Postrefinement: The model `rs`.

This is intended to be the simplest possible model for the reciprocal lattice point (RLP), describing the RLP as a sphere of radius r_s, which is globally constant over the whole dataset consisting of an ensemble of crystal lattices (or frames).

1 The size of the RLP model

The constant value of r_s is computed as follows. From model refinement and integration, each crystal has associated with it a list of Miller indices $\mathbf{h_i}$ and a reciprocal space orientation matrix $\mathbf{A}$ defined by Rossmann *et al.* (1979),

$$\mathbf{A} = \begin{pmatrix} a_x^* & b_x^* & c_x^* \\ a_y^* & b_y^* & c_y^* \\ a_z^* & b_z^* & c_z^* \end{pmatrix}. \tag{1}$$

The reciprocal space coordinates of RLP i are computed with

$$\mathbf{q} = \mathbf{A}\mathbf{h}, \tag{2}$$

leading to a reciprocal position Q, with a small distance offset r_h away from the Ewald sphere that represents the perfect diffracting condition. The fact that $|r_h|$ is non-zreo is indicative that Bragg observations from still shots represent partial reflections. Note that array index i denoting a specific Miller index is dropped on occasion for clarity. The geometry is explained in Fig. 1.

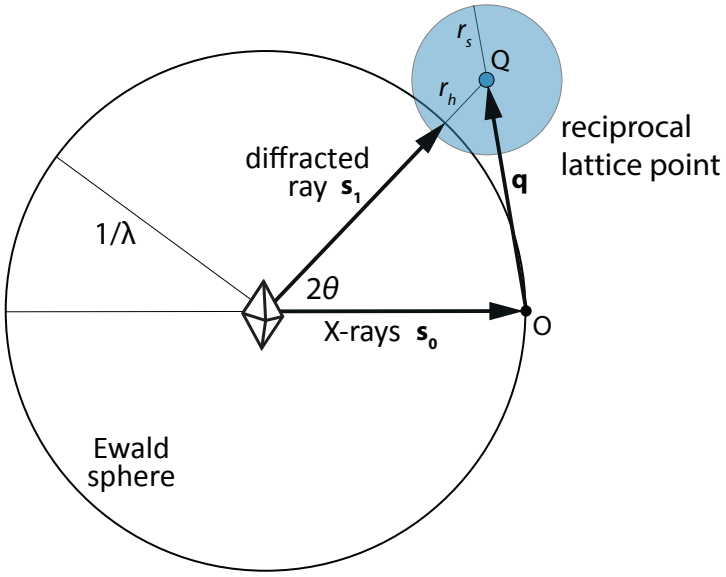

Fig. 1. Ewald sphere construction.

The quantity $|r_h|$ is given by

$$r_h = ||\mathbf{q} + \mathbf{s_0}|| - ||\mathbf{s_1}|| = ||\mathbf{q} + \mathbf{s_0}|| - \frac{1}{\lambda}, \tag{3}$$

where s_0 and s_1 are respectively the beam vector and the diffracted ray vector, each of length $1/\lambda$. For the model `rs`, the constant value of r_s is taken as the root mean-squared value of r_h over all Bragg spots

integrated from a given crystal. It therefore depends on whatever algorithm has been used to predict spots, regardless of whether there is measurable signal in the spots.

2 The geometry of the RLP model

The intention is to create a model of the RLP similar to a hard sphere, so that if any portion of the sphere touches the Ewald sphere there is signal expected, otherwise none. However, this is a discontinuous model (in terms of the spot partiality expressed as a function of r_h and therefore not easily amenable to parameter fitting. Therefore we relax the requirement for a hard sphere and adopt a radial profile somewhat smoother. For the Uervirojnangkoorn (2015) paper we used a profile based on a Lorentzian function. The derivation is as follows.

A suggestion from James Holton defines the Bragg spot partiality as

$$p = \frac{\text{Area of intersection between the Ewald sphere and } F_{hkl}}{\text{Area of intersection between the Ewald sphere and } F_{000}}. \tag{4}$$

The "areas of intersection" in question are really spherical caps that represent the Ewald sphere's intersection with the reciprocal space ball of radius r_s. However, we're not going to insist on such detail; instead we will simply take a circular area of radius r_p such that we have the right triangle

$$r_p^2 = r_s^2 - r_h^2, \tag{5}$$

and then the approximate expression for partiality becomes (model A),

$$p_A = \frac{\pi r_p^2}{\pi r_s^2} = 1 - \frac{r_h^2}{r_s^2} \text{ for } |r_h| < r_s, 0 \text{ otherwise.} \tag{6}$$

Partiality as a function of r_h is a simple inverted parabola with $p_A = 1$ at $r_h = 0$ and roots at $\pm r_s$ (Fig. 2). Outside of this domain the partiality is 0.

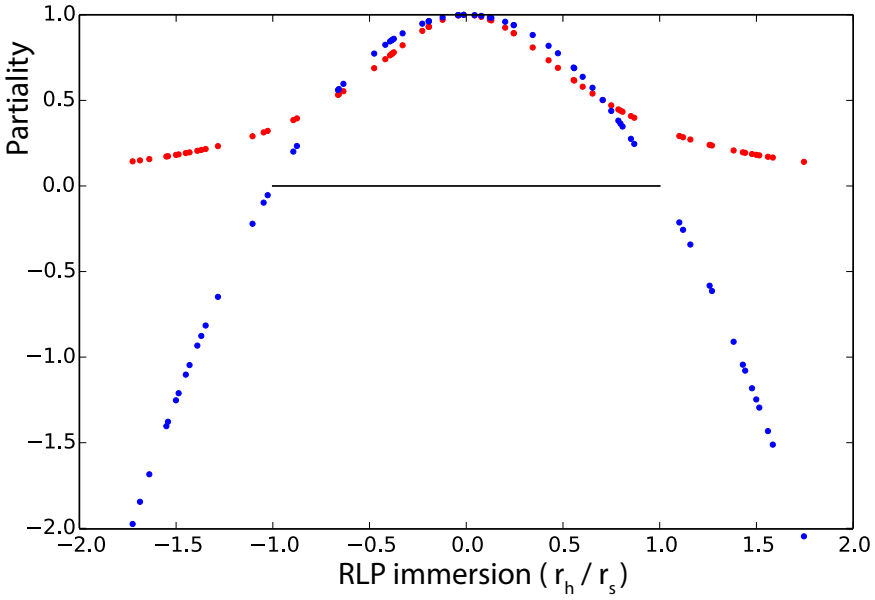

Fig. 2. Two partiality models: a simple hard-sphere model (p_A, blue), and a soft-sphere Lorentzian function (p_B, red).

However, having a mathematically discontinuous expression (p_A) will leave us at a disadvantage for postrefinement. The postrefinement strategy will be to express the lack of closure r_h in terms of model parameters such as the unit cell dimensions and crystal orientation. Then optimize a target function f expressed in terms of the partiality p, attempting to find parameter values to minimize f. It is crucial in this procedure to have an expression for partiality that is smooth and differentiable.

We will therefore have to modify our simple model of the Bragg spot as a reciprocal space ball. One functional form that might have the desired properties is the Lorentzian function

$$L = \frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{x^2 + (\frac{1}{2}\Gamma)^2}, \tag{7}$$

where Γ is the full-width at half maximum (FWHM).

Let's tinker with this expression so it conforms to expectation...first multiply by a scaling constant to get $L'(0) = 1$:

$$L' = \frac{\pi\Gamma}{2} L, \tag{8}$$

and finally setting the FWHM to the FWHM value obtained from eqn (6),

$$\Gamma = \frac{2r_s}{\sqrt{2}}, \tag{9}$$

so we get a new partiality expression (model B):

$$p_B = \frac{r_s^2}{2r_h^2 + r_s^2}. \tag{10}$$

Finally, for postrefinement we'll need the partial derivative of p_B with respect to r_h (use the quotient rule):

$$\frac{\partial p_B}{\partial r_h} = \frac{-4r_s^2 r_h}{(2r_h^2 + r_s^2)^2}. \tag{11}$$

3 Model parameters and target function

The goal of this work is to refine the parameters of the partiality model so that the observed intensities, corrected to their full spot equivalents, offer the best agreement over repeated measurements of the same asymmetric-unit Miller index. In practice, the parameters representing each crystal lattice are refined against a set of reference intensities I_{ref}. Program *prime* uses simple scaling to create an initial reference, after which repeated cycles of postrefinement are performed, with the reference being created from the corrected, merged intensities from the previous cycle. In *cxi.merge* the reference is an isomorphous atomic structure, from which intensities I_{ref} are calculated, and only one cycle is performed. The polarization-corrected measurements are denoted I_{obs}. The parameters refined for each crystal lattice are:

G: the scale factor.

B: the Wilson B-factor.

θ_x: incremental crystal rotation angle on x-axis ($\perp$ to beam).

θ_y: incremental crystal rotation angle on y-axis ($\perp$ to beam).

The least-squares target function used to achieve best agreement between model and observation is

$$\mathcal{F} = \sum_i (G \exp(\frac{-8B\sin^2\theta}{\lambda^2}) p_B I_{\mathrm{ref}} - I_{\mathrm{obs}})^2 \tag{12}$$

where θ is the Bragg diffraction angle defined in Fig. 1, and λ the wavelength, both treated as constants, and the sum is over all measurements integrated from a single crystal lattice.

4 Necessary derivatives for parameter refinement

Given the least-squares form, derivatives of the target functional with respect to parameter $\mathcal{P}$ are in general

$$\frac{\partial \mathcal{F}}{\partial \mathcal{P}} = 2 \sum_i \mathcal{R}_i \frac{\partial \mathcal{R}_i}{\partial \mathcal{P}}, \tag{13}$$

where the residual comparison on each observation is

$$\mathcal{R}_i = G \exp(\frac{-8B \sin^2 \theta}{\lambda^2}) p_B I_{\mathrm{ref}} - I_{\mathrm{obs}}. \tag{14}$$

The derivatives in the Jacobian matrix, required for parameter optimization, are more-or-less straightforward:

$$\frac{\partial \mathcal{R}_i}{\partial G} = \exp(\frac{-8B \sin^2 \theta}{\lambda^2}) p_B I_{\mathrm{ref}}, \tag{15}$$

$$\frac{\partial \mathcal{R}_i}{\partial B} = G \exp(\frac{-8B \sin^2 \theta}{\lambda^2}) p_B I_{\mathrm{ref}} \left(\frac{-8 \sin^2 \theta}{\lambda^2} \right). \tag{16}$$

The derivatives with respect to θ_x and θ_y require more work. All of the dependence on crystal orientation comes through the expression for partiality:

$$\frac{\partial \mathcal{R}_i}{\partial \theta_{x|y}} = \frac{\partial \mathcal{R}_i}{\partial p_B} \frac{\partial p_B}{\partial \theta_{x|y}}, \tag{17}$$

with

$$\frac{\partial \mathcal{R}_i}{\partial p_B} = G \exp(\frac{-8B \sin^2 \theta}{\lambda^2}) I_{\mathrm{ref}}. \tag{18}$$

As for the variation of the partiality model p_B defined in (10), the `rs` model assumes that the sphere radius r_s is fixed, thus the only remaining variable is the distance r_h between RLP and Ewald sphere:

$$\frac{\partial p_B}{\partial \theta_{x|y}} = \frac{\partial p_B}{\partial r_h} \frac{\partial r_h}{\partial \theta_{x|y}}. \tag{19}$$

An expression for $\frac{\partial p_B}{\partial r_h}$ has already been given in (11), so it now remains to investigate the derivative $\frac{\partial r_h}{\partial \theta_{x|y}}$, based on the definition of r_h given in (3).

Introduce the vector $\mathbf{S}$:

$$\mathbf{S} = \mathbf{q} + \mathbf{s_0}, \tag{20}$$

$$r_h = ||\mathbf{S}|| - \frac{1}{\lambda}, \tag{21}$$

$$\frac{\partial r_h}{\partial \theta_{x|y}} = \frac{\mathbf{S} \cdot \frac{\partial \mathbf{S}}{\partial \theta_{x|y}}}{||\mathbf{S}||}, \tag{22}$$

$$\frac{\partial \mathbf{S}}{\partial \theta_{x|y}} = \frac{\partial \mathbf{q}}{\partial \theta_{x|y}}. \tag{23}$$

Finally we investigate the derivative of the RLP position $\mathbf{q}$ with respect to the crystal rotations. The effective orientation matrix $\mathbf{A}$ may be expressed as the reference orientation matrix $\mathbf{A}_{\mathrm{ref}}$ determined during crystal refinement and integration, composed with additional rotational operators $\mathbb{R}_x$ and $\mathbb{R}_y$ determined by the postrefined angles θ_x and θ_y:

$$\mathbf{A} = \mathbb{R}_y(\mathbb{R}_x(\mathbf{A}_{\mathrm{ref}})). \tag{24}$$

The derivatives of $\mathbf{q}$ work out as follows:

$$\frac{\partial \mathbf{q}}{\partial \theta_x} = \mathbb{R}_y \frac{\partial \mathbb{R}_x}{\partial \theta_x} \mathbf{A}_{\mathrm{ref}} \mathbf{h}, \tag{25}$$

$$\frac{\partial \mathbf{q}}{\partial \theta_y} = \frac{\partial \mathbb{R}_y}{\partial \theta_y} \mathbb{R}_x \mathbf{A}_{\mathrm{ref}} \mathbf{h}. \tag{26}$$

The derivatives of the rotation operator are already encoded in the cctbx library (`scitbx/matrix/__init__.py`). Formulae for the rotation operator and its derivative with respect to angle θ are given in the LaTeX documentation included in that directory.