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

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

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

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,

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

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,

$$\begin{aligned} &\exp\left\{ i\left(\frac{K_\mathbf{h}}{2}\boldsymbol{\sigma}_3 + V^\mathrm{R}\boldsymbol{\sigma}_1 - V^\mathrm{I}\boldsymbol{\sigma}_2 \right) T \right\} \\ &\quad = \mathbf{E} + i\left(\frac{K_\mathbf{h}}{2}\boldsymbol{\sigma}_3 + V^\mathrm{R}\boldsymbol{\sigma}_1 - V^\mathrm{I}\boldsymbol{\sigma}_2 \right) T \\ &\qquad - \frac{1}{2}\left(\frac{K_\mathbf{h}}{2}\boldsymbol{\sigma}_3 + V^\mathrm{R}\boldsymbol{\sigma}_1 - V^\mathrm{I}\boldsymbol{\sigma}_2 \right)^2 T^2 + \ldots, \end{aligned}$$

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

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

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

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

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 $\mathbf{M}_{\rm p}$ (Goodman & Moodie, 1974), a process which involves the solution of the characteristic equation

$$|\mathbf{M}_{\rm p} - \gamma_j \mathbf{E}| = 0. \tag{5.2.8.2}$$

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

$$\mathbf{\Gamma} f(x) = f(x + t),$$

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

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

and

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

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

$$\mathbf{\Gamma}\psi(x) = \alpha\psi(x).$$

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

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

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, $\psi(x + t) = \mathbf{\Gamma}\psi(x) = \exp\{i2\pi kt\}\psi(x)$, 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 ultimately 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

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

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)].