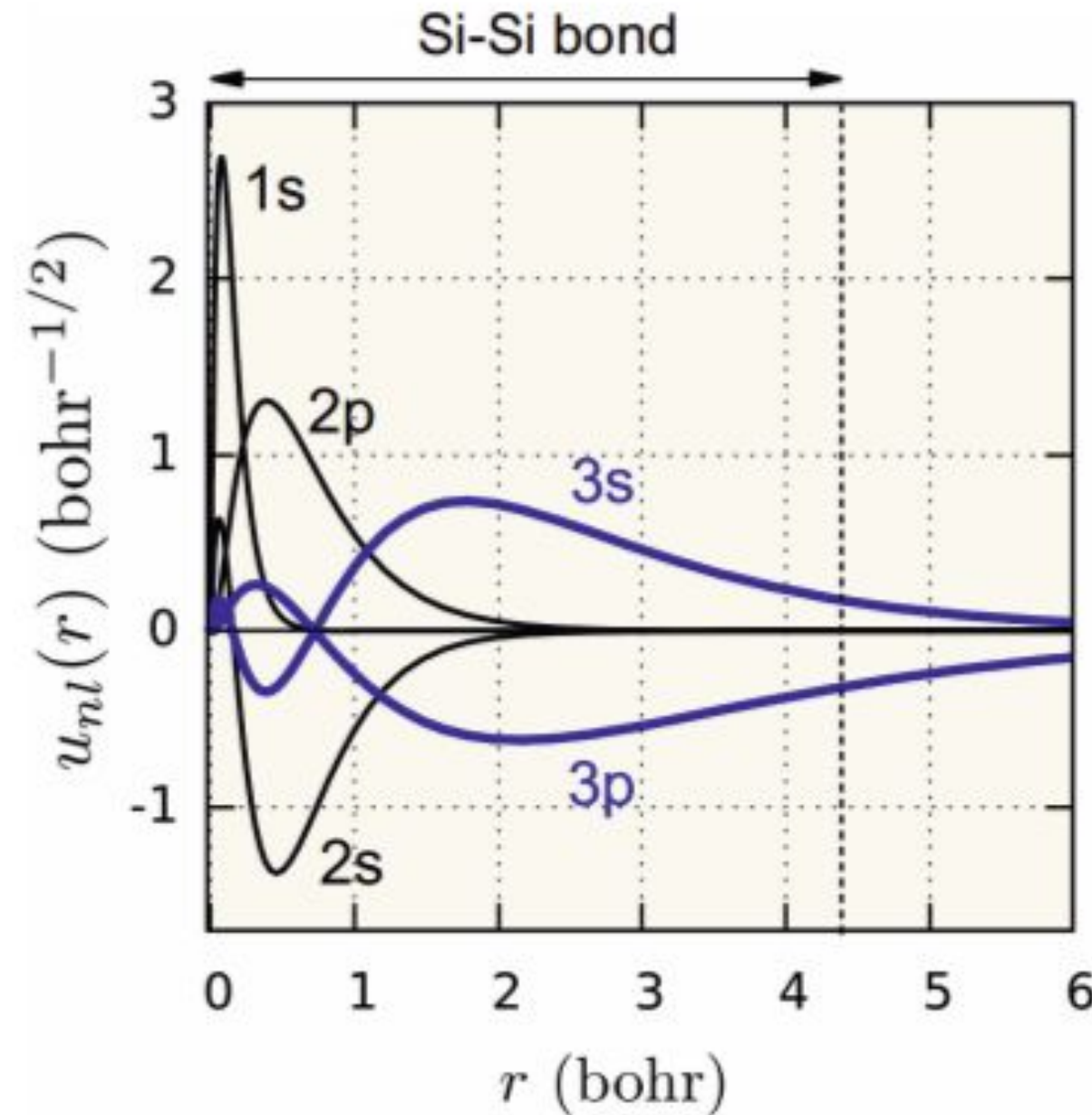


In VASP three energies are provided:

- **free energy** **TOTEN**
- **energy without entropy**
- **energy (sigma \rightarrow 0)**
- Do not mix with thermodynamic free energy

Plane-waves for valence and core electrons

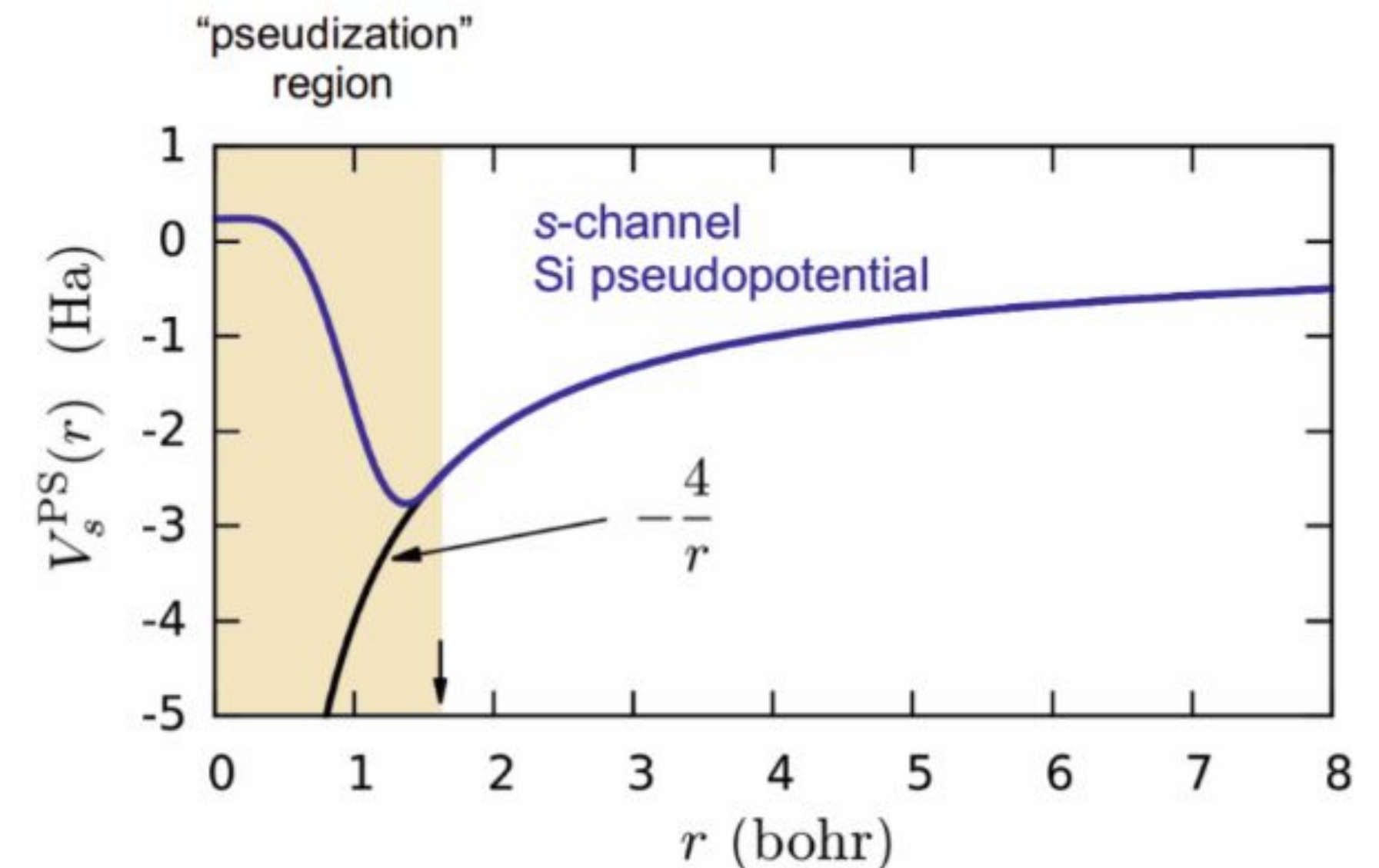
Giustino, F., (2014).
Oxford
University
Press.



- The valence electrons distributed mainly between Si atoms
- The core electrons localized near the cores and do not participate in bonding

- To describe core electrons a lot of plane waves are required
 - very computationally demanding!

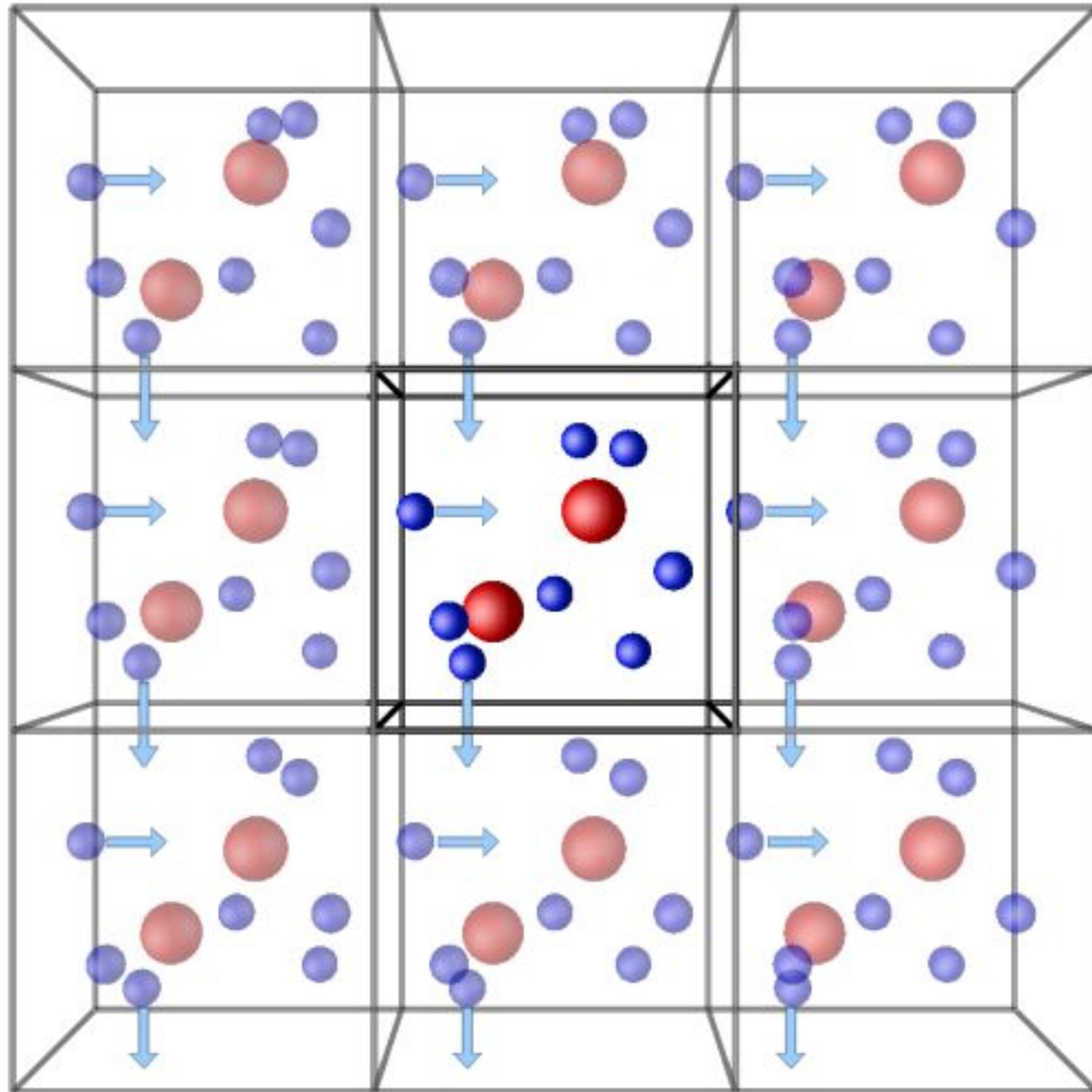
- **Solution: Pseudopotential**



Pseudopotential in DFT codes

- Hard and soft potentials – large and small E_{cut}
- ([POTCAR](#) in VASP)
- PAW – projected augmented wave method. See for VASP [PAW](#) (different number of valence electrons available, [sv, pv](#))
- Vanderbilt USP
- Check required pseudopotential for your task
 - number of electrons (more for small distances)
 - minimal energy cut-off (if several elements are used, the maximal should be chosen)
- Use the same pseudopotential for all calculations

Periodic Boundary conditions



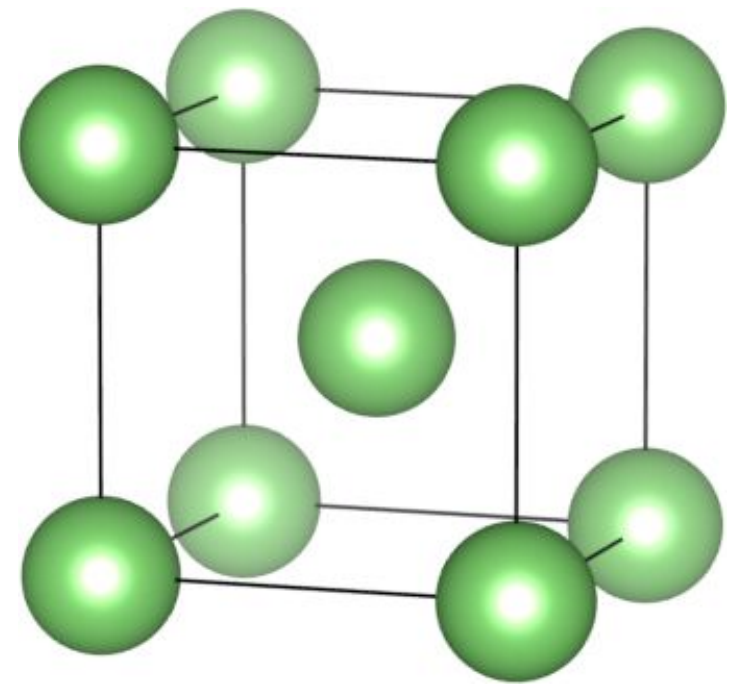
Periodic boundary conditions (PBC)

- when an object passes through one side of the unit cell, it reappears on the opposite side with the same velocity.
- Ideally suited for periodic systems.

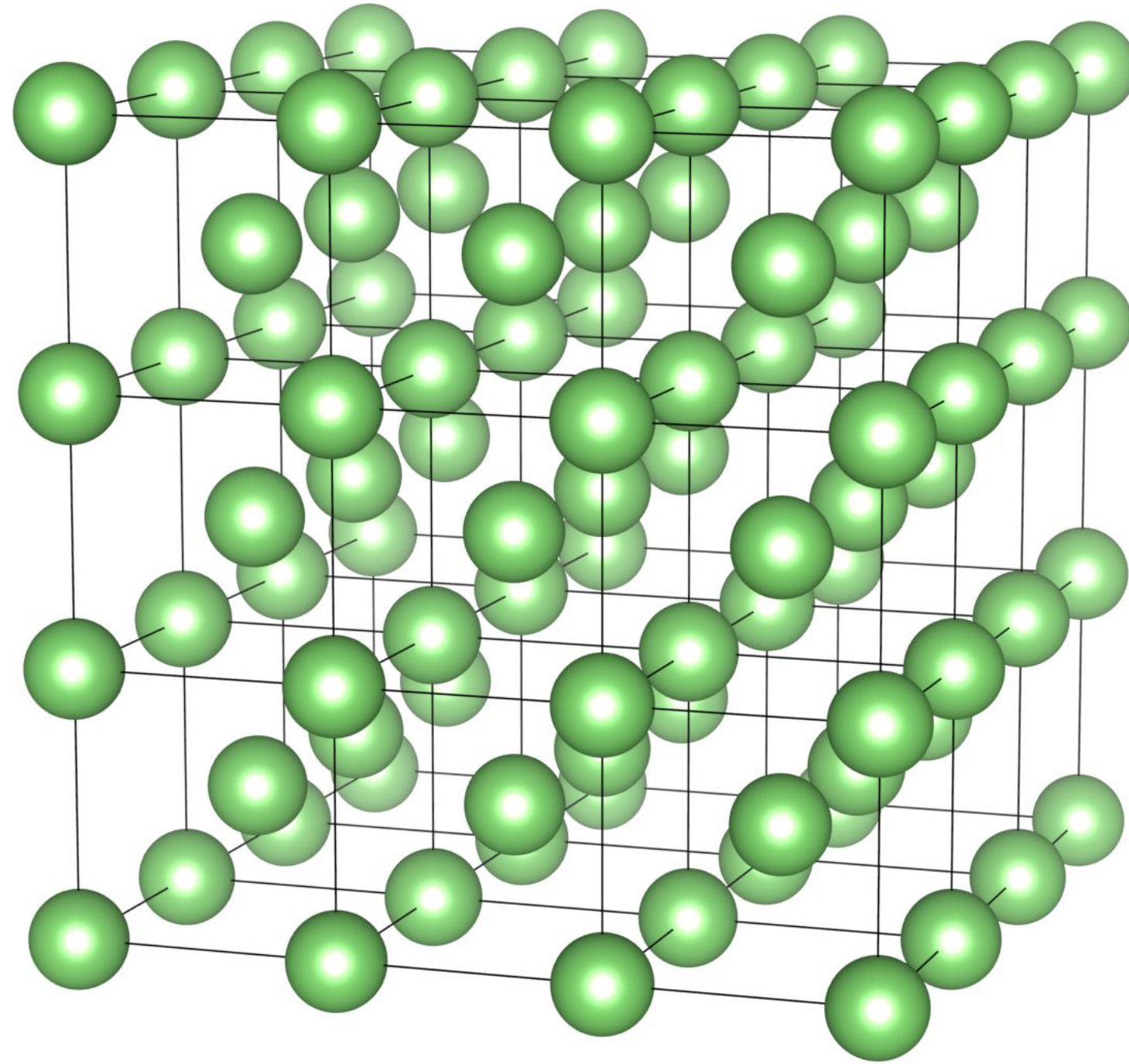
Keep in mind!

- Any atomic displacements or defects inside the unit cell are replicated infinitely, which may lead to artificial interactions.
- The net electrostatic charge of the system must be zero.
- Charged defects can be considered by adding a homogeneous background charge of opposite sign.

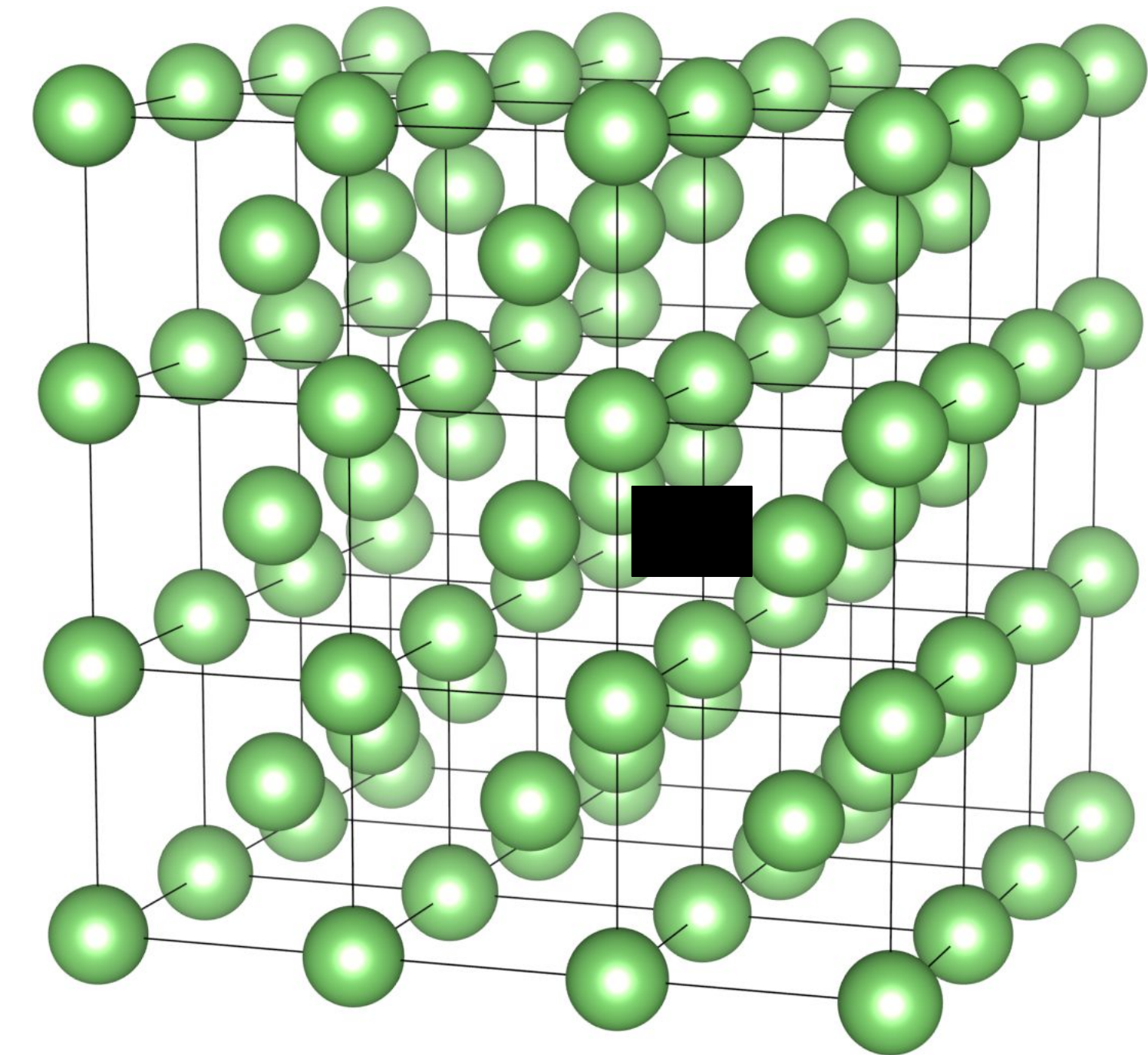
Supercell approach for non-periodicity



1. Take Unit cell

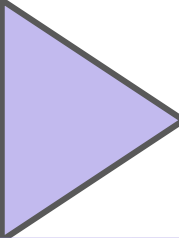


2. Create a supercell



3. Make a displacement of defect

- Remember that large supercell is still affected by PBC conditions
- Check convergence with respect to supercell size



Optimization of atoms in periodic systems

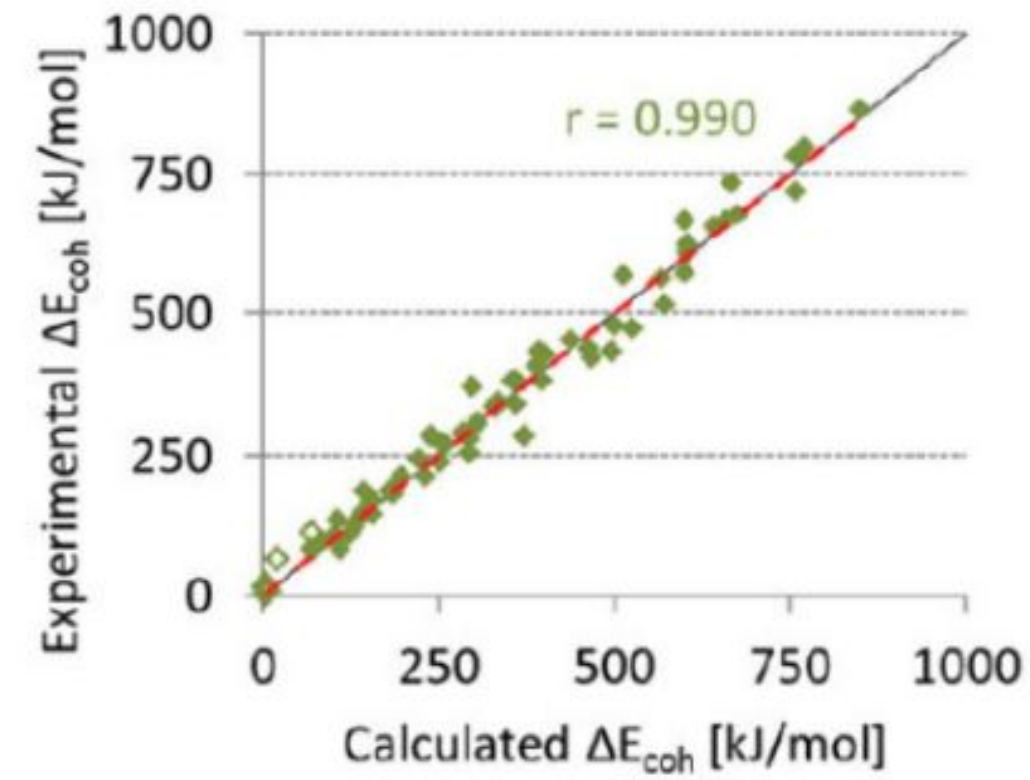
In VASP important parameters:

- [IBRION](#) – type of optimisation
 - 0 – molecular dynamics
 - 1 – quasi-Newton
 - 2 – Conjugate gradient
 - 3 – Damped MD
 - etc.
- [NSW](#) – number of steps
- [POTIM](#) – step in MD, fs

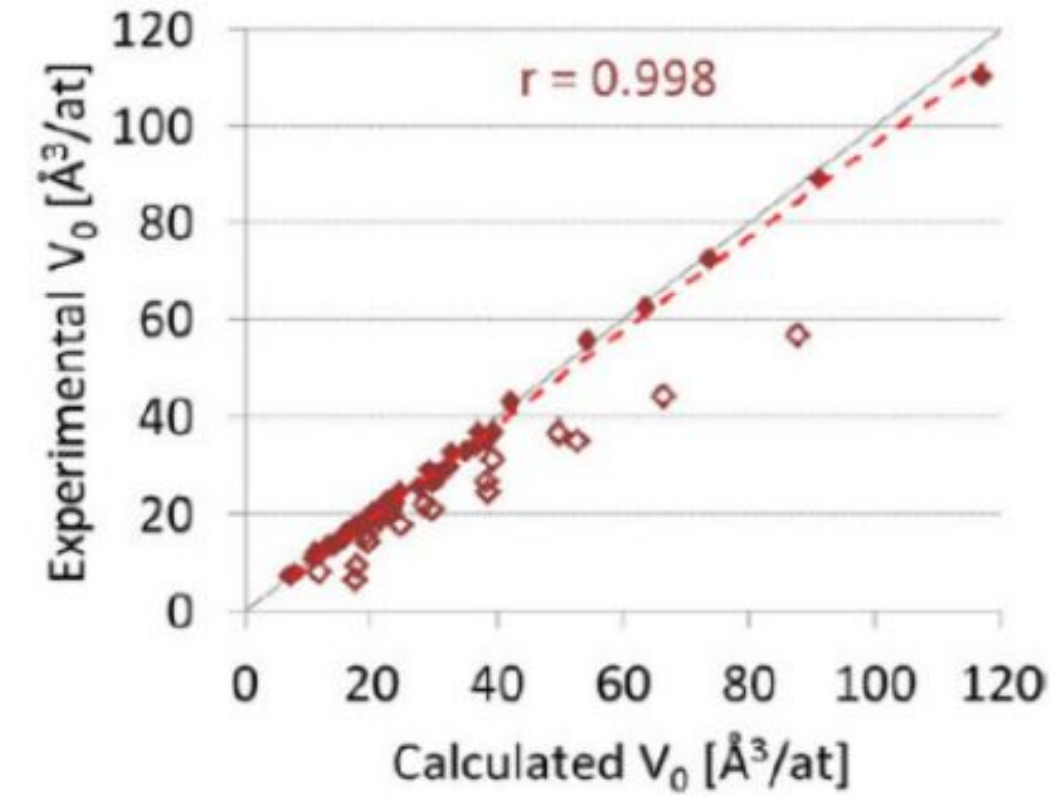
Accuracy of DFT calculations

Accuracy

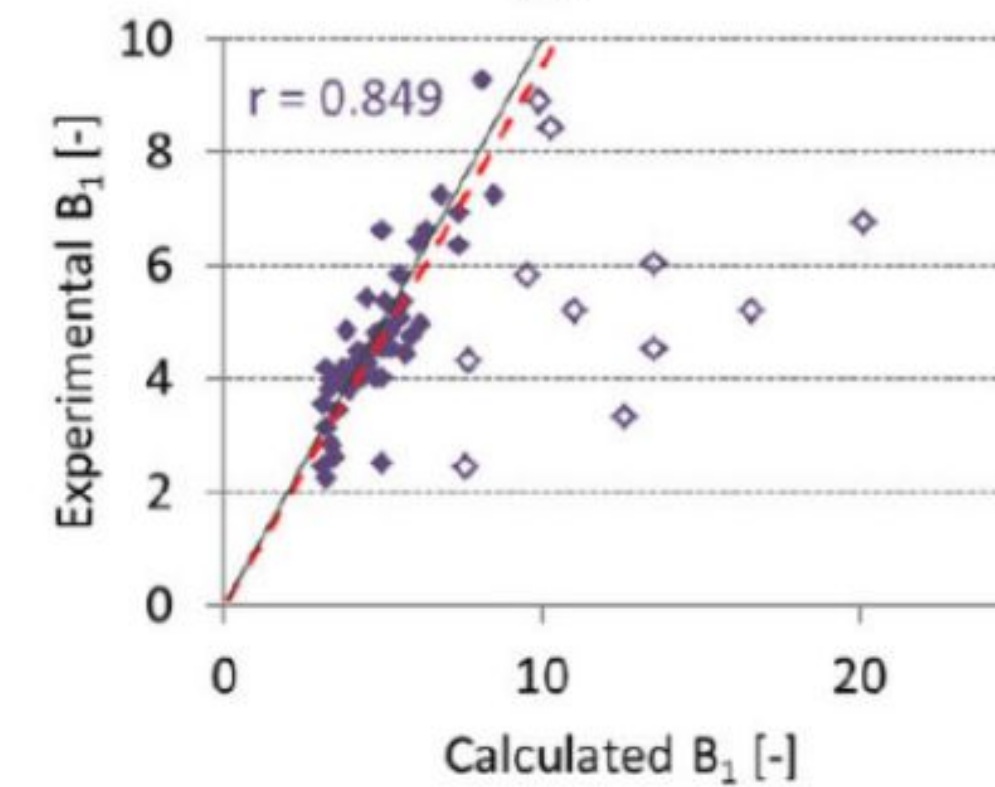
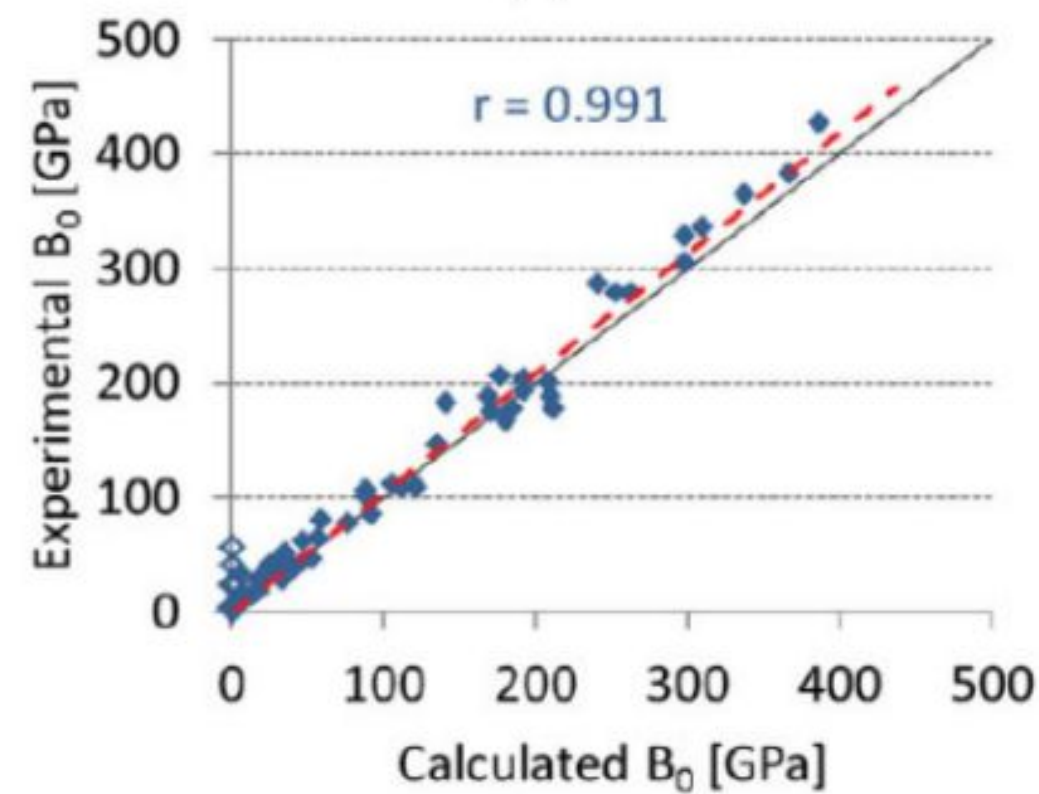
K Lejaeghere et al, Critical Reviews in Solid State and Materials Sciences 39, 1 (2014)



(a)



(b)

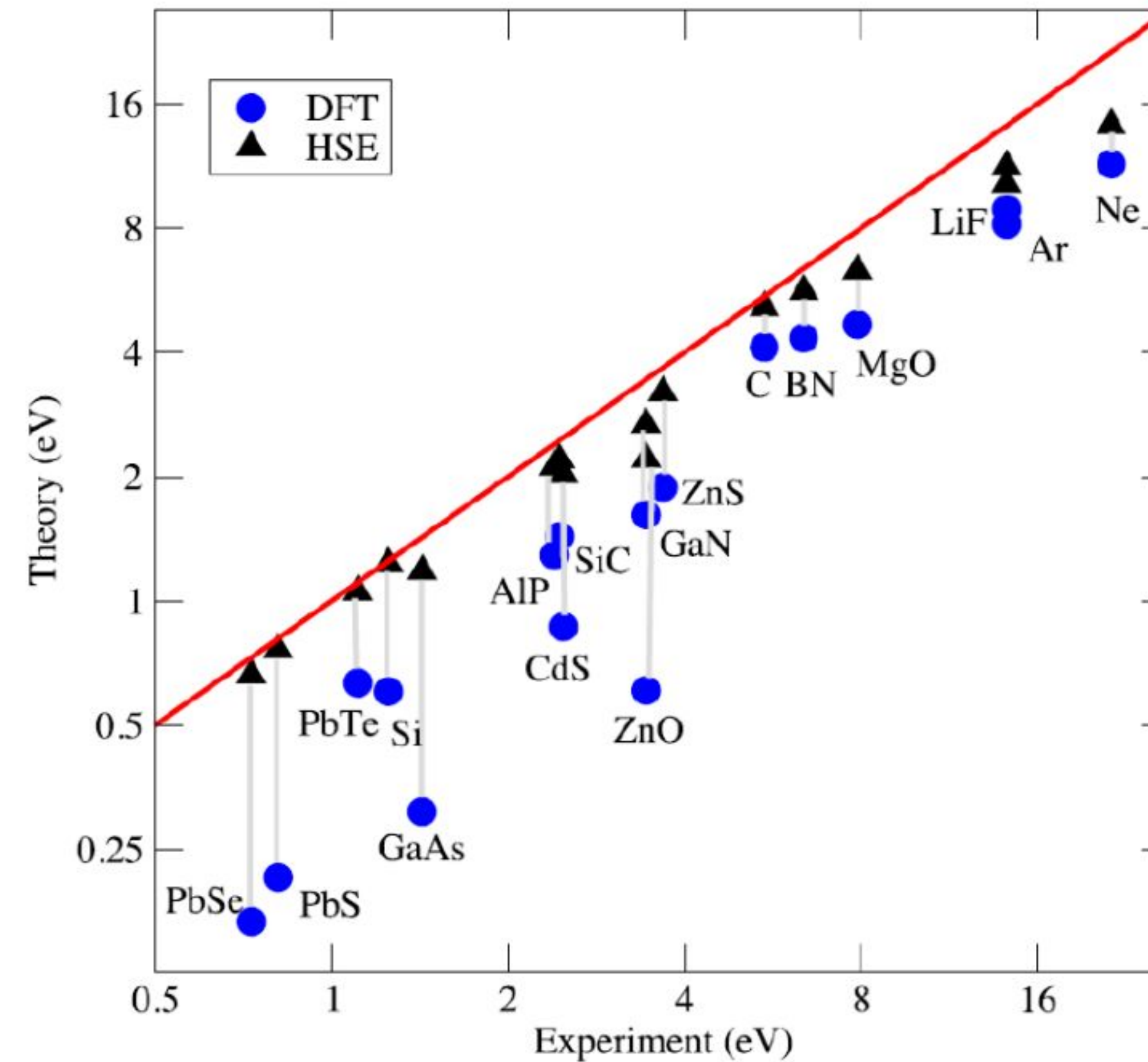


Geometry, cohesion energies, mechanical properties are generally not bad even for simple DFT (LDA, PBE – above)

Accuracy of bandgap calculations

Accuracy: bandgap

J Hafner, J Phys Condensed Matter 22, 384205 (2010)



For bandgaps use HSE functional or GW

► Calculation of Properties

- Electronic structure
- Lattice constants
- Elastic moduli
- Phonon bands
- Free energy
- Phase diagrams
- Defects

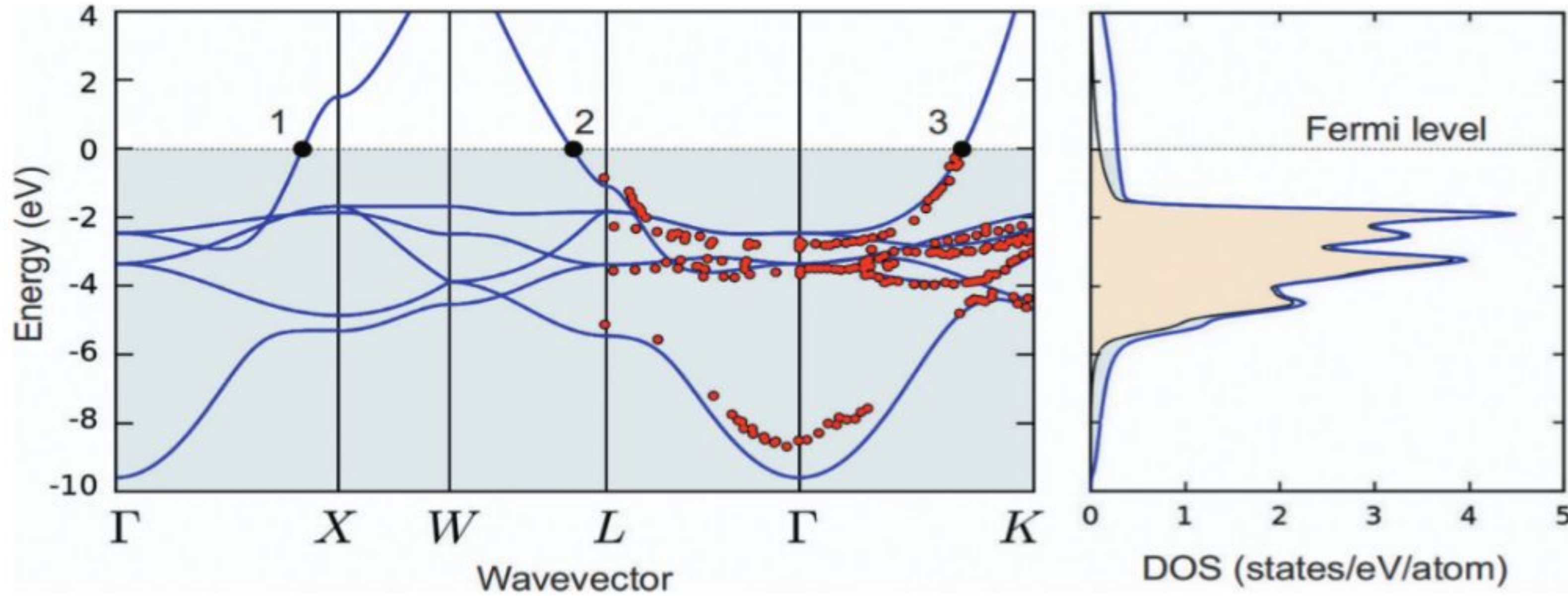
Density of states

Cu [Ar] 4s¹ 3d¹⁰ FCC lattice with 1 atom

11 Kohn-Sham electrons

$$\left[-\frac{1}{2}(\nabla + i\mathbf{k})^2 + V_{\text{tot}}(\mathbf{r}) \right] u_{i\mathbf{k}}(\mathbf{r}) = \varepsilon_{i\mathbf{k}} u_{i\mathbf{k}}(\mathbf{r}).$$

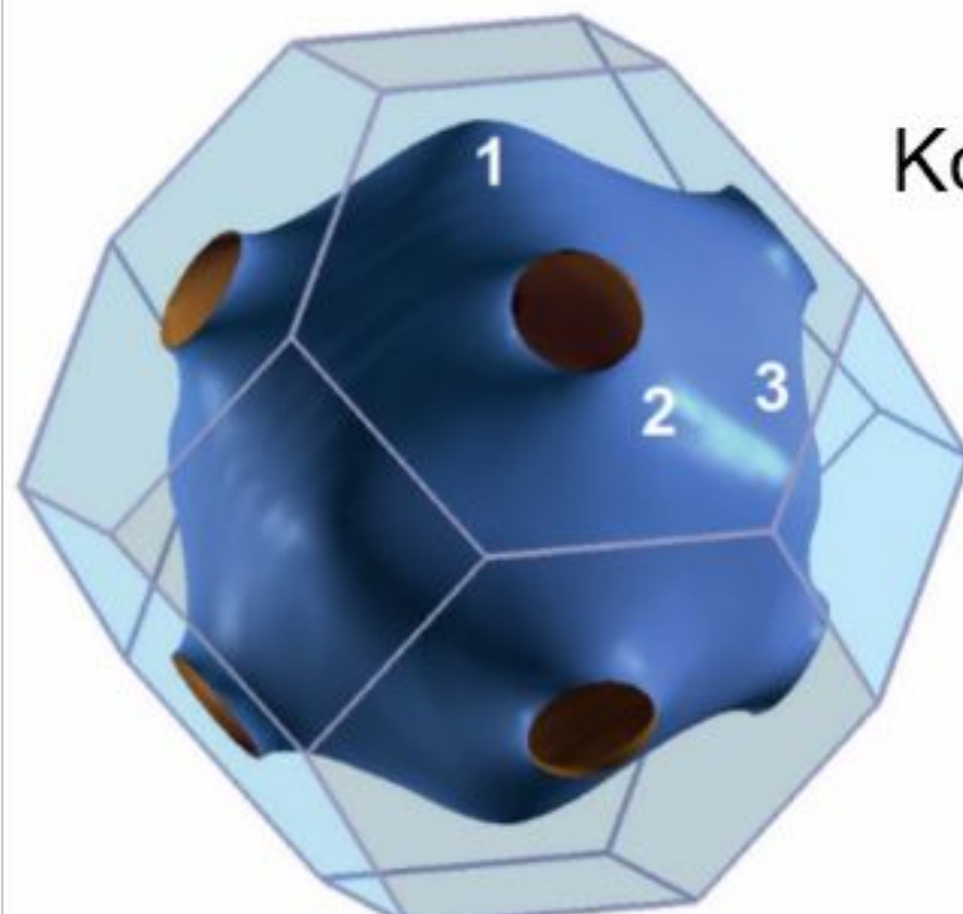
$$\rho(E) = \sum_i \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \delta(E - \varepsilon_{i\mathbf{k}}).$$



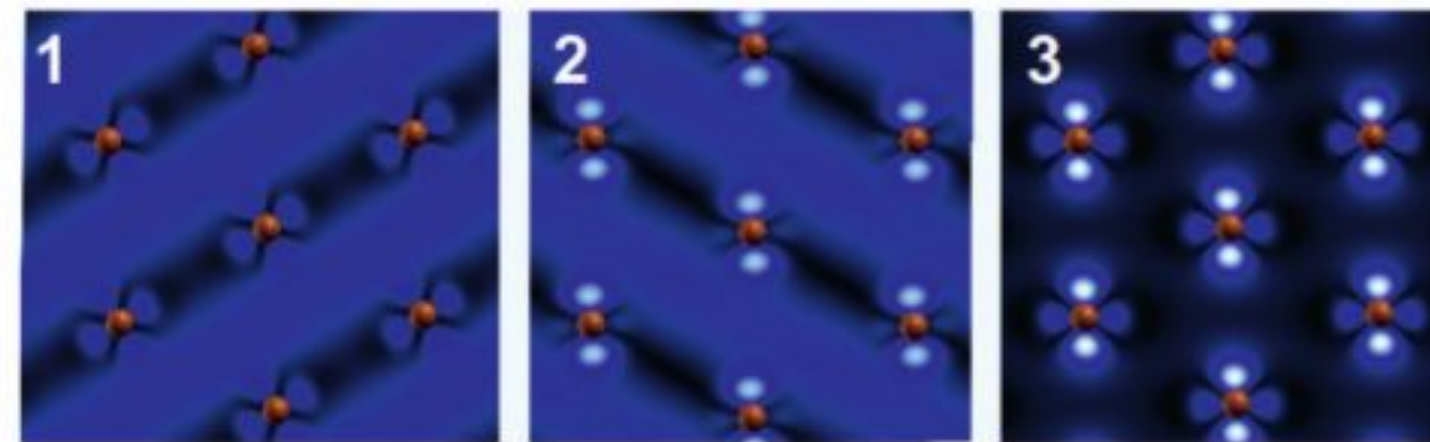
The parabolic behaviour in L-Γ-K region resembles free electron gas, however it is interrupted by spaghetti-like *d* states.

The red discs are from the experimental angle-resolved photoemission data – The Kohn-Sham eigenvalues has some physical reality

Fermi Surface



Kohn-Sham wavefunctions $|u_{n\mathbf{k}}(\mathbf{r})|^2$



d_{xy}

d_{z^2}

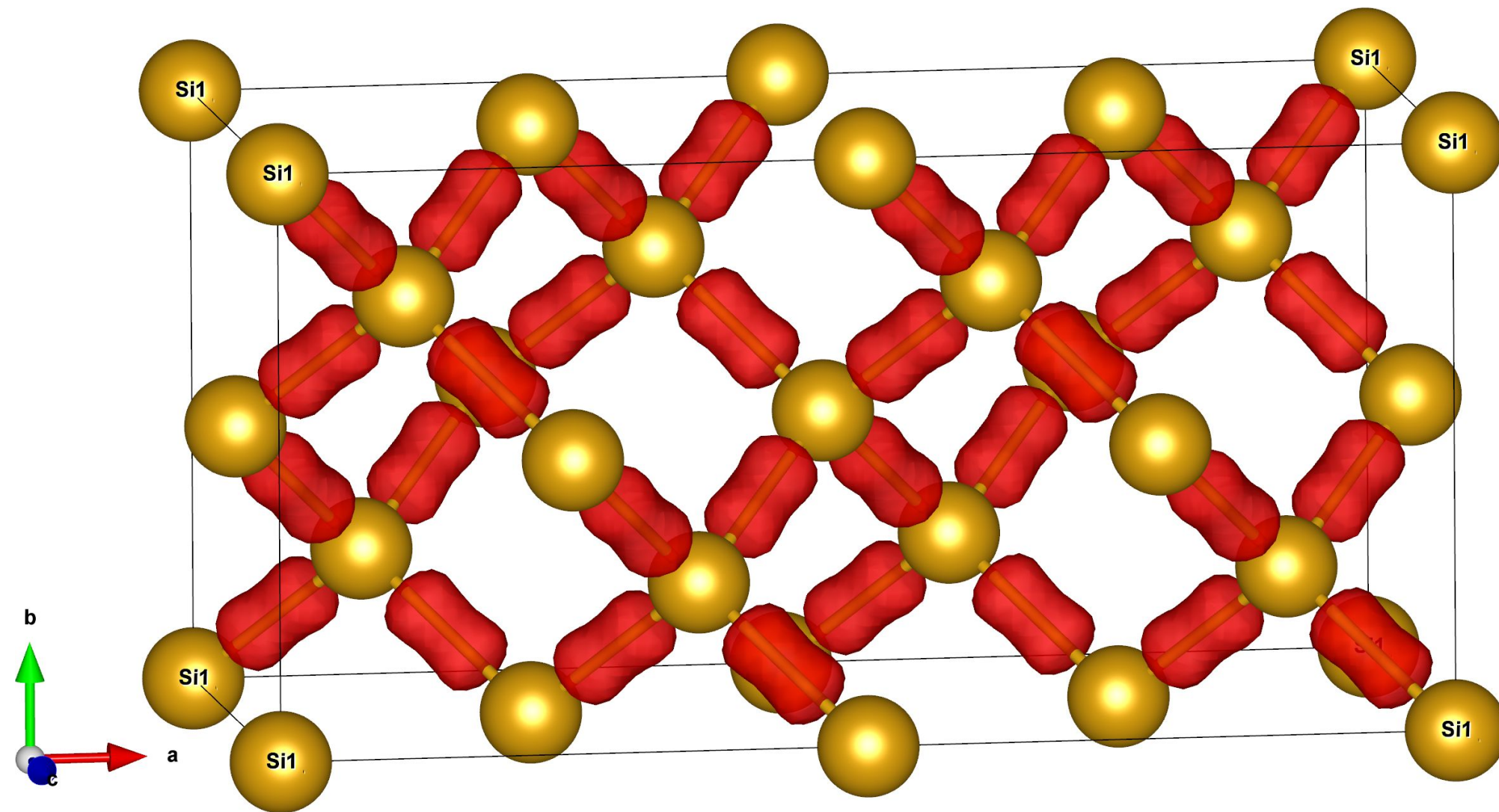
Significant differences between states across the Fermi surface.

Giustino, F., (2014).
Oxford University
Press.

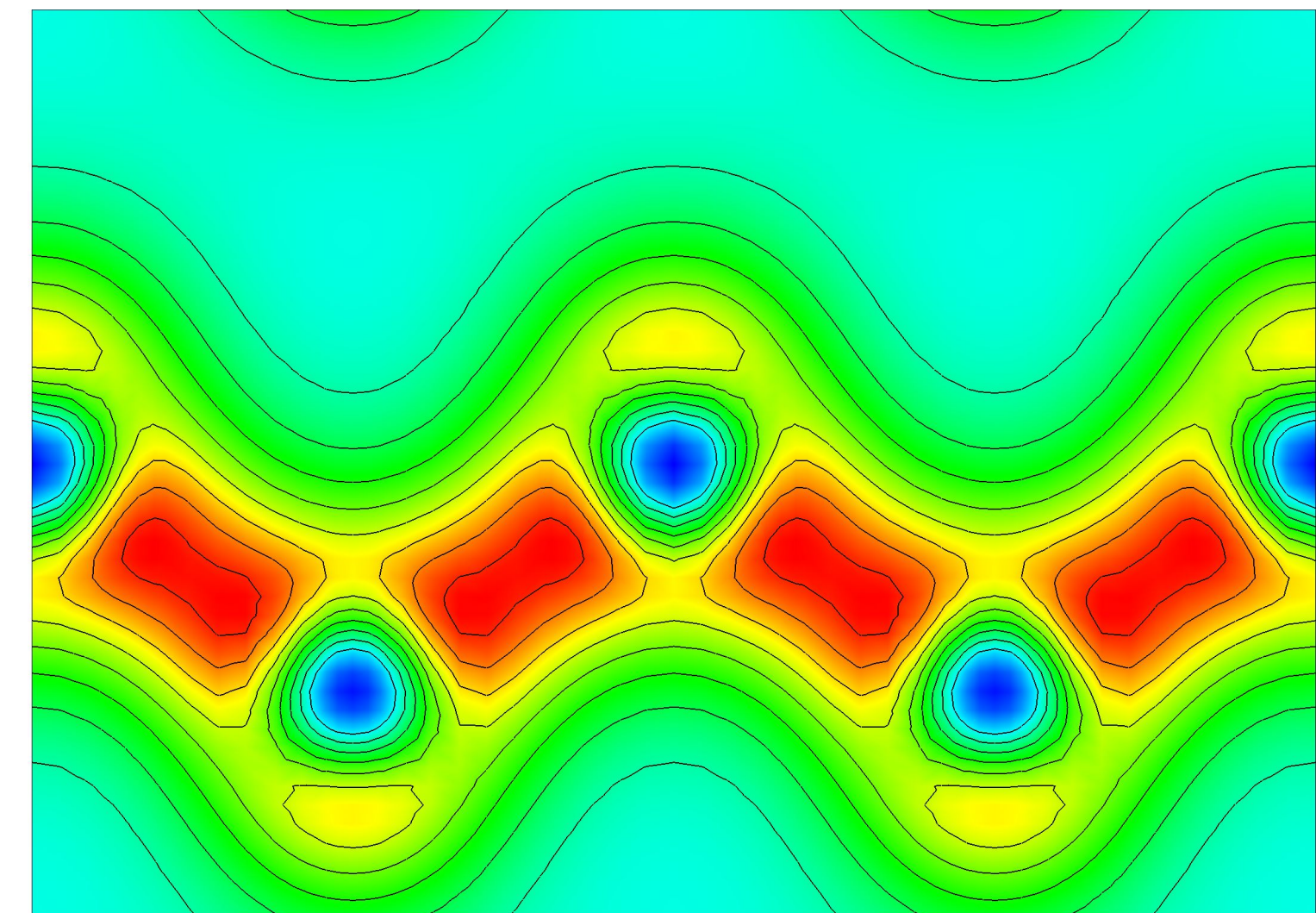
Charge density

$$n(\mathbf{r}) = \sum_i \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} f_{i\mathbf{k}} |u_{i\mathbf{k}}(\mathbf{r})|^2.$$

for VASP users
plot [CHGCAR](#) file in VESTA



Charge density for Silicon



- Plot charge density difference for fixed atomic positions

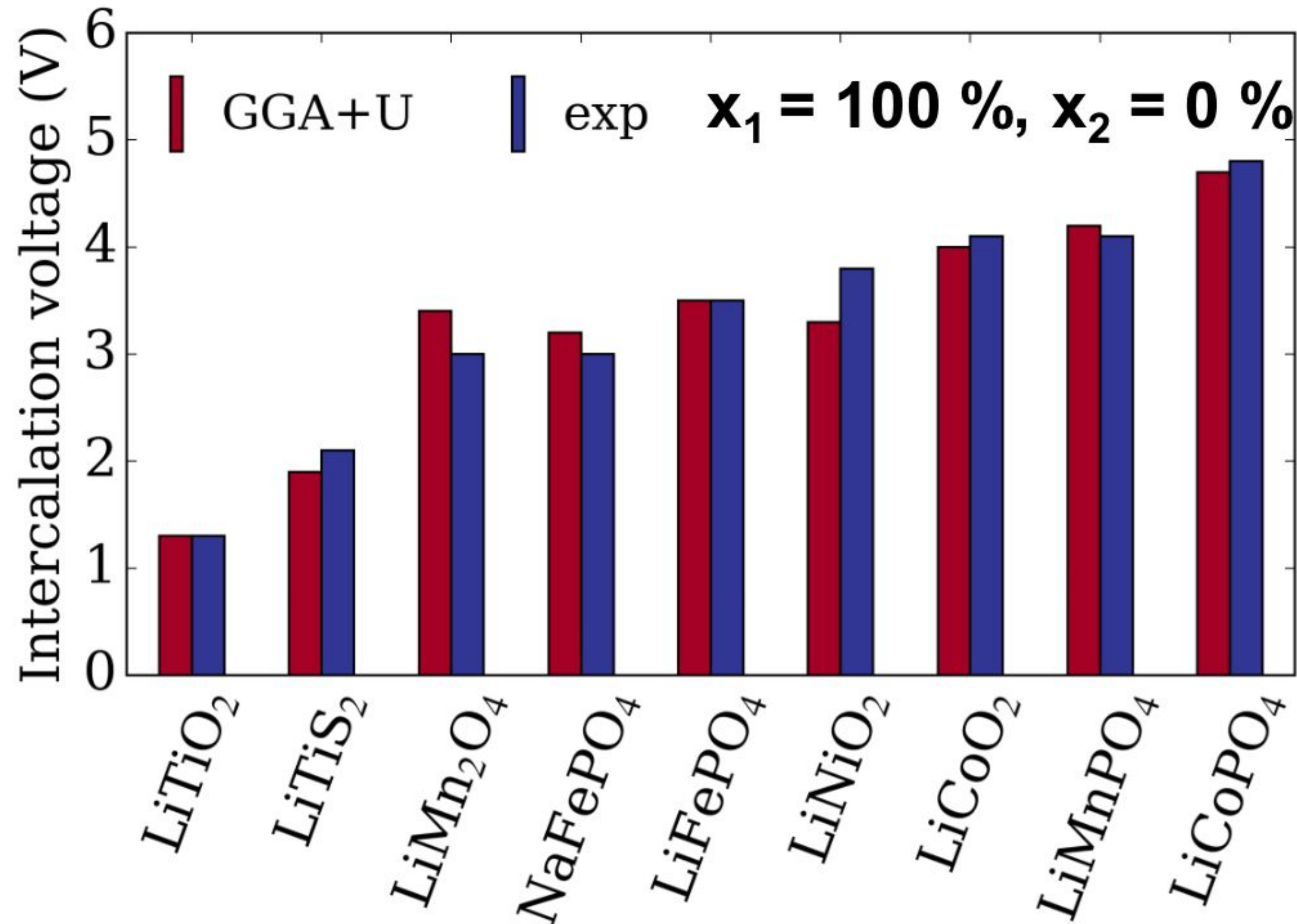
Example: Volume shrinkage/expansion of cathode materials

Reaction	DFT volume shrinkage, %	Experimental volume shrinkage, %
$\text{LiCoO}_2 \rightarrow \text{Li}_{0.25}\text{CoO}_2$	-4 (a)	-3/-4 (c)
$\text{LiFePO}_4 \rightarrow \text{FePO}_4$	7 (a)	6.5 (d)
$\text{Li}_4\text{Ti}_5\text{O}_{12} \rightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$	-0.2 (b)	~0 (e)

(a) Materials project, (b) Electrochem. Comm. 9 (2007) 1107–1112; (c) Measurement 94 (2016) 759–770; (d) J. Electrochem. Soc., 144, (1997) 4; (e) J. Electrochem. Soc., 142 (1995) 5.

Total energy example: Intercalation potentials

$$\bar{V}(x_1, x_2) \approx -\frac{E(\text{Li}_{x_1}\text{MO}_2) - E(\text{Li}_{x_2}\text{MO}_2) - (x_1 - x_2) E(\text{Li})}{(x_1 - x_2) F}$$



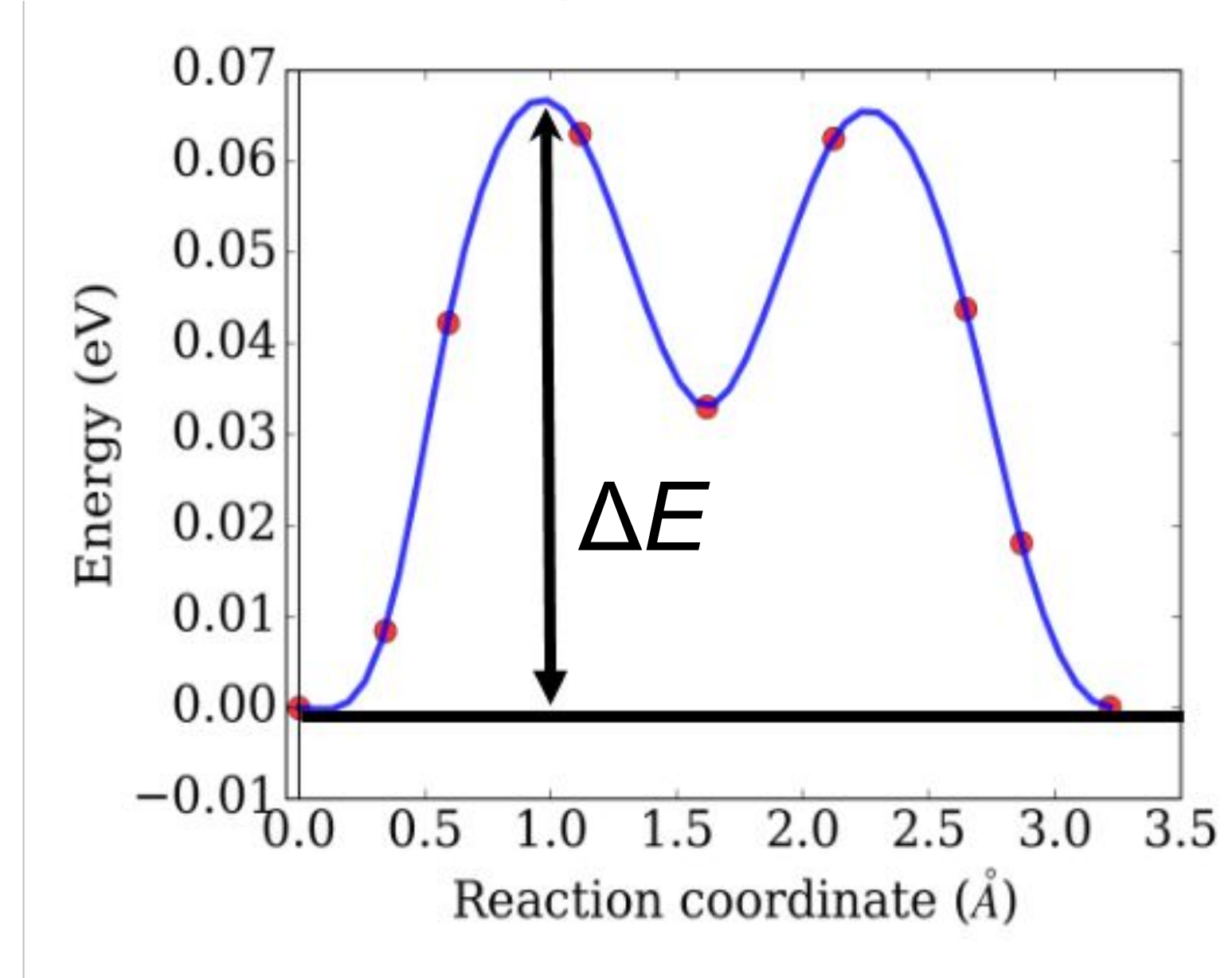
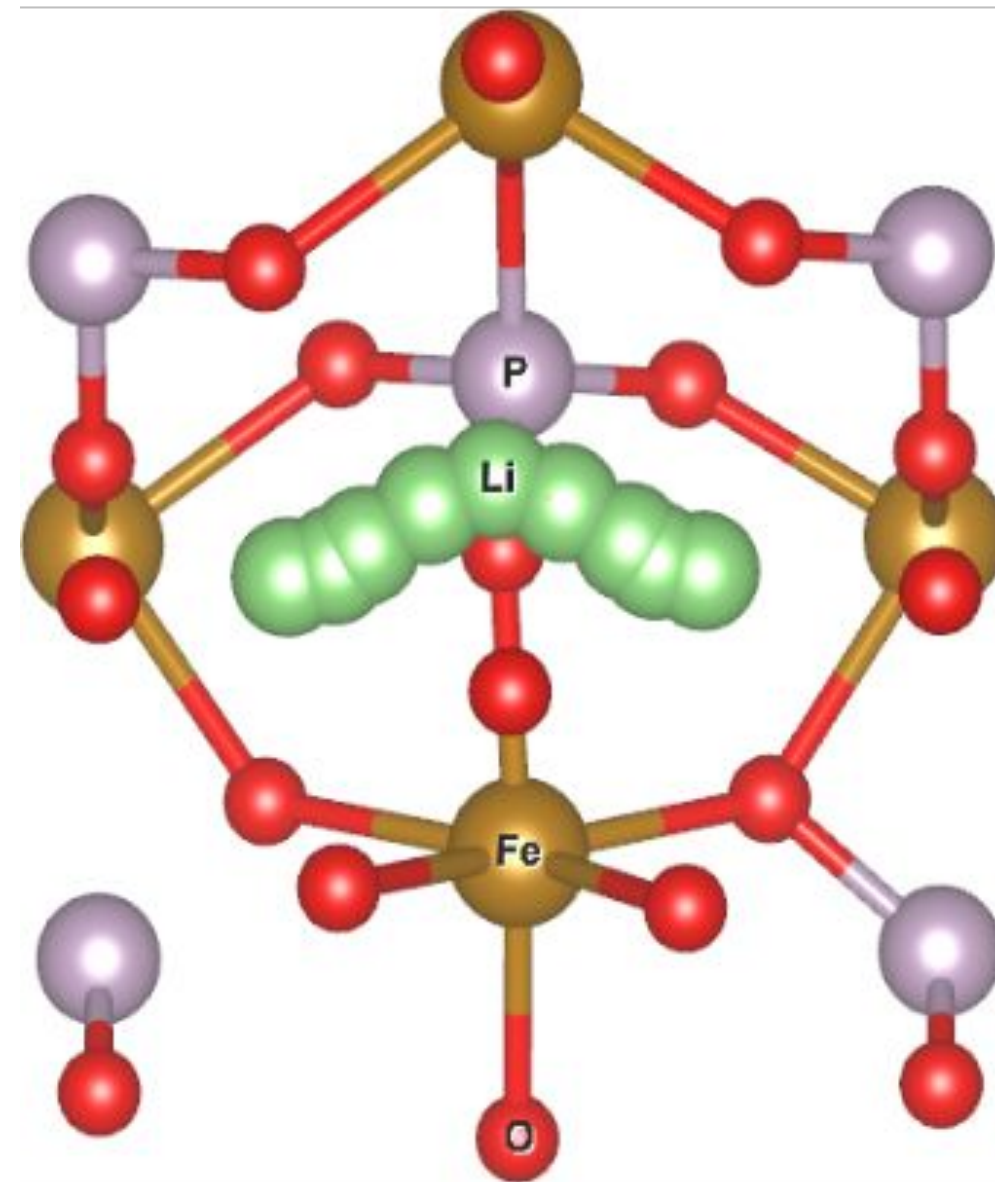
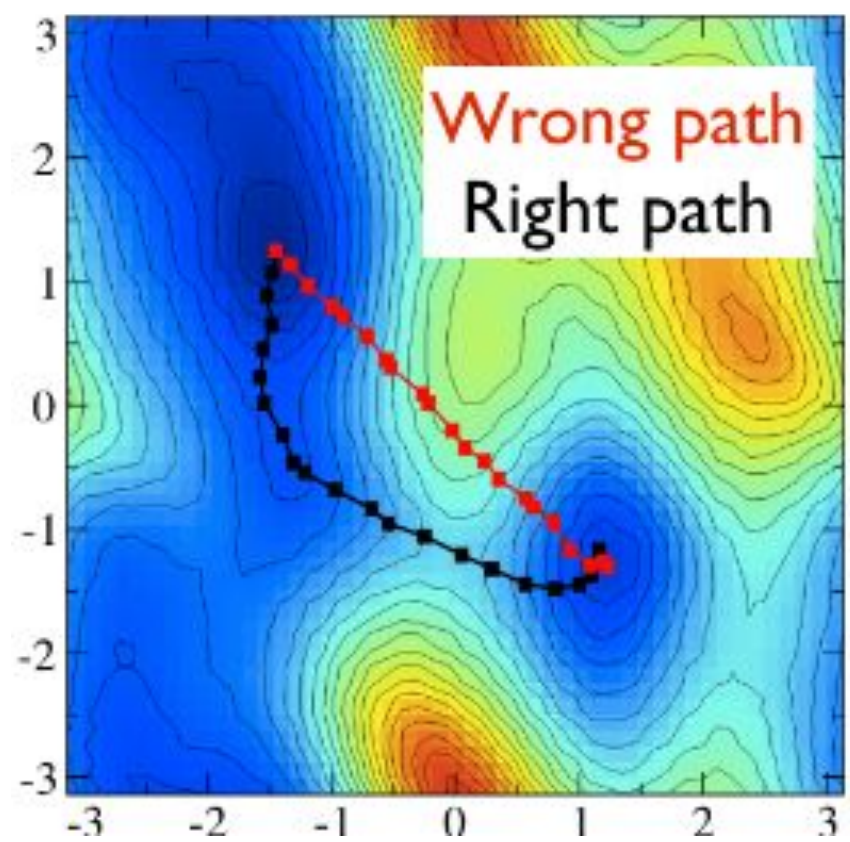
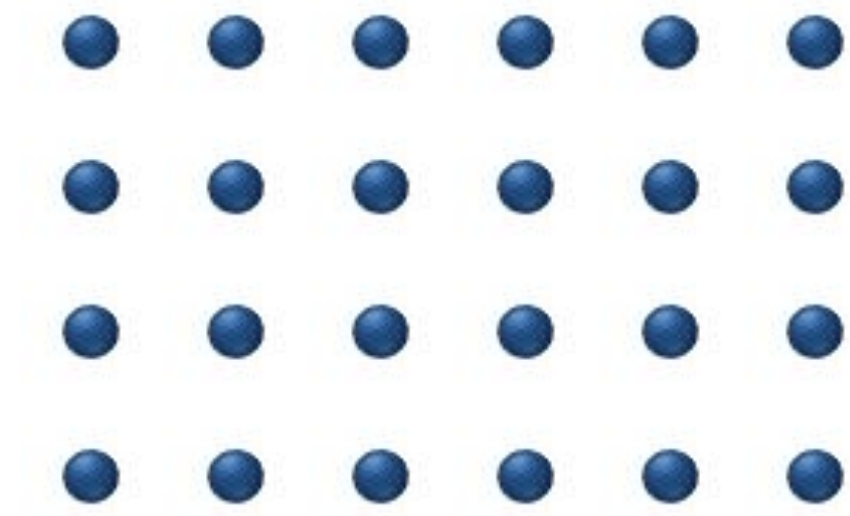
DFT+ U is required
The U value can be determined self-consistently from first-principles.
However, often it is fitted to experimental data

Another option is to use hybrid functionals, but in this case the calculation time increases by 3 orders of magnitude for plane-wave DFT codes

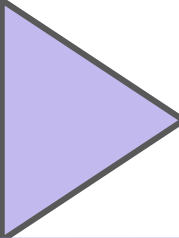
Ionic conductivity

- **Ionic** and electronic conductivity of electrodes determines C-rate
- Ionic conductivity depends on diffusivity of cations
- Migration barrier should be less 0.3–0.4 eV

$$D = 1/2\Gamma d^2 \quad \Gamma = \nu^* \exp\left(\frac{-\Delta E}{k_B T}\right)$$



- Migration barrier can be calculated with Nudge elastic band method (NEB).



Summary

Main definitions

- **Bands** – single particle solutions
- ***K*-points** – integration grid in 1st Brillouin zone
- **Smearing** – partial occupation of bands
- **Plane wave basis set** – wave function represented on reciprocal space grid within cut-off
- **Supercells** – approximating aperiodic system with a periodic one

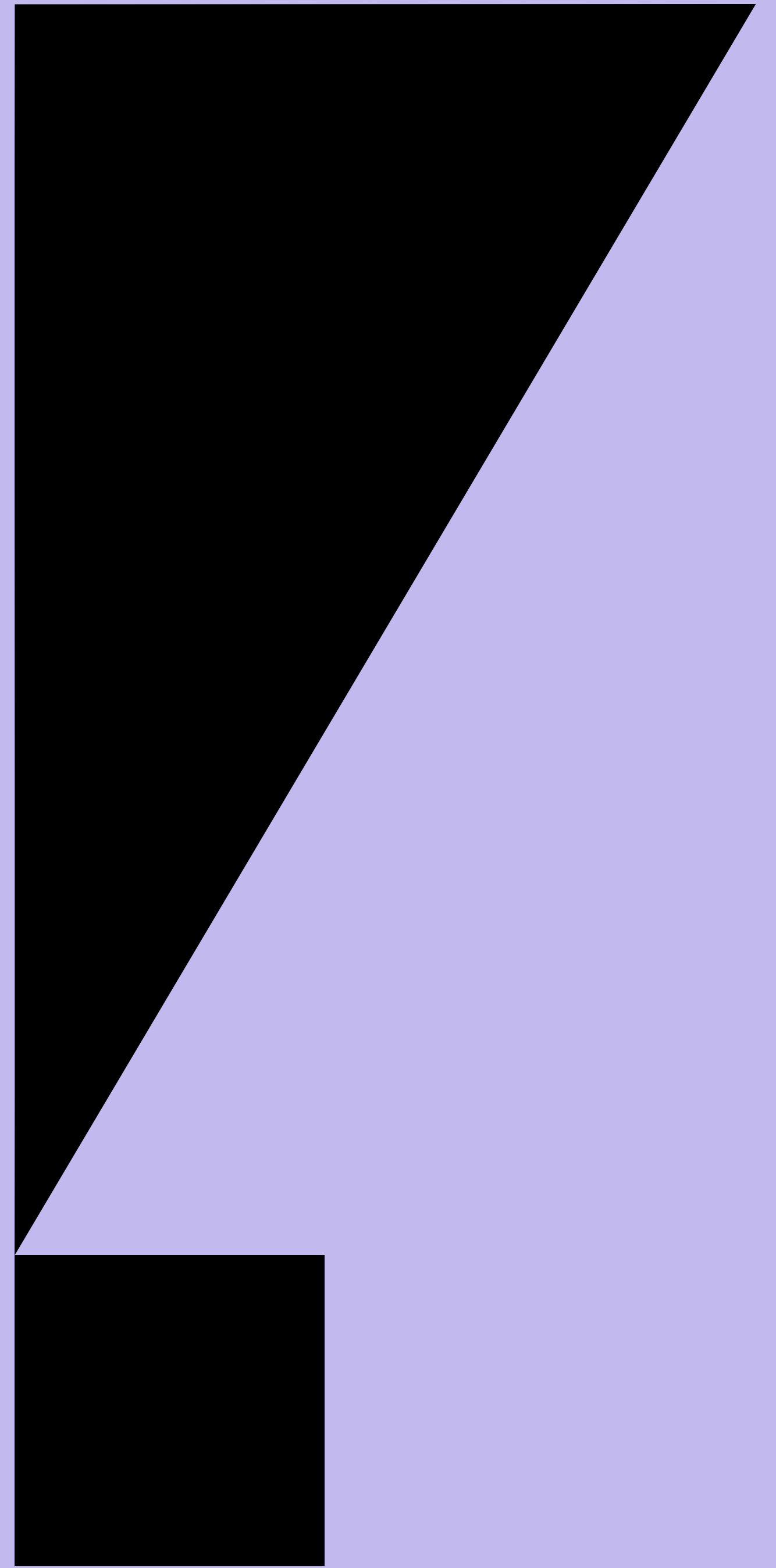
Principles

- Convergence with respect to basis set, *k*-points, smearing, supercell
- Compare only results obtained with the same setups

T

h

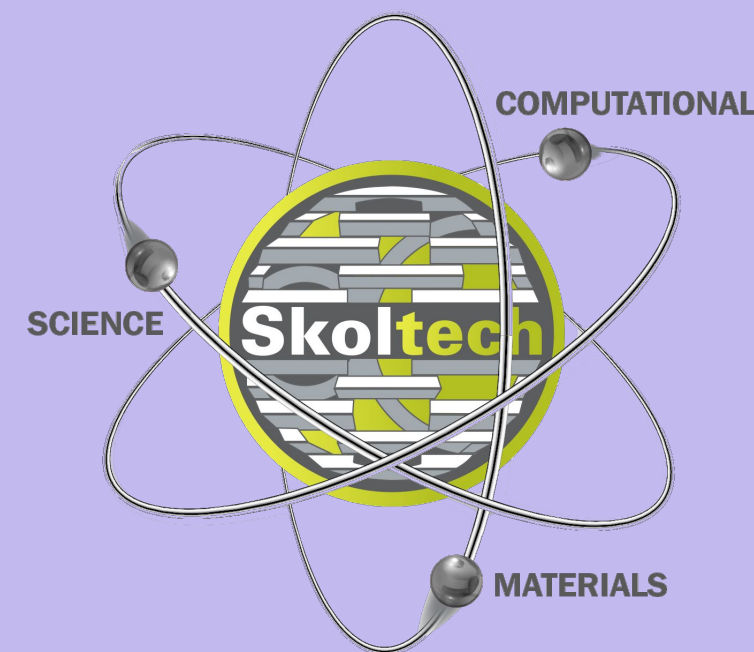
x



Acknowledgement

Skoltech
Energy

Center for
Energy Science
and Technology

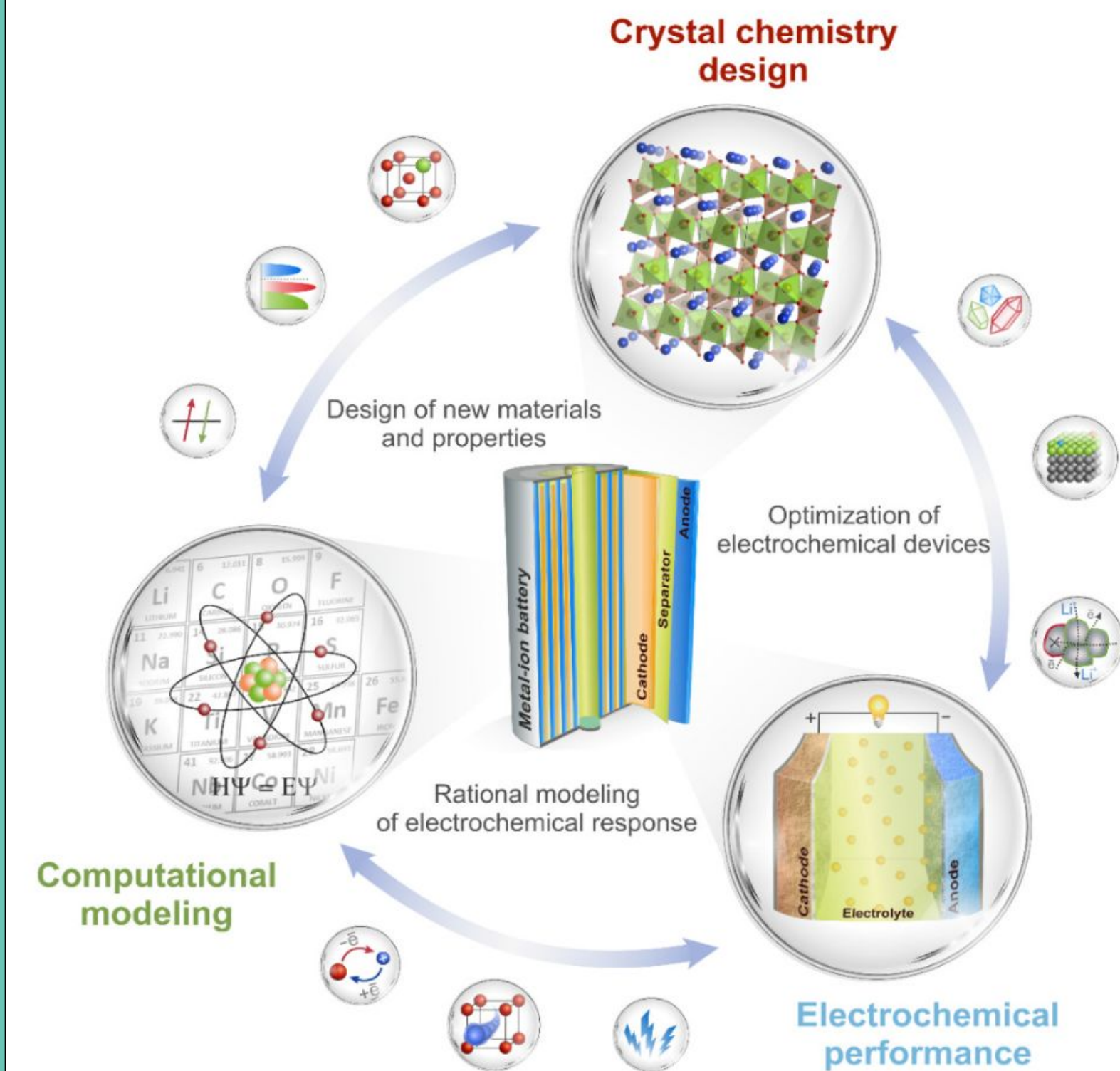


Russian Science
Foundation

Our group

Storion Research Lab

Center for Energy Science and Technology at Skoltech, Moscow



★ [MatSolver](#) - a web-service for predicting materials properties.