Gaussian constants are tabulated by Abramowitz & Stegun (1964).

Alternative schemes based on Monte Carlo and three-dimensional parabolic integration are described by de Graaff (1973, 1977).

6.3.3.5. *Empirical methods*

Some crystals do not have regular faces, or cannot be measured because these are obscured by the crystal mounting. If corrections based on measurements of the crystal shape are not feasible, absorption measurements may be estimated, either from the intensities of the same reflection at different azimuthal angles ψ (see Subsection 6.3.3.6), or from measurements of equivalent reflections, by empirical methods.

There are variants of the method related to differences in experimental technique. The principles may be illustrated by reference to the procedure for a four-circle diffractometer (Flack, 1977).

Intensities H_m are measurements for a reflection **S** at the angular positions Ω_m, 2θ, χ_m, φ_m. Corrected intensities I_m are to be derived from the measurements by means of a correction factor A_m^* such that

$$I_m = A_m^* H_m. \tag{6.3.3.40}$$

It is assumed that the correction can be written in the form of a rapidly converging Fourier series

$$A_m^* = \sum_{i,j,k,l=-\infty}^{\infty} a_{ijkl} \cos(i\Omega + j2\theta + k\chi + l\varphi) + b_{ijkl} \sin(i\Omega + j2\theta + k\chi + l\varphi). \tag{6.3.3.41}$$

The form of the geometrical terms may be simplified by taking advantage of the symmetry of the four-circle diffractometer. If it is assumed that diffraction is invariant to reversal of the incident and diffracted beams, the settings $\Omega, 2\theta, \chi, \varphi$; $\Omega, -2\theta, -\chi, \pi+\varphi$; $-\Omega, -2\theta, \pi+\chi, \varphi$; $-\Omega, 2\theta, \pi-\chi, \pi+\varphi$; $\pi+\Omega, -2\theta, \chi, \varphi$; $\pi+\Omega, 2\theta, -\chi, \pi+\varphi$; $\pi-\Omega, 2\theta, \pi+\chi, \varphi$; $\pi-\Omega, -2\theta, \pi-\chi, \pi+\varphi$ are equivalent. In shorthand notation, the series (6.3.3.41) reduces to

$$\begin{aligned} A_m^* = \sum a_{\rm cccc} + a_{\rm ccsc} + a_{\rm sccc} + a_{\rm scsc} + a_{\rm sssc} + a_{\rm sscc} \\ + a_{\rm cssc} + a_{\rm cscc} + b_{\rm cccs} + b_{\rm ccss} + b_{\rm sccs} + b_{\rm scss} \\ + b_{\rm ssss} + b_{\rm sscs} + b_{\rm csss} + b_{\rm cscs}. \end{aligned} \tag{6.3.3.42}$$

The range of indices for some terms may be restricted by noting other symmetries in the diffraction experiment. Thus, equation (6.3.3.40) will define the absorption correction for measurements of the incident-beam intensity, with $\Omega = 2\theta = 0$. Since with this geometry the correction will be invariant to rotation about the χ axis, the coefficients for the function involving $\cos(i\Omega)\cos(j2\theta)$ must vanish if the χ index, k, is non-zero. By similar reasoning with the φ axis along the incident beam, one may deduce that coefficients for $\sin(i\Omega)\cos(j2\theta)\sin(k\chi)$ will vanish unless $l = 0$.

Because for a given reflection all measurements are made at the same Bragg angle, the 2θ dependence of the correction cannot be determined by empirical methods. This factor in A is obtained from the absorption correction for a spherical crystal of equivalent radius.

Since an empirical absorption correction is defined only to within a scale factor, the scale must be specified by applying a constraint such that

$$\frac{1}{N_{\rm S}} \sum_{\rm S} A_{\rm S}^* = 1, \tag{6.3.3.43}$$

where $N_{\rm S}$ is the number of independent reflections. Equation (6.3.3.42) may be expressed in the shorthand notation

$$A_{\rm S}^* = \sum_{p=0} C_p f_{p\rm S}, \tag{6.3.3.44}$$

where C_p is the coefficient in a term such as $a_{\rm ccsc}$ or $b_{\rm ccss}$ and $f_{p\rm S}$ is the corresponding geometrical function. Labelling the constant geometrical term with a value of unity as f_0 and rearranging leads to

$$A_{\rm S}^* = 1 + \sum_{p=1} C_p \left\{ f_{p\rm S} - \frac{1}{N_{\rm S}} \sum_{\rm S} f_{p\rm S} \right\} = 1 + \sum_{p=1} C_p g_{p\rm S}, \tag{6.3.3.45}$$

which defines $g_{p\rm S}$.

Equation (6.3.3.40) is now expressed as

$$I_{m\rm S} = H_{m\rm S} + H_{m\rm S} \sum_{p=1} C_p g_{p\rm S}, \tag{6.3.3.46}$$

in which the coefficients C_p are to be chosen so that the values of $I_{m\rm S}$ for each **S** are as near equal as possible. Since the values within each set will not be exactly equal, we rewrite (6.3.3.46) as

$$\Delta_{m\rm S} - H_{m\rm S} = -I_{\rm S} + H_{m\rm S} \sum_{p=1} C_p g_{p\rm S}, \tag{6.3.3.47}$$

in which the mean intensity $I_{\rm S}$ and the C_p are chosen to minimize $\sum_{{\rm S},m} w_{\rm S}^2 \Delta_{m\rm S}^2$, where

$$\Delta_{m\rm S} = I_{m\rm S} - I_{\rm S}, \tag{6.3.3.48}$$

and $w_{\rm S}$ is the weight for that reflection.

If the equation to be solved

$$-w_{\rm S} H_{m\rm S} \simeq -w_{\rm S} I_m + \sum_{p=1} C_p g_{p\rm S} w_{\rm S} I_{m\rm S} \tag{6.3.3.49}$$

is written in the shorthand form

$$\boldsymbol{D} = \boldsymbol{F}\boldsymbol{C}, \tag{6.3.3.50}$$

in which $\boldsymbol{D}$ corresponds to $-w_{\rm S}H_{m\rm S}$, the I_m and C_p correspond to $\boldsymbol{C}$, with $(-w_{\rm S})$ and $w_{\rm S}g_{p\rm S}H_{m\rm S}$ corresponding to $\boldsymbol{F}$, the solution to (6.3.3.50) can be determined from the normal equations

$$\boldsymbol{C} = (\boldsymbol{F}^T\boldsymbol{F})^{-1}\boldsymbol{F}^T\boldsymbol{D}, \tag{6.3.3.51}$$

where $\boldsymbol{F}^T$ is the transpose of $\boldsymbol{F}$. This procedure suffers from the disadvantages of requiring a matrix inversion whenever the set of trial functions (*i.e.* those multiplied by the coefficients C_p) is modified. The tedious inversion of the normal equations, described by (6.3.3.51), may be replaced by a simple inversion *via* the Gram–Schmidt orthogonalizing process, *i.e.* by calculating a matrix $\boldsymbol{W}$ with mutually orthogonal columns $\boldsymbol{W}_j$ such that

$$\begin{aligned} \boldsymbol{W}_1 &= \boldsymbol{F}_1 \\ \boldsymbol{W}_j &= \boldsymbol{F}_j - \sum_{k=1}^{j-1} (\boldsymbol{F}_j \cdot \boldsymbol{W}_k)\boldsymbol{W}_k / \boldsymbol{W}_k^2. \end{aligned} \tag{6.3.3.52}$$

The minimizing of $(\boldsymbol{D} - \boldsymbol{F}\boldsymbol{C})^2$ is replaced by minimizing $(\boldsymbol{D} - \boldsymbol{W}\boldsymbol{A})^2$. Differentiating with respect to a_j yields

$$a_j = \frac{\boldsymbol{D} \cdot \boldsymbol{W}_j}{\boldsymbol{W}_j^2}. \tag{6.3.3.53}$$

If equation (6.3.3.52) is written as

$$\boldsymbol{F} = \boldsymbol{W}\boldsymbol{B},$$

where the upper triangular matrix $\boldsymbol{B}$ is

$$b_{ij} = \boldsymbol{F}_j \cdot \boldsymbol{W}_i / \boldsymbol{W}_i^2, \quad i < j; \quad b_{ij} = 1, i = j; \quad b_{ij} = 0, i > j, \tag{6.3.3.54}$$

the vector determining the coefficients is

$$\boldsymbol{C} = \boldsymbol{B}^{-1}\boldsymbol{A}, \tag{6.3.3.55}$$

in which the inversion of $\boldsymbol{B}$ is straightforward.

In difficult cases, with data affected by errors in addition to absorption, the method described may give physically unreasonable absorption corrections for some reflections. In such cases, it may help to impose the approximate constraints

$$\sum_{\mathbf{S}} w_{\mathbf{S}}^2 H_{m\mathbf{S}} \Big/ \sum_{\mathbf{S}} w_{\mathbf{S}}^2 = \sum_{\mathbf{S}} w_{\mathbf{S}}^2 I_{m\mathbf{S}} \Big/ \sum_{\mathbf{S}} w_{\mathbf{S}}^2. \tag{6.3.3.56}$$

If $m = 1, 2, \ldots, M$, this reduces to the M constraint equations

$$\sum_{p=1} C_p \left\{ \frac{\sum_{\mathbf{S}} w_{\mathbf{S}}^2 H_{m\mathbf{S}} g_{p\mathbf{S}}}{\sum_{\mathbf{S}} w_{\mathbf{S}}^2} \right\} = \sum_{p=1} C_p \left\{ \frac{\varepsilon w_m \sum_{\mathbf{S}} w_{\mathbf{S}}^2 H_{m\mathbf{S}} g_{p\mathbf{S}}}{\sum_{\mathbf{S}} w_{\mathbf{S}}^2} \right\} = 0, \tag{6.3.3.57}$$

where w_m is the square root of the weight for the weighted mean of the equivalent reflections H_m, defined as

$$H_m = \sum_{\mathbf{S}} w_{\mathbf{S}}^2 H_{m\mathbf{S}} \Big/ \sum_{\mathbf{S}} w_{\mathbf{S}}^2 \quad \text{for each } \mathbf{S}, \tag{6.3.3.58}$$

and the multiplier ε controls the strength with which the additional constraints are enforced. With the additional constraint equations, the sum of squares to be minimized, corresponding to (6.3.3.48), becomes

$$\sum_{\mathbf{S},m} w_{\mathbf{S}}^2 (I_{m\mathbf{S}} - I_m)^2 + \sum_{m} \varepsilon^2 w_m^2 (H_m - I_m)^2. \tag{6.3.3.59}$$

A closely related procedure expressing the absorption corrections as Fourier series in polar angles for the incident and diffracted beams is described by Katayama, Sakabe & Sakabe (1972). A similar method minimizing the difference between observed and calculated structure factors is described by Walker & Stuart (1983). Other experimental techniques for measuring data for empirical absorption corrections that could be analysed by the Fourier-series method are described by Kopfmann & Huber (1968), North, Phillips & Mathews (1968), Flack (1974), Stuart & Walker (1979), Lee & Ruble (1977*a*,*b*), Schwager, Bartels & Huber (1973), and Santoro & Wlodawer (1980).

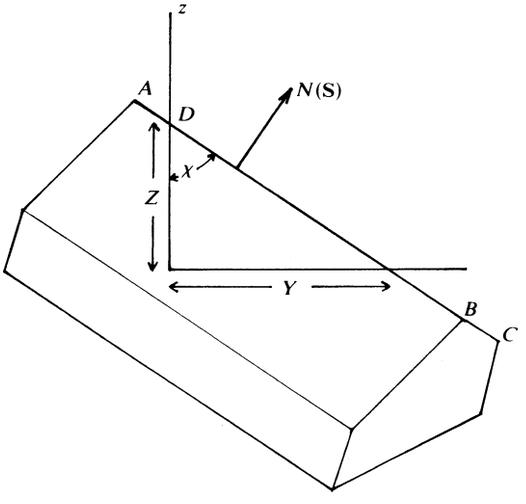

Fig. 6.3.3.4. Crystal oriented with the normal $N(\mathbf{S})$ to the face *ABCD* in the plane of view.

6.3.3.6. *Measuring crystals for absorption*

In general, A depends both on the shape of the crystal and on its orientation with respect to the incident and diffracted beams. To measure the shape of the crystal, a measuring microscope is mounted in the xy plane, and the crystal rotated about the z axis at right angles to that plane. A rotation about the z axis changes the orientation of the crystal x and y coordinates with respect to those (X and Y) for the measuring device. The x axis is directed from crystal to microscope when the angle of rotation about the z axis (φ) is zero. During rotation, each face will at some stage be oriented with its normal $N(\mathbf{S})$ perpendicular to the line of view, *i.e.* in the XY plane for instrument coordinates. If the angle of rotation at that orientation is denoted φ_N, the appearance of a typical face *ABCD* will be as indicated in Fig. 6.3.3.4.

The equation for the plane is

$$x \sin\varphi_N + y \cos\varphi_N + z \tan\chi = Y$$

or, equivalently,

$$(x \sin\varphi_N + y \cos\varphi_N) \cot\chi + z = Z.$$

For a crystal oriented on an Eulerian cradle, it is necessary to specify the orientation of the crystal, *i.e.* the angles Ω, χ, φ in which the measurements of the diffraction intensities are made. In a reflecting position, the reciprocal-lattice vector $\mathbf{S}$, which is normal to the Bragg planes, bisects the angle between the incident and diffracted beams, as shown in Fig. 6.3.3.5.

If the crystal is rotated about the reciprocal-lattice vector $\mathbf{S}$, varying the angle ψ, the crystal remains in a reflecting position. That is, there is a degree of freedom in the scattering experiment that enables the same reflection to be observed at different sets of Ω, χ, φ values. The path length varies with ψ, except for spherical crystals. In order to calculate an absorption correction, the value of ψ and its origin must be specified. For a crystal mounted on an Eulerian cradle, the bisecting position, with $\Omega = \theta$, is usually chosen as the origin for ψ.

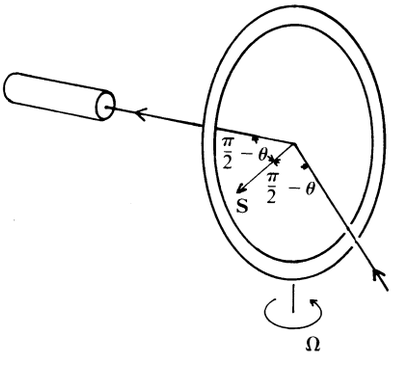

Fig. 6.3.3.5. Geometry of the Eulerian cradle in the bisecting position.

references