

# Electronic structure of solids: basic concepts and methods

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# Outline

A bit of formal mathematics for the beginning

Describing electronic states in a periodic system

Band structure of crystals: concepts and definitions

Electronic structure calculations: How to do it, what to expect

## Outline

## A bit of formal mathematics for the beginning

# Translation periodicity

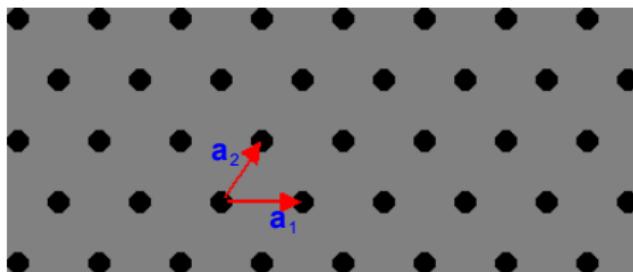
Primitive translation vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ :

Any translation can be written as

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

A set of all translations forms a lattice:

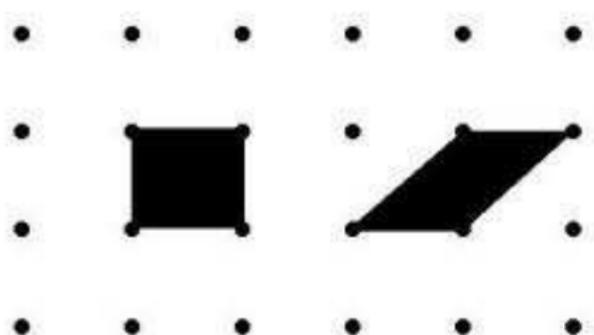
$$\mathbf{R}_i = \sum_i \left[ n_1^{(i)}\mathbf{a}_1 + n_2^{(i)}\mathbf{a}_2 + n_3^{(i)}\mathbf{a}_3 \right] .$$



## Primitive cell

**Primitive cell:** Tiny box chosen so that when stacked one next to another, the space is filled.

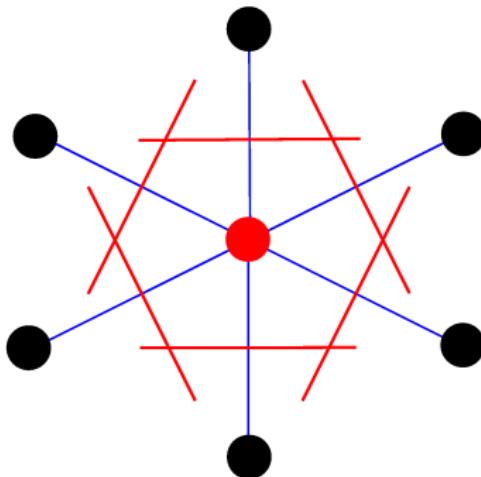
The primitive cell is *not uniquely defined*:



In praxis, we rely on **conventions**.

## Wigner-Seitz cell

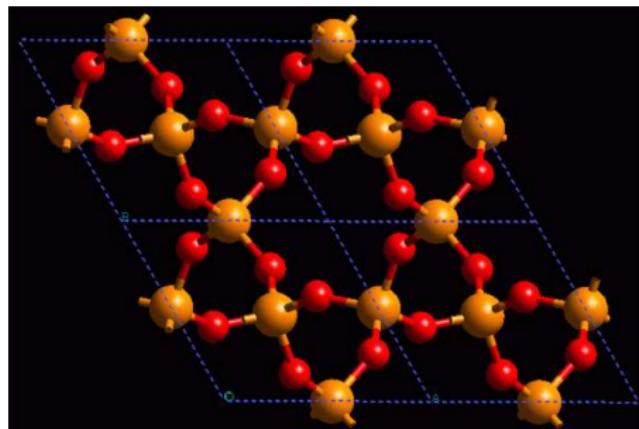
Wigner-Seitz cell: Region in space that is closer to a fixed lattice point than to any of the other lattice points.



Wigner-Seitz cell is a primitive cell. It is defined uniquely.

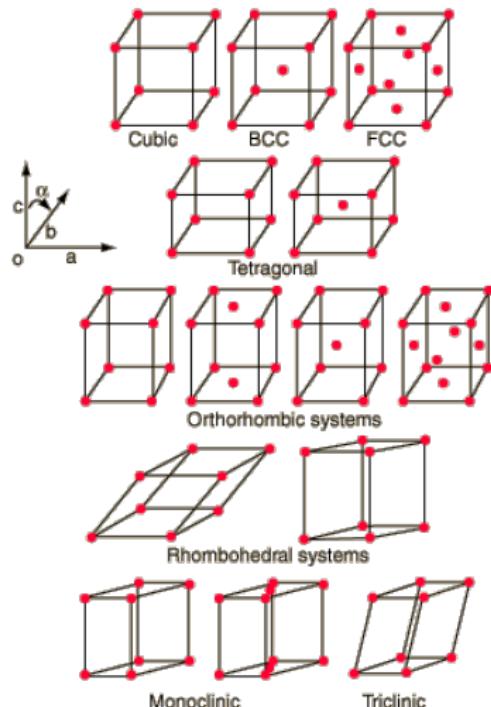
# Lattice vectors, basis

- ▶ Crystal structure =  
(Bravais) lattice + basis
  
- ▶ Symmetry of a crystal:
  - ▶ Translation symmetry
  - ▶ Point symmetry  
(rotations, reflections,  
inversions)



When dealing with formal matters in this talk, we will **focus on translation symmetry** only.

# Bravais lattices, space groups



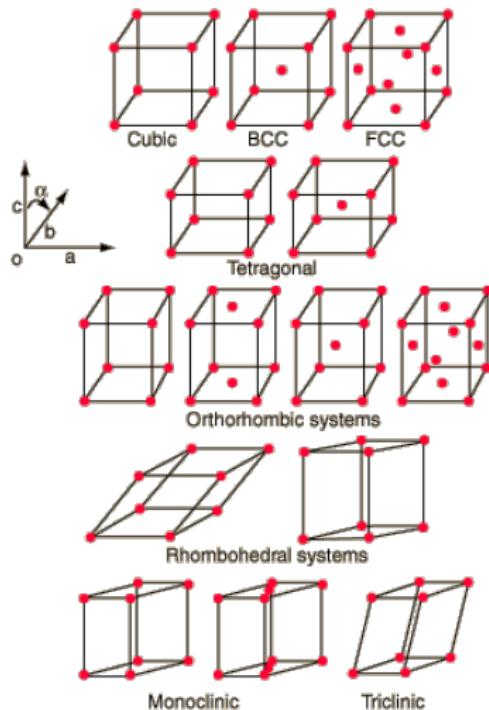
## 14 Bravais lattices:

Translations & operations that leave a particular point of the lattice fixed, assuming a *spherically symmetric basis*.

## 230 space groups:

Translations & operations that leave a particular point of the lattice fixed, assuming a *basis of arbitrary symmetry*.

# Bravais lattices, space groups



## 14 Bravais lattices:

Translations & operations that leave a particular point of the lattice fixed, assuming a *spherically symmetric basis*.

## 230 space groups:

Translations & operations that leave a particular point of the lattice fixed, assuming a *basis of arbitrary symmetry*.

Some of the **conventional unit cells** are not primitive cells (e.g. fcc, bcc). Different conventions, confusion is possible (probable).

## Representation of functions: *the basis*

Quantum states are represented by integrable (“normalizable”) functions. Integrable functions form a vector space.

Any vector can be expressed as a linear combination of a basis vectors.

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Any vector can be expressed as a linear combination of a basis vectors.

Fourier transformation: Plane waves  $e^{ik \cdot r}$  form a basis set in a space of functions integrable in a volume  $V$ :

$$f(\mathbf{r}) = \int_V d\mathbf{k} f(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} ,$$

expansion coefficients are the Fourier components

$$f(\mathbf{k}) = \frac{1}{V} \int_V d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} .$$

If no other requirements are laid on  $f(\mathbf{r})$ , this basis is continuous (integral instead of sum).

## Reciprocal lattice

For a given Bravais lattice  $\{\mathbf{R}_i\}$ , some plane waves  $e^{i\mathbf{k}\cdot\mathbf{r}}$  will have **the same periodicity** as this lattice, i.e., their wave vector  $\mathbf{k}$  is such that

$$e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{k}\cdot\mathbf{r}} \Leftrightarrow e^{i\mathbf{k}\cdot\mathbf{R}} = 1 .$$

Set of all such wave vectors  $\{\mathbf{K}_i\}$  forms a lattice in the  $\mathbf{k}$ -space. This lattice is called **reciprocal lattice**.

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Set of all such wave vectors  $\{\mathbf{K}_i\}$  forms a lattice in the  $\mathbf{k}$ -space. This lattice is called **reciprocal lattice**.

Any vector  $\mathbf{K}$  of the reciprocal lattice can be written as

$$\mathbf{K} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 ,$$

where the basis vectors of the reciprocal lattice  $\mathbf{b}_i$  are related to the basis vectors of the Bravais lattice  $\mathbf{a}_i$  via

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} .$$

## Functions with the periodicity of the lattice

If a function  $f(\mathbf{r})$  has the same periodicity as the lattice  $\{\mathbf{R}_i\}$ , only those components  $f(\mathbf{k})$  of its Fourier expansion are non-zero which correspond to reciprocal lattice vectors,  $\mathbf{k} \in \{\mathbf{K}_i\}$ ,

$$f(\mathbf{r}) = \int_V d\mathbf{k} f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad \longrightarrow \quad f(\mathbf{r}) = \sum_{\mathbf{K}} f(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}} .$$

To represent a function with the periodicity of the lattice, it is sufficient to take a **discrete sum**, with one term per each reciprocal lattice vector.  
(Otherwise, we would have a continuous subscript  $\mathbf{k}$ .)

Reciprocal lattice can be viewed as image of the Bravais lattice in the momentum space.

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## Quantum states for a periodic potential

The potential  $V(\mathbf{r})$  has the periodicity of the crystal:

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

Looking for a solution of a Schrödinger equation for an **electron in a periodic potential**:

$$\hat{H} \psi_i(\mathbf{r}) = \left[ \frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) .$$

Solutions  $\psi_i(\mathbf{r})$  *need not* have translational periodicity !

Recall: Solutions of Schrödinger equation in a spherically symmetric potential  $\psi_i(\mathbf{r}) = R_{nl} Y_{\ell m}(\hat{\mathbf{r}})$  are not spherically symmetric either.

# Finding the right quantum numbers

- ▶ How to find a complete set of solutions  $\psi_i(\mathbf{r})$  ?

$$|\psi\rangle = \sum_i |\psi_i\rangle$$

$$\langle \mathbf{r} | \psi \rangle = \sum_i \langle \mathbf{r} | \psi_i \rangle$$

$$\psi(\mathbf{r}) = \sum_i \psi_i(\mathbf{r})$$

- ▶ Good quantum numbers are eigenvalues of operators which commute with the Hamiltonian; then we can have wave functions which are simultaneously eigenvectors of the Hamiltonian and of those additional operators.
  - ▶ Recall: In case of spherical symmetric potential,  $\hat{H}$  commutes with  $\hat{L}^2$  and with  $\hat{L}_z$ , therefore we have quantum numbers  $\ell$  and  $m$ .

## The right symmetry operator for a crystal

- ▶ For a crystal, hamiltonian commutes with the translation operator  $T_{\mathbf{R}}$ , which is defined as

$$\hat{T}_{\mathbf{R}} \psi(\mathbf{r}) := \psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r} + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3) .$$

Translation  $T_{\mathbf{R}}$  leaves the Hamiltonian  $\hat{H}$  unchanged.

Suitable set of complete state vectors:

set of vectors which are simultaneously eigenvectors of the Hamiltonian operator  $H$  and of the transitions operator  $T_{\mathbf{R}}$ .

## Bloch theorem (1)

Eigenstates of Hamiltonian can be chosen with a definite value of the translation operator  $\hat{T}_{\mathbf{R}}$ , which can then be used to identify them.

Eigenvalues  $t_{\mathbf{R}}$  of the  $\hat{T}_{\mathbf{R}}$  operator:

$$\hat{T}_{\mathbf{R}} \psi(\mathbf{r}) = t_{\mathbf{R}} \psi(\mathbf{r}) .$$

By using **group properties of translations** and requiring that the wave function does not diverge, one gets

$$t_{\mathbf{R}} = e^{i\mathbf{k}\cdot\mathbf{R}} .$$

**Bloch theorem:**

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi(\mathbf{r}) .$$

## Bloch theorem (2)

Equivalent formulation: for a periodic potential, wave functions can be written as

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

where  $u_{\mathbf{k}}^n(\mathbf{r})$  has the periodicity of the crystal:

$$u_{\mathbf{k}}^n(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}^n(\mathbf{r}) .$$

Eigenstates with same eigenvalues of the translation operator  $\hat{T}_{\mathbf{R}}$  but different energies are distinguished by an **additional index  $n$** .

Analogy:

For an electron in a spherically symmetric potential, there is also a “**principal quantum number**”  $n$  apart from the  $\ell$  and  $m$  values (we have got  **$2p$**  states,  **$3p$**  states,  **$4p$**  states, ...).

## Band structure: Bands of eigenvalues $\varepsilon_{\mathbf{k}}^n$

Wave function  $\psi_{\mathbf{k}}^n(\mathbf{r})$  corresponds to energy  $\varepsilon_{\mathbf{k}}^n$ , i.e.,

$$\hat{H} \psi_{\mathbf{k}}^n(\mathbf{r}) = \varepsilon_{\mathbf{k}}^n \psi_{\mathbf{k}}^n(\mathbf{r}) .$$

Reminder:  $\mathbf{k}$  is linked to eigenvalues of translation operators  $\hat{T}_{\mathbf{R}}$ .

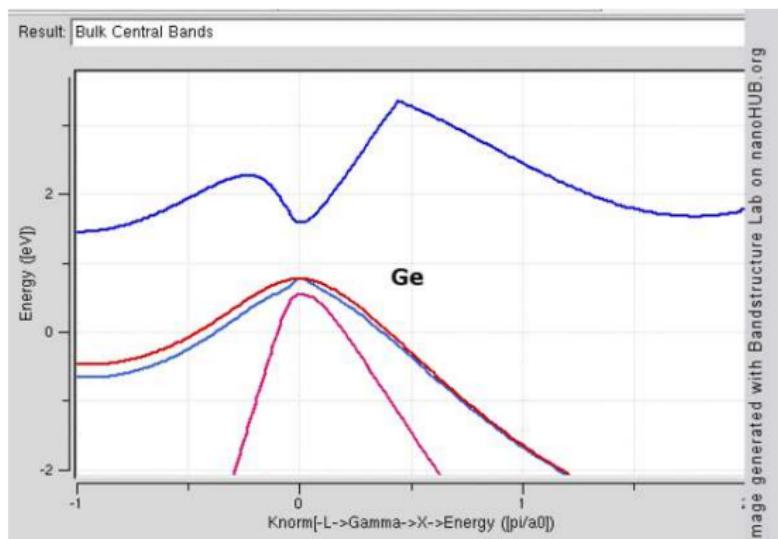
For macroscopic ("infinitely large") crystal, the wave vector  $\mathbf{k}$  is a continuous variable.

For each  $\mathbf{k}$  there is a discrete set of eigenstates labeled by the index  $n$ .

We have thus bands of energy eigenvalues  $\varepsilon_{\mathbf{k}}^n$ , for each  $n$  there is one band.

## Bands of eigenvalues $\varepsilon_{\mathbf{k}}^n$ : Example

For each  $\mathbf{k}$  there is a discrete set of eigenstates labeled by the index  $n$ .



<http://en.wikipedia.org/wiki/File:Bulkbandstructure.gif>

## Range of values of the quantum number $\mathbf{k}$

The quantum number  $\mathbf{k}$  is not uniquely defined.

Recall: if  $\mathbf{R}$  is a lattice vector and  $\mathbf{K}$  is a reciprocal lattice vector, then  $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ .

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}} e^{i\mathbf{K}\cdot\mathbf{R}} \psi(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}} \psi(\mathbf{r})$$

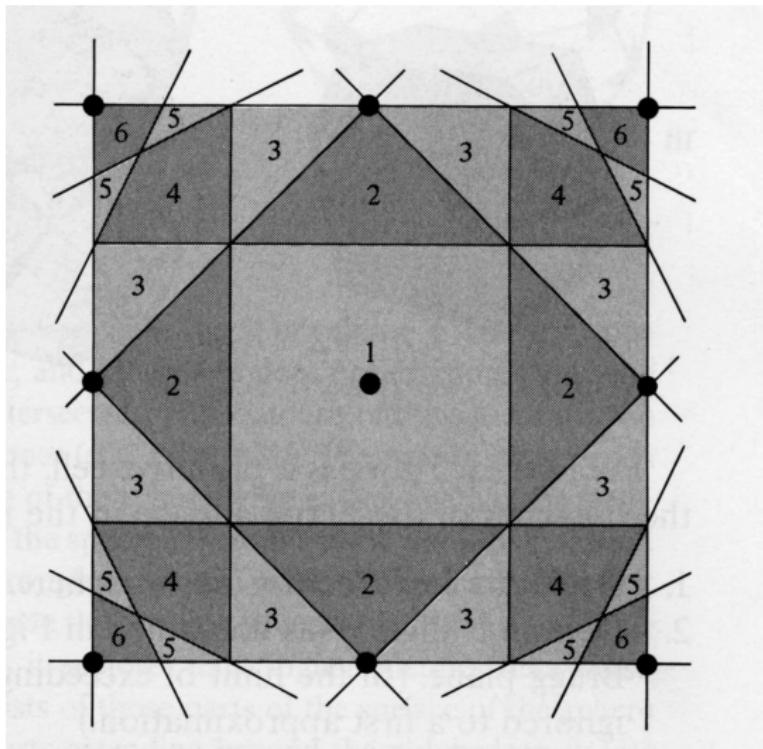
$\Rightarrow \mathbf{k}$  can be substituted by  $\mathbf{k}' = \mathbf{k} + \mathbf{K}$ , where  $\mathbf{K}$  is a reciprocal lattice vector.

In this way, the wave vector  $\mathbf{k}$  can be confined to a single primitive cell in the reciprocal space.

Conveniently (and conventionally), we use the Wigner-Seitz cell for this primitive cell in the reciprocal space. This cell is called the **first Brillouin zone**.

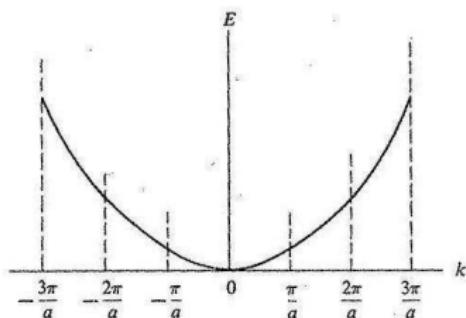
# More on Brillouin zones

Analogously to the first Brillouin zone (BZ), one can define second, third, forth, ... Brillouin zones.

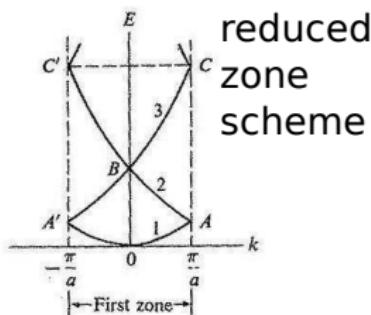


# Reduced, extended, repeated zone scheme

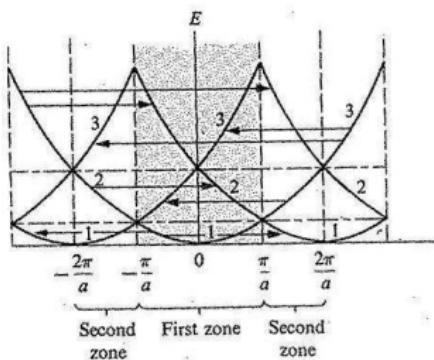
$\mathbf{k}$  is not unique  $\Rightarrow$  more equivalent ways to describe the band structure



repeated  
zone scheme



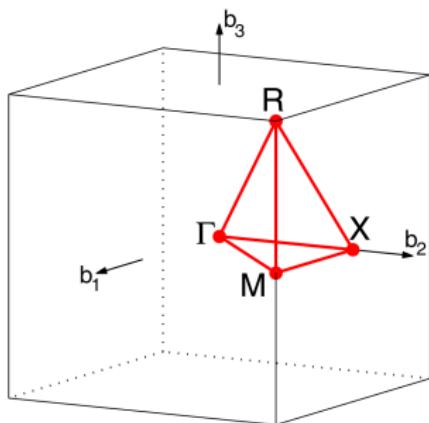
reduced  
zone  
scheme



repeated  
zone scheme

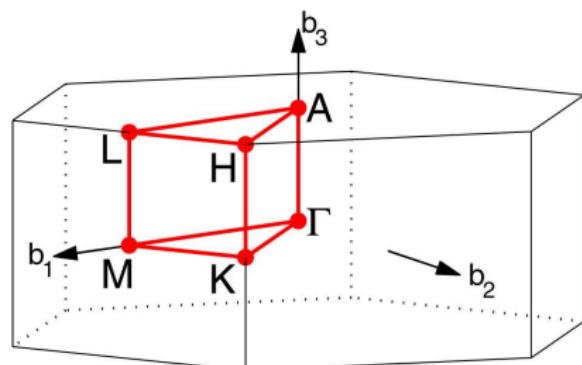
# Naming conventions

Some points in the Brillouin zone are given special “names”. Band-structure is usually shown along lines connecting these points.



CUB path:  $\Gamma$ -X-M- $\Gamma$ -R-X|M-R

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]



HEX path:  $\Gamma$ -M-K- $\Gamma$ -A-L-H-A|L-M||K-H

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

No science or mystique, just naming convention...

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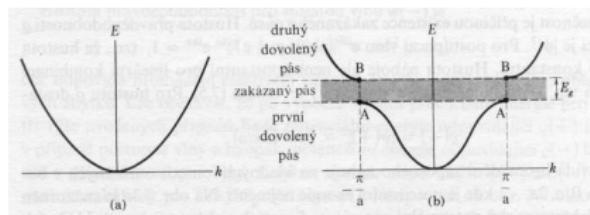
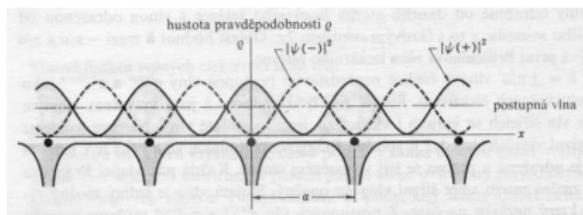
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# BZ boundary is the space to watch...

Plane waves with wave vector  $\mathbf{k}$  at BZ boundary satisfy the Bragg condition, so they will undergo subsequent reflections.



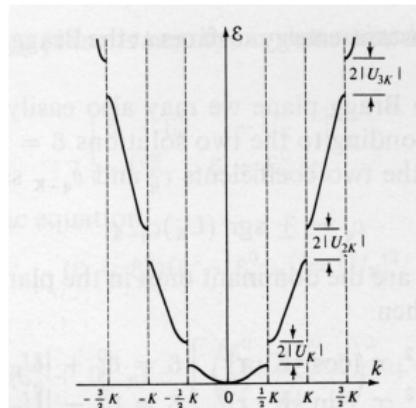
Kittel: Introduction to Solid State Physics

Bragg reflections at BZ boundary  
will make standing waves.

Waves  $\psi(+)$  and  $\psi(-)$  generate different charge distributions, these will lead to two different potential energies due to different repulsion from the ions.

The energy difference between the standing waves  $\psi(+)$  and  $\psi(-)$  is the origin to the energy gap  $E_g$ .

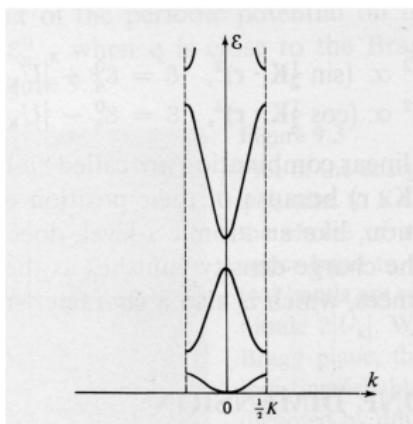
# Band structure of nearly free electrons



Energy of free electrons:

$$\epsilon_{\mathbf{k}}^n = \frac{\hbar^2}{2m} \mathbf{k}^2 .$$

If the crystal potential is weak,  $\epsilon_{\mathbf{k}}^n$  differs only slightly from the free electron case.

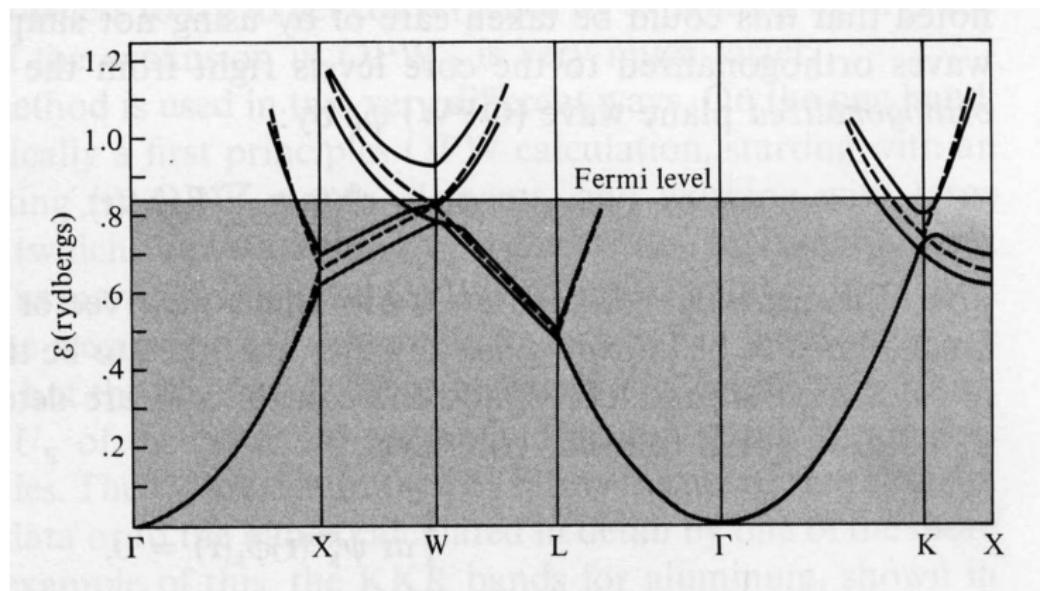


Main effects of the crystal potential:

1. The band structure can be folded into the first BZ.
2. At BZ boundaries, minigaps in the energy will appear.

## Real life example: aluminium

Band structure of aluminium is very close to free electron case.



Full lines represent energy band of aluminium, dashed lines represent energy bands of a free electron.

## Density of states (1)

How to sum over all electron states?

For systems with discrete energy levels:

Total energy  $E_{\text{TOT}}$  is obtained by a **sum** of energies  $\varepsilon_i$  over all the occupied states,

$$E_{\text{TOT}} = \sum_i 2\varepsilon_i$$

(the factor 2 accounts for spin degeneracy).

## Density of states (2)

For system with continuous energy levels:

Total energy  $E_{\text{TOT}}$  is obtained as an **integral**, weighting the energy  $\varepsilon$  by the density of states  $n(\varepsilon)$

$$E_{\text{TOT}} = \int d\varepsilon \varepsilon n(\varepsilon) .$$

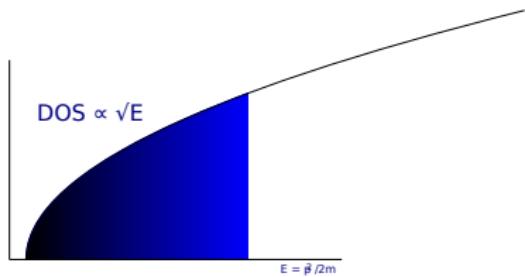
Intuitively:

Density of state (DOS) describes **how many electron states** are there **at certain energy**  $\varepsilon$ .

Formally:

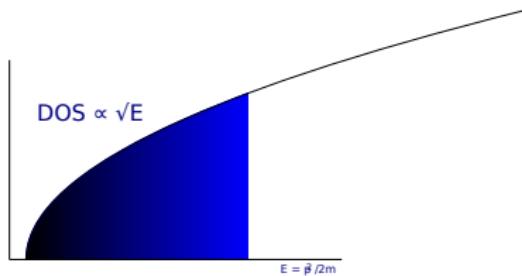
$$n(\varepsilon) = \sum_n \int_{1\text{BZ}} \frac{d\mathbf{k}}{4\pi} \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n) .$$

# Aluminium again

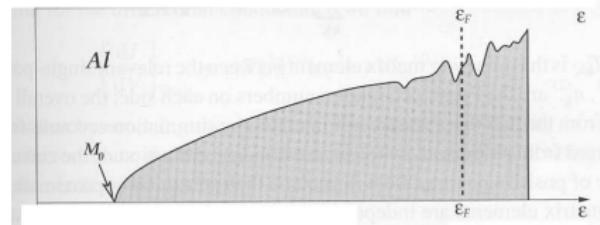


Free electrons: Density of states  
is proportional to  $\sqrt{\varepsilon}$ .

# Aluminium again

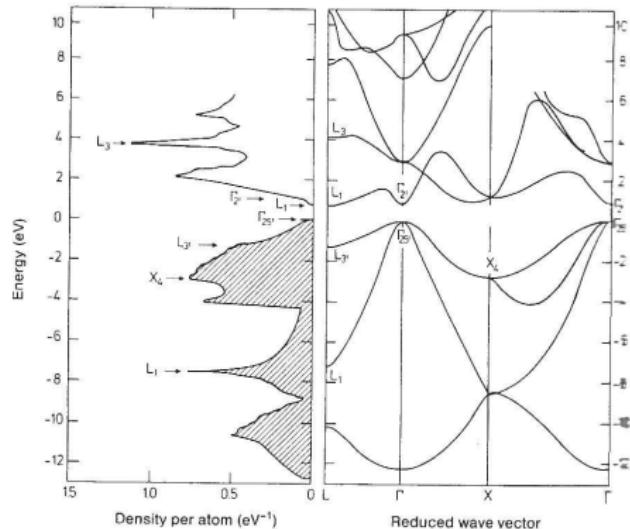


Free electrons: Density of states is proportional to  $\sqrt{\epsilon}$ .



Aluminium: its nearly free electron character gets revealed also in the DOS.

# Band structure and DOS



$$\begin{aligned} n(\varepsilon) &= \sum_n \int_{1\text{BZ}} \frac{d\mathbf{k}}{4\pi} \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n) \\ &= \sum_n \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{\nabla \varepsilon_{\mathbf{k}}^n} \end{aligned}$$

States with small  $\nabla \varepsilon_{\mathbf{k}}^n$  correspond to high DOS.

Peaks in DOS can be traced to local extrema of the band structure  $\varepsilon_{\mathbf{k}}^n$ .

## Local density of states

Intuitively: Local density of states (LDOS) at  $\mathbf{r}$  is

- ▶ the density of states with energy  $\varepsilon$  which results exclusively from electron states at site  $\mathbf{r}$ ,
- ▶ the electron density at site  $\mathbf{r}$  which results exclusively from states with energy  $\varepsilon$ .

$$\text{DOS} \quad n(\varepsilon) = \sum_n \int_{\text{1BZ}} \frac{d\mathbf{k}}{4\pi} \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

$$\text{LDOS} \quad n(\mathbf{r}, \varepsilon) = \sum_n \int_{\text{1BZ}} \frac{d\mathbf{k}}{4\pi} |\psi_{\mathbf{k}}^n(\mathbf{r})|^2 \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

Integral of  $n(\mathbf{r}, \varepsilon)$  over the unit cell gives total DOS  $n(\varepsilon)$ .

LDOS reflects the spatial inhomogeneity of electronic structure in a solid.

## Bloch spectral function $A(\mathbf{k}, \varepsilon)$

On a half-way between band structure  $\varepsilon_{\mathbf{k}}^n$  and the density of states  $n(\varepsilon)$ .

$$n(\varepsilon) = \sum_n \int_{1\text{BZ}} \frac{d\mathbf{k}}{4\pi} \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

$$n(\varepsilon) = \int_{1\text{BZ}} \frac{d\mathbf{k}}{4\pi} \sum_n \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

$$n(\varepsilon) = \int_{1\text{BZ}} \frac{d\mathbf{k}}{4\pi} A(\mathbf{k}, \varepsilon)$$

Bloch spectral function  $A(\mathbf{k}, \varepsilon)$  can be interpreted as a  $\mathbf{k}$ -resolved DOS.

$$A(\mathbf{k}, \varepsilon) = \sum_n \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

$$A(\mathbf{k}, \varepsilon, \mathbf{r}) = \sum_n |\psi_{\mathbf{k}}^n(\mathbf{r})|^2 \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

## Crystal momentum $\mathbf{k}$

Bloch wave functions  $\psi_{\mathbf{k}}^n(\mathbf{r})$  are not eigenvectors of the momentum operator: Momentum is conserved only if there is a full translation invariance, here we have only invariance w.r.t. lattice translations  $\{\mathbf{R}_i\}$ .

## Crystal momentum $\mathbf{k}$

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However,  $\psi_{\mathbf{k}}^n(\mathbf{r})$  are eigenvectors of the translation operator  $\hat{T}_{\mathbf{R}}$ :

$$\hat{T}_{\mathbf{R}} \psi_{\mathbf{k}}^n(\mathbf{r}) \equiv \psi_{\mathbf{k}}^n(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}^n(\mathbf{r}) .$$

Corresponding conserved quantity is the **crystal momentum**  $\hbar\mathbf{k}$ .

Recall: States described by  $\mathbf{k}$  can be described also by  $\mathbf{k}+\mathbf{K}$ , so  $\mathbf{k}$  can be always restricted to the first BZ.

$\mathbf{k}$  is conserved **up to a reciprocal lattice vector**.

*Crystal momentum  $\hbar\mathbf{k}$  is an analogy to the momentum  $\mathbf{p}$  but it is not the same.*

## Occupied and unoccupied states

Pauli exclusion principle: Electrons are **fermions**, so there can be only one electron per state.

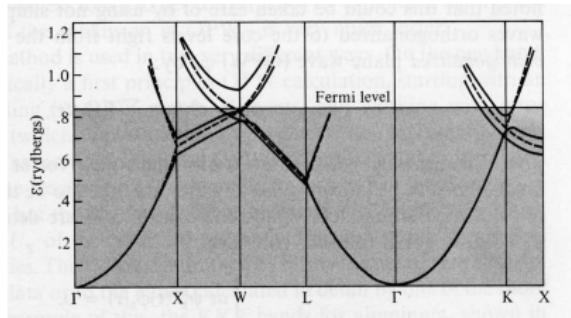
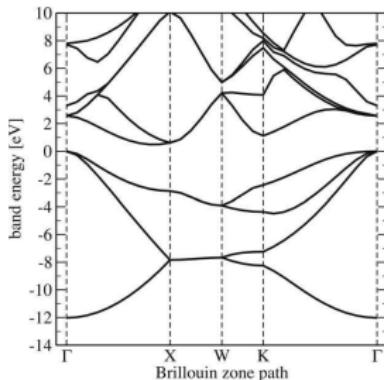
Spin degeneracy means that a state represented by particular  $n$  and  $\mathbf{k}$  can be occupied by two electrons at most.

In the ground state, electron states are being populated from bottom up. Energy levels  $\varepsilon_{\mathbf{k}}^n$  will be **occupied below** a certain energy and **unoccupied above** it.

In metals, this energy is called **Fermi energy**.

In molecules, it is called HOMO (highest occupied molecular orbital).

# Band gap (1)

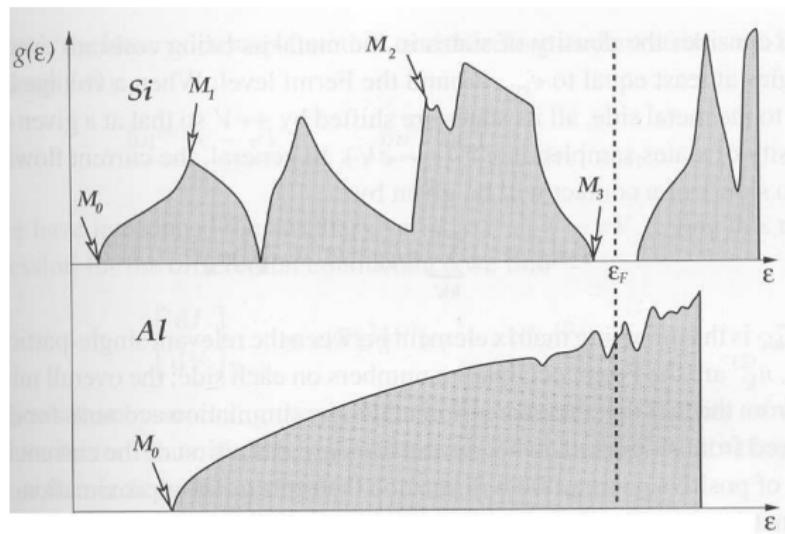


Band structure of silicon:  
for some energies, there  
are no corresponding  
states  $\Rightarrow$  energy gap.

Band structure of aluminium: for each  
energy there is a state  $\Rightarrow$  no band gap.

## Band gap (2)

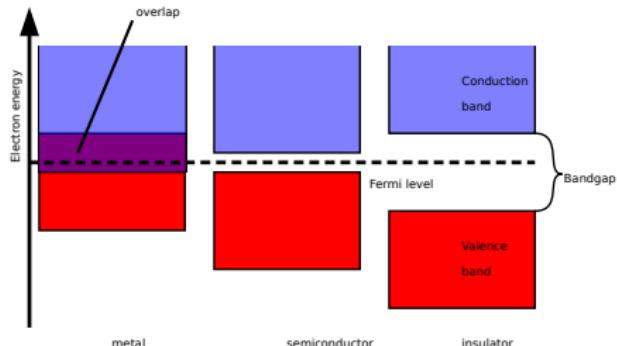
Density of states:



Si  
gap is present

Al  
no gap

# Metals and insulators



**Metals:** The border between occupied and unoccupied states goes through a band  $\Rightarrow$  infinitesimal energy is enough to excite the system.

**Insulators:** There is a completely filled band, then is an energy gap, then come empty bands  $\Rightarrow$  the energy gap has to be overcome to excite the system.

**Semiconductors:** the gap is small ( $\sim 1$  eV) and impurities “contaminate” it with additional energy levels.

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## What is knowing the band structure good for?

Solid material is a mixture of ions and electrons.

Electrons act as glue that keeps the material together.

Properties of the electron glue determine to large extent the properties of solids.

Ab-initio calculations of total energies: given just atomic numbers of constituting atoms, structure and properties of solids can be predicted.

# Model Hamiltonian or ab-initio ?

It depends...

**Model Hamiltonian:** All many body physics is in it. However, it has to be simplified so that it can be solved and the parameters have to be obtained by fits — it is not materially-specific. It can help us, though, to understand the principles.

**Ab-initio calculations:** Many-body physics has to be included in a simplified (mean-field) way. However, it is materially specific — it can be predictive !  
(Recall this during the talk on DFT on 4th November.)

## Finding $\psi_{\mathbf{k}}^n(\mathbf{r})$ , $\varepsilon_{\mathbf{k}}^n$ , and $V(\mathbf{r})$

We need to solve the Schrödinger equation for an electron in a given potential  $V(\mathbf{r})$ .

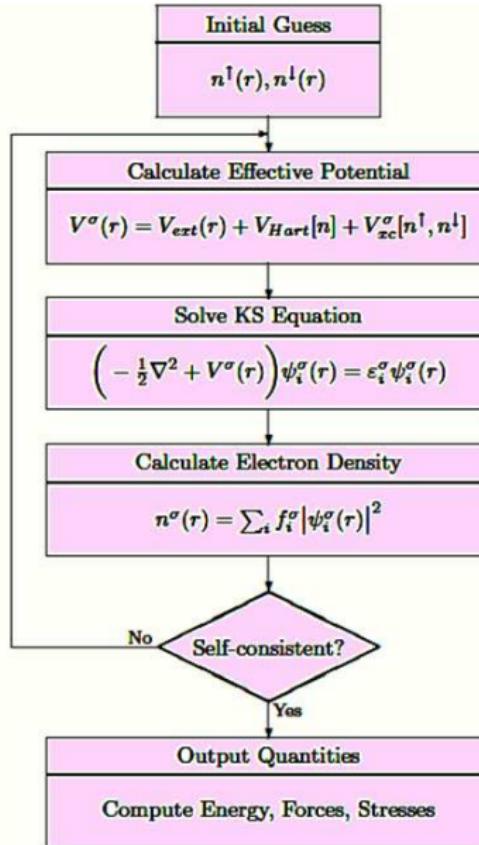
Wave functions  $\psi_{\mathbf{k}}^n(\mathbf{r})$  determine the electron density  $n(\mathbf{r})$ , electron density determines the potential  $V(\mathbf{r})$  potential  $V(\mathbf{r})$ .

The potential  $V(\mathbf{r})$  determines the wave functions  $\psi_{\mathbf{k}}^n(\mathbf{r})$ .

→ Need for **self-consistency** between  $V(\mathbf{r})$  and  $\psi_{\mathbf{k}}^n(\mathbf{r})$ .

Compare with the lecture on DFT and LDA on 4th November.

# Self-consistent scheme: $\psi_{\mathbf{k}}^n(\mathbf{r}) \Leftrightarrow V(\mathbf{r})$



# How to solve Schrödinger equation (1)

Solving Schrödinger equation numerically in 3D is a killer.

The way to proceed: Transform it into a matrix equation, using a suitable basis.

(Okay, there are other ways as well, e.g., the KKR and/or Green's function method.)

## How to solve Schrödinger equation (2)

Having a complete set of orthogonal functions  $\{\phi_i(\mathbf{r})\}$ , any function  $\psi(\mathbf{r})$  can be written as  $\psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$ .

Then, instead of

$$\hat{H} \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

we can solve

$$\sum_j H_{ij} a_j = \varepsilon a_i$$

with matrix elements  $H_{ij}$

$$H_{ij} := \langle \phi_i | \hat{H} | \phi_j \rangle = \int d\mathbf{r} \phi_i^*(\mathbf{r}) H(\mathbf{r}) \phi_j(\mathbf{r}) .$$

Matrix diagonalization is a **computer-friendly task**.

**Caveat:** The sum  $\sum_j$  is infinite (may even be continuous. . . ).

## How to solve Schrödinger equation (3)

Using a basis set  $\{\phi_i(\mathbf{r})\}$ , we have to find eigenvectors and eigenvalues of an infinite matrix,

$$\sum_j H_{ij} a_j = \varepsilon a_i .$$

The trick:

Choose the basis functions  $\{\phi_i(\mathbf{r})\}$  conveniently, so that only a finite (and small) number of them describes the problem with sufficient accuracy.

The choice of  $\{\phi_i(\mathbf{r})\}$  thus depends on what kind of system and what kind of property we are interested in.

# Which band structure method ?

We need to tailor our method to the problem.

There are **no “universal” methods** except for very simple problems (that need not be solved).

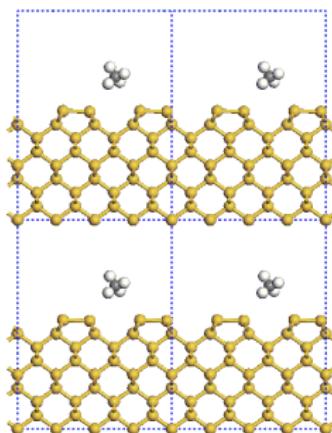
Criteria governing which method to choose:

- ▶ Metal or insulator? Covalent or ionic?
- ▶ Electron states localized or extended?
- ▶ High-symmetry or low-symmetry system? Layered?
- ▶ Ordered or disordered?
- ▶ Interested in ground-state or in excited state (spectroscopy)?
- ▶ ...

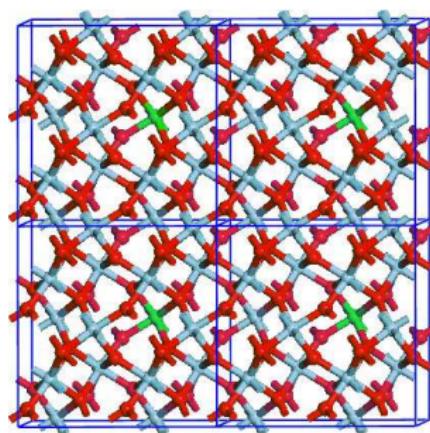
# Dealing with surfaces: Supercell calculations

Create a surface “artificially”, by forcing a periodicity to the system.

Advantage: Using all the polished tools of bulk calculations.



simulating adsorbate



simulating substitutional impurity

# Zoology of band structure methods (and codes)

- ▶ **All-electron** methods

Core and valence electrons are dealt with on the same footing.

- ▶ Augmented functions

- ▶ FLAPW (FLEUR, WIEN2K, ELK)
- ▶ KKR-GF (groups in Jülich, Osaka, Ames, FEFF)
- ▶ LMTO (Stuttgart, Turek and Kudrnovský in Prague)

- ▶ Localized orbitals

- ▶ LCAO (CRYSTAL)

- ▶ **Pseudopotential** methods

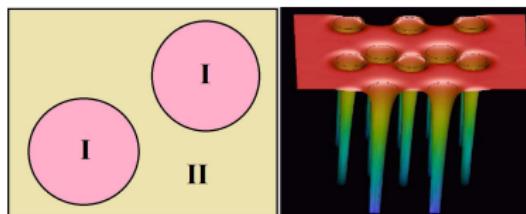
Core electrons are (semi-)ignored — they are effectively merged with the nucleus.

- ▶ Plane waves (ABINIT, QUANTUM ESPRESSO, VASP, CASTEP)
- ▶ LCAO (SIESTA)

“Method” and “code” are (unfortunately) often used interchangeably.

# FLAPW method

Full potential Linearized Augmented Plane Waves method.  
Considered (by some) to be the most accurate method.



Basis is made of augmented plane waves

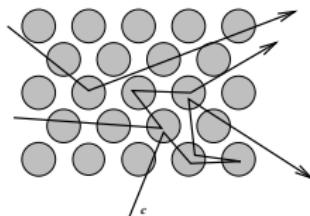
$$\text{muffin-tin spheres: } \phi(\mathbf{r}) \sim \sum_{\ell m} a_{\ell m} R_{\ell}(\mathbf{r}) Y_{\ell m}(\mathbf{r})$$

$$\text{interstitial region: } \phi(\mathbf{r}) \sim e^{i\mathbf{k}\mathbf{r}}$$

- ▶ Linearized method, same basis for each energy, Taylor expansion around the middle of the valence band
- ▶ Accurate
- ▶ Computer demanding, relatively slow

# KKR-Green's function method

Korringa-Kohn-Rostoker a.k.a. multiple-scattering method.



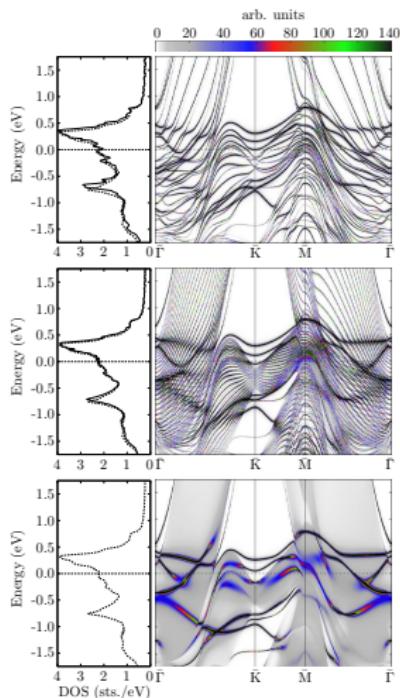
Reformulated version as a KKR-Green's function method.  
It is *not* a variational method.

It is not a linearized method:

- ▶ It is exact (specifically also concerning charge densities). However, for energies and consequently also atomic geometries accuracy of linearized methods is sufficient.
  - ▶ It is relatively slow and somewhat cumbersome.
- 
- ▶ Green's function → naturally suited for spectroscopy.
  - ▶ Green's function → naturally suited for many-body physics.
  - ▶ Efficient when treating surfaces, adsorbates, disorder.

# Surfaces via Green's function methods

Proper semi-infinite systems, no supercell.



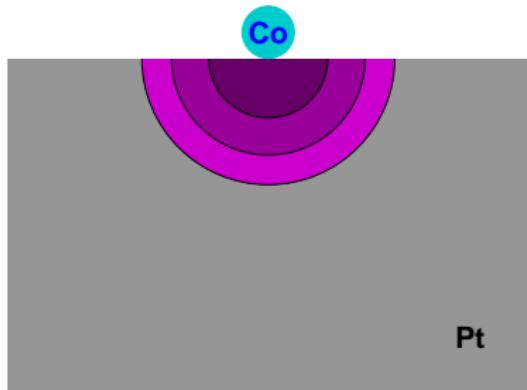
## Bloch spectral function: generalization of the band-structure for non-periodic systems

## Surface of a 14-layers slab.

## Surface of a 38-layers slab.

Surface of a semi-infinite layer.  
Only true surface states and resonances remain, **no spurious bands**.

# Adsorbates and impurities



Green's function formalism:  
**Embedded cluster** in an  
infinite host.

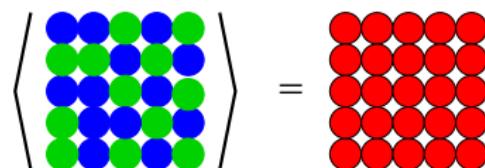
For small impurities such as adatoms, supercells can be used without creating any “issues”.

To deal with clusters of hundreds of atoms, Green's function formalism is more suitable.

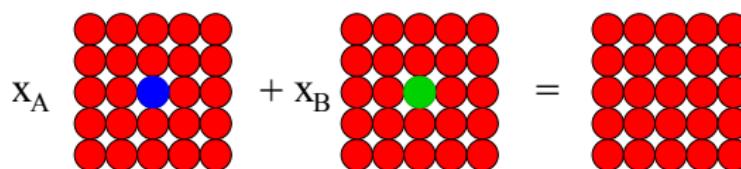
## Dealing with disorder

Disordered systems can be dealt with by averaging over many large supercells, spanning many different local environments.  
→ Accurate and slow.

Mean-field approach: define a suitable effective medium.



Coherent Potential Approximation (CPA) within the Green's function method.



# LMTO method

**Linear combination of Muffin-Tin Orbitals.**

LMTO is linearized version of KKR.

Basis is formed as a combination of solutions of Schrödinger equation inside the muffin-tin sphere.

As usually with linearized methods, it is **tuned to a fixed energy** and Taylor expansion is used around.

Employment of the LMTO method often leads to quick results even for complicated systems.

**Disclaimer:** The LMTO method is a powerful weapon in the hands of a powerful (knowledgeable) person.

# What is pseudopotential?

Operator simulating the effect

of [nucleus + core electrons]

on electronic states

in the energy range of interest

(valence states, unoccupied states — i.e. *not on any state!*)

Requirements, expected properties:

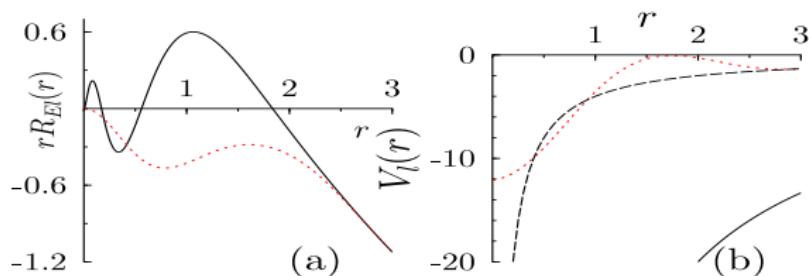
- ▶ Sufficient accuracy in a wide energy range (“transferability”)
- ▶ Real merit to computational efficiency (“softness”)
  - ▶ reducing the size of the basis set
  - ▶ eliminating large energies of the core states

# Constructing a pseudopotential

The calculation can be only as good as the pseudopotential is.

Pseudo-wavefunction is identical to true atomic wave-function outside the core region (for a given  $\ell$  and  $E$ ):

$$\psi_{I,E}^{\text{PS}}(r) \equiv \psi_{I,E}^{\text{true}}(r) \text{ for } r > R_C .$$



Equal scattering properties in the neighbourhood of  $E_{\text{ref}}$  (to the 1-st order).

## Desirable pseudopotential properties (... and problems)

The issue of **transferability**:

Ability to work properly in different environments (e.g., Na can be in metallic Na or in ionic NaCl).

Two main components:

- ▶ Ability to reproduce the scattering properties of an AE potential in some energy interval around  $E_{\text{ref}}$  — ***energy transferability***.
- ▶ Ability to reproduce all-electron eigenvalues under varying external conditions, i.e., under varying charge density — ***environmental transferability*** (among different compounds).

Whether the given pseudopotential is really suitable for the problem we solve is often hard to find out (and usually tacitly ignored).

## Pseudopotentials and plane waves and localized orbitals

Most often, pseudopotentials are used in connection with plane waves codes (because the pseudopotential is weak and only a decent number of plane waves are needed).

Common trick: Use a plane waves pseudopotential code to optimize geometry (quick) and then use a FLAPW code to calculate electronic struture (accurate).

Pseudopotentials can be used also with localized orbitals.

(First use of pseudopotential dates back to Fermi and atoms in 1934.)

# Accuracy of band structure calculations (1)

## Geometry and bulk modulus of bulk systems

	lattice constant [Å]	bulk modulus [Mbar]	
Al	4.01	0.82	theory
	4.03	0.79	experiment
Pd	3.85	2.35	
	3.88	1.95	
Ag	4.00	1.49	
	4.07	1.09	
Si	5.63	0.95	
	5.43	0.99	
Ge	5.63	0.76	
	5.65	0.76	

## Accuracy of band structure calculations (2)

Percentage of interlayer relaxation  $\Delta D_{ij}$  for several close-packed hexagonal metal surfaces

	$\Delta d_{12}$	$\Delta d_{23}$	$\Delta d_{34}$	
Al(111)	+1.35	+0.54	+1.04	theory
	+1.5	+0.5		experiment
Ti(0001)	-6.44	+2.64	0.37	
	-3.5	+1.4	-0.8	
Cu(111)	-1.58	-0.73	-0.43	
	-0.5			
Pd(111)	-0.22	-0.53	-0.33	
	+1.8	-0.3	+1.4	
Pt(111)	+0.88	-0.22	-0.17	
	+1.0			