

1964), although in these two examples the reduction already almost vanishes at the second reflexion, which is very close to the first one in angular position. The reduction found in the present study, however, is too small to conclude therefrom the existence of solid state effects. It is also to be mentioned that the present X-ray diffraction data do not give any information about the region below  $\sin \theta/\lambda = 0.25 \text{ \AA}^{-1}$ .

It is apparent that the contradictory results found by various authors are related to the techniques used for determining the intensity data on the absolute basis. In measurements of this kind, it is necessary to pay much attention to detailed experimental conditions. For example, we have found that an inaccuracy of  $\pm 0.2^\circ$  (in  $2\theta$ ) in the zero alignment (Batterman *et al.*, 1960) may result in an error of  $\pm 5\%$  in the integrated intensity when  $\theta = 10^\circ$ , if the receiving slit is very narrow.

As was pointed out at the Seventh International Congress of Crystallography in Moscow 1966 (Informal Session on the Powder Intensity Project), it is very desirable to have a standard powder specimen for X-ray intensity measurements, because with such a specimen a relative measurement can readily be converted to an absolute one. In the light of our measure-

ments, carbonyl iron seems to be suitable for the purpose. This powder is stable, and identical specimens will be available in different laboratories because of a well standardized procedure for the preparation of this substance.

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## A Linear Analysis of the Non-Crystallographic Symmetry Problem

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Linear equations are derived which express constraints on the structure factors of a crystal having more than one identical molecule or subunit in the asymmetric unit. Solution of these equations leads to a series of functions having the required non-crystallographic symmetry. Any structure having the postulated symmetry can be expressed as a linear combination of these functions. This approach has the advantage that far fewer variables are needed to describe the system to a given resolution than in the conventional method using amplitudes and phases. The reduction in the number of variables is used as a measure of the information content of the equations.

### Introduction

It has been shown (Rossmann & Blow, 1963; Main & Rossmann, 1966) that, when a crystal contains more than one identical molecule or subunit per asymmetric unit, equations can be set up which imply constraints on the phases of the structure factors. These equations contain certain parameters relating to the relative rotational and translational positioning of the subunits within the asymmetric unit. However, there exist methods for determining these parameters (Rossmann & Blow, 1962; Rossmann, Blow, Harding & Collier, 1964) and it is assumed in all that follows that their values are known.

Iterative methods for solution of the equations have been proposed which, for a number of simple trial structures, appear to converge to a unique answer, agreeing well with the known phases (Rossmann & Blow, 1964; Main & Rossmann, 1966). Both these papers attempt to derive values for the unknown phases and in doing so formally separate the amplitudes and phases of the structure factors as they appear in the equations. This means that the equations to be solved are non-linear from the beginning of the calculation.

The methods described in this paper formally keep the amplitude and phase together as an unknown complex structure factor. The equations are now linear in

these complex structure factors and the powerful techniques of linear analysis can be applied to the system. It will be shown that to a given resolution there is only a finite number of independent density distributions which satisfy the non-crystallographic symmetry and that this number is considerably less than the number of phases needed in a conventional description of the system to this resolution. These density distributions are the Fourier transforms of a degenerate set of eigenvectors corresponding to a multiple eigenvalue of the matrix describing the geometry of the system. Such degenerate systems of eigenfunctions are familiar in quantum mechanics and other branches of applied mathematics. The important point about them is that any function which satisfies the conditions of the problem can be expressed as a linear combination of the allowed eigenfunctions. Thus, to solve a structure having known non-crystallographic symmetry, it is necessary to determine the coefficients in the expansion of the structure in terms of the allowed eigenfunctions. Since only the intensities of the diffraction pattern are available the equations for these coefficients are non-linear, but the number of unknowns is now much smaller than the number of phases that would have to be found in a conventional structure determination.

### Setting up the equations

Let us now derive, in a suitably symmetrized form, the equations that the structure factors must obey when a crystal contains  $n$  identical subunits per asymmetric unit. For simplicity we consider space group  $P1$ , though the results can readily be extended to space groups of higher symmetry. In setting up the equations it is assumed that

- (a) the geometry of the subunits is known;
- (b) the subunits are identical;
- (c) the density between the subunits is zero;
- (d) the density is real.

One subunit  $U_1$  is taken as the reference subunit and the positions of the other subunits  $U_j$  are specified relative to this. Suppose the position  $\mathbf{x}_j$  of an element of density in the  $j$ th subunit is related to the position  $\mathbf{x}_1$  of the corresponding element of density in the reference subunit by

$$\mathbf{x}_j = \mathbf{C}_j \mathbf{x}_1 + \mathbf{d}_j, \quad (j = 1, n),$$

where  $\mathbf{C}_1 = \mathbf{I}$ ,  $\mathbf{d}_1 = \mathbf{0}$ ,

so that  $\varrho(\mathbf{C}_j \mathbf{x}_1 + \mathbf{d}_j) = \varrho(\mathbf{x}_1)$

when  $\mathbf{x}_1$  lies within  $U_1$ . We may write the complex structure factor  $F_{\mathbf{h}}$  as

$$F_{\mathbf{h}} = |F_{\mathbf{h}}| \exp(i\alpha_{\mathbf{h}}) = V \int_{\text{unit cell}} \varrho(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) d\mathbf{x}.$$

For reasons which will appear later it is more convenient to use assumption (d) and to work with the complex conjugate relation

$$F_{\mathbf{h}}^* = |F_{\mathbf{h}}| \exp(-i\alpha_{\mathbf{h}}) = V \int_{\text{unit cell}} \varrho(\mathbf{x}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}) d\mathbf{x}.$$

Using assumption (c) we may write this as a sum of integrals taken over the subunits

$$F_{\mathbf{h}}^* = V \sum_{j=1}^n \int_{U_j} \varrho(\mathbf{x}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}) d\mathbf{x}.$$

Transforming the variable of integration we have

$$F_{\mathbf{h}}^* = V \sum_{j=1}^n \int_{U_1} \varrho(\mathbf{x}_j) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) d\mathbf{x}_1.$$

We now have to express the identity of the subunits, assumption (b), in such a way that the algebraic symmetry is retained. This may be done by equating all the densities  $\varrho(\mathbf{x}_j)$  in turn to  $\varrho(\mathbf{x}_1)$ , then to  $\varrho(\mathbf{x}_2)$  and so on, thus generating the  $n$  relations

$$F_{\mathbf{h}}^* = V \sum_{j=1}^n \int_{U_1} \varrho(\mathbf{x}_k) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) d\mathbf{x}_1, \quad (k = 1, n).$$

We may now add these  $n$  expressions giving

$$nF_{\mathbf{h}}^* = V \sum_{j=1}^n \sum_{k=1}^n \int_{U_1} \varrho(\mathbf{x}_k) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) d\mathbf{x}_1.$$

Replacing  $\varrho(\mathbf{x}_k)$  by its Fourier series expansion

$$\varrho(\mathbf{x}_k) = \frac{1}{V} \sum_{\mathbf{p}} F_{\mathbf{p}} \exp(-2\pi i \mathbf{p} \cdot \mathbf{x}_k)$$

gives

$$F_{\mathbf{h}}^* = \frac{1}{n} \sum_{j=1}^n \sum_{k=1}^n \int_{U_1} \sum_{\mathbf{p}} F_{\mathbf{p}} \exp(-2\pi i \mathbf{p} \cdot \mathbf{x}_k) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) d\mathbf{x}_1,$$

which, after rearrangement, becomes

$$F_{\mathbf{h}}^* = \sum_{\mathbf{p}} F_{\mathbf{p}} \left\{ \frac{1}{n} \sum_{j=1}^n \sum_{k=1}^n \int_{U_1} \exp[-2\pi i (\mathbf{h} \cdot \mathbf{x}_j + \mathbf{p} \cdot \mathbf{x}_k)] d\mathbf{x}_1 \right\}.$$

This may be written more compactly as

$$F_{\mathbf{h}}^* = \sum_{\mathbf{p}} B_{\mathbf{hp}} F_{\mathbf{p}}, \quad (1)$$

where

$$B_{\mathbf{hp}} = \frac{1}{n} \sum_{j=1}^n \sum_{k=1}^n \int_{U_1} \exp[-2\pi i (\mathbf{h} \cdot \mathbf{x}_j + \mathbf{p} \cdot \mathbf{x}_k)] d\mathbf{x}_1.$$

It is shown in the Appendix that these equations relating the structure factors are not only a necessary consequence of the identity of the subunits, but are also sufficient to ensure that identity.

### Matrix formulation of the equations

The equations (1) express the value of an arbitrary structure factor  $F_{\mathbf{h}}^*$  as a weighted sum of structure factors  $F_{\mathbf{p}}$  taken over the whole of reciprocal space. The weighting factors  $B_{\mathbf{hp}}$  are expressed in terms of the shape and the relative rotational and translational parameters of the subunits within the asymmetric unit and are assumed calculable. For the purposes of computation it is necessary to truncate the summation over reciprocal space after a finite number of terms. Since

the weighting factor falls off fairly rapidly with increasing distance between the points  $\mathbf{p}$  and  $\mathbf{h}$  in reciprocal space, it may be assumed that the truncation affects significantly only those reflexions lying close to the boundary of the region of reciprocal space being considered.

It is convenient at this stage to denote the reflexions  $F_{\mathbf{h}}$  and  $F_{\mathbf{p}}$  by scalar suffixes as  $F_r$  and  $F_s$ , the Friedel-related reflexions being denoted by  $F_{-r}$  and  $F_{-s}$ . The equations (1) now become

$$\sum_{s=-N}^N B_{rs}F_s = F_r^*, \quad (r = -N, \dots, N),$$

or, writing this in matrix notation,

$$\mathbf{B}\mathbf{F} = \mathbf{F}^*, \quad (2)$$

where  $\mathbf{B}$  is the  $(2N+1) \times (2N+1)$  complex matrix of weighting factors and  $\mathbf{F}$  is the complex column vector of structure factors

$$\mathbf{F} = \begin{pmatrix} F_{-N} \\ \vdots \\ F_0 \\ \vdots \\ F_N \end{pmatrix}.$$

We now combine equation (2) with the Friedel relationship which can conveniently be written in matrix form as

$$\mathbf{T}\mathbf{F} = \mathbf{F}^*, \quad (3)$$

where  $\mathbf{T} = \begin{pmatrix} 0 & & & 1 \\ & \ddots & & \\ & & \ddots & \\ 1 & & & 0 \end{pmatrix}$ ,  $\mathbf{T}^2 = \mathbf{I}$ .

Premultiplication of the vector  $\mathbf{F}$  by the matrix  $\mathbf{T}$  has the effect of interchanging  $F_r$  and  $F_{-r}$ , ( $r=1, N$ ), so that  $\mathbf{T}$  is in fact a re-ordering matrix. Combining (2) and (3) we have

$$\mathbf{B}\mathbf{F} = \mathbf{T}\mathbf{F}$$

or

$$\mathbf{H}\mathbf{F} = \mathbf{F} \quad (4)$$

where  $\mathbf{H} = \mathbf{T}\mathbf{B}$ .

Therefore  $(\mathbf{H} - \mathbf{I})\mathbf{F} = 0$ . (5)

It can be seen from their definition that the elements of matrix  $\mathbf{B}$  obey the symmetry relation

$$B_{-s-r} = B_{rs}^*$$

so that  $\mathbf{B}$  is Hermitian about its second diagonal. Premultiplication by the matrix  $\mathbf{T}$  has the effect of interchanging the diagonals, so that the matrix  $\mathbf{H}$  is Hermitian about its leading diagonal (*i.e.*  $H_{sr} = H_{rs}^*$ ). The rather complicated manipulations used in deriving the equations were necessary in order to produce a matrix  $\mathbf{H}$  of Hermitian type, thus simplifying further theory and computation.

### Solution of the equations

The expression (5) represents a set of  $(2N+1)$  homogeneous linear equations in the  $(2N+1)$  complex variables  $F_r$ . Because of the way the equations were con-

structed, any solution of them will satisfy the Friedel relation and will have a Fourier transform which has identical density distributions inside the subunits and zero density outside the subunits. In general, however, there will be more than one independent solution and the general solution will be a linear combination of these.

To discover how many independent solutions there are to equations (5) we must consider (4) as a special case of the general eigenvalue problem

$$\mathbf{H}\mathbf{F} = \lambda\mathbf{F}. \quad (6)$$

By comparing (4) and (6) we see that any eigenvector of  $\mathbf{H}$  corresponding to an eigenvalue  $\lambda=1$  will be a solution of equation (5). Conversely the number of linearly independent solutions of (5) is equal to the number of unit eigenvalues of the matrix  $\mathbf{H}$ . Since  $\mathbf{H}$  is Hermitian all its eigenvalues are real and it is possible to construct a set of  $(2N+1)$  orthonormal eigenvectors.

Let us suppose that  $\mathbf{H}$  has  $m$  unit eigenvalues and let us denote the corresponding orthonormal eigenvectors by  $(\mathbf{u}_1, \dots, \mathbf{u}_m)$ . If we have a problem in which the density  $\varrho(\mathbf{x})$  satisfies the postulated conditions of localization and local symmetry, it is possible by the above argument to express its transform  $\mathbf{F}$  as a linear combination of the eigenvectors  $(\mathbf{u}_1, \dots, \mathbf{u}_m)$ , namely

$$\mathbf{F} = \sum_{j=1}^m \mu_j \mathbf{u}_j.$$

By taking the Fourier transform of this equation we could equally well express the relation in real space (to the resolution to which we are working) and write

$$\varrho(\mathbf{x}) = \sum_{j=1}^m \mu_j \varrho_j(\mathbf{x}),$$

where  $\varrho_j(\mathbf{x})$  represents the Fourier transform of the eigenvector  $\mathbf{u}_j$ . The functions  $\varrho_j(\mathbf{x})$  will be referred to as 'eigendensities'. It is important to note that the  $\mu_j$  are real, since  $\varrho(\mathbf{x})$  is real and since  $\varrho_j(\mathbf{x})$  are real because  $\mathbf{u}_j$  were constructed to satisfy the Friedel relation.

The eigendensities  $\varrho_j$  corresponding to an orthonormal set of eigenvectors  $\mathbf{u}_j$  are also orthonormal, in the sense that

$$I_{jk} = \int_{\text{unit cell}} \varrho_j(\mathbf{x}) \varrho_k(\mathbf{x}) d\mathbf{x} = \delta_{jk}.$$

This may be shown by replacing the densities by their Fourier series giving

$$\begin{aligned} I_{jk} &= \int_{\text{unit cell}} \sum_{\mathbf{h}} u_{j\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}) \sum_{\mathbf{p}} u_{k\mathbf{p}} \exp(-2\pi i \mathbf{p} \cdot \mathbf{x}) d\mathbf{x} \\ &= \sum_{\mathbf{h}} \sum_{\mathbf{p}} u_{j\mathbf{h}} u_{k\mathbf{p}} \int_{\text{unit cell}} \exp[-2\pi i (\mathbf{h} + \mathbf{p}) \cdot \mathbf{x}] d\mathbf{x}. \end{aligned}$$

The integral vanishes unless  $\mathbf{p} = -\mathbf{h}$  so that

$$I_{jk} = \sum_n u_{jn} u_{kn}^* \\ = \sum_n u_{jn} u_{kn}^*$$

since  $u_k$  satisfies the Friedel relation. Hence by the orthonormality of the eigenvectors we have

$$I_{jk} = \delta_{jk}.$$

We have so far considered only those eigenvectors and eigendensities corresponding to unit eigenvalues. What meaning can be attached to those eigenvalues

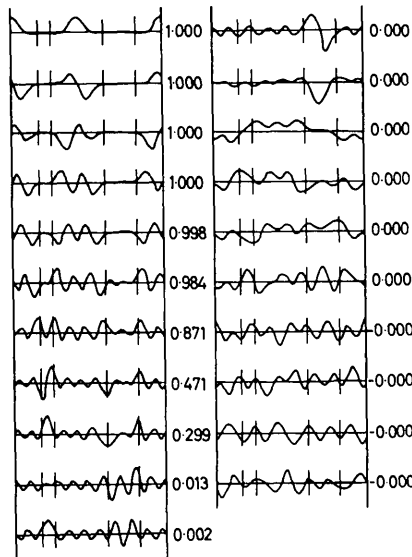


Fig. 1. Eigendensities and corresponding eigenvalues for a one-dimensional cell, line group 1, containing two identical subunits, each of fractional size 0.357 with centres at 0 and 0.431 respectively, reflexions from  $h = -10$  to  $h = +10$  being included.

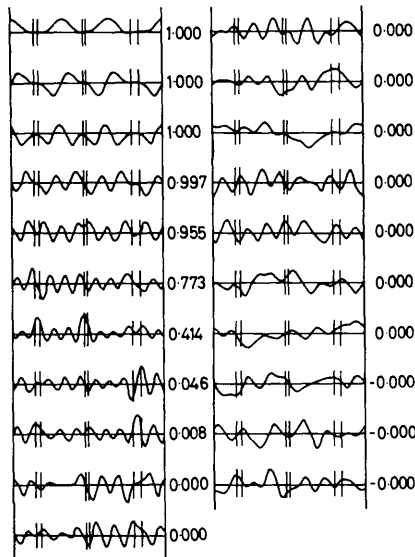


Fig. 2. Eigendensities and corresponding eigenvalues for a one-dimensional cell, line group 1, containing three identical subunits, each of fractional size 0.29 with centres at 0, 0.33 and 0.63 respectively (Main & Rossmann, 1966), reflexions from  $h = -10$  to  $h = +10$  being included.

which are not unity? It is shown in the Appendix that an eigenvalue  $\lambda_j$  can be expressed in terms of its corresponding eigendensity by

$$\lambda_j = \frac{\int_{\text{subunits}} [\rho_j(\mathbf{x})]^2 d\mathbf{x} - \sigma_j^2}{\int_{\text{unit cell}} [\rho_j(\mathbf{x})]^2 d\mathbf{x}}, \quad (7)$$

where  $\sigma_j^2$  is a measure of the lack of equality of density within the various subunits. The first term in the numerator is a measure of the fraction of the total density which lies within the subunits and the denominator is a normalizing factor. The form of (7) implies that  $0 \leq \lambda_j \leq 1$ . If there is no density outside the subunits and the densities within the subunits are identical, so that  $\sigma_j^2 = 0$ , equation (7) gives  $\lambda_j = 1$ , as expected. If all the density lies outside the subunits,  $\lambda_j = 0$ . Some combinations of non-zero densities within the various subunits can also lead to a zero eigenvalue, though the exact form of these densities depends on the number of subunits.

Figs. 1 and 2 show the eigendensities and corresponding eigenvalues for two one-dimensional examples containing 2 and 3 subunits respectively. In each case reflexions from  $h = -10$  to  $h = +10$  are included. Because we are considering a truncated system and because of rounding errors during calculation there are no exactly unit eigenvalues. Also in any real problem the postulated conditions, in particular that of vanishing density outside the subunits, will not be exactly fulfilled, so that it is not clear how far an eigenvalue can depart from unity, while still considering the corresponding eigendensity as allowable. This will be discussed further in the next section. If we consider an allowed eigendensity to be one corresponding to an eigenvalue  $\lambda \geq 0.95$ , the two subunit case has six allowed eigendensities and the three subunit case has five.

Fig. 3 shows the eigendensities corresponding to the six largest eigenvalues for a two-dimensional case with two identical subunits.

As might be expected the behaviour within the subunits of the one-dimensional eigendensities is similar to that of the classical orthogonal polynomials. With increasing number of zeros in the interval the fitting that can be achieved, while working to a given resolution, becomes steadily worse and this is reflected in an increasing departure from unity of the corresponding eigenvalue. In the two-dimensional example of Fig. 3 it can be seen that the behaviour of the eigendensities within the subunits is analogous to the normal modes of vibration of a rectangular membrane, though there are departures from this because of the unsymmetrical disposition of the subunits.

### Information content of the equations

Let us now consider the above problem in a different way. Suppose we have a structure which is unknown,

but which has the postulated local symmetry, and that to a given resolution we have measured the intensities of  $N$  independent reflexions. In a conventional structure determination  $N$  phases have to be found. Using the above analysis, however, only  $m$  real parameters have to be determined, namely the coefficients in the expansion of the transform in terms of the  $m$  known allowed eigenvectors. We may write

$$\mathbf{F} = \sum_{j=1}^m \mu_j \mathbf{u}_j. \quad (8)$$

Since only the intensities of the reflexions are available the equations from which  $\mu_j$  have to be found are non-linear, namely

$$|F_h|^2 = \sum_{j=1}^m \sum_{k=1}^m \mu_j \mu_k u_{jh}^* u_{kh}, \quad (h=0,1,\dots,N).$$

The number of equations is now much greater than the number of unknowns and it should be possible to find best values of the parameters  $\mu_j$  by a non-linear least-squares process, using a sliding filter of the type described by Diamond (1966). Using this technique it is possible to decide how many eigenvectors to include at each stage of the fitting procedure and in particular to decide how many eigenvectors are allowable. If the  $\mathbf{u}_j$  are orthonormal the form of (8) implies an overall scale factor for the problem, since the  $\mu_j$  must satisfy the relation

$$\sum_{j=1}^m \mu_j^2 = \sum_{h=-N}^N |F_h|^2.$$

In Fig. 4 the number of allowed eigendensities is plotted against the number of independent reflexions included, for a series of one-dimensional problems containing 2, 3 and 4 subunits respectively. In this context eigendensities corresponding to eigenvalues  $\lambda \geq 0.95$  have been considered allowable. It can be seen that the plots are linear, though their exact form for a given number of subunits will depend on the size and positioning of the subunits. The fact that the plots do not pass through the origin means that there is a certain minimum number of reflexions that has to be included before it is possible to generate an eigendensity which satisfies the conditions of the problem. The gradient of the plots, or the fractional decrease in the number of parameters needed to describe the system, can be considered to represent the information gained by this method of analysis. For reasons given below the expected fractional gain of information for the case of an asymmetric unit containing  $n$  subunits is about  $1/n$ . However it can be seen from Fig. 4 that, at least for one-dimensional problems, this expected gain is not in general achieved. In two and three dimensions the information gain should be closer to that expected.

To discover the information gain to be expected from the equations let us consider a degenerate case of 2 subunits, which completely fill a one-dimensional cell. The condition of equality of density within the subunits is now as strong as possible and the symmetry becomes truly crystallographic; we have a doubled unit

cell. The matrix  $\mathbf{H}$  for this system has alternating  $+1$  and  $-1$  along the diagonal and zeros off the diagonal, so that all its eigenvalues are  $\pm 1$ . For convenience let us truncate the system at  $h = \pm 2$ , so that

$$\mathbf{H} = \begin{pmatrix} 1 & & & 0 \\ & -1 & & \\ & & 1 & \\ 0 & & & -1 & \\ & & & & 1 \end{pmatrix}.$$

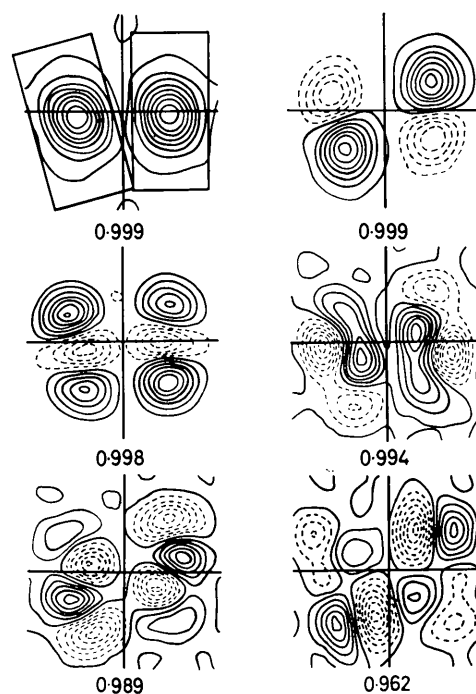


Fig. 3. Eigendensities corresponding to the six largest eigenvalues for a two-dimensional square cell, plane group  $p1$ , containing two identical subunits related by a rotation of  $194^\circ$  about the centre of the cell. The subunits are enclosed within rectangular boxes of fractional dimensions  $0.4 \times 0.8$  and the centre of the reference subunit is at  $x=0.25, y=0$ , as shown in the first diagram of the series. The innermost 49 reflexions are included.

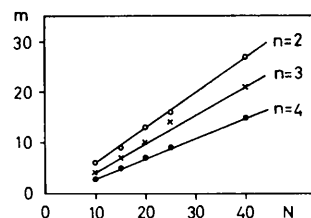


Fig. 4. Plots of  $m$ , the number of allowed eigenvectors, against  $N$ , the number of independent reflexions included, for one-dimensional examples containing 2, 3 and 4 identical subunits. Allowed eigenvectors are those corresponding to eigenvalues  $\lambda \geq 0.95$ . For  $n=2$ , subunit size =  $0.357$ , subunit centres at  $0$  and  $0.431$ . For  $n=3$ , subunit size =  $0.29$ , subunit centres at  $0, 0.33$  &  $0.63$ . For  $n=4$ , subunit size =  $0.21$ , subunit centres at  $0, 0.22, 0.46$  and  $0.72$ .

An orthogonal set of eigenvectors satisfying the Friedel relation can be constructed by inspection, namely

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \begin{pmatrix} i \\ 0 \\ 0 \\ 0 \\ -i \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \text{ for } \lambda = +1 ,$$

and

$$\begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ i \\ 0 \\ -i \\ 0 \end{pmatrix} \text{ for } \lambda = -1 .$$

According to our interpretation the transform of the structure must be expressible as a linear combination of eigenvectors corresponding to eigenvalue  $\lambda = +1$ , so that  $F_{-1} = F_1 = 0$ . By considering a more extended system it can be seen that  $F_h$  vanishes for all odd  $h$ , and this is of course what one expects for a doubled unit cell. The fractional gain in 'information' according to the above definition is thus  $\frac{1}{2}$ , meaning that the number of variables to be determined has been halved, though in this case it is because half the amplitudes are identically zero. A similar argument leads to an expected fractional gain of information of  $1/n$  in the  $n$  subunit case.

The preceding example takes into account only the identity of the subunits, which has been made as strong as possible, and does not consider the vanishing of density between subunits, which occurs in more realistic structures. It is possible however, while omitting the identity of the subunits, to set up structure factor equations of a very similar type to those already derived, relying only on the vanishing of the density outside the subunits to give phase information [*i.e.* using only assumptions (a), (c) and (d)]. A similar eigenvalue analysis shows that these weaker equations give little information unless the subunits are made to fill an unreasonably small fraction of the unit cell. Thus the above analysis, although of a degenerate system, indicates an expected fractional gain of approximately  $1/n$  in the general  $n$ -subunit case.

**Appendix**

We wish to derive the relation (7) between an eigenvalue  $\lambda_j$  and its corresponding eigendensity  $\varrho_j(x)$ . The eigenvalue equation is

$$\mathbf{H}\mathbf{u}_j = \lambda_j \mathbf{u}_j .$$

Taking the scalar products of this with  $\mathbf{u}_j^H$ , the Hermitian transpose of  $\mathbf{u}_j$ , gives

$$\mathbf{u}_j^H \mathbf{H}\mathbf{u}_j = \lambda_j \mathbf{u}_j^H \cdot \mathbf{u}_j .$$

Therefore

$$\lambda_j = \frac{\mathbf{u}_j^H \mathbf{H}\mathbf{u}_j}{\mathbf{u}_j^H \cdot \mathbf{u}_j} . \tag{9}$$

Now

$$\mathbf{u}_j^H \cdot \mathbf{u}_j = \sum_{h=-N}^N |u_{jh}|^2 = \int_{\text{unit cell}} [\varrho_j(\mathbf{x})]^2 d\mathbf{x} . \tag{10}$$

Also

$$\mathbf{u}_j^H \mathbf{H}\mathbf{u}_j = \sum_h \sum_p u_{jh}^* H_{hp} u_{jp} .$$

Substitution for  $H_{hp}$  gives

$$\mathbf{u}_j^H \mathbf{H}\mathbf{u}_j = \sum_h \sum_p u_{jh}^* u_{jp} \left\{ \frac{1}{n} \sum_{k=1}^n \sum_{l=1}^n \int_{U_1} \exp[-2\pi i (\mathbf{h} \cdot \mathbf{x}_k + p \cdot \mathbf{x}_l)] d\mathbf{x}_1 \right\} .$$

Therefore

$$\mathbf{u}_j^H \mathbf{H}\mathbf{u}_j = \frac{1}{n} \sum_{k=1}^n \sum_{l=1}^n \int_{U_1} \varrho_j(\mathbf{x}_k) \varrho_j(\mathbf{x}_l) d\mathbf{x}_1 \tag{11}$$

$$\begin{aligned} &= \int_{\text{sub-units}} [\varrho_j(\mathbf{x})]^2 d\mathbf{x} - \frac{1}{n} \sum_{k=1}^n \sum_{l=1}^{k-1} \int_{U_1} [\varrho_j(\mathbf{x}_k) - \varrho_j(\mathbf{x}_l)]^2 d\mathbf{x}_1 \\ &= \int_{\text{sub-units}} [\varrho_j(\mathbf{x})]^2 d\mathbf{x} - \sigma_j^2 , \end{aligned} \tag{12}$$

where  $\sigma_j^2$  is a measure of the lack of equality of the subunits, comparing them in pairs in every possible way. Combining (9), (10) and (12) leads to the required relation between an eigenvalue  $\lambda_j$  and the corresponding eigendensity  $\varrho_j(\mathbf{x})$ , namely

$$\lambda_j = \frac{\int_{\text{sub-units}} [\varrho_j(\mathbf{x})]^2 d\mathbf{x} - \sigma_j^2}{\int_{\text{unit cell}} [\varrho_j(\mathbf{x})]^2 d\mathbf{x}} .$$

The form of this expression implies that  $\lambda \leq 1$ , equality occurring only if all the subunits are equal, and if there is zero density outside the subunits. We have therefore shown that any solution of the structure factor equations (1) derived above does satisfy the assumptions (a)–(d).

By writing (11) in the form

$$\mathbf{u}_j^H \mathbf{H}\mathbf{u}_j = \frac{1}{n} \int_{U_1 k} [\sum \varrho_j(\mathbf{x}_k)]^2 d\mathbf{x}_1$$

we obtain the alternative expression for  $\lambda_j$ ,

$$\lambda_j = \frac{\frac{1}{n} \int_{U_1 k} [\sum \varrho_j(\mathbf{x}_k)]^2 d\mathbf{x}_1}{\int_{\text{unit cell}} [\varrho_j(\mathbf{x})]^2 d\mathbf{x}} ,$$

from which it follows that  $\lambda_j$  must be positive. We have therefore shown that the eigenvalues of the matrix  $\mathbf{H}$  satisfy  $0 \leq \lambda_j \leq 1$ .

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## An Optical Instrument for the Direct Interpretation of Laue Patterns

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An optical apparatus is described for the direct interpretation of Laue photographs. It presents the results in the form of radial projections of the lattice-plane normals on a spherical surface.

For the interpretation of Laue patterns graphical methods are available which lead either to the gnomonic or to the stereographic projection. In order to eliminate the point-by-point plotting involved in these procedures, we have tried to find an optical method capable of yielding the required projection of a large area of the film simultaneously. Moreover, we aimed at a radial projection of the lattice plane normals on a spherical surface, because this allows direct recognition of symmetry elements even for arbitrary crystal settings. Such elements are, indeed, hard to find from the above-mentioned plane projections. On the other hand, the advantages of the latter (angle-true image by stereographic projection, easy recognition of zones by the gnomonic one) are obviously retained in full in the radial projection.

The basic idea of the resulting method is explained in Fig. 1. A Laue photograph ( $L$ ) is placed before a point source ( $O$ ), in such a way that the geometry of light source and film, while being projected, is exactly the same as the geometry of crystal and film while the latter was exposed. A light-ray going from  $O$  to a spot  $S$  on the film then corresponds to the X-ray pencil which caused this spot.

After passing the film, the light-ray is reflected at  $P$  by a curved mirror to a ground glass sphere, intersection  $Q$ . Upon this sphere, a distorted shadow projection of the film is formed. Now the distortion has to be such that the line  $OQ$  be perpendicular to the lattice-plane ( $V$ ) which diffracted the X-rays in the direction  $OP$ .

The film is shown as a cylinder in Fig. 1, but it will be clear that any film shape can be used, provided the

geometry of the film-holder of the optical apparatus is again identical with that of the X-ray camera.

It will be equally clear that the mirror shows rotational symmetry, with  $XO$ , which corresponds to the direction of the incident X-rays, as axis. The shape of the mirror-curve is not yet fixed by the condition imposed. The condition leaves one degree of freedom so that the axial plane contains an infinite number of curves

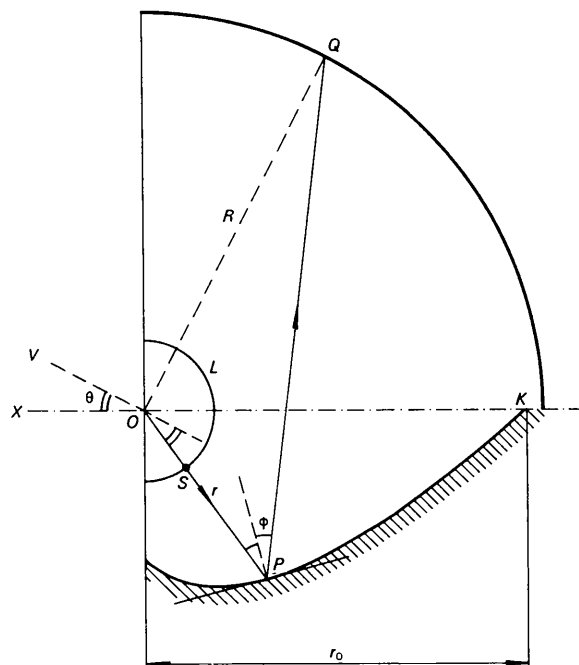


Fig. 1. Geometry of the instrument.