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Syntheses for the Deconvolution of the Patterson Function. Part IV. Refinement of the Theory and a General Comparison of the Various Syntheses

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The details of the γ class of syntheses are given in this paper. The theory of the standard syntheses namely, $|F|$, exp $[i\alpha]$, exp $[2i\alpha]$, $1/|F|$ and $1/F$ is refined to the next higher order of approximation. The results are then applied to work out the ratio ϱ of the strength of the peak at the unknown to that at the known atomic positions in the α, β, γ, α', β' and γ' syntheses. Finally a general comparison of the various syntheses is made using the above ratio as the criterion for judging their relative merits.

1. Introduction

In Part I (Ramachandran & Raman, 1959) of this series were outlined the general principles involved in certain classes of syntheses which were proposed for developing a structure from its Patterson function when a part of it is known. The more detailed mathematical aspects of the problem were presented in Part II (Raman, 1959) and the treatment there pertained to the general case of a non-centrosymmetric structure. The extension of the theory to the centrosymmetric case was considered in Part III (Raman, 1961).

Two of the classes, namely α and β were discussed at length in the earlier parts and it was pointed out that the third class, namely the γ, was likely to have properties in between the α and β classes. The existence

of another series of syntheses called the α', β' and γ' syntheses which are closely related to the α, β and γ classes respectively was also pointed out in Part I.

The interpretation of these different classes of syntheses demanded first the analysis of the significance of the standard classes of syntheses which employ as Fourier coefficients the quantities $|F|$, $\exp[i\alpha]$, $1/F$ etc. In the earlier parts, the properties of these standard syntheses were worked out only to the first order of approximation. This paper is primarily concerned with working out theoretically the various standard syntheses to the next higher order of approximation. The necessity of this refinement was actually felt while applying the earlier results to the interpretation of the various syntheses. As was mentioned in Part I, an exact interpretation is possible only for the α class of syntheses whereas the others could be worked out only to various degrees of approximation. The second order of approximation has therefore been applied to the different classes and their relative merits of each are discussed in this paper. The power of the different syntheses to reveal the unknown part of the structure is judged from the value of the ratio (ϱ) of the peak strengths at the required atomic positions to those at the known positions.

Further, for the sake of completeness, a brief discussion of the details of the γ class of syntheses is given in section 2. This should be reckoned along with those given for the α and β classes (Part II). Further, a close study of the nature of these syntheses and of the dashed series have revealed a striking fact which helps us to give a unified formulation of the whole theory. This is also considered in the next section. The notation follows that of the earlier parts.

2. The γ class of syntheses

The γ class of syntheses follows as a natural consequence of the study of the α and β classes. In the α class a known function of the quantities $|F_N|^2$ and $|F_P|^2$ is multiplied by the structure factor F_P (i.e., by $|F_P|\exp[i\alpha_P]$) of the known part, while in the β class the same function is divided by F_P^* (which is equivalent to multiplication by $(\exp[i\alpha_P]/|F_P|)$. The intermediate process would obviously be to use the phase factor $\exp[i\alpha_P]$ alone for multiplication. It is possible to show that this would also lead to the development of the unknown part of the structure by the following argument. A careful study of the nature of the α and β classes shows that the part used for the purpose of deconvolution resembles closely the structure of the known part. While in the case of the α class this is obvious, since F_P itself is used, it is not so evident in the case of the β class which uses $(1/F_P^*)$. But it has been pointed out in Part I that the synthesis $1/F_P^*$ resembles F_P to a first approximation. So also it has been shown that the phase synthesis $\exp[i\alpha_P]$ resembles, to a first approximation, the structure F_P and hence $\exp[i\alpha_P]$ itself can be used for the purpose of deconvolution.

A study of the synthesis using the modulus of the structure amplitude, namely, $|F|$ as coefficients (Part II) shows that it resembles closely the Patterson function. This immediately suggests that it should be possible to use $|F|$ itself, instead of the intensities, with either F_P, $1/F_P^*$ or $\exp[i\alpha_P]$ for extracting the unknown part of the structure. This gives rise to the new series of syntheses namely α', β' and γ' which make use of the Fourier coefficients $|F_N|F_P$, $|F_N|/F_P^*$ and $|F_N|\exp[i\alpha_P]$. In fact, a synthesis using any power of $|F|$ resembles, to a first approximation, the Patterson function. Thus calculation shows that a synthesis using $|F^2|^n$ as coefficients has, as a first approximation, an origin peak of strength S^{2n} and peaks at the same position as in the Patterson, namely at $(\mathbf{r}_i-\mathbf{r}_j)$ having strengths $nf_if_jS^{(2n-2)}$. Thus the relative weights of the non-origin to the origin peak in the $|F|^{2n}$ synthesis is n times that in the ordinary Patterson function.

Using this argument it is readily seen that even more generally the whole series of syntheses having Fourier coefficients of the form $|F_N|^m|F_P|^n\exp[i\alpha_P]$ are capable of revealing the unknown Q atoms. When $m=2$ and $n=1, -1, 0$, we get respectively the α, β, γ classes and when $m=1$, $n=1, -1, 0$, we get the α', β' and γ' classes of syntheses. It appears that the more general types are not so useful as the six types α, β, γ and the α', β', γ'.

The general γ synthesis (γ_{gen})

The γ_{gen} synthesis uses as its coefficients the function $|F_N|^2\exp[i\alpha_P]$. It can be shown that this reduces to

$$\gamma_{\text{gen}} = \underset{(9)}{|F_P|F_P} + \underset{(10)}{|F_Q|^2\exp[i\alpha_P]} + \underset{(11)}{F_P\exp[i\alpha_P]F_Q^*} + \underset{(12)}{F_Q|F_P|}\,.$$

(The numbering is in conformity with Parts I and II). The synthesis therefore consists of four parts, (9) to (12) as in the case of α_{gen} and β_{gen}, each of which can be interpreted as a modulation of the different standard syntheses discussed in Part II. The term (12) contains the required structure Q. The other terms besides containing the known peaks also contribute to the background. The term (11) consists of the modulation of three quantities F_P, $\exp[i\alpha_P]$ and F_Q^*. In working out the positions of the peaks and their strengths we need consider only the first-order interaction. Table 1 gives the number, position and weight of the various peaks in the γ_{gen} synthesis. This can be compared with Tables 1 and 2 (Part II) of the α_{gen} and β_{gen} syntheses respectively.

Modified γ synthesis (γ_{mod})

The modified γ synthesis takes the form

$$\gamma_{\text{mod}} = (|F_N|^2 - |F_P|^2 - \sum_j f_{Qj}^2) \exp[i\alpha_P]$$
$$= \exp[i\alpha_P] \left[\sum_i \sum_{i \neq j} f_{Qi} f_{Qj} \exp[2\pi i \mathbf{H}.(\mathbf{r}_{Qi} - \mathbf{r}_{Qj})]\right]$$
$$+ F_P F_Q^* \exp[i\alpha_P] + F_Q |F_P| .$$

The peaks of (10), (11) and (12) with the exception of (10·1) are present in γ_{mod}. The unwanted background is therefore lower here than in the case of γ_{gen}.

Isomorphous γ synthesis (γ_{is})

Analogous to the α_{is} and β_{is} we have

$$\gamma_{\text{is}} = [(|F_N^{(1)}|^2 - |F_N^{(2)}|^2) - (|F_P^{(1)}|^2 - |F_P^{(2)}|^2)] \exp[i\alpha_P] .$$

This is equivalent to (Part II)

$$\gamma_{\text{is}} = |F_P| F_Q + \exp[i\alpha_P] F_P F_Q^* .$$

Thus γ_{is} gives the structure against the background of (11·1) and (11·2) and is thus similar to β_{is}.

Anomalous γ synthesis (γ_{an})

It is clear that

$$\gamma_{\text{an}} = |F_P''| \beta_{\text{an}}$$
$$= |F_P''| (\tfrac{1}{2}\Delta |F_N|^2 - F_P' F_P''^* + F_P'^* F_P'') \exp[i\alpha_P] ,$$

which is equivalent to

$$(F_Q F_P''^* + F_Q^* F_P'') \exp[i\alpha_P''] = F_Q |F_P''^*| + F_P'' \exp[i\alpha_P''] F_Q^* .$$

Thus the structure F_Q is obtained against a background which is partly positive and partly negative and in this respect it resembles more the α_{an} than the β_{an} synthesis.

3. Refinement of the standard syntheses

The interpretation of the standard syntheses in the earlier parts was essentially based on an analysis of the nature of the modulus ($|F|$) synthesis. This was achieved first by taking $|F|$ in its equivalent form $(|F|^2)^{\frac{1}{2}}$ and expanding it as a 'Taylor series'. The knowledge of the properties of the modulus synthesis coupled with the principle of modulation led to the properties of the phase synthesis $\exp[i\alpha_P]$ from the equality $|F| \exp[i\alpha] = F$. A similar procedure was then adopted for interpreting the other types of syntheses. However, because of the very nature of the approximation involved, it was not possible to solve for the peak strengths exactly and the values given for the peak strengths in Part II correspond only to the first order of approximation.

The procedure adopted here for working out the next higher order of approximation is as follows. An examination of the results in Part II would show that the peak strengths are equal to some multiple of a product of the f_j's with a power of S_N; e.g., the peak at $(\mathbf{r}_i - \mathbf{r}_j)$ of the modulus synthesis has a strength $\frac{1}{2} \cdot f_i f_j / S_N$. It is obvious that the peak positions are unaffected by the order of approximation and also that the relative order of magnitude of the different types of peaks are also unaffected; e.g., the origin and the non-origin peaks of the modulus synthesis are of the order of S_N and $f_i f_j / S_N$. This is readily verified by checking the equations used for working out their strengths (also the equations to be given below), in which only quantities of the same order of magnitude are equated. On the other hand the coefficient which multiplies the product $(f_i f_j \ldots S_N^r)$ changes with the order of approximation used. Anticipating a result to be worked out below, the coefficients α and β of S_N and $f_i f_j / S_N$ for the $|F|$ synthesis are respectively 1 and $\frac{1}{2}$ to the first order of approximation while they become 0·92 and 0·38 to the second order.

The main principle used in working out the higher order of approximation is to take all terms to this order in the various equations and to equate them. The procedure is best understood with reference to the modulus synthesis which is obtained from the equation

$$|F||F| = |F|^2. \qquad (1)$$

It is now assumed that the $|F|$ synthesis contains a first-order peak of strength αS_N at the origin and second-order peaks of strengths $\beta f_i f_j / S_N$ at $(\mathbf{r}_i - \mathbf{r}_j)$, where α and β are the unknowns. On the right-hand side we have the Patterson synthesis which is known to contain a peak of strength S_N^2 at the origin and second-order peaks of strengths $f_i f_j$ at $(\mathbf{r}_i - \mathbf{r}_j)$. The contribution to the origin term from the left-hand side arises from two types of interaction between the $|F|$ syntheses:

(*a*) those between the origin peaks αS_N and
(*b*) those between the non-origin peaks $\beta f_i f_j / S_N$.

The total contribution to the origin term on the left-hand side can easily be shown to be† $(\alpha^2 + \beta^2) S_N^2$ and this is equated to the corresponding term on the right-hand side, giving the equation

$$\alpha^2 + \beta^2 = 1 . \qquad (2)$$

A similar calculation of the peak strength given by both sides of the equation at the position $(\mathbf{r}_i - \mathbf{r}_j)$ leads to the equation

$$2\beta(\alpha + \beta) = 1 . \qquad (3)$$

A solution of these two equations leads to the values $\alpha = 0{\cdot}924$ and $\beta = 0{\cdot}383$. It may be pointed out that taking the first approximation to α and β is equivalent to solving the two equations

$$\alpha^2 = 1 , \qquad (2a)$$

† There is a small approximation involved in writing the second term as $\beta^2 S_N^2$, in that $\sum_i \sum_j f_i^2 f_j^2 (i \neq j)$ is put equal to $(\sum f_i^2)^2$. The error is not serious if N is large.

$$2\alpha\beta=1\,, \tag{3a}$$

analogous to equations (2) and (3) above, which are obtained by taking only terms upto the first order in equation (1). These lead to the values of $\alpha=1$, $\beta=0{\cdot}5$ given in Part II. These refined values of $\alpha(=0{\cdot}924)$ and $\beta(=0{\cdot}383)$ are taken as the starting point for

Table 1. *Peaks in γ_{gen} synthesis*

Strength	Position	Designation	Corresponding peak in Table 1 (of Part II)	Table 2
$f_{Pj}S_P+\sum_{i\neq j} f_{Pi}^2/2S_P$	$\mathbf{r}_{Pj}$	9·1	1·1	5·1
$f_{Pi}f_{Pj}f_{Pk}/2S_P$	$\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Pk}$ $(i,j\neq k)$	9·2	1·2	—
$f_{Pj}S_Q^2/S_P$	$\mathbf{r}_{Pj}$	10·1	2·1	6·1
$f_{Pk}f_{Qi}f_{Qj}/S_P$	$\mathbf{r}_{Pk}+\mathbf{r}_{Qi}-\mathbf{r}_{Qj}$ $(i\neq j)$	10·2	2·2	6·2
$-f_{Pj}f_{Pk}f_{Pl}S_Q^2/2S_P^3$	$\mathbf{r}_{Pj}+\mathbf{r}_{Pk}-\mathbf{r}_{Pl}$ $(k\neq l)$	10·3	—	6·3
$f_{Qi}f_{Pj}^2/S_P$	$2\mathbf{r}_{Pj}-\mathbf{r}_{Qi}$	11·1	3·1	7·1
$2f_{Pi}f_{Pj}f_{Qk}/S_P$	$\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Qk}$ $(i\neq j)$	11·2	3·2	7·2
$f_{Qj}S_P$	$\mathbf{r}_{Qj}$	12·1	4·1	8·1
$f_{Pi}f_{Pj}f_{Qk}/S_P$	$\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Qk}$ $(i\neq j)$	12·2	4·2	—

Table 2. *Peaks in the standard syntheses*

Synthesis	Peak strength	Position	Value of the unknowns
$\lvert F\rvert$	αS_N	0	$\alpha=$ 0·92
	$\beta f_i f_j/S_N$	$\mathbf{r}_i-\mathbf{r}_j$	$\beta=$ 0·38
$\exp[i\alpha]$	xf_i/S_N	$\mathbf{r}_i$	$x=$ 0·90
	$yf_if_jf_k/S_N^3$	$\mathbf{r}_i+\mathbf{r}_j-\mathbf{r}_k$	$y=-0{\cdot}45$
$\exp[2i\alpha]$	Xf_if_j/S_N^2	$\mathbf{r}_i+\mathbf{r}_j$	$X=$ 0·85
	$Yf_if_jf_kf_l/S_N^4$	$\mathbf{r}_i+\mathbf{r}_j-\mathbf{r}_k+\mathbf{r}_l$	$Y=-2{\cdot}50$
$1/\lvert F\rvert$	γ/S_N	0	$\gamma=$ 1·2
	$\delta f_i f_j/S_N^3$	$\mathbf{r}_i-\mathbf{r}_j$	$\delta=-0{\cdot}27$
$1/F$	pf_i/S_N^2	$-\mathbf{r}_i$	$p=$ 0·95
	$qf_if_jf_k/S_N^4$	$-\mathbf{r}_i-\mathbf{r}_j+\mathbf{r}_k$	$q=-0{\cdot}66$

working out the results for the other standard syntheses such as $\exp[i\alpha]$, $\exp[2i\alpha]$ etc. However, unlike in Part II, where a particular equation alone is used for working out the results for each synthesis, a number of equations connecting these are used here. Thus, if we combine $|F|$ with $\exp[i\alpha]$ and $\exp[2i\alpha]$, we obtain the following simple combinations (4) to (10), connecting the above synthesis and the well-known syntheses F, F^2 and $|F|^2$.

$$|F|\exp[i\alpha] = F \tag{4}$$

$$\exp[i\alpha].\exp[-i\alpha] = 1 \tag{5}$$

$$|F|^2\exp[i\alpha] = |F|F \tag{6}$$

$$|F|^2\exp[i\alpha] = F^2\exp[-i\alpha] \tag{7}$$

$$|F|^2\exp[2i\alpha] = F^2 \tag{8}$$

$$\exp[i\alpha].\exp[i\alpha] = \exp[2i\alpha] \tag{9}$$

$$|F|\exp[2i\alpha] = F\exp[i\alpha]\,. \tag{10}$$

In each of these equations the peak strengths corresponding to the first and second order can be worked out from both sides and they lead to the following sets of equation. Using the designations adopted in Table 2,

$$\left.\begin{aligned} x(\alpha+\beta)+\beta y &= 1 \\ y(\alpha+2\beta)+2\beta x &= 0 \end{aligned}\right\} \quad \begin{matrix}(1{\cdot}00) & [1{\cdot}25] \\ (0{\cdot}08) & [0{\cdot}0]\end{matrix} \tag{11}$$

$$\left.\begin{aligned} x^2+y^2 &= 1 \\ x^2+2xy &= 0 \end{aligned}\right\} \quad \begin{matrix}(1{\cdot}01) & [1{\cdot}25] \\ (0{\cdot}0) & [0{\cdot}0]\end{matrix} \tag{12}$$

$$\left.\begin{aligned} 2x+y-\alpha-\beta &= 0 \\ 2x+3y-\beta &= 0 \end{aligned}\right\} \quad \begin{matrix}(0{\cdot}05) & [0{\cdot}0] \\ (0{\cdot}07) & [0{\cdot}0]\end{matrix} \tag{13}$$

$$x+2y = 0 \qquad (0{\cdot}0) \quad [0{\cdot}0] \tag{14}$$

$$\left.\begin{aligned} X-1 &= 0 \\ Y+3X &= 0 \end{aligned}\right\} \quad \begin{matrix}(-0{\cdot}10) & [0{\cdot}0] \\ (-0{\cdot}20) & [*]\end{matrix} \tag{15}$$

$$\left.\begin{aligned} 2x(x+y)-X &= 0 \\ 6xy-Y &= 0 \end{aligned}\right\} \quad \begin{matrix}(-0{\cdot}09) & [0{\cdot}0] \\ (-0{\cdot}07) & [*]\end{matrix} \tag{16}$$

$$\left.\begin{aligned} X(\alpha+2\beta)-2x-y &= 0 \\ \alpha Y+3\beta X-3y &= 0 \end{aligned}\right\} \quad \begin{matrix}(0{\cdot}16) & [0{\cdot}0] \\ (0{\cdot}08) & [*]\end{matrix} \tag{17}$$

All the equations (4) to (10) are exactly valid. However, the equations (11) to (17) worked out from these are valid only to the second order of approximation and therefore no values of α, β, x, y and X, Y will fit them all exactly. By a method of trial and error, the following set of values, correct to two significant figures have been deduced:

$$\alpha=0{\cdot}92,\ \beta=0{\cdot}38;\ x=0{\cdot}90,\ y=-0{\cdot}45;$$
$$X=0{\cdot}90,\ Y=-2{\cdot}5\,.$$

The values obtained for the right-hand sides of equations (11) to (17) using these values are given in round brackets which would give an idea of the accuracy of the approximation. The values obtained using the first approximation of Part II, namely,

$$\alpha=1,\ \beta=0{\cdot}5;\ x=1{\cdot}0,\ y=-0{\cdot}5;\ X=1{\cdot}0,\ Y=*;$$

are also given within square brackets. It will be seen that the first approximation leads to large errors in some cases.

Now for obtaining the values of p and q of the reciprocal synthesis $(1/F)$ it is found convenient to interpret $(1/F)$ as of the form

$$1/F=(1/|F|)\exp[-i\alpha]\,. \tag{18}$$

The unknowns γ and δ of the first term on the right-hand side, namely, the reciprocal modulus synthesis

* Y does not occur in the first-order calculations.

$(1/|F|)$ were first obtained as described above, using the set of equations

$$(1/|F|)|F|^2 = |F| \quad (19)$$

$$(1/|F|)|F| = 1 \quad (20)$$

$$F(1/|F|) = \exp[i\alpha] \quad (21)$$

$$F^2(1/|F|) = F\exp[i\alpha]\,. \quad (22)$$

Here, the quantities α, β and x, y of the modulus and the phase syntheses were assumed to have the values given above. The values of γ and δ thus deduced were then found to be $\gamma=1{\cdot}2$ and $\delta=-0{\cdot}27$. Using these values in the equation (18) we get $p=0{\cdot}95$ and $q=-0{\cdot}66$. These results are also included in Table 2. It should be mentioned here that when the peak strengths of the $(1/F)$ synthesis were directly calculated using various equations such as

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

inconsistent results were obtained when only quantities up to the second order were included. Since the $|F|$ synthesis has been taken as the main one in our discussions, the above method of working out the $(1/|F|)$ and then the $(1/F)$ synthesis in terms of this was adopted. The consistency of this procedure may be verified from the fact that the equations arising from the combinations (19) to (22) were fairly well satisfied by the above values of γ, δ, p and q. However, some caution is necessary in the use of these values of p and q for the synthesis $1/F$.

4. A general comparison of the α, β, and γ syntheses

In order to compare the relative merits of the various syntheses it is useful to have some criterion whereby their utility may be judged. We can adopt for this purpose the ratio ϱ which is the ratio of the strength of the peaks at the unknown positions to that at the known positions. This ratio can be calculated for the different classes of syntheses making use of the values of the various constants given in Table 2. The calculation of ϱ in these cases demands fairly accurate knowledge of the strengths and positions of the peaks in the standard syntheses and in fact, the refinement discussed in the last section was made mainly for this purpose. The values of ϱ for the different syntheses are listed in Table 3. ϱ' corresponds to the limiting case when P tends to N.

As expected, the γ class of syntheses has properties intermediate between the α and β classes. When the three general syntheses, namely, α_{gen}, β_{gen} and γ_{gen} are compared (Table 1) it is seen that the positions of the various peaks are the same in all of them though in some cases their relative weights are different. It is to be noted that the peak (4·2) of α_{gen} is present in γ_{gen} also, whilst it is absent from β_{gen}. In short γ_{gen} contains peaks corresponding to both α_{gen} and β_{gen} syntheses.

However, a comparison of the values of ϱ (Table 3) shows that the β synthesis is superior to both the α and γ syntheses as far as the peak strengths at the required positions are concerned. In fact of all the syntheses the β synthesis has the maximum value of ϱ, namely unity.

Table 3. *Values of the ratio ϱ of the strength of the peaks at the unknown to that at the known atomic positions in the various syntheses*

Synthesis	ϱ	$\varrho'(P \to N)$
α	$(S_P^2/S_N^2+S_P^2)$	0·50
β	$(S_P^2/S_P^2+0{\cdot}95S_Q^2)$	1·00
γ	$(S_P^2/1{\cdot}47S_P^2+0{\cdot}98S_Q^2)$	0·67
α'	$(S_P^2/2{\cdot}42S_N^2+S_P^2)$	0·29
β'	$(S_P^2/2{\cdot}42S_N^2+S_P^2-0{\cdot}70S_P^4/S_N^2)$	0·37
γ'	$(S_P^2/2{\cdot}80S_N^2+0{\cdot}43S_P^2)$	0·31

However, there arises one practical difficulty in performing the β synthesis, as already pointed out in Part II. Thus if some reflections have small values of $|F|$, the corresponding coefficients in the β synthesis tend to be large. Such terms should be neglected from the summation. In both the α and γ syntheses, this difficulty obviously does not arise. But it should also be noted that the ambiguity of phase for small values of $|F|$ is present in all types of syntheses, as for example even in the usual heavy-atom (γ') synthesis. This type of difficulty can therefore best be got over by omitting such ambiguous terms from the summation.

Coming to the dashed series, it is clear that all of them are in general inferior (judged from the value of ϱ) to the undashed syntheses. However, a word of caution is necessary when applying this criterion of ϱ. The value of ϱ given here refers only to the case when the background strength is zero. In an actual case this may not be true, since the number of peaks contributing to the background may be quite large even though individually the strength of each peak may not be high. The effect will be particularly serious in projections since a large number of them can add up to enhance the background strength. The value of ϱ in such cases should obviously correspond to the peak height over and above the background. Such practical aspects of this problem are reserved for a later paper.

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