

extinction length. It means that for a given crystal size, the scattering curve in the case of normal polarization of the incident radiation is shifted towards a larger angle than in the case of parallel polarization. The scattering curve shift for both modes of polarization is equal only for  $\tau \ll 1$ .

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## On the Separation of the Unknown Parameters of the Problem of Crystal-Structure Analysis

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#### Abstract

The problem of crystal-structure analysis can be given a form which exhibits dual quasi-symmetry. The orthogonality of the Fourier waves and the non-interpenetration of the atoms play a complementary role; this holds not only formally but also with respect to the separation of the coordinates of the atoms and the phases of the structure factors. The remarkable fact that the Patterson function is described by a convolution in direct space, while Sayre's equation is a convolution in reciprocal space may be understood as a part of the symmetry.

#### Introduction

The kinds of experiments and theoretical procedures which are used for crystal-structure analysis are numerous.

In most cases of structure analysis, the experimental investigations of the crystal to be analysed are restricted to:

- the quantitative chemical analysis,
- the determination of the density,
- the measurement of the Bragg angles of a number of reflexions, sufficient for the calculation of the lattice parameters,

the measurement of the integral intensities of the reflexions with scattering vectors of length less than the reciprocal of the desired resolution of the scattering density function of the crystal.

From the results of these experiments the following properties of the crystal structure, unknown as a whole, can be deduced by routine application of the laws of physics (see textbooks of crystal-structure analysis):

the lattice constants  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  and the volume  $V$  of the unit cell,

the number  $p$  of the chemical elements contained in the specimen and the numbers  $q(\mu)$ ,  $\mu = 1, 2, \dots, p$ , of the atoms of different kinds in its elementary cell,

the moduli  $I^{1/2}(\mathbf{m})$  of the structure factors of the scattering density function  $\rho(\mathbf{x})$  of the crystal on a relative scale for all lattice points  $\mathbf{m}$  with  $|\mathbf{m}|^{-1}$  less than the desired resolution,

the form factors  $\hat{\rho}_\mu(\mathbf{m})$  and hence the scattering density function  $\rho_\mu(\mathbf{x})$ ,  $\mu = 1, 2, \dots, p$ , of the atoms of the structure.

The system of information just described is necessary and sufficient for the application of the routine methods of crystal-structure analysis, now in common use, e.g. *MULTAN* (Germain, Main & Woolfson, 1971). Besides its practical importance, it is also of special theoretical interest because the problem of crystal-structure analysis, based on this class of information, can be formulated in a dual quasi-symmetric way.

We have denoted the form factor of  $\rho_\mu(\mathbf{x})$  by  $\hat{\rho}_\mu(\mathbf{m})$  and, in order to get a concise notation, we will in general use the symbols  $\hat{\psi}$  or  $\mathcal{F}\psi$  for the Fourier transform of any function  $\psi$  in the forthcoming part of the paper:

$$\mathcal{F}\psi(\mathbf{h}) = \hat{\psi}(\mathbf{h}) = \int \psi(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) dV_{\mathbf{x}}. \quad (1)$$

Let us choose any elementary cell in the crystal and define a function  $\chi(\mathbf{x})$  equal to 1 if  $\mathbf{x}$  is inside this cell, and equal to 0 if  $\mathbf{x}$  lies outside. Then the Fourier transform  $\hat{\rho}_0(\mathbf{m})$  of

$$\rho_0 = \chi\rho \quad (2)$$

at the reciprocal-lattice point  $\mathbf{m}$  represents the structure factors of the crystal (Bricogne, 1974) and we have

$$\hat{\rho}_0(\mathbf{m}) = \sigma_{\mathbf{m}} I^{1/2}(\mathbf{m}), \quad (3)$$

where  $\sigma_{\mathbf{m}}$  is a scale factor in most cases independent of  $m$ :

$$\sigma_{\mathbf{m}} = s. \quad (A1)$$

The diffraction experiments are in general performed at room temperature, which means that the atoms of the crystal are subject to thermal motion. The form factor  $\hat{\rho}_\mu(\mathbf{m})$  of the  $\mu$ th kind of atom must therefore be corrected by a temperature factor  $\hat{\tau}_{\mu\nu}(\mathbf{m})$  to give the effective form factor of the  $\nu$ th atom of the  $\mu$ th kind in the elementary cell:

$$\hat{\rho}_{\mu\nu}(\mathbf{m}) = \hat{\tau}_{\mu\nu}(\mathbf{m}) \rho_\mu(\mathbf{m}). \quad (4)$$

The temperature factor  $\hat{\tau}_{\mu\nu}(\mathbf{m})$  can be described to a good approximation by

$$\hat{\tau}_{\mu\nu}(\mathbf{m}) = \exp(-\mathbf{m} \cdot \mathbf{B}_{\mu\nu} \mathbf{m}), \quad (5)$$

where  $\mathbf{B}_{\mu\nu}$  is a positive-definite symmetrical tensor (Cochran, 1954; Rollett & Davies, 1955; Waser, 1955).

Denoting by  $\tau_{\mu\nu} * \rho_\mu$  the convolution of  $\tau_{\mu\nu}$  and  $\rho_\mu$ ,

$$\tau_{\mu\nu} * \rho_\mu(\mathbf{x}) = \int \tau_{\mu\nu}(\mathbf{y}) \rho_\mu(\mathbf{x} - \mathbf{y}) dV_{\mathbf{y}}, \quad (6)$$

the inverse Fourier transform of (4) can be written:

$$\rho_{\mu\nu}(\mathbf{x}) = \tau_{\mu\nu} * \rho_\mu(\mathbf{x}), \quad (7)$$

and from (5) we deduce

$$\tau_{\mu\nu}(\mathbf{x}) = \pi^{3/2} |\mathbf{B}_{\mu\nu}|^{-1/2} \exp(-\pi^2 \mathbf{x} \cdot \mathbf{B}_{\mu\nu}^{-1} \mathbf{x}). \quad (A2)$$

We may describe the direct lattice with the help of Dirac's  $\delta$ -function by

$$\xi(\mathbf{x}) = \sum_{m_1, m_2, m_3} \delta(\mathbf{x} - m_1 \mathbf{a}_1 - m_2 \mathbf{a}_2 - m_3 \mathbf{a}_3), \quad (8)$$

taking the summation over all integers  $m_1, m_2, m_3$ . We then have

$$\rho = \rho_0 * \xi. \quad (9)$$

The scattering density function of the crystal can now be written in two different ways: first as a Fourier series with unknown phases  $\varphi_{\mathbf{m}}$

$$\rho(\mathbf{x}) = 1/V \sum_{\mathbf{m}} \sigma_{\mathbf{m}} I^{1/2}(\mathbf{m}) \exp[2\pi i(\varphi_{\mathbf{m}} - \mathbf{m} \cdot \mathbf{x})] \quad (A3)$$

and secondly as a superposition of the scattering density function of the atoms with unknown positions  $\mathbf{x}_{\mu\nu}$

$$\rho(\mathbf{x}) = \sum_{\mu=1}^p \sum_{\nu=1}^{q(\mu)} \tau_{\mu\nu} * \rho_\mu * \xi(\mathbf{x} - \mathbf{x}_{\mu\nu}). \quad (A4)$$

Equations (A3) and (A4) must be valid for any value of  $\mathbf{x}$ . Hence they represent together with (A1) and (A2) a three-dimensional continuous system of determining equations for the unknown parameters – the coordinates  $\mathbf{x}_{\mu\nu}$  and temperature tensors  $\mathbf{B}_{\mu\nu}$  of the atoms and the phases  $\varphi_{\mathbf{m}}$  and the scale factor  $s$  of the Fourier coefficients – which determine the scattering density function  $\rho$  of the structure. All other quantities appearing in the equations of type (A) can be derived from the experiments mentioned at the beginning of the paper.

It is important to add to these equations a further restriction (Sayre, 1952; Woolfson, 1958a, b; Rothbauer, 1975). To a good approximation the atoms in a crystal structure do not inter-penetrate, therefore

$$\begin{aligned} & [\tau_{\mu\nu} * \rho_\mu * \xi(\mathbf{x} - \mathbf{x}_{\mu\nu})] \cdot [\bar{\tau}_{jk} * \bar{\rho}_j * \bar{\xi}(\mathbf{x} - \mathbf{x}_{jk})] \\ & = \delta_{\mu\nu, jk} |\tau_{\mu\nu} * \rho_\mu * \xi(\mathbf{x} - \mathbf{x}_{\mu\nu})|^2 \end{aligned} \quad (A5)$$

is valid, where

$$\begin{aligned} \delta_{\mu\nu, jk} &= 1 \quad \text{if } (\mu\nu) = (jk) \\ &= 0 \quad \text{if } (\mu\nu) \neq (jk) \end{aligned}$$

and  $\bar{\tau}$  is the complex conjugate of  $\tau$  etc. It is clear that with the assumption (A2) for the temperature factors, the condition (A5) cannot exactly be fulfilled.

No procedure is known up to now, by which all the solutions of the system of equations (A1) to (A5) for a given set of experimental derived quantities:  $I^{1/2}(\mathbf{m})$ ,  $\rho_\mu(\mathbf{x})$ ,  $p$  and  $q(\mu)$ , can be found in any case in the range of natural errors.

The problem of crystal-structure analysis as described in the equations (A), which we will call the 'normal problem', appears to be without inner symmetries. The non-interpenetration condition (A5), especially, seems to be of a somewhat accidental character without any obvious relation to the other equations. This is actually not the case. It was shown by Main (1974) that the non-interpenetration of the

atoms may be regarded as an orthogonality relation and, in fact, it turns out that (A5) plays a kind of complementary role to the orthogonality of the Fourier waves.

### Symmetrical formulation of the problem

We introduce the functions

$$\zeta_{\mathbf{m}}(\mathbf{x}) = \exp(2\pi i\varphi_{\mathbf{m}}), \quad (B1a)$$

$$\eta_{jk}(\mathbf{x}) = \delta(\mathbf{x} - \mathbf{x}_{jk}), \quad (B1b)$$

$$\alpha_{\mathbf{m}}(\mathbf{x}) = I^{1/2}(\mathbf{m}) \exp(-2\pi i\mathbf{m} \cdot \mathbf{x})/V, \quad (B2a)$$

$$\beta_j(\mathbf{x}) = \rho_j * \zeta(\mathbf{x}), \quad (B2b)$$

and get from (A3) and (A4)

$$\rho = \sum_{\mathbf{m}} \alpha_{\mathbf{m}} \cdot \sigma_{\mathbf{m}} \cdot \zeta_{\mathbf{m}}, \quad (B3a)$$

$$\rho = \sum_{jk} \beta_j * \tau_{jk} * \eta_{jk}, \quad (B3b)$$

respectively. From (B2a) we deduce the integral orthogonality relation

$$(\chi \cdot \alpha_{\mathbf{m}} \cdot \sigma_{\mathbf{m}} \cdot \zeta_{\mathbf{m}}) * \overline{(\alpha_{\mathbf{n}} \cdot \sigma_{\mathbf{n}} \cdot \zeta_{\mathbf{n}})} = \delta_{\mathbf{m}, \mathbf{n}} \overline{I\alpha_{\mathbf{m}}\sigma_{\mathbf{m}}|\alpha_{\mathbf{m}}|\sigma_{\mathbf{m}}V}, \quad (B4a)$$

where the inversion operator I is defined by  $I\psi(\mathbf{x}) = \psi(-\mathbf{x})$ , for any function  $\psi$ . From (A5) we have the corresponding local orthogonality

$$(\beta_j * \tau_{jk} * \eta_{jk}) \cdot \overline{(\beta_{\mu} * \tau_{\mu\nu} * \eta_{\mu\nu})} = \delta_{jk, \mu\nu} |\beta_{jk} * \tau_{jk}|^2 * \eta_{jk}. \quad (B4b)$$

As (B4a) is not only valid at the origin of the direct lattice, it represents in fact a generalized orthogonality of the Fourier waves. In order to complete the series (B1) to (B4) we add the approximations (A1) and (A2) for the scale and temperature factors

$$\sigma_{\mathbf{m}} = s, \quad (B5a)$$

$$\tau_{jk}(\mathbf{x}) = \pi^{3/2} |\mathbf{B}_{jk}|^{-1/2} \exp(-\pi^2 \mathbf{x} \cdot \mathbf{B}_{jk}^{-1} \mathbf{x}). \quad (B5b)$$

The 'normal problem' consists of a wave (B3a) and a particle (B3b) representation of the scattering density function of the crystal. For the waves there exists an integral (B4a) and for the particles a local (B4b) orthogonality relation. Known from experiments are the waves  $\alpha_{\mathbf{m}}$  and the particles  $\beta_j$ . Unknown are their positions, described by the shift functions  $\zeta_{\mathbf{m}}$  and  $\eta_{jk}$  — or the  $\varphi_{\mathbf{m}}$  and  $\mathbf{x}_{jk}$ , respectively — and the scale and temperature factors  $\sigma_{\mathbf{m}}$  and  $\tau_{jk}$ , described by  $s$  and the tensors  $\mathbf{B}_{jk}$ . The orientation of the waves is given; the orientation of the particles is irrelevant, because they are assumed to be spherically symmetric.

If one takes the Fourier transform of the system (B), the equations of type (a) and (b) interchange their character to a certain extent because the multiplications become convolutions and *vice versa*. Since for any  $\psi$

$$\overline{(\mathcal{F}\psi)} = I\mathcal{F}\bar{\psi},$$

in particular, the integral orthogonality of the waves (B4a) becomes a local orthogonality of type (B4b) and the local orthogonality of the atoms (B4b) becomes an integral orthogonality of type (B4a). However, the symmetry is not perfect: e.g. on the right hand side of (B4b) appears the shift function  $\eta_{jk}$  while the shift function  $\zeta_{\mathbf{m}}$  does not appear on the right hand side of (B4a). This is one of the reasons why the derivation of the structure factor equations and the Patterson (1934) function run along different lines.

The unknown quantities of the normal problem may be divided into three parts:  $(\mathbf{x}_{jk}, \mathbf{B}_{jk})$ ,  $(\varphi_{\mathbf{m}}, s)$  and  $\rho$ . It is plain that if one of these has been derived the rest of the solution may easily be found.

By equating (A3) and (A4) or (B3a) and (B3b), respectively,  $\rho$  can immediately be eliminated from the determinantal equations. We will now proceed to separate the following three classes of parameters:  $(\mathbf{x}_{jk}, \mathbf{B}_{jk}, s)$ ,  $(\varphi_{\mathbf{m}}, s, \mathbf{B}_{jk})$  and  $(\mathbf{B}_{jk}, s)$  from the normal problem. It is convenient to start with a short discussion of the locally defined mappings of density functions, which form an important tool for this purpose.

### Local mappings of density functions

The directional derivative of the scattering density function

$$\psi(\mathbf{x}) = \int \hat{\psi}(\mathbf{m}) \exp(-2\pi i\mathbf{m} \cdot \mathbf{x}) dV_{\mathbf{m}}$$

along an arbitrary vector  $\mathbf{v}$  is

$$d\psi(\mathbf{x})/d\mathbf{v} = \int (-2\pi i\mathbf{m} \cdot \mathbf{v}) \hat{\psi}(\mathbf{m}) \exp(-2\pi i\mathbf{m} \cdot \mathbf{x}) dV_{\mathbf{m}}.$$

If D is a differential operator representing a linear combination of directional derivatives of different order along different directions  $\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3, \dots$ , we have

$$D * \rho(\mathbf{x}) = \int \hat{D}(\mathbf{m}) \psi(\mathbf{m}) \exp(-2\pi i\mathbf{m} \cdot \mathbf{x}) dV_{\mathbf{m}},$$

where  $\hat{D}(\mathbf{m})$  is a polynomial of the scalar products,  $\mathbf{m} \cdot \mathbf{v}_1, \mathbf{m} \cdot \mathbf{v}_2, \mathbf{m} \cdot \mathbf{v}_3, \dots$ , and hence a polynomial of the coefficients,  $m_1, m_2, m_3$ , of  $\mathbf{m}$ . Conversely, any polynomial of  $m_1, m_2, m_3$  represents a differential operator D.

The differential operator D applied to  $\psi$  may be regarded as the limit of the convolutions of a certain sequence of proper functions with  $\psi$ . We write therefore  $D * \psi$  rather than  $D\psi$  and think of  $\hat{D}(\mathbf{m})$  as the Fourier transform of  $D(\mathbf{x})$ . The Fourier transform of  $D * \psi$  is then given by

$$\mathcal{F}(D * \psi)(\mathbf{h}) = \hat{D}\hat{\psi}(\mathbf{h}).$$

The convolution of the wave  $\alpha_{\mathbf{m}}$  with any function C is equal to the product of the Fourier transform of C and  $\alpha_{\mathbf{m}}$ :

$$C * \alpha_{\mathbf{m}} = \hat{C}(\mathbf{m})\alpha_{\mathbf{m}}. \quad (10a)$$

For the particles  $\beta_{jk}$  there exists a similar equation: as any function  $D * \psi$  cannot be more extensive than  $\psi$ , there are functions  $D'_{jk}$  such that

$$D * \beta_j * \tau_{jk} = D'_{jk}(\beta_j * \tau_{jk}), \quad j = 1, 2, \dots, p, \quad (10b)$$

$$k = 1, 2, \dots, q(j).$$

Equation (10b) holds for any  $D$ , proper function or operator, with

$$\text{support}(D * \beta_j * \tau_{jk}) \subset \text{support}(\beta_j * \tau_{jk}) \quad j = 1, 2, \dots, p,$$

$$k = 1, 2, \dots, q(j).$$

Therefore, special classes of atoms  $\beta_j * \tau_{jk}$  may also allow proper functions  $D$  to be inserted into (10b). For this reason one can use (10b) to give a more general definition of the  $D$ 's for certain crystals.

We deduce from (B4a)

$$(C_1 * \alpha_m \sigma_m \zeta_m \chi) * \overline{(IC_2 * \alpha_n \sigma_n \zeta_n)}$$

$$= \delta_{m,n} C_1 * \overline{IC_2 * \alpha_m \sigma_m | \alpha_m | \sigma_m} V \quad (11a)$$

and from (B4b)

$$(D_1 * \beta_j * \tau_{jk} * \eta_{jk}) \cdot \overline{(D_2 * \beta_\mu * \tau_{\mu\nu} * \eta_{\mu\nu})}$$

$$= \delta_{jk, \mu\nu} [(D_1 * \beta_j * \tau_{jk}) \cdot \overline{(D_2 * \beta_j * \tau_{jk})}] * \eta_{jk}, \quad (11b)$$

where  $C_1, C_2$  are arbitrary and  $D_1, D_2$  are defined by (10b).

Let now  $\gamma$  be any scalar function with one or more arguments, then

$$\Gamma(\psi) = \gamma(D_1 * \psi, D_2 * \psi, \dots) - \gamma(0, 0, \dots) \quad (12)$$

describes a mapping of density functions  $\psi$ , which has the property

$$\Gamma(\psi * \eta) = \Gamma(\psi) * \eta, \quad \text{if } \eta(\mathbf{x}) = \delta(\mathbf{x} - \mathbf{x}_1) \quad (13)$$

for arbitrary  $D_1, D_2, \dots$  and any vector  $\mathbf{x}_1$ .

If  $D_1, D_2, \dots$  are defined by (10b), one finds, because of the non-interpenetration relation (11b) and because of (13),

$$\Gamma\left(\sum_{jk} \beta_j * \tau_{jk} * \eta_{jk}\right) = \sum_{jk} \Gamma(\beta_j * \tau_{jk}) * \eta_{jk}. \quad (14)$$

### Separation of the coordinates of the atoms, the temperature and scale factors

We take the convolution of (B3a) and (B3b) with  $C_1$ , eliminate  $\rho$  and get

$$\sum_m C_1 * \alpha_m \sigma_m \zeta_m = \sum_{jk} C_1 * \beta_j * \tau_{jk} * \eta_{jk} \quad (15)$$

and similarly

$$\sum_m IC_2 * \alpha_m \sigma_m \zeta_m = \sum_{jk} IC_2 * \beta_j * \tau_{jk} * \eta_{jk}. \quad (16)$$

We multiply (15) with  $\chi$ , take the complex conjugate of (16), convolute the right and left hand sides and find with the integral orthogonality (11a) the equation:

$$\sum_m C_1 * \overline{IC_2 * \alpha_m \sigma_m | \alpha_m | \sigma_m} V$$

$$= \sum_{jk\mu\nu} [\chi(C_1 * \beta_j * \tau_{jk} * \eta_{jk})] * \overline{IC_2 * \beta_\mu * \tau_{\mu\nu} * \eta_{\mu\nu}}, \quad (17)$$

which does not contain the unknown phases. If  $C_1$  and  $C_2$  are chosen to be Dirac's  $\delta$  function, (17) is nothing but the Patterson function (Patterson, 1934).

The Fourier transform of (17) gives the intensity equations used for least-squares refinement of the atom coordinates and the temperature and scale factors in the final stages of a crystal-structure analysis.

We notice that the phases have been eliminated with the help of the integral orthogonality. In the next chapter it will be shown that the atomic coordinates can be eliminated with the help of the local orthogonalities.

### Separation of the phases, the temperature and scale factors

Eliminating  $\rho$  from (B3), we find

$$\sum_m \alpha_m \sigma_m \zeta_m = \sum_{jk} \beta_j * \tau_{jk} * \eta_{jk}, \quad (18)$$

applying the mapping  $\Gamma$  on both sides of (18), we deduce with the help of (14), which is a consequence of the local orthogonality (B4b):

$$\Gamma\left(\sum_m \alpha_m \sigma_m \zeta_m\right) = \sum_{jk} \Gamma(\beta_j * \tau_{jk}) * \eta_{jk}. \quad (19)$$

Because of (2) and (9) the identities

$$\alpha_m = (\chi^{\alpha_m}) * \xi$$

and

$$\beta_j * \tau_{jk} = [\chi(\beta_j * \tau_{jk})] * \xi$$

are valid. Inserting the two expressions into (19) we get by application of (13)

$$\Gamma\left(\chi \sum_m \alpha_m \sigma_m \zeta_m\right) * \xi = \sum_{jk} \Gamma[\chi(\beta_j * \tau_{jk})] * \eta_{jk} * \xi.$$

The Fourier transform of this equation is

$$\hat{F}\left(\chi \sum_{\mathbf{m}} \alpha_{\mathbf{m}} \sigma_{\mathbf{m}} \zeta_{\mathbf{m}}\right) \cdot \hat{\xi} = \sum_{jk} \hat{F}[\chi(\beta_j * \tau_{jk})] \cdot \hat{\eta}_{jk} \cdot \hat{\xi}, \quad (20)$$

the Fourier transform of (8) becomes

$$\hat{\xi}(\mathbf{h}) = 1/V \sum_{m_1, m_2, m_3} \delta(\mathbf{h} - m_1 \mathbf{a}'_1 - m_2 \mathbf{a}'_2 - m_3 \mathbf{a}'_3),$$

where  $m_1, m_2, m_3$  run over all integers and  $\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3$  are the reciprocal basis vectors

$$\mathbf{a}_j \cdot \mathbf{a}'_k = \delta_{j,k}, \quad j, k = 1, 2, 3,$$

and that of  $\eta_{jk}$  ( $B1b$ ) is

$$\hat{\eta}_{jk}(\mathbf{h}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_{jk}). \quad (21)$$

By integration of (20) over the neighbourhood of the reciprocal-lattice point  $\mathbf{h}'$  one derives

$$\hat{F}\left(\chi \sum_{\mathbf{m}} \alpha_{\mathbf{m}} \sigma_{\mathbf{m}} \zeta_{\mathbf{m}}\right)(\mathbf{h}') = \sum_{jk} \hat{F}[\chi(\beta_j * \tau_{jk})](\mathbf{h}') \cdot \hat{\eta}_{jk}(\mathbf{h}'). \quad (22)$$

We now choose  $n$  arbitrary local mappings  $\Gamma_{\mu}$ ,  $\mu = 1, 2, \dots, n$ , and introduce the  $n \times [q(1) + q(2) + \dots + q(p)]$  matrix  $\hat{\beta}$ , which contains in the  $\mu$ th row the elements  $\Gamma_{\mu}[\chi(\beta_j * \tau_{jk})](\mathbf{h}')$  in the lexicographic order of  $j$  and  $k$ ; this means the element  $\hat{F}_{\mu}[\chi(\beta_j * \tau_{jk})]$  in the  $[q(1) + q(2) + \dots + q(j-1) + k]$ th column. The rank of the matrix  $\hat{\beta}$  is less than or equal to the number of atoms,  $q(1) + q(2) + \dots + q(p)$ , in the elementary cell, because this is equal to the number of columns of  $\hat{\beta}$ . For the purpose of crystal-structure analysis it will be sufficient to assume in most cases that the temperature factors of the atoms of one kind are all the same, so that the rank  $r$  of  $\hat{\beta}$  does not exceed  $p$ . Special cases with  $r$  less than  $p$  have been described (Rothbauer, 1975, 1977).

Let us now build up a matrix  $\hat{\beta}$  by successively adding new rows, representing generalized local mappings  $\Gamma_{\mu}$ , until the number of rows  $n$  is equal to  $r + 1$ . Then numbers  $b_1, b_2, \dots, b_n$  will exist such that

$$0 = \sum_{j=1}^n b_j (\hat{\beta})_{jk}, \quad k = 1, 2, \dots, \sum_{v=1}^p q(v), \quad (23a)$$

and therefore because of (22)

$$0 = \sum_{j=1}^n b_j \hat{F}_j \left[ \chi \left( \sum_{\mathbf{m}} \alpha_{\mathbf{m}} \sigma_{\mathbf{m}} \zeta_{\mathbf{m}} \right) \right](\mathbf{h}'). \quad (23b)$$

In (23) the coordinates  $\mathbf{x}_{jk}$  of the atoms, contained in the shift functions  $\eta_{jk}$ , are eliminated. As  $n$  is chosen to be equal to  $r + 1$ , the numbers  $b_1, b_2, \dots, b_{n-1}$ , are uniquely determined by (23a), if we require  $b_n = 1$ .

The elimination procedure was introduced by Sayre (1952) and more generally by Woolfson (1958a, b),

using the mappings  $\Gamma_{\mu}(\rho) = \rho^{\mu}$ ,  $\mu = 1, 2, \dots$ ; for  $p = 1$  and  $\Gamma_1(\rho) = \rho$ ,  $\Gamma_2(\rho) = \rho^2$ , (23) represents Sayre's equation, for  $p = r = n - 1$  and  $\Gamma_{\mu}(\rho) = \rho^{\mu}$ ,  $\mu = 1, 2, \dots, n$ , (21) becomes Woolfson's equation and  $\Gamma_{\mu}(\rho) = (D_{1\mu} * \rho)(D_{2\mu} * \rho)$  generates the convolutional structure factor equations (Rothbauer, 1975, 1976, 1977).

We may also write (23) in the form of a determinant. Let us choose  $r$  linear independent columns out of  $\hat{\beta}$  and add the column  $\hat{F}_{\mu}(\chi \sum_{\mathbf{m}} \alpha_{\mathbf{m}} \sigma_{\mathbf{m}} \zeta_{\mathbf{m}})$ ,  $\mu = 1, 2, \dots, n$ , to get an  $n \times n$  matrix  $\mathbf{B}$ . This matrix is singular because of (22) and the structure factor equations appear in the simple form

$$|\mathbf{B}| = 0. \quad (24)$$

### Separation of the scale and temperature factors

Scale and temperature factors can be separated out of the 'normal problem' by inserting the local mapping

$$\Gamma_{\mu}(\rho) = (D_{\mu 1} * \rho) \overline{(D_{\mu 2} * \rho)} \quad (25)$$

into (22), which is a consequence of (B4b), at reciprocal-lattice point  $\mathbf{h}' = \mathbf{0}$ . The left hand side of (22) then becomes

$$\begin{aligned} & \sum_{\mathbf{m}, \mathbf{n}} \int \chi(D_{\mu 1} * \alpha_{\mathbf{m}} \sigma_{\mathbf{m}} \zeta_{\mathbf{m}}) \overline{(D_{\mu 2} * \alpha_{\mathbf{n}} \sigma_{\mathbf{n}} \zeta_{\mathbf{n}})} dV \\ & = \sum_{\mathbf{m}, \mathbf{n}} [\chi(D_{\mu 1} * \alpha_{\mathbf{m}} \sigma_{\mathbf{m}} \zeta_{\mathbf{m}})] * \overline{(ID_{\mu 2} * \alpha_{\mathbf{n}} \sigma_{\mathbf{n}} \zeta_{\mathbf{n}})}(\mathbf{0}). \end{aligned}$$

The phases  $\varphi_{\mathbf{m}}$ , contained in the shift functions  $\zeta_{\mathbf{m}}$ , disappear, if we apply (11a) to the above expression. We derive

$$\sum_{\mathbf{m}} D_{\mu 1} * \overline{ID_{\mu 2} * \alpha_{\mathbf{m}} \sigma_{\mathbf{m}} | \alpha_{\mathbf{m}} | \sigma_{\mathbf{m}} V(\mathbf{0})}.$$

Since because of (21)

$$\hat{\eta}_{jk}(\mathbf{0}) = 1,$$

we find for the right hand side of (22), if  $\Gamma_{\mu}$  is given by (25), at the origin of the reciprocal lattice

$$\begin{aligned} & \sum_{jk} \int \chi(D_{\mu 1} * \beta_j * \tau_{jk}) \overline{(D_{\mu 2} * \beta_j * \tau_{jk})} dV \\ & = \sum_{jk} \hat{\chi} * (\hat{D}_{\mu 1} \hat{\beta}_j \hat{\tau}_{jk}) * \overline{[I(\hat{D}_{\mu 2} \hat{\beta}_j \hat{\tau}_{jk})]}(\mathbf{0}), \end{aligned}$$

an expression which does not depend on the coordinates of the atoms. Hence the following system of equations,

$$\begin{aligned} & \sum_{\mathbf{m}} D_{\mu 1} * \overline{I(D_{\mu 2} * \alpha_{\mathbf{m}} \sigma_{\mathbf{m}}) | \alpha_{\mathbf{m}} | \sigma_{\mathbf{m}} V(\mathbf{0})} \\ & = \sum_{jk} \hat{\chi} * (\hat{D}_{\mu 1} \hat{\beta}_j \hat{\tau}_{jk}) * \overline{[I(\hat{D}_{\mu 2} \hat{\beta}_j \hat{\tau}_{jk})]}(\mathbf{0}), \quad (26) \end{aligned}$$

labelled by the  $D_{\mu 1}$ ,  $D_{\mu 2}$ ,  $\mu = 1, 2, \dots$ , may be used for the determination of the scale and temperature factors (Rothbauer, 1978). We note that for the derivation of (26) both the local and integral orthogonalities have been used.

### Conclusions

A mathematical formulation, (A) or (B), of the problem of crystal-structure analysis has been given on the basis of simple accessible experimental information.

It has been shown that the Patterson function is derived if one eliminates the phases of the structure factors from the equations of the 'normal problem', and that Sayre's, Woolfson's and the convolutional structure factor equations are the result if one eliminates the coordinates of the atoms. In addition, a method has been given to eliminate both the phases of the structure factors and the coordinates of the atoms.

The importance of the orthogonality relations for the elimination processes has been stressed and it has become intelligible why the Patterson function is described by a convolution in direct space and the simplest structure factor equations are convolutions in reciprocal space.

If  $\mathbf{x}_{jk}$ ,  $\mathbf{B}_{jk}$ ,  $\varphi_{\mathbf{m}}$ ,  $s$ , represents a solution of (A) or (B),  $\mathbf{x}_{jk} - \mathbf{u}$ ,  $\mathbf{B}_{jk}$ ,  $\varphi_{\mathbf{m}} - \mathbf{u} \cdot \mathbf{m}$ ,  $s$ , for arbitrary  $\mathbf{u}$ , is also a solution describing the same structure, with the origin shifted by  $\mathbf{u}$ . There may also occur non-trivial ambiguities of the solution. From the theory of homometric sets (Pauling & Shappell, 1930) – see for example Hosemann & Bagchi (1954) and Bullough (1961, 1964) – it becomes obvious that under certain conditions several non-congruent structures may satisfy the same system of determinantal equations (A) or (B).

In practice, 'solution of the normal problem' means solution in the range of natural errors. Beside the usual errors, resulting from measurement and the application of approximate physical models, we are here concerned with termination effects, (A3) or (B3a), because only a finite number of integral intensities of Bragg reflexions can be collected. As far as we have described the problem in this paper, we did not need to discuss the influence of all the approximations and errors, which characterize the real situation. However, any method of crystal-structure analysis must somehow take into account that an exact solution cannot exist.

The 'normal problem' formulated in (A) or (B) is overdetermined in the sense that many more intensities are known than atomic coordinates and that temperature and scale factors are to be calculated. It is underdetermined in the sense that there might exist multiple, e.g. homometric, solutions.

No method is known up to now by which the solutions of (A) or (B) can be found in any case; and we have not even a criterion to prove that a structure, which has been found to satisfy (A) or (B), is the only

one with this property or not. The latter seems to embarrass the theoreticians more than the practical structure analyst.

Equation (17) forms the basis of the Patterson methods of structure analysis and (23) is used in the form of Sayre's equation for phase extension (Sayre, 1972, 1974). Scale and temperature factors may be derived with the help of (26).

The powerful computing methods of crystal-structure analysis now in common use have been developed by the introduction of additional statistical assumptions, not contained in the propositions of the 'normal problem'. Further information, not contained in the formulation of (A) and (B), but frequently used for structure analysis, involves the knowledge of whole molecules (Karle, 1976; Main, 1976), also sets of diffraction data gained by molecular replacement and non-crystallographic symmetries (Crowther, 1969; Main, 1967; Rossmann, 1972; Bricogne, 1974).

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