Although this involves a lot of labour, the solution thereafter is simple, for the deconvolution of the Patterson (or the autocorrelation function of the structure) is straightforward, using vector shift methods (Buerger, 1951). In fact, if a single peak is present in the Patterson, then even a single shift of the origin to this peak is sufficient to extract the structure, for the coincident peaks would give the structure straightway, but for a duplication by inversion at the midpoint of the shift vector. (A detailed theory of the superposition methods will be presented elsewhere). Chance coincidences can be eliminated by making more than one vector shift, and the same thing holds for the extra coincidences which occur when shifting to a double peak. In any case, if the peak positions are accurately known, then these operations can be made algebraically, and techniques can be developed for mechanising them.

The essential point is that, in this technique, one deals directly with the intensity data and considers them as the structure amplitudes of the 'Patterson structure' (see Part II). One then uses the usual methods of Fourier and least squares refinements for obtaining the 'peaks' $\mathbf{p}_k$ in this structure. The number and relative heights of these peaks are known beforehand. Thereafter, using the relation that $\mathbf{p}_k=\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, the Patterson structure is analyzed for the crystal structure. This last part is facilitated by making use of vector shift methods. This approach eliminates all need for phase determination by trial and error or other auxiliary techniques. It makes use only of the information regarding the contents of the unit cell, namely, the number and types of atoms occurring in the repeating unit, and the intensity data.

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Syntheses for the Deconvolution of the Patterson Function. Part II. Detailed Theory for Non-Centrosymmetric Crystals

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This part contains the more detailed mathematical portion of theory discussed in Part I. First, the significance of various syntheses using as coefficients F, $|F|^2$, F^2, $|F|$, $\exp[i\alpha]$, $\exp[2i\alpha]$, $1/F$, $|F|\exp[i(\pi-\alpha)]$ and also products of the type F_1F_2, where F_1 and F_2 are the structure amplitudes of two portions of a structure, is discussed. It is then used to work out the positions and strengths of the peaks in the different types of alpha and beta syntheses. The new syntheses are also compared with the known types of syntheses, such as the 'heavy atom-phased synthesis'. The main theoretical results have been verified by detailed numerical computation made with a hypothetical non-centric structure containing 6 atoms.

1. Introduction

In Part I, the general principles involved in the alpha- and the beta-types of syntheses were discussed, and it was shown how it is possible to obtain more information about a crystal structure, if a part of it (viz. the positions of some of the atoms) is known, making use of intensity data alone. In the alpha type of syntheses, a suitable function of the measured intensity is *multiplied* by the structure factor of the known atoms for the same reflection and the resulting quantity is used as the coefficient in a Fourier synthesis. In the beta syntheses, on the other hand, a function of the measured intensity is *divided* by the complex conjugate of the structure factor of the known atoms and then used as a coefficient in the Fourier syntheses. In this paper, the detailed theory of these syntheses is worked out and the proofs of the various statements made in Part I are given. The theoretical results have been verified by means of numerical calculation in the case of hypothetical two-dimensional model structures, which is presented in the last section.

2. Basic definitions

(*a*) *A structure*: F_N

The notation generally follows that in Part I. We consider a crystal containing N atoms in the unit cell, with position vectors $\mathbf{r}_{Nj}$ and scattering powers f_{Nj}. The double subscript Nj implies that the suffix j assumes all values from 1 to N; thus if the suffix Pj is used, j goes from 1 to P and so on. The structure factor of the reflection hkl whose reciprocal vector is $\mathbf{H}$ is given by

$$F_N = \sum_{j=1}^{N} f_{Nj} \exp 2\pi i \mathbf{H}.\mathbf{r}_{Nj} \qquad (1)$$

where

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \qquad (2)$$

and

$$\mathbf{r}_{Nj} = x_{Nj}\mathbf{a} + y_{Nj}\mathbf{b} + z_{Nj}\mathbf{c} \qquad (3)$$

where x_{Nj}, y_{Nj}, z_{Nj} are the fractional coordinates of atom j and $\mathbf{a}, \mathbf{b}, \mathbf{c}$, and $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ are the real and reciprocal lattice vectors respectively.

It is well known from Fourier transform theory that the electron-density distribution function in the crystal structure can be developed as a triple Fourier series whose coefficients are the structure factors $F_N(\mathbf{H})$. Thus, a set of structure factors F_N defines a crystal structure of N atoms, and so the latter structure may be identified with the structure factors themselves, and may be called 'the structure F_N'.

Now, suppose we divide the N atoms into two groups containing P and Q atoms respectively, and suppose that F_P and F_Q are the structure factors (both in magnitude and phase) of the two parts, then we have the algebraic equation

$$F_N = F_P + F_Q\,. \qquad (4)$$

It is obvious that the following equation also holds:

$$\text{Structure } F_N = \text{structure } F_P + \text{structure } F_Q\,. \qquad (5)$$

This is true mathematically because of the linear property of the Fourier transform. Physically also, it is obvious, because the Fourier syntheses using F_P and F_Q as coefficients would lead to the P- and Q-group of atoms, and if the two functions are superposed, all the N atoms would be obtained.

(*b*) *Inverse structure*: F_N^*

The inverse structure is defined to be the structure obtained by using the complex conjugate of F_N in the Fourier synthesis. Clearly, if F_N is given by equation (1) then

$$F_N^* = \sum_{j=1}^{N} f_{Nj}^* \exp -2\pi i \mathbf{H}.\mathbf{r}$$
$$= \sum_{j=1}^{N} f_{Nj} \exp 2\pi i \mathbf{H}.(-\mathbf{r}), \quad \text{if } f \text{ is real.} \qquad (6)$$

A complex scattering factor f arises only in the case of anomalous scatterers. Leaving out this case, it follows that F_N^* is the structure amplitude of a group of N atoms having the same scattering factors as the original structure F_N, but occurring at positions related to it by inversion at the origin. We shall call this structure the 'inverse structure' and it is obvious that it is the 'structure F_N^*', namely what would be obtained if F_N^* is used as coefficient in a Fourier synthesis.

(*c*) *Modulation of structures* F_P *and* F_Q: F_PF_Q

The modulation of one structure F_P by another structure F_Q is that structure which is obtained by using the product F_PF_Q as the coefficient in the Fourier synthesis. The former consists of P atoms, f_{Pj} at $\mathbf{r}_{Pj}$ and the latter consists of Q atoms f_{Qj} at $\mathbf{r}_{Qj}$. The product F_PF_Q is obviously given by

$$F_PF_Q = \sum_{i=1}^{P} \sum_{j=1}^{Q} f_{Pi} f_{Qj} \exp 2\pi i \mathbf{H}.(\mathbf{r}_{Pi} + \mathbf{r}_{Qj})\,. \qquad (7)$$

It is the same as the structure factor of a crystal whose unit cell consists of PQ atoms each of strength $f_{Pi}f_{Qj}$ occurring at $\mathbf{r}_{Pi}+\mathbf{r}_{Qj}$. This is what would be obtained if F_PF_Q is used as coefficient in a Fourier synthesis. Thus the modulation of two structures is an interesting type of multiplication in which the scattering powers have to be multiplied and the coordinates have to be added.

(*d*) *Patterson of a structure*: $|F_N|^2$

The Patterson of a structure F_N is the modulation of the structure by its inverse. Thus the Patterson is given by the coefficients

$$|F_N|^2 = F_NF_N^* = \sum_i \sum_j f_{Ni} f_{Nj}^* \exp 2\pi i \mathbf{H}.(\mathbf{r}_{Ni} - \mathbf{r}_{Nj})$$
$$= \sum_i f_{Ni}^2 + \sum_{\substack{i \\ i \neq j}} \sum_j f_{Ni} f_{Nj} \exp 2\pi i \mathbf{H}.(\mathbf{r}_{Ni} - \mathbf{r}_{Nj})\,. \qquad (8)$$

This equation shows that the Patterson function contains a single peak of weight Σf_{Ni}^2 obtained from the coincidence of the N vectors $\mathbf{r}_i - \mathbf{r}_j$ of the type $i=j$. The remaining (N^2-N) peaks of the type $i \neq j$ fall under two groups, each containing $\frac{1}{2}(N^2-N)$ peaks. These are at $(\mathbf{r}_{Ni}-\mathbf{r}_{Nj})$ with respect to the single peak, Σf_{Ni}^2, which constitutes the origin of the Patterson function. Thus the two groups are related by inversion about the origin of the Patterson.

(*e*) *Squared structure*: F_N^2

The squared structure is the modulation of a structure by itself and its Fourier coefficients are given by

$$F_N^2 = \sum_i \sum_j f_{Ni} f_{Nj} \exp 2\pi i \mathbf{H}.(\mathbf{r}_{Ni} + \mathbf{r}_{Nj})$$
$$= \sum_i f_{Ni}^2 \exp 2\pi i \mathbf{H}.2\mathbf{r}_{Ni} + \sum_{\substack{i \\ i \neq j}} \sum_j 2 f_{Ni} f_{Nj}$$
$$\times \exp 2\pi i \mathbf{H}.(\mathbf{r}_{Ni} + \mathbf{r}_{Nj})\,. \qquad (9)$$

This equation shows that the squared structure consists of N peaks, each of weight f_{Ni}^2 at $2\mathbf{r}_{Ni}$ and $\frac{1}{2}(N^2-N)$ peaks, each of weight

$$2f_{Ni}f_{Nj} \quad \text{at} \quad \mathbf{r}_{Ni}+\mathbf{r}_{Nj}\,, \qquad (i \neq j)\,.$$

(*f*). *Modulus structure*: $|F_N|$

The complete theory of the structure whose structure factor is equal to the modulus of F_N is rather difficult to work out. An approximate theory (given in Appendix I) shows that it must be quite similar to the Patterson diagram, i.e., structure $|F_N|^2$. It may be expected to give a peak of weight $(\Sigma f_{Nk}^2)^{1/2}$ at the origin and (N^2-N) peaks of weight

$$\tfrac{1}{2}f_{Ni}f_{Nj}/(\Sigma f_{Nk}^2)^{1/2} \quad \text{at} \quad \mathbf{r}_{Ni}-\mathbf{r}_{Nj}, \qquad (i \neq j)\,,$$

these being centrosymmetrically disposed about the single peak at the origin.

(*g*) *The phase-structure*: $\exp\,[i\alpha_N]$

The nature of the Fourier synthesis calculated with just the phase term $\exp\,[i\alpha_N]$ as the coefficient is also not fully known. An approximate theory (see Appendix II) shows that it must consist of N positive peaks, each of strength $f_{Ni}/(\Sigma f_{Nl}^2)^{1/2}$ at $\mathbf{r}_{Ni}$, i.e. at the atomic positions of the structure F_N, and second order negative peaks of strength

$$-\tfrac{1}{2}f_{Ni}f_{Nj}f_{Nk}/(\Sigma f_{Nl}^2)^{3/2} \quad \text{at} \quad \mathbf{r}_{Ni}+\mathbf{r}_{Nj}-\mathbf{r}_{Nk}, \qquad (j \neq k)\,.$$

Thus, the modulus structure would resemble the Patterson, while the phase structure would resemble the Fourier diagram.

(*h*) *The phase-squared structure*: $\exp\,[i2\alpha_N]$

This is the square of the phase structure and is the modulation of $\exp\,[i\alpha_N]$ with itself. It consists of N peaks of weight

$$f_{Ni}^2/\sum_k f_{Nk}^2 \quad \text{at} \quad 2\mathbf{r}_{Ni}$$

and $\frac{1}{2}(N^2-N)$ peaks of weight

$$2f_{Ni}f_{Nj}/\sum_k f_{Nk}^2 \quad \text{at} \quad \mathbf{r}_{Ni}+\mathbf{r}_{Nj}\,, \qquad i \neq j\,.$$

This discussion takes into account only the positive peaks of the phase structure and is approximate.

(*i*) *Reciprocal structure*: $1/F_N$

This structure is obtained by using

$$1/F_N \equiv \exp\,[-i\alpha_N]/|F_N|$$

as the coefficient in the Fourier series. The main peaks can be worked out (see Appendix III). It consists of N positive peaks at $-\mathbf{r}_{Ni}$ (i.e. at positions inverse to the original structure) of strength

$$f_{Ni}/\sum_l f_{Nl}^2$$

and second order negative peaks at

$$-\mathbf{r}_{Ni}-\mathbf{r}_{Nj}+\mathbf{r}_{Nk}\,, \qquad (j \neq k)$$

of strength

$$-f_{Ni}f_{Nj}f_{Nk}/(\sum_l f_{Nl}^2)^2.$$

To the first order, therefore, it resembles the inverse structure.

It follows that the reciprocal inverse structure ($1/F_N^* \equiv \exp\,[i\alpha_N]/|F_N|$) will resemble the original structure to the first order. It would be just the inverse of the reciprocal structure.

(*j*) *Negative inverse structure*: $|F_N|\exp\,[i(\pi-\alpha_N)]$

This is the structure obtained by changing the phases of the structure factors from α to $(\pi-\alpha)$, without changing their magnitudes. From the identity

$$|F|\exp\,[i(\pi-\alpha)] = -|F|\exp\,[-i\alpha] = -F^*,$$

it follows that it would have negative peaks at atomic positions corresponding to the inverse structure, the absolute value of each negative peak in this case being exactly equal to that of the corresponding positive peak in the inverse structure. This justifies the term 'negative inverse structure'. The properties of this synthesis and of its combination with the ordinary Fourier synthesis, leading to the sine synthesis, have been discussed by the author (Raman, 1958) in another connection.

The definitions given above will be used in the succeeding sections in connection with the new Fourier syntheses suggested in this paper for the deconvolution of the Patterson function. We assume, as in Part I, that the positions of P out of the total of N atoms are known, and we wish to find those of the remaining Q atoms. We shall now proceed to consider these syntheses and start with the alpha class of syntheses.

3. The class of alpha-syntheses

(*a*) *The general synthesis*: (α_{gen})

We shall first investigate the nature of the Fourier synthesis employing the product $|F_N|^2F_P$ as coefficients. Since $|F_N|^2 = F_NF_N^*$ and $F_N = F_P+F_Q$, we have

$$\begin{aligned}|F_N|^2 &= (F_P+F_Q)(F_P^*+F_Q^*)\\ &= F_PF_P^*+F_QF_Q^*+F_PF_Q^*+F_P^*F_Q\,. \qquad (11)\end{aligned}$$

Thus,

$$\begin{aligned}\alpha_{\text{gen}} = |F_N|^2F_P = \underset{(1)}{F_P|F_P|^2} + \underset{(2)}{|F_Q|^2F_P}\\ + \underset{(3)}{F_P^2F_Q^*} + \underset{(4)}{|F_P|^2F_Q}\,. \qquad (12)\end{aligned}$$

The coefficient used in α_{gen}, which is the product of $|F_N|^2$ and F_P, thus consists of four terms each one of which is the structure factor of the modulation of two structures. Because of this method of looking at the

Table 1. *List of peaks in the alpha-general synthesis*

Description	No. of peaks	Position	Weight	Designation
Known	P	$\mathbf{r}_{Pj}$	$f_{Pj}\sum_i f^2_{Pi}$	**1.1**
Unwanted	$P(P^2-P)$	$\mathbf{r}_{Pk}+\mathbf{r}_{Pi}-\mathbf{r}_{Pj}$ $(i\neq j)$	$f_{Pi}f_{Pj}f_{Pk}$	**1.2**
Known	P	$\mathbf{r}_{Pj}$	$f_{Pj}\sum_i f^2_{Qi}$	**2.1**
Unwanted	$P(Q^2-Q)$	$\mathbf{r}_{Pk}+\mathbf{r}_{Qi}-\mathbf{r}_{Qj}$ $(i\neq j)$	$f_{Qi}f_{Qj}f_{Pk}$	**2.2**
Unwanted	PQ	$2\mathbf{r}_{Pi}-\mathbf{r}_{Qk}$	$f^2_{Pi}f_{Qk}$	**3.1**
Unwanted	$\frac{1}{2}(P^2-P)Q$	$\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Qk}$ $(i\neq j)$	$2f_{Pi}f_{Pj}f_{Qk}$	**3.2**
Wanted	Q	$\mathbf{r}_{Qk}$	$f_{Qk}\sum_i f^2_{Pi}$	**4.1**
Unwanted	$(P^2-P)Q$	$\mathbf{r}_{Pi}-\mathbf{r}_{Pj}+\mathbf{r}_{Qk}$ $(i\neq j)$	$f_{Pi}f_{Pj}f_{Qk}$	**4.2**

problem, it is possible to write down the various peaks which a Fourier synthesis calculated with α_{gen} as the coefficient will contain. The peaks are listed below in Table 1 those which result from term (**1**) being designated as (**1·1**, **1·2** etc.) and so on.

(*b*) *Modified synthesis*: (α_{mod})

Out of these eight sets of peaks two of which (**1·1**) and (**2·1**) are superposed, only those under (**4·1**) refer to the absolute positions $\mathbf{r}_{Qj}$ of the Q unknown atoms. They are the only wanted peaks, while all the others are unwanted. The unwanted background can be considerably reduced by modifying the coefficient α_{gen} and calculating the synthesis employing the coefficient:

$$\alpha_{\text{mod}}=\left(|F_N|^2-|F_P|^2-\sum_{j=1}^{Q}f^2_{Qj}\right)|F_P|\exp i\alpha_P\,. \quad (13)$$

This modification is possible even in the most general case because $|F_P|$ is a known quantity when the positions of the P atoms are known and

$$\sum_j f^2_{Qj}$$

is only the sum over the square of the scattering powers of the Q unknown atoms. This modified coefficient may be expressed in the form

$$\alpha_{\text{mod}}=\underbrace{\left[\sum_{\substack{i\\i\neq j}}\sum_{j}f_{Qi}f_{Qj}\exp 2\pi i\mathbf{H}.(\mathbf{r}_{Qi}-\mathbf{r}_{Qj})\right]F_P}_{(2\cdot2)}+\underbrace{F^2_PF^*_Q}_{(3)}+\underbrace{|F_P|^2F_Q}_{(4)}\,. \quad (14)$$

The synthesis will thus give only the peaks **2·2**, **3·1**, **3·2**, **4·1** and **4·2** and will have less of a background than the alpha-general synthesis. In particular, the peaks at the positions of the known atoms will be suppressed.

(*c*) *Isomorphous alpha-synthesis*: (α_{is})

Further reduction of the background is possible if a pair of isomorphous crystals are available. Let us consider the case when there are two crystals, 1 and 2 say. The difference between the two crystals is that a group of P atoms in crystal 1 has been isomorphously replaced by a group of P others in 2. Let $F_N^{(1)}$ and $F_N^{(2)}$ be the structure factors of the corresponding reflections hkl of the two crystals, and let $F_P^{(1)}$ and $F_P^{(2)}$ be the contribution from the group of P replaceable atoms in each case. Then it is possible to derive the quantity $(F_PF^*_Q+F_QF^*_P)$ alone from the intensity-differences of the two crystals, provided the positions of the replaceable atoms are known. This follows from the following consideration:

Since $F_N^{(1)}=F_P^{(1)}+F_Q$,

$$|F_N^{(1)}|^2=|F_P^{(1)}|^2+|F_Q|^2+F_P^{(1)}F^*_Q+F_P^{(1)*}F_Q\,. \quad (15)$$

Also, from $F_N^{(2)}=F_P^{(2)}+F_Q$,

$$|F_N^{(2)}|^2=|F_P^{(2)}|^2+|F_Q|^2+F_P^{(2)}F^*_Q+F_P^{(2)*}F_Q\,. \quad (16)$$

Hence,

$$|F_N^{(1)}|^2-|F_N^{(2)}|^2=|F_P^{(1)}|^2-|F_P^{(2)}|^2+(F_P^{(1)}-F_P^{(2)})F^*_Q+(F_P^{(1)}-F_P^{(2)})^*F_Q\,. \quad (17)$$

Let us denote by F_P the contribution $F_P^{(1)}-F_P^{(2)}$, the difference between those from the replaceable atoms of the two crystals. Then it is obvious from (17) that

$$|F_N^{(1)}|^2-|F_N^{(2)}|^2-(|F_P^{(1)}|^2-|F_P^{(2)}|^2)=F_PF^*_Q+F^*_PF_Q\,. \quad (18)$$

Thus the quantity on the right hand side can be obtained from an experimental measurement of

$$|F_N^{(1)}|^2 \quad\text{and}\quad |F_N^{(2)}|^2$$

provided the positions of the replaceable atoms (P) are known, so that $|F_P^{(1)}|^2$ and $|F_P^{(2)}|^2$ can be calculated.

One can then calculate the α_{is} synthesis using the coefficient

$$\alpha_{\mathrm{is}}=\{(|F_N^{(1)}|^2-|F_N^{(2)}|^2)-(|F_P^{(1)}|^2-|F_P^{(2)}|^2)\}F_P\,, \quad (19)$$

which can be obtained from the intensity data of the two crystals.

The positions of the peaks in this synthesis may be obtained by using the right hand side of equation (18) from which it follows that the coefficient is

$$\alpha_{\mathrm{is}}=\underset{(3)}{F_P^2F_Q^*}+\underset{(4)}{|F_P|^2F_Q}\,. \quad (20)$$

As indicated in equation (20) this would lead only to the peaks of the type **3·1**, **3·2**, **4·1**, and **4·2** listed in Table 1. The relative strengths are, however, slightly different from what is given in Table 1. The difference is that instead of f_{Pj} one has to use the difference $(f_{Pj}^{(1)}-f_{Pj}^{(2)})$. The wanted peaks **4·1** are thus obtained against a background of **3·1**, **3·2**, and **4·2** only.

It must be noted that in the case of an isomorphous pair, even the predetermination of the positions of the P atoms is rendered easy. It can be done either from a study of the Difference-Patterson diagram (Kartha & Ramachandran, 1955) or by using the synthesis employing the coefficient $(|F_N^{(1)}|-|F_N^{(2)}|)^2$, as suggested by Perutz (1956), for centrosymmetric crystals. For non-centrosymmetric crystals also, this synthesis is likely to work, as has been recently shown in this laboratory (unpublished).

(*d*) *Anomalous alpha-synthesis*: (α_{an})

A more favourable case occurs when the known P atoms become anomalous scatterers, that is to say, have complex atomic scattering factors f_{Pj}. A complex atomic scattering factor can be obtained by choosing a radiation whose wavelength lies on the short wavelength side of the absorption edge of the atoms P. It is well known that the effect of a complex atomic scattering factor is to make the intensities of the pairs of inverse reflections hkl and $\bar{h}\bar{k}\bar{l}$ unequal and introduce a certain difference, say $\Delta|F|^2$, between them. The latter is a quantity that can be measured experimentally. If the positions and nature of the anomalous scatterers are known, then it is possible to calculate the anomalous imaginary vector F_P'', which is the contribution from the imaginary component $i\Delta f_{Pj}''$ of the atomic scattering powers of the P atoms. The formula is

$$F_P''=i\sum_j \Delta f_{Pj}''\exp 2\pi i\mathbf{H}.\mathbf{r}_{Pj}\,. \quad (21)$$

It is, therefore, possible to calculate a synthesis (the alpha-anomalous synthesis) with the coefficient

$$\alpha_{\mathrm{an}}=\{\tfrac{1}{2}\Delta|F_N|^2-(F_P'F_P''^*+F_P'^*F_P'')\}F_P''\,. \quad (22)$$

To understand the nature of this synthesis, let us suppose, as before, that F_Q is the contribution from the remaining Q atoms and that F_P' is the contribution from the real part of the atomic scattering powers of the P atoms. Then

$$F_N=F_Q+F_P'+F_P'' \quad (23)$$

so that

$$\begin{aligned}|F_N|^2=F_NF_N^*=|F_Q|^2+|F_P'|^2+|F_P''|^2\\ +(F_QF_P'^*+F_Q^*F_P')+(F_P'F_P''^*+F_P''F_P'^*)\\ +(F_QF_P''^*+F_Q^*F_P'')\,. \end{aligned} \quad (24)$$

Denoting by a bar above the corresponding quantities for the inverse reflection, we have

$$\bar{F}_N=\bar{F}_Q+\bar{F}_P'+\bar{F}_P'' \quad (25)$$

so that

$$|\bar{F}_N|^2=(\bar{F}_Q+\bar{F}_P'+\bar{F}_P'')(\bar{F}_Q^*+\bar{F}_P'^*+\bar{F}_P''^*)\,. \quad (26)$$

It is obvious that

$$\bar{F}_Q=F_Q^*,\quad \bar{F}_P'=F_P'^*, \quad (27a)$$

but

$$\bar{F}_P''=-F_P''^*. \quad (27b)$$

Using these relations,

$$\begin{aligned}|\bar{F}_N|^2=|F_Q|^2+|F_P'|^2+|F_P''|^2+(F_QF_P'^*+F_Q^*F_P')\\ -(F_P'F_P''^*+F_P''F_P'^*)-(F_QF_P''^*+F_Q^*F_P'')\,. \end{aligned} \quad (28)$$

Thus,

$$\begin{aligned}\Delta|F_N|^2=|F_N|^2-|\bar{F}_N|^2=2(F_P'F_P''^*+F_P''F_P'^*)\\ +2(F_QF_P''^*+F_Q^*F_P'') \end{aligned} \quad (29)$$

so that

$$\tfrac{1}{2}\{\Delta|F_N|^2-2(F_P'F_P''^*+F_P''F_P'^*)\}=F_QF_P''^*+F_Q^*F_P''\,. \quad (30)$$

The quantity $\Delta|F_N|^2$ can be experimentally measured and the quantity $2(F_P'F_P''^*+F_P'^*F_P'')$ can be obtained by calculation, provided the positions and the scattering powers of the P atoms are known. As was mentioned in Part I, the anomalous scatterers are invariably heavy atoms and so their positions may be obtained from the Patterson itself. Therefore, the left hand side of equation (30) can be obtained. Suppose now, that this is multiplied by F_P'' and the product used as coefficient in a Fourier series, one obtains what might be called the α-anomalous synthesis (α_{an}). The coefficient of this synthesis is given by equation (22). From equation (30) the R.H.S. of this equation is given by

$$\alpha_{\mathrm{an}}=F_P''^2F_Q^*+F_Q|F_P''|^2. \quad (31)$$

Thus the synthesis with α_{an} as coefficient will consist of the modulation of the square structure $F_P''^2$ by the structure F_Q^* plus the modulation of the Patterson $|F_P''|^2$ by the structure F_Q. Now, the structure $F_P''^2$ will consist of P peaks of weight $(-\Delta f_{Pi}''^2)$ at $2\mathbf{r}_{Pi}$ and $\frac{1}{2}(P^2-P)$ peaks of weight

$$-2\Delta f_{Pi}''\Delta f_{Pj}'' \quad \text{at} \quad \mathbf{r}_{Pi}+\mathbf{r}_{Pj} \qquad (i\neq j)\,,$$

while the Patterson $|F_P''|^2$ will consist of a single peak of weight

$$\sum_i \Delta f''^2_{Pi}$$

at the origin and (P^2-P) peaks centrosymmetrically disposed about the origin at $\mathbf{r}_{Pi}-\mathbf{r}_{Pj}$ $(i\neq j)$, their weights being $\Delta f''_{Pi}\Delta f''_{Pj}$.

Therefore the α_{an} synthesis will consist of PQ peaks of weight $-f_{Qj}\Delta f''_{Pi}$ at $2\mathbf{r}_{Pi}-\mathbf{r}_{Qj}$ and $\frac{1}{2}(P^2-P)Q$ peaks of weight

$$-2\Delta f''_{Pi}\Delta f''_{Pj}f_{Qk} \quad \text{at} \quad \mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Qk} \qquad (i\neq j)\,,$$

derived from the first term of (31) and Q (wanted peaks) of weight

$$f_{Qj}\sum_i \Delta f''^2_{Pi} \quad \text{at} \quad \mathbf{r}_{Qj} \text{ plus } (P^2-P)Q$$

peaks (unwanted) of weight

$$f_{Qk}\Delta f''_{Pi}\Delta f''_{Pj} \quad \text{at} \quad \mathbf{r}_{Pi}-\mathbf{r}_{Pj}+\mathbf{r}_{Qk}\,.$$

The positions of the peaks will be seen to be the same as the α_{is}-structure **3·1**, **3·2**, **4·1**, **4·2** of Table 1, but the first two sets are now negative peaks. Thus the α_{an}-synthesis gives the structure Q against a background, which is partly positive and partly negative. Since some of the unwanted peaks are negative, it is easy to distinguish them, and also the general background will be less than in the α_{is}-synthesis.

The particular case in which the P anomalous scatterers are all of the same kind of atom is interesting. In this case, it can be readily shown that $(F'_P F''^*_P + F'^*_P F''_P)$ is zero, so that

$$\alpha_{\text{an}} = \tfrac{1}{2}\Delta|F_N|^2 F''_P\,. \tag{32}$$

4. The class of beta-syntheses

(*a*) *General beta-synthesis*: (β_{gen})

We will now consider the class of β-syntheses, that is, the syntheses of the division technique. In this case, the coefficient of the synthesis is the quotient of $|F_N|^2$ with F^*_P. It is interesting to note at the outset that the very process of division reduces the unwanted background considerably. This follows from the following considerations:

Using equation (11), the coefficient in the β_{gen}-synthesis is

$$\begin{aligned}\beta_{\text{gen}} &= \frac{|F_N|^2}{|F_P|}\exp i\alpha_P = |F_N|^2/F^*_P \\ &= \underset{(5)}{F_P} + \underset{(6)}{|F_Q|^2/F^*_P} + \underset{(7)}{\exp[i2\alpha_P]\,F^*_Q} + \underset{(8)}{F_Q}\end{aligned} \tag{33}$$

The structure given by this synthesis consists of four parts (5) to (8) as in the case of α_{gen}, each of which can be interpreted as a modulation of the different standard structures. The first term (5) of equation (33) leads to the known structure $P(f_{Pj}$ at $\mathbf{r}_{Pj})$ and the last term (8) leads to the required unknown structure $Q(f_{Qj}$ at $\mathbf{r}_{Qj})$. Thus, the unwanted background is produced by the other two terms (6) and (7).

The structure arising from (6) is the modulation of the Patterson of the Q-atoms with the reciprocal inverse of the P atoms. Taking only first order interactions, this would lead to the following peaks

$$f_{Pj}\sum_i f^2_{Qi}\Big/\sum_k f^2_{Pk} \quad \text{at} \quad \mathbf{r}_{Pj} \tag{6·1}$$

$$f_{Pk}f_{Qi}f_{Qj}\Big/\sum_l f^2_{Pl} \quad \text{at} \quad \mathbf{r}_{Pk}+\mathbf{r}_{Qi}-\mathbf{r}_{Qj} \quad (i\neq j) \tag{6·2}$$

$$f_{Pi}f_{Pj}f_{Pk}\sum_l f^2_{Ql}\Big/\Big(\sum_m f^2_{Pm}\Big)^2 \quad \text{at} \quad \mathbf{r}_{Pk}+\mathbf{r}_{Pi}-\mathbf{r}_{Pj} \quad (i\neq j)\,. \tag{6·3}$$

Similarly term (7) would lead to a structure which is a modulation of the phase-squared structure of the P atoms with the inverse of the Q atoms, which would contain the following peaks

$$f^2_{Pi}f_{Qj}\Big/\sum_k f^2_{Pk} \quad \text{at} \quad 2\mathbf{r}_{Pi}-\mathbf{r}_{Qj} \tag{7·1}$$

$$2f_{Pi}f_{Pj}f_{Qk}\Big/\sum_l f^2_{Pl} \quad \text{at} \quad \mathbf{r}_{Pi}+\mathbf{r}_{Pj}-r_{Qk} \quad (i\neq j)\,. \tag{7·2}$$

The number, position, and weight of the various peaks occurring in the β_{gen}-synthesis are given in Table 2, which is similar to Table 1. The last column gives the designation of the corresponding peaks which occur in the same position in the α_{gen}-synthesis. Note that while the positions closely agree in the two

Table 2. *List of peaks in the beta-general synthesis*

No. of peaks	Position	Weight	Designation	Corresponding peak in Table 1
P	$\mathbf{r}_{Pj}$	f_{Pj}	**5.1**	**1.1**
P	$\mathbf{r}_{Pj}$	$f_{Pj}\Sigma f^2_{Qi}/\Sigma f^2_{Pk}$	**6.1**	**2.1**
$P(Q^2-Q)$	$\mathbf{r}_{Pk}+\mathbf{r}_{Qi}-\mathbf{r}_{Qj}$ $(i\neq j)$	$f_{Pk}f_{Qi}f_{Qj}/\Sigma f^2_{Pl}$	**6.2**	**2.2**
$P(P^2-P)$	$\mathbf{r}_{Pk}+\mathbf{r}_{Pi}-\mathbf{r}_{Pj}$ $(i\neq j)$	$\{-f_{Pi}f_{Pj}f_{Pk}\Sigma f^2_{Ql}\}/\Sigma f^2_{Pm}$	**6.3**	**1.2**
PQ	$2\mathbf{r}_{Pi}-\mathbf{r}_{Qk}$	$f^2_{Pi}f_{Qk}/\Sigma f^2_{Pl}$	**7.1**	**3.1**
$(P^2-P)Q$	$\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Qk}$	$2f_{Pi}f_{Pj}f_{Qk}/\Sigma f^2_P$	**7.2**	**3.2**
Q	$\mathbf{r}_{Qk}$	f_{Qk}	**8.1**	**4.1**

cases, the relative weights are in some cases different.

Comparing the β-general with the α-general synthesis, it is seen that the peaks corresponding to **4.2** of α_{gen} are absent in the former. This reduction is a result of the division process used in the β class.

(b) *Modified β-synthesis*: (β_{mod})

Here again, it is unnecessary to evaluate β_{gen} and it is always possible to modify the coefficient as in the α-class and calculate a synthesis with the coefficient β_{mod} given by

$$\beta_{\text{mod}}=(|F_N|^2-|F_P|^2-\Sigma f_{Qj}^2)\exp i\alpha_P/|F_P|\,. \tag{34}$$

The coefficient β_{mod} is equal to

$$\frac{1}{F_P^*}\Bigg\{\underset{(\mathbf{6\cdot 2})}{\sum_{\substack{i \\ i\neq j}}\sum_{j} f_{Qi}f_{Qj}\exp 2\pi i\mathbf{H}.(\mathbf{r}_{Qi}-\mathbf{r}_{Qj})}\Bigg\} + \underset{(7)}{\exp[i2\alpha_P]\,F_Q^*}+\underset{(\mathbf{8})}{F_Q}\,. \tag{35}$$

This equation shows that β_{mod} will give only the unknown atoms Q but will not contain the known atoms P.

(c) *Isomorphous β-synthesis* (β_{is})

In the favourable case of a pair of isomorphous crystals, it is possible to evaluate a synthesis with the coefficient

$$\beta_{\text{is}}=\{(|F_N^{(1)}|^2-|F_N^{(2)}|^2)-(|F_P^{(1)}|^2-|F_P^{(2)}|^2)\}\exp i\alpha_P/|F_P| \tag{36}$$

analogous to the α-isomorphous synthesis.

The coefficient β_{is} is from equation (18) equivalent to

$$\beta_{\text{is}}=F_Q+\exp[i2\alpha_P]\,F_Q^*\,. \tag{37}$$

It is thus obvious that β_{is} gives the structure Q against the background (**7.1**) and (**7.2**) alone, which again is superior to the α_{is}-synthesis, as the peaks (**4.2**) of the latter are suppressed.

(d) *Anomalous β-synthesis* (β_{an})

In the still more favourable case of anomalous scatterers, it is possible to evaluate the synthesis with coefficient β_{an} given by

$$\begin{aligned}\beta_{\text{an}}&=\alpha_{\text{an}}/|F_P''|^2\\ &=\{\tfrac{1}{2}\Delta|F_N|^2-(F_P'F_P''^*+F_P'^*F_P'')\}\exp i\alpha_P''/|F_P''|\,,\end{aligned} \tag{38}$$

which from equation (31) is equivalent to

$$\beta_{\text{an}}=F_Q-\exp[i2\alpha_P'']\,F_Q^*\,. \tag{39}$$

The latter equation shows that β_{an} will give the required structure Q as a set of positive peaks against a background of the type of (7), but which is now negative. The background is now completely negative, the advantage of which is obvious. The unwanted peaks would show themselves up as negative peaks and the possibility of mistaking a strong spurious peak as a structure peak is eliminated. Herein lies the superiority of the β_{an}-synthesis over all the others discussed in this paper.

It is interesting to note that β_{is} and β_{an} are the same as the isomorphous and the anomalous syntheses calculated by using the two possible values of the phase angle obtained in the ambiguous phase-determination by the two techniques, the isomorphous replacement technique, and the anomalous dispersion technique. The former one has been discussed by Bijvoet *et al.* (1954), Harker (1956), and Perutz (1956). The latter one has been developed by Ramachandran & Raman (1956) and Raman (1958).

5. Symmetry of the syntheses

The symmetry of the various syntheses discussed above depends upon the symmetry of the known group of P atoms. The particular case which is of interest is when the structure is non-centrosymmetric, but the group P is centrosymmetric. Then all the syntheses are centrosymmetric and, therefore, give diagrams which involve an artificial centre of inversion. In this case the phase of the contribution α_P from the P-atoms is either 0 or π so that $F_P^2=|F_P|^2$. Consequently the squared structure and the Patterson of the P-group are identical. As a result the following circumstances arise:

(a) *Modified α-synthesis*

Now,

$$\alpha_{\text{mod}}=\Bigg\{\underset{(\mathbf{2\cdot 2})}{\sum_{\substack{i \\ i\neq j}}\sum_{j} f_{Qi}f_{Qj}\exp 2\pi i\mathbf{H}.(\mathbf{r}_{Qi}-\mathbf{r}_{Qj})}\Bigg\}F_P + \underset{(\mathbf{3})}{|F_P|^2F_Q^*}+\underset{(\mathbf{4})}{|F_P|^2F_Q}\,. \tag{40}$$

It is obvious that term (**4**) leads to the required structure of Q atoms and the usual background of $Q(P^2-P)$ peaks at $\mathbf{r}_{Pi}-\mathbf{r}_{Pj}+\mathbf{r}_{Qk}$. The term (**3**) leads to the inverse structure and a background of $Q(P^2-P)$ peaks, but at $\mathbf{r}_{Pj}-\mathbf{r}_{Pi}-\mathbf{r}_{Qk}$. It is obvious that the two sets are related by inversion about the origin of the Patterson, which is the same as the centre of inversion of the group P. The term (**2·2**) will lead to the usual $P(Q^2-Q)$ background peaks, but these are also centric about the origin, whence it is clear that the synthesis will give the structure and a set of unwanted peaks and the entire set will be duplicated by inversion about the inversion-centre of the known group P.

(b) *Isomorphous α-synthesis*

In this case

$$\alpha_{\text{is}}=\underset{(\mathbf{3})}{|F_P|^2F_Q}+\underset{(\mathbf{4})}{|F_P|^2F_Q^*} \tag{41}$$

The discussion is identical with that for the α_{mod}-

synthesis except that now the peaks (**2.2**) will get suppressed.

(*c*) *Anomalous α-synthesis*

In this case, the important point to be noted is that

$$F_P''^2 = -|F_P''|^2 \tag{42}$$

whence,

$$\alpha_{\mathrm{an}} = \underset{(\mathbf{3})}{|F_P''|^2 F_Q} - \underset{(\mathbf{4})}{|F_P''|^2 F_Q^*} \tag{43}$$

It is obvious that (**3**) will lead to the structure Q against a background and (**4**) will lead to the inverse structure and a background. The two sets are related by inversion, but the second set of peaks are all *negative*. Thus, the anomalous α-synthesis gives the structure and a certain background and both are duplicated by an equivalent negative series, the duplication being by inversion at the centre of inversion of the P-group.

(*d*) *Modified β-synthesis*

In this case since $\exp[i\alpha_P] = \pm 1$ and so $\exp[i2\alpha_P] = 1$, the coefficient β_{mod} takes the form

$$\beta_{\mathrm{mod}} = \underset{(\mathbf{6{\cdot}2})}{\frac{1}{F_P} \sum_{i} \sum_{\substack{j \\ i \neq j}} f_{Qi} f_{Qj} \exp 2\pi i \mathbf{H}.(\mathbf{r}_{Qi} - \mathbf{r}_{Qj})} + \underset{(\mathbf{7})}{F_Q} + \underset{(\mathbf{8})}{F_Q^*}. \tag{44}$$

It is obvious that term (**7**) will lead to the required structure of Q atoms, term (**8**) will lead to its inverse structure and term (**6.2**) will lead to a background which again is centrosymmetric about the inversion centre of the P atoms. Thus, the β_{mod} synthesis in this case will give the structure and a certain background, duplicated by inversion at the inversion-centre of the P-group.

(*e*) *Isomorphous β-synthesis*

In this case,

$$\beta_{\mathrm{is}} = F_Q + F_Q^* \tag{45}$$

from which it is clear that β_{is} gives just the structure duplicated by its inverse, there being no background whatsoever. It is interesting to note that when the P-group is centric, the isomorphous β-synthesis gives just the structure and its inverse about the inversion-centre of the P-group. If the P-group is non-centric, the latter set of duplication peaks gets dispersed into a general background.

(*f*) *Anomalous β-synthesis*

In this case,

$$\beta_{\mathrm{an}} = F_Q - F_Q^*. \tag{46}$$

This shows that β_{an} will give the structure duplicated by its inverse, but the latter will be negative in sign. Thus the structure peaks are positive, while the duplication peaks are negative so that the former can be easily distinguished from the latter. Here also it may be noted that when the P-group is non-centric, the duplication peaks get dispersed into a general background.

6. A comparison of the different syntheses

From the above discussion it follows that preference must be given always to the β-type of syntheses, since the background of any β-synthesis is always less than the background of the corresponding α-synthesis.

Among the four types of β-syntheses, the order of preference is β_{an}, β_{is} and then β_{mod}. The superiority of β_{an} consists in its negative background. Because of this, there is no possibility of mistaking an atom at a wrong spurious peak to be a real atom. In the other two syntheses, the background is positive so that it is always possible to mistake a strong spurious peak for a possible atomic site. The chances of such an occurrence are again greater in β_{mod} than in β_{is} because of the larger background.

However, in the absence of either anomalous scatterers or an isomorphous pair of crystals the only course open is to calculate the β_{mod}-synthesis. It is interesting to compare this synthesis with the usual 'heavy-atom' or 'partially phased' synthesis, viz., $|F_N| \exp i\alpha_P$, calculated under similar circumstances. The latter procedure is very common, more so if the P atoms are heavy atoms. It is obvious that this synthesis will be inferior to the β_{mod} synthesis for the reason that it tends to emphasise the known atoms, while the known atoms are suppressed in the β_{mod} synthesis. Thus, the synthesis employing $|F_N| \exp i\alpha_P$ as coefficients will include over and above the peaks of the β_{mod}-synthesis, the known atomic peaks of the type (**1·1**) and (**2·1**) and also (**1·2**).* Of course, it may be possible to remove the peaks (**1·1**) by taking as Fourier coefficients the terms $(|F_N| - |F_P|) \exp i\alpha_P$, but the peaks of the type (**2·1**) and (**1·2**) will still persist. These, however, get eliminated in the β_{mod} synthesis and hence the superiority of the latter over the former.

A certain precaution must, however, be always taken when performing the β-class of syntheses. Since terms contain $1/|F_P|$ as a factor, some of the coefficients become very large when $|F_P| \rightarrow 0$. It is obvious that such terms must be omitted from the Fourier summation, for when $|F_P|$ is small, the phase α_P is indefinite. A small change in the assumed positions of the P atoms would produce a large change in the phase. As a practical proposition it is suggested that all those terms for which $|F_P|$ is less than one-fifth the mean value in that particular range of $(\sin\theta)/\lambda$ be omitted from the β-synthesis summations.

It may be mentioned that a similar difficulty arises

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* The nature of this synthesis will be discussed in full in a later part.

even in the heavy-atom method, where, if the heavy atom contribution tends to zero, the phase is indeterminate, and the corresponding term is best omitted from the partially phased synthesis. No such difficulty occurs with the α-class of syntheses, because of the multiplicative process.

7. Choice of the *P*-group

The success of the methods described here depends on the number and nature of the known atoms. Both classes of syntheses tend to present the unknown atoms with weights enhanced by the factor P over those of the unwanted background peaks. This alone may make it appear that the larger the number of known atoms, the greater are the chances of success. But actually, increase of P results in an undesirable increase in the number of unwanted peaks and therefore in the possibility of some of them coming together and standing out as a strong peak, comparable to a wanted structure peak. Thus the most favourable case is a small group of heavy atoms for the P-group. However, if all the atoms are equal then it may be better to have a small P than a large one. The number of unwanted peaks is small if either P is small, or when P is very large, and is largest when $P=\frac{1}{2}N$. As the latter is impractical one is forced to prefer a small P, say 3 or 4. It is preferable that the syntheses are evaluated in three dimensions so that the number of chance coincidences of the unwanted peaks is reduced.

8. Verification

The above conclusions have been verified with hypothetical two-dimensional model structures. The model proposed consisted of a non-centric disposition of six atoms, all of unit strength. The symmetry of the configuration is that of the space-group $P1$ though the axes have been taken to be equal and orthogonal for the purpose of easy computation. The unit-cell edge was divided into ten equal parts and the atomic coordinates were specified on the basis of this unit, that is, one tenth of the cell, so that the structure factors were all periodic with period 10. The positions of the known (P) and unknown (Q) atoms are given in Table 3. The complex structure factors were evaluated and these were then used to calculate the coefficients of the various syntheses.

At first, the position of the three P atoms were assumed to be known and the isomorphous α-synthesis

Table 3. *Coordinates of the known* (P) *and the unknown* (Q) *atoms in the unit cell*

The numbers given are fractional coordinates, in multiples of 1/10 of the cell edge

Atom	x	y
P-group:		
1	0	0
2	2	4
3	7	5
Q-group:		
4	6	1
5	9	4
6	5	7

Table 4. *Test of the isomorphous α-synthesis*

The calculated values are given at intervals of 0·1 of the unit cell.
The quantities in brackets shown below are the theoretically expected values

$x \backslash y$	0	1	2	3	4	5	6	7	8	9
0	0·02 (0)	0·06 (0)	−0·02 (0)	0·000 (0)	−0·038 (0)	2·00 (2)	1·00 (1)	0·02 (0)	1·02 (1)	0·06 (0)
1	1·03 (1)	−0·10 (0)	1·03 (1)	−0·08 (0)	2·00 (2)	−0·04 (0)	1·00 (1)	0·01 (0)	1·02 (1)	−0·02 (0)
2	0·01 (0)	0·02 (0)	0·97 (1)	−0·04 (0)	−0·03 (0)	−0·08 (0)	−0·04 (0)	0·02 (0)	2·06 (2)	1·02 (1)
3	2·04 (2)	0·06 (0)	−0·01 (0)	1·00 (1)	0·05 (0)	0·00 (0)	1·00 (1)	−0·02 (0)	1·98 (2)	0·10 (0)
4	0·01 (0)	0·02 (0)	2·01 (2)	1·02 (1)	−0·03 (0)	1·00 (1)	0·00 (0)	0·97 (1)	0·06 (0)	1·02 (1)
5	0·03 (0)	−0·06 (0)	−0·01 (0)	1·00 (1)	1·03 (1)	0·00 (0)	1·00 (1)	3·02 (3)	0·02 (0)	−0·02 (0)
6	0·01 (0)	3·02 (3)	−0·03 (0)	2·00 (2)	−0·03 (0)	0·00 (0)	0·00 (0)	0·02 (0)	0·02 (0)	1·06 (1)
7	1·03 (1)	1·06 (1)	−0·01 (0)	−0·04 (0)	−0·01 (0)	−0·04 (0)	0·00 (0)	2·02 (2)	0·02 (0)	0·02 (0)
8	0·01 (0)	1·98 (2)	1·05 (1)	−0·04 (0)	−0·02 (0)	0·96 (0)	0·00 (0)	0·98 (1)	0·06 (0)	0·98 (1)
9	0·03 (0)	0·94 (1)	−0·01 (0)	1·00 (1)	3·00 (3)	0·00 (0)	1·04 (1)	−0·02 (0)	0·02 (0)	0·02 (0)

Table 5. *Test of the isomorphous β-synthesis*

The calculated values are given at intervals of 0·1 of the unit cell. The positions of the Q-atoms are indicated by rings around the corresponding numbers. The theoretically expected spurious peaks are indicated by symbols (*a*) and (*b*), which stand for those listed under (**7.1**) and (**7.2**) respectively in Table 2

$x \backslash y$	0	1	2	3	4	5	6	7	8	9
0	−0·7	−0·4	−1·9	−2·2	−1·7	5·2 (*a*)	−1·5	−0·8	0·3	0·2
1	0·3		−2·0	−0·4	5·2 (*a*)	0·4	3·4 (*b*)	−2·2	0·5	1·2
2	1·2	0·4	−0·3	0·2	0·1	−0·4	−2·0	1·6	3·6 (*b*)	−2·8
3	4·0 (*a*)	0·8	−1·6	−0·6	0·3	0·8	0·6	0·4	4·5 (*b*)	−0·3
4	−0·2	0·9	4·0 (*a*)	1·4	−0·7	−1·2	0·8	1·2	0·2	1·4 (*b*)
5	0·6	1·6	−2·0	2·2 (*b*)	1·6 (*b*)	0·6	2·1 (*b*)	$\boxed{10\cdot4}$	−0·4	−0·1
6	−0·4	$\boxed{11\cdot2}$	0·3	3·2 (*a*)	0·0	−1·6	−1·6	−1·2	−0·4	−1·6
7	−2·4	0·4	0·2	−0·3	−0·5	0·5	1·6	4·0 (*a*)	0·9	−2·0
8	0·8	3·2 (*a*)	1·2	1·0	−0·1	−0·8	−0·4	2·2 (*b*)	−0·4	0·4 (*b*)
9	−1·2	2·4 (*b*)	−2·0	2·4 (*b*)	$\boxed{11\cdot2}$	0·0	−1·6	−0·4	−1·2	−0·3

Table 6. *Modulus synthesis of the Q-atoms*

The peaks corresponding to the Patterson are indicated by rings, the origin peak by a double ring. Note the very low background elsewhere, the more prominent of which is negative. The expected ratio of first order non-origin to origin peak is $\frac{1}{8}$

$x \backslash y$	0	1	2	3	4	5	6	7	8	9
0	$\boxed{\boxed{16}}$	0	0	0	0·2	0·2	0·2	0	0	0
1	−0·4	−0·4	0	−0·4	$\boxed{2\cdot8}$	−0·2	−0·4	−0·4	0	0
2	0	0	0	0·4	0	0	0	0·4	0	−0·4
3	−0·8	0	0	$\boxed{2\cdot4}$	0	0	−0·8	0	0	0
4	0	0·4	0	0	0·4	−0·2	−0·4	$\boxed{2\cdot4}$	0	0
5	0	−0·8	0	−0·4	−0·2	0·2	−0·2	−0·4	0	−0·4
6	0	0	0	$\boxed{2\cdot4}$	−0·4	−0·2	−0·4	0	0	0·4
7	−0·8	0	0	0	−0·8	0	0	$\boxed{2\cdot4}$	0	0
8	0	−0·4	0	0·4	0	0	0	0·4	0	0
9	−0·4	0	0	−0·4	−0·4	−0·2	$\boxed{2\cdot8}$	−0·4	0	−0·4

was calculated. As expected, the synthesis gave the three unknown atoms, each of weight 3 against a background of twenty seven points of weight 1 and nine points of weight 2. The agreement between the numerically calculated and theoretically expected values was exact as regards the weight as well as the positions of the various points. These values are given in Table 4. The deviations in the third significant figure are due to rounding off errors.

Next the isomorphous β-synthesis was calculated. This synthesis gave the three wanted peaks against a much reduced background of eighteen peaks only. The results are shown in Table 5. Theory and calculations agreed only in that there should be three major

Table 7. *Phase synthesis of the Q-atoms*

The peaks at the assumed atomic positions are shown by solid rings. The negative peaks expected from theory are indicated by broken rings. Note the low background elsewhere

$x \backslash y$	0	1	2	3	4	5	6	7	8	9
0	−02	−02	02	−01	01	−02	04	−02	−18	−05
1	−05	−04	05	04	02	02	00	01	−02	−02
2	−02	06	01	03	−16	02	−01	−04	−03	−04
3	−02	−05	01	−04	−02	−01	−02	−03	−02	−01
4	−01	−01	06	−04	−03	06	02	01	02	02
5	−02	01	−01	02	−04	02	−02	52	−01	−06
6	−01	55	−02	01	10	00	−01	−02	−02	−06
7	00	00	05	−01	−01	−06	−08	01	−04	−02
8	−19	−02	−02	01	−02	02	−02	04	01	00
9	−01	09	00	03	52	02	01	−01	−02	−02

peaks at the wanted positions and eighteen minor peaks at the expected unwanted positions, but not as to the weights of the various peaks. Surprisingly it was found that the ratio of the unwanted to the wanted peaks was much less than the expected value of $\frac{1}{3}$ and $\frac{2}{3}$. The reason for this is that in the theoretical discussion, we have ignored the negative second order terms of the phase structure. The effect of this is apparently to interfere with the general background and reduce it further. The numerical calculation of a phase synthesis with $\exp i\alpha_P$ as coefficient indicated that there are minor negative peaks at the expected second order positions and this confirms the above conclusion to some extent. The details are not given here. Anyway, the numerical check confirms the statement made earlier that it is more difficult to work out the nature of the β-class of syntheses to the same degree of exactitude as the α-class of syntheses. However, the computation shows that the required peaks show up quite prominently in the β-synthesis, in fact more prominently than in the α-synthesis. The isomorphous β-synthesis was also tested in another model with four known atoms and two unknown atoms. Here again, there were prominent peaks at the expected positions and the ratio of unwanted to wanted peaks was less than what is given by elementary theory.

No numerical calculations were made to verify the anomalous β-synthesis. But an experimental verification has been already given in the application of the anomalous dispersion method to L(+)-ephedrine hydrochloride (Ramachandran & Raman (1956), Raman (1958)). The phase and modulus syntheses of the Q atoms of Table 3 were also made and are given in Tables 6 and 7. These indicate good agreement with theory, and confirm that the first order peaks in the former case occur in the same positions as in the simple Fourier and in the latter in the same positions as in the simple Patterson synthesis.

APPENDIX I

Nature of the modulus structure: $|F_N|$

We shall omit the subscript N for convenience in these appendices. We have

$$|F_N|^2=\sum_{i=1}^{N} f_i^2+\sum_{j=1}^{N}\sum_{\substack{k=1\\ j\neq k}}^{N} f_j f_k^* \exp 2\pi i\mathbf{H}.(\mathbf{r}_j-\mathbf{r}_k)\,. \qquad (\text{I·1})$$

Now $|F_N|=(|F_N|^2)^{1/2}$ and so we may take the square root of the above expression and expand it by the binomial theorem, assuming the first term to be large compared with the second. This is not mathematically quite valid, but a sort of justification can be given from the fact that when a Fourier synthesis is performed with the above coefficient, the origin peak given by the first term is much stronger than any of the peaks given by the second term. It is hoped to be able to justify the procedure adopted here by a full mathematical theory at a later date. However, it may be mentioned that the results derived below have been tested numerically on examples and found to be in agreement with the calculations:

Thus,

$$\begin{aligned}|F_N|&=(\Sigma f_i^2)^{1/2}\left[1+\frac{1}{\Sigma f_i^2}\sum_{j\neq k}\sum f_j f_k^* \exp 2\pi i\mathbf{H}.(\mathbf{r}_j-\mathbf{r}_k)\right]^{1/2}\\ &=S_N+\frac{1}{2S_N}\sum_{j\neq k}\sum f_j f_k^* \exp 2\pi i\mathbf{H}.(\mathbf{r}_j-\mathbf{r}_k)\\ &\quad-\frac{1}{8S_N^2}\left[\sum_{j\neq k}\sum f_j f_k^* \exp 2\pi i\mathbf{H}.(\mathbf{r}_j-\mathbf{r}_k)\right]^2+\dots\end{aligned} \qquad (\text{I·2})$$

where
$$S_N=\left[\sum_{i=1}^{N} f_i^2\right]^{1/2}. \qquad (\mathrm{I}\cdot3)$$

Equation (I·2) shows that a Fourier synthesis employing $|F_N|$ as the coefficient will give a peak of weight S_N at the origin and (N^2-N) peaks of weight $\frac{1}{2}f_jf_k/S_N$ at $\mathbf{r}_j-\mathbf{r}_k$ centrosymmetrically disposed about the origin and a series of higher order peaks, alternately positive and negative. The strengths of the higher order peaks decrease rapidly, and they are, therefore, not significant and have not been considered. However, some of them may occur together at the origin or at the positions of the lower order peaks and thus slightly modify the strengths of the latter. This part is also difficult to work out and is reserved for the more detailed theory.

As a first approximation, therefore, we find that the structure $|F_N|$ consists of the following peaks:

$$S_N \quad \text{at} \quad 0$$

and
$$f_jf_k/2S_N \quad \text{at} \quad \mathbf{r}_j-\mathbf{r}_k \quad (j\neq k)\,.$$

It is interesting to note that the ratio of the strengths of a non-origin peak and the origin peak is $f_jf_k/2S_N^2$, which is half the ratio found in the Patterson diagram, namely f_jf_k/S_N^2. In this respect, the modulus synthesis differs from the Patterson synthesis, although to a first order of approximation the peaks occur in the same places in both cases.

APPENDIX II

Nature of the phase structure: exp i α_N

We shall work out the nature of the phase synthesis, making use of our knowledge of the modulus synthesis. Since it follows that the modulation of the modulus structure ($|F_N|$) by the phase structure ($\exp i\alpha_N$) must lead just to the original structure, viz., atoms f_j at $\mathbf{r}_j$; thus, the phase structure must first of all consist of N peaks of strength f_j/S_N at $\mathbf{r}_j$ so that the modulation of these with the origin peak of strength S_N of the modulus structure will give the required peaks at $\mathbf{r}_j$.

However, the modulation of these peaks with the non-origin peaks of the modulus structure will lead to $N(N^2-N)$ second order peaks of strength $\frac{1}{2}f_jf_kf_l/S_N^2$ at $\mathbf{r}_j+\mathbf{r}_k-\mathbf{r}_l$ $(k\neq l)$, which are not present in the F_N-structure. Therefore, the phase-structure must consist of second order *negative* peaks

$$\text{at} \quad \mathbf{r}_j+\mathbf{r}_k-\mathbf{r}_l$$

i.e. of strength $-\frac{1}{2}f_jf_kf_l/S_N^3$, so that their modulation with the origin peak of strength S_N will result in just the right number of peaks of the right strength to annul the former unwanted set.

This argument may be continued for working out still higher order peaks if necessary. However, since the modulus structure is itself only known to the second order, this is not worthwhile. Thus, as a first approximation, the structure $\exp i\alpha$ consists of the following peaks:

$$f_j/S_N \quad \text{at} \quad \mathbf{r}_j$$
$$-\tfrac{1}{2}f_jf_kf_l/S_N^3 \quad \text{at} \quad \mathbf{r}_j+\mathbf{r}_k-\mathbf{r}_l \quad (k\neq l)\,.$$

The phase-squared structure may be obtained by squaring the phase structure and its peaks have been listed in section 2.

APPENDIX III

Nature of reciprocal structure: $1/F_N$

Just as in the case of the phase structure, we shall make use of the result

$$1/F\,.\,|F|^2=F^*$$

i.e. the modulation of the Patterson structure by the reciprocal structure leads to the inverse structure, i.e., peaks of strength f_j at $-\mathbf{r}_j$. Now the Patterson consists of an origin peak of strength S_N^2 and peaks of strength f_kf_l at $\mathbf{r}_k-\mathbf{r}_l$. Thus the reciprocal structure must first of all contain peaks of strength f_j/S_N^2 at $-\mathbf{r}_j$, which on modulation with the origin peak of the Patterson leads to the required peaks. However, its modulation by the non-origin peaks of the Patterson leads to false positive peaks of strength $f_jf_kf_l/S_N^2$ at $-\mathbf{r}_j+\mathbf{r}_k-\mathbf{r}_l$, to cancel which, there must be negative peaks of strength $-f_jf_kf_l/S_N^2$ at $-\mathbf{r}_j+\mathbf{r}_k-\mathbf{r}_l$ in the reciprocal structure. These negative peaks combining with the origin peak of the Patterson will give a negative contribution to the electron-density distribution, which will exactly cancel the false positive peaks mentioned above.

Thus to a first order of approximation, the reciprocal structure $1/F$ consists of the following peaks:

$$f_j/S_N^2 \quad \text{at} \quad -\mathbf{r}_j$$
$$-f_jf_kf_l/S_N^4 \quad \text{at} \quad -\mathbf{r}_j+\mathbf{r}_k-\mathbf{r}_l \quad (k\neq l).$$

Its principal peaks occur at the positions corresponding to the inverse structure, with additional minor negative peaks.

It is obvious that the structure obtained by using $1/F_N^*$ as coefficient would closely approximate to the original structure F_N and that its main peaks will be as follows:

$$f_j/S_N^2 \quad \text{at} \quad \mathbf{r}_j$$
$$-f_jf_kf_l/S_N^4 \quad \text{at} \quad \mathbf{r}_j+\mathbf{r}_k-\mathbf{r}_l \quad (k\neq l).$$

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