

SOLID STATE PHYSICS

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Lectures and tutorials

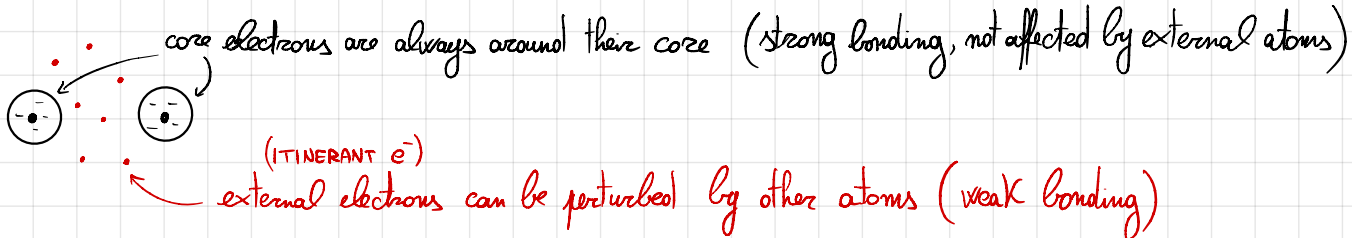
Lecture #1

Introduction

Crystals are the main topic of this course; part A ends with some concepts about holes and electrons. There are a lot of topics which are not included in this course. The topics are very heterogeneous, so it is very important to find a suitable approach for each of them. Some lectures are on WEBEEP. The exam lasts 30-45 minutes on average (theory + calculations).

Solid body

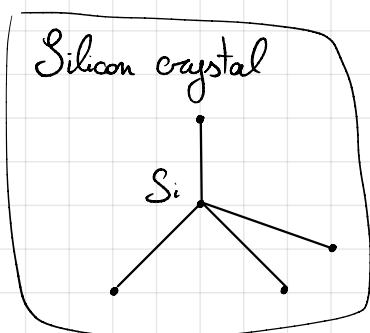
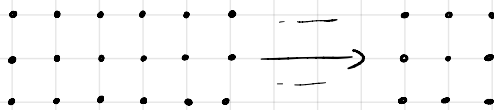
A solid body is something that has proper shape and volume (approximation). We are interested in optical and transport properties. Solid body is made of ions and electrons. Quantum Physics and Electromagnetism are the main tools; the number of particles is huge, not suitable for a macroscopic approach. We have to simplify the problem.



Splitting between ions and itinerant electrons is a good approach; studying both of them separately is also a good approximation, introducing reciprocal interaction as a perturbation. To start the course, we can study one electron in a periodic potential (quasi-particles as the holes are also introduced). Periodic configuration is the minimum energy configuration available; equilibrium state is achievable through periodicity.

Simple crystals

Before we start talking about simple crystals, it is recommended to introduce the Bravais Lattice: it is a geometrical concept; in particular we are talking about a set of point with translational symmetry. A crystal, then, is a material with long range positional order, meaning that the order is kept regardless the distance.



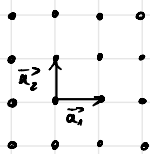
Bravais Lattice is described through a set of vectors

$$\vec{m} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$$

NOT IN THE SAME PLANE

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ are PRIMITIVE vectors

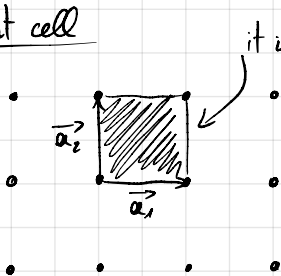
m_1, m_2, m_3 are INTEGERS



Primitive vectors describe all the points because they can be shifted with the integers

A crystal is simple when it has one atom in each point of the BL

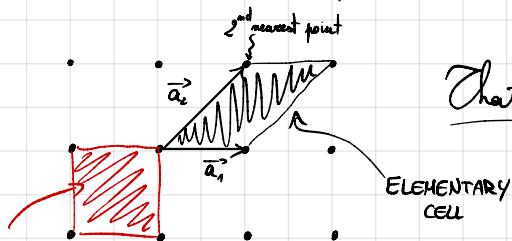
Unit cell



it is the ^(or volume) area generated by the primitive vectors

This cell repeated for each translation fills the space without leaving any void and without overlapping

Primitive vectors are not unique:

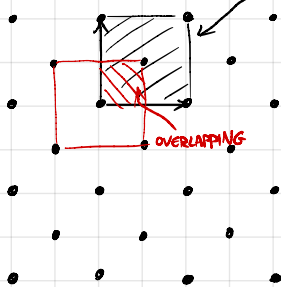


That is also a good choice

PRIMITIVE CELL

each point is connected to the others with minimum distance (nearest neighbor points, NNP)

Conventional cell



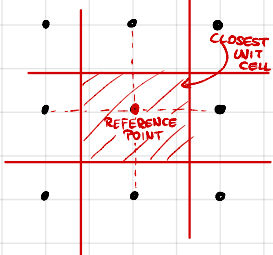
primitive cell with a point inside
↳ this partially overlaps during translations

Volume is bigger than the unit cell and is not generated by the primitive vectors. It is mostly used for simplicity purposes (i.e. cubic systems)

Lecture #2

Wigner-Seitz cell

BRAGG PLANES: PLANES BUILT CLOSE TO THE NEAREST POINT TO THE REFERENCE

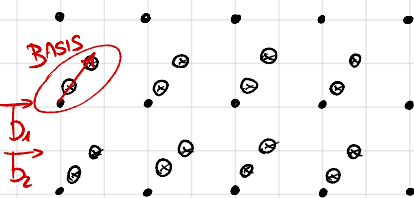


The Wigner-Seitz cell is the region of space closer to a lattice point taken as reference.

Complex crystal

Starting point is the Bravais lattice

We can group the atoms that repeat with a clear order into a basis, creating a complex crystal.

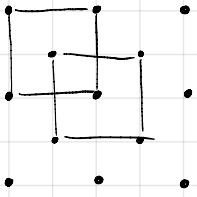


Lattice translation

All crystals have translational symmetry. We have lattice translation when we move the crystal by one of the Bravais vectors. We can define

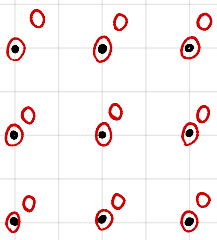
$$\vec{T}_{\vec{m}} = \vec{m} - \vec{m}' = (m_1 - m_1')\vec{a}_1 + (m_2 - m_2')\vec{a}_2 + (m_3 - m_3')\vec{a}_3$$

In particular, $\vec{T}_{0\vec{m}} = \vec{m}$



Which one is the point in the centre?
All are equivalent due to translational symmetry.

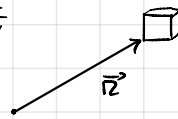
It is also very important to consider that ANY LOCAL PROPERTY IS PERIODIC WITH TRANSLATIONAL SYMMETRY.



LATTICE ATOMS

i.e. Charge density: $\rho(\vec{r}) = \frac{dQ}{dV}$

$$\rho(\vec{r}) = \rho(\vec{r} + \vec{a}_i)$$



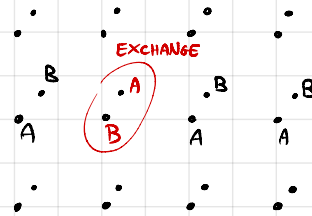
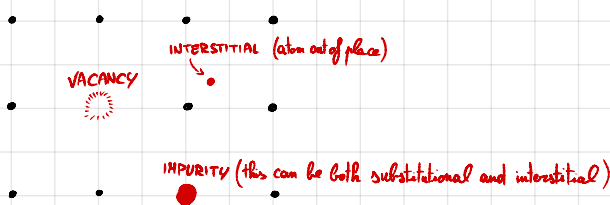
Imperfections

In a real crystal it is impossible to have a perfect translational symmetry, because of the defects, such as

- ① POINT DEFECTS
- ② LINE DEFECTS
- ③ SURFACE DEFECTS

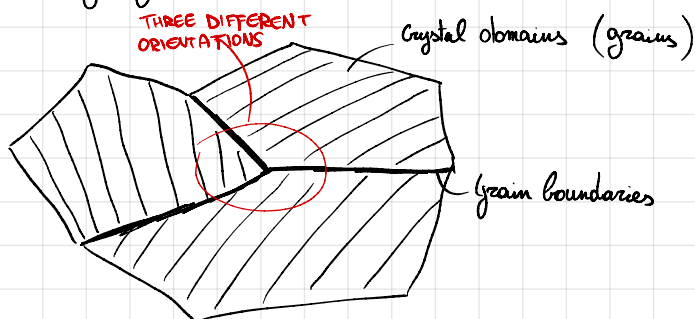
Mechanical, optical and electrical properties are strongly affected by defects.

①



② and ③ are not treated in detail (just dislocations^②).

Polycrystal

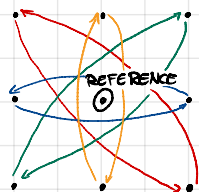


Other symmetries

Symmetries are very important in Physics; we can have

- POINT SYMMETRIES

① INVERSION $\vec{m} \rightarrow -\vec{m}$

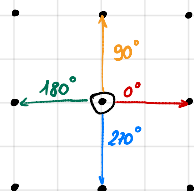


ALL POINTS ARE FLIPPED TO THEIR OPPOSITE

This symmetry is always present

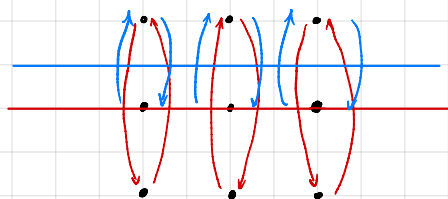
N.B. Symmetry operations leave the crystal UNCHANGED

② ROTATIONS (2,3,4,6) $\int_0^{2\pi} \frac{2\pi}{M}$



In this case, the order is 4

③ REFLECTION



④ ROTATION INVERSION

⑤ ROTOREFLECTION

} Combinations of the previous ones

In general, it is true that, considering symmetry operation, $AA^{-1} = I$ and $(AB)C = A(BC)$, but $AB \neq BA$. There are 7 possible crystalline systems, according to point symmetry; if we combine point and translational, they become 14. (SYLLOQUES)

Considering complex crystals, new symmetries appear, like screw axis and glide planes, for a total of 32 point groups and 230 space groups (point + translational).

Bonding classification of the solids

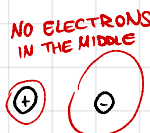
It is known that considering $\Psi(\vec{r}) \rightarrow |\Psi(\vec{r})|^2 dV = dP$ is the infinitesimal probability to find an electron. Charge density, then, is defined as $\rho(\vec{r}) = -e \sum_i |\Psi(\vec{r})|^2$; if we were to make a classification, that would be

A) METALS $\rightarrow \Delta \rho$ SMALL (ρ is almost constant) \rightarrow ALKALI



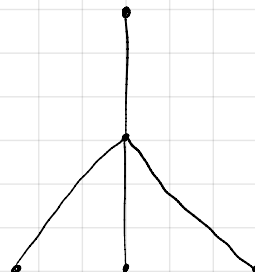
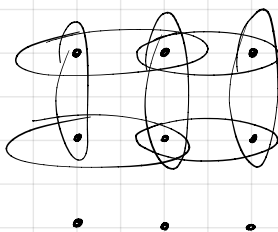
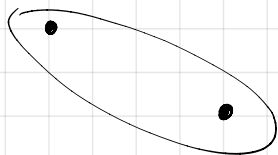
Free electrons $\Psi = A e^{i\vec{k} \cdot \vec{r}}$

B) IONIC CRYSTALS such as NaCl

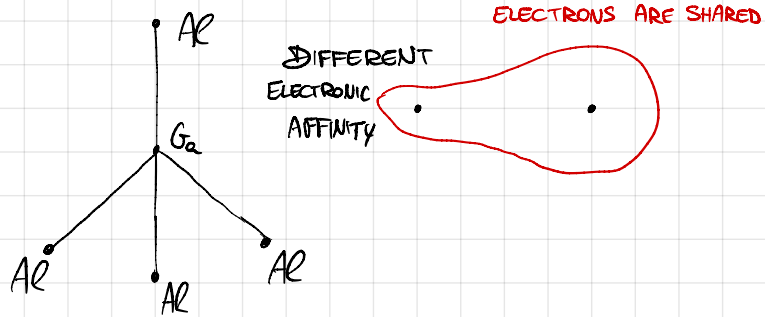


Bonding is made through Coulombian force

C) COVALENT SOLIDS

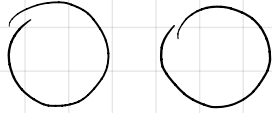


D) INTERMEDIATE



E) NOBLE GAS CRYSTALS

The bonding is due to Van der Waals forces (very weak).



Cohesive energy

It is also called binding energy; it is the energy needed to tear apart the atoms in the crystal $[\frac{eV}{atom}]$. We can define strong and weak binding.

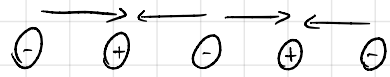
$$\rho(\vec{r}) = \rho(\vec{r} + \vec{a})$$

Macroscopic properties (observables)

$$\bar{\rho} = \frac{1}{V_p} \int_{V_p} \rho(\vec{r}) d\vec{r} \quad \text{mean charge density}$$

$$\vec{P} = \epsilon_0 \chi \vec{E} \quad \text{polarization}$$

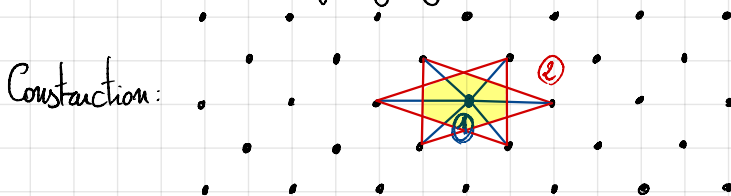
$$\vec{P}_i = \epsilon_0 \sum_j \chi_{ij} E_j \quad \text{local polarization}$$



Tutorial #1

Crystalline structure

Every crystal has translational symmetry; as approximations, we assume that crystals have infinite extent, no defects and we use mean positions. We describe the crystals with the Bravais lattice, defined as an infinite set of points (integer sums of primitive lattice vectors). Primitive vectors are not unique: we have to choose the most appropriate set according to the lattice. The honeycomb arrangement is not a Bravais lattice. The unit cell is the region of space generated from the PLVs that can cover the whole crystal just by translations without void or overlapping (just the primitive cell). The elementary cell, then, is the minimal volume cell but with not the nearest point taken. The most important primitive cell is the **Wigner-Seitz cell**, because it encloses just one lattice point, has minimal volume and is perfectly symmetric.

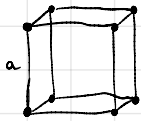


PRIMITIVE CELL VOLUME

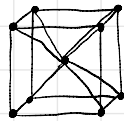
$$\Omega = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|$$

Conventional cells may or may not be primitive cells; what is important is just the symmetry axes of the crystal structure. Considering 3D, there are 14 lattices in 7 systems.

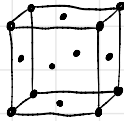
Cubic lattices



SIMPLE
 $\Omega = a^3$



BODY CENTERED
 $\Omega = \frac{a^3}{2}$



FACE CENTERED
 $\Omega = \frac{a^3}{4}$

Lattice planes

A lattice plane is by definition a plane containing 3 non collinear points, thus infinite lattice points forming a 2D Bravais lattice within the plane. Infinite sets of equally spaced lattice planes are classified as families. Miller indices define the lattice planes through the method of intercepts.

$$(h \ k \ l) = \left(\frac{a_1}{x_{int}}, \frac{a_2}{y_{int}}, \frac{a_3}{z_{int}} \right) \cdot \text{l.c.m.} (x_{int}, y_{int}, z_{int})$$

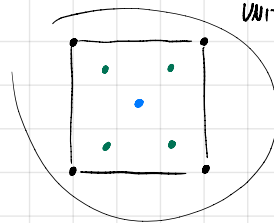
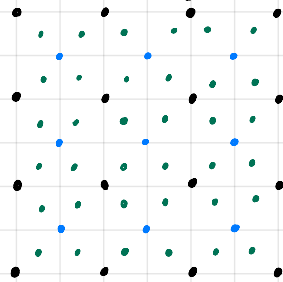
Brackets: {family of equivalent lattice planes}

[direction perpendicular to the plane]

< family of equivalent directions >

Physical crystal

A basis is a specific set of atoms decorating every primitive cell of the Bravais lattice.



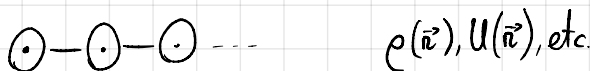
Diamond structure

It is a very rare structure; it can be seen as two FCCs with a basis of two atoms compensated. Si has the diamond structure as well as C (graphene/graphite).

Supporting lecture #1

Fourier series

A crystal is intrinsically a periodic function:

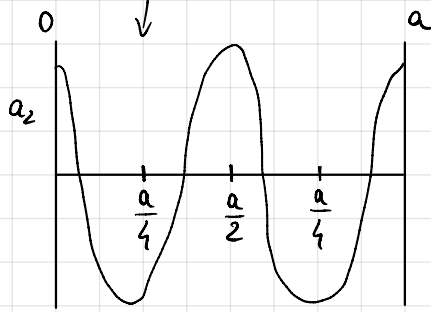
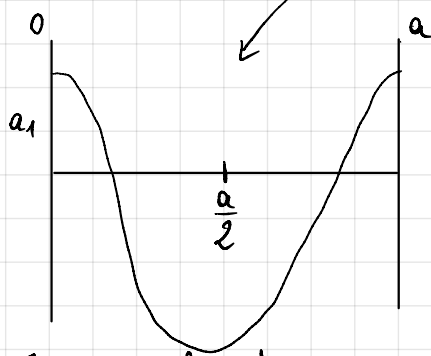


Fourier series is a periodic function defined as $f(x) = f(x+a) = f(x+ma)$ with $m = 0, 1, 2, \dots$

$$f(x) = \frac{a_0}{2} + \sum_{m=1}^{+\infty} \left[a_m \cos\left(\frac{2\pi}{a} mx\right) + b_m \sin\left(\frac{2\pi}{a} mx\right) \right]$$

If we stop to $m=2$ we get

$$f(x) = \frac{a_0}{2} + a_1 \cos\left(\frac{2\pi}{a}x\right) + b_1 \sin\left(\frac{2\pi}{a}x\right) + a_2 \cos\left(\frac{4\pi}{a}x\right) + b_2 \sin\left(\frac{4\pi}{a}x\right)$$



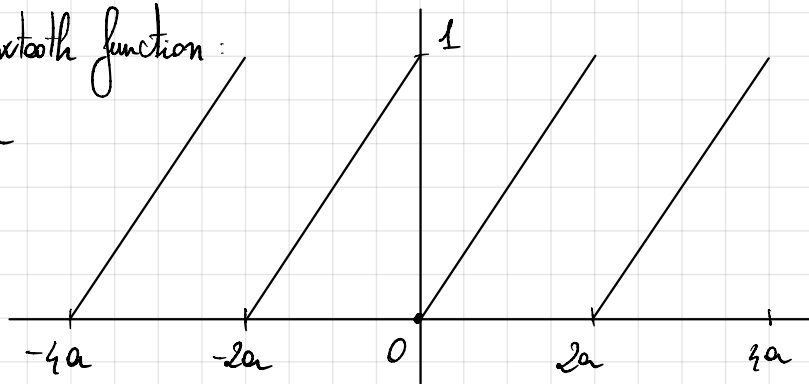
Fourier coefficients

$$a_n = \frac{2}{a} \int_0^a f(x) \cos\left(n \frac{2\pi}{a} x\right) dx$$

$$b_n = \frac{2}{a} \int_0^a f(x) \sin\left(n \frac{2\pi}{a} x\right) dx$$

We now want to build the sawtooth function:

$$f(x) = \frac{x}{2a} \quad 0 \leq x \leq 2a$$



Let's find the Fourier coefficients then

$$a_0 = \frac{2}{2a} \int_0^{2a} \frac{x}{2a} dx = 1 \quad \text{for } m=0$$

$$a_m = \frac{2}{2a} \int_0^{2a} \frac{x}{2a} \cos\left(m \frac{2\pi}{2a} x\right) dx = 0 \quad \forall m$$

$$b_m = \frac{2}{2a} \int_0^{2a} \frac{x}{2a} \sin\left(m \frac{2\pi}{a} x\right) dx = -\frac{1}{m\pi}$$

Thus

$$\frac{x}{2a} = \frac{1}{2} - \frac{1}{\pi} \sum_{m=1}^{+\infty} \frac{1}{m} \sin\left(m \frac{2\pi}{2a} x\right)$$

Exponential form

$$\cos\left(m \frac{2\pi}{a} x\right) + i \sin\left(m \frac{2\pi}{a} x\right) = e^{i m \frac{2\pi}{a} x}$$

much more compact

NEW COEFFICIENT

$$C_m = \frac{1}{a} \int_0^a f(x) e^{-i m \frac{2\pi}{a} x} dx$$

$$m = n \frac{2\pi}{a}$$

$$C_m = \frac{1}{a} \int_0^a f(x) e^{-imx} dx \rightsquigarrow a_m = \frac{2}{a} \int_0^a f(x) \cos(mx) dx = \frac{2}{a} \int_0^a f(x) \frac{e^{imx} + e^{-imx}}{2} dx =$$

$$C_0 = \frac{1}{a} \int_0^a f(x) dx \rightsquigarrow a_0 = \frac{2}{a} \int_0^a f(x) dx = \underbrace{\frac{1}{a} \int_0^a f(x) e^{-i0x} dx}_{C_{-m}} + \underbrace{\frac{1}{a} \int_0^a f(x) e^{-i0x} dx}_{C_m}$$

$$\boxed{C_0 = \frac{a_0}{2}}$$

$$= C_{-m} + C_m$$

If we repeat the same with b_m we get

$$b_m = \frac{2}{a} \int_0^a f(x) \sin(mx) dx = \frac{2}{a} \int_0^a f(x) \frac{e^{imx} - e^{-imx}}{2i} dx = -i \left(\frac{1}{a} \int_0^a f(x) e^{-i(-m)x} dx - \frac{1}{a} \int_0^a f(x) e^{-imx} dx \right)$$

$$= -i(C_{-m} - C_m) = i(C_m - C_{-m})$$

If we combine all

$$C_m = \frac{1}{2}(a_m - ib_m)$$

$$C_{-m} = \frac{1}{2}(a_m + ib_m)$$

$$C_m^* = C_{-m}$$

Then

$$a_m \cos(mx) + b_m \sin(mx) = (C_m + C_{-m}) \frac{e^{imx} + e^{-imx}}{2} + i(C_m - C_{-m}) \frac{e^{imx} - e^{-imx}}{2} = C_m e^{imx} + C_{-m} e^{-imx}$$

$$f(x) = C_0 + \sum_{m=1}^{+\infty} (C_m e^{imx} + C_{-m} e^{-imx}) = \sum_{m=-\infty}^{+\infty} C_m e^{imx} = \sum_{m=-\infty}^{+\infty} C_m e^{im \frac{2\pi}{a} x}$$

Complex number

$$C_n^* = C_{-n}$$

We can assume then

$$C_m = P_m e^{i\varphi_m} \Rightarrow f(x) = \sum_{n=-\infty}^{+\infty} P_n e^{i \left(n \frac{2\pi}{a} x + \varphi_n \right)}$$

2D and 3D functions

$f(x, y)$ with two periodicities $\begin{matrix} x \rightarrow a_1 \\ y \uparrow a_2 \end{matrix}$

$$f(x, y) = \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} \alpha_{n,m} \cos\left(n \frac{2\pi}{a_1} x\right) \cos\left(m \frac{2\pi}{a_2} y\right) + \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} \beta_{n,m} \cos\left(n \frac{2\pi}{a_1} x\right) \sin\left(m \frac{2\pi}{a_2} y\right) +$$

$$+ \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} \gamma_{n,m} \sin\left(n \frac{2\pi}{a_1} x\right) \cos\left(m \frac{2\pi}{a_2} y\right) + \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} \delta_{n,m} \sin\left(n \frac{2\pi}{a_1} x\right) \sin\left(m \frac{2\pi}{a_2} y\right) =$$

$$= \sum_{n=-\infty}^{+\infty} \sum_{m=-\infty}^{+\infty} C_{n,m} e^{im \frac{2\pi}{a_2} y} e^{in \frac{2\pi}{a_1} x} = \sum_{n,m=-\infty}^{+\infty} C_{n,m} e^{i \left(n \frac{2\pi}{a_1} x + m \frac{2\pi}{a_2} y \right)}$$

For 3D function it is the same procedure:

$$f(x, y, z) = \sum_{m, n, t} e^{i(m \frac{2\pi}{a_1} x + n \frac{2\pi}{a_2} y + t \frac{2\pi}{a_3} z)} C_{m, n, t}$$

If we do want to use the scalar product: $e^{i \left[\left(m \frac{2\pi}{a_1} ; n \frac{2\pi}{a_2} ; t \frac{2\pi}{a_3} \right) \cdot (x, y, z) \right]}$

$$f(\vec{r}) = \sum_{m, n, t} C_{m, n, t} e^{i \vec{g}_{m, n, t} \cdot \vec{r}}$$

$$C_{m, n, t} = \frac{1}{V} \int_V f(x, y, z) e^{-i \vec{g}_{m, n, t} \cdot \vec{r}}$$

$a_1 a_2 a_3$

$$(a_1, a_2, a_3) \rightarrow \vec{m} = (m_1 a_1, m_2 a_2, m_3 a_3)$$

$$f(\vec{r}) = f(\vec{r} + \vec{m}) = \left(\sum_{h, k, l} f_{h, k, l} e^{i \vec{g}_{h, k, l} \cdot \vec{r}} \right) \underbrace{e^{i \vec{g}_{h, k, l} \cdot \vec{m}}}_1$$

Lecture #3

Tensors and reciprocal lattice

Macroscopic properties

Every local property is periodic, like charge density: $\rho(\vec{r}) = \rho(\vec{r} + \vec{m})$. The mean value of a specific property for a cell can be extended to the whole crystal.

$$\bar{\rho} = \frac{1}{V} \int_V \rho(\vec{r}) d\vec{r}$$

HOMOGENEOUS (translational symmetry) TENSOR

$\vec{P} = \epsilon_0 \chi \vec{E}$

ISOTROPIC CRYSTAL

 \rightarrow

$P_i = \epsilon_0 \sum_j \chi_{ij} E_j$

IN GENERAL

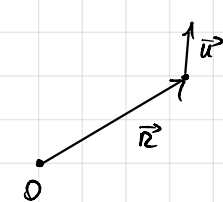
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$\begin{bmatrix} \chi & 0 & 0 \\ 0 & \chi & 0 \\ 0 & 0 & \chi \end{bmatrix}$

In general, properties can be represented by tensors. Another example of tensorial dependence could be the stress applied to a solid material in mechanical deformations, known as σ_{ij} .

STIMULUS (2nd RANK) $\sigma_{ij} = \sum_{r, s} \overset{\substack{\text{ELASTIC} \\ \text{TENSOR (4th RANK)}}}{\chi_{ijrs}} \overset{\substack{\text{EFFECT} \\ \text{(2nd RANK)}}}{\epsilon_{rs}}$

STRAIN $\epsilon_{rs} = \frac{1}{2} \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} \right)$



What happens if we apply point symmetry operations?

- ROTATION

$$x'_i = \sum_j \alpha_{ij} x_j$$

$$\chi'_{ij} = \sum_{k, s} \alpha_{ik} \alpha_{js} \chi_{ks}$$

NEW SYSTEM (left), OLD SYSTEM (right), ROTATION SENSOR (middle)

This is how tensors transform

If α_{ij} is a symmetry operation, the new component will be equal to the old.

$$\chi'_{ij} = \chi_{ij} \implies \chi_{ij} = \sum_{k, s} \alpha_{ik} \alpha_{js} \chi_{ks}$$

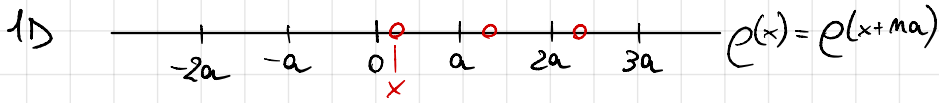
If a system is isotropic, every rotation is a symmetry operation.

In an isotropic system we have just one component in the diagonal of the tensor.

Reciprocal Lattice

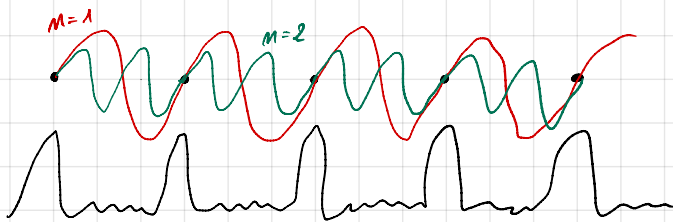
We have only talked about direct lattice until now. Let's start with 1D situation, obviously periodic.

$$\rho(\vec{r}) = \rho(\vec{r} + \vec{a})$$



Every periodic function can be represented with the Fourier series (sin+cos OR exp).

$$\rho(x) = \sum_m \rho_m e^{i \frac{2\pi}{a} m x} \quad \rho_m = \frac{1}{a} \int_0^a \rho(x) e^{-i \frac{2\pi}{a} m x} dx \quad \text{if } \rho(x) \text{ is real, } \rho_m^* = \rho_{-m}$$

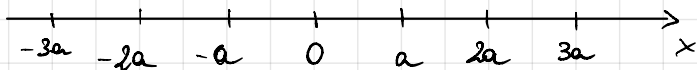


$$e^{iKx} \rightarrow K = \frac{2\pi}{\lambda} \rightarrow \lambda = \frac{a}{m} \text{ is the wavelength}$$

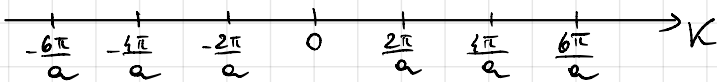
$$\begin{aligned} \lambda_1 &= a \\ \lambda_2 &= \frac{a}{2} \\ \lambda_3 &= \frac{a}{3} \\ &\vdots \end{aligned}$$

Reciprocal lattice vectors: $\vec{g}_m = \frac{2\pi}{a} m$

DIRECT LATTICE



RECIPROCAL LATTICE (abstract concept)



This is a discrete space

$$\rho(x+ma) = \sum_m \rho_m e^{i \frac{2\pi}{a} m (x+ma)} = \underbrace{\sum_m \rho_m e^{i \frac{2\pi}{a} m x}}_{\rho(x)} \underbrace{e^{i 2\pi m}}_1 \quad \text{IT IS PERIODIC (complex number properties)}$$

Now we consider a 3D situation.

$$\rho(\vec{r}) = \rho(\vec{r} + \vec{a}) \xrightarrow{\text{Fourier}} \rho(\vec{r}) = \sum_{\vec{g}} \rho_{\vec{g}} e^{i \vec{g} \cdot \vec{r}} \quad \text{PLANE WAVE}$$

If for the direct lattice $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are all \perp , $\vec{g} = 2\pi \left(\frac{h}{a_1} \hat{u}_x + \frac{k}{a_2} \hat{u}_y + \frac{l}{a_3} \hat{u}_z \right)$ with h, k, l integers

Fourier coefficients: $\rho_{\vec{g}} = \frac{1}{V_p} \int_{V_p} \rho(\vec{r}) e^{-i \vec{g} \cdot \vec{r}} d\vec{r}$

It is important to remember that all the waves have the same periodicity of the crystal.

$$\rho(\vec{r} + \vec{a}) = \sum_{\vec{g}} \rho_{\vec{g}} e^{i \vec{g} \cdot (\vec{r} + \vec{a})} = \sum_{\vec{g}} \rho_{\vec{g}} e^{i \vec{g} \cdot \vec{r}} \underbrace{e^{i \vec{g} \cdot \vec{a}}}_1 \quad (\text{if } \vec{a}_1 \perp \vec{a}_2 \perp \vec{a}_3)$$

Alternatively $e^{i\vec{g} \cdot \vec{m}} = 1 \iff e^{i\vec{g} \cdot (\vec{r} + \vec{m})} = e^{i\vec{g} \cdot \vec{r}}$ PLANE WAVE

$\vec{m} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$

DEFINITION OF \vec{g}

MILLER INDICES

(generic primitive vectors) $\vec{g}_{hkl} = 2\pi (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)$

$\vec{b}_1 = \frac{\vec{a}_2 \times \vec{a}_3}{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|} = \frac{\vec{a}_2 \times \vec{a}_3}{V_p}$

$\vec{b}_2 = \frac{\vec{a}_3 \times \vec{a}_1}{V_p}$

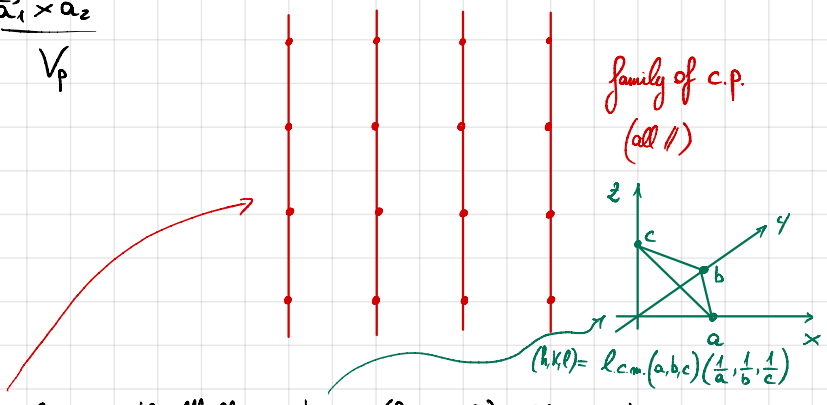
$\vec{b}_3 = \frac{\vec{a}_1 \times \vec{a}_2}{V_p}$

Linear combination among $2\pi\vec{b}_1, 2\pi\vec{b}_2, 2\pi\vec{b}_3$

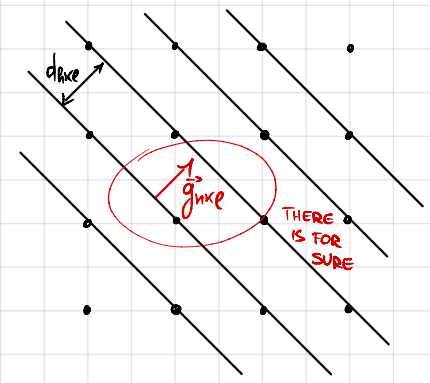
A very interesting property is $\vec{a}_i \cdot \vec{b}_j = \delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases}$

Properties of the reciprocal lattice

- 1) RL is a Bravais lattice;
- 2) RL of RL is DL;
- 3) $V_{p,RL} = \frac{(2\pi)^3}{V_p}$ (in 1D $k = \frac{2\pi}{a}$);



4) Given DL and a family of crystallographic planes with Miller indices (h, k, l) , $\exists \vec{g}_{hkl} \perp$ PLANES:



5) $d_{hkl} = \frac{2\pi}{|\vec{g}_{hkl}|}$ where the $|\vec{g}_{hkl}|$ is the smallest possible.

Lecture #4

Diffraction

$e^{i\vec{g} \cdot \vec{m}} = 1 \implies e^{i\vec{g} \cdot (\vec{r} + \vec{m})} = e^{i\vec{g} \cdot \vec{r}}$

$\vec{g}_n = \frac{2\pi}{a} n \quad \vec{g}_{hkl} = 2\pi (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)$

RECAP

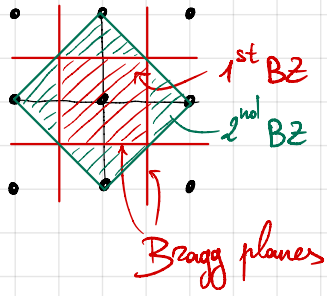
It is interesting to notice that FCC \rightarrow BCC and so BCC \rightarrow FCC.

PLANES (h, k, l) $\implies \exists \vec{g}_{hkl} \perp$ PLANES

$d_{hkl} = \frac{2\pi}{|\vec{g}_{hkl}|}$

Brillouin zones

The 1st Brillouin zone is the Wigner-Seitz cell of RL.

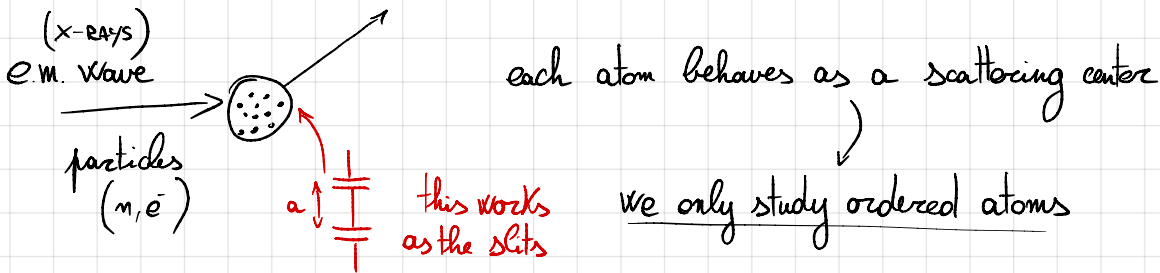


The 1st BZ is the closest region to the origin without crossing Bragg planes.

Now we must talk about diffraction

Scattering

In reality, periodicity is given by the average position of the atoms, as they move due to atomic vibrations. If the material is a crystal, we can talk about diffraction because the atoms are ordered.

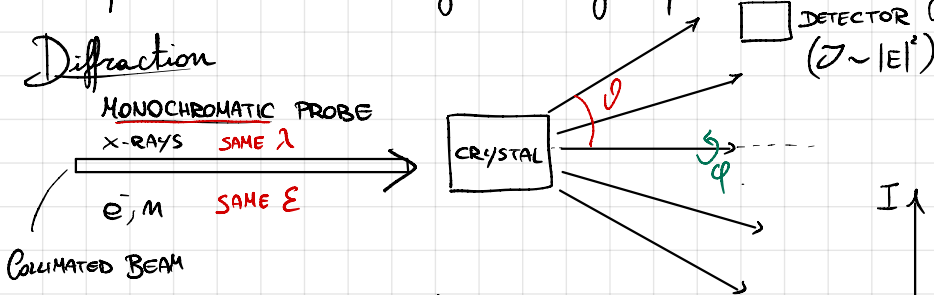


each atom behaves as a scattering center

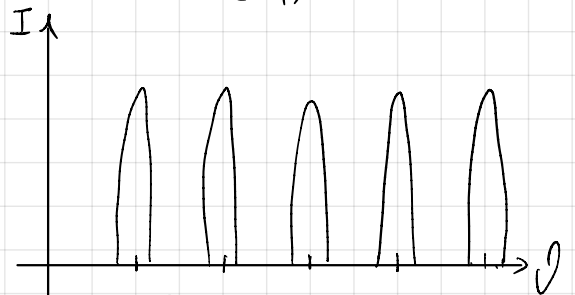
we only study ordered atoms

X-rays have a wavelength similar to the distance between the scattering atoms (light doesn't work), while electrons are surface sensitive. Neutrons identify the nuclei inside the material, while x-rays just the distribution of electrons (they are easier to use). A possible approach using x-rays involves Maxwell equations, but we are going to use the **Von Laue semiempirical laws**. Bragg law can be derived from these. For particles, we have to study Schrodinger equation. Mathematically, both are the same.

Diffraction



We measure the intensity (# particles vs direction)
 $I = I(\theta, \phi)$



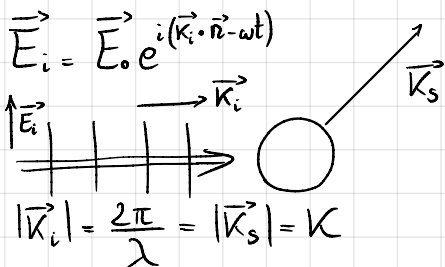
Just some angles are good due to interference

There are some approximations to be done.

1) Elastic scattering: after the scattering, we still have same λ/E (position informations).

X-RAYS

$e^- - m$



$$\psi = A e^{i(\vec{k}_i \cdot \vec{r} - \omega t)}$$

$$\epsilon = \frac{|\vec{p}|^2}{2m} = \frac{\hbar^2 |\vec{k}_i|^2}{2m} = \frac{\hbar^2 |\vec{k}_s|^2}{2m} = \frac{\hbar^2 |\vec{k}|^2}{2m}$$

$$\vec{p} = \hbar \vec{k}$$

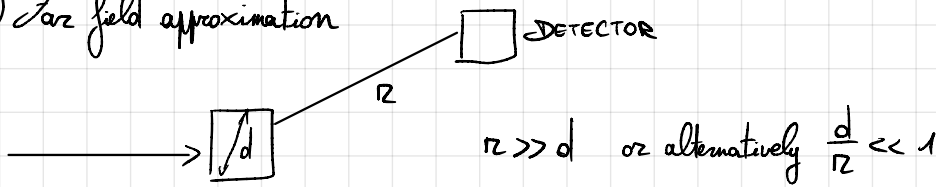
$$\lambda = \frac{2\pi}{|\vec{k}|} = \frac{h}{|\vec{p}|}$$

Energy doesn't change

$c = \lambda \omega \rightsquigarrow E_{ph} = \hbar \omega$ constant

Sometimes electrons may lose energy, but in our approximation they just change direction.

2) Far field approximation



Very useful

3) Born approximation (1st order): we just consider ONE interaction (single scattering).

WEAK INTERACTION

4) NO small angles

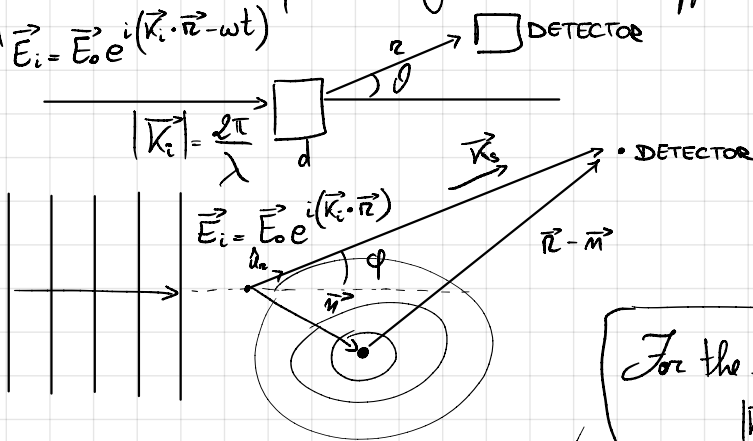
Lecture #5

Von Laue semiempirical laws and Schrödinger equation

Von Laue

We would use Maxwell equations for a stricter approach.

$$\vec{E}_i = \vec{E}_0 e^{i(\vec{k}_i \cdot \vec{r} - \omega t)}$$



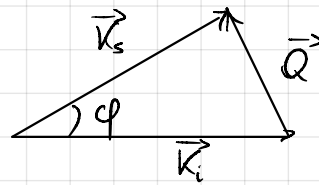
SCATTERED WAVE AMPLITUDE

$$\vec{E}_s = \vec{E}_0 e^{i\vec{k}_s \cdot \vec{r}} A \frac{e^{iK|\vec{r}-\vec{m}|}}{|\vec{r}-\vec{m}|}$$

scattering amplitude

For the elastic approximation $|\vec{k}_s| = |\vec{k}_i| = K$

$$\vec{k}_s = K \frac{\vec{r}}{r} = K \hat{u}_r$$



$\vec{Q} = \vec{k}_s - \vec{k}_i$
SCATTERING WAVE VECTOR SCATTERED WAVE VECTOR

THEN

$$|\vec{r}-\vec{m}| = \sqrt{(\vec{r}-\vec{m}) \cdot (\vec{r}-\vec{m})} = \sqrt{r^2 + m^2 - 2\vec{r} \cdot \vec{m}} = r \sqrt{1 - 2\vec{m} \cdot \frac{\vec{r}}{r} + \frac{m^2}{r^2}} \approx r \left(1 - \frac{\vec{m} \cdot \vec{r}}{r^2}\right)$$

for far field approximation

$$K|\vec{r}-\vec{m}| = Kr - K\hat{u}_r \cdot \vec{m} = Kr - \vec{k}_s \cdot \vec{m}$$

$$A \vec{E}_0 e^{i\vec{k}_i \cdot \vec{r}} \frac{e^{iKr} e^{-i\vec{k}_s \cdot \vec{m}}}{r}$$

There is also the incident wave

$$\vec{E}(\vec{r}) = \left(\sum_{\vec{m}} A \vec{E}_0 e^{i\vec{k}_i \cdot \vec{m}} e^{-i\vec{k}_s \cdot \vec{m}} \right) \frac{e^{iKr}}{r} + \vec{E}_0 e^{i\vec{k}_i \cdot \vec{r}}$$

negligible

NO SMALL ANGLE



$$\vec{E}(\vec{r}) = \vec{E}_0 A \frac{e^{iKr}}{r} \left(\sum_{\vec{m}} e^{-i\vec{Q} \cdot \vec{m}} \right)$$

ALL THE PROBLEMS COME FROM HERE

interference

spherical wave

Let's rewrite \vec{Q} as

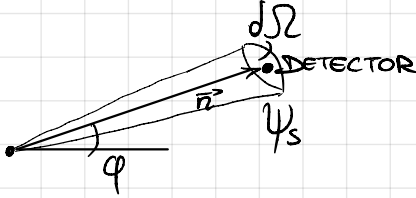
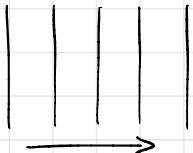
$$|\vec{Q}| = 2K \sin \frac{\varphi}{2} = \frac{4\pi}{\lambda} \sin \frac{\varphi}{2}$$

With the detector we measure intensity

$$I \sim |\vec{E}(\vec{r})|^2 \sim \left| \sum_{\vec{m}} e^{-i\vec{Q} \cdot \vec{m}} \right|^2$$

Now we move to particles.

Schrödinger equation



$$\psi = A e^{i(\vec{k}_i \cdot \vec{r} - \omega t)}$$

With the detector we measure the flux of particles

$$d\sigma = \frac{\text{\# PARTICLES SCATTERED IN } d\Omega}{\text{UNIT TIME}} \cdot \frac{\text{UNIT TIME} \cdot \text{UNIT SURFACE}}{\text{\# PARTICLES INCIDENT}}$$

DIFFERENTIAL CROSS SECTION [m²]
RECAP

$$d\sigma \sim |\psi_s|^2$$

SCHRÖDINGER EQUATION T.I.S.E.

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

 \rightsquigarrow

$$\hat{H}\psi = E\psi$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})$$

We know how much is the energy.

$$|\vec{k}_i| = |\vec{k}_s| = K$$

$$E = \frac{\hbar^2 K^2}{2m} \quad \text{just kinetic energy (elastic scattering)} \implies \hat{H}\psi = \frac{\hbar^2 K^2}{2m} \psi$$

we have to solve this

$$(\nabla^2 + K^2)\psi = \frac{2m U(\vec{r})}{\hbar^2} \psi$$

Helmholtz operator

Helmholtz equation

SOURCE

$$\text{in general } (\nabla^2 + K^2)\psi = f(\vec{r})$$

$\left\{ \begin{array}{l} \text{if } f(\vec{r}) = 0 \rightsquigarrow \text{homogeneous} \\ \text{if } f(\vec{r}) \neq 0 \rightsquigarrow \text{inhomogeneous} \end{array} \right.$

The problem is that here the source depends on the solution.

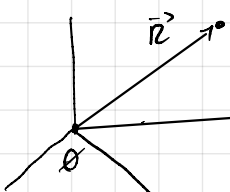
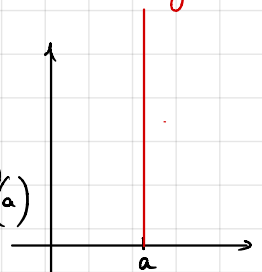
Green function method

$$(\nabla^2 + K^2)G(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}')$$

Dirac function

$$\int_{-\infty}^{+\infty} \delta(x) dx = 1$$

$$\int_{-\infty}^{+\infty} f(x) \delta(x-a) dx = f(a)$$



function exists only here

The solution for a point-like source is $G(\vec{r}, \vec{r}') = -\frac{1}{4\pi} \frac{e^{iK|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}$ spherical wave

$$\Psi(\vec{r}) = \int \underbrace{G(\vec{r}, \vec{r}')}_{\text{convolution with the source}} \underbrace{f(\vec{r}')}_{\text{source}} d\vec{r}' + \underbrace{\Psi_i(\vec{r})}_{\text{homogeneous solution}}$$

Source is both the potential of the crystal and the solution.

solution for ONE point

SOLUTION!!!

negligible for BIG ANGLES

$$\Psi_s(\vec{r}) = -\frac{2m}{4\pi\hbar^2} \int \frac{e^{iK|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} U(\vec{r}') \Psi(\vec{r}') d\vec{r}' + \Psi_i$$

Detector is distant, far field approximation $\frac{|\vec{r}'|}{|\vec{r}|} \ll 1$

SOURCE

We get an implicit equation

Born approximation

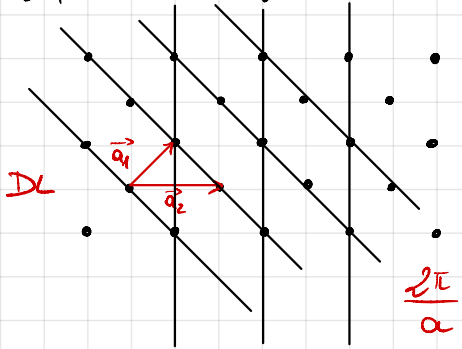
SCATTERED WAVE FUNCTION

Eventually

$$\Psi_s(\vec{r}) = -\frac{2mA}{\hbar^2 4\pi} \int \frac{e^{iKz} e^{-i\vec{k}_s \cdot \vec{r}'} e^{i\vec{k}_i \cdot \vec{r}'} U(\vec{r}') d\vec{r}'}{r} = -\frac{2mA}{4\pi\hbar^2} \frac{e^{iKz}}{r} \int U(\vec{r}') e^{-i\vec{Q} \cdot \vec{r}'} d\vec{r}'$$

Tutorial #2

We are going to study crystals with the reciprocal lattice. Lattice is described through its spatial frequencies instead of point positions; we enter in the world of waves ($K \rightarrow \lambda$).



Of course there has to be periodicity ($f(r) = f(r + T_n)$). This kind of function can be represented as a Fourier series.

$$f(r) = \sum_{\vec{k} \in \text{RL}} A_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

The reciprocal lattice is a set of vectors $\vec{k} = \vec{g}_{\vec{k}}$ such that $e^{i\vec{g}_{\vec{k}} \cdot \vec{T}_n} = 1$ (plane wave has the same periodicity as the crystal).

$$\vec{g}_{\vec{k}} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$$\Omega_{\vec{k}} = \frac{(2\pi)^3}{\Omega}$$

Volume RL Volume DL

PRIMITIVE VECTORS OF RL

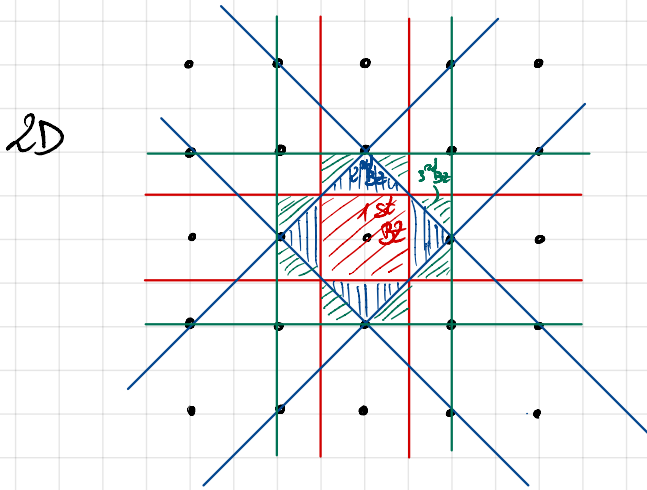
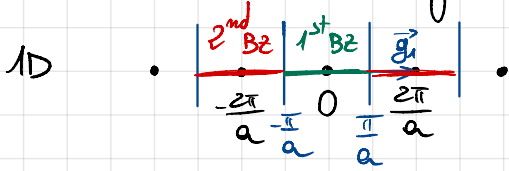
$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{|\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)|}$$

The 1st Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice; its center is called Γ point. It is important to remember that a family of lattice planes is perpendicular to a reciprocal lattice vector \vec{g} and further the spacing between neighbor planes is $d = \frac{2\pi}{|\vec{g}_{\text{min}}|}$.

shortest RLV in direction of \vec{g}

$$|\vec{g}_{hkl}| = \sqrt{h^2 |\vec{b}_1|^2 + k^2 |\vec{b}_2|^2 + l^2 |\vec{b}_3|^2}$$

Higher Brillouin zones can be found over Bragg planes.



Each Brillouin zone has the same size

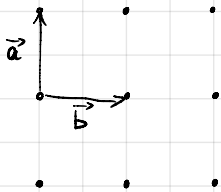
Tutorial #3

This is about chemical bondings. In general, a system is kept together because it has minimum energy.

$$U = Nu$$

TOTAL ENERGY UNIT ENERGY

Crystal structures are various.



both modules can be written as

$$\begin{cases} a = aR \\ b = bR \end{cases}$$

We want to condense informations into R so that $u = u(R)$

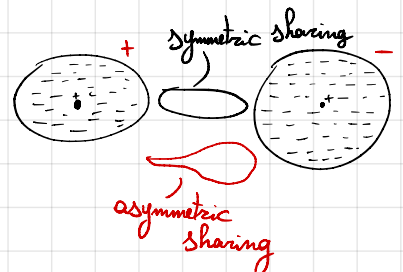
We impose that $\frac{du}{dR} = 0$ to have a minimum potential, therefore $u(R_0) = u$ constant. Why is there a binding energy?

Pauli's principle

Two fermions with same spin cannot occupy the same state; this, along with electrostatics gives us the answer.

Bonding types

			u [eV]
1	NEUTRAL (ATOMS, MOLECULES, ETC)	NOBLE GASES	0,1 @ $T = 83K$
2	COVALENT	C, Si, Ge... ~ 0	$C_{DIAMOND} \sim 5,4$
		GaAs ~ 0,67	NaCl ~ 7,8
3	IONIC	NaCl ~ 0,94	
4	METALLIC	ALKALI	0,8 - 8,9



Neutral crystals are also called molecular crystals; they are very common in nature

Shell structure

$$s \rightarrow l=0, m_l=0, m_s = \left\langle \begin{matrix} \frac{1}{2} \\ -\frac{1}{2} \end{matrix} \right\rangle$$

$$p \rightarrow l=1, m_l = \left\langle \begin{matrix} 1 \\ 0 \\ -1 \end{matrix} \right\rangle \dots$$

- MOLECULAR
- METALLIC
- PURE COVALENT

NOBLE GASES

ALKALINE

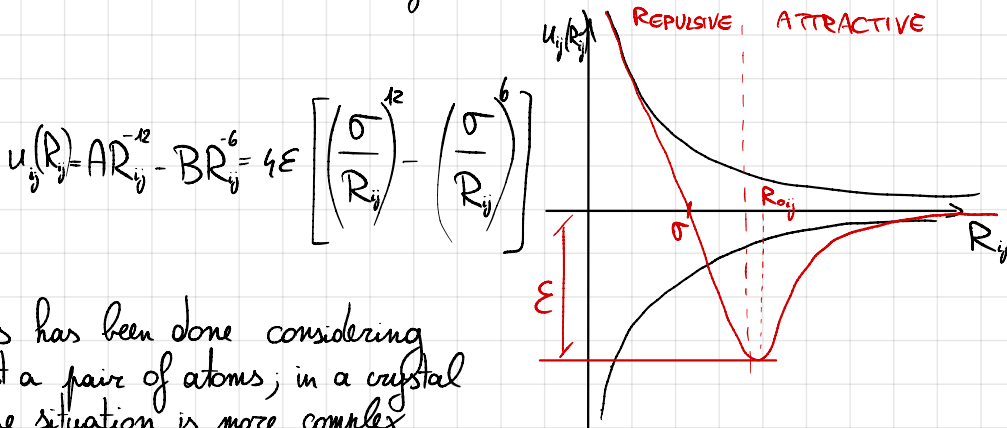
TEST

THIS IS JUST A MESS

Covalent bonding has the most symmetric directionality

Molecular crystals

Ice is a molecular crystal with a metal-like melting temperature. We have to consider also noble gases, which are attracted to one another by Van der Waals interactions.

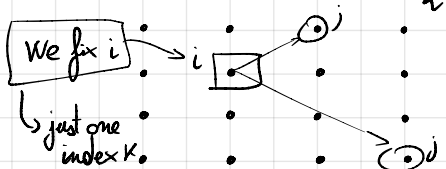


This has been done considering just a pair of atoms; in a crystal the situation is more complex.

$$U_{TOT} = \frac{1}{2} \sum_i \sum_{j \neq i} u_{ij} = \frac{1}{2} N \sum_K 4\epsilon \left[\left(\frac{\sigma}{R_K} \right)^{12} - \left(\frac{\sigma}{R_K} \right)^6 \right] = \frac{1}{2} N 4\epsilon \left[\frac{\sigma^{12}}{R^{12}} \sum_K \frac{1}{R_K^{12}} - \frac{\sigma^6}{R^6} \sum_K \frac{1}{R_K^6} \right]$$

$R_K = R_{PK}$ NON-DIMENSIONAL QUANTITY

$u = \frac{U_{TOT}}{N}$



We need to know what the shape of the crystal is. Typically, $K_{(12)} \approx 12, 13$ and $K_{(6)} \approx 14, 45$.

$$U'(R) = 2\epsilon \left[\frac{\sigma^6}{R^{13}} (-12) K_{(12)} - \frac{\sigma^6}{R^7} (-6) K_{(6)} \right] = 2\epsilon \frac{\sigma^6}{R^7} \left[\frac{\sigma^6}{R^6} (-12) K_{(12)} + 6 K_{(6)} \right] = 0$$

$$\frac{\sigma^6}{R_0^6} = \frac{K_{(6)}}{2K_{(12)}} \rightarrow R_0 = \sigma \sqrt[6]{\frac{2K_{(12)}}{K_{(6)}}}$$

CONSTANT

$$\frac{R_0}{\sigma} = 1.09$$

	Ne	Ar	Kr	Xe
$\frac{R}{\sigma} _{\text{exp}}$	1.14	1.11	1.1	1.09

PERFECT FOR HEAVY NOBLE GASES

Lecture #6

Diffraction again

Each atom in the crystal is a source of electromagnetic wave. We have already seen that

X-RAYS $I \sim \left| \sum_{\vec{n}} e^{-i\vec{Q} \cdot \vec{n}} \right|^2$ $\vec{Q} = \vec{k}_s - \vec{k}_i$

PARTICLES $\Psi_s(\vec{r}) \approx -\frac{2m A}{4\pi \hbar^2} \frac{e^{i\vec{k}_s \cdot \vec{r}}}{r} \int_V U(\vec{r}') e^{-i\vec{Q} \cdot \vec{r}'} d\vec{r}'$ SCATTERING AMPLITUDE $A_{si}(\vec{Q})$

Until this moment we have considered a generic crystal, but now we want to consider a periodic potential.

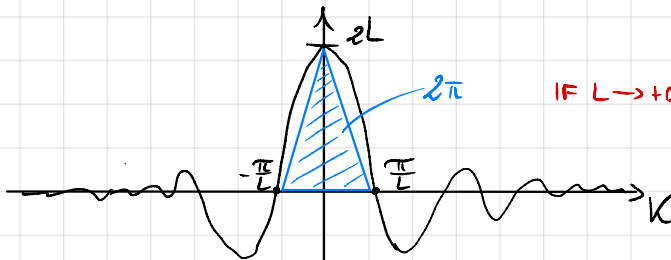
$$U(\vec{r}) = U(\vec{r} + \vec{n}) \Rightarrow U(\vec{r}) = \sum_{\vec{g}} U_{\vec{g}} e^{i\vec{g} \cdot \vec{r}} \quad \text{where } U_{\vec{g}} = \frac{1}{V_p} \int_{V_p} U(\vec{r}) e^{-i\vec{g} \cdot \vec{r}} d\vec{r}$$

If we do this, then $A_{si}(\vec{Q}) \sim \int_{V_p} e^{-i\vec{Q} \cdot \vec{r}} \sum_{\vec{g}} U_{\vec{g}} e^{i\vec{g} \cdot \vec{r}} d\vec{r} = \sum_{\vec{g}} U_{\vec{g}} \int_V e^{-i(\vec{Q} - \vec{g}) \cdot \vec{r}} d\vec{r}$ \rightarrow if the volume of the crystal is large enough

Considering a periodic potential, $A_{si}(\vec{Q}) = 0$ unless $\vec{Q} = \vec{g}$ (DIFFRACTION CONDITION) $\rightarrow \propto \delta(\vec{Q} - \vec{g})$

Demonstration of δ

$$\int_{-L}^{+L} e^{-ikx} dx = \frac{e^{-ikx}}{-ik} \Big|_{-L}^{+L} = -\frac{1}{ik} [e^{-iKL} - e^{iKL}] = \frac{2}{k} \sin(KL) = 2L \frac{\sin(KL)}{KL}$$



$$\text{If } L \rightarrow +\infty, \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-ikx} dx = \delta(x)$$

$$\vec{Q} = \vec{k}_s - \vec{k}_i = \vec{g}_{hke}$$

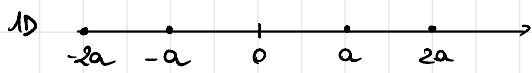
DIFFRACTION CONDITION

$$A_{S_i}(\vec{Q}) \sim \sum_{\vec{g}} U_{\vec{g}} \int_V e^{-i(\vec{Q}-\vec{g}) \cdot \vec{r}} d\vec{r} \quad \text{In this case } |A|^2 \propto |U_{\vec{g}}|^2$$

↑
INTENSITY OF THE PEAK

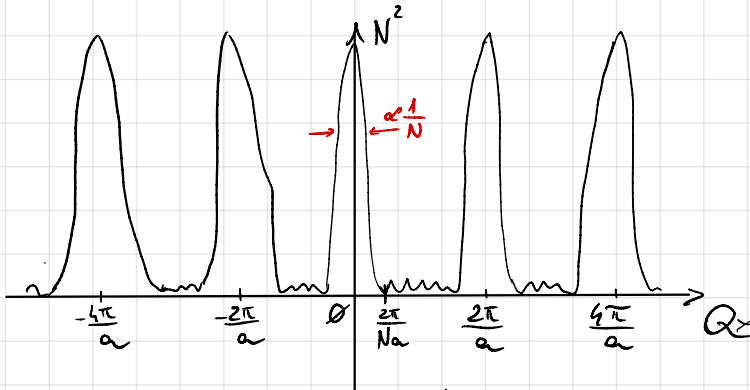
The Von Laue result is the same.

$$\mathcal{I} \sim \left| \sum_{\vec{r}} e^{i\vec{Q} \cdot \vec{r}} \right|^2 \sim \delta(\vec{Q}-\vec{g})$$



$$\vec{r} = ma\hat{x}$$

$$\vec{Q} \cdot \vec{r} = Q_x ma \rightarrow \left| \sum_{m=0}^{N-1} e^{-iQ_x ma} \right|^2 = \frac{\sin^2\left(\frac{Q_x Na}{2}\right)}{\sin^2\left(\frac{Q_x a}{2}\right)}$$



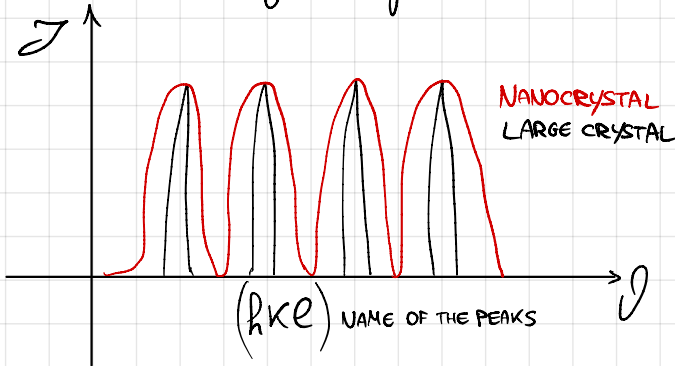
We have the maxima when both the sin go to zero $\rightarrow \frac{Q_x a}{2} = m\pi$

$$Q_x = \frac{2\pi}{a} m$$

We have the first zero when the numerator goes to zero $\rightarrow \frac{Q_x Na}{2} = \pi$

$$Q_x = \frac{2\pi}{Na}$$

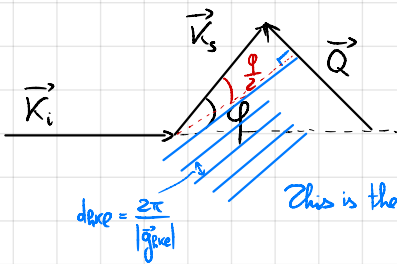
Typically we consider a crystal infinite when $a > 100 \text{ nm}$.



Bragg law of diffraction

$$2d \sin \vartheta = m\lambda$$

$$\vec{Q} = \vec{g}_{hke}$$



$$|\vec{Q}| = \frac{4\pi}{\lambda} \sin \frac{\varphi}{2}$$

if \vec{g} is not the shortest

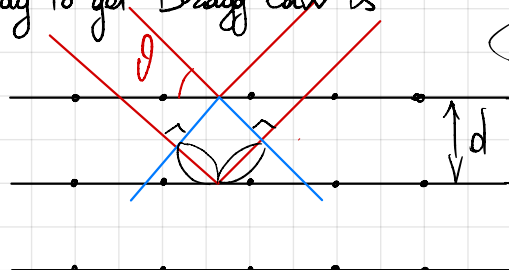
$$|\vec{g}_{hke}| = \frac{2\pi}{d_{hke}} m = \frac{4\pi}{\lambda} \sin \frac{\varphi}{2}$$

$$2d_{hke} \sin \frac{\varphi}{2} = m\lambda$$

where $\vartheta = \frac{\varphi}{2}$

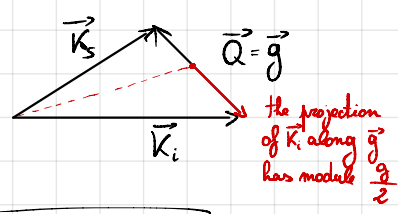
Diffraction condition is equivalent to Bragg law

Fastest way to get Bragg Law is



$$2d \sin \theta = n \lambda$$

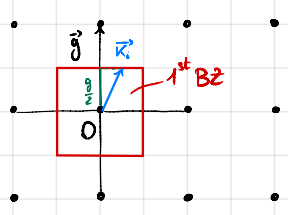
Von Laue diffraction condition



$$\vec{K}_s = \vec{K}_i + \vec{g}$$

$$K^2 = (\vec{K}_i + \vec{g}) \cdot (\vec{K}_i + \vec{g}) = K^2 + g^2 + 2\vec{K}_i \cdot \vec{g} \Rightarrow \vec{K}_i \cdot \vec{g} = -\frac{g^2}{2} \Rightarrow \vec{K}_i \cdot \frac{\vec{g}}{g} = -\frac{g}{2}$$

$$\vec{K}_i \cdot \frac{\vec{g}}{g} = -\frac{g}{2}$$



RECIPROCAL LATTICE

\vec{K}_i IS ON A BRAGG PLANE

What happens if we have a basis? DIFFRACTION IS THE SAME

$$\mathcal{I} \sim |U_{\vec{g}}|^2$$

NEUTRONS
$$U(\vec{r}) = \sum_{\vec{m}} \sum_{p=1}^s b_p \delta(\vec{r} - \vec{m} - \vec{r}_p)$$

atoms of the basis

$$U_{\vec{g}} = \frac{1}{V_p} \int_{V_p} U(\vec{r}) e^{-i\vec{g} \cdot \vec{r}} d\vec{r} = \frac{1}{V_p} \int_{V_p} \sum_p b_p \delta(\vec{r} - \vec{r}_p) e^{-i\vec{g} \cdot \vec{r}} d\vec{r} = \frac{1}{V_p} \sum_p b_p \int_{V_p} \delta(\vec{r} - \vec{r}_p) e^{-i\vec{g} \cdot \vec{r}} d\vec{r} = \frac{1}{V_p} \sum_p b_p e^{-i\vec{g} \cdot \vec{r}_p}$$

GEOMETRICAL STRUCTURE FACTOR

$$\mathcal{I}_{hke} \sim \left| \sum_p b_p e^{-i\vec{g}_{hke} \cdot \vec{r}_p} \right|^2$$

IF THE ATOMS ARE ALL EQUAL, ~~b_p~~

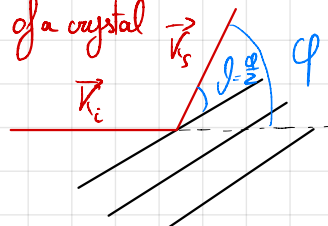
We have a missing peak if the structure factor goes to zero, even though $\vec{Q} = \vec{g}_p$ for destructive interference.

Lecture #7

Electronic structure of a crystal

$$\vec{Q} = \vec{K}_s - \vec{K}_i = \vec{g}_{hke}$$

$$2d \sin \theta = n \lambda$$



$$\vec{K}_i \cdot \frac{\vec{g}}{g} = \frac{g}{2}$$

We start from these considerations.

$$\frac{d\sigma}{d\Omega}(\vec{r}) \sim |U_{\vec{g}}|^2; \text{ for neutrons } \mathcal{I}_{hke} \sim \left| \sum_p b_p e^{-i\vec{g}_{hke} \cdot \vec{r}_p} \right|^2, \text{ while for the electrons } U(\vec{r}) \text{ depends on charge distribution}$$

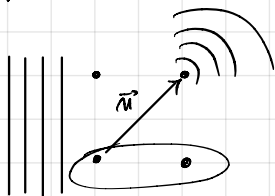
X-ray approach

We don't use the potential, but charge density: $U(\vec{r}) \rightarrow \rho(\vec{r})$

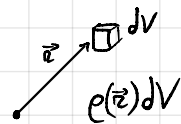
REMEMBER FOR PARTICLES

$$A_s = \int_V U(\vec{r}) e^{-i\vec{Q}\cdot\vec{r}} d\vec{r}$$

$\vec{E}_s \sim \int_V \rho(\vec{r}) e^{-i\vec{Q}\cdot\vec{r}} d\vec{r}$, then $\mathcal{I} \sim \left| \sum_{\vec{g}} \rho_{\vec{g}} \delta(\vec{Q}-\vec{g}) \right|^2$ and when the diffraction condition is satisfied $\mathcal{I} \sim |\rho_{\vec{g}}|^2$.



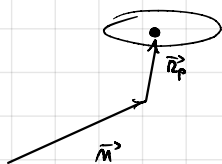
Each infinitesimal volume has a charge density:



$$\vec{E}_s \sim \int_V \rho(\vec{r}) dV e^{-i\vec{Q}\cdot\vec{r}}$$

Now let's find the Fourier coefficient.

$$\rho(\vec{r}) = \sum_{\vec{r}_p} \rho_p(\vec{r} - \vec{r}_p)$$



This is the charge distribution

$$\begin{aligned} \rho_{\vec{g}} &= \frac{1}{V_P} \int_{V_P} \sum_P \rho_P(\vec{r} - \vec{r}_P) e^{-i\vec{g}\cdot\vec{r}} d\vec{r} = \frac{1}{V_P} \int_{V_P} \sum_P \rho_P(\vec{r} - \vec{r}_P) e^{-i\vec{g}\cdot(\vec{r} - \vec{r}_P)} e^{-i\vec{g}\cdot\vec{r}_P} d(\vec{r} - \vec{r}_P) = \\ &= \frac{1}{V_P} \sum_P e^{-i\vec{g}\cdot\vec{r}_P} \int_{V_P} \rho_P(\vec{r}) e^{-i\vec{g}\cdot\vec{r}} d\vec{r} = \frac{1}{V_P} \sum_P f_P(\vec{g}) e^{-i\vec{g}\cdot\vec{r}_P} \end{aligned}$$

similar to the neutron one ($U_{\vec{g}} = \frac{1}{V_P} \sum_P b_P e^{-i\vec{g}\cdot\vec{r}_P}$)

$f_P(\vec{g})$ ATOMIC FORM FACTOR

It is important to highlight the dependence on g

Electronic structure

The goal is to find the stationary states of e^- (not considering core electrons). There are some issues though, like many-body (huge presence of particles), interactions e^-/e^- and $e^-/ions$ and ions vibrations. How is it possible to solve Schrödinger equation? We do some approximations.

1) FROZEN CRYSTAL

Ions are fixed in equilibrium lattice positions. It is also known as Born-Oppenheimer or adiabatic approximation.

$$\hat{H}_{TOT} \Psi = E_{TOT} \Psi$$

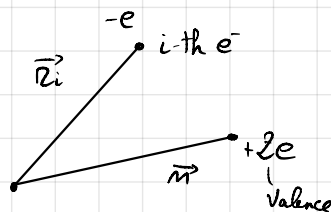
$$\hat{H}_{TOT} = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] - \sum_i \left[\sum_{ions} \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \right] + \frac{1}{2} \sum_i \sum_{j \neq i} \left[\frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \right]$$

THIRD TERM CANNOT BE MERGED

$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$

Coulomb force

Coulomb repulsive force



Interaction ions/ions is not considered.

$$\hat{H}_{TOT} = \sum_i \hat{H}_i + \frac{1}{2} \sum_{i,j} V_{ij}$$

Other approximations are needed (we must reduce a complex problem for N particles to N single particle problems)

we want a sum over electrons

$$\frac{1}{2} \sum_{i,j} V_{ij} \rightarrow \sum_i \bar{U}(\vec{r}_i)$$

NO MORE MUTUAL INTERACTION

Each electron is now separated from any other

Now we have a new hypothesis:

$$\hat{H}_{TOT} = \hat{H}_1(1) + \hat{H}_2(2)$$

in quantum physics it is referred as non-interacting particles.

$$\hat{H}_{TOT} \Psi(1,2) = E_{TOT} \Psi(1,2) \Rightarrow \begin{cases} \Psi(1,2) = \Psi(1)\Psi(2) \\ E_{TOT} = E_1 + E_2 \end{cases}$$

$$\begin{cases} \hat{H}_1 \psi_1 = \epsilon_1 \psi_1 \\ \hat{H}_2 \psi_2 = \epsilon_2 \psi_2 \end{cases}$$

We don't solve a problem for two particles, but we solve two problems for single particles!

Then $\hat{H}_{TOT} \psi_1 \psi_2 = \epsilon_{TOT} \psi_1 \psi_2$

$$(\hat{H}_1 + \hat{H}_2) \psi_1 \psi_2 = \epsilon_{TOT} \psi_1 \psi_2$$

$$\underbrace{\psi_2 \hat{H}_1 \psi_1}_{\epsilon_1 \psi_1} + \underbrace{\psi_1 \hat{H}_2 \psi_2}_{\epsilon_2 \psi_2} = (\epsilon_1 + \epsilon_2) \psi_1 \psi_2$$

2) EXCHANGE SYMMETRY

We introduce an exchange operator $\hat{P}(1,2)$: $\hat{P}(1,2) \psi(1,2) = \psi(2,1)$

The two electrons change position

$$[\hat{H}(1,2), \hat{P}(1,2)] = \hat{H}\hat{P} - \hat{P}\hat{H} = 0 \quad \text{it commutes with the Hamiltonian}$$

Stationary states are eigenfunctions of \hat{P} .

$$\hat{P}(1,2) \psi(1,2) = \lambda \psi(1,2) = \psi(2,1) \xrightarrow{\text{APPLY AGAIN } \hat{P}} \hat{P}[\psi(2,1)] = \hat{P}[\lambda \psi(1,2)] \Rightarrow \psi(1,2) = \lambda^2 \psi(1,2) \Rightarrow \lambda^2 = 1$$

$\lambda = \pm 1$

So we get $\hat{P}(1,2) \psi(1,2) = \pm \psi(1,2) \rightsquigarrow \psi(2,1) = \pm \psi(1,2)$ always true

- ⊕ symmetric BOSONS (integer spin)
- ⊖ anti-symmetric FERMIONS (half-integer spin)

↳ Pauli exclusion principle

Tutorial #4

We acknowledge that $u = u(R)$ and $u'(R_0) = 0$ where $R_0 = 1,030$.

↳ Lennard Jones potential

$$u_T = u_{REP} + u_{Coul}$$

$$u_{Coul,i} = \sum_j \frac{e z_j}{4\pi \epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

TOTAL CHARGE

} this does not depend on the lattice site

Let's start from a 1D crystal:

$$z = \pm 1 \quad \vec{r}_i - \vec{r}_j = \vec{r}_K - R \vec{p}_K$$

- + - + - +

$$u_i = \frac{e^2}{4\pi \epsilon_0} \sum_K \frac{(-1)^K}{R^K}$$

harmonic series log 2

For a generic situation though

$$u_i = \frac{e^2}{4\pi \epsilon_0 R} \sum_K \frac{m_K}{p_K} \text{ sign of } 1$$

molecule	a
NaCl	1,74
CsCl	1,763
GaAs	1,638

$$u_r = A e^{-\frac{R}{P}} \left\{ \frac{e^2}{4\pi\epsilon_0 R} a \right\}$$

$$u' = -\frac{A}{P} e^{-\frac{R}{P}} + \frac{e^2}{4\pi\epsilon_0 R^2} a \quad \text{for } R=R_0 \Rightarrow \frac{A}{P} e^{-\frac{R_0}{P}} = \frac{e^2}{4\pi\epsilon_0 R_0^2} a$$

Typically $P \sim \frac{R_0}{10}$; for NaCl, $R_0 = 2.82 \text{ \AA}$
 $P = 0.321 \text{ \AA}$

SPATIAL DISTRIBUTION OF MATTER RESPONSIBLE FOR DIFFRACTION

ATOMIC FORM FACTOR

$$F(\vec{g}) = \sum_j f_p(\vec{g}) e^{-i\vec{r}_p \cdot \vec{g}}$$

This expresses the summation of the amplitudes of two incidental waves. Now we are going to see how these terms behave in cubic systems.

$$A e^{-\frac{R_0}{P}} = \frac{e^2}{4\pi\epsilon_0 R_0} a \frac{P}{R_0} \Rightarrow u(R_0) = \left(\frac{P}{R_0} - 1\right) \frac{e^2}{4\pi\epsilon_0 R_0} a$$

constant

$U_{\text{Coul}}(R_0)$
Coulomb interaction energy in equilibrium

$$u = 7.81 \text{ eV}$$

Simple cubic

$$\vec{r}_p = (0, 0, 0)$$

$$\vec{g} = h \frac{2\pi}{a} \hat{u}_x + k \frac{2\pi}{a} \hat{u}_y + l \frac{2\pi}{a} \hat{u}_z \rightsquigarrow \vec{r}_p \cdot \vec{g} = 0 \Rightarrow e^{-i \cdot 0} = 1$$

$$F(\vec{g}) = f(\vec{g})$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{just for SC}$$

→ it is easier to consider BCC and FCC as SC with a basis

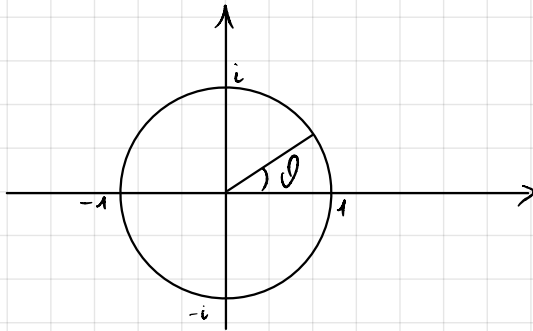
BCC

$$\vec{r}_p = \begin{cases} (0, 0, 0) \\ \frac{a}{2}(1, 1, 1) \end{cases}$$

$$\vec{g} \text{ is the same as before } \rightsquigarrow \vec{r}_p \cdot \vec{g} = \begin{cases} 0 \\ \pi(h+k+l) \end{cases}$$

$$\Rightarrow e^{-i\vec{r}_p \cdot \vec{g}} = \begin{cases} 1 \\ e^{-i\pi(h+k+l)} = (-1)^{h+k+l} \end{cases}$$

we are moving on the complex plane with jumps of π (RHS)
Since $e^{i\pi} = -1$



$$F(\vec{g}) = f(\vec{g}) \underbrace{(1 + e^{-i\pi(h+k+l)})}_{\pm 1} = \begin{cases} 0 & \text{if } h+k+l \text{ is odd} \\ 2f(\vec{g}) & \text{if } h+k+l \text{ is even} \end{cases}$$

COUNTER-PHASE

PHASE

FCC

$$\vec{r}_p = \begin{cases} (0, 0, 0) \\ \frac{a}{2}(1, 0, 1) \\ \frac{a}{2}(0, 1, 1) \\ \frac{a}{2}(1, 1, 0) \end{cases}$$

$$\rightsquigarrow \vec{r}_p \cdot \vec{g} = \begin{cases} 0 \\ (h+l)\pi \\ (k+l)\pi \\ (h+k)\pi \end{cases}$$

$$\Rightarrow e^{-i\vec{r}_p \cdot \vec{g}} = \begin{cases} 1 \\ e^{i\pi(h+l)} = (-1)^{h+l} \\ e^{i\pi(k+l)} = (-1)^{k+l} \\ e^{i\pi(h+k)} = (-1)^{h+k} \end{cases}$$

$$F(\vec{g}) = f(\vec{g}) \left[1 + (-1)^{h+l} + (-1)^{k+l} + (-1)^{h+k} \right] = \begin{cases} 4f(\vec{g}) & \text{if all even/odd} \\ 0 & \text{if one odd/one even} \end{cases}$$

To condense everything

$$F(\vec{g}) = f(\vec{g}) \left[1 + (-1)^{h_1} + (-1)^{k_1} + (-1)^{h+k} \right] \left(1 + e^{-i\frac{\pi}{2}(h+k+l)} \right) = \begin{cases} 0 & \text{if one odd/one even} \\ 8f(\vec{g}) & \text{if all even and } h+k+l=4m \\ 0 & \text{if all even but } h+k+l \neq 4m \\ 4(1+i)f(\vec{g}) & \text{if all odd} \end{cases}$$

we are moving in the complex plane with jumps of $\frac{\pi}{2}$

Lecture #8

Electrons in a crystal

$$\hat{H}_{TOT} = \sum_i \hat{H}_i + \frac{1}{2} \sum_{i,j} V_{ij}$$

$$\hat{H} = \hat{H}_A + \hat{H}_B$$

Exchange symmetry: $\psi(2,1) = \pm \psi(1,2)$

$\sum_i U_{MEAN}(\vec{r}_i)$ } First simplification

$$\psi(A,B) = \psi_A(A) \psi_B(B)$$

Now we consider independent e⁻

THIS DOES NOT SATISFY EXCHANGE SYMMETRY

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{m_1}(\vec{r}_1) \psi_{m_2}(\vec{r}_2) \neq \psi_{m_1}(\vec{r}_2) \psi_{m_2}(\vec{r}_1)$$

QUANTUM NUMBERS (STATES)

$$\Psi(1,2) = \psi(\vec{r}_1, \vec{r}_2) \chi(1,2) = -\Psi(2,1)$$

SPATIAL WAVE FUNCTION

+	-	} ANTI-SYMMETRIC
-	+	

SPIN

A new function is needed

$$\Psi_S = \frac{1}{\sqrt{2}} \left[\psi_{m_1}(\vec{r}_1) \psi_{m_2}(\vec{r}_2) + \psi_{m_1}(\vec{r}_2) \psi_{m_2}(\vec{r}_1) \right]$$

PARTICLES IN THE SAME STATE

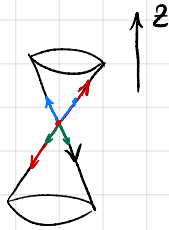
if $m_1 = m_2$, $\Psi_S = \psi_{m_1}(\vec{r}_1) \psi_{m_1}(\vec{r}_2)$

$$\Psi_{AS} = \frac{1}{\sqrt{2}} \left[\psi_{m_1}(\vec{r}_1) \psi_{m_2}(\vec{r}_2) - \psi_{m_1}(\vec{r}_2) \psi_{m_2}(\vec{r}_1) \right]$$

What about the spin?

$$s = \frac{1}{2} \Rightarrow S^2 = \hbar s(s+1)$$

$$m_s = \pm \frac{1}{2} \quad S_z = \hbar m_s$$



SINGLET

$$\chi_{AS}(1,2) = \frac{1}{\sqrt{2}} \left[\chi_{\frac{1}{2}}(1) \chi_{-\frac{1}{2}}(2) - \chi_{-\frac{1}{2}}(2) \chi_{\frac{1}{2}}(1) \right]$$

TRIPLET

$$\chi_S(1,2) = \frac{1}{\sqrt{2}} \left[\chi_{\frac{1}{2}}(1) \chi_{\frac{1}{2}}(2) + \chi_{\frac{1}{2}}(2) \chi_{\frac{1}{2}}(1) \right]$$

It is the same, but for the spin

if they have the same spin, $\chi_S = \chi_{\frac{1}{2}}(1) \chi_{\frac{1}{2}}(2)$ BOTH UP

$\chi_S = \chi_{-\frac{1}{2}}(1) \chi_{-\frac{1}{2}}(2)$ BOTH DOWN

The final product must be anti-symmetric.

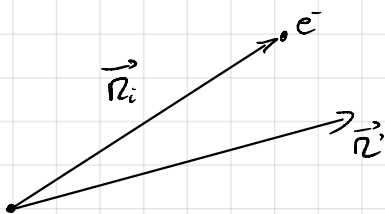
Hartree approach

It is an approach to find U_{MEAN} . We want a mean field generated by the electrons in an atom.

$$\Psi = \psi_{m_1}(\vec{r}_1) \psi_{m_2}(\vec{r}_2) \dots \psi_{m_N}(\vec{r}_N)$$

Symmetry is not considered along with the spin

$U(\vec{r}_i)$?



$$\rho_i(\vec{r}) = -e \sum_{j \neq i} |\psi_{m_j}(\vec{r})|^2$$

Electron potential $V_i(\vec{r}_i) = \int_V \frac{\rho_i(\vec{r}') d\vec{r}'}{4\pi \epsilon_0 |\vec{r}_i - \vec{r}'|}$

Potential is not discrete because electrons are uniformly distributed.

As final result

$$U_i(\vec{r}_i) = \frac{e^2}{4\pi\epsilon_0} \int \frac{\sum_{j \neq i} |\psi_{m_j}(\vec{r}_j)|^2 d\vec{r}_j}{|\vec{r}_i - \vec{r}_j|}$$

we don't know this

The wave function of an electron depends on the wave function of the others

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{\vec{r}} \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}|} + \frac{e^2}{4\pi\epsilon_0} \int \frac{|\psi_{m_j}(\vec{r}_j)|^2 d\vec{r}_j}{|\vec{r}_i - \vec{r}_j|} \right] \psi_{m_i}(\vec{r}_i) = \epsilon_i \psi_{m_i}(\vec{r}_i)$$

SELF-CONSISTENT MEAN FIELD

An iterative method must be used.

$$\psi_{m_j}^{(0)}(\vec{r}_j) \rightarrow \psi_{m_i}^{(1)}(\vec{r}_i)$$

Hartree-Fock approach

$$\Psi = \Psi(\vec{r}_1, \vec{S}_1; \vec{r}_2, \vec{S}_2; \dots; \vec{r}_N, \vec{S}_N)$$

SLATER DETERMINANT

$$\begin{vmatrix} \psi_{m_1}(\vec{r}_1, \vec{S}_1) & \dots & \psi_{m_1}(\vec{r}_N, \vec{S}_1) \\ \vdots & & \vdots \\ \psi_{m_N}(\vec{r}_1, \vec{S}_1) & \dots & \psi_{m_N}(\vec{r}_N, \vec{S}_1) \end{vmatrix}$$

For the rest of the course, we substitute the mutual interaction with the mean energy.

In order to jump to another energy level, an energy quantity $\Delta\epsilon = \epsilon_j - \epsilon_i$ is needed.

$$\hat{H}_{TOT} = \sum_i \hat{H}_i \quad \hat{H}_i = -\frac{\hbar^2}{2m} \nabla^2 + U_{e-ion}(\vec{r}_i) + U_{e-e}(\vec{r}_i)$$

$U_{CRYSTAL}(\vec{r}_i) \leftarrow$ whatever method we choose, that is periodic

This has become a single particle problem.

Crystal models

1) $U(\vec{r}) = 0$ suitable for electrons in a metal

2) $U(\vec{r})$ small PERTURBATION THEORY

3) $U(\vec{r})$ big TIGHT BINDING

Electrons in periodic potential

A single particle state in a periodic potential is called Bloch state; also $U(\vec{r}) = U(\vec{r} + \vec{m})$.

$$\hat{H}\psi = \epsilon\psi \quad \text{where} \quad \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})$$

$$\hat{T}_{\vec{m}}: \hat{T}_{\vec{m}}\psi(\vec{r}) \hat{=} \psi(\vec{r} + \vec{m})$$

$\rightarrow [\hat{H}, \hat{T}_{\vec{m}}] = 0$ if the potential is periodic

$$\hat{T}_{\vec{m}}(\hat{H}\psi) = \hat{H}(\vec{r} + \vec{m})\psi(\vec{r} + \vec{m}) = \hat{H}(\vec{r})\psi(\vec{r} + \vec{m}) = \hat{H}\hat{T}_{\vec{m}}\psi(\vec{r})$$

Stationary states are eigenfunction of the translational operator: $\hat{T}_{\vec{m}}\psi = \lambda(\vec{m})\psi$

Lecture #3

Bloch theorem

$$\hat{H}_i = -\frac{\hbar^2}{2m} \nabla^2 + \underbrace{U(\vec{r})}_{U_{el-ion} + U_{phon-procs}}$$

$$U(\vec{r}) = U(\vec{r} + \vec{m})$$

$$\hat{T}_{\vec{m}} \psi(\vec{r}) = \psi(\vec{r} + \vec{m})$$

$$[\hat{H}, \hat{T}_{\vec{m}}] = 0 \text{ same eigenfunctions} \rightarrow \hat{T}_{\vec{m}} \psi = \lambda(\vec{m}) \psi$$

$$\hat{T}_{\vec{m}_1} \hat{T}_{\vec{m}_2} \psi(\vec{r}) = \psi(\vec{r} + \vec{m}_1 + \vec{m}_2) = \hat{T}_{\vec{m}_1 + \vec{m}_2} \psi(\vec{r})$$

$$\lambda(\vec{m}_1) \lambda(\vec{m}_2) \psi = \lambda(\vec{m}_1 + \vec{m}_2) \psi \Rightarrow \lambda(\vec{m}_1) \lambda(\vec{m}_2) = \lambda(\vec{m}_1 + \vec{m}_2) \text{ important property; just one solution: } \lambda(\vec{m}) = e^{i\vec{s} \cdot \vec{m}}$$

\vec{s} is a constant vector defined as $\vec{s} = \vec{\alpha} + i\vec{k}$

$$\vec{m} = n\vec{a}$$

$$\hat{T}_{\vec{m}} \psi = \psi(x + na) = e^{sna} \psi(x)$$



$$\int \psi^* \psi dV = \int |\psi|^2 dV = 1$$

$$\int |\psi(x+na)|^2 dx = \int |e^{sna}|^2 |\psi|^2 dx = |e^{sna}|^2 \int |\psi|^2 dx = 1 \Rightarrow |e^{sna}|^2 = 1$$

$$|e^{sna}|^2 = |e^{i\vec{k} \cdot n\vec{a}}|^2 = 1$$

$\lambda(\vec{m})$ is a pure imaginary function

$$\lambda(\vec{m}) = e^{i\vec{k} \cdot \vec{m}}$$

$$[\vec{k}] = [m^{-1}] \vec{k} \text{ is a wavevector}$$

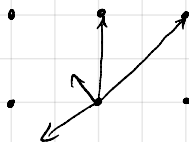
$\hat{T}_{\vec{m}} \psi(\vec{r}) = \psi(\vec{r} + \vec{m}) = e^{i\vec{k} \cdot \vec{m}} \psi(\vec{r})$ if ψ is a stationary state; we've just expressed the first form of the Bloch theorem.

Some considerations

1) Wavefunction is not periodic

2) Wavefunction is periodic only if $\vec{k} = \vec{g}$

$$\psi(\vec{r} + \vec{m}) = e^{i\vec{g} \cdot \vec{m}} \psi(\vec{r})$$



The eigenvalue depends on the wavevector.

$$\psi_{\vec{k}}(\vec{r} + \vec{m}) = e^{i\vec{k} \cdot \vec{m}} \psi_{\vec{k}}(\vec{r}) \text{ (function not periodic, just a phase factor } e^{i\vec{k} \cdot \vec{m}})$$

Quantum numbers

$$\hat{H} \psi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}(\vec{k}) \psi_{\vec{k}}(\vec{r})$$

energy depends on \vec{k}

for each \vec{k} there can be more solutions

Now we consider the second form of Bloch theorem.

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \text{ with } u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{m}) \text{ Bloch function}$$

$$\psi_{\vec{k}}(\vec{r} + \vec{m}) = u_{\vec{k}}(\vec{r} + \vec{m}) e^{i\vec{k} \cdot (\vec{r} + \vec{m})} = \underbrace{u_{\vec{k}}(\vec{r})}_{\psi} e^{i\vec{k} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{m}} = \psi(\vec{r}) e^{i\vec{k} \cdot \vec{m}}$$

$$\begin{cases} \hat{H}\psi_{\vec{k}} = E(\vec{k})\psi_{\vec{k}} \\ \psi_{\vec{k}} = u_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \end{cases} \Rightarrow \left[\frac{|\hat{p} + \hbar\vec{k}|^2}{2m} + U(\vec{r}) \right] u_{\vec{k}}(\vec{r}) = E(\vec{k})u_{\vec{k}}(\vec{r})$$

$$\hat{p} = -i\hbar\nabla$$

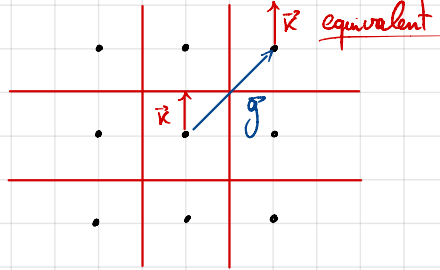
$$|\hat{p}|^2 = \hat{p}\cdot\hat{p} = -\hbar^2\nabla^2$$

We can see how Bloch function depends on \vec{k} . For each \vec{k} we have a family of solutions. Let's come back to the translation operator.

$$\lambda_{\vec{k}}(\vec{m}) = e^{i\vec{k}\cdot\vec{m}} \quad \text{what if } \vec{k} \rightarrow \vec{k} + \vec{g} ? \quad \lambda_{\vec{k}+\vec{g}}(\vec{m}) = e^{i(\vec{k}+\vec{g})\cdot\vec{m}} = e^{i\vec{k}\cdot\vec{m}} e^{i\vec{g}\cdot\vec{m}} = e^{i\vec{k}\cdot\vec{m}} = \lambda_{\vec{k}}(\vec{m})$$

And so $\psi_{\vec{k}}(\vec{r}+\vec{m}) = e^{i\vec{k}\cdot\vec{m}}\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}+\vec{g}}(\vec{r}+\vec{m})$. It is sufficient to consider \vec{k} in just one cell, the first Brillouin zone.

NOTHING CHANGES



Stationary states are periodic in \vec{k} space with \vec{g}

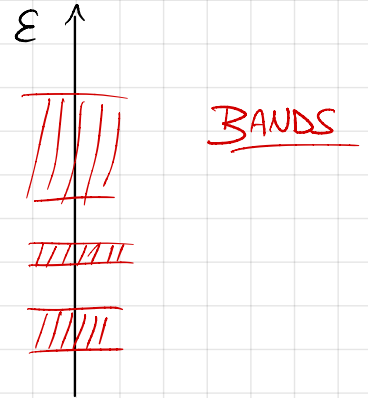
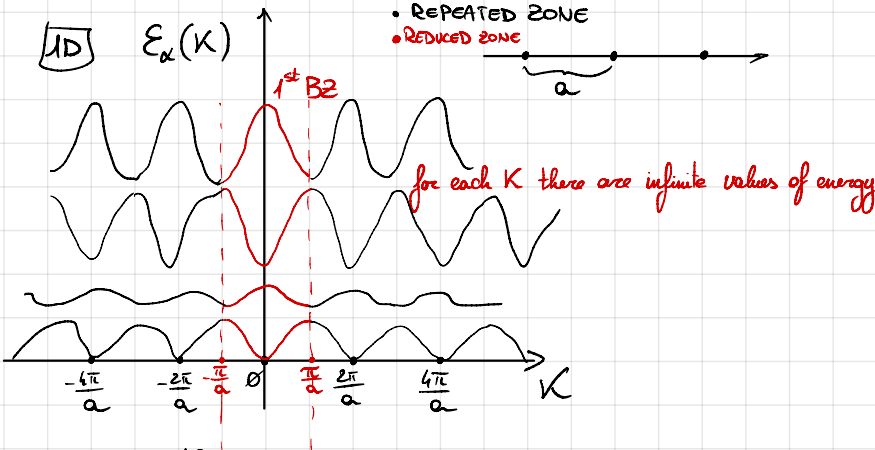
$$\psi_{\alpha, \vec{k}+\vec{g}}(\vec{r}) = \psi_{\alpha, \vec{k}}(\vec{r})$$

REDUCED ZONE SCHEME

$$\hat{H}\psi_{\alpha, \vec{k}} = E_{\alpha}(\vec{k})\psi_{\alpha, \vec{k}}$$

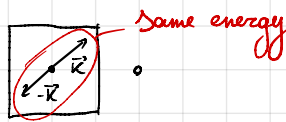
$$E_{\alpha}(\vec{k}+\vec{g}) = E_{\alpha}(\vec{k})$$

Also $E(\vec{k})$ is called DISPERSION RELATION, while α represents its different branches.



Kramers theorem

$$E_{\alpha}(\vec{k}) = E_{\alpha}(-\vec{k})$$



For a free electron ($U=0$), we are considering a plane wave $\psi = e^{i\vec{k}\cdot\vec{r}} \Rightarrow \vec{p} = \hbar\vec{k}$, $E = \frac{\hbar^2 k^2}{2m}$ parabolic

$$\text{2D/3D} \quad E_{\alpha}(\vec{k}) = E_{\alpha}(k_x, k_y, k_z)$$

Usually the dispersion relation is represented only in particular symmetry directions.

