

# Electronic structure of solids: basic concepts and methods

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Winter Term 2023 - 2024

Troja, 20. October 2023

# Outline

Describing electronic states in a periodic system

Band structure of crystals: concepts and definitions

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

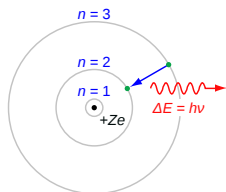
# Outline

Describing electronic states in a periodic system

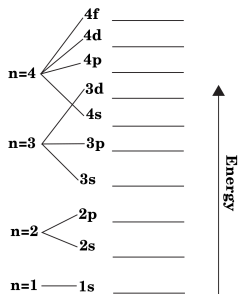
Band structure of crystals: concepts and definitions

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# Electron energy levels in atom (1)



atom is **spherically symmetric**



1s 2s 2p<sub>x</sub> 2p<sub>y</sub> 2p<sub>z</sub>

<https://commons.wikimedia.org>

Electron energy levels  $E_{nl}$ .

Wave functions  $\psi_{nlms}$ .

**Quantum numbers:**

principal	$n$	$1, 2, 3, \dots$
orbital	$l$	$0, 1, 2, \dots$
magnetic	$m$	$-l, \dots, -1, 0, 1, \dots, l$
spin	$s$	$\pm \frac{1}{2}$

Spin operates in another Hilbert space: decoupling of  $s$  from  $n$ ,  $l$  and  $m$ .

## Intermezzo: Why care about quantum numbers? (1)

**Classical mechanics:** state of a system determined by positions and velocities of constituting particles.

**Quantum mechanics:** state of a system represented by a vector in a Hilbert space.

Physical quantities (“observables”) are represented by operators.

Possible outcomes of measuring an observable are the eigenvalues of the respective operator.

A pure quantum state can be characterized by this eigenvalue.

Position and momentum (“velocity”) are observables. Knowing the position or momentum of an electron is equivalent to knowing the eigenvalue of the position operator or of the momentum operator.

## Why care about quantum numbers? (2)

Some operators do not commute. The system cannot be in a state where the respective observables are well-defined: such a state would have to be an eigenvector of both operators which is not possible for non-commuting operators.

Recall the Heisenberg uncertainty principle.

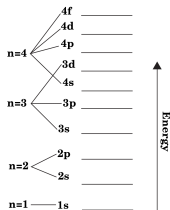
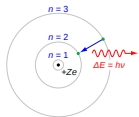
To characterize the system, we should find **which operators commute**.

The most definite information can be obtained about states which are **eigenvectors of all these operators simultaneously**.

This information comprises the eigenvalues of these operators.

**Stationary states**, i.e., states which do not evolve in time, are **eigenvectors of the Hamiltonian**.

# Electron energy levels in atom (2)



Electron in a spherically symmetric potential.

Commuting operators:

energy	$\hat{H}$	$E$
size of the angular momentum	$\hat{\mathbf{L}}^2$	$l(l+1)$
z-component of the ang. mom.	$\hat{L}_z$	$m$
spin	$\hat{S}$	$s$

Eigenvectors of operators  $\hat{H}$ ,  $\hat{\mathbf{L}}^2$ ,  $\hat{L}_z$ , and  $\hat{S}$  form a complete set of solutions of the Schrödinger equation for an atom.

Spin operator works in a Hilbert space that is decoupled from the space where  $\hat{H}$ ,  $\hat{\mathbf{L}}^2$ , and  $\hat{L}_z$  operators works (in the non-relativistic case).

# Solids: Quantum states for a periodic potential

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

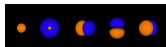
$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}) .$$

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!

Solutions of Schrödinger equation in a spherically symmetric potential  $\psi_i(\mathbf{r}) = R_{nl} Y_{lm}(\hat{\mathbf{r}})$  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 atoms: In case of spherical symmetric potential,  $\hat{H}$  commutes with  $\hat{L}^2$  and with  $\hat{L}_z$ , therefore we have quantum numbers  $n$ ,  $\ell$  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 complete set of 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  $T_{\mathbf{R}}$ , which can then be used to identify these eigenstates.

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

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

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:**

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

$e^{i\mathbf{k}\cdot\mathbf{R}}$  is the eigenvalue of the translation operator,  $\mathbf{k}$  is the corresponding quantum number.

## 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 the same eigenvalue of the translation operator  $\hat{T}_{\mathbf{R}}$  (which is  $e^{i\mathbf{k}\mathbf{R}}$ ) but with 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 finite systems, allowed values of  $\mathbf{k}$  are discrete but dense (typically, determined by *Born-Karmán conditions*). This is needed for theoretical considerations. For praxis, think of  $\mathbf{k}$  as continuous.

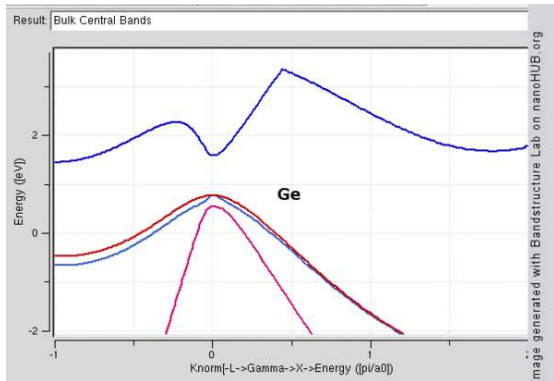
For each  $\mathbf{k}$  there is a discrete set of eigenstates labeled by  $n$ .

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

Spin  $s$  can be added onto it:  $\varepsilon_{\mathbf{k}}^{n,s}$ ,  $\psi_{\mathbf{k}}^{n,s}(\mathbf{r})$ .

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

For each (semi)continuous  $\mathbf{k}$  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  $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ . Bloch theorem then reads:

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

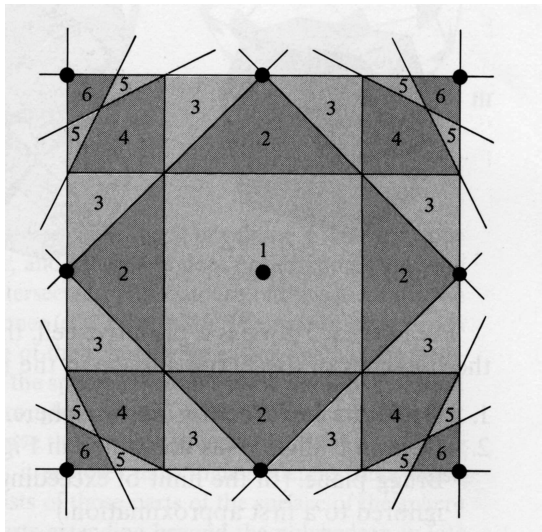
$\Rightarrow$   $\mathbf{k}$  can be substituted by  $\mathbf{k}' = \mathbf{k} + \mathbf{K}$ , where  $\mathbf{K}$  is a reciprocal lattice vector. Quantum numbers  $\mathbf{k}$  and  $\mathbf{k}'$  correspond to the same eigenvalues.

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

Conventionally, we take the *Wigner-Seitz cell* as the defining primitive cell in the reciprocal space. This cell is called the **first Brillouin zone**.

## More on Brillouin zones

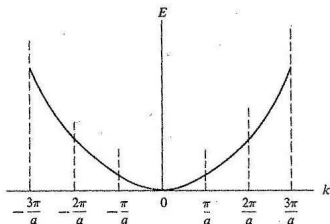
Analogously to the first Brillouin zone (BZ), one can define second, third, fourth, ... Brillouin zones.



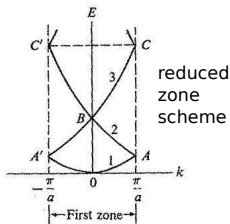


# Reduced, extended, repeated zone scheme

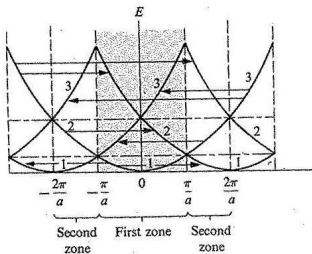
$k$  is not unique  $\Rightarrow$  more equivalent ways to describe the band structure



extended zone scheme



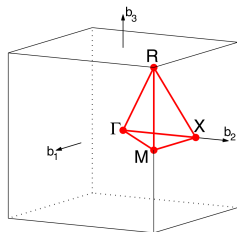
reduced zone scheme



repeated zone scheme

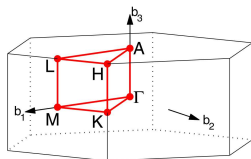
# Naming conventions

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



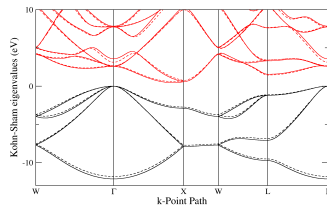
CUB path:  $\Gamma$ -X-M- $\Gamma$ -R-X|M-R

[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]



<https://stackoverflow.com/questions/61995566>

No science or mystique, just naming convention...

## 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  $\{\mathbf{R}_i\}$ .

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 describe 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*.

# Outline

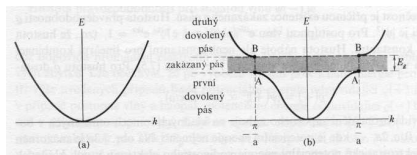
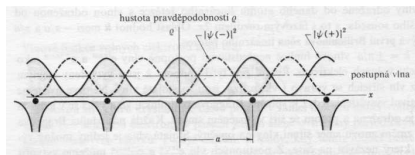
Describing electronic states in a periodic system

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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**  $(\mathbf{k} + \mathbf{K})^2 = k^2$ , so they will undergo **subsequent reflections**.



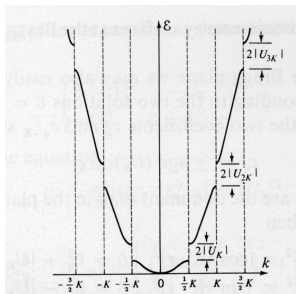
Kittel: Introduction to Solid State Physics

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**.

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

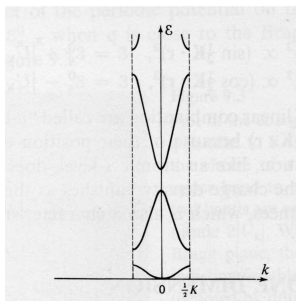
# Band structure of nearly free electrons



Energy of free electrons:

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

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

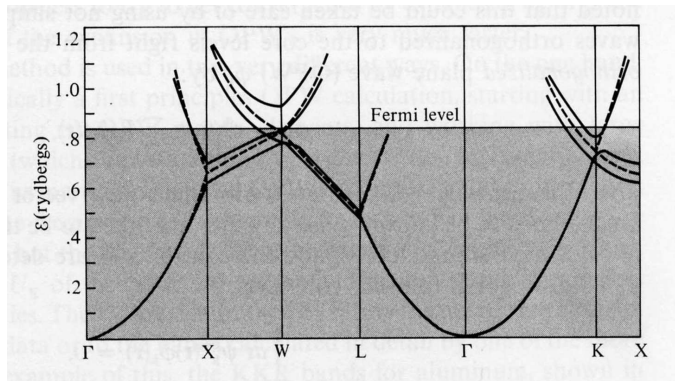


Main effects of the crystal potential:

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  $n(\varepsilon)$

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

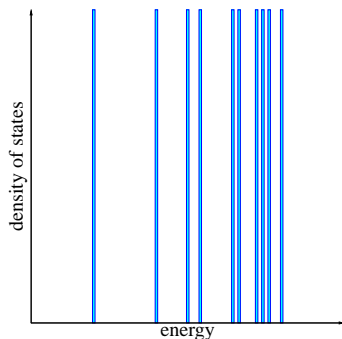
Intuitively:

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

Formally:

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

# DOS for atoms

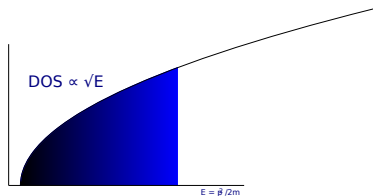


Set of  $\delta$ -functions:

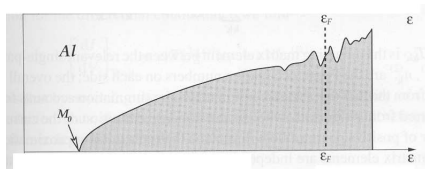
$$n(\varepsilon) = \sum_j \delta(\varepsilon - \varepsilon_j) .$$

$$\begin{aligned} E_{\text{TOT}} &= \int d\varepsilon \varepsilon n(\varepsilon) \\ &= \int d\varepsilon \varepsilon \sum_j \delta(\varepsilon - \varepsilon_j) \\ &= \sum_j \varepsilon_j \end{aligned}$$

# DOS for aluminium (nearly free electrons)



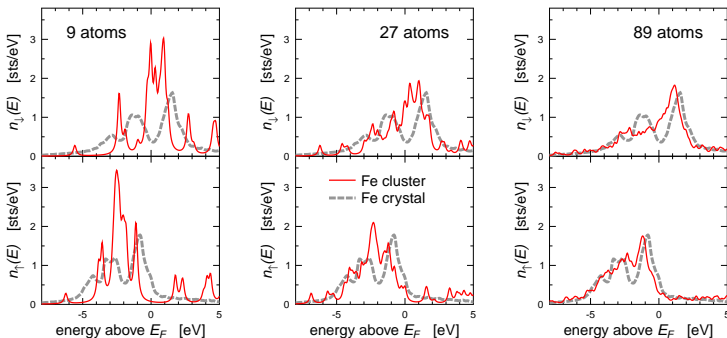
Free electrons: Density of states is proportional to  $\sqrt{E}$ .



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

# DOS of clusters and DOS of crystals

Series of free Fe clusters of increasing size compared to bulk Fe:

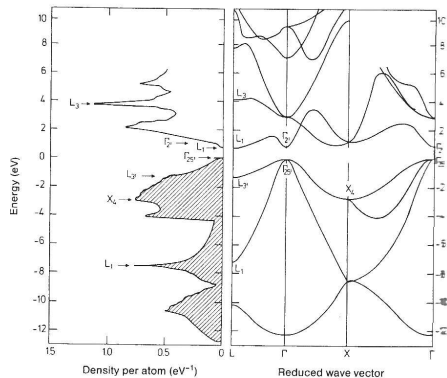


PRB **70**, 174423 (2004)

Small clusters have atomic-like character.

If the size of the crystal increases, the character of the DOS approaches the bulk.

# Band structure and DOS



The expression for DOS can be transformed so that it includes the band structure:

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

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  $\varepsilon$ .

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

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

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

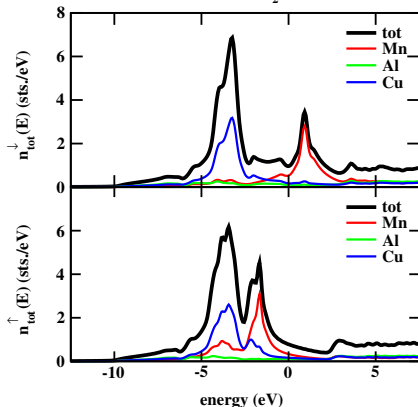
LDOS reflects the spatial inhomogeneity of electronic structure in a solid.

# Total DOS, local DOS, site-resolved DOS

$$n_j(\varepsilon) = \sum_n \int_{1\text{BZ}} \frac{d\mathbf{k}}{4\pi} \int_0^{R_j} r^2 dr |\psi_{\mathbf{k}}^n(\mathbf{r})|^2 \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

Total and site-projected DOS

MnAlCu<sub>2</sub>



Site-resolved DOS:  
LDOS integrated inside  
a sphere around specific  
site at  $\mathbf{R}_j$

Heusler alloy MnAlCu<sub>2</sub>.

Projected not only  
according to the site but  
also according to the spin.

$$n_j = \sum_{s=\pm 1/2} n_{j,s}$$

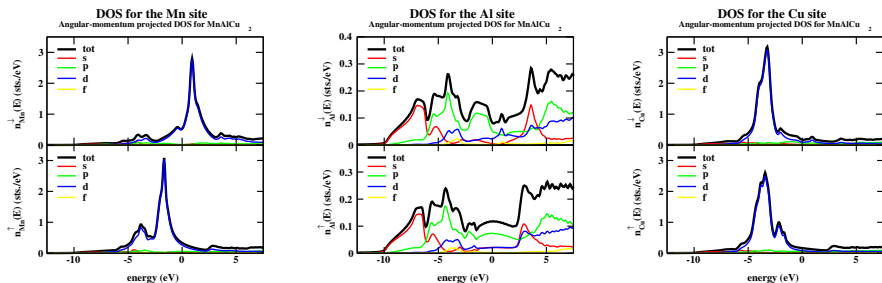
# Angular-momentum-projected site-resolved DOS

Atoms: distinguish between  $s$  ( $\ell=0$ ),  $p$  ( $\ell=1$ ),  $d$  ( $\ell=2$ ) levels.

Solids: projecting LDOS on angular momenta represented by spherical harmonics  $Y_{\ell m}(\hat{\mathbf{n}})$ .

$$n_{j,\ell m}(\varepsilon) = \sum_n \int_{1\text{BZ}} \frac{d\mathbf{k}}{4\pi} \int_0^{R_j} r^2 dr \int d\hat{\mathbf{n}} |\psi_{\mathbf{k}}^n(\mathbf{r})|^2 Y_{\ell m}(\hat{\mathbf{n}}) \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$$

Usually summing over magnetic quantum numbers:  $n_{\ell} = \sum_m n_{\ell m}$ .





## Occupied and unoccupied states

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

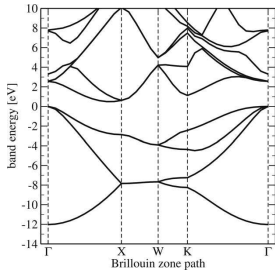
Spin degeneracy means that a state represented by particular  $n$  and  $\mathbf{k}$  can be occupied by two electrons at most.

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.

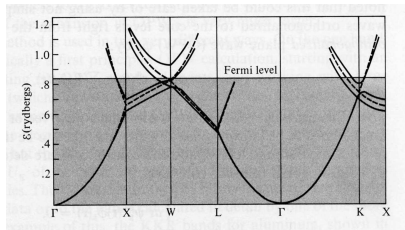
In metals, this energy is called **Fermi energy**.

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

# Band gap (1)



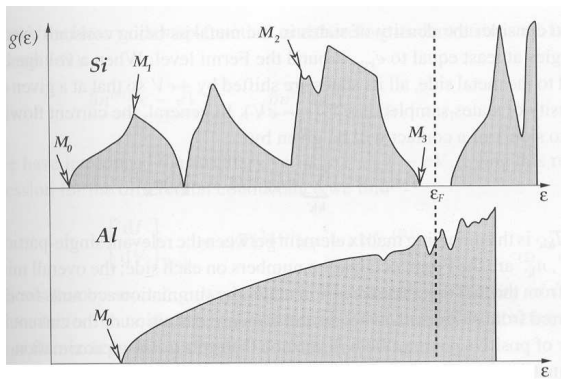
Band structure of silicon:  
for some energies, there  
are no corresponding  
states  $\Rightarrow$  energy gap.



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

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

Band structure:  $\varepsilon_{\mathbf{k}}$  is an eigenvalue of operators  $\hat{H}$  and  $\hat{T}_{\mathbf{R}}$ .

Eigenstates of  $\hat{H}$  are stationary (basic quantum mechanics), their lifetime is infinite.

Probability that we find an electron with energy  $\varepsilon = \varepsilon_{\mathbf{k}}$  and crystal momentum  $\mathbf{k}$  is one. Probability that we find an electron with energy and crystal momentum outside the  $\varepsilon_{\mathbf{k}}$  range is zero.

The Bloch spectral function  $A(\mathbf{k}, \varepsilon)$  describes the probability that an electron with crystal momentum  $k$  has energy  $\varepsilon$ .

For non-interacting electrons:

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

Density of states:

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

## 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.

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

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

## Intermezzo: Heisenberg uncertainly relations

Heisenberg uncertainly relation:

It is impossible to determine exactly both the position and the momentum of an object.

$$\Delta x \Delta p_x \leq \frac{1}{2} \hbar$$

Formally, it is a consequence that operators of position and momentum do not commute.

Time-energy uncertainty relation:

$$\Delta E \Delta t \leq \frac{1}{2} \hbar$$

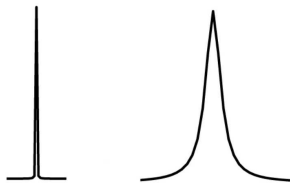
Principally different from  $\Delta x \Delta p_x$  relation:  $\Delta t$  is lifetime of the state, not eigenvalue of an operator.

Quantum state that exists for only a short time cannot have a definite energy.

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

What if the electron is not a true eigenstate of the single-particle Hamiltonian satisfying the crystal periodicity?

Many body effects, disorder  $\Rightarrow$  finite lifetime of single-particle electron state.



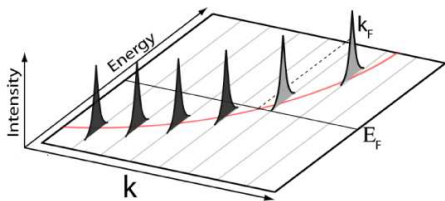
$$\delta(\varepsilon - \varepsilon_{\mathbf{k}})$$

$$A(\mathbf{k}, \varepsilon)$$

Quantum state that exists for only a short time cannot have a definite energy.

Spectral function  $A(\mathbf{k}, \varepsilon)$  is a generalization of the band structure.

## Generalizing the $\varepsilon_n(\mathbf{k})$ picture



LeBlanc *et al.* PRB **83**, 184506 (2011)

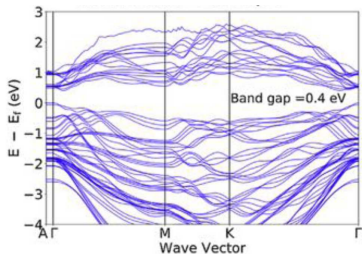
Band structure of a crystal in a single-electron picture: single sharp  $\delta$ -function-like peaks corresponding to  $\varepsilon_{\mathbf{k}}$ .

Spectral function  $A(\mathbf{k}, \varepsilon)$  of an alloy or when including many-body effects: broadened Lorentzian-like peaks.

For practical purposes: View the Bloch spectral function  $A(\mathbf{k}, \varepsilon)$  just as a blurred generalization of the band structure  $\varepsilon_{\mathbf{k}}$ .



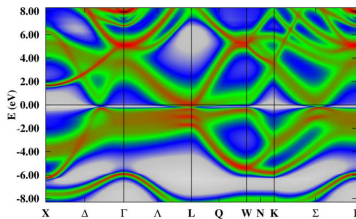
# Example: band structure and Bloch spectral function



Behera *et al.* J Mater Sci Technol (2020)

Band structure:  
fully ordered  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  crystal

sharp lines



Sinha-Roy *et al.* PRB (2029)

Bloch spectral function:  
disordered  $\text{Ge}_{2.005}\text{Sb}_2\text{Te}_5$  alloy

blurred lines, areas

# Wannier functions (1)

Bloch wave functions  $\psi_{\mathbf{k}}^n(\mathbf{r})$  form a complete set of eigenvectors of the periodic crystal Hamiltonian  $\hat{H}$ .

However, one can choose **other complete sets to describe the system.**

Bloch wave functions

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

are delocalized.

By Fourier transforming the  $\psi_{\mathbf{k}}^n(\mathbf{r})$  functions one gets **Wannier functions,**

$$\phi_{\mathbf{R}}^n(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}^n(\mathbf{r}) .$$

The sum  $\sum_{\mathbf{k}}$  goes over the appropriate  $\mathbf{k}$  values in the first Brillouin zone.

Wannier functions are localized (each of them at different site).

## Wannier functions (2)

Description of electronic states via Bloch functions and via Wannier functions is equivalent.

Both sets form a complete orthonormal basis.

Bloch functions can be obtained from Wannier functions by a back Fourier transformation,

$$\psi_{\mathbf{k}}^n(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_{\mathbf{R}}^n(\mathbf{r})$$

where  $\sum_{\mathbf{R}}$  sums over all lattice vectors  $\mathbf{R}$  of the crystal.

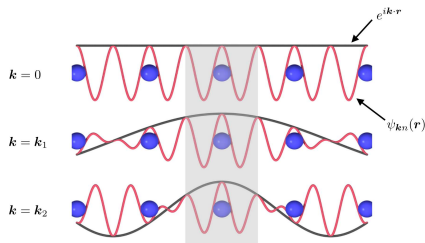
Individual Bloch wave functions or Wannier functions do not necessarily describe any particular electron.

They matter as a complete set (basis) which enables to describe the system.

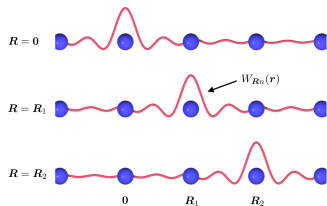
We just choose the basis so that it describes the system in the most simple and intuitive way.

# Wannier functions vers. Bloch functions

Wannier functions are localized.



Bloch



<https://www.flapw.de>

Wannier

Wannier functions have been used lately in many practical applications where the formally local approach is technically and intuitively convenient.

# Outline

Describing electronic states in a periodic system

Band structure of crystals: concepts and definitions

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

# 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**.

To calculate the real (atomic) structure you need to know the electronic structure.

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

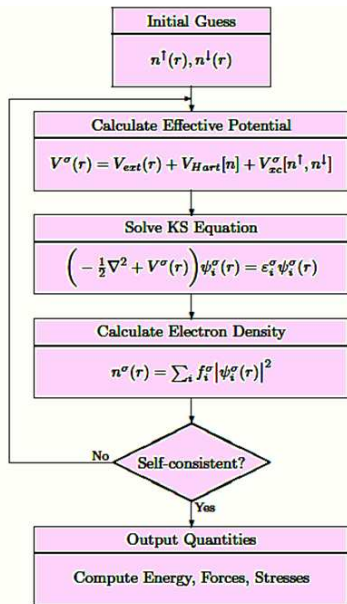
We need to solve the Schrödinger equation for an electron in a given potential  $V(\mathbf{r})$ .

1. The wave functions  $\psi_{\mathbf{k}}^n(\mathbf{r})$  determine the electron density  $n(\mathbf{r})$ .
2. The electron density determines the potential  $V(\mathbf{r})$ .
3. 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 24<sup>th</sup> November.

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



Solve the Schrodinger equation iteratively:

1. Start with an initial guess for the charge density  $n(\mathbf{r})$ .
2. Use density  $n(\mathbf{r})$  to generate the potential  $V(\mathbf{r})$ .
3. Solve the Schrodinger equation to get the wave functions  $\psi(bmr)$ .
4. Use wave functions  $\psi(bmr)$  to generate the density  $n(\mathbf{r})$ .
5. Go back to step 2 until the initial density and the final density do not agree.



# How to solve Schrödinger equation (1)

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

Solving Schrödinger equation numerically in 3D is a killer.

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

(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

$$\sum_j H_{ij} c_j = \varepsilon c_i$$

with matrix elements  $H_{ij}$

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

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

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

## How to solve Schrödinger equation (3)

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

$$\sum_j H_{ij} c_j = \varepsilon c_i .$$

Methods based on this approach are called variational.

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.

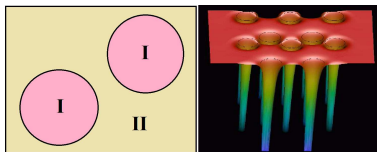
There are **no “universal” methods** except for very simple problems (that need not be solved anyhow).

Criteria governing which method to choose:

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

# FLAPW method

Full potential **L**inearized **A**ugmented **P**lane **W**aves method.  
Considered (by some) to be the most accurate method.



Basis is made of augmented plane waves.

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

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.

## Plane waves methods

Plane waves  $e^{i\mathbf{k}\cdot\mathbf{r}}$  form an orthogonal 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

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

Plane waves are computer-friendly.

☹️ The potential has a **singularity close to the nuclei** and to describe this singularity properly, on needs a **huge** number of plane waves, making their use impractical.

😊 This problem can be by-passed by introducing **pseudopotentials**.

# What is pseudopotential?

Operator simulating the effect

of [nucleus + core electrons]

on electronic states

in the energy range of interest

(i.e. *not on any state!*)

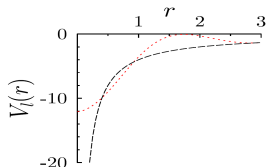
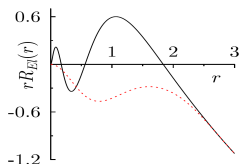
Requirements, expected properties:

- ▶ 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

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

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



Equal scattering properties **in the neighbourhood of  $E_{\text{ref}}$** .

Smooth pseudopotential means that the expansion of the wave functions in terms of plane waves is efficient: one needs a relatively small basis.



## Pseudopotentials: Looking under the bonnet

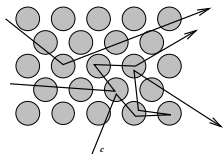
The calculation can be only as good as the pseudopotential is.

The issue of **transferability**, i.e., the ability to describe properly the scattering on atom in different environments (e.g., Na atom can be in metallic Na but also in ionic NaCl).

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

# KKR-Green's function method

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



Old method, subsequently reformulated as a KKR-Green's function method.

KKR-Green's function method does not rely on a fixed basis.

- ▶ It is exact, specifically also concerning charge densities. However, for energies and consequently also geometries the accuracy of linearized methods is usually sufficient.
- ▶ It is relatively slow and somewhat cumbersome.
- ▶ Often used in its linearized version (LMTO).
- ▶ Green's function → naturally suited for **spectroscopy**.
- ▶ Green's function → naturally suited for **many-body physics**.

# 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 (i.e., knowledgeable) person.

# 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 (Jülich, München, Osaka, Ames, Oak Ridge, FEFF)
- ▶ LMTO (Stuttgart code and its derivatives, Turek in Brno)

### ▶ 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.

## Picking the cherries: jumping from one method to another

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 but less accurate) and then use an all-electron (e.g., FLAPW) code to calculate electronic structure and other properties (slow but accurate).

Find the timetable and slides on the web

`http://crysa.fzu.cz/ondra/teor-surf-phys`

