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Ewald's Extended Dynamical Theory of Diffraction on a Crystal of Finite Thickness

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Abstract

Exact formulae of Ewald's conception of the extended dynamical theory of diffraction are applied to a crystal of finite thickness. The results obtained are compared with those yielded by conventional and extended Laue theory.

1. Introduction

In the so-called 'conventional' dynamical theory of diffraction some approximations are used, with the consequence that the final formulae are not valid in some extreme cases. This unfavorable situation occurs, for example, when the Bragg angle is near $\pi/2$. This case has been dealt with by Kohra & Matsushita (1972), Caticha & Caticha-Ellis (1982), Brümmer, Höche & Nieber (1979) and Litzman & Dub (1990). Considerations in these papers are limited to a semi-infinite crystal. The aim of the present paper is to generalize the method of the papers of Litzman (1986) and Litzman & Dub (1990) to a crystal of finite thickness. The formulae of these papers will be referred to as I and II followed by the number of the relevant equation.

2. Exact and approximate formulae for the reflectivity on a slab

As in the papers by Litzman (1986) and Litzman & Dub (1990), in the following the diffraction of a scalar wave on a system of Fermi delta potentials will be discussed. The notation of these papers with some small exceptions will be used. The solutions of the dispersion equation (II.11*ab*) will be denoted by ψ_{pq}^{+-}. Though the general formula (I.38) is invariant to the choice of the indices +, −, *pq*, for practical cases it is advantageous to denote the solution ψ that is near [see § 3 of Litzman & Dub (1990)] to the pole θ_{pq}^{+-} as ψ_{pq}^{+-}. Further, the assumption is made that the diffraction takes place on a crystal of finite thickness, *i.e.* the diffraction centers form a simple lattice

$$\begin{gathered}\mathbf{R}_\mathbf{m}=m_1\mathbf{a}_1+m_2\mathbf{a}_2+m_3\mathbf{a}_3,\\ m_1,m_2=0,\pm1,\pm2,\dots,\pm\infty,\\ m_3=0,1,2,\dots,N.\end{gathered}\tag{1}$$

Similarly, as in Litzman & Dub (1990), the reflectivity $\mathcal{R}(\theta_{pq}^-)$ in the direction of the vector $\mathbf{K}_{pq}^-$ is given by

$$\begin{aligned}\mathcal{R}(\theta_{pq}^-)&=\left|\frac{\mathbf{j}_r(\theta_{pq}^-)}{\mathbf{j}_{\rm inc}}\right|\frac{\cos\xi_{pq}}{\cos\xi}\\ &=\left|\frac{\det\mathbf{M}^-(pq)}{\det\mathbf{H}}\right|^2\frac{\cos\xi}{\cos\xi_{pq}}.\end{aligned}\tag{2}$$

The matrices $\mathbf{H}, \mathbf{M}^-(pq)$ were defined by Litzman (1986). In the case of a simple lattice without basis they can be written in the partitioned form

$$\mathbf{H}=\left\|\begin{matrix}H_{11}&H_{12}\\ H_{21}&H_{22}\end{matrix}\right\|,\tag{3}$$

with blocks

$$H_{11}=\left\|\frac{1}{x_{ij}^+-y_{pq}^+}\right\|,\tag{4a}$$

$$H_{12}=\left\|\frac{1}{x_{ij}^--y_{pq}^+}\right\|,\tag{4b}$$

$$H_{21}=\left\|\frac{1}{x_{ij}^+-y_{pq}^-}\right\|\langle(x_{00}^+)^{N+1},\dots,(x_{uv}^+)^{N+1}\rangle,\tag{4c}$$

$$H_{22}=\left\|\frac{1}{x_{ij}^--y_{pq}^-}\right\|\langle(x_{00}^-)^{N+1},\dots,(x_{uv}^-)^{N+1}\rangle,\tag{4d}$$

$$\begin{gathered}(i,j),(p,q)=(0,0),\dots,(u,v),\\ x_{pq}^{+-}=\exp(i\psi_{pq}^{+-}),\qquad y_{pq}^{+-}=\exp(i\theta_{pq}^{+-}),\end{gathered}\tag{4e}$$

whereby (i,j) are the indices of the columns, (p,q) are those of the rows and $\langle a_1,\dots,a_n\rangle$ denotes a diagonal matrix with elements $a_1,\dots,a_n$ on the main diagonal. The matrix $\mathbf{M}^-(rs)$ in (2) differs from the matrix $\mathbf{H}$ defined by (3) in the first row only. This

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row has the form

$$\|M^-(rs)_{00,ij}\| = \left[\frac{1}{x_{00}^+ - y_{rs}^-}, \ldots, \frac{1}{x_{uv}^+ - y_{rs}^-}, \frac{1}{x_{00}^- - y_{rs}^-}, \ldots, \frac{1}{x_{uv}^- - y_{rs}^-}\right]. \quad (5)$$

In the case of a semi-infinite crystal, formula (I.38) can be simplified to the form (I.55), discussed by Litzman & Dub (1990). Litzman & Rózsa (1980) tried to find a more explicit expression for (I.38) in the case of a crystal of finite thickness; their result, however, was of no practical use. That is why we content ourselves in the present paper with the following approximations.

(i) From the physical arguments given at the beginning of § 3 of Litzman & Dub (1990), the distances $|\psi_{pq}^+ - \theta_{pq}^+|$ and $|\psi_{pq}^- - \theta_{pq}^-|$ are assumed to be small. Let us consider the Bragg reflection in the direction of the wave vector $\mathbf{K}_{rs}^-$. Thus (see II.20),

$$\theta_{00}^+(\mathbf{k}) = \theta_{rs}^-(\mathbf{k}) + 2\pi j + \eta, \qquad j \text{ integer}, \ |\eta| \ll 1, \quad (6)$$

for one pair of indices (rs) only and the poles θ_{00}^+ and θ_{rs}^- of the dispersion equation (II.11*ab*) nearly coincide. (The case when more than two poles coincide is discussed in the Appendix.) In the matrices $\mathbf{H}$ and $\mathbf{M}_{pq}^-(rs)$ let us omit all terms except those for which

$$|x_{ij}^{+-} - y_{pq}^{+-}| \ll 1 \quad (7)$$

holds. Then the non-zero elements of $\mathbf{H}$ are the terms along the main diagonal plus the terms

$$\frac{1}{x_{00}^+ - y_{rs}^-}, \frac{1}{x_{rs}^- - y_{00}^+}. \quad (8)$$

Similarly, the non-zero elements in the first row of $\mathbf{M}^-(rs)$ are

$$\frac{1}{x_{00}^+ - y_{rs}^-}, \frac{1}{x_{rs}^- - y_{rs}^-} \quad (9)$$

only. In this approximation,

$$\frac{\det \mathbf{M}^-(rs)}{\det \mathbf{H}} = [(x_{rs}^-)^{N+1} - (x_{00}^+)^{N+1}] \times \left[\frac{x_{00}^+ - y_{rs}^-}{x_{00}^+ - y_{00}^+}(x_{rs}^-)^{N+1} - \frac{x_{rs}^- - y_{rs}^-}{x_{rs}^- - y_{00}^+}(x_{00}^+)^{N+1}\right]^{-1} \quad (10)$$

is obtained.

(ii) A further approximation will be made by the solution of the dispersion equation (II.11*ab*, II.22). Denoting

$$x_{00}^+ = x_1 = \exp(i\psi_1), \qquad x_{rs}^- = x_2 = \exp(i\psi_2) \quad (11)$$

and using the same procedure as in Litzman & Dub (1990), we get

$$x_{1,2} = [\exp(i\theta_{rs}^-)/(F + b_{rs}^0)] \exp(i\eta/2) \times [H_{rs} \cos \eta/2 - \tfrac{1}{2}(\beta_{00} + \beta_{rs}) \sin \eta/2 \pm i(\beta_{00}\beta_{rs})^{1/2}(Y^2 - 1)^{1/2}]. \quad (12)$$

The definitions of symbols β_{00}, β_{rs}, b_{rs}^0, H_{rs}, F, Y, η used in (12) are explained in Litzman & Dub (1990) [(II.12*a*), (II.24), (II.28), (II.23*a*), (II.25), (II.20)]. From (12) it follows that

$$x_1/x_2 = 1 + (2/\{H_{rs}^2 + [(\beta_{00} - \beta_{rs}/2)]^2\}) \times [-\beta_{00}\beta_{rs}(Y^2 - 1) + i(\beta_{00}\beta_{rs})^{1/2} \times \{H_{rs} \cos \eta/2 - [(\beta_{00} + \beta_{rs})/2] \sin \eta/2\} \times (Y^2 - 1)^{1/2}]. \quad (13)$$

Using (II.23*b*), the formula for reflectivity (2) can be written as [see (10)]

$$\mathcal{R}(\theta_{rs}^-) = |[(x_{rs}^-)^{N+1} - (x_{00}^+)^{N+1}] \times \{[Y + (Y^2 - 1)^{1/2}](x_{rs}^-)^{N+1} - [Y - (Y^2 - 1)^{1/2}](x_{00}^+)^{N+1}\}^{-1}|^2. \quad (14)$$

3. Crystal without absorption

In the following, a crystal without absorption will be dealt with. In this case, Q_0, β_{00}, β_{rs}, H_{rs} and Y are real and the cases $Y^2 > 1$ and $Y^2 < 1$ will be considered separately.

(*a*) $Y^2 > 1$ (the region outside the total reflection of a semi-infinite crystal). In this case, from (12) follows $|x_{1,2}|^2 = 1$. Thus ψ_1 and ψ_2 in (11) are real and

$$\psi_1 - \psi_2 = -i \ln x_1/x_2, \quad (15)$$

where x_1 and x_2 are given by (13) as functions of the known parameters β_{00}, β_{rs} and η. By simple algebraic operations we get [see (11)]

$$|(x_{rs}^-)^{N+1} - (x_{00}^+)^{N+1}|^2 = 4 \sin^2 (N+1)(\psi_1 - \psi_2)/2,$$

$$|(x_{rs}^+)^{N+1} + (x_{00}^+)^{N+1}|^2 = 4 \cos^2 (N+1)(\psi_1 - \psi_2)/2.$$

Finally, (14) yields

$$\mathcal{R}(\theta_{rs}^-) = \frac{\sin^2 [(N+1)/2](\psi_1 - \psi_2)}{Y^2 - 1 + \sin^2 [(N+1)/2](\psi_1 - \psi_2)}. \quad (16)$$

(*b*) $Y^2 < 1$ (the region of the total reflection of the semi-infinite crystal). In this case, from (12) it follows that $x_1 x_2^* = 1$. Thus we put in (11)

$$x_{00}^+ = x_1 = \exp \psi, \qquad x_{rs}^- = x_2 = \exp(-\psi^*), \quad (17)$$

ψ is complex. Then,

$$\psi + \psi^* = \ln x_1/x_2. \quad (18)$$

Proceeding similarly as above, in this case

$$\mathcal{R}(\theta_{rs}^-) = \frac{\sinh^2 [(N+1)/2](\psi + \psi^*)}{1 - Y^2 + \sinh^2 [(N+1)/2](\psi + \psi^*)} \quad (19)$$

is obtained.

Let us remark that (16) and (19) are valid for skew reflection as well.

In standard textbooks on conventional dynamical theory of diffraction [*e.g.* Zachariasen (1946), equations (3.143), (3.144); Pinsker (1978), equations (8.33), (8.36)], the formulae for the reflectivity in the case of zero absorption read

$$\mathcal{R}(\theta_{rs}^-)=\frac{\sin^2[A(y^2-1)^{1/2}]}{y^2-1+\sin^2[A(y^2-1)^{1/2}]},\qquad y^2>1 \quad (20)$$

(outside the region of total reflection),

$$\mathcal{R}(\theta_{rs}^-)=\frac{\sinh^2[A(1-y^2)^{1/2}]}{1-y^2+\sinh^2[A(1-y^2)^{1/2}]},\qquad y^2<1 \quad (21)$$

(in the region of total reflection), where

$$A=[k|\chi_h|/2(\cos\xi\cos\xi_{rs})^{1/2}](N+1)a_{3z}. \quad (22)$$

In both (20) and (21), the reflected beam is assumed to be in the plane of incidence.

In order to compare our formulae for the diffraction of neutrons with those for the X-ray diffraction we substitute in our formulae above [see (II.5)]

$$Q_0=-k^2\Omega_0\chi_0/4\pi. \quad (23)$$

The correspondence between the parameters Y in (16), (19) and y in (20), (21) has been discussed in § 4 of the paper by Litzman & Dub (1990). Now, let us investigate the properties of the parameters $\psi_1-\psi_2$ and $\psi+\psi^*$ given by (15) and (18), respectively. Since

$$|\beta_{pq}|,|\eta|,|1-H_{rs}|\simeq|Q_0/a|,|Q_0/a|\ll 1 \quad (24)$$

(a is the lattice constant), (13) and (23) yield

$$\ln x_1/x_2=(ika_{3z}/H_{rs})[\chi_0^2/\cos\xi\cos\xi_{rs}]^{1/2}\times(Y^2-1)^{1/2}+O(Q_0/a)^2. \quad (25)$$

Using (15) and (18) and neglecting in (25) terms of order $(Q_0/a)^2$, we can write our formulae (16) and (19) for the reflectivity in a formally analogous form to that of formulae (20) and (21) of the conventional theory:

$$\mathcal{R}(\theta_{rs}^-)=\frac{\sin^2[\mathcal{A}(Y^2-1)^{1/2}]}{Y^2-1+\sin^2[\mathcal{A}(Y^2-1)^{1/2}]},\qquad Y^2>1 \quad (26)$$

(outside the region of total reflection),

$$\mathcal{R}(\theta_{rs}^-)=\frac{\sinh^2[\mathcal{A}(1-Y^2)^{1/2}]}{1-Y^2+\sinh^2[\mathcal{A}(1-Y^2)^{1/2}]},\qquad Y^2<1 \quad (27)$$

(in the region of total reflection), where

$$\mathcal{A}=[k|\chi_0|/2(\cos\xi\cos\xi_{rs})]a_{3z}[(N+1)/H_{rs}],$$
$$H_{rs}=1+O(Q_0/a). \quad (28)$$

Thus, the difference between A (28) and $\mathcal{A}$ (34) is negligible.

4. Concluding remarks

In Litzman & Dub (1990), the exact formula (II.29)

$$\mathcal{R}^\infty(\theta_{rs}^-)=|Y(\psi_1)\mp[Y^2(\psi_1)-1]^{1/2}|^2|R_2(\theta_{rs}^-)|^2 \quad (29)$$

was given for the Bragg reflectivity on a semi-infinite crystal. In this paper the approximate formula (14) for the Bragg reflection on a crystal of finite thickness has been obtained. Since the dispersion equation (II.11*a*) for the evaluation of x_{00}^+, x_{rs}^- (11) and the definition of the parameter Y (II.25) are the same in the case of the semi-infinite and the finite crystals, we can conclude that the validity of the approximation (14) corresponds to the validity of the approximation in (II.18): $R_2(\theta_{rs}^-)^2=1$.

In order to compare our results with those of the conventional dynamical theory of diffraction, in § 3 the crystal without absorption was considered. In this case, the reflection coefficients of the conventional theory are of the simple form (20), (21). Making use of the approximation (25) it was shown that (as in the case of a semi-infinite crystal) the formulae of the conventional theory, (20), (21), and those of the extended theory (26), (27), are formally identical, the meaning of the parameters y, A and/or Y, $\mathcal{A}$ are however different. The difference between the parameters y and Y was discussed by Litzman & Dub (1990): it is important when the Bragg angle is near $\pi/2$ (Brümmer, Höche & Nieber, 1979). The parameters A (22) and $\mathcal{A}$ (28) differ in the coefficient H_{rs} only. Since $H_{rs}=1+O(Q_0/a)$, this difference is negligible.

Let us mention that (16) and (19) are valid for skew reflection as well, while in the conventional formulae, (20), (21), the reflected beam is assumed to be in the plane of incidence.

The reflectivity of a crystal with absorption is given in the conventional theory by formula (3.139) in Zachariasen (1946). In this case (when Y, β_{00}, β_{rs} are complex), the algebraic rearrangement of our formula (14) to a form similar to the conventional one is much more complicated. Obviously, a formally analogous formula to the conventional one has to be obtained in this case, containing, however, the parameters Y and $\mathcal{A}$ instead of y and A.

APPENDIX

Let us suppose that, besides (6),

$$\theta_{pq}^+(\mathbf{k})=\theta_{mn}^-(\mathbf{k})+2\pi j+\eta,$$
$$(pq)\neq(00),\qquad (mn)\neq(rs) \quad (A.1)$$

also holds, *i.e.* more than two poles of the dispersion equation (II.11*ab*) coincide. Then, in the matrices **H** and $\mathbf{M}^-(rs)$ also the great terms

$$(x^+_{pq} - y^+_{pq})^{-1},\ (x^+_{pq} - y^-_{mn})^{-1},$$
$$(x^-_{mn} - y^-_{mn})^{-1},\ (x^-_{mn} - y^+_{pq})^{-1} \qquad (A.2)$$

are to be taken into consideration. Since these additional large terms are outside the first row of the matrix $\mathbf{M}^-(rs)$, a simple consideration shows that the coincidence of the poles in (*A*.1) does not change the value of the quotient det $\mathbf{M}^-(rs)$/det **H**, (10). Another situation appears if (6) is satisfied for two (or more) different pairs of indices (rs), *i.e.* when as well as (6)

$$\theta^+_{00}(\mathbf{k}) = \theta^-_{ab}(\mathbf{k}) + 2\pi j + \eta,$$
$$(ab) \neq (rs), \qquad (A.3)$$

also holds. In this case, additional large terms appear in the first rows of the matrices $\mathbf{M}^-(rs)$ and **H** and they change quotient (10). The conditions (6) and (*A*3) mean physically that either the Bragg reflection condition is satisfied for two wave vectors $\mathbf{K}^-_{rs}$ and $\mathbf{K}^-_{ab}$ or the incident wave is near the grazing reflection angle [see § 3(iii) of Litzman & Dub (1990)]. These cases were not considered in the present paper.

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Structure-Factor Probabilities for Related Structures

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Abstract

Probability relationships between structure factors from related structures have allowed previously only for either differences in atomic scattering factors (isomorphous replacement case) or differences in atomic positions (coordinate error case). In the coordinate error case, only errors drawn from a single probability distribution have been considered, in spite of the fact that errors vary widely through models of macromolecular structures. It is shown that the probability relationships can be extended to cover more general cases. Either the atomic parameters or the reciprocal-space vectors may be chosen as the random variables to derive probability relationships. However, the relationships turn out to be very similar for either choice. The most intuitive is the expected electron-density formalism, which arises from considering the atomic parameters as random variables. In this case, the centroid of the structure-factor distribution is the Fourier transform of the expected electron-density function, which is obtained by smearing each atom over its possible positions. The centroid estimate has a phase different from, and more accurate than, that obtained from the unweighted atoms. The assumption that there is a sufficient number of independent errors allows the application of the central limit theorem. This gives a one- (centric case) or two-dimensional (non-centric) Gaussian distribution about the centroid estimate. The general probability expression reduces to those derived previously when the appropriate simplifying assumptions are made. The revised theory has implications for calculating more accurate phases and maps, optimizing molecular replacement models, refining structures, estimating coordinate errors and interpreting refined *B* factors.

1. Introduction

A model of a crystal structure always has errors in any parameters used to describe the structure: atomic coordinates, atomic scattering factors, thermal motion parameters, or even cell dimensions. In addition, the approximations of spherically symmetric atoms and of harmonic (or even isotropic) thermal motion will lead to small errors. In refining a structure, we attempt to minimize these errors as far as possible, but it is best to keep their existence in mind and to be aware of their effects.

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