Diffracted intensities measured in the Laue technique

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The object of this document is to summarise the formulae for treating the measured intensities using the Laue technique. This step is absolutely necessary for refining a crystal or magnetic structure.

One can use two methods: the first one consists on extracting the structure factors from the measured intensities using the intrinsic redundancy of the way we collect data in the Laue technique and the second one models directly the raw intensities. Instead of extracting the structure factors form the measured intensities (as done by **LAUENORM** or **LAUE4**) one can model directly the intensity in the refinement program. In the future we will implement this method within **FullProf** in order to avoid the necessity of coming back to the normalisation when one realises that something has gone wrong. This method is much more flexible; it uses all the available Laue spots and allows also extracting the structure factors as a sub-product if one uses the squares of structure factors of independent reflections as free variables using a method similar to the Le Bail or Pawley fits in powder diffraction.

For the moment we have used the first method in the new program **Normalize_Laue**, so that the extracted structure factors can be used in a conventional single refinement program like **SHELX** (of course also with **FullProf** in conventional mode).

A high degree of redundancy is needed for properly refine all the free parameters contained in the pre-factors of the structure factor squared.

The general expression of the diffracted intensity in a Laue diffraction pattern may be written as:

$$I(\mathbf{h})_{xz} = s\, Lp(\theta,\varphi)\Phi(\lambda,\mathbf{p}_{\phi})\lambda^3 E_{ff}(\lambda,x,z)A(\lambda,x,z,\mathbf{p}_{abs})G(\mathbf{h},\mathbf{p}_g)\,E(\lambda,|F(\mathbf{h})|,\mathbf{p}_{ext})F^2(\mathbf{h},\mathbf{p}_s) \qquad [1]$$

In the above expression **h**, represent the scattering vector and $F^2(\mathbf{h},\mathbf{p}_s)$ is the square of the structure factor (or the square of the magnetic interaction vector $\mathbf{M}_{\perp}^2(\mathbf{h},\mathbf{p}_s)$) of the current reflection that depends on the structural parameters represented by the vector $\mathbf{p}_s$. The (x, z) variables are the coordinates of the spot in the 2D detector used to collect the diffraction pattern. Here we have included the term λ^3 that comes from the reflectivity of the sample. This term may be included within the flux factor but we will keep it explicitly in the expression of the integrated intensity.
In many cases a single observation contains several reflections. In such a case the total observed intensity can be written as:

$$I_{xz} = s\, Lp(\theta,\varphi)\sum_i \Phi(\lambda_i,\mathbf{p}_{\phi})\lambda_i^3 E_{ff}(\lambda_i,x,z)A(\lambda_i,x,z,\mathbf{p}_{abs})G(\mathbf{h}_i,\mathbf{p}_g)E(\lambda_i,|F(\mathbf{h}_i)|,\mathbf{p}_{ext})F^2(\mathbf{h}_i,\mathbf{p}_s) \qquad [2]$$

The quantity s is a constant scale factor. Additional scale factors have to be considered for different images if they have been measured in different conditions. The list of contributing factors is described below.

The Lorentz and Polarisation factor

The coefficient $Lp(\theta,\varphi)$ is reduced to the Lorentz factor in neutron diffraction and contents a polarisation factor for X-ray diffraction. The combined coefficient is given by:

$$Lp(\theta,\varphi) = \frac{1}{\sin^2\theta}\frac{1+\cos^2 2\theta - \tau\cos 2\varphi \sin^2 2\theta}{2} \qquad [3]$$

This is valid for synchrotron radiation. The variable φ is the azimuth angle and τ is the degree of polarisation. It may be written as $\tau = \sin\rho$ because τ verifies $-1 \le \tau \le 1$. Only the first factor ($1/\sin^2\theta$) is operative in neutron diffraction.

Incident spectrum

It is described by the factor: $\Phi(\lambda, \mathbf{p}_\phi)$. It may be given as a histogram or modelled by a Maxwellian function (idealised case in neutron scattering) or, better, parameterized using Chebychev polynomials as given, for instance, in Z. Ren and K. Moffat (*J. App. Cryst*. **28**, 461 (1995)):

$$\Phi(\lambda, \mathbf{p}_\phi) = \exp\{-\sum_{i=1}^{n_\phi} c_i[\cos(i\cos^{-1}\lambda') - \cos(i\cos^{-1}\lambda_r')]\} \qquad [4]$$

$$\mathbf{p}_\phi = (c_1, c_2, \ldots c_{n_\phi}); \qquad \lambda' = \frac{\lambda - \frac{1}{2}(\lambda_{\max} + \lambda_{\min})}{\frac{1}{2}(\lambda_{\max} - \lambda_{\min})} = \frac{2\lambda - (\lambda_{\max} + \lambda_{\min})}{(\lambda_{\max} - \lambda_{\min})} \qquad [5]$$

The normalization wavelength is such that when $\lambda=\lambda_r$, the flux is $\Phi(\lambda_r, \mathbf{p}_\phi) = 1$. It may be selected arbitrarily between $\lambda_{\min}$ and $\lambda_{\max}$. The best is to select $\lambda=\lambda_r$ for which the number of measured reflections is the higher.

Efficiency of the detector

The coefficient $E_{ff}(\lambda, x, z, \mathbf{p}_E)$ should be determined or modelled. In general, what is determined is the combined effect ΦE_{ff}. However one can use a geometrical term depending on the angle between the scattered beam (along **u**) and the normal to the detector in the impact point (**n**) together with the absorption cross section of the neutron detecting element $\sigma(\lambda)$. The expression of the efficiency can be written as:

$$E_{ff}(\lambda, x, z, \mathbf{p}_E) = E_{ff}(\lambda, \nu, \mathbf{p}_E)_{cyl} = 1 - \exp\{-\frac{\sigma(\lambda) p_E}{\mathbf{nu}}\} \qquad [6]$$

The function $\sigma(\lambda)$ depends on the material of the detector and may be modelled read from a table for each λ. For a cylindrical detector $\mathbf{nu}=\cos\nu$. In the above expression the parameter p_E represents the thickness of the absorbing element. If the expression of $\sigma(\lambda)$ or the tables are not available, one can use a two parameter efficiency correction using the expression:

$$E_{ff}(\lambda, \mathbf{nu}, \mathbf{p}_E) = 1 - \exp\{-\frac{p_E(1) + p_E(2)\lambda}{\mathbf{nu}}\} \qquad [7]$$

Absorption

It is described by the factor $A(\lambda, x, z, \mathbf{p}_{abs})$. One can use simplified expressions for spheres or cylinders as approximate models for absorption. The only free parameter is μR. The expression given in the ITC Vol. C for the transmission factor is:

$$A(\lambda, \theta, \mathbf{p}_{abs}) = \exp\{-\sum_{m=1}^{M} K_m(\theta)(\mu R)^m\} = \exp\{-\sum_{m=1}^{M} K_m(\theta)(a_0 + a_1\lambda)^m\} \qquad [8]$$

The coefficients $K_m(\theta)$ are known for discrete values of θ but can be determined and interpolated. Another possibility is to consider an approximation similar to that used in XABS2 (S. Parkin et *al*., *J. Appl.Cryst.* **28**, 53 (1995)) for monochromatic single crystal experiments:

$$A(\theta, \mathbf{p}_{abs}) = a_1 \sin^6\theta + a_2 \sin^4\theta + a_3 \sin^2\theta + a_4 \qquad [9]$$

For Laue data, a dependency of the coefficients a_i on λ should be introduced. This has to be explored more deeply.

However the general case is quite complicated because it depends on the shape of the crystal, the path in air, screens in the cryostat, etc. In any case we can consider that the final correction for a particular image depends on a generalized path p_g (see *J. App. Cryst*. **28**, 461 (1995)) and use Chebychev polynomials for its modelling. We can use the following expression generalising that given by Ren & Moffat:

$$A(\lambda, x, z, \mathbf{p}_{abs}) = \exp\{-(A + B\lambda + C\lambda^3 - D\lambda^4) p_g(x, z, \mathbf{p}_{abs})\} \qquad [10]$$

For neutrons C=D=0.0 and for X-rays B=0.0. The generalised path p_g can be written as:

$$p_g(x, z, \mathbf{p}_{abs}) = \left(\sum_{i=1}^{n_A} c_{xi}[\cos(i\cos^{-1}x') - \cos(i\cos^{-1}x_r')]\right) \times \left(\sum_{j=1}^{n_A} c_{zj}[\cos(j\cos^{-1}z') - \cos(j\cos^{-1}z_r')]\right) \qquad [11]$$

$$\mathbf{p}_{abs} = (c_{x1}, c_{x2}, \ldots c_{xn_A}, c_{z1}, c_{z2}, \ldots c_{zn_A})$$

The primed variables are obtained with a normalisation expression similar to that of the wavelength distribution.

Geometrical or undetermined corrections

The coefficient $G(\mathbf{h},\mathbf{p}_g)$ represents undetermined corrections to the intensity that come from systematic errors of different origins that cannot be determined with precision. We will consider only some expressions given by Ren & Moffat that may be fixed to 1 in practical cases.

The so called anisotropic scale factor:

$$G(h,k,l,\mathbf{p}_g) = \exp\{-(a_1h + a_2k + a_3l + a_4h^2 + a_5k^2 + a_6l^2 + a_7hk + a_8hl + a_9hl)\} \qquad [12]$$

$$\mathbf{p}_g = (a_1, a_2, \quad ... \quad a_9)$$

may be used, with caution, to take into account radiation damage (or event a part of the absorption)

Secondary extinction

It is described by the factor $E(\lambda,|F(\mathbf{h})|,\mathbf{p}_{ext})$. A simplified model, as those used in SHELX or FullProf, can be used. The isotropic version of the model corresponds to the expression:

$$E(\lambda,|F(\mathbf{h})|,\mathbf{p}_{ext}) = \frac{1}{\sqrt{1 + c_e p_{ext} \lambda^3 \frac{|F(\mathbf{h})|^2}{\sin 2\theta}}} \qquad \mathbf{p}_{ext} = (p_{ext}) \qquad [13]$$

The anisotropic version of the model corresponds to the expression:

$$E(\lambda,|F(\mathbf{h})|,\mathbf{p}_{ext}) = \frac{1}{\sqrt{1 + c_e d_{hkl}^2 \lambda^3 \frac{|F(\mathbf{h})|^2}{\sin 2\theta}(p_1h^2 + p_2k^2 + p_3l^2 + p_4hk + p_5hl + p_6kl)}} \qquad [14]$$

$$\mathbf{p}_{ext} = (p_1, p_2, p_3, p_4, p_5, p_6)$$

Notice that the structure factor is considered here without its dependence with respect to structural parameters.

Extracting structure factors using the first method as implemented in Normalize_Laue

In the program **Normalize_Laue** we use a least squares two-step method: we assume an initial value of the correction parameters and we use the set of equivalent reflections measured at different conditions (different wavelength, positions in the detector, etc.) to extract the square of the structure factors of the independent reflections.

Least squares refinements for implementing the second method in FullProf

In least squares (LSQ) refinement one considers to minimise the following cost function:

$$\chi^2 = \sum_{p=1}^{N_p} \sum_{n=1}^{N_{obs}^p} w_n^p \{I_{obs,n}^p - I_{calc,n}^p(\boldsymbol{\alpha})\}^2$$

with respect to the P unknown parameters $\boldsymbol{\alpha}$=($\mathbf{p}_\varphi$, $\mathbf{p}_E$, $\mathbf{p}_{abs}$, $\mathbf{p}_g$, $\mathbf{p}_{ext}$, $\mathbf{p}_s$)=(α_1,... α_P). The index *p* makes reference to a particular image and the number *n* indexes a single observation. The weight factors are normally the inverse of the variance of the observation, but different weight schemes can be used. The expression of the calculated intensity for a single observation is given by:

$$I_{calc,n}^p = s_p Lp(\theta_n) \sum_{i=1}^{N_n^p} \Phi(\lambda_i, \mathbf{p}_\phi) \lambda_i^3 E_{ff}(\lambda_i, \mathbf{p}_E) A(\lambda_i, \mathbf{p}_{abs}) G(\mathbf{h}_i, \mathbf{p}_g) E(\lambda_i, |F(\mathbf{h}_i)|, \mathbf{p}_{ext}) F^2(\mathbf{h}_i, \mathbf{p}_s)$$

After data reduction, the wavelength and geometrical parameters of each reflection are known. For finding an improvement of the initial parameters $\boldsymbol{\alpha}_0$, ($\boldsymbol{\alpha}_1 = \boldsymbol{\alpha}_0 + \boldsymbol{\delta}$) one has to solve the LSQ linear equations:

$$\mathbf{A}(\boldsymbol{\alpha}_0)\boldsymbol{\delta} = \mathbf{b}(\boldsymbol{\alpha}_0)$$

where the components of the P x P matrix $\mathbf{A}(\boldsymbol{\alpha}_0)$ and vector $\mathbf{b}(\boldsymbol{\alpha}_0)$ in the Gauss-Newton algorithm are given by the expressions:

$$A_{kl} = \sum_{p=1}^{N_p} \sum_{n=1}^{N_{obs}^p} w_n^p \frac{\partial I_{calc,n}^p(\boldsymbol{\alpha}_0)}{\partial \alpha_k} \frac{\partial I_{calc,n}^p(\boldsymbol{\alpha}_0)}{\partial \alpha_l}$$

$$b_k = \sum_{p=1}^{N_p} \sum_{n=1}^{N_{obs}^p} w_n^p (I_{obs,n}^p - I_{calc,n}^p) \frac{\partial I_{calc,n}^p(\boldsymbol{\alpha}_0)}{\partial \alpha_k}$$

For calculating the derivatives with respect to a particular group of parameters of type H (H being one of the factor functions: Φ, E_{ff}, A, ...), in the case of a single reflection contributing to $I_{calc,n}^p$ we have:

$$\frac{\partial I_{calc,n}^p(\boldsymbol{\alpha}_0)}{\partial p_H} = \frac{I_{calc,n}^p(\boldsymbol{\alpha}_0)}{H(\mathbf{p}_{H0})} \frac{\partial H(\mathbf{p}_{H0})}{\partial p_H}$$

All derivatives can be calculated easily from the expressions given above. In the case of several reflections contributing to the same observation this factorization cannot be used and the calculation should be done explicitly. Some examples are given below

$$\frac{\partial I^p_{calc,n}(\boldsymbol{\alpha}_0)}{\partial s_p} = \frac{I^p_{calc,n}(\boldsymbol{\alpha}_0)}{s_p} = Lp(\theta_n)\sum_{i=1}^{N^p_n}\Phi(\lambda_i,\mathbf{p}_\phi)\lambda_i^3 E_{ff}(\lambda_i,\mathbf{p}_E)A(\lambda_i,\mathbf{p}_{abs})G(\mathbf{h}_i,\mathbf{p}_g)E(\lambda_i,|F(\mathbf{h}_i)|,\mathbf{p}_{ext})F^2(\mathbf{h}_i,\mathbf{p}_s)$$

$$\frac{\partial I^p_{calc,n}(\boldsymbol{\alpha}_0)}{\partial p_{\phi,k}} = s_p Lp(\theta_n)\sum_{i=1}^{N^p_n}\frac{\partial\Phi(\lambda_i,\mathbf{p}_\phi)}{\partial p_{\phi,k}}\lambda_i^3 E_{ff}(\lambda_i,\mathbf{p}_E)A(\lambda_i,\mathbf{p}_{abs})G(\mathbf{h}_i,\mathbf{p}_g)E(\lambda_i,|F(\mathbf{h}_i)|,\mathbf{p}_{ext})F^2(\mathbf{h}_i,\mathbf{p}_s)$$

$$with \quad \frac{\partial\Phi(\lambda_i,\mathbf{p}_\phi)}{\partial p_{\phi,k}} = -\Phi(\lambda_i,\mathbf{p}_\phi)[\cos(k\cos^{-1}\lambda'_i) - \cos(k\cos^{-1}\lambda'_{r,i})]$$

$$\frac{\partial I^p_{calc,n}(\boldsymbol{\alpha}_0)}{\partial p_{E,k}} = s_p Lp(\theta_n)\sum_{i=1}^{N^p_n}\Phi(\lambda_i,\mathbf{p}_\phi)\lambda_i^3\frac{\partial E_{ff}(\lambda_i,\mathbf{p}_E)}{\partial p_{E,k}}A(\lambda_i,\mathbf{p}_{abs})G(\mathbf{h}_i,\mathbf{p}_g)E(\lambda_i,|F(\mathbf{h}_i)|,\mathbf{p}_{ext})F^2(\mathbf{h}_i,\mathbf{p}_s)$$

$$with \quad \frac{\partial E_{ff}(\lambda_i,\mathbf{p}_E)}{\partial p_{E,k}} = \frac{1}{\cos\nu_n}\frac{\partial f(\lambda_i,\mathbf{p}_E)}{\partial p_{E,k}} = \frac{\lambda^k}{\cos\nu_n}$$

etc.

In FullProf we use the following notation (*not finished*!):

$$I^p_{calc,n}(\boldsymbol{\alpha}_0) = s_p Corr_n(\mathbf{p}_\phi,\mathbf{p}_E,\mathbf{p}_{abs},\mathbf{p}_g,\mathbf{p}_{ext})F^2(\mathbf{h}_i,\mathbf{p}_s)$$

$$Corr_n(\mathbf{p}_\phi,\mathbf{p}_E,\mathbf{p}_{abs},\mathbf{p}_g,\mathbf{p}_{ext}) = Lp\,.\,Flux\_corr\,.\,Ext\_corr\,.\,Eff\_corr$$