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# Time-Like Perturbation Method in High-Energy Electron Diffraction

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## Abstract

The small-angle approximation usually encountered in dynamical theories of fast electrons essentially leads to a transformation of the propagation-direction variable $z$ into a time-like parameter [Berry (1971). *J. Phys. C*, 4, 697–722]. The three-dimensional stationary Schrödinger equation is then approximated by a two-dimensional 'time'-dependent equation which may be solved by using the standard time-perturbation techniques encountered in quantum mechanics. The basic idea of the present approach consists in studying the evolution operator $U(z,z_0)$ instead of the wave function. Depending on the choice of bases, the matrix elements of $U(z,z_0)$ represent either the transition probabilities of diffraction or the kernel function of the propagation issued from Feynman-path integral theory [Berry & Mount (1972). *Rep. Prog. Phys.* 35, 315–397; Van Dyck (1975). *Phys. Status Solidi,* 72, 321–336;
Jap & Glaeser (1978). *Acta Cryst.* A34, 94–102]. Special attention is devoted to the so-called 'Bloch waves' and 'physical-optics' formulations which both correspond to the same perturbation expansion but with two different unperturbed 'Hamiltonians'.

## I. Introduction

The dynamical theory of elastic scattering of fast electrons is of great importance for the understanding of contrast formation in electron microscopy and diffraction images. The methods which have been derived in the past twenty years may be classified in two general classes, those formally considering the crystal as an infinite three-dimensional medium (Bethe, 1928; Darwin, 1914) and those considering the crystal as an infinite number of successive planes of infinitesimal thickness (Cowley & Moodie, 1957a,b).

Several discussions have clearly demonstrated the equivalence of these two types of approaches for small-angle scattering (Goodman & Moodie, 1974; Moodie, 1981; Van Dyck, 1980; Buxton, 1979).

The purpose of the present paper is to derive a simple formalism based on quantum-mechanical perturbation theory.

## II. Evolution operator for small-angle elastic scattering

The basic equation for time-independent elastic scattering is given by (in relativistic units) (Fujiwara, 1961)

$$(\nabla^2 + k_0^2)\,\Psi = V\Psi, \tag{1}$$

where $k_0$ is the relativistic wave vector and $V$ the corrected scattering potential given respectively by

$$k_0 = \frac{1}{\hbar}\left(2m_0E + \frac{E^2}{c^2}\right)^{1/2} \tag{2}$$

$$V = 2\left(m_0 + \frac{E}{c^2}\right)v(r)/\hbar^2. \tag{3}$$

Let $z$ be the optical axis assumed to be close to the initial propagation direction $k_0$ and let $K$ be the component of $k_0$ along $z$ and $\chi$ the component of $k_0$ in the $x,y$ plane (Fig. 1).
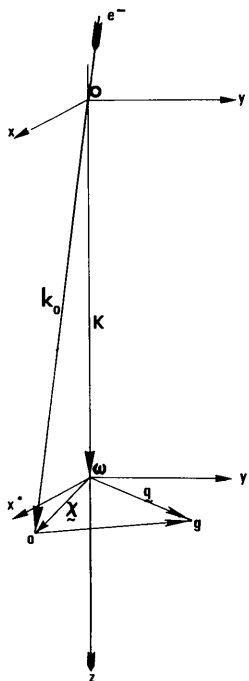


Fig. 1. The $x,y$ plane is defined by the entrance surface of the sample and is supposed to be nearly perpendicular to $k_0$. The small-angle-scattering approximation consists in assuming that the large component $K$ of $k_0$ along $z$ remains almost unchanged during the scattering. The small component $\chi$ of $k_0$ in the $x,y$ plane corresponds to the obliquity of the incident wave.

Extracting the chief component of the $z$ dependence of $\Psi$ in the form

$$\Psi = \psi \exp(iKz) \tag{4}$$

and neglecting the second derivative of $\psi$ with respect to $z$, one obtains

$$i\frac{\partial}{\partial z}\,\psi = \frac{1}{2K}\left(-\nabla^2_{x,y} - \chi^2 + V\right)\psi. \tag{5}$$

Equation (5) makes explicit use of the fact that the scattering potential is sufficiently small with respect to the incident energy that the component of the motion along $z$ remains almost unchanged during the scattering process. Equation (5) is formally similar to a Schrödinger equation for a two-dimensional system with a time-dependent potential (Berry, 1971).

The causal evolution operator $U(z,z_0)$ with respect to $z$ is defined by

$$i\frac{\partial}{\partial z}\,U(z,z_0) = H(z)\,U(z,z_0) \tag{6}$$

or

$$U(z,z_0) = 1 - i\int_{z_0}^{z} U(z,\tau)\,H(\tau)\,\mathrm{d}\tau. \tag{7}$$

$H(z)$ is the 'Hamiltonian' of the 2D system:

$$H(z) = \frac{1}{2K}\left(-\nabla^2 - \chi^2 + V\right), \tag{8}$$

where $\nabla^2$ stands for the 2D Laplacian.

In the 2D configurational space the eigenvectors $|\rho_0\rangle$ and $|q_0\rangle$ of position $\rho_0$ and momentum $q_0$ are

$$\langle\rho|\rho_0\rangle = \delta(\rho - \rho_0) \tag{9}$$

$$\langle\rho|q_0\rangle = \exp i q_0 \cdot \rho, \tag{10}$$

where, in (10), the normalization constant $1/2\pi$ has been dropped for simplicity.

As usual, the Hermitian scalar product is defined by

$$\langle\psi|\rho_0\rangle = \psi(\rho_0) = \int \psi(\rho)\,\delta(\rho - \rho_0)\,\mathrm{d}^2\rho \tag{11}$$

in the $\{\rho\}$ representation, and

$$\langle\psi|q_0\rangle = \mathscr{F}(\psi) \tag{12}$$

with

$$\mathscr{F}(\psi) = \int \psi(\rho)\exp(i q_0 \cdot \rho)\,\mathrm{d}^2\rho \tag{13}$$

in the $\{q\}$ representation.

The initial state, say $|0\rangle$, is an eigenvector of the $q$ momentum corresponding to the projection of $k_0$ in the $x,y$ plane:

$$\langle\rho|0\rangle = \langle\rho|\chi\rangle = \exp(i\chi\rho). \tag{14}$$

In these standard bracket notations, diffraction and

images correspond to the following transition probabilities:

$$\{q\}; \omega_{0 \to q}(z, z_0) = |\langle q | U(z, z_0) | 0 \rangle|^2 \qquad (15)$$

$$\{p\}; \omega_{0 \cdot p}(z, z_0) = |\int \langle p | q \rangle F(\mathbf{q})$$
$$\times \langle q | U(z, z_o) | 0 \rangle \, d^2 q|^2, \qquad (16)$$

where, in (16), $F(\mathbf{q})$ stands for the filter function* due to the different aberrations of the microscope (objective aperture, spherical aberration, defocus, astigmatism, ...).

The purpose of the dynamical theories of high-energy electron diffraction consists in finding some approximate solutions of the master equation (6). Subsequent use of (15) or (16) will lead to the diffraction or image intensities.

Both initial and final states $|0\rangle$ and $|q\rangle$ (which correspond to the usual boundary conditions) are known; the only remaining problem consists in the determination of the transition probabilities from the initial to the final states.

Equation (6) may generally not be integrated analytically and standard time-dependent perturbation theory has to be used: we will see in § IV that the perturbation series leads to the Cowley–Moodie (1957a,b) formulation when the unperturbed Hamiltonian is the free propagator. In § III we will derive some of the possible solutions for $U(z, z_0)$ when the potential is $z$ independent or when the sudden-perturbation approximation may be used.

### III. Special integrated expressions of the $z$-evolution operator

III-1. *Projected potential and free propagation approximations*

If $H(z)$ and $(\partial/\partial z) H(z)$ commute, $U(z, z_0)$ takes the simple form

$$U(z, z_0) = \exp - i \int_{z_0}^{z} H(\tau) \, d\tau. \qquad (17)$$

The commutation relation

$$\left[ H(z), \frac{\partial}{\partial z} H(z) \right] = 0 \qquad (18)$$

is certainly satisfied if the potential $V$ is assumed to be $z$ independent. In practical cases this assumption consists in replacing the actual potential $V(\tau)$ by the projected average potential $\bar{V}$:

$$\bar{V} = \frac{1}{z - z_0} \int_{z_0}^{z} V(\tau) \, d\tau. \qquad (19)$$

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* For a non-linear transfer, $F(\mathbf{q})$ is no longer diagonal on the $\{q\}$ basis.

The approximate Hamiltonian is then

$$H \simeq \frac{1}{2K} (-\nabla^2 - \chi^2 + \bar{V}). \qquad (20)$$

Substituting (20) in (17) we obtain the $z$-evolution operator

$$U(z, z_0) = \exp[-iH(z - z_0)]. \qquad (21)$$

Designating by $|j\rangle$ and $\gamma_j$ the eigenvectors and eigenvalues of $H$,

$$H|j\rangle = \gamma_j |j\rangle, \qquad (22)$$

we obtain the standard form of the $z$-evolution operator (see, for instance, Messiah, 1965):

$$U(z, z_0) = \int |j\rangle \exp[-i\gamma_j(z - z_0)]\langle j| \, dj. \qquad (23)$$

In $\{q\}$ representation (22) can be written

$$\left( \frac{q^2 - \chi^2}{2K} - \gamma_j \right) \langle q | j \rangle$$
$$+ \frac{1}{2K} \int \langle q | \bar{V} | q' \rangle \langle q' | j \rangle \, dq' = 0, \qquad (24)$$

where $\langle q | j \rangle$ is the Fourier transform of $|j\rangle$ and $\langle q | \bar{V} | q' \rangle$ the 2D Fourier coefficient of the projected potential $\bar{V}$ for the $\mathbf{q}' - \mathbf{q}$ vector. If $\bar{V}$ is periodic in the $(x, y)$ plane, then the matrix elements are discrete and so are the $|j\rangle$'s and $\gamma_j$'s. Equation (24) may then be solved from the usual eigenvalue equation,

$$\det(M - \gamma I) = 0, \qquad (25)$$

where $I$ is the identity matrix and $M$ the so-called scattering matrix defined by (Tournarie, 1960, 1961, 1962)

$$M_{ij} = \frac{q_j^2 - \chi^2}{2K} \delta_{ij} + \frac{1}{2K} \bar{V}_{q_j - q_i}. \qquad (26)$$

One recognizes here the Sturkey (1962) formulation. The $|j\rangle$ eigenfunctions are the usual Bloch waves (for periodic $x, y$ potential) of the two-dimensional system whereas the eigenvalues are the *Anpassung* parameters (see, for instance, Hirsch, Howie, Nicholson, Pashley & Whelan, 1965).

The transition probability from state $|0\rangle$ to state $|q\rangle$, which is usually designated by $|\varphi_q|^2$, is directly obtained from (23):

$$|\varphi_q|^2 = |\langle q | U(z, z_0) | 0 \rangle|^2$$
$$= |\int \exp[-i\gamma_j(z - z_0)] \langle q | j \rangle \langle j | 0 \rangle \, dj|^2. \qquad (27)$$

For an $(x, y)$ periodic crystal the probability amplitude $\varphi_q$ is

$$\varphi_q = \sum_j \exp[-i\gamma_j(z - z_0)] \langle q | j \rangle \langle j | 0 \rangle, \qquad (28)$$

where $\langle q | j \rangle$ and $\langle j | 0 \rangle$ are respectively the component

of the $|q\rangle$ state on the $|j\rangle$ state and of the $|j\rangle$ state on the $|0\rangle$ state. These components are generally denoted by (Howie & Whelan, 1961)

$$\langle q|j\rangle = C_q^j; \quad \langle j|0\rangle = C_0^{*j}. \tag{29}$$

A special case arises when the potential $\bar{V}$ vanishes: this corresponds to the free propagation in vacuum. The Hamiltonian $H^0$ becomes then

$$H^0 = \frac{1}{2K}(-\nabla^2 - \chi^2) \tag{30}$$

and is diagonal on the $\{q\}$ basis

$$H^0|q\rangle = \frac{q^2 - \chi^2}{2K}|q\rangle. \tag{31}$$

The corresponding $U^0(z - z_0)$ evolution operator may be written as [from (23)]

$$U^0(z,z_0) = \int |q\rangle \exp\left[-i\frac{q^2 - \chi^2}{2K}(z - z_0)\right]\langle q| \, dq. \tag{32}$$

This operator is one of the basic ingredients of the multislice method and is called the propagator. Expressed in direct space (on the $\{\rho\}$ basis) the propagator is no longer diagonal and can be written as

$$\langle\rho_1|U^0(z,z_0)|\rho_0\rangle = \int \langle\rho_1|q\rangle\langle q|U^0(z,z_0)|q\rangle\langle q|\rho_0\rangle \, dq \tag{33}$$

leading to

$$\langle\rho_1|U^0(z,z_0)|\rho_0\rangle = C^{te} \exp\left[i\frac{K(\rho_1 - \rho_0)^2}{2(z - z_0)}\right], \tag{34}$$

which corresponds to the Fresnel propagator initially introduced by Cowley & Moodie (1957a,b) in the 'physical optics' approach (see Cowley, 1975).

### III-2. The sudden-perturbation approximation

For very short interaction times (here for very thin crystals), the sudden-perturbation approximation may be used, stipulating that the evolution operator may be approximated by the identity

$$U^0(z,z_0) \simeq I. \tag{35}$$

The perturbed evolution operator $U(z,z_0)$ is then expanded in a perturbation series:

$$U(z,z_0) = U^0(z,z_0) + \sum_{n=1}^{\infty} U^{(n)}(z,z_0), \tag{36}$$

where the $n$th-order term has the general form

$$U^{(n)}(z,z_0) = (-i)^n \int_{z \geq \tau_n \geq \tau_{n-1} \geq \ldots \geq \tau_1 \geq z_0} d\tau_n d\tau_{n-1} \ldots d\tau_1$$
$$\times U^0(z,\tau_n) V(\tau_n) U^0(\tau_n,\tau_{n-1}) \times \ldots$$
$$\times U^0(\tau_2,\tau_1) V(\tau_1) U^0(\tau_1,z_0). \tag{37}$$

We will come back to this general standard formula in § IV. For the present context, introducing (35) into (37), we simply obtain

$$U^{(n)}(z,z_0) = (-i)^n I^{n+1} \int_{z \geq \tau_n \geq \tau_{n-1} \geq \ldots \geq \tau_1 \geq z_0} V(\tau_n)$$
$$\times V(\tau_{n-1}) \ldots V(\tau_1) \, d\tau_n d\tau_{n-1} \ldots d\tau_1, \tag{38}$$

which, after some algebraic manipulations, leads to

$$U^{(n)}(z,z_0) = \frac{(-i)^n}{n!} I^{n+1} \left[\int_{z_0}^{z} V(\tau) \, d\tau\right]^n. \tag{39}$$

Then, from (36), the perturbed evolution operator reduces to

$$U(z,z_0) = I \exp -i\int_{z_0}^{z} V(\tau) I \, d\tau. \tag{40}$$

This operator is diagonal on the $\rho$ basis with eigenvalues $\exp -i\int_{z_0}^{z} V(\rho,z) \, d\tau$, where $\rho$ explicitly defines the $x,y$ dependence of $V$:

$$U(z,z_0) = \int |\rho\rangle \exp -i\int_{z_0}^{z} V(\rho,z) \, d\tau\langle\rho| \, d\rho. \tag{41}$$

This operator (41), which we call the diffractor, corresponds to the usual phase-grating approximation: it is the perturbed evolution operator in the sudden-perturbation approximation. In the first order, it simplifies to

$$U(z,z_0) = \int |\rho\rangle \left[1 - i\int_{z_0}^{z} V(\rho,z)\right]\langle\rho| \, d\rho, \tag{42}$$

which is the so-called weak-phase-object approximation; in this approximation only one interaction is supposed to occur between $z_0$ and $z$, meaning that the perturbation potential is very small with respect to the incident energy and that the crystal is thin enough for the sudden perturbation to be valid. In order to have a criterion of validity for such an approximation we can expend the evolution operator in a Born-like series. From (7),

$$U(T,0) = 1 - i^{-1} T\int_{0}^{T} H(\tau) \, d\tau + (i)^{-2} T^2 \int_{0}^{T} d\tau_1$$
$$\times \int_{0}^{\tau_1} d\tau_2 H(\tau_1) H(\tau_2) + \ldots, \tag{43}$$

where it has been assumed that the Hamiltonian $H^0$ for $z < z_0 = 0$, suddenly changes to $H^0 + V$ during the passage of the electrons through a crystal of thickness $T$ and then back to $H^0$ for $z > T$. Since the sudden perturbation consists in approximating the final state $|f\rangle$ as equal to the initial one, $|0\rangle$, simply multiplied by a phase factor,

$$|f\rangle = U(T,0)|0\rangle \simeq \exp(i\theta)|0\rangle, \tag{44}$$

we may calculate the probability $\omega$ of finding the system in a state different from $|0\rangle$ and determine the thickness such that this probability is negligible. Then, let $Q$ be the operator of projection on the space orthogonal to $|0\rangle$:

$$Q = I - |0\rangle\langle 0|. \qquad (45)$$

The probability $\omega$ is then

$$\omega = |\langle 0|U^+(t,0) \, QU(T,0)|0\rangle|^2 \qquad (46)$$

and has to be small with respect to 1.

Replacing now $U(T,0)$ by (43), we obtain, to second order in $T$,

$$\omega = T^2\{\langle 0|\bar{H}^2|0\rangle - \langle 0|\bar{H}|0\rangle^2\} + T^3 \ldots, \qquad (47)$$

where $\bar{H} = \int_0^T H(\tau)\,d\tau$ and $H(\tau)$ is given by (8). Choosing as initial state $|0\rangle$ the plane wave

$$\langle \rho|0\rangle = \exp(i\boldsymbol{\chi}\boldsymbol{\rho}), \qquad (48)$$

and assuming the potential to be periodic in the $x,y$ plane, we obtain finally

$$T \ll \frac{2K}{\left(\displaystyle\sum_{g \neq 0} |\bar{V}_g|^2\right)^{1/2}}, \qquad (49)$$

where the $\bar{V}_g$ are the two-dimensional Fourier coefficients of the projected potential $\bar{V}(\boldsymbol{\rho})$. Condition (49) stipulates the range of validity of the phase-grating approximation. As expected, this approximation is better for increasing voltage and for atoms of low atomic number.

### III-3. The multislice method (Goodman & Moodie, 1974)

Initially considered as an approximate expression suitable for numerical calculations of the Cowley–Moodie expansion (see § IV-2), the multislice method consists of successive and repeated use of propagator and diffractor: the crystal is considered as a stacking sequence of 'slices' separated by vacuum. In each slice the scattering is treated as a sudden perturbation; the thickness of the slice is chosen to be thin enough for inequality (49) to be satisfied. Between two successive slices the free propagator $U^0$ is used.

$$U_{MS}(nT) = U_0(T) \, U_d^{(n)}(T) \ldots U_0(T) \, U_d^{(2)}(T)$$
$$\times \, U_0(T) \, U_d^{(1)}(T). \qquad (50)$$

### IV. Approximate evolution operator for $z$-dependent potential

For a $z$-dependent potential the integrated form (17) is no longer valid. One has therefore either to evaluate the differential equation (7) numerically step by step or to expand $U(z,z_0)$ in a perturbation series. The first case corresponds to the so-called Darwin (1914) approach, while the second one leads either to the Cowley–Moodie formulation or to a slightly modified form of the Buxton (1976) approach according to the type of the chosen unperturbed Hamiltonian.

### IV-1. The Darwin-type approach (Darwin, 1914)

In order to integrate (7) numerically, $U(z,z_0)$ has to be expressed on an appropriate basis. The natural one is the $q$ basis since the initial state is an eigenvector of the $q$ momentum. Choosing, for simplicity, $z_0 > 0$, we obtain

$$i\frac{\partial}{\partial z} \langle q|U(z)|0\rangle = \frac{q^2 - \chi^2}{2K} \langle q|U(z)|0\rangle$$
$$+ \frac{1}{2K} \int \langle q|V(z)|q'\rangle$$
$$\times \langle q'|U(z)|0\rangle \, dq'. \qquad (51)$$

The amplitudes of transition probability from the initial state $|0\rangle$ to the final state $|q\rangle$ are usually denoted by $\varphi_q(z)$:

$$\varphi_q(z) = \langle q|U(z)|0\rangle. \qquad (52)$$

For an $x,y$ periodic potential the only non-zero transition probabilities are those corresponding to the nodes of the 2D reciprocal lattice; (51) then becomes

$$\frac{\partial}{\partial z} \varphi_g(z) = i\pi\left[2\zeta(g)\,\varphi_g(z) + \sum_{g'} v_{g-g'}(z)\,\varphi_{g'}(z)\right], \qquad (53)$$

where

$$\zeta(g) = \frac{\chi^2 - (\chi + g)^2}{4\pi K};$$

$$v_{g-g'}(z) = -\frac{\langle g|V(z)|g'\rangle^*}{2\pi K} \qquad (54)$$

are the usual 2D excitation-error parameter and reduced 2D scattering potential, respectively, both well-known in the Darwin theory.

### IV-2. General perturbation expansion

The general Hamiltonian may be written as a sum of a $z$-independent operator $H^0$ plus a $z$-dependent perturbation $W(z)$:

$$H(z) = H^0 + W(z).$$

Two natural choices are possible for $H^0$ and $W(z)$:
(i) If $H^0$ is simply the free propagator Hamiltonian

$$H^0 = \frac{1}{2K}(-\nabla^2 - \chi^2), \qquad (55)$$

then the perturbation term is the whole potential

$$W(z) = \frac{V(z)}{2K};\qquad (56)$$

the unperturbed eigenfunctions, eigenvalues and evolution operator are respectively the plane waves $|q\rangle$, the excitation errors $(q^2 - \chi^2)/2K$ and the free propagator (32).

(ii) If $H^0$ is the sum of the free propagator plus the projected potential (or average potential)

$$H_0 = \frac{1}{2K}(-\nabla^2 - \chi^2 + \bar{V})\qquad (57)$$

then the perturbation term is the oscillating part of the potential along $z$

$$W(z) = [V(z) - \bar{V}]/2K \qquad (58)$$

and the eigenfunctions, eigenvalues and unperturbed evolution operator are now respectively the Bloch waves, the *Anpassung* parameters and the evolution operator given by (23).

Case (i) corresponds to the so-called 'physical-optics' approach proposed by Cowley & Moodie (1957*a,b*) while case (ii) corresponds to the more recent derivation of Buxton (1976). Both of these theories may be obtained from standard time-dependent perturbation theory given in (36) and (37). The physical significance of the $n$th-order term [(37)] is straightforward: After a free propagation from $z_0$ to $\tau_1$, electrons interact with the perturbation potential at the level $\tau_1$ and then propagate freely to $\tau_2$, where a second interaction occurs, *etc.*; the $n$th order corresponds to $n$ interactions so that the electrons pass through $n-1$ virtual states (Fig. 2). Between two successive inter-
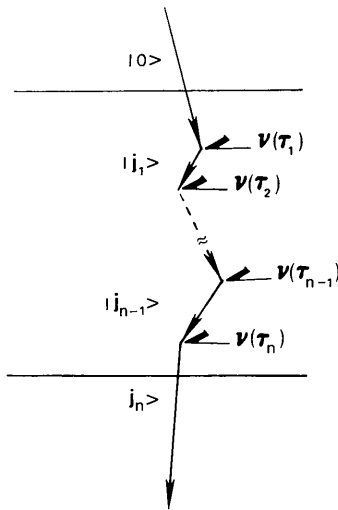


Fig. 2. The $n$th-order perturbation term corresponds to a succession of $n$ interactions between the electrons and the perturbation potential. It is a multiple-diffraction term. Obviously, all intermediate states $|j_1\rangle$, $|j_2\rangle$, $|j_{n-1}\rangle$ are virtual states, the actual measured transition being from $|0\rangle$ to $|j_n\rangle$.

actions the electrons propagate according to the eigenstates of the unperturbed Hamiltonian. The perturbation introduces transitions between the original eigenstates.

Let $|j\rangle$ and $\gamma_j$ be the eigenfunctions and eigenvalues of the unperturbed Hamiltonian [which may be case (i) or (ii)]. The $n$th-order perturbation term may be written as [from (37)]

$$U^{(n)}(z,z_0) = (-i)^n \int_{z > \tau_n \geq \tau_{n-1} \geq \ldots \geq \tau_1 \geq z_0} d\tau_n \ldots d\tau_1$$

$$\times \sum_{j_n}\sum_{j_{n-1}} \ldots \sum_{j_1}\sum_{j_0} \langle j_n|W(\tau_n)|j_{n-1}\rangle$$

$$\times \langle j_{n-1}|W(\tau_{n-1})|j_{n-2}\rangle \ldots \langle j_1|W(\tau_1)|j_0\rangle$$

$$\times \exp -i[\gamma_{j_n}(z - \tau_n)$$

$$+ \gamma_{j_{n-1}}(\tau_n - \tau_{n-1}) + \ldots$$

$$+ \gamma_{j_0}(\tau_1 - z_0)]|j_n\rangle\langle j_0|,\qquad (59)$$

where the perturbation terms of successive order satisfy the following recursive relation:

$$U^{(n+1)}(z,z_0) = -i \int_{z_0}^{z} d\tau \sum_{j,j'} |j\rangle \exp[-i\gamma_j(z - \tau)]$$

$$\times \langle j|W(\tau)|j'\rangle\langle j'|U^{(n)}(\tau,z_0). \qquad (60)$$

The matrix elements of the perturbation potential $\langle j|W(z)|j'\rangle$ are either the usual 2D Fourier transform of the potential when the $|j\rangle$ basis is the $q$ basis

$$\langle q|W(z)|q'\rangle = W'(z)_{q'-q},\qquad (61)$$

or the components of $W$ on the Bloch-wave $|j\rangle$ basis. Explicitly stated with respect to the usual Fourier coefficients they are given by

$$\langle j|W(z)|j'\rangle = \sum_{q,q'}\langle j|q\rangle\langle q|W(z)|q'\rangle\langle q'|j'\rangle \qquad (62)$$

or, with notations (29),

$$\langle j|W(z)|j'\rangle = \sum_{q,q'} C_q^{*j} W(z)_{q'-q} C_{q'}^{j'}.\qquad (63)$$

IV-2-1. *First-order expansions.* The first-order term is easily obtained from (60) by taking $n = 0$:

$$U^{(1)}(z,z_0) = -i \int_{z_0}^{z} d\tau \sum_{j}\sum_{j'} |j\rangle \exp\{-i[\gamma_j(z - \tau)$$

$$+ \gamma_{j'}(\tau - z_0)]\} \langle j|W(z)|j'\rangle\langle j'|.$$

$$(64)$$

This term, corresponding to the single-transition approximation, leads to both the $z$-dependent kinematical theory ($|j\rangle = |q\rangle$) and the first-order interband transition in the Bloch-wave formulation (Buxton, 1976).

The most important feature arising from the present

approach is the resonance-like effect which occurs for a periodic potential along $z$ [actually the only requirement is that the perturbation potential $W(z)$ be periodic between $z_0$ and $z$]. Then, supposing $W(z)$ to be periodic along $z$, we expand it in Fourier series:

$$W(z) = \sum_l W_l \exp(-il\omega z), \qquad (65)$$

where $\omega = 2\pi/c$, $c$ being the period along $z$. The matrix elements of $W_l$ on the $q$ basis are now the usual 3D Fourier coefficients of the potential

$$\langle q | W_l | q' \rangle = W_{q'-q,b} \qquad (66)$$

the term $l = 0$ being zero for case (ii).

Introducing (65) into (64), we obtain, after integration ($z_0 = 0$),

$$U^{(1)}(z,0) = -i \sum_l \sum_{jj'} | j \rangle \exp(-i\gamma_j z) \exp(i\theta_{ljj'} z)$$

$$\times \langle j | W_l | j' \rangle \frac{\sin \theta_{ljj'} z}{\theta_{ljj'}} \langle j' | \qquad (67)$$

with

$$\theta_{ljj'} = \frac{\gamma_j - \gamma_{j'} - l\omega}{2} \qquad (68)$$

so that the amplitude of transition probability from $| j_0 \rangle$ to $| j_1 \rangle$ is given by

$$\langle j_1 | U^{(1)}(z,0) | j_0 \rangle = -i \sum_l \exp(-i\gamma_{j_1} z) \exp(i\theta_{lj_1 j_0} z)$$

$$\times \langle j_1 | W_l | j_0 \rangle \frac{\sin \theta_{lj_1 j_0} z}{\theta_{lj_1 j_0}}. \qquad (69)$$

The contribution of the different harmonics is governed by the argument of the sine function and will be important only if

$$|\theta_{lj_1 j_0}| \lesssim \frac{1}{z}, \qquad (70)$$

i.e. if the difference between the two involved eigenvalues is close to an integer value of the reciprocal-lattice vector $c^*$.

Let us first consider the Cowley–Moodie formulation: as initial state we have to choose the $| 0 \rangle$ vector. The eigenvalues involved in the transition to the $| q \rangle$ state are respectively

$$\gamma_{j_1} = \frac{q^2 - \chi^2}{2K} \quad \text{and} \quad \gamma_{j_0} = \frac{\chi^2 - \chi^2}{2K} = 0, \qquad (71)$$

so that the $\theta$ term becomes

$$\theta_{lj_1 j_0} = \frac{1}{2}\left(\frac{q^2 - \chi^2}{2K} - l\omega\right). \qquad (72)$$

This term corresponds to the Bohr frequency of the

transition through the $l$th harmonic and defines the excitation parameters which have to be used for upper-layer diffraction spots ($l \neq 0$):

$$s(q,l) = \zeta(q,l) - l/c. \qquad (73)$$

It is now easily shown that the resonance peak of this $l$th harmonic is centred on the usual $q,l$ Bragg peak of the 3D reciprocal lattice. In fact, let $\mathbf{k}_l$ be the 3D wave vector defined by (Fig. 3)

$$\mathbf{k}_l = \left(K + 2\pi\frac{l}{c}\right)\mathbf{n}_z + \mathbf{q}, \qquad (74)$$

where $\mathbf{n}_z$ is the unit vector along the $z$ direction. A simple calculation shows that

$$\frac{k_l^2 - k_0^2}{2K} = 2\pi\left[\frac{l}{c} - \zeta(q)\right] + O\left(\frac{1}{2K}\right), \qquad (75)$$

so that the centre of the resonance peak ($\theta = 0$) corresponds to $|k_l| = |k_0|$, i.e. to the 3D $q$–$l$ reciprocal node being on the Ewald sphere.

According to the present approach the Ewald sphere may be considered as the geometrical locus of zero Bohr frequency. As usual in the small-angle scattering approximation, the Ewald 'sphere' is a paraboloid defined by

$$\frac{(x - x_0)^2 + (y - y_0)^2}{2K} + z = 0, \qquad (76)$$



Fig. 3. For a periodic potential along $z$ resonance-like peaks appear, the maxima of which are located on the nodes of the 3D reciprocal lattice: for thick crystals, the 3D reciprocal space is essentially recovered.

where $x_0$ and $y_0$ designate the coordinates of the $\chi$ vector.

The width of the resonance peak being approximately $1/z$, the contributions of the different $l$ harmonics will not overlap for crystals sufficiently thick: the 3D reciprocal space will be essentially recovered. This fact may equally be understood as a time–energy Heisenberg inequality. Thick crystals give rise to a long interaction time and therefore the transition levels are well defined (sharp resonance peaks). On the contrary, for thin crystals corresponding to short interaction times, the resonance peaks are broadened and different Bragg reflections of different layers of the reciprocal lattice may overlap. At the limit of infinitesimal thickness (sudden perturbation), the resonance peaks become continuous lines along $z$. Hence the progressive passage from two- to three-dimensional diffraction as the thickness increases is naturally described by the present approach.

A similar analysis may be performed starting with the Hamiltonian of case (ii) (free propagation plus projected potential). The transition probability at the first order is found to be

$$\langle q|U^{(1)}(z,0)|0\rangle = -i \sum_{j,j'} \sum_{g,g'} \sum_l \exp(-i\gamma_j z) \exp(i\theta_{ljj'} z)$$

$$\times C_q^j C_g^{*j} \langle g|W_l|g'\rangle$$

$$\times C_{g'}^{j'} C_0^{*j'} \frac{\sin \theta_{ljj'} z}{\theta_{ljj'}}, \qquad (77)$$

whereas the transition-probability amplitude between two Bloch waves (eigenstates of the unperturbed system) given by (69) has exactly the same form as the kinematical probabilities. However, it is clear that the $|j\rangle$ basis is, without doubt, a well adapted basis convenient for a perturbation treatment: the zero order leads to the usual 2D dynamical theory, whereas the $|q\rangle$ basis gives the kinematical one. Even at first order [(77)] this treatment is expected to be a challenge to the general Cowley–Moodie expansion.

*IV-2-2. General perturbation expansion.* It is easily shown from (59) that the general perturbation term is the Cowley–Moodie expansion when the unperturbed Hamiltonian is the free propagator. The matrix element $\langle q|U^{(n)}(z,z_0)|0\rangle$ can then be written as

$$\langle q|U^{(n)}(z,z_0)|0\rangle = (-i)^n \int_{z>\tau_n>\tau_{n-1}>\ldots>\tau_1>z_0} d\tau_n \ldots d\tau_1$$

$$\times \sum_{q_{n-1}} \sum_{q_{n-2}} \ldots \sum_{q_1} \langle q|V(\tau_n)|q_{n-1}\rangle$$

$$\times \langle q_{n-1}|V(\tau_{n-1})|q_{n-2}\rangle \cdots$$

$$\times \langle q_1|V(\tau_1)|0\rangle \exp -i[\gamma_q(z-z_n)$$

$$+ \gamma_{q_{n-1}}(\tau_n-\tau_{n-1}) + \cdots$$

$$+ \gamma_{q_1}(\tau_2 - \tau_1)], \qquad (78)$$

where $\gamma_q = (q^2 - \chi^2)/2K$. Using now the recursive relation (60) and introducing

$$\varphi_q^{(n)}(z,z_0) = i \exp[i\gamma_q(z - z_0)]\langle q|U^{(n)}(z,z_0)|0\rangle, \qquad (79)$$

we obtain

$$\varphi_q^{(n+1)}(z,z_0) = -i \sum_{q'} \int_{z_0}^{z} d\tau \exp\{[\gamma(q) - \gamma(q')]\tau\}$$

$$\times \langle q|V(\tau)|q'\rangle \varphi_{q'}^{(n)}(\tau,z_0). \qquad (80)$$

Here again, we infer from (80) that the relative contributions of the different harmonics of a periodic potential along $z$ are governed by the argument of the exponential, namely

$$2\theta_{qq'l} = \gamma(q) - \gamma(q') - l\omega, \qquad (81)$$

showing, as is well known, that the only important terms are those arising from reciprocal-lattice nodes located near the Ewald 'sphere'. If we now choose the unperturbed Hamiltonian by including the average projected potential, (59) gives the general $n$th-order transition between Bloch waves. Unfortunately, like the original Cowley–Moodie formulation, this expression is not suitable for numerical calculations. However, a multislice-like method may be used by replacing the optical propagator (32) by (23) where the unperturbed Hamiltonian includes the average projected potential $\bar{V}$. The diffractor is calculated in the sudden-perturbation approximation [(40)] where the potential has been replaced by
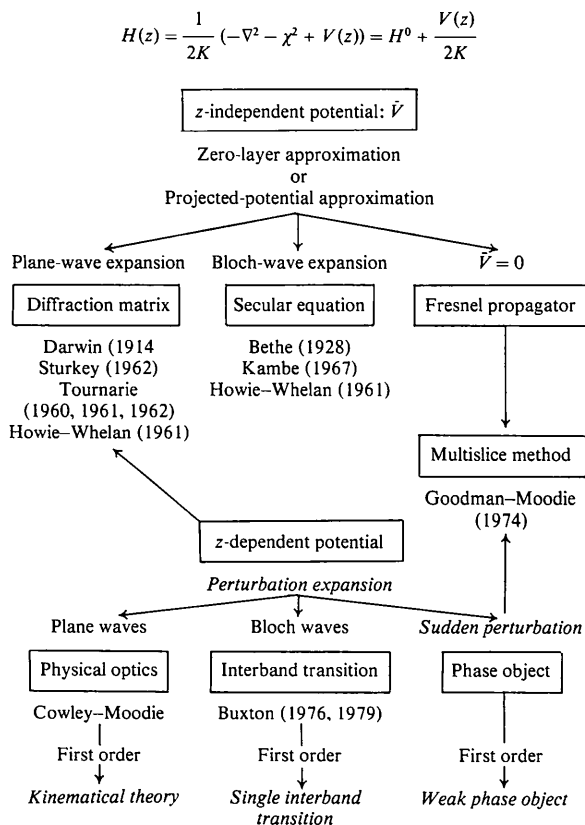
$$W(\tau) = (V(\tau) - \bar{V})/2K. \qquad (82)$$

Such a method essentially consists in replacing the crystal by a $z$-independent crystal with slices corresponding to the local $z$ variation of the potential.

## V. Conclusion

Time-dependent perturbation theory provides a natural and straightforward way to derive pre-existing theories of dynamical diffraction of fast electrons. This derivation is based fundamentally on the small-angle-scattering approximation, the principal effect of which is to transform one of the dynamical variables into a time-like parameter. As a result, the usual Schrödinger stationary-state equation becomes a time-dependent causal equation of a two-dimensional system. The introduction of the evolution operator leads to a simple and direct expression of the transition probabilities. Existing theories actually correspond to the different ways of calculating the evolution operator (Table 1).

So far, all possibilities offered by the time-dependent perturbation theory have not been used in the present study. For example, if a relatively smooth $z$ variation of the potential inside the crystal may be assumed then the adiabatic approximation gives new possibilities to solve

Table 1. *Correlations between some of the principal descriptions of the elastic scattering of electrons*

$$H(z) = \frac{1}{2K}(-\nabla^2 - \chi^2 + V(z)) = H^0 + \frac{V(z)}{2K}$$

z-independent potential: $\bar{V}$

Zero-layer approximation
or
Projected-potential approximation

| Plane-wave expansion | Bloch-wave expansion | $\bar{V} = 0$ |

| Diffraction matrix | Secular equation | Fresnel propagator |

Darwin (1914)  Bethe (1928)
Sturkey (1962)  Kambe (1967)
Tournarie  Howie–Whelan (1961)
(1960, 1961, 1962)
Howie–Whelan (1961)

Multislice method

Goodman–Moodie
(1974)

z-dependent potential

*Perturbation expansion*

| Plane waves | Bloch waves | *Sudden perturbation* |

| Physical optics | Interband transition | Phase object |

Cowley–Moodie  Buxton (1976, 1979)
First order  First order  First order
*Kinematical theory*  *Single interband transition*  *Weak phase object*

the problems by the so-called 'turning-axes' technique (for example, defects).

Also of great interest is the fact that the present description may provide an elegant way of studying the symmetry properties of the diffraction process. In fact, since any unitary or antiunitary operators leave the Hermitian scalar product invariant, the symmetry properties of both diffraction and images may be derived by studying the commutation properties between the evolution operator and the usual symmetry operators (Portier & Gratias, 1981).

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