

function after the origin peak and the intramolecular vectors have been removed. This corresponds to an extension of the point made in PT that the origin peak may lead to false peaks in the  $Q$ -function, but can be removed.

The expression for  $T(\mathbf{t})$  obtained by CB represents in one respect a more general form of the  $Q$ -functions than that given by PT. Since  $T(\mathbf{t})$  is expressed in terms of  $F_m(\mathbf{h})$ , the transform of the individual molecule, it need not be calculated, as suggested by the expressions given above, in terms of a set of discrete atoms. If, for example, a molecule of a protein has been obtained at less than atomic resolution, its transform may still be calculated by numerical methods from the electron density. The possibility of such an extension has been suggested previously (Tollin, 1966*b*) in terms of the  $Q$ -functions. In this case the quantities  $CC'$  and  $SS'$  in the notation of PT must be obtained by such numerical integration. At what resolution such a function will prove useful is a matter for experiment.

The  $Q$ -functions have now been successfully applied to the determination of the structure of a number of molecular crystals (for example, Young, Tollin & Sutherland, 1968; Tollin, Young & Wilson, 1968). Recently the author has applied the  $Q$ -function to the determination of the position in the unit cell of the seal myoglobin molecule (Scouloudi, 1960) once its orientation had been determined. The orientation was found using the rotation function (Rossmann & Blow, 1962) to compare the 5.8 Å resolution data for seal and sperm whale myoglobin (Tollin, 1966*b*). A report of the details of this determination is in preparation. However, it is worth noting here that since the protein molecule is so large that many atoms are in positions

which would give rise to non-Harker peaks in the Harker section, it is essential in this case to remove the origin peak from the Patterson.

It should be noted that, as Hoppe & Paulus (1967) mention in a footnote, 'it is possible to translate operations with convolution molecules into reciprocal space. . .'. The  $Q$ -functions are closely similar to the reciprocal space equivalent of the convolution molecule method where the sum of the convolution molecule and the Patterson structure is used as the criterion of fit.

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## A Contribution to the Dynamical Diffraction Theory of Scalar Waves in Crystals

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A matrix formalism is developed for calculating the elastically scattered waves diffracted by an infinite plane parallel crystal. Introduction of projection operators makes it possible to cover both Laue and Bragg reflected waves under the same formalism.

### 1. Introduction

The basic problem to be considered is the solving of the time-independent Schrödinger equation

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = u(\mathbf{r})\psi(\mathbf{r}) \quad (1.1)$$

for a potential  $V(\mathbf{r}) = (\hbar^2/2\mu)u(\mathbf{r})$ , periodic inside a three-dimensional crystal lattice and zero outside.  $k$  is the

wave number and  $\mu$  the mass of the particle associated with the scalar field  $\psi(\mathbf{r})$ . In diffraction experiments an incident wave falls upon the crystal and an outgoing wave scattered by the crystal is detected. This is described more adequately by the integral equation

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) - \frac{1}{4\pi} \int_V \frac{\exp ik|\mathbf{r}-\mathbf{r}'|}{|\mathbf{r}-\mathbf{r}'|} u(\mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}' \quad (1.2)$$

than by equation (1.1) itself. Here  $\psi_0(\mathbf{r})$  represents the incident wave and the integral, carried out over the crystal volume  $V$  represents the diffracted wave. The advantage of equation (1.2) over equation (1.1) is that it automatically takes care of all the boundary conditions, which are rather complicated if correctly applied to equation (1.1). For small crystals a reasonable approximation is obtained by substituting  $\psi(\mathbf{r}')$ , in the integrand, by the incident wave  $\psi_0(\mathbf{r}')$ . This is known as the first order Born approximation in quantum mechanics, and one arrives at the kinematical theory of diffraction (or geometrical), according to terminology commonly used in the literature. In this case every atom of the crystal is assumed to be illuminated by the same incident wave and all the multiple-scattering effects, which play an important role in large crystals, are neglected. Thus for large crystals better approximations are needed. Every theory extending beyond the first order Born approximation is called a dynamical theory.

In this paper we consider only the diffraction of plane waves by an infinite plane parallel crystal, whose unit cells are centred at  $\mathbf{r}_h = h_1\mathbf{a}_1 + h_2\mathbf{a}_2 + h_3\mathbf{a}_3$ .  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  are three lattice vectors, which form a right hand system ( $\mathbf{a}_1 \times \mathbf{a}_2 \cdot \mathbf{a}_3 > 0$ ), and  $h_1, h_2$  are integers taking values  $0, \pm 1, \dots, \pm \infty$  and  $h_3$  is an integer taking values  $0, 1, 2, \dots, N-1$ . The crystal is thus described by  $N$  infinite crystal planes each obtained from the former by the same translation  $\mathbf{a}_3$ . One way of treating the problem is to introduce a three-dimensional Fourier-expansion for the potential and the amplitude of the field, first applied to X-rays by Ewald (1916, 1917) and to electrons by Bethe (1928). The disadvantages of this method are that it does not account satisfactorily for absorption and incoherent scattering, and the calculations are very difficult if the Bragg condition is to be nearly satisfied for more than one set of crystal planes simultaneously. These difficulties can be avoided, however, if the symmetry of the situation is taken into account from the very beginning and if it is realized that the problem is essentially one-dimensional, the relevant variable being the depth from the upper surface of the crystal. This is the basic idea of the matrix-multiplication method introduced in the electron diffraction case by Sturkey (1957), Fujimoto (1959), and Howie & Whelan (1961).

A comparison of the different forms of the dynamical diffraction theory and later developments can be found in a review article by Molière (1966). Most of the matrix methods presented so far are limited to small scattering angles and are therefore not directly applicable to neutrons or X-rays. Kato (1963) has, however, considered the forward scattering, or Laue case, where the scattering angle may be large, but does not account for the backward scattered waves.

We shall first solve the diffraction pattern from an infinite doubly periodic crystal plane, for which a diffraction matrix can be defined. With the help of the diffraction matrix and projection operators the case of

$N$  crystal planes can be conveniently treated by matrix-multiplication no matter through which face the diffracted waves leave the crystal.

## 2. Diffraction by an infinite doubly periodic crystal plane

Let us suppose that only one of the planes is present with  $h_3$  fixed. Let us further suppose that a plane wave  $\exp i\mathbf{k}_0 \cdot \mathbf{r}$  is impinging on the plane from the negative side, by which we mean that the relation  $\mathbf{k}_0 \cdot \mathbf{a}_1 \times \mathbf{a}_2 > 0$  holds. Consider first a system of point scatterers such that the scattering power of each unit cell is concentrated at its centre, characterized by scattering length  $b$ . Hence  $u(\mathbf{r})$  is represented by the following sum of  $\delta$ -functions:  $u(\mathbf{r}) = 4\pi b \sum_{h_1} \sum_{h_2} \delta(\mathbf{r} - \mathbf{r}_h)$  and equation (1.2) takes the form

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}_0 \cdot \mathbf{r}) - b \int_V \frac{\exp ik_0|\mathbf{r} - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}'|} \times \left[ \sum_{h_1} \sum_{h_2} \delta(\mathbf{r}' - \mathbf{r}_h) \right] \psi(\mathbf{r}') d^3\mathbf{r}', \quad (2.1)$$

where the volume  $V$  encompasses the whole scattering plane. We start with the first order Born approximation and accordingly the scattered wave  $\psi_s(\mathbf{r}) = \psi(\mathbf{r}) - \exp i\mathbf{k}_0 \cdot \mathbf{r}$  is given by the expression

$$\psi_s(\mathbf{r}) = -b \sum_{h_1} \sum_{h_2} \exp(i\mathbf{k}_0 \cdot \mathbf{r}_h) \frac{\exp ik_0|\mathbf{r} - \mathbf{r}_h|}{|\mathbf{r} - \mathbf{r}_h|}. \quad (2.2)$$

We are more interested in the plane wave expansion of  $\psi_s(\mathbf{r})$  and therefore consider the scalar product

$$S^\pm = \frac{1}{(2\pi)^3} \int_{\text{all space}} \psi_s^\pm(\mathbf{r}) \exp(-i\mathbf{k}_1 \cdot \mathbf{r}) d^3\mathbf{r}. \quad (2.3)$$

Because the analytic expressions of  $\psi_s(\mathbf{r})$  are eventually different in the upper half space (limited to the positive side of the scattering plane) and in the lower half space (limited to the negative side)  $\psi_s^+(\mathbf{r})$  is defined as an analytic function of  $\mathbf{r}$  in all space such that the relationship  $\psi_s^+(\mathbf{r}) = \psi_s(\mathbf{r})$  holds in the upper half space and  $\psi_s^-(\mathbf{r})$  is defined as another analytic function of  $\mathbf{r}$  such that the relationship  $\psi_s^-(\mathbf{r}) = \psi_s(\mathbf{r})$  holds in the lower half space. When calculating  $S^\pm$  it is convenient to introduce a rectangular coordinate system  $(x, y, z)_h$ , whose  $x$  and  $y$  axes lie on the scattering plane and whose  $z$  coordinate is given by the equation  $z = (\mathbf{r} - h_3\mathbf{a}_3) \cdot \mathbf{a}_1 \times \mathbf{a}_2 / |\mathbf{a}_1 \times \mathbf{a}_2|$ . The direction of the  $x$  axes can be fixed by choosing  $k_{1x} = 0$ . Inserting (2.2) into (2.3) and partially changing the order of summation and integration we get

$$S^\pm = - \frac{b}{(2\pi)^3} \int_{-\infty}^{+\infty} dz \sum_{h_1} \sum_{h_2} \exp[i(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{r}_h - ik_{1z}z] \times \int_{-\infty}^{+\infty} dx dy \exp(-ik_{1y}y) \frac{\exp ik_0 \sqrt{x^2 + y^2 + z^2}}{|\sqrt{x^2 + y^2 + z^2}|}$$

when the origin of the coordinate system  $(x, y, z)_h$  is at  $\mathbf{r}_h$ . The integral over  $x$  and  $y$  is calculated in the Appendix and found to be  $(2\pi i/k'_z) \exp ik'_z|z|$ , where

$$k'_z = \sqrt{k_0^2 - k_{1y}^2} . \quad (2.4)$$

$k_{1y}$  is the projection of  $\mathbf{k}_1$  onto the scattering plane. Obviously the exponential  $\exp ik'_z|z|$  must be written as  $\exp ik'_z z$ , when dealing with  $S^+$  and as  $\exp -ik'_z z$ , when dealing with  $S^-$  according to the previous convention. The remaining summations over  $h_1$  and  $h_2$  and the integration over  $z$  can be performed separately and  $S^\pm$  may be written as

$$\begin{aligned} S^\pm = & - \frac{2\pi ib}{k'_z} \exp (ih_3(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_3) \\ & \times \left[ \frac{1}{2\pi} \int_{-\infty}^{+\infty} dz \exp i(\pm k'_z - k_{1z})z \right] \\ & \times \left[ \frac{1}{2\pi} \sum_{-\infty}^{+\infty} \exp ih_1(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_1 \right] \\ & \times \left[ \frac{1}{2\pi} \sum_{-\infty}^{+\infty} \exp ih_2(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_2 \right] . \end{aligned}$$

From the theory of spectral representations Friedman (1965) we know that the first bracket is the  $\delta$ -function  $\delta(\pm k'_z - k_{1z})$  and the last two brackets can be written as sums of the  $\delta$ -functions:

$$\begin{aligned} \sum_l \delta[(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_1 - 2\pi l]; \quad l=0, \pm 1, \pm 2, \dots \\ \sum_m \delta[(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_2 - 2\pi m]; \quad m=0, \pm 1, \pm 2, \dots \end{aligned}$$

Thus we obtain

$$\begin{aligned} S^\pm = & - \frac{2\pi ib}{k'_z} \exp [ih_3(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_3] \delta(\pm k'_z - k_{1z}) \\ & \times \left\{ \sum_l \delta[(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_1 - 2\pi l] \right\} \left\{ \sum_m \delta[(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_2 - 2\pi m] \right\} . \end{aligned} \quad (2.5)$$

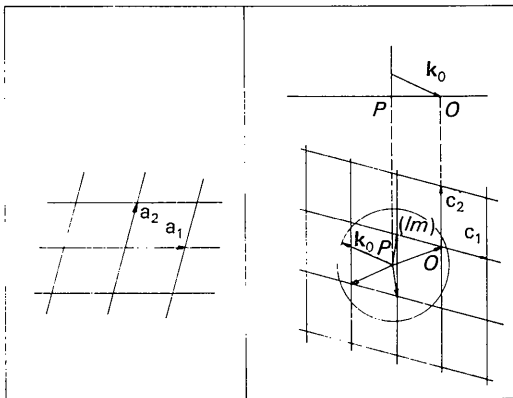


Fig. 1. The scattering plane (left) and its reciprocal lattice plane (right). Reciprocal lattice points inside the circle are responsible for the diffracted waves.

For the lattice plane  $(\mathbf{a}_1, \mathbf{a}_2)$  a reciprocal lattice plane  $(\mathbf{c}_1, \mathbf{c}_2)$  can be defined with the property  $\mathbf{a}_i \cdot \mathbf{c}_j = \delta_{ij}$  where  $\delta_{ij}$  is the Kronecker symbol. With the help of a construction in the reciprocal lattice plane it is very easy to see which are the effective terms of equation (2.5). Referring to Fig. 1 we project on the reciprocal lattice plane the vector  $\mathbf{k}_0$  ending at the origin  $O$ . With the projection point  $P$  as its centre we draw a circle with radius  $|\mathbf{k}_0|$  in the reciprocal lattice plane. Each index pair  $(l, m)$  of equation (2.5) defines a product of three  $\delta$ -functions, the arguments of which can only be zero simultaneously when  $l, m$  take values such that the reciprocal lattice points are inside, or at, this circle. Thus these are the only reciprocal lattice points capable of generating diffracted waves.

From the equations (2.3) and (2.5) and from the identity

$$\frac{1}{(2\pi)^3} \int_{\text{all space}} \exp [i(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{r}] d^3\mathbf{r} \equiv |\mathbf{a}_1 \times \mathbf{a}_2| \delta(k_{0z} - k_{1z}) \delta[(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_1] \delta[(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{a}_2]$$

we find the following plane wave expansion for  $\psi_s^\pm(\mathbf{r})$

$$\psi_s^\pm(\mathbf{r}) = -i \sum_{lm} q_{lm}^\pm \exp ih_3(\mathbf{k}_0 - \mathbf{k}_{lm}^\pm) \cdot \mathbf{a}_3 \exp i\mathbf{k}_{lm}^\pm \cdot \mathbf{r} . \quad (2.6)$$

Here the reflexion coefficients  $q_{lm}^\pm$  are given by the formula

$$q_{lm}^\pm = \frac{2\pi b}{|k_{lmz} \mathbf{a}_1 \times \mathbf{a}_2|} = \frac{2\pi N_0 b}{|k_{lmz}|} . \quad (2.7)$$

$N_0$  being the number of unit cells/cm<sup>2</sup> at the scattering planes. The wave vectors  $\mathbf{k}_{lm}$  of the diffracted waves are most conveniently obtained from Fig. 1. The projection of  $\mathbf{k}_{lm}$  on the reciprocal lattice plane is simply the vector originating at  $P$  and ending at the reciprocal lattice point  $(l, m)$ . Because of the condition  $|\mathbf{k}_0| = |\mathbf{k}_{lm}|$  the wave vectors  $\mathbf{k}_{lm}$  are thus completely solved. The point  $l=0, m=0$  always lies inside the circle and it gives rise to the forward scattered wave when taking the  $+$  sign ( $\mathbf{k}_{00} = \mathbf{k}_0$ ) and the mirror reflected wave when taking the  $-$  sign.

Since the domain of our wave functions is an infinite three-dimensional space, the expansion (2.6) does not have to be equal to  $\psi_s^\pm(\mathbf{r})$  everywhere in space. In fact, one can say that the expansion (2.6) converges to  $\psi_s^\pm(\mathbf{r})$  when  $|z|$  tends to infinity. In other words, the scattered wave field is well described by expansion (2.6) at large distances from the scattering plane. From equation (2.2) we see that the amplitude of the scattered wave field tends to infinity, when  $\mathbf{r}$  approaches one of the vectors  $\mathbf{r}_h$ , whereas this behaviour cannot be deduced from (2.6). Now the order of magnitude of  $b$  is  $10^{-12}$  cm in a typical case for X-rays or neutrons, and the reflexion coefficients  $q_{lm}^\pm$  are about  $10^{-5} \dots 10^{-4}$  unless  $|k_{lmz}|$  is exceedingly small. Hence one might say that within a sphere of radius  $10^{-8} \dots 10^{-7}$  cm around each scatterer the scattered wave field is mainly determined

by this scatterer alone, whereas outside these spheres the resultant field from all the scatterers prevails. The radius  $10^{-8} \dots 10^{-7}$  cm is of the order of the interatomic distance between nearest neighbours, but, because the amplitude of the incident wave at each scatterer is about  $10^4 \dots 10^5$  times larger than the amplitude of the scattered field due to all the other scatterers, it is justifiable, when considering multiple scattering effects, to describe the scattered wave field by a sum of plane waves in all space.

A typical feature of the solution (2.6) is that the reflexion coefficients are real for real values of  $b$ , as a result of the first order Born approximation. This indicates a small violation of the energy conservation law, since the outgoing flux of particles is not exactly equal to the incident flux, but deviates from it by a quantity of the order  $|q_{lm}^{\pm}|^2$ . Because of the smallness of this quantity, excluding very small glancing angles of any diffracted wave, the first order Born approximation is a good one. Higher approximations could be obtained by solving the integral equation (1.2) for one layer of unit cells with the method of successive approximations, which converges very rapidly in this case.

Up to now we have been discussing the case of point scatterers only, but the generalization to diffuse scatterers is quite obvious. In fact, let the scattering power inside each unit cell be given by a distribution  $bf(\mathbf{r})$ , normalized by the relation

$$\int_{\text{unit cell}} f(\mathbf{r}) d^3\mathbf{r} = 1.$$

The unit cell is here the parallelepiped, the centre of which coincides with  $\mathbf{r}_h$  and the edges with the vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ . Then it is easily found that the formula (2.6) remains valid, if the reflexion coefficients are readjusted according to the formula

$$q_{lm}^{\pm} = \frac{2\pi N_0 b}{|k_{lmz}|} \int_{\text{unit cell}} (f\mathbf{r}) \exp [i(\mathbf{k}_0 - \mathbf{k}_{lm}^{\pm}) \cdot \mathbf{r}] d^3\mathbf{r} \quad (2.8)$$

so the above conclusions need not be altered.

### 3. The diffraction matrix

In the previous section we saw that for a given incident plane wave a definite even number ( $M$ ) of diffracted waves are generated due to the periodicity of the scattering plane. If we choose any of these diffracted waves as a new incident wave, the same assembly of diffracted waves is again generated. Thus this assembly of waves behaves like a closed system: if the scattering plane is illuminated simultaneously by several waves, which belong to the same assembly, the outgoing wave field is made up exclusively of members of the same assembly. Such a situation occurs in plane parallel crystals, which are composed of several identical parallel crystal planes, and is most conveniently described with the help of a diffraction matrix.

Let us order the plane wave components of the assembly according to index  $j$ , ranging from 1 to  $M$ , and let the corresponding wave amplitude be denoted by  $\varphi_j(\mathbf{r})$ . We now form a column vector  $\xi_v^{\text{in}}$ , where  $v$  replaces the previous index  $h_3$ , in such a way that its  $j$ th component is given by the formula

$$\xi_{vj}^{\text{in}} = \sqrt{\frac{|k_{jz}|}{|\mathbf{k}_j|}} \varphi_j^{\text{in}}(v\mathbf{a}_3). \quad (3.1)$$

Because  $\varphi_j(\mathbf{r})$  is a two-valued function at the scattering planes, we have to distinguish between the incoming wave  $\varphi_j^{\text{in}}(\mathbf{r})$  and the outgoing wave  $\varphi_j^{\text{out}}(\mathbf{r})$ . The factor  $\sqrt{\frac{|k_{jz}|}{|\mathbf{k}_j|}}$  is a cosine factor and takes care of the fact that the incident flux of particles passing through a unit area of the scattering plane is simply proportional to the norm

$$\|\xi_v^{\text{in}}\| = \sum_{j=1}^M \xi_{vj}^{\text{in}} \overline{\xi_{vj}^{\text{in}}},$$

where the bar designates the complex conjugate. In a similar way we define another column vector  $\xi_v^{\text{out}}$  to describe the assembly of waves propagating outwards from the scattering plane and write for its  $j$ th component the formula

$$\xi_{vj}^{\text{out}} = \sqrt{\frac{|k_{jz}|}{|\mathbf{k}_j|}} \varphi_j^{\text{out}}(v\mathbf{a}_3). \quad (3.2)$$

The relation between  $\xi_v^{\text{out}}$  and  $\xi_v^{\text{in}}$  is given by the equation

$$\xi_v^{\text{out}} = D \xi_v^{\text{in}} \quad (3.3)$$

which defines the diffraction matrix  $D$ .  $D$  is independent of  $v$  and its matrix elements are easily written down with the help of the results of the preceding section and definitions (3.1) ... (3.3). We obtain

$$D_{jj'} = \delta_{jj'} - i \frac{2\pi N_0 b}{\sqrt{|k_{jz}| |k_{j'z}|}} \times \int_{\text{unit cell}} f(\mathbf{r}) \exp [i(\mathbf{k}_{j'} - \mathbf{k}_j) \cdot \mathbf{r}] d^3\mathbf{r}. \quad (3.4)$$

For non-absorbing crystals the incident flux of particles must be equal to the departing flux and this is expressed by the unitary property of the diffraction matrix  $D$ . Especially, the formula (3.4) satisfies the unitary condition within the framework of the first order Born approximation only, upon which its derivation was based. Absorption, incoherent scattering, and inelastic scattering represent loss channels, through which a net flux of particles is escaping out of the wave assembly and can phenomenologically be taken into account by defining extra components for  $\xi_v^{\text{in}}$  and  $\xi_v^{\text{out}}$ , whence the dimension of  $D$  becomes larger than  $M \times M$ . If these loss effects are not strong, and if we want to calculate only members of the assembly emerging out of the crystal, the calculation can be reduced to

$(M \times M)$  space by modifying the elements of  $D$  in the same way as the ordinary absorption is usually taken into account by complex values of the scattering length  $b$ . Having developed the theory for scalar waves, we would like to point out that the two polarization components of X-rays, and the existence of spin correlation between nuclei in the neutron case, do not essentially complicate the theory. The dimension of  $D$  is merely  $(2M \times 2M)$  instead of  $(M \times M)$ , although some difficulties may be encountered in working out the matrix elements of  $D$ .

#### 4. Diffraction by $N$ infinite crystal planes

##### 4.1. The general solution

The diffraction matrix  $D$  was very easily defined with the help of column vectors  $\xi_v^{\text{in}}$  and  $\xi_v^{\text{out}}$ . When combining the effect of all  $N$  scattering planes, however, two new column vectors  $\zeta_v^+$  and  $\zeta_v^-$  are introduced, defined by formulae:

$$\zeta_v^+ = P^+ \xi_v^{\text{out}} + P^- \xi_v^{\text{in}} \quad (4.1)$$

$$\zeta_v^- = P^- \xi_v^{\text{out}} + P^+ \xi_v^{\text{in}}, \quad (4.2)$$

which are much more convenient.  $P^+$  and  $P^-$  are projection operators which pick up waves propagating in the positive and negative directions among the members of the assembly. Thus  $\zeta_v^+$  represents the wave field at the positive side of the  $v$ th plane, and  $\zeta_v^-$  at the negative side. The relation between  $\zeta_{v+1}^-$  and  $\zeta_v^+$  is now given by the formula

$$\zeta_{v+1}^- = \Phi \zeta_v^+, \quad (4.3)$$

where the phase matrix  $\Phi$  takes care of the phase differences over the translation  $\mathbf{a}_3$  between two successive planes.  $\Phi$  is a diagonal matrix, the elements of which are given by the formula

$$\Phi_{jj'} = \exp(i\mathbf{k}_j \cdot \mathbf{a}_3) \delta_{jj'}. \quad (4.4)$$

With the help of definitions (3.1) ... (3.3) and (4.1) ... (4.3) we are able to derive the recurrence formula

$$\zeta_{v+1}^+ = T \zeta_v^+, \quad (4.5)$$

where  $T$  is given as the matrix product

$$T = [P^+ D + P^-] [P^- D + P^+]^{-1} \Phi. \quad (4.6)$$

Because the index  $v$  ranges from 0 to  $N-1$ , we find that the column vector  $\xi^{\text{in}}$  describing the wave field incident on the whole crystal is represented by the combination

$$\xi^{\text{in}} = P^+ \xi_0^{\text{in}} + P^- \xi_{N-1}^{\text{in}}. \quad (4.7)$$

In a similar way the column vector,

$$\xi^{\text{out}} = P^- \xi_0^{\text{out}} + P^+ \xi_{N-1}^{\text{out}}, \quad (4.8)$$

represents the wave field emerging from the crystal. The effect of the whole crystal is to transform the incident wave field to the departing one according to the formula

$$\xi^{\text{out}} = S_N \xi^{\text{in}}. \quad (4.9)$$

The matrix  $S_N$  can be considered as our final result. Making use of the definitions of the column vectors and the given relations between them we obtain

$$S_N = \{P^- D + P^+ T^N \Phi^{-1} [P^- D + P^+]\} \{P^+ + P^- T^N \Phi^{-1} [P^- D + P^+]\}^{-1}. \quad (4.10)$$

It is easy to prove that from the unitarity of  $D$  (non-absorbing crystal) the unitarity of  $S_N$  follows, expressing the conservation of flux of particles. In practice we want to calculate the waves emerging from the crystal, when it is illuminated by one plane wave only.  $\xi^{\text{in}}$  then takes the form

$$\xi^{\text{in}} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \quad (4.11)$$

and it is necessary to calculate only the elements  $S_{Nj}$  ( $j=1 \dots M$ ) which are then equal to the desired components  $\xi_j^{\text{out}}$ . Defining the power reflexion coefficient  $P_r$ , and power transmission coefficient  $P_t$  of the crystal as the flux of particles in the reflected, or transmitted beam, through a unit surface of the plane parallel crystal, relative to unit incident flux, we find the simple connexions:

$$P_t = |S_{N11}|^2 \quad (4.12)$$

$$P_{rj} = |S_{N1j \neq 1}|^2. \quad (4.13)$$

For a unitary  $S_N$  the equation  $P_t + \sum_{j=2}^M P_{rj} = 1$  is satisfied.

The most difficult point in applying the formula (4.10) is the calculation of  $T^N$  since the interesting values of  $N$  range from  $10^3$  up to  $10^5$  in a typical case. If the calculations are carried out numerically with a computer, this is no problem, but if analytic expressions are desired, one has to solve the eigenvalues of  $T$ , with the help of which  $T^N$  can be written down explicitly. Let us consider  $T$  in more detail. From formulae (3.4), (4.4) and (4.6) we conclude that all the off-diagonal elements of  $T$  are small and the main diagonal elements are approximately the same as those of  $\Phi$ . The eigenvalues of  $T$  are thus roughly  $\lambda_j = \exp i\mathbf{k}_j \cdot \mathbf{a}_3$ . The off-diagonal elements of  $T^N$ , for large  $N$ , are in general also small, unless two or more eigenvalues  $\lambda_j$  happen to be very near to each other. Because of the form (4.11) for  $\xi^{\text{in}}$ , at least one of the eigenvalues  $\lambda_{j \neq 1}$  must be very near to  $\lambda_1$  if any considerable flux of particles is expected to emerge from the crystal, excluding the forward scattered wave. The so called two-wave approximation is based on the assumption that only one of the eigenvalues, say  $\lambda_2$  is in the immediate vicinity of  $\lambda_1$ . In this case the whole calculation can be performed in  $(2 \times 2)$  space. Let us assume that  $\mathbf{k}_1$  points in the positive direction. Now, depending on

whether  $\mathbf{k}_2$  points in the positive or negative direction we can distinguish two cases. The former is called the Laue case and the latter the Bragg case in the diffraction literature. Because the solutions differ considerably from each other, we shall, in what follows, consider each case in a separate sub-section.

#### 4.2. The two-wave approximation in the Laue case

Here the reduction in  $(2 \times 2)$  space means that  $P^+$  is replaced by the identity matrix 1 and  $P^-$  by zero. From equation (4.6) we see that  $T$  reduces to  $D\Phi$  and from equation (4.10) we see that  $S_N$  reduces to  $[D\Phi]^N \Phi^{-1}$ .

With the help of the definitions

$$\begin{aligned} (\mathbf{k}_2 + \mathbf{k}_1) \cdot \mathbf{a}_3 &= 2\varrho \\ (\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{a}_3 &= 2(n\pi + \varphi), \end{aligned} \quad (4.14)$$

$\Phi$  can be written as

$$\Phi = e^{i\varphi} \begin{bmatrix} e^{-i\varphi} & 0 \\ 0 & e^{+i\varphi} \end{bmatrix}. \quad (4.15)$$

An explicit representation for the diffraction matrix

$$D = \begin{bmatrix} 1 - i\gamma_{11} & -i\gamma_{12} \\ -i\gamma_{21} & 1 - i\gamma_{22} \end{bmatrix} \quad (4.16)$$

is obtained from formula (3.4) adopting the notation

$$\begin{aligned} \gamma_{jj'} &= \frac{2\pi N_0 b}{\sqrt{|k_{jz}| |k_{j'z}|}} \\ &\times \int_{\text{unit cell}} f(\mathbf{r}) \exp [i(\mathbf{k}_{j'} - \mathbf{k}_j) \cdot \mathbf{r}] d^3\mathbf{r}. \end{aligned} \quad (4.17)$$

The eigenvalues of

$$T = e^{i\varphi} \begin{bmatrix} (1 - i\gamma_{11}) e^{-i\varphi} & -i\gamma_{12} e^{+i\varphi} \\ -i\gamma_{21} e^{-i\varphi} & (1 - i\gamma_{22}) e^{+i\varphi} \end{bmatrix} \quad (4.18)$$

calculated in the lowest order approximation are:

$$\lambda_{\pm} = \exp i\varrho \exp [i\{-\frac{1}{2}(\gamma_{11} + \gamma_{22}) \pm \tau_L\}], \quad (4.19)$$

where we have used the notation

$$\tau_L = \sqrt{[\varphi + \frac{1}{2}(\gamma_{11} - \gamma_{22})]^2 + \gamma_{12}\gamma_{21}}. \quad (4.20)$$

Since  $T$  is a  $(2 \times 2)$  matrix,  $T^N$  can be written as  $T^N = \alpha T + \beta 1$  where the coefficients  $\alpha, \beta$  solved from the equations  $\lambda_{\pm}^N = \alpha \lambda_{\pm} + \beta$  are:

$$\alpha = \exp \{i(N-1) [\varrho - \frac{1}{2}(\gamma_{11} + \gamma_{22})]\} \sin N\tau_L / \sin \tau_L$$

$$\beta = - \exp \{iN[\varrho - \frac{1}{2}(\gamma_{11} + \gamma_{22})]\} \sin (N-1)\tau_L / \sin \tau_L.$$

The desired matrix elements  $S_{N11}$  and  $S_{N12}$  can now be calculated by dropping the higher order terms, and are given by formulae:

$$S_{N11} = (\alpha T_{11} + \beta) \Phi_{11}^{-1}, \quad S_{N12} = \alpha T_{12} \Phi_{11}^{-1}.$$

By substitution of the relevant quantities, the following well known result, for real values of  $\gamma_{11}$ ,  $\gamma_{22}$  and  $\gamma_{12}\gamma_{21}$ , is obtained from formulae (4.12) and (4.13):

$$\begin{aligned} P_t &= \cos^2 N\tau_L + \frac{\tau_L^2 - \gamma_{12}\gamma_{21}}{\tau_L^2} \sin^2 N\tau_L \\ P_r &= \frac{\gamma_{12}\gamma_{21}}{\tau_L^2} \sin^2 N\tau_L. \end{aligned} \quad (4.21)$$

The condition  $P_t + P_r = 1$  is satisfied by formula (4.21).

#### 4.3. The two-wave approximation in the Bragg case

Here the representations of the projection operators are

$$P^+ = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad P^- = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix},$$

and no simplification in the form of  $T$  or  $S_N$  can be made. From formulae (4.6), (4.15), and (4.16), by dropping the second order terms in  $\gamma$  we get the representation:

$$T = e^{i\varphi} \begin{bmatrix} (1 - i\gamma_{11}) e^{-i\varphi} & -i\gamma_{12} e^{+i\varphi} \\ +i\gamma_{21} e^{-i\varphi} & (1 + i\gamma_{22}) e^{+i\varphi} \end{bmatrix}. \quad (4.22)$$

The eigenvalues of  $T$  in the lowest order approximation are

$$\lambda_{\pm} = \exp i\varrho \exp [-i\frac{1}{2}(\gamma_{11} - \gamma_{22}) \pm \tau_B], \quad (4.23)$$

where

$$\tau_B = \sqrt{\gamma_{12}\gamma_{21} - [\varphi + \frac{1}{2}(\gamma_{11} + \gamma_{22})]^2}. \quad (4.24)$$

As a  $(2 \times 2)$  matrix  $T^N$  can be written as  $T^N = \alpha T + \beta 1$  where the coefficients  $\alpha, \beta$  solved from the equations  $\lambda_{\pm}^N = \alpha \lambda_{\pm} + \beta$  are:

$$\alpha = \exp \{i(N-1) [\varrho - \frac{1}{2}(\gamma_{11} - \gamma_{22})]\} \sinh N\tau_B / \sinh \tau_B$$

$$\beta = - \exp \{iN[\varrho - \frac{1}{2}(\gamma_{11} - \gamma_{22})]\} \sinh (N-1)\tau_B / \sinh \tau_B.$$

The required elements of  $S_N$  can now be calculated with the help of formulae (4.10), (4.16), and (4.22). Dropping the higher order terms one can write

$$S_{N11} = [(\alpha T_{11} + \beta)(\alpha T_{22} + \beta) - \alpha^2 T_{12} T_{21}] / (\alpha T_{22} + \beta) e^{-i\varphi},$$

$$S_{N12} = -\alpha T_{21} e^{2i\varphi} / (\alpha T_{22} + \beta).$$

Substituting the expressions for the relevant quantities, and making use of the definitions (4.12) and (4.13) one arrives at the results:

$$\begin{aligned} P_t &= (\tau_B^2 \coth^2 N\tau_B - \tau_B^2) / (\gamma_{12}\gamma_{21} - \tau_B^2 + \tau_B^2 \coth^2 N\tau_B) \\ P_r &= \gamma_{12}\gamma_{21} / (\gamma_{12}\gamma_{21} - \tau_B^2 + \tau_B^2 \coth^2 N\tau_B) \end{aligned} \quad (4.25)$$

for real values of  $\gamma_{11}$ ,  $\gamma_{22}$  and  $\gamma_{12}\gamma_{21}$ . Here again  $P_t + P_r = 1$  is true.

## 5. Discussion

The matrix formalism developed in this paper can also be considered as a system of difference equations, which as a special case include both Darwin's (1914) classical treatment and the equations recently given by Borie (1966). At this point a comment can be made

on Raith's (1966) remark on page 31 of his thesis. He states that the factor 'i', in an expression of Darwin's theory corresponding to our formula (2.6), is due to a calculation error. This confusion is best explained by referring to Fig. 2. In case (a) there is an infinitely large crystal plane and a 'plane wave', modified by a slowly varying exponential attenuation factor, which makes the field vanish at infinity. After carrying out the integration involved (see Appendix) this attenuation factor is made to converge to 1 and this procedure gives the above mentioned factor 'i'. In case (b) there is a large finite crystal plane and a plane wave. Here the diffracted field does not converge to any definite limit as the crystal is made larger and larger. Therefore, at small distances from the crystal the phase of the diffracted field is a function of position and cannot be given by a single phase factor. However, at distances large compared with the crystal dimensions the diffracted wave can be described by spherical waves with definite phase compared with the incident wave.

Let us briefly summarize the essential features of the formalism developed above. It is sufficient to define one wave number only, namely that in vacuum. The system of equations is finite and the number of equations is twice the number of reciprocal lattice points within the circle constructed in Fig. 1. The major components are found by considering the eigenvalues of matrix  $T$  or diagonal elements of the phase matrix  $\Phi$ . All the physically interesting information is contained in the matrix  $T$ , from the properties of which one can deduce such typical phenomena of the dynamical diffraction theory as anomalous absorption and 'umweganregung'. Because of the simple framework of the theory calculations are easily programmed for a computer.

For comparison, let us list the typical features of the conventional theory, based on ordinary Fourier-expansions

[see e.g. James (1963)]. Distinction between wave numbers in vacuum and in crystal matter must be made. The number of unknowns and equations is infinite. The large components are those in the immediate vicinity of the Ewald sphere. Programming the problem for a computer is not straightforward.

For crystals composed of atoms with finite mass the thermal motion of the crystal can be taken into account only by averaging the static potential over the assumed motion of atoms. Hence the formula (2.8) can be thought to include the Debye-Waller factor. The effect of inelastic scattering on coherent elastic scattering can be phenomenologically treated in a similar way to ordinary absorption, as stated in § 3. However, to calculate the inelastically scattered waves themselves would require a much more complicated theory than the present one.

## APPENDIX

### Calculation of the integral

$$\mathcal{J} = \iint_{-\infty}^{+\infty} dx dy \exp(-ik_{1y}y) \frac{\exp ik_0 \sqrt{x^2 + y^2 + z^2}}{\sqrt{x^2 + y^2 + z^2}}.$$

Let us introduce new variables  $(u, \varphi)$  defined by equations:

$$\begin{cases} x = \frac{\sqrt{u^2 - k_z'^2 z^2}}{k_z'} \sin \varphi \\ y = \frac{k_0}{k_z'} \sqrt{(u^2 - k_z'^2 z^2)} \cos \varphi + uk_{1y}/k_z'^2 \end{cases} \quad (A1)$$

where

$$k_z' = \sqrt{k_0^2 - k_{1y}^2}. \quad (A2)$$

$u$  is the phase angle of the integrand of  $\mathcal{J}$  and the curves  $u = \text{constant}$  on the plane  $(x, y)$  are ellipses, the parameter equations of which are given in (A1). In order to calculate the surface element  $dA = dx dy = J du d\varphi$  the Jacobian

$$J = \begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial \varphi} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial \varphi} \end{vmatrix}$$

must be evaluated. The required partial derivatives are obtained from equation (A1) and with the help of these the Jacobian is found to be

$$J = k_0 u / k_z'^3 + k_{1y} \cos \varphi \sqrt{u^2 - k_z'^2 z^2} / k_z'^3. \quad (A3)$$

On the other hand for the denominator of the integrand of  $\mathcal{J}$  the following expression can be derived

$$\sqrt{x^2 + y^2 + z^2} = k_0 u / k_z'^2 + k_{1y} \cos \varphi \sqrt{u^2 - k_z'^2 z^2} / k_z'^2.$$

Combining this with (A3) we find that  $J$  is simply given by the formula

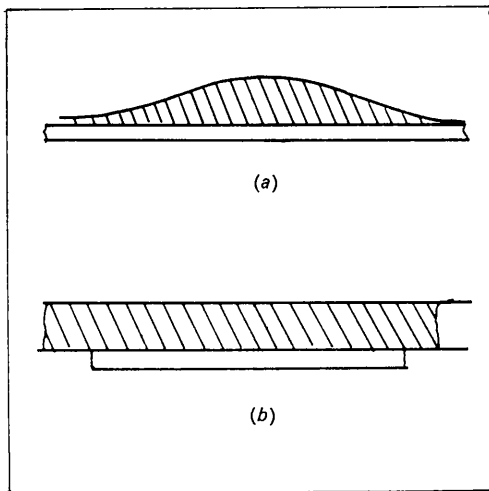


Fig. 2. An infinite crystal plane illuminated by a modified plane wave (a), and a finite crystal plane illuminated by an unmodified plane wave (b).

$$J = \sqrt{x^2 + y^2 + z^2/k'_z}. \quad (\text{A4})$$

The integral  $\mathcal{J}$  can now be written as

$$\mathcal{J} = \int_{u_{\min}}^{u_{\max}} du \int_0^{2\pi} d\varphi \exp iu/k'_z = \frac{2\pi i}{k'_z} \times [\exp iu_{\min} - \exp iu_{\max}] \quad (\text{A5})$$

where  $u_{\min} = k'_z|z|$  and  $u_{\max} \rightarrow \infty$ . Because  $u$  is real  $\mathcal{J}$  does not converge to any definite limit but oscillates along a closed curve in the complex plane, when  $u_{\max}$  tends to infinity. This difficulty, due to the fact that plane waves do not vanish at infinity, can be overcome by multiplying the integrand in (A5) by a factor  $\exp -\varepsilon u$ , where  $\varepsilon$  is a small positive number. In this case we can write

$$\mathcal{J}_\varepsilon = \frac{2\pi i}{k'_z(1+i\varepsilon)} \exp(i-\varepsilon)k'_z|z|.$$

Now, letting  $\varepsilon$  converge to zero the result

$$\mathcal{J} = \frac{2\pi i}{k'_z} \exp ik'_z|z| \quad (\text{A6})$$

is obtained.

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