

11. DATA PROCESSING

$$\mathbf{Y} = [\mathbf{R}_{2\theta}]^{-1} \lambda (\mathbf{S} - \mathbf{S}_0), \quad (11.4.6.3)$$

$$\mathbf{H} = [\mathbf{R}_z]^{-1} [\mathbf{R}_y]^{-1} [\mathbf{R}_x]^{-1} \mathbf{G}, \quad (11.4.6.4)$$

$$\mathbf{X} = [\mathbf{R}_{2\theta}] \frac{\mathbf{H} \cdot \mathbf{H}}{\mathbf{Y} \cdot \mathbf{H}} \mathbf{Y}. \quad (11.4.6.5)$$

Then, by inverting equation (11.4.2.8), the position in pixels, $\{p, q\}$, of the reflection can be calculated:

$$\{p, q\} = [\mathbf{D}]^{-1} [\mathbf{K}]^{-1} ([\mathbf{L}]^{-1} ([\mathbf{R}_{2\theta}]^{-1} ([\mathbf{R}_z]^{-1} [\mathbf{R}_y]^{-1} [\mathbf{R}_x]^{-1} (\mathbf{X} - T_D) + T_D) - T_D) + B). \quad (11.4.6.6)$$

11.4.6.1. Refinement of crystal and detector parameters

The precision of the integration step depends on precise knowledge of the peak position. The autoindexing step provides only the approximate orientation of the crystal, and the result of that step is imprecise if the initial values of the detector parameters are poorly known. A nonlinear least-squares refinement process is used to improve the prediction (*EEC Cooperative Workshop on Position-Sensitive Detector Software*, 1986). Depending on the particulars of the experiment, the same parameters (*e.g.* crystal-to-detector distance) are more precisely known *a priori*, or are better estimated from the diffraction data. *DENZO* allows for the choice of fixing or refining each of the parameters separately. This flexibility is important to characterize a detector, but when detector parameters are already known, the *fit all* option and detector-specific default values are quite reliable.

DENZO can refine the position and orientation of the detector (six parameters). It can also refine internal parameters of the detector including:

- (1) curvature radius and rotation of active surface – *film rotation*, for cylindrical detectors;
- (2) *x* to *y* scale and *x* to *y* skew;
- (3) radial/angular distortion for spiral scanners; and
- (4) polynomial distortion, separate for each module of multi-module CCD detectors (Naday *et al.*, 1998).

Detector- and crystal-parameter refinement in *DENZO* is achieved by minimizing the sum of the three functions of the type in equation (11.4.5.1). The contribution resulting from the measurement of position *p* of the reflection is

$$\chi_p^2 = \sum_{hkl} (p_{\text{pred}} - p_{\text{cent}})^2 / \sigma_p^2. \quad (11.4.6.7)$$

The measurement of position *q* contributes a similar term.

11.4.6.2. Bragg's law for non-ideal conditions: mosaicity

The Bragg condition [equation (11.4.2.1)] assumes ideal crystals and a parallel X-ray beam. In reality, crystals are mosaic and the beam has some angular spread. The value of *mosaicity* describes the range of orientations of the crystal lattice within a sample. As the impacts of mosaicity and the beam's angular spread on the angular width of reflections are equivalent, the keyword *mosaicity* describes the sum of both effects.

DENZO assumes the following model of angular shape of diffraction peaks:

$$M = \frac{\text{mos}}{\pi} \left[1 + \cos \frac{\pi(\varphi - \varphi_c)}{\text{mos}} \right] \quad (11.4.6.8)$$

for φ_c in the range $(\varphi_c - \text{mos}/2; \varphi_c + \text{mos}/2)$, otherwise $M = 0$,

$$P_{\varphi_1 \varphi_2} = \int_{\varphi_1}^{\varphi_2} M(\varphi) d\varphi, \quad (11.4.6.9)$$

where *mos* is mosaicity, φ_c is the predicted angle and *P* is the predicted partiality of data collected by oscillating from φ_1 to φ_2 .

Partiality is a number that represents what fraction of the reflection intensity is present in one image. If partiality is 1, such reflections are called fully recorded; otherwise they are called partials. For partials, predictions of partiality can be compared with the observed fraction P_0 of the reflection intensity present in one image. The partiality model contributes the following term to the refinement:

$$\chi_P^2 = (P_{\varphi_1 \varphi_2} - P_0)^2 / \sigma_{P_0}^2. \quad (11.4.6.10)$$

The combined positional and partiality refinement used in *DENZO* is both stable and very accurate. The power of this method is in proper weighting (by estimated error) of two very different terms – one describing positional differences and the other describing intensity differences. Both detector and crystal variables are uniformly treated in the refinement process.

11.4.6.3. Detector distortions

The design of detectors results in pixels not being positioned on an exact square or rectangular grid. A correct understanding of the detector distortions is essential to accurate positional refinement. The types of distortions are detector-specific. The primary sources of error include misalignment of the detector position sensors and optical or magnetic distortion in CCD-based detectors. If the detector distortion can be parameterized, then these parameters should be added to the refinement. For example, in the case of spiral scanners, there are two parameters describing the end position of the scanning head. In a perfectly adjusted scanner, these parameters would be zero. In practice, however, they may deviate from zero by as much as 1 mm. Such misalignment parameters can correlate very strongly with other detector and crystal parameters, particularly for low-symmetry lattices or in the case of low-resolution data. If the distortions are stable, it is better to determine them in a separate experiment optimized for that task.

Fibre-optic tapers used in many CCD detectors have distortion that has to be individually determined for each instrument. The distortion is stable over time and its spatial characteristics are dominated by a smooth component and a small local shear. In high-quality tapers used in X-ray instruments, the small local shear can be ignored. The smooth component can be parameterized in a number of ways, for example by splines (Hammersley, 1998) or polynomials (Messerschmidt & Pflugrath, 1987). *DENZO* uses two-dimensional Chebyshev polynomials (Press *et al.*, 1989) in $\{x, y\}$ or $\{p, q\}$ coordinates, normalized to the range $\{[-1, +1], [-1, +1]\}$. Typically, fifth- or seventh-order polynomials result in a positional error (r.m.s.) lower than 7 μm (about one tenth of the detector pixel). *DENZO* can use either a grid mask pattern or the X-ray diffraction pattern to refine the coefficients of the Chebyshev polynomials. If a grid mask is used, it has to be precisely made and positioned. The use of crystallographic data requires precise knowledge of detector and crystal parameters that are not known *a priori* with the required precision. The crystal and detector parameters can be determined in the same experiment as detector distortion. However, this experiment needs to be designed to minimize the impact of correlations between the parameters involved. The data analysis requires the description of the distortion function and its inverse. In *DENZO*, both are approximated in terms of Chebyshev polynomials. The magnitude of the approximation error is the same for the distortion function and its inverse.