

Phase Determination and Structure Refinement by Density and Shift Functions

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Any crystal structure may be described in terms of a sublattice of points, each of which represents a certain fraction of the electron density. Multiplying this sublattice by a density function $f(x)$ and applying a shift function $s(x)$, which brings the atoms into the right positions, the correct crystal structure can be given in many different ways. It is shown that the shift function $s(x)$ yields phase relations between the structure factors $F(h)$, which may be evaluated directly, if the coefficients of the Fourier representation of $s(x)$ converge rapidly. This behaviour is demonstrated for the case of a one-dimensional acentric model structure consisting of 50 atoms. Complete information on the structure may be obtained by routine methods with the aid of 5 given phases of the structure factor. This procedure may also be applied to three-dimensional structures, if the corresponding computer programs are available.

1. Introduction

The existence of satellites in any diffraction pattern indicates a simple lattice superstructure. This superstructure may be described in terms of the coefficients of the corresponding Fourier-representation of density or shift functions.

In the case of X-ray diffraction examples with one or two Fourier coefficients have been discussed by Dehlinger (1938), Preston (1938), Kochendörfer (1939), Daniel & Lipson (1943, 1944), Hargreaves (1951) and others. A more general treatment of this problem has been published by Korekawa & Jagodzinski (1967) for the case of plagioclases of various compositions, where complex behaviour of satellites is observed. A full account of the mathematical background to their method has been given by Korekawa (1967). It can be shown that phase relations between density and shift functions may be derived directly from the diffraction pattern.

Any crystal structure may be described in this way, if the restriction of convergent Fourier coefficients of density and shift functions is removed. In this case the diffraction pattern cannot be described in terms of 'main' reflexions and 'satellites', as each observed Bragg-reflexion may be attributed to either group. It is possible to judge from the diffraction pattern whether a rapidly convergent set of Fourier coefficients of density or displacement can be found, but this is only true in very special cases which will not be considered here. We shall introduce complete chemical information in order to obtain a unique description of the structure; this is necessary because there are a very large number of possible pseudo-homometric structures which can only be excluded by chemical considerations.

It will be shown that this kind of treatment of the diffraction pattern yields phase relations between structure factors, and more efficient refinement procedures.

2. Qualitative description of the new method

Let us discuss our method in terms of a one-dimensional model. We start with a sublattice of M equidistant points, each of which represents one electron or a fraction (or multiple) of it. The number of electrons n_M to be represented by one point is given by

$$n_M = N/M \quad (1)$$

where N is the total number of electrons in the unit cell [Fig. 1(b)]. There appear to be two possible simple representations of the structure:

(1) By multiplying the various points of the sublattice with a normalized density function $f^M(x)$ according to Fig. 1(a).

(2) By applying the shift function $s^M(x)$, which displaces the lattice points corresponding to the value of $s^M(x)$, in the positive or negative direction, according to Fig. 1(c).

The result of this operation is shown in Fig. 1(d). It may easily be seen that both representations should result in the same structure for $M \rightarrow \infty$, although their structure factor is described in completely different ways, as will be shown in the mathematical § 3 of this paper.

The first description of the structure corresponds exactly to the usual Fourier-representation of the electron density with the integrated electron density normalized to unity. Therefore the Fourier coefficients are – neglecting the constant – exactly the same. The second representation is completely different, neither the amount nor the phase of the Fourier coefficients of $s^M(x)$ being known, but whatever the function $s^M(x)$ may be, the electron density remains everywhere positive. Some correlation exists between the structure factors $F(h)$ and the Fourier coefficients of the Fourier-representation of $s^M(x)$, but this will not be discussed here.

The usual procedure of solving a complicated struc-

ture is stepwise by restricting the 'resolution power' and we will describe a similar method in terms of our model for the case of point atoms (the use of 'unitary' struc-

ture factors will be assumed). Fig. 1(e) shows a sublattice consisting of 16 points, which can be used for the construction of the point model of the same structure

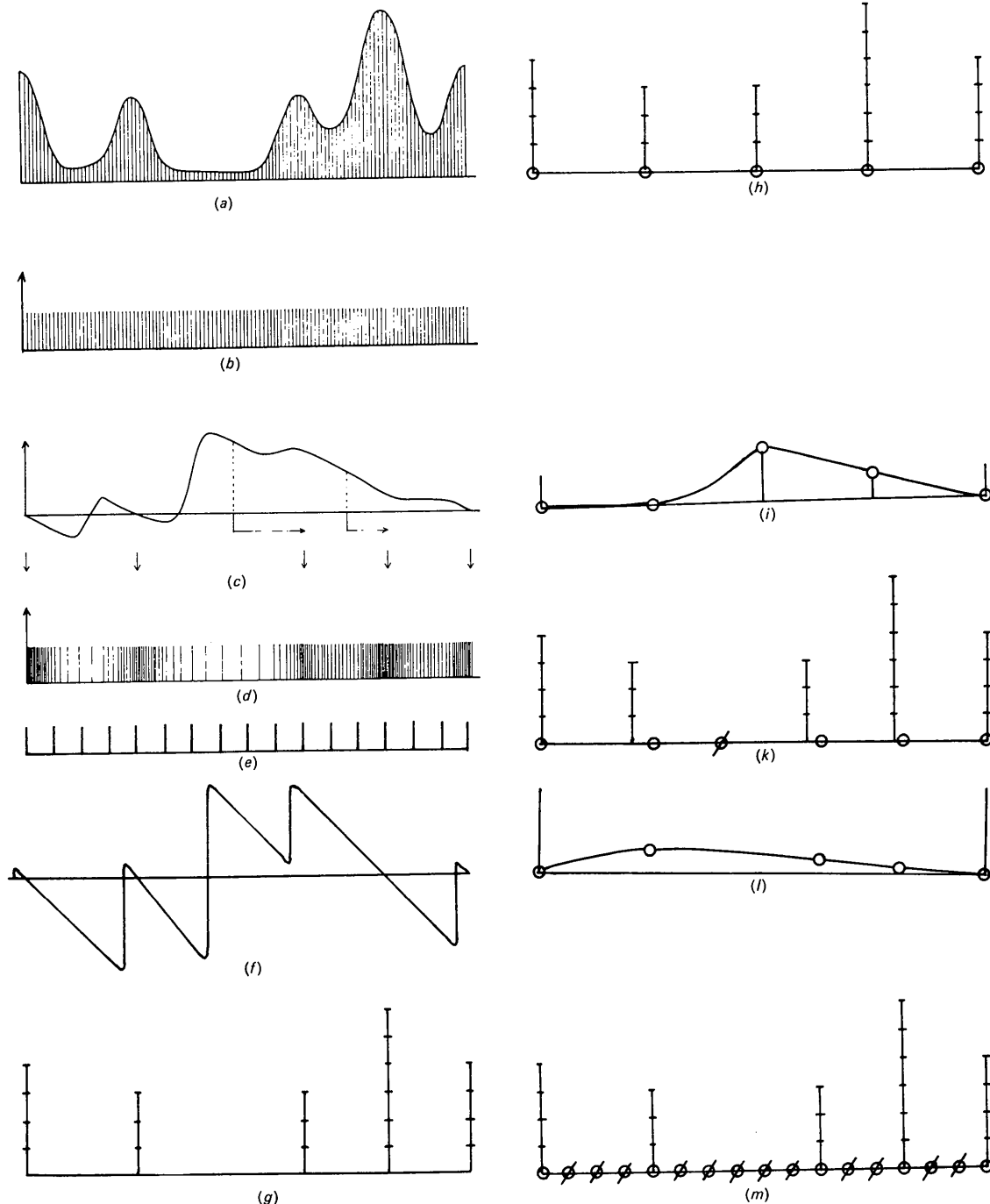


Fig. 1. Possible different representations of the same structure. (a) A sublattice of M equidistant points is multiplied by the normalized density function. (b-d) The points (b), which represent a certain number of electrons or fraction of it, are displaced (c) by a shift function $s(x)$; the arrows indicate the displacement and the positions of the maxima respectively (d). (e-g) Approximate description by a sublattice of 16 points (e); (f) $s(x)$ brings the points to the atom positions [cf. (a)]. (h-i) The weighted sublattice (h) yields the description of the structure given in (g) by a more rapidly convergent set of Fourier coefficients of $s(x)$, shown in (i). (k-l) A sublattice of five points (k) gives another possible representation of the structure with a slightly different density function and a still more rapidly convergent set of Fourier coefficients (l). (m) Representation with the aid of a density function, for the case of rational atomic coordinates only (12 of the 16 points have to be cancelled by the density function in this particular case).

with four atoms. This may be done by taking into account the chemistry of the compound. The corresponding shift function $s^{16}(x)$, which has to be introduced to bring atoms of the required height into the correct positions [Fig. 1(g)], is shown in Fig. 1(f). It should be pointed out that the function $s^M(x)$, given in Fig. 1(c), is very similar to the one shown in Fig. 1(f).

The convergence of the Fourier coefficients S_n^M attributed to $s^M(x)$ is proportional to $1/n$. This result may be obtained by assuming abrupt jumps of $s^M(x)$ between the straight regions representing the atoms and their 'heights'. However, as $s^M(x)$ has only to be defined at the sublattice positions, a different function with more rapidly convergent Fourier coefficients, may be chosen. The use of incorrect shift functions will generally lead to a 'chemically different' structure, as the number of atoms and their heights are not yet fixed; they depend on the choice of the shift function.

A better solution should be found if complete chemical information is introduced for the sublattice itself. This may be done by choosing a sublattice with four atoms, the points of which are multiplied by a density function, which has only to be defined at the sublattice positions; thus the function $f^4(x)$ with the most rapidly convergent set of Fourier coefficients may be chosen. The number of ways of distributing the four atoms, two of which are alike in our example, on the four positions, leads formally to $4!/2! = 12$ models, which are mostly equivalent by translation or centrosymmetry. Thus only two essentially different structures remain, one of which has only unlike atoms as neighbours, and the other has not. If the 'chemistry' of our compound is known, only one of the two models in question is probable, and the 'model' structure is already found. Since the maximum shift of any atom is restricted by the sum of the minimum separation d of the atoms $+a-d$ (a = lattice constant), a very rapid convergent function $s^4(x)$ may be expected for the solution of the correct structure, as demonstrated in Fig. 1(i).

However, the convergence of the Fourier coefficients, determining $s^M(x)$, may still be improved, especially if the atoms are not uniformly distributed. Introducing a sublattice with five points, a slightly different density function $f^5(x)$ has to be defined, which should be zero at the site of the most appropriate point of the sublattice as shown in Fig. 1(k). In this case a shift function with better convergence of its Fourier coefficients results [Fig. 1(l)]; it should be pointed out that the number five for optimal convergence is accidental. On the other hand the X-ray pattern itself gives information about which values of M are best suited for rapid convergence. This procedure may be continued by the use of an increasing number of points of the sublattice, thus introducing more holes into the structure, until the shift function is zero and the normal density representation is reached, which gives correct amplitudes and phases as determined by the convergent procedure of the new method. This is shown on Fig. 1(m), but it

should be pointed out that in general, with non-rational atomic coordinates the shift function 'zero' will be obtained only for $M \rightarrow \infty$, because the last small atom displacements may be better corrected with normal atomic coordinate refinement procedures.

At the beginning of a structure determination, representation of the structure by shifts in the sublattice points is most convenient, because correlations between phases of structure factors $F(h)$ are given with most reliable information for small values of h . Chemical information may be introduced gradually in order to determine density functions, which describe the correct sequence of atoms. Thus an early introduction of the maximum chemical information may easily be achieved and a more rapid convergence may be expected; this method seems to be especially useful where normal refinement procedures do not converge.

3. Mathematical formulae

The mathematical relationship between the structure factors $F(h)$ and the Fourier coefficient of the density functions $f^M(x)$ and shift functions $s^M(x)$ is given by

$$F(h) = \sum_{\{p_n\}} F^M(h + \sum np_n) \times \prod_{n=1}^{M/2} J_{p_n}(2\pi h S_n^M) \exp 2\pi i p_n \phi_n^M \quad (2)$$

where

$$F(h) = \sum_{k=1}^N f_k \exp 2\pi i h x_k$$

$$F^M(h) = \sum_{k=0}^{M-1} \rho_k^{(M)} \exp 2\pi i h k / M$$

$\rho_k^{(M)}$ = the density of the k th point of the sublattice with M points,

$J_{p_n}(2\pi h S_n^M)$ = the Bessel function of p_n th order, (p_n = integer),

S_n^M, ϕ_n^M = the amplitudes and phases of the Fourier coefficients of the shift function

$$s(x) = \sum_{n=1}^{M/2} S_n^M \sin 2\pi(n x + \phi_n^M).$$

The summation over $\{p_n\}$ involves sets of all possible combinations of products $J_{p_1} \cdot J_{p_2} \cdot \dots \cdot J_{p_{M/2}}$ with

$$-\infty < p_n < \infty \quad \text{for } n = 1, 2, \dots, M/2.$$

In the case of a vanishing function $s^M(x) = 0$ all Fourier coefficients S_n^M are zero and according to the relations

$$J_n(0) = 0 \quad \text{and}$$

$$J_0(0) = 1,$$

$$F(h) = F^M(h) \text{ results.}$$

This relation may occur accidentally in the case of rational atomic coordinates. If M approaches infinity, the shift function will become zero, consequently we have

$$S_n^M = 0 \text{ for all values of } n,$$

and therefore

$$F^M(h) = F(h).$$

As long as the values of $2\pi h S_n^M$ are sufficiently small, only the zero and first order Bessel function are important. Starting with a given density function $f^M(x)$ incorporating the necessary number of atoms, the arrangement of which may still be wrong, the structure factors can be calculated from a first order approximation with respect to the shift function for $h \neq 0$:

$$F(h) = \prod_{n=1}^{M/2} J_0(2\pi h S_n^M) \cdot \sum_{n=1}^{M/2} \frac{J_1(2\pi h S_n^M)}{J_0(2\pi h S_n^M)} \{F^M(h+n) \exp 2\pi i \phi_n^M - F^M(h-n) \exp(-2\pi i \phi_n^M)\} \quad (3)$$

In this equation the unknown phases of the structure factors $F(h)$ are correlated with the known Fourier coefficients of the density function $F^M(h)$ by the parameters of the shift function which brings the atoms into the right positions.

The efficiency of this procedure is strongly dependent on the choice of $F^M(h)$. But there is another way of determining $F(h)$. For small values of h a sublattice containing a smaller number of points than atoms may be chosen. In this case each point of the sublattice represents a group of atoms, the interference of which may be taken into account by introducing a homogeneous density. If the number of points of the sublattice is M , $M/2$ Fourier coefficients are needed for the shift function; thus a modified equation (3) may be used in a similar way to that indicated above and the phases of $F(h)$ ($h \leq h_0$) may be determined.

After each step the agreement between the calculated structure factors and the observed structure amplitudes, within the region of convergence ($h \leq h_0$), must improve until the structure is finally solved with limited resolution.

The procedure described above is very tedious without the corresponding computer program. Therefore we will not illustrate the procedure of phase determination itself, but will show that the information from a very small $F(h)$ set is sufficient for refinement based on our method. In the following example we have homogeneous density at the sublattice points. The Fourier coefficients of the density function are known

in this case:

$$F^M(h) = \begin{cases} M & \text{for } h=0 \text{ mod } M \\ 0 & \text{elsewhere.} \end{cases} \quad (4)$$

This equation is approximately valid for lattices where the density distribution is almost uniform; this may be verified by checking the observed $F(h)$ for small values of h ($F(h)$ must be small compared with $F(0)$, if almost equal atoms are distributed uniformly in the cell).

For uniform density equation (3) is simplified to

$$F(h) = \prod_{n=1}^{M/2} J_0(2\pi h S_n^M) \cdot M \times \frac{J_{-1}(2\pi h S_n^M) \exp(-2\pi i \phi_n^M)}{J_0(2\pi h S_n^M)}. \quad (5)$$

The initial information on the shift function in the following example is obtained from this equation.

4. One dimensional example

In order to give some idea of the usefulness of the new method, and of the number of Fourier coefficients necessary to fix the shift function, a one-dimensional example of an acentric structure, containing 50 atoms of equal scattering length, has been chosen. Table 1 gives the atomic coordinates of the structure, which were fixed subject to the condition that distance extrema were not exceeded, which seems to be plausible for normal crystal structures; it may be easily shown that this condition improves the convergence of possible S_n^M according to equation (2) or (3). For the sake of simplicity four sets of equidistant atoms were chosen. A possible objection that this example is too specialized can be dismissed on the grounds that small fluctuations in atomic distances within one set of atoms would not influence the Fourier coefficients used for refinement.

In order to show the improved convergence of our method, compared with usual procedures, we apply our method to this structure. We assume the first six phases of $F(h)$, one of which may be arbitrarily chosen, to be given. Thus only five pieces of information were used to obtain complete information on 49 atomic coordinates. The results of the calculation of the Fourier

Table 1. Atomic coordinates of a one-dimensional acentric model structure (50 points of equal scattering length)

i	$X(i)$	i	$X(i)$	i	$X(i)$	i	$X(i)$	i	$X(i)$
0	0.000	10	0.180	20	0.350	30	0.560	40	0.800
1	0.018	11	0.193	21	0.371	31	0.584	41	0.824
2	0.036	12	0.214	22	0.392	32	0.608	42	0.848
3	0.054	13	0.231	23	0.413	33	0.632	43	0.867
4	0.072	14	0.248	24	0.436	34	0.656	44	0.886
5	0.090	15	0.265	25	0.455	35	0.680	45	0.905
6	0.108	16	0.282	26	0.476	36	0.704	46	0.924
7	0.126	17	0.299	27	0.497	37	0.728	47	0.943
8	0.144	18	0.316	28	0.518	38	0.752	48	0.962
9	0.162	19	0.333	29	0.539	39	0.776	49	0.981

Table 2. Result of the zero-approximation for S_n^M and φ_n^M , as calculated from the first six given phases $F(h)$ according to equation (5), compared with the exact values

h, n	Structure factor		Fourier coefficients			
	$ F(h) $	$\chi(h) \cdot 2\pi$	Approximate		Exact values	
			S_n	$\varphi_n \cdot 2\pi$	S_n	$\varphi_n \cdot 2\pi$
0	100.00	0.00	0.0000	0.00	0.0000	0.00
1	8.30	0.17	0.0266	0.33	0.0263	0.31
2	0.56	-0.16	0.0009	0.66	0.0031	0.64
3	1.92	-0.24	0.0022	0.74	0.0020	0.71
4	0.62	0.03	0.0005	0.47	0.0008	0.11
5	1.86	0.49	0.0012	0.01	0.0007	-0.14
6	0.64	0.07	0.0004	0.43	0.0001	0.26

coefficients of the shift function, according equation (5), for the first six S_n^M and φ_n^M are given in Table 2, and compared with their exact values. The agreement between the calculated function $s(x)$ (full line) and the correct function (dotted line) is given in Fig. 2. That these first few Fourier coefficients are sufficient to solve the complete structure determination can be shown in the following way:

(1) A least-squares refinement of the phases and amplitudes of the Fourier coefficients S_n^M , φ_n^M was carried out, using the 20 most intense $F(h)$. The R index decreased from 0.49 to 0.12 after four cycles.

(2) The subsequent refinement of coordinates started with $R=0.20$ which decreased to 0.05 after two cycles. The atomic positions were found in this way with sufficient accuracy (better than 0.05%).

It should be pointed out that the usual atomic coordinates refinement procedure did not converge before the refinement of the S_n^M , φ_n^M had been completed. This indicates that the present method is superior to normal refinement methods. This is due to the fact that all displacements are introduced in a strictly correlated way by the shift function; the convergence of the Fourier series of this function is guaranteed by chemical considerations.

5. Conclusions

The extension of this method to three-dimensions is in preparation. It is self-evident that all equations and relations are much more complex than for the one-dimensional case, but in principle it should be possible to develop this method in three dimensions. The dif-

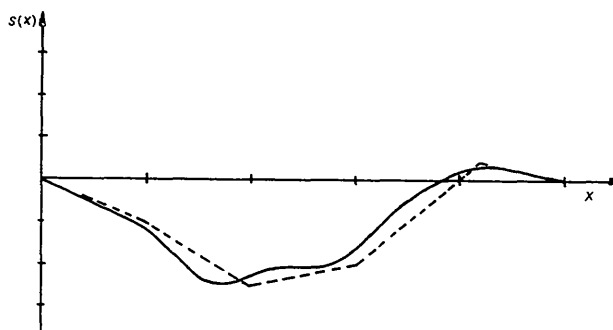


Fig. 2. Exact shift function (dotted line) of the structure, given in Table 1, compared with the shift function (full line) calculated with the approximation given in equation (4).

ficulty that the displacement of the points of the sublattice cannot be given uniquely can be overcome by introducing limiting conditions, imposed by the convergence properties of the shift functions.

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