FULL PATTERN DECOMPOSITION

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The structure determination maze

The problems to be overcome in structure determination from powder diffraction data are twofold:

1) **the basic phase problem**, which is central to all crystallographic structure analyses, whether the data be from a single-crystal or a powder diffraction experiment

2) **the reflection overlap problem**, which is specific to powder diffraction data

No single approach to these two problems has emerged as the optimal one. The best approach always depends upon the nature and complexity of the material under investigation, and the quality of the diffraction data

The whole process can be viewed as finding a practicable path through a maze of possibilities

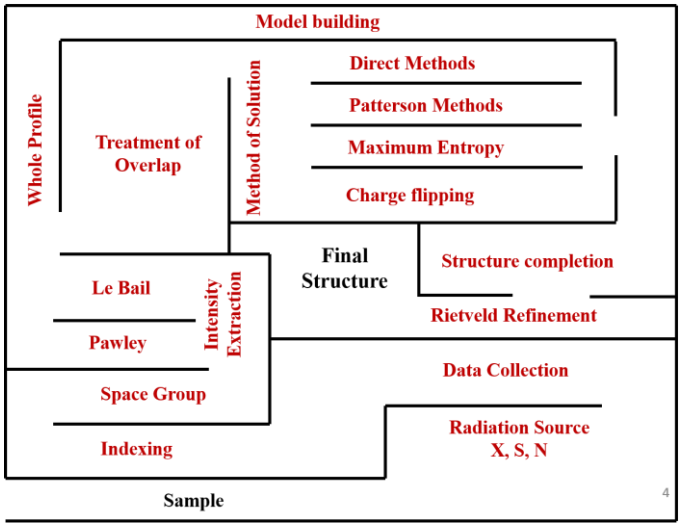
The powder structure determination maze

The structure determination process is a sequential one

That is, each step depends upon the previous one being correct

A mistake made early on in the procedure can make all subsequent steps useless

When the positions of the reflections are known, their intensities can be estimated



Two methods can produce a set of extracted intensities suitable for attempting a structure solution. Both derived from the Rietveld method:

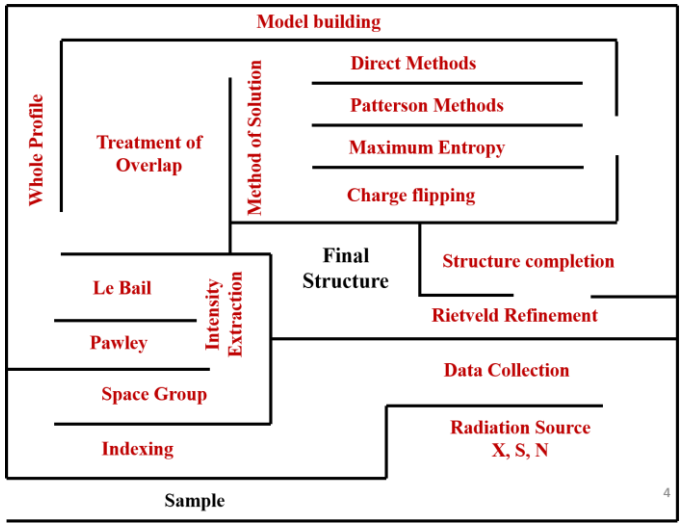
LE BAIL (1988)

The process of using iteratively the Rietveld decomposition formula, combined with a *full profile fitting* procedure

PAWLEY (1981)

Removing the crystal structure refinement and adding the refinement of the individual intensity for every expected Bragg peak

The intensities estimation is best done with a **whole profile fit**, where a peak shape is assigned to each reflection and its intensity is either refined (Pawley method) or adjusted in an iterative procedure (Le Bail method) to fit the measured data



This approach to the determination of the reflection intensities can be described as a model-free Rietveld refinement, where the intensities of the reflections rather than the atomic coordinates are optimized

Profile fitting

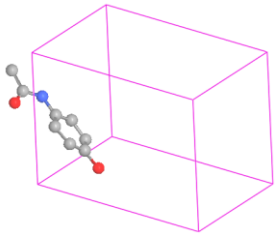
The background is described by a polynomial

The peak shape is described by some appropriate analytical functions (*gaussian*, *lorentzian*, *pearson VII*…..)

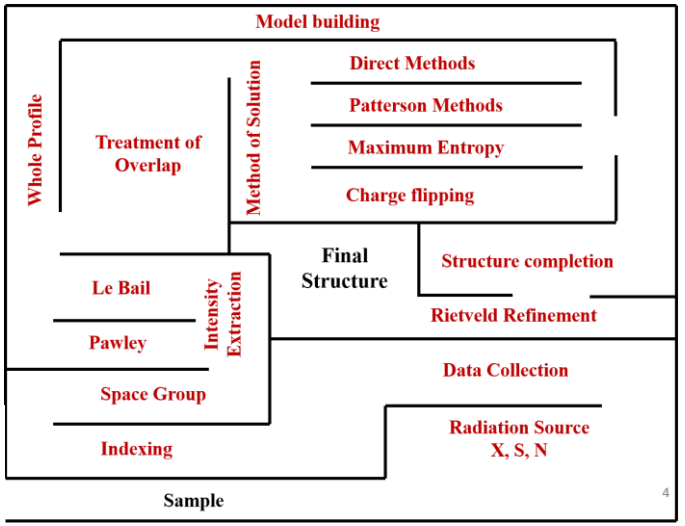
The FWHM, peak asymmetry, etc, are described with analytical functions, variable with 2θ

During the profile fitting the refinable parameters are: unit cell, 2θ zero, background, shape function, FWHM, asymmetry

The individual reflection intensities can be used as input to the traditional structure solution methods



$$\rho_{xyz} = 1/V \sum_{hkl} \boxed{F_{hkl}} \exp\{-2\pi i(hx + ky + lz)\}$$



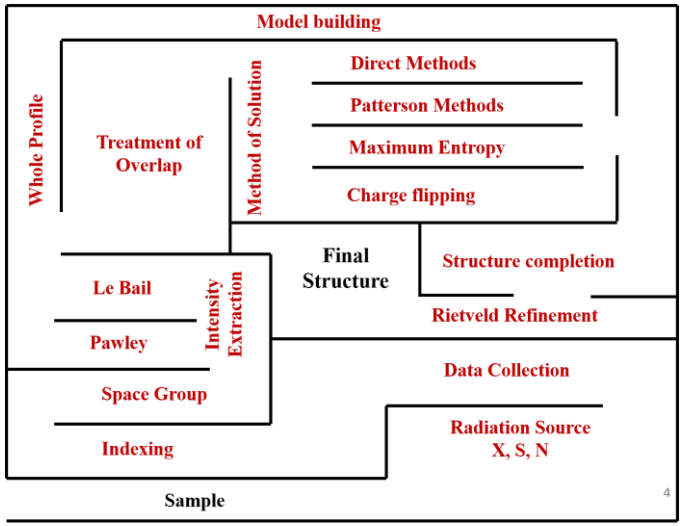
The structure factor F_{hkl} sums the result of scattering from all of the atoms in the unit cell from the (hkl) planes, to form a diffraction peak

$$F_{hkl} = |F_{hkl}| \exp(2\pi i \varphi_{hkl})$$

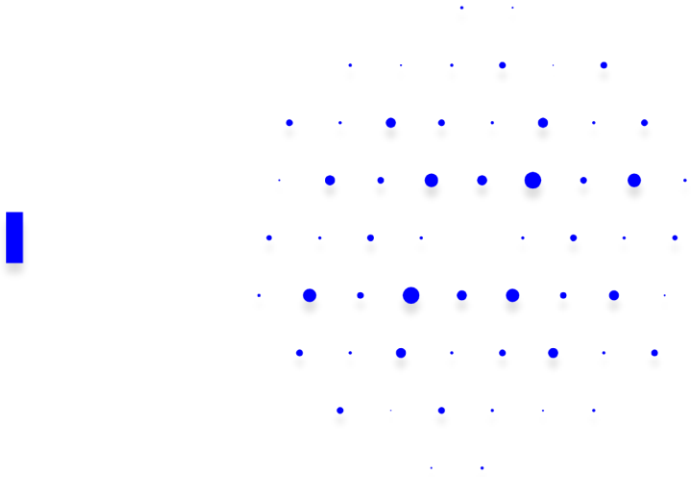
$$I_{hkl} \propto |F_{hkl}|^2$$

lost in a XRD experiment

If the extracted intensities are to be used as input to the structure solution program, something has to be done about the **overlapping reflections**

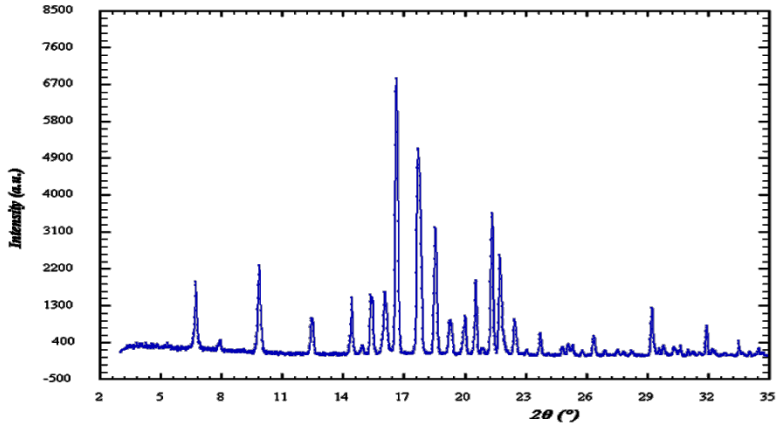


Single Crystal Diffraction



This information is distributed in a 3D space

Powder Diffraction

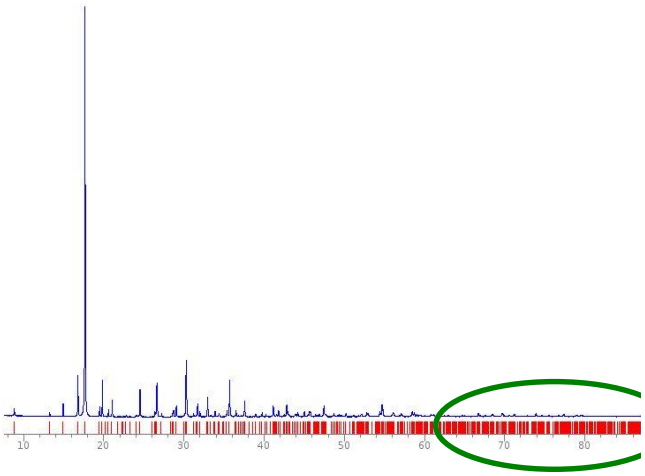


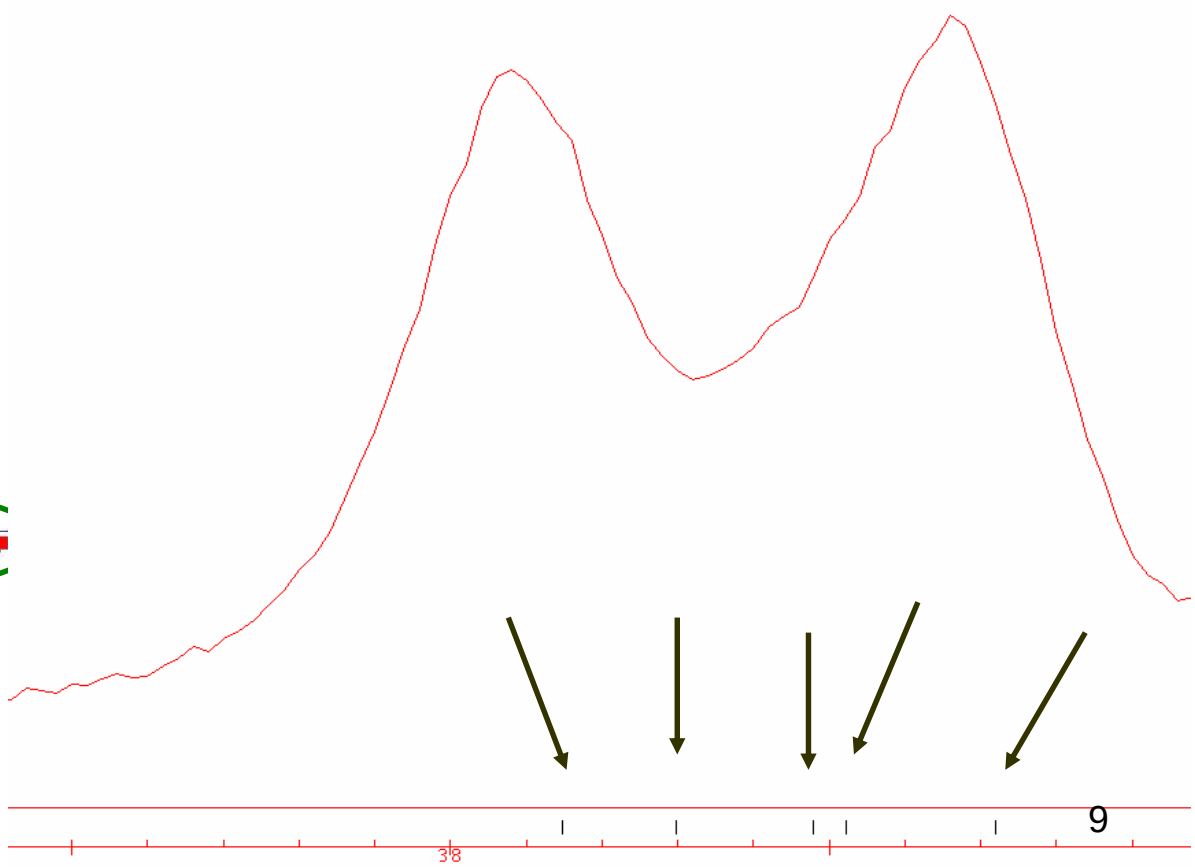
The 3D diffraction data are “compressed” into one-dimension

As a consequence

Overlap

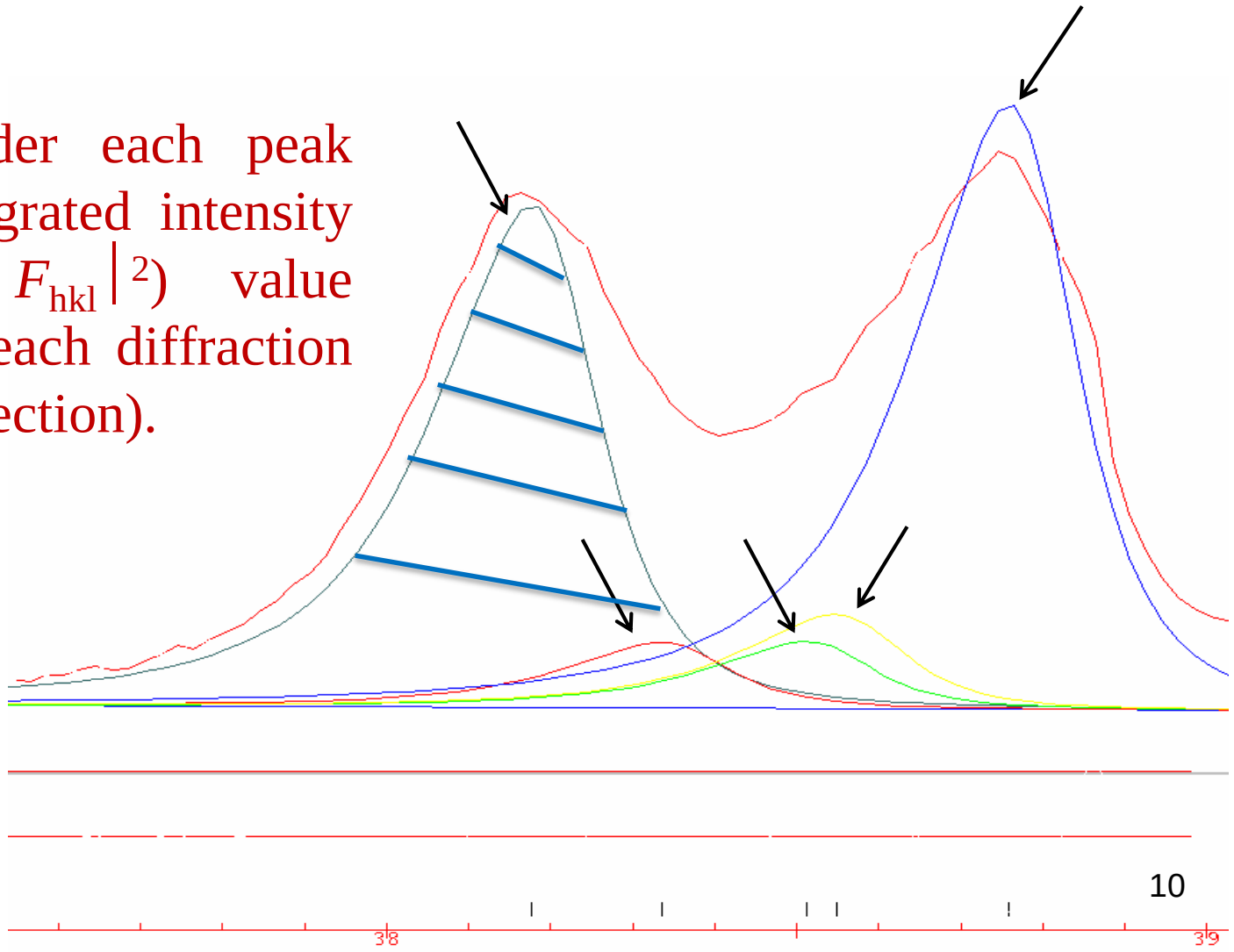
Considerable **overlap** of peaks leading to severe ambiguities in extracting the intensities I_{hkl} of individual diffraction maxima





The experimental diffraction profile must be decomposed into single peaks in order to extract the integrated intensities corresponding to each hkl reflection

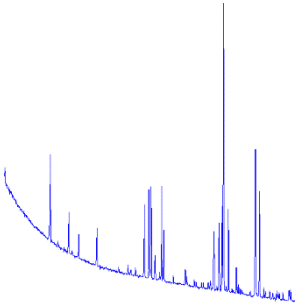
The area under each peak gives the integrated intensity I_{hkl} ($I_{hkl} \propto |F_{hkl}|^2$) value associated to each diffraction effect (hkl reflection).



Other problems

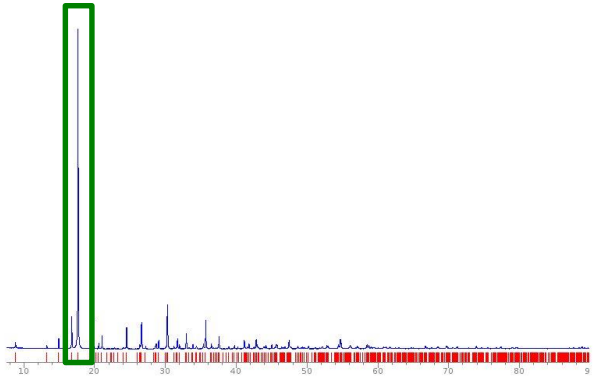
Background

not always easy to be correctly defined

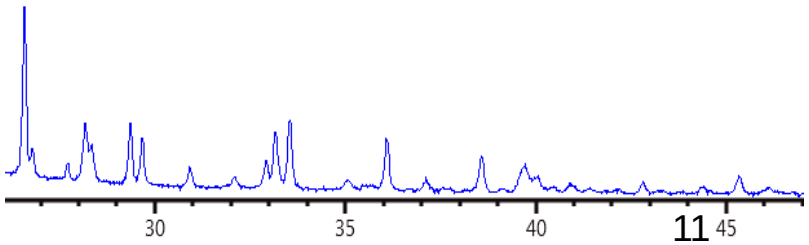


Preferred orientation

The crystallites are not always randomly oriented. This behaviour modifies the real ratios of the experimental integrated intensities



If the scattering power is weak (light atoms) the **experimental resolution** is very far from being atomic



COMMENTS

The quantity of information present in a powder diffraction experiment is the same as in the single crystal

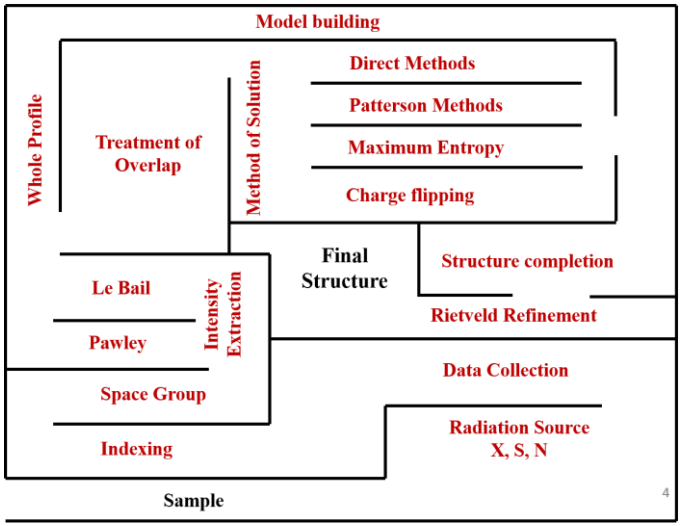
The difficulty is in the possibility to recover the complete and correct information

The experimental structure factor moduli are generally determined with errors of about 40% when good quality laboratory X-ray data are used

The success of powder TRADITIONAL structural solution methods depends on the extraction step:
the more reliable the extracted integrated intensity values, the larger the success probability of solving the structure

Treatment of overlapping

Usually, the intensity of a peak resulting from several overlapping reflections is simply divided equally over the contributing reflections



This is known as equipartitioning

Although this approach necessarily yields a number of incorrect intensities, it has proven to be sufficient for structure solution in many cases

For the more difficult cases, more sophisticated approaches can be used

The random decomposition approach in EXPO

For each group of **severely** overlapping reflections, a random partition of the integrated intensities is performed

```
%nowindow
%structure mes
%job MES - data from home diffractometer
%data pattern mes.pow
cell 8.588 9.931 11.105  90.0  93.754 90.0
content C 24 N 4 O 20 S 4 H 52
spacegroup p 21/c
wavelength 1.5406
%extraction
random p
%continue
```

To activate the random procedure (Altomare *et al.*, 2001) in order to improve the quality of the extracted structure factor moduli values.
p is the coefficient for the reflection overlapping definition ($2\vartheta_i - 2\vartheta_{i-1} \leq p\mathrm{FWHM}_{i-1}$. Default *p* value is 0.5)

The random decomposition approach: the main steps

An EXPO default run extracts the intensities (I_h) *via* Le Bail algorithm

Groups of **severely** overlapping reflections are defined

the total integrated intensity of the group is partitioned according to:

$$I_h^{'} = \sum_h I_h * \left(r_h \Big/ \sum_k r_k \right)$$

r_h is a random number associated with the reflection **h**, $I_h^{'}$ is consequently a random integrated intensity value

The random decomposition approach: the main steps

The profile discrepancy factor is calculated to evaluate the efficiency of the random decomposition process:

$$R'_p = \sum_j \left(Y_{oj} - SY'_{cj}\right)^2$$

If $R'_p \leq R_p$ the I'_h are accepted as trial integrated intensities and the R_p value of the cluster is updated

The procedure is cyclically repeated

The I'_h set having the minimum R'_p is saved and used in the phasing step

AGREEMENT FACTOR

to estimate behaviour and efficiency of the decomposition process

On the profile:

$$R_P = \frac{\sum_i \left| y_{oss}(i) - y_{calc}(i) \right|}{\sum_i y_{oss}(i)}$$

The summations go over the total number of profile points

Assesses the quality of the fit between observed and calculated profiles

Low R_p value is necessary and not sufficient condition for a reliable extraction

The Le Bail method: limit

If two reflections strongly or completely overlap, the Le Bail approach assigns equal starting intensity values to the reflections

The Le Bail method: advantage

Is very sensitive to the starting intensity values

↓

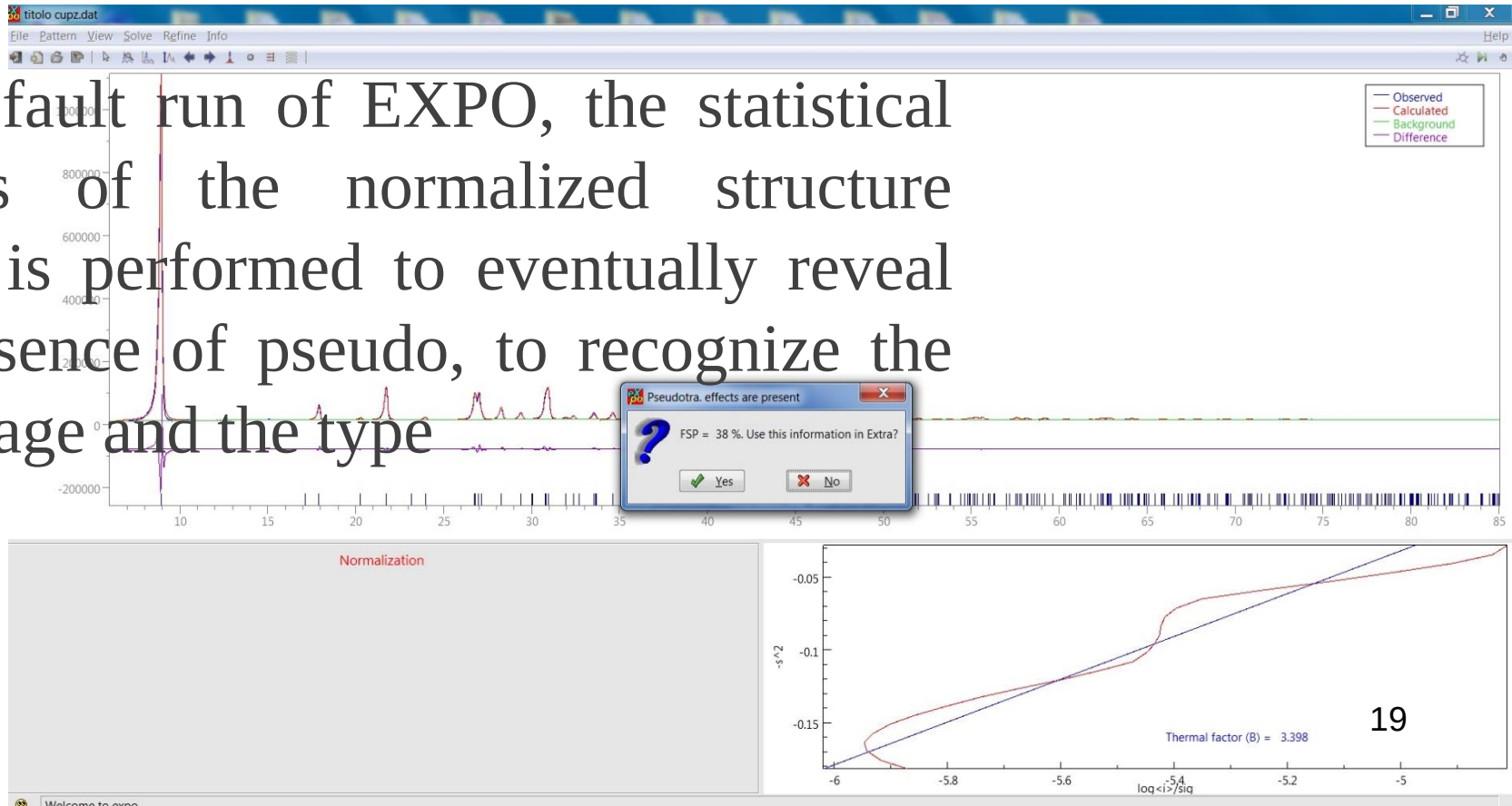
The Le Bail method can exploit some prior information in the intensity-recycled extraction process, eventually available during the solution process

If the starting integrated intensities are less arbitrary and closer to the true ones, the amplitude estimate is improved

The Le Bail method may benefit from the following information:

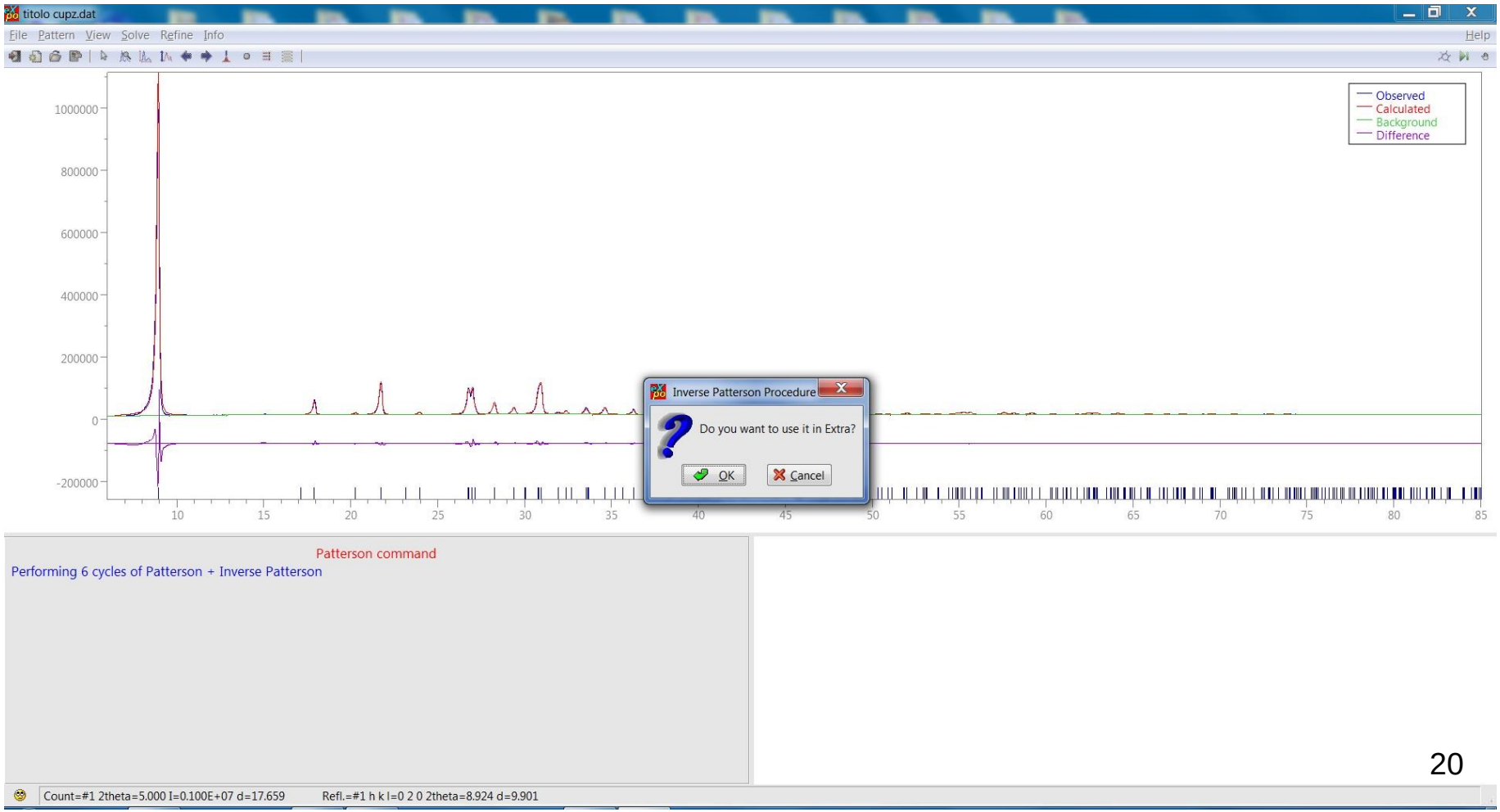
The presence of Pseudo symmetry

In a default run of EXPO, the statistical analysis of the normalized structure factors is performed to eventually reveal the presence of pseudo, to recognize the percentage and the type



The Le Bail method can exploit some prior information in the extraction process, eventually available during the solution process

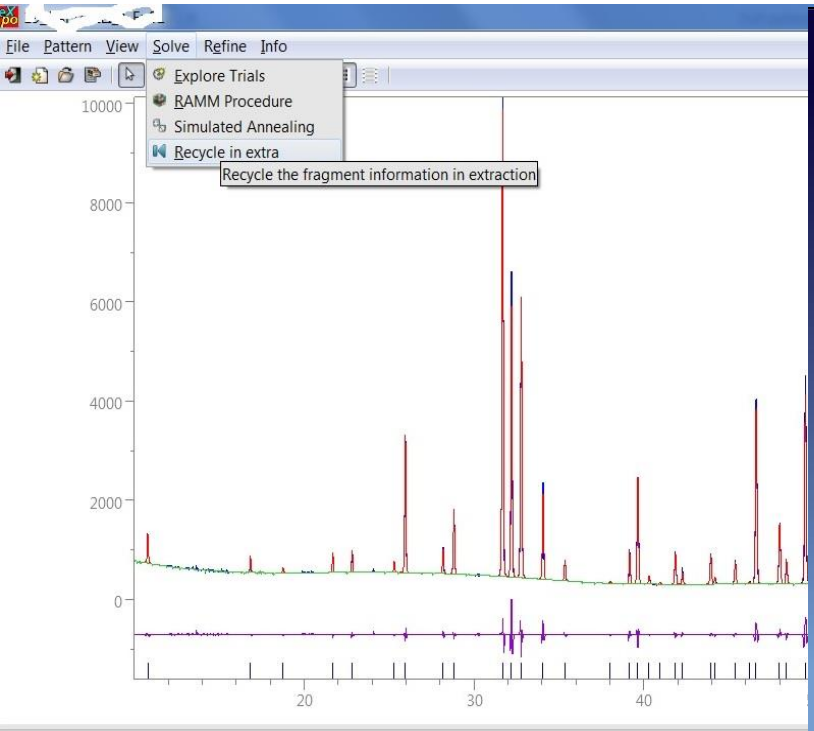
It may benefit from the following information:

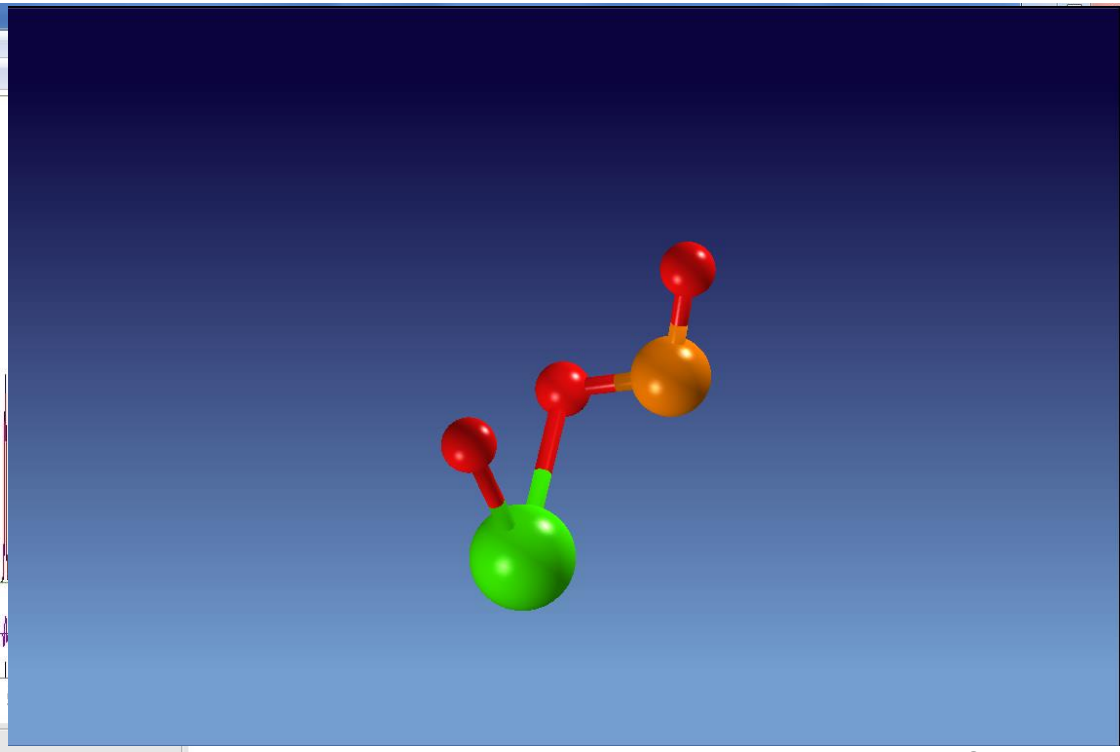


The Le Bail method can exploit some prior information in the extraction process, eventually available during the solution process

It may benefit from the following information:

The localization of a structure fragment





The use of the information which become available during the structure solution process, reduces the tendency of the Le Bail formula to equiportion the intensity of a group of strongly overlapping reflections and **improves (on average) the accuracy of the decomposition process and than of the total structural solution process**

EXPO Profile Decomposition and Intensity Extraction: an application

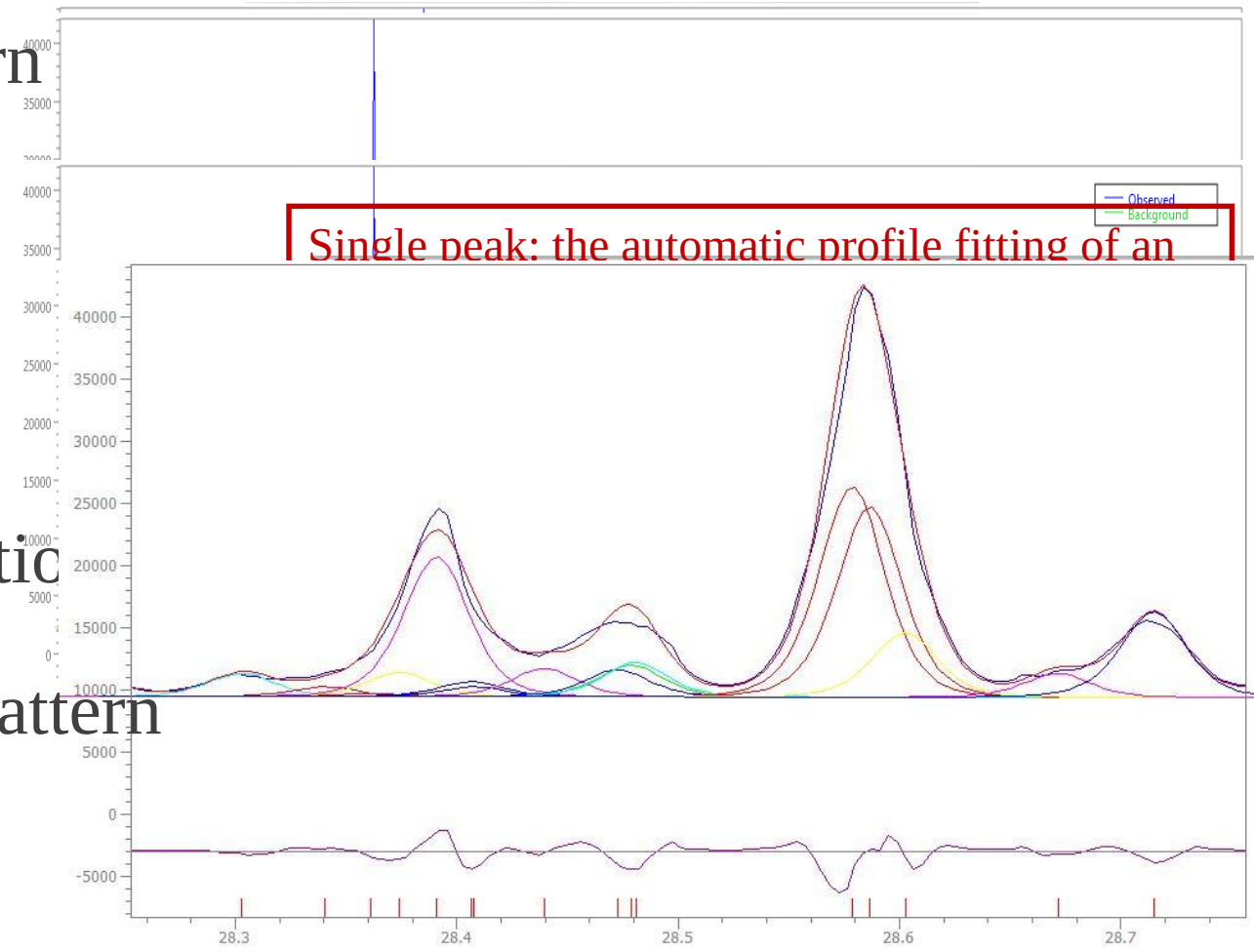
Experimental pattern

The pattern is divi
intervals. A single
also singled out

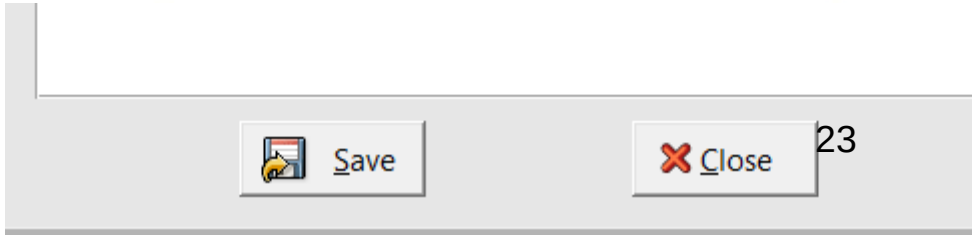
Background estimatic

Profile fitting and pattern decomposition via Le Bail method

Integrated intensity values calculation



Single peak: the automatic profile fitting of an



Conclusions

Crystal structure solution by powder diffraction data is not a trivial task and is still a challenge in many cases

A preliminary and critical point is represented by the decomposition of the experimental diffraction pattern into single integrated intensity values

Great experimental, methodological and computing progress has been reached and implemented in many available software.

crystals

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Special Issue

Crystal Structure Characterization by Powder Diffraction

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Submission Deadline: 31 December 2019

We invite contribute of papers that, while discussing the followed computational, methodological, and/or experimental strategies, point out the essential and advanced contribution of powder diffraction in identifying the unknown crystal structure of a compound.

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