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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

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

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 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

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

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.

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

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,

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

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, *i.e.* $V_{\mathbf{h}} = V^R + iV^I$. Expanding,

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

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 $[(K_{\mathbf{h}}/2)^2 + V(\mathbf{h})V^*(\mathbf{h})] = \Omega$, $\mathbf{M}_2 = [(K_{\mathbf{h}}/2)\boldsymbol{\sigma}_3 + V^R\boldsymbol{\sigma}_1 - V^I\boldsymbol{\sigma}_2]$, 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

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

the evolution operator can be written as

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

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

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

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

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

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

$$|\mathbf{M}_p - \gamma_j\mathbf{E}| = 0. \tag{5.2.8.2}$$

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

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

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

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

and

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

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

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

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

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

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

references