

Electronic structure of solids: basic concepts and methods

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III.

NEVF 514 Surface Physics

Winter Term 2018 - 2019

Troja, 19. October 2018

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

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Translation periodicity

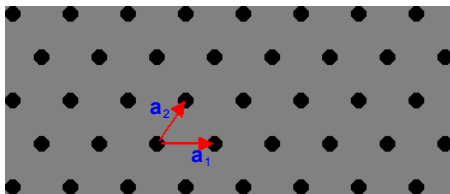
Primitive translation vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 :

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:

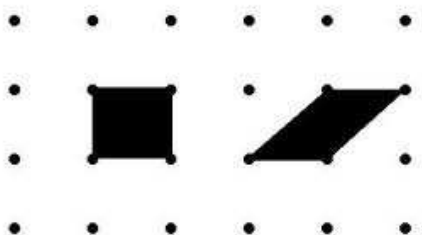
$$\mathbf{R}_i = \sum_i \left[n_1^{(i)} \mathbf{a}_1 + n_2^{(i)} \mathbf{a}_2 + n_3^{(i)} \mathbf{a}_3 \right] \ .$$



Primitive cell

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

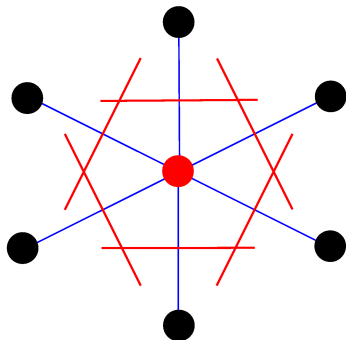
The primitive cell is *not uniquely defined*:



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

Wigner-Seitz cell

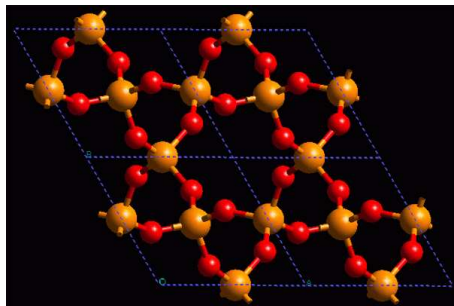
Wigner-Seitz cell: Region in space that is closer to a fixed lattice point than to any of the other lattice points.



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

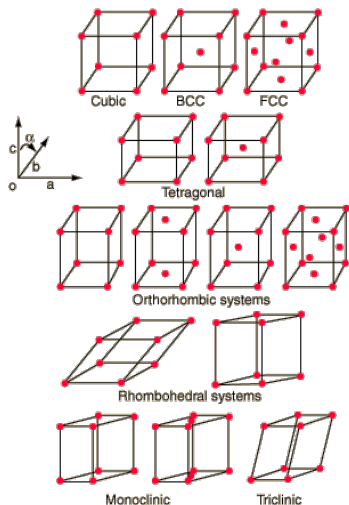
Lattice vectors, basis

- ▶ 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



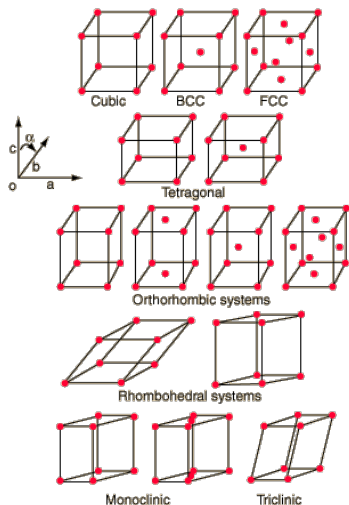
14 Bravais lattices:

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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Fourier transformation: Plane waves $e^{i\mathbf{k}\cdot\mathbf{r}}$ 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 ℓ 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 $T_{\mathbf{R}}$, 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 ℓ 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 $\hat{T}_{\mathbf{R}}$.

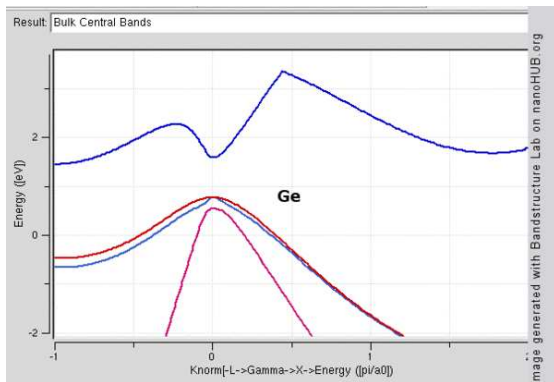
For macroscopic (“infinitely large”) crystal, the wave vector \mathbf{k} is a continuous variable.

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 $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$.

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

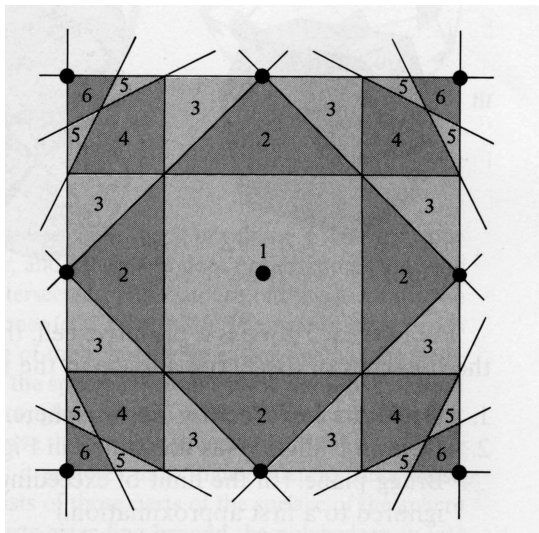
$\Rightarrow \mathbf{k}$ can be substituted by $\mathbf{k}' = \mathbf{k} + \mathbf{K}$, where \mathbf{K} is a reciprocal lattice vector.

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**.

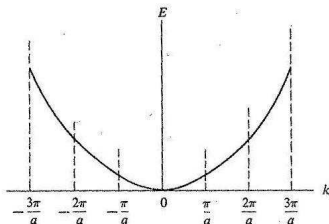
More on Brillouin zones

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

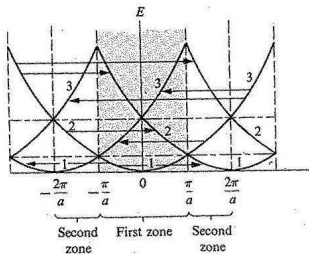
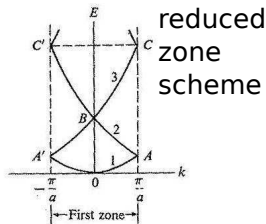


Reduced, extended, repeated zone scheme

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



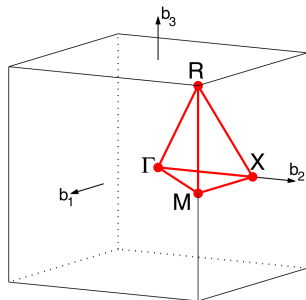
repeated
zone scheme



repeated
zone scheme

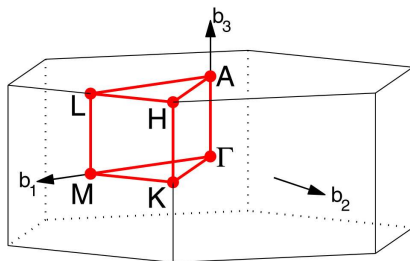
Naming conventions

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



CUB path: Γ -X-M- Γ -R-X|M-R

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



HEX path: Γ -M-K- Γ -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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A bit of formal mathematics for the beginning

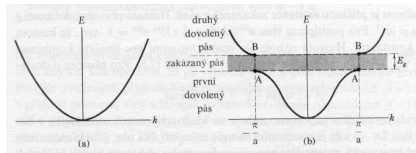
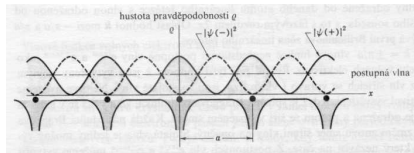
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BZ boundary is the space to watch...

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



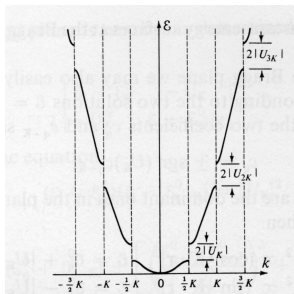
Kittel: Introduction to Solid State Physics

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 .

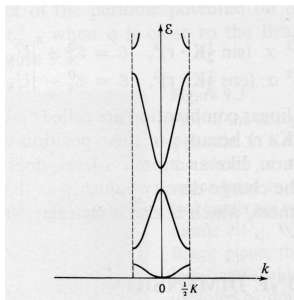
Band structure of nearly free electrons



Energy of free electrons:

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

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

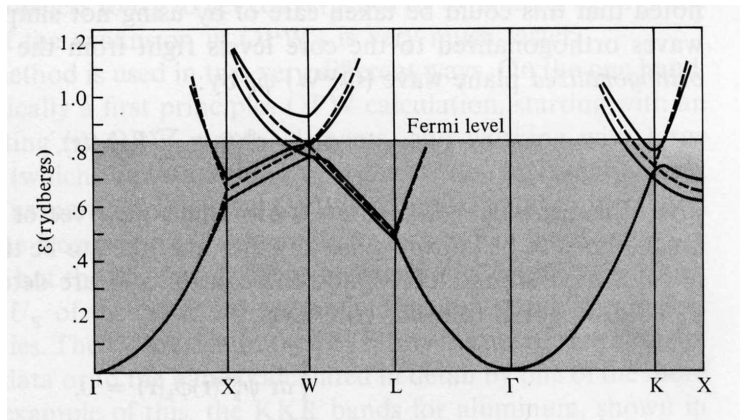


Main effects of the crystal potential:

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_{TOT} is obtained by a **sum** of energies ε_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_{TOT} is obtained as an **integral**, weighting the energy ε by the density of states $n(\varepsilon)$

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

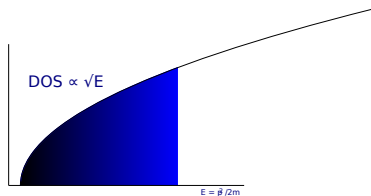
Intuitively:

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

Formally:

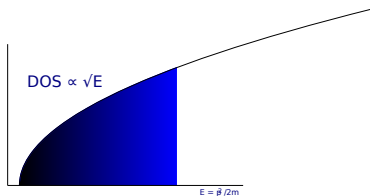
$$n(\varepsilon) = \sum_n \int_{\text{1BZ}} \frac{d\mathbf{k}}{4\pi} \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n) .$$

Aluminium again

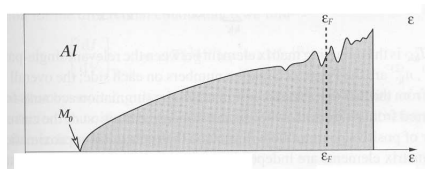


Free electrons: Density of states
is proportional to $\sqrt{\epsilon}$.

Aluminium again

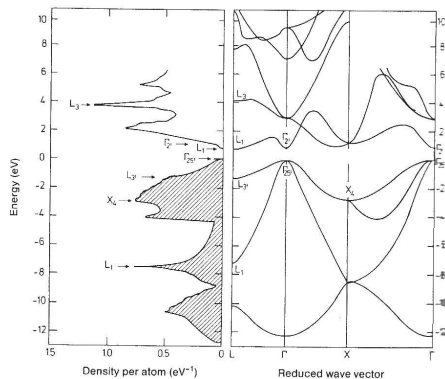


Free electrons: Density of states is proportional to \sqrt{E} .



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 $\nabla \epsilon_{\mathbf{k}}^n$
correspond to high DOS.

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

Local density of states

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

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

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

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

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}

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.

Occupied and unoccupied states

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

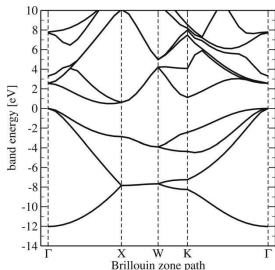
Spin degeneracy means that a state represented by particular n and \mathbf{k} can be occupied by two electrons at most.

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.

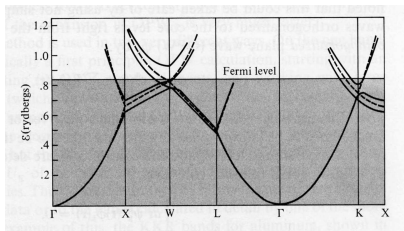
In metals, this energy is called **Fermi energy**.

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

Band gap (1)



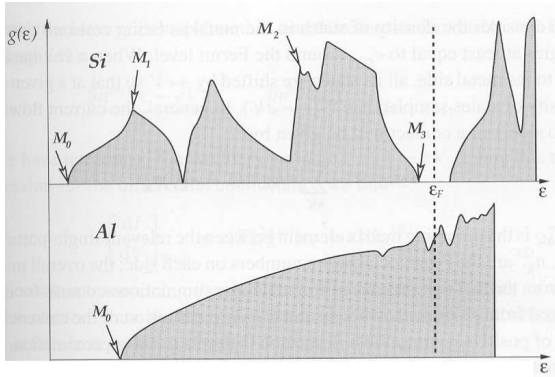
Band structure of silicon:
for some energies, there
are no corresponding
states \Rightarrow energy gap.



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

Band gap (2)

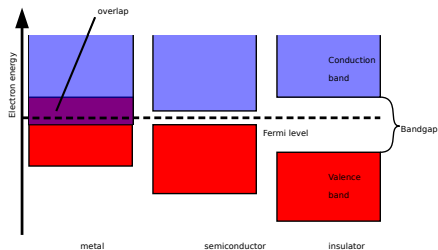
Density of states:



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 (~ 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 $V(\mathbf{r})$.

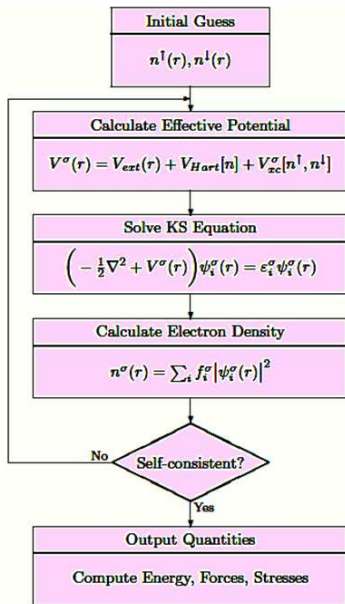
Wave functions $\psi_{\mathbf{k}}^n(\mathbf{r})$ determine the electron density $n(\mathbf{r})$, electron density determines the potential $V(\mathbf{r})$.

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).

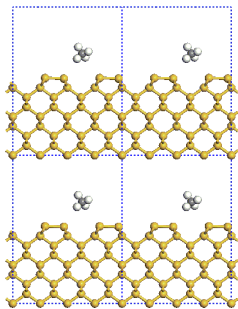
Criteria governing which method to choose:

- ▶ 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)?
- ▶ ...

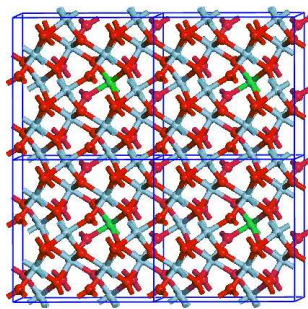
Dealing with surfaces: Supercell calculations

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

Advantage: Using all the polished tools of bulk calculations.



simulating adsorbate



<http://www.tcm.phy.cam.ac.uk/castep>

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

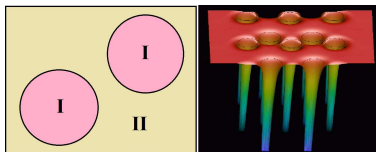
Core electrons are (semi-)ignored — they are effectively merged with the nucleus.

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

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

FLAPW method

Full potential **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

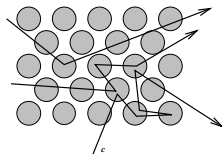
muffin-tin spheres: $\phi(\mathbf{r}) \sim \sum_{\ell m} a_{\ell m} R_{\ell}(\mathbf{r}) Y_{\ell m}(\mathbf{r})$

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

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 \rightarrow naturally suited for spectroscopy.
- ▶ Green's function \rightarrow naturally suited for many-body physics.
- ▶ Efficient when treating surfaces, adsorbates, disorder.

Surfaces via Green's function methods

Proper semi-infinite systems, no supercell.

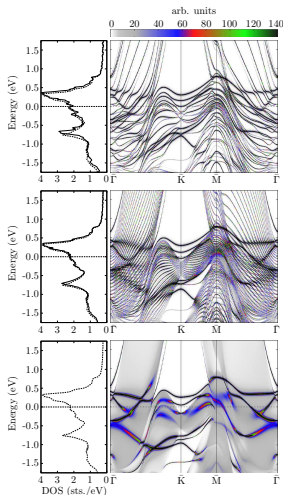
Bloch spectral function: generalization of the band-structure for non-periodic systems

Surface of a 14-layers slab.

Surface of a 38-layers slab.

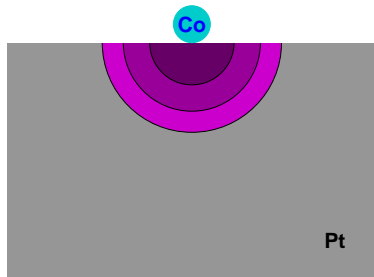
Surface of a semi-infinite layer.

Only true surface states and resonances remain, **no spurious bands**.



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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”.

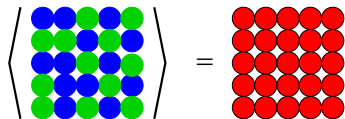
To deal with clusters of hundreds of atoms, Green's function formalism is more suitable.

Dealing with disorder

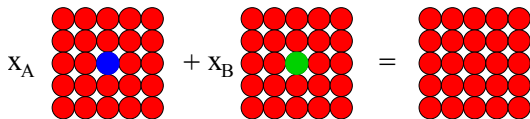
Disordered systems can be dealt with by averaging over many large supercells, spanning many different local environments.

→ **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 **M**uffin-**T**in **O**rbitals.

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:

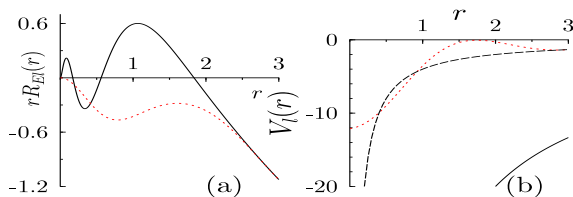
- ▶ Sufficient accuracy in a wide energy range (“transferability”)
- ▶ Real merit to computational efficiency (“softness”)
 - ▶ reducing the size of the basis set
 - ▶ eliminating large energies of the core states

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 ℓ 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_{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_{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 structure (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 [\AA]	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 ΔD_{ij} for several close-packed hexagonal metal surfaces

	Δd_{12}	Δd_{23}	Δd_{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			