Acta Cryst. (1996). A52, 675-680

The Phase Problem in Structure Analysis and its One-Dimensional Solution

H. Jagodzinski

Institut für Kristallographie und Mineralogie der Universität, Theresienstrasse 41, D-80333 München, Germany

(Received 27 December 1995; accepted 28 March 1996)

Dedicated to Professor Dr H. Maier-Leibnitz on the occasion of his 85th birthday

Abstract

In a preceding paper, the author has developed a new method of phase determination using latent lattices. The structure is generated by a shift function which displaces the atoms from their idealized position into the correct one. As a consequence, the number of phases to be determined in reciprocal shift space is reduced to $m/2$ (M = number of atoms in the unit cell). The application of the new method is subject to a transformation of conventional Fourier coefficients to those of the shift function. This is greatly facilitated by some known conventional phases. In the case of little phase information, a rough proposal may suffice to start the solution of certain sets of linear equations. Each atomic distance in the unit defines a system of $M - 1$ independent equations. In spite of their interdependence, each system yields just one solution of the phase problem. Two different methods may be applied: (i) $(M - 1)/2$ exact independent pieces of information on distances may be used to evaluate the corresponding system of linear equations; or (ii) a rough model of the structure with averaged atomic distances or coordinates may serve to apply certain sets of 'joker' equations, providing displacements of atoms into the correct direction. In this way, a refined model can be proposed for a repeated use of the joker equations. At the end of this process, a conventional refinement of the structure should be performed. The principles of the new method are explained with the aid of a simple one-dimensional model structure containing one kind of atom only.

1. Introduction

In a preceding paper, the author (Jagodzinski, 1994; hereafter I) suggested a new method for the solution of the phase problem in diffraction, using latent lattices (= primitive lattice of point scatterers). The effectiveness of this method is demonstrated in this paper for the one-dimensional (1D) case only, but its extension to 3D structures is a question of an adequate computer program rather than a question of principle. For a 1D crystal containing a single kind of atom, the lattice constant a_l of the latent lattice is nothing more than the average distance $\langle d\rangle$ of the structure consisting of M atoms, which may be described in a cell with the lattice constant Ma_l. As shown in I, the mathematical treatment of the diffraction problem demands the following slightly different definition of the normalized structure factor:

$$E'(h) = a_h \exp i\varphi_h = (1/M) \sum_{\nu} \exp(2\pi i h x_\nu). \quad (1)$$

With the latent lattice, x_ν in (1) can be replaced by

$$x_\nu = \nu/M + s(\nu/M),$$

where the shift function $s(\nu/M)$ describes the displacement of the νth atom from its ideal position ν/M. Fig. 1 shows a typical picture of $s(\nu/M)$ for two molecules separated by a large distance. The construction is nothing more than an inclined projection. With the definition given for $s(\nu/M)$, (1) becomes (M = odd)

$$E'(h) = (1/M) \sum_{\nu=-(M-1)/2}^{(M-1)/2} \exp\{2\pi i h[\nu/M + s(\nu/M)]\}. \quad (2)$$

For even M, the sum in (2) has to be extended from $-M/2$ to $+M/2$. The evaluation of (2) with the aid of Bessel functions has been described in I for the general 3D case, using a conventional Fourier series for $s(\nu/M)$:

$$s(\nu/M) = a_0 + 2 \sum_{h'=1}^{(M-1)/2} a_{h'} \cos[2\pi h'(\nu/M) + \varphi_{h'}] \quad (3)$$

and its inverse

$$a_{h'} \exp i\varphi_{h'} = (1/M) \sum_{\nu=-(M-1)/2}^{(M-1)/2} s(\nu/M) \exp\{2\pi i[h'(\nu/M)]\}. \quad (4)$$

It should be pointed out that a new reciprocal space has been defined in (3) with the property that a_0 can be omitted (displacement of the origin in real space). Since the Fourier coefficients $a_{h'}$ (hereafter Fc's) describe shifts of atoms, they are different from the conventional Fc's for electron density. For this reason, we shall use the terms real and reciprocal shift space in the following. As shown in I, only $(M - 1)/2$ (M = odd)

Fc's, $a_{h'}\exp(i\varphi_{h'})$, are needed for the full description of the structure. For $M=\text{even}$, $M/2$ Fc's, $a_{h'}$, are necessary, with the restriction that the phase of $a_{M/2}$ is 0 or π. Since both phases describe the two structures correlated by a centre of symmetry, there is a free choice of them. In order to avoid confusion, we shall derive all formulae for $M=\text{odd}$, unless it is explicitly stated that $M=\text{even}$.

The fundamental difference between (1) and (3) can easily be demonstrated. Equation (1) yields Fc's, restricted to points in reciprocal space, but no periodic property is involved. Equation (3) represents points in real and reciprocal shift space and both have periodic properties. It will be shown below that this almost complete equivalence in real and reciprocal shift space yields strong correlations between different $a_{h'}$ and $\varphi_{h'}$. These correlations do not exist at all if the electron-density concept is used. Statistical phase relations originate from the use of point scatterers in the calculation of structure factors. They are considerably weaker than those caused by using the shift space.

The transformation of conventional Fc's $a_h\exp(i\varphi_h)$ into $a_{h'}\exp(i\varphi_{h'})$ has been described in I for the 3D case. Since only relative phases may be determined, some other information is necessary. As has been stated in I, the applicability of the method depends largely on the existence of reflections with small diffraction angles (larger distance fluctuations). Since they are correlated with fluctuations of observed intensities, it may be concluded that (almost) random distributions of atoms in the unit will cause considerable difficulties in the transformation of the experimental data. This difficulty will never occur in periodically ordered structures, however, where the atoms are far from being randomly distributed. The transformation of Fc's from conventional reciprocal to reciprocal shift space may be simple, as long as the a_h ($a_{h'}$) are not too large. Since mutual trespassing of points is prohibited, this condition is satisfied in most cases, as has been discussed in I. Therefore, we shall postpone the discussion of the practical procedure to a later paper, dealing with its application in three dimensions. One point, however, should be added here: the transformation of a_h and φ_h to $a_{h'}$ and $\varphi_{h'}$ cannot be done separately because of the interdependence of the two quantities. In the case of very small $a_{h'}$, the information on phases $\varphi_{h'}$ may be lost. For this reason, only the information on $a_{h'}$ is reliable. This connection between $a_{h'}$ and $\varphi_{h'}$ might be used to argue that all phase information is lost by this transformation. This conclusion seems to be supported by the fact that each set of phases yields a different real function $s(\nu/M)$. This argument is as wrong as it is plausible, however. It is the main object of this paper to show that $a_{h'}$ still contains more phase information than any other statistical method.

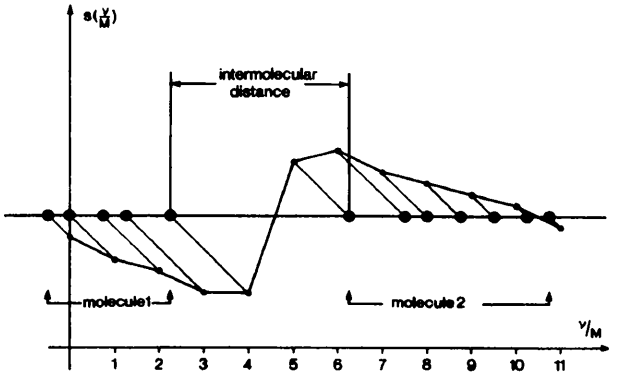

Fig. 1. Reconstruction of two molecules, separated by a large distance, as a projection of the displacement function $s(\nu/M)$.

2. Latent lattices

The shift function $s(\nu/M)$ replaces electron density in the conventional theory of diffraction. Consequently, all laws for Fourier transformation can also be applied to real and reciprocal shift space, the displacement law excepted, where discrete displacements only are admitted. $a_0=0$ is valid if the average over all displacements is zero. At small diffraction angles, the diffraction effects between density and displacement waves are similar as far as the amplitudes are concerned. The phases, φ_h and $\varphi_{h'}$, however, differ by $\pi/2$ in a fair approximation as long as their Fc's describe density waves. It should be stressed once more that this relationship holds for small h, h' only. It should be added that the treatment of the diffraction problem using real and reciprocal shift space is a 6D representation for 3D crystals, and a 2D representation for chain structures.

A simple formula for the difference $s[(\nu+1)/M]-s(\nu/M)$ has been given in I [equation (15) in I]. It determines the corresponding difference of distances between two neighbours:

$$\Delta d_{1\nu}=s[(\nu+1)/M]-s(\nu/M).$$

In this paper, we generalize this definition to any pair (next, next but one *etc.*) of neighbours using the corresponding relation

$$\Delta d_{n\nu}=s[(\nu+n)/M]-s(\nu/M), \tag{5}$$

representing the distance $d_{n\nu}=n\,a_l+\Delta d_{n\nu}$.

With this new definition, equation (15) in I becomes

$$\Delta d_{n\nu}=-4\sum_{h'=1}^{(M-1)/2}\{a_{h'}\sin(\pi nh'/M)[\sin(\alpha_{nh'\nu})x_{h'}+\cos(\alpha_{nh'\nu})y_{h'}]\} \tag{6}$$

with $\alpha_{nh'\nu}=(2\pi h'/M)(\nu+n/2)$, $x_{h'}=\cos\varphi_{h'}$, $y_{h'}=\sin\varphi_{h'}$.

Since $a_{h'}$ are considered to be known, (6) represents a two-dimensional system (ν, n) of equations that have to be solved with respect to the unknown variables $\varphi_{h'}$ and

$\Delta d_{n\nu}$. Each $n\,(= n_0)$ represents a solution of the problem if $\Delta d_{n_0\nu}$ is known. Since $x_{h'}$, $y_{h'}$ are not independent variables, and small $a_{h'}$ excludes the corresponding $x_{h'}$, $y_{h'}$, the number of equations necessary for the solution is reduced. On the other hand, $\Delta d_{n\nu}$ are unknown, but it should be remembered that $\Delta d_{n\nu} \equiv 0$ represents a kind of zero approximation, namely the latent lattice itself. Now we have two possibilities to solve the phase problem: (i) to introduce a proposed structure in order to evaluate the (overdetermined) set of equations statistically; or (ii) to select the necessary number of most reliable equations for the direct mathematical solution. Small $a_{h'}$ reduce the number of variables, while small $\Delta d_{n\nu}$ reduce the number of necessary equations. These two important properties emphasize the effectivity of the new method. Another property of (6) should be briefly discussed. There are two ways to develop the structure. For fixed ν, the structure is determined by the variable n; this is a local approach to the correct structure. On the other hand, for each n and variable ν, the structure is developed in terms of a series, using next ($n = 1$), next but one ($n = 2$) *etc.* nearest neighbours. This seems to be trivial for $n = 1$ only, but for $n = 2$ the situation is essentially the same: for all pairs involved, each position appears twice, namely as starting and as reference atom. Although correlated with the distances for $n = 1$, however, different distances are involved resulting in a different set of equations (compare Fig. 3*c*). Moreover, the coefficients $a_{nh'}$ in (6*a*) are different in so far as for small n the reflections with low h' have a lower weight because of the factor $\sin(\pi n h')$. The author admits that the situation seems to be confusing, but this may be explained by the fact that the Fc's (amplitudes and phases) have to satisfy numerous conditions in order to arrive at a unique solution. In other words, different ways may be taken, which end at the same structure. Since we take care in satisfying these conditions, many equations, although interdependent, may be used for the solution. We have $M - 1$ equations for ν and $(M - 1)/2$ for n, hence the number of equations corresponds exactly to the number of distances in the structure or the corresponding peaks in the Patterson function. Each distance represents one equation for phase determination. Dependent equations are dropped by avoiding closed cycles of distances.

It is useful to separate the sine and the cosine parts in (6). This can be done in the following way. With a rearrangement of the set of equations given by (6) and with the aid of $\nu' = \nu + n/2$, (6) can be transformed to

$$\Delta d_{n\nu'} = -4 \sum_{h'=1}^{(M-1)/2} \{a_{nh'}[\sin(2\pi h'\nu'/M)\,x_{h'} + \cos(2\pi h'\nu'/M)\,y_{h'}]\} \qquad (6a)$$

with $a_{nh'} = a_{h'} \sin(\pi n h'/M)$.

Now any pair of equations ν', $-\nu'$, can be replaced by their sum and their difference:

$$\Delta d_{n,\nu'} + \Delta d_{n,-\nu'} = -8 \sum_{h'=1}^{(M-1)/2} a_{nh'} \cos(2\pi h'\nu'/M)\,y_{h'}, \qquad (7a)$$

$$\Delta d_{n,\nu'} - \Delta d_{n,-\nu'} = -8 \sum_{h'=1}^{(M-1)/2} a_{nh'} \sin(2\pi n h'\nu'/M)\,x_{h'}. \qquad (7b)$$

For a centrosymmetric structure, we have

$$\Delta d_{n,\nu'} - \Delta d_{n,-\nu'} \equiv 0,$$

therefore (7*b*) vanishes, all phases must be $\pi/2$ or $3\pi/2$, and all $y_{h'}$ become ± 1. This property of (7*a*) seems to be similar to conventional sign-determination methods. It should be noted, however, that the conditions imposed on (7*a*) are considerably stronger than those derived for usual sign determination. Since equations have to be satisfied for factors ± 1, the distribution law of signs can be found.

The advantage of (6) and (7) is easily recognized. Structural information as well as transformed phase information from experimental methods enter the same equations. Each n represents just one system of independent equations. The phases are the same in all systems but the $a_{nh'}$ are different for each n. As a consequence, a statistical evaluation with different weights due to $a_{nh'}$ is possible. Small $a_{nh'}$ cancel the influence of their corresponding phases $\varphi_{h'}$. This property allows for direct phase determination using known structural information. This method may be developed for the 3D case in a straightforward manner. Since weak $a_{nh'}$ reduce the number of unknown phases, fewer equations are needed for phase determination. In this way, uncertain structural elements may be neglected in the course of the various approximations to the structure.

At the beginning of this procedure, (7*a*), (7*b*) may be used to determine the signs of all $y_{h'}$ and $x_{h'}$. After having resolved the ambiguities of signs, (6*a*) has to be used in the following way. As soon as the phases $\varphi_{h'}$ are known within a certain limit of error, it may be replaced by $\varphi^0_{h'} + \Delta\varphi_{h'}$. With this definition, (6*a*) transforms to

$$\Delta d_{n\nu} = -4 \sum_{h'=1}^{(M-1)/2} \{a_{nh'}[\cos(\alpha_{nh'\nu} + \varphi^0_{h'}) \sin \Delta\varphi_{h'} + \sin(\alpha_{nh'\nu} + \varphi^0_{h'}) \cos \Delta\varphi_{h'}]\}.$$

With

$$\Delta d^0_n = -4 \sum_{h'=1}^{(M-1)/2} a_{nh'}[\sin(\alpha_{nh'\nu} + \varphi^0_{h'}) \cos \Delta\varphi_{h'}],$$

we get

$$\Delta d_{n\nu} - \Delta d^0_{n\nu} = -4 \sum_{h'=1}^{(M-1)/2} a_{nh'} \cos(\alpha_{nh'\nu} + \varphi^0_{h'}) \sin \Delta\varphi_{h'}. \tag{8}$$

As soon as the $\Delta\varphi_{h'}$ are small, $\cos \Delta\varphi_{h'}$ in (8) approaches unity and $\Delta d^0_{n\nu}$ represents an approximated $\Delta d_{n\nu}$, differing only slightly from the correct value. Since this property will not be used in this paper, its application will be discussed in a later investigation.

Finally, it should be mentioned that (6) may be transformed into a Fourier series in the following way. Using

$$a'_{nh'} = -2a_{nh'}, \varphi_{nh'} = \pi n(h'/M) + \pi/2 + \varphi_{h'},$$

we get

$$\Delta d_{n\nu} = 2 \sum_{h'=1}^{(M-1)/2} a'_{nh'} \cos[(2\pi h'\nu/M) + \varphi_{nh'}]. \tag{9}$$

Equation (9) is nothing more than the Fourier series for $\Delta d_{n\nu}$. Its inverse is

$$a'_{nh'} \exp(i\varphi_{nh'}) = (1/M) \sum_{\nu=-(M-1)/2}^{(M-1)/2} \Delta d_{n\nu} \exp(2\pi i h'\nu/M). \tag{10}$$

Let us now briefly discuss the meaning of (3) and (9) for the new method of phase determination. They represent a kind of 'joker' in the following sense: once an approximate proposal of the structure has been found that yields a set of amplitudes $a_{nh'}$ different from the corresponding known values and phases $\varphi_{nh'}$, (3) and (9) may be applied using the phases with the correct $a_{nh'}$. If the proposal was acceptable, this procedure yields displacement towards an improved structure. Since we have one basic joker of type (3), but $(M-1)/2$ special jokers of type (9), each of them will contribute to a different proposal according to their value n: the large n will yield better information on long distances, while the reverse is true of the small ones. The basic joker (3) is a neutral one and may be used as a kind of 'referee'. After having received these sets of information, a new proposal to the correct structure has to be given. This procedure may be repeated as long as the use of (4) and (10) result in $a_{nh'}$, different from the experimental ones. Since they are known within certain limits of error only, the dead end of this process may be reached at an early stage. It should be emphasized, however, that a proposal of the complete structure has to be developed. In the case that no final proposal can be offered, solutions for phases using (6), (8) and (9) have to be found.

Summarizing, we may conclude that any structure determination can be performed in several approximations. Since the latent lattice with the assignment of atomic positions to the points of the lattice represents the zero approximation to the structure, the next step must use some further information on phases or structure in order to get a first approximation to the structure. Phases known from experimental data or by the $a_{h'}$ transformation reduce the number of unknown phases by one (or two). More effective is the chemical method, which may be applied if some information on the structure is available. This information may be introduced directly into the set of equations (6) or (9), with the effect that the addition of a single position to M_0 known positions may result in M_0 new equations, subject to the condition that they are independent. If sufficient equations have been found, the phases may directly be determined. For a protein structure, this number is still very large but the method of using latent superlattices may be used to solve the problem with a reduced number of equations. Since this method is useful only for 3D structures, it will be discussed very briefly in the following chapter.

3. Latent superlattices

Let us now define the nth latent superlattice. If M is not divisible by n, a new lattice can be defined with the n-fold lattice constant na_l. As shown in Fig. 2(b) for $n = 2$, the points of this superlattice coincide with the same $s(\nu/M)$ but in another sequence. The unit cell of the structure is doubled with respect to the lattice with $n = 1$ and the first half of this larger cell covers the even-numbered points, the second half the odd-numbered ones. Since this latent superlattice contains the same number of points as the basic latent lattice, the number of Fc's is invariant and it may be shown with the aid of Fourier transforms that the Fc's are the same in another sequence. This property yields strong correlations between Fc's. This may easily be seen in the case of M = even (compare with Fig. 2a). Obviously, the latent superlattice decomposes into two (displaced) structures, each of them containing just half the number of points of the basic latent lattice. Consequently, the structure is described by two

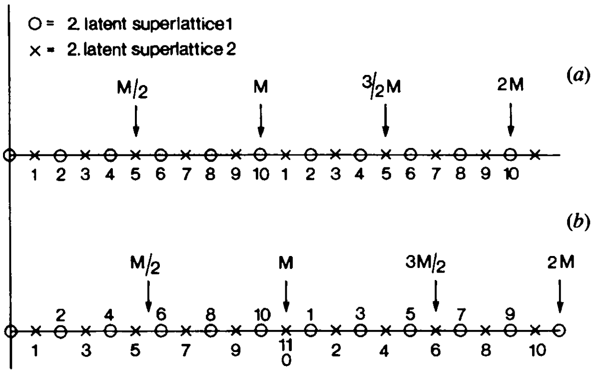

Fig. 2. Correlations between latent lattice and second latent superlattices: (a) M = even, (b) M = odd.

interpenetrating lattices, one of them being a kind of raster with respect to the second one. In a first approximation to the correct structure, the atoms of the interpenetrating lattice may be placed exactly in between the first using Fc's that have to be calculated according to the displacement law of Fourier transformation. Obviously, there is no significant difference between the even and the odd case for complicated structures. Therefore, similar correlations exist between the two corresponding sets of Fc's for $M = \text{odd}$.

Summarizing, we may conclude that the reduction of the number of Fc's seems to be important in the case of very complicated structures such as proteins or compounds of similar complexity. In the 3D case, the $2 \times 2 \times 2$ superlattice yields a fair description of the structure with a lower resolution given by the raster. Once this problem has been solved, the transition to high resolution is no more than a question of computer capacity. The reason for the correlation of phases is obvious: the interpenetration avoids mutual trespassing of neighbouring points even at a long distance. The complete discussion of the powerful properties of latent superlattices will be given in a later paper, treating the 3D theory of phase determination using generalized latent lattices.

4. Example

Let us now discuss the following simple 1D structure in order to elucidate the procedure, rather than to demonstrate its effectiveness. A chain structure with 11 atoms is defined, consisting of three molecules, two of them with four atoms (Figs. 3*a–c*). The following distances are assumed:

(i) (three atoms) $d_{10} = 1.3$, $d_0 = 1.5$ Å, intermolecular distance between 1 and 2 $d_1 = 3.9$ Å;

(ii) (four atoms), $d_2 = 1.3$, $d_3 = 1.2$, $d_4 = 1.5$ Å, intermolecular distance $d_5 = 3.5$;

(iii) (four atoms) $d_6 = 1.6$, $d_7 = 1.5$, $d_8 = 1.3$ Å, intermolecular distance $d_9 = 3.4$ Å.

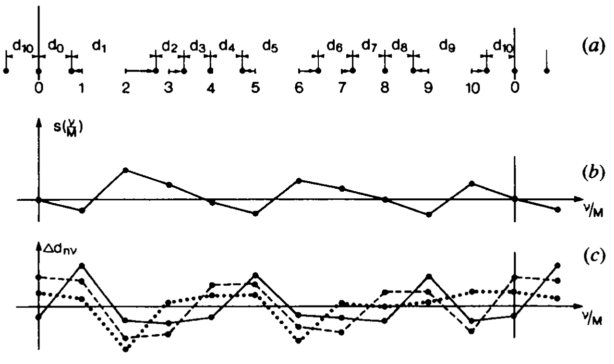

Fig. 3. Hypothetical structure of three molecules and some of their derived functions: (*a*) molecular structure, (*b*) $s(\nu/M)$, (*c*) full line $\Delta d_{1\nu}$, broken line $\Delta d_{2\nu}$, dotted line $\Delta d_{3\nu}$.

Table 1. *$s(\nu/M)$, $\Delta d_{1\nu}$ and $\Delta d_{3\nu}$ for the hypothetical structure consisting of three molecules*

Str = hypothetical structure, I = approximation I, II = approximation II.

	$s(\nu/M)$			$\Delta d_{1\nu}$			$\Delta d_{3\nu}$		
ν	Str	I	II	Str	I	II	Str	I	II
0	0	0	0	−0.5	−0.6	−0.6	+0.7	+0.6	+0.7
1	−0.5	−0.6	−0.6	+1.9	+1.8	+1.9	+0.4	+0.6	+0.7
2	+1.4	+1.2	+1.3	−0.7	−0.6	−0.6	−2.0	−1.8	−1.8
3	+0.7	+0.6	+0.7	−0.8	−0.6	−0.6	+0.2	+0.3	+0.3
4	−0.1	0	+0.1	−0.5	−0.6	−0.6	+0.6	+0.3	+0.3
5	−0.6	−0.6	−0.5	+1.5	+1.5	+1.5	+0.6	+0.3	+0.3
6	+0.9	+0.9	+1.0	−0.4	−0.6	−0.6	−1.6	−1.8	−1.8
7	+0.5	+0.3	+0.4	−0.5	−0.6	−0.6	+0.2	+0.3	+0.2
8	+0	−0.3	−0.2	−0.7	−0.6	−0.6	0	+0.3	+0.2
9	−0.7	−0.9	−0.8	+1.4	+1.5	+1.4	+0.2	+0.3	+0.2
10	+0.7	+0.6	+0.6	−0.7	−0.6	−0.6	+0.7	+0.6	+0.7

Table 2. *(a) $\Delta d_{l,\nu} \pm d_{l,-\nu}$ and (b) $\Delta d_{3\nu} \pm d_{3,-\nu}$ for the hypothetical structure and models I and II*

	Str	I	II		Str	I	II
(*a*)							
$\Delta d_{1,0} + \Delta d_{1,10}$	−1.2	−1.2	−1.2	$\Delta d_{1,0} - \Delta d_{1,10}$	+0.2	0	0
$\Delta d_{1,1} + \Delta d_{1,9}$	+3.3	+3.3	+3.3	$\Delta d_{1,1} - \Delta d_{1,9}$	+0.5	0.3	0.5
$\Delta d_{1,2} + \Delta d_{1,8}$	−1.4	−1.2	−1.2	$\Delta d_{1,2} - \Delta d_{1,8}$	0	0	0
$\Delta d_{1,3} + \Delta d_{1,7}$	−1.3	−1.2	−1.2	$\Delta d_{1,3} - \Delta d_{1,7}$	−0.3	0	0
$\Delta d_{1,4} + \Delta d_{1,6}$	−0.9	−1.2	−1.2	$\Delta d_{1,4} - \Delta d_{1,6}$	−0.1	0	0
(*b*)							
$\Delta d_{3,10} + \Delta d_{3,9}$	+0.9	+0.9	+0.9	$\Delta d_{3,10} - \Delta d_{3,9}$	+0.5	0.3	0.5
$\Delta d_{3,0} + \Delta d_{3,8}$	+0.7	+0.9	+0.9	$\Delta d_{3,0} - \Delta d_{3,8}$	+0.7	0.3	0.5
$\Delta d_{3,1} + \Delta d_{3,7}$	+0.6	+0.9	+0.9	$\Delta d_{3,1} - \Delta d_{3,7}$	+0.2	0.3	0.5
$\Delta d_{3,2} + \Delta d_{3,6}$	−3.6	−3.6	−3.6	$\Delta d_{3,2} - \Delta d_{3,6}$	−0.4	0	0
$\Delta d_{3,3} + \Delta d_{3,5}$	+0.8	+0.6	+0.6	$\Delta d_{3,3} - \Delta d_{3,5}$	−0.4	0	0

With these distances, $s(\nu/M)$, $\Delta d_{1\nu}$ and $\Delta d_{3\nu}$ were calculated (Table 1). Using (4), their Fc's $a_{h'} \exp i\varphi_{h'}$ (Table 3) were determined. The following structural information was demanded: (i) lattice constant = 22 Å; (ii) average intramolecular distances = 1.4 Å; (iii) three molecules as described above; (iv) acentric structure. Using this information, we get the following idealized structural distances: $d_0 = d_2 = d_3 = d_4 = d_6 = d_7 = d_8 = d_{10} = 1.4$ Å, $d_1 = d_5 = d_9 = 3.6$ Å. Unfortunately, this idealized structure is centrosymmetric. For this reason, the second molecule was arbitrarily displaced by 0.2 Å ($d_1 = 3.8$, $d_5 = d_9 = 3.5$ Å) in order to break this unwanted symmetry (model I). For a second (better) model II, the correct intermolecular distances (3.9, 3.5, 3.4 Å) were used. The $s(\nu/M)$ values calculated from the distances of both models are given in Table 1. $a_{h'}$ and $\varphi_{h'}$ were calculated according to (4) (see Table 3): their agreement with the 'true' values of the structure is poor.

In order to get better phases, the second possibility of phase determination was tested. Using (6), tables of

$$\Delta d_{n\nu}, \quad a_{h'} \sin(\pi n h'/M) \cos(\alpha_{nh'\nu})$$

and

Table 3. *$a_{h'}$ and $\varphi_{h'}$ as calculated from equation (3)*

Last column: calculated phases $\varphi_3, \varphi_4, \varphi_5$ are averaged phases from models I and II.

	Str	I	II	
a_1	0.995	0.1496	0.1414	
φ_1	−100.0	−114.0	−105.0	−109.3
a_2	0.1731	0.1295	0.1252	
φ_2	−116.6	−108.7	−101.5	−115.8
a_3	0.3530	0.3543	0.3541	
φ_3	94.0	92.6	91.6	92
a_4	0.1286	0.1110	0.1109	
φ_4	86.0	86.4	87.8	87
a_5	0.1713	0.1834	0.1827	
φ_5	88.1	83.5	86.1	84.2

$$a_{h'} \sin(\pi n h'/M) \sin(\alpha_{nh'\nu})$$

as well as their sums and differences according to (7) were calculated. Two of the latter are given in Table 2. Astonishingly, there were some sums of $\Delta d_{nh'}$ almost independent of the model used, namely $\Delta d_{1,1} + \Delta d_{1,9}$ and $\Delta d_{3,2} + \Delta d_{3,6}$. As factors of the corresponding $y_{h'} = \sin \varphi_{h'}$ and $x_{h'} = \cos \varphi_{h'}$, they yield equations which were selected for a first calculation of phases. They are:

$$\begin{aligned} &\Delta d_{11} + \Delta d_{19} \\ &\quad = -0.15 y_1 + 0.11 y_2 + 1.80 y_3 + 0.90 y_4 + 0.56 y_5 \\ &\quad = 3.3\text{Å}, \\ &\Delta d_{32} + \Delta d_{36} \\ &\quad = 0.25 y_1 + 0.90 y_2 - 1.47 y_3 - 0.0412 y_4 - 1.05 y_5 \\ &\quad = -3.6\text{Å}. \end{aligned}$$

The reader may check that these equations determine the approximate values of the phase satisfactorily to:

$$y_1 = -0.95, \quad y_2 = -0.90, \quad y_3 = y_4 = y_5 = 1;$$
$$\varphi_1 = -109.3, \quad \varphi_2 = -115.8,$$
$$\varphi_3 = \varphi_4 = \varphi_5 = 90^\circ \quad (\cos\varphi_1, \cos\varphi_2 \text{ negative}).$$

According to Table 3, the values of the last three $y_{h'}$ are so near to unity that they could be excluded from a more precise evaluation. From (3), these phases were used to calculate a new set of $s(\nu/M)$. The resulting distances compared with the correct ones in parentheses are: $d_0 = 1.43\,(1.50)$, $d_1 = 3.92\,(3.90)$, $d_2 = 1.31\,(1.30)$, $d_3 = 1.26\,(1.20)$, $d_4 = 1.47\,(1.50)$, $d_5 = 3.50\,(3.50)$, $d_6 = 1.65\,(1.60)$, $d_7 = 1.43\,(1.50)$, $d_8 = 1.29\,(1.30)$, $d_9 = 3.38\,(3.40)$, $d_{10} = 1.36\,(1.30)$ Å. Remembering the simplified procedure applied, the result is convincing because all displacement involved occurs in the correct direction. Since no chemical feeling can be developed for this model, the author had to stop here. In the next step, improbable distances have to be excluded. This results in a new proposal for a second application of the whole procedure.

It should be pointed out that the phases $\varphi_{h'}$ used in the new method are much more sensitive to structural changes than the phases in conventional structure analysis. This is because these phases determine displacements rather than electron density. It is self-evident that the accuracy of phases is essentially determined by the errors in $a_{h'}$. Consequently, much care has to be taken for their correct determination. This procedure will be effectively supported by some phases, determined experimentally in conventional reciprocal space. Their transformation to reciprocal shift space has been described in I.

5. Conclusions

The method of latent lattices and superlattices has been explained in the 1D case only. Obviously, there is no difficulty in rewriting all equations used in this paper in their 3D form. All scalar quantities, typical for the 1D case, have to be replaced by their corresponding vectors and their scalar products. There is only one essential difference: the arrangement of phase equations (6) and (7) is more complicated and it may become difficult to correlate all structural information with the system of equations. This is more or less a question of computer programs, however, which have to be developed for the new method. For this reason, experimental measurements of phases may become very important. As pointed out above, the crucial point of this method is to get sufficient information to start the approximations. Experimental measurements of phases and their transformation to phases of the latent lattice as described in I may be determined with a considerable amount of error. As has been shown above, this does not hamper the new method in principle.

The author regrets that, because of the lack of an effective computer program, the example given above was too poor to elucidate the power of the new method adequately. Since it is based on equations rather than on statistics, there is no doubt that the method should be superior to any other theoretical method presently in use. The great advantage results from the fact that all information available can be used, and that the weak intensities are as important as the strong ones. The inclusion of disorder, anomalous scattering and other properties modifies the equations to be used but does not exclude their application. This is specifically valid for proteins, where the short-range order of the water molecules has to be included for a reliable structure determination.

The author thanks Mrs R. Wunderlich for her kind assistance in preparing the manuscript of this paper.

References

Jagodzinski, H. (1994). *Phys. Status Solidi*, pp. 477–490.