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5.2. Dynamical theory of electron diffraction

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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

$$\nabla^2\psi_b + \frac{8\pi^2 m|e|\varphi}{h^2}\psi_b + \frac{8\pi^2 m_0|e|W}{h^2}\left(1+\frac{|e|W}{2m_0c^2}\right)\psi_b = 0.$$

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, $|e|$,

$$\lambda = h[2m_0eW(1 + eW/2m_0c^2)]^{-1/2},$$

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

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

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

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

where

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

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,

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

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

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

The equation for ψ^{+} 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,

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

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 (5.2.4.1*b*) 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 (5.2.4.1*a*).

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 (5.2.6.1*b*) 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 (5.2.6.1*a*,*b*) now in semi-reciprocal space, and define an operator $\mathbf{Q}(z)$ [compare with equation (5.2.4.1*a*)] 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 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

$$|U\rangle = \exp\{i\mathbf{M}_pT\}|0\rangle \qquad (5.2.6.2)$$

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.

$$\mathbf{S} = \exp\{i\mathbf{M}_pT\}$$

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,

$$\exp\left\{i\begin{pmatrix} 0 & V^*(\mathbf{h}) \\ V(\mathbf{h}) & K_{\mathbf{h}} \end{pmatrix}T\right\}$$
$$= \exp\left\{i\frac{K_{\mathbf{h}}T}{2}\right\}\mathbf{E}\exp\left\{i\left(\frac{K_{\mathbf{h}}}{2}\boldsymbol{\sigma}_3 + V^R\boldsymbol{\sigma}_1 - V^I\boldsymbol{\sigma}_2\right)T\right\}.$$

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,

references