PART II SOME STATISTICAL STUDIES
CHAPTER 6

PROBABILITY DISTRIBUTION OF X-RAY INTEGRALES OF APPROXIMATELY CENTROSYMMETRIC STRUCTURES

6.1 INTRODUCTION

Recently a number of papers have been published from this laboratory dealing with the probability distribution of structure factors (Part I: Ramachandran, Srinivasan and Raghupathy Sarma, 1963; Part II: Srinivasan, Raghupathy Sarma and Ramachandran, 1963a; Part III: Srinivasan, Subramanian and Ramachandran, 1964; Part IV: Srinivasan and Ramachandran, 1965a; Part V: Srinivasan and Ramachandran, 1965b; Part VI: Srinivasan and Ramachandran, 1966; see also Ramachandran and Srinivasan, 1963; Srinivasan, Raghupathy Sarma and Ramachandran, 1963b; Srinivasan and Chandrasekaran, 1966; Parthasarathy and Srinivasan, 1967). The basic problem considered may be stated as the probability distribution of the structure factor of the true structure containing $N$ atoms at locations $x_j$ and another assumed model containing a part $P$ of the atoms ($P < N$) with coordinate errors. The probability distribution function of the structure
factors $F_N$ and $F_P^o$ when $F_N$ corresponds to the true structure and $F_P^o$ the 'assumed model' was established. Based on the theoretical distributions a number of statistical tests such as the test for isomorphism between a pair of crystals, discrepancy indices for use in crystal structure analysis have been deduced. Two main cases were considered, namely, case I: when both $F_N$ and $F_P$ are non-centrosymmetric; case II: when both $F_N$ and $F_P^o$ are centrosymmetric.

The cases when one of the two is non-centrosymmetric and the other centrosymmetric (case III), and vice versa (case IV) were not considered then since no immediate practical application was then envisaged. However, it has been realised now that the situations of this type could arise in practice and these can lead to, as we shall see presently, distributions corresponding to pseudosymmetric structures. For instance, it is possible that the true structure is approximately centrosymmetric. If the assumed model is exactly centrosymmetric, the coordinates $F_{Nj}$ of the true model would then be related to the coordinates $F_{Nj}^o$ of the assumed model by the shifts $\Delta F_{Nj}$ which would correspond to the perturbation of the centrosymmetric model to yield the non-centrosymmetric one.*

*For convenience we consider only the case when $P = N$
This problem has been considered recently in this laboratory and reported briefly (Srinivasan and Swaminathan, 1974). The present chapter deals with working out in detail the joint probability distribution of the structure factors $F_N$ and $F_C$ for such a situation. This further enables us to work out several of other statistical distributions such as the difference, quotient, reciprocal quotient and phase angle difference connected with the structure factors $F_N$ and $F_C$ etc., which are of prime interest from the point of view of application. So also it is obvious that the converse case of $F_N$ corresponding to a centrosymmetric model and $F_C$ to a non-centrosymmetric one, can be deduced from the results of case III.

It appears that this type of pseudosymmetric distribution was first considered by Trucco (1953) who applied his (1952) earlier analysis to the above situation. He deduced theoretically, for example, the values of a type of discrepancy index involving $F_N$ and $F_C$ which would enable one to estimate this in a practical situation. Here we treat this problem more systematically following the type of analysis used for cases I and II. In particular, the distributions for
the difference, quotient, reciprocal quotient of the normalised structure factors as well as their phase angle difference will be arrived at. Since most of the steps for the derivation are common to the earlier parts reference to equations etc of the earlier parts will be made by a prefix denoting the part concerned.

It is not out of place to mention here that the treatment of the present problem of the degree of centrosymmetry of a non-centrosymmetric structure arose in another context in this laboratory (Srinivasan and Vijayarajalakshmi, 1972; Srinivasan, Swaminathan and Shackle, 1972; Srinivasan, Vijayarajalakshmi and Parthasarathy, 1974).

6.2 BASIC PROBABILITY DISTRIBUTION

6.2.1 Derivation of the Joint Probability Distribution of \( |P_\alpha| \) and \( \alpha \) for a Given \( F_\lambda \)

We consider here the triclinic case only. Let \( F_{\lambda j} \) denote the coordinates of the structure which is approximately centrosymmetric. This may be considered to have been
derived by giving random and independent displacements
to the coordinates of a perfectly centrosymmetric assumed
model with coordinates $F_{ij}$. It is assumed that the
shifts $\Delta y_{ij}$ and $\Delta y_{ij'}$, for the atoms $j$ and $j'$ which
are related by a centre of symmetry are random and independ-
ent where $n = N/2$. Let $F_N$ and $F_N^c$ denote the
structure factors of the true and assumed model. It is
also assumed that both the true and assumed models contain
a large number of similar atoms.

Since we are going to derive our basic proba-
bility distributions starting from the joint distribution
of $|F_N|$ and the phase angle difference $\phi$ for a given
$F_N^c$, derived earlier by Srinivasan and Chandrasekaran
(1966), we give some of the essential steps involved in
deriving the joint distribution of $|F_N|$ and $\phi$ for a
given $F_N^c$ for the sake of continuity. However, in the
reference cited above the distribution had been derived
for the case when $P \neq N$. Thus Figure 6.1 gives the
relationship between the various vectors
where $F_N$ is the total structure factor, $F_P$ and $F_Q$
are the structure factors due to $P$ and $Q$ atoms
is the calculated structure factor of the $P$ atoms. The

---

There has been an error in Figure 4 of the paper by
Srinivasan and Chandrasekaran (1966) in that the vector
is marked as $(F_N - F_{ij})$ instead of $(F_N - F_{ij'}$. The argu-
ments in the text are however unaffected.
vector \[ U = \Delta F_P^c - (\psi_P, -1) \psi_P. \]

As far as the pair of vectors \( \psi_N \) and \( \psi_P \) are concerned the former can be considered to be made up of three vectors \( \psi' \) and \( \psi'' \) and \( \psi''' \) where \( \Delta \psi_P = \psi^c_P \).

The distributions governing the real and imaginary components of \( U \) can be shown to be Gaussian and further it is independent of the orientation of the vector \( \psi_P \) on the Argand plane. Thus the distributions of \( \psi' \) and \( \psi'' \) are given by

\[
P(\psi') d\psi' = \frac{1}{\sqrt{2\pi} \Delta \psi_P} e^{-\frac{\psi'^2}{2\Delta \psi_P^2}} d\psi',
\]

\[
P(\psi'') d\psi'' = \frac{1}{\sqrt{2\pi} \Delta \psi_P} e^{-\frac{\psi''^2}{2\Delta \psi_P^2}} d\psi''.
\]

where \( \Delta \psi_P \) denotes the root mean square value of the structure amplitude \( \psi^c_P \) or \( \psi_P \).
It is well known that the components \( y_{i\alpha} \) and \( y_{\alpha} \) of the vector \( F_\alpha \) have also a Gaussian distribution given by (Wilson, 1949)

\[
P(x_{i\alpha}) \, dx_{i\alpha} = \frac{1}{\sqrt{2\pi} \sigma_{x_{i\alpha}}} \exp\left(-\frac{1}{2\sigma_{x_{i\alpha}}^2} x_{i\alpha}^2\right) \]

\[
P(y_{\alpha}) \, dy_{\alpha} = \frac{1}{\sqrt{2\pi} \sigma_{y_{\alpha}}} \exp\left(-\frac{1}{2\sigma_{y_{\alpha}}^2} y_{\alpha}^2\right)
\]

where \( \sigma_{x_{i\alpha}} = \sqrt{\langle x_{i\alpha}^2 \rangle} \)

The two vectors \( U \) and \( F \) arise due to entirely different causes and hence by the well-known addition theorem of Gaussian distribution, the components of the sum of two vectors \( U + F \) (say) will also have a Gaussian distribution with the characteristic \( \sigma \) value equal to the sum of the corresponding ones for the individual cases; i.e.,

\[
\sigma_{\alpha}^2 = \sigma_{x_{i\alpha}}^2 + \sigma_{y_{\alpha}}^2
\]
Thus we can write

\[ P(x_\Delta) \, dx_\Delta = \frac{1}{\sqrt{2\pi}} e^{-x_\Delta^2/2} \, dx_\Delta \]

\[ P(y_\Delta) \, dy_\Delta = \frac{1}{\sqrt{2\pi}} e^{-y_\Delta^2/2} \, dy_\Delta \]

Hence the joint probability distribution of \( x_\Delta \) and \( y_\Delta \) is given by

\[ P(x_\Delta, y_\Delta) \, dx_\Delta \, dy_\Delta = \frac{1}{2\pi} e^{-x_\Delta^2/2 - y_\Delta^2/2} \, dx_\Delta \, dy_\Delta \tag{4} \]

These formulae enable us now to work out the distribution in terms of amplitudes and phases which are required for the evaluation of the various correlation functions. It is obvious from Figure 6.1 that given \( x_\Delta \), the probability that the vector \( y_\Delta \) lies in an element of area \( da(y_\Delta) \) at the terminus of \( x_\Delta \) is the same as the probability that the vector \( x_\Delta \) lies in an element
on the element \( dA \). The distribution governing this is known and hence substituting 1 for \( dA \) in (4) and replacing the area \( 4\pi \alpha^2 \) by 1, we obtain the joint distribution of \( |F_N| \) and \( \alpha \) for a given \( F_P^0 \)

\[
P(|F_N|, \alpha; \alpha; F_P^0) = \frac{|F_N|^2}{\pi} e^{-\frac{|F_N|^2}{\pi}} \left( 1 + \frac{|F_N|}{\pi} \right)
\]

or equivalently

\[
P(|F_N|, \alpha; \alpha; F_P^0) = \frac{|F_N|^2}{\pi} e^{-\frac{|F_N|^2}{\pi}} \left( 1 + \frac{|F_N|}{\pi} \right)
\]

Equation (6) can be used for the present case when \( P = N \), since it has been derived based on the distributions of \( U \) and \( F_P^0 \) which are independent of the orientation of the vector \( F_P^0 \) on the Argand plane. The distribution (6) is valid even when \( F_P^0 \) lies on the

---

We use a comma between two variables to denote the joint distribution and a semicolon to denote the conditional distribution of the variable preceding it given the quantity (quantities) following it. Thus the use of the above, \( P(|F_N|, \alpha; F_P^0) \), denotes the joint probability distribution of \( |F_N| \) and \( \alpha \) for a given \( F_P^0 \).
real axis (i.e. when the assumed model is centrosymmetric).
For the present case when \( P = N \) becomes equal to \( J_N^{-1} \) where \( D = \frac{1}{2} \).
Hence, Equation (6) becomes

\[
F(\{F_N\}, \alpha ; F_N^c) = \frac{1}{\pi \sqrt{1 - D^2}} \sum_{\alpha} F_N^c \exp \left( \frac{i2\pi \alpha N}{\lambda} \right)
\]

(7)

In terms of the normalised structure amplitudes \( y_N \) and \( y_N^c = \frac{|F_N^c|}{y_N} \), Equation (7) takes the form

\[
P( y_N, \alpha ; y_N^c ) = \frac{y_N}{\pi (1 - D^2)} \exp \left( \frac{i2\pi \alpha N}{\lambda} \right)
\]

(8)

6.2.2 Derivation of Probability Distribution of the Normalised Amplitude \( y_N \)

The conditional distribution of amplitude \( y_N \) alone can be obtained by integrating Equation (8) with respect to \( \alpha \) (Appendix XII) which yields

\[
P( y_N ; y_N^c ) = \int P( y_N, \alpha ; y_N^c ) d\alpha
\]

\[
= \frac{2y_N}{\pi (1 - D^2)} \left[ \frac{1}{1 - D^2} + \frac{1}{(1 - D^2)^2} \right] \left( \frac{\sin \frac{\pi \lambda}{\lambda} y_N}{\sin \frac{\pi \lambda}{\lambda} \lambda} \right)
\]

(9)
Equation (9) is identical in form with Equation (9) of Srinivasan and Ramachandra (1955b). It is important to note here that for the present case \( \phi \) has both magnitude and phase while \( \phi_n \) is real since it corresponds to a centrosymmetric model. Thus, the conditional distribution \( P(\phi_n | \phi) \) for the present case and case I turns out to be the same, the distinction arising at the next stage namely in trying to arrive at the joint distribution \( P(\phi_n, \phi) \) which needs assumption about the distribution \( \phi_n \).

Thus assuming a centric distribution \( \phi_n \),

\[
P(\phi_n) = \frac{1}{\sqrt{2\pi}} e^{-\phi_n^2/2}
\]  

(10)

The joint distribution \( P(\phi_n, \phi) \) is deduced to be

\[
P(\phi_n, \phi) = P(\phi_n) \cdot P(\phi)
\]

\[
= \frac{1}{\sqrt{2\pi}} e^{-\phi_n^2/2} \cdot 1
\]

(11)

The distribution of \( \phi_n \) alone can be deduced by integrating Equation (11) with respect to \( \phi \). (Appendix VII)
\[ P(y_N) = \int_0^\infty P\left(y_N, y_N\right) \, dy_N \]

\[ = \int_0^\infty \frac{2}{\sqrt{\pi}} \frac{y_N}{(1 + p^2)^{1/2}} e^{-y_N^2/(4(1+p^2))} \, dy_N \]

\[ = \frac{2}{\sqrt{1-p^2}} \left( \frac{y_N}{(1+p^2)^{1/2}} \right) \left( \frac{4}{4} \right) \]

The results are given in Figure 6.2 and also in Table 6.1.

6.2.3 Derivation of Probability Distribution of the Phase Angle Difference

In an analogous fashion the conditional distribution \[ P(y_N|\alpha) \]

could be arrived at from Equation (13) by integrating over \( y_N \). This turns out to be

\[ P(\alpha, y_N) = \int_0^\infty P\left(\alpha, y_N\right) \, dy_N \]

\[ = \int_0^\infty \frac{2}{\sqrt{\pi}} \frac{y_N}{(1 + p^2)^{1/2}} e^{-y_N^2/(4(1+p^2))} \, dy_N \]

(13)
FIG 6.2 The $P(Y_n)$ distribution for an approximately centrosymmetric structure for different $D$ values.
\[ = \frac{1}{\pi (1-D^2)} \int_0^{\nu_0} \exp \left( -\frac{D^2}{2} \right) \ldots \text{Eq. (14)} \]

Equation (14) can be simplified as (Ref. Appendix VIII)

\[ P(\chi; y_N^k) = K \left[ \prod_{i=1}^{m} \left( \frac{1}{\sqrt{2\pi}} \int \exp \left( -\frac{D^2}{2} \right) \ldots \right) \right] \]

where \[ K = \frac{1}{\sqrt{\pi}} \]

On further simplification equation (15) takes the form

\[ P(\chi; y_N^k) = \frac{1}{2\pi} \exp \left( -\frac{D^2}{2} \right) \ldots \]

The distribution of \( \chi \) is then given by

\[ P(\chi) = \int_{-\infty}^{\infty} P(\chi; y_N^k) d\chi \]

Using Equations (10), (15) and (17) we get
\[ P(x) = \int_{-\infty}^{\infty} \frac{1}{\pi} \frac{1}{1 + x^2} \, dx \\
+ \int_{0}^{\infty} D_y \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{y}{\sqrt{1 + y^2}} \, dy \, dx \\
\left[ 1 + \ldots \right] \\
\] (1) 

Integral (1) can be simplified as (Ref. Appendix IX)

\[ P(x) = \sqrt{1 - y^2} + \ldots \frac{1}{\pi} \frac{1}{\sqrt{1 + y^2}} \\
\left[ 1 + \ldots \right] \\
\] (1)

6.2.4 Derivation of the Probability Distribution of the Normalized Difference

From our previous experience we find that among several variables connected with the normalized quantities \( y_N \) and \( y_N^s \) such as sum, difference, product and quotient it is essentially the difference and the quotient variables which are of primary interest and lead to interesting
applications. Accordingly we shall consider the distribution of the difference variable in this section and the quotient in the next. Although the distribution of the difference and quotient variable were derived by a particular method by Srinivasan and Ramanathan (1965a) and Srinivasan, Subramanian and Ramanathan (1964), this could be done by a slightly different procedure (Parthasarathy and Srinivasan, 1967) which incidentally gives as a bonus the distribution of the sum variable. Thus the joint probability distribution of the variables

\[ y_s = x + y \]  \hspace{1cm} (20a)  \\
and \[ y_d = x - y \]  \hspace{1cm} (20b)

is given by

\[ P(\{ y_s, y_d \} = \{ s, d \} ) \]

where $1/2$ is Jacobian of transformation

\[ P( y_s, y_d ) = \exp \left[ -\frac{1}{2} X^T \Lambda X \right] \]

where

$P( y_s, y_d ) = \exp \left[ -\frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} y_s \\ y_d \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right] \]

We follow uniformly the revised notation for these variables. Thus $a, d, p$ and $q$ are used as subscripts to denote sum, difference, product and quotient.
It can be easily shown that the function is non-zero only in the region

\[-\infty \leq y_d \leq \eta \]  \hspace{1cm} (22)

and is zero elsewhere in the \( k - \lambda \) plane. The distribution of \( y_d \) can be obtained from Equation (21) and (22) as

\[ P(y_d) = \frac{1}{2} \left( \frac{y_d}{\eta} \right) \]  \hspace{1cm} (23)

Substituting for \( y_d \), we have

\[ P(y_d) = \frac{1}{2} \left( \frac{y_d}{\eta} \right) \]  \hspace{1cm} (24)

Integral (24) was evaluated by numerical methods and the results are given in the form of curves in Figure (6.4) for different values of \( D \). Numerical values are given in Table 6.2.
6.2.5 Derivation of the Probability Distribution of the Normalised Quotient

As stated earlier following the earlier treatment (Fartheswarathy and Srinivasan, 1967) the joint distribution of the product \( y_p \) and quotient \( y_q \) variables, defined as

\[
\begin{align*}
y_p &= \ln P \quad (25a) \\
y_q &= \ln q \quad (25b)
\end{align*}
\]

is given by

\[
P(y_p, y_q) = |y_q|^{-1} f(y_p, y_q) \quad (26)
\]

where \( 1/2y_q \) is the Jacobian of transformation.

It can be easily shown that the function \( \phi \)  is non-zero in the domain

\[
\phi = y_p - y_q \quad (27)
\]

and is zero elsewhere.
The distribution of $y_q$ is then given by

$$P(y_q) = \frac{1}{y_q!} \int_{y_q}^{\infty} \cdots$$

substituting for $P(y_p, y_q)$ we get

$$P(y_q) = \frac{1}{y_q!} \int_{y_q}^{\infty} \cdots$$

Equation (29) can be simplified (Appendix X) as

$$P(y_q) = \frac{1}{y_q!} \int_{y_q}^{\infty} \cdots$$

where $_2F_1$ is the hypergeometric function.
6.2.6 Derivation of the Probability Distribution of the Normalised Reciprocal Quotient

In cases I and II considered in earlier parts certain symmetry properties of the normalised variables were emphasised. For instance, the function \( p(y_q) \) was symmetrical about the origin (Part IV). This was also reflected in the quotient distribution. That is, the distribution of the quotient and its reciprocal were the same (Grimvassan, Subramanian and Ramachandran, 1964). It turns out that in the present case such symmetry properties are absent.

For instance the distribution of \( y_q \) is asymmetric (see next section) unlike for cases I and II. This is obviously reflected also in the quotient variable. Thus it becomes necessary to work out the distribution of the reciprocal quotient \( u = 1/y_q = y_q^o/y_q^r \). This is readily done by making appropriate transformations (Refer Appendix II) in the expression for \( P(y_q) \).

Thus we obtain for the distribution of \( u \) the following expression

\[
P(u) = \frac{2}{\pi} \frac{\sqrt{2 + u^4 + \left( \frac{u}{\sqrt{1 + u^2}} \right)^2}}{\left( 2 + u^4 + \left( \frac{u}{\sqrt{1 + u^2}} \right)^2 \right)^{\frac{3}{2}}}
\] (31)
Thus the above expression is different from that of $P(y_q)$ excepting when $D = 1$.

6.3 DISCUSSION OF THE RESULTS

The various probability distributions derived in earlier sections may all be seen to be characterised by a single parameter $D$ defined in the earlier section. It will be useful therefore to discuss the properties of the various distributions in terms of the parameter $D$. We shall discuss these one by one. It may be noted that $D = 0$ when the errors $y_q$ are very large and $D = 1$ when all the errors are zero. Physically these two correspond respectively to the true structure being completely non-centrosymmetric and completely centrosymmetric. For intermediate values of $D$ the situation may be described as the true model being approximately centrosymmetric. In essence therefore $D$ is a measure of the degree of centrosymmetry of the true structure.
6.3.1 Distribution of the Normalised Amplitude of an Approximately Centrosymmetric Situation

The way normalised structure amplitude of an approximately centrosymmetric structure is distributed is readily available in the marginal distribution \( P(y_y) \) deduced in Equation (12b). As is to be expected this is characterised by the parameter \( D \). It is readily shown that the equation (12b) reduces to basic acentric and centric distributions respectively for \( D = 0 \) and \( D = 1 \). Figure 6.2 gives a family of curves of \( P(y_y) \) for different values of \( D \) including the limiting cases. The numerical values are given in Table 6.1.

It is interesting to note that the distribution \( P(y_y) \) is identical in form with the distribution of the normalised amplitude for another type of situation which could also be characterised as "approximately centrosymmetric". This has been considered earlier in the literature by Srinivasan (1965a)(see also Parthasarathy and Parthasarathi, 1974). Thus the situation considered earlier was the distribution of the normalised structure amplitude of a structure in a non-centrosymmetric space group \( P1 \) containing centrosymmetric (\( P \)) and non-centrosymmetric (\( C \)) groups of atoms. If the ratio of the
contribution to the mean intensity by the centrosymmetric group to that of the whole structure is denoted by the distribution for such a case turns out to be

$$P(y_N) = \frac{2y_N}{\sqrt{1-v}}$$

(32)

The parallel roles of $v$ and $D$ are now obvious. Thus the two limits $D = 0$ (or $v = 0$) and $D = 1$ (or $v = 1$) correspond to acentric and centric distributions. Intermediate values of $D$ (or $v$) correspond to different degrees of centrosymmetry of the respective structures. Physically the two situations are quite different although one could describe both as approximately centrosymmetric structures. For convenience, we shall refer (if the need arises) the situation considered in this chapter as that of an approximately centrosymmetric structure (distortion type) to distinguish it from the other types referred to earlier. From the above it is also obvious that the parameter $D$ may conveniently replace $v$ in other statistical distributions, considered earlier. The present results only supply a sound theoretical justification for the same.

Although in the reference cited the distribution $P(y_N)$ has been given in the form of an integral it can be reduced to the above form using the Table of Integral Transforms (Gradstein et al. (1965), p.721, 6.644).
6.3.2 The Distribution of the Phase Angle Difference

The distribution \( P(\alpha) \) available in Equation (19) is exactly the same as the one derived earlier by Parthasarathy for a non-centrosymmetric crystal (Equation (23) of Parthasarathy, 1965) if \( D \) is replaced by \( D^* \) and \( \sigma \) by \( \sigma_2 \). As mentioned in the previous section, this is another evidence to indicate the parallel roles of \( D \) and \( \sigma_1 \). The \( P(\alpha) \) distribution is given in the form of curves in Figure 6.3(a). The limiting values of \( P(\alpha) \) are \( 1/2 \pi \) (for \( D = 0 \)) and \( \pi \) (for \( D = 1 \)). It is clear from the \( P(\alpha) \) curves that the values of \( \alpha \) crowd near the origin for high values of \( D \). It is obvious since for large values of \( D \) the true model and the assumed model agree better and hence the difference in the phase angle diminishes. The cumulative function of \( \|\alpha\| \) given by \( W(\|\alpha\|) = \frac{1}{2} \) for different values of \( D \) are shown in Figure 6.3(b).

*In the reference cited above, the distribution is for \( \alpha \).
Since \( P(\alpha) \) distribution is symmetrical about the origin

\[ P(\|\alpha\|) = \]
FIG. 6.3(b) The theoretical solid curves for various values of D
6.3.3 Probability Distribution of the Normalized Difference

The distributions of the difference variable $y_d$ for different values of $D$ are shown in Figure 6.4. It is interesting to note that unlike case I and II the $P(y_d)$ distributions for the present case are asymmetric. The maxima of $P(y_d)$ occur on the positive side of $y_d$ (see Figure 6.4). The asymmetry is maximum for $D = 0$ and it vanishes in the other limit $D = 1$ when the $P(y_d)$ function is a delta function at the origin. Physically these features are understandable. For example, the maximum asymmetry for $D = 0$ correspond to the true model being completely non-centrosymmetric while the assumed model is centrosymmetric. For the general case the lack of symmetry may be seen to be a consequence of the fact that $y_N$ and $y_0$ correspond to approximately non-centrosymmetric and centrosymmetric structures respectively.

The above curves in this form are useful in a practical situation when the true structure is approximately centrosymmetric while the trial model is assumed to be centrosymmetric. One would then expect that the $y_d$ will not be as often negative as positive, the positive
being slightly in excess to that of the negative. The proportion of the positive and negative values of \( y_d \) may be calculated from the curves in Figure 5.4 by working out the area under the curve for \( y_d > 0 \) and \( y_d < 0 \). These are given as a function of \( D \), in Table 6.3. It is needless to discuss the distribution of the difference \( (y^*_n - y_n) \), which will be obviously related to the above curves \( P(y_d) \) by a mirror at \( y_d = 0 \).

6.3.4 Probability Distribution of the Normalised Quotient and Reciprocal Quotient

The quotient distribution \( P(y_q) \) for different values of \( D \) are shown in Figure 6.5. For the limit \( D = 1 \) we obtain a delta function at the origin and for \( D = 0 \) we obtain a distribution similar to the eccentric distribution \( P(y) \). It is interesting to observe that the symmetry property associated with the quotient distribution for the cases I and II is absent here. Thus for cases I and II both \( P(y_q) \) and \( P(1/y_q) \) had identical forms. However, for the present case the reciprocal \( y_q \) (\( = 1/y_q \))
FIG. 6.5 Theoretical $P(y_q)$ curves for various values of $D$. 
of \( y_q \) has a different distribution from that of \( y_q \). The \( P(u) \) curves are given in Figure 5.8. Here again for \( D = 1 \) we get a delta function at \( u = 1 \) and for \( D = 0 \), we get a distribution somewhat similar to the centric distribution \( P(y) \). The numerical values of \( P(u) \) and \( P(y_q) \) are given in Tables 5.4 and 5.5.

### 6.4 DISCREPANCY INDEX

Several types of discrepancy indices have been discussed earlier for cases I and II which could be deduced theoretically from the distribution \( P(y_q) \), \( P(y_q) \) etc (see Srinivasan and Ramachandran, 1955; Parthasarathy and Srinivasan, 1967; For a recent account see Srinivasan and Parthasarathy, 1974). We shall adopt here for convenience the Booth type of index in the normalised form defined by

\[
R_B (F) = \frac{R_1 (F)}{R_0 (F)}
\]

or equivalently

\[
R_B (F) = \frac{R_1 (F)}{R_0 (F)}
\]
This index has the advantage in the present case that the denominator is the same whether the model is centrosymmetric or non-centrosymmetric or approximately centrosymmetric and is equal to unity. The various values of $p_y(r)$ for different $D$ values are shown in Figure 6.12.

6.5 TEST OF THE THEORETICAL CURVES

The theoretical distributions $P(y_d)$, $P(y_q)$, $P(u)$ and $P(\alpha)$ have been tested using a hypothetical model shown in Figure 6.7. The molecules (1) and (2) form the asymmetric unit in the two-dimensional plane group $P1$. To start with the molecules (1) and (2) were assumed to be exactly related by a centre of inversion. The calculated structure factors with this model formed the $F_h$. Keeping one of the molecules fixed small shifts were given to the atoms of the other to yield an approximately centrosymmetric structure. Care was taken so that the shifts given to the atoms were randomly distributed. The calculated structure factors with the distorted model
values are ranked by sales and success
FIG 6.11  Theoretical P(U) curves for D = 0.6 and 0.9. Experimental values are given by circles and crosses.
FIG 6.12  Variation of $\rho_1(\theta)$ with $\theta$
formed the $P_n$. The tests were carried out for D-values equal to 0.9 and 0.6. The results are given in Figures 6.8, 6.9, 6.10 and 6.11. The agreement of the experimental results with the theory is reasonable.
TABLE - 6.1

PROBABILITY DISTRIBUTION OF THE NORMALISED AMPLITUDE $q_n$ FOR VARIOUS VALUES OF $D$

<table>
<thead>
<tr>
<th>$q_n$</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000</td>
<td>0.171</td>
<td>0.380</td>
<td>0.609</td>
<td>0.855</td>
<td>0.999</td>
<td>0.798</td>
</tr>
<tr>
<td>0.1</td>
<td>0.019</td>
<td>0.196</td>
<td>0.374</td>
<td>0.614</td>
<td>0.860</td>
<td>0.998</td>
<td>0.794</td>
</tr>
<tr>
<td>0.2</td>
<td>0.038</td>
<td>0.184</td>
<td>0.351</td>
<td>0.587</td>
<td>0.854</td>
<td>0.996</td>
<td>0.782</td>
</tr>
<tr>
<td>0.3</td>
<td>0.048</td>
<td>0.160</td>
<td>0.319</td>
<td>0.548</td>
<td>0.846</td>
<td>0.993</td>
<td>0.762</td>
</tr>
<tr>
<td>0.4</td>
<td>0.061</td>
<td>0.147</td>
<td>0.287</td>
<td>0.509</td>
<td>0.837</td>
<td>0.989</td>
<td>0.736</td>
</tr>
<tr>
<td>0.5</td>
<td>0.078</td>
<td>0.135</td>
<td>0.256</td>
<td>0.470</td>
<td>0.827</td>
<td>0.984</td>
<td>0.704</td>
</tr>
<tr>
<td>0.6</td>
<td>0.095</td>
<td>0.123</td>
<td>0.226</td>
<td>0.432</td>
<td>0.816</td>
<td>0.977</td>
<td>0.666</td>
</tr>
<tr>
<td>0.7</td>
<td>0.113</td>
<td>0.112</td>
<td>0.206</td>
<td>0.394</td>
<td>0.805</td>
<td>0.970</td>
<td>0.625</td>
</tr>
<tr>
<td>0.8</td>
<td>0.133</td>
<td>0.102</td>
<td>0.186</td>
<td>0.358</td>
<td>0.794</td>
<td>0.963</td>
<td>0.579</td>
</tr>
<tr>
<td>0.9</td>
<td>0.154</td>
<td>0.092</td>
<td>0.167</td>
<td>0.323</td>
<td>0.784</td>
<td>0.956</td>
<td>0.532</td>
</tr>
<tr>
<td>1.0</td>
<td>0.176</td>
<td>0.083</td>
<td>0.148</td>
<td>0.290</td>
<td>0.777</td>
<td>0.949</td>
<td>0.484</td>
</tr>
<tr>
<td>1.5</td>
<td>0.216</td>
<td>0.075</td>
<td>0.127</td>
<td>0.257</td>
<td>0.771</td>
<td>0.942</td>
<td>0.439</td>
</tr>
<tr>
<td>2.0</td>
<td>0.257</td>
<td>0.068</td>
<td>0.107</td>
<td>0.226</td>
<td>0.764</td>
<td>0.935</td>
<td>0.398</td>
</tr>
</tbody>
</table>
TABLE 6.3
RATIO OF THE AREA $A_t$ (FOR $D > 0$) TO
$A_L$ (FOR $R_L > 0$) UNDER THE
$P$ ($R_L R_L$) CURVE

<table>
<thead>
<tr>
<th>$D$</th>
<th>$A_t$</th>
<th>$A_L$</th>
<th>$A_t/A_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.577</td>
<td>0.423</td>
<td>1.364</td>
</tr>
<tr>
<td>0.2</td>
<td>0.577</td>
<td>0.423</td>
<td>1.364</td>
</tr>
<tr>
<td>0.4</td>
<td>0.577</td>
<td>0.423</td>
<td>1.364</td>
</tr>
<tr>
<td>0.5</td>
<td>0.577</td>
<td>0.423</td>
<td>1.364</td>
</tr>
<tr>
<td>0.6</td>
<td>0.576</td>
<td>0.424</td>
<td>1.355</td>
</tr>
<tr>
<td>0.7</td>
<td>0.575</td>
<td>0.426</td>
<td>1.352</td>
</tr>
<tr>
<td>0.8</td>
<td>0.572</td>
<td>0.428</td>
<td>1.336</td>
</tr>
<tr>
<td>0.9</td>
<td>0.566</td>
<td>0.435</td>
<td>1.298</td>
</tr>
<tr>
<td>0.95</td>
<td>0.557</td>
<td>0.444</td>
<td>1.257</td>
</tr>
<tr>
<td>0.99</td>
<td>0.538</td>
<td>0.462</td>
<td>1.164</td>
</tr>
</tbody>
</table>
### Table 6.4

**Probability Distribution of the Normalised Quotient $\gamma_n$ for Various $D$**

<table>
<thead>
<tr>
<th>$D$</th>
<th>$\gamma_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>0.2</td>
<td>0.356</td>
</tr>
<tr>
<td>0.4</td>
<td>0.528</td>
</tr>
<tr>
<td>0.6</td>
<td>0.637</td>
</tr>
<tr>
<td>0.8</td>
<td>0.670</td>
</tr>
<tr>
<td>1.0</td>
<td>0.528</td>
</tr>
<tr>
<td>1.2</td>
<td>0.343</td>
</tr>
<tr>
<td>1.4</td>
<td>0.277</td>
</tr>
<tr>
<td>1.6</td>
<td>0.214</td>
</tr>
<tr>
<td>1.8</td>
<td>0.177</td>
</tr>
<tr>
<td>2.0</td>
<td>0.177</td>
</tr>
<tr>
<td>2.2</td>
<td>0.149</td>
</tr>
<tr>
<td>2.4</td>
<td>0.149</td>
</tr>
<tr>
<td>2.6</td>
<td>0.126</td>
</tr>
<tr>
<td>2.8</td>
<td>0.126</td>
</tr>
<tr>
<td>3.0</td>
<td>0.160</td>
</tr>
<tr>
<td>3.2</td>
<td>0.118</td>
</tr>
<tr>
<td>3.4</td>
<td>0.094</td>
</tr>
<tr>
<td>3.6</td>
<td>0.084</td>
</tr>
<tr>
<td>3.8</td>
<td>0.082</td>
</tr>
<tr>
<td>4.0</td>
<td>0.072</td>
</tr>
</tbody>
</table>
### Table 6.5

**Probability Distribution of the Normalised Reciprocal Quotient $\alpha$ for Various $D$**

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.707</td>
<td>0.693</td>
<td>0.649</td>
<td>0.566</td>
<td>0.424</td>
<td>0.308</td>
</tr>
<tr>
<td>0.2</td>
<td>0.686</td>
<td>0.676</td>
<td>0.641</td>
<td>0.573</td>
<td>0.444</td>
<td>0.330</td>
</tr>
<tr>
<td>0.4</td>
<td>0.693</td>
<td>0.627</td>
<td>0.617</td>
<td>0.489</td>
<td>0.507</td>
<td>0.405</td>
</tr>
<tr>
<td>0.6</td>
<td>0.557</td>
<td>0.572</td>
<td>0.572</td>
<td>0.554</td>
<td>0.613</td>
<td>0.570</td>
</tr>
<tr>
<td>0.8</td>
<td>0.466</td>
<td>0.476</td>
<td>0.509</td>
<td>0.577</td>
<td>0.721</td>
<td>0.857</td>
</tr>
<tr>
<td>1.0</td>
<td>0.389</td>
<td>0.386</td>
<td>0.401</td>
<td>0.511</td>
<td>0.713</td>
<td>1.008</td>
</tr>
<tr>
<td>1.2</td>
<td>0.313</td>
<td>0.323</td>
<td>0.357</td>
<td>0.415</td>
<td>0.549</td>
<td>0.676</td>
</tr>
<tr>
<td>1.4</td>
<td>0.254</td>
<td>0.269</td>
<td>0.281</td>
<td>0.417</td>
<td>0.562</td>
<td>0.636</td>
</tr>
<tr>
<td>1.6</td>
<td>0.204</td>
<td>0.216</td>
<td>0.221</td>
<td>0.336</td>
<td>0.472</td>
<td>0.695</td>
</tr>
<tr>
<td>1.8</td>
<td>0.167</td>
<td>0.166</td>
<td>0.174</td>
<td>0.275</td>
<td>0.452</td>
<td>0.717</td>
</tr>
<tr>
<td>2.0</td>
<td>0.136</td>
<td>0.137</td>
<td>0.137</td>
<td>0.134</td>
<td>0.710</td>
<td>0.775</td>
</tr>
<tr>
<td>2.2</td>
<td>0.112</td>
<td>0.112</td>
<td>0.109</td>
<td>0.171</td>
<td>0.774</td>
<td>0.852</td>
</tr>
<tr>
<td>2.4</td>
<td>0.093</td>
<td>0.092</td>
<td>0.089</td>
<td>0.177</td>
<td>0.658</td>
<td>0.931</td>
</tr>
<tr>
<td>2.6</td>
<td>0.077</td>
<td>0.076</td>
<td>0.071</td>
<td>0.061</td>
<td>0.441</td>
<td>0.428</td>
</tr>
<tr>
<td>2.8</td>
<td>0.062</td>
<td>0.063</td>
<td>0.055</td>
<td>0.045</td>
<td>0.322</td>
<td>0.221</td>
</tr>
<tr>
<td>3.0</td>
<td>0.055</td>
<td>0.055</td>
<td>0.049</td>
<td>0.039</td>
<td>0.225</td>
<td>0.117</td>
</tr>
</tbody>
</table>