EXPO&more International Workshop

Rietveld Refinement

The Rietveld Method

Based on the idea suggested in the middle 1960s by Rietveld

Aim of the method

All structural and instrumental parameters are refined by fitting a calculated profile to the observed data without extraction of the individual integrated intensities

- Nonlinear least squares method
- Requires a model of a crystal structure

Fundamentals of the Rietveld Method

The minimized function is given by:

$$\chi^2 = \sum_{i=1}^{N} w_i [y_{i,obs} - y_{i,calc}]^2$$

$y_{i,obs}$ is the observed intensity at the *i*th data point

$y_{i,calc}$ is the calculated intensity at the *i*th data point

The weight is given by $w_i = \frac{1}{y_{i,obs}}$

Peak-Shape Functions

The diffracted profile is expressed by the equation:

$$y_{i,calc} = b_i + S \sum_{k=1}^{m} I_k y_k(x_k)$$

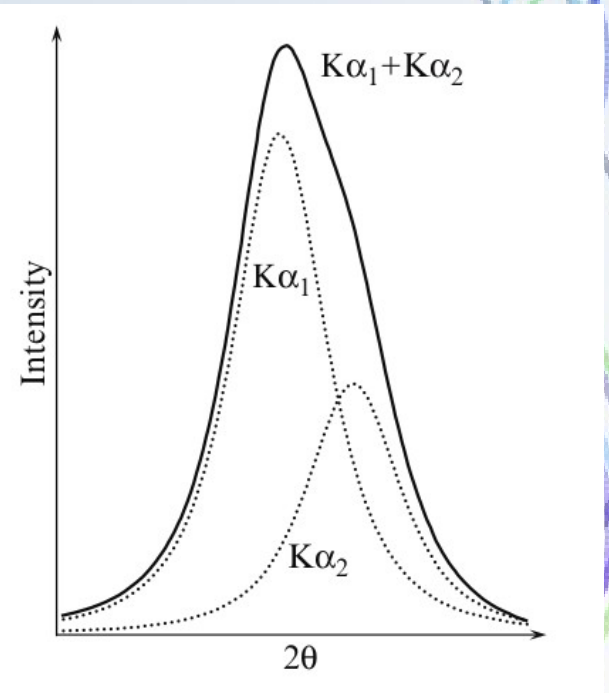
$y_{i,calc}$ is the total intensity calculated at the point *i*

b_i is the background intensity

S is the phase scale factor

y_{ik} is the contribution from the *k*th individual Bragg peak

I_k is the intensity of the *k*th Bragg reflection and the sum is extended over all *m* reflections contributing the intensity to point *i*



$$x_k = 2\theta_i - 2\theta_k$$

$$y_{i,calc} = b_i + S \sum_{k=1}^{m} I_k [y_k(x_k) + 0.5 y_k(x_k + \Delta x_k)]$$

wavelength 1.54059 1.54443 0.5

Fundamentals of the Rietveld Method

The intensity I_k is given by the expression:

$$I_k = M_k L_k |F_k|^2 P_k$$

M_k is the multiplicity

L_k is the Lorentz-polarisation factor

F_k is the structure factor

P_k is the preferred orientation

Fundamentals of the Rietveld Method

Single phase crystalline material:

$$y_{i,calc} = b_i + S \sum_{k=1}^{m} I_k y_{ik}$$

Mixture of several N_p phases:

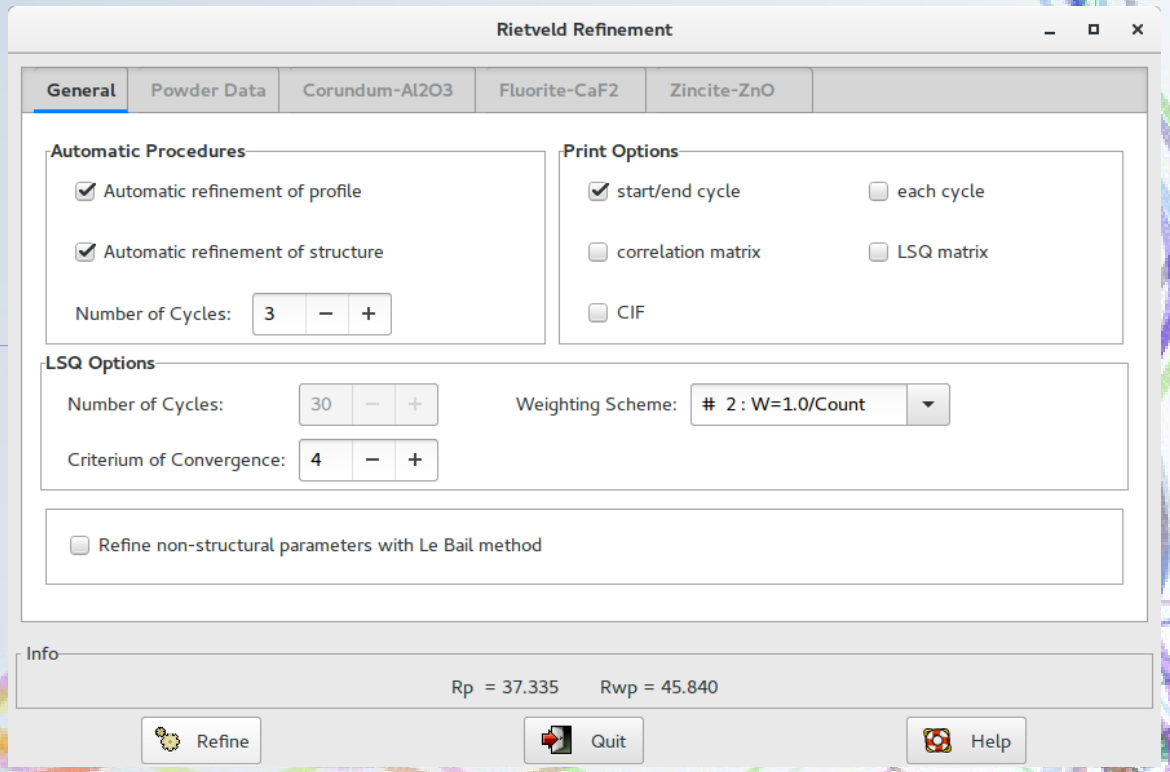
$$y_{i,calc} = b_i + \sum_{p=1}^{N_p} S_p \sum_{k=1}^{m} I_k^p y_{ik}^p$$

For mixture of several phases, the contribution from every crystalline phase is accounted in the expression of y_{ci}.

Quantitative analysis of a multiple phase crystalline material

Multiple phase powder diffraction patterns

```
%job Sample_ID_1e  (Corundum 55.12%, Fluorite 29.62%, Zincite
15.25%)

%structure Sample_ID_1e

%data
pattern cpd-1e.dat
wave 1.54056 1.54439 0.5

%crystal Corundum-Al2O3.cif

%crystal Fluorite-CaF2.cif

%crystal Zincite-ZnO.cif

%rietveld
```



J. Appl. Cryst. (2001). 34, 409-426

Fundamentals of the Rietveld Method

$$\chi^2 = \sum_{i=1}^{N} w_i [y_{i,obs} - y_{i,calc}]^2$$

$$y_{i,calc} = b_i + S \sum_{k=1}^{m} I_k y_{ik}$$

$$I_k = M_k L_k |F_k|^2 P_k$$

The Rietveld method is similar to the full pattern decomposition using:

- **Pawley algorithms**: the integrated intensities are treated as free least squares variables. We minimize χ^2 respect to $|F_k|$ (non linear least-squares) or $|F_k|^2$ (linear least-squares).

- **Le Bail algorithms**: the integrated intensities are determined iteratively after each refinement cycle

Mathematical procedure*

$$\chi^2 = \sum_{i=1}^{N} w_i [y_{i,obs} - y_{i,calc}]^2$$

$y_{i,calc}$ is a non linear function with respect to the unknown parameters, $x_1, x_2, ..., x_m$ and a system of equations can be assumed:

$$y_{1,calc} = M_1(x_1, x_2, ..., x_m)$$
$$y_{2,calc} = M_2(x_1, x_2, ..., x_m)$$
.....
$$y_{N,calc} = M_N(x_1, x_2, ..., x_m)$$

In the matrix form:

$$\chi^2 = [\mathbf{y} - \mathbf{M(x)}]^T \mathbf{W} [\mathbf{y} - \mathbf{M(x)}]$$

* Chapter 3 of the monograph The Rietveld method, R.A. Young, Ed., Oxford University Press, Oxford, New York (1993)

Linear Least Squares

$$\chi^2 = [\mathbf{y} - \mathbf{M}(\mathbf{x})]^T \mathbf{W} [\mathbf{y} - \mathbf{M}(\mathbf{x})]$$

$\mathbf{y}$ is the set of observable quantities $y_{1,obs}, y_{2,obs}, \ldots, y_{N,obs}$

$\mathbf{W}$ is a diagonal matrix whose diagonal elements are $w_1, w_2, \ldots, w_N$

If the model function is linear

$$\mathbf{M}(\mathbf{x}) = \mathbf{A}\mathbf{x} + \mathbf{b}$$

The set of parameters $\mathbf{x}$ that minimizes χ^2 is the solution of normal equations

$$\mathbf{J}^T \mathbf{W} \mathbf{J} \mathbf{x} = \mathbf{J}^T \mathbf{W} (\mathbf{y}\text{-}\mathbf{b})$$

$\mathbf{J}(\mathbf{x})$ is the **Jacobian matrix** $J(x)_{ij} = \frac{\partial M_i(x)}{\partial x_j}$ $\quad 1 < i < N$, $1 < j < m$

Example of linear least squares: background in a polynomial approximation, phase scale, are linear, $|F_k|^2$ in the Pawley full pattern decomposition

Nonlinear Least Squares

Expanding the model function $\mathbf{M}(\mathbf{x})$ around the starting point $\mathbf{x}_0$ in Taylor's series and retaining only the linear terms we obtain the equation:

$$\mathbf{M}(\mathbf{x}) \approx \mathbf{M}(\mathbf{x}_0) + \mathbf{J}(\mathbf{x}_0)(\mathbf{x} - \mathbf{x}_0)$$

Gauss Newton algorithm for each k iteration

(1) Compute the search direction $\mathbf{d}$ as the solution of the linear system

$$\mathbf{J}^T\mathbf{W}\mathbf{J}\mathbf{d} = \mathbf{J}^T\mathbf{W}[\mathbf{y} - \mathbf{M}(\mathbf{x})]$$

(2) Set $\mathbf{x}_k = \mathbf{x}_{k-1} + \mathbf{d}$

(3) If not converged go to **(1)**, else stop.

Gauss-Newton-Type Methods

- Gauss-Newton method with a **line search**

Set $\mathbf{x}_{k-1} = \mathbf{x}_k + \alpha\mathbf{d}$

where called step length, is such that the algorithm is in descendant condition:

$$\chi^2(\mathbf{x}_k + \alpha\mathbf{d}) < \chi^2(\mathbf{x}_k)$$

is chosen by a line-search procedure

- Levenberg–Marquardt algorithm modify the normal equations in

$$(\mathbf{J}^T\mathbf{W}\mathbf{J} + \lambda\mathbf{I})\mathbf{d} = \mathbf{J}^T\mathbf{W}[\mathbf{y} - \mathbf{M}(\mathbf{x})]$$

where I is the identity matrix, λ is a damping factor

Standard deviations

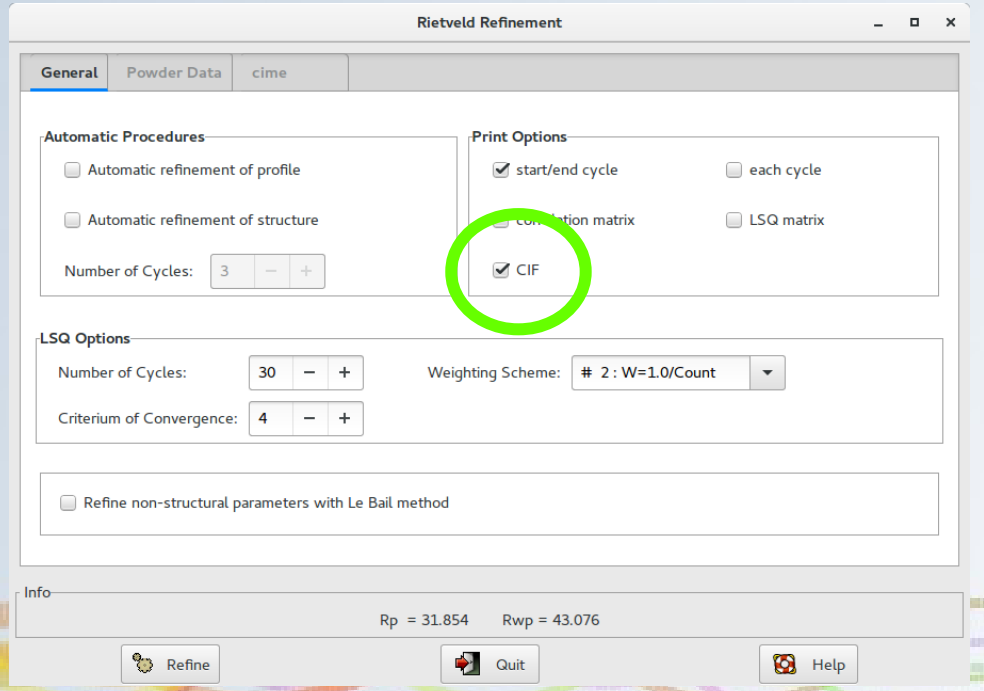
Variance-covariance matrix: $\mathbf{V}_x = (\mathbf{J}^T\mathbf{W}\mathbf{J})^{-1}$

$$\sigma(x_j) = \sqrt{\frac{(V_x)_{jj}\chi^2}{n-m}}$$

n is the number of observations

m is the number of unknown parameters

$(V_x)_{jj}$ is the corresponding diagonal element of the variance-covariance matrix



Classes of Rietveld Refinement Parameters

$$\chi^2 = \sum_{i=1}^{N} w_i (y_{i,obs} - [b_i + S \sum_{k=1}^{m} I_k y_k(x_k)])^2$$

- Background coefficients
- Sample displacement, sample transparency or zero-shift corrections
- Peak-shape function parameters
- Unit cell dimensions
- Preferred orientation
- Scale factors
- Positional parameters
- Atomic site occupancies
- Atomic displacement parameters

Background Functions

- Polynomial function

$$b_i = \sum_{j=1}^{m} B_j \left(\frac{2\theta_i}{2\theta_0} - 1\right)^{j-1}$$

where $2\theta_0$ is the the origin of the background polynomial and B_j are the parameters to be refined

- Chebyshev polynomial

$$b_i = \sum_{j=1}^{m} B_j T_{j-1}(x)$$

where

$$x = \frac{2(2\theta_i - 2\theta_{min})}{2\theta_{max} - 2\theta_{min}}$$

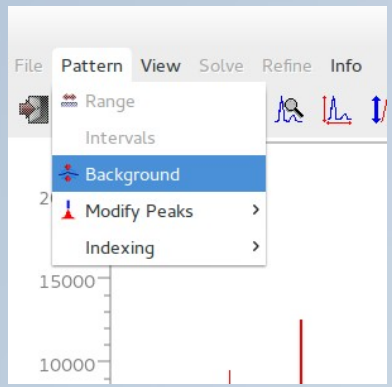
and $T_{j-1}(x)$ are the Chebyshev polynomials:

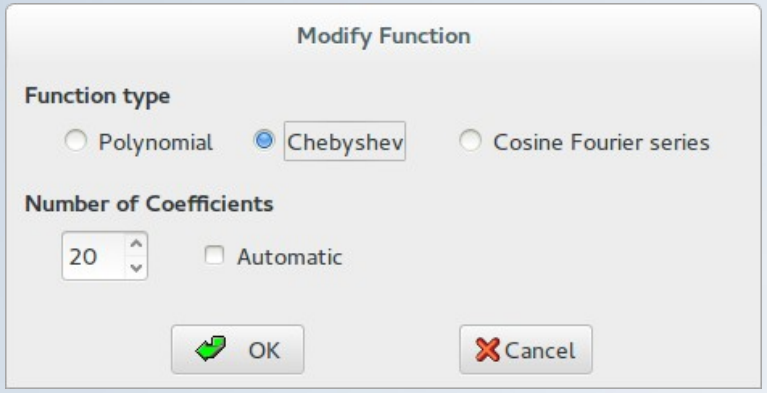
$$T_0(x) = 0$$
$$T_1(x) = x$$
$$T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$$

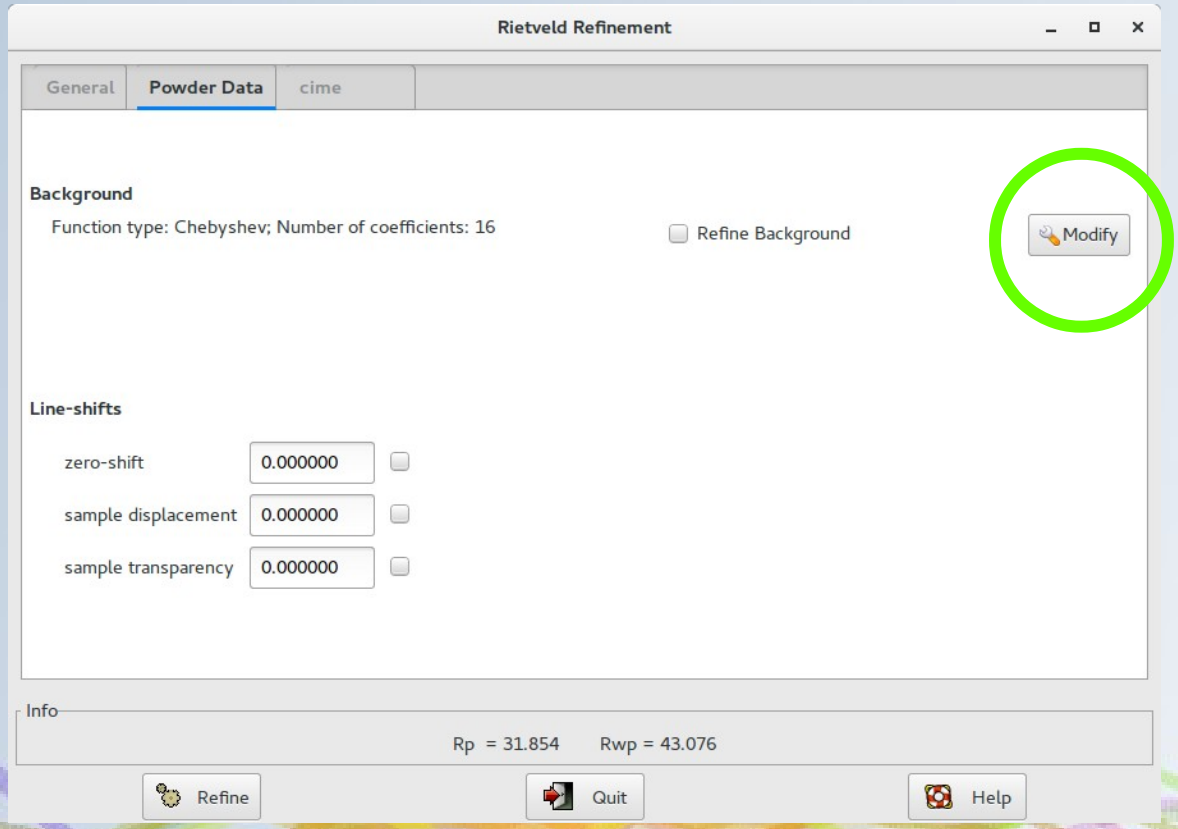
- Cosine Fourier series

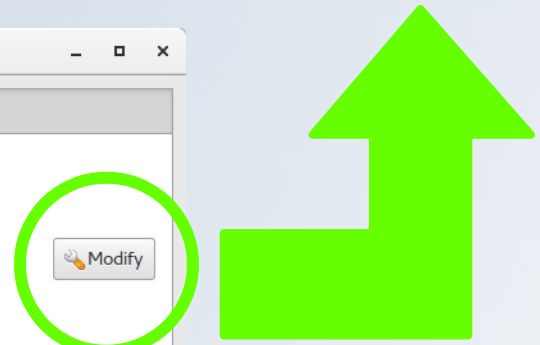
$$b_i = \sum_{j=1}^{m} B_j cos(2(j-1)2\theta_i)$$

Background function

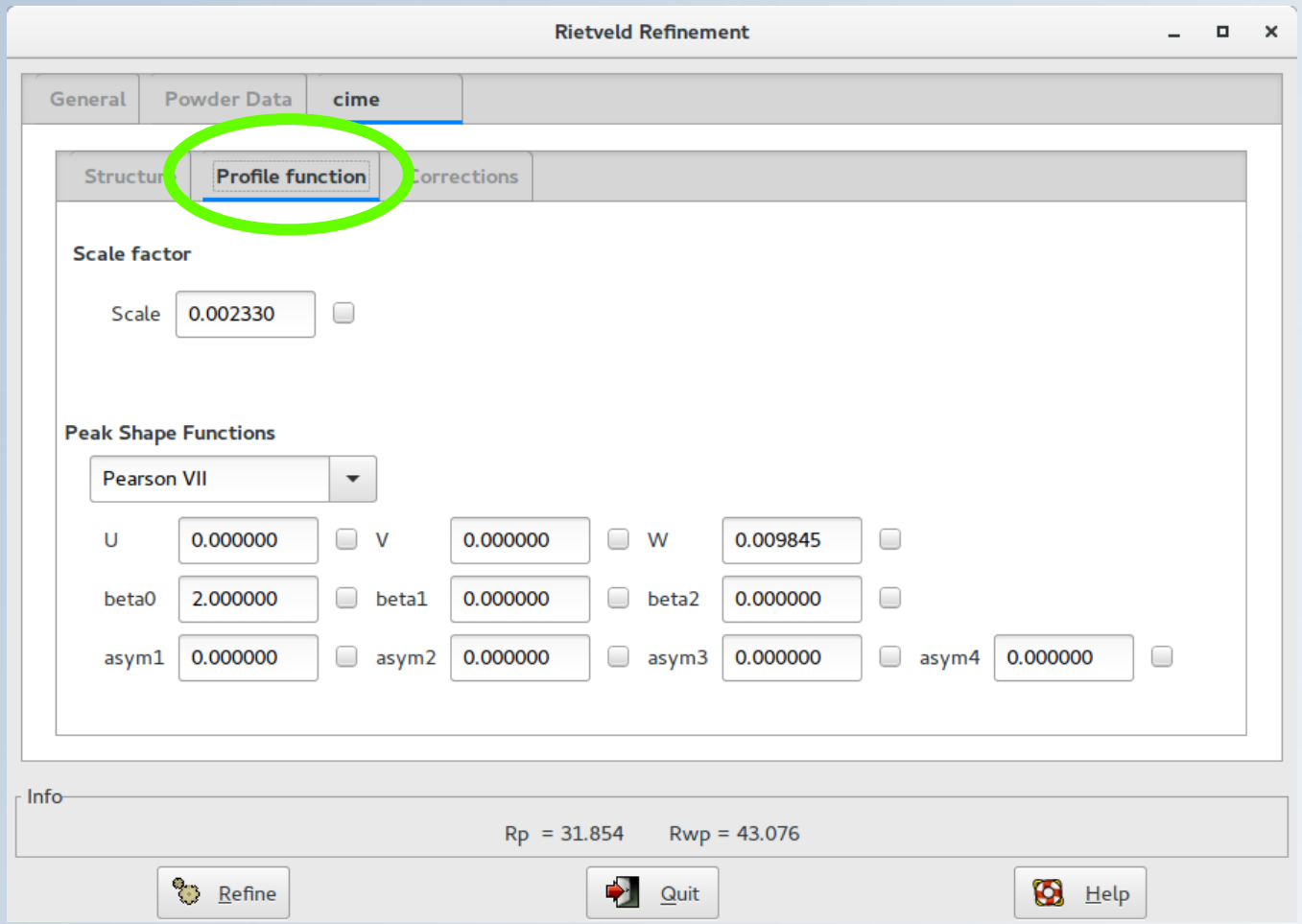








Peak shape functions



Pseudo-Voigt profile function

$$y(x) = \eta \frac{C_G^{1/2}}{\sqrt{\pi} H} \mathrm{e}^{(-C_G x^2)} + (1-\eta) \frac{C_L^{1/2}}{\pi H} (1 + C_L x^2)^{-1}$$

$$x = \frac{(2\theta_i - 2\theta_k)}{H_k}$$

$$C_G = 4ln2, C_L = 4, C_G^{1/2}/\sqrt{\pi} H \text{ with } \int_{-\infty}^{\infty} y(x)dx = 1$$

$$\eta = \eta_0 + \eta_1 2\theta + \eta_2 2\theta^2, \text{ where } 0 \leq \eta \leq 1$$

$$H = \sqrt{U tan^2\theta + V tan\theta + W}$$ **Caglioti formula**

$\eta_0, \eta_1, \eta_2, U, V$ and W are refined variables

Modified Thompson-Cox-Hastings pseudo-Voigt

$$y(x) = \eta \frac{C_G^{1/2}}{\sqrt{\pi} H} \mathrm{e}^{(-C_G x^2)} + (1-\eta) \frac{C_L^{1/2}}{\pi H} (1 + C_L x^2)^{-1}$$

$$H = \sum_{i=0}^{5} a_i H_G^{5-i} H_L^i$$

$$H_G = \sqrt{U tan^2\theta + V tan\theta + W + Z/cos^2\theta}$$

$$H_L = X/cos\theta + Y tan\theta$$

$$\eta = \sum_{i=1}^{3} b_i (\frac{H_L}{H})$$

U, V, W, Z, X and Y are refined variables

Pearson-VII profile function

$$y(x) = \frac{\Gamma(\beta)}{\Gamma(\beta - 1/2)} \frac{C_p^{1/2}}{\sqrt{\pi} H} (1 - C_p x^2)^{-\beta}$$

Default choice

$$\beta = \beta_0 + \beta_1/2\theta + \beta_2$$

$\beta = 1$ Cauchy function
$\beta = 2$ Lorentz function
$\beta = \infty$ Gauss function

The FWHM (H) is modeled by using the **Caglioti formula** as in the case of the pseudo-Voigt function

$\beta_0, \beta_1, \beta_2, U, V, W$ are refined variables

Peak Asymmetry

The correction for the peak asymmetry is applied by using as multiplier the semi-empirical function given in Bérar & Baldinozzi, (1993). J. Appl. Cryst. 26, 128-129

$$A_{ik} = 1 + P_1(\theta_k)F_a(z) + P_2(\theta_k)F_b(z)$$

$$P_1(\theta_k) = A_0/tan(\theta_k) + A_1/tan(2\theta_k)$$
$$P_2(\theta_k) = B_0/tan(\theta_k) + B_1/tan(2\theta_k)$$

$$F_a(z) = 2z\mathrm{e}^{-z^2} \quad F_b(z) = (8z^3 - 12z)\mathrm{e}^{-z^2} \quad z = \frac{\theta_i - \theta_k - S}{H_k}$$

$A_0, A_1, B_1,$ and B_2 are refined variables

Preferred orientation

The preferred orientation P_k is calculated using the March-Dollase function (Dollase, 1986):

$$P_k = \frac{1}{N}\sum_{i=1}^{N}(G^2 cos^2\phi_k^i + \frac{1}{G} sin^2\phi_k^i)^{-3/2}$$

where Φ_k is the angle between the reciprocal lattice vector $\mathbf{d_k}^*$ corresponding to a Bragg reflection k and the reciprocal lattice vector parallel to the preferred orientation axis.

G is the refined parameter

Line-shifts corrections

$$2\theta_{obs} = 2\theta_{calc} + \Delta 2\theta$$

$$\Delta 2\theta_s = -2s\frac{cos\theta}{R} = Scos\theta$$

Sample displacement error in Bragg-Brentano geometry

$$\Delta 2\theta_t = \frac{1}{2\mu R} sin2\theta = Tsin2\theta$$

Transparency correction in Bragg-Brentano geometry

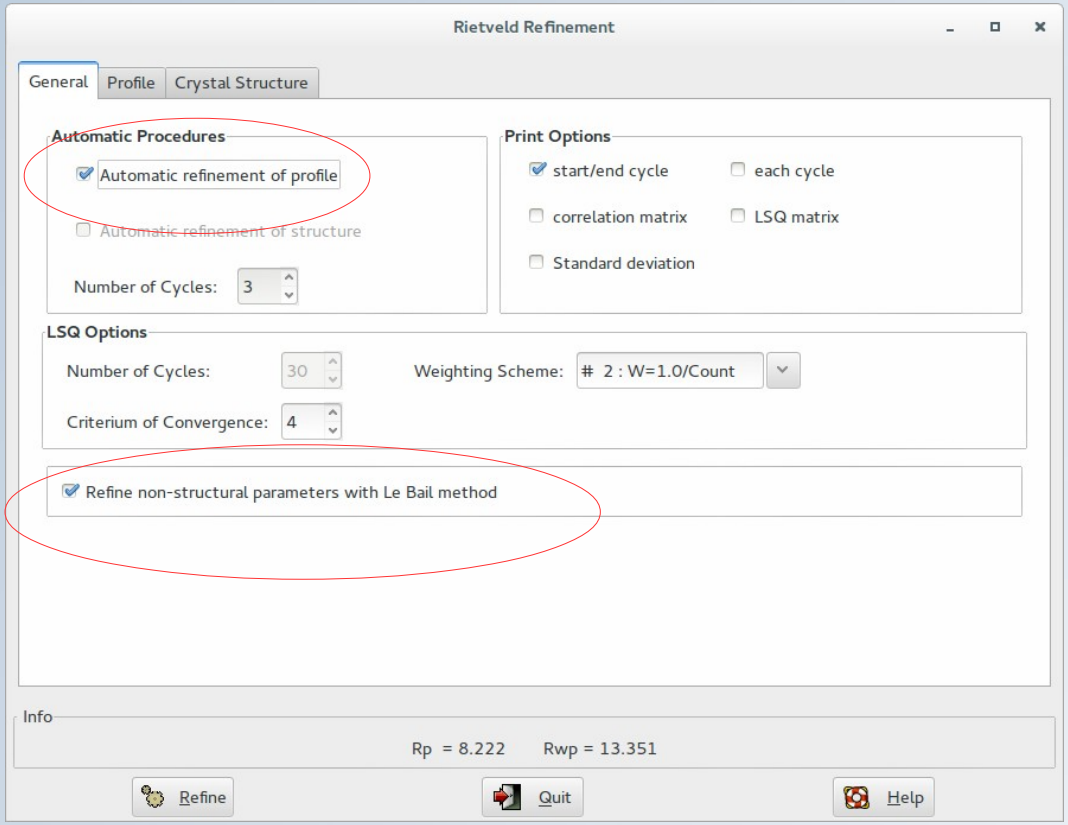
$$\Delta 2\theta = Scos\theta + Tsin2\theta + Z$$

The constant term *Z* is the zero-shift error

$S, T,$ and Z are refined variables

Profile parameters

The Le Bail technique can be adopted to perform a full pattern decomposition prior to Rietveld refinement



This strategy is suggested especially if the available structure model is not completed
(Rietveld refinement guidelines, L.B. McCusker, R.B. Von Dreele, D.E. Cox, D. Louer, P. Scardi, *J. Appl. Cryst.* **32** (1999) 36)

Refinement strategies

The refinement can be carried out by following two alternative approaches:

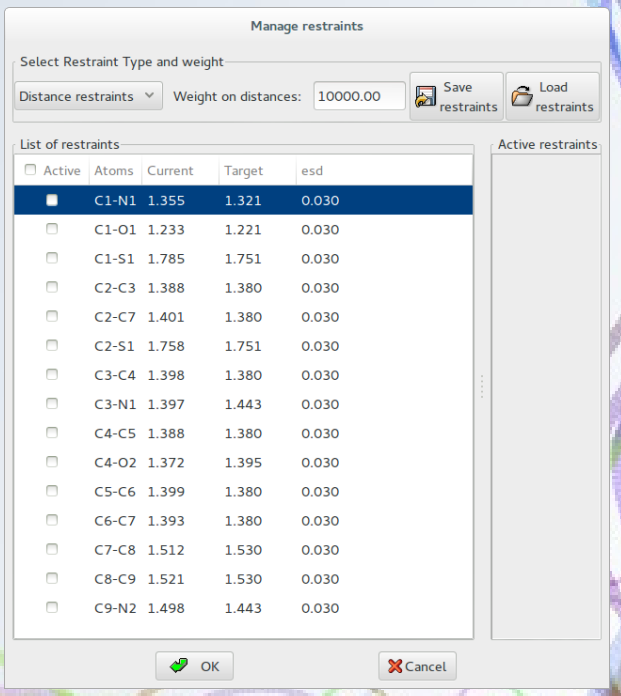
- The user can decide the refinement strategy via graphical interface
- An automatic refinement schedule can be applied
  - Scale
  - 2Θ correction
  - Background coefficients
  - *W*
  - *U, V*, other profile parameters
  - Coordinates of atoms
  - Isotropic displacements

Restraints

$$\Phi = \sum_{i=1} w_i \cdot (y_{i,obs} - y_{i,calc})^2 + w_{dist} \sum_{i=1} w_i \cdot (dist_i^{exp} - dist_i^{calc})^2 +$$

$$w_{ang} \sum_{i=1} w_i \cdot (a_i^{exp} - a_i^{calc})^2 + w_{plane} \sum_{i=1} w_i \cdot (p_i^{exp} - p_i^{calc})^2$$

Each type of restraints is included in the refinement as a set of observations, in addition to the main set



Constraints

Constraints are mathematical relationships between parameters

Symmetry constraints are mandatory and automatically imposed by the program

- *Special position*

  e.g., atom on special position $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ should non be refined,

  atom on special position (x, x, x) in space group P23 should have equal shift on x,y,z

- *Unit cell dimension*

  e.g., a=b=c and α=β=γ in cubic crystal system

Constraints

Constraints imposed by the user to reduce the number of parameters

- Riding model (move H atoms synchronously with the C atoms)
- Constraints on ADPs (ADPs are made to shift synchronously)
- Occupation factor

  e.g., A,B atoms in same site: occA + occB = 1

Statistical measures of a refinement

- Unweighted profile R-factor

$$R_p = \frac{\sum_i^N |y_{i,obs} - y_{i,calc}|}{\sum_i^N y_{i,obs}} \times 100$$

- Weighted profile R-factor

$$R_{wp} = \sqrt{\frac{\sum_i^N w_i \cdot (y_{i,obs} - y_{i,calc})^2}{\sum_i^N w_i \cdot (y_{i,obs})^2}} \times 100$$

Profile residual with the background subtracted

$$R'_p = \frac{\sum_i^N |y_{i,obs} - y_{i,calc}| \cdot \frac{|y_{i,obs} - b_i|}{y_{i,obs}}}{\sum_i^N y_{i,obs} - b_i} \times 100$$

$$R'_{wp} = \sqrt{\frac{\sum_i^N w_i \cdot \left((y_{i,obs} - y_{i,calc}) \frac{(y_{i,obs} - b_i)}{y_{i,obs}} \right)^2}{\sum_i^N w_i \cdot (y_{i,obs} - b_i)^2}} \times 100$$

Statistical measures of a refinement

- Expected R value

$$R_{exp} = \sqrt{\frac{N-p}{\sum_{i}^{N} w_i \cdot (y_{i,obs})^2}} \times 100$$

- Goodness-of-fit

$$\chi^2 = \frac{\sum_{i}^{N} w_i \cdot (y_{i,obs} - y_{i,calc})^2}{N-P} = \left[\frac{R_{wp}}{R_{exp}}\right]^2$$

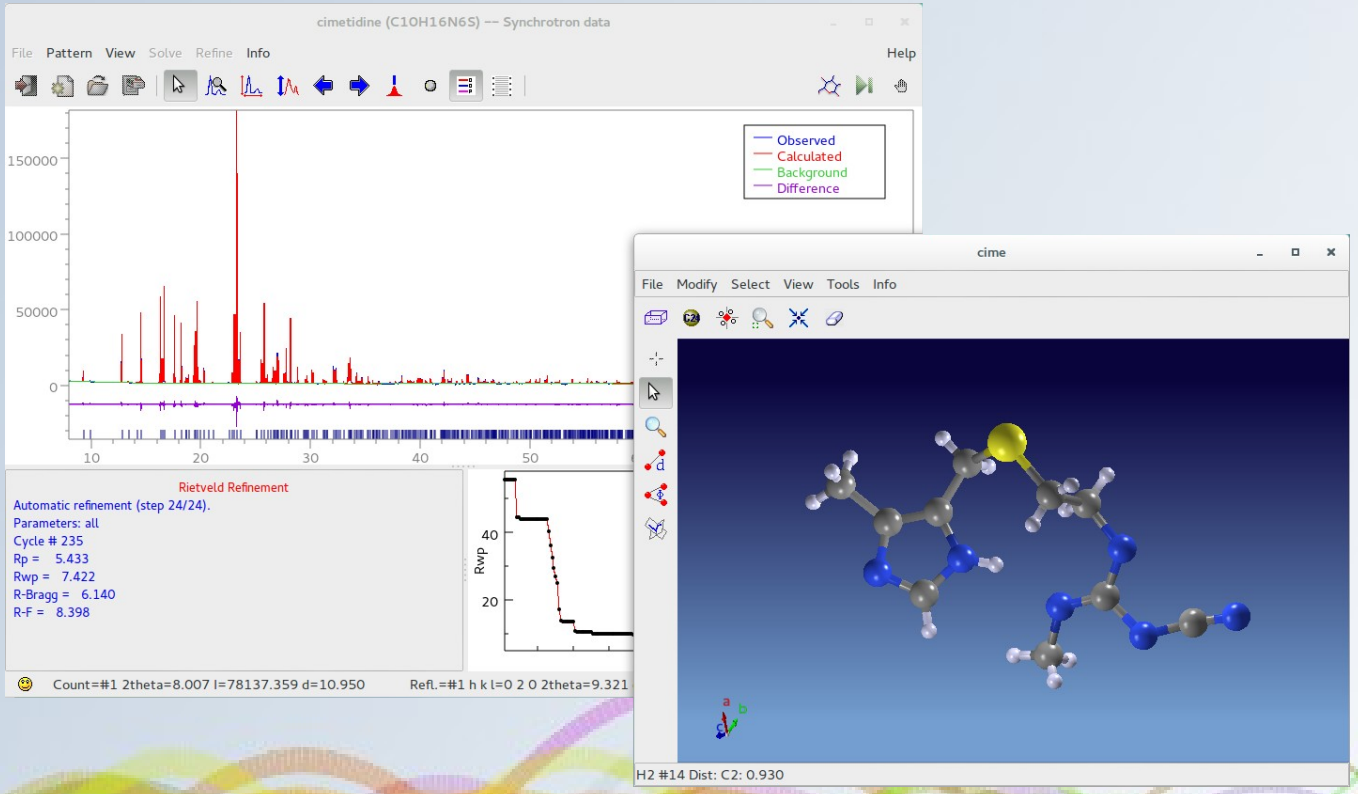
- Other residual on *F* or *F*²:

$$R_F = \frac{\sum_{j}^{m} |F_{j,obs} - F_{j,calc}|}{\sum_{j}^{m} F_{j,obs}} \times 100 \qquad R_B = \frac{\sum_{j}^{m} |I_{j,obs} - I_{j,calc}|}{\sum_{j}^{m} I_{j,obs}} \times 100$$

Quality of refinement

Important criteria for the quality of the refinement:

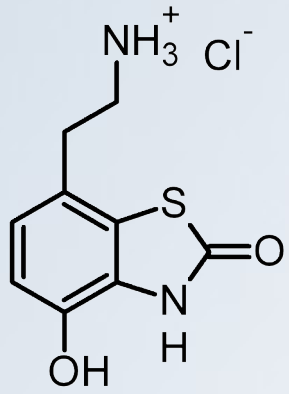
- the fit of the calculated pattern to the observed data and
- the chemical sense of the structural model



Structure refinement of $C_9H_{11}N_2O_2S{\cdot}Cl$

Input file for Rietveld refinement:

```
%Structure ammonium
%Job ethylammonium chloride (C9H11N2O2SCl)
%Data
   Pattern ammonium.xy
   Wavelength 1.54056
%crystal ammonium_riet.cif
%rietveld
```



2-(4-Hydroxy-2-oxo-2,3-dihydro-1,3-benzothiazol-7-yl) ethylammonium chloride

$C_9H_{11}N_2O_2S{\cdot}Cl$

From graphical interface:

- File > Import Diffraction Pattern
- File > Import Structure
- Refine > Rietveld

Contact, software download and info
http://www.ba.ic.cnr.it/softwareic/expo/

Acknowledgements

Colleagues of the research team
A. Altomare, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio