Electronic Structure Theory for Periodic Systems: The Concepts

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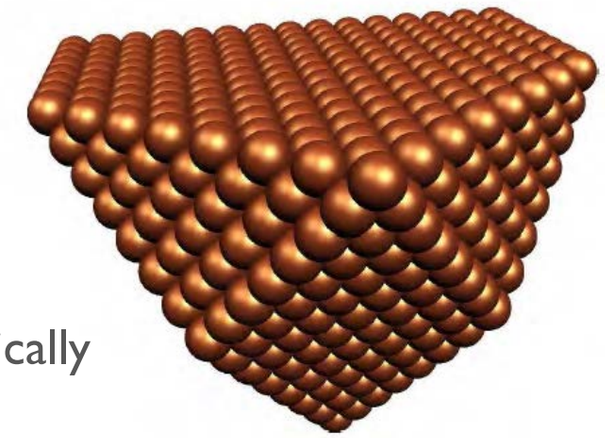
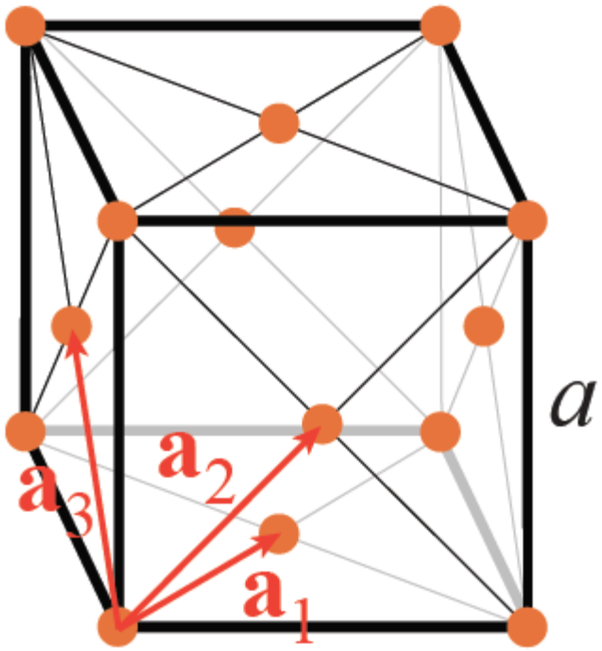
Motivation

- There are 10^{20} atoms in 1 mm^3 of a solid.
- It is impossible to track all of them.
- But for most solids, atoms are arranged periodically

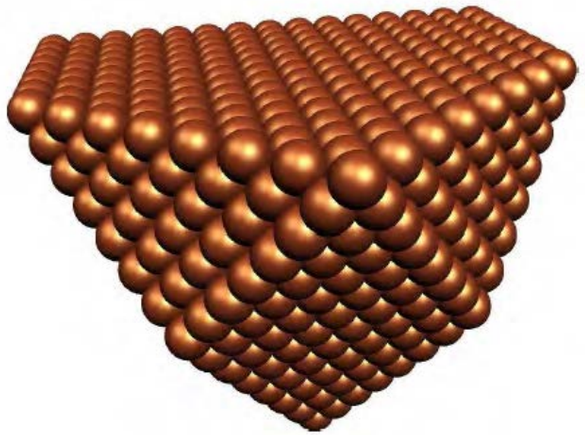




Outline

Part 1

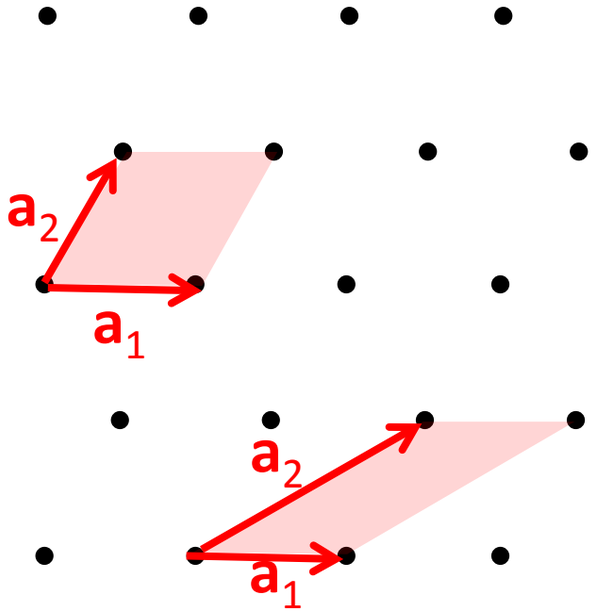
- Periodicity in real space
  - Primitive cell and Wigner Seitz cell
  - 14 Bravais lattices
- Periodicity in reciprocal space
  - Brillouin zone, and irreducible Brillouin zone
- Bandstructures
- Bloch theorem
- K-points



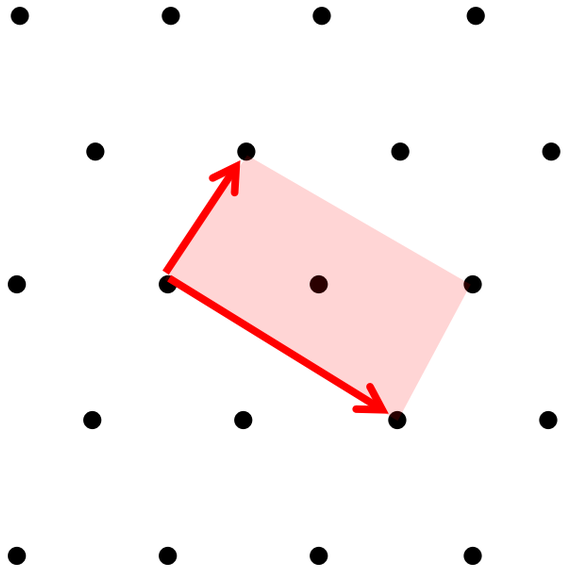
Part 2

- The supercell approach
- Application: Adatom on a surface (to calculate for example a diffusion barrier)
- Surfaces and Surface Energies
- Surface energies for systems with multiple species, and variations of stoichiometry
- Ab-Initio thermodynamics

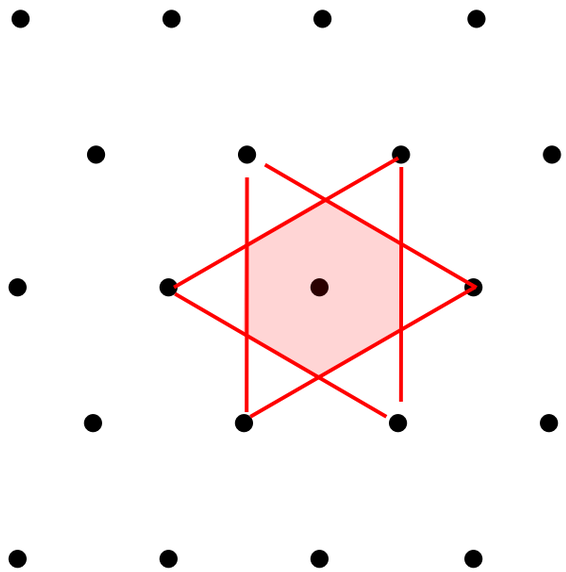
Primitive Cell and Wigner Seitz Cell



primitive cell



Non-primitive cell



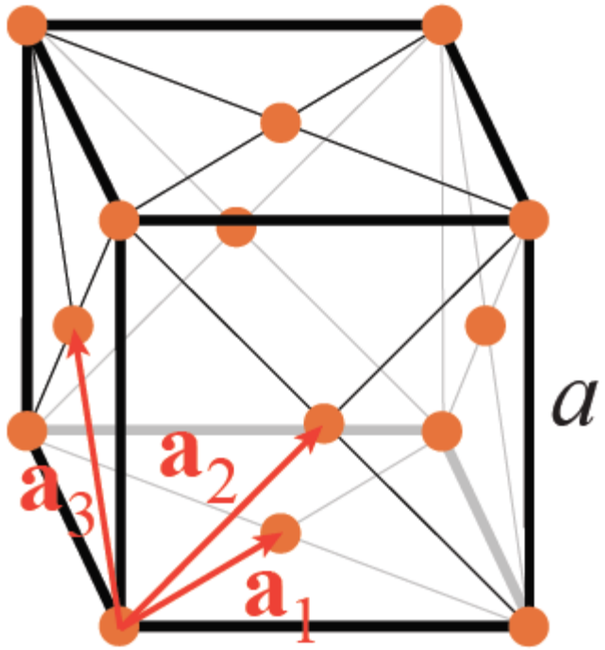
Wigner-Seitz cell

$$\boldsymbol{R} = N_1\boldsymbol{a}_1 + N_2\boldsymbol{a}_2$$

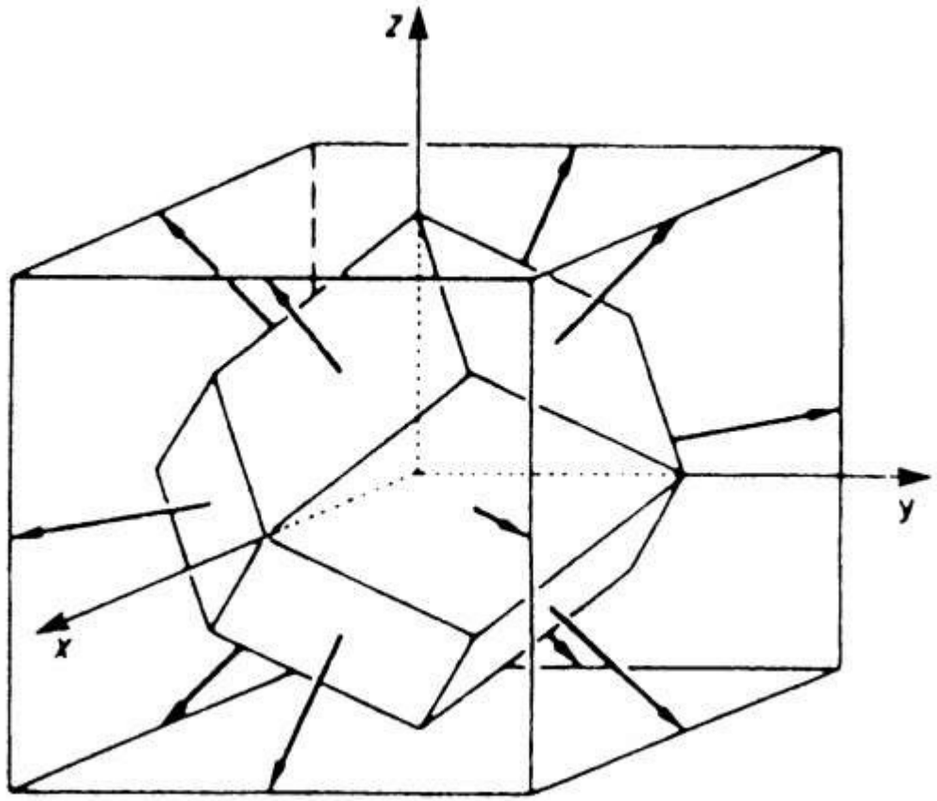
Primitive Cell and Wigner Seitz Cell

Face-center cubic (fcc) in 3D:

Primitive cell



Wigner-Seitz cell

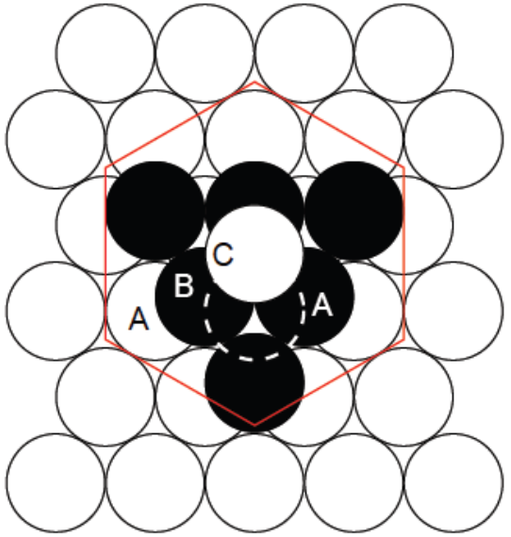


$$\boldsymbol{R} = N_1\boldsymbol{a}_1 + N_2\boldsymbol{a}_2 + N_3\boldsymbol{a}_3$$

How Do Atoms arrange in Solid

Atoms with no valence electrons:
(noble elements)

- all electronic shells are filled
- weak interactions
- arrangement is closest packing of hard shells, i.e., fcc or hcp structure

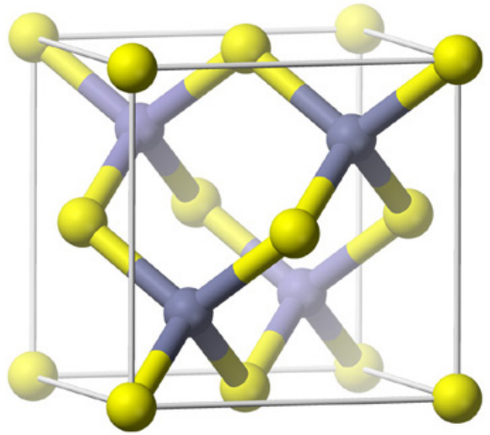


Atoms with s valence electrons:
(alkalis)

- s orbitals are spherically symmetric
- no particular preference for orientation
- electrons form a sea of negative charge, cores are ionic
- Resulting structure optimizes electrostatic repulsion (bcc, fcc, hcp)

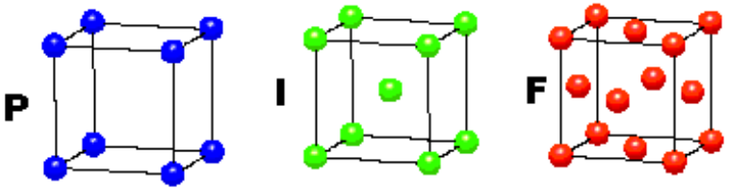
Atoms with s and p valence electrons:
(group IV elements)

- Linear combination between s and p orbitals form directional orbitals, which lead to directional, covalent bonds.
- Structure is more open than close-packed structures (diamond, which is really a combination of 2 fcc lattices)

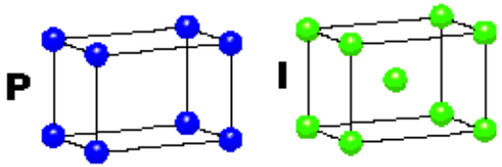


14 Bravais Lattices

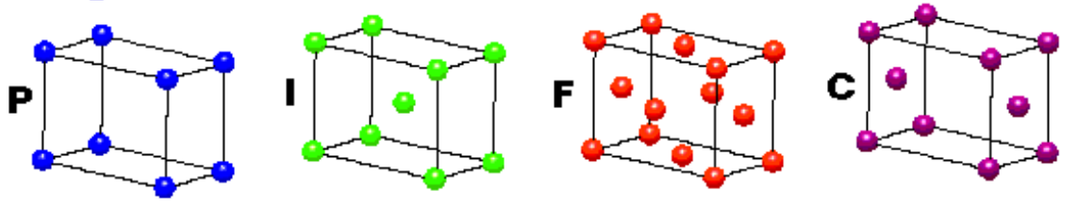
CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$



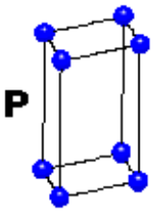
TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



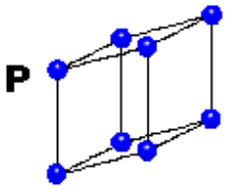
ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



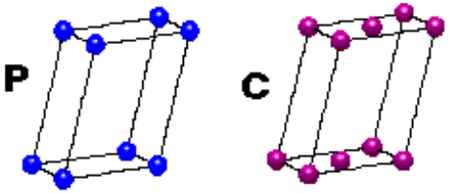
HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$



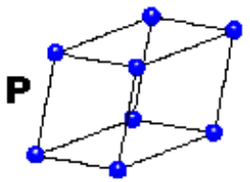
TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$



MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$



TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

Reciprocal Lattice

- The reciprocal lattice is a mathematically convenient construct; it is the space of the Fourier transform of the (real space) wave function.
- It is also known as k-space or momentum space

The reciprocal lattice is defined by

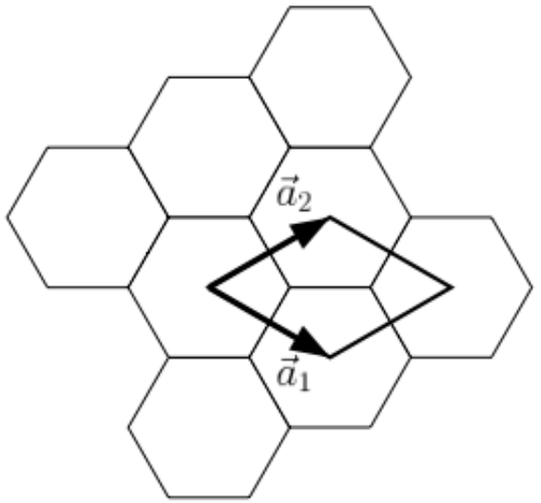
$$\boldsymbol{b}_1 = 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{|\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)|}$$

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

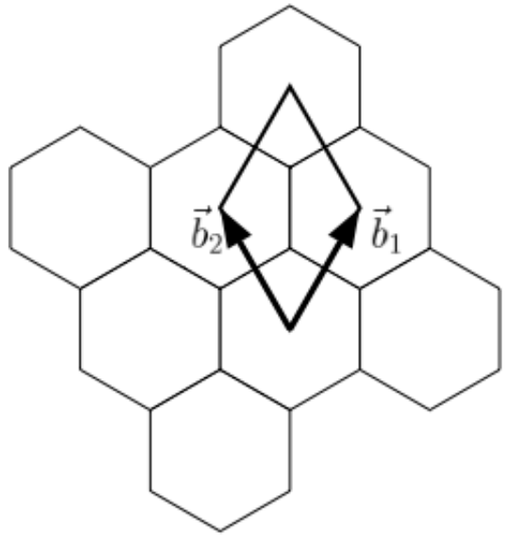
$$\boldsymbol{b}_3 = 2\pi \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{|\boldsymbol{a}_3 \cdot (\boldsymbol{a}_1 \times \boldsymbol{a}_2)|}$$

Example: Honeycomb lattice

Real space



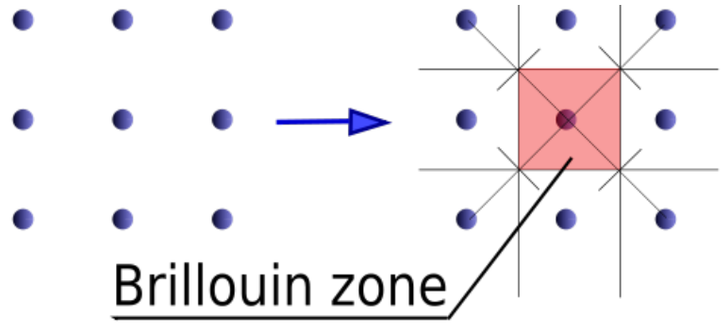
Reciprocal space



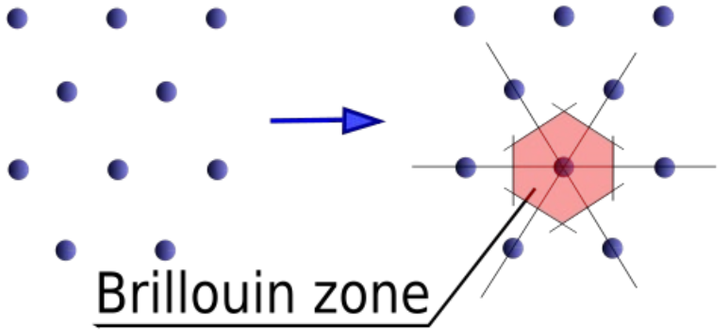
Brillouin Zone

The Brillouin Zone is the Wigner-Seitz cell of the reciprocal space

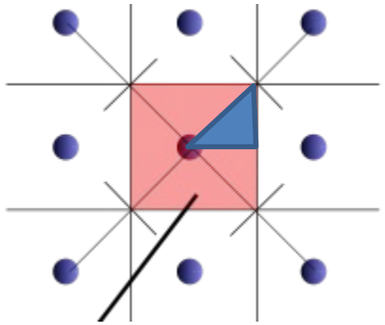
Square lattice (2D) ⟶ square lattice



Hexagonal lattice (2D) ⟶ hexagonal lattice

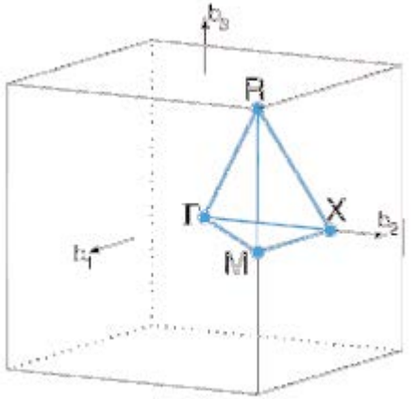


The Irreducible Brillouin Zone is the Brillouin Zone reduced by all symmetries

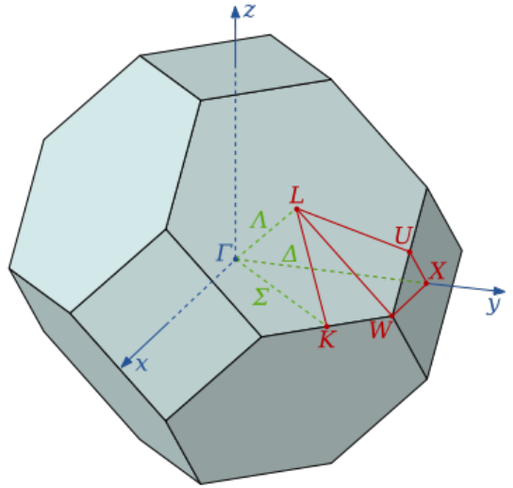


3D

Cubic structure



Body-centered cubic



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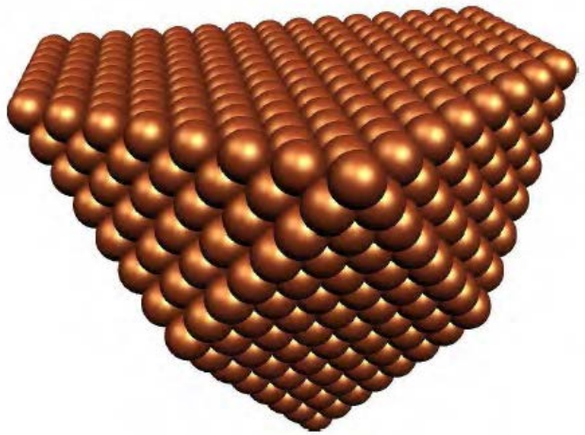
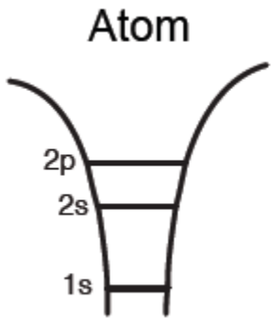
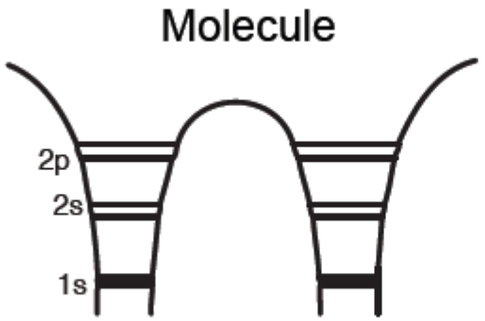


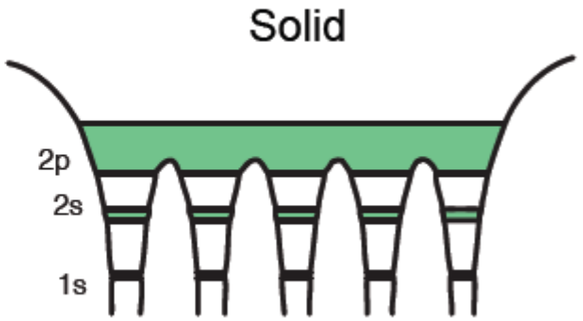
From Atoms to Molecules to Solids: The Origin of Electronic Bands



Discrete states

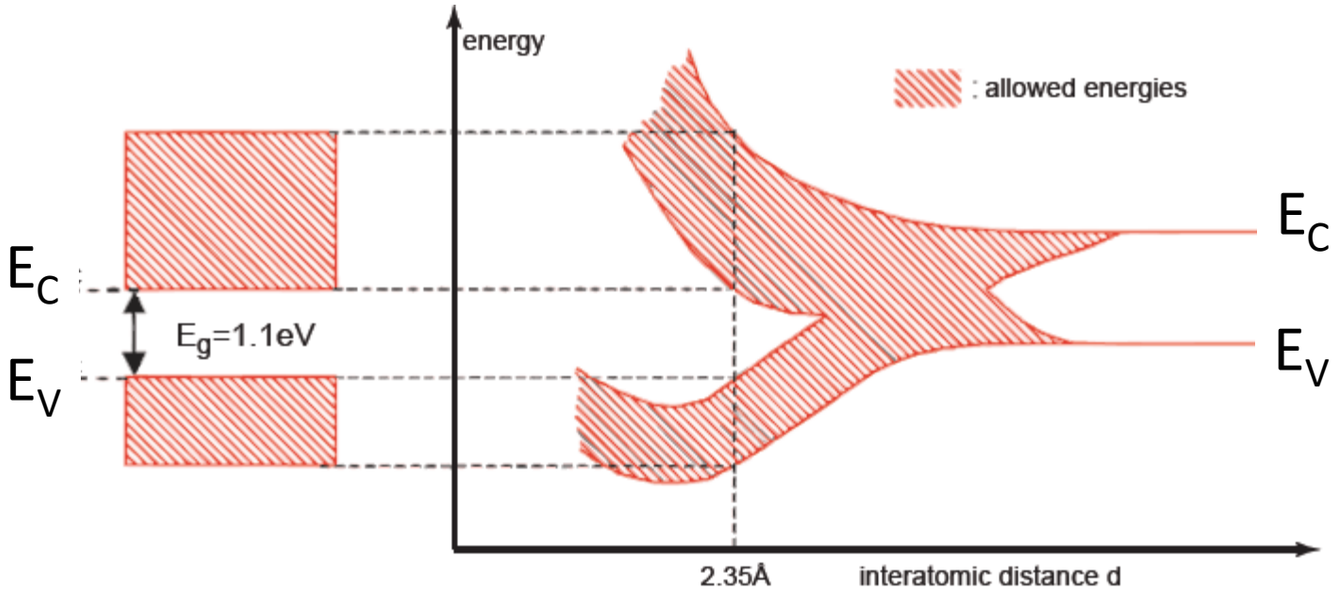


Localized discrete states



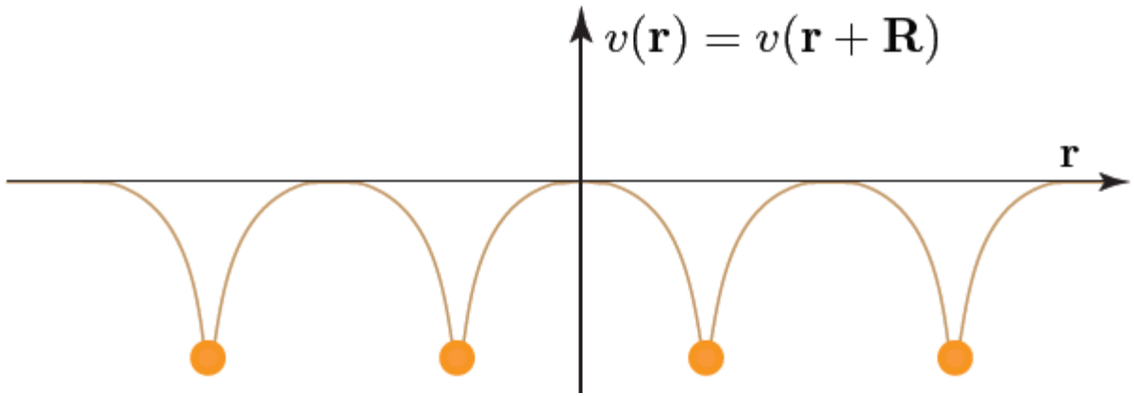
Many localized discrete states, effectively a continuous band

Silicon



Bloch Theorem

Suppose we have a periodic potential



where $\boldsymbol{R}$ is the lattice vector

$$\boldsymbol{R} = N_1\boldsymbol{a}_1 + N_2\boldsymbol{a}_2 + N_3\boldsymbol{a}_3$$

Bloch theorem for wave function (Felix Bloch, 1928):

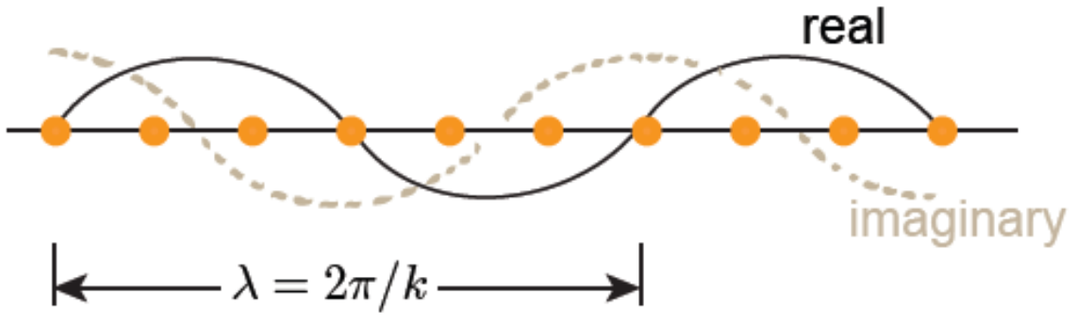
$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{\boldsymbol{k}}(\boldsymbol{r})$$

phase factor

$$u_{\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{\boldsymbol{k}}(\boldsymbol{r})$$

The meaning of k

Free electron wavefunction



$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r})$$

$k = 2\pi/a$ $\quad$ $k = 0$

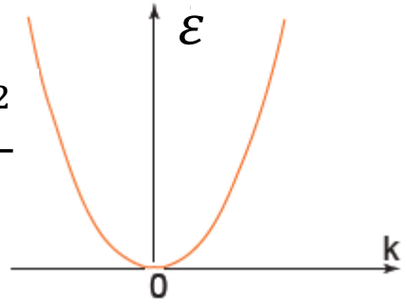
$k \neq 0$

$k = \pi/a$

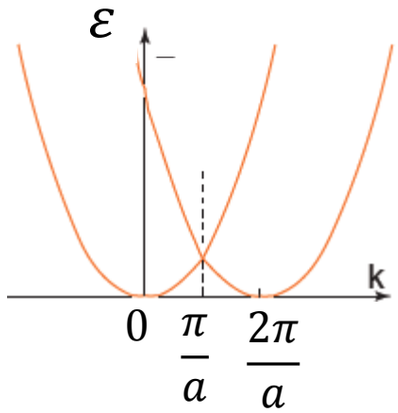
Band structure in 1D

Energy of free electron in 1D

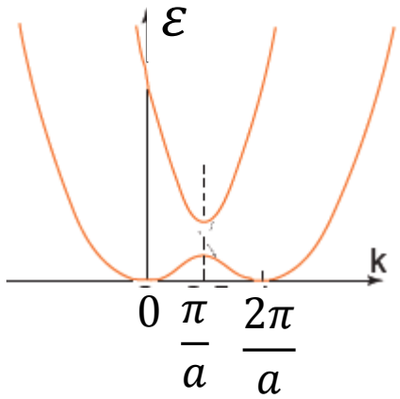
$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$



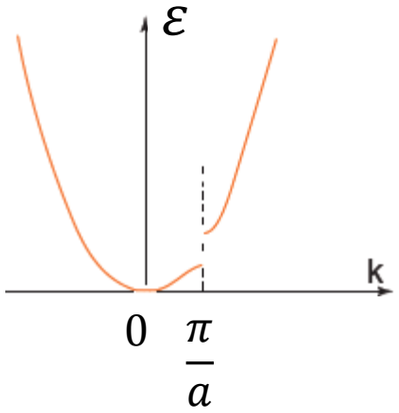
periodic potential



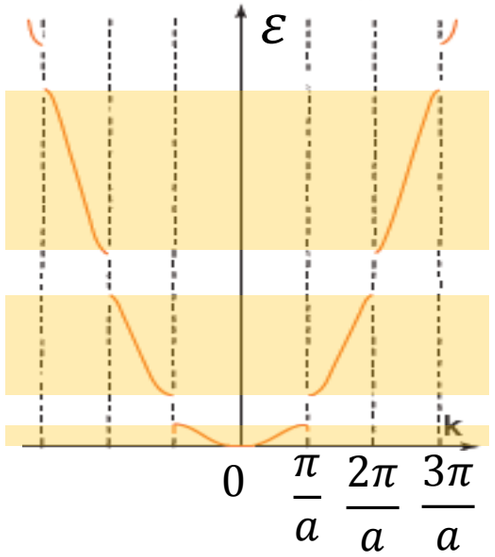
weak interactions



Only first parabola

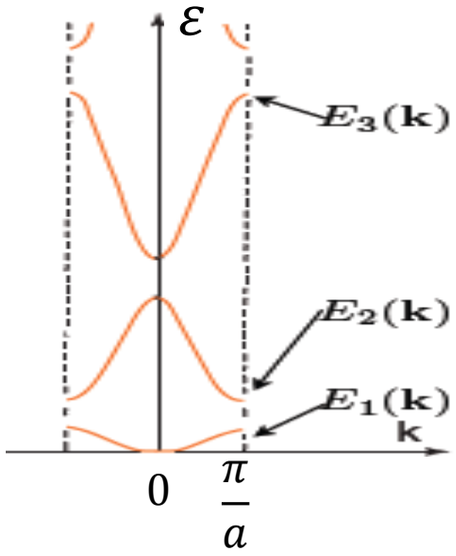


Extended zone scheme of similar split at $k = \frac{\pi}{a}, k = \frac{2\pi}{a}$

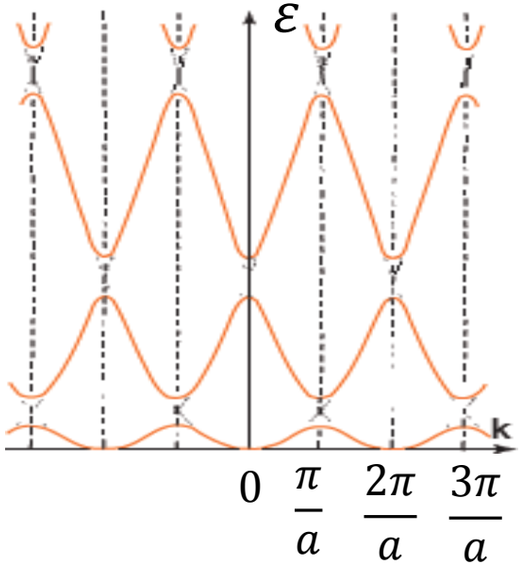


Energy bands

Reduced zone scheme



Repeated zone scheme

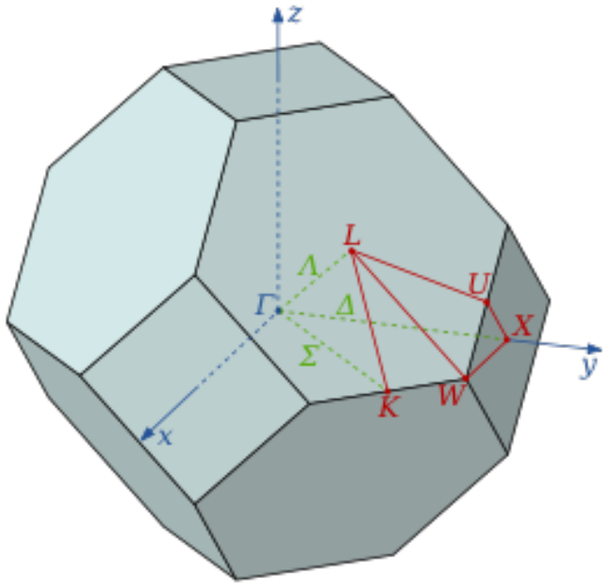


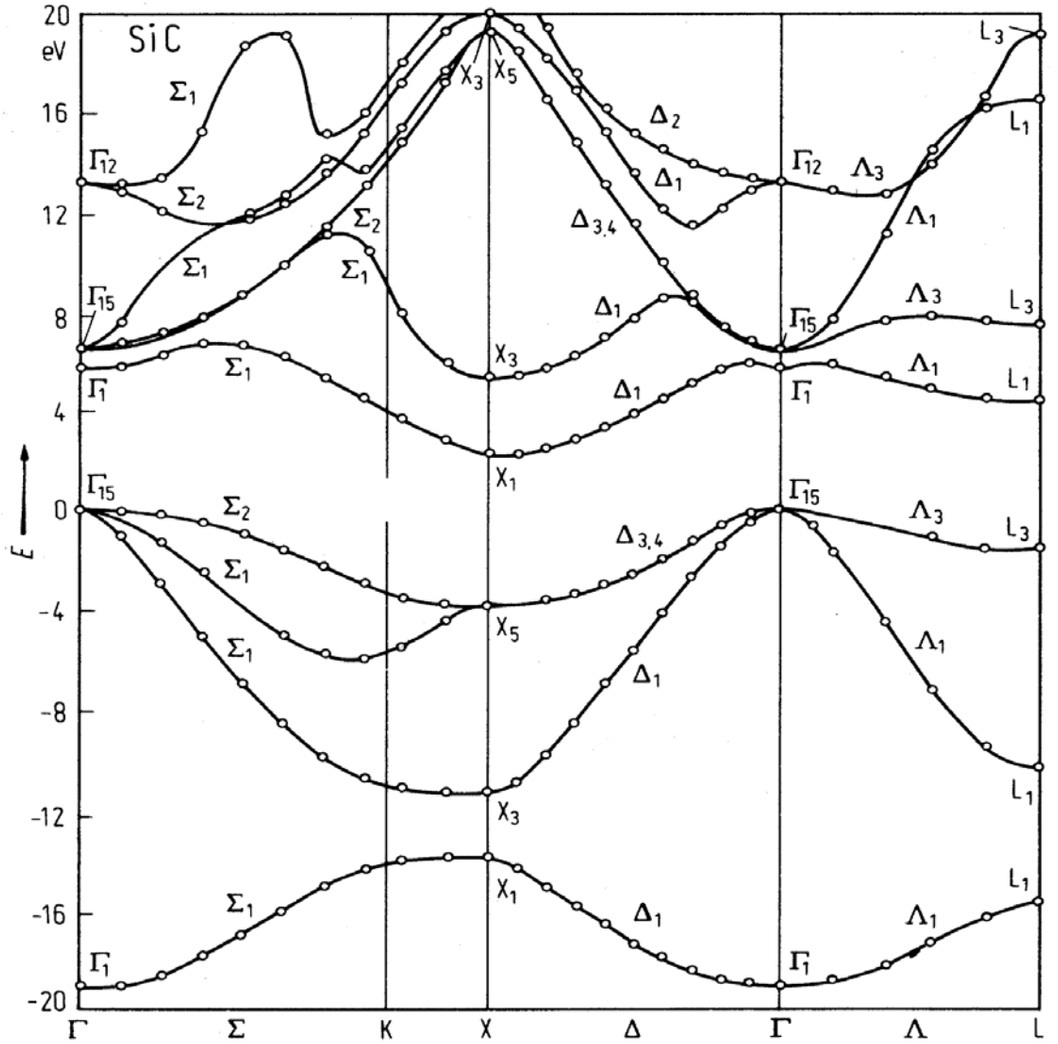
- We have 2 quantum numbers **k** and n
- Eigenvalues are $E_n(\mathbf{k})$

Band Structure in 3D

- In principle, we need a 3+1 dimensional plot.
- In practise, instead of plotting "all" k-points, one typically plots band structure along high symmetry lines, the vertices of the Irreducible Brillouin Zone.

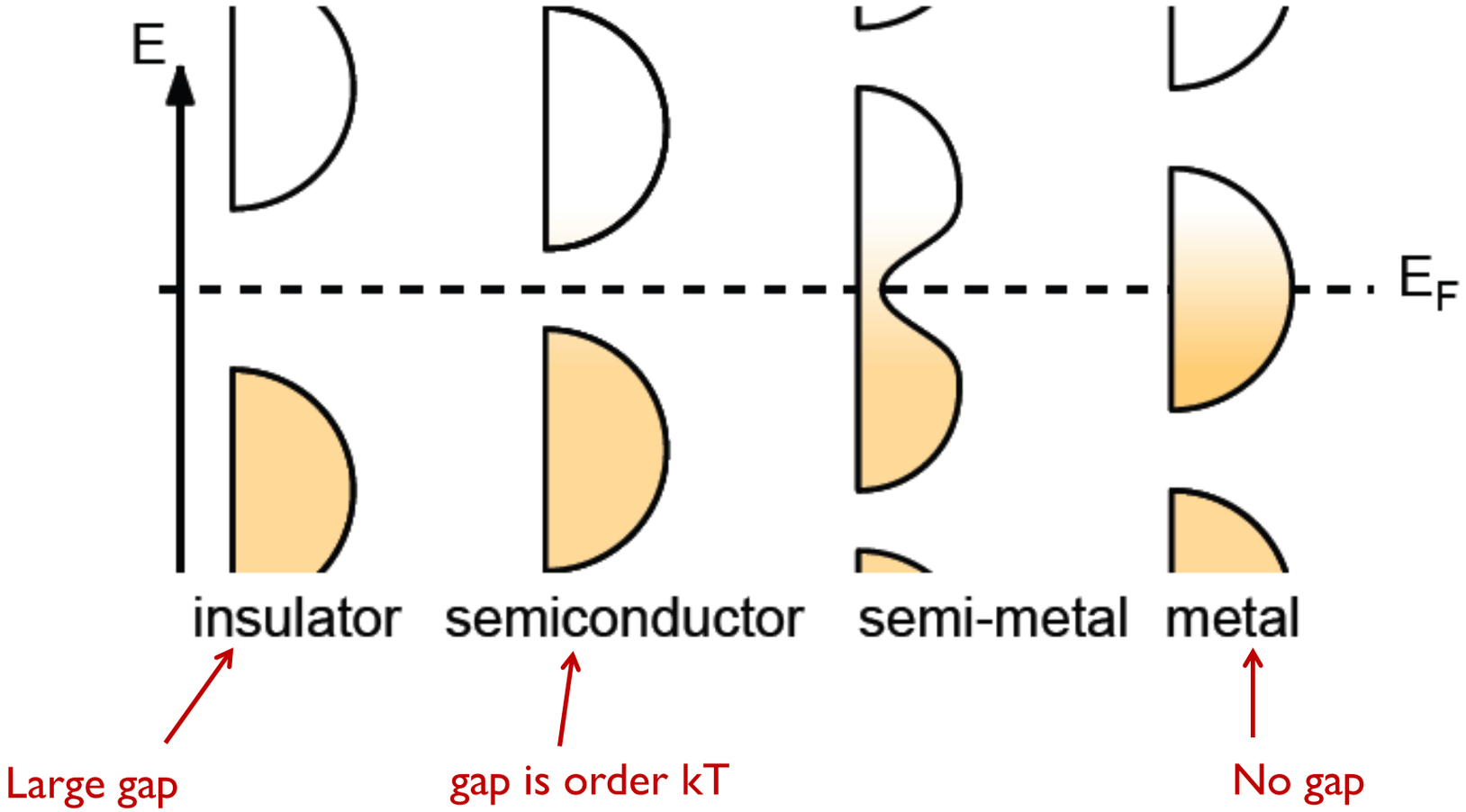
Example: Silicon





- The band gap is the difference between highest occupied band and lowest unoccupied band.
- Distinguish direct and indirect bandgap.

Insulator, Semiconductors, and Metals

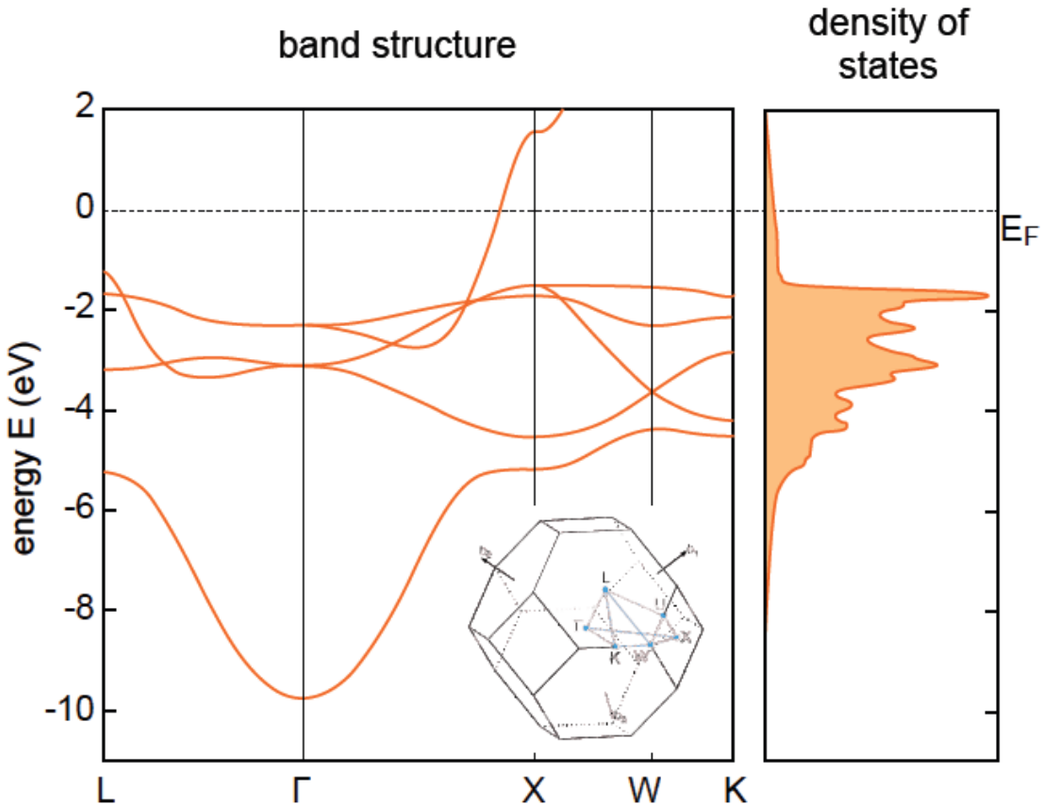


The Fermi Surface E_F separates the highest occupied states from the lowest un-occuppied states

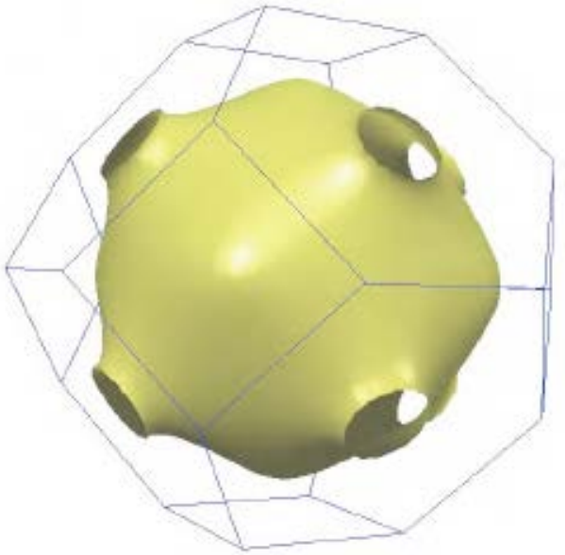
Fermi Surface

In a metal, some (at least one) energy bands are only partially occupied by electrons. The Fermi energy ε_F defines the highest occupied state(s). Plotting the relation $\epsilon_j(\boldsymbol{k}) = \epsilon_F$ in reciprocal space yields the Fermi surface(s).

Example: Copper



Fermi Surface



How to Treat Metals

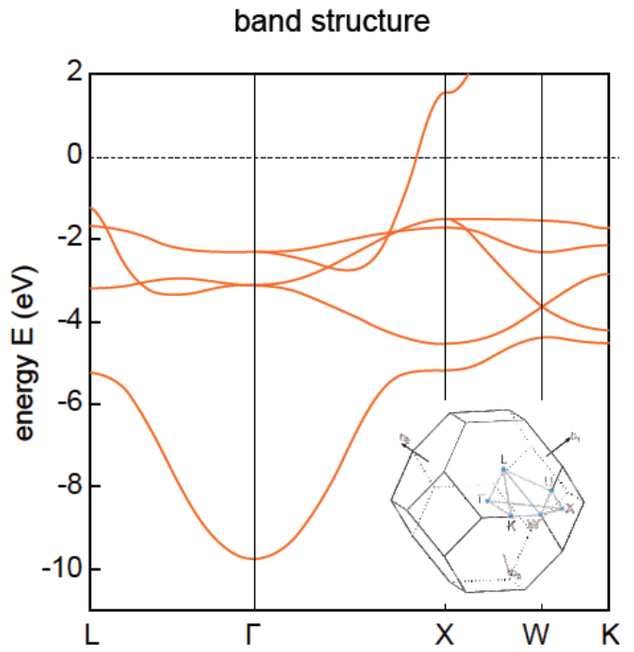
Fermi distribution function f_F enters Brillouin zone integral:

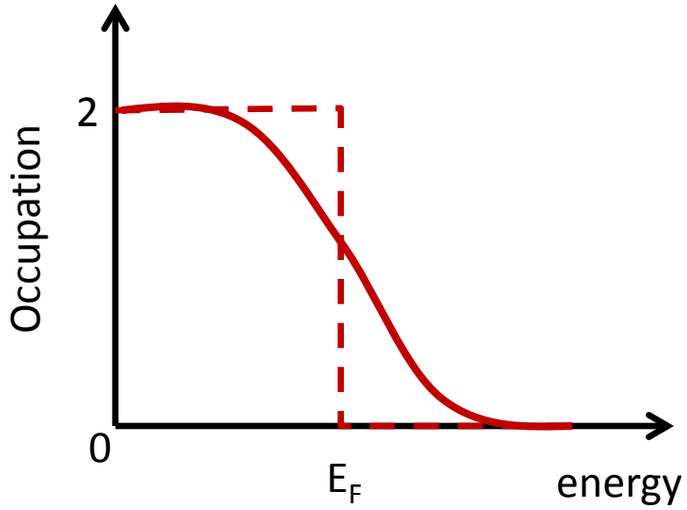
$$n(\boldsymbol{r}) = \sum_j \int_{\Omega_{BZ}} f(\epsilon_j) \left|\psi_{j,\boldsymbol{k}}(\boldsymbol{r})\right|^2 \frac{d^3\boldsymbol{k}}{\Omega_{BZ}}$$

- A dense k-point mesh is necessary.
- Numerical limitations can lead to errors and bad convergence.
- Possible solutions:
  - Smearing of the Fermi function: artificial increase $k_B T^{el}$ ~ 0.2 eV; then extrapolate to T^{el} = 0.

$$f(\epsilon_j) = \frac{1}{1 + e^{(\epsilon_j - \epsilon_F)/k_B T^{el}}}$$

  - Tetrahedron method [P. E. Blöchl et al., PRB 49, 16223 (1994)]
  - Methfessel-Paxton distribution [PRB 40, 3616 (1989)]
  - Marzari-Vanderbilt ensemble-DFT method [PRL 79, 1337 (1997)]





k-Point Sampling

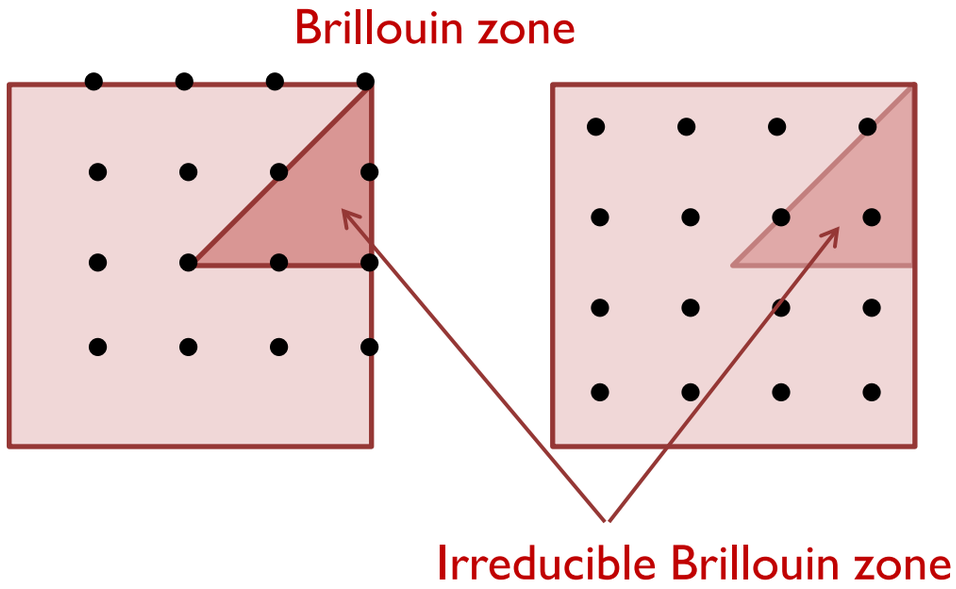
Charge densities (and other quantities) are represented by Brillouin-zone integrals

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

replace integral by discrete sum:

$$n(\mathbf{r}) \approx \sum_{j}^{\mathrm{occ}} \sum_{n=1}^{N_{\mathrm{kpt}}} w_n |\psi_{j,\mathbf{k}_n}(\mathbf{r})|^2$$

- For smooth, periodic function, use (few) special k-points (justified by mean value theorem).

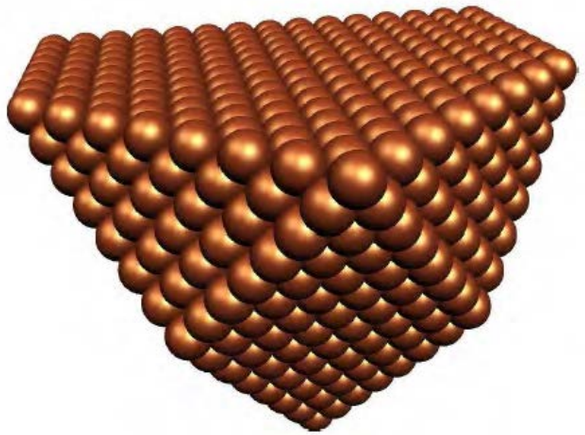


- Most widely used scheme proposed by Monkhorst and Pack.
- Monkhorst and Pack with an even number omits high symmetry points, which is more efficient (especially for cubic systems)

Outline

Part 1

- Periodicity in real space
  - Primitive cell and Wigner Seitz cell
  - 14 Bravais lattices
- Periodicity in reciprocal space
  - Brillouin zone, and irreducible Brillouin zone
- Bandstructures
- Bloch theorem
- K-points

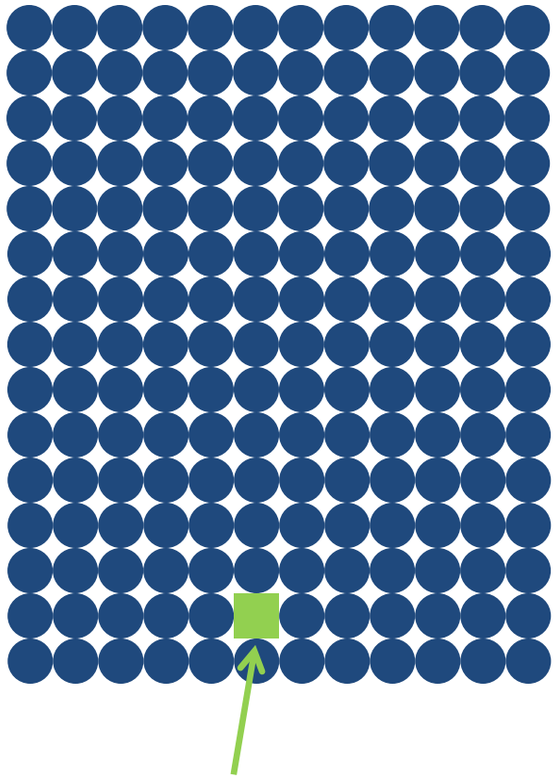


Part 2

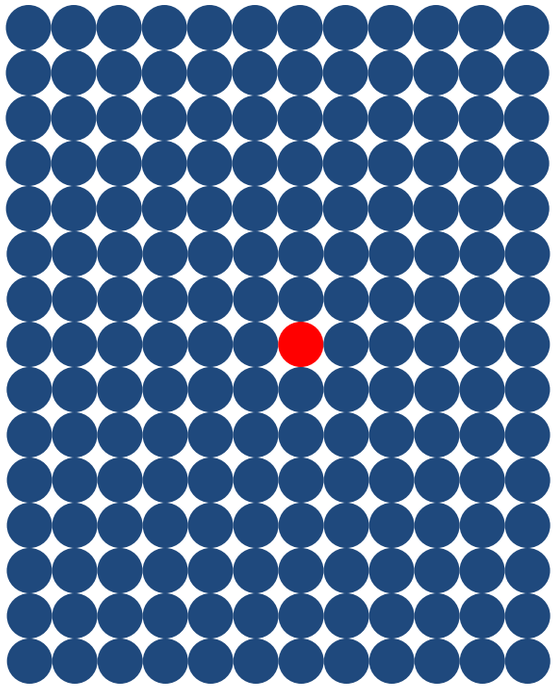
- The supercell approach
- Application: Adatom on a surface (to calculate for example a diffusion barrier)
- Surfaces and Surface Energies
- Surface energies for systems with multiple species, and variations of stoichiometry
- Ab-Initio thermodynamics

Supercell Approach to Describe Non-Periodic Systems

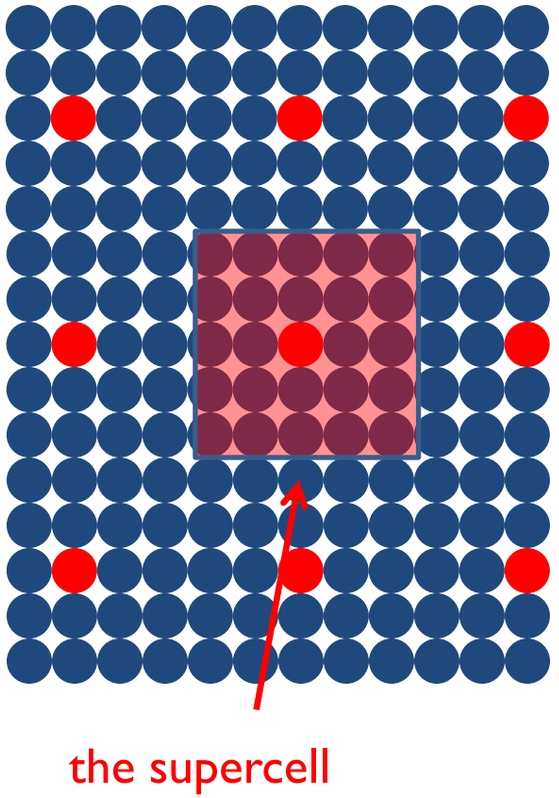
A infinite lattice



A defect removes periodicity



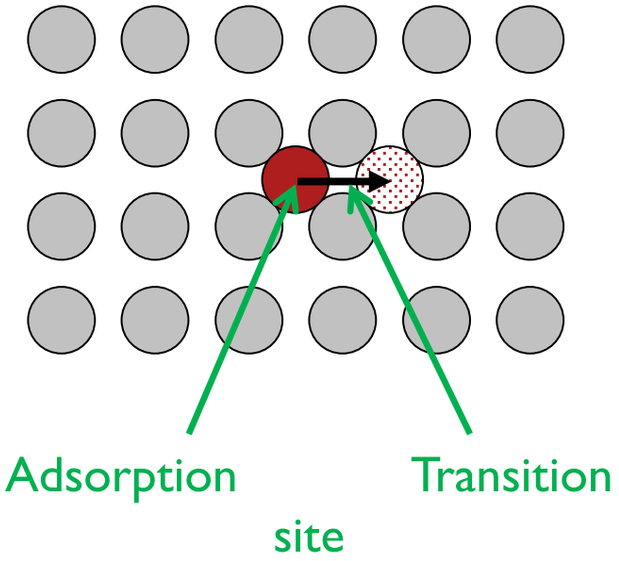
Define supercell to get back a periodic system



Size of supercell has to be tested: does the defect "see itself"?

Adatom Diffusion Using the Supercell Approach

Diffusion on (100) Surface



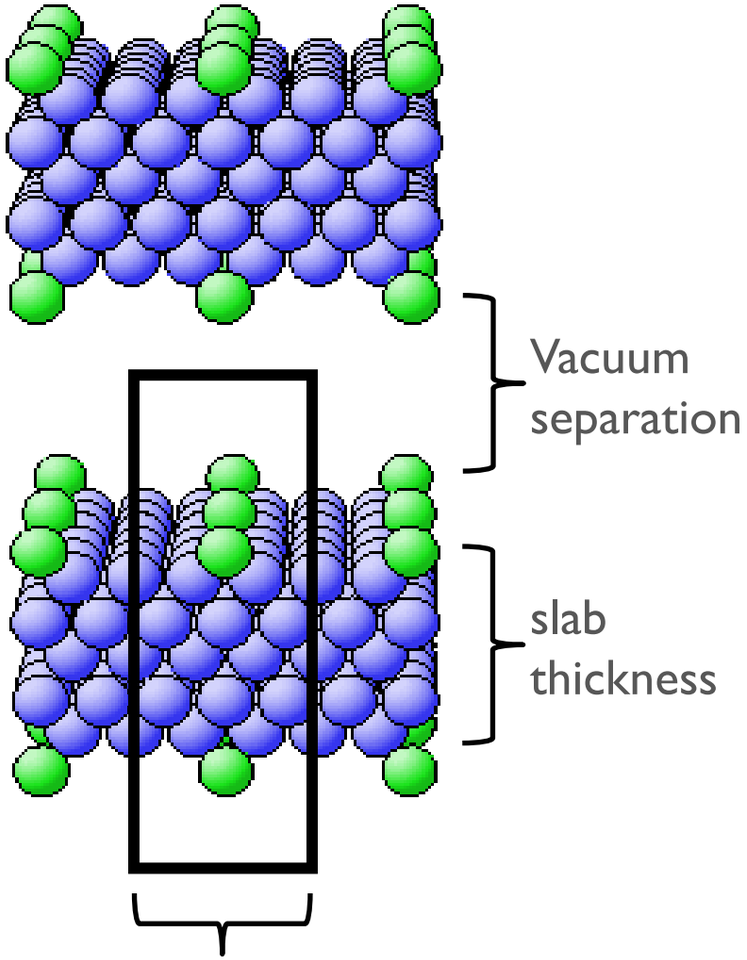
Transition state theory (Vineyard, 1957):

$$D = \Gamma_0 \exp(-\Delta E_d / kT)$$

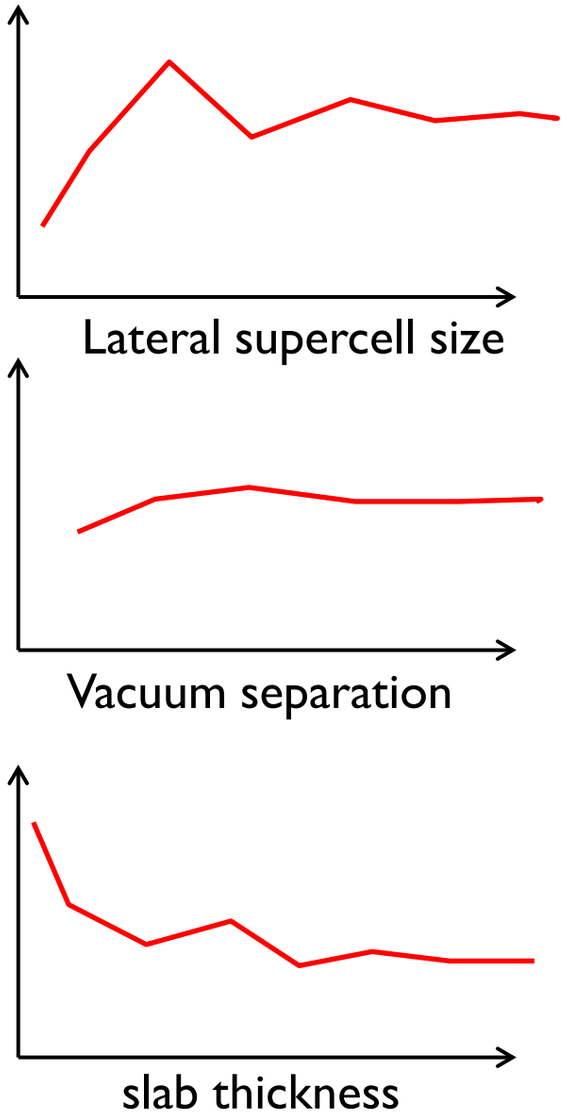
$$\Delta E_d = E_{trans} - E_{ad}$$

Attempt frequency $\Gamma_0 = \dfrac{\prod_{j=1}^{3N} \nu_j}{\prod_{j=1}^{3N-1} \nu_j^*}$

Supercell

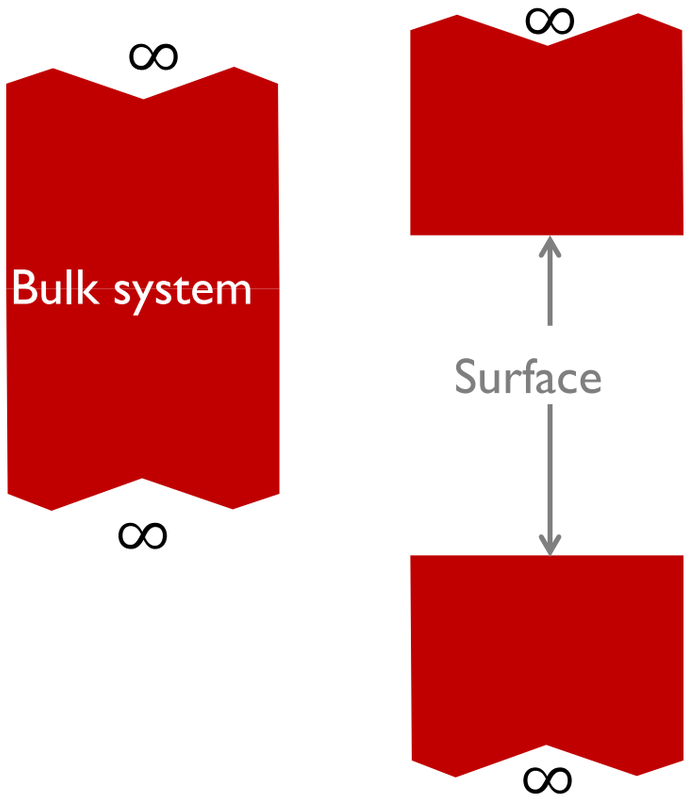


Need to test



Surface Energies

Surface energy is the energy cost to create a surface (compared to a bulk configuration)



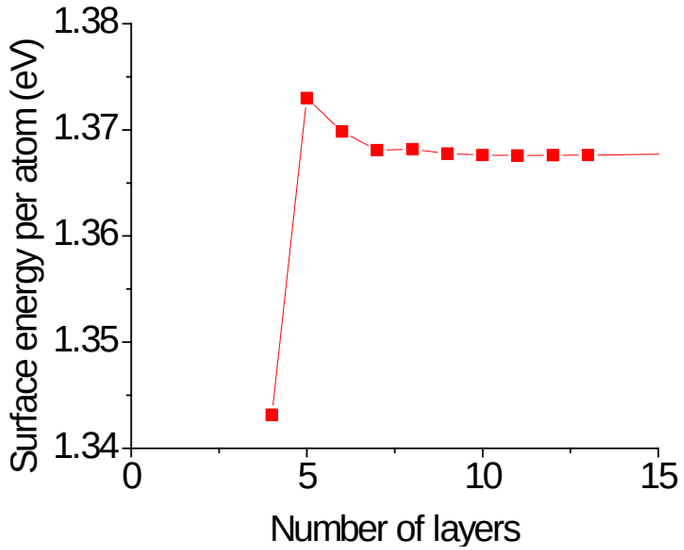
Example: Si(111)

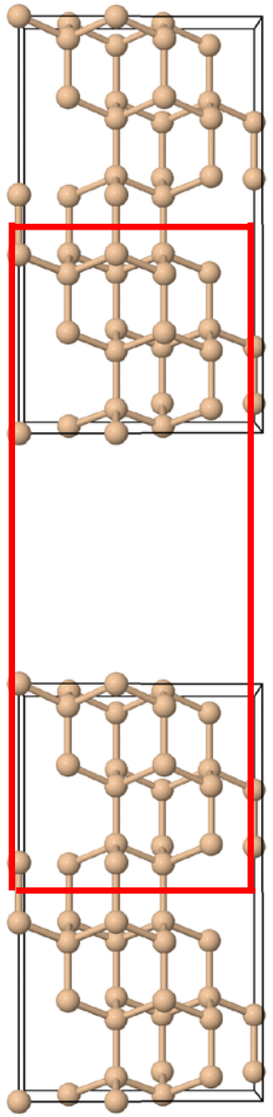
$$\gamma_{Surface} = \frac{1}{2}\frac{(E^{(DFT)} - N\mu)}{area}$$

$E^{(DFT)}$: Energy of DFT slab calculation

N : Number of atoms in slab

μ : Chemical potential of material

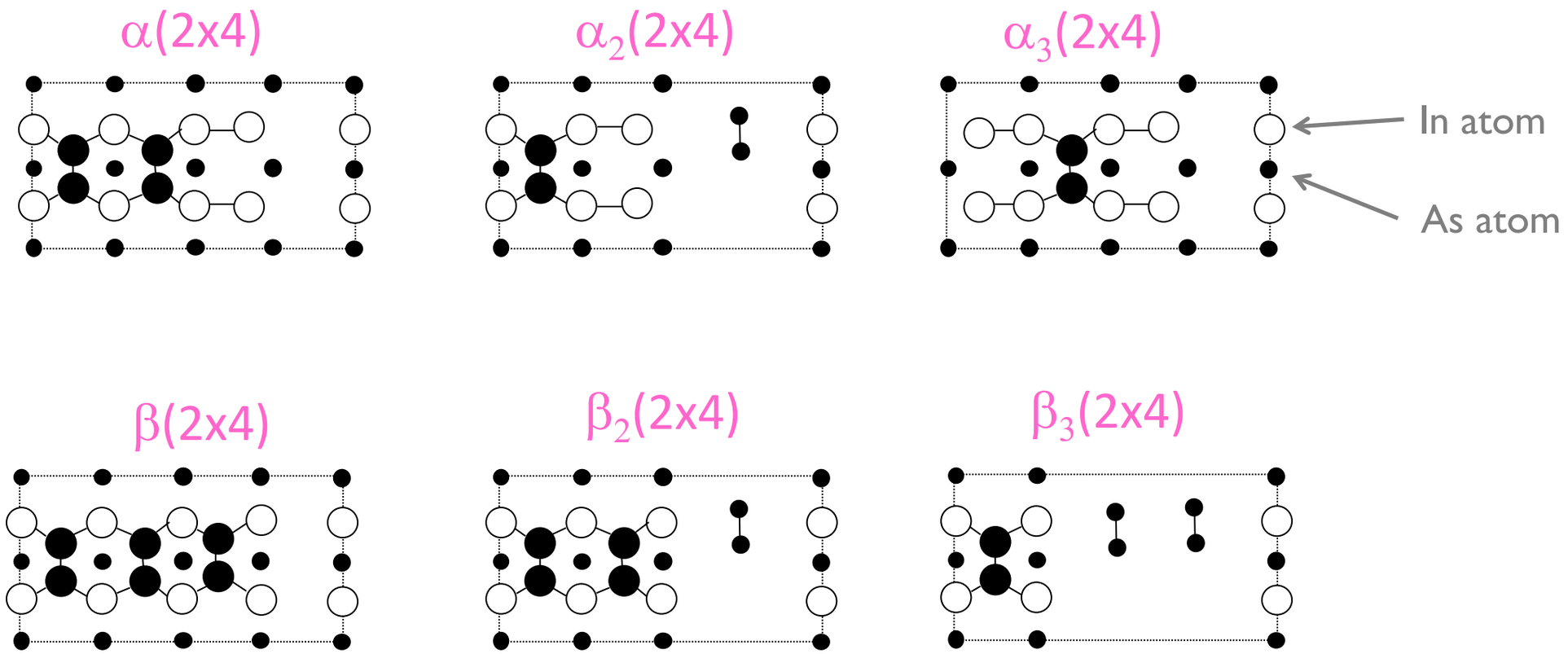




Ab-Initio Thermodynamics to Calculate Surface Energies

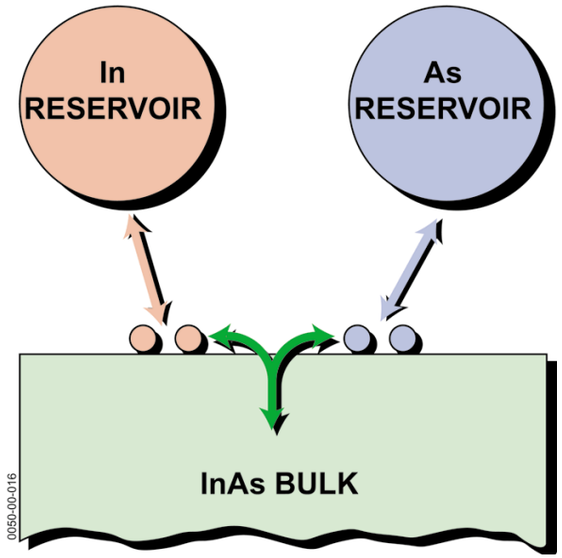
For systems that have multiple species, things are more complicated, because of varying stoichiometries

Example: Possible surface structures for InAs(001)



Surface Energy for InAs(100)

$$\gamma_{InAs-Surface} = E^{(DFT)}_{InAs-slab} - N_{In}\mu_{In} - N_{As}\mu_{As}$$



with $\mu_i \le \mu_i^{(bulk)}$

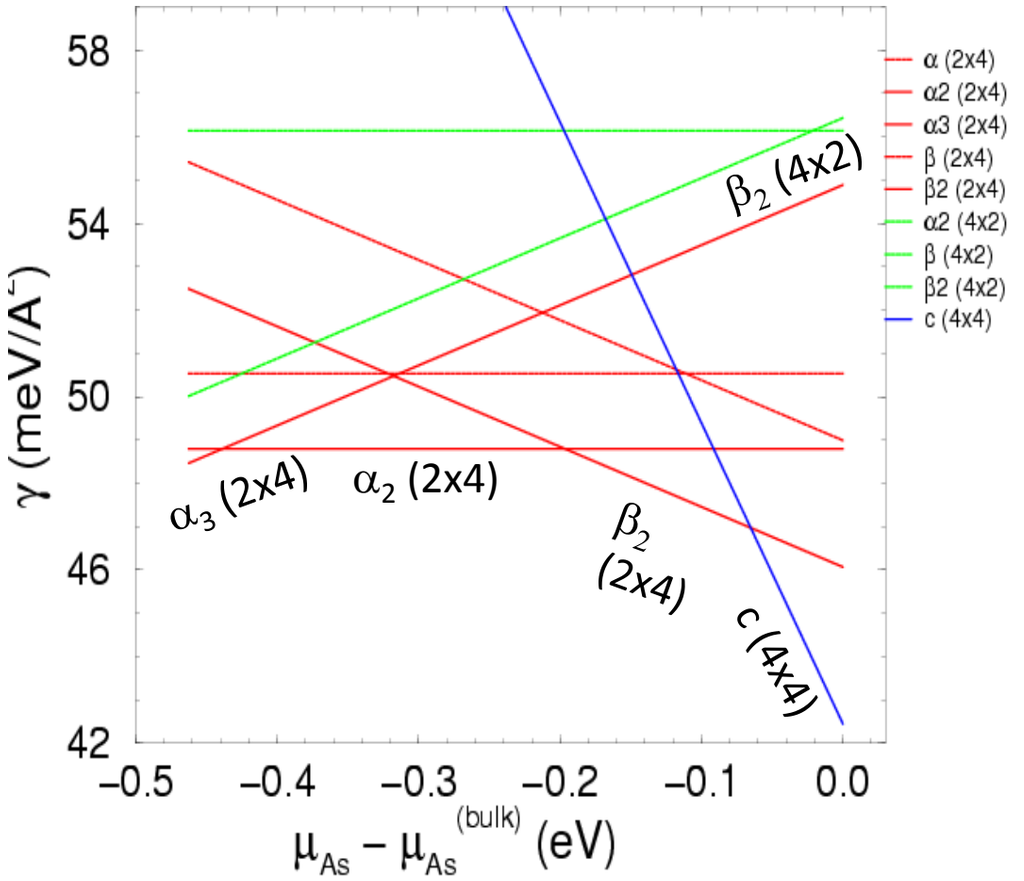
Equilibrium condition:

$$\mu_{In} + \mu_{As} = \mu_{InAs} = \mu^{(bulk)}_{InAs}$$

This can be re-written as:

$$\gamma_{InAs-Surface} = E^{(DFT)}_{InAs-slab} - N_{In}\mu_{InAs} - (N_{As} - N_{In})\mu_{As}$$

with $\mu^{(bulk)}_{InAs} - \mu^{(bulk)}_{In} \le \mu_{As} \le \mu^{(bulk)}_{As}$



Conclusions

Thank you for your attention!!