$$I_{theoretical}(\vec{H}) \approx |F(\vec{H})|^2 \frac{Vcry}{V_{EC}^2} \underbrace{K(2\theta)}_{correction factor}$$

we want to compare the theoretical and the experimental intensities.
It's required to introduce a scale factor S related to the experimental set-up (that accounts for the crystal size, incident intensity, detector efficiency and more):

$$|F(\vec{H})|^2 \frac{Vcry}{V_{EC}^2} \underbrace{K(2\theta)}_{correction factor} \mathcal{S}cale \leftrightarrow I_{exp}(\vec{H})$$

we thus define $\Omega = \sum_{\vec{H}} \frac{[I_{theo}(\vec{H}) - I_{exp}(\vec{H})]^2}{\sigma^2(\vec{H})}$ in order to minimise this function.

$$F(\vec{H}) \approx \sum_{j=1}^{N_{atoms}} e^{2\pi i \vec{H} \cdot \vec{R}_{j,0}} e^{-B_j \vec{H}^2} f_j(\vec{H})$$

we start from the condition that we are approximating the coordinates of the atoms $\vec{R}_{j,0}$, then we will refine them. Same for B_j and $\mathcal{S}$. This procedure is called STRUCTURE REFINEMENT.

B_j is known as thermal parameter or as "atomic displacement parameter".

STRUCTURE SOLVING
electron density is lattice invariant:

$$\rho(\vec{x}) = \rho(\vec{x} + \vec{T}) = \frac{1}{V} \sum_{\vec{H}} A(\vec{H}) e^{-2\pi i \vec{H} \cdot \vec{x}}$$

where $\vec{T} = m\vec{a} + n\vec{b} + p\vec{c} \in \mathbb{N}$ and where the summation over $\vec{H}$ means the sum of hkl from $+\infty$ to $-\infty$ and $A(\vec{H})$ is a series of Fourier coefficients.
The Fourier coefficients correspond to the structure factor:

$$F(\vec{H}) \rightarrow A(\vec{H}) = \int_{V_{EC}} e^{2\pi i \vec{H} \cdot \vec{x}} \rho(\vec{x}) dV$$

experimentally is possible to notice that:

$$I_{observed}(\vec{H}) \propto |F(\vec{H})|^2$$

so, just because the structure factor is a complex function, we can just know its modulus.
$F(\vec{H}) = |F(\vec{H})| e^{i\phi(\vec{H})}$ ----> that's why the problem of defining the structure factor is called "the phase problem".
There are 3 methods used for structure solving:

1. maximum entropy method (MEM) we just want to find the electron density in a grid of pixels inside the elementary cell (see picture 1)
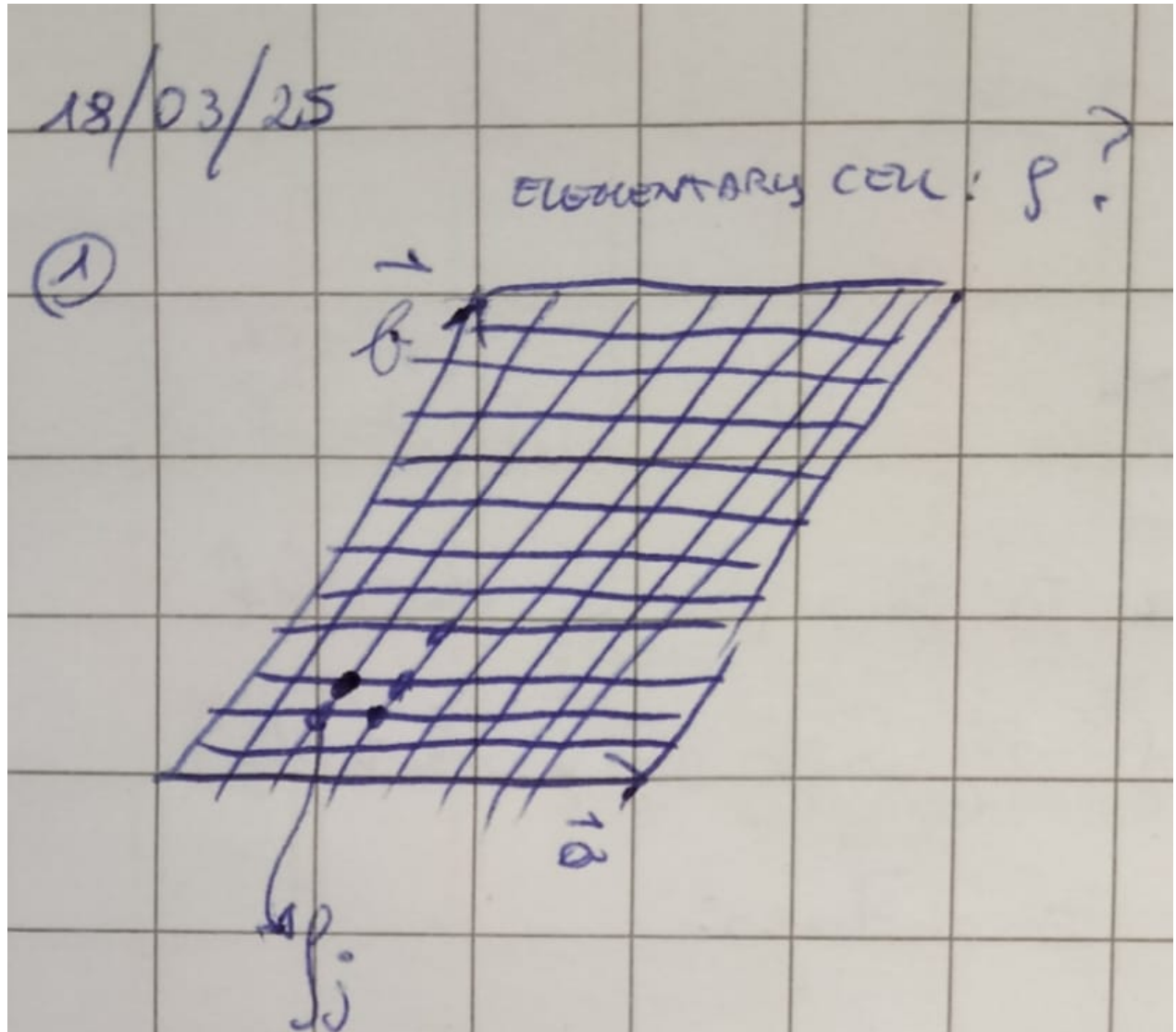
and we sink the electron density at each node (in the picture we see the jth pixel). We don't know nothing about ρ_j, but we assume that ρ_j must be the best possible values that maximise the function

$$\Omega = \sum_{j=1}^{pixels} \rho_j ln(\rho_j)$$

which is called "ENTROPY". So searching the $max(\Omega)$ (with the Lagrange multipliers method), we find the electron density.

When we have a set of $\{\rho_j\}$, we are able to calculate $F_{theo}(\vec{H})$. We also know that

$$\sum_{j=1} \rho_j = \text{n electrons}$$

and we have the constraint that $\underbrace{\{\rho_j\} \rightarrow F_{theo}(\vec{H}) \text{ where } |F_{theo}(\vec{H})| = |F_{exp}(\vec{H})|}$

3) charge flipping method: tricky but effective

It exist a set of structure factors written as $F(\vec{H}) = |F_{exp}(\vec{H})|e^{i\phi_{guess}(\vec{H})} \rightarrow \rho_j^{[0]}$ where the apex $[0]$ is the zero level of approximation and it's preferable to pixel the cell;

so we use the guess phase for the electron density: $\rho(\vec{x}) = \frac{1}{V}\sum_{\vec{H}} F(\vec{H})e^{-2\pi i \vec{H}\cdot\vec{x}}$
and we take $|\rho_j^{[0]}|$, meaning that we change the negative sign in positive, when it occurs(we thus flip the charge). We this obtain $\rho_j^{[1]}$. Now we calculate the structure factor associated with this electron density: $F^{[1]}(\vec{H})$. For each structure factor, I can determine the phases $\phi^{[1]}(\vec{H})$. Taking these phases, I reconstruct a new structure factor, that is $|F_{exp}(\vec{H})|e^{i\phi^{[1]}(\vec{H})}$. I repeat the procedure as an iterative process.

4. direct methods (set of methods with common basic idea): we know how to solve

$$F(\vec{H}) = \underbrace{|F(\vec{H})|}_{experimental} * \underbrace{e^{i\phi}}_{missing}$$

we will not see in detail, but there are techniques able to investigate the probability of having a given phase ϕ.

- $$f_j(\vec{H}) = \int e^{2\pi i \vec{H}\cdot\vec{x}} \rho_{j,atom}(\vec{x})dV \approx \int e^{2\pi i \vec{H}\cdot\vec{x}} \rho(|\vec{x}|)dV = f_j(|\vec{H}|)$$

by the way, using the Bragg's law, we have that $|\vec{H}| = \frac{2}{\lambda}sin\theta$. We find in the literature a dependance $f_j(\frac{sin\theta}{\lambda})$ instead of $f_j(|\vec{H}|)$.

- $\rho_{j,atoms}(\vec{x})$ can be modelled (with LDA, DFT, HF ...) and minimized with the refinement but the position j^{th} has to be known
Parametrisation of $f_j(|\vec{H}|)$:

$$f_j(\frac{sin\theta}{\lambda}) = c_0 + \sum_{k=1}^{4,6} a_k e^{-(\frac{sin\theta}{\lambda})^2 b_k}$$

where the summation goes to 4,5,6 because it's enough to have a good estimation. In order to have a good precision, we can stop to 6.

ANOMALOUS SCATTERING
Larmor law: $\mathcal{P} \propto q^2\vec{a}^2$
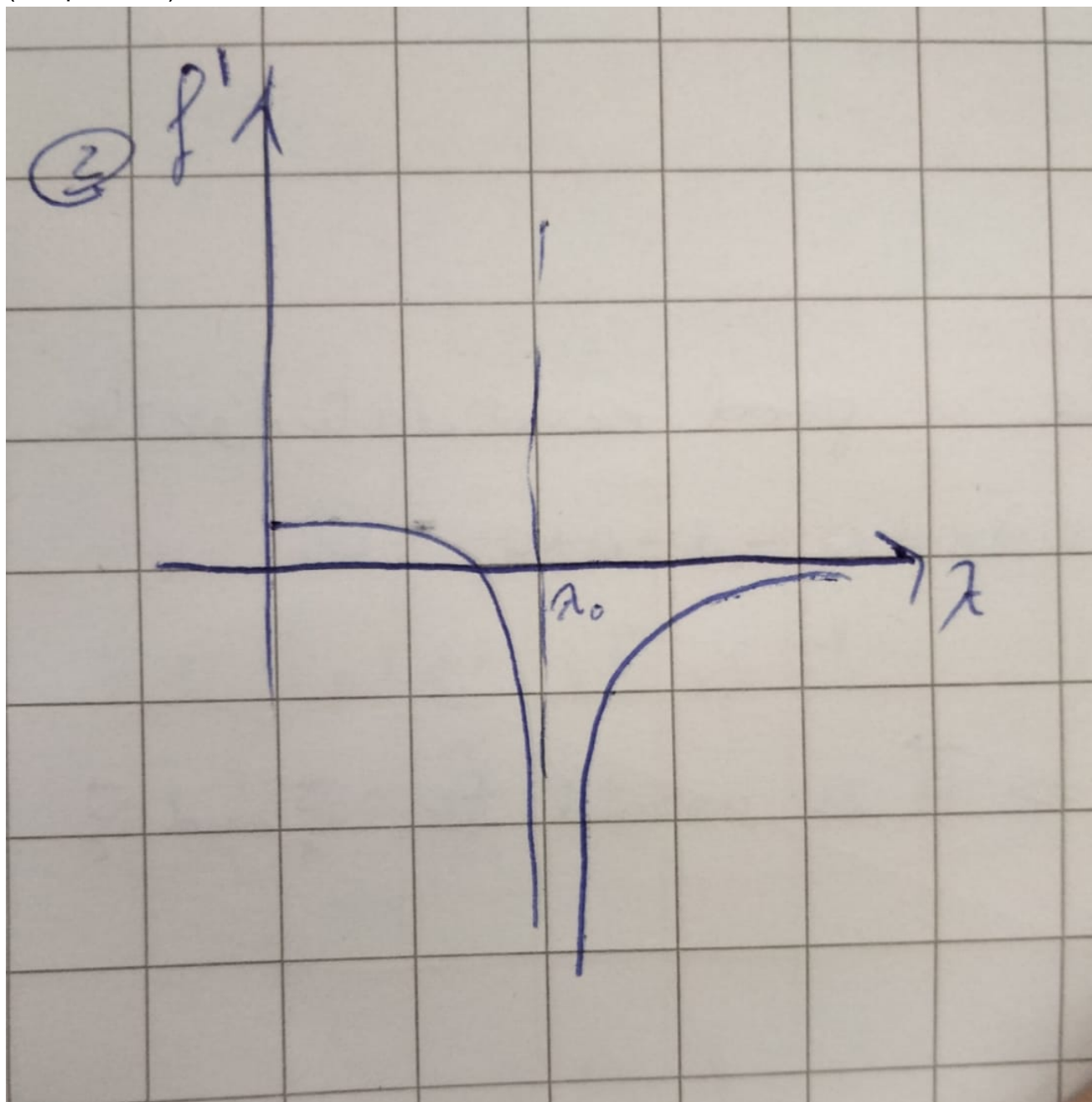The acceleration, $\vec{a} = \ddot{\vec{x}} = \frac{\vec{E}q}{m}$ can be expressed introducing a term of velocity,

$$\ddot{x} + \underbrace{\gamma\dot{x}}_{damping\ factor} = \frac{\vec{E}q}{m}$$

by introducing the damping factor, we cannot describe $f(\vec{H})$ as we said before, but we have to introduce a couple of terms more:

$$f(\vec{H}) = \underbrace{\int e^{2\pi i \vec{H}\cdot\vec{x}} \rho_{atom}(\vec{x})dV}_{f_0(\vec{H})} + \underbrace{f'(\lambda) + if''(\lambda)}_{anomalous\ contribution}$$
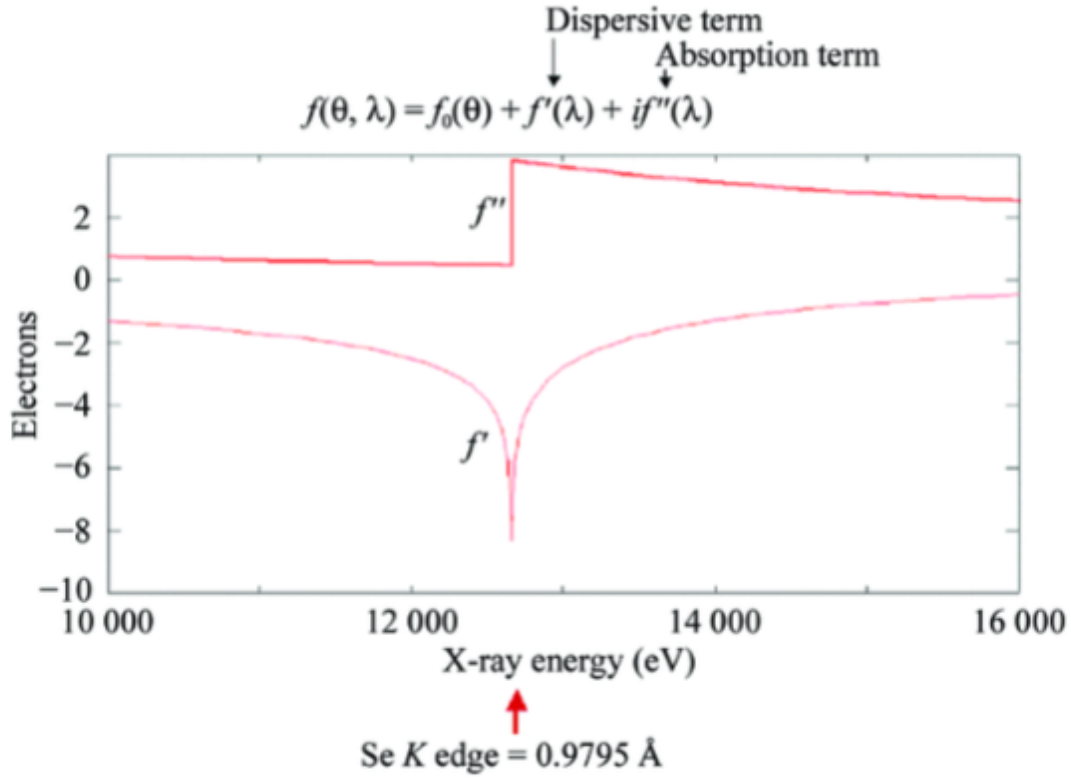
the anomalous contribution is relevant only in resonant conditions.

(see picture 2)

where λ_0 is the resonance wavelength, at which f' becomes extremely important. λ_0 depends on the chemical species.

By looking at f'', we see a step at the resonance wavelength (or resonance energy):

Dispersive term

Absorption term

$$f(\theta, \lambda) = f_0(\theta) + f'(\lambda) + if''(\lambda)$$

Se K edge $= 0.9795$ Å

HOW TO TREAT THE CASE OF SOLID SOLUTION

$$F(\vec{H}) = \sum_{j=1}^{atoms} e^{2\pi i \vec{H} \cdot \vec{x}_{j,0}} * e^{B_j \vec{H}^2} \underbrace{[f_{0j}(\frac{sin\theta}{\lambda}) + f'_j(\lambda) + if''_j(\lambda)]}_{\text{anomalous scattering } f_j(\frac{sin\theta}{\lambda}, \lambda)}$$

and we assume that there are no vacancies, so the sum of each probability of occupancy in each site j is 1: $P_j^{Mg} + P_j^{Fe} = 1$ for instance. The contribution of occupancy of each site is represented generally by

$$e^{2\pi i \vec{H} \cdot \vec{x}_{j0}} e^{-B_j \vec{H}^2} [P_j^{Mg} f_{Mg}(\frac{sin\theta}{\lambda}, \lambda) + P_j^{Fe} f_{Fe}(\frac{sin\theta}{\lambda}, \lambda)]$$