

## 5. DYNAMICAL THEORY AND ITS APPLICATIONS

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

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

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 Gratiias & 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

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

or

$$\mathbf{U}(z, z_0) = 1 - i \int_{z_0}^z \mathbf{U}(z, z_1) \mathbf{H}(z_1) dz_1. \quad (5.2.4.1b)$$

**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

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

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

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

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

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

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

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

where

$$\begin{aligned} \mathbf{M}^\pm(z) &= \pm [\mathbf{K} + (1/2)\mathbf{K}^{-1}V(z)], \\ [K_{ij}] &= \delta_{ij}K_i, \end{aligned}$$

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 wavevector, 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  $\theta_i$  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

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$$|U\rangle = \exp\{i\mathbf{M}_p T\}|0\rangle \quad (5.2.6.2)$$

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.

$$\mathbf{S} = \exp\{i\mathbf{M}_p T\}$$

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

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

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,

$$\begin{aligned} & \exp\left\{i\begin{pmatrix} 0 & V^*(\mathbf{h}) \\ V(\mathbf{h}) & K_h \end{pmatrix} T\right\} \\ &= \exp\left\{i\frac{K_h T}{2}\right\} \mathbf{E} \exp\left\{i\left(\frac{K_h}{2}\sigma_3 + V^R\sigma_1 - V^I\sigma_2\right) T\right\}. \end{aligned}$$

Here, the  $\sigma_i$  are the Pauli matrices

$$\begin{aligned} \sigma_1 &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \\ \mathbf{E} &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \end{aligned}$$

and  $V^R, V^I$  are the real and imaginary parts of the complex scattering coefficients appropriate to a noncentrosymmetric crystal, *i.e.*  $V_h = V^R + iV^I$ . Expanding,

$$\begin{aligned} & \exp\left\{i\left(\frac{K_h}{2}\sigma_3 + V^R\sigma_1 - V^I\sigma_2\right) T\right\} \\ &= \mathbf{E} + i\left(\frac{K_h}{2}\sigma_3 + V^R\sigma_1 - V^I\sigma_2\right) T \\ & \quad - \frac{1}{2}\left(\frac{K_h}{2}\sigma_3 + V^R\sigma_1 - V^I\sigma_2\right)^2 T^2 + \dots, \end{aligned}$$

using the anti-commuting properties of  $\sigma_i$ :

$$\begin{cases} \sigma_i \sigma_j + \sigma_j \sigma_i = 0 \\ \sigma_i \sigma_i = 1 \end{cases}$$

and putting  $[(K_h/2)^2 + V(\mathbf{h})V^*(\mathbf{h})] = \Omega$ ,  $\mathbf{M}_2 = [(K_h/2)\sigma_3 + V^R\sigma_1 - V^I\sigma_2]$ , 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

$$\mathbf{Q}_2 = \exp\{i(K_h/2)T\} \mathbf{E} \left[ (\cos \Omega^{1/2} T) \mathbf{E} + i \left( \frac{\sin \Omega^{1/2} T}{\Omega^{1/2}} \right) \mathbf{M}_2 \right]. \quad (5.2.7.2)$$

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

$$\mathbf{H}_p |j\rangle = \gamma_j |j\rangle,$$

the evolution operator can be written as

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

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

$$U_h = \sum_j \psi_0^{j*} \psi_h^j \exp\{-i2\pi\gamma_j T\}, \quad (5.2.8.1)$$

where  $\psi_h^j$  is the  $h$  component of the  $j$  eigenvector with eigenvalue  $\gamma_j$ .

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

$$\Phi_h = \exp(i\mathbf{M}_p z) = \sum \mathbf{P}_j \exp\{i2\pi\gamma_j z\}$$

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

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