Calculation of Reflected Intensities for Medium and High Energy Electron Diffraction

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Dedicated to Professor K. Molière on the occasion of his sixtieth birthday

The Bethe theory of electron diffraction is used to calculate reflection electron diffraction intensities for medium and high energy electrons. A generalized Hill's determinant method is used for the numerical calculations instead of the more common but slower matrix-eigenvalue technique. Results of a "systematics" calculation of the specular intensity as a function of incident angle are compared with some experimental values for the Si (111) surface. The application of the Bethe theory to crystals where the surface structure differs from the bulk is also considered.

1. Introduction

The Bethe theory ¹ of electron diffraction, so useful in Transmission microscopy (TM) studies ², has also been used for calculating reflection electron diffraction intensities ³–⁵. The infinite number of dynamical equations obtained from the theory is first reduced to a finite number \( N \) in a manner similar to that used in TM calculations. These \( N \) coupled equations of second order in the wave vector component normal to the crystal surface may be transformed into a \( 2N \times 2N \) matrix eigenvalue equation. (The small \( \lambda \), linearisation approximations of TM are no longer valid for reflection calculations.) Bloch wave components corresponding to each of the \( 2N \) eigenvalues are then calculated and the amplitudes of the various Bloch waves are found from the boundary condition (BC) equations. Here a difficulty arises. In the transmission case there are exactly enough BC equations to provide solutions for all unknown quantities. In the reflection case this is no longer so. This problem arises because some of the eigenvalues are physically equivalent to each other and thus produce identical Bloch wave components. If the amplitudes of the Bloch waves associated with these equivalent eigenvalues are then treated as separate and distinct unknown quantities, then it is not surprising that there are insufficient BC equations. Thus to calculate the reflected intensities using matrix eigenvalue techniques one eigenvalue from each set should be chosen and only these eigenvalues should be used to calculate the Bloch wave components and amplitudes.

Unfortunately, because of the equivalence of many of the eigenvalues, matrix eigenvalue techniques are inefficient in use of computer time. Eigenvalue algorithms generally calculate all eigenvalues even though only one from each set of equivalent eigenvalues is required in the intensity calculation. A more efficient procedure in such cases is the generalized Hill's determinant method proposed by Lamla ⁶, ⁷.

This article describes the development of the Hill's determinant (HD) approach, showing how the problem of equivalent eigenvalues arises, is resolved and efficiently solved. As far as possible Lamla's notation has been retained. The application of the Bethe theory to crystals where the surface structure differs from the bulk is also discussed.

2. Bethe Theory

An electron incident on a crystal finds itself in a region of potential \( V(\mathbf{r}) \). For an electron of energy \( E \) (eV) the Schroedinger equation is

\[
\nabla^2 \Psi + \left(2 m/e^2\right)(E + V) \Psi = 0
\]

which has solution in vacuum

\[
\Psi = \exp\left\{-2 \pi i \mathbf{k}_a \cdot \mathbf{r}\right\},
\]

where \( |\mathbf{k}_a| = 1/2 \gg \sqrt{E/150} \text{ Å}^{-1} \). The primitive translations of the crystal lattice \( a_1, a_2, a_3 \) are so

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chosen that \( \mathbf{a}_1, \mathbf{a}_2 \) lie on the boundary plane of the crystal surface. The corresponding vectors of the reciprocal net are defined by \( \mathbf{b}_i = \mathbf{a}_i \times \mathbf{a}_h, \mathbf{Q}, \) where \( \mathbf{Q} = \mathbf{a}_1, \mathbf{a}_2 \times \mathbf{a}_h. \) A right hand cartesian coordinate system is chosen such that the boundaries of the crystal are defined by \( z = 0 \) and \( z = D \) (which may be finite or infinite). The potential \( V \) possesses the lattice periodicity and may be expanded in a Fourier series

\[
(2 \pi \omega V/\hbar^2) = \sum_{\mathbf{g}} v_\mathbf{g} \exp\{-2 \pi i \mathbf{b}_\mathbf{g} \cdot \mathbf{r}\}
\]

where \( \mathbf{g} \) represents the number triple such that \( \mathbf{b}_\mathbf{g} = g_1 \mathbf{b}_1 + g_2 \mathbf{b}_2 + g_3 \mathbf{b}_3 \). The wave function may be expanded as a linear combination of Bloch wave expressions of the form

\[
\psi = \sum_{\mathbf{g}} \psi_\mathbf{g} \exp\{-2 \pi i \mathbf{b}_\mathbf{g} \cdot \mathbf{r}\}
\]

where \( \mathbf{k}_g = \mathbf{K}_0 + \mathbf{b}_g \). Substitution of the expressions for \( \Psi \) and \( V \) into (1) yields (after rearrangement)

\[
\sum_{\mathbf{h}} \{ (\mathbf{k}_g^2 \mathbf{h}^2 - 1) \delta_{\mathbf{gh}} - \mathbf{h}^2/4 \pi^2 v_{\mathbf{g} - \mathbf{h}} \} \psi_\mathbf{h} = 0,
\]

where \( \delta_{\mathbf{gh}} \) is the Kronecker \( \delta \)-function. The condition for solution of the (infinite) equation system is the vanishing of the determinant of the coefficients

\[
\det | (\mathbf{k}_g^2 \mathbf{h}^2 - 1) \delta_{\mathbf{gh}} - \mathbf{h}^2/4 \pi^2 v_{\mathbf{g} - \mathbf{h}} | = 0.
\]

The \( X \) - and \( Y \)-components of \( \mathbf{K}_0 \) (crystal) are written as \( \alpha_0/\lambda, \beta_0/\lambda \) (\( \lambda \) is the vacuum wavelength) and the \( Z \)-component as \( x_0/\lambda \). Defining

\[
\begin{align*}
\gamma_g &= \gamma_g \mathbf{z}^2 = \gamma_g (g_1 \mathbf{b}_1^2 + g_2 \mathbf{b}_2^2), \\
\alpha_g &= \alpha_g \mathbf{b}_g^0 = \gamma_g (g_1 \mathbf{b}_1^2 + g_2 \mathbf{b}_2^2) \quad \text{and} \quad g_0 = x_0 + \tau_g.
\end{align*}
\]

Now \( k_g^2 \mathbf{h}^2 - 1 \) may be rewritten as

\[
x_g^2 - \gamma_g^2 = (x_0 + \tau_g)^2 - \gamma_g^2
\]

where

\[
\gamma_g = \sqrt{1 - \alpha_g^2 - \beta_g^2}
\]

and writing \( v_g^2/4 \pi^2 g = \sqrt{V}/E \) and \( v_g = a_g v_0 \) the dynamical equations may be rewritten as

\[
\sum_{\mathbf{h}} [((x_0 + \tau_g)^2 - \gamma_g^2) \delta_{\mathbf{gh}} - a_{\mathbf{g} - \mathbf{h}}] \psi_\mathbf{h} = 0
\]

which have a solution provided

\[
det | [((x_0 + \tau_g)^2 - \gamma_g^2) \delta_{\mathbf{gh}} - a_{\mathbf{g} - \mathbf{h}} | = 0.
\]

Distinguishing the various solutions \( z_0 \) of this equation by the index \( i \) the wave function in the interior may be written as

\[
\Psi = \sum_{\mathbf{g}, i} \psi_{\mathbf{g}, i} \exp\{-2 \pi i/\lambda (a_g X + \beta_g Y + x_0^i Z)\}.
\]

Now a plane wave (direction cosines \( \alpha, \beta, \gamma \) and amplitude 1) has wave function

\[
\Psi_0 = \exp\{-2 \pi i/\lambda (a_0 X + \beta_0 Y + \gamma_0 Z)\}.
\]

Continuity conditions at the surface require that

\[
a_g = a_0 \quad \text{and} \quad \beta_g = \beta_0.
\]

and thus \( a_g = a_0 + \gamma_0 \) and \( \beta_g = \beta_0 + \gamma_0 \).

Now because of the existence of the waves \( \mathbf{k}_g \) in the crystal diffracted waves appear in the vacuum with wave vectors \( a_g/\lambda, \beta_g/\lambda, \gamma_g/\lambda \) where \( \gamma_g \) is determined by Equation (7). The negative sign corresponds to a reflected wave and the positive sign to the transmitted wave. The wave function (in vacuum) for the reflected wave \( (Z \leq 0) \) is

\[
\Psi^R = \sum_{\mathbf{g}} \psi_{\mathbf{g}, 0} \exp\{-2 \pi i/\lambda (a_g X + \beta_g Y + \gamma_g Z)\},
\]

and for the transmitted wave \( (Z \geq D) \)

\[
\Psi^T = \sum_{\mathbf{g}} \Phi_{\mathbf{g}} \exp\{-2 \pi i/\lambda (a_g X + \beta_g Y + \gamma_g Z)\}.
\]

The requirements of continuity of the wave function and its normal derivative on the upper surface \( Z = 0 \) yields the equations

\[
1 + \varphi_0 = \sum_{g_0} \psi_{g_0}^i , \quad \gamma(1 - \varphi_0) = \sum x_{g_0}^i \psi_{g_0}^i , \quad g_1, g_2 = 0
\]

and

\[
\varphi_g = \sum_{g_0} \psi_{g_0}^i \quad \gamma_0 \varphi_g = \sum_{g_0} x_{g_0}^i \psi_{g_0}^i \quad \text{for all other cases.}
\]

On the lower surface \( Z = D \) the corresponding equations are found

\[
\Phi_g \exp\{-2 \pi i/\lambda \gamma_0 D\} = \sum_{g_0} \psi_{g_0}^i \exp\{-2 \pi i/\lambda x_{g_0}^i D\},
\]

\[
\gamma_0 \Phi_g \exp\{-2 \pi i/\lambda \gamma_0 D\} = \sum_{g_0} x_{g_0}^i \psi_{g_0}^i \exp\{-2 \pi i/\lambda x_{g_0}^i D\}.
\]

Eliminating the quantities \( \Phi_g \) and \( \varphi_g \) from these equations the boundary condition equations are ob-
tained.
\[ \sum_{\nu, \xi} (\gamma_\nu + x_\nu) \psi_{\gamma, \nu} = 2 \gamma \quad \text{for} \quad g_1, g_2 = 0 \]
\[ = 0 \quad \text{for all other cases} \quad (18) \]
\[ \sum_{\nu, \xi} (\gamma_\nu - x_\nu) \psi_{\gamma, \nu} \exp\{-2 \pi i / h x_\nu D\} = 0. \quad (19) \]

From the direction cosines \( a, \beta, \gamma \) of the incident wave the (infinitely) many corresponding directions \( \gamma_\nu, \beta_\nu, \alpha_\nu \) of the diffracted wave vector in vacuum are calculated. The various \( x_\nu \) are calculated from Eq. (9) and back-substitution into the dynamical equations (8) provides the ratios \( \psi_{\gamma, \nu} / \psi_{\gamma} \).

The \( \psi_{\gamma, \nu} \) are calculated from the BC equations (18) and (19), and finally the amplitudes of the reflected and transmitted waves are calculated from the Equations (14) – (16). If absorption processes are included in the description of the potential, and provided \( D \) is sufficiently large, all \( \Phi_\nu \) will be zero and thus only those \( x_{\gamma, \nu} \) corresponding to waves propagating down into the crystal need be considered.

If the calculation is limited to \( N \) different \( g \) values (including \( g = 0 \) then the determinant (9) is of order \( N \) and yields then an equation of order \( 2N \) for \( x_\nu \). The solution of an equation
\[ \det (Q - B x + x^2) = 0, \]
such as Eq. (9), is provided by the eigenvalue solutions of the equation
\[ \det \left( \begin{array}{cc} B-x I & -Q \\ I & 0 -x I \end{array} \right) = 0 \quad (20) \]
where the matrices \( B, Q, I, 0 \) are of order \( N \), and \( I \) and \( 0 \) are the identity and null matrices respectively. To each of the \( 2N \) values \( x_{\gamma, \nu} \) correspond \( N \) values \( x_{\gamma, \nu} \) and thus there are, in toto, \( 2N^2 \) values \( x_{\gamma, \nu} \) and correspondingly \( 2N^2 \) values \( \psi_{\gamma, \nu} \) (2 \( N \) wave fields each with \( N \) waves). From (8) the \( \psi_{\gamma, \nu} \) may be expressed as ratios of the \( \psi_{\gamma} \) leaving \( 2N \psi_{\gamma} \) to be found from the BC Eqs. (18) and (19). The totality of these equations is twice the number of different pairs \((g_1, g_2)\) and is equal to \( 2N \) only if, of the \( N \) number triples originally chosen, no two triples are such that they differ only in their \( g_3 \) values. If such number triples do occur then the number of BC equations is insufficient to solve for all unknowns. This problem arises because the eigenvalues with number triples differing only in their \( g_3 \) values are physically equivalent to each other, and including them in the calculation means counting the same Bloch wave more than once. If matrix eigenvalue techniques are used to calculate the eigenvalues only one eigenvalue from each set of equivalent eigenvalues should be used.

It is assumed of course that \( N \) was chosen large enough to ensure that the eigenvalues had converged in value. For reflection calculations the generalized Hill’s determinant method is a more efficient technique in cases where many number triples must be included which differ only in their \( g_3 \) values.

### 3. The Hill’s Determinant Method

The dynamical equations (8) may be rewritten as
\[ \psi_{g} - \sum_{k} \frac{q a_{g-k}}{(k + t_g + g_k)^2 - c_{g}^2} \psi_{k} = 0 \quad (21) \]
where
\[ q = q/c^2, \quad x = x_0/c, \quad t_g = \lambda (g_1 b_1^2 + g_2 b_2^2), \quad c = \lambda b_3^2 \quad (22) \]
and
\[ c_g = (\gamma_g^2 + q)/c^2. \quad (23) \]

The quantities \( a_g = v_g/v_0 \) are such that the sum \( \sum_{k} q a_g \) is absolutely convergent. The equation system (21) has solutions provided the determinant \( A_1(x) \) of the coefficient vanishes. If only three pairs \((g_1, g_2)\) need be considered \((0, G, H)\), then this determinant \( A_1(x) \) may be written as
\[ A_1(x) = \begin{bmatrix} 1 & -a_{-1} q & \cdots & -a_{-g} q & 1 \\ -a_{1} q & (x-1)^2 - c_{0}^2 & \cdots & -a_{-g} q & (x-1)^2 - c_{0}^2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ -a_{g} q & (x+g)^2 - c_{g}^2 & \cdots & 1 & -a_{-g+1} q \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ -a_{h+1} q & (x+h)^2 - c_{h}^2 & \cdots & \cdots & 1 \end{bmatrix} \quad (24) \]

Apart from simple poles at the positions
\[ x = \pm c_{0} + n, \quad \pm c_{g} - t_{g} + n \quad \text{and} \quad \pm c_{h} - t_{h} + n \quad (n \text{ any integer}) \]
this infinite determinant is unconditionally convergent, since the products of the main diagonal elements \((= 1)\) and the sum of all elements not on the main diagonal are absolutely convergent (because
of the convergence of the sums $\sum g a_g$ and $\sum l/n^2$.
In addition $A_1(x)$ is a simple periodic function of $x$ with period 1. Thus if $x$ is a solution of the equation $A_1(x) = 0$ then so is $x + n$, where $n$ is any integer. These solutions $x(+n)$ are physically equivalent. The simplest periodic function of $x$ with period 1 and simple poles at the points $x = \pm c_0 + n$ is the function $\cot\pi(x - c_0)$. If constants $A_1, B_0, A_2, B_2, A_3, B_3, \ldots$, etc., are then found to satisfy the condition $\Sigma(A_g + B_g) = 0$. The solutions of the equation $A_1(x) = 0$ are then found as solutions of the polynomial equation

$$1 + \sum g \{A_g \cot(x + t_g - c_g) + B_g \cot(x + t_g + c_g)\} = 0. \quad (26)$$

The coefficients $A_g, B_g$ may simply be found by expanding (26) in the vicinity of $x = c_g - t_g$, etc., and thus

$$A_g = \pi L t \left[ (x - c_g - t_g) A_1(x) \right]_{x = c_g - t_g}$$

and

$$B_g = \pi L t \left[ (x + t_g + c_g) A_1(x) \right]_{x = -c_g - t_g}. \quad (27)$$

It is assumed that $\pm c_0$ and $\pm c_0 - t_g$ differ by more than an integer. The determinants may be evaluated conveniently using the Gaussian elimination procedure. The order of the determinant is increased until convergence of the coefficients (to working accuracy) is achieved. The approximation suggested by LAMLA for the evaluation of the coefficients [expansion of (27) in powers of $\varphi^2$] is insufficiently accurate, at least for the low order expansion.

For a centro-symmetric crystal where the $a_3$ axis is normal to the crystal surface, all $t_g = 0$ and $A_g = -B_g$. Defining $y = \tan \pi x$, $y_0 = \tan \pi c_0$, $y_2 = \tan \pi c_2$, etc., the Eq. (26) reduces to a bi-cubic equation in $y$,

$$3 \sum K_i(y^2)^i = 0. \quad (28)$$

If only two pairs $0, G$ need be considered (26) reduces to a bi-quadratic equation in $y$, and if a "systematics" calculation only is required [i.e., only reciprocal lattice points $(0, 0, g_3)$ need be considered] then the equation system reduces to a bi-linear equation in $y$.

$$(1 + 2 A_0 y_0) y^2 + (2 A_0 y_0 - y_0^2) = 0. \quad (28)$$

In the general case where many pairs $(g_1, g_2)$ must be considered a polynomial in $y$ must be solved. Nickel's algorithm readily provides the roots of such a general polynomial.

4. An Application

The simplest application of this theory is to the "systematics" case. If it is possible to choose azimuth angles experimentally so that the interference from non-systematic diffracted beams is greatly minimized, then in the theoretical calculation only those reciprocal lattice (RL) points lying on the 0000 and normal to the surface need be considered. To calculate the Fourier coefficients of the potential, Doyle-Turner parameters were used for the electron scattering factors. The approximations inherent in the calculations leading to these parameters should remain valid for both MEED (1-10 keV) and RHEED (10-50 keV) energy regions. The likely advantages of MEED over both RHEED and LEED have been pointed out elsewhere. The effect of absorption on the intensity may be included by means of an imaginary part added to the potential coeffi-

![Fig. 1. A “systematics” calculation of the specular intensity as a function of incident angle compared with the experimental values of MENADUE for the Si (111) surface. The incident energy is 40 keV and the inner potential is 12 V for curve 1 and 8 V for curve 2. The origin has been displaced in curve 2 so that the peak position still coincide.](image-url)
cients. In the absence of good theoretical values the absorptive part of the potential may be treated as a parameter in the calculations.

Figure 1 is a comparison of the experimental results of MENADUE \textsuperscript{13} for the Si (111) surface with a “systems” calculation. The incident energy was 40 keV. To provide best agreement with the 555 peak $V_0$, the inner potential, was chosen as 12 volt and $V_{\text{imaginary}}$ was chosen as $V_{\text{real}}/8.0$ to account for absorption. A Debye parameter of 0.5 Å\textsuperscript{2} was assumed. Using the HD method each intensity point required one second computation time (using a CDC 6400 computer). Matrix eigenvalue methods (e.g., the QR algorithm\textsuperscript{14}) are at least an order of magnitude slower. The discrepancy between theory (curve 1) and experiment, especially noticeable at very low angles of incidence, may be attributed to two main factors:

1. Neglect of non-systematic interactions. This would cause the minima to be greater than observed experimentally. The peak intensities should not be significantly changed because the azimuth angles were chosen experimentally to minimize non-systematic interactions at the Bragg positions.

2. “Surface flatness.” At very low angles of incidence there will be a significant variation in penetration and refraction effects if the surface departs at all from the ideal flat state. In addition, especially at very low angles, the abrupt potential cut-off required by the Bethe theory (planar surface at $Z=0$) causes the reflected intensity to be much larger than would be expected for a potential which actually decreases gradually.

Curve 2 (Fig. 1) shows the effect of decreasing the inner potential on the reflected intensity at low angles. (The origin has been shifted in this curve so that the peak positions still coincide with the experimental positions.) Similar effects occur in LEED calculations\textsuperscript{15}.

5. An Extension of the Bethe Theory to Non-Perfect Crystals

The crystal model assumed by the Bethe theory is an infinitely (3-D) periodic array of scattering units (Figure 2 a). The BC equations account for the finite nature of the actual crystal by providing the right linear combination of Bloch waves (infinite crystal solutions). If absorption is included in the theory this linear combination is such that the electron wave is strongly attenuated within the first few layers of atoms. That is to say, the reflected intensity is largely unaffected by the crystal structure below the first few layers of atoms. By applying the Bethe theory to a model crystal whose unit cell corresponds in structure to the uppermost layers of the actual crystal, reflection calculations can be performed for non-perfect crystals, i.e., those crystals whose surface layers differ from the bulk. This model crystal will have an elongated unit cell (Fig. 2 b) and reciprocal lattice points in the direction of the surface normal will thus be very close together. To achieve convergence, many Fourier coefficients must then be included in the calculations. While this would present a serious problem if matrix-eigenvalue techniques were used, this should not be the case for the Hill's determinant method.

This approach is formally equivalent to the multi-layer scattering matrix approach suggested for LEED\textsuperscript{16} and RHEED\textsuperscript{5} calculations. It corresponds however to the case where absorption is so strong and the first layer so thick that the back-scattering from the second and subsequent layers may be neglected in the calculations. A comparison of these two approaches is now under way.

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Berücksichtigung der Gitterperiodizität bei der Elektron-Plasmon-Streuung. I.

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Herrn Prof. Dr. K. MOLIÈRE zu seinem 60. Geburtstag gewidmet

Consideration of Lattice Periodicity at the Electron Plasmon Scattering. I.

Einleitung


1. Es wird untersucht, ob zusätzlich zu der oben beschriebenen 'astisch-unelastischen Zweifachstreuung eine direkte unelastische Streuung in die Reflexrichtung erfolgt. Eine schematische Darstellung dieses Sachverhalts ist aus Abb. 1 zu entnehmen (s. Diskussion).

2. Es wird eine Formel für den Imaginärteil des komplexen Streupotentials angegeben, die die wegen der zusätzlichen Streuprozesse zu erwartende Änderung der Absorption beschreibt (anomale Absorption).