where the nth derivative of $h(x)$ is

$$h_n(x) = (-)^n h(x) - \{(-)^n + n h_{n-1}(x)\}/x. \qquad (6.3.3.25)$$

An alternative method of calculating the scattering power of each Howells polyhedron is based on a subdivision into slices. Within each polyhedron, the loci of constant absorption are planes, equivalent to the dotted lines for the two-dimensional example in Fig. 6.3.3.3. The loci may be determined from the path lengths of rays diffracted at each vertex of the polyhedron. The sum of the path lengths in the incident and diffracted directions is found for each vertex, and the loci determined by interpolation. The slices into which each polyhedron is divided are bounded at the upper and lower faces by planes parallel to the loci of constant absorption, such that at least one vertex of the polyhedron lies on those planes.

The volume of the slice is determined from the coordinates of the vertices on each of the opposite faces. Dummy vertices are inserted if necessary to make the number of vertices on the top and bottom faces identical. For simplicity, an axis (z) is chosen perpendicular to the upper face. This locus of constant absorption with N_v vertices x_i, y_i, z_i has an area

$$D_U = 1/2 \sum_{i=1}^{N_v} (x_i y_{i+1} - y_i x_{i+1}) = E/2. \qquad (6.3.3.26)$$

The corresponding vertices on the lower face may be written $x_i + q\Delta x_i, y_i + q\Delta y_i, z_i + q\Delta z$, with $q = 1$. The lower face has an area

$$D_L = 1/2(E + qF + q^2 G), \quad q = 1, \qquad (6.3.3.27)$$

where

$$F = \sum_{i=1}^{N_v} \Delta x_i y_{i+1} + \Delta y_{i+1} x_i - \Delta x_{i+1} y_i - \Delta y_i x_{i+1}$$

and

$$G = \sum_{i=1}^{N_v} \Delta x_i \, \Delta y_{i+1} - \Delta y_i \, \Delta x_{i+1} \qquad (6.3.3.28)$$

so that the volume of the slice is

$$V_s = 1/2(z_L - z_U)(E + F/2 + G/3). \qquad (6.3.3.29)$$

The diffracting power of an element of the slice, allowing for absorption, is $D(q)\exp(-\mu T)\,\mathrm{d}z$, where T is the total path length of the rays diffracted from this plane. Because of the definition of the Howells polyhedron, the path length

$$T = T_U + q(T_L - T_U) = T_U + q\Delta T. \qquad (6.3.3.30)$$

Thus, the total diffracting power of the slice

$$\begin{aligned} R_s &= 1/2(z_L - z_U)\exp(-\mu T_U) \\ &\quad \times \int_0^1 (E + qF + q^2 G)\exp(-\mu q \Delta T)\,\mathrm{d}q \\ &= 1/2(z_L - z_U)\exp(-\mu T_L)\left\{\frac{-E}{\mu\Delta T} - \frac{F(\mu\Delta T + 1)}{(\mu\Delta T)^2}\right. \\ &\quad \left. - G\frac{(\mu\Delta T^2 + 2\mu\Delta T + 2)}{(\mu\Delta T)^3}\right\} \\ &\quad - 1/2(z_L - z_U)\exp(-\mu T_U)\left\{\frac{-E}{\mu\Delta T} - \frac{F}{(\mu\Delta T)^2} - \frac{2G}{(\mu\Delta T)^3}\right\}. \end{aligned} \qquad (6.3.3.31)$$

The transmission factor for the Howells polyhedron is obtained by summing over the slices, and that for the whole crystal is obtained by summing over the polyhedra, *i.e.*

$$A = \sum R_s / \sum V_s, \qquad (6.3.3.32)$$

where the crystal volume is $\sum V_s$.

$\mathrm{d}A/\mathrm{d}\mu$, required in calculating $\bar{T}$ for the extinction correction, can be obtained by differentiating R_s for each slice with respect to μ, summing the derivatives for each slice, and dividing by $\sum V_s$. To reduce rounding errors in calculation, it may be desirable to rescale the crystal dimensions so that the path lengths are of the order of unity, multiplying the absorption coefficient by the inverse of the scale factor. Further details are given by Alcock, Pawley, Rourke & Levine (1972).

The number of component tetrahedra or slices, which determines the time and precision required for calculation, is a rapidly increasing function of the number of crystal faces. The method may be computationally prohibitive for crystals with complex shapes.

6.3.3.4. *Gaussian integration*

The integral in the transmission factor in equation (6.3.3.1) may be approximated by a sum over grid points spaced at intervals through the crystal volume. It is usually convenient to orient the grid parallel to the crystallographic axes. The grid is non-isometric, the points being chosen weighted by Gaussian constants to minimize the difference between the weighted sum at those points and the exact value of the integral.

Thus, an integral such as $\int_a^b f(y)\,\mathrm{d}y$ may be approximated (Stroud & Secrest, 1966) by

$$\int_a^b f(y)\,\mathrm{d}y = \frac{b-a}{2}\sum_{i=1}^{n} w_i f(y_i) + R_n, \qquad (6.3.3.33)$$

where

$$y_i = \left(\frac{b-a}{2}\right)X_i + \left(\frac{b+a}{2}\right),$$

X_i is the ith zero of the Legendre polynomial $P_n(X)$,

$$w_i = \frac{2}{(1 - X_i^2)}[P_n'(X_i)]^2, \qquad (6.3.3.34)$$

and

$$R_n = \frac{(b-a)^{2n+1}(n!)^4}{(2n+1)[(2n!)]^3}\, 2^{2n+1} f^{(2n)}(\xi), \quad -1 < \xi < 1. \qquad (6.3.3.35)$$

When applying this to the calculation of a transmission coefficient (Coppens, 1970), we commence with the a-axis grid points x_i selected such that

$$x_i = x_{\min} + (x_{\max} - x_{\min})X_i, \qquad (6.3.3.36)$$

where the X_i are the Gaussian constants.

For each x_i, a line is drawn parallel to **b** and points are then selected such that

$$y_{ij} = y_{\min}(x_i) + [y_{\max}(x_i) - y_{\min}(x_i)]\,X_j. \qquad (6.3.3.37)$$

The procedure is repeated for the c direction, yielding

$$z_{ijk} = z_{\min}(x_i, y_j) + [z_{\max}(s_i, y_j) - z_{\min}(x_i, y_j)]\,X_k. \qquad (6.3.3.38)$$

To calculate the absorption corrections, the incident and diffracted wavevectors are determined. For each grid point, the sum T_{ijk} of the path lengths for the incident and diffracted beams is evaluated. The sum that approximates the transmission coefficient is then

$$A = 1/V \sum_{i,j,k} w_i w_j w_k \exp(-\mu T_{ijk}). \qquad (6.3.3.39)$$

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

references