



# Full powder pattern decomposition

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## Introduction

After that the cell parameters and the space group have been determined, the *ab-initio* crystal structure solution from X-ray powder diffraction data (XRPD) can be attained by the application of the single-crystal-like two-stage method [1, 2]:

1. The experimental powder diffraction profile is decomposed in order to extract the integrated intensities of the individual reflections.
2. The structure factor moduli are derived from the extracted intensities and processed by Direct Methods (or Patterson Methods or Maximum Entropy), which carry out the phasing process. The inverse Fourier transform of the structure factors, so determined in both moduli and phases, gives the electron density map from which the structure model can be recovered.

If compared with the single crystal case, the complexity of the structure solution process by XRPD arises from the nature of powder, which consists of several crystallites randomly oriented in the space. These crystallites can simultaneously result in diffraction, making the diffraction profile complex to be analyzed and processed. The single crystal diffraction pattern is made by spots, one spot for each diffraction effect. The powder diffraction pattern consists of a series of one-dimensional peaks whose intensities degrade at increasing the  $\theta$  angle of diffraction, resulting in a profile where the entire three-dimensional reciprocal lattice collapses onto one dimension of the  $2\theta$  axis. The consequence of the collapse is the overlapping of diffraction peaks. A diffraction peak can correspond to more than one reflection in such a way that the information associated to the diffraction intensity of each reflection cannot be easily derived. The overlapping problem becomes critical when the ratio  $\sin\theta/\lambda$  ( $\lambda$  is the wavelength of the radiation) increases. Moreover, at high  $2\theta$  values, peak overlap combines with the decrease of the atomic scattering factor, also.

The main obstacles to the extraction process are:

- peak overlap;
- background estimation. It cannot be always unambiguously modelled;
- preferred orientation. Sometimes, powder crystallites are not randomly oriented in the space, but they align along preferred directions. When present, the preferred orientation effect modifies the diffraction intensity ratios.

Peak overlap, background and preferred orientation can introduce strong correlations among reflection intensities and heavy errors in their estimates.

## The extraction methods

The accuracy of the extracted integrated intensity values depends on the quality of the experimental data (*e.g.*, synchrotron data are less affected by peak overlap, but the problems of intrinsic peak broadening from the sample itself still remain) as well as on the mathematical algorithm used for the decomposition of the diffraction profile. The success probability of solving crystal structures by using the so called 'traditional' approaches like Direct Methods or Patterson Methods (or Maximum Entropy) strongly depends on the reliability of the extracted intensities.

Several theoretical methods have been developed to carry out and, in particular, improve more and more the procedure of extraction of the structure factor amplitudes.

The structure factor modulus  $|F_h|$  of each  $\mathbf{h}$  reflection can be derived from the integrated intensity  $I_h$  ( $I_h \propto |F_h|^2$ ), which is given by the area under the peak, in the experimental powder profile, corresponding to the  $\mathbf{h}$  reflection. The operation of extracting  $I_h$  from the powder pattern requires that the observed experimental profile  $y_i(\mathbf{obs})$  at the  $i$ -th step is mathematically described by means of the calculated profile  $y_i(\mathbf{calc})$ :

$$y_i(\mathbf{calc}) = s \sum_{\mathbf{h}} y_{i,\mathbf{h}}(\mathbf{calc}) + y_i(\mathbf{b}) = s \sum_{\mathbf{h}} m_{\mathbf{h}} \mathbf{LP}_{\mathbf{h}} |F_{\mathbf{h}}|^2 P_{i,\mathbf{h}} A_{i,\mathbf{h}} + y_i(\mathbf{b}),$$

where  $s$  is a scale factor; the summation is over the reflections contributing to the profile intensity;  $y_{i,\mathbf{h}}(\mathbf{calc})$  represents the calculated contribution of the  $\mathbf{h}$  reflection;  $m_{\mathbf{h}}$  is the reflection multiplicity;  $\mathbf{LP}_{\mathbf{h}}$  is the Lorentz-polarization factor;  $P_{i,\mathbf{h}}$  and  $A_{i,\mathbf{h}}$  are the peak shape and asymmetry function, respectively, corresponding to the peak associated to the  $\mathbf{h}$  reflection and evaluated at the  $i$ -th step. Several kinds of profile analytical functions (Gaussian, Lorentzian, Pearson VII, ...) can be used for describing  $P_{i,\mathbf{h}}$ . Analytical functions, variable with the  $2\theta$  value, are adopted for fitting the full width at half maximum (FWHM) and the asymmetry of peak;  $y_i(\mathbf{b})$  is the background term which can be described by a polynomial function. Peak shape, background, asymmetry, FWHM parameters are refined by least-squares.

The quantity  $m_{\mathbf{h}} \mathbf{LP}_{\mathbf{h}} |F_{\mathbf{h}}|^2$  gives  $I_h$ .

Two methods are mainly used to evaluate the  $I_h$  values:

- the *Pawley method* [3].

It is based on a non-linear least-squares procedure that refines scale factor, lattice parameters ( $2\theta_{\mathbf{h}}$  depends on them), peak shape, asymmetry parameters and integrated intensities. Sometimes this method can be faulty because the correlation of the integrated intensities, due to peak overlap, often leads to ill-conditioning least-squares which provide negative integrated intensities. The method has been improved, *e.g.* by the introduction of a Bayesian probability approach, able to provide positive intensities [4].

- the *Le Bail method* [5].

It is based on the iterative use of the following equation:

$$I_{\mathbf{h}} = \sum_i \{y_i(\mathbf{obs}) - y_i(\mathbf{b})\} * y_{i,\mathbf{h}}(\mathbf{calc}) / \sum_k y_{i,k}(\mathbf{calc}),$$

where the summation at the numerator is over the peak range corresponding to the  $\mathbf{h}$  reflection and the summation at the denominator is over the reflections contributing to the  $i$ -th step observation. The formula starts with arbitrary integrated intensity values in  $y_{i,\mathbf{h}}(\mathbf{calc})$ , then the algorithm is iteratively applied. Moreover, the profile parameters are optimized by least-squares cycles. The method is convergent, provides positive integrated intensities but tends to equipartition the peak intensity of a group of strongly overlapping reflections.

Both the Pawley and Le Bail method are based on the minimization of the difference between the observed and calculated profiles. The  $R_p$  profile reliability parameter is used for evaluating the efficiency of the powder decomposition process:

$$R_p = \frac{\sum_i |y_i(\text{obs}) - y_i(\text{calc})|}{\sum_i y_i(\text{obs})}$$

The summation is extended over the number of experimental profile counts. A small  $R_p$  value means a good fit of the observed profile by means of the calculated profile, but it does not ensure free error extracted amplitudes.

In spite of great efforts to improve the extraction procedures, whatever the method used to calculate them (Pawley or Le Bail), the experimental structure factor moduli, especially of overlapping reflections, are not often well determined and errors of about 40% are quite common in case of good quality laboratory X-ray data. This occurrence is so critical that it can reduce the success probability of solving crystal structures when the traditional approaches like Direct Methods are used.

The Le Bail method has the great advantage with respect to the Pawley method to be sensitive to the starting point [6]: if the starting integrated intensities are less arbitrary and closer to the true ones, their estimate is improved. According to this feature, procedures have been developed for optimizing the extraction process routine [7]. They have been introduced in the EXPO package [8], the program devoted to the *ab-initio* crystal structure solution by powder data, able to carry out all the steps of the solution process, from the indexation to the structure refinement. Among them, we quote the approaches, which exploit the following additional information made available during the phasing process:

- pseudo-translational symmetry [9],
- Patterson function [10],
- location of a partial structure fragment [11],
- preferred orientation [12,13].

Le Bail based algorithms using a random approach [14] and a systematic decomposition process [15, 16] have also been developed and successfully applied.

## Conclusions

The step of extracting the structure factor amplitudes from the powder diffraction profile is critical in the *ab-initio* solution process, which depends on the quality of the extracted intensities.

When the *ab-initio* solution process is executed by using the computer program EXPO and the default run fails the following rule of thumb can be applied for improving the result of the extraction procedure and, consequently, increasing the probability of success of the solution process:

It is advisable to use the pseudo-symmetry procedure when the percentage of the detected pseudo-translational symmetry is large; the Patterson approach in case of heavy atom structure; the located fragment procedure when a reasonable fragment is recognized; the preferred orientation correction when it is revealed. Random or systematic partition strategy can be generally applied.

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