Testing of spherical harmonics absorption correction.

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November 20, 2017

1 Simulation dataset

A test dataset was generated under the following assumptions; the crystal remains fully in the uniform parallel beam, the crystal dimensions are small relative to the crystal-detector distance - i.e. parallel diffracted beam onto small detector spot. To model diffraction from a cuboid crystal, the dimensions were defined and the crystal volume was sampled at 10 points along each dimension i.e. 1000 points define the body of the crystal. The planes defining the surfaces of the crystal are also generated.

To model an experiment, the reciprocal lattice points were generated, the crystal was rotated through 360° in 2° steps and the reciprocal lattice points meeting the elastic diffraction condition were determined (within a suitable tolerance). A square detector was defined at a distance of 10 along the beam axis (x), which extended by ± y_det, z_det in the y, z directions. Two cases are typically considered, a small detector (y_det, z_det = 4) and a large detector (y_det, z_det = 20), to investigate the impact of having high angle data (for all other factors being equal). Diffraction vectors that coincided with the detector were selected to form the dataset. To calculate the intensity of each reflection, the path-distance d through the crystal for the given k_0, k_1 was calculated for each point in the crystal, and the sum of exp(-μ d) was calculated over the whole crystal to give the intensity of the reflection. The variance was set equal to the intensity.

2 Absorption correction for a cuboid-shaped crystal

2.0.1 Large detector ($2\theta \leq 63.4°$)

First a cuboid shaped crystal of dimensions $1.5 \times 1.0 \times 1.0$ was investigated (beam along x, rotation axis z). The absorption surface terms were not tied to one, and an absorption coefficient $\mu = 0.2$ was used, such that the sample was 26% and 18% absorbing along the x/y directions - this should be higher than any samples measured experimentally as multiple scattering will become a problem before this level of absorption, but gives a good upper limit to test the effectiveness of an absorption correction for a 'regular' shaped sample. I guess this corresponds to an in-plane anisotropy of around 10%. Following aimless, we are

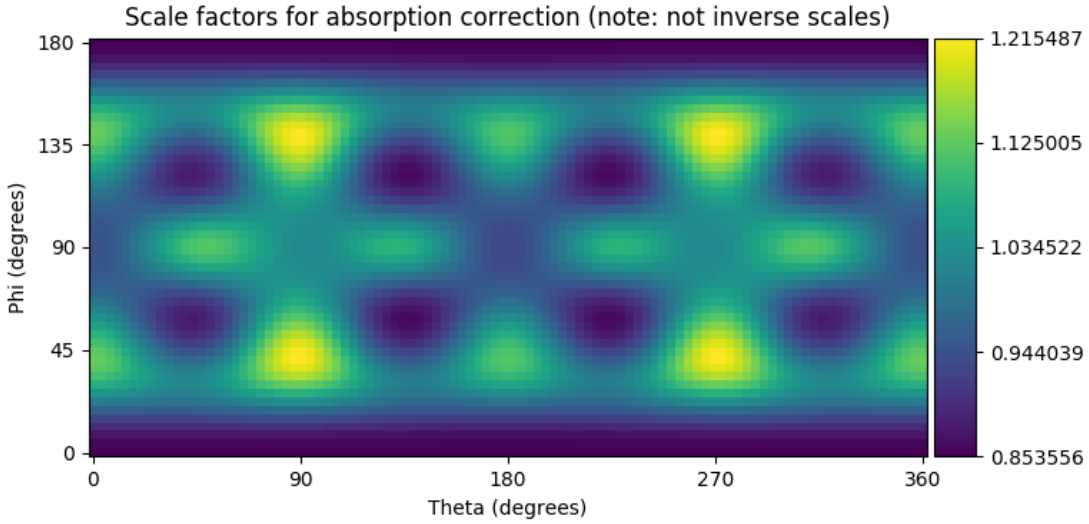

Figure 1: absorption correction for P4, rectangular cuboid, with 6 orders of spherical harmonics.

working in the diffractometer frame, where the vector defining the absorption surface is the scattering vector $\mathbf{s_{2d}} = -\mathbf{\Phi}(\mathbf{k_1} - \mathbf{k_0})$.

The space group of P4 was chosen (with the c axis along z), as this gives good 'connectivity' between different directions in reciprocal space without any systematic absences. Figure 1 show a pure absorption correction, with no tying to 1, using $l\_\mathrm{max} = 6$. The brighter colours are where absorption is greatest: this can be seen at the sides of the cuboid at around 60° in the equatorial plane and 45° out of the equatorial plane at 90° intervals. This gives an $R_{\mathrm{p.i.m.}}$ of 0.298% and an R_{meas} of 1.38%, with the absorption scaling varying between 0.853 and 1.215.

Interestingly, if the scale factor term is included in the scaling, the scale term takes on the majority of the scale variation as a function of rotation, with the absorption correction being a small correction on-top of this term: see Figures 2 and 3. The additional correction appears to correct the in-plane edges in this case, and does not show the underlying crystal-

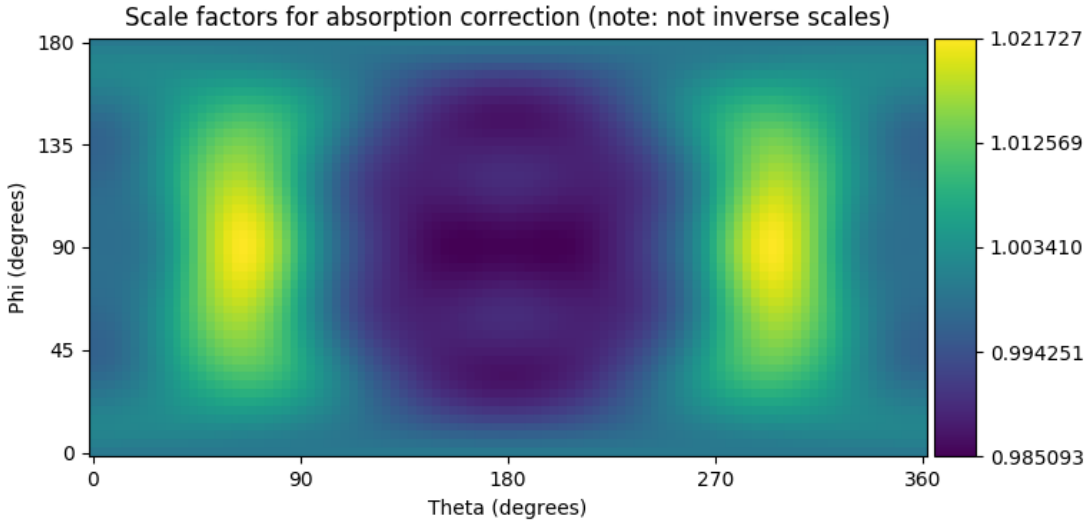

Figure 2: absorption correction for P4, rectangular cuboid with scale factor

shape symmetry. This resulted in the absorption term varying only from 1.022 to 0.985. There was also a significant improvement to the R-factors (on a relative scale), with an $R_{\text{p.i.m.}}$ of 0.164% and an R_{meas} of 0.50%. The smooth inverse scale factor varied from around 0.99 to 1.08 - i.e. it shows the $\sim 10\%$ in-plane anisotropy expected.

The effect of setting $l\_\text{max} = 4$ gave a different absorption pattern to $l\_\text{max} = 6$ (less nodes), giving a higher range of values for the absorption correction, however once the scale term is included, things end up only slightly worse ($R_{\text{p.i.m.}}$ of 0.172% and R_{meas} of 0.54%), with similar patterns for the absorption correction and smooth scales. Similarly, setting $l\_\text{max} = 8$ gets a little better again but is significantly slower. So at least for this simple shape, $l\_\text{max} = 4$ is probably sufficient if both the scale and absorption term are determined simultaneously.

The effect of rotation of the reciprocal lattice by 20° relative the the crystal shape didn't have any significant effect on the scaling (except a global 20° rotation of the absorption surface). Changing to a higher symmetry P4mm space group also did not have a significant

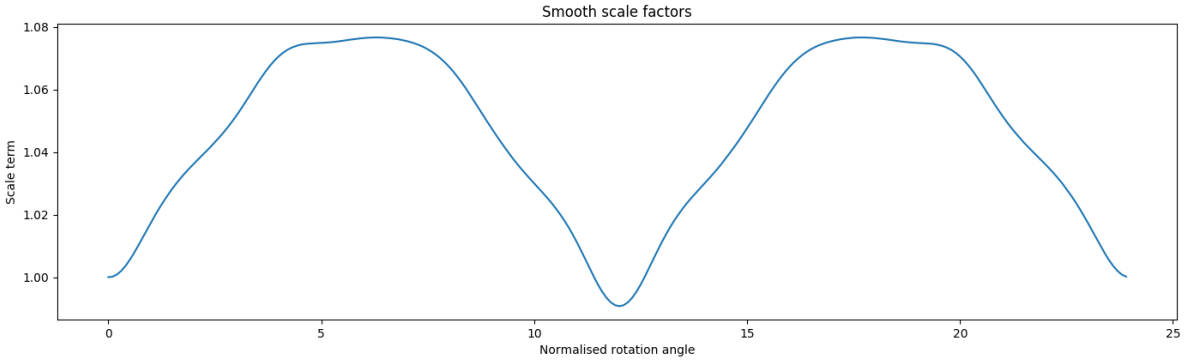

Figure 3: Smooth scale factors for P4, rectangular cuboid with scale factor

effect.

All these tests were done without tying the absorption surface to one. Including a tie weight of 1000 caused an increase in the R values from $R_{\text{p.i.m.}}$, R_{meas} = 0.164%, 0.54% to 0.204%, 0.58%, with a range of absorption factors from 0.994 to 1.006 (was 0.985 to 1.022). Including a tie weight of 100 gave $R_{\text{p.i.m.}}$, R_{meas} = 0.173%, 0.52% and a range of absorption factors 0.988 to 1.017. Therefore it seems that some weighting to restrict the absorption scales is fine, but that too much weight could start to affect the quality of scaling - the precise tie weight that is good to use will unfortunately be dataset dependent. Also, with no tie and scale term, the polar regions acquired low values, so a weak tie is useful to restrain the polar regions.

2.0.2 Small detector ($2\theta \leq 21.8°$)

The case of a small detector was also considered - this is equivalent to only selecting lower reflection angles (i.e. excluding weak higher angle reflections). Overall, a similar pattern is obtained, however by not tying the scale factors to one, the polar regions acquire large scale corrections if only an absorption correction is applied. This effect is still evident but significantly reduced when a scale term is included or if the scales are tied to one (but not completely removed?). With both scale and absorption factors refined simultaneously,

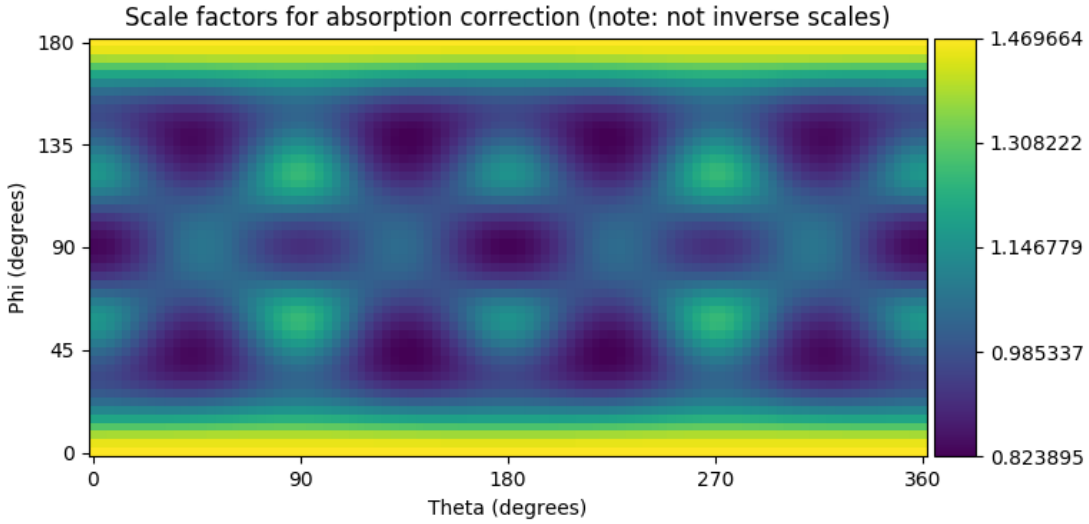

Figure 4: absorption correction for P4, rectangular cuboid, with 6 orders of spherical harmonics, for a 'small' detector/low angle reflections.

with a tie weight of 100 gave $R_{\text{p.i.m.}}$, $R_{\text{meas}} = 0.157\%$, 0.465%, with a range of absorption factors from 0.990 to 1.013.

2.1 Summary

In summary, the spherical harmonics absorption correction seems largely sufficient to correct for anisotropy of a regular shape, when using 4 or 6 orders of spherical harmonics and a low absorption tie weight. Significant improvements are obtained by including the smooth scale factor term in the minimisation. So nothing that we didn't really know already, but good to confirm that we seems to be getting sensible results with our version of the aimless code.

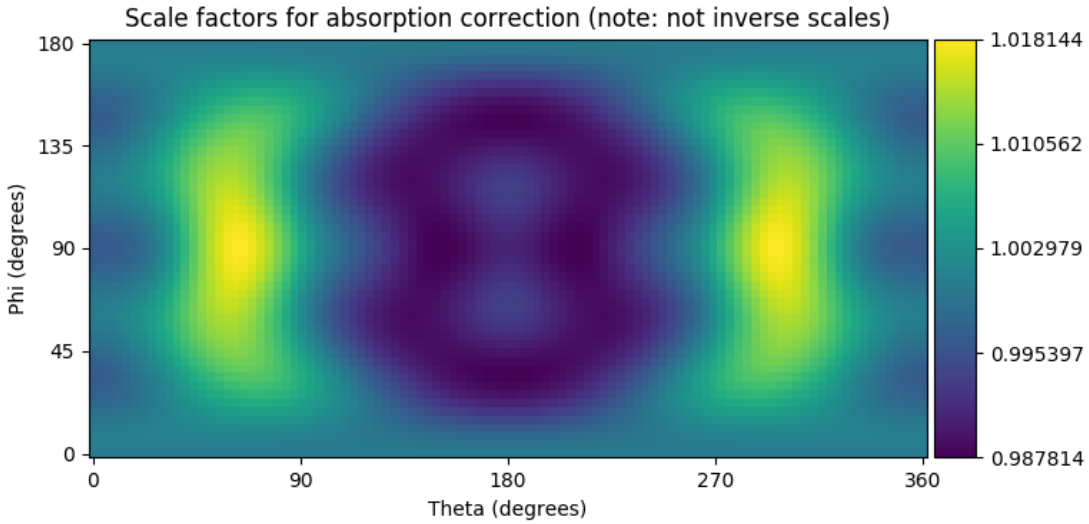

Figure 5: absorption correction for P4, rectangular cuboid with scale factor, for a 'small' detector/low angle reflections