5.2. Dynamical theory of electron diffraction

By A. F. Moodie, J. M. Cowley† and P. Goodman†

5.2.1. Introduction

Since electrons are charged, they interact strongly with matter, so that the single scattering approximation has a validity restricted to thin crystals composed of atoms of low atomic number. Further, at energies of above a few tens of keV, the wavelength of the electron is so short that the geometry of two-beam diffraction can be approximated in only small unit cells.

It is therefore necessary to develop a scattering theory specific to electrons and, preferably, applicable to imaging as well as to diffraction. The development, started by Born (1926) and Bethe (1928), and continuing into the present time, is the subject of an extensive literature, which includes reviews [for instance: Howie (1978), Humphreys (1979)] and historical accounts (Goodman, 1981), and is incorporated in Chapter 5.1. Here, an attempt will be made to present only that outline of the main formulations which, it is hoped, will help the nonspecialist in the use of the tables. No attempt will be made to follow the historical development, which has been tortuous and not always logical, but rather to seek the simplest and most transparent approach that is consistent with brevity. Only key points in proofs will be sketched in an attempt to display the nature, rather than the rigorous foundations of the arguments.

5.2.2. The defining equations

No many-body effects have yet been detected in the diffraction of fast electrons, but the velocities lie well within the relativistic region. The one-body Dirac equation would therefore appear to be the appropriate starting point. Fujiwara (1962), using the scattering matrix, carried through the analysis for forward scattering, and found that, to a very good approximation, the effects of spin are negligible, and that the solution is the same as that obtained from the Schrödinger equation provided that the relativistic values for wavelength and mass are used. In effect a Klein–Gordon equation (Messiah, 1965) can be used in electron diffraction (Buxton, 1978) in the form

$$\nabla^2 \psi_b + \frac{8\pi^2 m|e|\varphi}{h^2}\psi_b + \frac{8\pi^2 m_0|e|W}{h^2}\left(1 + \frac{|e|W}{2m_0 c^2}\right)\psi_b = 0.$$

Here, W is the accelerating voltage and φ, the potential in the crystal, is defined as being positive. The relativistic values for mass and wavelength are given by $m = m_0(1 - v^2/c^2)^{-1/2}$, and taking 'e' now to represent the modulus of the electronic charge, $|e|$,

$$\lambda = h[2m_0 eW(1 + eW/2m_0 c^2)]^{-1/2},$$

and the wavefunction is labelled with the subscript b in order to indicate that it still includes back scattering, of central importance to LEED (low-energy electron diffraction).

In more compact notation,

$$[\nabla^2 + k^2(1 + \varphi/W)]\psi_b = (\nabla^2 + k^2 + 2k\sigma\varphi)\psi_b = 0. \quad (5.2.2.1)$$

Here $k = |\mathbf{k}|$ is the scalar wavenumber of magnitude $2\pi/\lambda$, and the interaction constant $\sigma = 2\pi me\lambda/h^2$. This constant is approximately 10^{-3} for 100 kV electrons.

For fast electrons, φ/W is a slowly varying function on a scale of wavelength, and is small compared with unity. The scattering will therefore be peaked about the direction defined by the incident beam, and further simplification is possible, leading to a forward-scattering solution appropriate to HEED (high-energy electron diffraction).

5.2.3. Forward scattering

A great deal of geometric detail can arise at this point and, further, there is no generally accepted method for approximation, the various procedures leading to numerically negligible differences and to expressions of precisely the same form. Detailed descriptions of the geometry are given in the references.

The entrance surface of the specimen, in the form of a plate, is chosen as the x, y plane, and the direction of the incident beam is taken to be close to the z axis. Components of the wavevector are labelled with suffixes in the conventional way; $\mathbf{K}_0 = \mathbf{k}_x + \mathbf{k}_y$ is the transverse wavevector, which will be very small compared to $\mathbf{k}_z$. In this notation, the excitation error for the reflection is given by

$$\zeta_h = \frac{K_0^2 - |\mathbf{K}_0 + 2\pi\mathbf{h}|^2}{4\pi|\mathbf{k}_z|}.$$

An intuitive method argues that, since $\varphi/W \ll 1$, then the component of the motion along z is little changed by scattering. Hence, making the substitution $\psi_b = \psi \exp\{ik_z z\}$ and neglecting $\partial^2\psi/\partial z^2$, equation (5.2.2.1) becomes

$$\frac{\partial\psi}{\partial z} = i\left[\frac{1}{2k_z}(\nabla_{x,y}^2 + K_0^2) + \sigma\varphi\right]\psi, \quad (5.2.3.1)$$

where

$$\nabla_{x,y}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2},$$

and $\psi(x, y, 0) = \exp\{i(k_x x + k_y y)\}$.

Equation (5.2.3.1) is of the form of a two-dimensional time-dependent Schrödinger equation, with the z coordinate replacing time. This form has been extensively discussed. For instance, Howie (1966) derived what is essentially this equation using an expansion in Bloch waves, Berry (1971) used a Green function in a detailed and rigorous derivation, and Goodman & Moodie (1974), using methods due to Feynman, derived the equation as the limit of the multislice recurrence relation. A method due to Corones *et al.* (1982) brings out the relationship between the HEED and LEED equations. Equation (5.2.2.1) is cast in the form of a first-order system,

$$\frac{\partial}{\partial z}\begin{pmatrix} \psi_b \\ \frac{\partial\psi_b}{\partial z} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -(\nabla_{x,y}^2 + k^2 + 2k\sigma\varphi) & 0 \end{pmatrix}\begin{pmatrix} \psi_b \\ \frac{\partial\psi_b}{\partial z} \end{pmatrix}.$$

† Deceased.

A splitting matrix is introduced to separate the wavefunction into the forward and backward components, $\psi_b^{\pm}$, and the fast part of the phase is factored out, so that $\psi_b^{\pm} = \psi^{\pm} \exp\{\pm ik_z z\}$. In the resulting matrix differential equation, the off-diagonal terms are seen to be small for fast electrons, and equation (5.2.2.1) reduces to the pair of equations

$$\frac{\partial \psi^{\pm}}{\partial z} = \pm i \left[\frac{1}{2k_z}(\nabla_{x,y}^2 + K_0^2) + \sigma\varphi \right] \psi^{\pm}. \qquad (5.2.3.2)$$

The equation for $\psi^{\pm}$ is the Lontovich & Fock (1946) parabolic equation.

5.2.4. Evolution operator

Equation (5.2.3.1) is a standard and much studied form, so that many techniques are available for the construction of solutions. One of the most direct utilizes the causal evolution operator. A recent account is given by Gratias & Portier (1983).

In terms of the 'Hamiltonian' of the two-dimensional system,

$$-\mathbf{H}(z) \equiv \frac{1}{2k_z}(\nabla_{x,y}^2 + K_0^2) + \sigma\varphi,$$

the evolution operator $\mathbf{U}(z, z_0)$, defined by $\psi(z) = \mathbf{U}(z, z_0)\psi_0$, satisfies

$$i\frac{\partial}{\partial z}\mathbf{U}(z, z_0) = \mathbf{H}(z)\mathbf{U}(z, z_0), \qquad (5.2.4.1a)$$

or

$$\mathbf{U}(z, z_0) = 1 - i\int_{z_0}^{z} \mathbf{U}(z, z_1)\mathbf{H}(z_1)\,\mathrm{d}z_1. \qquad (5.2.4.1b)$$

5.2.5. Projection approximation – real-space solution

Many of the features of the more general solutions are retained in the practically important projection approximation in which $\varphi(x, y, z)$ is replaced by its projected mean value $\varphi_p(x, y)$, so that the corresponding Hamiltonian $\mathbf{H}_p$ does not depend on z. Equation (5.2.4.1b) can then be solved directly by iteration to give

$$\mathbf{U}_p(z, z_0) = \exp\{-i\mathbf{H}_p(z - z_0)\}, \qquad (5.2.5.1)$$

and the solution may be verified by substitution into equation (5.2.4.1a).

Many of the results of dynamical theory can be obtained by expansion of equation (5.2.5.1) as

$$\mathbf{U}_p \equiv \mathbf{1} - i\mathbf{H}_p(z - z_0) + \frac{i^2}{2!}\mathbf{H}_p^2(z - z_0) - \ldots,$$

followed by the direct evaluation of the differentials. Such expressions can be used, for instance, to explore symmetries in image space.

5.2.6. Semi-reciprocal space

In the derivation of electron-diffraction equations, it is more usual to work in semi-reciprocal space (Tournarie, 1962). This can be achieved by transforming equation (5.2.2.1) with respect to x and y but not with respect to z, to obtain Tournarie's equation

$$\frac{\mathrm{d}^2 |U\rangle}{\mathrm{d}z^2} = -\mathbf{M}_b(z)|U\rangle. \qquad (5.2.6.1a)$$

Here $|U\rangle$ is the column vector of scattering amplitudes and $\mathbf{M}_b(z)$ is a matrix, appropriate to LEED, with $\mathbf{k}$ vectors as diagonal elements and Fourier coefficients of the potential as nondiagonal elements.

This equation is factorized in a manner parallel to that used on the real-space equation [equation (5.2.3.1)] (Lynch & Moodie, 1972) to obtain Tournarie's forward-scattering equation

$$\frac{\mathrm{d}|U^{\pm}\rangle}{\mathrm{d}z} = \pm i\mathbf{M}^{\pm}(z)|U^{\pm}\rangle, \qquad (5.2.6.1b)$$

where

$$\mathbf{M}^{\pm}(z) = \pm[\mathbf{K} + (1/2)\mathbf{K}^{-1}V(z)],$$

$$[K_{ij}] = \delta_{ij}K_i,$$

and

$$[V_{ij}] = 2k_z\sum_l V_{i-j}\exp\{-2\pi i l z\},$$

where $V_i \equiv \sigma v_i$ are the scattering coefficients and v_i are the structure amplitudes in volts. In order to simplify the electron-diffraction expression, the third crystallographic index 'l' is taken to represent the periodicity along the z direction.

The double solution involving $\mathbf{M}$ of equation (5.2.6.1b) is of interest in displaying the symmetry of reciprocity, and may be compared with the double solution obtained for the real-space equation [equation (5.2.3.2)]. Normally the $\mathbf{M}^+$ solution will be followed through to give the fast-electron forward-scattering equations appropriate in HEED. $\mathbf{M}^-$, however, represents the equivalent set of equations corresponding to the z reversed reciprocity configuration. Reciprocity solutions will yield diffraction symmetries in the forward direction when coupled with crystal-inverting symmetries (Section 2.5.3).

Once again we set out to solve the forward-scattering equation (5.2.6.1a,b) now in semi-reciprocal space, and define an operator $\mathbf{Q}(z)$ [compare with equation (5.2.4.1a)] such that

$$|U_z\rangle = \mathbf{Q}_z|U_0\rangle \quad \text{with} \quad U_0 = |0\rangle;$$

i.e., $\mathbf{Q}_z$ is an operator that, when acting on the incident wave-vector, generates the wavefunction in semi-reciprocal space.

Again, the differential equation can be transformed into an integral equation, and once again this can be iterated. In the projection approximation, with $\mathbf{M}$ independent of z, the solution can be written as

$$\mathbf{Q}_p = \exp\{i\mathbf{M}_p(z - z_0)\}.$$

A typical off-diagonal element is given by $V_{i-j}/\cos\theta_i$, where θ_i is the angle through which the beam is scattered. It is usual in the literature to find that $\cos\theta_i$ has been approximated as unity, since even the most accurate measurements are, so far, in error by much more than this amount.

This expression for $\mathbf{Q}_p$ is Sturkey's (1957) solution, a most useful relation, written explicitly as

$$|U\rangle = \exp\{i\mathbf{M}_{\mathrm{p}}T\}|0\rangle \qquad (5.2.6.2)$$

with T the thickness of the crystal, and $|0\rangle$, the incident state, a column vector with the first entry unity and the rest zero.

$$\mathbf{S} = \exp\{i\mathbf{M}_{\mathrm{p}}T\}$$

is a unitary matrix, so that in this formulation scattering is described as rotation in Hilbert space.

5.2.7. Two-beam approximation

In the two-beam approximation, as an elementary example, equation (5.2.6.2) takes the form

$$\begin{pmatrix} u_0 \\ u_{\mathbf{h}} \end{pmatrix} = \exp\left\{ i \begin{pmatrix} 0 & V^*(\mathbf{h}) \\ V(\mathbf{h}) & K_{\mathbf{h}} \end{pmatrix} T \right\} \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \qquad (5.2.7.1)$$

If this expression is expanded directly as a Taylor series, it proves surprisingly difficult to sum. However, the symmetries of Clifford algebra can be exploited by summing in a Pauli basis thus,

$$\exp\left\{ i \begin{pmatrix} 0 & V^*(\mathbf{h}) \\ V(\mathbf{h}) & K_{\mathbf{h}} \end{pmatrix} T \right\}$$

$$= \exp\left\{ i\frac{K_{\mathbf{h}}T}{2} \right\} \mathbf{E} \exp\left\{ i\left(\frac{K_{\mathbf{h}}}{2}\boldsymbol{\sigma}_3 + V^{\mathrm{R}}\boldsymbol{\sigma}_1 - V^{\mathrm{I}}\boldsymbol{\sigma}_2 \right)T \right\}.$$

Here, the $\boldsymbol{\sigma}_i$ are the Pauli matrices

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \ \boldsymbol{\sigma}_3 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix},$$

$$\mathbf{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

and V^{R}, V^{I} are the real and imaginary parts of the complex scattering coefficients appropriate to a noncentrosymmetric crystal, *i.e.* $V_{\mathbf{h}} = V^{\mathrm{R}} + iV^{\mathrm{I}}$. Expanding,

$$\exp\left\{ i\left(\frac{K_{\mathbf{h}}}{2}\boldsymbol{\sigma}_3 + V^{\mathrm{R}}\boldsymbol{\sigma}_1 - V^{\mathrm{I}}\boldsymbol{\sigma}_2 \right)T \right\}$$

$$= \mathbf{E} + i\left(\frac{K_{\mathbf{h}}}{2}\boldsymbol{\sigma}_3 + V^{\mathrm{R}}\boldsymbol{\sigma}_1 - V^{\mathrm{I}}\boldsymbol{\sigma}_2 \right)T$$

$$- \frac{1}{2}\left(\frac{K_{\mathbf{h}}}{2}\boldsymbol{\sigma}_3 + V^{\mathrm{R}}\boldsymbol{\sigma}_1 - V^{\mathrm{I}}\boldsymbol{\sigma}_2 \right)^2 T^2 + \dots,$$

using the anti-commuting properties of $\boldsymbol{\sigma}_i$:

$$\left. \begin{aligned} \boldsymbol{\sigma}_i\boldsymbol{\sigma}_j + \boldsymbol{\sigma}_j\boldsymbol{\sigma}_i &= 0 \\ \boldsymbol{\sigma}_i\boldsymbol{\sigma}_i &= 1 \end{aligned} \right\}$$

and putting $[(K_{\mathbf{h}}/2)^2 + V(\mathbf{h})V^*(\mathbf{h})] = \Omega$, $\mathbf{M}_2 = [(K_{\mathbf{h}}/2)\boldsymbol{\sigma}_3 + V^{\mathrm{R}}\boldsymbol{\sigma}_1 - V^{\mathrm{I}}\boldsymbol{\sigma}_2]$, so that $\mathbf{M}_2^2 = \Omega\mathbf{E}$ and $\mathbf{M}_2^3 = \Omega\mathbf{M}_2$, the powers of the matrix can easily be evaluated. They fall into odd and even series, corresponding to sine and cosine, and the classical two-beam approximation is obtained in the form

$$\mathbf{Q}_2 = \exp\{i(K_{\mathbf{h}}/2)T\}\mathbf{E}\left[(\cos \Omega^{1/2}T)\mathbf{E} + i\left(\frac{\sin \Omega^{1/2}T}{\Omega^{1/2}} \right)\mathbf{M}_2 \right].$$

$$(5.2.7.2)$$

This result was first obtained by Blackman (1939), using Bethe's dispersion formulation. Ewald and, independently, Darwin, each with different techniques, had, in establishing the theoretical foundations for X-ray diffraction, obtained analogous results (see Section 5.1.3).

The two-beam approximation, despite its simplicity, exemplifies some of the characteristics of the full dynamical theory, for instance in the coupling between beams. As Ewald pointed out, a formal analogy can be found in classical mechanics with the motion of coupled pendulums. In addition, the functional form $(\sin ax)/x$, deriving from the shape function of the crystal emerges, as it does, albeit less obviously, in the N-beam theory.

This derivation of equation (5.2.7.2) exhibits two-beam diffraction as a typical two-level system having analogies with, for instance, lasers and nuclear magnetic resonance and exhibiting the symmetries of the special unitary group SU(2) (Gilmore, 1974).

5.2.8. Eigenvalue approach

In terms of the eigenvalues and eigenvectors, defined by

$$\mathbf{H}_{\mathrm{p}}|j\rangle = \gamma_j|j\rangle,$$

the evolution operator can be written as

$$\mathbf{U}(z, z_0) = \int |j\rangle \exp\{\gamma_j(z - z_0)\}\langle j| \, \mathrm{d}j.$$

This integration becomes a summation over discrete eigen states when an infinitely periodic potential is considered.

Despite the early developments by Bethe (1928), an N-beam expression for a transmitted wavefunction in terms of the eigenvalues and eigenvectors of the problem was not obtained until Fujimoto (1959) derived the expression

$$U_{\mathbf{h}} = \sum_j \psi_0^{j*} \psi_{\mathbf{h}}^j \exp\{-i2\pi\gamma_j T\}, \qquad (5.2.8.1)$$

where $\psi_{\mathbf{h}}^j$ is the h component of the j eigenvector with eigenvalue γ_j.

This expression can now be related to those obtained in the other formulations. For example, Sylvester's theorem (Frazer *et al.*, 1963) in the form

$$f(\mathbf{M}) = \sum_j \mathbf{A}_j f(\gamma_j)$$

when applied to Sturkey's solution yields

$$\boldsymbol{\Phi}_{\mathbf{h}} = \exp(i\mathbf{M}_{\mathrm{p}}z) = \sum \mathbf{P}_j \exp\{i2\pi\gamma_j z\}$$

(Kainuma, 1968; Hurley *et al.*, 1978). Here, the $\mathbf{P}_j$ are projection operators, typically of the form

$$\mathbf{P}_j = \prod_{n \neq j} \frac{(\mathbf{M}_{\mathrm{p}} - \mathbf{E}\gamma_n)}{\gamma_j - \gamma_n}.$$

On changing to a lattice basis, these transform to $\psi_0^{j*}\psi_{\mathbf{h}}^j$.

Alternatively, the semi-reciprocal differential equation can be uncoupled by diagonalizing $\mathbf{M}_{\mathrm{p}}$ (Goodman & Moodie, 1974), a process which involves the solution of the characteristic equation

$$|\mathbf{M}_{\mathrm{p}} - \gamma_j \mathbf{E}| = 0. \qquad (5.2.8.2)$$

5.2.9. Translational invariance

An important result deriving from Bethe's initial analysis, and not made explicit in the preceding formulations, is that the fundamental symmetry of a crystal, namely translational invariance, by itself imposes a specific form on wavefunctions satisfying Schrödinger's equation.

Suppose that, in a one-dimensional description, the potential in a Hamiltonian $\mathbf{H}_t(x)$ is periodic, with period t. Then,

$$\varphi(x + t) = \varphi(x)$$

and

$$\mathbf{H}_t \psi(x) = \mathbf{E}\psi(x).$$

Now define a translation operator

$$\Gamma f(x) = f(x + t),$$

for arbitrary $f(x)$. Then, since $\Gamma\varphi(x) = \varphi(x)$, and ∇^2 is invariant under translation,

$$\Gamma \mathbf{H}_t(x) = \mathbf{H}_t(x)$$

and

$$\Gamma \mathbf{H}_t(x)\psi(x) = \mathbf{H}_t(x + t)\psi(x + t) = \mathbf{H}_t(x)\Gamma\psi(x).$$

Thus, the translation operator and the Hamiltonian commute, and therefore have the same eigenfunctions (but not of course the same eigenvalues), i.e.

$$\Gamma\psi(x) = \alpha\psi(x).$$

This is a simpler equation to deal with than that involving the Hamiltonian, since raising the operator to an arbitrary power simply increments the argument

$$\Gamma^m \psi(x) = \psi(x + mt) = \alpha^m \psi(x).$$

But $\psi(x)$ is bounded over the entire range of its argument, positive and negative, so that $|\alpha| = 1$, and α must be of the form $\exp\{i2\pi kt\}$.

Thus, $\psi(x + t) = \Gamma\psi(x) = \exp\{i2\pi kt\}\psi(x)$, for which the solution is

$$\psi(x) = \exp\{i2\pi kt\}q(x)$$

with $q(x + t) = q(x)$.

This is the result derived independently by Bethe and Bloch. Functions of this form constitute bases for the translation group, and are generally known as Bloch functions. When extended in a direct fashion into three dimensions, functions of this form ulti-

mately embody the symmetries of the Bravais lattice; i.e. Bloch functions are the irreducible representations of the translational component of the space group.

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 (2004, 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 (2004, 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

$$U_n(h, k) = \sum_l \sum_{h_1 k_1 l_1} \ldots \sum_{h_{n-1} k_{n-1} l_{n-1}} i^n V(h_1, k_1, l_1)$$
$$\ldots V\left(h - \sum_{r=1}^{n-1} h_r, k - \sum_{r=1}^{n-1} k_r, l - \sum_{r=1}^{n-i} l_r\right)$$
$$\times [\exp\{-2\pi i\zeta T\}/(2\pi i)^n]$$
$$\times \left(\exp\{i\pi\zeta T\}(\sin \pi\zeta T/\zeta)\big[(\zeta - \zeta_1)\ldots(\zeta - \zeta_{n-1})\big]^{-1}\right.$$
$$+ \sum_{m=1}^{n-1} \exp\{i\pi\zeta_m T\}(\sin \pi\zeta_m T/\zeta_m)\big[(\zeta_m - \zeta_1)$$
$$\left.\ldots(\zeta_m - \zeta_{m-1})(\zeta_m - \zeta_{m+1})\ldots(\zeta_m - \zeta)\big]^{-1}\right)$$
$$(5.2.13.1a)$$

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

$$U_n = \sum_{r=0}^{\infty} E_n(h)\big[(2\pi iT)^{n+r}/(n+r)!\big]h_r(\zeta, \zeta_1 \ldots \zeta_{n-1}), \quad (5.2.13.1b)$$

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

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

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 (2004, 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.

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