HARDGROVE, G. L. & TEMPLETON, D. H. (1959). *Acta Cryst.* **12**, 28.

HOCK, A. A. & MILLS, O. S. (1958). *Proc. Chem. Soc.* p. 233.

MILLS, O. S. (1958). *Acta Cryst.* **11**, 620.

MILLS, O. S., HOCK, A. A. & ROBINSON, G. (1959). XVIIth Intern. Congr. Pure and Appl. Chem., Munich. (Abstr. A, 143).

MILLS, O. S. & ROBINSON, G. (1959). *Proc. Chem. Soc.* p. 156.

POWELL, H. M. & EWENS, R. V. G. (1939). *J. Chem. Soc.* p. 286.

REPPE, W. & VETTER, H. (1953). *Ann. Chem.* **582**, 133.

SLY, W. G. (1959). *J. Amer. Chem. Soc.* **81**, 18.

STERNBERG, H. W., MARKBY, R. & WENDER, I. (1956). *J. Amer. Chem. Soc.* **78**, 3621.

STERNBERG, H. W., MARKBY, R. & WENDER, I. (1958). *J. Amer. Chem. Soc.* **80**, 1009.

WILSON, F. C. & SHOEMAKER, D. P. (1957). *J. Chem. Phys.* **27**, 809.

Syntheses for the Deconvolution of the Patterson Function. Part III: Theory for Centrosymmetric Crystals

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This part deals with the syntheses for the deconvolution of the Patterson function when the structure is centrosymmetric. The interesting result is obtained that the isomorphous β-synthesis gives just the structure with no background at all.

1. Introduction

In Parts I and II (Ramachandran & Raman, 1959) of this series of papers, three classes of Fourier syntheses were proposed, which can be used when part of the structure is known for the determination of the remaining atoms in the structure. In Part II, the theory was fully worked out for the case of a non-centrosymmetric crystal. It is the purpose of the present paper to extend the theory to the case of a centrosymmetric crystal.

Let us suppose that the unit cell of the crystal contains N atoms. It is convenient to take $N = 2n$ in view of the centrosymmetry. The structure is then given by atoms of strength f_j at $\pm \mathbf{r}_j$ where $j = 1$ to $n (= N/2)$.

Let us next investigate the nature of the Fourier synthesis calculated with the product $F_P F_Q$ as the coefficient where F_P and F_Q refer to the structure factors of two centrosymmetric structures, P and Q respectively. Let f_{pi} denote the strengths of the equivalent atoms at $\pm \mathbf{r}_{pi}$.† In working out the modulation of the two structures P and Q, it is convenient to divide each of them into its two non-equivalent parts, whose structure factors may be denoted by F_P, $F_{P'}$, F_Q, $F_{Q'}$ respectively. Then,

$$F_P F_Q = (F_P + F_{P'})(F_Q + F_{Q'})$$
$$= F_P F_Q + F_P F_{Q'} + F_{P'} F_Q + F_{P'} F_{Q'} . \quad (1)$$

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† The symbols p, q are the number of atoms of type P and Q in the asymmetric unit. The symbols P and Q agree with those in the earlier part, being the total number of atoms of each type. Clearly, $P = 2p$, $Q = 2q$.

Applying the principle of modulation (Raman, 1959), the peaks in the resultant structure are obtained as follows:

$$f_{pi}f_{qj} \text{ at } \pm(\mathbf{r}_{pi}+\mathbf{r}_{qj}) \;\;\} \;\; i=1 \text{ to } p \;(=P/2)$$
$$f_{pi}f_{qj} \text{ at } \pm(\mathbf{r}_{pi}-\mathbf{r}_{qj}) \;\;\} \;\; j=1 \text{ to } q \;(=Q/2) .$$

The peaks therefore correspond to sums and differences of vectors of the atoms p_i, q_j and their inverses. This particular property of the resultant structure plays an important part in the interpretation of the Patterson diagram in centrosymmetric crystals, as we shall see below.

2. The Patterson function and the squared structure

It is interesting to note that the Patterson function and the squared structure become identical, when a structure is centrosymmetric. The reason for this is that a centrosymmetric structure is identical with its inverse, so that the structure factor F_N is the same as its complex conjugate F_N^*. It follows that the Patterson function becomes identical with the squared structure. It suffices therefore to study the properties of either one. Interpreting the Patterson function of a centrosymmetric structure as the modulation of the structure with itself we get the following peaks:

a strong peak $\sum\limits_{1}^{N} f_{Nj}^2$ at the origin,

$N(=2n)$ peaks of strength f_{nj}^2 at $\pm 2r_{nj}$ these referring to the interatomic vectors between equivalent atoms related by inversion and

$\frac{1}{4}(N^2-2N)$ peaks of strength $2f_{ni}f_{nj}$ at $\pm(\mathbf{r}_{ni}-\mathbf{r}_{nj})$ and an equivalent set of $\frac{1}{4}(N^2-2N)$ peaks each of strength $2f_{ni}f_{nj}$ at $\pm(\mathbf{r}_{ni}+\mathbf{r}_{nj})$.

The state of affairs may be compared with that in the non-centrosymmetric case where we have a single peak Σf_{Nj}^2 at origin, $\frac{1}{2}(N^2-N)$ peaks at $\mathbf{r}_{ni}-\mathbf{r}_{nj}$ of strength $f_{ni}f_{nj}$ and an equivalent set of $\frac{1}{2}(N^2-N)$ peaks at $\mathbf{r}_{nj}-\mathbf{r}_{ni}$. Thus there are N^2-N+1 peaks when there is no centrosymmetry but only $\frac{1}{2}N^2+1$ peaks when it is present, where N is the number of atoms in the fundamental structure. This brings to light the interesting fact that the number of distinct peaks in the Patterson is much less (nearly halved) if a structure is centrosymmetric than if it is non-centrosymmetric.

3. The 'modulus', the 'phase' and the 'reciprocal' structures

(a) The modulus structure

This is obtained by employing $|F_N|$ as the Fourier coefficient. It is that structure which when modulated by itself yields the Patterson structure. This argument leads to the result that $|F_N|$ structure should consist of the following peaks: A peak of strength $S_N(=\sqrt{(2S_n^2)})$ at the origin, and peaks of strength $f_{ni}^2/2S_N$ at $\pm2\mathbf{r}_{ni}$ and of $2f_{ni}f_{nj}/(2S_N)$ at both $\pm(\mathbf{r}_{ni}+\mathbf{r}_{nj})$ and $\pm(\mathbf{r}_{ni}-\mathbf{r}_{nj})$.

(b) The phase structure

The phase synthesis employs the coefficient $\exp i\alpha_N$ which reduces now to plus or minus unity. The nature of the phase structure can be understood from the fact that the modulation of the phase structure and the modulus structure will yield the direct structure F_N (or its equivalent F_N^*). It will therefore consist of peaks of strength f_{ni}/S_N at $\pm r_{ni}$ and lower order negative peaks $-f_{ni}^2f_{nk}/(2S_N^3)$ at $\pm2\mathbf{r}_{ni}\pm\mathbf{r}_{nk}$ and $-f_{ni}f_{nj}f_{nk}/S_N^3$ at $\pm(\mathbf{r}_{ni}+\mathbf{r}_{nj})\pm r_{nk}$ and at $\pm(\mathbf{r}_{ni}-\mathbf{r}_{nj})\pm r_{nk}$ $(i\neq j\neq k)$.

(c) The reciprocal structure

The reciprocal synthesis employs the coefficient $1/F_N$. In the case of a non-centrosymmetric crystal, it was shown that the reciprocal structure resembles the inverse structure to a first approximation. As centrosymmetry leads to $F_N=F_N^*$ it is natural to expect that the reciprocal of a centrosymmetric structure will resemble the structure itself. Actually, one obtains peaks of strength f_{nj}/S_N^2 at $\pm\mathbf{r}_{nj}$ and second-order negative peaks of strength $f_{ni}^2f_{nj}/S_N^4$ at $\pm2\mathbf{r}_{ni}\pm\mathbf{r}_{nj}$ and $2f_{ni}f_{nj}f_{nk}/S_N^4$ at $\pm(\mathbf{r}_{ni}+\mathbf{r}_{nj})\pm r_{nk}$ and also at $\pm(\mathbf{r}_{ni}-\mathbf{r}_{nj})\pm r_{nk}$.

Using these results we shall now investigate the nature of the various syntheses, α, β and γ. It is proposed to discuss the case of α thoroughly and merely quote the results for the others.

4. The α-class of syntheses

The general type of this class of syntheses employs the Fourier coefficient $\alpha_{gen}=|F_N|^2F_P$, where F_P denotes the contribution of the known part P of the structure. It was shown in Part II (Raman, 1959) that α_{gen} can be expanded as follows:

$$\alpha_{gen}=|F_P|^2F_P+|F_Q|^2F_P+F_P^2F_Q^*+|F_P|^2F_Q . \quad (2)$$
$$\quad\text{I}\qquad\quad\text{II}\qquad\quad\text{III}\qquad\quad\text{IV}$$

In the centrosymmetric case the expression simplifies, in view of the fact that $F_Q^*=F_Q$ and $|F_P|^2=F_P^2$, to

$$\alpha_{gen}=|F_P|^2F_P+|F_Q|^2F_P+2|F_P|^2F_Q . \quad (3)$$
$$\quad\text{I}\qquad\quad\text{II}\qquad\quad\text{III}$$

It is to be noted that terms III and IV of expression (2) (of the non-centrosymmetric case) have combined into a single term in expression (3) (centrosymmetric case). Term I refers to the modulation of the Patterson of P by the structure P, term II to the modulation of the Patterson of Q by the structure of P, and term III to the Patterson of P by the structure of Q. The peaks given by the syntheses and the strengths have been worked out from an application of the principle of modulation and are given in Table 1. The required peaks are 3·1 while the known peaks are 1·1, 2·1 and 1·2. The others are unwanted background peaks.

Table 1. *Peak strength and position*

Designation	Peak strength	Peak position	Nature
1·1	$f_{pi}\Sigma f_{Pj}^2$	$\pm \mathbf{r}_{pi}$	Known atoms
1·2	$f_{pi}f_{Pj}^2$	$\pm2\mathbf{r}_{pj}\pm\mathbf{r}_{pi}$	Known background
1·3	$2f_{pi}f_{pj}f_{pj}$	$\pm\ \mathbf{r}_{pi}\pm(\mathbf{r}_{pj}+\mathbf{r}_{pk})$	Known background
1·4	$2f_{pi}f_{pj}f_{pk}$	$\pm\ \mathbf{r}_{pi}\pm(\mathbf{r}_{pj}-\mathbf{r}_{pk})$	Known background
2·1	$f_{pi}\Sigma f_{Qj}^2$	$\pm\ \mathbf{r}_{pi}$	Known atoms
2·2	$f_{pi}f_{Qj}^2$	$\pm\ \mathbf{r}_{pi}\pm2\mathbf{r}_{qj}$	Unwanted background
2·3	$2f_{pi}f_{qj}f_{qk}$	$\pm\ \mathbf{r}_{pi}\pm(\mathbf{r}_{qj}+\mathbf{r}_{qk})$	Unwanted background
2·4	$2f_{pi}f_{qj}f_{qk}$	$\pm\ \mathbf{r}_{pi}\pm(\mathbf{r}_{qj}-\mathbf{r}_{qk})$	Unwanted background
3·1	$2f_{qi}\Sigma f_{Pj}^2$	$\pm\ \mathbf{r}_{qi}$	Required atoms
3·2	$4f_{qi}f_{pj}f_{pk}$	$\pm\ \mathbf{r}_{qi}\pm(\mathbf{r}_{pj}+\mathbf{r}_{pk})$	Unwanted background
3·3	$4f_{qi}f_{pj}f_{pk}$	$\pm\ \mathbf{r}_{qi}\pm(\mathbf{r}_{pj}-\mathbf{r}_{pk})$	Unwanted background
3·4	$2f_{qi}f_{Pj}^2$	$\pm\ \mathbf{r}_{qi}\pm2\mathbf{r}_{pj}$	Unwanted background

The modified α-synthesis employs the coefficient $\alpha_{\mathrm{mod}} = \{|F_N|^2 - |F_P|^2 - \Sigma f_Q^2\} F_P$ and contains all the peaks of Table 1 with the elimination, however, of the known atoms and the known background, i.e., the peaks 1·1, 1·2, 1·3, 1·4 and 2·1. The isomorphous α-synthesis employs the coefficient

$$\alpha_{\mathrm{is}} = \{|F_N^1|^2 - |F_N^2|^2 - |F_P^1|^2 + |F_P^2|^2\} F_P$$

and gives only the peaks under term III viz., the required peaks 3·1, with only the peaks in 3·2, 3·3 and 3·4 as background. The anomalous α-synthesis does not exist for centrosymmetric structures.

5. The β-class and the γ-class

We will now briefly outline the properties of the other types of syntheses. The β-class of syntheses employs the coefficient $(1/F_P^*)|F_N|^2$ which is the same as $(1/F_P)|F_N|^2$, while the γ-class employs the coefficient $|F_N|^2 \exp i\alpha_P$. (It is to be noted that $\exp i\alpha_P$ is just plus or minus unity in the present case.) The detailed results are not given here to conserve space. The most interesting result is that the isomorphous β-synthesis gives only the structure with no background at all in the case of a centrosymmetric structure. The coefficient β_{is} of equation (37) Part II now reduces to $2F_Q$ since $\exp i2\alpha_P = 1$, and the synthesis gives just the structure alone. The weights are, however, doubled with respect to the non-centrosymmetric case. The anomalous β-synthesis does not exist. The γ-synthesis has properties intermediate between those of α and β.

6. Comparison of centrosymmetric and non-centrosymmetric cases

It is worthwhile to compare the properties of the various syntheses in the centrosymmetric and non-centrosymmetric cases. Two important features emerge in this connection. The first is that the number of distinct background peaks is much less in the centro-symmetric case as compared with that in the non-centrosymmetric case. The reason for this is that the Patterson of the latter contains many fewer peaks than the former. Since the background peaks arise because of the modulation of the non-origin peaks of the Patterson with the peaks of the deconvoluting agent, the background is considerably reduced in the centrosymmetric case. This particular point is best appreciated by considering the β_{is}-synthesis. Whereas with a non-centrosymmetric crystal the above synthesis gives the structure against a small background, for a centro-symmetric crystal it gives just the structure and the background is nil.

The second point to be noted is that the ratio of the strengths of the unknown atoms to known atoms is higher when centrosymmetry is present than when it is not present. This again is due to the fact that all the non-origin peaks of the Patterson, except those at $\pm 2r_j$, are double peaks. An exact result can be obtained in the case of the α-synthesis. Here the ratio works out to be $2S_P^2 f_{Qj}/(S_N^2 + 2S_P'^2) f_{Pj}$ in the centro-symmetric and $S_P^2 f_{Qj}/(S_N^2 + S_P'^2) f_{Pj}$ in the non-centro-symmetric case, which leads to an increase by a factor of 2 when the number of P atoms is small (i.e., $S_P \ll S_N$). In the case of β- and γ-syntheses also there is an increase in the strength, but the exact value is not worked out here. It is found that the value depends on the approximations employed in working out the modulus, phase, reciprocal etc., syntheses. Higher-order approximations are being worked out in this laboratory and these will be presented in a later part.

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References

RAMACHANDRAN, G. N. & RAMAN, S. (1959). *Acta Cryst.* **12**, 957.
RAMAN, S. (1959). *Acta Cryst.* **12**, 964.

Absorption Corrections for Diffraction Measurements from Large Single Crystals

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General expressions are derived for the absorption corrections required in evaluating the intensities of beams diffracted from large crystal blocks.

1. Introduction

An account of the absorption corrections used in evaluating the intensities of beams diffracted from crystal specimens is given in the new edition of Vol. II of the *International Tables for X-ray Crystallography* (1959). Formulae are included for the absorption cor-