Supplementary Materials

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1 Extra constraint for the weighted least-squares (WLS) scaling method

In the WLS method described in the section 4.2 of the article, the scaling of different ratio data sets is performed by minimizing the error function ϵ^R_{min}. This function depends on the variable vector $\mathbf{x}$ consisting of the different Ratio model variables,

$$\epsilon^R_{\text{min}}(\mathbf{x}) = \sum\nolimits_{i\in\{\text{sets}\}}\left[\sum\nolimits_{\mathbf{H}\in\{\mathbf{H}\}^i}\left[\sum\nolimits_{j\in\{R_{\text{obs}}\}^i_{\mathbf{H}}} w^{(i,j)}_{\text{obs}}(\mathbf{H})\Big(R^{(i,j)}_{\text{obs}}(\mathbf{H}) - R^i_{\text{model}}(\mathbf{H})\Big)^2\right]\right] \tag{1}$$

where $\{\mathbf{H}\}^i_{\text{unique}}$ is the set of unique reflections of data set i, $\{R_{\text{obs}}\}^i_{\mathbf{H}}$ is the set of observed ratios of the unique reflection $\mathbf{H}$ in the data set i, $R^{(i,j)}_{\text{obs}}(\mathbf{H})$ the j^{th} observed ratio in the set $\{R_{\text{obs}}\}^i_{\mathbf{H}}$, and $w^{(i,j)}_{\text{obs}}(\mathbf{H})$ the corresponding weight (by default $w^{(i,j)}_{\text{obs}}(\mathbf{H}) = 1/s^2_{R^{(i,j)}_{\text{obs}}(\mathbf{H})}$ with $s^2_{R^{(i,j)}_{\text{obs}}(\mathbf{H})}$ the estimated variance of $R^{(i,j)}_{\text{obs}}(\mathbf{H})$).

The ratio model of the unique reflection $\mathbf{H}$ in data set i is defined as

$$\mathrm{R}^i_{\text{model}}(\mathbf{H}) \simeq K^i_{\text{ratio}}\big[1 + Q^i\eta_{\text{model}}(\mathbf{H})\big] \tag{2}$$

in which $\eta_{\text{model}}(\mathbf{H})$ is the calculated average η for the reflection $\mathbf{H}$, Q^i the relative population and K^i_{ratio} the global ratio scaling factor of set i.

The minimization of ϵ^R_{min} is done under the constraint $m_1 = 0$ defined in the section 4.2.2.

When the laser-ON and laser-OFF intensities are collected on the same sample with the same X-ray beam setting, all factors K_{ratio} equal 1.0. If they are not, after appropriate corrections done the sets of intensities with and without laser-exposure do not share the same global scale. Thus, for each ratio data set i, a global ratio scaling factor K^i_{ratio} must be refined and an extra constraint $m_2 = 0$ is necessary to properly scale the observations. This constraint consists in setting to 1.0 the intercept of the linear regression on the calculated average η variables η_{model} as function of the squared reciprocal space resolution $\omega^2 = \sin^2\theta/\lambda^2$. The application of this constraint helps to decorrelate the factors K_{ratio} and the relative populations Q. The expression of a linear regression intercept is well known which leads to the following expression for the constrain $m_2 = 0$ with

$$m_2(\mathbf{x}) = \frac{\sum_{X^2}\sum_Y - \sum_X\sum_{XY}}{N_{\mathbf{H}}\sum_{X^2} - \left(\sum_X\right)^2} \tag{3}$$

with $\sum_{XY}$, $\sum_Y$, $\sum_X$ and $\sum_{X^2}$ defined as

$$\sum_{XY} = \sum_{\mathbf{H}\in\{\mathbf{H}\}^{\text{all}}_{\text{unique}}} \eta_{\text{model}}(\mathbf{H})\omega^2(\mathbf{H}) \tag{4a}$$

$$\sum_{Y} = \sum_{\mathbf{H}\in\{\mathbf{H}\}^{\text{all}}_{\text{unique}}} \eta_{\text{model}}(\mathbf{H}) \tag{4b}$$

$$\sum_{X} = \sum_{\mathbf{H}\in\{\mathbf{H}\}^{\text{all}}_{\text{unique}}} \omega^2(\mathbf{H}) \tag{4c}$$

$$\sum_{X^2} = \sum_{\mathbf{H}\in\{\mathbf{H}\}^{\text{all}}_{\text{unique}}} \omega^4(\mathbf{H}) \tag{4d}$$

2 Estimation of standard deviations

The minimization of the error function Φ^R_{min} under a set of linear constraints $\{m_i\}$ can be treated using the Lagrangian method as the optimization of the following function ψ^R_{min}

$$\psi^R_{\text{min}}(\mathbf{x}, \mathbf{\Lambda}) = \Phi^R_{\text{min}}(\mathbf{x}) + \sum_{i\in\{\text{constraints}\}} \lambda_i m_i(\mathbf{x}) \tag{5}$$

in which $\mathbf{x}$ is the vector of the refined ratio model variables and $\mathbf{\Lambda}$ the vector of the lagrangian multipiers λ_i.

At the convergence of the ψ^R_{min} optimization at $\left(\tilde{\mathbf{x}}; \tilde{\Lambda}\right)$, the following relations are satisfied,

$$\frac{\partial\psi^R_{\text{min}}}{\partial\mathbf{x}}(\mathbf{x}, \mathbf{\Lambda}) = \frac{\partial\Phi^R_{\text{min}}}{\partial\mathbf{x}}(\mathbf{x}) + \sum_{i\in\{\text{constraints}\}} \lambda_i \frac{\partial m_i}{\partial\mathbf{x}}(\mathbf{x}) = 0 \tag{6a}$$

$$\text{For each constraint } i, \quad m_i(\mathbf{x}) = 0 \tag{6b}$$

In the vicinity of $\tilde{\mathbf{x}}$, the first-order Taylor expansions of these expressions with respect of $\Delta\mathbf{x} = \mathbf{x} - \tilde{\mathbf{x}}$ give

$$\frac{\partial^2\Phi^{\text{R}}_{\text{min}}}{\partial^2\mathbf{x}}(\tilde{\mathbf{x}})\Delta\mathbf{x} + \sum_{i\in\{\text{constraints}\}} \tilde{\lambda}_i \frac{\partial m_i}{\partial\mathbf{x}}(\tilde{\mathbf{x}}) = -\frac{\partial\Phi^{\text{R}}_{\text{min}}}{\partial\mathbf{x}}(\tilde{\mathbf{x}}) \tag{7a}$$

$$\text{For each constraint } i, \quad \frac{\partial m_i}{\partial\mathbf{x}}(\tilde{\mathbf{x}})\Delta\mathbf{x} = 0 \tag{7b}$$

These conditions can be rewritten as a matrix expression

$$\underbrace{\begin{pmatrix} \mathbf{H} & \mathbf{M} \\ \mathbf{M^T} & \mathbf{0} \end{pmatrix}}_{\mathbf{H}_\mathrm{B}} \underbrace{\begin{pmatrix} \Delta\mathbf{x} \\ \boldsymbol{\Lambda} \end{pmatrix}}_{\mathbf{X}} = \underbrace{\begin{pmatrix} \mathbf{B} \\ \mathbf{0} \end{pmatrix}}_{\mathbf{C}} \tag{8}$$

with the matrices $\mathbf{H}$ (Hessian matrix of the function Φ^R_{min} at $\mathbf{x}$), $\mathbf{B}$ and $\mathbf{M}$ defined as

$$\mathbf{H} = \left[\frac{\partial^2 \Phi^R_{\mathrm{min}}}{\partial^2 \mathbf{x}} (\tilde{\mathbf{x}}) \right] \tag{9a}$$

$$\mathbf{M} = \left[\frac{\partial m_i}{\partial \mathbf{x}} (\tilde{\mathbf{x}}) \right] \tag{9b}$$

$$\mathbf{B} = \left[-\frac{\partial \Phi^R_{\mathrm{min}}}{\partial \mathbf{x}} (\tilde{\mathbf{x}}) \right] \tag{9c}$$

The estimation of variance-covariance matrix of the variable vector $\mathbf{x}$ at $\tilde{\mathbf{x}}$ consists of inversing $\mathbf{H}_\mathrm{B}$ named the bordered Hessian matrix, selecting the subpart of this inverse matrix corresponding to the variable vector $\mathbf{x}$ and multiplying this submatrix by the squared goodness of fit.

The estimated uncertainties of the variable vector $\mathbf{x}$ elements corresponds to the square root of the diagonal elements in the estimated variance-covariance matrix.