5.2. DYNAMICAL THEORY OF ELECTRON DIFFRACTION

5.2.10. Bloch-wave formulations

In developing the theory from the beginning by eigenvalue techniques, it is usual to invoke the periodicity of the crystal in order to show that the solutions to the wave equation for a given wavevector $\mathbf{k}$ are Bloch waves of the form

$$\psi = C(\mathbf{r})\exp\{i\mathbf{k}\cdot\mathbf{r}\},$$

where $C(\mathbf{r})$ has the periodicity of the lattice, and hence may be expanded in a Fourier series to give

$$\psi = \sum_{\mathbf{h}} C_{\mathbf{h}}(\mathbf{k})\exp\{i(\mathbf{k}+2\pi\mathbf{h})\cdot\mathbf{r}\}. \qquad (5.2.10.1)$$

The $C_{\mathbf{h}}(\mathbf{k})$ are determined by equations of consistency obtained by substitution of equation (5.2.10.1) into the wave equation.

If N terms are selected in equation (5.2.10.1) there will be N Bloch waves where wavevectors differ only in their components normal to the crystal surface, and the total wavefunction will consist of a linear combination of these Bloch waves. The problem is now reduced to the problem of equation (5.2.8.2).

The development of solutions for particular geometries follows that for the X-ray case, Chapter 5.1, with the notable differences that:

(1) The two-beam solution is not adequate except as a first approximation for particular orientations of crystals having small unit cells and for accelerating voltages not greater than about 100 keV. In general, many-beam solutions must be sought.

(2) For transmission HEED, the scattering angles are sufficiently small to allow the use of a small-angle forward-scattering approximation.

(3) Polarization effects are negligible except for very low energy electrons.

Humphreys (1979) compares the action of the crystal, in the Bloch-wave formalism, with that of an interferometer, the incident beam being partitioned into a set of Bloch waves of different wavevectors. 'As each Bloch wave propagates it becomes out of phase with its neighbours (due to its different wavevector). Hence interference occurs. For example, if the crystal thickness varies, interference fringes known as thickness fringes are formed.' For the two-beam case, these are the fringes of the pendulum solution referred to previously.

5.2.11. Dispersion surfaces

One of the important constructs of the Bloch-wave formalism is the dispersion surface, a plot of the permitted values of the z component of a Bloch wavevector against the component of the incident wavevector parallel to the crystal surface. The curve for a particular Bloch wave is called a branch. Thus, for fast electrons, the two-beam approximation has two branches, one for each eigenvalue, and the N-beam approximation has N.

A detailed treatment of the extensive and powerful theory that has grown from Bethe's initial paper is to be found, for example, in Hirsch *et al.* (1965). Apart from its fundamental importance as a theoretical tool, this formulation provides the basis for one of the most commonly used numerical techniques, the essential step being the estimation of the eigenvalues from equation (5.2.8.2) [see *IT* C (1999, Section 4.3.6.2)].

5.2.12. Multislice

Multislice derives from a formulation that generates a solution in the form of a Born series (Cowley & Moodie, 1962). The crystal is treated as a series of scattering planes on to which the potential from the slice between z and $z+\Delta z$ is projected, separated by vacuum gaps Δz, not necessarily corresponding to any planes or spacings of the material structure. The phase change in the electron beam

produced by passage through a slice is given by

$$q = \exp\left\{-i\sigma \int_{z_1}^{z_1+\Delta z} \varphi(x,y,z)\,dz\right\},$$

and the phase distribution in the x, y plane resulting from propagation between slices is given by

$$p = \exp\left\{\frac{ik(x^2+y^2)}{2\Delta z}\right\},$$

where the wavefront has been approximated by a paraboloid. Thus, the wavefunction for the $(n+1)$th slice is given by

$$\psi_{n+1} = \left[\psi_n * \exp\left\{\frac{ik(x^2+y^2)}{2\Delta z}\right\}\right]\exp\{-i\sigma\varphi_{n+1}\}$$

$$= [\psi_n * p]q, \qquad (5.2.12.1)$$

where $*$ is the convolution operator (Cowley, 1981).

This equation can be regarded as the finite difference form of the Schrödinger equation derived by Feynman's (1948) method. The calculation need be correct only to first order in Δz. Writing the convolution in equation (5.2.12.1) explicitly, and expanding in a Taylor series, the integrals can be evaluated to yield equation (5.2.3.1) (Goodman & Moodie, 1974).

If equation (5.2.12.1) is Fourier transformed with respect to x and y, the resulting recurrence relation is of the form

$$U_{n+1} = [U_n P] * Q_n, \qquad (5.2.12.2)$$

where P and Q are obtained by Fourier transforming p and q above. This form is convenient for numerical work since, for a perfect crystal, it is: discrete, as distinct from equation (5.2.12.1) which is continuous in the variables [see *IT* C (1999, Section 4.3.6.1)]; numerically stable at least up to 5000 beams; fast; and only requires a computer memory proportional to the number of beams (Goodman & Moodie, 1974).

5.2.13. Born series

In the impulse limit of equation (5.2.12.2), the integrals can be evaluated to give the Born series (Cowley & Moodie, 1957)

$$U(h,k) = \sum_n U_n(h,k),$$

where

$$U_n(h,k) = \sum_l \sum_{h_1 k_1 l_1} \cdots \sum_{h_{n-1} k_{n-1} l_{n-1}} i^n V(h_1,k_1,l_1)$$

$$\ldots V\left(h - \sum_{r=1}^{n-1} h_r, k - \sum_{r=1}^{n-1} k_r, l - \sum_{r=1}^{n-i} l_r\right)$$

$$\times [\exp\{-2\pi i\zeta T\}/(2\pi i)^n]$$

$$\times \left(\exp\{i\pi\zeta T\}(\sin \pi\zeta T/\zeta)[(\zeta - \zeta_1)\ldots(\zeta - \zeta_{n-1})]^{-1}\right.$$

$$+ \sum_{m=1}^{n-1} \exp\{i\pi\zeta_m T\}(\sin \pi\zeta_m T/\zeta_m)[(\zeta_m - \zeta_1)$$

$$\left.\ldots(\zeta_m - \zeta_{m-1})(\zeta_m - \zeta_{m+1})\ldots(\zeta_m - \zeta)]^{-1}\right)$$

$$(5.2.13.1a)$$

and where n is the order of interaction. Here ζ is the excitation error of the reflection with index h, k, and ζ_i are the excitation errors for the reflections with indices h_i, k_i, l_i. Thus each constituent process may be represented by a diagram, starting on the origin of reciprocal

space, possibly looped, and ending on the point with coordinates (h, k).

This solution can also be obtained by iteration of the Green-function integral equation, the integrals being evaluated by means of suitably chosen contours on the complex k_z plane (Fujiwara, 1959), as well as by expansion of the scattering matrix (Fujimoto, 1959).

Clearly, two or more of the ζ_i will, in general, be equal in nearly all of the terms in equation (5.2.13.1a). Confluence is, however, readily described, the divided differences of arbitrary order transforming into differentials of the same order (Moodie, 1972).

The physical picture that emerges from equation (5.2.13.1a) is that of n-fold scattering, the initial wave being turned through $n-1$ intermediate states, processes that can be presented by scattering diagrams in reciprocal space (Gjønnes & Moodie, 1965).

For a given scattering vector, constituent functions are evaluated for all possible paths in three dimensions, and those functions are then summed over l. There are therefore two distinct processes by which upper-layer lines can perturb wavefunctions in the zone, namely: by scattering out of the zone and then back in; and by intrusion of the effective shape function from another zone, the latter process being already operative in the first Born, or kinematical approximation.

The constituent functions to be evaluated can be transformed into many forms. One of the more readily described is that which assigns to each diagram an effective dynamical shape function. If there are no loops in the diagram of order n, this effective shape function is the $(n+1)$th divided difference of the constituent phase-shifted kinematical shape transforms. For general diagrams, divided differences in loops are replaced by the corresponding differentials. The resulting function is multiplied by the convolution of the contributing structure amplitudes and diagrams of all orders summed (Moodie, 1972).

While scattering diagrams have no utility in numerical work, they find application in the analysis of symmetries, for instance in the determination of the presence or absence of a centre of inversion [for a recent treatment, see Moodie & Whitfield (1995)] and in the detection of screw axes and glide planes (Gjønnes & Moodie, 1965). Methods for the direct determination of all space groups are described by Goodman (1975) and by Tanaka *et al.* (1983) (see Section 2.5.3).

Equation (5.2.13.1a) can be rewritten in a form particularly suited to the classification of approximations, and to describing the underlying symmetry of the formulation. The equation is written for compactness as

$$U_n(h) = E_n(h)Z_n(\zeta),$$

so that $E_n(h)$ depends only on crystal structure and $Z_n(\zeta)$ only on diffraction geometry. A transformation (Cowley & Moodie, 1962) involving bialternants leads to

$$U_n = \sum_{r=0}^{\infty} E_n(h)\left[(2\pi iT)^{n+r}/(n+r)!\right]h_r(\zeta, \zeta_1 \ldots \zeta_{n-1}),$$

$$(5.2.13.1b)$$

where h_r is the complete homogeneous symmetric polynomial function of n variables of order r.

Upper-layer-line effects can, of course, be calculated in any of the formulations.

5.2.14. Approximations

So far, only the familiar first Born and two-beam approximations and the projection approximation have been mentioned. Several others, however, have a considerable utility.

A high-voltage limit can be calculated in standard fashion to give

$$U_{HVL}(h, k) = \mathscr{F}\exp\left\{-i\sigma_c\int_0^T \varphi(x, y, z)\,\mathrm{d}z\right\}, \qquad (5.2.14.1)$$

where $\mathscr{F}$ is the Fourier transform operator, and $\sigma_c = 2\pi m_0 e\lambda_c/h^2$ with $\lambda_c = (h/m_0 c)$, the Compton wavelength. The phase-grating approximation, which finds application in electron microscopy, involves the assumption that equation (5.2.14.1) has some range of validity when σ_c is replaced by σ. This is equivalent to ignoring the curvature of the Ewald sphere and can therefore apply to thin crystals [see Section 2.5.2 and *IT* C (1999, Section 4.3.8)].

Approximations that involve curtailing the number of beams evidently have a range of validity that depends on the size of the unit cell. The most explored case is that of three-beam interactions. Kambe (1957) has demonstrated that phase information can be obtained from the diffraction data; Gjønnes & Høier (1971) analysed the confluent case, and Hurley & Moodie (1980) have given an explicit inversion for the centrosymmetric case. Analyses of the symmetry of the defining differential equation, and of the geometry of the noncentrosymmetric case, have been given by Moodie *et al.* (1996, 1998).

Niehrs and his co-workers (*e.g.* Blume, 1966) have shown that, at or near zones, effective two-beam conditions can sometimes obtain, in that, for instance, the central beam and six equidistant beams of equal structure amplitude can exhibit two-beam behaviour when the excitation errors are equal. Group-theoretical treatments have been given by Fukuhara (1966) and by Kogiso & Takahashi (1977). Explicit reductions for all admissible noncentrosymmetric space groups have been obtained by Moodie & Whitfield (1994). Extensions of such results have application in the interpretation of lattice images and convergent-beam patterns.

The approximations near the classical limit have been extensively explored [for instance, see Berry (1971)] but channelling has effectively become a separate subject and cannot be discussed here.