

SOLID STATE PHYSICS

Professor: Li Bassi Andrea

Lectures and tutorials

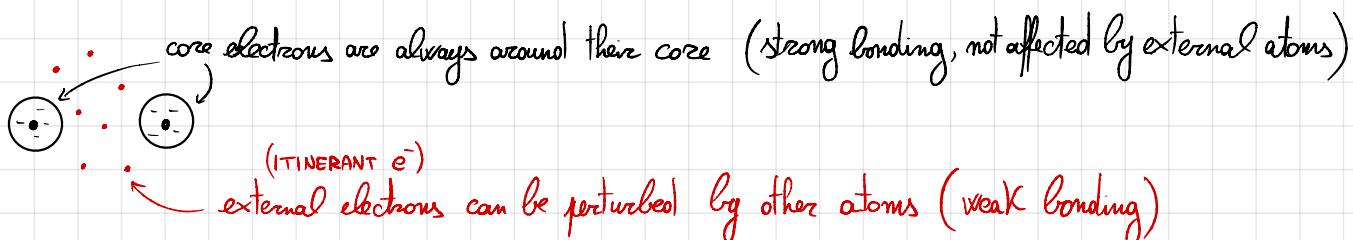
Lecture #1

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

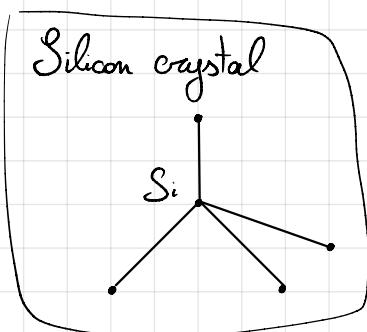
A solid body is something that has proper shape and volume (approximation). We are interested in optical and transport properties. Solid body is made of ions and electrons. Quantum Physics and Electromagnetism are the main tools; the number of particles is huge, not suitable for a macroscopic approach. 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 points with translational symmetry. A crystal, then, is a material with long range positional order, meaning that the order is kept regardless the distance.



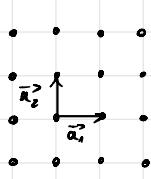
Bravais lattice is described through a set of vectors

$$\vec{M} = M_1 \vec{a}_1 + M_2 \vec{a}_2 + M_3 \vec{a}_3$$

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

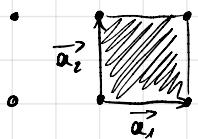


Primitive vectors describe all the points because they can be shifted with the integers

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

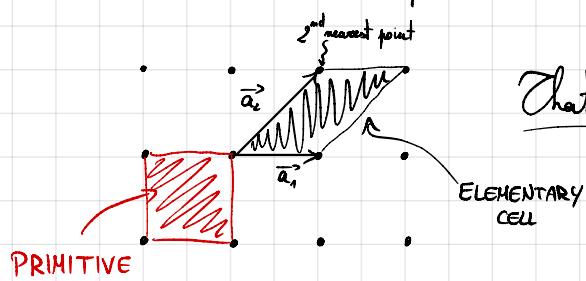
Unit cell

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

each point is connected

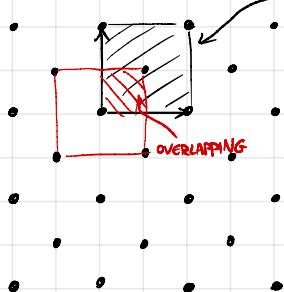
to the others with minimum

distance (nearest neighbor points, NNP)

Conventional cell

primitive cell with a point inside

↳ this partially overlaps during translations

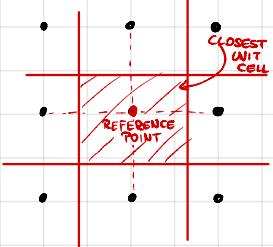


Volume is bigger than the unit cell and is not generated by the primitive vectors.
It is mostly used for simplicity purposes (i.e. cubic systems).

Lecture #2

Wigner - Seitz cell

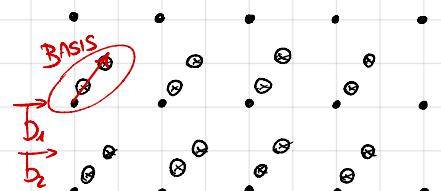
BRAGG PLANES: PLANES BUILT CLOSE TO THE NEAREST POINTS TO THE REFERENCE



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



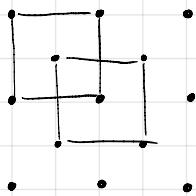
We can group the atoms that repeat with a clear order into a basis, creating a complex crystal

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

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

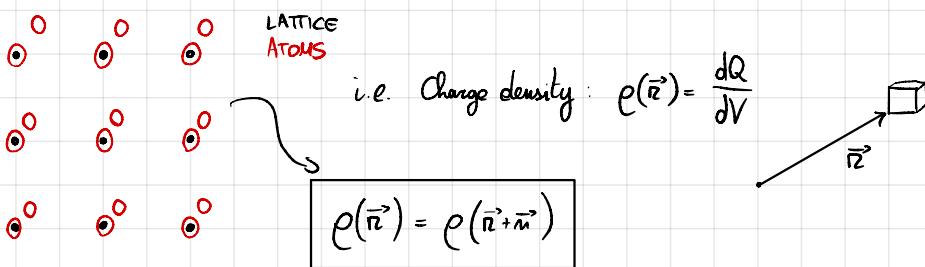
In particular, $\vec{T}_{\vec{0}\vec{m}} = \vec{m}$



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.



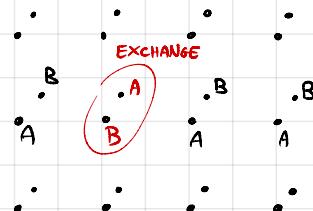
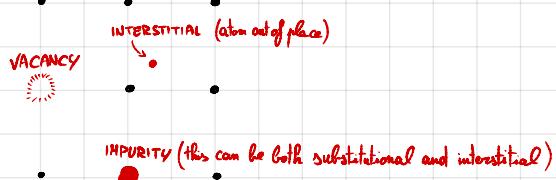
Imperfections

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

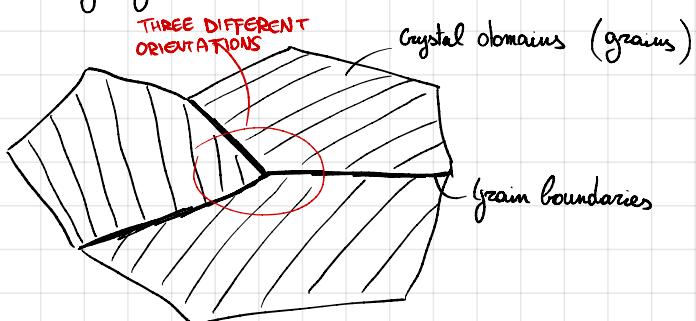
Mechanical, optical and electrical properties are strongly affected by defects.

①



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

Polycrystal

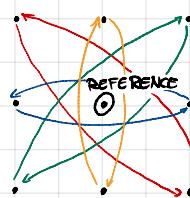


Other symmetries

Symmetries are very important in Physics; we can have

- POINT SYMMETRIES

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

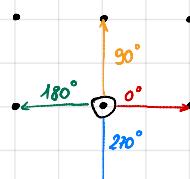


ALL POINTS ARE FLIPPED TO THEIR OPPOSITE

This symmetry is always present

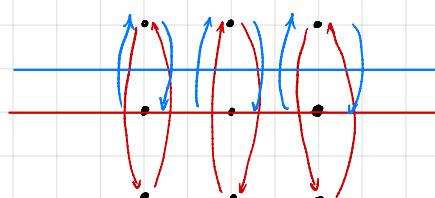
N.B. Symmetry operations leave the crystal UNCHANGED

② ROTATIONS $(2, 3, 4, 6)$ $J_m = \frac{2\pi}{M}$



In this case, the order is 4

③ REFLECTION



④ ROTOTOINVERSION

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.

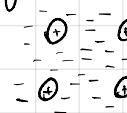
Considering complex crystals, new symmetries appear, like screw axis and glide planes, for a total of 32 point groups and 230 space groups (point + translational).

Bonding classification of the solids

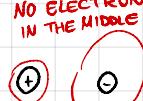
It is known that considering $\Psi(\vec{r}) \rightarrow |\Psi(\vec{r})|^2 dV = dP$ is the infinitesimal probability to find an electron. Charge density, then, is defined as $\rho(\vec{r}) = -e \sum_i |\Psi_i(\vec{r})|^2$; if we were to make a classification, that would be

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

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

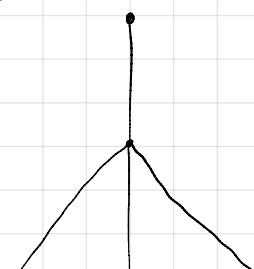
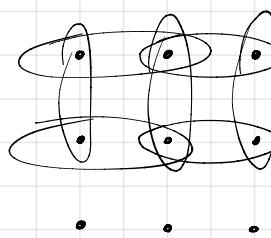


B) IONIC CRYSTALS such as NaCl

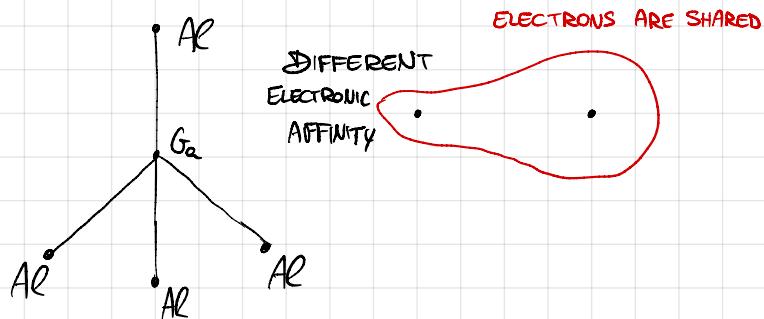


Bonding is made through coulombian force

c) COVALENT SOLIDS

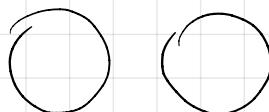


D) INTERMEDIATE



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 [eV/atom]. We can define strong and weak binding.

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

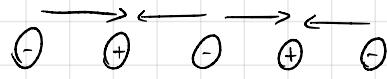
Macroscopic properties (observables)

$$\bar{\rho} = \frac{1}{V_p} \int \rho(\vec{r}) d\vec{r}$$

mean charge density

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

polarization



$$\vec{P}_i = \epsilon_0 \sum_j \chi_{ij} E_j$$

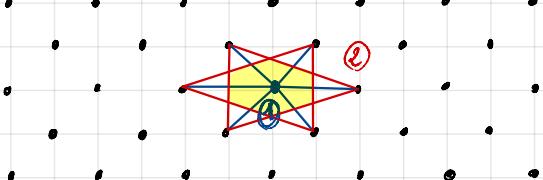
local polarization

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 P.L.V.s 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.

Construction:

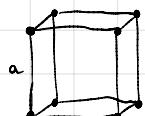


PRIIMITIVE CELL VOLUME

$$V = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$$

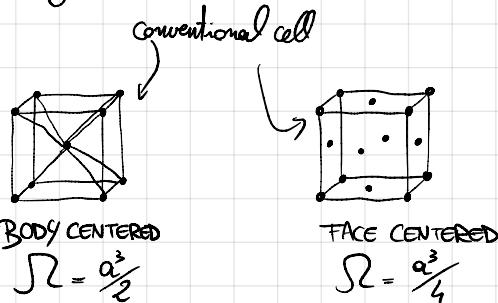
Conventional cells may or may not be primitive cells; what is important is just the symmetry axes of the crystal structure. Considering 3D, there are 14 lattices in 7 systems.

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.

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

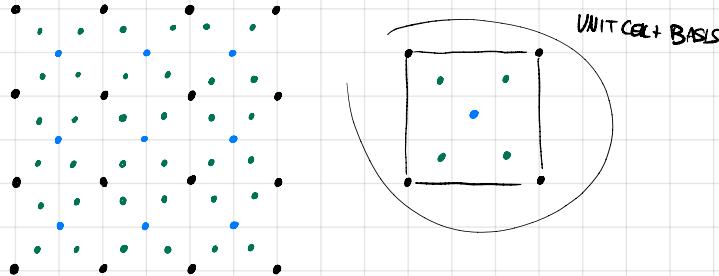
Brackets: $\{$ family of equivalent lattice planes $\}$

[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:

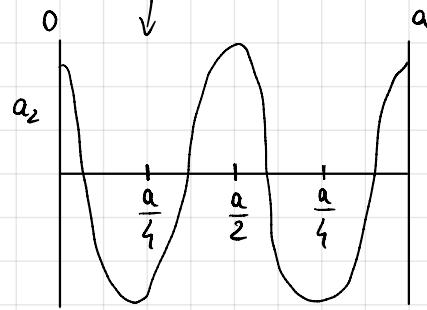
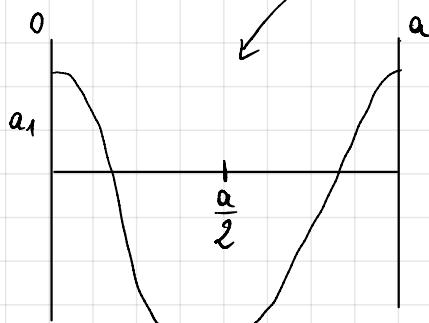
$$\bullet - \bullet - \bullet - \dots \quad \rho(\vec{r}), U(\vec{r}), \text{etc.}$$

(1) 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

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



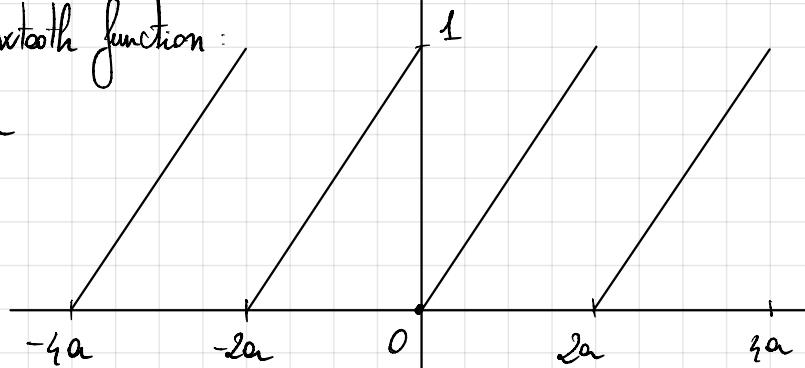
Fourier coefficients

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

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

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

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

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

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

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

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

much more compact

NEW COEFFICIENT

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

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

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

$$C_0 = \frac{1}{a} \int_0^a f(x) dx \rightsquigarrow a_0 = \frac{2}{a} \int_0^a f(x) dx$$

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

$$= \frac{1}{a} \int_0^a f(x) e^{-imx} dx + \frac{1}{a} \int_0^a f(x) e^{imx} dx = C_{-m} + C_m$$

If we repeat the same with b_m we get

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

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

If we combine all

$$\left. \begin{aligned} C_m &= \frac{1}{2} (a_m - ib_m) \\ C_{-m} &= \frac{1}{2} (a_m + ib_m) \end{aligned} \right\} C_m^* = C_{-m}$$

Then

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

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

Complex number

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

We can assume then

$$C_m = p_m e^{i\varphi_m} \Rightarrow f(x) = \sum_{m=-\infty}^{+\infty} p_m e^{i(m \frac{2\pi}{a} + \varphi_m)}$$

2D and 3D functions

$f(x, y)$ with two periodicities $\xrightarrow{\frac{x}{a_1}} \xrightarrow{\frac{y}{a_2}}$

$$\begin{aligned} f(x, y) &= \sum_{m=0}^{+\infty} \sum_{m=0}^{+\infty} \alpha_{m,m} \cos\left(m \frac{2\pi}{a_1} x\right) \cos\left(m \frac{2\pi}{a_2} y\right) + \sum_{m=0}^{+\infty} \sum_{m=0}^{+\infty} \beta_{m,m} \cos\left(m \frac{2\pi}{a_1} x\right) \sin\left(m \frac{2\pi}{a_2} y\right) + \\ &+ \sum_{m=0}^{+\infty} \sum_{m=0}^{+\infty} \gamma_{m,m} \sin\left(m \frac{2\pi}{a_1} x\right) \cos\left(m \frac{2\pi}{a_2} y\right) + \sum_{m=0}^{+\infty} \sum_{m=0}^{+\infty} \delta_{m,m} \sin\left(m \frac{2\pi}{a_1} x\right) \sin\left(m \frac{2\pi}{a_2} y\right) = \\ &= \sum_{m=-\infty}^{+\infty} \sum_{m=-\infty}^{+\infty} C_{m,m} e^{im \frac{2\pi}{a_1} x} e^{im \frac{2\pi}{a_2} y} = \sum_{m,m=-\infty}^{+\infty} C_{m,m} e^{i(m \frac{2\pi}{a_1} x + m \frac{2\pi}{a_2} y)} \end{aligned}$$

For 3D function it is the same procedure:

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

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

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

$$C_{m, m, t} = \frac{1}{V} \int_V f(x, y, z) e^{-i \vec{g}_{m, m, t} \cdot \vec{r}} d^3r$$

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

$$f(\vec{r}) = f(\vec{r} + \vec{m}) = \left(\sum_{-\infty}^{+\infty} f_{m, m, t} e^{i \vec{g}_{m, m, t} \cdot \vec{r}} \right) e^{i \vec{g}_{m, m, t} \cdot \vec{m}}$$

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.

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

~~HOLOGENEOUS (translational symmetry)~~

IN GENERAL

$$\vec{P} = \epsilon_0 \chi \vec{E} \quad \longrightarrow \quad P_i = \epsilon_0 \sum_j \chi_{ij} E_j$$

TENSOR

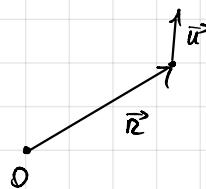
$$\begin{bmatrix} \chi & 0 & 0 \\ 0 & \chi & 0 \\ 0 & 0 & \chi \end{bmatrix}$$

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} .

$$\text{STIMULUS (2nd RANK)} \quad \sigma_{ij} = \sum_{rs} c_{ijrs} \epsilon_{rs} \quad \text{EFFECT (2nd RANK)}$$

ELASTIC TENSOR (4th RANK)

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



What happens if we apply point symmetry operations?

$$\text{- ROTATION} \quad x'_i = \sum_j \alpha_{ij} x_j \quad \text{OLD SYSTEM}$$

New System Rotation Sensor

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

This is how tensors transform

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

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

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.

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

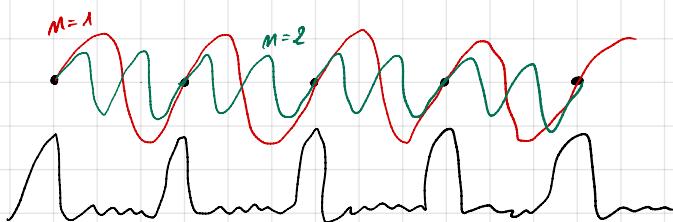


Every periodic function can be represented with the Fourier series (sin+cos OR exp).

$$\rho(x) = \sum_m \rho_m e^{i \frac{2\pi}{a} mx}$$

$$\rho_m = \frac{1}{a} \int_0^a \rho(x) e^{-i \frac{2\pi}{a} mx} dx$$

if $\rho(x)$ is real, $\rho_m^* = \rho_{-m}$

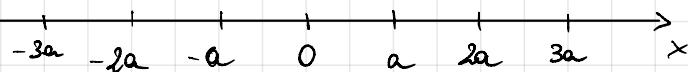


$$e^{ikx} \rightarrow K = \frac{2\pi}{\lambda} \rightarrow \lambda = \frac{a}{m} \text{ is the wavelength}$$

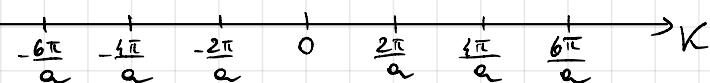
$$\begin{aligned} \lambda_1 &= a \\ \lambda_2 &= \frac{a}{2} \\ \lambda_3 &= \frac{a}{3} \\ &\vdots \end{aligned}$$

Reciprocal lattice vectors: $g_m = \frac{2\pi}{a} n$

DIRECT LATTICE



RECIPROCAL LATTICE (abstract concept)



This is a discrete space

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

(complex number properties)

Now we consider a 3D situation.

$$\rho(\vec{r}) = \rho(\vec{r} + \vec{m}) \xrightarrow{\text{Fourier}} \rho(\vec{r}) = \sum_{\vec{q}} \rho_{\vec{q}} e^{i \vec{q} \cdot \vec{r}}$$

PLANE WAVE

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

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

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

$$\rho(\vec{r} + \vec{m}) = \sum_{\vec{q}} \rho_{\vec{q}} e^{i \vec{q} \cdot (\vec{r} + \vec{m})} = \underbrace{\sum_{\vec{q}} \rho_{\vec{q}} e^{i \vec{q} \cdot \vec{r}} e^{i \vec{q} \cdot \vec{m}}}_{\rho(\vec{r})} \quad \text{1 (if } \vec{a}_1 \perp \vec{a}_2 \perp \vec{a}_3 \text{)}$$

Alternatively

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

DEFINITION OF \vec{g}

$$\vec{m} = M_1 \vec{a}_1 + M_2 \vec{a}_2 + M_3 \vec{a}_3$$

MILLER INDICES

$$\vec{g}_{hkl} = 2\pi(h\vec{b}_1 + K\vec{b}_2 + \ell\vec{b}_3)$$

(generic primitive vectors)

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

A very interesting property is

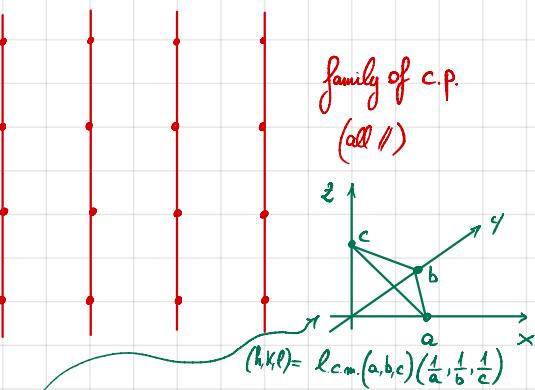
$$\vec{a}_i \cdot \vec{b}_j = \delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases}$$

Properties of the reciprocal lattice

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

family of c.p.

(all //)

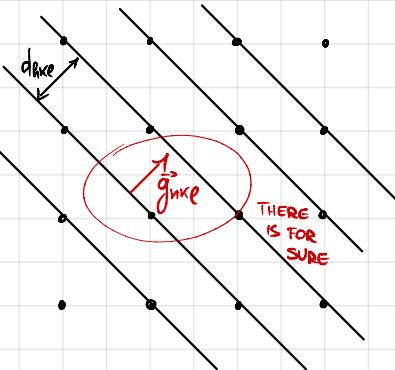


1) RL is a Bravais Lattice;

2) RL of RL is DL;

$$3) V_{P, RL} = \frac{(2\pi)^3}{V_p} \quad (\text{in 1D } K = \frac{2\pi}{a});$$

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



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

Lecture #4

Diffraction

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

$$g_m = \frac{2\pi}{a} m \quad \vec{g}_{hkl} = 2\pi(h\vec{b}_1 + K\vec{b}_2 + \ell\vec{b}_3)$$

RECAP

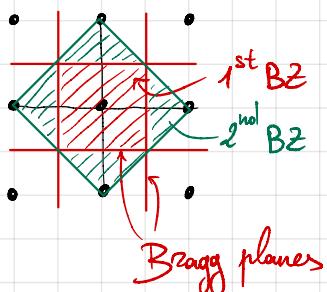
It is interesting to notice that FCC \rightarrow BCC and so BCC \rightarrow FCC.

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

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

Brillouin zones

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

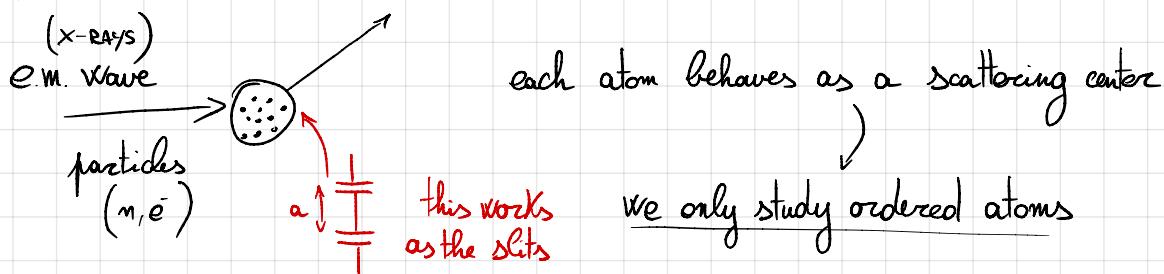


The 1st BZ is the closest region to the origin without crossing Bragg planes.

Now we must talk about diffraction

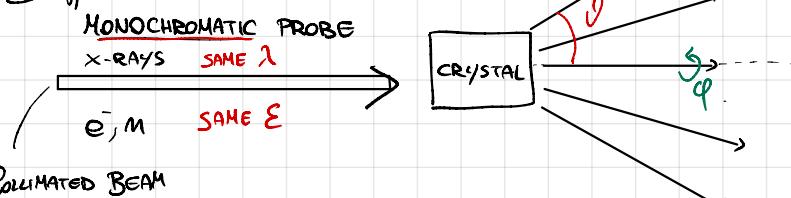
Scattering

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.

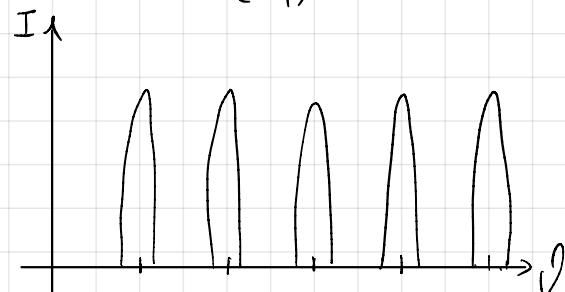


X-rays have a wavelength similar to the distance between the scattering atoms (light doesn't work), while electrons are surface sensitive. Neutrons identify the nuclei inside the material, while x-rays just the distribution of electrons (they are easier to use). A possible approach using x-rays involves 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 Schrödinger equation. Mathematically, both are the same.

Diffraction



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



Just some angles are good due to INTERFERENCE

X-RAYS

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

$$|\vec{E}_i| = \frac{2\pi}{\lambda} = |\vec{k}_s| = K$$

$$c = \lambda \nu \sim E_{ph} = h\nu \text{ constant}$$

e-m

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

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

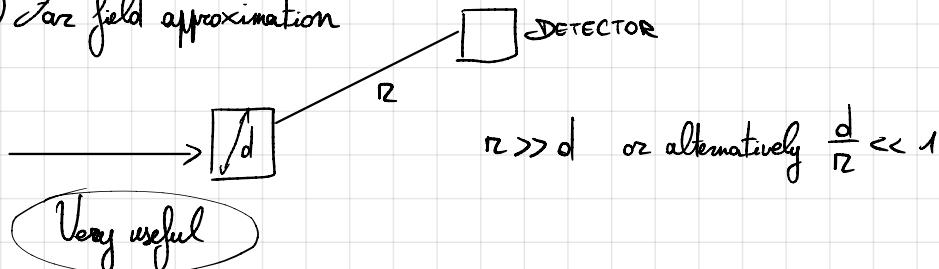
$$\vec{p} = \hbar \vec{k}$$

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

Energy doesn't change

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

2) Far field approximation



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

WEAK INTERACTION

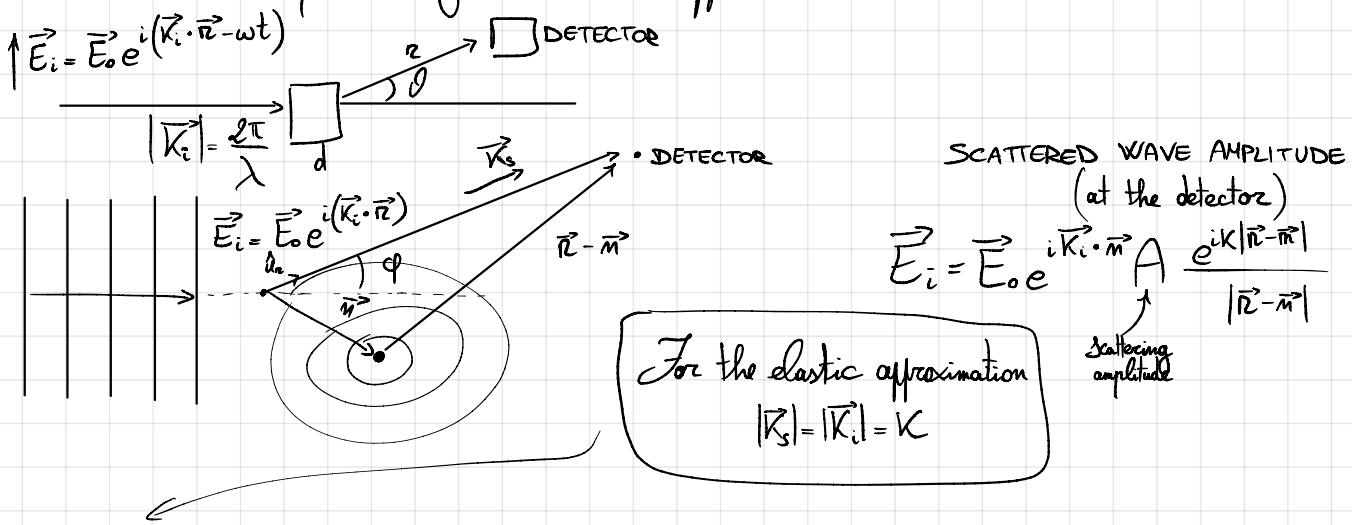
i) NO small angles

Lecture #5

Von Laue

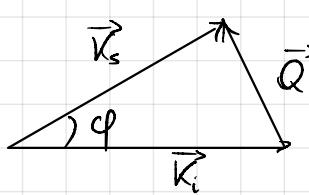
Von Laue semiempirical laws and Schrödinger equation

We would use Maxwell equations for a stricter approach.



$$\vec{K}_s = K \frac{\vec{r}}{R} = K \vec{u}_R \quad \vec{K}_s$$

\sim



$\vec{Q} = \vec{K}_s - \vec{K}_i$

SCATTERING WAVE VECTOR

SCATTERED WAVE VECTOR

THEN

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

for far field approximation

$$K |\vec{r} - \vec{m}| = K_R - K \vec{u}_R \cdot \vec{m} = K_R - \vec{K}_s \cdot \vec{m}$$

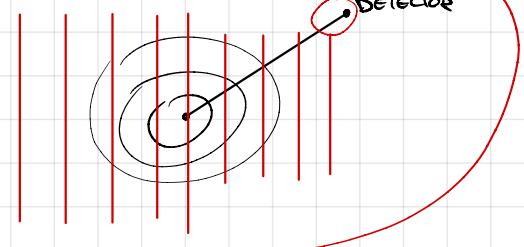
$$(A \vec{E}_0 e^{i\vec{K}_i \cdot \vec{r}} \frac{e^{-iK_R} - e^{-i\vec{K}_s \cdot \vec{m}}}{R})$$

$$\vec{E}(\vec{r}) = \left(\sum_m A \vec{E}_0 e^{i\vec{K}_i \cdot \vec{m}} e^{-i\vec{K}_s \cdot \vec{m}} \right) \frac{e^{-iK_R}}{R} + \vec{E}_0 e^{i\vec{K}_i \cdot \vec{r}}$$

negligible

There is also the incident wave

NO SMALL ANGLE



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

ALL THE PROBLEMS COME FROM HERE

← interference

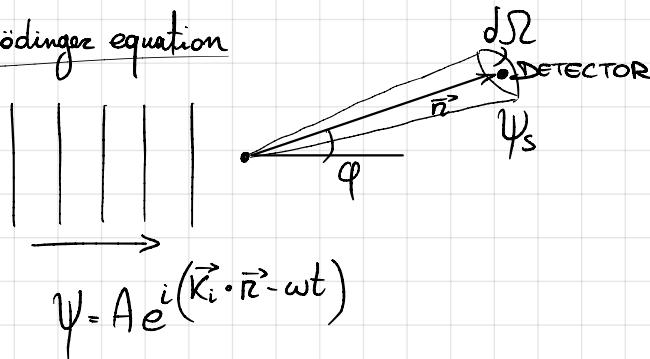
spherical wave

Let's rewrite \vec{Q} as

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

Now we move to particles.

Schrödinger equation



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

DIFFERENTIAL CROSS SECTION $[m^2]$

RECAP

SCHRÖDINGER EQUATION

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \sim \hat{H}\Psi = \mathcal{E}\Psi$$

T. I. S. E.

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

We know how much is the energy.

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

$$\mathcal{E} = \frac{\hbar^2 K^2}{2m} \quad \text{just Kinetic energy (elastic scattering)} \Rightarrow \hat{H}\Psi = \frac{\hbar^2 K^2}{2m} \Psi \quad \text{we have to solve this}$$

$$\underbrace{(\nabla^2 + K^2)}_{\text{Helmoltz operator}} \Psi = \frac{2m U(\vec{r})}{\hbar^2} \Psi$$

Helmoltz equation

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

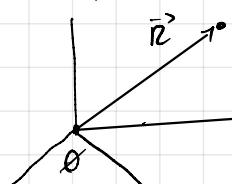
{ if $f(\vec{r}) = 0 \rightarrow$ homogeneous
if $f(\vec{r}) \neq 0 \rightarrow$ inhomogeneous }

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

(green function method)

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

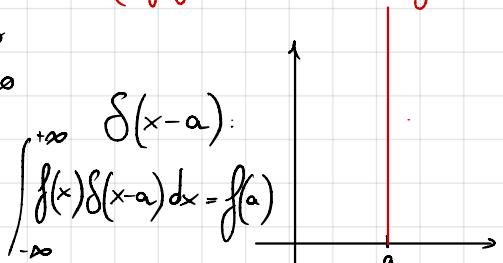
Dirac function



function exists only here

$$1D \quad \delta(x) = \begin{cases} 0 & \text{if } x \neq 0 \\ +\infty & \text{if } x = 0 \end{cases}$$

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



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

$$\Psi(\vec{r}) = \int G(\vec{r}, \vec{r}') f(\vec{r}') d\vec{r}' + \Psi_i(\vec{r})$$

convolution with the source

solution for one point

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

SOLUTION!!! negligible for BIG ANGLES

SOURCE

K|\vec{r}-\vec{r}'| \approx K\vec{r} - \vec{K}_s \cdot \vec{r}'

SCATTERED WAVE FUNCTION

We get an implicit equation
Detector is distant
far field approximation
Born approximation

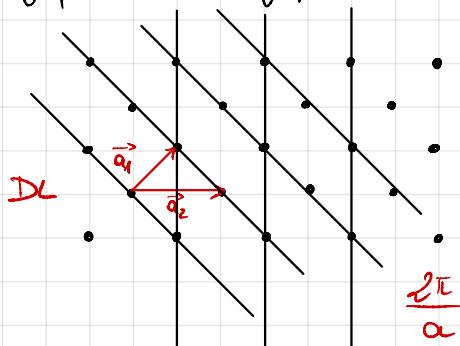
$$\frac{|\vec{r}'|}{|\vec{r}|} \ll 1$$

Eventually

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

Tutorial #2

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



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

$$f(r) = \sum_{k \in \mathbb{Z}^3} A_{k \in \mathbb{Z}^3} e^{i g_{k \in \mathbb{Z}^3} r}$$

The reciprocal lattice is a set of vectors $K = g_{k \in \mathbb{Z}^3}$ such that $e^{ig_{k \in \mathbb{Z}^3} T_m} = 1$ (plane wave has the same periodicity as the crystal).

$$\vec{g}_{k \in \mathbb{Z}^3} = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3$$

$$S_K = \frac{(2\pi)^3}{V_{DL}}$$

Volume RL Volume DL

PRIMITIVE VECTORS OF RL

$$b_i = \frac{a_j \times a_k}{|a_i \cdot (a_j \times a_k)|}$$

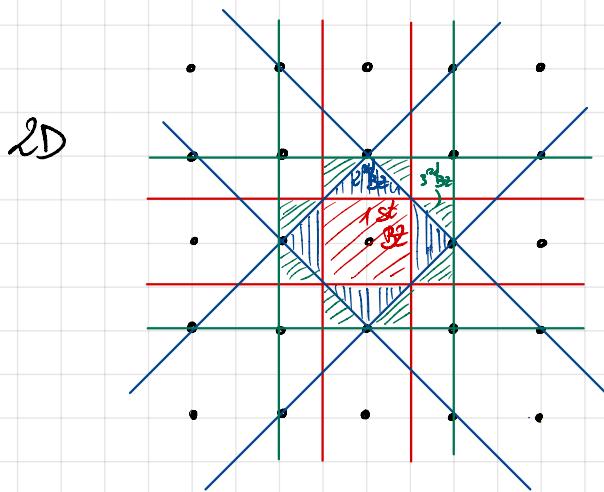
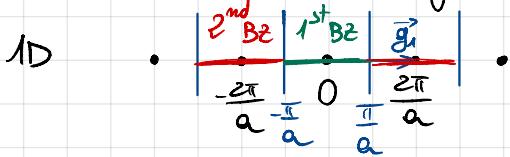
S2

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 $d = \frac{2\pi}{|g_{min}|}$.

shortest RLV in direction of \vec{g}

$$|\vec{g}_{\text{here}}| = \sqrt{P^2 |\vec{b}_1|^2 + K^2 |\vec{b}_2|^2 + L^2 |\vec{b}_3|^2}$$

Higher Brillouin zones can be found over Bragg planes.

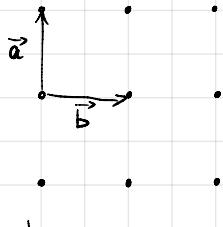


Each Brillouin Zone has the same size

Tutorial #3

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

Crystal structures are various.



both modules can be written as

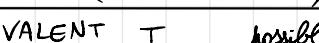
We want to condense informations into R so that $u = u(R)$

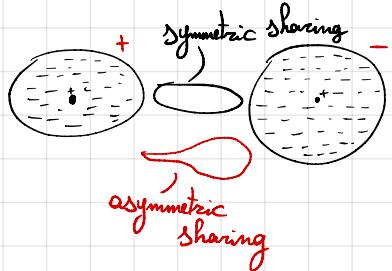
We impose that $\frac{du}{dR} \Big|_{R=R_0} = 0$ to have a minimum potential, therefore $u(R_0) = u_{\text{constant}}$. Why is there a binding energy?

Pauli's principle

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

Bonding types

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



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

Shell structure

$$S \rightarrow l=0, m_l=0, m_s=\begin{cases} +\frac{1}{2} \\ -\frac{1}{2} \end{cases}$$

$$P \rightarrow l=1, m_l=\begin{cases} +1 \\ 0 \\ -1 \end{cases}$$

- MOLECULAR
- METALLIC
- PURE COVALENT

NOBLE GASES

ALKALINE

Gruppo	1 IA	2 IIA	3 IIIA	4 IVB	5 VB	6 VIIB	7 VIIIB	8 - VIII	9 -	10 -	11 -	12 -
1	H											
2	Litio	Borillo										
3	Sodio	Magnesio										
4	Potassio	Calcio	Scandio	Titanio	Vanadio	Cromo	Manganese	Ferro	Cobalto	Nichel	Rame	Zinco
5	Rubidio	Sterzio	Ytrio	Zirconio	Niodio	Molibdeno	Tecneta	Rutenio	Rodium	Palladio	Argento	Cadmio
6	Cesio	Bario	Lantaniidi	Atrio	Tantalio	Wolframio	Rhenio	Osmio	Iridio	Platino	Oro	Mercurio
7	Francio	Rado	Actinidi	Rutherfordio	Dubonio	Seaborgio	Baltorio	Hassio	Meltnerio	Unomolio	Ununmonio	Ununknio

Tavola Periodica degli elementi

Numero atomico → 20
Simbolo → Ca
Nome → Calcio

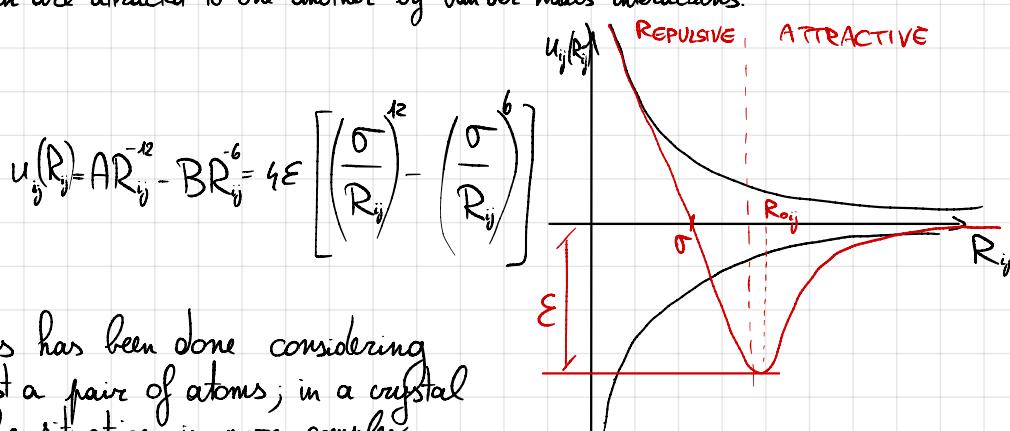
13 IIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
Boro	Carbonio	Aresto	Oxigeno	Fluoro	Neon
Al	Si	P	S	Cl	Ar
Gallo	Germanio	Asenico	Se	Br	Kr
Zinco	Antimonio	Selenio	Te	I	Xe
Tellurio	Radone				
Indio	Stagno				
Talio	Plomo				
Bismuto	Poliuro				
Po	At				
	Rn				

57 Lanthanidi	58 Cerio	59 Praseodimio	60 Neodimio	61 Prometio	62 Samario	63 Europa	64 Gadolinio	65 Terbio	66 Disprosio	67 Holmia	68 Erbio	69 Tmbo	71 Yttrio	72 Lu
Actinidi	Torio	Protortio	Uranio	Nettunio	Plutonio	Americio	Curio	Berkello	Californio	Einsteinio	Fermio	Mendelevio	Noberio	Lorenzio

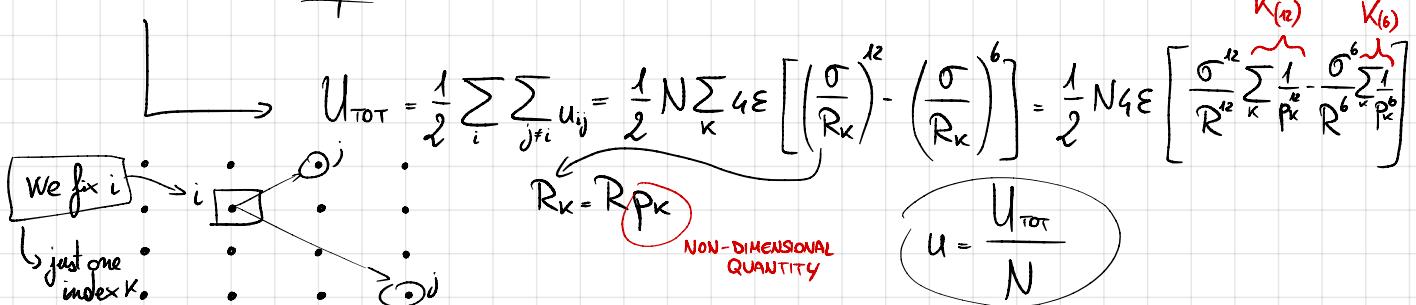
Covalent bonding has the most symmetric directionality.

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.



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

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

CONSTANT

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

$$\frac{R_0}{\sigma} = 1,09$$

N_e	A_Z	K_2	χ_e
$\frac{R}{\sigma}_{\text{exp}}$	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

$$x\text{-RAYS} \quad J \sim \left| \sum_{\vec{m}} e^{-i\vec{Q} \cdot \vec{m}} \right|^2 \quad \vec{Q} = \vec{K}_s - \vec{K}_i$$

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

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

$$U(\vec{r}) = U(\vec{r} + \vec{m}) \Rightarrow U(\vec{r}) = \sum_{\vec{g}} U_{\vec{g}} e^{i\vec{g} \cdot \vec{r}}$$

$$\text{where } U_{\vec{g}} = \frac{1}{V_p} \int_V U(\vec{r}) e^{-i\vec{g} \cdot \vec{r}} d\vec{r}$$

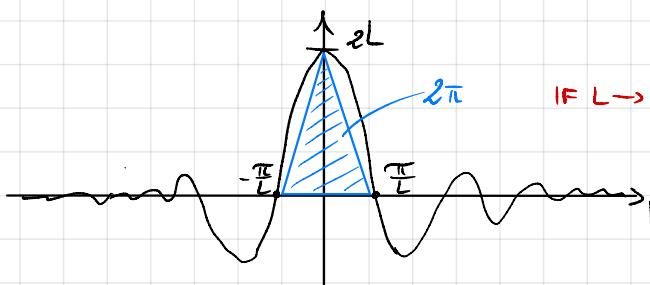
$$\text{If we do this, then } A_{Si}(\vec{Q}) \sim \int_V e^{-i\vec{Q} \cdot \vec{r}} \sum_{\vec{g}} U_{\vec{g}} e^{i\vec{g} \cdot \vec{r}} d\vec{r} = \sum_{\vec{g}} U_{\vec{g}} \int_V e^{-i(\vec{Q}-\vec{g}) \cdot \vec{r}} d\vec{r}$$

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 8

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



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

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

DIFFRACTION CONDITION

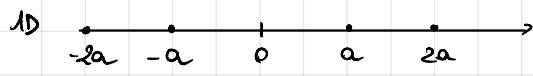
$$A_{S_i}(\vec{Q}) \sim \sum_{\vec{g}} U_{\vec{g}} \int_V e^{-i(\vec{Q}-\vec{g}) \cdot \vec{r}} d\vec{r}$$

In this case $|A|^2 \propto |U_{\vec{g}}|^2$

INTENSITY OF THE PEAK

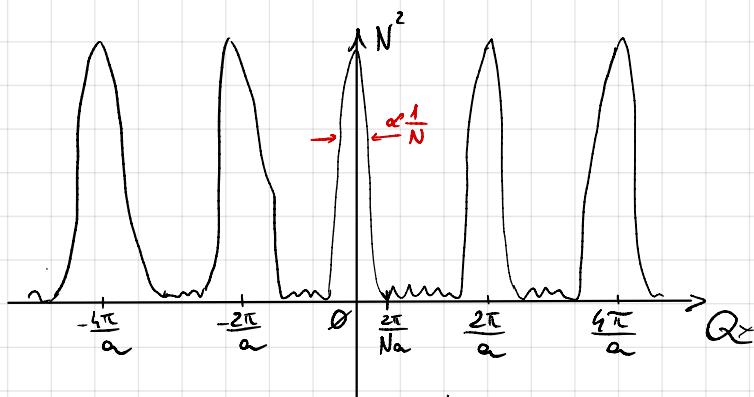
The Von Laue result is the same.

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



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

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



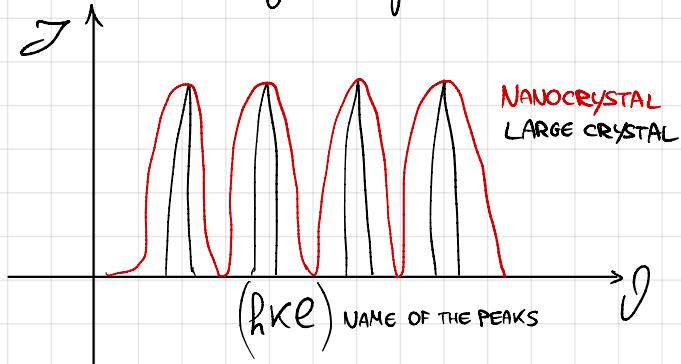
We have the maxima when both the \sin go to zero $\rightarrow \frac{Q_x a}{2} = m\pi$

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

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

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

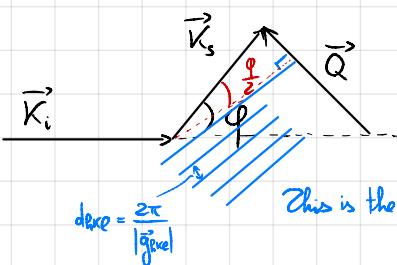
Typically we consider a crystal infinite when $a > 100$ nm.



Bragg law of diffraction

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

$$(\vec{Q} = \vec{g}_{hkl})$$



This is the family of planes $\perp \vec{g}$

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

if \vec{g} is not the shortest

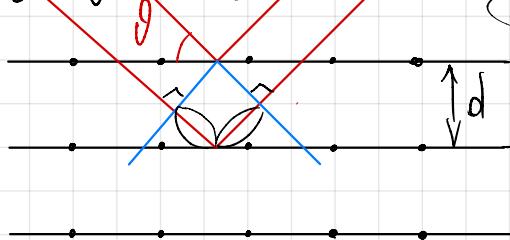
$$|\vec{g}_{hkl}| = \frac{2\pi}{d_{hkl}} m = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$

$$2d_{hkl} \sin \frac{\theta}{2} = m\lambda$$

where $\theta = \frac{\theta}{2}$

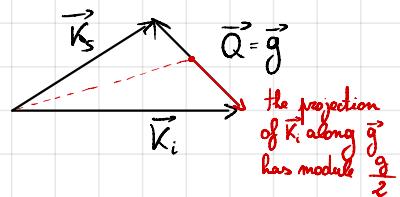
Diffraction condition is equivalent to Bragg Law

Fastest way to get Bragg law is



$$ds \sin \theta = m \lambda$$

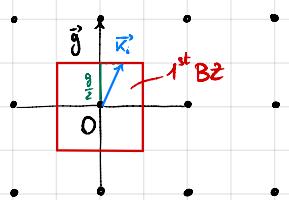
Von Laue diffraction condition



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

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

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



RECIPROCAL LATTICE

\vec{K}_i IS ON A BRAGG PLANE

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

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

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

atoms of the basis

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

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

properties of δ

GEOMETRICAL STRUCTURE FACTOR

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

IF THE ATOMS ARE ALL EQUAL, b_p

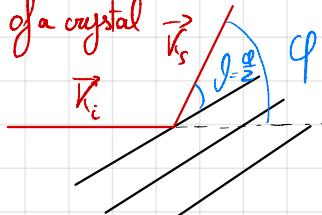
We have a missing peak if the structure factor goes to zero, even though $\vec{Q} = \vec{g}$ for destructive interference.

Lecture #7

Electronic structure of a crystal

$$\vec{Q} = \vec{K}_s - \vec{K}_i = \vec{g}_{\text{like}} \quad 2d \sin \theta = m \lambda$$

We start from these considerations.



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

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

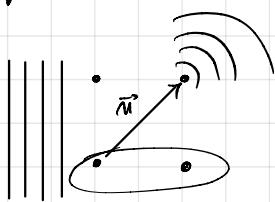
X-ray approach

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

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

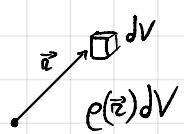
REMEMBER
FOR PARTICLES

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



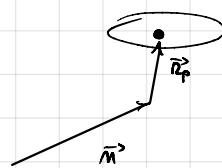
Each infinitesimal volume has a charge density:

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



Now let's find the Fourier coefficient.

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



This is the charge distribution

$$\begin{aligned} \rho_g &= \frac{1}{V_p} \int_{V_p} \sum_p \rho_p(\vec{r} - \vec{r}_p) e^{-i\vec{g} \cdot \vec{r}} d\vec{r} = \frac{1}{V_p} \int_{V_p} \sum_p \rho_p(\vec{r} - \vec{r}_p) e^{-i\vec{g} \cdot (\vec{r} - \vec{r}_p)} e^{-i\vec{g} \cdot \vec{r}_p} d\vec{r} = \\ &= \frac{1}{V_p} \sum_p e^{-i\vec{g} \cdot \vec{r}_p} \underbrace{\int_{V_p} \rho_p(\vec{r}) e^{-i\vec{g} \cdot \vec{r}} d\vec{r}}_{f_p(\vec{g})} = \frac{1}{V_p} \sum_p f_p(\vec{g}) e^{-i\vec{g} \cdot \vec{r}_p} \end{aligned}$$

Similar to the neutron one
 $(U_g = \frac{1}{V_p} \sum_p b_p e^{i\vec{g} \cdot \vec{r}_p})$
 \vec{g} is important to highlight the dependence on \vec{g}

ATOMIC FORM FACTOR

Electronic structure

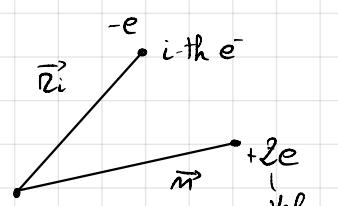
The goal is to find the stationary states of e^- (not considering core electrons). There are some issues though, like many-body (huge presence of particles), interactions e^-/e^- and e^-/ions and ions vibrations. How is it possible to solve Schrödinger equation? We do some approximations.

1) FROZEN CRYSTAL

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

$$\begin{aligned} \hat{H}_{\text{TOT}} \Psi &= E_{\text{tot}} \Psi \\ \hat{H}_{\text{TOT}} &= \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_i \underbrace{\sum_j \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}}_{\text{Coulomb force}} + \frac{1}{2} \sum_i \sum_{j \neq i} \underbrace{\frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}}_{\text{Coulomb repulsive force}} \right] \end{aligned}$$

THIRD TERM CANNOT BE MERGED



Interaction ions/ions is not considered.

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

we want a sum over electrons

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

NO MORE MUTUAL INTERACTION

Now we have a new hypothesis:

Each electron is now separated from any other

$$\begin{aligned} \hat{H}_{\text{TOT}} &= \hat{H}_1(1) + \hat{H}_2(2) \quad \text{in quantum physics it is referred as non-interacting particles} \\ \hat{H}_{\text{TOT}} \Psi_{1,2} &= E_{\text{tot}} \Psi_{1,2} \Rightarrow \begin{cases} \Psi_{1,2} = \Psi_1(1)\Psi_2(2) \\ E_{\text{tot}} = E_1 + E_2 \end{cases} \end{aligned}$$

$$\left. \begin{array}{l} \hat{H}_1 \Psi_1 = E_1 \Psi_1 \\ \hat{H}_2 \Psi_2 = E_2 \Psi_2 \end{array} \right\} \text{We don't solve a problem for two particles, but we solve two problems for single particles!}$$

Then

$$\begin{aligned} \hat{H}_{\text{TOT}} \Psi_1 \Psi_2 &= E_{\text{TOT}} \Psi_1 \Psi_2 \\ (\hat{H}_1 + \hat{H}_2) \Psi_1 \Psi_2 &= E_{\text{TOT}} \Psi_1 \Psi_2 \\ \underbrace{\Psi_2 \hat{H}_1 \Psi_1 + \Psi_1 \hat{H}_2 \Psi_2}_{E_1 \Psi_1 \quad E_2 \Psi_2} &= (E_1 + E_2) \Psi_1 \Psi_2 \end{aligned}$$

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} .

$$\begin{aligned} \hat{P}(1,2) \Psi(1,2) &= \lambda \Psi(1,2) = \Psi(2,1) & \xrightarrow{\substack{\text{APPLY} \\ \text{AGAIN } \hat{P}}} \hat{P} [\Psi(2,1)] &= \hat{P} [\lambda \Psi(1,2)] \Rightarrow \Psi(1,2) = \lambda^2 \Psi(1,2) \Rightarrow \lambda^2 = 1 \\ &\text{definition} \\ &\text{of eigenvalues} & & \lambda = \pm 1 \end{aligned}$$

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

$\begin{cases} \textcircled{+} \text{ symmetric } \text{BOSONS (integer spin)} \\ \textcircled{-} \text{ anti-symmetric } \text{FERMIONS (half-integer spin)} \end{cases}$
 \hookrightarrow Pauli exclusion principle

Tutorial #4

We acknowledge that $U = U(R)$ and $U'(R_0) = 0$ where $R_0 = 1,080$.

Lennard Jones potential

$$U_T = U_{\text{REP}} + U_{\text{COUR}} \quad U_{\text{COUR},i} = \frac{V_i}{V(\vec{r}_i)} e^{-\frac{V_i}{V(\vec{r}_i)}} \quad \left. \begin{array}{l} \text{TOTAL CHARGE} \\ V(\vec{r}_i) = \sum_{j \neq i} \frac{e^2 z_{ij}}{4\pi \epsilon_0 |\vec{r}_i - \vec{r}_j|} \end{array} \right\} \text{this does not depend on the lattice site}$$

Let's start from a 1D crystal:

$$\begin{array}{ccccccc} \vec{r}_i & - & \vec{r}_j & = & \vec{r}_K & - & R \vec{p}_K \\ \vdots & ; & \vdots & ; & \boxed{+} & ; & \vdots \end{array}$$

$$U_i = \frac{e^2}{4\pi \epsilon_0} \sum_K \frac{(1-i)^K}{R^K} \quad \text{harmonic series}$$

For a generic situation though

$$U_i = \frac{e^2}{4\pi \epsilon_0 R} \sum_K m_K \frac{s_K}{p_K} \quad \text{sign of } i$$

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

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

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

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

SPATIAL DISTRIBUTION OF MATTER
RESPONSIBLE FOR DIFFRACTION

ATOMIC FORM
FACTOR

$$\frac{A}{P} e^{-\frac{R_0}{P}} = \frac{e^2}{4\pi\epsilon_0 R_0} a$$

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

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

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

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

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

Simple cubic

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

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

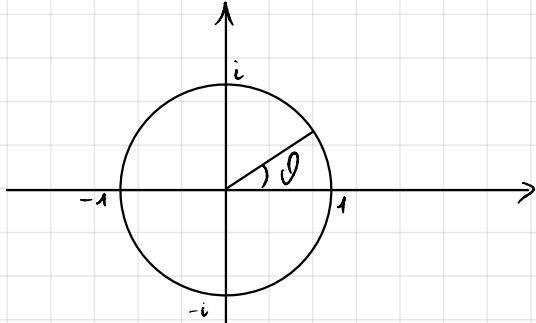
$$F(\vec{g}) = f(\vec{g})$$

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

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

BCC

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



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

COUNTER-PHASE

PHASE

FCC

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

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

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

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

To condense everything

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

Lecture #8

Electrons in a crystal

$$\hat{H}_{\text{TOT}} = \sum_i \hat{H}_i + \frac{1}{2} \sum_{ij} V_{ij} \quad \left. \begin{array}{c} \text{First} \\ \text{simplification} \end{array} \right\}$$

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

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

Now we consider independent e^-

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{m_1}(\vec{r}_1) \psi_{m_2}(\vec{r}_2) \quad \left. \begin{array}{c} \text{THIS DOES NOT SATISFY EXCHANGE SYMMETRY} \\ \text{QUANTUM NUMBERS (STATES)} \end{array} \right\}$$

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

$\underbrace{+}_{\text{SPATIAL WAVE FUNCTION}}$ $\underbrace{-}_{-}$ $\underbrace{-}_{+}$ $\underbrace{+}_{\text{SPIN}}$ $\underbrace{\text{ANTI-SYMMETRIC}}$

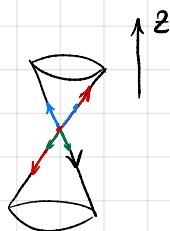
$$\Psi_S = \frac{1}{\sqrt{2}} [\psi_{m_1}(\vec{r}_1) \psi_{m_2}(\vec{r}_2) + \psi_{m_1}(\vec{r}_2) \psi_{m_2}(\vec{r}_1)]$$

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

What about the spin?

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

$$m_S = \pm \frac{1}{2} \quad S_x = \hbar m_S$$



PARTICLES
IN THE SAME STATE

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

$$\text{SINGLET} \quad \chi_{AS}(1,2) = \frac{1}{\sqrt{2}} [\chi_{\frac{1}{2}}(1) \chi_{\frac{1}{2}}(2) - \chi_{\frac{1}{2}}(2) \chi_{\frac{1}{2}}(1)]$$

$$\text{TRIPLET} \quad \chi_s(1,2) = \frac{1}{\sqrt{2}} [\chi_{\frac{1}{2}}(1) \chi_{\frac{1}{2}}(2) + \chi_{\frac{1}{2}}(2) \chi_{\frac{1}{2}}(1)]$$

It is the same, but for the spin

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

$$\chi_s = \chi_{-\frac{1}{2}}(1) \chi_{-\frac{1}{2}}(2) \quad \text{BOTH DOWN}$$

The final product must be anti-symmetric.

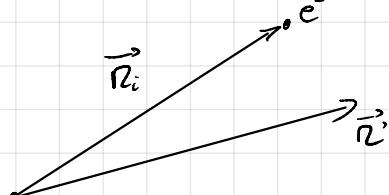
Hartree approach

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

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

Symmetry is not considered along with the spin

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



$$\rho_i(\vec{r}) = -e \sum_j |\psi_{mj}(\vec{r})|^2$$

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

Potential is not discrete because electrons are uniformly distributed.

As final result

$$U_i(\vec{r}_i) = \frac{e^2}{4\pi\epsilon_0} \left(\sum_{j \neq i} \frac{|\Psi_{m_j}(\vec{r}')|^2 d\vec{r}'}{|\vec{r}_i - \vec{r}'|} \right)$$

we don't know this

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

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_m \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}|} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \frac{|\Psi_{m_j}(\vec{r}')|^2 d\vec{r}'}{|\vec{r}_i - \vec{r}'|}}_{\text{SELF-CONSISTENT MEAN FIELD}} \right] \Psi_{m_i}(\vec{r}_i) = E_i \Psi_{m_i}(\vec{r}_i)$$

An iterative method must be used.

$$\Psi_{m_j}^{(0)}(\vec{r}_j) \rightarrow \Psi_{m_j}^{(1)}(\vec{r}_j)$$

Hartree-Fock approach

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

SALTER DETERMINANT

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

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 $\Delta E = E_j - E_i$ is needed.

$$\hat{H}_{\text{TOT}} = \sum_i \hat{H}_i \quad \hat{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 + U_{\text{e-ion}}(\vec{r}_i) + \underbrace{U_{\text{mean e-o}}(\vec{r}_i)}_{U_{\text{CRYSTAL}}(\vec{r}_i)}$$

$U_{\text{CRYSTAL}}(\vec{r}_i)$ ← 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 $U(\vec{r}) = U(\vec{r} + \vec{m})$.

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

TRANSLATION OPERATOR
 $\hat{T}_m: \hat{T}_m \psi(\vec{r}) \cong \psi(\vec{r} + \vec{m})$

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

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

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

Lecture #3

Bloch theorem

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

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

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

?

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

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

$$\lambda(\vec{m}_1) \lambda(\vec{m}_2) \Psi = \lambda(\vec{m}_1 + \vec{m}_2) \Psi \implies \lambda(\vec{m}_1) \lambda(\vec{m}_2) = \lambda(\vec{m}_1 + \vec{m}_2)$$

important property; just one solution: $\lambda(\vec{m}) = e^{\frac{i\vec{s} \cdot \vec{m}}{\hbar}}$

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

$$\text{and } \vec{m} = m\vec{a}$$

$$\hat{T}_{\vec{m}} \Psi = \Psi(x + ma) = e^{\frac{i\vec{s} \cdot \vec{m}}{\hbar}} \psi(x)$$



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

$$\int |\Psi(x+ma)|^2 dx = \int |e^{sma}|^2 |\psi|^2 dx = |e^{sma}|^2 \int |\psi|^2 dx = 1 \implies |e^{sma}|^2 = 1$$

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

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

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

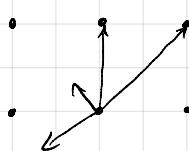
$\hat{T}_{\vec{m}} \Psi(\vec{r}) = \Psi(\vec{r} + \vec{m}) = e^{i\vec{k} \cdot \vec{m}} \Psi(\vec{r})$ if Ψ is a stationary state; we've just expressed the first form of the Bloch theorem.

Some considerations

1) Wavefunction is not periodic

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

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



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

Quantum numbers

$$\hat{H} \Psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}(\vec{k}) \Psi_{\vec{k}}(\vec{r})$$

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

energy depends on \vec{k}

The eigenvalue depends on the wavevector.

Now we consider the second form of Bloch theorem.

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

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

$$\left\{ \begin{array}{l} \hat{H}\Psi_{\vec{K}} = \mathcal{E}(\vec{K})\Psi_{\vec{K}} \\ \Psi_{\vec{K}} = U_{\vec{K}} e^{i\vec{K} \cdot \vec{r}} \end{array} \right. \Rightarrow \left[\frac{|\vec{p} + \hbar\vec{K}|^2}{2m} + U(\vec{r}) \right] U_{\alpha\vec{K}}(\vec{r}) = \mathcal{E}_{\alpha}(\vec{K}) U_{\alpha\vec{K}}(\vec{r})$$

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

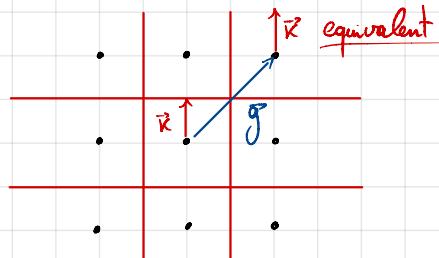
$$|\hat{\vec{p}}|^2 = \hat{\vec{p}} \cdot \hat{\vec{p}} = -\hbar^2 \vec{\nabla}^2$$

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



REDUCED ZONE SCHEME

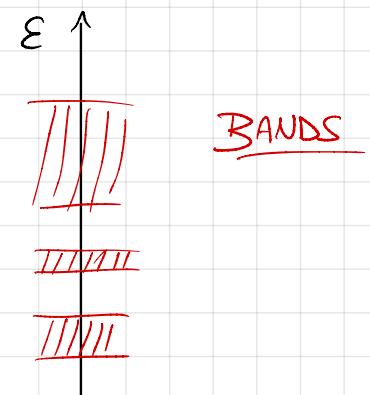
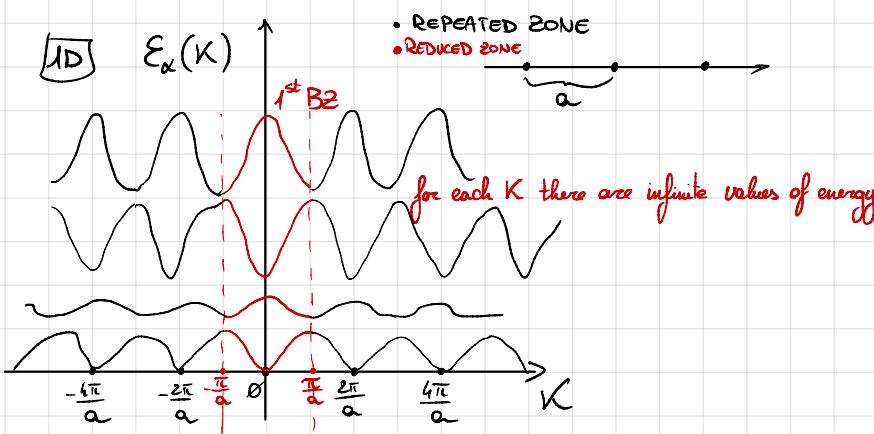
Stationary states are periodic in \vec{K} space with \vec{g}

$$\Psi_{\alpha, \vec{K} + \vec{g}}(\vec{r}) = \Psi_{\alpha, \vec{K}}(\vec{r})$$

$$\hat{H}\Psi_{\alpha, \vec{K}} = \underbrace{\mathcal{E}_{\alpha}(\vec{K})}_{\downarrow} \Psi_{\alpha, \vec{K}}$$

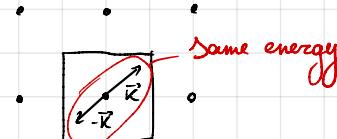
$$\mathcal{E}_{\alpha}(\vec{K} + \vec{g}) = \mathcal{E}_{\alpha}(\vec{K})$$

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



Kramers theorem

$$\mathcal{E}_{\alpha}(\vec{K}) = \mathcal{E}_{\alpha}(-\vec{K})$$



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

2D/3D $\mathcal{E}_{\alpha}(\vec{K}) = \mathcal{E}_{\alpha}(K_x, K_y, K_z)$

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

