Dynamical theory of elastic electron diffraction at small angles

Introduction

The dynamical theory of elastic electron diffraction at small angles is very important to understand both diffraction patterns and images. It uses several approximations, in particular the small angle diffraction approximation. This approximation is satisfied when the energy of the incident electrons is equal or larger than 50 kV (depending on crystal mean atomic number). This theory is presented here following Portier and Gratias [Portier, 1981].

Before its formal description a few remarks are required:

i) The electron microscope destroys the space isotropy as the electron are propagating thousand times faster in the direction defined by the optical column of the microscope (z direction) than in a plane perpendicular to it ({x,y} plane). In the small angles approximation the 3 dimensional stationary problem is replaced by a 2 dimensional problem where time is replaced by z. This problem can be solved using the theory of time dependant perturbation.

ii) The diffraction problem can be considered as a transition process using the following scheme:

-given known initial state $|i\rangle$ (direction of the incident electrons or wave vector), what is the transition probability after interaction with a diffusion potential during a time z (crystal thickness) to a particular final state $|f\rangle$ (i.e. a diffracted beam).

The dynamical theory of elastic diffraction calculates the amplitude and phase diffracted in a set of directions {|f>} selected by the Bragg law. It is equivalent to calculate the transition probabilities from an initial state |i> towards these directions |f>.

The fundamental equation of the elastic diffusion of electrons in a potential V is given in the stationary mono-electronic approximation (constant electron flux, no energy dispersion) [Humphreys, 1979]:

$$(\Delta + k^2)\Phi = V\Phi \tag{1}$$

where the wave vector k is given by:

$$k = \frac{\sqrt{2meE}}{\hbar}$$

$m = \gamma m_o$ = mass of the electron corrected for relativistic effect,

$$\gamma = 1 + \frac{e^2 E^2}{2m_o c^2} = \text{relativistic correction (2 à 511 KeV)},$$

e = electron charge,

E = accelerating voltage,

c = speed of light in vacuum,

$$V = -\frac{2me}{\hbar^2}V_{volt}(\rho;z) = \text{ diffusing potential.}$$

In this description of the dynamical theory we use $\quad \dfrac{\hbar^2}{2m} = 1 \quad$.

Table 1 shows a few values of the relativistic correction, the wavelength and speed of electron accelerated in a potential from 50 kV to 1000kV.

E_O kV	γ	λ [pm]	v/c
50	1.098	5.362	0.412
100	1.119	3.706	0.548
200	1.391	2.511	0.695
500	1.978	1.423	0.862
1000	2.957	0.873	0.941

TABLE 1. *Relativistic correction, wavelength and speed of the electron*

The electron microscope destroys the space isotropy because of the very high kinetic energy of the electrons. The 3-D space is thus described by {**r**; z} where $\rho = (x, y)$. At very high energy Bragg angles are very small. The Bragg law $2d_q\sin\theta = \lambda$ is nothing else but a consequence of elastic diffusion. Figure 1 shows the wave vectors $\underline{\mathbf{k}}_\mathbf{o}$ and $\underline{\mathbf{k}}_\mathbf{q}$ the incident beam and of a diffracted beam respectively. They are both located on the Ewald sphere, i.e. the sphere of all possible direction of elastic diffusion. Elastic diffusion will occur when $\underline{\mathbf{k}}_\mathbf{q} = \underline{\mathbf{k}}_\mathbf{o} + \mathbf{q}.$
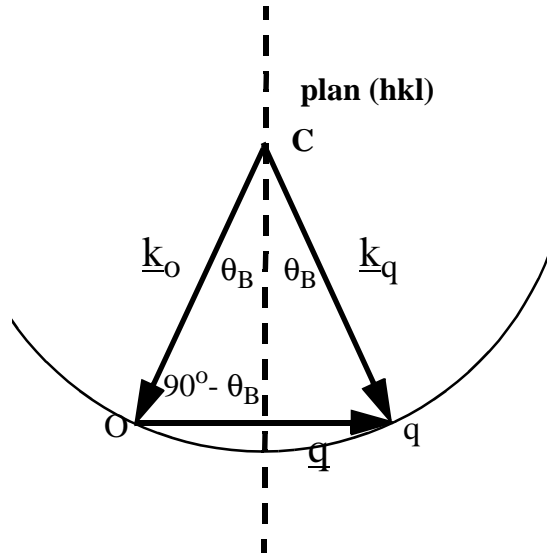
FIGURE 1. *Geometry of elastic diffraction (Bragg condition satisfied)*

Elastic diffraction satisfies $\left| \underline{k}_q \right| = \left| \underline{k}_o \right|$ and $\underline{k}_q - \underline{q} = \underline{k}_o$. Combining these 2

equations one obtain: $2 \left| \underline{k}_o \right| \cos\left(\dfrac{\pi}{2} - \theta_B \right) = \left| \underline{q} \right|$. And finally the Bragg law:

$$2 d_q \sin\theta_B = \lambda$$

For typical d_q of 10 nm^{-1} and wave vector of 400 nm^{-1} (at 200 kV), the Bragg angle is of the order of 0.15 degree. Thus the small angles approximation is well verified in transmission electron microscopy.

The geometry of the dynamical theory is defined in figure 2. The wave vector **k** of the incident electron is close to a [u,v,w] crystal direction (zone axis): the miss orientation is given by **c**, projection of **k** on the {x,y}plane ($|c| \sim 1$-10 nm^{-1}). The z component k_z of **k** is very large (~ 400 nm^{-1}). As a result the electron wave oscillates with a very high frequency in the z direction. The electron wave function F(r; z) is written as:

$$\Phi(\underline{r})= \Phi(\rho;z) = e^{ik_z z}\psi(\rho;z) \tag{2}$$

where $\psi(\rho;z)$ is a slowly varying function of z.

Putting equation (2) in equation (1) and neglecting $\dfrac{\partial^2 \psi}{\partial z^2}$ because:

$$\left|\frac{\partial \psi}{\partial z}\right| \gg \frac{1}{2k_z}\left|\frac{\partial^2 \psi}{\partial z^2}\right| \quad \text{and} \quad |\psi| \gg \frac{1}{2k_z}\left|\frac{\partial^2 \psi}{\partial z^2}\right| \quad \text{(at 200 kV, l = 2.5 pm, } k_z = 400 \text{ nm}^{-1}) \text{ the}$$

fundamental equation of the dynamical theory of elastic diffraction at small angles is obtained:

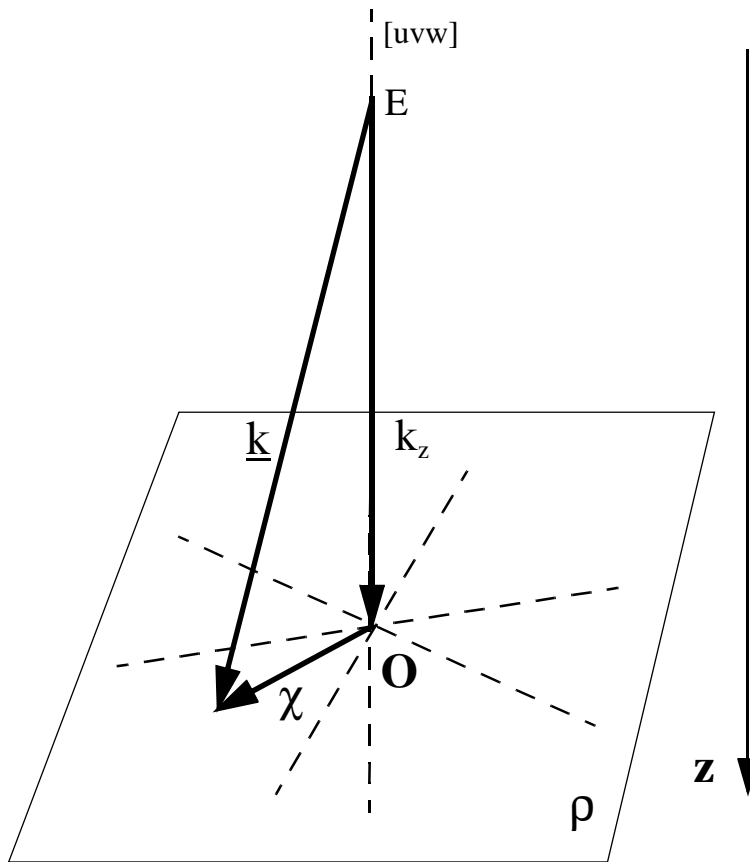$$i\frac{\partial}{\partial z}\psi(\rho;z) = \frac{1}{2k_z}[-\Delta_\rho - \chi^2 + V(\rho;z)]\psi(\rho;z) \tag{3}$$

FIGURE 2. *Geometry of the electron diffraction problem. The incident wave vector $|\underline{k}|$ is very large compared to its projection $|c|$ on the $\{r,0\} = (x, y)$ plane.*

Remarks:

i) The approximation of the fundamental equation is equivalent to assume that the diffusing potential is very small compared to the incident electron energy and that the z component of k only varies very slightly during the diffusion process. This is a good approximation as the mean crystal potential is of the order of 10~30 V.

ii) Electron back scattering is neglected (as the z movement is almost constant in the z direction).

Equation 3 is formally equivalent to a time-dependent Schroedinger equation in 2 dimensions **r**, where **z** plays the role of time. The evolution of the system is

absolutely causal, i.e. *from the past to the future without any interaction towards the past.* The -z movement of the electrons does not interfere with the +z movement.

Using a hamiltonian notation equation (3) becomes:

$$i\frac{\partial \psi}{\partial z} = H\psi \qquad \text{where} \quad H = \frac{1}{2k_z}[-\Delta_\rho - \chi^2 + V(\rho;z)]$$

Let us introduce H_o as:

$$H_o = -\Delta_\rho + V(\rho;z)$$

H_o is the hamiltonian of a system where $\underline{\mathbf{k}}$ is parallel to [u,v,w].

Thus:

$$H = \frac{1}{2k_z}[H_o - \chi^2] \qquad \text{where } c^2 \text{ is the transverse kinetic energy of the}$$

incident electrons (it is null when the electron beam is along [u,v,w]).

H depends of **z** through V(r; z). When one assumes that V *does not depend* on **z**, one can define a *causal evolution operator* U(z, o) such that:

$$\Psi(\rho;z) = U(z,o)\psi(\rho;o) \tag{4}$$

Assuming that V = V(r) does not depend on z, is equivalent to replace the crystal by a stack of small slices of thickness t, with constant projected potential V'(r) (in a given slice):

$$V'(\rho) = \frac{1}{\tau} \int_{z}^{(z+\tau)} V(\rho;z')dz' \tag{5}$$

The causal evolution operator is thus:

$$U(z_n, o) = U(z_n, z_{n-1})...U(z, o) \tag{6}$$

The evolution operator obeys the following differential equation (postulate of quantum mechanics) [Messiah, 1964, Shankar, 1994]:

$$i\frac{\partial}{\partial z}U(z, o) = H(\rho, z)U(z, o) \tag{7}$$

Hence, the small angle approximation of the dynamical theory of elastic electron diffraction is solved when the solutions of (7) are found.

Reminder on the notation used in the following pages

In the crystal space at 2 dimensions {x,y} or r (**r** representation), the position eigenvectors are given by:

$$|\rho\rangle = \delta(\rho' - \rho) \tag{8}$$

where d(r'-r) is the Dirac distribution (or function). In the dual space or reciprocal space or momentum space (**q** representation or plane waves basis) the eigenvectors of the momentum are given by:

$$|q\rangle = \frac{1}{2\pi}e^{i(q \cdot \rho)} \tag{9}$$

In the $\{|\rho\rangle\}$ basis the electron wave function is:

$$\langle\rho|\psi\rangle = \int\psi(\rho')\delta(\rho' - \rho)d\rho' \tag{10}$$

In the $\{|q\rangle\}$ basis (plane wave representation) the wave function projected in the $|q\rangle$ direction is:

$$\langle q|\psi\rangle = \int\psi(\rho)e^{-i(q \cdot \rho)}d\rho \tag{11}$$

i.e. $\langle q|\psi\rangle$ is the complex amplitude diffracted in the $|q\rangle$ direction.

The wave function $\psi(\rho) = \sum_{|q\rangle} |q\rangle\langle q|\psi\rangle$ is thus decomposed on the basis of plane waves, i.e. a Fourier decomposition.

The initial state characterized by c is represented by a state $|\psi_o\rangle$. Hence its wave function is written as: $\psi(\rho;o) = \langle\rho|\psi_o\rangle$.

Similarly, the final state at thickness z is $|\psi_z\rangle$ and its wave function is

$$\psi(\rho;z) = \langle\rho|\psi_z\rangle \quad .$$

Hermitic or self-adjoint operators can be decomposed on the basis formed by their eigenvectors (spectral decomposition).

For example $\quad H = \sum_i \lambda_i |\lambda_i\rangle\langle\lambda_i| \quad$ (***spectral decomposition of H***).

Or: $\quad H = \sum_i \lambda_i P_{\lambda_i} \quad$ where $P_{\lambda_i} = |\lambda_i\rangle\langle\lambda_i|$ are the projection operators.

Using the spectral decomposition any function of an hermitic operator (i.e. f(H)) can be written as:

$$f(H) = \sum_i f(\lambda_i)|\lambda_i\rangle\langle\lambda_i| \quad .$$

(this follows from the fact that $P^2{}_{\lambda_i} = P_{\lambda_i}$).

Transition probability

The electron wave function at thickness **z** after interaction with the crystal potential is given by $|\psi_z\rangle = U(z, o)|\psi_o\rangle$. The **_intensity diffracted_** in the $|q\rangle$ direction is the _transition probability_ $\omega_{o \to q}(z, o)$ from the initial state $|q = o\rangle = |o\rangle$ to the final state $|q\rangle$ (figure 3). It is given by:

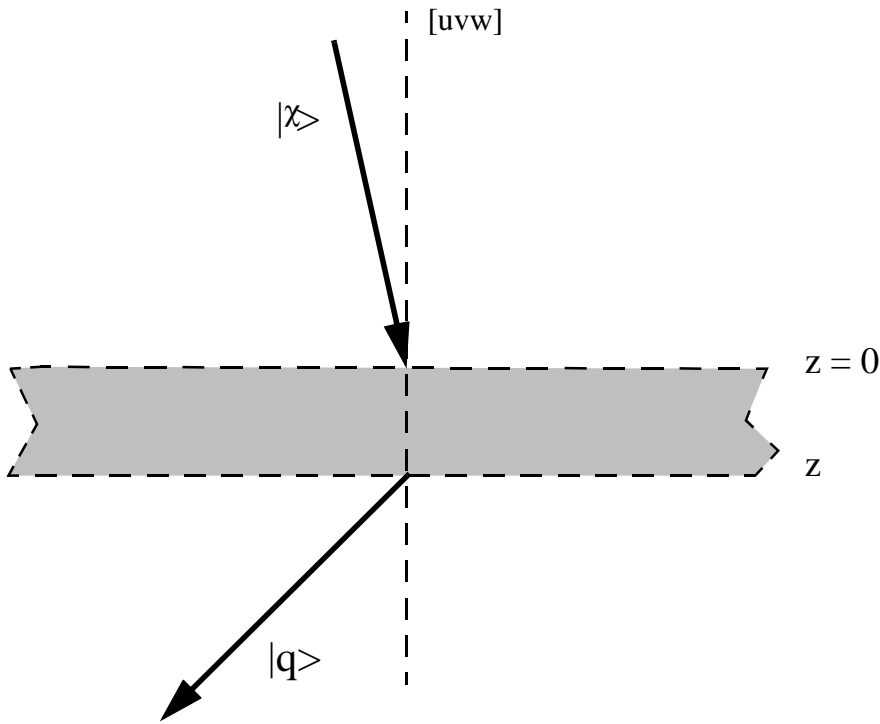$$\omega_{o \to q}(z, o) = \left|\langle q|U(z, o)|o\rangle\right|^2 \tag{12}$$

FIGURE 3. _Transition from the initial state $|o\rangle$ to a final state $|q\rangle$._

The intensity at a point **r** of the exit face of the crystal is similarly given by:

$$\omega_{o \to \rho}(z, o) = \left|\langle\rho|U(z, 0)|o\rangle\right|^2 = \left|\sum_q \langle\rho|q\rangle\langle q|U(z, 0)|o\rangle\right|^2$$

where the closure relation for a periodic specimen has been used: $\sum_q |q\rangle\langle q| = 1$.

The intensity observed at a point **r** located in the image plane (observation plane) is modified by the transfer function $T(q', q)$ of the electron microscope. It is given by:

$$\omega_{o \to \rho}(z, o) = \left| \sum_{q'} \sum_{q} \langle \rho | q' \rangle \langle q' | T(q', q) | q \rangle \langle q | U(z, o) | o \rangle \right|^2$$

where the exit wave function components $\langle q | U(z, 0) | o \rangle)$ are modified by the microscope (terms $\langle q' | T(q', q) | q \rangle$). The terms $\sum_{q'} \langle \rho | q' \rangle$ are related to the inverse Fourier transform that provides the image wave function.

In the back focal plane of the objective lens the $|q'\rangle$ wave function component is:

$$\sum_{q'} \langle q' | T(q', q) | q \rangle \langle q | U(z, o) | o \rangle$$

One sees that a coupling of the diffracted beams is introduced during the transfer by the objective lens.

When the transfer is linear (i.e. for a weak phase object), the transfer matrix is diagonal $\langle q' | T(q', q) | q \rangle = T(q)\delta(q' - q)$. In that particularly simple case, the image intensity is given by:

$$\omega_{o \to \rho}(z, o) = \left| \sum_{q} \langle \rho | q \rangle T(q) \langle q | U(z, 0) | o \rangle \right|^2 \tag{13}$$

Furthermore the symmetry properties of the diffraction patterns and of the high resolution images are intrinsic properties of the transition probability functions $\omega_{o \to q}(z, o)$ and $\omega_{o \to \rho}(z, o)$.

To summarize, one have to calculate the evolution operator $U(z, o)$ in order to solve the fundamental equation.

$U(z, o)$, a unitary operator, is not in general directly integrable. But, when $H(z)$ and $\frac{\partial}{\partial z}H(z)$ commute one has the general solution:

$$U(z, o) = \exp\left[-i\int_{o}^{z}H(\tau)d\tau\right] \qquad \textbf{(14)}$$

$H(z)$ and $\frac{\partial}{\partial z}H(z)$ commute when:

- $V(\rho, z)$ does not depend on z,
- $V(\rho;z)$ can be neglected,
- $H(z)$ reduces to its potential term.

These approximations are considered below. They are very useful for the electron microscopes, as they explain both the Bloch wave and the multislice approach.

Approximations

The diffusing potential does not depend on z

When the diffusion potential does not depend on z, the evolution operator

$$U(z, o) = \exp{-i\int_{o}^{z}H(\tau)d\tau} \text{ is reduced to } U(z, o) = \exp{-i\int_{o}^{z}H(\tau)d\tau}.$$

As H is a hermitic (self-adjoint) operator it can be represented in its eigenstates basis $\{|\alpha\rangle\}$ by a *diagonal matrix* where the γ_{α} are the (real) associated eigenvalues:

$$H|\alpha\rangle = \gamma_{\alpha}|\alpha\rangle \qquad \textbf{(15)}$$

The eigenstates $|\alpha\rangle$ are Bloch waves that characterize the propagation of the electron wave in a periodic continuum (crystal) and the eigenvalues γ_α give the kinetic energy of the Bloch waves. The unitary operators $P_\alpha = |\alpha\rangle\langle\alpha|$ are projectors on the eigenstates of the Hamiltonian $H(z)$:

$$H = \sum_\alpha \gamma_\alpha |\alpha\rangle\langle\alpha| = \sum_\alpha \gamma_\alpha P_\alpha \tag{16}$$

The evolution operator is a function of H and is written as:

$$U(z, o) = \sum_\alpha e^{-\gamma_\alpha z} |\alpha\rangle\langle\alpha|.$$

When V (**r**) does not depend on z, $U(z, o)$ is also diagonal on $\{|\alpha\rangle\}$. Therefore there is no possibility of transition between Bloch states.

The incident wave function $|o\rangle$ is a plane wave (or a sum of plane waves). Using the principle of superposition, it suffices to consider only one plane wave to calculate the wave function $\psi(\rho, z)$ at the exit plane of the crystal:

$$\psi(\rho, z) = \sum_q \phi_q(\rho, z)|q\rangle.$$

But:

$$|\psi_z\rangle = \sum_\alpha e^{-\gamma_\alpha z} |\alpha\rangle\langle\alpha|\psi_o\rangle$$

As a consequence the (complex) projected amplitude of $|\psi_z\rangle$ on $|q\rangle$ (Fourier coefficient of the wave transmitted by the crystal, i.e diffracted beam) is:

$$\phi_q(\rho, z) = \langle q|\psi_z\rangle = \langle q|U(z, o)|o\rangle = \sum_\alpha e^{-\gamma_\alpha z}\langle q|\alpha\rangle\langle\alpha|o\rangle \qquad \text{(17)}$$

Many books and research papers use excitation and Bloch wave coefficients. They are expressed in function of $|q\rangle$ and $|\alpha\rangle$ as:

$$\langle\alpha|o\rangle = (c_o^\alpha)^* = c_o^{\alpha*} \quad \text{projection of } |o\rangle \text{ on } |\alpha\rangle : \text{excitation coeff.} \qquad ,$$

$$\langle q|\alpha\rangle = c_q^\alpha \quad \text{projection of } |\alpha\rangle \text{ on } |q\rangle \qquad .$$

Using the microscopes notation:

$$\phi_q(\rho, z) = \langle q|U(z, o)|o\rangle = \sum_\alpha e^{-\gamma_\alpha z} c_q^\alpha c_o^{\alpha*} \qquad \text{(18)}$$

And the exit wave function is:

$$\psi(\rho;z) = \sum_q \phi_q(\rho, z)|q\rangle = \sum_\alpha c_o^{\alpha*} e^{-\gamma_\alpha z} \sum_q c_q^\alpha |q\rangle \qquad \text{(19)}$$

The eigenstates or Bloch waves are linear combinations of the plane waves:

$$|\alpha\rangle = \sum_q c_q^\alpha |q\rangle.$$

Equation (19) gives the representation of the wave function on the plane wave basis $\{|q\rangle\}$, i.e. its Fourier decomposition. The eigenstates define the dispersion surfaces, surfaces of constant total energy, but different kinetic energy.

How to determine the eigenstates?

In the plane waves basis $\{|q\rangle\}$ (q representation) $H|\alpha\rangle = \gamma_\alpha|\alpha\rangle$ is written as:

$$\langle q|H|\alpha\rangle = \gamma_\alpha \langle q|\alpha\rangle.$$

Using the closure relation $\sum_{q'} |q'\rangle\langle q'| = \mathbf{1}$, the matrix elements of H ($\{|q\rangle\}$ basis)

are obtained:

$$\sum_{q'} \langle q|H|q'\rangle\langle q'|\alpha\rangle = \gamma_\alpha \langle q|\alpha\rangle \tag{20}$$

For the hamiltonian $H = \dfrac{1}{2k_z}[-\Delta_\rho - \chi^2 + V(\rho;z)]$, the matrix elements of

$-\Delta_\rho - \chi^2$ are diagonal and consequently equation (20) reduces to:

$$\frac{q^2 - \chi^2}{2k_z}\langle q|\alpha\rangle + \sum_{q'} \langle q|\frac{V}{2k_z}|q'\rangle\langle q'|\alpha\rangle = \gamma_\alpha\langle q|\alpha\rangle \tag{21}$$

Using the microscopiste excitation error and Bloch wave coefficients and the fact that the matrix element of V(r) are:

$$V_{q'-q} = \langle q|V|q'\rangle,$$

the usual secular equation is obtained:

$$\frac{q^2 - \chi^2}{2k_z}c_q^\alpha + \sum_{q'} \frac{V_{q'-q}}{2k_z}c_{q'}^\alpha = \gamma_\alpha c_q^\alpha \tag{22}$$

It is simpler to write it in matrix form: $\{M\}\underline{c} = \gamma\{I\}\underline{c}$

where $\{I\}$ is the identity matrix and the matrix elements of M are:

$$M_{ij} = \frac{q_i^2 - \chi^2}{2k_z}\delta_{ij} + \frac{1}{2k_z}V_{q_j - q_i}.$$

A necessary condition to solve equation (22) is:

$$Det[\{M\} - \gamma\{I\}] = o.$$

When the dimension of the $\{|q\rangle\}$ basis is n (1 transmitted and n -1 diffracted beams), the eigensystem will provide n eigenvalues γ_α and n eigenvectors $|\alpha\rangle$ called eigenstates (i.e. Bloch waves). Some of the eigenstates can be degenerated depending of the symmetry of the diffraction experiment. When there is no degenerate state, each state corresponds to a Bloch wave with a different kinetic energy, but the same total energy.

Example

Here one considers a diffraction experiment where only 5 beams are excited (figure 4):
- crystal is Al fcc,
- zone axis is [0,0,1],
- exact zone axis condition (c = 0),
- accelerating voltage is 100 kV.

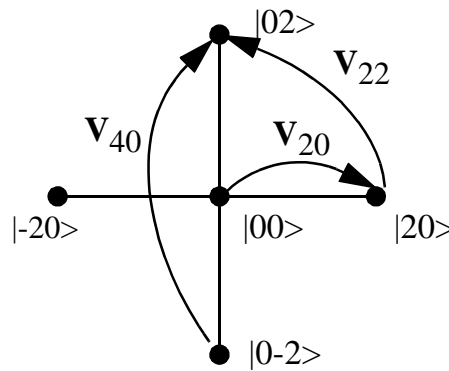- $\{|q\rangle\}$ basis: $\{|00\rangle, |20\rangle, |02\rangle, |\bar{2}0\rangle, |\bar{2}\bar{2}\rangle\}$

FIGURE 4. *5 beams diffraction experiment. The arrows show the interaction between the different diffracted beams.*

The secular matrix is:

	$|00>$	$|20>$	$|02>$	$|-20>$	$|0-2>$
$|00>$	0	V_{20}	V_{20}	V_{20}	V_{20}
$|20>$	V_{20}	h_{22}	V_{22}	V_{40}	V_{22}
$|02>$	V_{20}	V_{22}	h_{22}	V_{22}	V_{40}
$|-20>$	V_{20}	V_{40}	V_{22}	h_{22}	V_{22}
$|0-2>$	V_{20}	V_{22}	V_{40}	V_{22}	h_{22}

TABLE 2. *Secular matrix of the 5 beams diffraction experiment.*

The Fourier coefficients of the potential $V_{|00>-|20>}, V_{|20>-|02>}, V_{|20>-|-20>}$ (matrix elements $V_{q'-q}$) have been identified as U_{20}, U_{22} et U_{40} respectively. The "strength" of the dynamical interaction between the transmitted beam $|00>$ and the diffracted beams $|20>$ is proportional to U_{20}. It is proportional to U_{22} for the interaction between beams $|20>$ and $|02>$, and to U_{40} for $|20>$ et $|-20>$. The numerical values are given below (arbitrary units).

$$\begin{pmatrix} 0 & -3.946 & -3.946 & -3.946 & -3.946 \\ -3.946 & 24.39 & -2.392 & -2.392 & -1.443 \\ -3.946 & -2.392 & 24.39 & -1.443 & -2.392 \\ -3.946 & -2.392 & -1.443 & 24.39 & -2.392 \\ -3.946 & -1.443 & -2.392 & -2.392 & 24.39 \end{pmatrix}$$

FIGURE 5. *Numerical coefficients of the secular matrix (5 beams experiment)*

The eigenvalues correspond to Bloch waves of different energy. The lowest energy (-2.95) is attributed to a core state written as state 1s. In this particular diffraction experiment only 2 states are excited, state 1s and state 2s (21.1). These states are totally symmetric, they correspond to type A_1 irreducible representation of C_{4v}.

$$\{27.7\,,\ 25.8\,,\ 25.8\,,\ 21.1\,,\ -2.95\}$$

FIGURE 6. *Eigenvalues of the 5 beams diffraction experiment. Eigenstate 25.8 suffers is 2 fold degenrated.*

α	$c^{\alpha}_{\lvert oo \rangle}$	$c^{\alpha}_{\lvert 2o \rangle}$	$c^{\alpha}_{\lvert o2 \rangle}$	$c^{\alpha}_{\lvert \bar{2}o \rangle}$	$c^{\alpha}_{\lvert o\bar{2} \rangle}$	
1	0	0.5	-0.5	-0.5	0.5	B_1
2	0	0.353	-0.613	0.613	-0.353	$\Big\}E$
3	0	-0.613	-0.353	0.353	0.613	
4	-0.35	0.468	0.468	0.468	0.468	A_1
5	-0.937	-0.175	-0.175	-0.175	-0.175	A_1

FIGURE 7. *Eigenstate |a> coefficients. The excitation coefficients of the anti symmetric eigenstates are null. The irreducible decomposition of the C_{4v} representation in the 5 plane waves basis is $2A_1 + B_1 + E$. Only the eigenstates $\lvert \alpha \rangle$ with the symmetry of the irreducible representation A_1 are excited.*

As stated above the Bloch wave approach to the dynamical theory of electron diffraction has the advantage to place the symmetry properties of the eigenstates in the forefront. Furthermore using these symmetries it is possible to put the secular matrix into a block diagonal form and to reduce the size and time of the calculation.

$$\begin{pmatrix} h_{11} & h_{12} & h_{12} & h_{12} & h_{12} \\ h_{12} & h_{22} & h_{23} & h_{23} & h_{25} \\ h_{12} & h_{23} & h_{22} & h_{25} & h_{23} \\ h_{12} & h_{23} & h_{25} & h_{22} & h_{23} \\ h_{12} & h_{25} & h_{23} & h_{23} & h_{22} \end{pmatrix}$$

$$\downarrow$$

$$\begin{pmatrix} h_{11} & h_{12} & 0 & 0 & 0 \\ 4\,h_{12} & h_{22} + 2\,h_{23} + h_{25} & 0 & 0 & 0 \\ 0 & 0 & h_{22} - h_{25} & 0 & 0 \\ 0 & 0 & 0 & h_{22} - h_{23} & h_{23} - h_{25} \\ 0 & 0 & 0 & h_{23} - h_{25} & h_{22} - h_{23} \end{pmatrix}$$

FIGURE 8. *With a symmetry adapted basis, the secular matrix is put into a block diagonal form.*

In our case it is also immediate to obtain an analytical expression of the eigenstates. Without such a reduction there will not be an analytical solution as the characteristic polynomial is of degree 5. With the reduction of C_{4v} to $2A_1 + B_1 + E$, the analytical eigenvalues are given by the solutions of 3 characteristic polynomials, two of degree 2 and one of degree 1! Finally the 5 beams diffraction problem reduces to find the solutions of the following secular matrix.

$$\begin{pmatrix} 0 & h_{12} \\ 4\,h_{12} & h_{22} + 2\,h_{23} + h_{25} \end{pmatrix}$$

FIGURE 9. *Using group theory and a symmetry adapted basis the secular matrix of the 5 beams problem reduces to a 2x2 matrix.*

The approximation of the Fresnel propagator

This is the approximation that corresponds to the propagation of the incident electron in vacuum or between thin crystal slices where the crystal potential V(r;z) is null. In that case H reduces $H = \dfrac{1}{2k_z}(-\Delta_\rho - \chi^2)$.

H is then diagonal in the $\{|q\rangle\}$ basis (plane waves):

$$H|q\rangle = \frac{q^2 - \chi^2}{2k_z}|q\rangle.$$

The evolution operator is also diagonal in $\{|q\rangle\}$:

$$U(z, o) = e^{-Hz} = \int dq\, e^{-i\frac{q^2 - \chi^2}{2k_z}z}|q\rangle\langle q| \tag{23}$$

Without a diffusing potential, the incident wave function is not modified:

$$U(z, o)|o\rangle = |o\rangle.$$

In real space propagation from point $|\rho_1\rangle$ to point $|\rho_2\rangle$ is given by:

$$\langle \rho_2|U(z, o)|\rho_1\rangle = \int dq\, e^{-i\frac{q^2 - \chi^2}{2k_z}z}\langle \rho_2|q\rangle\langle q|\rho_1\rangle \tag{24}$$

But:

$$\langle \rho_2|q\rangle = \int dq\, \delta(\rho - \rho_2)e^{iq \cdot \rho}$$

and

$$\langle q | \rho_1 \rangle = \int dq\, \delta(\rho - \rho_1) e^{-iq \cdot \rho} \ .$$

Finally when $\chi = 0$:

$$\langle \rho_2 | U(z, o) | \rho_1 \rangle = \int dq\, e^{-i\frac{q^2}{2k_z}z} e^{-iq \cdot (\rho_1 - \rho_2)} = e^{\frac{-ik_z(\rho_1 - \rho_2)^2}{z}} \tag{25}$$

This is the *Fresnel propagator* expressed in direct space ($\{|\rho\rangle\}$ basis).

Phase grating approximation

Here H is assumed to be:

$$H = \frac{1}{2k_z} V(\rho; z) \ .$$

H is then diagonal $|\rho\rangle$ representation.

$$H(z)|\rho\rangle = \frac{1}{2k_z} V(\rho; z) |\rho\rangle \ .$$

The evolution operator is:

$$U(z, o) = \int d\rho\, e^{\left[\frac{-i}{2k_z} \int_o^z V(\rho; \tau) d\tau \right]} |\rho\rangle\langle\rho| \tag{26}$$

At thickness z, the wave function is:

$$|\psi_z\rangle = U(z, o)|o\rangle = e^{\left[\frac{-i}{2k_z} \int_o^z V(\rho; \tau) d\tau \right]} |o\rangle = e^{-i\sigma V_p(\rho)} |o\rangle \tag{27}$$

This is the phase grating approximation, that is the base of the multislice approach for the calculation of the complex exit wave function. The crystal is sliced into thin enough, the potential of each slice is projected on a plane and form a phase grating. The incident wave function is multiplied by the phase grating of the slice and propagated to the next. The propagation is usually performed in dual space.

Power series method

When H does not depend on **z**, the evolution operator $U(z, o) = e^{-iHz}$ can be developed in a power series of **z**:

$$U(z, o) = 1 - iHz + \frac{(-iH)^2}{2!}z^2 - \frac{(-iH)^3}{3!}z^3 + \dots \tag{28}$$

To third order the diffracted beam $|q\rangle$ is:

$$\langle q|U(z, o)|o\rangle = \langle q|o\rangle - i\langle q|H|o\rangle - \frac{1}{2}\langle q|H^2|o\rangle - \frac{i}{6}\langle q|H^3|o\rangle$$

Because $\langle q|H^2|o\rangle = \langle q|HH|o\rangle = \sum_{q'}\langle q|H|q'\rangle\langle q'|H|o\rangle$

and $\langle q|H^3|o\rangle = \langle q|HHH|o\rangle = \sum_{q''}\sum_{q'}\langle q|H|q''\rangle\langle q''|H|q'\rangle\langle q'|H|o\rangle$,

$\langle q|U(z, o)|o\rangle$ is calculated by summing the power series of the diffraction matrix

$\{H_{q'q}\} = \langle q'|H|q\rangle$.

To first order (kinematical approximation), diffraction introduces a $\dfrac{\pi}{2}$ dephasing of diffracted beams. One has to remember that in this approximation, the diffracted beams do not interfere with the transmitted beam. In high resolution electron microscopy this dephasing is more or less compensated by the phase changes introduced by the specimen defocus and by the spherical aberration of the objective lens of the microscope.

z dependent crystal potential

In that case the evolution of a diffracted beam $|q\rangle$ is given by:

$$i\frac{\partial}{\partial z}\langle q|U(z, o)|o\rangle = \langle q|H(z)U(z, o)|o\rangle \tag{29}$$

Using the closure relation one obtain:

$$i\frac{\partial}{\partial z}\langle q|U(z, o)|o\rangle = \sum_{q'} \langle q|H(z)|q'\rangle\langle q'|U(z, o)|o\rangle \tag{30}$$

Writing $|q\rangle$ as $\phi_q(z) = \langle q|U(z, o)|o\rangle$, the matrix elements of H are:

$$i\frac{\partial}{\partial z}\phi_q(z) = \frac{q^2 - \chi^2}{2k_z}\phi_q(z) + \frac{1}{2k_z}\sum_{q'} \langle q|V(z)|q'\rangle\phi_{q'}(z)$$

This equation shows clearly the coupling of the diffracted beams due to the crystal potential. In many books and research papers on the theory of electron diffraction the coefficient $\dfrac{-1}{2\pi}\left(\dfrac{q^2 - \chi^2}{2k_z}\right)$ is known as the excitation error $s_{|q\rangle}$. It is proportional to the distance of the reciprocal node $|q\rangle$ to the Ewald sphere.

Reflections at Bragg conditions are such that $s_{|q\rangle}$ is zero. With the $s_{|q\rangle}$ equation 30 becomes:

$$\frac{\partial}{\partial z}\phi_q(z) \;=\; i\pi\left[2s_q\phi_q(z) - \sum_{q'}\frac{V_{q'-q}}{2\pi k_z}\phi_{q'}(z)\right]$$

This equation has been first proposed by Howie-Whelan [Hirsch, 1977]. They are of great practical importance in the frame of the column approximation employed to calculate the contrast of crystalline defects such as dislocations or interfaces. Their numerical solution is obtained by Runge-Kutta integration.

Final remarks

All these different techniques are equivalent for the calculation of the exit wave function, but each has a specific domain where it performs better in terms of computation ease or speed. Figure 10 shows two calculations, one using the Bloch wave approach and the other using the multislice method. There are indeed small differences in the intensity, but it obvious that such differences will not appear in simulated images.
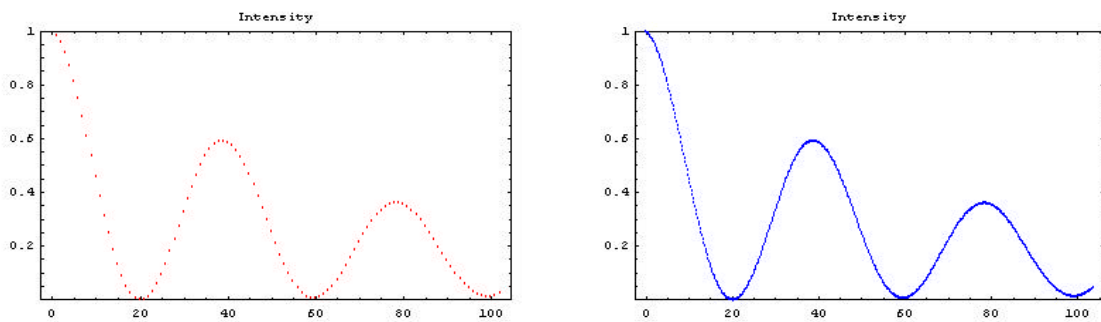
Bloch wave approach is more accurate when the dynamical calculations must include High Order Laue Zone reflections, like CBED and LACBED patterns (figures 11, 12) while multislice is definitely the method to use for the simulation of HREM images of defects (figure 13).
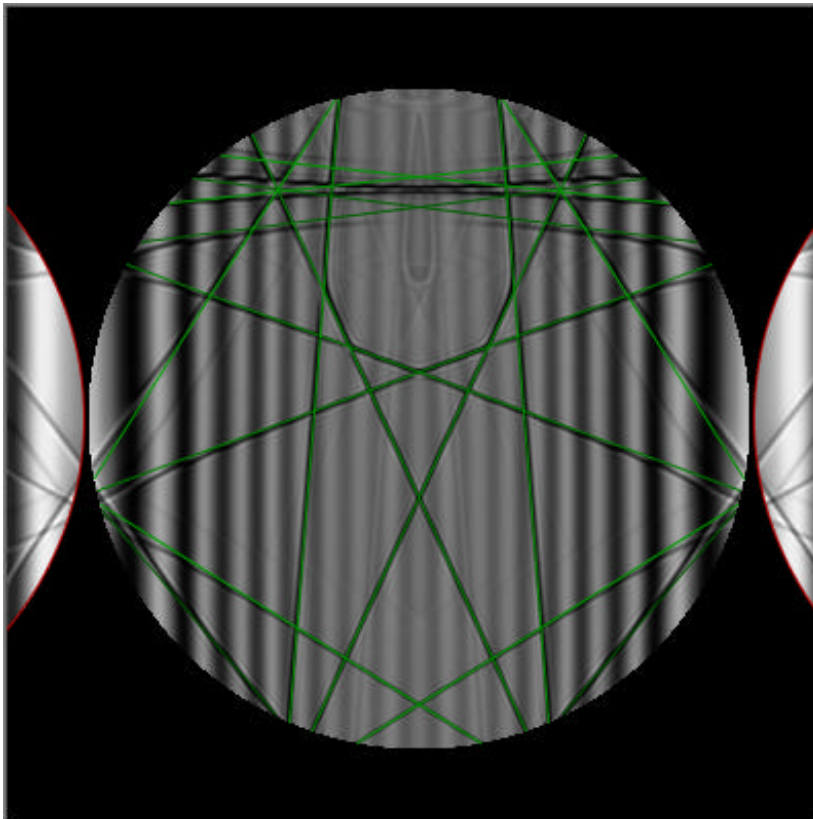

FIGURE 11. *Bloch wave calculation Al [1,3,3]. Kinematical HOLZ lines are superimposed (HOLZ shift included).*
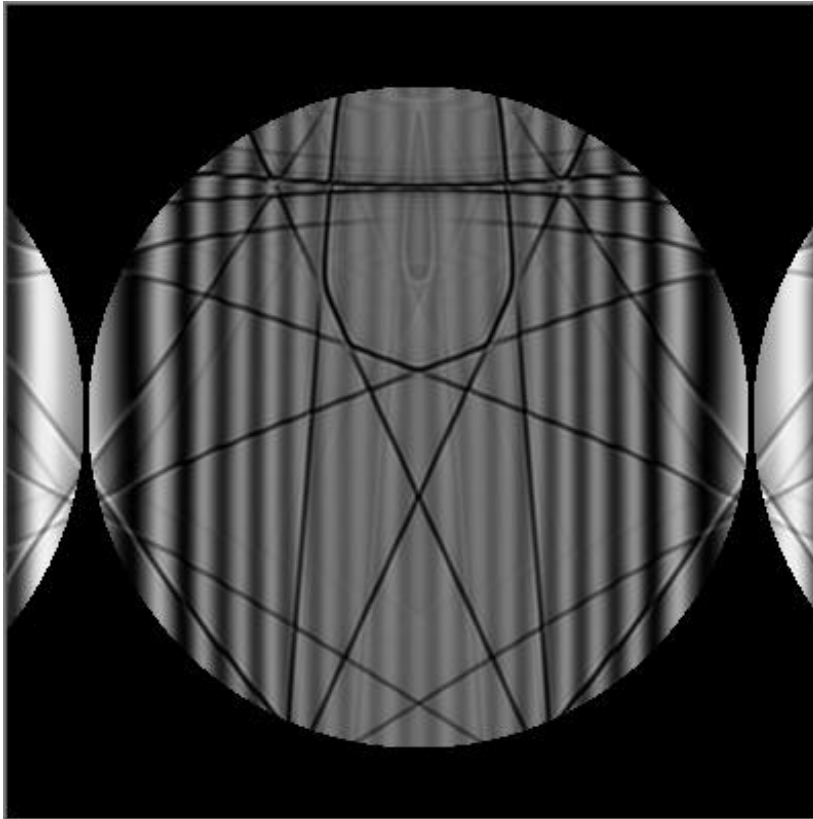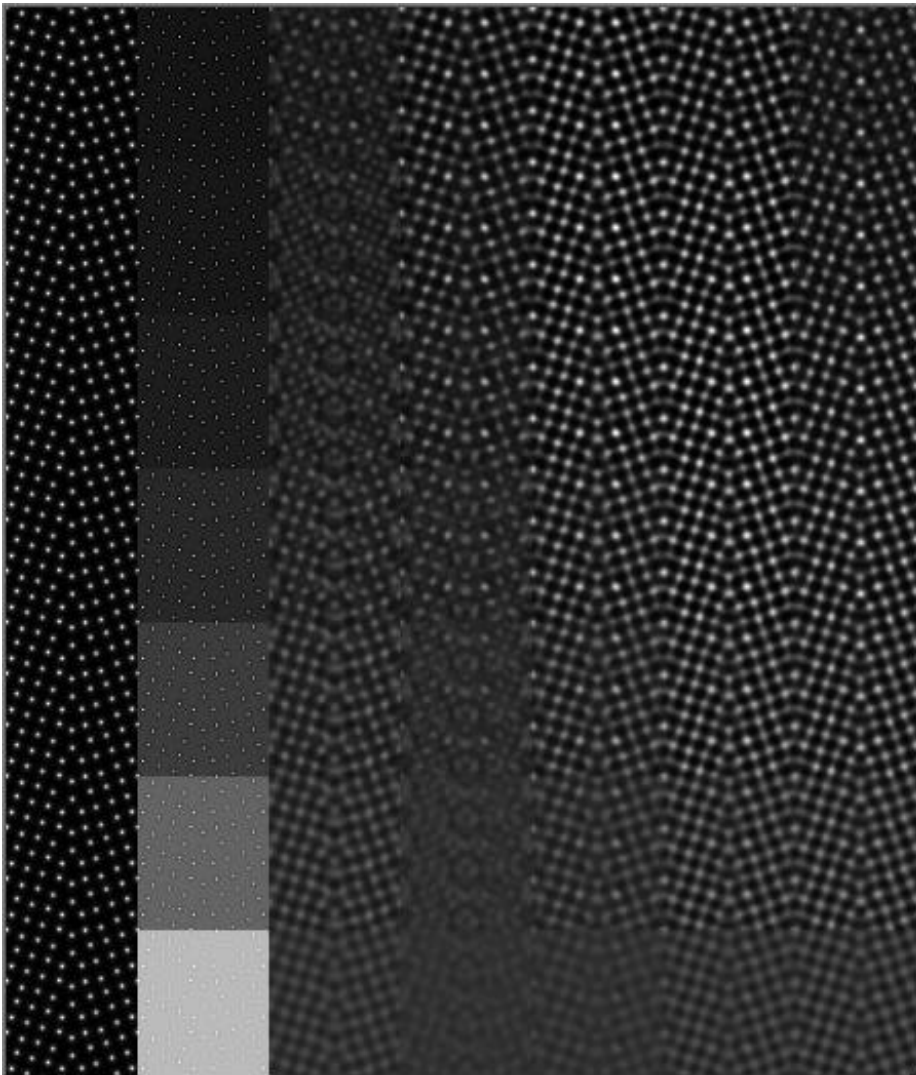
FIGURE 12. *Bloch wave calculation Al [1,3,3].*

FIGURE 13. *HREM image map Au* S_{53} *001.*

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Dynamical theory of elastic electron diffraction at small angles

Introduction

The dynamical theory of elastic electron diffraction at small angles is very important to understand both diffraction patterns and images. It uses several approximations, in particular the small angle diffraction approximation. This approximation is satisfied when the energy of the incident electrons is equal or larger than 50 kV (depending on crystal mean atomic number). This theory is presented here following Portier and Gratias [Portier, 1981].

Before its formal description a few remarks are required:

i) The electron microscope destroys the space isotropy as the electron are propagating thousand times faster in the direction defined by the optical column of the microscope (z direction) than in a plane perpendicular to it ({x,y} plane). In the small angles approximation the 3 dimensional stationary problem is replaced by a 2 dimensional problem where time is replaced by z. This problem can be solved using the theory of time dependant perturbation.

ii) The diffraction problem can be considered as a transition process using the following scheme:

-given known initial state $|i\rangle$ (direction of the incident electrons or wave vector), what is the transition probability after interaction with a diffusion potential during a time z (crystal thickness) to a particular final state $|f\rangle$ (i.e. a diffracted beam).

The dynamical theory of elastic diffraction calculates the amplitude and phase diffracted in a set of directions {|f>} selected by the Bragg law. It is equivalent to calculate the transition probabilities from an initial state |i> towards these directions |f>.

The fundamental equation of the elastic diffusion of electrons in a potential V is given in the stationary mono-electronic approximation (constant electron flux, no energy dispersion) [Humphreys, 1979]:

$$(\Delta + k^2)\Phi = V\Phi \tag{1}$$

where the wave vector k is given by:

$$k = \frac{\sqrt{2meE}}{\hbar}$$

$m = \gamma m_o =$ mass of the electron corrected for relativistic effect,

$$\gamma = 1 + \frac{e^2 E^2}{2m_o c^2} =$$ relativistic correction (2 à 511 KeV),

$e =$ electron charge,

$E =$ accelerating voltage,

$c =$ speed of light in vacuum,

$$V = -\frac{2me}{\hbar^2}V_{volt}(\rho;z) = \text{diffusing potential.}$$

In this description of the dynamical theory we use $\quad \dfrac{\hbar^2}{2m} = 1 \qquad .$

Table 1 shows a few values of the relativistic correction, the wavelength and speed of electron accelerated in a potential from 50 kV to 1000kV.

E_O kV	γ	λ [pm]	v/c
50	1.098	5.362	0.412
100	1.119	3.706	0.548
200	1.391	2.511	0.695
500	1.978	1.423	0.862
1000	2.957	0.873	0.941

TABLE 1. *Relativistic correction, wavelength and speed of the electron*

The electron microscope destroys the space isotropy because of the very high kinetic energy of the electrons. The 3-D space is thus described by {**r**; z} where $\rho = (x, y)$. At very high energy Bragg angles are very small. The Bragg law $2d_q \sin\theta = \lambda$ is nothing else but a consequence of elastic diffusion. Figure 1 shows the wave vectors $\underline{\mathbf{k}}_0$ and $\underline{\mathbf{k}}_q$ the incident beam and of a diffracted beam respectively. They are both located on the Ewald sphere, i.e. the sphere of all possible direction of elastic diffusion. Elastic diffusion will occur when $\underline{\mathbf{k}}_q = \underline{\mathbf{k}}_0 + \underline{\mathbf{q}}.$
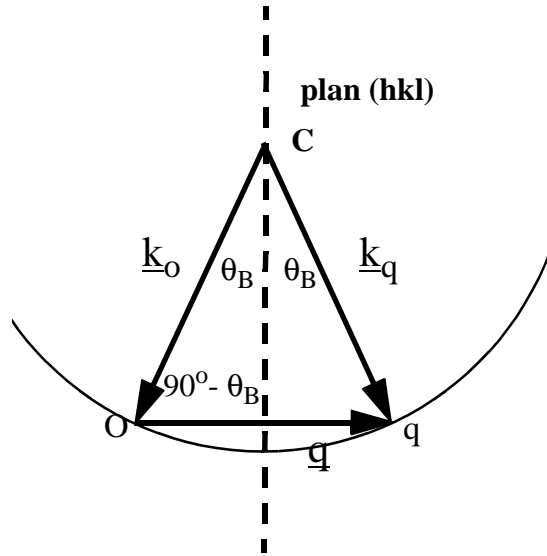
FIGURE 1. *Geometry of elastic diffraction (Bragg condition satisfied)*

Elastic diffraction satisfies $\left|\underline{k}_q\right| = \left|\underline{k}_o\right|$ and $\underline{k}_q - \underline{q} = \underline{k}_o$. Combining these 2

equations one obtain: $2\left|\underline{k}_o\right| \cos\left(\dfrac{\pi}{2} - \theta_B\right) = \left|\underline{q}\right|$. And finally the Bragg law:

$$2d_q \sin\theta_B = \lambda$$

For typical d_q of 10 nm^{-1} and wave vector of 400 nm^{-1} (at 200 kV), the Bragg angle is of the order of 0.15 degree. Thus the small angles approximation is well verified in transmission electron microscopy.

The geometry of the dynamical theory is defined in figure 2. The wave vector **k** of the incident electron is close to a [u,v,w] crystal direction (zone axis): the miss orientation is given by **c**, projection of **k** on the {x,y}plane ($|c| \sim$ 1-10 nm^{-1}). The z component k_z of **k** is very large ($\sim$400 nm^{-1}). As a result the electron wave oscillates with a very high frequency in the z direction. The electron wave function F(r; z) is written as:

$$\Phi(\underline{r}) = \Phi(\rho;z) = e^{ik_z z}\psi(\rho;z) \tag{2}$$

where $\psi(\rho;z)$ is a slowly varying function of z.

Putting equation (2) in equation (1) and neglecting $\dfrac{\partial^2\psi}{\partial z^2}$ because:

$$\left|\frac{\partial\psi}{\partial z}\right| \gg \frac{1}{2k_z}\left|\frac{\partial^2\psi}{\partial z^2}\right| \quad \text{and} \quad |\psi| \gg \frac{1}{2k_z}\left|\frac{\partial^2\psi}{\partial z^2}\right| \quad \text{(at 200 kV, l = 2.5 pm, } k_z = 400 \text{ nm}^{-1}\text{) the}$$

fundamental equation of the dynamical theory of elastic diffraction at small angles is obtained:

$$i\frac{\partial}{\partial z}\psi(\rho;z) = \frac{1}{2k_z}[-\Delta_\rho - \chi^2 + V(\rho;z)]\psi(\rho;z) \tag{3}$$

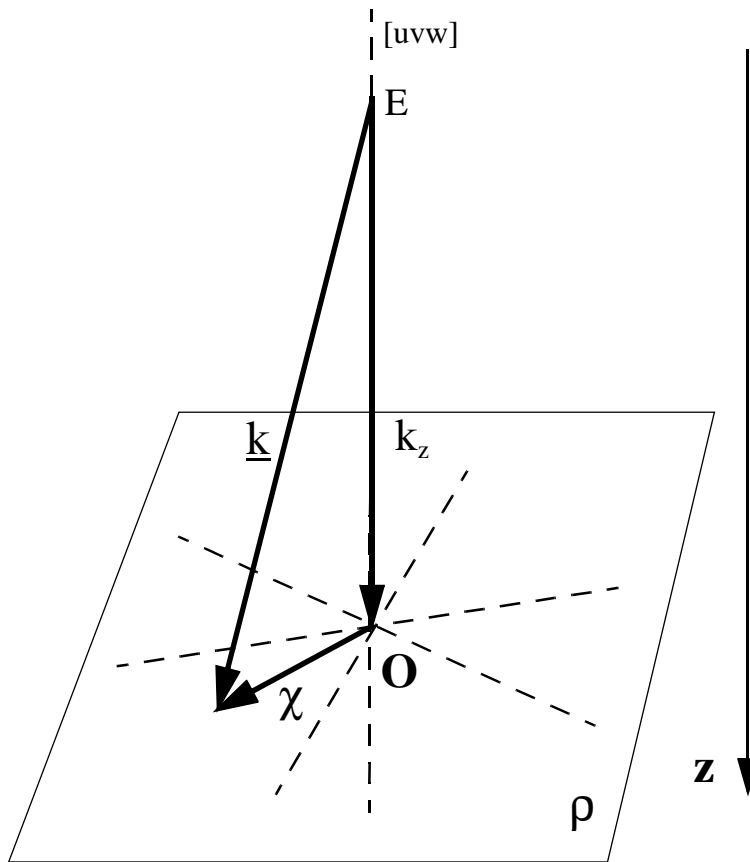**FIGURE 2.** *Geometry of the electron diffraction problem. The incident wave vector $|\underline{k}|$ is very large compared to its projection $|c|$ on the $\{r,0\} = (x, y)$ plane.*

Remarks:

i) The approximation of the fundamental equation is equivalent to assume that the diffusing potential is very small compared to the incident electron energy and that the z component of k only varies very slightly during the diffusion process. This is a good approximation as the mean crystal potential is of the order of 10~30 V.

ii) Electron back scattering is neglected (as the z movement is almost constant in the z direction).

Equation 3 is formally equivalent to a time-dependent Schroedinger equation in 2 dimensions **r**, where **z** plays the role of time. The evolution of the system is

absolutely causal, i.e. *from the past to the future without any interaction towards the past.* The -z movement of the electrons does not interfere with the +z movement.

Using a hamiltonian notation equation (3) becomes:

$$i\frac{\partial \psi}{\partial z} = H\psi \qquad \text{where} \quad H = \frac{1}{2k_z}[-\Delta_\rho - \chi^2 + V(\rho;z)]$$

Let us introduce H_o as:

$$H_o = -\Delta_\rho + V(\rho;z)$$

H_o is the hamiltonian of a system where **k** is parallel to [u,v,w].

Thus:

$$H = \frac{1}{2k_z}[H_o - \chi^2] \qquad \text{where } c^2 \text{ is the transverse kinetic energy of the}$$

incident electrons (it is null when the electron beam is along [u,v,w]).

H depends of **z** through V(r; z). When one assumes that V *does not depend* on **z**, one can define a *causal evolution operator* U(z, o) such that:

$$\Psi(\rho;z) = U(z, o)\psi(\rho;o) \tag{4}$$

Assuming that V = V(r) does not depend on z, is equivalent to replace the crystal by a stack of small slices of thickness t, with constant projected potential V'(r) (in a given slice):

$$V'(\rho) = \frac{1}{\tau} \int\limits_{z}^{(z+\tau)} V(\rho;z')dz' \tag{5}$$

The causal evolution operator is thus:

$$U(z_n, o) = U(z_n, z_{n-1})...U(z, o) \tag{6}$$

The evolution operator obeys the following differential equation (postulate of quantum mechanics) [Messiah, 1964, Shankar, 1994]:

$$i\frac{\partial}{\partial z}U(z, o) = H(\rho, z)U(z, o) \tag{7}$$

Hence, the small angle approximation of the dynamical theory of elastic electron diffraction is solved when the solutions of (7) are found.

Reminder on the notation used in the following pages

In the crystal space at 2 dimensions {x,y} or r (**r** representation), the position eigenvectors are given by:

$$|\rho\rangle = \delta(\rho' - \rho) \tag{8}$$

where d(r'-r) is the Dirac distribution (or function). In the dual space or reciprocal space or momentum space (**q** representation or plane waves basis) the eigenvectors of the momentum are given by:

$$|q\rangle = \frac{1}{2\pi}e^{i(q \cdot \rho)} \tag{9}$$

In the $\{|\rho\rangle\}$ basis the electron wave function is:

$$\langle\rho|\psi\rangle = \int \psi(\rho')\delta(\rho' - \rho)d\rho' \tag{10}$$

In the $\{|q\rangle\}$ basis (plane wave representation) the wave function projected in the $|q\rangle$ direction is:

$$\langle q|\psi\rangle = \int \psi(\rho)e^{-i(q \cdot \rho)}d\rho \tag{11}$$

i.e. $\langle q|\psi\rangle$ is the complex amplitude diffracted in the $|q\rangle$ direction.

The wave function $\psi(\rho) = \sum_{|q\rangle} |q\rangle\langle q|\psi\rangle$ is thus decomposed on the basis of plane waves, i.e. a Fourier decomposition.

The initial state characterized by c is represented by a state $|\psi_o\rangle$. Hence its wave function is written as: $\psi(\rho;o) = \langle\rho|\psi_o\rangle$.

Similarly, the final state at thickness z is $|\psi_z\rangle$ and its wave function is

$\psi(\rho;z) = \langle\rho|\psi_z\rangle$.

Hermitic or self-adjoint operators can be decomposed on the basis formed by their eigenvectors (spectral decomposition).

For example $H = \sum_i \lambda_i |\lambda_i\rangle\langle\lambda_i|$ (*spectral decomposition of H*).

Or: $H = \sum_i \lambda_i P_{\lambda_i}$ where $P_{\lambda_i} = |\lambda_i\rangle\langle\lambda_i|$ are the projection operators.

Using the spectral decomposition any function of an hermitic operator (i.e. f(H)) can be written as:

$f(H) = \sum_i f(\lambda_i)|\lambda_i\rangle\langle\lambda_i|$.

(this follows from the fact that $P^2_{\lambda_i} = P_{\lambda_i}$).

Transition probability

The electron wave function at thickness **z** after interaction with the crystal potential is given by $|\psi_z\rangle = U(z, o)|\psi_o\rangle$. The **intensity diffracted** in the $|q\rangle$ direction is the *transition probability* $\omega_{o \to q}(z, o)$ from the initial state $|q = o\rangle = |o\rangle$ to the final state $|q\rangle$ (figure 3). It is given by:

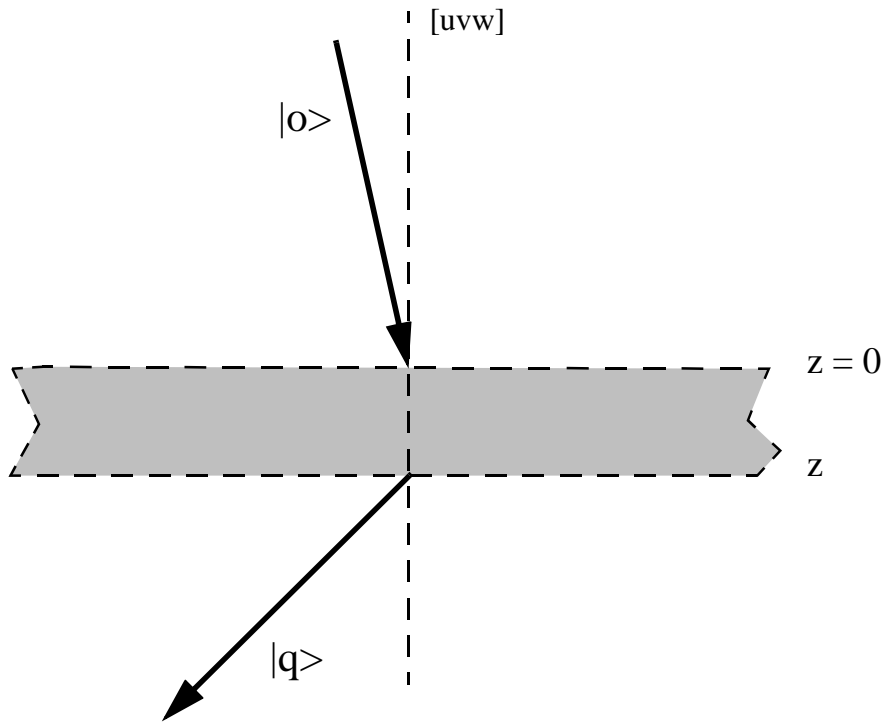$$\omega_{o \to q}(z, o) = |\langle q|U(z, o)|o\rangle|^2 \tag{12}$$

FIGURE 3. *Transition from the initial state | o> to a final state | q>.*

The intensity at a point **r** of the exit face of the crystal is similarly given by:

$$\omega_{o \to \rho}(z, o) = |\langle \rho|U(z, 0)|o\rangle|^2 = \left|\sum_q \langle \rho|q\rangle\langle q|U(z, 0)|o\rangle\right|^2$$

where the closure relation for a periodic specimen has been used: $\sum_q |q\rangle\langle q| = 1$.

The intensity observed at a point **r** located in the image plane (observation plane) is modified by the transfer function $T(q', q)$ of the electron microscope. It is given by:

$$\omega_{o \to \rho}(z, o) = \left| \sum_{q'} \sum_{q} \langle \rho | q' \rangle \langle q' | T(q', q) | q \rangle \langle q | U(z, o) | o \rangle \right|^2$$

where the exit wave function components $\langle q | U(z, 0) | o \rangle)$ are modified by the microscope (terms $\langle q' | T(q', q) | q \rangle$). The terms $\sum_{q'} \langle \rho | q' \rangle$ are related to the inverse Fourier transform that provides the image wave function.

In the back focal plane of the objective lens the $|q'\rangle$ wave function component is:

$$\sum_{q'} \langle q' | T(q', q) | q \rangle \langle q | U(z, o) | o \rangle$$

One sees that a coupling of the diffracted beams is introduced during the transfer by the objective lens.

When the transfer is linear (i.e. for a weak phase object), the transfer matrix is diagonal $\langle q' | T(q', q) | q \rangle = T(q) \delta(q' - q)$. In that particularly simple case, the image intensity is given by:

$$\omega_{o \to \rho}(z, o) = \left| \sum_{q} \langle \rho | q \rangle T(q) \langle q | U(z, 0) | o \rangle \right|^2 \tag{13}$$

Furthermore the symmetry properties of the diffraction patterns and of the high resolution images are intrinsic properties of the transition probability functions $\omega_{o \to q}(z, o)$ and $\omega_{o \to \rho}(z, o)$.

To summarize, one have to calculate the evolution operator $U(z, o)$ in order to solve the fundamental equation.

$U(z, o)$, a unitary operator, is not in general directly integrable. But, when

$H(z)$ and $\frac{\partial}{\partial z} H(z)$ commute one has the general solution:

$$U(z, o) = \exp\left[-i \int_o^z H(\tau)\,d\tau \right] \tag{14}$$

$H(z)$ and $\frac{\partial}{\partial z} H(z)$ commute when:

- $V(\rho, z)$ does not depend on z,
- $V(\rho; z)$ can be neglected,
- $H(z)$ reduces to its potential term.

These approximations are considered below. They are very useful for the electron microscopes, as they explain both the Bloch wave and the multislice approach.

Approximations

The diffusing potential does not depend on z

When the diffusion potential does not depend on z, the evolution operator

$U(z, o) = \exp{-i} \int_o^z H(\tau)\,d\tau$ is reduced to $U(z, o) = \exp{-i} \int_o^z H(\tau)\,d\tau$.

As H is a hermitic (self-adjoint) operator it can be represented in its eigenstates basis $\{|\alpha\rangle\}$ by a *diagonal matrix* where the γ_α are the (real) associated eigenvalues:

$$H|\alpha\rangle = \gamma_\alpha |\alpha\rangle \tag{15}$$

The eigenstates $|\alpha\rangle$ are Bloch waves that characterize the propagation of the electron wave in a periodic continuum (crystal) and the eigenvalues γ_α give the kinetic energy of the Bloch waves. The unitary operators $P_\alpha = |\alpha\rangle\langle\alpha|$ are projectors on the eigenstates of the Hamiltonian $H(z)$:

$$H = \sum_\alpha \gamma_\alpha |\alpha\rangle\langle\alpha| = \sum_\alpha \gamma_\alpha P_\alpha \tag{16}$$

The evolution operator is a function of H and is written as:

$$U(z, o) = \sum_\alpha e^{-\gamma_\alpha z}|\alpha\rangle\langle\alpha|.$$

When V (**r**) does not depend on z, $U(z, o)$ is also diagonal on $\{|\alpha\rangle\}$. Therefore there is no possibility of transition between Bloch states.

The incident wave function $|o\rangle$ is a plane wave (or a sum of plane waves). Using the principle of superposition, it suffices to consider only one plane wave to calculate the wave function $\psi(\rho, z)$ at the exit plane of the crystal:

$$\psi(\rho, z) = \sum_q \phi_q(\rho, z)|q\rangle.$$

But:

$$|\psi_z\rangle = \sum_\alpha e^{-\gamma_\alpha z}|\alpha\rangle\langle\alpha|\psi_o\rangle$$

As a consequence the (complex) projected amplitude of $|\psi_z\rangle$ on $|q\rangle$ (Fourier coefficient of the wave transmitted by the crystal, i.e diffracted beam) is:

$$\phi_q(\rho, z) = \langle q|\psi_z\rangle = \langle q|U(z, o)|o\rangle = \sum_{\alpha} e^{-\gamma_{\alpha}z}\langle q|\alpha\rangle\langle\alpha|o\rangle \qquad (17)$$

Many books and research papers use excitation and Bloch wave coefficients. They are expressed in function of $|q\rangle$ and $|\alpha\rangle$ as:

$$\langle\alpha|o\rangle = (c_o^{\alpha})^* = c_o^{\alpha*} \quad \text{projection of } |o\rangle \text{ on } |\alpha\rangle : \text{excitation coeff.} \qquad ,$$

$$\langle q|\alpha\rangle = c_q^{\alpha} \quad \text{projection of } |\alpha\rangle \text{ on } |q\rangle \qquad \qquad .$$

Using the microscopes notation:

$$\phi_q(\rho, z) = \langle q|U(z, o)|o\rangle = \sum_{\alpha} e^{-\gamma_{\alpha}z} c_q^{\alpha} c_o^{\alpha*} \qquad (18)$$

And the exit wave function is:

$$\psi(\rho;z) = \sum_{q} \phi_q(\rho, z)|q\rangle = \sum_{\alpha} c_o^{\alpha*} e^{-\gamma_{\alpha}z} \sum_{q} c_q^{\alpha} |q\rangle \qquad (19)$$

The eigenstates or Bloch waves are linear combinations of the plane waves:

$$|\alpha\rangle = \sum_{q} c_q^{\alpha} |q\rangle.$$

Equation (19) gives the representation of the wave function on the plane wave basis $\{|q\rangle\}$, i.e. its Fourier decomposition. The eigenstates define the dispersion surfaces, surfaces of constant total energy, but different kinetic energy.

How to determine the eigenstates?

In the plane waves basis $\{|q\rangle\}$ (q representation) $H|\alpha\rangle = \gamma_{\alpha}|\alpha\rangle$ is written as:

$$\langle q|H|\alpha\rangle = \gamma_{\alpha}\langle q|\alpha\rangle.$$

Using the closure relation $\sum_{q'}|q'\rangle\langle q'| = \mathbf{1}$, the matrix elements of H ($\{|q\rangle\}$ basis)

are obtained:

$$\sum_{q'}\langle q|H|q'\rangle\langle q'|\alpha\rangle = \gamma_{\alpha}\langle q|\alpha\rangle \tag{20}$$

For the hamiltonian $H = \dfrac{1}{2k_z}[-\Delta_{\rho} - \chi^2 + V(\rho;z)]$, the matrix elements of

$-\Delta_{\rho} - \chi^2$ are diagonal and consequently equation (20) reduces to:

$$\frac{q^2 - \chi^2}{2k_z}\langle q|\alpha\rangle + \sum_{q'}\langle q|\frac{V}{2k_z}|q'\rangle\langle q'|\alpha\rangle = \gamma_{\alpha}\langle q|\alpha\rangle \tag{21}$$

Using the microscopiste excitation error and Bloch wave coefficients and the fact that the matrix element of V(r) are:

$$V_{q'-q} = \langle q|V|q'\rangle,$$

the usual secular equation is obtained:

$$\frac{q^2 - \chi^2}{2k_z}c_q^{\alpha} + \sum_{q'}\frac{V_{q'-q}}{2k_z}c_{q'}^{\alpha} = \gamma_{\alpha}c_q^{\alpha} \tag{22}$$

It is simpler to write it in matrix form: $\{M\}\underline{c} = \gamma\{I\}\underline{c}$

where $\{I\}$ is the identity matrix and the matrix elements of M are:

$$M_{ij} = \frac{q_i^2 - \chi^2}{2k_z}\delta_{ij} + \frac{1}{2k_z}V_{q_j - q_i}.$$

A necessary condition to solve equation (22) is:

$$Det[\{M\} - \gamma\{I\}] = o.$$

When the dimension of the $\{|q\rangle\}$ basis is n (1 transmitted and n -1 diffracted beams), the eigensystem will provide n eigenvalues γ_α and n eigenvectors $|\alpha\rangle$ called eigenstates (i.e. Bloch waves). Some of the eigenstates can be degenerated depending of the symmetry of the diffraction experiment. When there is no degenerate state, each state corresponds to a Bloch wave with a different kinetic energy, but the same total energy.

Example

Here one considers a diffraction experiment where only 5 beams are excited (figure 4):
- crystal is Al fcc,
- zone axis is [0,0,1],
- exact zone axis condition (c = 0),
- accelerating voltage is 100 kV.

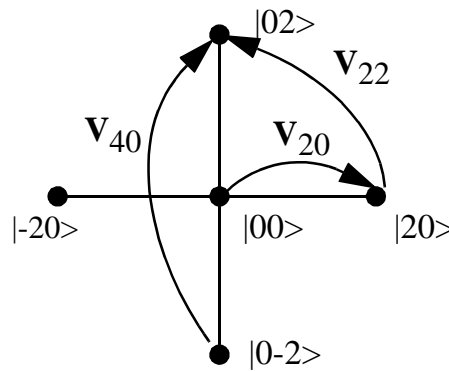- $\{|q\rangle\}$ basis: $\{|00\rangle, |20\rangle, |02\rangle, |\bar{2}0\rangle, |\bar{2}\bar{2}\rangle\}$

FIGURE 4. *5 beams diffraction experiment. The arrows show the interaction between the different diffracted beams.*

The secular matrix is:

	$|00\rangle$	$|20\rangle$	$|02\rangle$	$|-20\rangle$	$|0-2\rangle$
$|00\rangle$	0	V_{20}	V_{20}	V_{20}	V_{20}
$|20\rangle$	V_{20}	h_{22}	V_{22}	V_{40}	V_{22}
$|02\rangle$	V_{20}	V_{22}	h_{22}	V_{22}	V_{40}
$|-20\rangle$	V_{20}	V_{40}	V_{22}	h_{22}	V_{22}
$|0-2\rangle$	V_{20}	V_{22}	V_{40}	V_{22}	h_{22}

TABLE 2. *Secular matrix of the 5 beams diffraction experiment.*

The Fourier coefficients of the potential $V_{|00\rangle-|20\rangle}, V_{|20\rangle-|02\rangle}, V_{|20\rangle-|-20\rangle}$ (matrix elements $V_{q'-q}$) have been identified as U_{20}, U_{22} et U_{40} respectively. The "strength" of the dynamical interaction between the transmitted beam $|00\rangle$ and the diffracted beams $|20\rangle$ is proportional to U_{20}. It is proportional to U_{22} for the interaction between beams $|20\rangle$ and $|02\rangle$, and to U_{40} for $|20\rangle$ et $|-20\rangle$. The numerical values are given below (arbitrary units).

$$
\begin{pmatrix}
0 & -3.946 & -3.946 & -3.946 & -3.946 \\
-3.946 & 24.39 & -2.392 & -2.392 & -1.443 \\
-3.946 & -2.392 & 24.39 & -1.443 & -2.392 \\
-3.946 & -2.392 & -1.443 & 24.39 & -2.392 \\
-3.946 & -1.443 & -2.392 & -2.392 & 24.39
\end{pmatrix}
$$

FIGURE 5. *Numerical coefficients of the secular matrix (5 beams experiment)*

The eigenvalues correspond to Bloch waves of different energy. The lowest energy (-2.95) is attributed to a core state written as state 1s. In this particular diffraction experiment only 2 states are excited, state 1s and state 2s (21.1). These states are totally symmetric, they correspond to type A_1 irreducible representation of C_{4v}.

$$\{ 27.7 , 25.8 , 25.8 , 21.1 , -2.95 \}$$

FIGURE 6. *Eigenvalues of the 5 beams diffraction experiment. Eigenstate 25.8 suffers is 2 fold degenrated.*

α	$c^{\alpha}_{\lvert oo \rangle}$	$c^{\alpha}_{\lvert 2o \rangle}$	$c^{\alpha}_{\lvert o2 \rangle}$	$c^{\alpha}_{\lvert \bar{2}o \rangle}$	$c^{\alpha}_{\lvert o\bar{2} \rangle}$	
1	0	0.5	-0.5	-0.5	0.5	B_1
2	0	0.353	-0.613	0.613	-0.353	}E
3	0	-0.613	-0.353	0.353	0.613	
4	-0.35	0.468	0.468	0.468	0.468	A_1
5	-0.937	-0.175	-0.175	-0.175	-0.175	A_1

FIGURE 7. *Eigenstate $\lvert a \rangle$ coefficients. The excitation coefficients of the anti symmetric eigenstates are null. The irreducible decomposition of the C_{4v} representation in the 5 plane waves basis is $2A_1 + B_1 + E$. Only the eigenstates $\lvert \alpha \rangle$ with the symmetry of the irreducible representation A_1 are excited.*

As stated above the Bloch wave approach to the dynamical theory of electron diffraction has the advantage to place the symmetry properties of the eigenstates in the forefront. Furthermore using these symmetries it is possible to put the secular matrix into a block diagonal form and to reduce the size and time of the calculation.

$$\begin{pmatrix} h_{11} & h_{12} & h_{12} & h_{12} & h_{12} \\ h_{12} & h_{22} & h_{23} & h_{23} & h_{25} \\ h_{12} & h_{23} & h_{22} & h_{25} & h_{23} \\ h_{12} & h_{23} & h_{25} & h_{22} & h_{23} \\ h_{12} & h_{25} & h_{23} & h_{23} & h_{22} \end{pmatrix}$$

$$\downarrow$$

$$\begin{pmatrix} h_{11} & h_{12} & 0 & 0 & 0 \\ 4\,h_{12} & h_{22} + 2\,h_{23} + h_{25} & 0 & 0 & 0 \\ 0 & 0 & h_{22} - h_{25} & 0 & 0 \\ 0 & 0 & 0 & h_{22} - h_{23} & h_{23} - h_{25} \\ 0 & 0 & 0 & h_{23} - h_{25} & h_{22} - h_{23} \end{pmatrix}$$

FIGURE 8. *With a symmetry adapted basis, the secular matrix is put into a block diagonal form.*

In our case it is also immediate to obtain an analytical expression of the eigenstates. Without such a reduction there will not be an analytical solution as the characteristic polynomial is of degree 5. With the reduction of C_{4v} to $2A_1 + B_1 + E$, the analytical eigenvalues are given by the solutions of 3 characteristic polynomials, two of degree 2 and one of degree 1! Finally the 5 beams diffraction problem reduces to find the solutions of the following secular matrix.

$$\begin{pmatrix} 0 & h_{12} \\ 4\,h_{12} & h_{22} + 2\,h_{23} + h_{25} \end{pmatrix}$$

FIGURE 9. *Using group theory and a symmetry adapted basis the secular matrix of the 5 beams problem reduces to a 2x2 matrix.*

The approximation of the Fresnel propagator

This is the approximation that corresponds to the propagation of the incident electron in vacuum or between thin crystal slices where the crystal potential V(r;z) is null. In that case H reduces $H = \dfrac{1}{2k_z}(-\Delta_\rho - \chi^2)$.

H is then diagonal in the $\{|q\rangle\}$ basis (plane waves):

$$H|q\rangle = \frac{q^2 - \chi^2}{2k_z}|q\rangle.$$

The evolution operator is also diagonal in $\{|q\rangle\}$:

$$U(z, o) = e^{-Hz} = \int dq\, e^{-i\frac{q^2 - \chi^2}{2k_z}z}|q\rangle\langle q| \tag{23}$$

Without a diffusing potential, the incident wave function is not modified:

$$U(z, o)|o\rangle = |o\rangle.$$

In real space propagation from point $|\rho_1\rangle$ to point $|\rho_2\rangle$ is given by:

$$\langle\rho_2|U(z, o)|\rho_1\rangle = \int dq\, e^{-i\frac{q^2 - \chi^2}{2k_z}z}\langle\rho_2|q\rangle\langle q|\rho_1\rangle \tag{24}$$

But:

$$\langle\rho_2|q\rangle = \int dq\, \delta(\rho - \rho_2)e^{iq\cdot\rho}$$

and

$$\langle q|\rho_1\rangle = \int dq\, \delta(\rho - \rho_1)e^{-iq\cdot\rho}\,.$$

Finally when $\chi = 0$:

$$\langle\rho_2|U(z,o)|\rho_1\rangle = \int dq\, e^{-i\frac{q^2}{2k_z}z}\, e^{-iq\cdot(\rho_1-\rho_2)} = e^{\frac{-ik_z(\rho_1-\rho_2)^2}{z}} \tag{25}$$

This is the *Fresnel propagator* expressed in direct space ($\{|\rho\rangle\}$ basis).

Phase grating approximation

Here H is assumed to be:

$$H = \frac{1}{2k_z}V(\rho;z)\,.$$

H is then diagonal $|\rho\rangle$ representation.

$$H(z)|\rho\rangle = \frac{1}{2k_z}V(\rho;z)|\rho\rangle\,.$$

The evolution operator is:

$$U(z,o) = \int d\rho\, e^{\left[\frac{-i}{2k_z}\int_o^z V(\rho;\tau)d\tau\right]}|\rho\rangle\langle\rho| \tag{26}$$

At thickness z, the wave function is:

$$|\psi_z\rangle = U(z,o)|o\rangle = e^{\left[\frac{-i}{2k_z}\int_o^z V(\rho;\tau)d\tau\right]}|o\rangle = e^{-i\sigma V_p(\rho)}|o\rangle \tag{27}$$

This is the phase grating approximation, that is the base of the multislice approach for the calculation of the complex exit wave function. The crystal is sliced into thin enough, the potential of each slice is projected on a plane and form a phase grating. The incident wave function is multiplied by the phase grating of the slice and propagated to the next. The propagation is usually performed in dual space.

Power series method

When H does not depend on **z**, the evolution operator $U(z, o) = e^{-iHz}$ can be developed in a power series of **z**:

$$U(z, o) = 1 - iHz + \frac{(-iH)^2}{2!}z^2 - \frac{(-iH)^3}{3!}z^3 + \dots \tag{28}$$

To third order the diffracted beam $|q\rangle$ is:

$$\langle q|U(z, o)|o\rangle = \langle q|o\rangle - i\langle q|H|o\rangle - \frac{1}{2}\langle q|H^2|o\rangle - \frac{i}{6}\langle q|H^3|o\rangle$$

Because $\langle q|H^2|o\rangle = \langle q|HH|o\rangle = \sum_{q'} \langle q|H|q'\rangle\langle q'|H|o\rangle$

and $\langle q|H^3|o\rangle = \langle q|HHH|o\rangle = \sum_{q''}\sum_{q'} \langle q|H|q''\rangle\langle q''|H|q'\rangle\langle q'|H|o\rangle$,

$\langle q|U(z, o)|o\rangle$ is calculated by summing the power series of the diffraction matrix

$\{H_{q'q}\} = \langle q'|H|q\rangle$.

To first order (kinematical approximation), diffraction introduces a $\frac{\pi}{2}$ dephasing of diffracted beams. One has to remember that in this approximation, the diffracted beams do not interfere with the transmitted beam. In high resolution electron microscopy this dephasing is more or less compensated by the phase changes introduced by the specimen defocus and by the spherical aberration of the objective lens of the microscope.

z dependent crystal potential

In that case the evolution of a diffracted beam $|q\rangle$ is given by:

$$i\frac{\partial}{\partial z}\langle q|U(z, o)|o\rangle = \langle q|H(z)U(z, o)|o\rangle \tag{29}$$

Using the closure relation one obtain:

$$i\frac{\partial}{\partial z}\langle q|U(z, o)|o\rangle = \sum_{q'}\langle q|H(z)|q'\rangle\langle q'|U(z, o)|o\rangle \tag{30}$$

Writing $|q\rangle$ as $\phi_q(z) = \langle q|U(z, o)|o\rangle$, the matrix elements of H are:

$$i\frac{\partial}{\partial z}\phi_q(z) = \frac{q^2 - \chi^2}{2k_z}\phi_q(z) + \frac{1}{2k_z}\sum_{q'}\langle q|V(z)|q'\rangle\phi_{q'}(z)$$

This equation shows clearly the coupling of the diffracted beams due to the crystal potential. In many books and research papers on the theory of electron diffraction

the coefficient $\frac{-1}{2\pi}\left(\frac{q^2 - \chi^2}{2k_z}\right)$ is known as the excitation error $s_{|q\rangle}$. It is

proportional to the distance of the reciprocal node $|q\rangle$ to the Ewald sphere.

Reflections at Bragg conditions are such that $s_{|q\rangle}$ is zero. With the $s_{|q\rangle}$ equation 30 becomes:

$$\frac{\partial}{\partial z}\phi_q(z) \;=\; i\pi\left[2s_q\phi_q(z) - \sum_{q'}\frac{V_{q'-q}}{2\pi k_z}\phi_{q'}(z)\right]$$

This equation has been first proposed by Howie-Whelan [Hirsch, 1977]. They are of great practical importance in the frame of the column approximation employed to calculate the contrast of crystalline defects such as dislocations or interfaces. Their numerical solution is obtained by Runge-Kutta integration.

Final remarks

All these different techniques are equivalent for the calculation of the exit wave function, but each has a specific domain where it performs better in terms of computation ease or speed. Figure 10 shows two calculations, one using the Bloch wave approach and the other using the multislice method. There are indeed small differences in the intensity, but it obvious that such differences will not appear in simulated images.
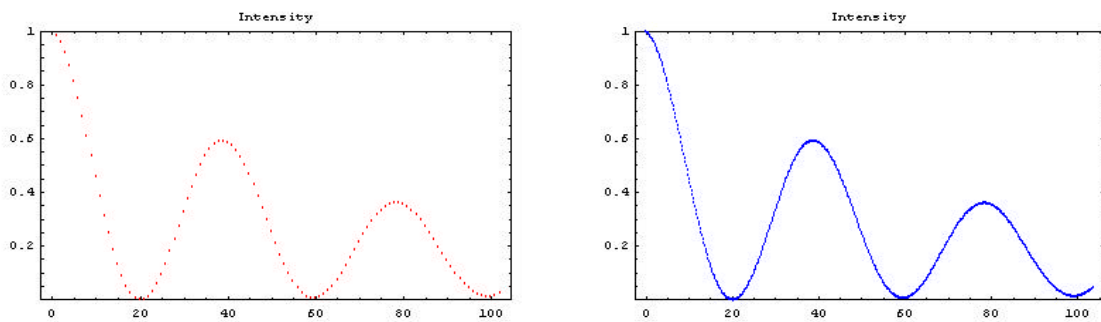
FIGURE 10. *Multislice & Bloch wave simulation of (2,0,0) beam. Al 400kV, zone Axis [0,0,1]*

Bloch wave approach is more accurate when the dynamical calculations must include High Order Laue Zone reflections, like CBED and LACBED patterns (figures 11, 12) while multislice is definitely the method to use for the simulation of HREM images of defects (figure 13).
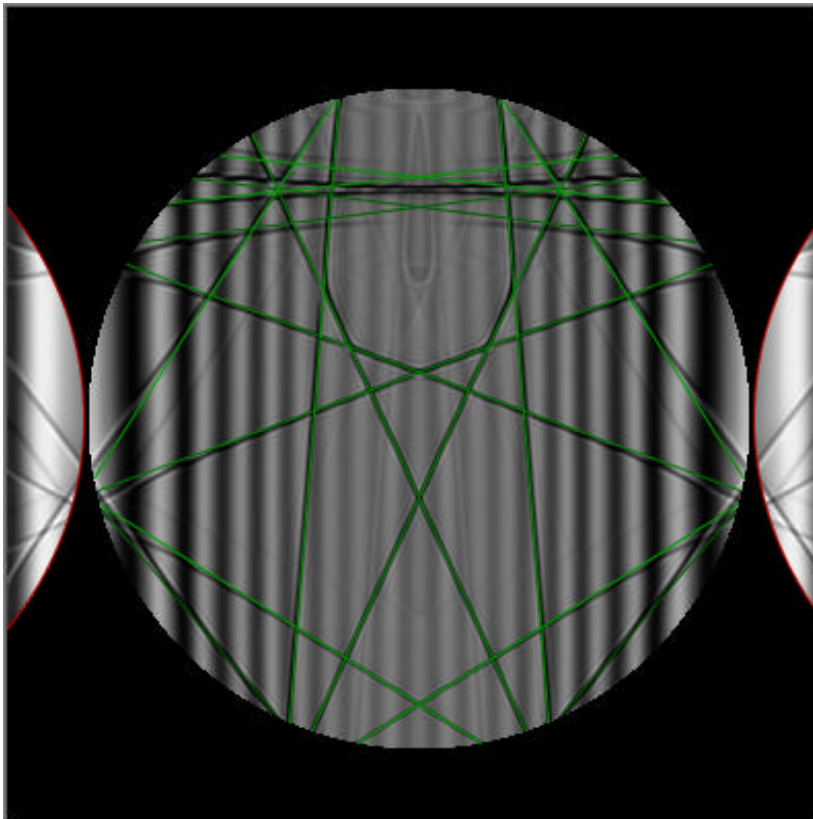

FIGURE 11. *Bloch wave calculation Al [1,3,3]. Kinematical HOLZ lines are superimposed (HOLZ shift included).*
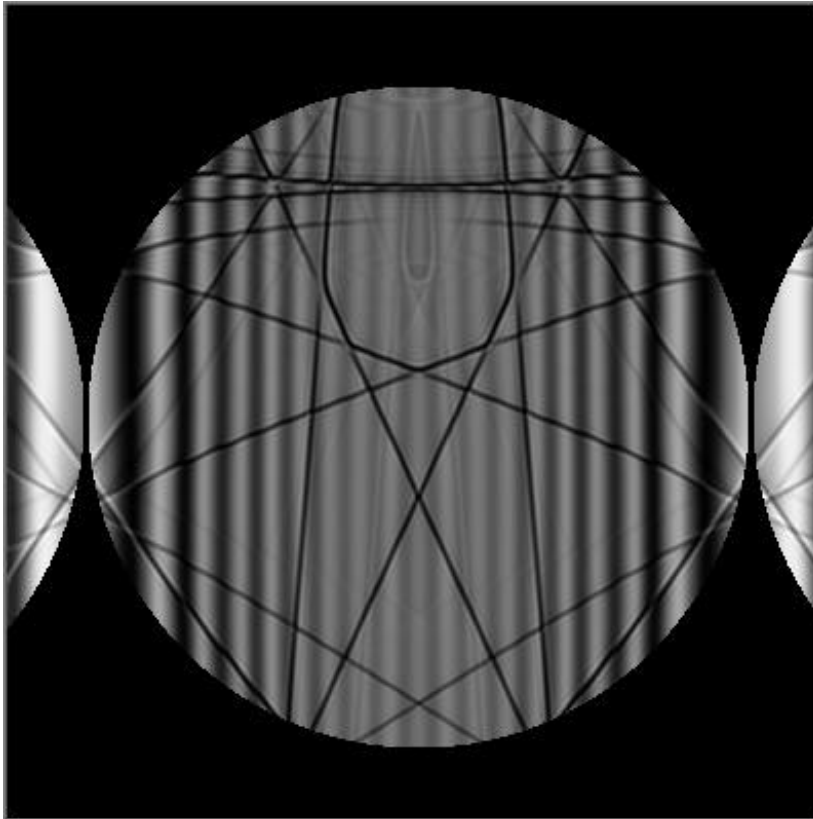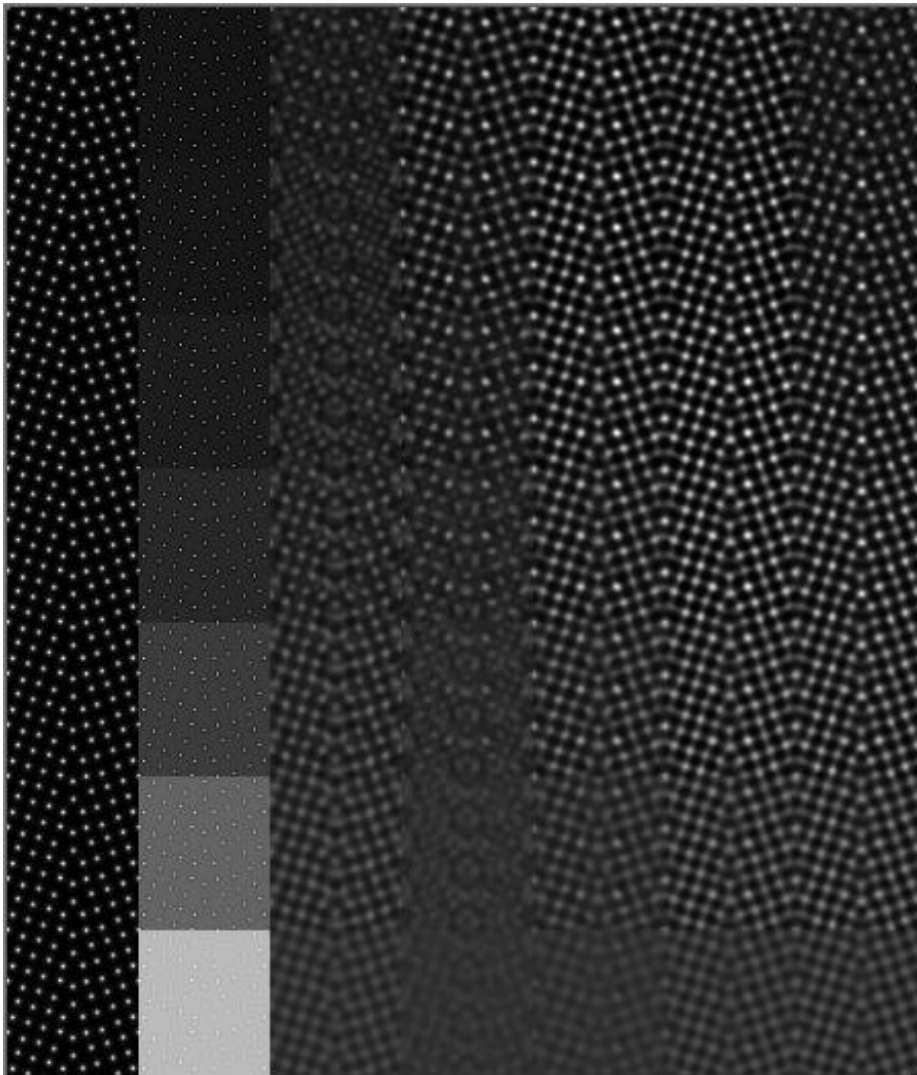
FIGURE 12. *Bloch wave calculation Al [1,3,3].*

FIGURE 13. *HREM image map Au* S_{53} *001.*

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