

by any slight shifts of neighbouring oxygen atoms, to make the coordination polyhedron contracted so as to fit a calcium atom. This situation may be relevant to the difference in the amount of alkali contents in these minerals, namely phillipsite contains two alkali atoms per unit cell, while harmotome only one atom or less. Thus, the arrangement of metal atoms and water molecules in phillipsite is probably considerably different from that in harmotome. In fact, the results of our preliminary investigation into the structure of phillipsite seem to suggest that its aluminosilicate framework may take a configuration somewhat different from the one in harmotome, though we still believe that these two are essentially of identical structural scheme.

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## On the Method of Least Squares as Applied to the Refinement of Crystal Structures

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The effect of off-diagonal terms of the normal equations of least-squares on the refinement of parameters (both positional and thermal) is discussed critically. It is shown that the usual procedure of neglecting the off-diagonal terms during refinement of positional parameters in a three-dimensional structure, or in a projection without overlap of atoms, is valid only if the structure or the projection concerned is centrosymmetric and the axes are orthogonal. If the structure is non-centrosymmetric and contains atoms or groups of atoms which are centrosymmetric and which contribute predominantly to the structure factor, then a new type of overlap termed 'inverse overlap' has to be taken into account. The inverse overlap is particularly significant since it can occur in three dimensions. Finally it is shown that in the refinement of thermal parameters the linear approximation formula is not valid and all the off-diagonal terms involving the  $B_{ij}$ 's which occur for the particular symmetry have to be included in the refinement.

### 1. Introduction

Since it was first suggested by Hughes (1941), the method of least-squares has been widely used in crystal-structure analysis. However, no critical examination of the method, particularly the effect of off-diagonal terms, as applied to the structural refinement seems to be available in the literature. Such a study was undertaken by the author and the results obtained are presented in this paper.

The usual procedure of neglecting the off-diagonal terms in the refinement of three-dimensional structures, and in two dimensional projections without overlap, although justifiable in centrosymmetric structures, is not valid for non-centrosymmetric structures containing atoms or groups which are centrosymmetric and which contribute predominantly to the structure factor. Under these conditions it is necessary to take into account what may be termed the 'inverse overlap' of atoms. The linear-approximation formula

is also found not to be valid when applied to the refinement of anisotropic thermal parameters.

## 2. Effect of off-diagonal terms

First, let us assume that only positional parameters are refined. Also, for convenience, we shall consider only a two-dimensional case (say the projection down the  $c$  axis). The extension of the results to three dimensions is quite straightforward.

The normal equation for the shift  $\Delta x_i$  in the  $x$  co-ordinate of an atom  $i$  can be written in the form

$$\sum_{h,k} \Delta F \frac{\partial |F_c|}{\partial x_i} = \sum_{h,k} \left\{ \left( \frac{\partial |F_c|}{\partial x_i} \right)^2 \Delta x_i + \frac{\partial |F_c|}{\partial x_i} \frac{\partial |F_c|}{\partial y_i} \Delta y_i \right\} + \sum_{h,k} \sum_{i \neq j} \left\{ \frac{\partial |F_c|}{\partial x_i} \frac{\partial |F_c|}{\partial x_j} \Delta x_j + \frac{\partial |F_c|}{\partial x_i} \frac{\partial |F_c|}{\partial y_j} \Delta y_j \right\}, \quad (1)$$

where  $\Delta F = (|F_o| - |F_c|)$ . In this equation the off-diagonal terms can, in general, be divided into two categories. The first consists of interactions of an atom with itself, namely of the type  $(\partial |F_c| / \partial x_i) \cdot (\partial |F_c| / \partial y_i)$ ; we shall denote such a term by  $[X_i Y_i]$ . The second group of terms involves interactions of different atoms, of the type  $[X_i X_j]$  and  $[X_i Y_j]$ . It is usual to assume that all interactions excepting the diagonal one, namely  $[X_i X_i]$ , are negligible so that the determination of the shift  $\Delta x_i$  of an atom reduces to a single linear equation

$$\Delta x_i = \frac{\sum_{h,k} \Delta F \frac{\partial |F_c|}{\partial x_i}}{\sum_{h,k} \left( \frac{\partial |F_c|}{\partial x_i} \right)^2}. \quad (2)$$

The conditions under which this holds good are usually taken to be the following.

(1) If the axes are orthogonal or nearly so the contribution due to  $[X_i Y_i]$  may be neglected.

(2) The interactions of the type  $[X_i X_j]$  and  $[X_i Y_j]$  may be neglected in all three-dimensional work and also in two-dimensional projections if there is no overlap of atoms. These points will now be examined more closely.

### (i) Centrosymmetric case

When the structure is centrosymmetric we can write

$$F_c = \sum_i f_i \cos 2\pi(hx_i + ky_i) = \sum_i f_i \cos \theta_i. \quad (3)$$

Consider first the interaction between the different co-ordinates of the same atom, i.e., of the type  $[X_i Y_i]$ , which is given by

$$[X_i Y_i] = \sum_{h,k} \frac{\partial F_c}{\partial x_i} \frac{\partial F_c}{\partial y_i} = \sum_{h,k} 4\pi^2 f_i^2 h k \sin^2 \theta_i \quad (4)$$

$$= \sum_{h,k} 2\pi^2 f_i^2 h k - \sum_{h,k} 2\pi^2 f_i^2 h k \cos 2\theta_i. \quad (5)$$

When  $\theta_i$  goes through a range greater than  $2\pi$  for

different values of  $h, k$  we have to consider the following three cases:

(I) The symmetry is orthogonal, which would result in  $(\theta_i)_{hk} = (\theta_i)_{\bar{h}\bar{k}}$ .

(II) Axes are orthogonal, but the symmetry is not. This would give only a relation of the type  $(f_i)_{hk} = (f_i)_{\bar{h}\bar{k}}$ .

(III) Both symmetry and axes are non-orthogonal.

For case (I), it is possible to group properly terms of the type  $(\cos 2\theta_i)_{hk}$  and  $(\cos 2\theta_i)_{\bar{h}\bar{k}}$  so that the first and second terms in (5) vanish identically. Hence all the non-diagonal terms  $[X_i Y_i]$  vanish. For case (II), the second term in (5) becomes negligible since  $\cos 2\theta_i$  is an oscillatory function. Regarding the first term, since  $(f_i)_{hk} = (f_i)_{\bar{h}\bar{k}}$  a proper grouping of the terms will make it vanish so that in this case also the non-diagonal terms  $[X_i Y_i]$  become negligible although they are not identically zero as in case (I). For case (III), it can be shown that (5) is not negligible. Firstly  $(f_i)_{hk} \neq (f_i)_{\bar{h}\bar{k}}$  because of the non-orthogonality of the axes. Therefore the grouping of the terms as devised earlier cannot be adopted. However, neglecting for the present the above factor  $(f_i)^2$ , the non-vanishing of the sum of the product terms  $hk, \bar{h}\bar{k}$  can be understood by reference to Fig. 1 which represents the situation in a two-dimensional reciprocal lattice. The circle represents the limiting sphere and the axes  $a^*$  and  $b^*$  are non-orthogonal with an included angle  $\gamma^*$  ( $\neq 90^\circ$ ). It is clear from the diagram that the number of product terms of the type  $hk, \bar{h}\bar{k}$  which have positive values is much less than the number of terms of the type  $\bar{h}k, h\bar{k}$ , which have negative values. Therefore the sum (5) will not vanish. It is also obvious that the positive and negative terms become nearly equal in number when  $\gamma^* \simeq 90^\circ$  so that the sum (5) becomes negligible (i.e., it tends to case (II) discussed above).

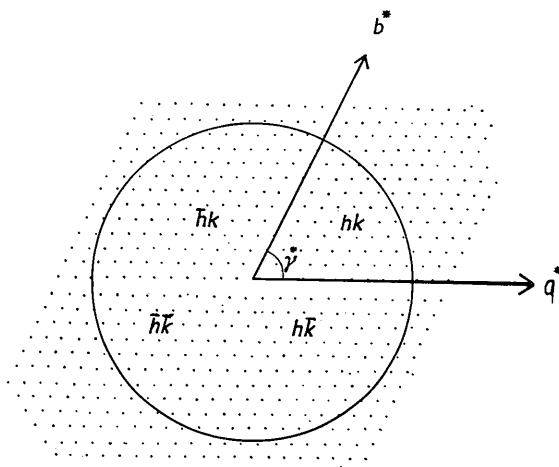


Fig. 1. Two-dimensional reciprocal lattice with non-orthogonal axes. The circle represents the limiting sphere of reflection.

Before considering the interaction between different atoms it is necessary to consider one other possible

case for (5), namely when the atom lies close to the origin, so that  $\theta_i$  will not be distributed over a range of  $2\pi$  for different values of  $h$  and  $k$ . Here again we can consider the three cases (I), (II) and (III).

For case (I), obviously the sum (5) is zero. For case (II) it is seen that the first term in (5) is zero because of  $(f_i)_{hk} = (f_i)_{\bar{h}\bar{k}}$  but the second term will not vanish. For, by grouping terms of the type  $hk, \bar{h}\bar{k}$  and  $\bar{h}k, h\bar{k}$  the second term in (5) can be written as

$$\begin{aligned}
 & - \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} 4\pi^2 (f_i)^2 hk [\cos 2\pi(2hx_i + 2ky_i) \\
 & \qquad \qquad \qquad - \cos 2\pi(2hx_i - 2ky_i)] \quad (6) \\
 & = \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} 8\pi^2 f_i^2 \sin 2\pi \cdot 2hx_i \sin 2\pi \cdot 2ky_i. \quad (7)
 \end{aligned}$$

Suppose  $H$  and  $K$  are the largest values of  $h$  and  $k$  occurring in the summation. Then if neither  $|2Hx_i|$  nor  $|2Ky_i|$  is greater than  $\frac{1}{2}$ , the two sine functions do not change sign throughout the interval and so this sum cannot vanish. This condition for non-vanishing of the sum can be put in the form  $x_i < \frac{1}{4}H$ ,  $y_i < \frac{1}{4}K$  or more generally, if  $\mathbf{s}$  is the reciprocal vector and  $\mathbf{r}_i$  the position vector of the atom,  $\mathbf{s} \cdot \mathbf{r}_i < \frac{1}{4}$  or  $r_i < \lambda/4$ . This means that in a centrosymmetric structure if an atom occurs at a distance less than  $\lambda/4$  from the origin, the sum (5) is non-negligible. Physically this is plausible because the atom  $i$  will then overlap with its inverse ( $i'$ ). Obviously the minimum separation of  $i$  and  $i'$  for non-vanishing of (5) becomes  $|\mathbf{r}_i - \mathbf{r}_j| < \lambda/2$ . This condition is exactly the same as the condition for the resolution of the two atoms  $i$  and  $i'$  and is similar to the more general result to be obtained below for the case of two different atoms.

Case (III) need not be discussed separately here since the non-diagonal terms have to be included even when the atom is in a general position.

Let us now consider the interaction between different atoms. The two types of interactions can be written

$$[X_i X_j] = \sum_{h,k} 2\pi^2 h^2 f_i f_j [\cos(\theta_i - \theta_j) - \cos(\theta_i + \theta_j)] \quad (8)$$

and

$$[X_i Y_j] = \sum_{h,k} 2\pi^2 h k f_i f_j [\cos(\theta_i - \theta_j) - \cos(\theta_i + \theta_j)]. \quad (9)$$

Taking first equation (8), since only  $h^2$  which is always positive appears in the summation, the following

discussion will hold good for all the three cases (I), (II), and (III).

The sum (8) will have a large value when either  $(\theta_i - \theta_j)$  or  $(\theta_i + \theta_j) \simeq 0$  for various values of  $h, k$ . Now,  $(\theta_i - \theta_j) = 2\pi \mathbf{s} \cdot (\mathbf{r}_i - \mathbf{r}_j)$  and  $(\theta_i + \theta_j) = 2\pi \mathbf{s} \cdot (\mathbf{r}_i + \mathbf{r}_j)$ . So the sum will be large if  $\mathbf{r}_i \simeq \mathbf{r}_j$  or if  $\mathbf{r}_i \simeq -\mathbf{r}_j$ . This means that if an atom  $i$  overlaps another atom  $j$  or its inverse ( $j'$ ), then the corresponding co-ordinates have to be taken together in the refinement. In a centrosymmetric crystal the two conditions  $\mathbf{r}_i \simeq \mathbf{r}_j$  and  $\mathbf{r}_i \simeq -\mathbf{r}_j$  are equivalent and so it is enough to consider one of them, say the former. Hence using an argument similar to that used for  $[X_i Y_i]$ , it is seen that for the non-vanishing of (8),  $(\mathbf{r}_i - \mathbf{r}_j)$  should be less than  $\lambda/2$ . Thus if two atoms  $i$  and  $j$  are separated by a distance greater than  $\lambda/2$  their interactions may be neglected.

It is seen that sum (9) is similar to (5) and if  $\theta_i = \theta_j$ , it is identically the same as (5), as obviously it should be. In fact, the discussions pertaining to (5) hold here practically always with slight modifications and the results will be stated without detailing the proofs. For case (I), (9) vanishes whether the atoms  $i$  and  $j$  overlap or not. For case (II), however, (9) becomes negligible provided the two atoms are well resolved; otherwise these terms have to be included. Lastly, for case (III), it will be clear that (9) will always be large since it has been shown to be so even if the atoms do not overlap.

In the case of non-centrosymmetric structures a further condition arises.

(ii) *Non-centrosymmetric case*

For a non-centrosymmetric projection it is easy to show that

$$\frac{\partial |F_c|}{\partial x_i} = \frac{1}{|F_c|} \left( A \frac{\partial A}{\partial x_i} + B \frac{\partial B}{\partial x_i} \right). \quad (10)$$

Making use of the relations,

$$|F_c| \cos \alpha = A, \quad |F_c| \sin \alpha = B, \quad |F_c|^2 = A^2 + B^2, \quad (11)$$

we get

$$\frac{\partial |F_c|}{\partial x_i} = \cos \alpha \left( \frac{\partial A}{\partial x_i} \right) + \sin \alpha \left( \frac{\partial B}{\partial x_i} \right). \quad (12)$$

Taking first the interactions between the different co-ordinates of the same atom, we get the following equation after some manipulation:

Table 1. *Terms to be included in the normal equations of least-squares under various situations in a two dimensional case*

Situations (B) and (D) do not arise in a three dimensional case

Description	(A) No overlap (both centric and non-centric)	(B) Overlap (both centric and non-centric) $\theta_i \simeq \theta_j$	(C) Inverse overlap (non-centric) $\theta_i \simeq 2\alpha - \theta_j$	(D) Inverse overlap (centric) $\theta_i \simeq 0$
	(i) Symmetry orthogonal	$[X_i X_i]$	$[X_i X_i][X_i X_j]$	Same types as for (B)
(ii) Axes orthogonal	$[X_i X_i]$	$[X_i X_i][X_i X_j][X_i Y_j]$		excepting that, now, $j = i'$
(iii) Both non-orthogonal	$[X_i X_i][X_i Y_i]$	$[X_i X_i][X_i Y_i]$ $[X_i X_j][X_i Y_j]$		

$$[X_i Y_i] = \sum_{h,k} \frac{\partial |F_c|}{\partial x_i} \cdot \frac{\partial |F_c|}{\partial y_i} = \sum_{h,k} 4\pi^2 h k f_i^2 \sin^2 (\theta_i - \alpha). \quad (13)$$

This is identical with (4) excepting that  $(\theta_i - \alpha)$  replaces  $\theta_i$ . In fact, all the other expressions below for the non-centrosymmetric case can be obtained by replacing  $\theta_i$  in the corresponding formulae for the centrosymmetric case by  $(\theta_i - \alpha)$ . The detailed derivations are omitted.

It is clear from the nature of the expression (13) that the results obtained while discussing (5) should hold good here also. However, the overlap of an atom with its inverse does not arise here. On the other hand a slightly different form of overlap between different atoms arises in the non-centrosymmetric case as will be shown below.

Considering the  $[X_i X_j]$  interaction, we have,

$$\sum_{h,k} \frac{\partial |F_c|}{\partial x_i} \frac{\partial |F_c|}{\partial x_j} = \sum_{h,k} 2\pi^2 h^2 f_i f_j \times \{\cos (\theta_i - \theta_j) - \cos (\theta_i + \theta_j - 2\alpha)\}. \quad (14)$$

This expression with  $\alpha = 0$  or  $\pi$  agrees with equation (8) of the centrosymmetric case as obviously it should. Now the above sum (14) will be large if, for various values of  $h, k$ ,

- (a)  $(\theta_i - \theta_j) \simeq 0$ ,
- (b)  $(\theta_i + \theta_j) \simeq 2\alpha$ .

The first condition leads to the case of overlap between atoms  $i$  and  $j$  discussed already in connection with the centrosymmetric case. The second condition shows that when  $(\theta_i + \theta_j) \simeq 2\alpha$  each term in (14) will have a large value and hence the sum will also be large. In general,  $\alpha$  will be highly variable (0 to  $2\pi$ ) so that the condition  $(\theta_i + \theta_j) \simeq 2\alpha$  will be satisfied only very rarely for certain reflections.

But suppose the structure contains a group of heavy atoms which is centrosymmetric, though the structure as a whole is non-centrosymmetric. Suppose also that the origin is chosen at the point of inversion of the centrosymmetric group. The majority of reflections will have their phases ( $\alpha$ ) close to 0 or  $\pi$ , depending on  $\alpha_H$ . Hence for these reflections  $2\alpha \simeq 0$ . The second condition,  $(\theta_i + \theta_j) \simeq 2\alpha$ , now reduces to  $(\theta_i + \theta_j) \simeq 0$ . This could now be satisfied for all these reflections provided that an atom  $i$  is related to another atom  $j$  by the relation  $\theta_i \simeq -\theta_j$ . Consequently, the second term in (14) will have a large value. The condition  $\theta_i \simeq -\theta_j$  is equivalent to saying that the atoms  $i$  and  $j$  are related to each other by an inversion at the centre of symmetry of the centrosymmetric group.

Although we have proved this result taking the origin at the centre of inversion of the heavy atoms, it is true whatever be the choice of the origin. Thus, during the refinement of an atom  $i$  in a structure containing heavy atoms, or group of atoms which are centrosymmetric, though the structure as a whole is non-centrosymmetric, the interaction of the atom  $i$

with another atom  $j$  which may be accidentally related to it by inversion at the centre of symmetry of the heavy atoms (or the centrosymmetric group) will have to be taken into account. By analogy with the usual notion of 'overlap' the above situation may be called the 'inverse overlap'.

The interaction of the type  $[X_i Y_j]$  does not require special treatment. It is in fact similar to the corresponding type in the centrosymmetric case (equation (9)), the only difference being that we have to consider the possible inverse overlaps along with the usual ordinary overlap.

### 3. Refinement of thermal parameters

These results pertain only to the refinement of the positional parameters. Strictly speaking each atom has also six thermal parameters, which correspond to the possible anisotropic vibration of an atom, in the most general case of a triclinic crystal. We shall, however, consider a case where the anisotropic thermal parameters are applied to the whole structure factor, which would occur when all the atoms have identically the same thermal parameters. This assumption is purely for convenience of mathematical manipulations and it will be obvious that the discussion to be given below will be equally applicable for the refinement of the thermal parameters of individual atoms.

Now we can write

$$\left. \begin{aligned} F_c(hkl) &= F_c'(hkl) \exp - [B_{11}h^2 + B_{22}k^2 + B_{33}l^2 \\ &\quad + 2B_{12}hk + 2B_{23}kl + 2B_{13}hl] \\ F_c' &= \sum_j f_j^0 \exp 2\pi i(hx_j + ky_j + ly_j), \end{aligned} \right\} \quad (15)$$

where  $B_{11}$ ,  $B_{12}$ , etc., denote the overall anisotropic thermal parameters and  $f_j^0$  corresponds to the scattering factor without application of the temperature factor. The initial values of  $B_{11}$ ,  $B_{12}$ , etc., can be found from the usual isotropic temperature factor by the relation

$$B_{ij} = \frac{1}{4} B a_i^* \cdot a_j^*, \quad (16)$$

where  $a_i^*$  ( $i = 1$  to 3) are the reciprocal vectors. We have to include now the refinement of these parameters  $B_{ij}$  also in the normal equations (1). For convenience, let  $X$  denote any positional parameter, and  $T$  denote any thermal parameter. The normal equations for the positional parameters will contain  $[XX]$  and  $[XT]$  types of interactions while those for thermal parameters will contain  $[TX]$  and  $[TT]$  types. Of these, the  $[XX]$  type has already been considered in section 2.

Consider now an  $[XT]$  type of interaction. We get from (15)

$$\frac{\partial F_c}{\partial B_{11}} = -h^2 F_c, \quad \frac{\partial F_c}{\partial B_{12}} = -hk F_c \text{ etc.} \quad (17)$$

Hence for a typical  $[XT]$  interaction we have

$$\sum_s \frac{\partial F_c}{\partial B_{11}} \frac{\partial F_c}{\partial x_i} = \sum_s 2\pi h^3 f_i F_c \sin \theta_i, \quad (18)$$

where the suffix  $s$  denotes summation over all reflections  $hkl$ . Now  $\sin \theta_i$ ,  $h^3$  and  $F_c$  can all be as often positive as negative and therefore the sum (18) will, in general, be negligible. The result will be found to hold good for any type of  $[XT]$  interaction. *The above result shows that the refinement of positional and thermal parameters can be treated independently.*

Considering now the thermal parameters alone we may write the normal equations as

$$\sum_s (F_o - F_c) \frac{\partial F_c}{\partial B_{ij}} = \sum_s \sum_{p,q} \left( \frac{\partial F_c}{\partial B_{ij}} \right) \left( \frac{\partial F_c}{\partial B_{pq}} \right) \Delta B_{pq} \quad (i, j, p, q = 1 \text{ to } 3; j > i, q > p). \quad (19)$$

The terms in (19) fall under three categories which are of the types

$$[B_{11}B_{11}] = \sum_s \left( \frac{\partial F_c}{\partial B_{11}} \right)^2 = \sum_s h^4 F_c^2 \quad (20)$$

$$[B_{11}B_{22}] = \sum_s \left( \frac{\partial F_c}{\partial B_{11}} \right) \left( \frac{\partial F_c}{\partial B_{22}} \right) = \sum_s h^2 k^2 F_c^2 \quad (21)$$

$$[B_{11}B_{13}] = \sum_s \left( \frac{\partial F_c}{\partial B_{11}} \right) \left( \frac{\partial F_c}{\partial B_{13}} \right) = \sum_s hl h^2 F_c^2. \quad (22)$$

Since all the quantities,  $h^2$ ,  $k^2$  and  $F_c^2$  occurring in (21) are positive the sum (21) is comparable in magnitude to the term  $[B_{11}B_{11}]$  given by (20). On the other hand, in (22), the term  $hl$  occurs which can take both positive and negative values. It will be obvious that if the  $a$  and  $c$  axes are not orthogonal, then the sum (22) will not be negligible (see case (III) under equation (5)). A similar result also holds for other cross terms of the type (22), namely that they are not negligible if the corresponding axes are non-orthogonal.

Even if the axes  $a$  and  $c$  are orthogonal, but the symmetry is not, the sum (22) is not negligible since the only equality for the structure factors is  $|F_c(hkl)|^2 = |F_c(\bar{h}\bar{k}\bar{l})|^2$  for both of which  $hl$  is the same and no cancellation occurs. However, if the symmetry is orthogonal we may adopt the method described in section 2 of grouping terms of the type  $hl$  and  $h\bar{l}$  (for a fixed  $k$ ) and the sum (22) will then be seen to vanish. Obviously the term  $B_{13}$  itself does not exist. From this it will be clear that, for a triclinic crystal, the refinement of the six possible thermal parameters

Table 2. *Terms to be included in the refinement of anisotropic thermal parameters for different symmetries*

System	Types of terms
Triclinic	$[B_{ii}B_{jj}]$ and $[B_{ii}B_{jk}]$
Monoclinic	$[B_{ii}B_{jj}]$ and $[B_{ii}B_{13}]$ ( $b$ axis unique)
Orthorhombic	$[B_{ii}B_{jj}]$
Higher symmetries	Same as orthorhombic, but equalities like $B_{11} = B_{22}$ etc., to be noted

consists in solving the six simultaneous equations (19). In the monoclinic system the number of equations reduces to four while in orthogonal systems there will be a maximum of three. All the non-vanishing parameters which have to be refined together are listed in Table 2.

#### 4. Discussion

The various results obtained for the refinement of positional parameters are summarized in Table 1. In general, the problems in a non-centrosymmetric structure are very similar to those in a centrosymmetric structure and Table 1 can be used for both. They may be classified as follows.

- All the atoms are well resolved.
- Atoms, say  $i$  and  $j$  overlap.
- Atom  $i$  overlaps with its inverse  $i'$  (centrosymmetric projection).
- Atom  $i$  is related to another atom  $j$  by  $\theta_i \simeq -\theta_j$  (non-centrosymmetric case).

The situation (a) is common to both three and two dimensions. However, the overlap of atoms (b) does not arise in three dimensions, because the minimum separation required for resolution, which has been shown to be  $\lambda/2$ , is much less than the usual interatomic distances. But in two-dimensional projections overlap of atoms can occur. Situation (c), obviously, can arise only in a two-dimensional centrosymmetric case. However, the last one, (d), can occur both in three dimensions and in a two-dimensional projection of a non-centrosymmetric structure. Its occurrence in three dimensions is important because inverse overlap can occur.

It is clear that, even if a structure does not contain heavy atoms, if it contains a centrosymmetric group of atoms which contributes predominantly to the structure factor, the above discussions will still apply. Such cases are likely to occur in structures of compounds which contain a benzene ring and other types of highly symmetrical molecules and crystallize in non-centrosymmetric space groups.

As regards the refinement of thermal parameters it is clear from the last section that the linear approximation formula (2) does not hold good and all the terms like  $[B_{11}B_{22}]$  and  $[B_{11}B_{23}]$  have to be included in solving the normal equations of refinement of these parameters.

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#### Reference

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