International Tables for Crystallography (2006). Vol. C, Section 4.3.6.2, pp. 415–416.

$$U(x, y) = \sum_{h=-n_h}^{n_h} \sum_{k=-n_k}^{n_k} u(h, k) \exp\left\{2\pi i \left[\frac{hx}{n_x}, \frac{ky}{n_y}\right]\right\},$$

where $n_h = (n_x/2) - 1$, $n_k = (n_y/2) - 1$, and n_x, n_y are the sampling intervals in the unit cell. The array sizes used in the calculations of the Fourier transforms are commonly powers of 2 as is required by many fast Fourier subroutines. The array for $u_n(h, k)$ is usually defined over the central portion of the reserved computer array space in order to avoid oscillation in the Fourier transforms (Gibbs instability). It is usual to carry out a 64×64 beam calculation in an array of 128×128, hence the critical timing interval in a multislice calculation is that interval taken by a fast Fourier transform for $4N$ coefficients. If the number of beams, N, is such that there is still appreciable intensity being scattered outside the calculation aperture, then it is usually necessary to impose a circular aperture on the calculation in order to prevent the symmetry of the calculation aperture imposing itself on the calculated wavefunction. This is most conveniently achieved by setting all $p(h, k)$ coefficients outside the desired circular aperture to zero.

It is clear that the iterative procedure of (4.3.6.1) means that care must be taken to avoid accumulation of error due to the precision of representation of numbers in the computer that is to be used. Practical experience indicates that a precision of nine significant figures (decimal) is more than adequate for most calculations. A precision of six to seven (decimal) figures (a common 32-bit floating-point representation) is only barely satisfactory. A computer that uses one of the common 64-bit representations (12 to 16 significant figures) is satisfactory even for the largest calculations currently contemplated.

The choice of slice thickness depends upon the maximum value of the projected potential within a slice and upon the validity of separation of the calculation into transmission function and propagation function. The second criterion is not severe and in practice sets an upper limit to slice thickness of about 10 Å. The first criterion depends upon the atomic number of atoms in the trial structure. In practice, the slice thickness will be too large if two atoms of medium to heavy atomic weight ($Z \geq 30$) are projected onto one another. It is not necessary to take slices less than one atomic diameter for calculations for fast electron (acceleration voltages greater than 50 keV) diffraction or microscopy. If the trial structure is such that the symmetry of the diffraction pattern is not strongly dependent upon the structure of the crystal parallel to the slice normal, then the slices may be all identical and there is no requirement to have a slice thickness related to the periodicity of the structure parallel to the surface normal. This is called the 'no upper-layer-line' approximation. If the upper-layer lines are important, then the slice thickness will need to be a discrete fraction of the c axis, and the contents of each slice will need to reflect the actual atomic contents of each slice. Hence, if there were four slices per unit cell, then there would need to be four distinct $q(h, k)$, each taken in the appropriate order as the multislice operation proceeds in thickness.

The multislice procedure has two checks that can be readily performed during a calculation. The first is applied to the transmission function, $q(h, k)$, and involves the evaluation of a unitarity test by calculation of

$$\sum_{h'} \sum_{k'} q(h', k') q^*(h + h', k + k') = \delta(h, k) \qquad (4.3.6.5)$$

for all h, k, where q^* denotes the complex conjugate of q, and $\delta(h, k)$ is the Kronecker delta function. The second test can be applied to any calculation for which no phenomenological absorption potential has been used in the evaluation of the $q(h, k)$. In that case, the sum of intensities of all beams at the final thickness should be no less than 0.9, the incident intensity being taken as 1.0. A value of this sum that is less than 0.9 indicates that the number of beams, N, has been insufficient. In some rare cases, the sum can be greater than 1.0; this is usually an indication that the number of beams has been allowed to come very close to the array size used in the convolution procedure. This last result does not occur if the convolution is carried out directly rather than by use of fast-Fourier-transform methods.

A more complete discussion of the multislice procedure can be obtained from Cowley (1975) and Goodman & Moodie (1974). These references are not exhaustive, but rather an indication of particularly useful articles for the novice in this subject.

4.3.6.2. *The Bloch-wave method (By A. Howie)*

Bloch waves, familiar in solid-state valence-band theory, arise as the basic wave solutions for a periodic structure. They are thus always implicit and often explicit in dynamical diffraction calculations, whether applied in perfect crystals, in almost perfect crystals with slowly varying defect strain fields or in more general structures that (see Subsection 4.3.6.1) can always, for computations, be treated by periodic continuation.

The Schrödinger wave equation in a periodic structure,

$$\nabla^2 \psi + 4\pi^2 \left[\chi^2 + \sum_{\mathbf{g}} U_{\mathbf{g}} \exp(2\pi i \mathbf{g} \cdot \mathbf{r})\right] \psi = 0, \qquad (4.3.6.6)$$

can be applied to high-energy, relativistic electron diffraction, taking $\chi = \lambda^{-1}$ as the relativistically corrected electron wave number (see Subsection 4.3.1.4). The Fourier coefficients in the expression for the periodic potential are defined at reciprocal-lattice points $\mathbf{g}$ by the expression

$$U_{\mathbf{g}} = U^*_{-\mathbf{g}} = \frac{m}{m_0} \frac{\exp(-M_{\mathbf{g}})}{\pi \Omega} \sum_j f_j[\sin(\theta_{\mathbf{g}})/\lambda] \exp(-2\pi i \mathbf{g} \cdot \mathbf{r}_j), \qquad (4.3.6.7)$$

where f_j is the Born scattering amplitude (see Subsection 4.3.1.2) of the jth atom at position $\mathbf{r}_j$ in the unit cell of volume Ω and $M_{\mathbf{g}}$ is the Debye–Waller factor.

The simplest solution to (4.3.6.6) is a single Bloch wave, consisting of a linear combination of plane-wave beams coupled by Bragg reflection.

$$\psi(\mathbf{r}) = b(\mathbf{k}, \mathbf{r}) = \sum_h C_{\mathbf{h}} \exp[2\pi i (\mathbf{k} + \mathbf{h}) \cdot \mathbf{r}]. \qquad (4.3.6.8)$$

In practice, only a limited number of terms N, corresponding to the most strongly excited Bragg beams, is included in (4.3.6.8). Substitution in (4.3.6.6) then yields N simultaneous equations for the wave amplitudes $C_{\mathbf{g}}$.

$$[\chi^2 + U_0 - (\mathbf{k} + \mathbf{g})^2] C_{\mathbf{g}} + \sum_{\mathbf{g}' \neq 0} U_{\mathbf{g}'} C_{\mathbf{g}-\mathbf{g}'} = 0. \qquad (4.3.6.9)$$

Usually, χ and the two tangential components k_x and k_y are fixed by matching to the incident wave at the crystal entrance surface. k_z then emerges as a root of the determinant of coefficients appearing in (4.3.6.9).

Numerical solution of (4.3.6.9) is considerably simplified (Hirsch, Howie, Nicholson, Pashley & Whelan, 1977) in cases of transmission high-energy electron diffraction where all the important reciprocal-lattice points lie in the zero-order Laue zone $g_z = 0$ and $\chi^2 \gg |U_{\mathbf{g}}|$. The equations then reduce to a standard matrix eigenvalue problem (for which efficient subroutines are widely available):

$$\sum_{\mathbf{h}} M_{\mathbf{gh}} C_{\mathbf{h}} = \gamma C_{\mathbf{g}}, \qquad (4.3.6.10)$$

where $M_{\mathbf{gh}} = U_{\mathbf{g-h}}/2\chi + s_{\mathbf{g}}\delta_{\mathbf{gh}}$ and $s_{\mathbf{g}} = [k^2 - (\mathbf{k}+\mathbf{g})^2]/2\chi$ is the distance, measured in the z direction, of the reciprocal-lattice point $\mathbf{g}$ from the Ewald sphere.

There will in general be N distinct eigenvalues $\gamma = k_z - \chi_z$ corresponding to N possible values $k_z^{(j)}$, $j = 1, 2, \cdots N$, each with its eigenfunction defined by N wave amplitudes $C_0^{(j)}, C_{\mathbf{g}}^{(j)}, \ldots, C_{\mathbf{h}}^{(j)}$. The waves are normalized and orthogonal so that

$$\sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)*} C_{\mathbf{g}}^{(l)} = \delta_{jl}; \quad \sum_{j} C_{\mathbf{g}}^{(j)*} C_{\mathbf{h}}^{(l)} = \delta_{\mathbf{gh}}. \qquad (4.3.6.11)$$

In simple transmission geometry, the complete solution for the total coherent wavefunction $\psi(\mathbf{r})$ is

$$\psi(\mathbf{r}) = \sum_{j} \psi^{(j)} \exp[-2\pi q^{(j)} z] \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} \exp[2\pi i(\chi + \mathbf{g})\cdot \mathbf{r}]. \qquad (4.3.6.12)$$

Inelastic and thermal-diffuse-scattering processes cause anomalous absorption effects whereby the amplitude of each component Bloch wave decays with depth z in the crystal from its initial value $\psi^{(j)} = C_0^{(j)*}$. The decay constant is computed using an imaginary optical potential $iU'(\mathbf{r})$ with Fourier coefficients $iU'_{\mathbf{g}} = iU'^{*}_{-\mathbf{g}}$ (for further details of these see Humphreys & Hirsch, 1968, and Subsection 4.3.1.5 and Section 4.3.2).

$$q^{(j)} = \frac{m}{h^2 \chi_z} \sum_{\mathbf{g},\mathbf{h}} C_{\mathbf{g}}^{(j)*} U'_{\mathbf{h}} C_{\mathbf{g-h}}^{(j)}. \qquad (4.3.6.13)$$

The Bloch-wave, matrix-diagonalization method has been extended to include reciprocal-lattice points in higher-order Laue zones (Jones, Rackham & Steeds, 1977) and, using pseudopotential scattering amplitudes, to the case of low-energy electrons (Pendry, 1974).

The Bloch-wave picture may be compared with other variants of dynamical diffraction theory, which, like the multislice method (Subsection 4.3.6.1), for example, employ plane waves whose amplitudes vary with position in real space and are determined by numerical integration of first-order coupled differential equations. For cases with $N < 50$ beams in perfect crystals or in crystals containing localized defects such as stacking faults or small point-defect clusters, the Bloch-wave method offers many advantages, particularly in thicker crystals with $t > 1000$ Å. For high-resolution image calculations in thin crystals where the periodic continuation process may lead to several hundred diffracted beams, the multislice method is more efficient. For cases of defects with extended strain fields or crystals illuminated at oblique incidence, coupled plane-wave integrations along columns in real space (Howie & Basinski, 1968) can be the most efficient method.

The general advantage of the Bloch-wave method, however, is the picture it affords of wave propagation and scattering in both perfect and imperfect crystals. For this purpose, solutions of equations (4.3.6.9) allow dispersion surfaces to be plotted in k space, covering with several sheets j all the wave points $\mathbf{k}^{(j)}$ for a given energy E. Thickness fringes and other interference effects then arise because of interference between waves excited at different points $\mathbf{k}^{(j)}$. The average current flow at each point is normal to the dispersion surface and anomalous-absorption effects can be understood in terms of the distribution of Bloch-wave current within the unit cell. Detailed study of these effects, and the behaviour of dispersion surfaces as a function of energy, yields accurate data on scattering amplitudes *via* the critical-voltage effect (see Section 4.3.7). Static crystal defects induce elastic scattering transitions $\mathbf{k}^{(j)} \rightarrow \mathbf{k}^{(l)}$ on sheets of the same dispersion surface. Transitions between points on dispersion surfaces of different energies occur because of thermal diffuse scattering, generation of electronic excitations or the emission of radiation by the fast electron. The Bloch-wave picture and the dispersion surface are central to any description of these phenomena. For further information and references, the reader may find it helpful to consult Section 5.2.10 of Volume B (*IT* B, 1996).

4.3.7. Measurement of structure factors and determination of crystal thickness by electron diffraction (by J. Gjønnes and J. W. Steeds)

Current advances in quantitative electron diffraction are connected with improved experimental facilities, notably the combination of convergent-beam electron diffraction (CBED) with new detection systems. This is reflected in extended applications of electron diffraction intensities to problems in crystallography, ranging from valence-electron distributions in crystals with small unit cells to structure determination of biological molecules in membranes. The experimental procedures can be seen in relation to the two main principles for measurement of diffracted intensities from crystals:

– *rocking curves*, *i.e.* intensity profiles measured as function of deviation, s_g, from the Bragg condition, and

– *integrated intensities*, which form the well known basis for X-ray and neutron diffraction determination of crystal structure.

Integrated intensities are not easily defined in the most common type of electron-diffraction pattern, *viz* the selected-area (SAD) spot pattern. This is due to the combination of dynamical scattering and the orientation and thickness variations usually present within the typically micrometre-size illuminated area. This combination leads to spot pattern intensities that are poorly defined averages over complicated scattering functions of many structure factors. Convergent-beam electron diffraction is a better alternative for intensity measurements, especially for inorganic structures with small-to-moderate unit cells. In CBED, a fine beam is focused within an area of a few hundred ångströms, with a divergence of the order of a tenth of a degree. The diffraction pattern then appears in the form of discs, which are essentially two-dimensional rocking curves from a small illuminated area, within which thickness and orientation can be regarded as constant. These intensity distributions are obtained under well defined conditions and are well suited for comparison with theoretical calculations. The intensity can be recorded either photographically, or with other parallel recording systems, *viz* YAG screen/CCD camera (Krivanek, Mooney, Fan, Leber & Meyer, 1991) or image plates (Mori, Oikawa & Harada, 1990) – or sequentially by a scanning system. The inelastic background can be removed by an energy filter (Krahl, Pätzold & Swoboda,1990; Krivanek, Gubbens, Dellby & Meyer, 1991). Detailed intensity profiles in one or two dimensions can then be measured with high precision for low-order reflections from simple structures. But there are limitations also with the CBED technique: the crystal should be fairly perfect within the illuminated area and the unit cell relatively small, so that overlap between discs can be avoided. The current development of electron diffraction is therefore characterized by a wide range of techniques, which extend from the traditional spot pattern to two-dimensional, filtered rocking curves, adapted to the

references