

Lecture 6

Computational Chemistry of Crystals

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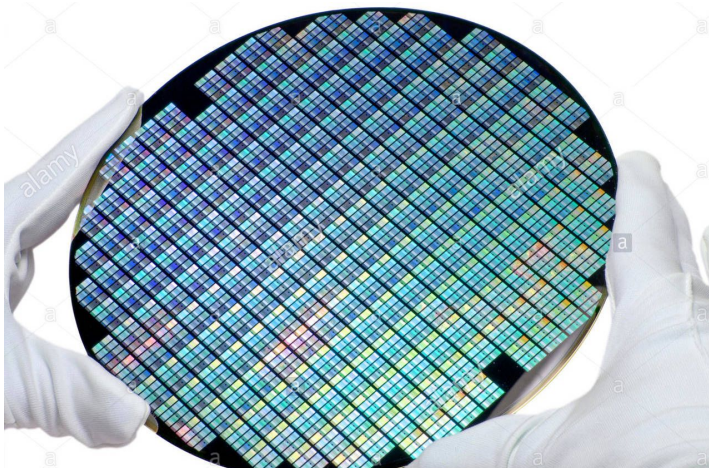
Arseniy Burov (TA)

What are the examples of crystals?

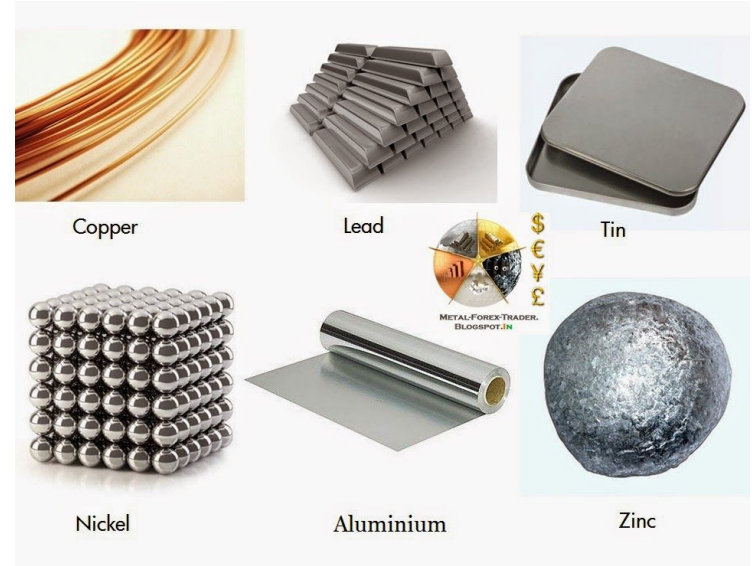
- Minerals (insulating)



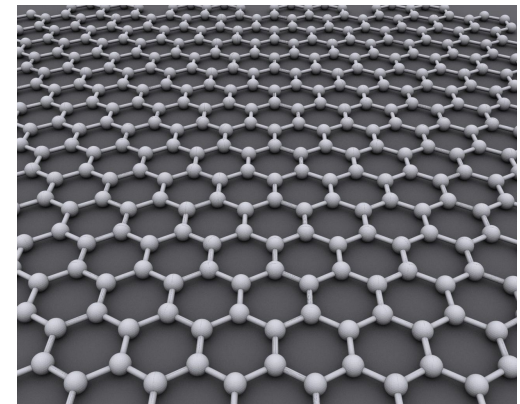
- Semiconductors



- Metals and alloys

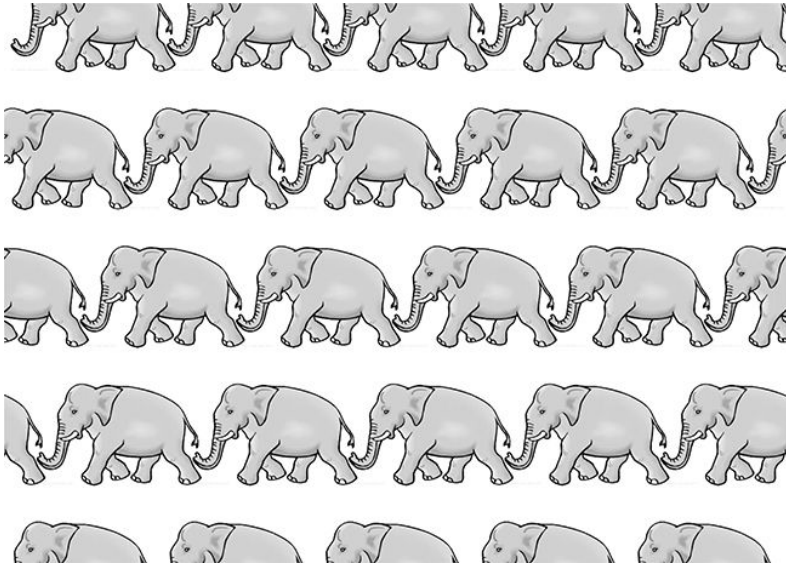


- 2D materials



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

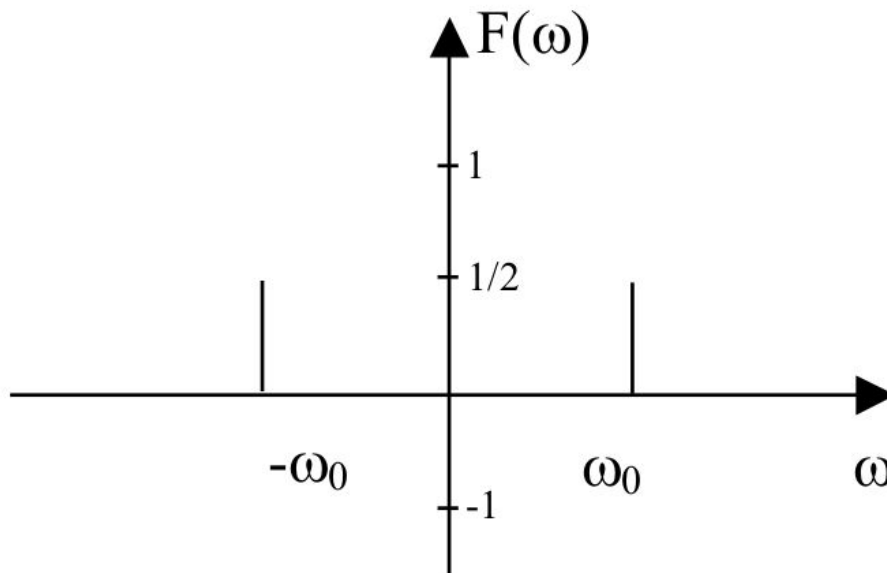
Problem: How to represent the infinite system?

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

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

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

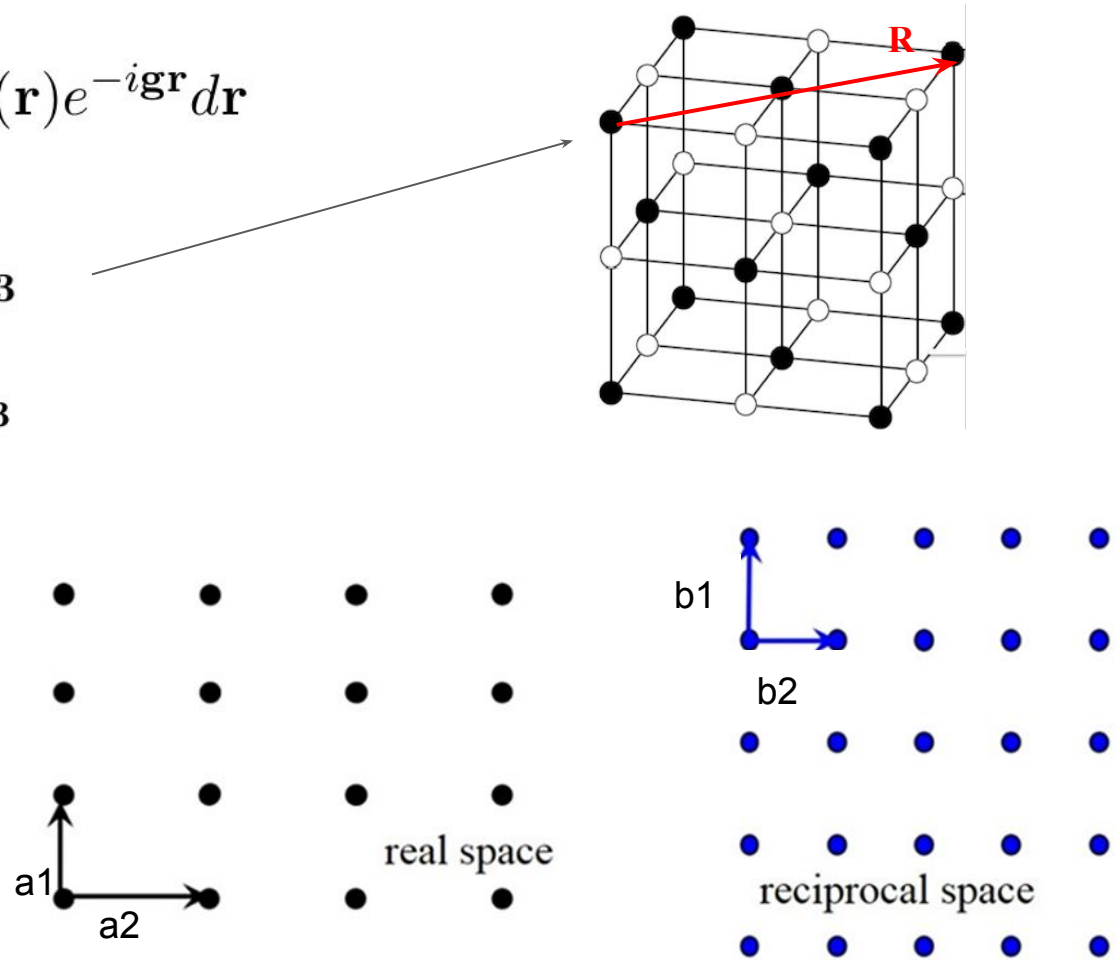
$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$$

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

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

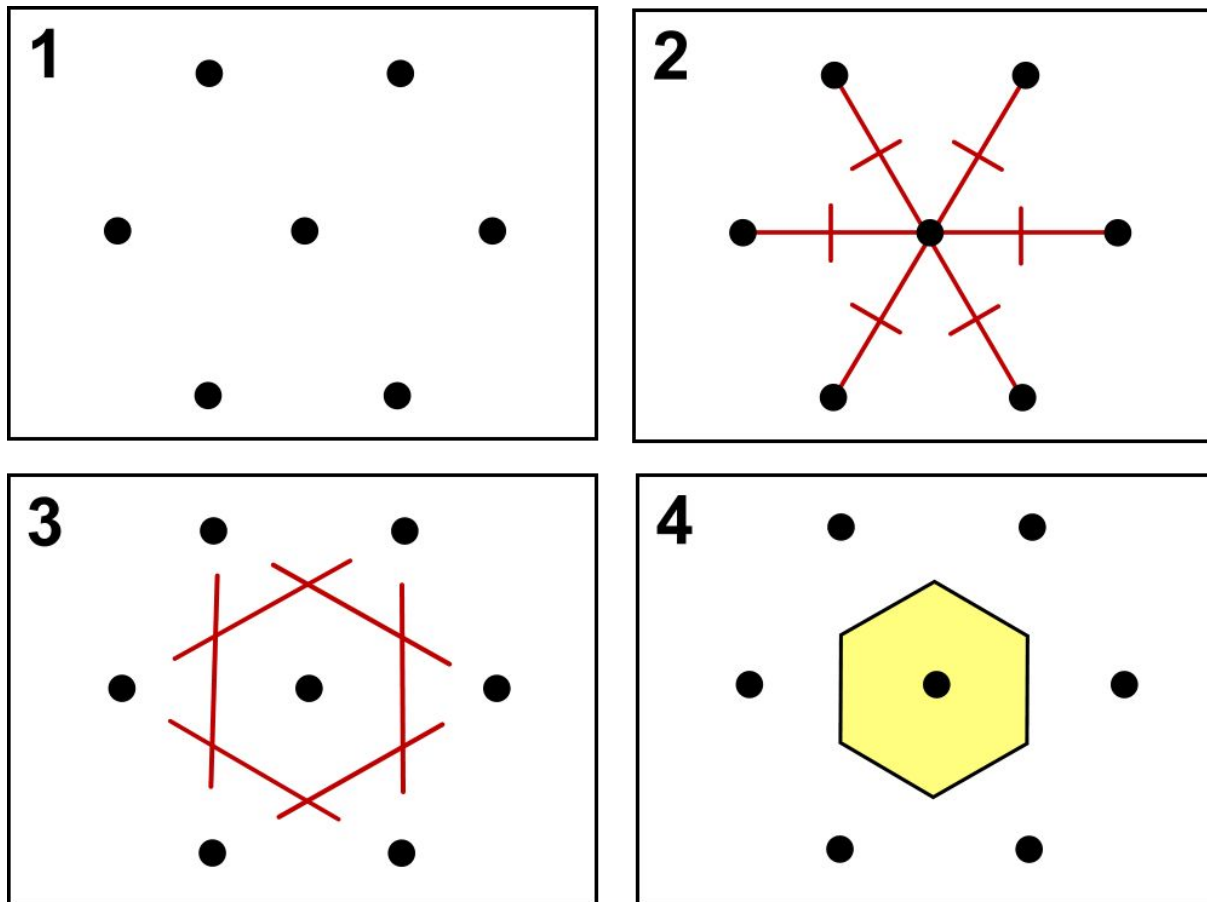
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

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

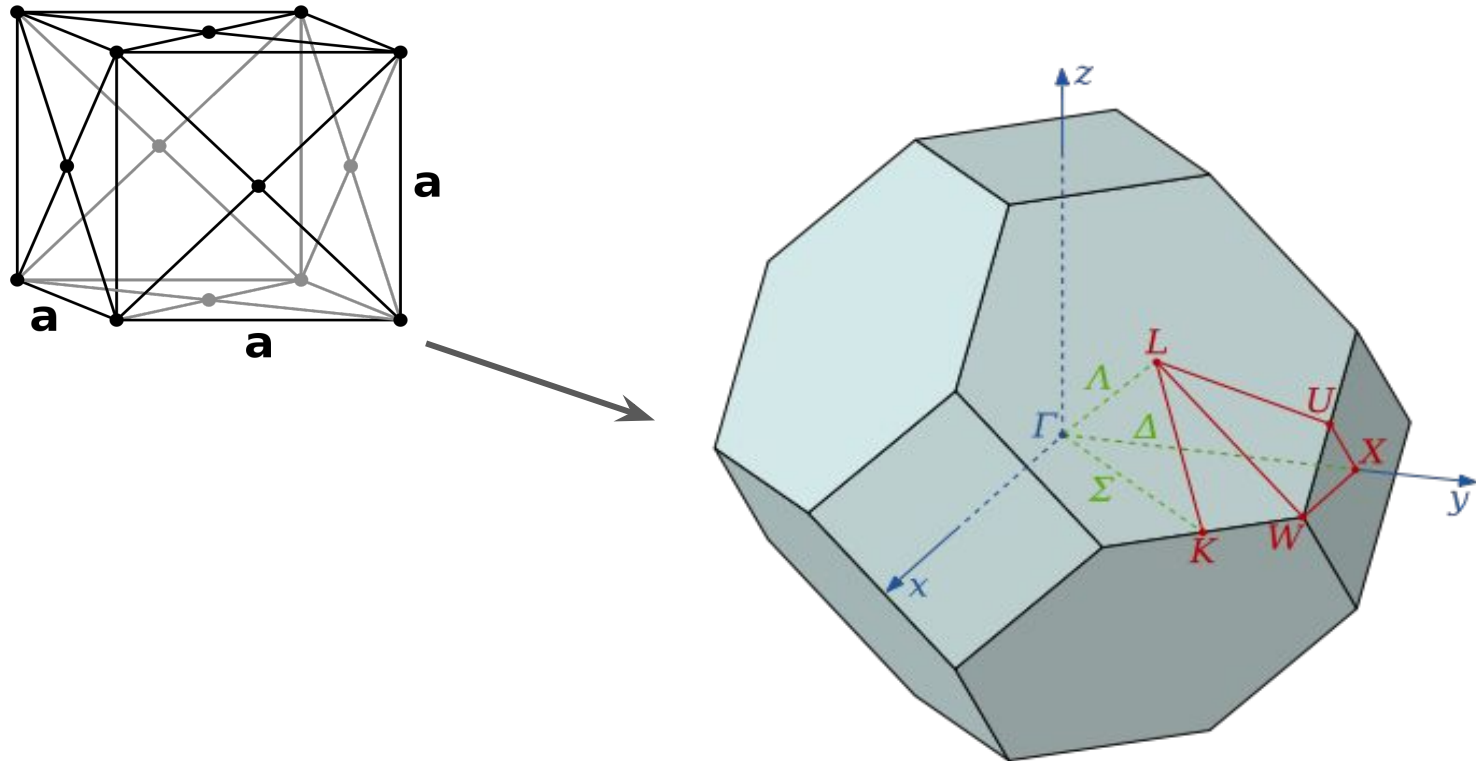


Brillouin zone and Wigner seitz cell

- 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



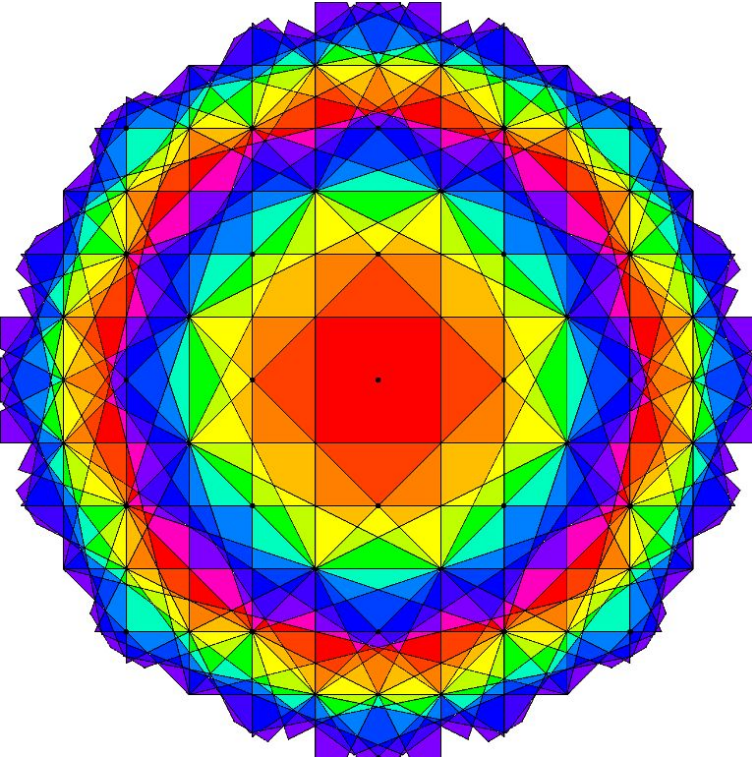
First BZ for FCC lattice



- The reciprocal lattice for FCC lattice is BCC
- 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)**

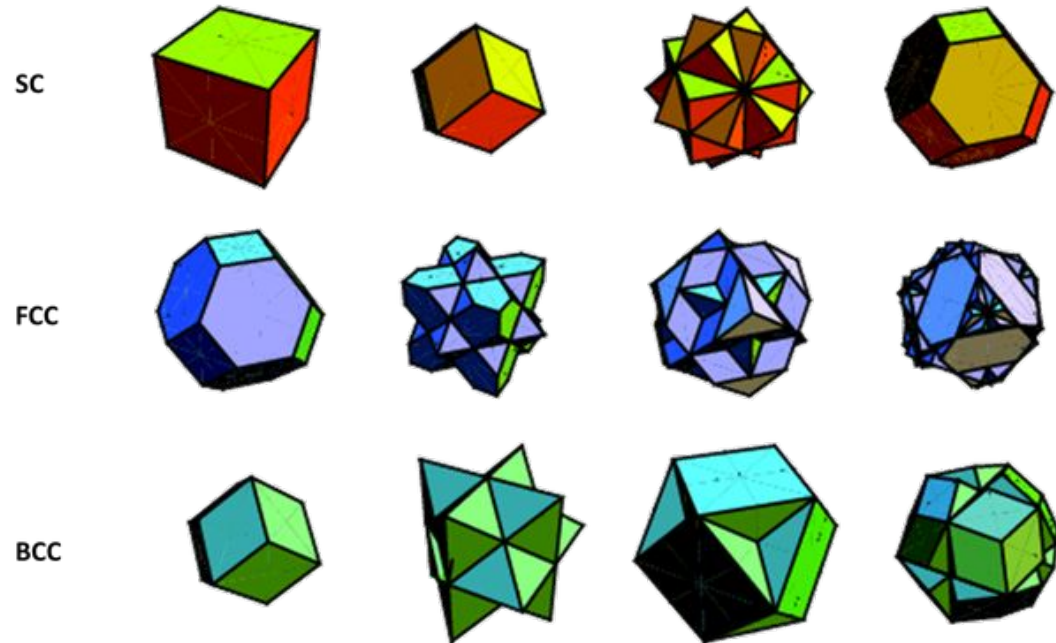
Understanding Brillouin zones

First 27 BZ for 2D square lattice



All BZ are of equal volume

First 4 BZ for 3D lattices:

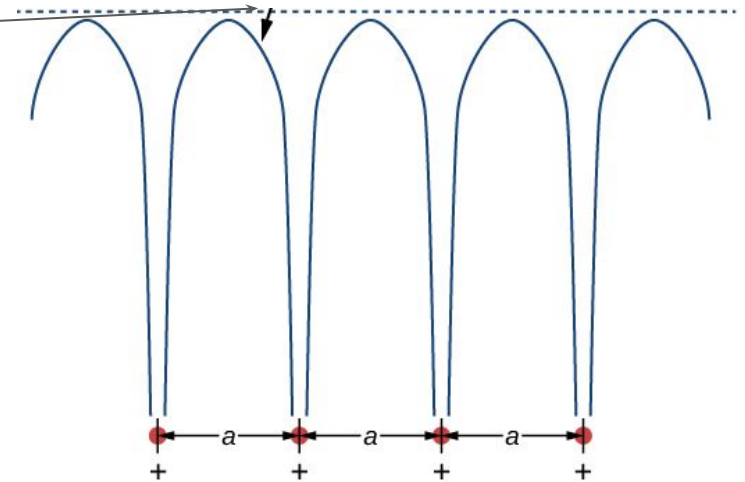


Electrons in periodic potential of ions

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

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

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:

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



Felix Bloch
Nobel prize in
1952

- \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 $\mathbf{k} = \mathbf{k} + \mathbf{G}$, where \mathbf{G} is translation vector

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

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

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

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

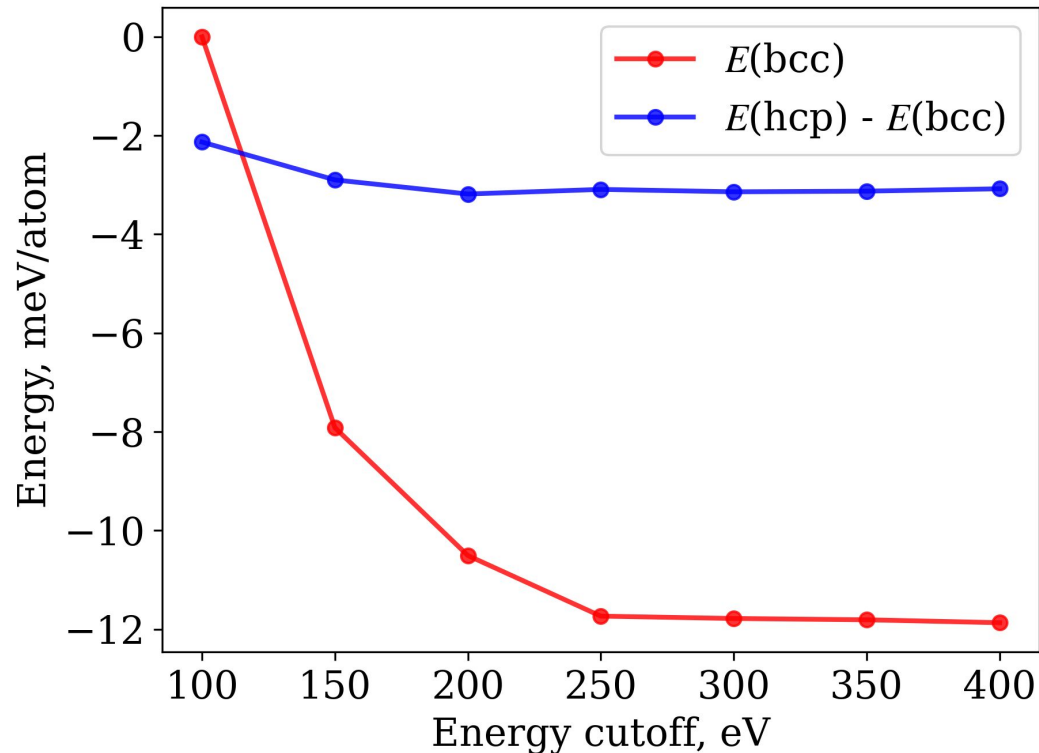
$$E = \frac{h^2}{2m} |\mathbf{k} + \mathbf{G}|^2. \quad E_{\text{cut}} = \frac{h^2}{2m} G_{\text{cut}}^2.$$

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

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!

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

Bloch theorem for Kohn-Sham equations

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

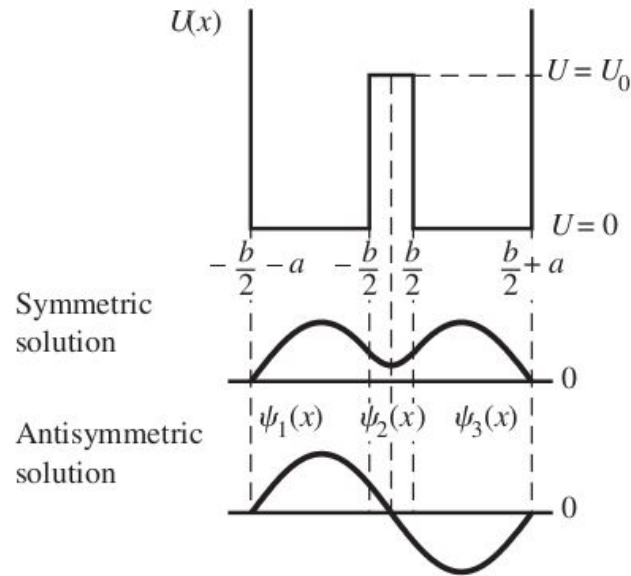
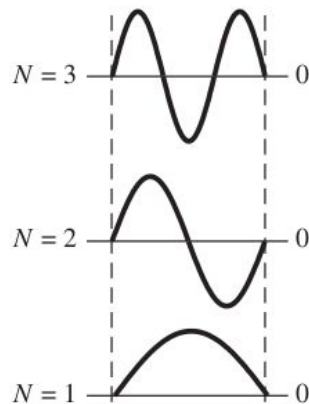
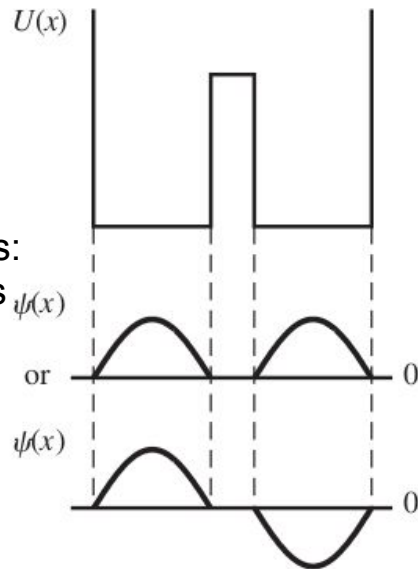
↓ Kohn-Sham equations can be solved separately for each point at k-space

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

- 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**

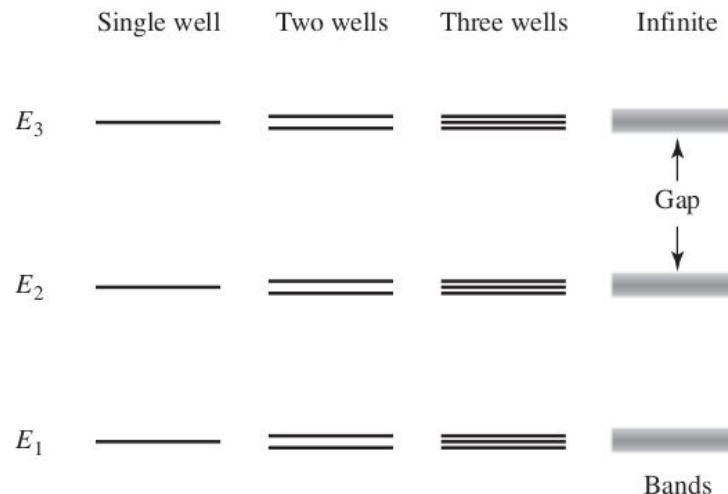
Simple picture for band formation in quantum wells (Kronig-Penney model)

Infinite barrier
between two wells:
degenerate states



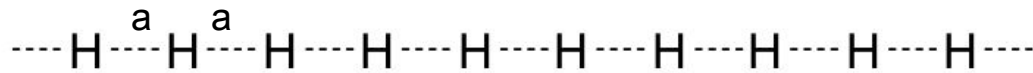
Finite barrier:
small splitting in
energy between
states due to
coupling

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



D. Snoke /Solid
state physics

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



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

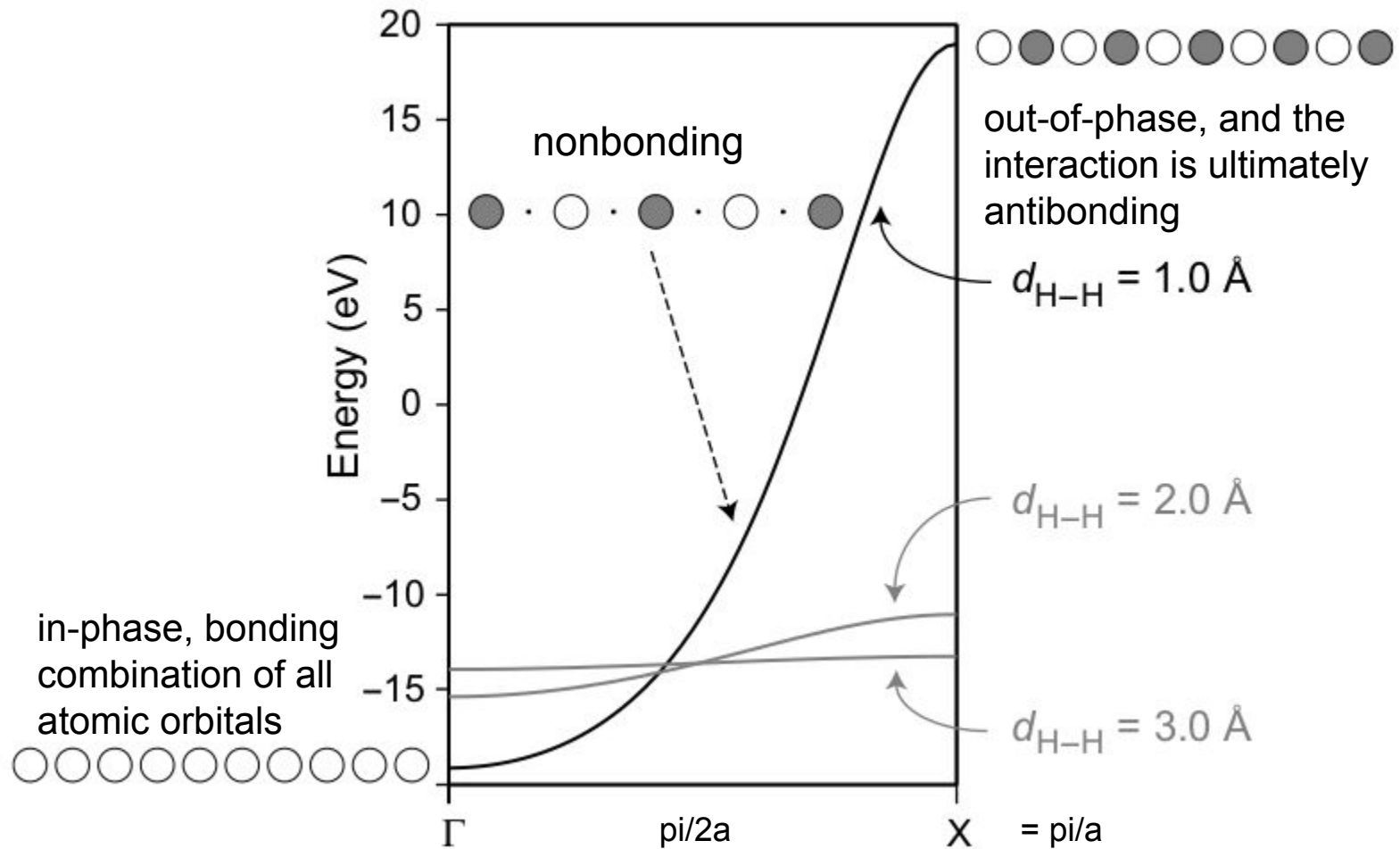
$$\psi(0) = \sum_{n=1}^N \phi_n = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 \dots, \quad \text{At } k = 0, \text{ also known as } \Gamma$$

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

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

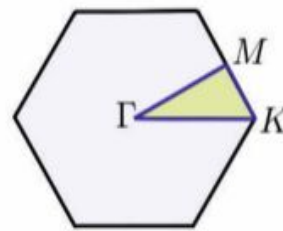
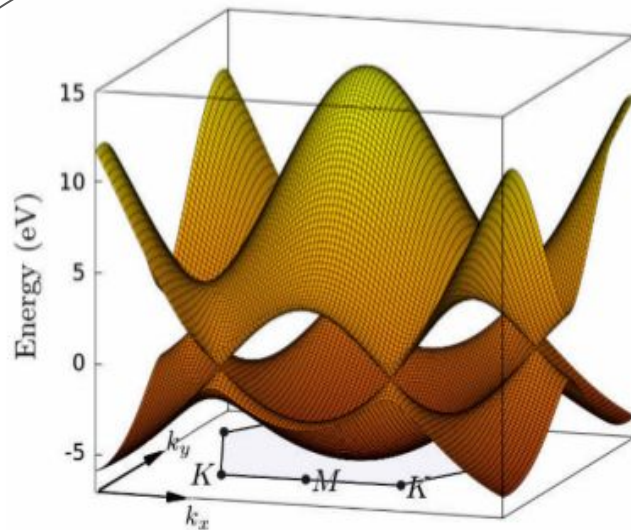


First Brillouin zone in 1D case

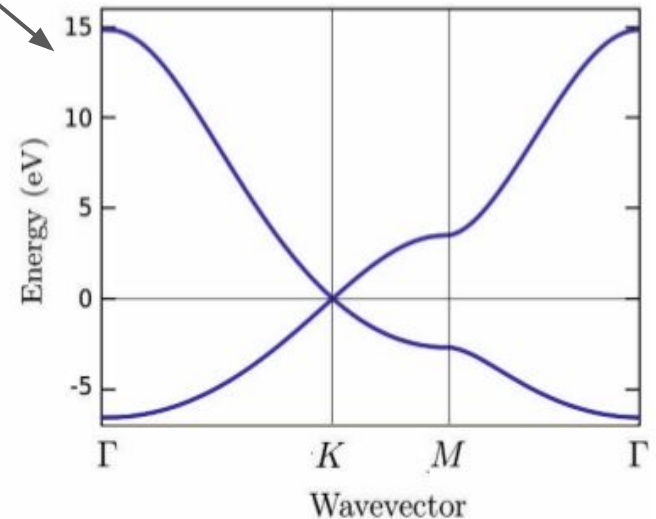
Dronskowski

Example of band structure for graphene

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



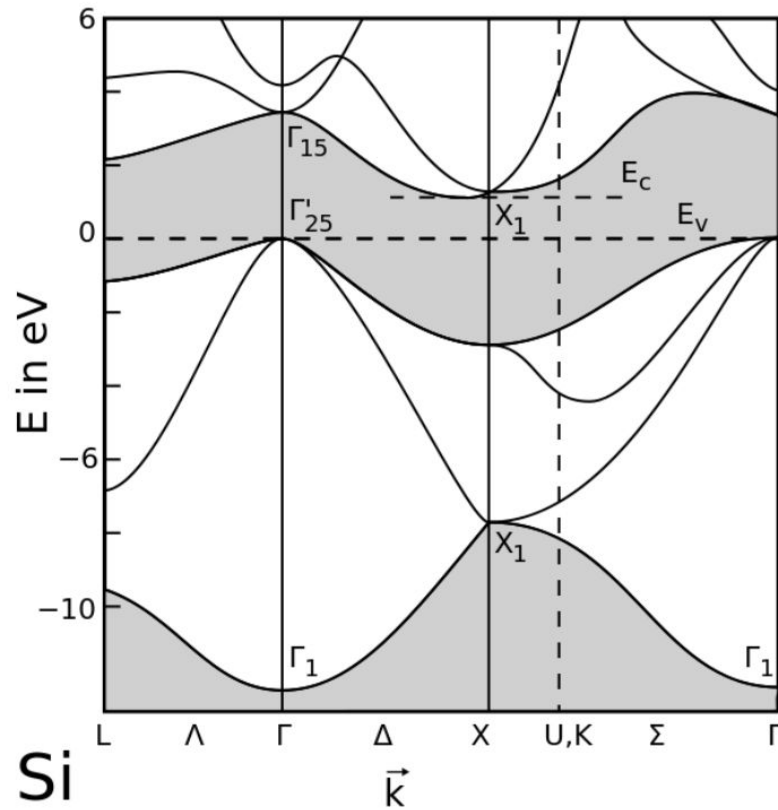
BZ and IBZ



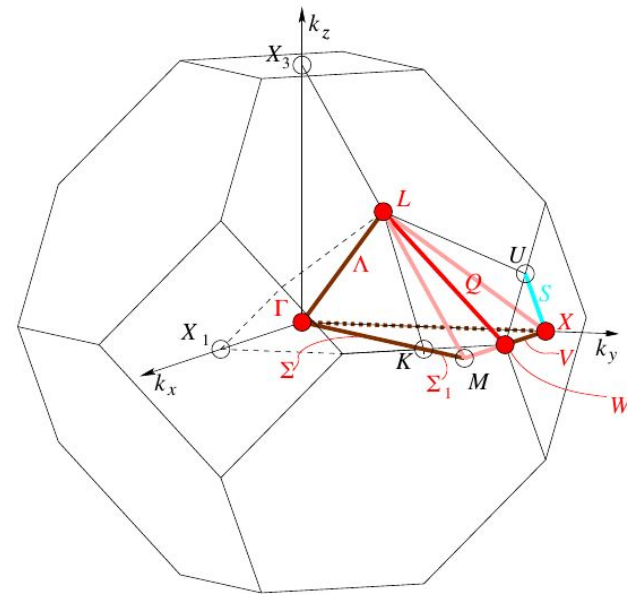
one-dimensional cross-sections is the most common way to visualize bands

Change of energy along high-symmetry direction

Example of band structure for silicon



Band structure of Si

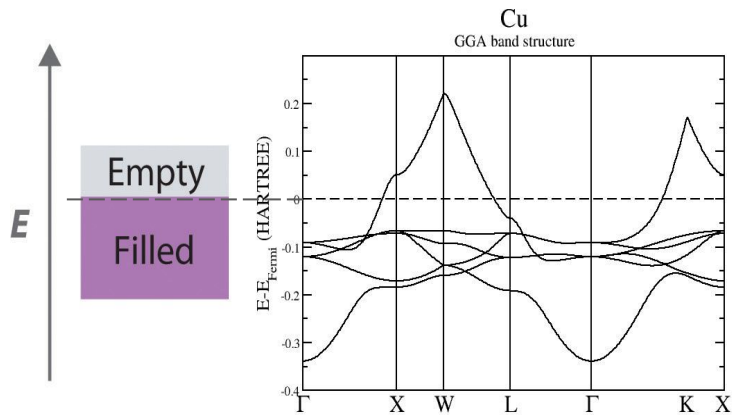


Brillouin zone for $Fm-3m$

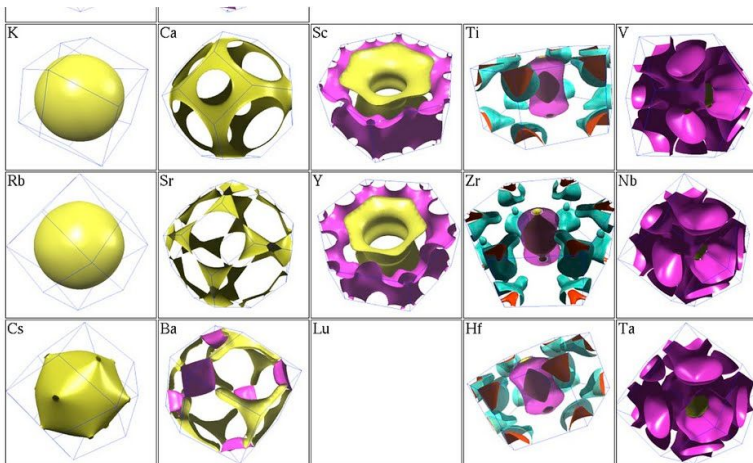
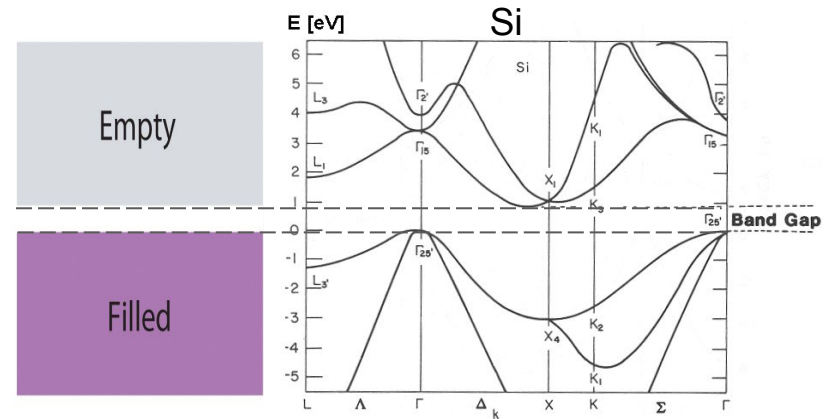
Ground state and Fermi surface

The ground state of N electrons is obtained by filling one-electron bands with energies $\varepsilon_n(\mathbf{k})$ 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



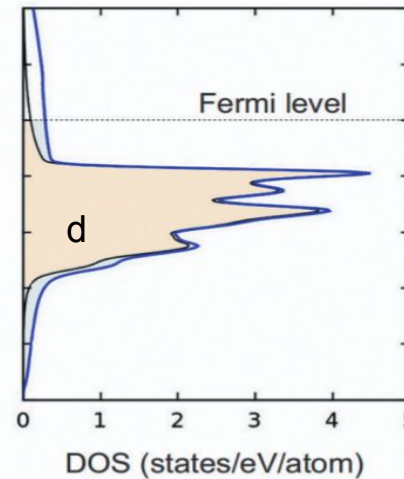
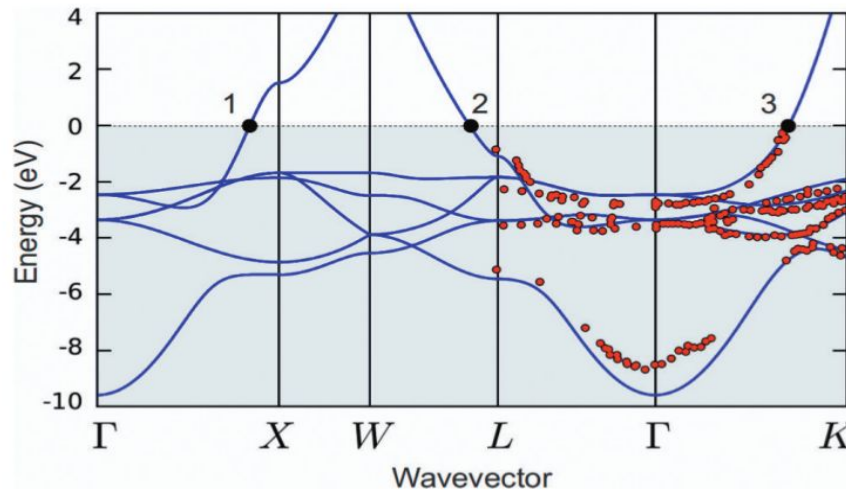
No Fermi surface for band gap materials! -> definition for metals

Density of states

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

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

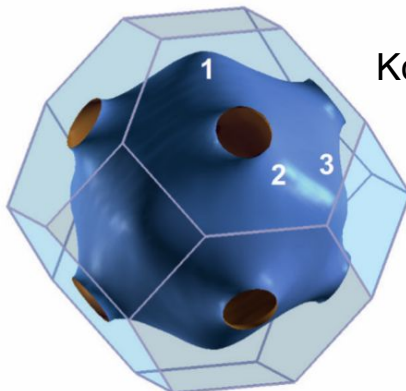
11 Kohn-Sham electrons



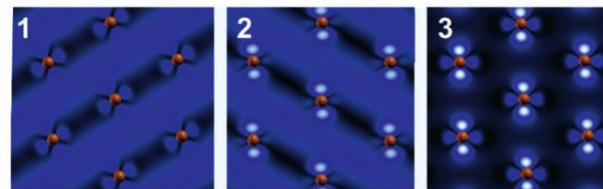
The parabolic behaviour in L- Γ -K region resembles free electron gas, however it is interrupted by spaghetti-like d states

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}

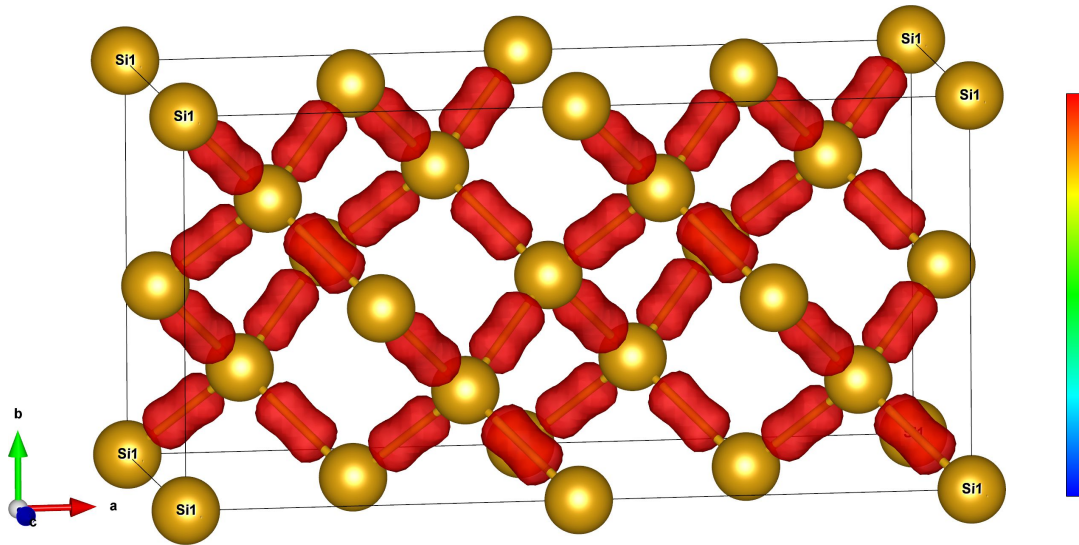
Significant differences between states across the Fermi surface.

from Giustino

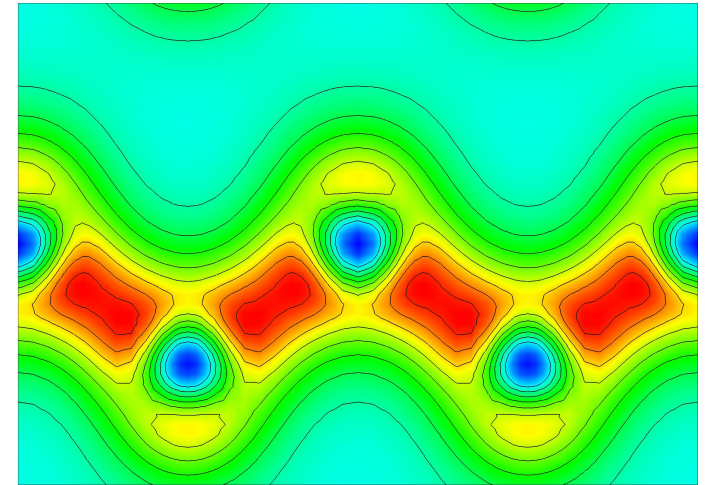
Charge density

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

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



Charge density for Silicon



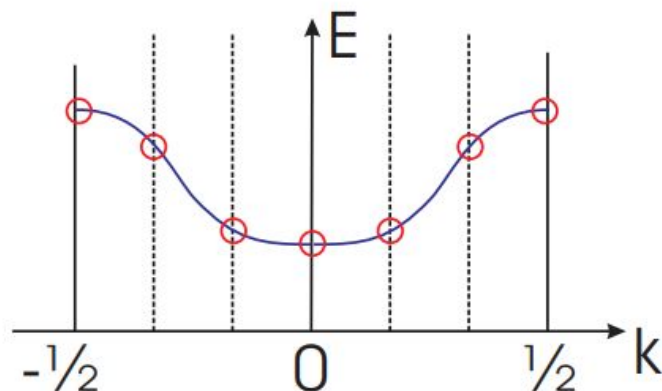
- Plot charge density difference for fixed atomic positions

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

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



- 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

Monkhorst-Pack - regular equispaced mesh

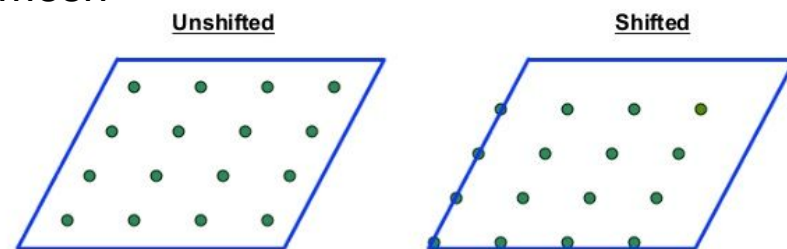


TABLE 3.1 Approximations to the Integral $\int_{-1}^1 \frac{\pi x}{2} \sin(\pi x) dx = 1$ Using the Trapezoidal and Legendre Quadrature Methods

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

Sholl p.54

Choosing k-points mesh

How to choose N_1, N_2, N_3 ?

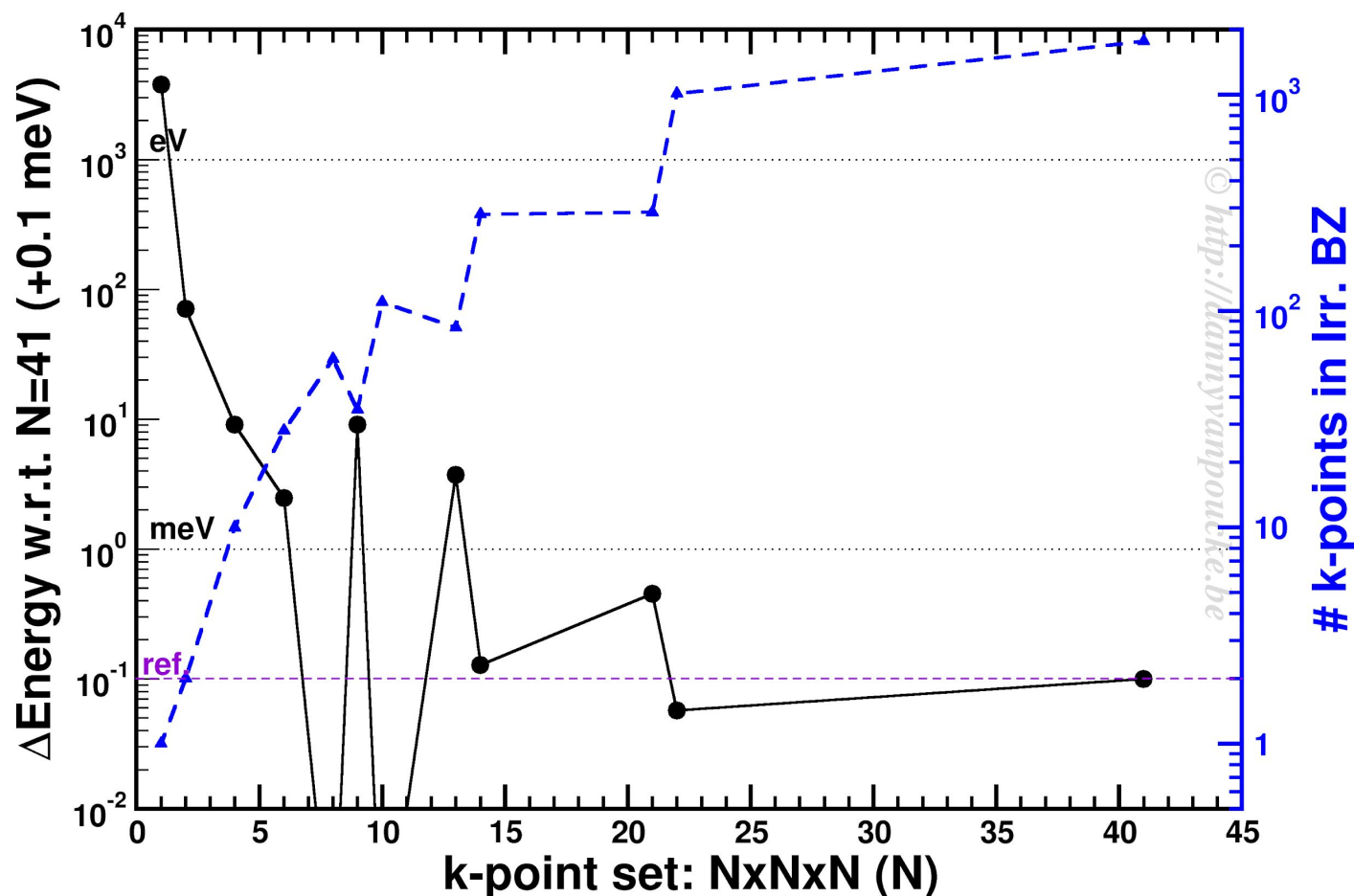
Commonly the following rule of thumb applies:

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

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 \AA^{-1} !
 - k-spacing 0.5 \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/>

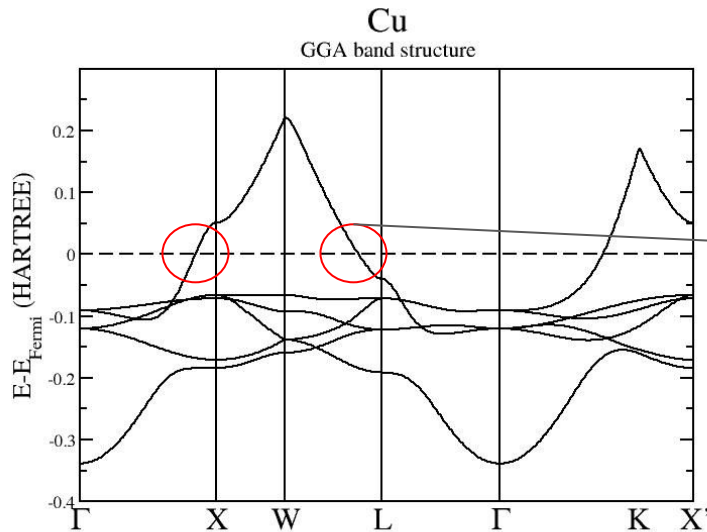
Smearing at Fermi level

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

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

Q?

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



Sholl, p. 60

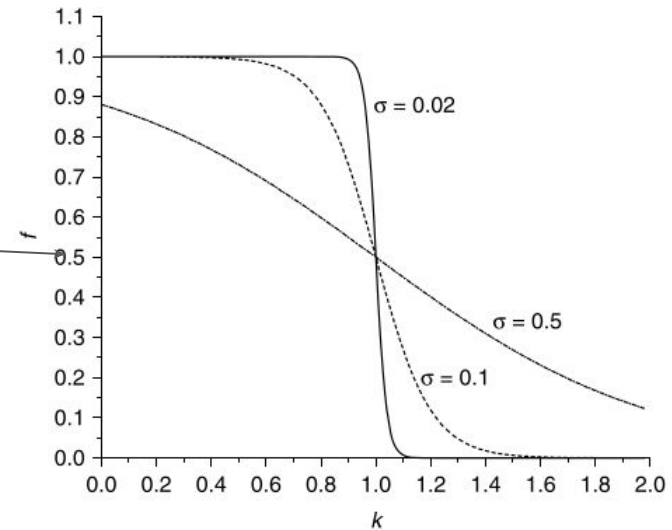


Figure 3.3 Fermi Dirac function [Eq. (3.10)] with $k_0 = 1$ and several values of σ .

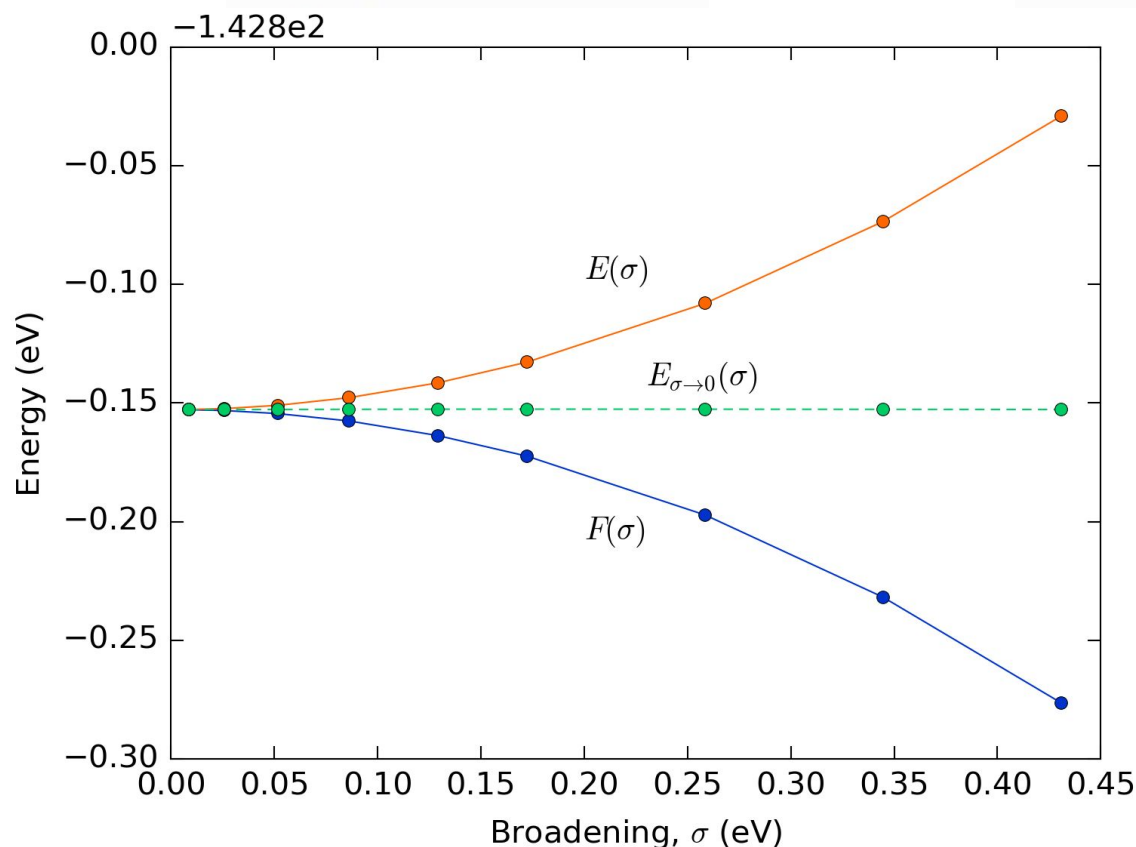
- Smearing is needed to make function continuous, [ISMEAR](#)
- In VASP: **ISMEAR** - chose method for smearing, [SIGMA](#) - the value of smearing
- Check smearing parameter!
- More k-points for metals, density $< 0.15 \text{ \AA}^{-1}$ (**KSPACING**)

(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->0)**
- Do not mix with thermodynamic free energy

Convergence with respect to k-points and smearing

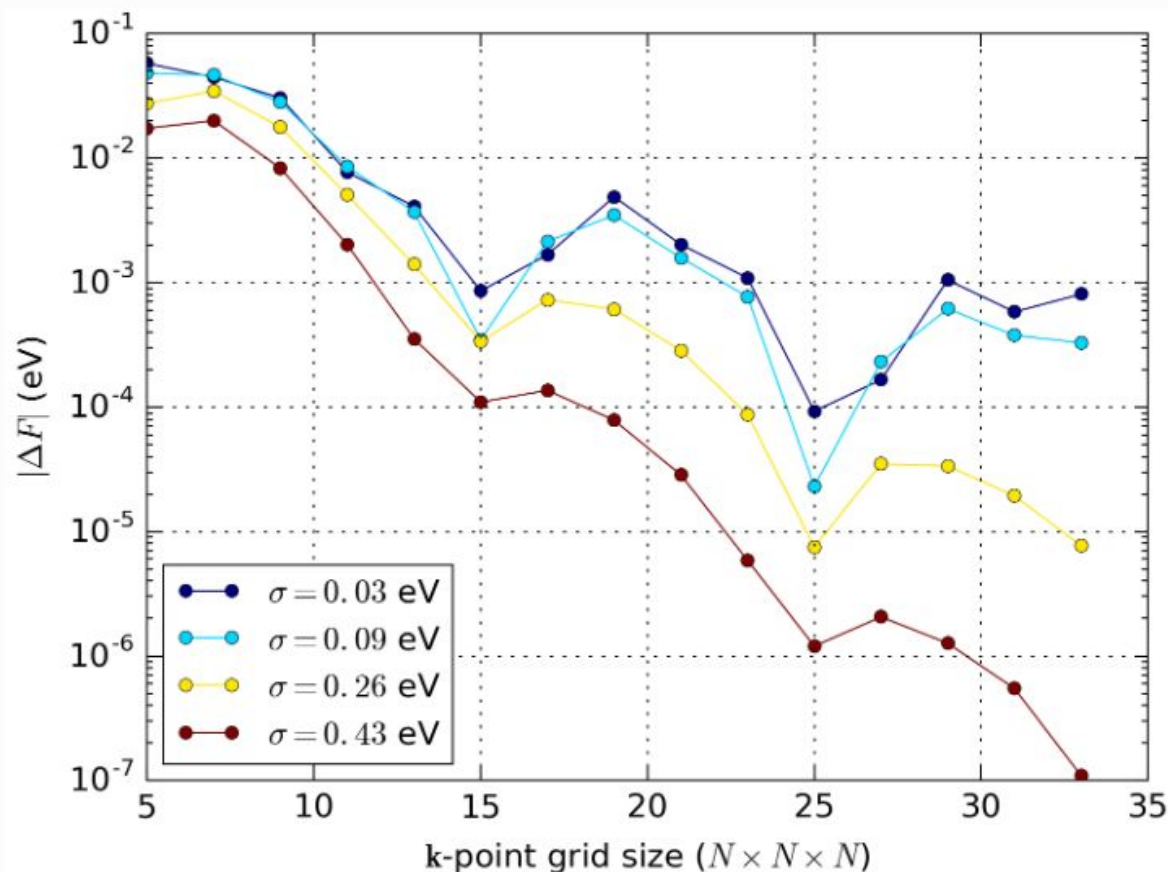


Fig. 105 Convergence of the free energy of bulk Aluminum with respect to the k-point sampling using the *Fermi-Dirac* occupation function with different broadenings. The free energy difference, ΔF , is calculated as the difference between the calculation at the given \mathbf{k} -point sampling and one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

https://docs.quantumatk.com/manual/technicalnotes/occupation_methods/occupation_methods.html

Smearing methods

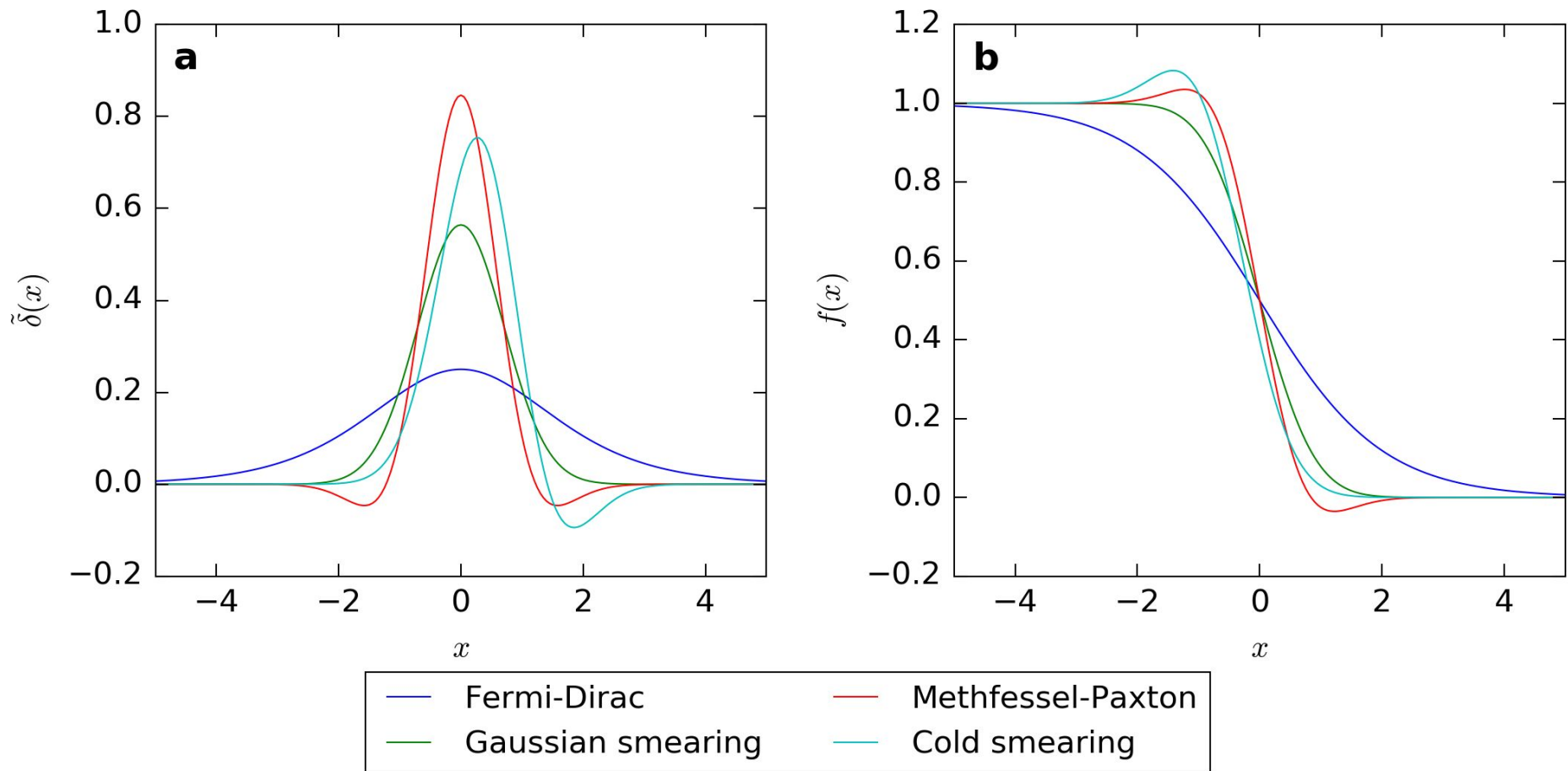
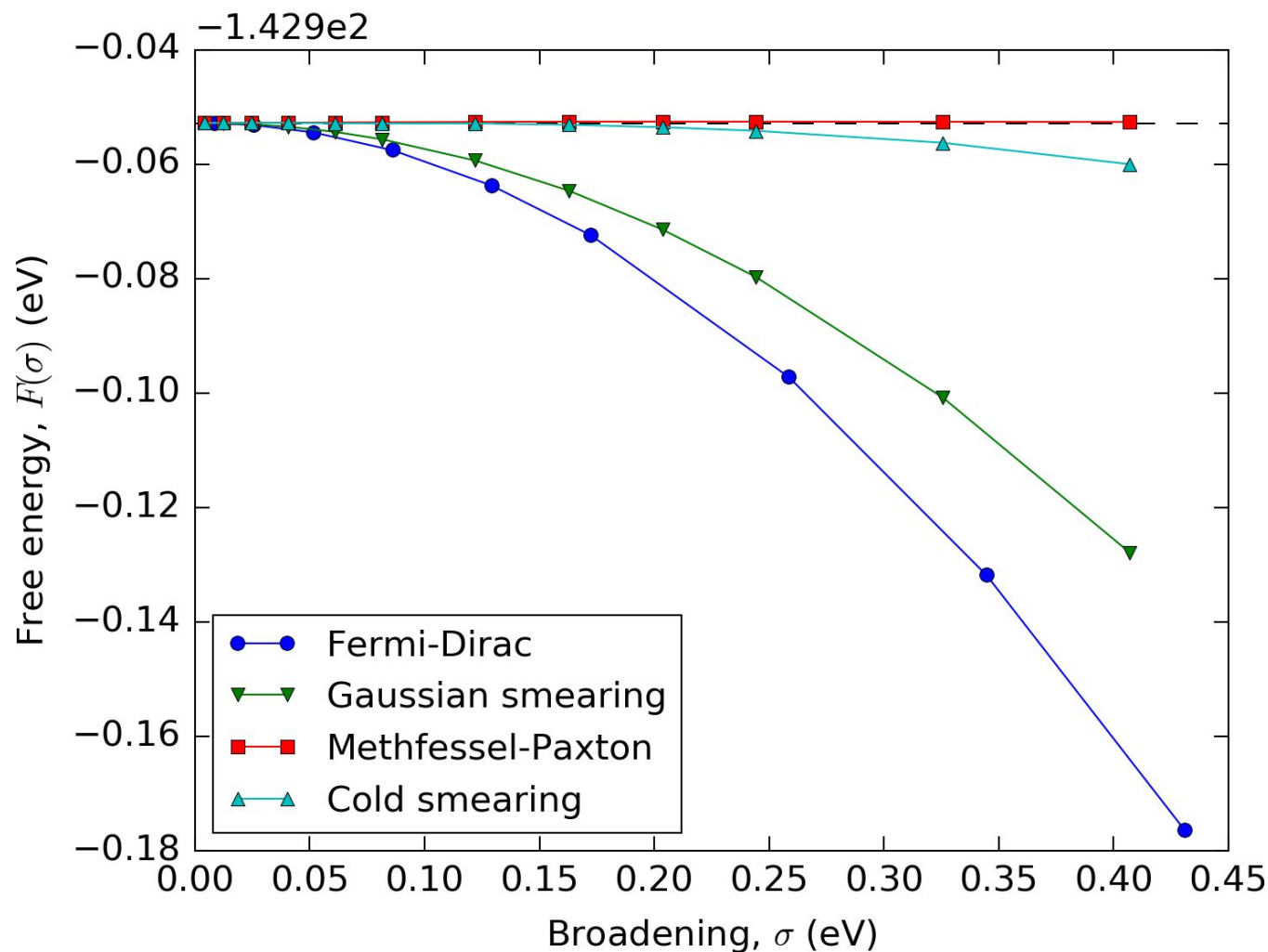
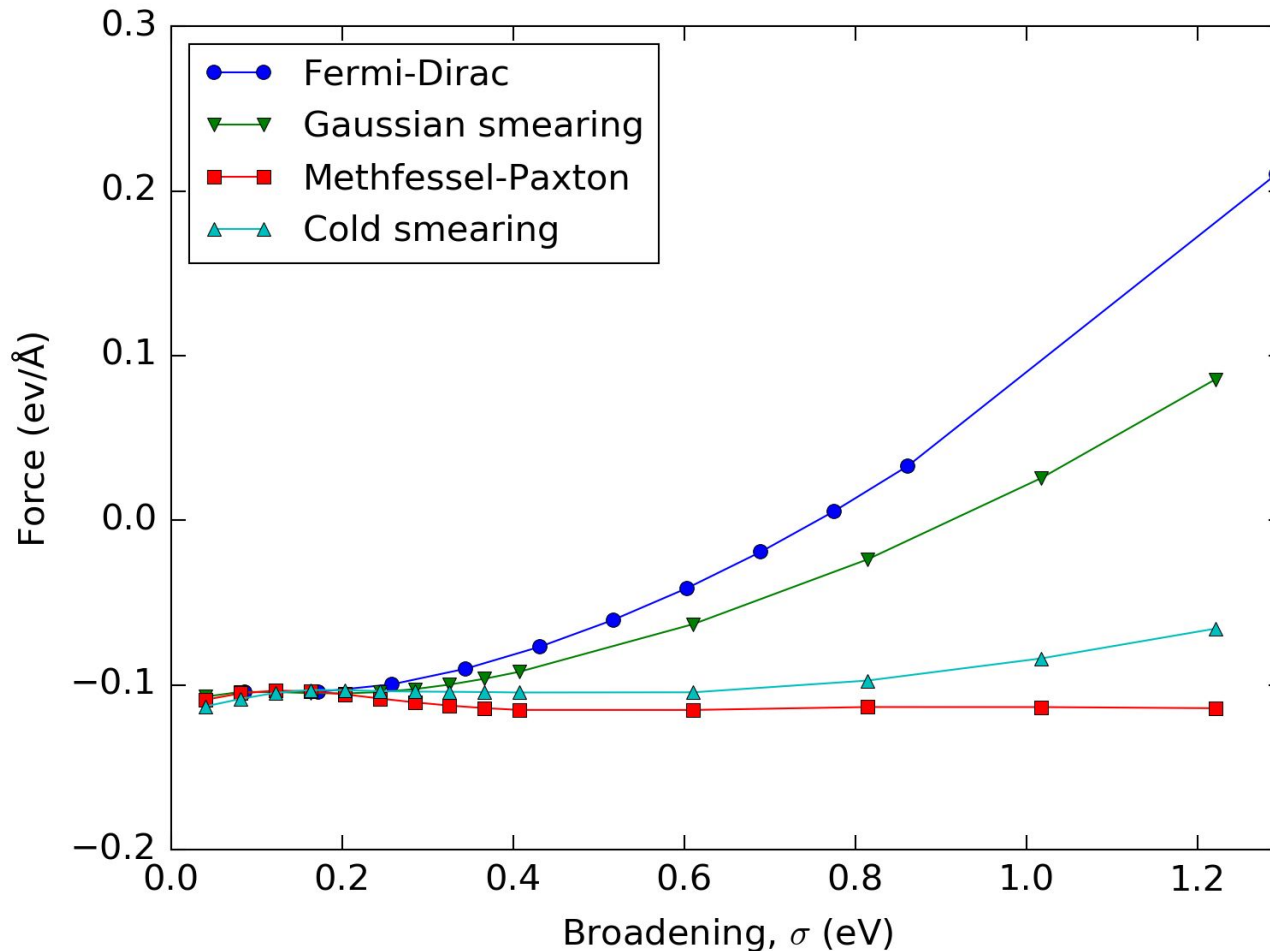


Fig. 107 (a) Plots of the different smeared delta functions, $\tilde{\delta}(x)$, and (b) their corresponding occupation functions $f(x)$, shown as functions of $x = \frac{\epsilon - \mu}{\sigma}$.

Energy error for different smearing methods



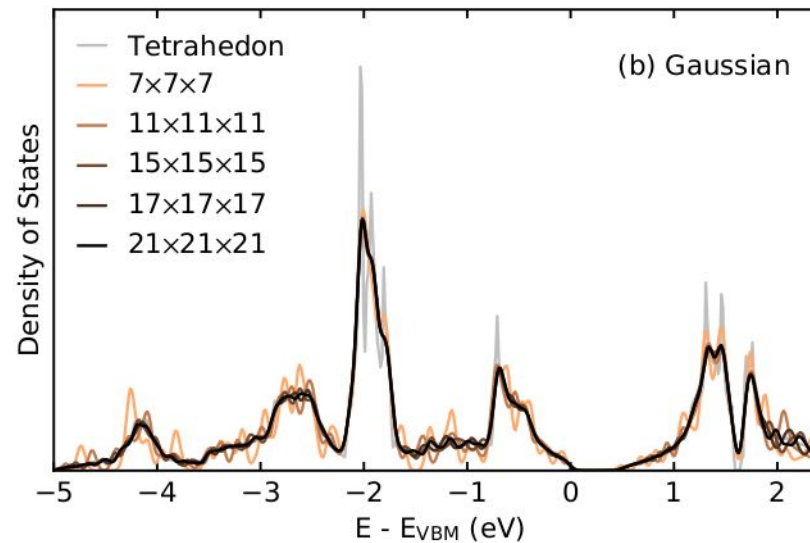
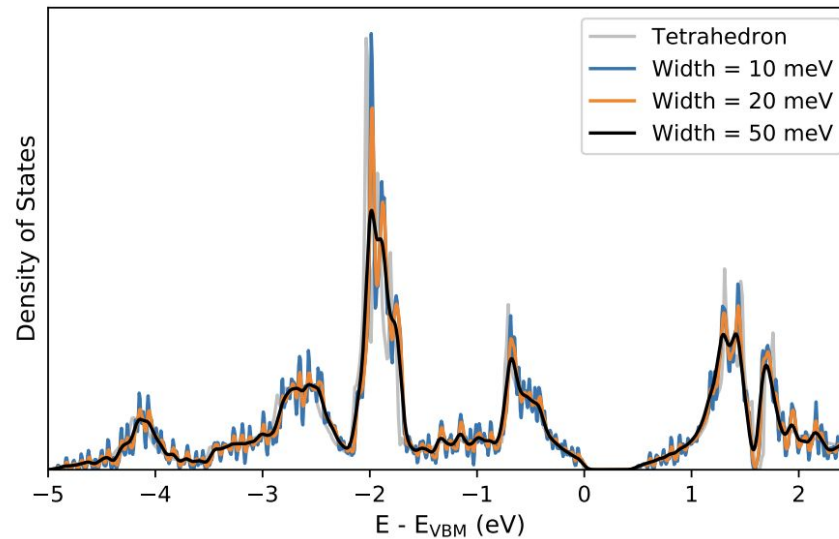
Force error for different smearing methods



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.

Smearing of DOS

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



SIGMA=50 meV

Advices on choosing k-grid and smearing

K-grids

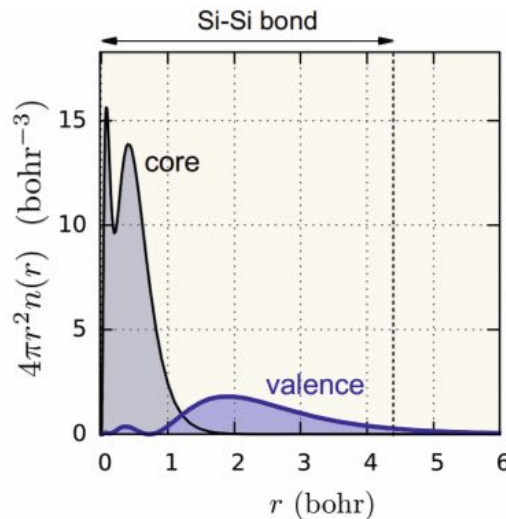
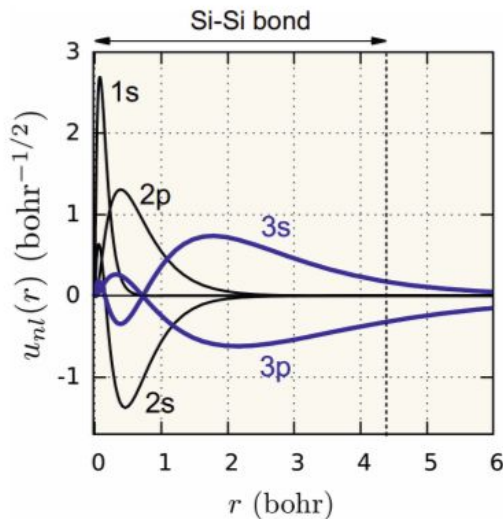
- Use equally spaced grids of points, a shift can reduce number of k-points
- Try Gamma-centered k-grid if you have problem with off-center Monkhorst-Pack
- Use fine grid for DOS
- Use equivalent k-points meshes when comparing different cells

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>)

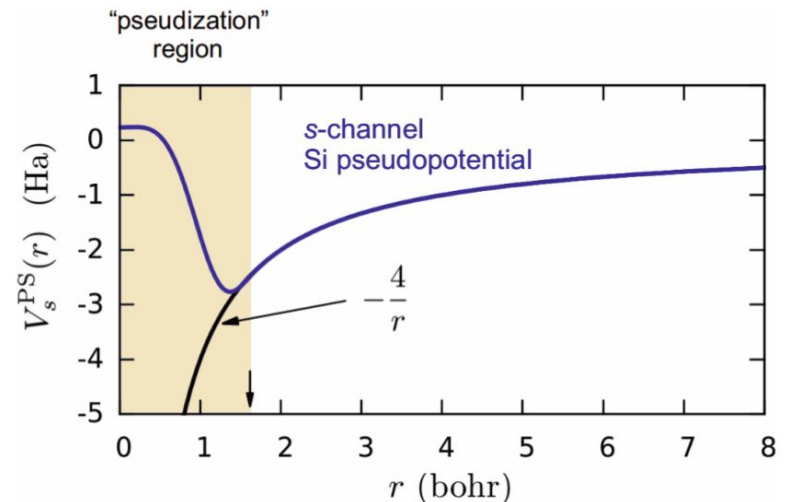
Plane-waves for valence and core electrons

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**



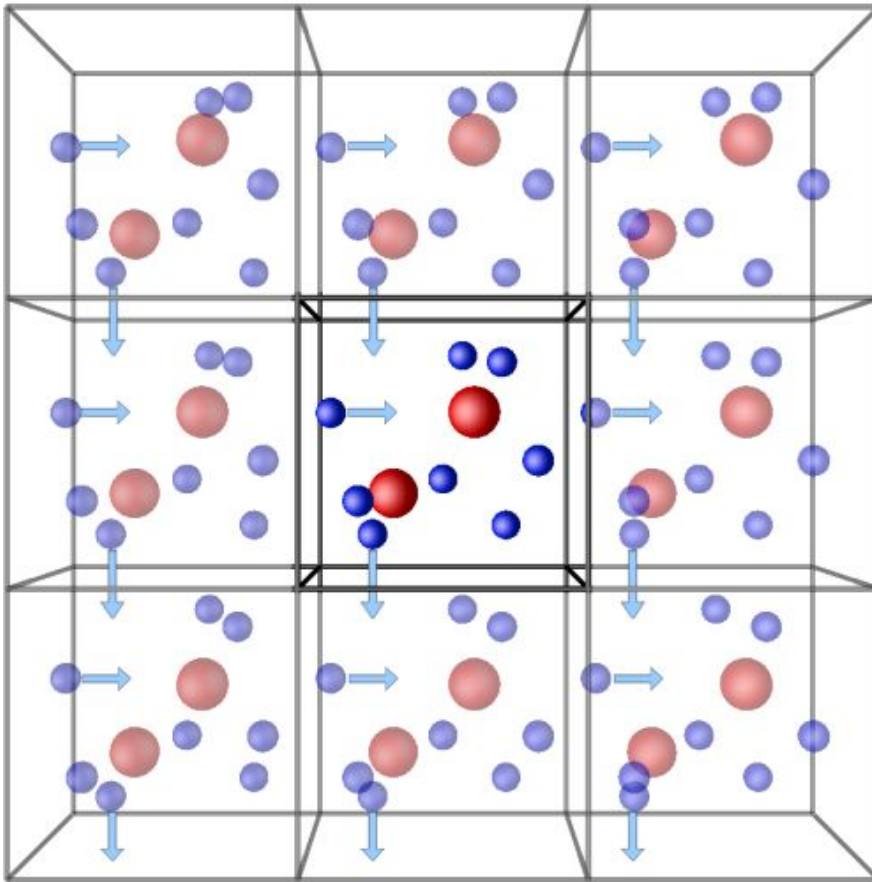
Pseudopotential in DFT codes

- 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, norm-conserving
- 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



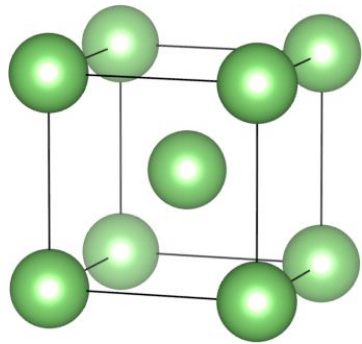
Periodic boundary conditions (PBC) -

- 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

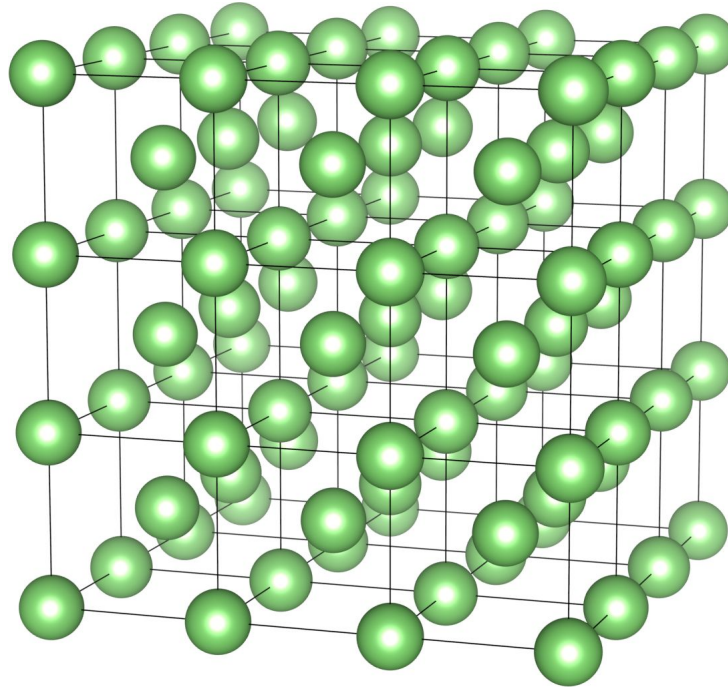
Keep in mind!

- 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

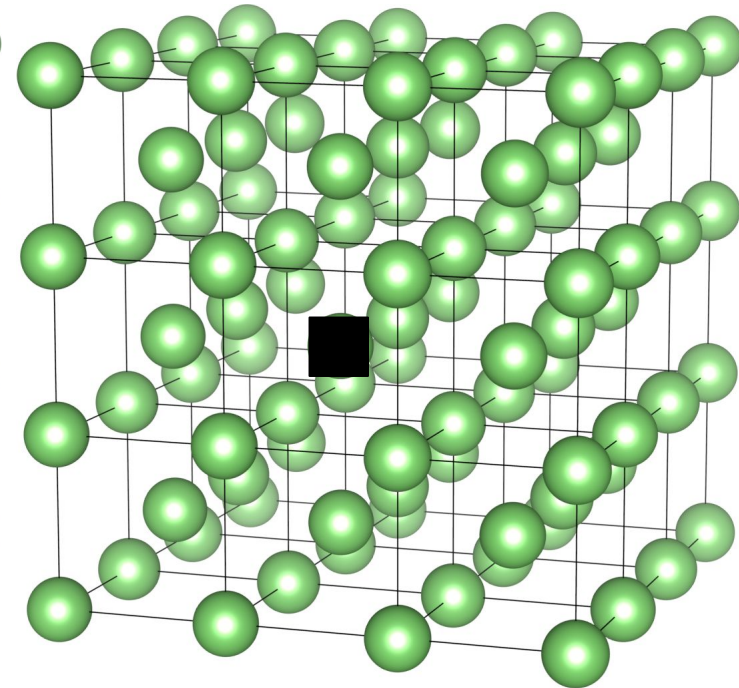
Supercell approach for non-periodicity



1. Take Unit cell



2. Create a supercell

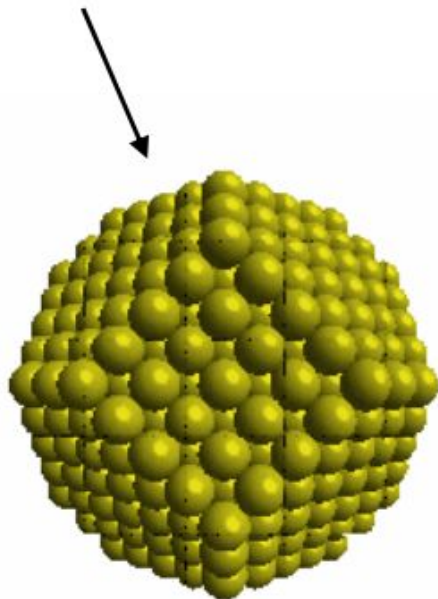


3. Make a displacement of defect

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

Free boundary conditions

Free cluster



No translation symmetry!

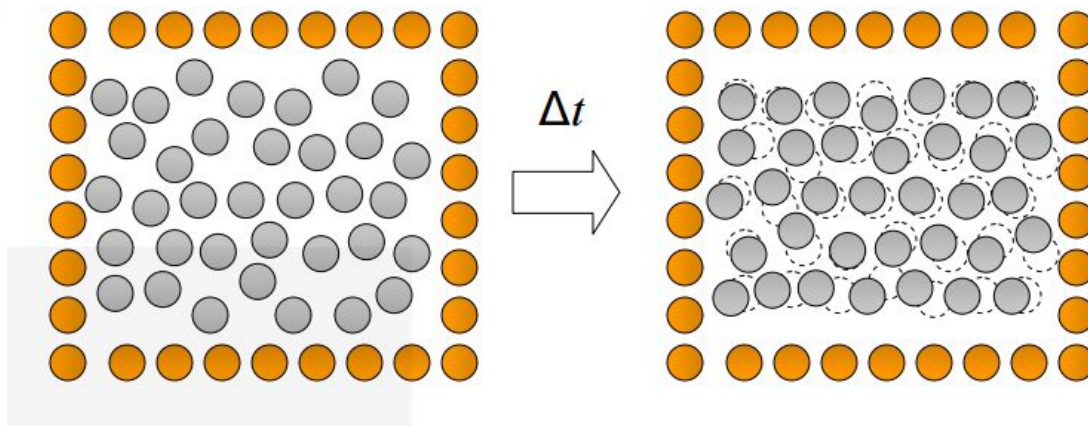
Cons:

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

Therefore:

For molecules, clusters, disordered solids in classical MD simulations

Rigid shell, still
unphysical, but better than
open



Optimization of atoms in periodic systems

Similar to molecular, see previous lecture

In VASP important parameters:

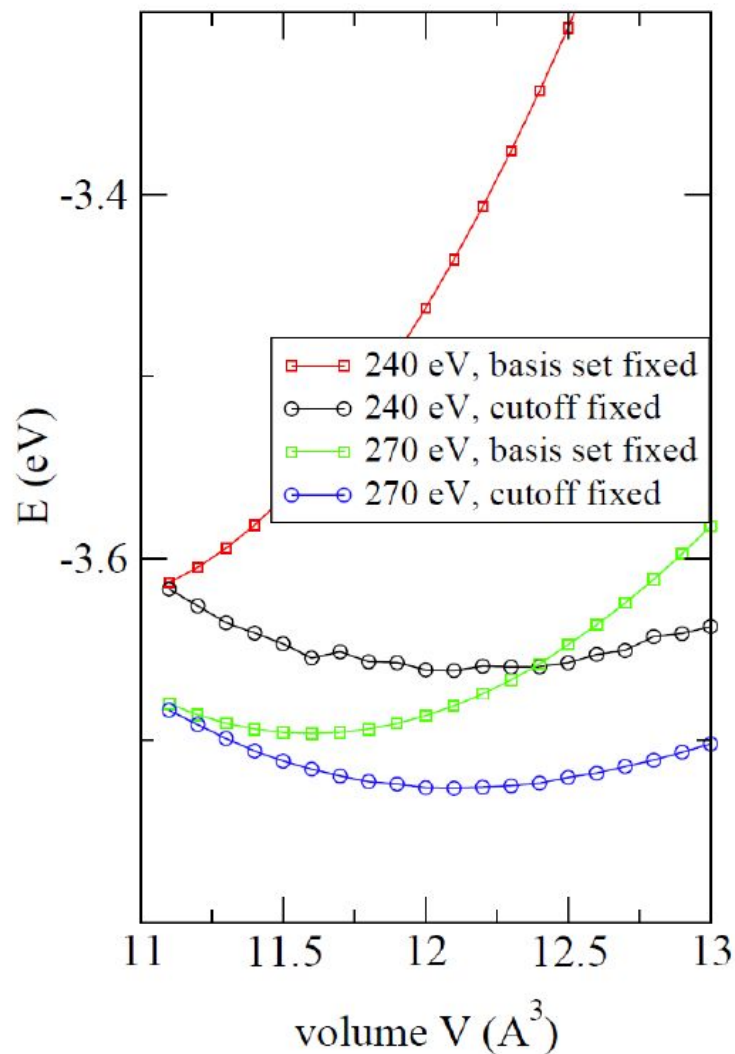
- IBRION - type of optimisation
 - 0 - molecular dynamics
 - 1 - quasi-Newton
 - 2 - Conjugate gradient
 - 3 - Damped MD
 - etc
- NSW - number of steps
- POTIM - step in MD, fs

Unit cell optimization

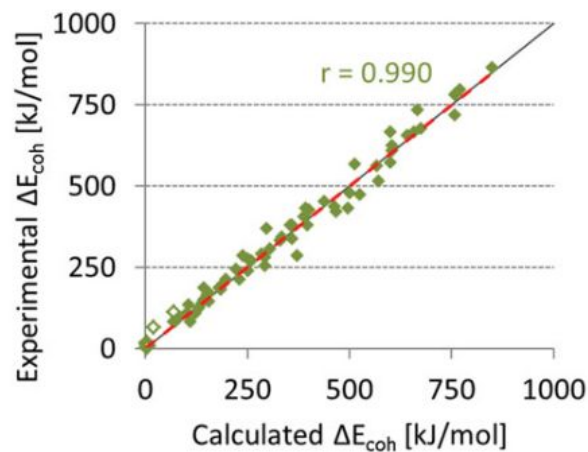
- Pulay stress: increase plane wave cutoff or do volume scan
- Use the same plane wave cutoff for different volumes
- Use consistent k-grids for different volumes

In VASP [ISIF](#) :

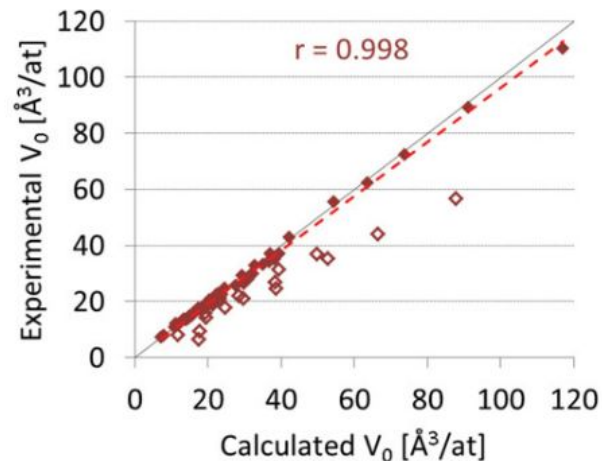
- 2 - only atoms
- 4 - shape
- 3 - shape and volume



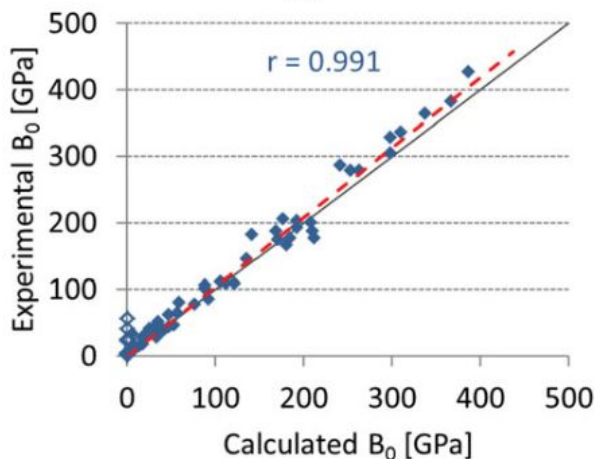
Accuracy: geometry and elastic (PBE/PW91)



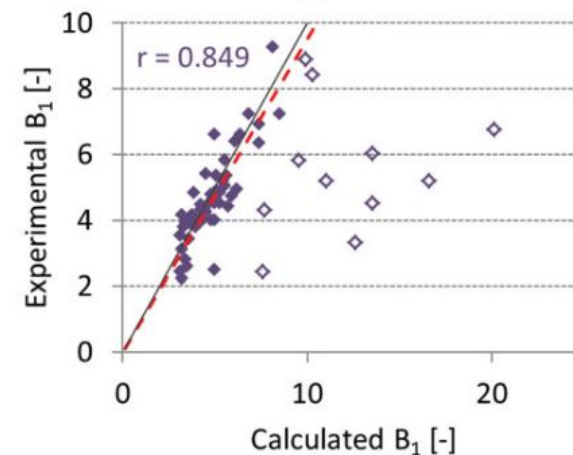
(a)



(b)



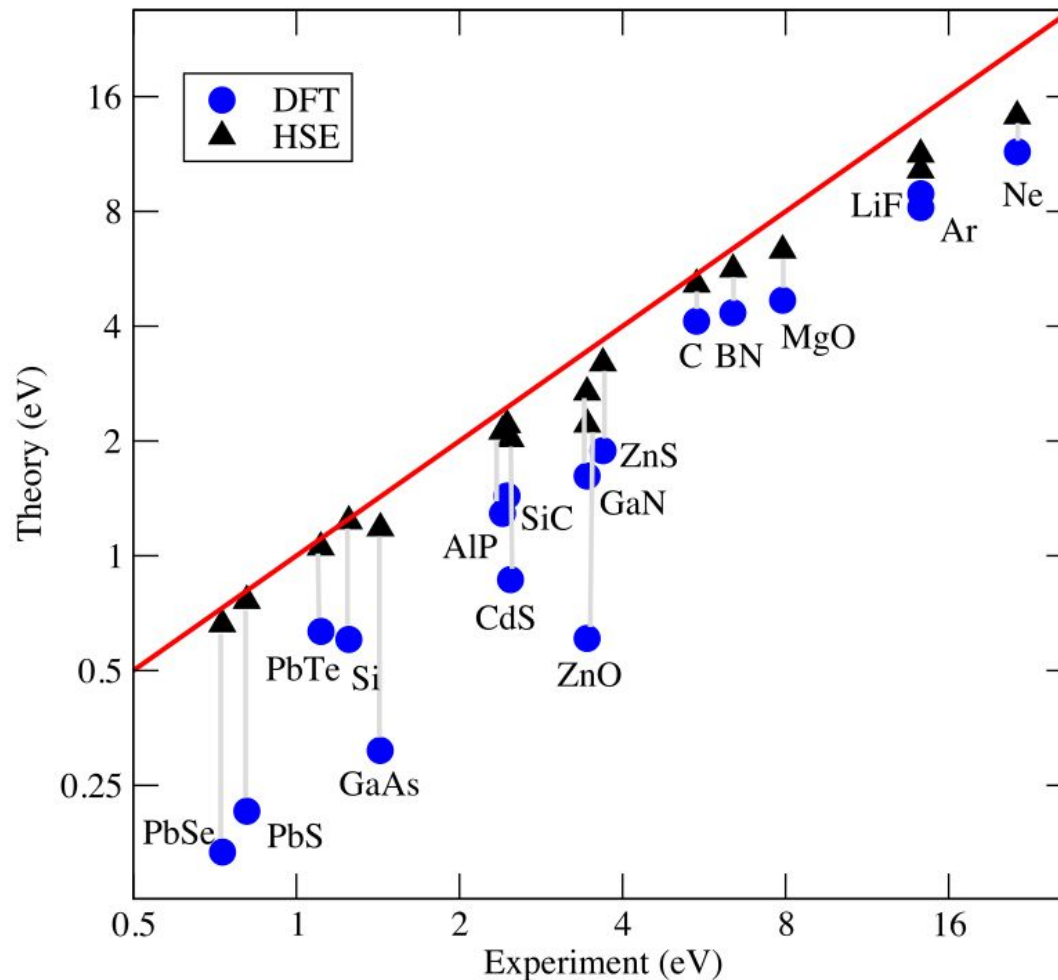
(c)



(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; open symbols are excluded from the fit, see details in article

Accuracy: band gap



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

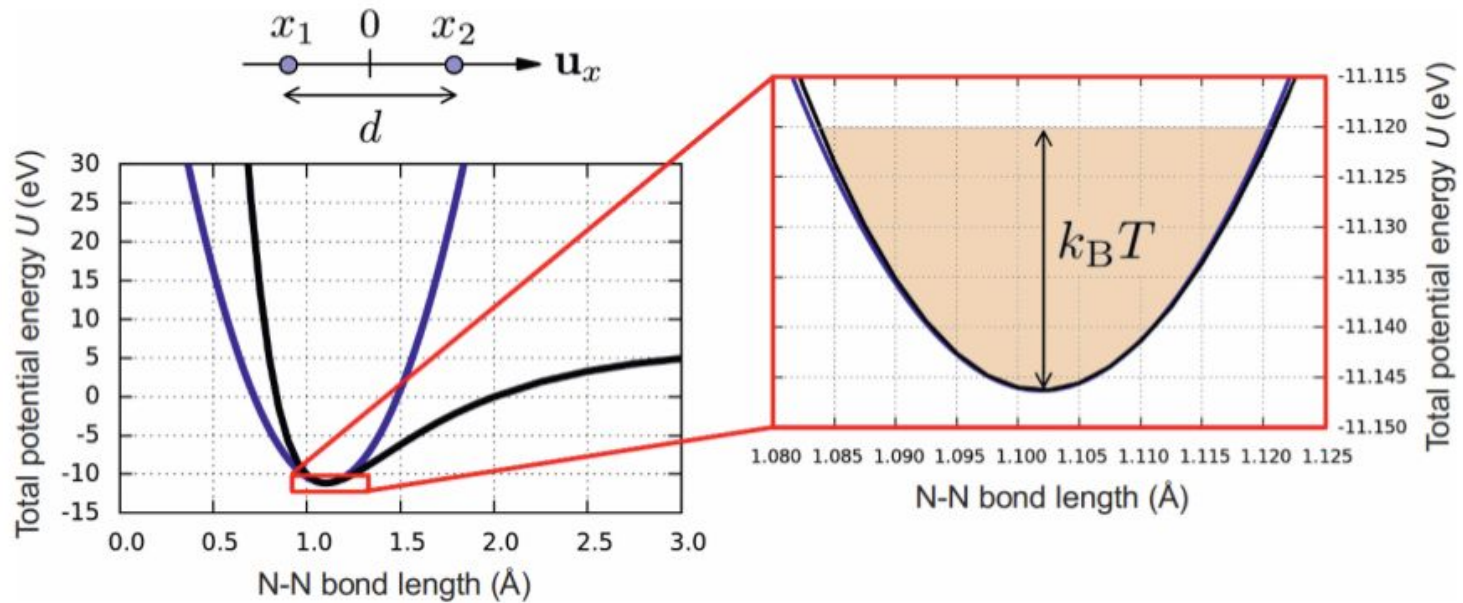
Other things to keep in mind

- Kohn-Sham orbitals are supposed to give one-electron orbitals and approximation to elementary excitations
- 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 **k**-grid along the reduced dimension

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

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

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

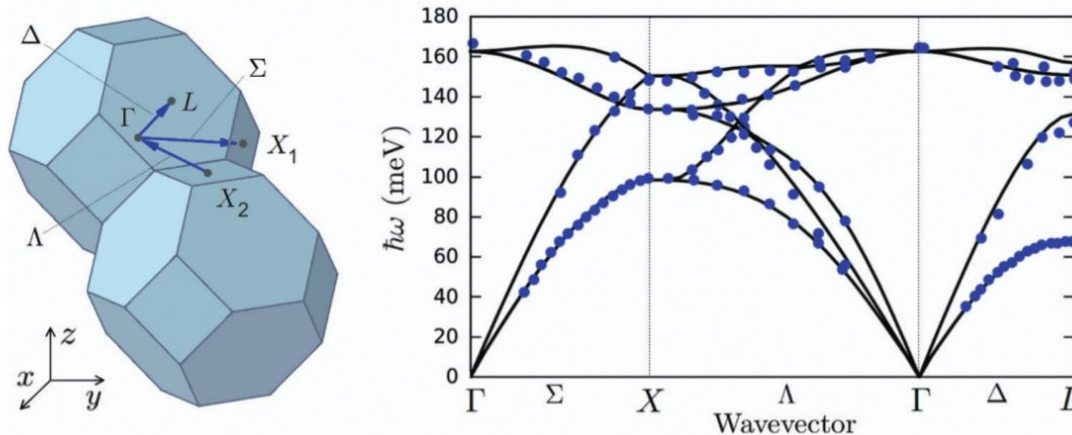
The eigenvalues of mass-weighted Hessian are called normal modes and have frequency ω , $3N$ in total, where N is number of atoms

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

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

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

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

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

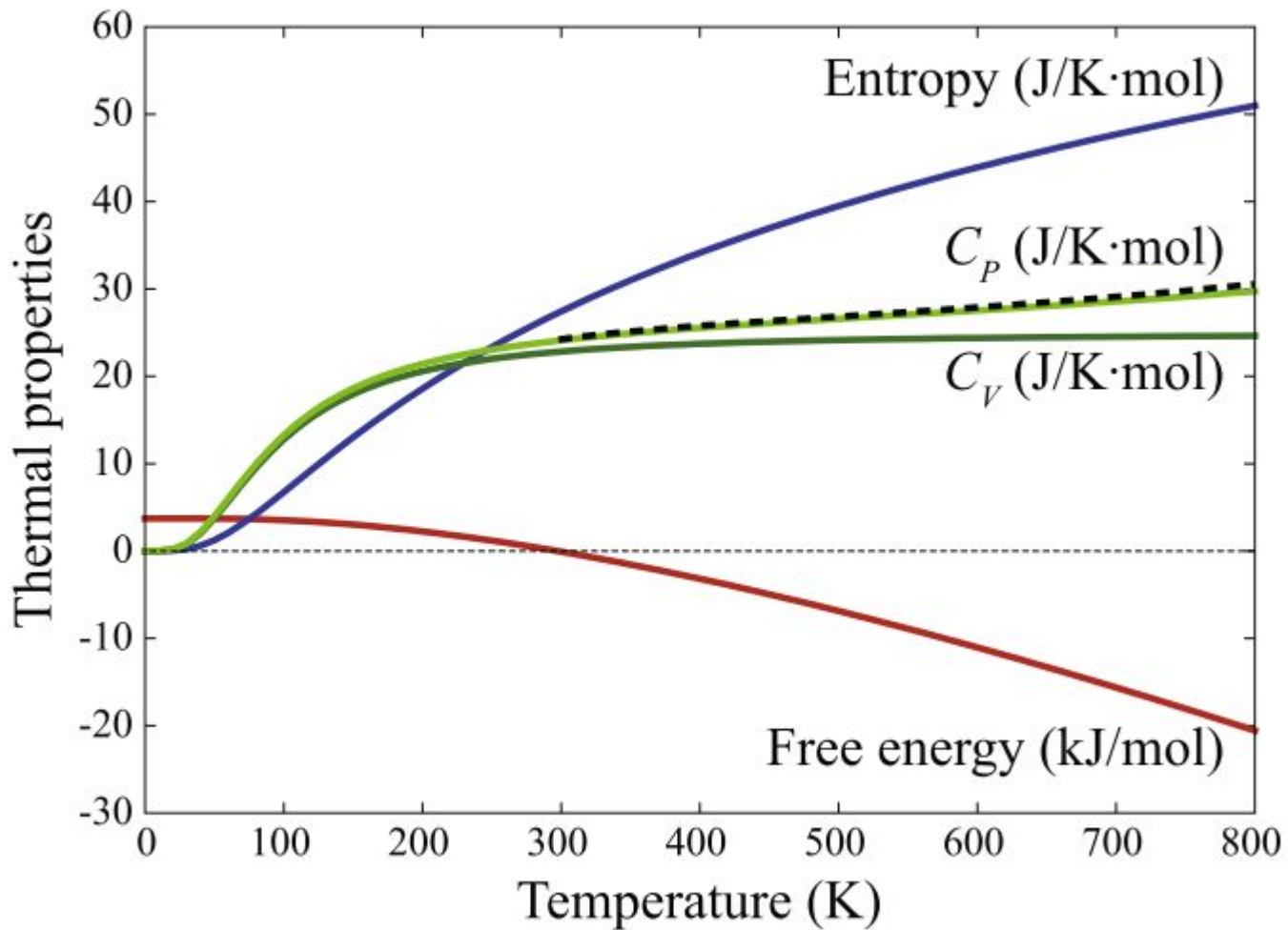
Helmholtz free energy F :

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

Entropy:

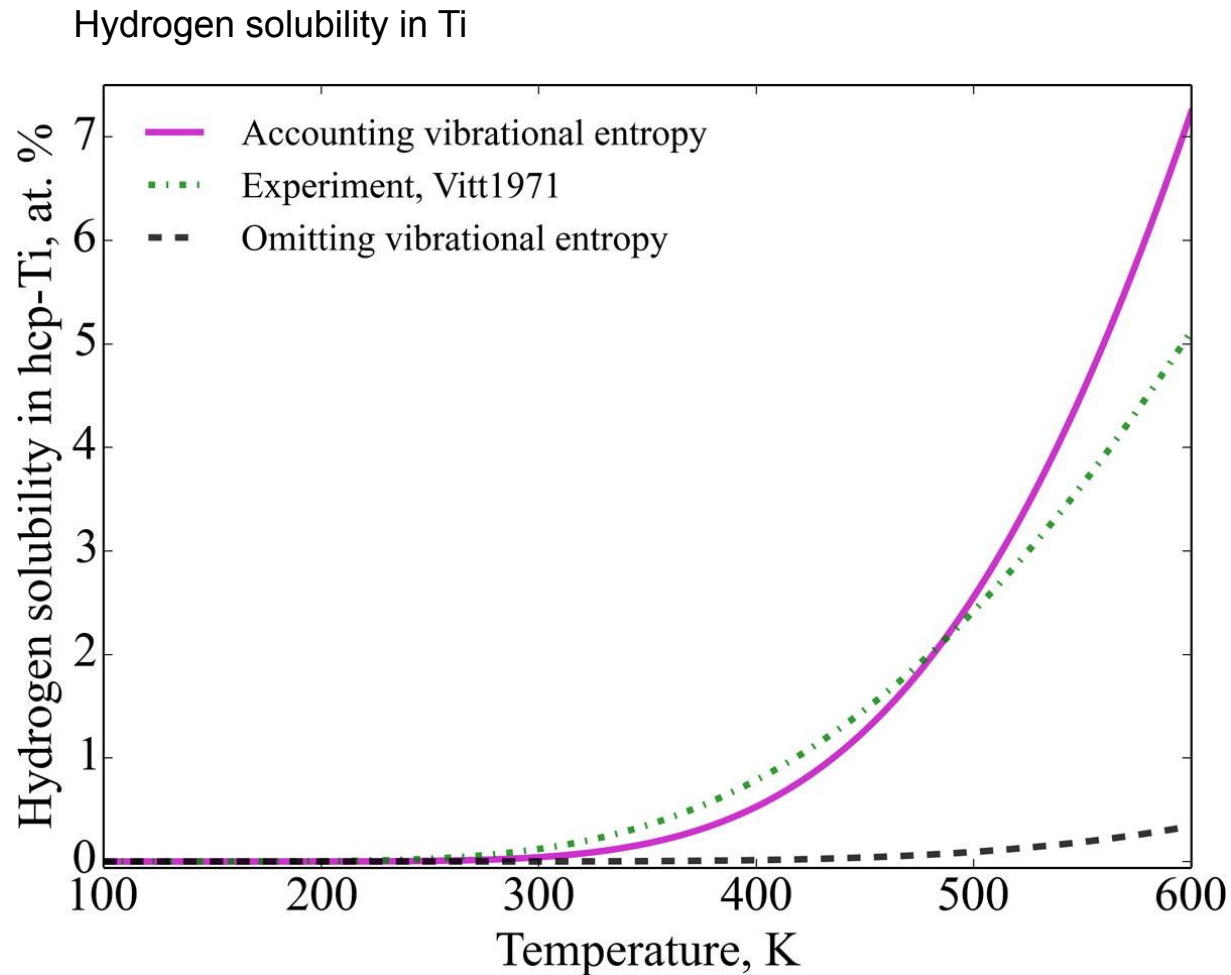
$$S = \frac{1}{2T} \sum_{\mathbf{qj}} \hbar \omega_{\mathbf{qj}} \coth [\hbar \omega_{\mathbf{qj}}/2k_B T] - k_B \sum_{\mathbf{qj}} \ln [2 \sinh(\hbar \omega_{\mathbf{qj}}/2k_B T)].$$

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://atztoigo.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

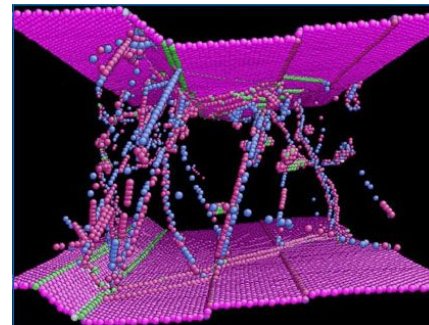
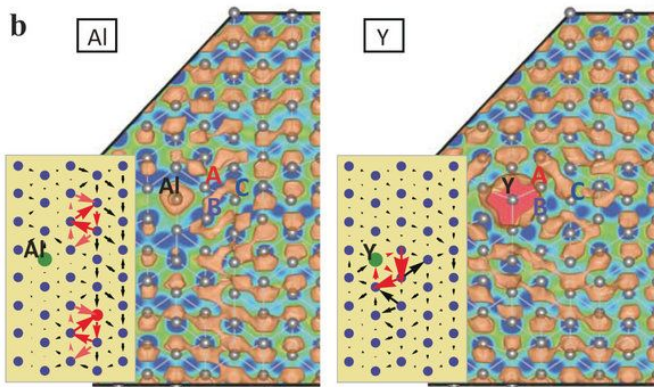
Methods vs scales

Quantum methods

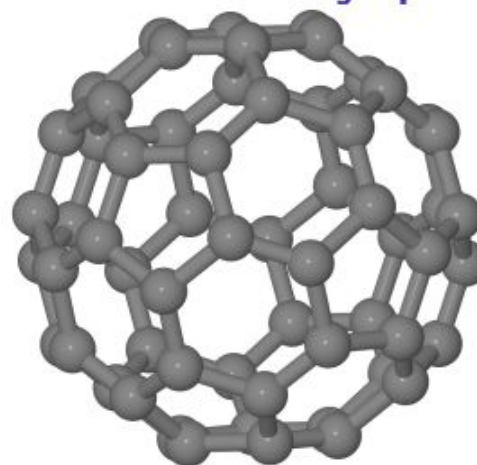
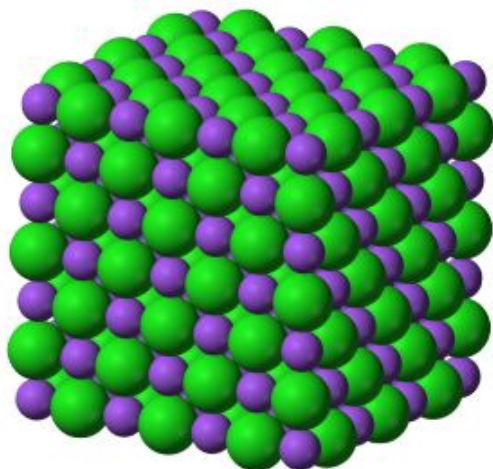
- **Schrödinger** equation for atomic interaction
 - DFT (Density Functional Theory) and flavours
 - VASP, Abinit, QE, etc.
- **Electronic structure**
- Almost all properties!!!
- Restricted in system sizes (1000 atoms) and simulation time (1000 of steps per day)

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

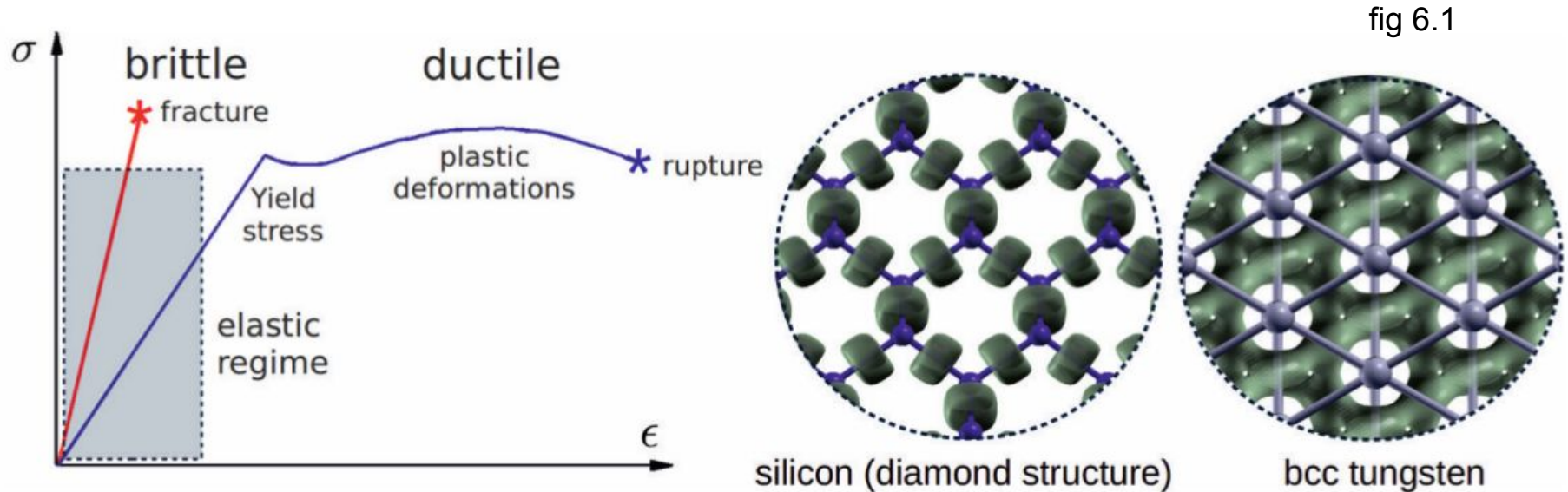


Crystal vs molecule: computational chemistry perspective



- 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

Mechanical properties



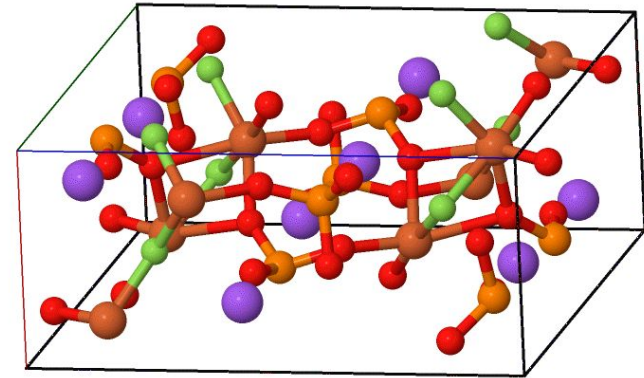
- The mechanical properties in brittle and ductile regimes depends on defects of crystal structure - an active research area for computational materials
- However, the elastic regime depends only on ideal crystal structure and can be easily described

Equation of state and elastic properties

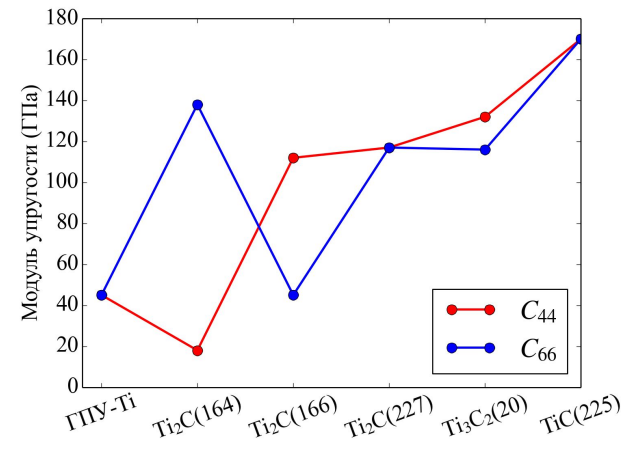
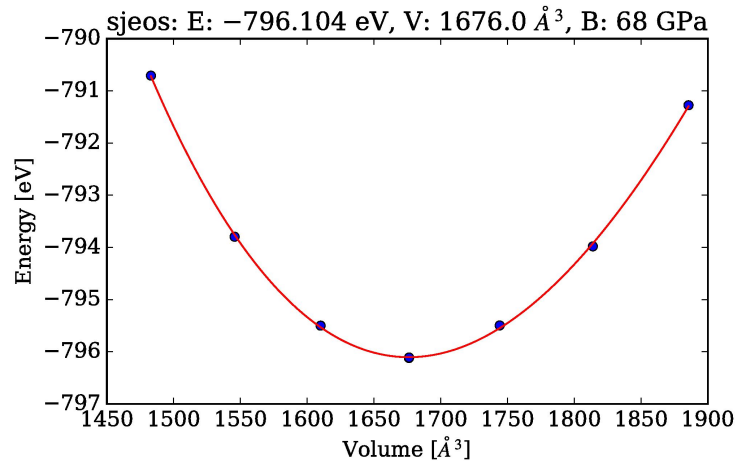
$$\mathbf{R} = \begin{pmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{c}{a} \end{pmatrix}$$

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

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



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



D.Aksyonov et al, Computational Materials Science 65 (2012): 434-441

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:

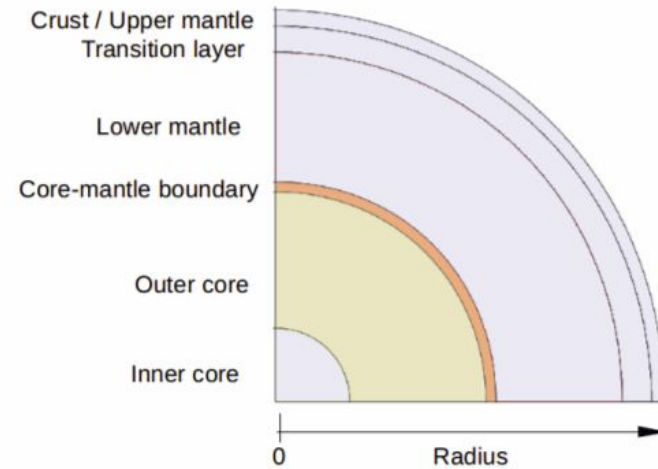
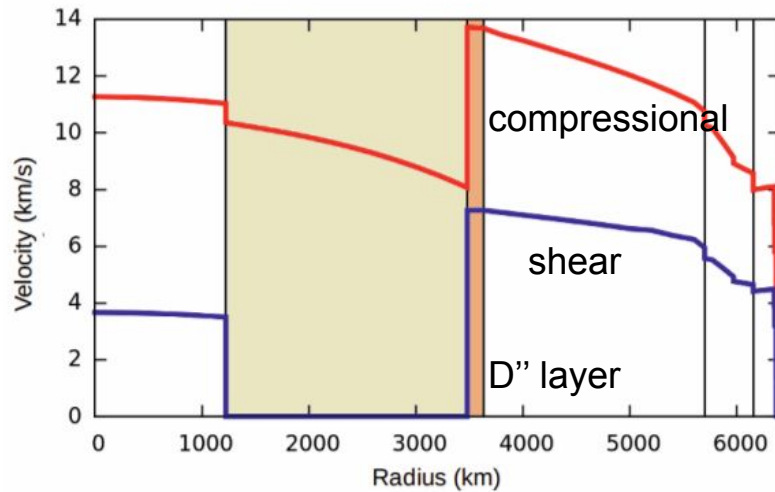
$$\tilde{\boldsymbol{\sigma}} = (\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{xz}, \sigma_{xy}) \equiv (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6)$$

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

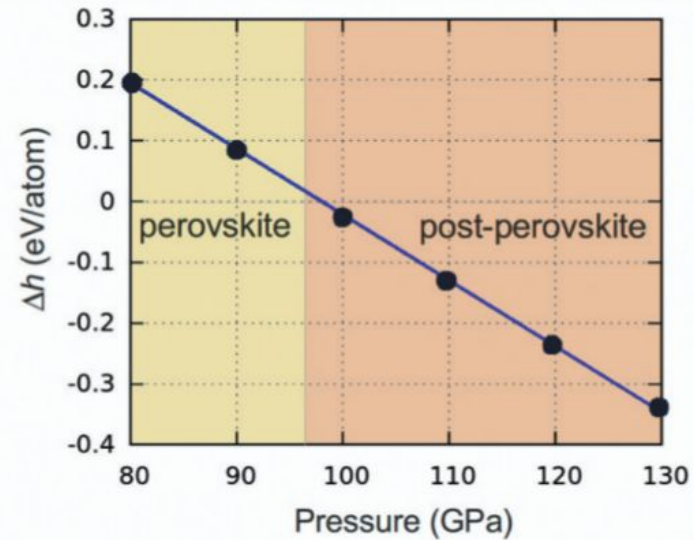
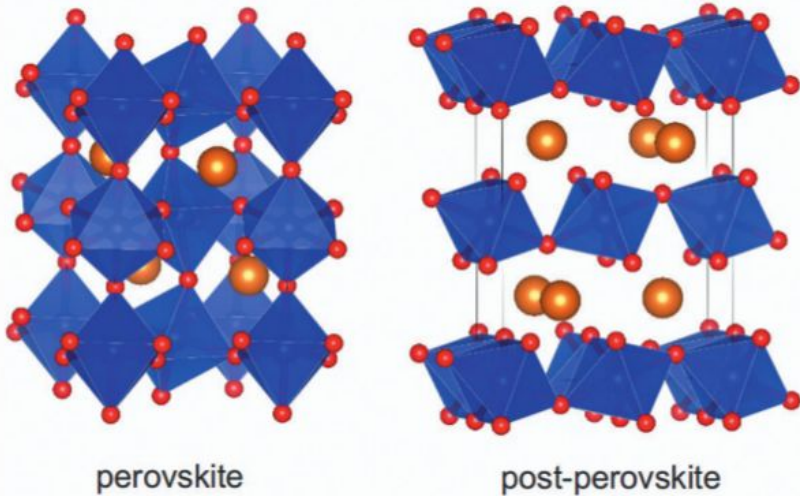
$$\sigma_{ij} = \sum_{k=1}^3 \sum_{l=1}^3 c_{ijkl} \epsilon_{kl}$$

$C_{25} = C_{yyxz}$ gives relationship between ϵ_{xz} deformation component σ_{yy} stress component

Influence of pressure



from
Giustino



A.Oganov, S. Ono, Nature 430.6998 (2004): 445-448

Temperature-pressure phase diagram

Giustino fig 8.8

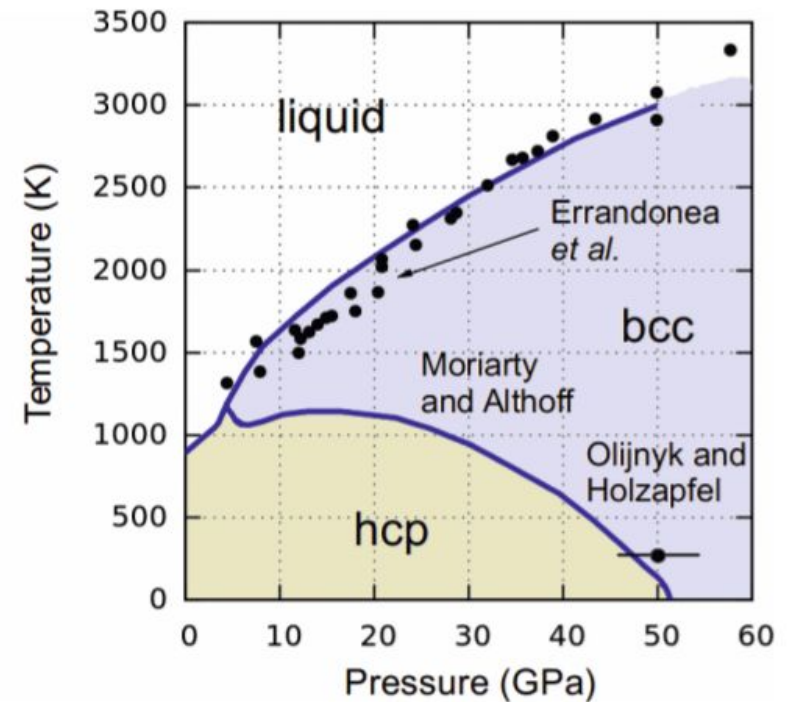
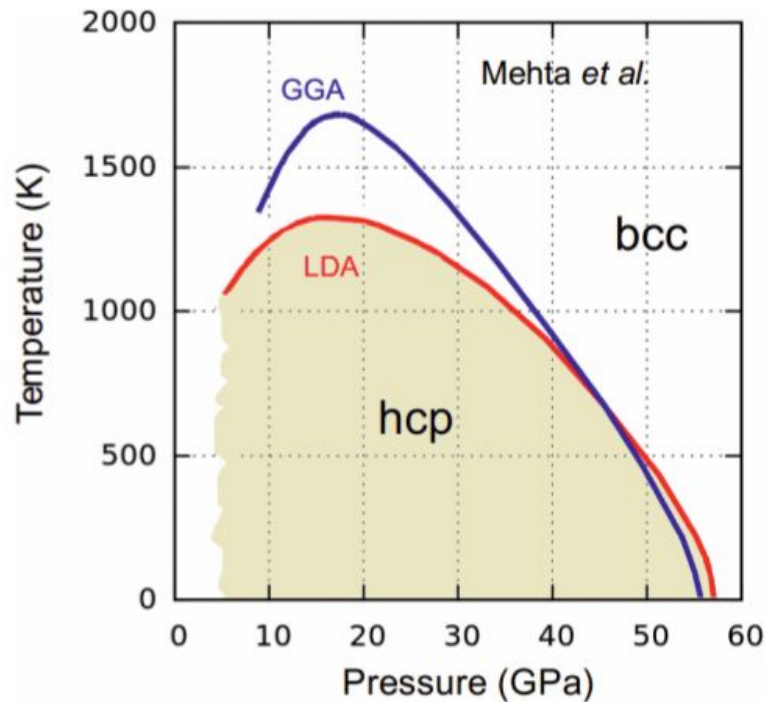


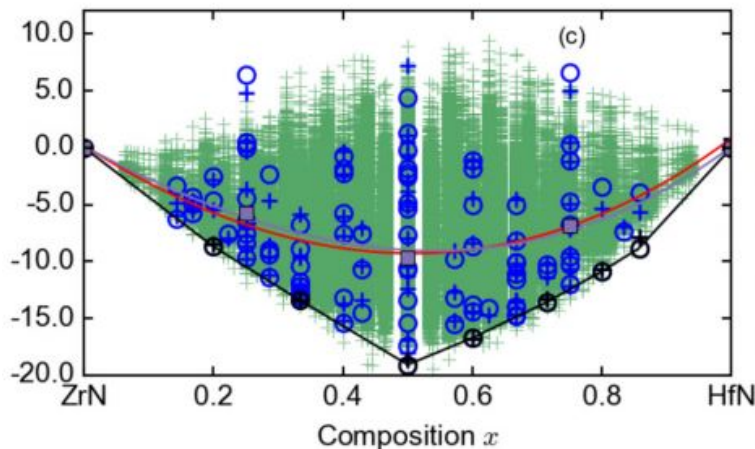
Fig. 8.8 The phase diagram of Mg from first principles. The left panel shows the calculations

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

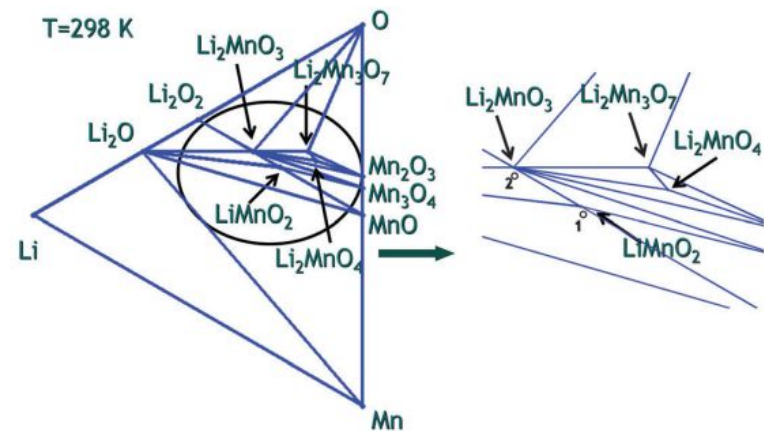
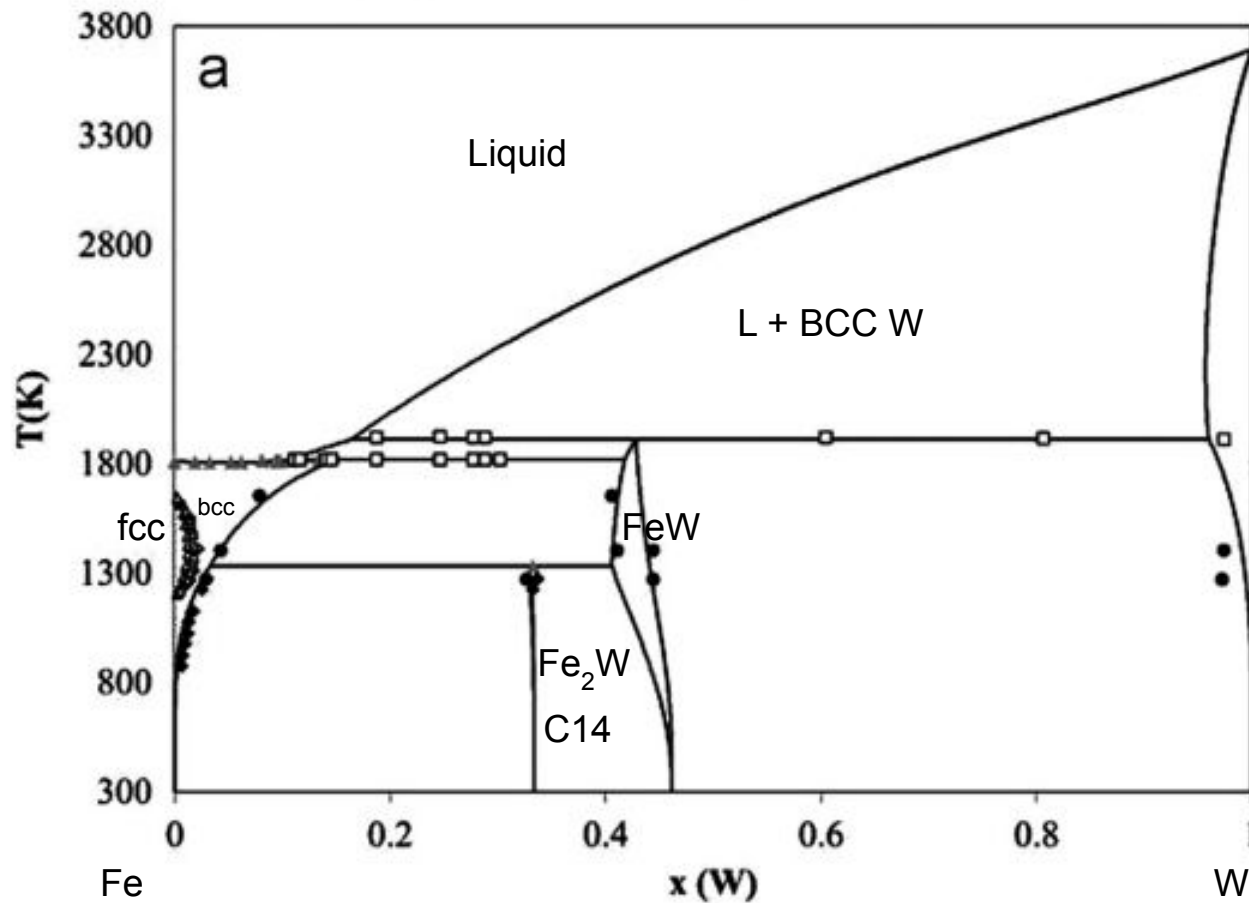


Fig. 4 Calculated ternary phase diagram of the Li-Mn-O system at room temperature. Points 1 and 2 show the position of the Li-O vacancy pair for LiMnO_2 and Li_2MnO_3 , respectively (see the text for details).

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

Case study Fe–W phase diagram from DFT



- DFT
- phonon calculations
- Calphad

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

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

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

- 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 $12 \times 12 \times 12$ for a cubic unit cell. What is an equivalent k-grid for $3 \times 2 \times 1$ supercell?

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!