

Computational Chemistry and Materials Modeling

## Lecture 6

# Computational Chemistry of Crystals

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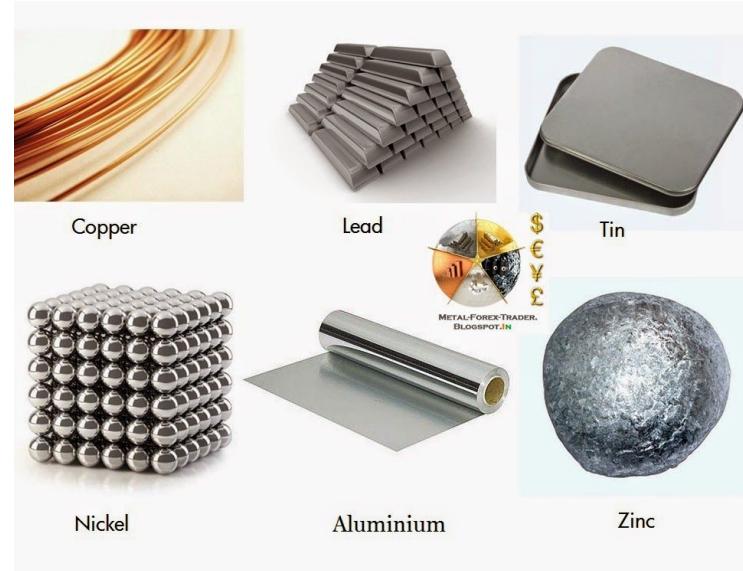
November 12, 2021

# What are the examples of crystals?

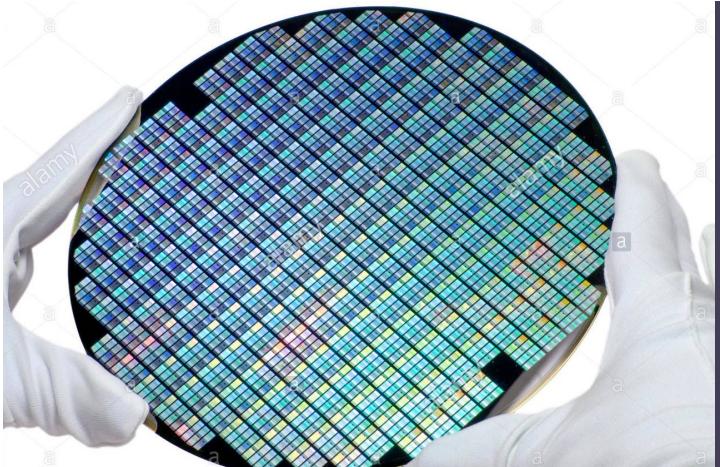
- Minerals (insulating)



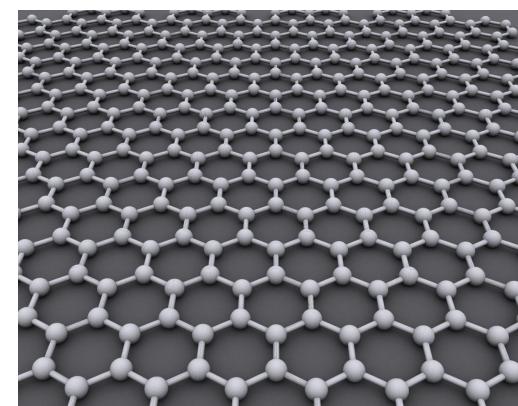
- Metals and alloys



- Semiconductors

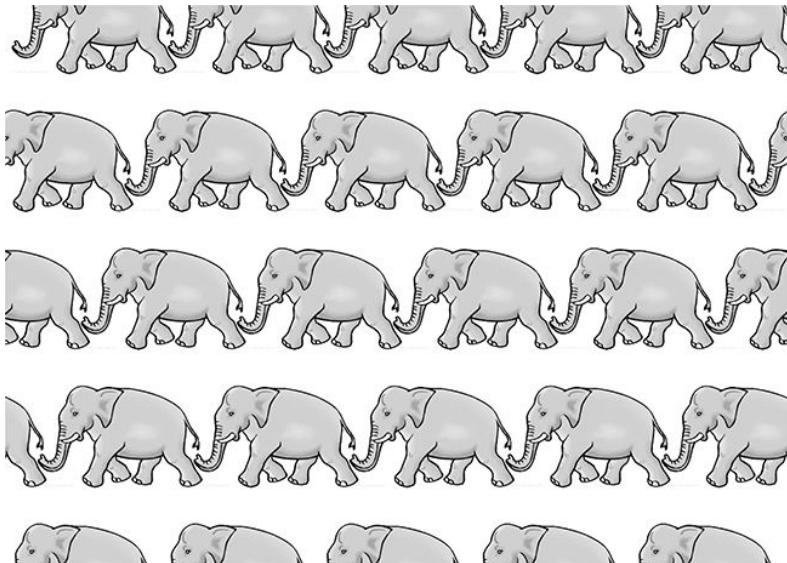


- 2D materials



# What is the main difference of crystals from molecules?

- 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

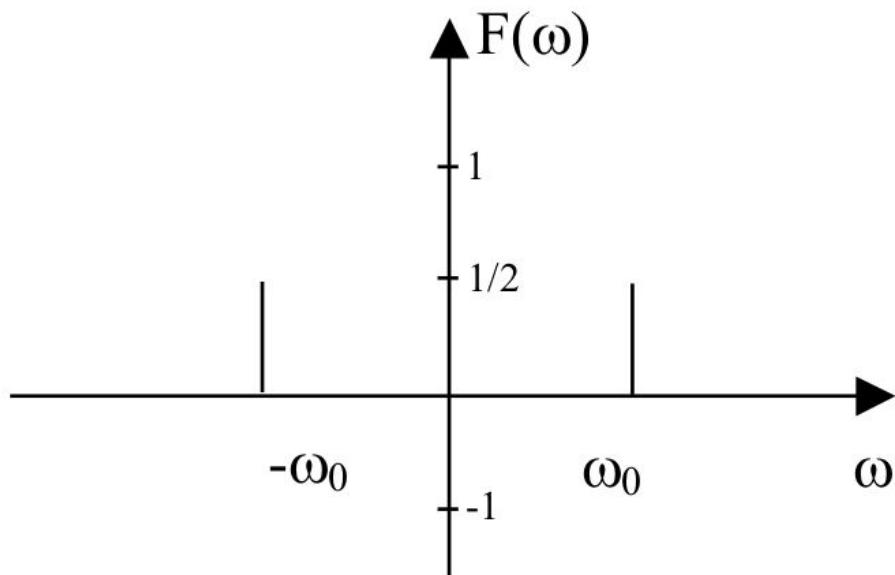
**Problem: How to represent the infinite system?**

# Fourier transform: functions of time

The Fourier transform  $F$  of a function  $f(t)$  is a function  $F(\omega)$  in frequency domain, and is defined as:

$$F(\omega) = \mathcal{F}\{f\} = \int_{-\infty}^{\infty} f(t)e^{-i\omega t} dt$$

Fourier transform of  $\cos(\omega_0 t)$ :



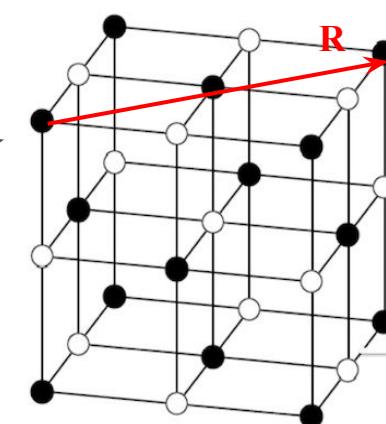
# Fourier transform: functions of space

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

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

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

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

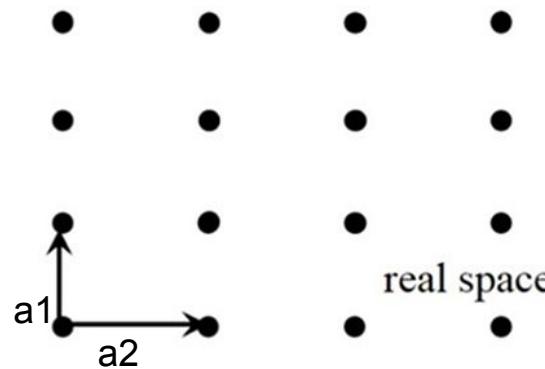


$$\mathbf{G}_m \cdot \mathbf{R}_n = 2\pi N$$

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

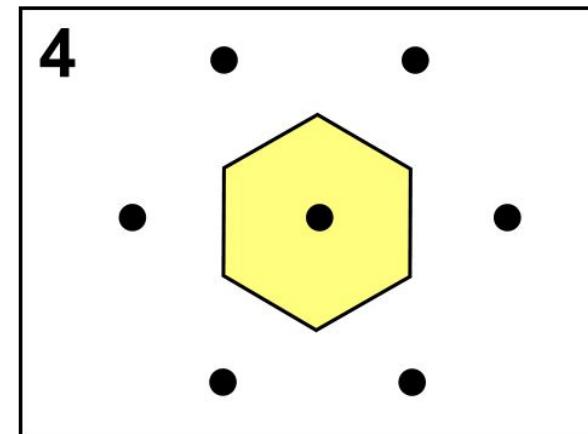
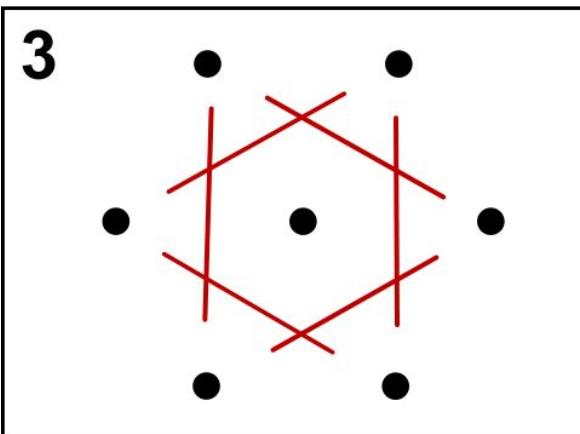
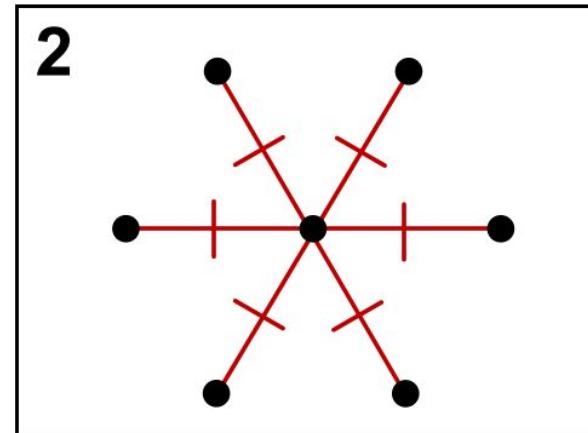
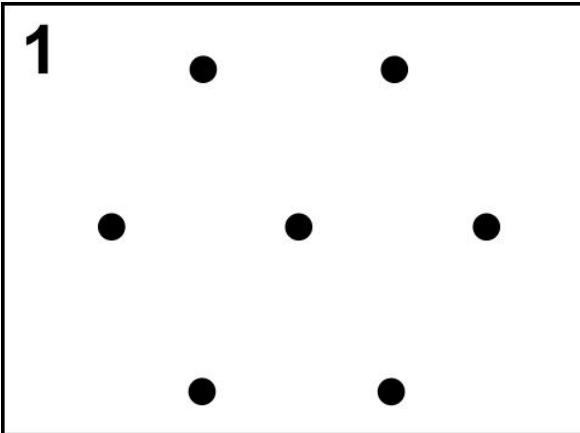
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

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

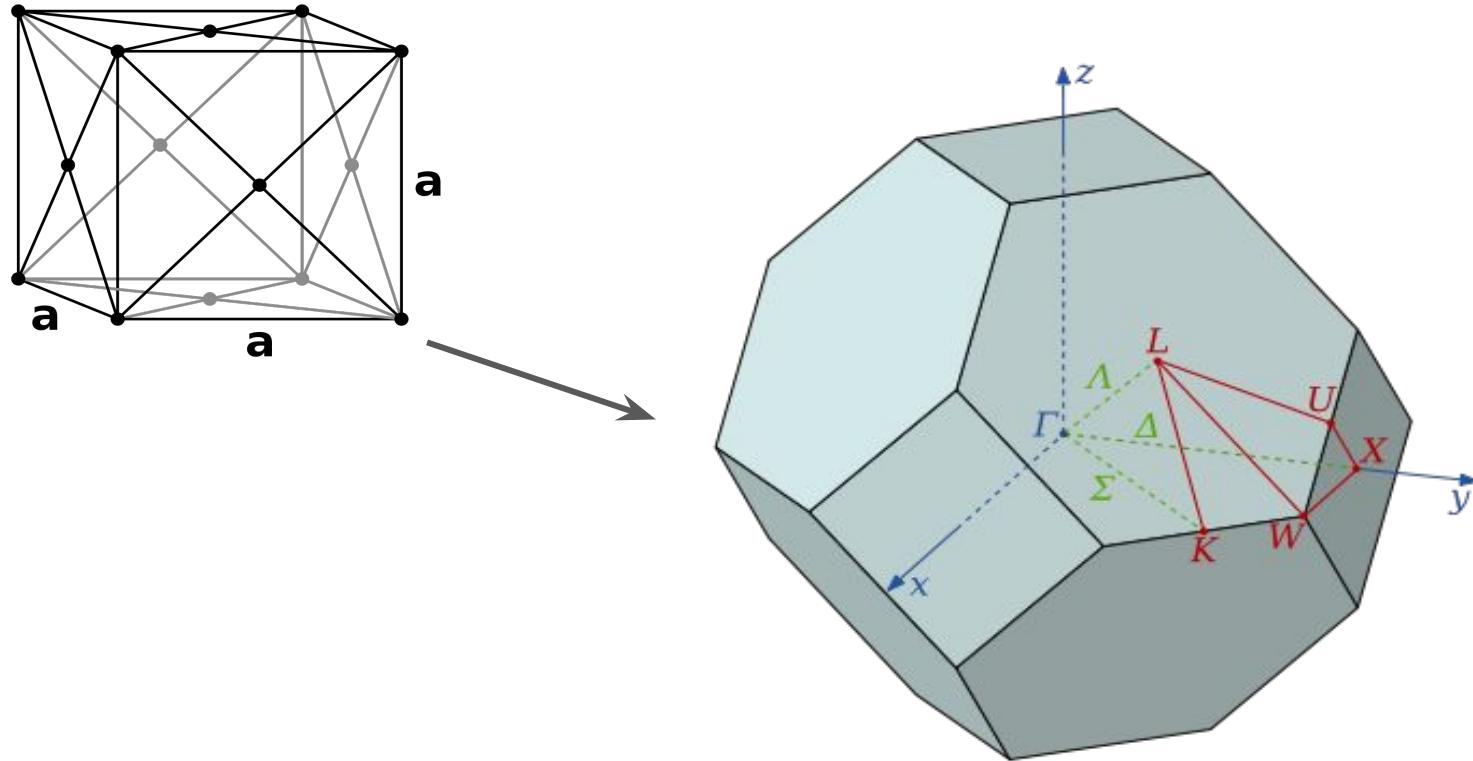


# Brillouin zone and Wigner seitz cell

- Primitive cell - cell with minimal volume, infinite number of possibilities
- First Brillouin zone (BZ) is a primitive cell in reciprocal space with the symmetry of the reciprocal lattice
- Wigner-seitz cell - the primitive cell with the symmetry of the Bravais lattice



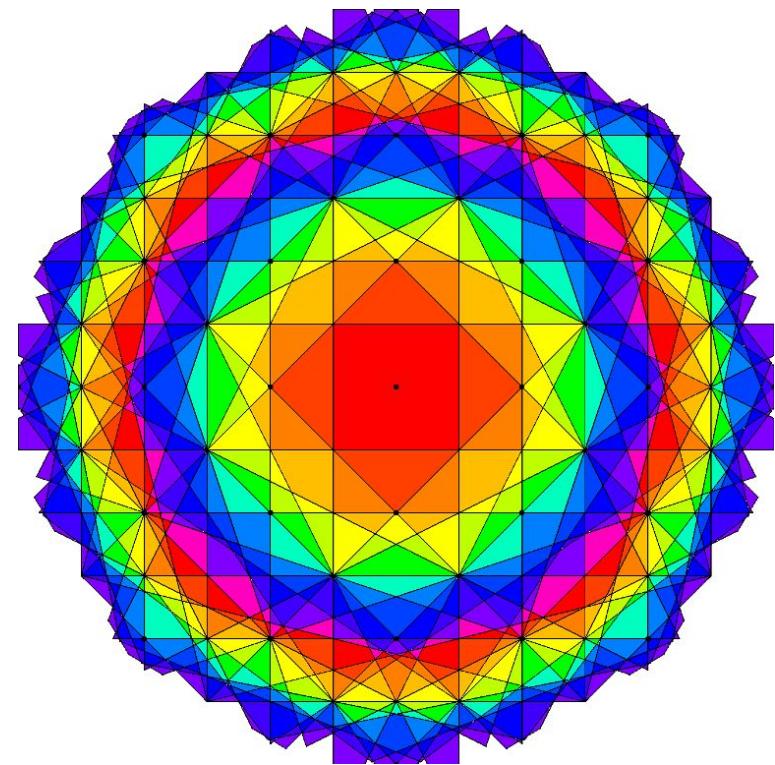
# First BZ for FCC lattice



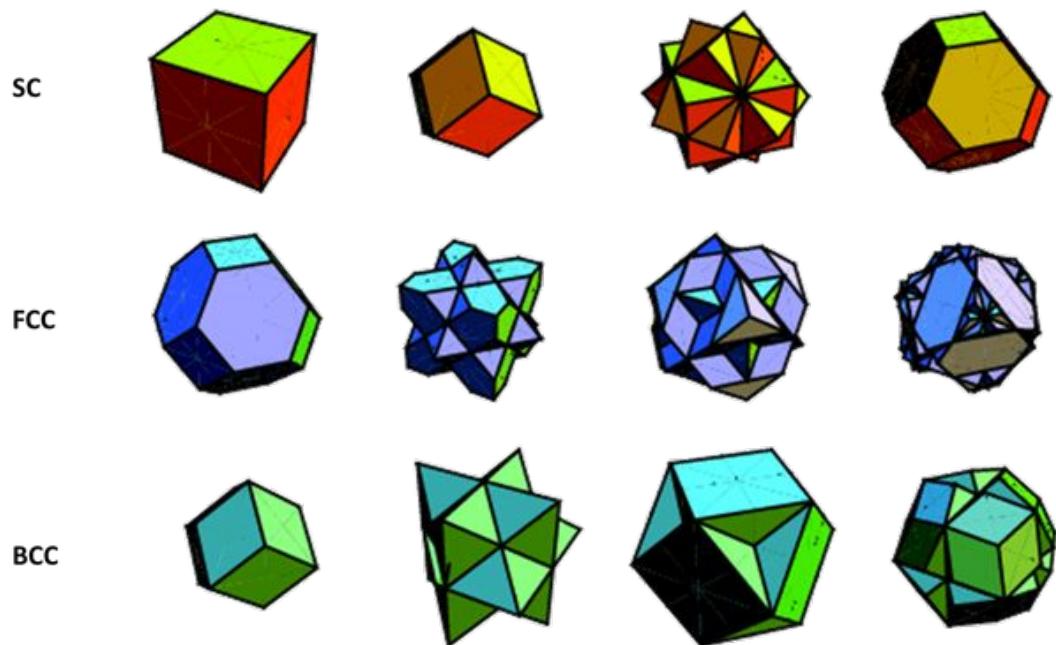
- The reciprocal lattice for FCC lattice is BCC
- $\Gamma$  is the center of Brillouin zone
- High-symmetry directions are called with Greek letters ([see here](#)), high symmetry points with Latin
- Fundamental domain of BZ is often called **irreducible Brillouin zone (IBZ)**

# Understanding Brillouin zones

First 27 BZ for 2D square lattice



First 4 BZ for 3D lattices:



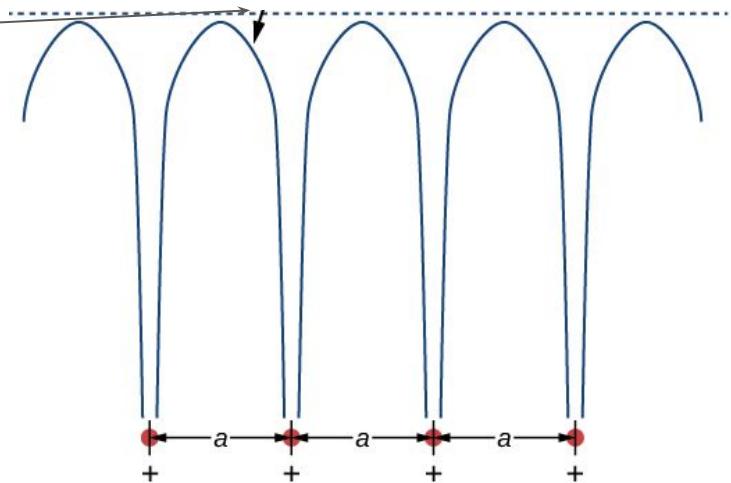
All BZ are of equal volume

# 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:



Felix Bloch  
Nobel prize in  
1952

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

- $\mathbf{k}$  - 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
- $e^{i\mathbf{kr}}$  - invariant with respect  $\mathbf{k} = \mathbf{k} + \mathbf{G}$ , where  $\mathbf{G}$  is translation vector

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

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}], \quad \mathbf{G} \text{ is translation vector of reciprocal lattice}$$

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  $E_{\text{cut}}$  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

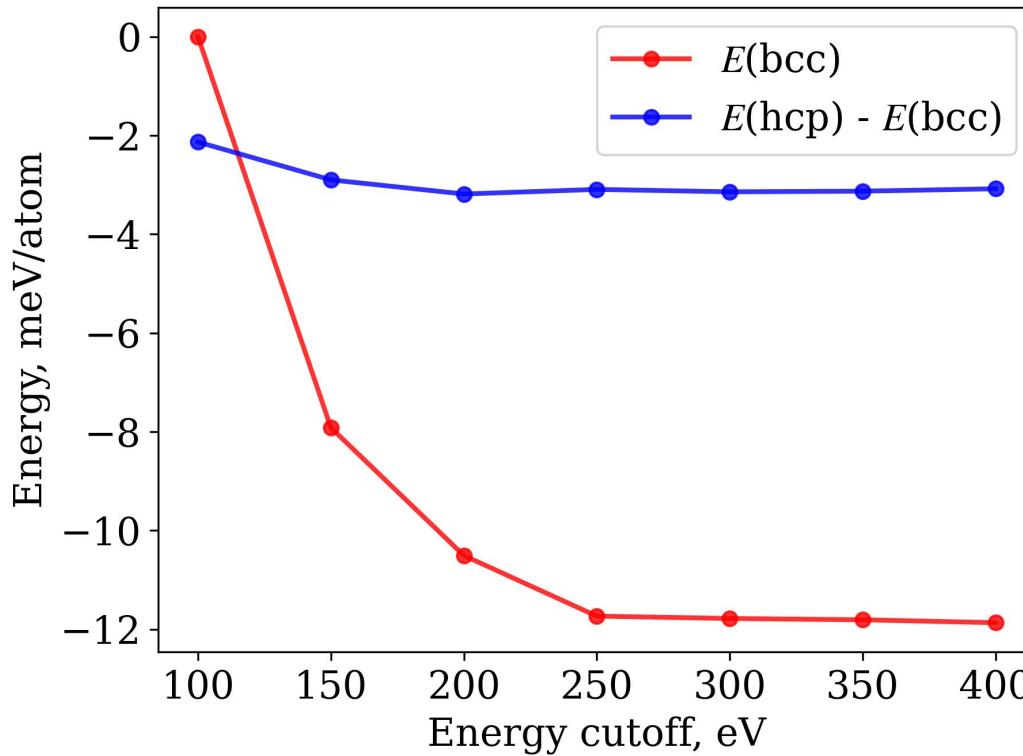
$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{tot}}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \varepsilon_n \phi_n(\mathbf{r})$$

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

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

- In analogy to the particle in the box there are infinite number of solutions  $n$ ,  $u_{n\mathbf{k}+\mathbf{G}} = u_{n\mathbf{k}}$  where  $n$  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  $n$ ,  $\varepsilon_n(\mathbf{k})$  - this is called **band dispersion**

# Convergence with respect to e-cut

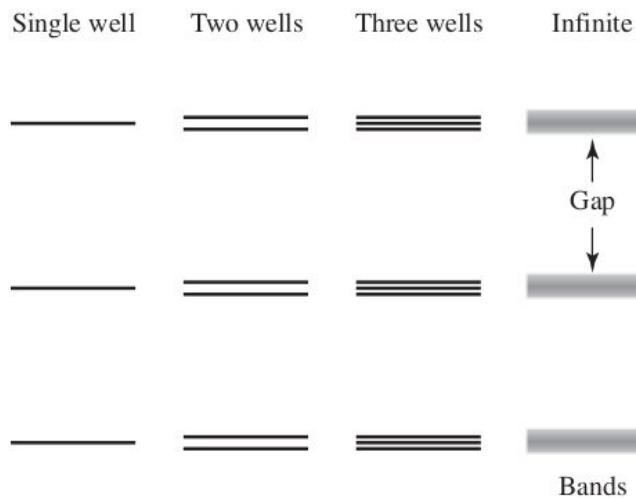
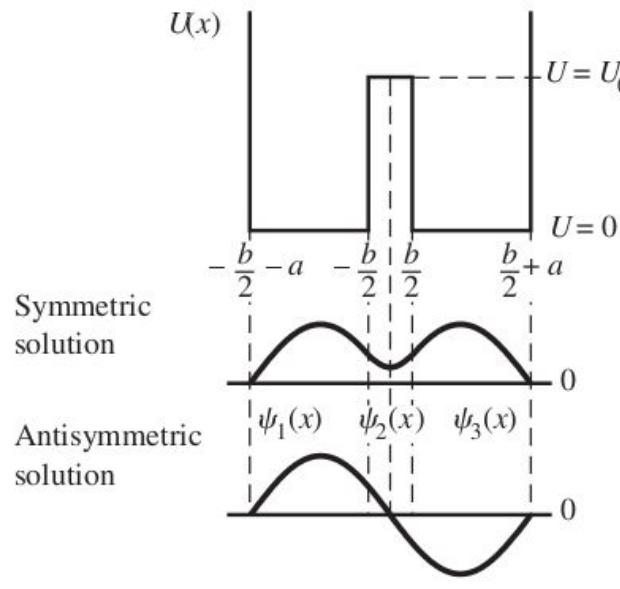
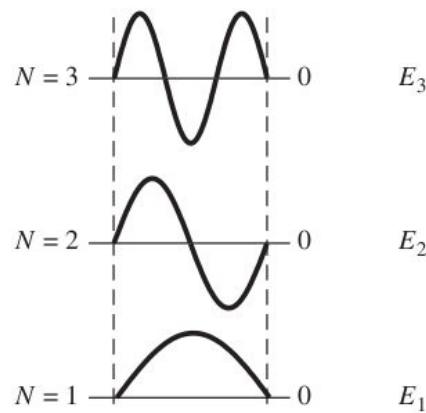
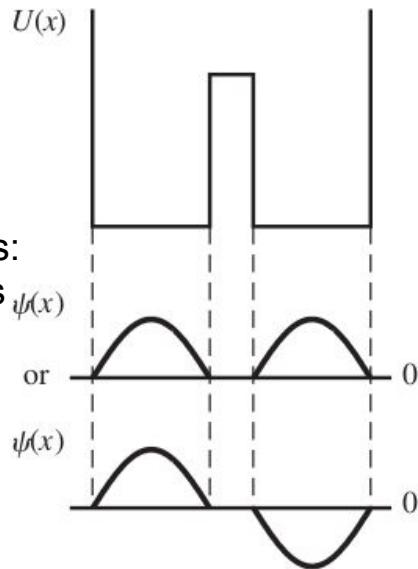


*Convergence of the energy cut-off for bcc Li and energy difference using the PBE functional and a 8x8x8 k-point grid for conventional cell.*

- Make all calculations at fixed cut-off
- The absolute energy has little sense, use differences
- Check convergence for property of interest

# Simple picture for band formation in quantum wells (Kronig-Penney model)

Infinite barrier  
between two wells:  
degenerate states



Finite barrier:  
small splitting in  
energy between  
states due to  
coupling

States with more  
nodes (shorter  
wavelength) will  
have higher  
energy, while  
states with fewer  
nodes will have  
lower energy.

D. Snake /Solid  
state physics

# 1D case, infinite chain of H atoms with non-interacting electrons



$$\psi(k) = \sum_{n=1}^N e^{ikna} \phi_n \quad \text{with} \quad 0 \leq |k| \leq \frac{\pi}{a}, \quad a - \text{interatomic distance, } \phi - \text{atomic orbital}$$

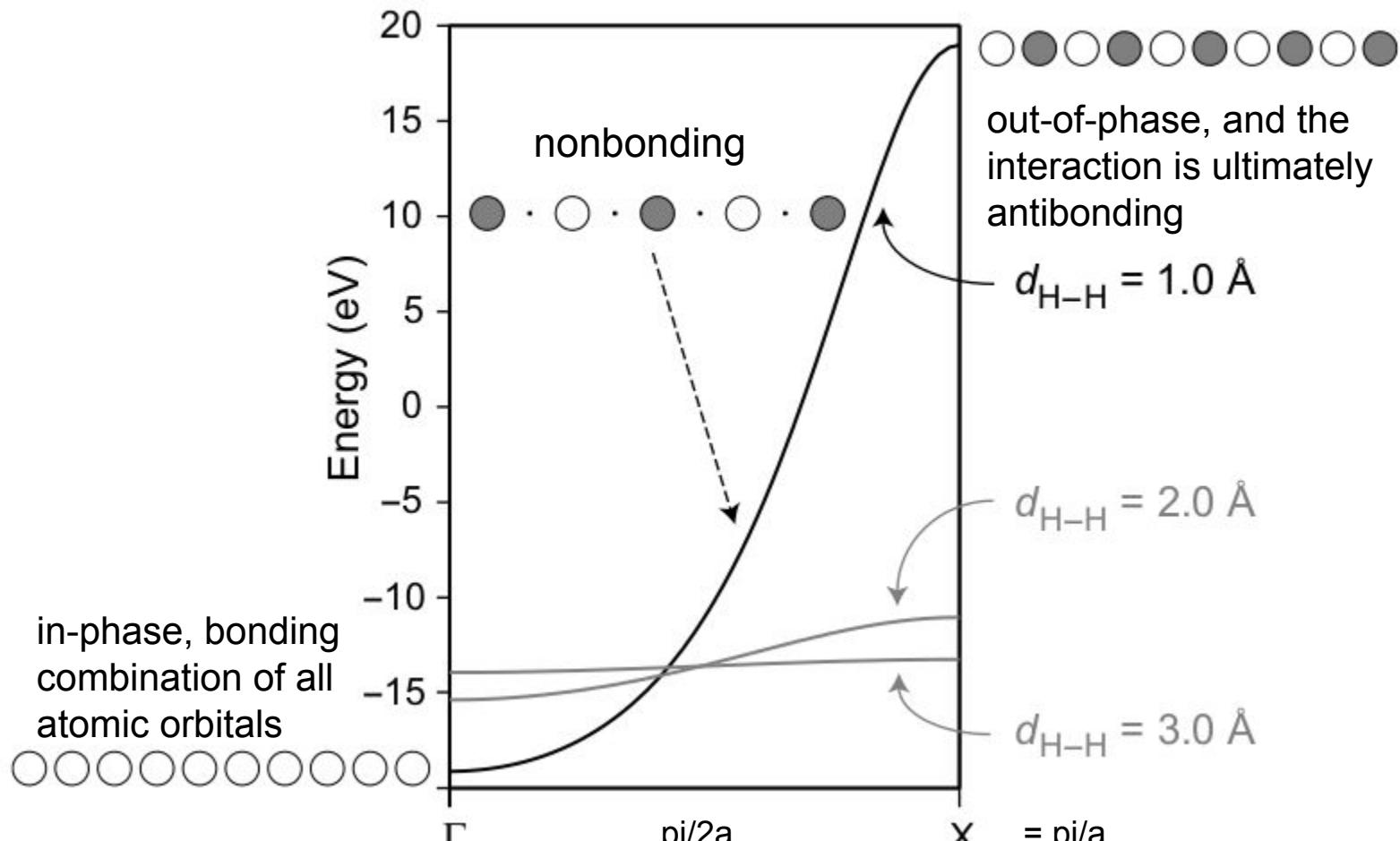
$$\psi(0) = \sum_{n=1}^N \phi_n = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 \dots, \quad \text{At } k = 0, \text{ also known as } \Gamma$$

$$\psi\left(\frac{\pi}{a}\right) = \sum_{n=1}^N e^{i\pi n} \phi_n = -\phi_1 + \phi_2 - \phi_3 + \phi_4 - \phi_5 \dots, \quad \text{At } k = \pi/a, \text{ also known as } X$$

The same procedure for intermediate k values

$$E(k) = \frac{\langle \psi(k) | \mathcal{H} | \psi(k) \rangle}{\langle \psi(k) | \psi(k) \rangle}$$

# Band structure for hydrogen chain

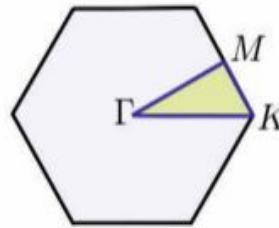
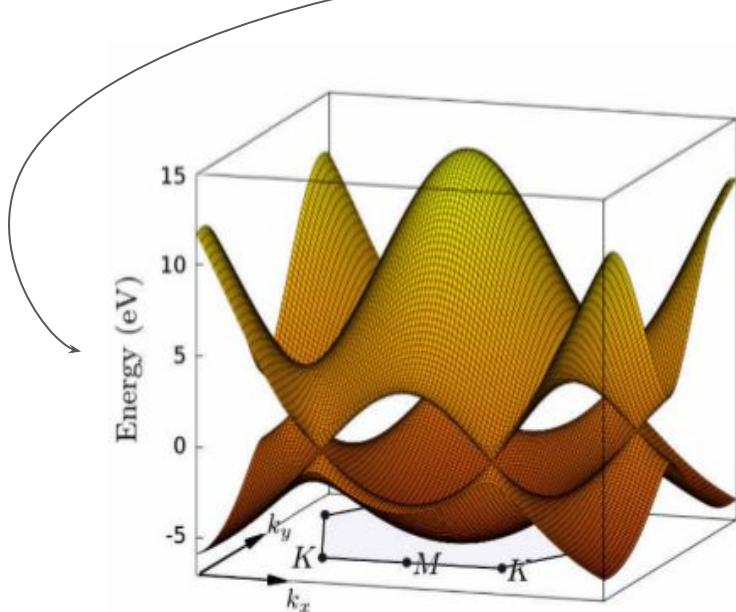


First Brillouin zone in 1D case

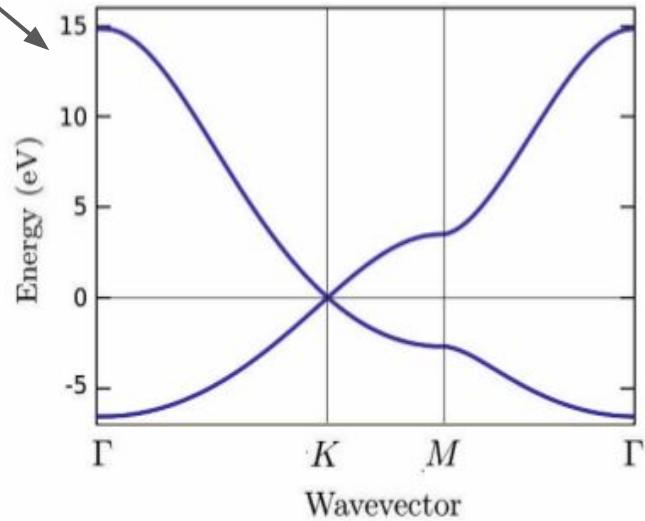
Dronskowski

# Example of band structure for graphene

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



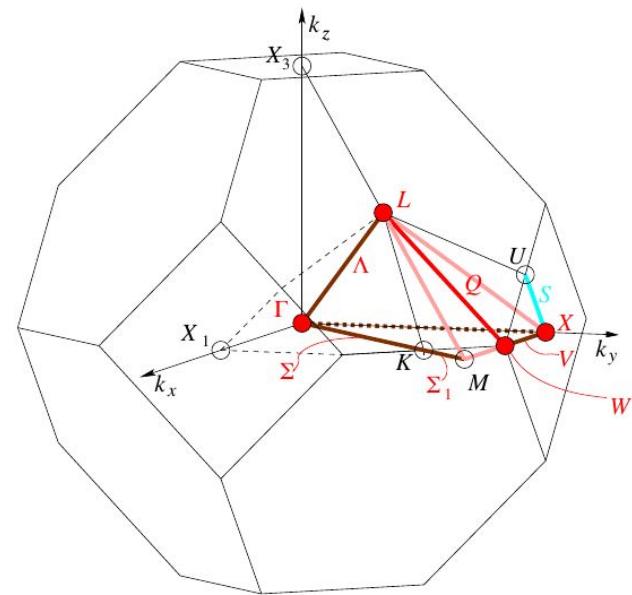
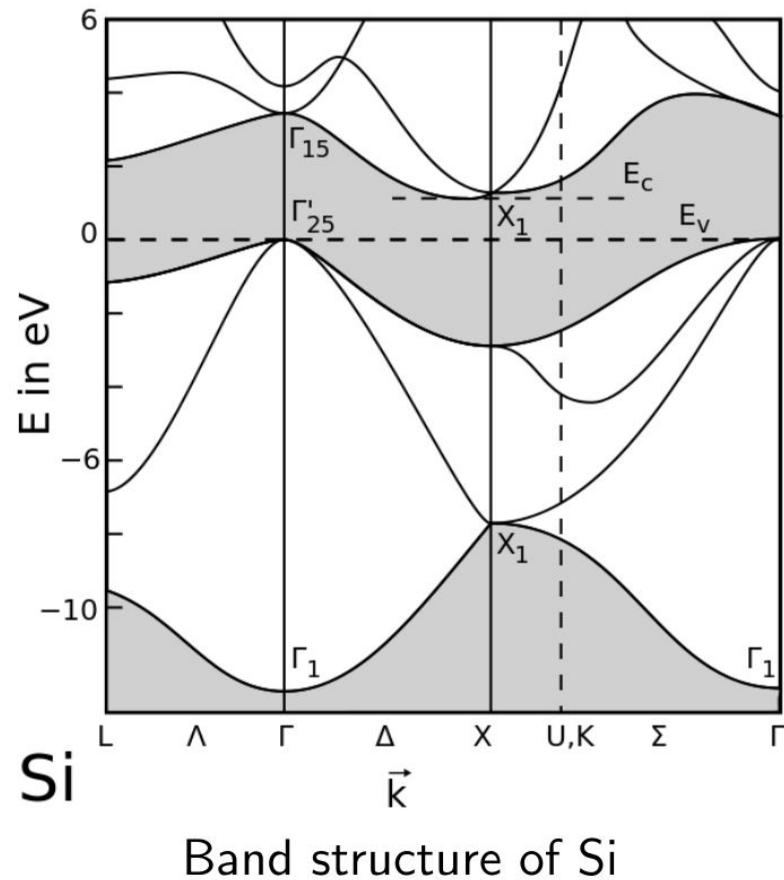
BZ and IBZ



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

Change of energy along  
high-symmetry direction

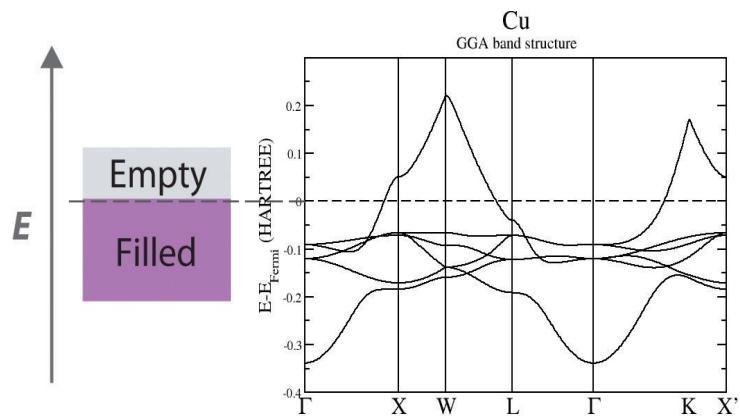
# Example of band structure for silicon



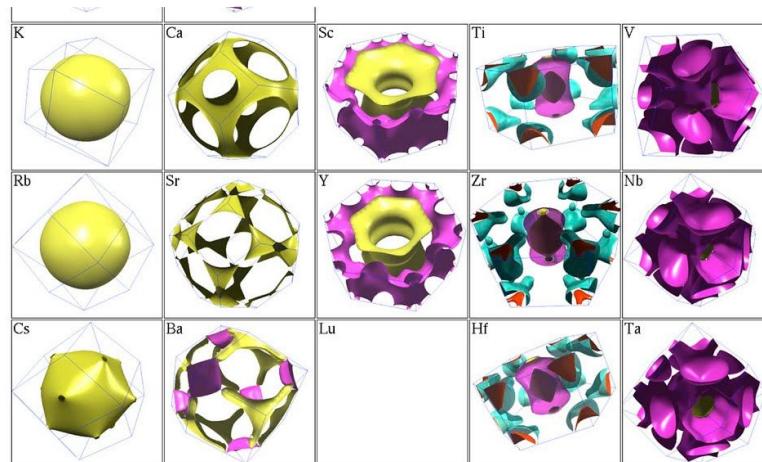
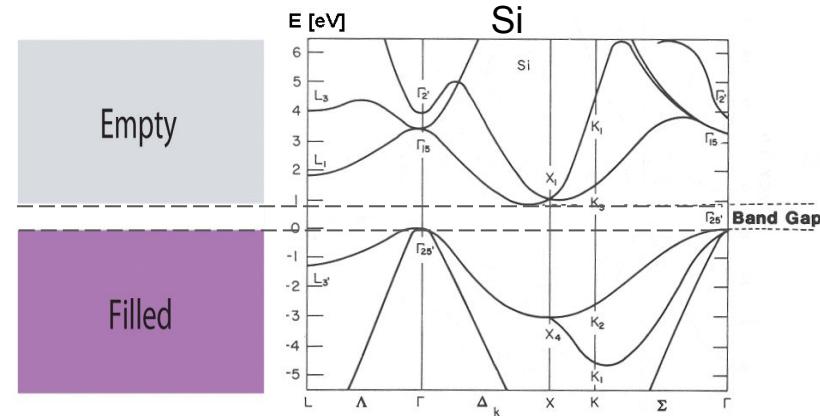
# Ground state and Fermi surface

The ground state of  $N$  electrons is obtained by filling one-electron bands with energies  $\epsilon_n(\mathbf{k})$  up to the Fermi energy.  
Some bands are fully filled, the others are empty

Case 1: The band is partially filled or overlapped



Case 2: The band is either completely filled or empty

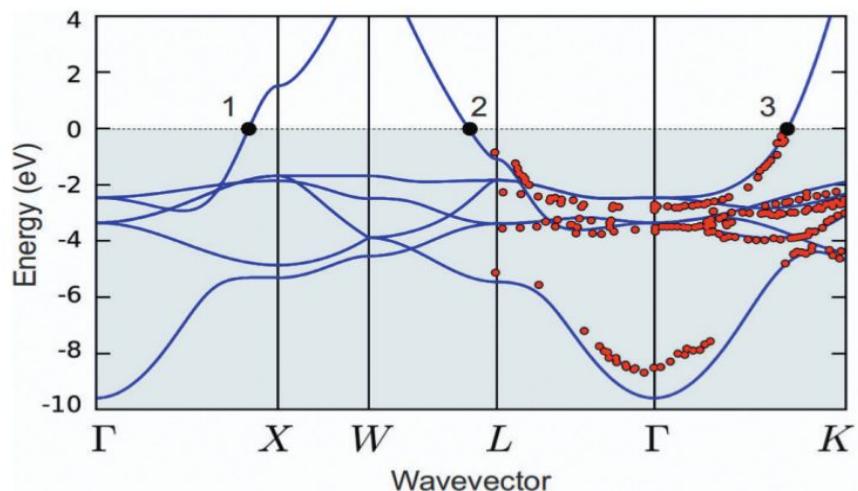


No Fermi surface for band gap materials!  $\rightarrow$  definition for metals

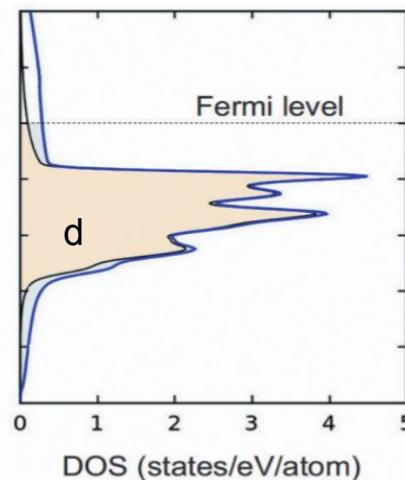
# Density of states

$$DOS(E) = \sum_n \int_{BZ} \frac{d\mathbf{k}}{\Omega_{BZ}} \delta(E - \varepsilon_{n,\mathbf{k}})$$

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

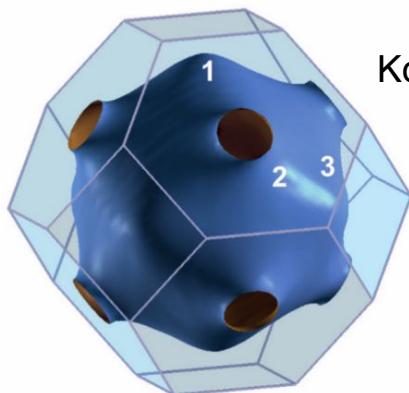


11 Kohn-Sham electrons

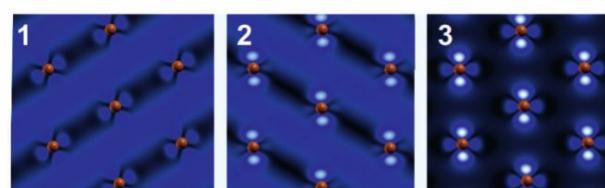


The parabolic behaviour in L- $\Gamma$ -K region resembles free electron gas, however it is interrupted by spaghetti-like d states

Fermi Surface



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



from  
Giustino

$d_{xy}$

$d_{z2}$

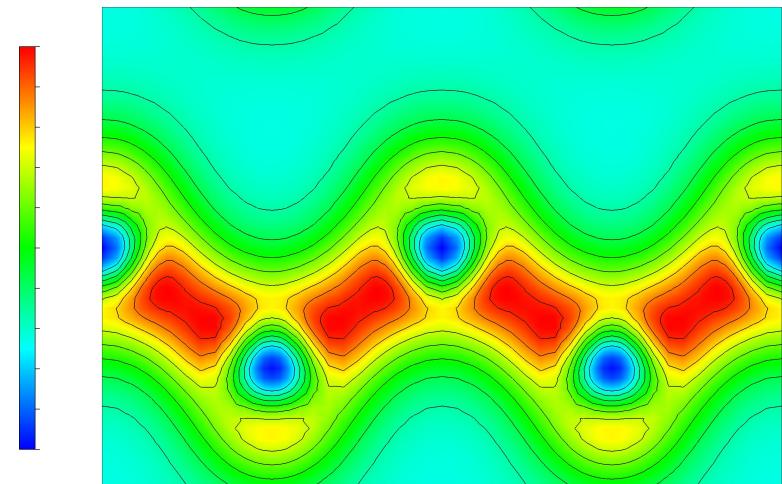
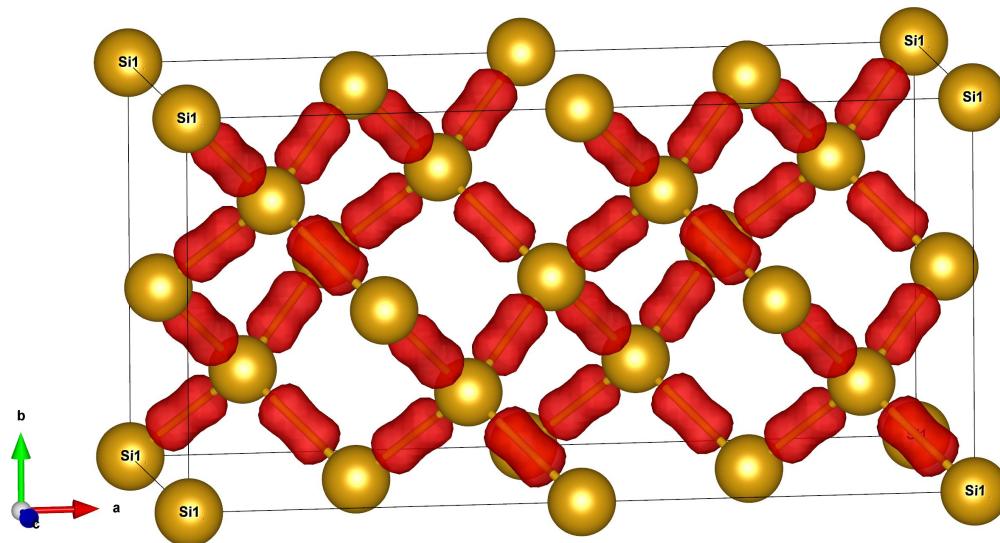
The red discs are from the experimental angle-resolved photoemission data - The Kohn-Sham eigenvalues has some physical reality

Significant differences between states across the Fermi surface.

# Charge density

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

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



Charge density for Silicon

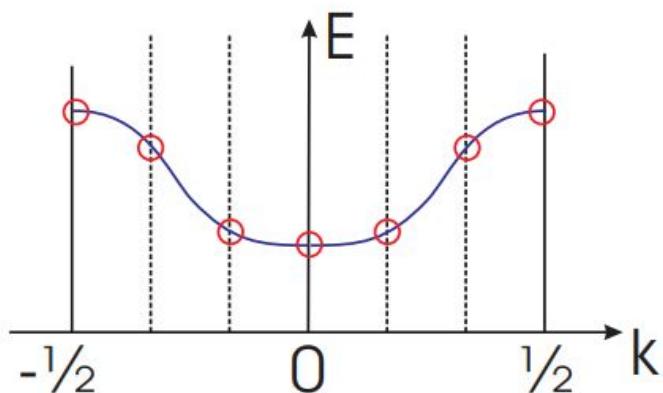
- Plot charge density difference for fixed atomic positions

# Discussion

- What is the difference of Brillouin zone from other primitive cells in the reciprocal space?
- Why do we need smearing of a Fermi-level?
- Why antisymmetric solution has higher energy compared to the symmetric one?
- What is the difference of real crystal from ideal periodic crystal?

# k-point sampling

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



Monkhorst-Pack - regular equispaced mesh

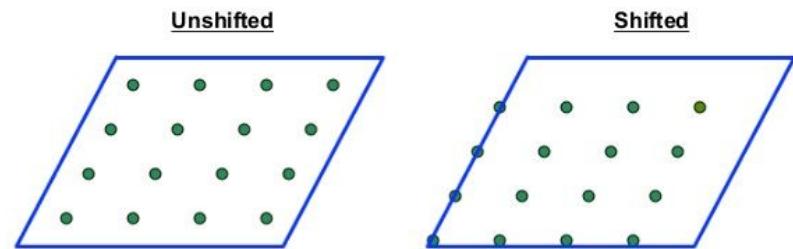


TABLE 3.1 Approximations to the Integral  $\int_{-1}^1 \frac{\sin(\pi x)}{x} dx = 1$  Using the Trapezoidal and Legendre Quadrature Methods

$N$	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

- 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

Sholl p.54

# Choosing k-points mesh

How to choose  $N_1, N_2, N_3$ ?

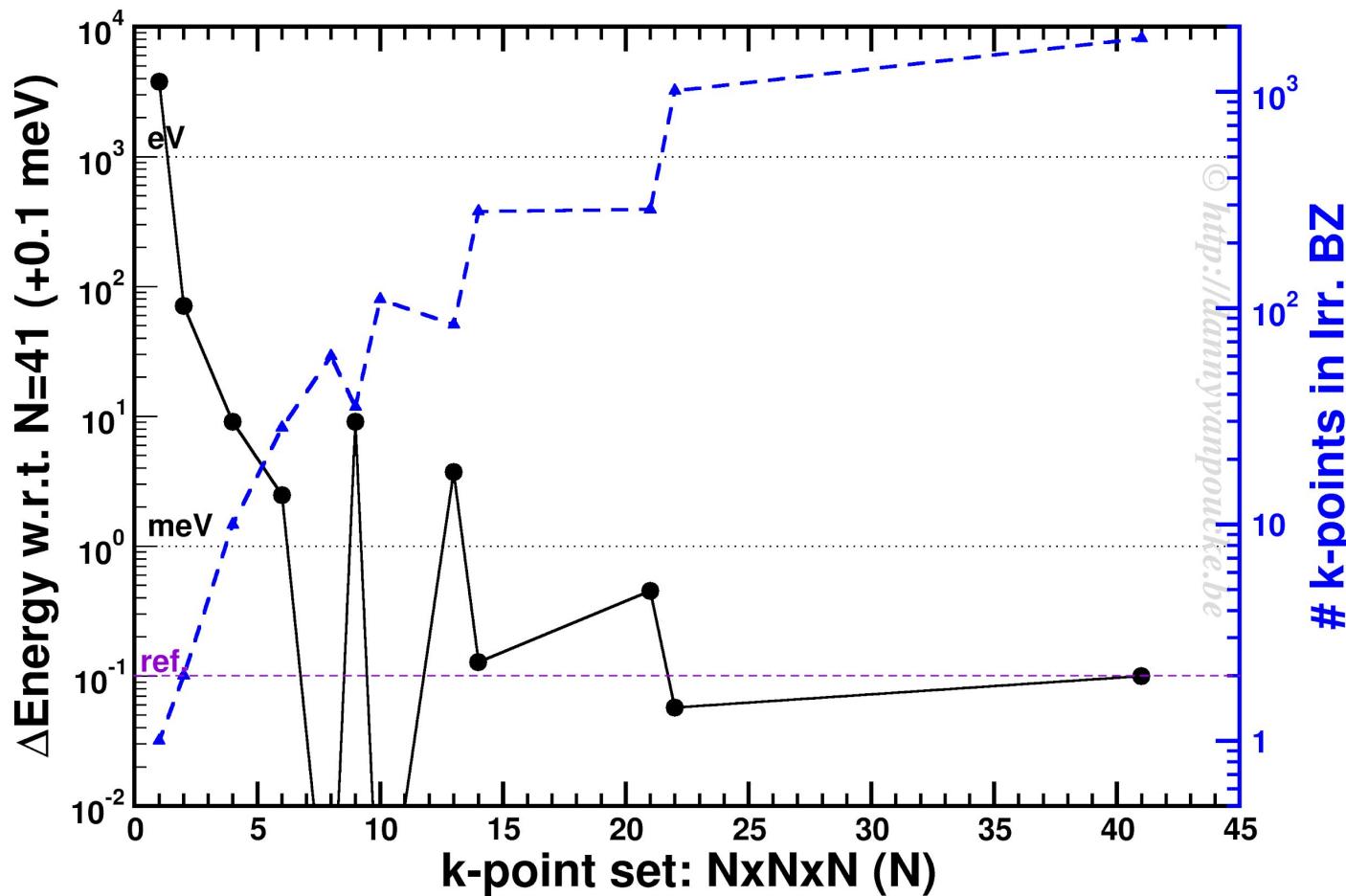
Commonly the following rule of thumb applies:

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

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  $0.05 \text{ \AA}^{-1}$ !
  - k-spacing  $0.5 \text{ \AA}^{-1}$  risk of large errors

# Convergence with respect to k-grid



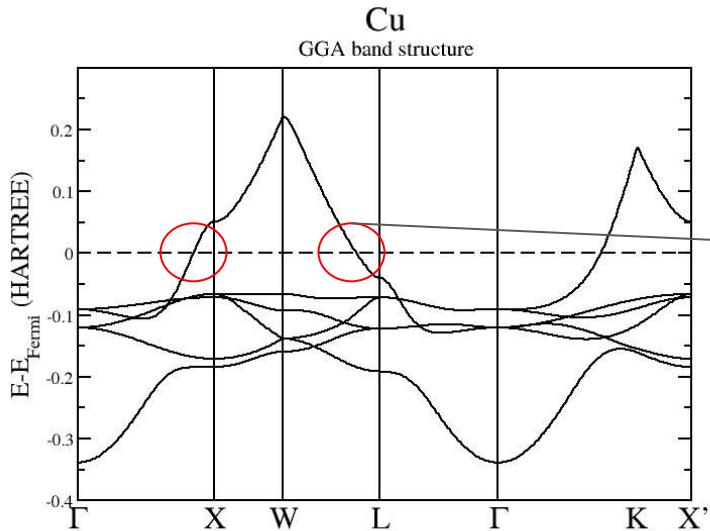
K-point convergence of alpha-Cerium using the PBE functional and ENCUT=500 eV.

<https://dannyvanpoucke.be/vasp-tutor-convergence-testing-en/>

# Smearing at Fermi level

$$E = \sum_i \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} f_{i\mathbf{k}} \varepsilon_{i\mathbf{k}} - \left[ E_{\text{H}} + \int d\mathbf{r} V_{xc}(\mathbf{r}) n(\mathbf{r}) - E_{xc} \right] \quad f_{i\mathbf{k}} = \frac{1}{e^{(\varepsilon_{i\mathbf{k}} - \mu)/\sigma} + 1} \quad \text{Q?}$$

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



Sholl, p. 60

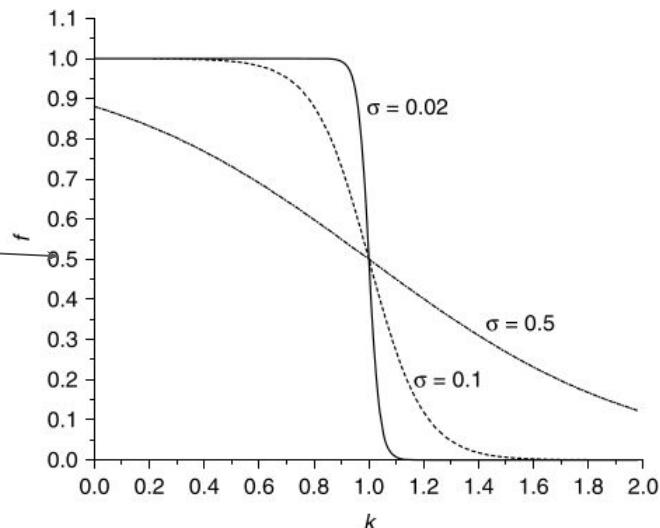


Figure 3.3 Fermi Dirac function [Eq. (3.10)] with  $k_0 = 1$  and several values of  $\sigma$ .

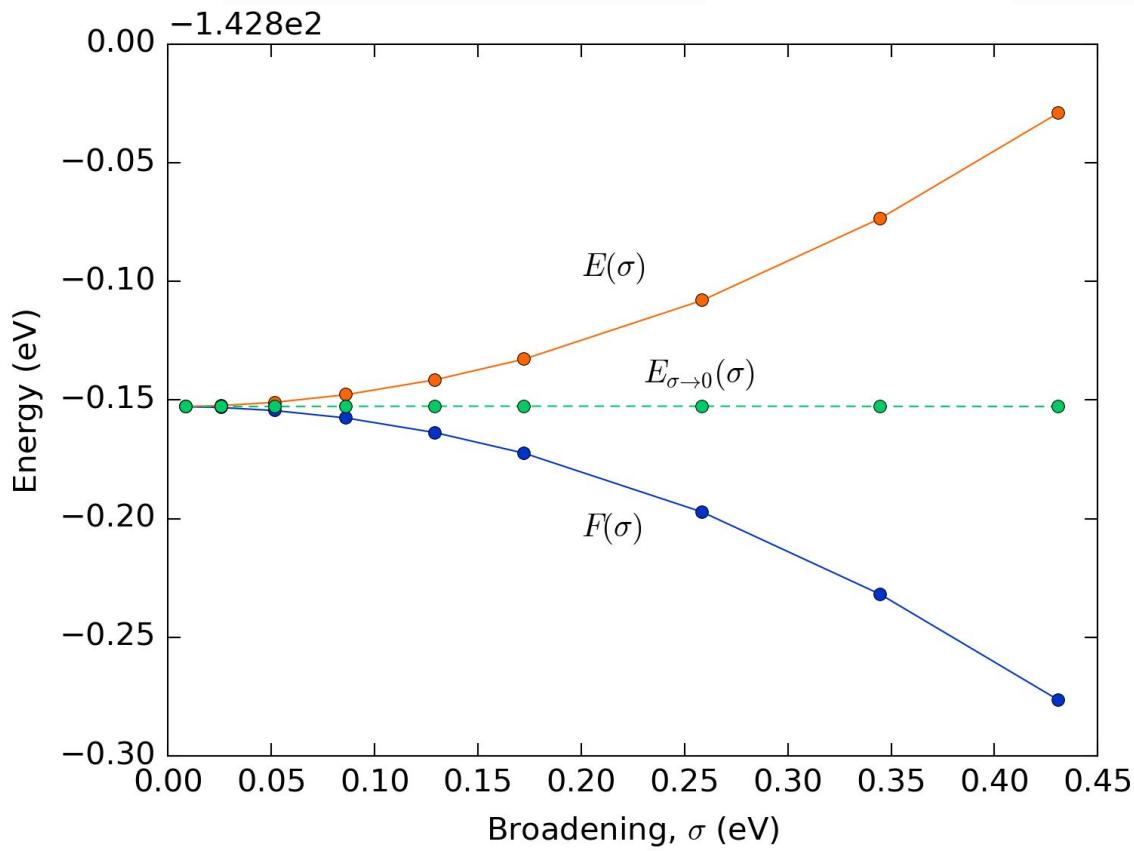
- Smearing is needed to make function continuous, [ISMEAR](#)
- In VASP: **ISMEAR** - chose method for smearing, [SIGMA](#) - the value of smearing
- Check smearing parameter!
- More k-points for metals, density < 0.15 Å<sup>-1</sup> (**KSPACING**)

# (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

# Convergence with respect to k-points and smearing

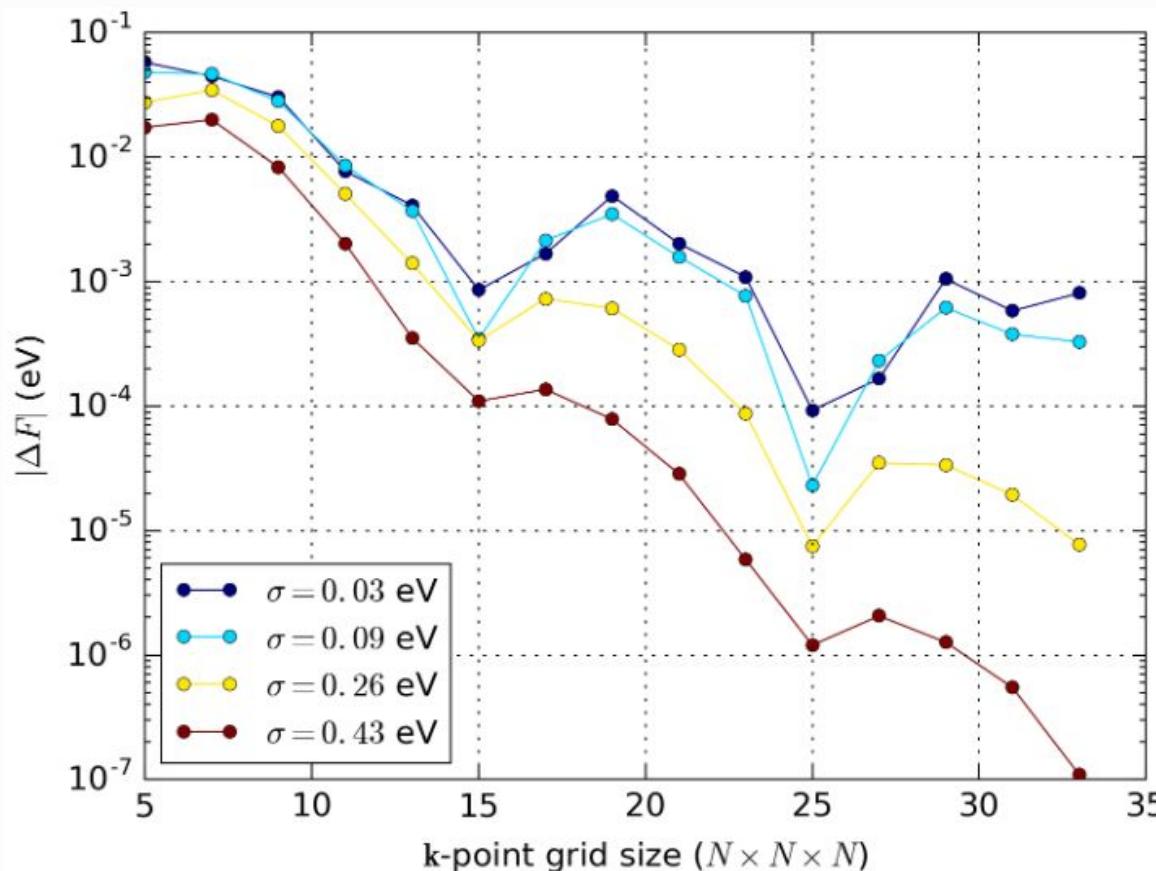


Fig. 105 Convergence of the free energy of bulk Aluminum with respect to the k-point sampling using the *Fermi-Dirac* occupation function with different broadenings. The free energy difference,  $\Delta F$ , is calculated as the difference between the calculation at the given k-point sampling and one at  $35 \times 35 \times 35$ .

[https://docs.quantumatk.com/manual/technicalnotes/occupation\\_methods/occupation\\_methods.html](https://docs.quantumatk.com/manual/technicalnotes/occupation_methods/occupation_methods.html)

# Smearing methods

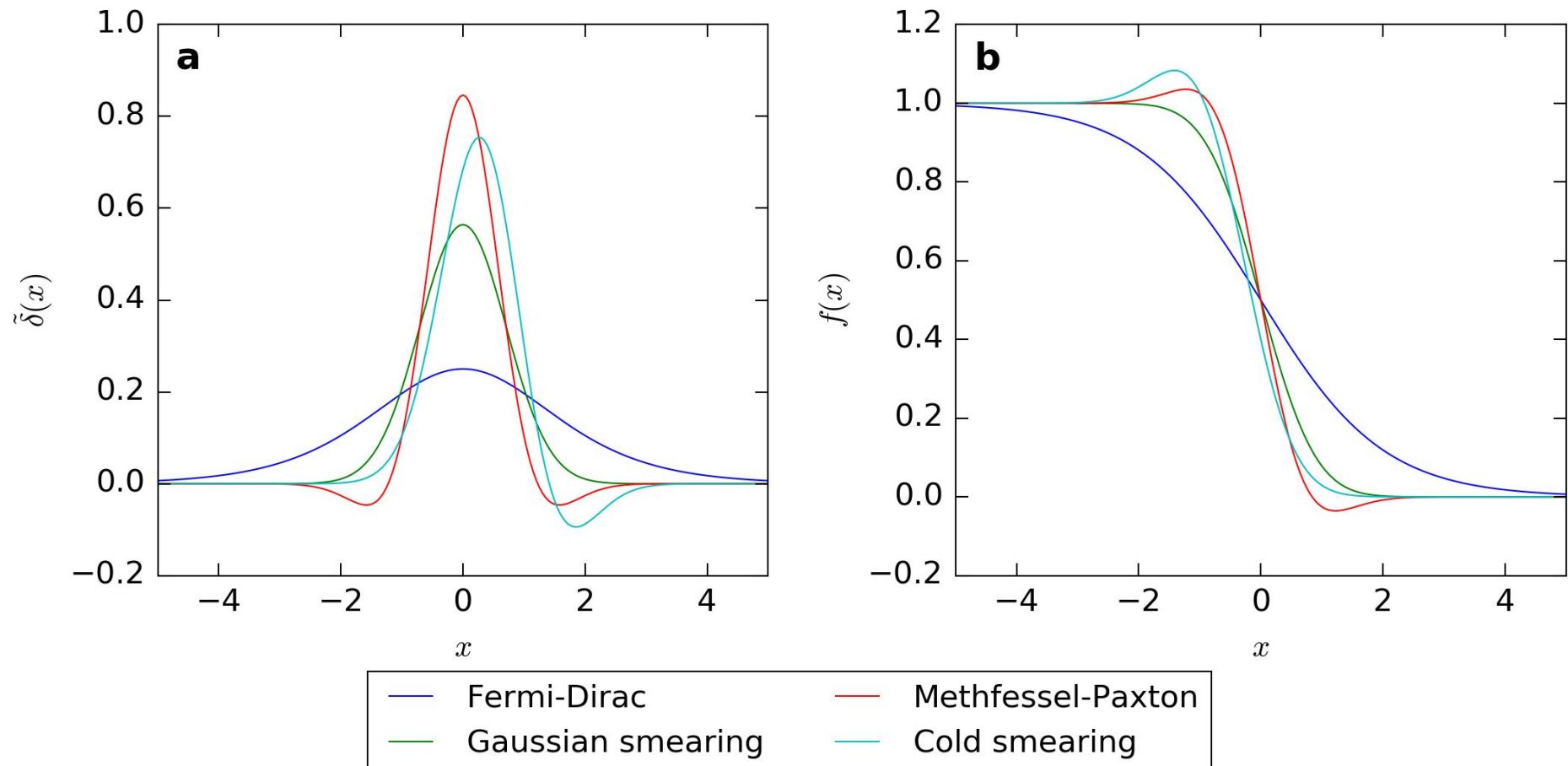
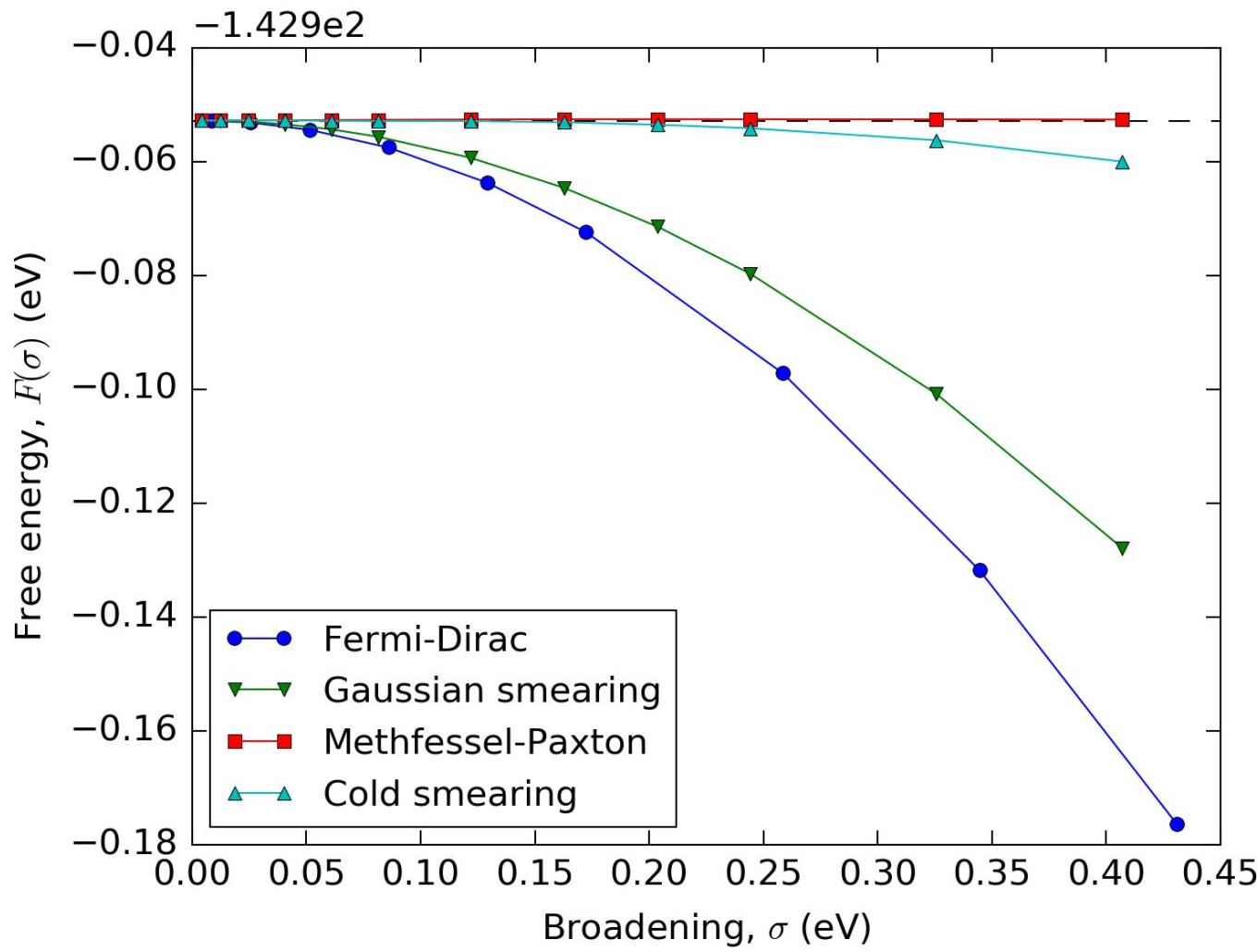
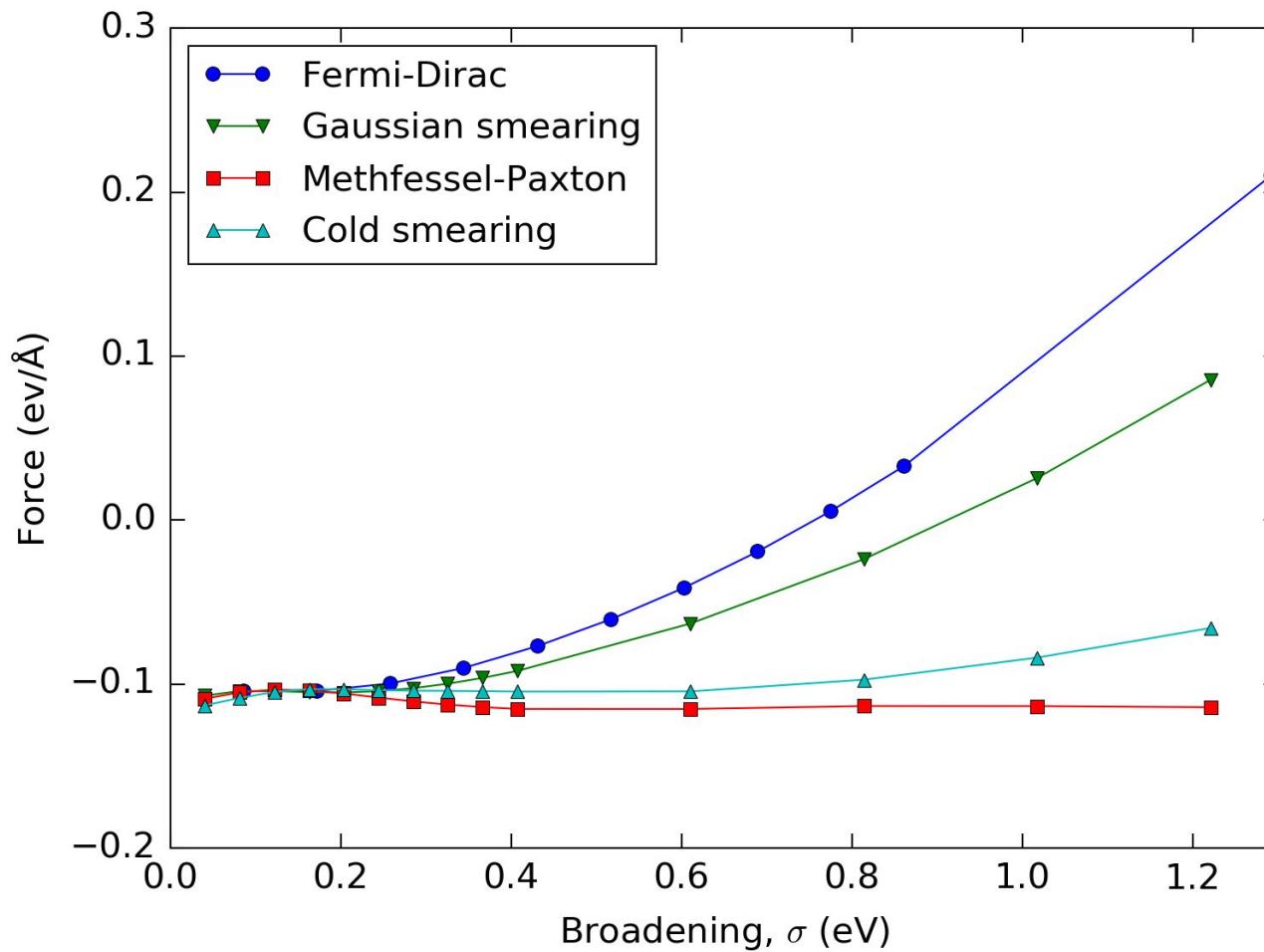


Fig. 107 (a) Plots of the different smeared delta functions,  $\tilde{\delta}(x)$ , and (b) their corresponding occupation functions  $f(x)$ , shown as functions of  $x = \frac{\epsilon-\mu}{\sigma}$ .

# Energy error for different smearing methods



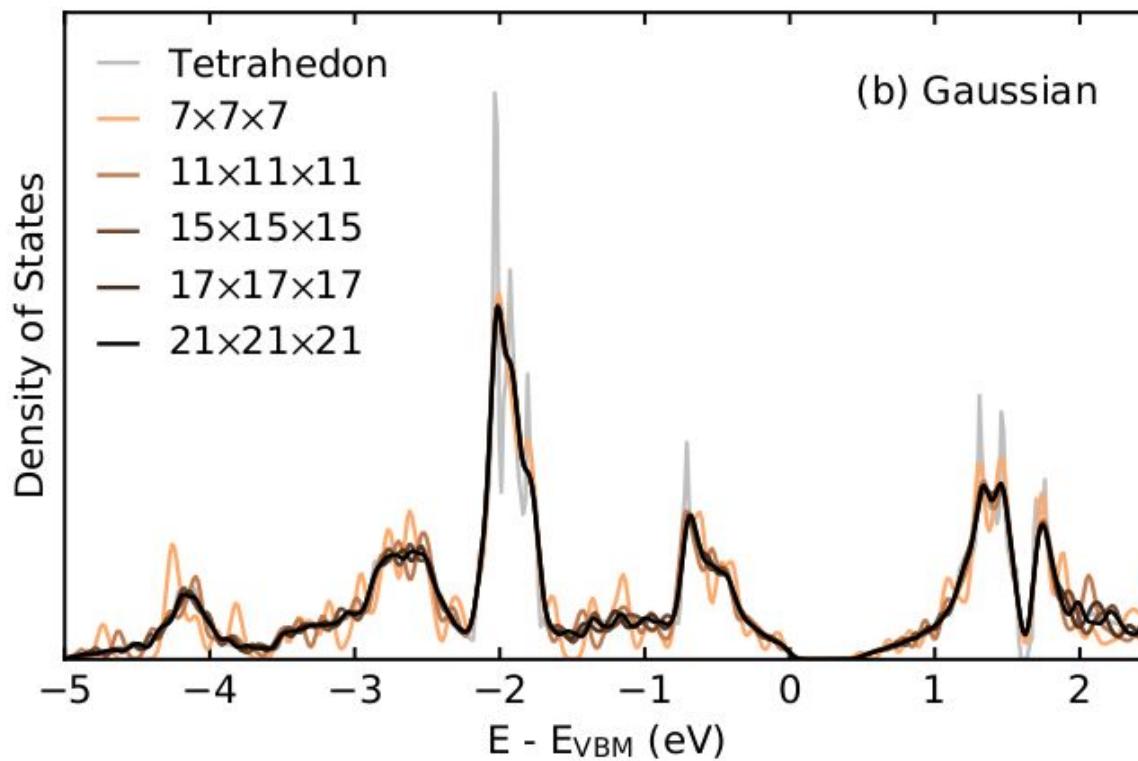
# Force error for different smearing methods



Force on the outermost atom in a 6 layer Aluminum 111 slab as a function of the broadening using the different occupation methods. In order to keep the different methods comparable, the broadening has been multiplied by 2.117 for all but the Fermi-Dirac distribution.

# DOS

<https://arxiv.org/pdf/2103.03469.pdf>



# Advices on choosing k-grid and smearing

## K-grids

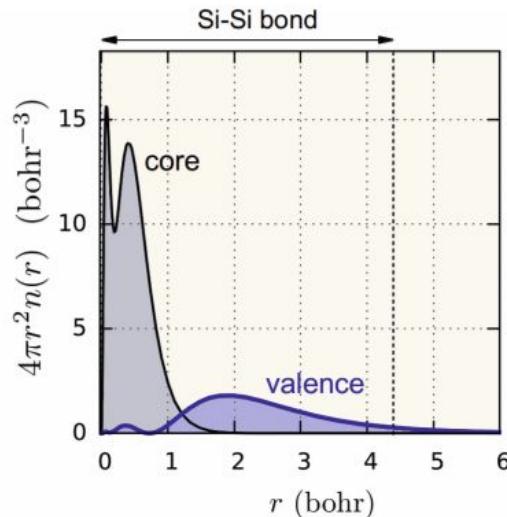
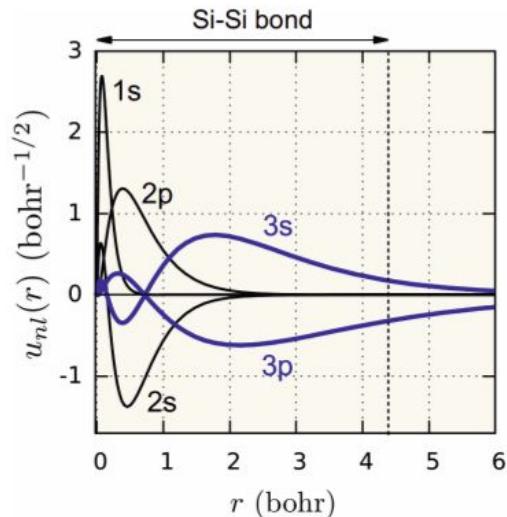
- Use even number of points, a shift can reduce number of k-points
- Try Gamma-centered k-grid if you have problem with off-center Monkhorst-Pack
- Use fine grid for DOS
- Use equivalent k-points meshes when comparing different cells

## Orbital occupation (smearing)

- **Systems with a band-gap** (semiconductors, insulators, molecules): Use either *Fermi-Dirac* (fictitious temperatures) or *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 either *Methfessel-Paxton* or *cold* smearing 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 (<https://arxiv.org/pdf/2103.03469.pdf>)

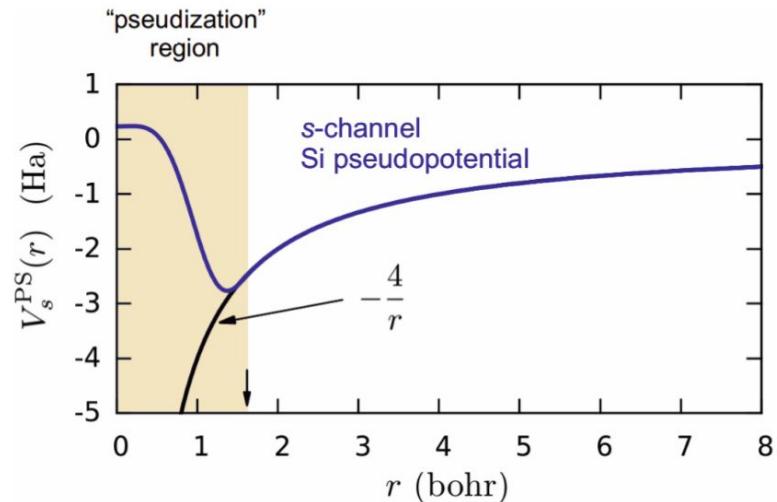
# Plane-waves for valence and core electrons

Guistino E1



- 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**



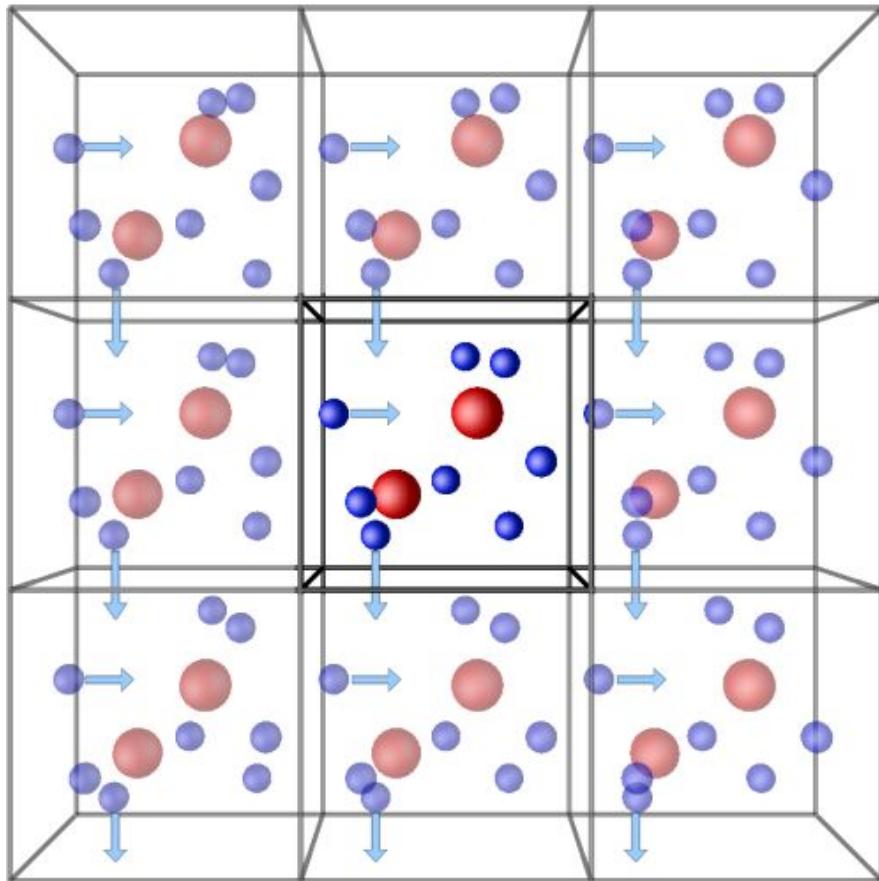
# Pseudopotential in DFT codes

- 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

# 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 - fix delocalization problems of PBE when higher level methods are not available, improves description of 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, many-body dispersion (MBD) method of Tkatchenko, etc

# Periodic Boundary conditions



Periodic boundary conditions (PBC) -

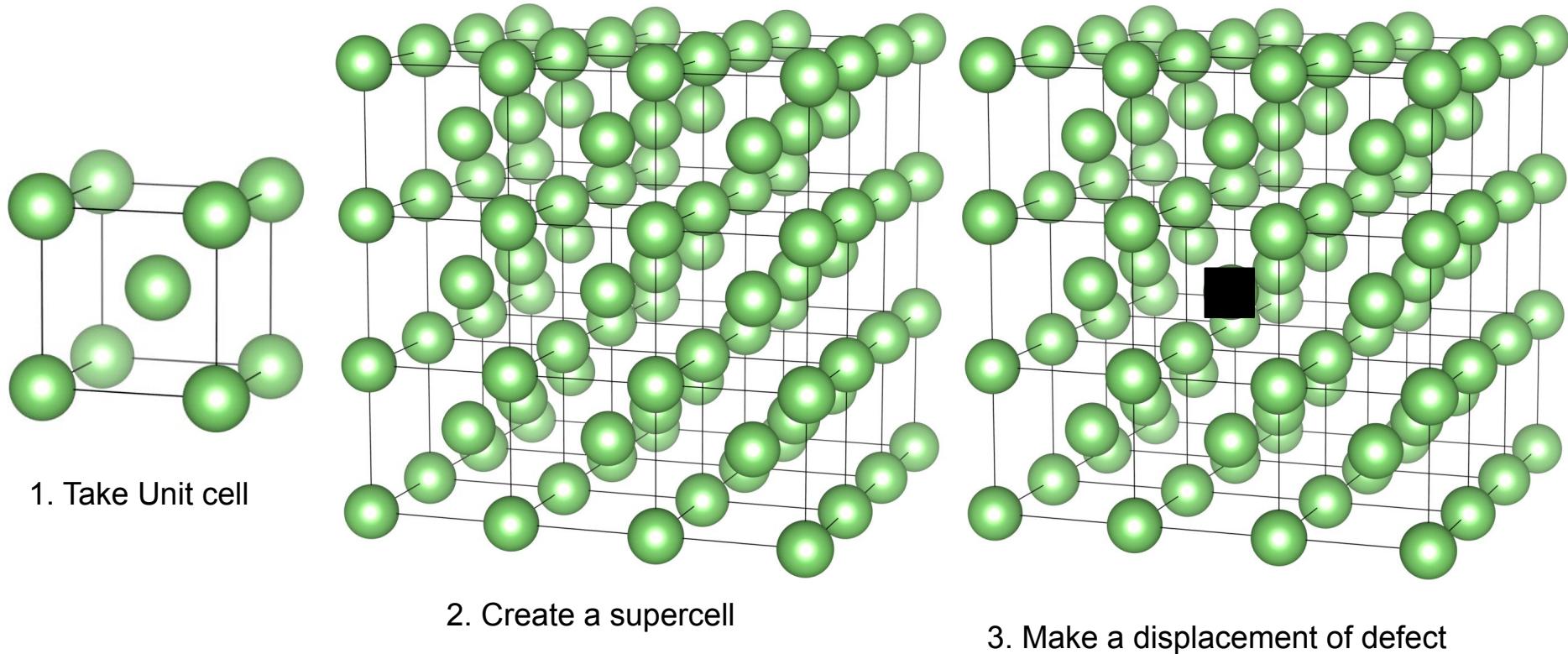
- when an object passes through one side of the unit cell, it reappears on the opposite side with the same velocity.
- Ideally suited for periodic systems

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

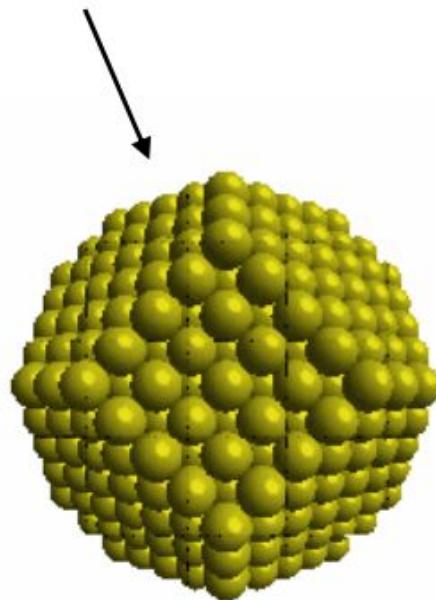
# Supercell approach for non-periodicity



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

# Free boundary conditions

Free cluster



Rigid shell, still unphysical, but better than open

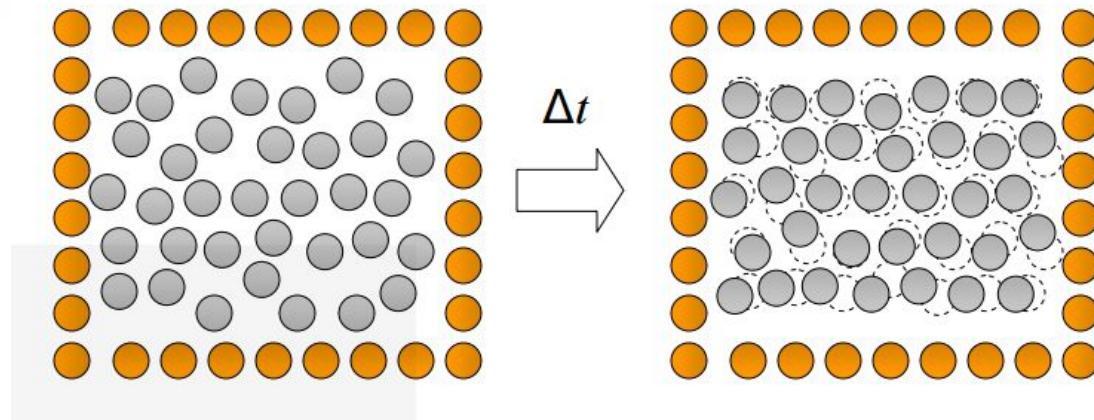
No translation symmetry!

Cons:

- non physical electronic states
- levels in the gap
- finite size quantum effects

Therefore:

For molecules, clusters, disordered solids in classical MD simulations



# Discussion

- Why full CI can not be used to describe periodic systems?
- Why do we need smearing of bands?
- What is the physical meaning of energy cut-off?
- What is pseudopotential and why it used?
- The k-grid is 12x12x12 for a cubic unit cell. Write in the chat an equivalent k-grid for 3x2x1 supercell.

# Optimization of atoms in periodic systems

Similar to molecular, see previous lecture

In VASP important parameters:

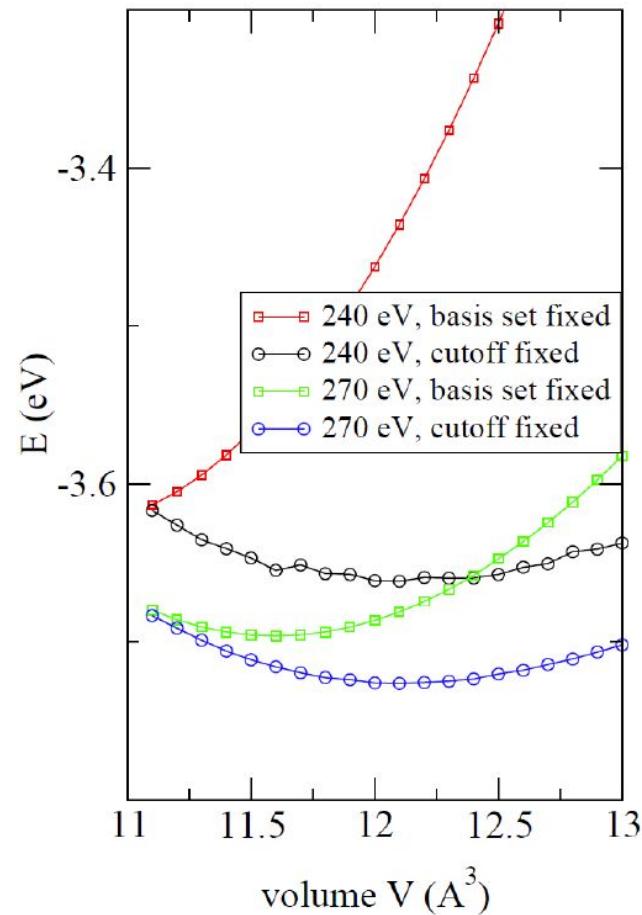
- IBRION - type of optimisation
  - 0 - molecular dynamics
  - 1 - quasi-Newton
  - 2 - Conjugate gradient
  - 3 - Damped MD
  - etc
- NSW - number of steps
- POTIM - step in MD, fs

# Unit cell optimization

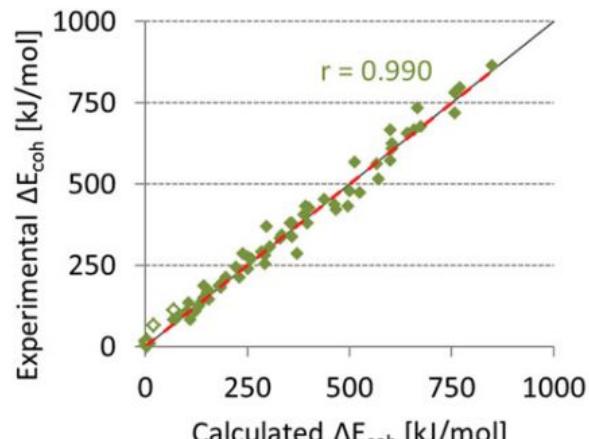
- Pulay stress: increase plane wave cutoff or do volume scan
- Use the same plane wave cutoff for different volumes
- Use consistent k-grids for different volumes

In VASP ISIF :

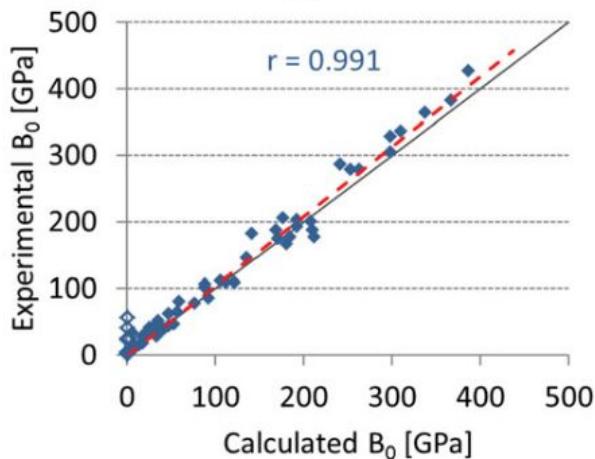
- 2 - only atoms
- 4 - shape
- 3 - shape and volume



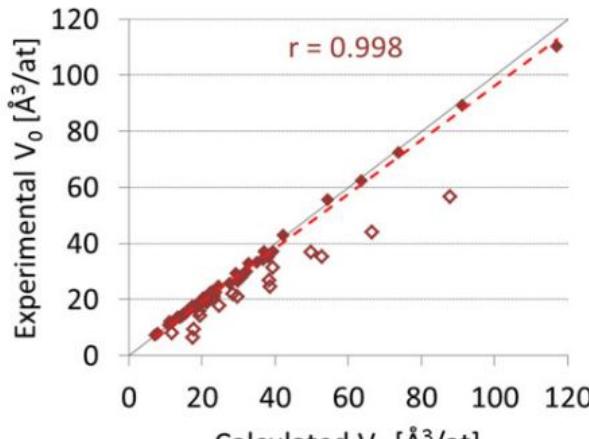
# Accuracy: geometry and elastic



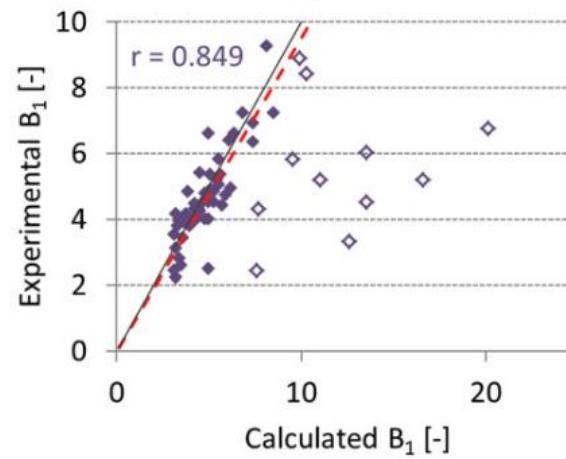
(a)



(c)



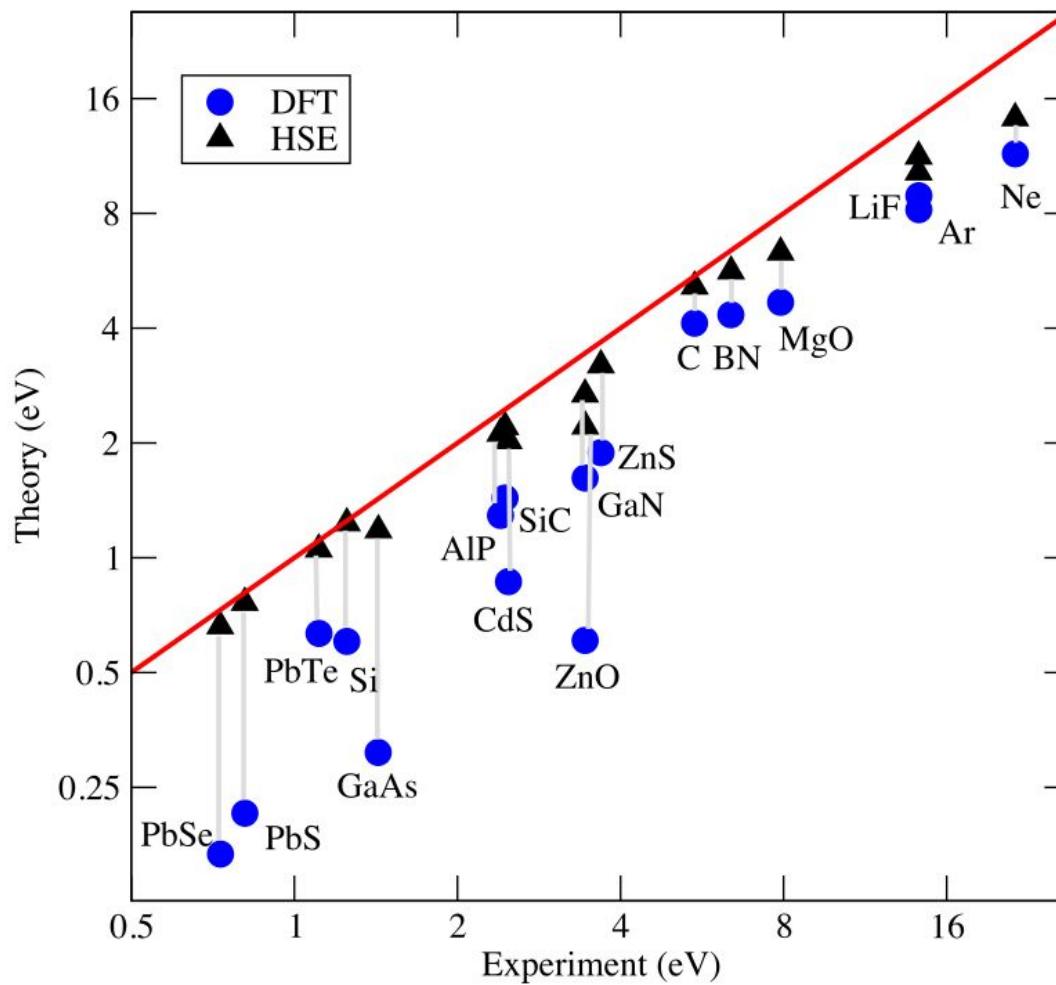
(b)



(d)

Geometry, cohesion energies, mechanical properties for elemental crystals are quite accurate even for simple DFT (LDA, PBE) from Lejaeghere *et al.*, *Crit. Rev. Solid State Mater. Sci.* 39 (2014) 1-24

# Accuracy: band gap

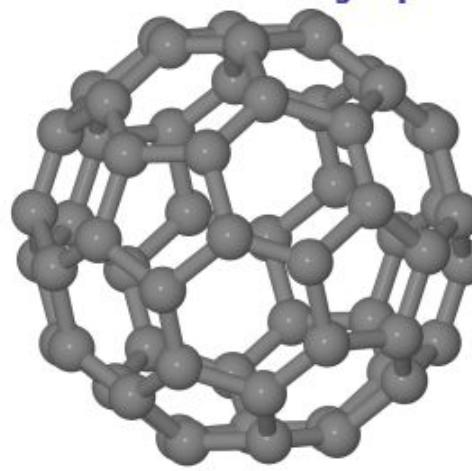
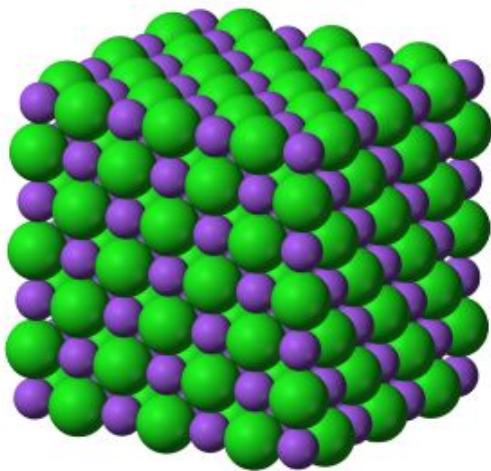


For band gap calculations use HSE or GW methods, J. Hafner, *J. Phys.: Condens. Matter* 22 (2010) 384205

# Other things to keep in mind

- Use primitive unit cell instead of symmetric one (e.g. VASP recognizes diamond lattice but misinterprets  $\mathbf{k}$ -points)
- Kohn-Sham orbitals are supposed to give one-electron orbitals and elementary excitations:
  - No cations and anions
  - TDDFT does not work, for bandgap use GW or HSE06
- Beyond DFT:
  - GW is good for excitations
  - DFT+U is a ``patch" for valence  $d$ - and  $f$ -electrons
  - CI/CC are conceptually challenging
  - QMC is technically challenging (``sign" problem)
  - DMFT is computationally demanding
  - Overall, no reliable methods for strongly correlated systems (high-T superconductors, actinides)
- Surfaces and interfaces, 1D and 2D materials - use appropriate supercell and  $\mathbf{k}$ -grid along the reduced dimension

# Crystal vs molecule: computational chemistry perspective

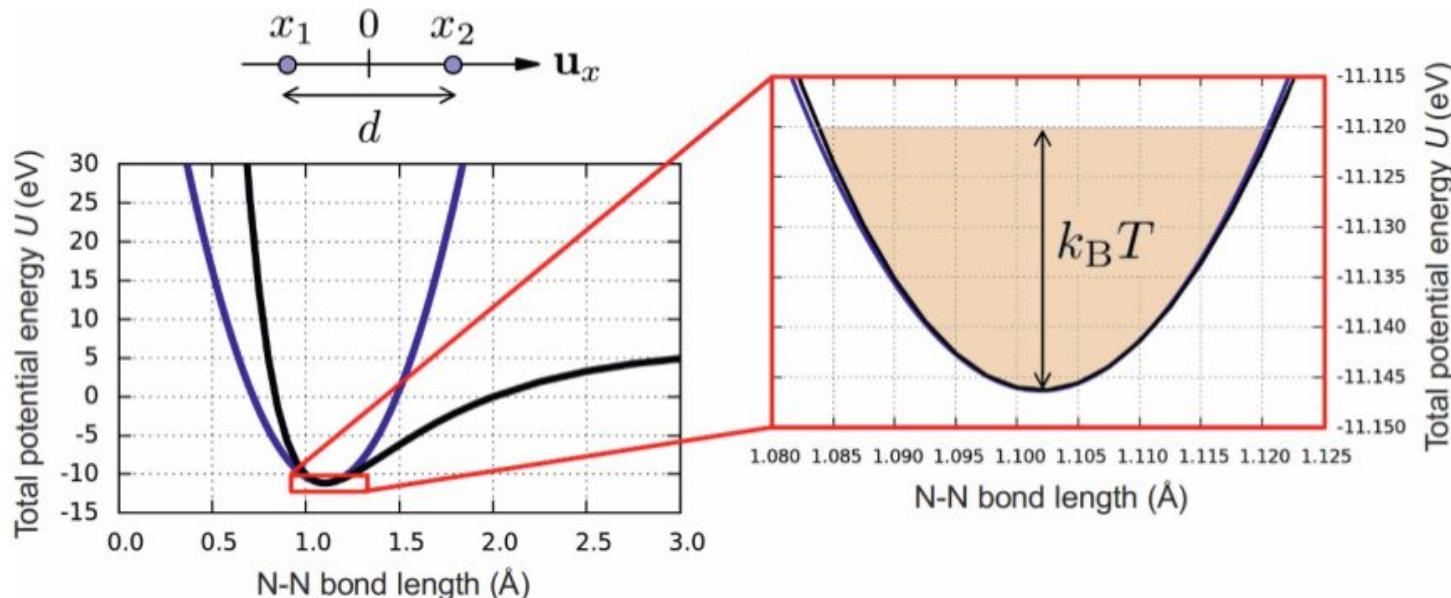


- Brute force approach (large supercell or supermolecule) does not always work (e.g. metals) and is always inefficient (by orders of magnitude)
- Infinite symmetry due to translations (space group)
- Finite sums to lattice sums (or integrals)
- Essentially infinite system (thermodynamic limit) implies no exact answer like ``full CI'' + phase transitions (both classical and quantum)
- Metals (no molecular analogues)
- Nuclei motion breaks translation symmetry

# Influence of temperature?

- thermal conductivity
- thermal expansion
- electrical resistivity
- heat capacity
- optical absorption
- superconductivity
- thermopower
- structural phase transitions.

# Vibrations in crystals



Taylor expansion in harmonic approximation

$$E = E_0 + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left[ \frac{\partial^2 E}{\partial x_i \partial x_j} \right]_{\mathbf{x}=0} x_i x_j$$

$$H_{ij} = \left[ \frac{\partial^2 E}{\partial x_i \partial x_j} \right]_{\mathbf{x}=0} \quad A_{ij} = H_{ij}/m_i$$

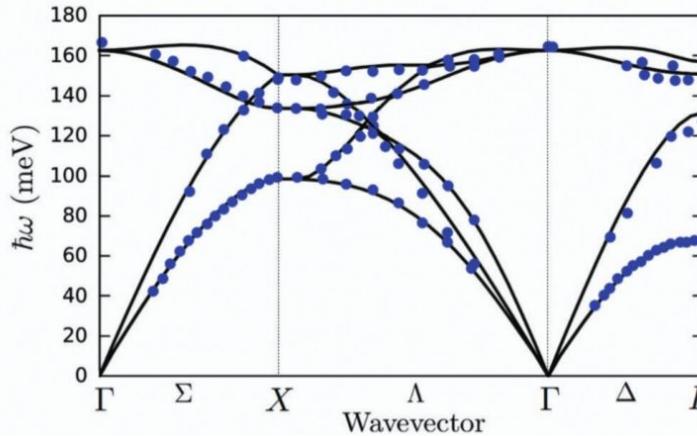
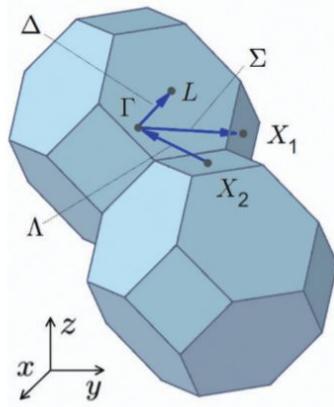
The eigenvalues of mass-weighted Hessian are called normal modes and have frequency  $\omega$ ,  $3N$  in total, where  $N$  is number of atoms

# The dependence on $\mathbf{q}$ (phonon wave vector)

But in periodic crystal the normal modes obey the Bloch theorem:

$$\mathbf{u}_n(\mathbf{R}) = \mathbf{u}_{n,q} e^{i\mathbf{q}\mathbf{R}} \quad n - \text{mode number}$$

As a result normal modes got dispersion in  $\mathbf{q}$  space



Vibrational spectra of diamond)

# Thermodynamics

Once phonon frequencies over Brillouin zone are known , the energy E of phonon system is given as

$$E = \sum_{\mathbf{q}j} \hbar \omega_{\mathbf{q}j} \left[ \frac{1}{2} + \frac{1}{\exp(\hbar \omega_{\mathbf{q}j}/k_B T) - 1} \right],$$

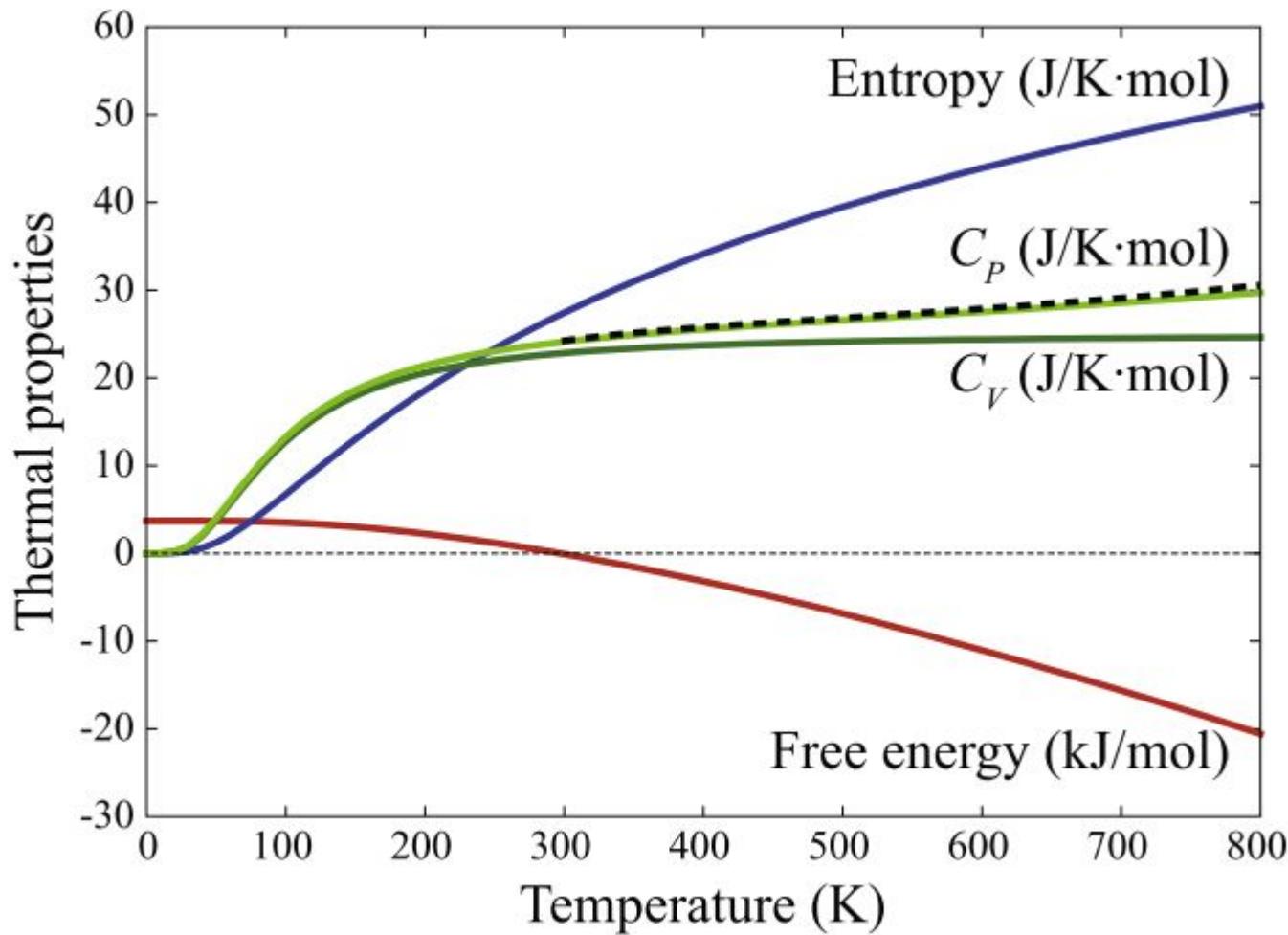
Helmholtz free energy F:

$$F = \frac{1}{2} \sum_{\mathbf{q}j} \hbar \omega_{\mathbf{q}j} + k_B T \sum_{\mathbf{q}j} \ln [1 - \exp(-\hbar \omega_{\mathbf{q}j}/k_B T)],$$

Entropy:

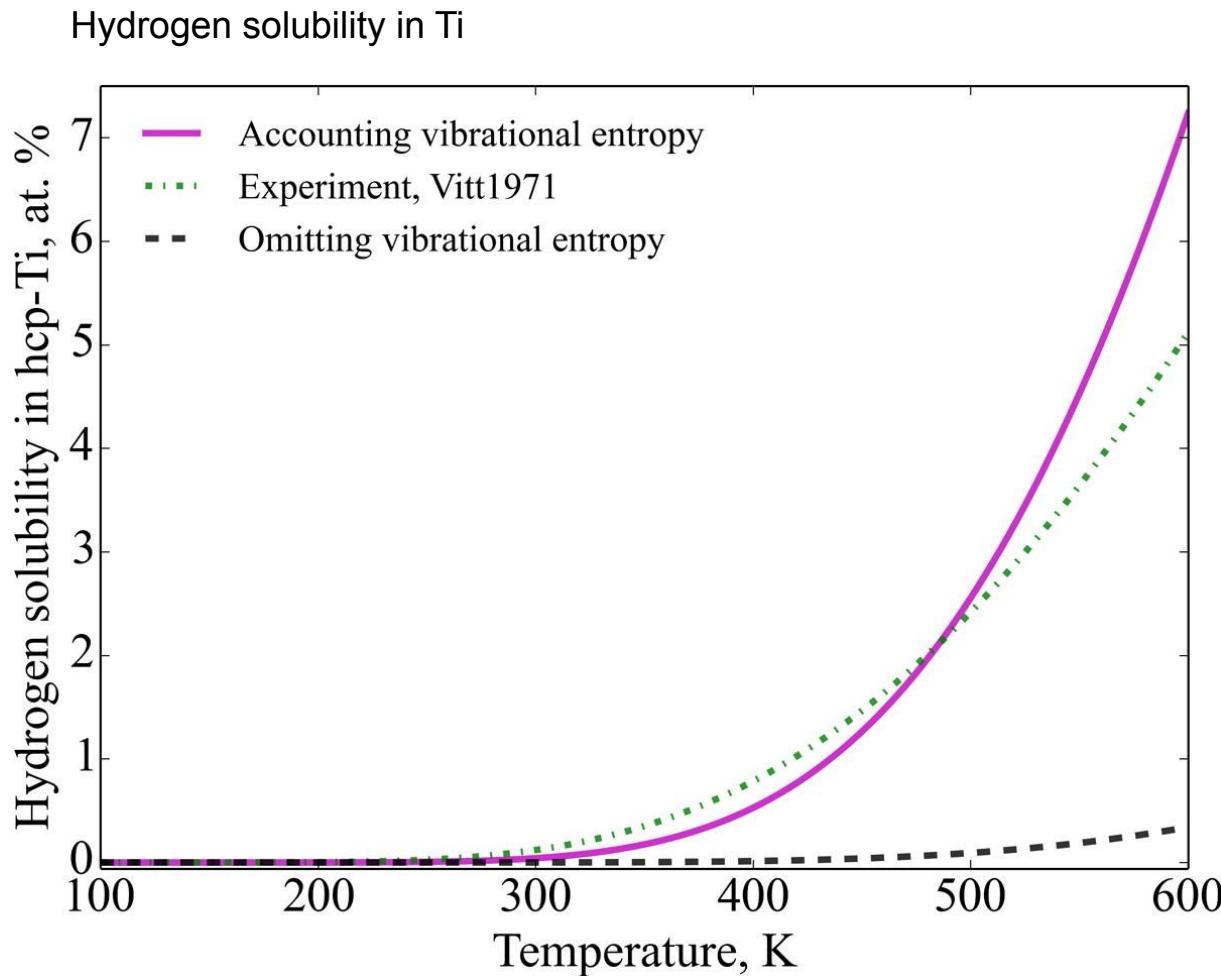
$$S = \frac{1}{2T} \sum_{\mathbf{q}j} \hbar \omega_{\mathbf{q}j} \coth [\hbar \omega_{\mathbf{q}j}/2k_B T] - k_B \sum_{\mathbf{q}j} \ln [2 \sinh(\hbar \omega_{\mathbf{q}j}/2k_B T)].$$

# Thermodynamics



Thermal properties of Aluminium

# Influence of vibrational entropy



Poletaev, D. O., et al. Computational Materials Science 114 (2016): 199-208.

# Phonon Calculation

- Two methods:
  - Finite differences - creates a set of cell with small atom displacements.
    - IBRION = 5,6 in VASP
  - DFPT (Perturbation theory) primitive cell can be used
    - IBRION = 7,8 in VASP
  - VASP calculates frequencies only at Gamma point!
    - For other points use Supercell
- To plot phonon band structure at other points and calculate thermodynamic properties use combination of DFT code and **phonopy** (<http://atztogo.github.io/phono3py/vasp.html>)

# Stability

- Check stability of lattice by looking on frequencies
  - There should be no imaginary frequencies
  - Three translation modes
- Check mechanical stability
  - Eigenvalues of elastic tensor should be positive

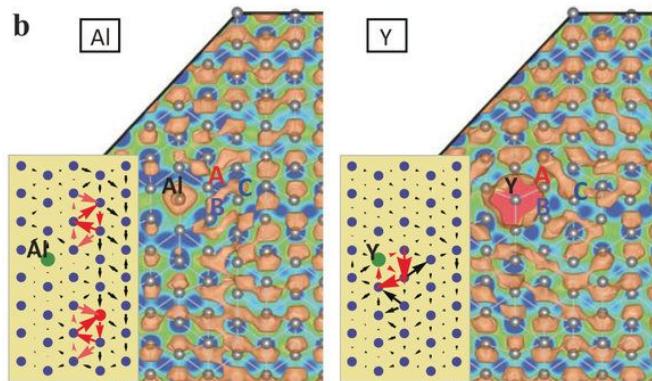
# Calculation of Properties

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

# Methods vs scales

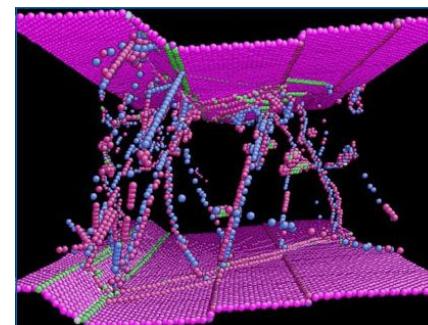
## Quantum methods

- Schrödinger equation for atomic interaction
  - DFT (Density Functional Theory) and flavours
    - VASP, Abinit, QE, etc.
- Electronic structure
- Almost all properties!!!
- Restricted in system sizes (1000 atoms) and simulation time (1000 of steps per day)

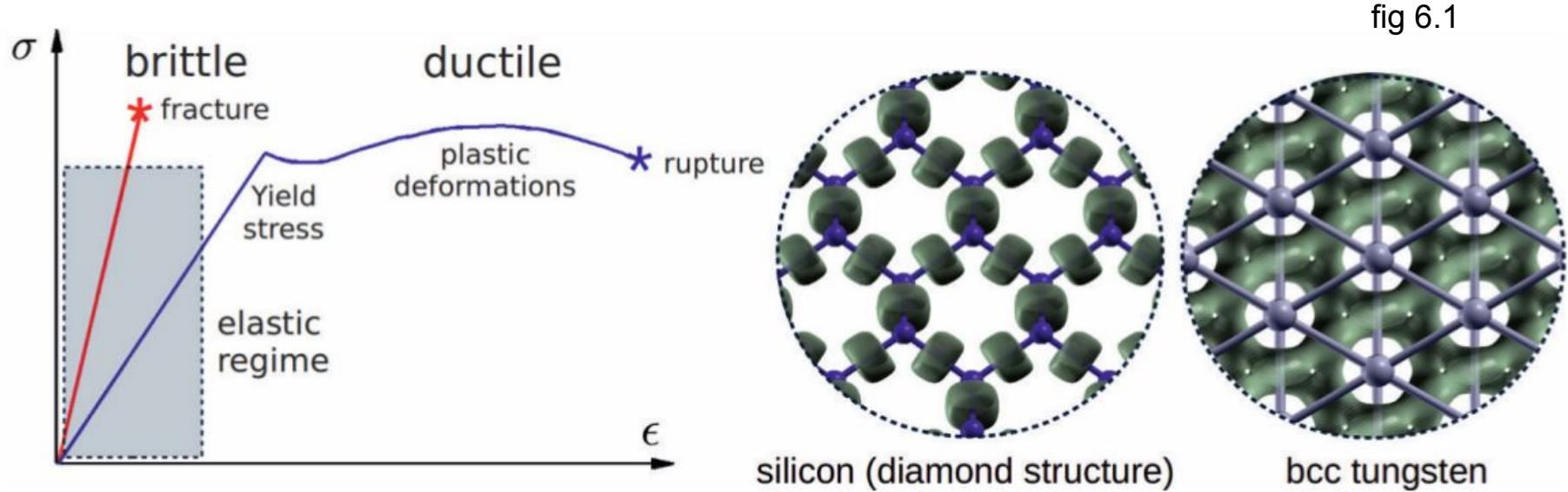


## Classical methods

- The interaction between atoms described empirically:
  - pair potentials, force fields, (EAM) Embedded Atom Method
    - LAMMPS code
- Atomic dynamics
- 20x20x20 nm, nanoseconds
  - Radiation cascades
  - Diffusion phenomena
  - Phase transitions
  - Plastic deformation



# Mechanical properties



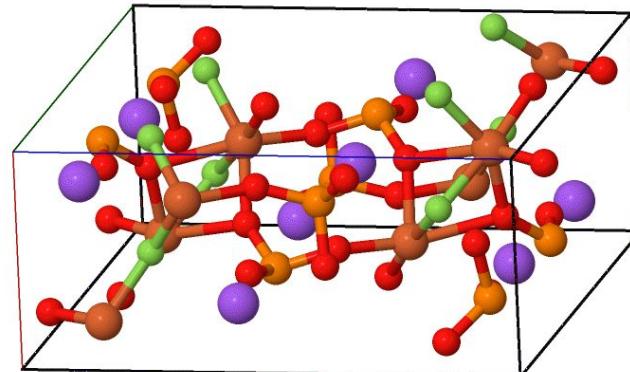
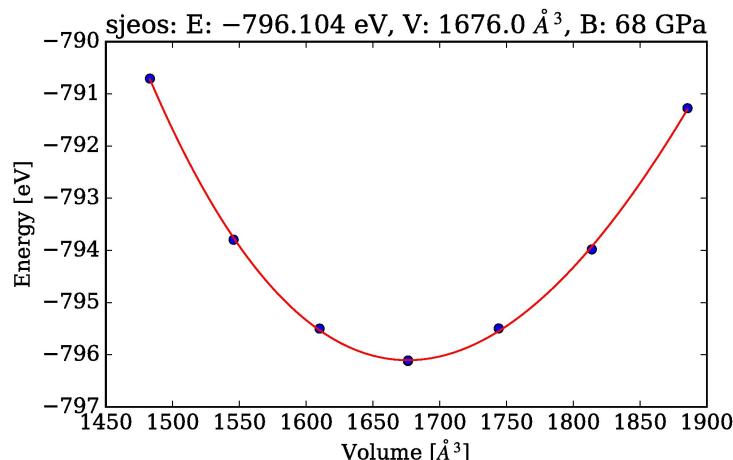
- The mechanical properties in brittle and ductile regimes depends on defects of crystal structure - an active research area for computational materials
- However, the elastic regime depends only on ideal crystal structure and can be easily described

# Equation of state and elastic properties

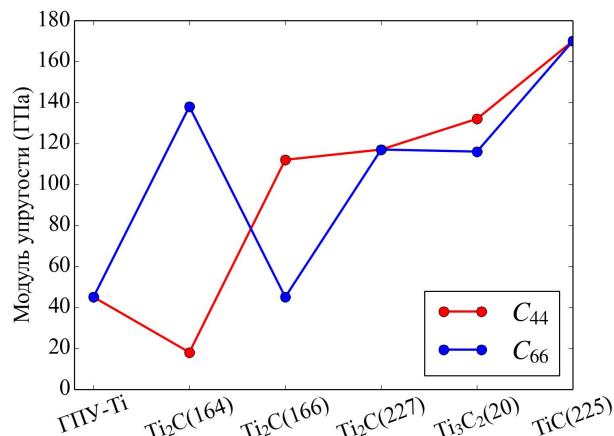
$$\mathbf{R} = \begin{pmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{c}{a} \end{pmatrix}$$

$$\begin{pmatrix} 1 + \alpha & 0 & 0 \\ 0 & 1 - \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$E(V, \alpha) = E(V_0, 0) + V_0[(\tau_1 - \tau_2)\alpha + (C_{11} - C_{12})\alpha^2].$$



$$C_{ijkl} \Rightarrow C_{\alpha\beta} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix}.$$



# Elastic tensor notations

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \quad \boldsymbol{\epsilon} = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

In Voigt notation:

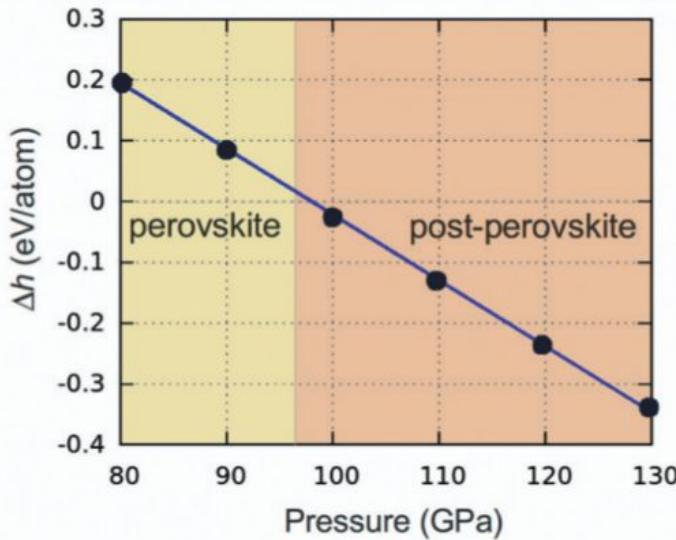
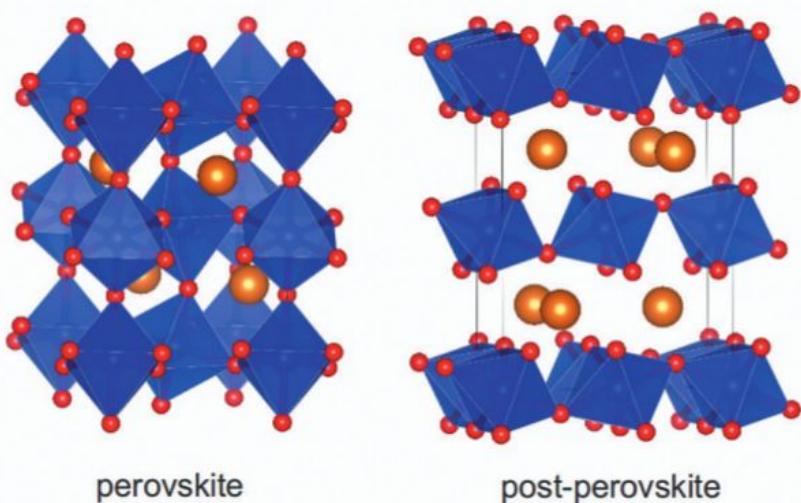
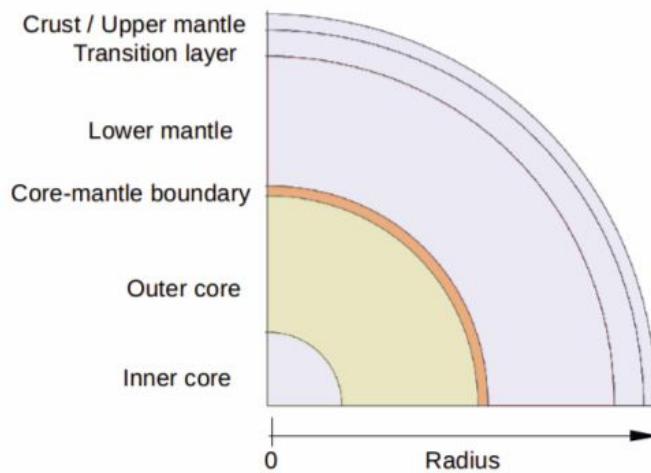
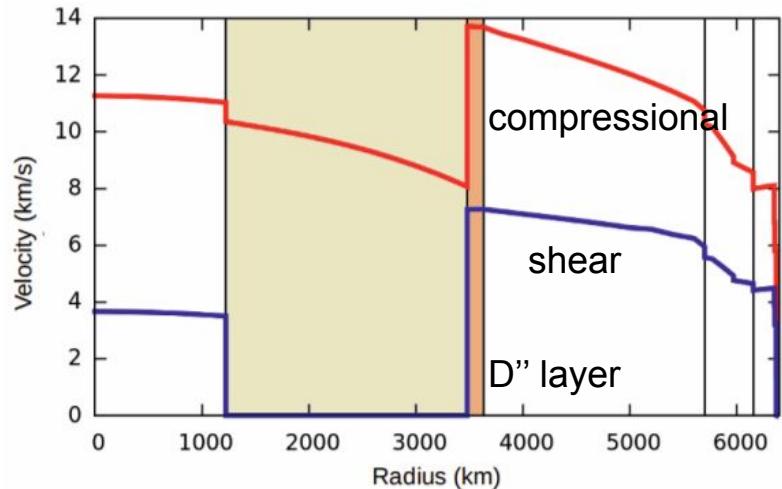
$$\tilde{\boldsymbol{\sigma}} = (\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{xz}, \sigma_{xy}) \equiv (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6)$$

$$\tilde{\boldsymbol{\epsilon}} = (\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}, \gamma_{yz}, \gamma_{xz}, \gamma_{xy}) \equiv (\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6)$$

$$\sigma_{ij} = \sum_{k=1}^3 \sum_{l=1}^3 c_{ijkl} \epsilon_{kl}$$

$C_{25} = C_{yyxz}$  gives relationship between  $\epsilon_{xz}$  deformation component  $\sigma_{yy}$  stress component

# Influence of pressure



from  
Giustino

# Temperature-pressure phase diagram

Giustino fig 8.8

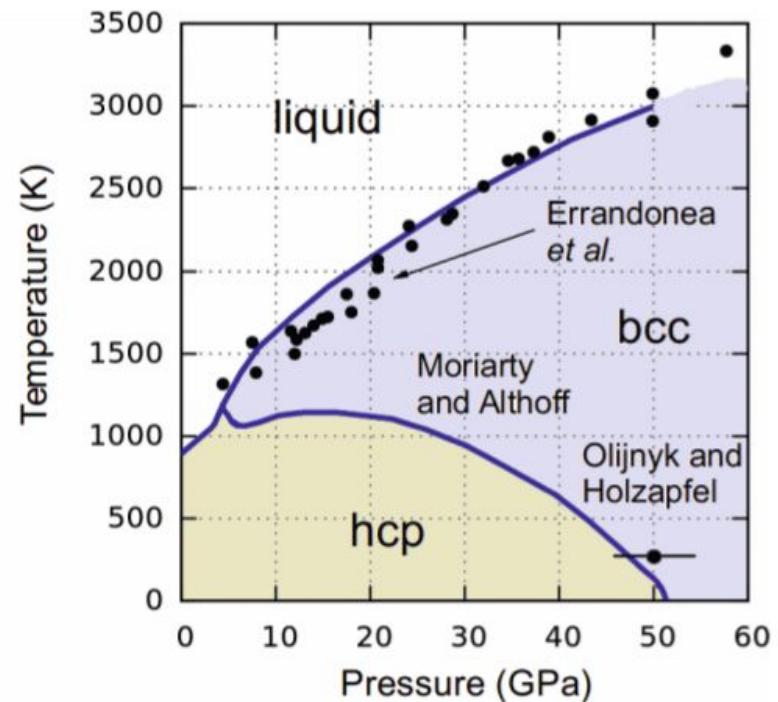
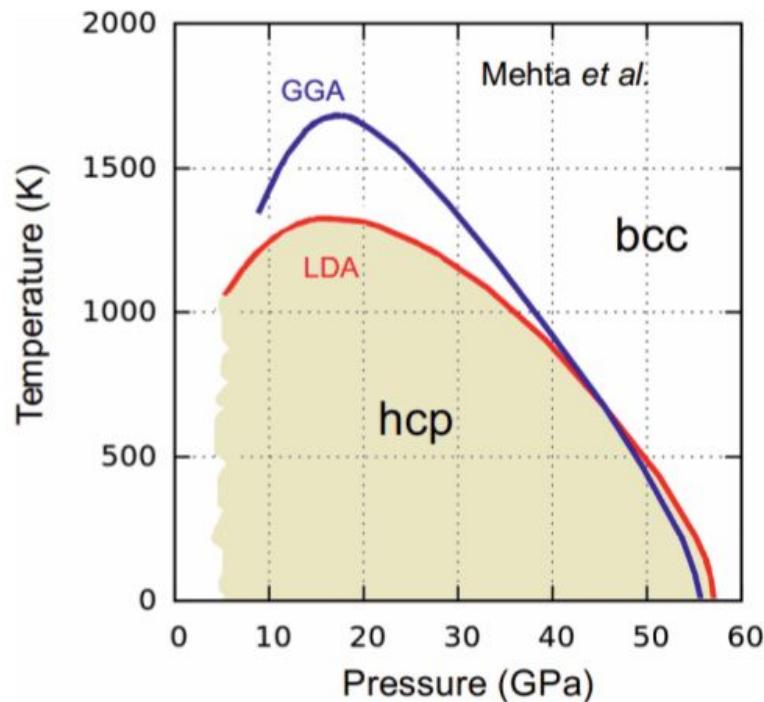


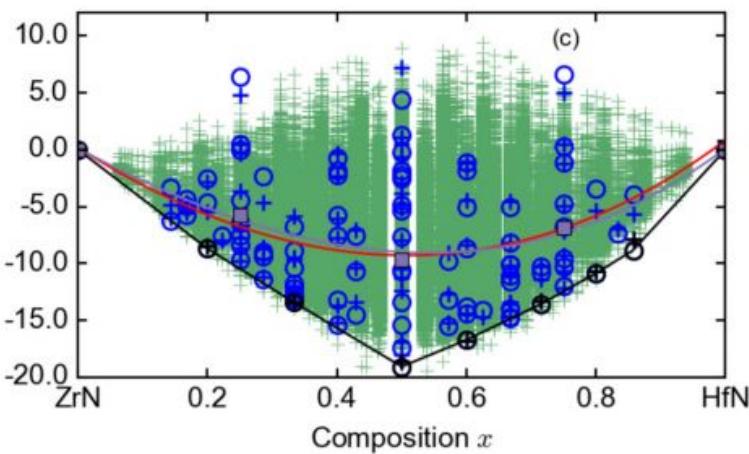
Fig. 8.8 The phase diagram of Mg from first principles. The left panel shows the calculations

# Temperature-chemical phase diagrams

More complicated:

- 1) Find all phases in chemical space - for example with USPEX code
- 2) Study solid solutions - use cluster expansion method (ATAT) and Monte-Carlo
- 3) Study the influence of temperature by making phonon calculations
- 4) Plot phase diagrams

DFT and cluster expansion, ZrN-HfN



J. Phys.: Condens. Matter 29 (2017) 035401

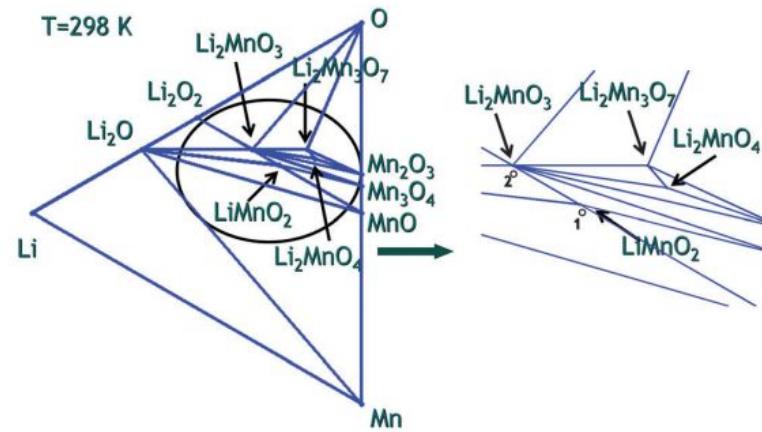
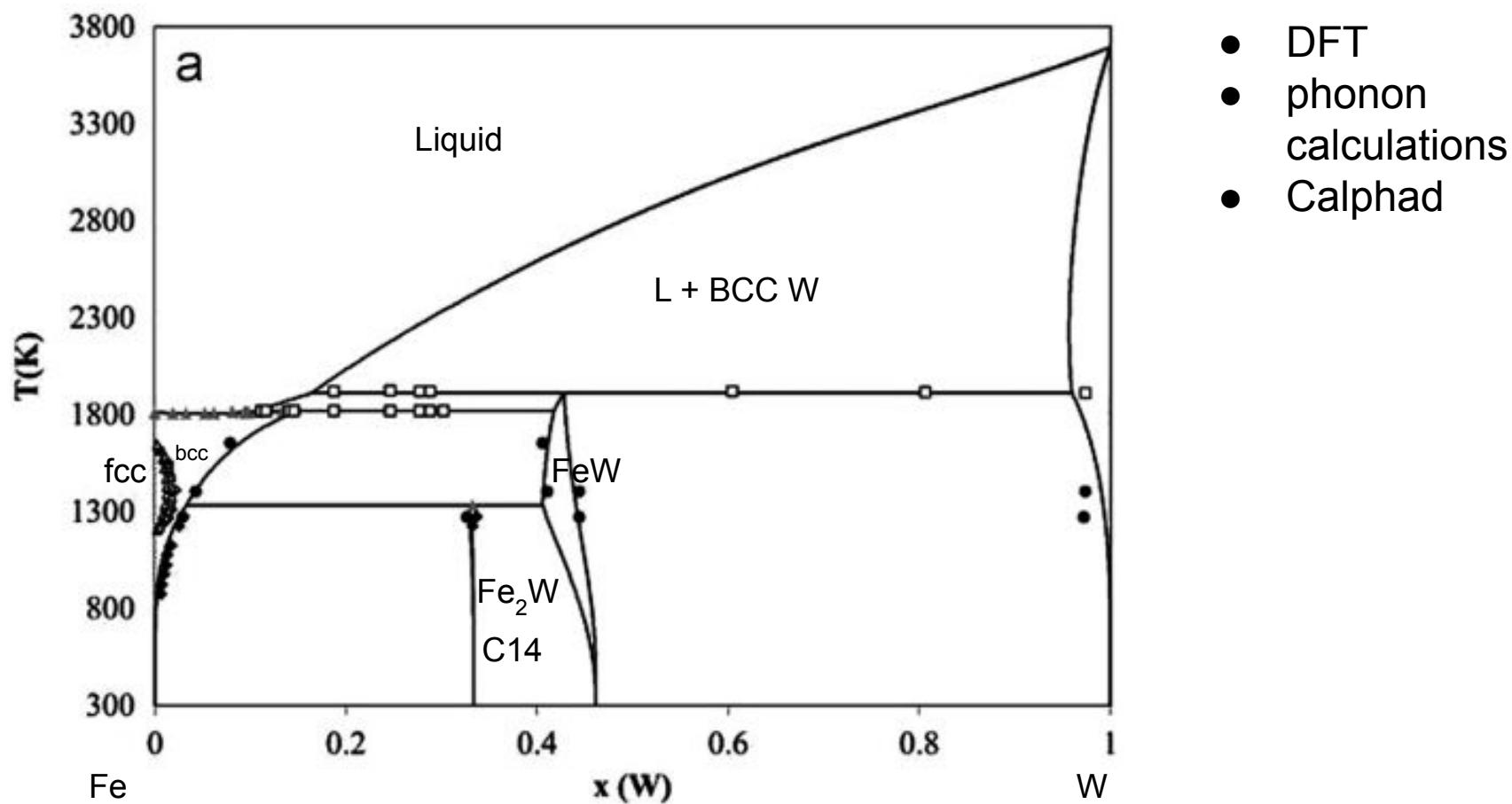


Fig. 4 Calculated ternary phase diagram of the Li–Mn–O system at room temperature. Points 1 and 2 show the position of the Li–O vacancy pair for  $\text{LiMnO}_2$  and  $\text{Li}_2\text{MnO}_3$ , respectively (see the text for details).

Longo Phys. Chem. Chem. Phys., 2014, 16, 11218

# Case study Fe–W phase diagram from DFT



A. Jacob, et al., CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 50 (2015) 92–104

$$\begin{aligned}G^{C14} = & y_{Fe}^1 y_W^2 G_{Fe:W}^0 + y_W^1 y_{Fe}^2 G_{W:Fe}^0 + y_W^1 y_W^2 G_{W:W}^0 + \\& y_{Fe}^1 y_{Fe}^2 G_{Fe:Fe}^0 \\& + RT \left[ 2(y_{Fe}^1 \ln y_{Fe}^1 + y_W^1 \ln y_W^1) + (y_{Fe}^2 \ln y_{Fe}^2 + y_W^2 \ln y_W^2) \right]\end{aligned}$$

# Summary

## Main definitions

- **Bands** – single particle solutions
- **K-points** – integration grid in 1st Brillouin zone
- Partial occupation of bands (smearing)
- **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

# Discussion

- What convergence tests should be performed in DFT calculations for periodic systems ?
- How to estimate dynamical and mechanical stability of the lattice?
- Which class of materials requires less k-points: metals or insulators? Why?

# Individual studies:

- **Reading**

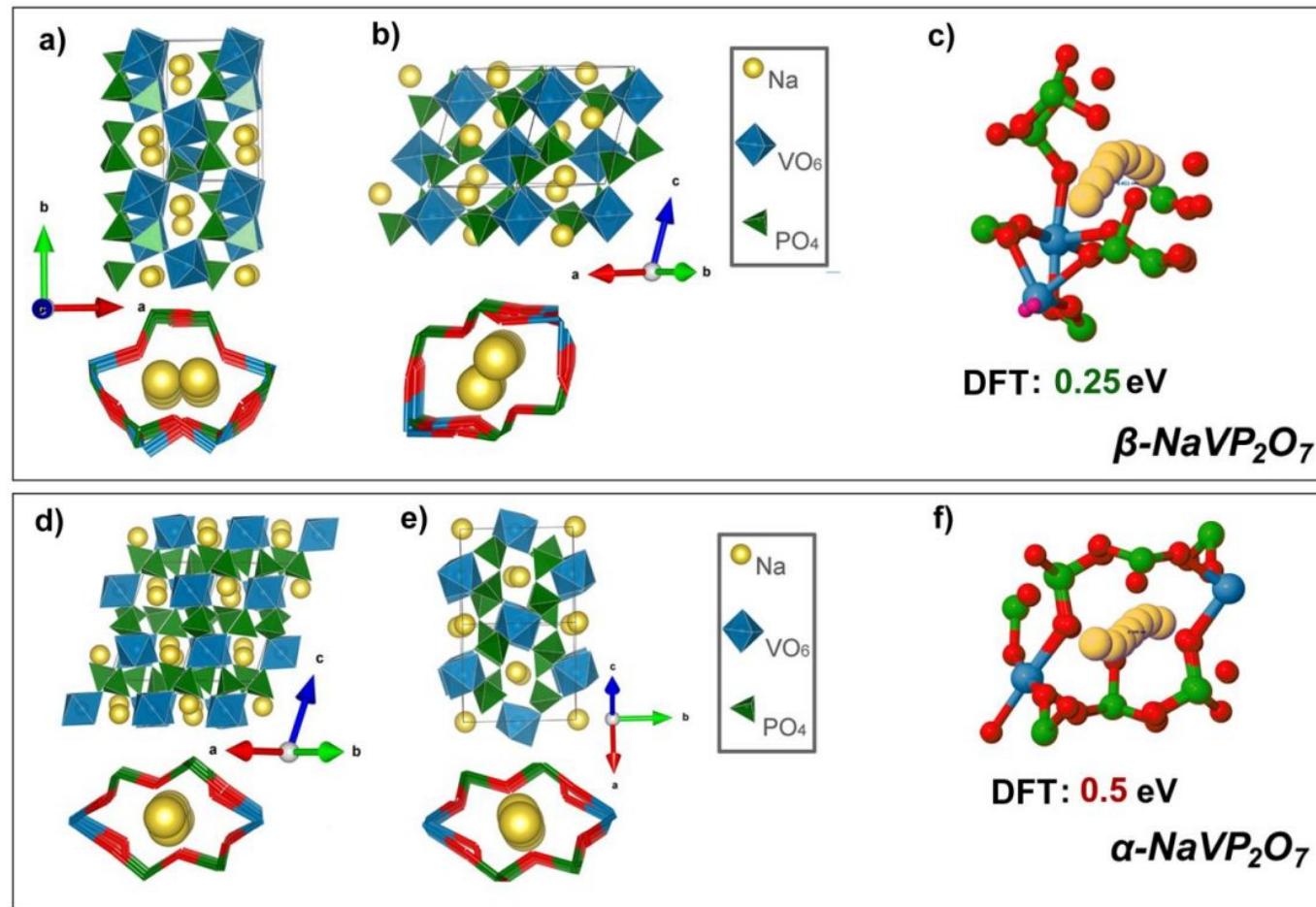
**Required:** Giustino (9.1-9.2, 9.4-9.5, 6.1-6.4, 7.1-7.4, 8.2-8.4)

**Additional:** Sholl (Ch.3)

1. **F. Giustino**, Materials Modelling using Density Functional Theory, Oxford, 2014
2. **D. Sholl**, Density functional theory  
A Practical Introduction, New Jersey, Wiley, 2009

**Thank you for your attention!**

# Case study: Migration of Na in $\text{NaVP}_2\text{O}_7$



Drozhzhin, O.A., Tertov, I.V., Alekseeva, A.M., **Aksyonov, D.A.**, Stevenson, K.J., Abakumov, A.M. and Antipov, E.V., //.  
*Chemistry of Materials*, 2019