PART I: GENERAL INTRODUCTION
CHAPTER 3: 1

INTRODUCTORY SURVEY

This chapter gives a summary of crystallographic methods and is oriented in such a way as to form an introduction to the matter in the thesis. It also contains a summary of the notation and nomenclature used in the succeeding chapters.

1. THE ANOMALOUS DISPERSION METHOD

The phenomenon of anomalous dispersion is well-known. When an atom exhibits anomalous dispersion, its atomic scattering factor can be written in the form

\[ f = f^0 + \Delta f' + i \Delta f'' \]  \hspace{1cm} (1)

following a standard notation (James, 1958). The values of \( \Delta f' \) and \( \Delta f'' \), for different atoms and different X-ray wavelengths, have been tabulated by Dauben and Templeton (1955) (see also International
Tables, 1962) and recently by Cromer (1965) and by Saravia and Caticha-Ellis (1966; only $\Delta f'$ values).

Equation (1) can be written as

$$ f = f' + if'' \quad (2a) $$

where

$$ f' = f^0 + \Delta f' \quad \text{and} \quad f'' = \Delta f'' \quad (2b) $$

Here $f'$ and $f''$ are the real and imaginary parts of the total atomic scattering factor ($f$) of the anomalous scatter. This complex nature of the atomic scattering factor makes the intensities of inverse reflections (namely, the reflection $H(=hkl)$ and $\bar{H}(=-h\bar{k}\bar{l})$) unequal in a non-centrosymmetric crystal, thereby causing a break down of the well-known Friedel's Law. Since Bijvoet was the first to clearly point out the practical use of this difference in the intensities of inverse reflections (hereafter denoted by $\Delta I$) for the determination of the absolute configuration of optically active crystals (Bijvoet, 1951; 1954; 1955) and for resolving the well-known two-fold ambiguity in the phase determined by the single isomorphous replacement method (Bijvoet, 1951,
1954), this difference $\Delta I$ is known as the Bijvoet difference. The scope of the anomalous dispersion method in crystal structure analysis was widened by the work of Peterson (1955) and the possible uses of this method may be summarised as follows:

(a) To determine the structure of non-centro-symmetric crystals using the Bijvoet difference data alone (Phase Methods: Ramachandran and Raman, 1956; Peerdeeman and Bijvoet, 1956; Patterson Methods: Pepinsky and Okaya, 1956; Okaya and Pepinsky, 1956; Ramachandran and Raman, 1959; Raman, 1959b).

(b) To complement the multiple isomorphous replacement method in its various stages (see Rossman, 1961; North, 1965; Kartha and R.Parthasarathy, 1965a, 1965b; Kartha, 1965; Matthews, 1966a, 1966b).

(c) To establish the absolute configuration of optically active crystals (Bijvoet et al, 1951; Saito et al, 1955a, 1955b; Grenville-Wells and Lonsdale, 1954; Ramachandran and Chandrasekaran, 1957; Beurskens-Kersten et al, 1963).

(d) To determine the space group of crystals (Ramachandran and R.Parthasarathy, 1963).
(e) To determine experimentally the value of $\Delta f^* \ (R.\ Parthasarathy, \ 1962b; \ Hall \ and \ Maslen, \ 1966)$.

It is clear that the success of the anomalous dispersion method for such applications depends on the possibility of measuring, fairly accurately, the Bijvoet differences of a large percentage of reflections. A question of practical importance and utility now arises, namely, "what are the optimum conditions for observing large Bijvoet differences?" The answer for this is discussed in Chapters 2 and 3 where the probability distribution of Bijvoet differences and the expectation value of the Bijvoet ratio (which is the ratio of the Bijvoet difference to the mean intensity of inverse reflections) are considered.

It is well-known that the phase of a reflection can be determined from the value of $\Delta I$ but for an inherent two-fold ambiguity and the easiest method of resolving this ambiguity is to use the phase closer to the heavy-atom (i.e. anomalous scatterer) contribution (Ramachandran and Ramaswamy, 1956). We shall hereafter call this method as the quasi-anomalous method (or QAM briefly)
and the Fourier synthesis computed using the phases obtained by the QAM as the quasi-anomalous synthesis (or QAS briefly). However, a few questions of practical importance arise such as "what will be the probable percentage of reflections for which QAM can give correct phases, under specified conditions? Is it justifiable to use the QAM even when the contribution of the anomalous scatterers to the local mean intensity is small? What is the effect of the number of anomalous scatterers on the QAM?" The answers to these interesting questions are discussed in Chapter 4 where the probability distribution of phases in crystals containing anomalous scatterers is dealt with. It may, however, be asked whether the QAM is the best way of resolving the two-fold ambiguity. This aspect is discussed in Chapter 5 where a new probability method for resolving this two-fold ambiguity is developed. This method satisfies the criterion of Blow and Crick (1959) for the "best Fourier" (which is one in which the mean square error in the electron density distribution is a minimum) and leads to a new weighting function. The Fourier synthesis using this weighting function will be hereafter called the weighted anomalous syntheses (or WAS briefly). In this chapter the QAS and WAS are compared using suitable 2-dimensional hypothetical models, in order to find out the relative merits of the two syntheses.
2. THE ISOMORPHOUS REPLACEMENT METHOD

This method makes use of the differences in the intensities of a reflection \( \bar{h} \) from a pair of isomorphous crystals for determining the phases of X-ray reflections. This leads to a unique determination of the signs of reflections in centrosymmetric crystals, while in the case of a non-centrosymmetric crystal the phase is determined but for an inherent two-fold ambiguity (Bokhoven et al, 1949; 1951). However, the phases of reflections in non-centrosymmetric crystals can be uniquely determined by the double isomorphous replacement method (Bokhoven et al, 1951; Harker, 1956). In actual crystals, disturbing factors such as the errors in the intensity data, lack of isomorphism between the pair of crystals etc arise and this makes it necessary to use the multiple isomorphous replacement method which is often used in protein crystallography (see Dickerson et al, 1961).

The success of the isomorphous replacement method depends on how well the two crystals are isomorphous and thus a test for isomorphism of the pair of crystals would be necessary and useful (Dickerson et al, 196
The tests that have been proposed for this may be summarised as follows:

(a) The simplest is to compare the unit cell dimensions of the pair of crystals. This test is not only qualitative but also not confirmative since a pair of crystals with practically the same cell dimensions may have different molecular arrangements (Trommel and Bijvoet, 1954; Corey et al., 1962).

(b) Since the intensities of X-ray reflections are structure-dependent quantities, the intensity data from the two must contain information about the isomorphism of the pair of crystals. Thus the isomorphism between two crystals can be tested by the following methods: (i) By comparing the Patterson synthesis for the two structures (Bernal et al., 1959); (ii) By studying the variation in $\langle (\Delta I)^2 \rangle / \langle I \rangle$ with $\sin \theta$ (Crick and Magdoff, 1956; Carlisle and Palmer, 1962) and (iii) By studying the probability distribution of certain random variables defined in terms of the intensity data from the two crystals (Ramachandran et al., 1963; Srinivasan et al., 1963a; 1963b; Srinivasan et al., 1964; Srinivasan and Ramachandran, 1965a; 1965b). Of these
methods, (i) and (ii) are of a qualitative nature but (iii) is quantitative in the sense that it can give a measure of the degree of isomorphism. However, the results obtained by Ramachandran and co-workers are not applicable for studying the isomorphism of the simple substitution type (such as that which exists in Cl and Br derivatives) and are also not applicable to crystals in which the replaceable group contains a small number of atoms. An extension of method (iii) to such cases involves theoretical difficulties. Such difficulties can be easily overcome if moments of the distribution of intensities are used for this purpose, instead of the distribution function of structure amplitudes. Details of the calculation of the higher moments of simple functions of normalised intensities from a pair of crystals under general conditions is given in Chapter 9. The advantage of this higher moment test over that using distribution functions is that the value of the higher moments differ widely for the isomorphous and non-isomorphous pair of crystals and can therefore be expected to give better results.

It is well-known that a combination of the single isomorphous replacement method and the anomalous dispersion method can, in principle, lead to a unique
determination of structure in non-centrosymmetric crys-
tals (Ramachandran and Raman, 1956; Ramachandran and
Ayyar, 1963; Okaya and Pepinsky, 1956). In this con-
nection it might be useful if we could test the isomor-
phism of the pair of crystals by using the anomalous
dispersion data from them. This possibility is discussed
in Chapter 10 where the probability distribution of
the sum, difference, product and the quotient of the
normalised Bijvoet differences from a pair of non-
centrosymmetric crystals containing anomalous scatterers
is considered.

3. THE HEAVY ATOM METHOD

The heavy atom method is one of the earliest
and simplest attempts to circumvent the phase problem
(Åbberthson and Woodward, 1937; 1940; Carlisle and Crow-
foot, 1945). This method is based on the principle that
if a few atoms of larger scattering power than the others
are present in the structure (these heavy atoms can be
easily located from the Patterson) the phase of the con-
tribution to the structure factor from these heavy atoms
(denoted by $\alpha_p$) would be close to the true phase
(denoted by $\alpha_N$) of the reflection, so that the Fourier
synthesis with $|F_o| \exp(i\alpha_p)$ as Fourier coefficients
(where $|F_o|$ is the observed structure amplitude cor-
rected for various factors) leads to a Fourier map which
would be an approximation to the true Fourier and can
in general be interpreted to determine the positions of
the unknown atoms. The success of this method will
therefore depend on the closeness of $\alpha_p$ to $\alpha_N$ for
most of the reflections. Thus, the distribution of the
phase-angle-error $\Theta(= \alpha_N - \alpha_p)$ can be used to under-
stand the general features of the heavy atom method.

Sim (1957b) has worked out this distribution for the
particular case of a non-centrosymmetric crystal contain-
ing a single heavy atom in addition to a large number of
light atoms in the unit cell. However, the effect of
the number and 'heaviness' of the atoms on the dis-
tribution of $\Theta$ and the consequent effect on the heavy-
atom method have not been considered by Sim (1957b).

This problem is therefore considered in Chapter 6 where
the distribution of $\Theta$ for a unit cell containing
different number of heavy atoms is dealt with.
The heavy atom method for a centrosymmetric crystal consists in using $|F_0|s_p$ as the Fourier coefficients, where $s_p(=\pm 1)$ is the sign of the reflection due to contributions from the heavy atoms. The success of this method will therefore depend on using a suitable heavy-atom derivative of the molecule for which the sign $(s_H)$ of most of the reflections are determined by the sign of $(s_p)$ of the heavy atom contribution. In this connection it would be useful to determine the probable percentage of reflections (denoted by $P(\pm)$) which have the same sign as the heavy atom contribution, as a function of the number and 'heaviness' of the heavy atoms. The expression for $P(\pm)$ has been worked out by Sim (1957a) for two cases, namely, those of a centrosymmetric crystal having two and many atoms respectively (besides a large number of light atoms) and his expression for the many-atom case is in the form of an integral which has to be evaluated by a numerical method. The effects of the number and 'heaviness' of the dominating atoms on the heavy-atom method were not discussed by him. This problem is tackled in Chapter 6, by following an independent method, where the probability distribution of a discrete variable $s(=s_HS_P)$, which is the product of the sign $(s_H)$ of the reflection and
the sign \((s_p)\) of the heavy-atom contribution, is worked for four cases, namely, the cases of a centrosymmetric crystal containing one, two, four and many heavy atoms (besides a large number of light atoms). The value of \(P(+)\) can be directly deduced from the distribution of \(a\) as a particular case. It is also found that the expression for \(P(+)\) now turns out to be a simple function, namely, an Arctan function which can be easily evaluated. The theoretical results obtained from the distributions of \(a\) and \(\theta\) are also used to compare the heavy atom method in centrosymmetric and non-centrosymmetric crystals.

4. SPACE GROUP DETERMINATION USING INTENSITY STATISTICS

Wilson (1949a) was the first to show that the distribution of X-ray intensities can be used for testing the centrosymmetry of crystals. Since then several statistical tests for centrosymmetry, based on Wilson's distributions, have been proposed and they are (a) the test ratio of Wilson, \(F\) \((= \langle F^2 \rangle / \langle F^2 \rangle)\) (Wilson, 1949a; 1949b); (b) the variance test of the
normalised intensity $\mathbf{z}$, i.e. $v(s)$ (Wilson, 1951); (c) the average multiple test (Wilson, 1950; Rogers, 1950); (d) the cumulative function of $\mathbf{z}$, $N(s)$ (Howells et al., 1950); (e) the probability density function of $y(=\sqrt{s})$ (Ramachandran and Srinivasan, 1959), (f) the higher moment test, $\langle s^n \rangle$ (Srinivasan and Subramanian, 1964); and (g) the test based on the probability distribution of new intensity functions (Srinivasan and Sriskrishnam, 1966). Since Wilson's distributions are applicable only to crystals containing a large number of atoms at random positions in the unit cell (International Tables, 1959), such tests may lead to ambiguous and some times even wrong results, when applied to crystals containing dominating atoms or to crystals with pseudo-symmetric distribution of atoms (Whittaker, 1953; Eriks and MacGillavry, 1954; Paton and MacDonald, 1957; Robertson and Shearer, 1956; Robertson et al., 1958). The probability distribution of X-ray intensities for these non-Wilson cases have been considered by various workers (Lipson and Woolfson, 1952; Rogers and Wilson, 1953; Karle and Hauptman, 1953; Hauptman and Karle, 1953; Collin, 1955; Hargreaves, 1955; 1956; Wilson, 1956; Herbstein and Schoening, 1957; Klug, 1956; Sim, 1958a; 1958b; 1960a; Srinivasan, 1960; 1961.

* A recent study by Hargreaves and Coggi (1966) using a modified $N(s)$ test has shown the structure to be centrosymmetric.
Ilyukhin and Nikitin, 1963). Recently, Foster and Har- 
greaves (1963a; 1963b) have worked out the higher 
moments of X-ray intensities and their results have 
greater scope for space group determination. However, 
a quantitative treatment of the effect of the number of 
heavy atoms and their 'heaviness' on the statistical 
criteria such as $\rho$, $v(s)$ and $\langle s^n \rangle$ were not considered 
earlier. This study is particularly interesting in view 
of the fact that usually a few heavy atoms are intro-
duced in the molecule to circumvent the phase problem. 
This study is therefore undertaken in Chapter 7 where 
the general expressions for the $n$th moment of the 
normalised structure amplitude $y$ are worked out for 
crystals (both centrosymmetric and non-centrosymmetric) 
containing different number of heavy atoms in the unit 
cell (besides a large number of light atoms). The 
theoretical treatment in this chapter has some advanta-
ages which are (a) the expressions for $\rho$, $\langle y \rangle$, $v(y)$, 
v($s$) and $\langle s^n \rangle$ can all be deduced as particular 
cases from the expression for $\langle f^n \rangle$ and (b) the 
expressions of all these statistical criteria turn out 
to be functions of a single parameter $\sigma^{-2}$ which is the 
fractional contribution to the local mean intensity from 
the heavy atoms in the unit cell. It may be noted here
since \( \sigma^{-2} \) is a good measure for the 'heaviness' of the dominating atoms and since it can also be easily calculated by knowing the contents of the unit cell, it is best suited for the problem at hand. It may be mentioned here that Sim (1958b) has obtained the value of \( \rho \) as a function of \( \eta_{\sigma} (= \sigma^{-2}/\sqrt{1-\sigma^{-2}}) \) which is not a good measure of the 'heaviness' of the dominating atoms when compared with \( \sigma^{-2} \) in the presence of heavy atoms.

One point which is worthy of notice is that the presence of dominating atoms in the unit cell and the pseudo-symmetry are not the only causes for deviations from Wilson's distributions in actual crystals. Even in the absence of such disturbing features, which are structural in nature, the distributions obtained in actual cases may deviate from Wilson's distributions due to the use of the inaccurate intensity data (i.e. data with errors of observation). It will therefore be useful to study the influence of intensity errors on the statistical criteria for centrosymmetry. Such a study helps one to find a rough upper limit for the discrepancy that can be allowed in practical cases where intensities with errors of observations are involved and thereby
enables one to avoid correlating such deviations (i.e. the statistical anomalies arising from the use of inaccurate intensity data) to structural peculiarities.

Rogers et al (1955) have studied this problem with reference to four statistical criteria, \( P, \beta, v(s), \) and average multiple test. Such a study will be particularly interesting and useful for the higher moment test, in view of the relative importance of the higher moments for space group determination. The influence of different types of intensity errors on the higher moment test for centrosymmetry is therefore considered in Chapter 8.

5. NOMENCLATURE FROM THE THEORY OF PROBABILITY

We shall denote the probability density function (hereafter briefly referred to as PDF) of a random variable \( x \) by \( P(x) \) and the cumulative distribution function (or simply called the cumulative function) by \( N(x) \). If the random variable under consideration is of the discrete type, we shall use the term "probability function" instead of the term PDF. We
shall denote the expectation value of $x$ by $\langle x \rangle$ and the variance of $x$ by $\nu(x)$. Whenever necessary, we shall attach subscripts to $P(-)$ and $\langle - \rangle$ for the purpose of identification. We shall introduce the theorems from the theory of probability at the appropriate places in the text.

6. NOTATION OF SPECIAL FUNCTIONS

$\text{erf}(x)$ - Error function
$\text{erfc}(x)$ - Complementary error function
$\Gamma(n)$ - Gamma function
$\Gamma(a,x)$ - Incomplete gamma function
$\gamma(a,x)$ - Incomplete gamma function
$B(m,n)$ - Beta function
$J_\nu(x)$ - Bessel function of the first kind of order $\nu$
$I_\nu(x)$ - Modified Bessel function of the first kind of order $\nu$
$K_\nu(x)$ - Modified Bessel function of the second kind of order $\nu$
$K(k)$ - Complete elliptic integral of the first kind
$E(k)$ - Complete elliptic integral of the second kind
$\delta(x)$ - Dirac delta function

$_pF_q(a_1, a_2, \ldots, a_p; b_1, b_2, \ldots, b_q; x)$ - Generalised hypergeometric function with $p$ numerator parameters and $q$ denominator parameters. This will be briefly called the $_pF_q$ function

$_1F_1(a; b; x)$ - Kummer's confluent hypergeometric function or simply called $_1F_1$ function

$_2F_1(a, b; c; x)$ - Gauss' hypergeometric function (or simply called $_2F_1$ function)

$M_{k, \mu}(x)$ - Whittaker's confluent hypergeometric function

$W_{k, \mu}(x)$ - Whittaker's confluent hypergeometric function

$D_v(x)$ - Parabolic cylinder function

$P_v(x)$ - Legendre function of the first kind of order $\nu$

These functions are defined in Appendix A and the formulae involving these functions, which are necessary for the study in this thesis are given in the various appendices.
7. DESCRIPTION OF THE CONTENTS OF THE UNIT CELL OF A CRYSTAL

We shall consider a centrosymmetric crystal of space group $P\bar{1}$ (hereafter simply referred to as a centrosymmetric crystal) or a non-centrosymmetric crystal of space group $P1$ (hereafter simply called a non-centrosymmetric crystal) containing $N$ atoms in the unit cell. Let $P$ of the $N$ atoms represent the known atoms and the remaining $Q = N - P$ atoms represent the unknown atoms. For simplicity, we shall refer to the known and unknown groups of atoms as the P-group (or P-atoms) and the Q-group (or Q-atoms) respectively. The Q-group is assumed to contain a large number of atoms of similar scattering power (for example, light atoms such as O, N and C) which are randomly distributed in the unit cell (subject to the crystal symmetry) so that the structure factors due to contributions from the Q-atoms satisfy Wilson's distributions (Wilson, 1949a) depending on the symmetry of the Q-group. The P-group is assumed to contain only atoms of a single type (for example all chlorines or all bromines, etc) which are distributed at random in the unit cell subject to the crystal symmetry. The
P-group will be generally assumed to consist of heavy atoms or anomalous scatterers or replaceable atoms (the latter two types of atoms are also usually heavy atoms) and this will be clear from the context. The number of atoms in the P-group is assumed to be small (say \( P = 1 \) or 2) or large (i.e. \( P = \text{many} \)). When \( P = \text{many} \), the P-group will have a centric configuration if the crystal is centrosymmetric and may have either a centric or acentric configuration if the crystal is non-centrosymmetric and these three cases will be briefly denoted by \( P = M, MC \) and \( MA \) respectively. That is, we shall consider three cases in a centrosymmetric crystal, namely, the cases when \( P = 1, 2 \) and \( M \) and four cases in a non-centrosymmetric crystal, namely the cases when \( P = 1, 2, MC \) and \( MA \). We shall, as usual, choose the origin conveniently at the centre of the P-group (whether the crystal is centrosymmetric or non-centrosymmetric) if the P-group is centric and this is true for the cases \( P = 1, 2, M \) and \( MC \). We shall assume the number of P-atoms for the case \( P = \text{many} \) to be large enough so that the structure factors due to contributions from the P-atoms for the cases \( P = M \) and \( MC \) satisfy Wilson's distribution for the centrosymmetric crystal that for the case \( P = MA \) satisfies that for a non-centrosymmetric crystal.
For convenience, we shall term the cases when \( P = 1, 2 \) and many (\( = M, MC \) or \( MA \)) as the one-atom case, two-atom case and many-atom case respectively. It is to be noted that though we have designated the crystal by the number of \( P \)-atoms alone, it is always taken that the crystal contains the \( Q \)-atoms (already described) in addition to the \( P \)-atoms.

Why We Consider \( P \)-groups with Different Number of Atoms

The dominant role of heavy atoms (or known atoms) to circumvent the phase problem is well-known (for example we have the heavy-atom method, the anomalous dispersion method, and the isomorphous replacement method). However, in the presence of heavy atoms in the unit cell, various interesting effects occur. The peculiar distribution of intensities for a two atom structure (Srinivasan, 1960) and the occurrence of pronounced anomalous scattering effect in structures with two anomalous scatterers (see Section (2-1)) are but a few interesting examples for this. Thus, a systematic study of the effect of the number of heavy atoms in the unit cell on the statistical criteria obtainable from random variables of crystallographic interest would be useful. We shall therefore make such an attempt by considering the cases with \( P = 1, 2 \) and many (\( = M, MC \) or \( MA \)) as specific examples.
8. SUMMARY OF NOTATION AND SOME STANDARD RESULTS

(a) Normal Scattering

We shall consider a crystal (centrosymmetric or non-centrosymmetric) containing $N$ atoms of which $P$ are known and the remaining $Q (= N - P)$ are unknown. The structure factor $F_{N}(H)$ for a reflection $H(=h\,k\,l)$ due to all the $N$ atoms can be written in terms of the contributions from the $P$- and the $Q$-atoms as (see Figure 1)

$$F_{N}(H) = F_{P}(H) + F_{Q}(H)$$  \hfill (3)

where

$$F_{S}(H) = \sum_{j=1}^{S} f_{Sj} \exp(2\pi i H \cdot R_{Sj}) = |f_{S}| \exp(i \alpha_{S})$$  \hfill (4)

where $S$ is a dummy subscript standing for $N$, $P$ and $Q$. Here $f_{Nj}$, $f_{Pj}$ and $f_{Qj}$ represent the atomic scattering factors of atoms in the $N$-, $P$- and $Q$-groups respectively. The structure factors $F_{S}(S = P, Q$ and $N)$ become real quantities in a centrosymmetric crystal.
Argand Diagram Representing the Structure Factor of a Reflection $\mathbf{H} = (h \, k \, l)$ in terms of the contributions from the P- and the Q-atoms. If the P-atoms are anomalous scatterers, the same diagram shows the relationship of the structure factors $P_H'(H)$, $P_P'(H)$, and $P_Q$ due to contributions from the real part of the atomic scattering factor of the atoms in the Unit Cell.

Argand Diagram showing the Relationship between the various components of the structure factor of the pair of inverse reflections $\mathbf{H}$ and $\mathbf{H}$ (i.e. the Bijvoet pair). This figure enables one to obtain the expression for Bijvoet difference as $\Delta I = 4 |F_H''| |F_P''| \sin \theta$.
We shall denote the contributions to the local mean intensity from the \( N \), \( P \) and \( Q \)-atoms by \( \sigma_N^2 \), \( \sigma_P^2 \) and \( \sigma_Q^2 \) respectively and the fractional contribution to the local mean intensity from the \( P \) and \( Q \)-atoms by \( \sigma_{1}^2 \) and \( \sigma_{2}^2 \) respectively. That is (Wilson, 1942)

\[
\sigma_S^2 = \left< |F_S|^2 \right> = \sum_{f=1}^{S} \sigma_{f}^2, \quad S = N, P \text{ and } Q \tag{5}
\]

\[
\sigma_{1}^2 = \frac{\sigma_P^2}{\sigma_N^2}, \quad \sigma_{2}^2 = \frac{\sigma_Q^2}{\sigma_N^2} \tag{6}
\]

From (5) and (6) it is clear that

\[
\sigma_P^2 + \sigma_Q^2 = \sigma_N^2 \tag{7}
\]

\[
\sigma_1^2 + \sigma_2^2 = 1 \tag{8}
\]

Equation (8) is an important relation and will be frequently used in the thesis for simplifying many theoretical expressions. Let us define

\[
r = \frac{\sigma_P^2}{\sigma_Q^2} = \frac{\sigma_1^2}{\sigma_2^2} \tag{9}
\]

We shall denote the normalised structure amplitudes due to
contributions from the $N$-, $P$- and $Q$-atoms respectively by $y_N$, $y_P$ and $y_Q$ and the corresponding normalised intensities by $s_N$, $s_P$ and $s_Q$ respectively. That is,

$$y_S = \frac{|F_S|}{\sigma_S}, \quad S = N, P \text{ and } Q \quad (10)$$

$$s_S = \frac{|F_S|^2}{\sigma_S^2} = y_S^2, \quad S = N, P \text{ and } Q \quad (11)$$

We shall denote the angle which $F_N$ makes with $F_P$ by $\theta$. That is,

$$\alpha_N - \alpha_P = \theta \quad (12)$$

Geometrically $\theta$ represents the angle made by $F_N$ with $F_P$ as the reference line (Figure 1).

(b) Anomalous Scattering

When the $P$-atoms become anomalous scatterers for the given wavelength of X-rays, the atomic scattering factor $f_P$ can be written as (see Section (1))

$$f_P = f_P^0 + \Delta f_P' + i \Delta f_P'' = f_P' + if_P'' \quad (13)$$
We shall denote the ratio of the imaginary part to the total real part of the complex atomic scattering factor \( f_p \) by \( k \). That is,

\[
k = \frac{\Delta f_p''}{f_p'' + \Delta f_p'} = \frac{f_p''}{f_p'}
\]  

(14)

The structure factor equation for a reflection \( \overline{hkl} \) can be written from (3), (4) and (13) as

\[
F_N(\overline{hkl}) = F'_P(\overline{hkl}) + F''_P(\overline{hkl}) + F_Q(\overline{hkl})
\]

\[
= F'_N(h) + F''_P(h)
\]  

(15)

where

\[
F'_P(\overline{h}) = \sum_{j=1}^{P} f_{pj}' \exp(2\pi i \overline{h} \cdot \overline{r}_{pj}) = |F'_P| \exp(i \alpha'_P)
\]  

(16)

\[
F''_P(\overline{h}) = i \sum_{j=1}^{P} f_{pj}'' \exp(2\pi i \overline{h} \cdot \overline{r}_{pj}) = |F''_P| \exp(i \alpha''_P)
\]  

(17)

\[
F'_N(\overline{h}) = F'_P(\overline{h}) + F_Q(\overline{h}) = |F'_N| \exp(i \alpha'_N)
\]  

(18)

Here \( F_P(\overline{h}) \) and \( F_Q(\overline{h}) \) are the contributions to reflection \( \overline{h} \) from the real and the imaginary parts of the
atomic scattering factor of the anomalous scatterers and \( P'(H) \) represents that from the real parts of the scattering factor of all the atoms in the unit cell. We shall represent the angle between \( P'_N(H) \) and \( P'_P(H) \) by \( \theta \). That is

\[
\lambda'_N - \lambda'_P = \theta
\]  

(19)

In the commonly occurring cases, the \( P \)-group contains only anomalous scatterers of a single type. We shall therefore consider only such cases. For this case it is clear from (16) and (17) that \( P''_P \) is perpendicular to \( P'_P \). That is

\[
\lambda''_P = \lambda'_P + \eta/2
\]  

(20)

The relationship of the various structure factor components for inverse reflections (i.e. \( \overline{H} \) and \( \overline{H} \)) can be conveniently represented in an Argand diagram (Figure 2). In order to bring out the geometrical relations clearly,

* It may be noted that \( \theta \) defined in (19) becomes identical with that defined in (12) in the absence of anomalous scattering. The use of \( \theta \) in both the places would not cause confusion, since the context would indicate which is meant
the part of the diagram pertaining to the reflection $\bar{H}$ (i.e. that below the $x$-axis), is reflected about the $x$-axis so that $F_N(\bar{H})$ coincides with $F_N(H)$. The Bijvoet difference $(\Delta I)$ and the arithmetic mean $(I)$ of the intensities of the inverse reflections can be obtained from the geometry of Figure 2 (Ramachandran and Kahan, 1956) as

$$\Delta I = |F_N(H)|^2 - |F_N(\bar{H})|^2 = 4|F'_N||F''_P| \cos \phi$$

$$= 4|F'_N||F''_P| \sin \phi$$

(21)

$$I = \left(\frac{1}{2}\right)[|F_N(H)|^2 + |F_N(\bar{H})|^2] = |F'_N|^2 + |F''_P|^2$$

(22)

where we have used the relation $\phi + \phi = \pi/2$ (Figure 2).

From (14) and (16) to (18) we obtain the following results

$$F''_P(H) = \sum_{j=1}^{P} f''_{Pj} \exp\left(2\pi i \frac{H}{a} \cdot \frac{j}{P}\right) = i k f'_{P} F'(H)$$

(23)

$$\langle |F'_N|^2 \rangle = \sum_{j=1}^{P} f'_{Pj}^2 = P f'_{P}^2 = \sigma_{P}^2, \quad \sigma_{P}$$

(24)

$$\langle |F''_P|^2 \rangle = \sum_{j=1}^{P} f''_{Pj}^2 = P f''_{P}^2 = \sigma_{P''}^2, \quad \sigma_{P''}$$

(25)

$$\sigma_{P''}^2 = k^2 \sigma_{P}^2$$

(26)
\[ \langle |F|^2 \rangle = \sigma_p^2 + \sigma_Q^2 = \sigma_N^2, \text{ say}^* \]  

(27)

The definition of other quantities such as \( \sigma_{-1}^2, \sigma_{-2}^2 \) etc. follows exactly as for normal scattering (Section (8a)).

Using (23) and (26) we obtain

\[ y_p = \frac{|F_p'|}{\sigma_p} = \frac{|F_p'|}{(k \sigma_p)} = \frac{|F_p''|}{\sigma_p''} \quad (28) \]

which shows that the normalised variables \( |F_p''|/\sigma_p'' \), \( |F_p'|/\sigma_p \) and the variable \( y_p \) defined in (10) have the same value.

9. THE PDF AND THE nTH MOMENT OF \( Y_Q \) AND \( Y_P \)

(a) The PDF of \( Y_Q \) and \( Y_P \)

Since \( Y_Q \) satisfies Wilson's distributions (depending on crystal symmetry), the PDF of \( Y_Q \) will be given by** (Ramachandran and Srinivasan, 1959)

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* For convenience, we use \( \sigma_p^{-2} \) to stand for \( \sigma_{-2}^{-2} \) and \( \sigma_N^{-2} \) for \( \sigma_{-N}^{-2} \) (see foot-note in p. 26).

** In this section \( C \) and \( A \) are used as subscripts to denote that the subscripted quantity belongs to a centrosymmetric or to a non-centrosymmetric crystal respectively.
\[ P_Q(y_Q) = \left( \frac{2}{\pi} \right)^{\frac{1}{4}} \exp(-y_Q^2/2), \quad 0 \leq y_Q < \infty \quad (29) \]

\[ P_A(y_Q) = 2y_Q \exp(-y_Q^2), \quad 0 \leq y_Q < \infty \quad (30) \]

when \( P = 1 \), if we choose the origin on this single P-atom, it is clear that \( P_P = f_P \) and \( \sigma_P^2 = f_P^2 \), so that \( \gamma_P = |f_P|/\sigma_P = 1 \) for any reflection.

The PDF of \( y_P \) in this case will therefore be a delta function at \( y_P = 1 \). The PDF of \( y_P \) for the case \( P = 2 \) has been obtained by Srinivasan (1960). As assumed earlier (section (7)), the PDF of \( y_P \) for the cases \( P = M \) and \( \text{MC} \) will be that for Wilson's distribution for a centrosymmetric crystal (i.e. (29)) and that for the case \( P = MA \) will be that for a non-centrosymmetric crystal (i.e. (30)). For the case \( P = 4 \) (P-centric) the PDF of \( y_P \) (this is required in Chapter 6) is worked out in Appendix G. Thus, the PDF of \( y_P \) in the various cases are given by

\[ P(y_P) = \]

\[ \delta (y_P - 1), \quad 0 \leq y_P < \infty \quad \text{when } P = 1 \quad (31) \]

\[ \left( \frac{2}{\pi} \right)^{\frac{1}{4}} (2 - y_P)^{-\frac{1}{4}}, \quad 0 \leq y_P \leq \sqrt{2} \quad \text{when } P = 2 \quad (32) \]
\[ (2/\pi)^{\frac{1}{2}} \exp(-y_P^2/2), \quad 0 \leq y_P < \infty \text{ when } P = M \text{ or } MC \] (33)

\[ 2y_P \exp(-y_P^2), \quad 0 \leq y_P < \infty \text{ when } P = MA \] (34)

\[ (1/\pi) 2F_1(1/2, 1/2; 1; 1-y_P^2/4), \quad 0 \leq y_P \leq 2 \]
when \( P = 4 \) (P-centric) (35)

(b) The \( n \)-th Moment of \( y_Q \) and \( y_P \) for \( P = 1, 2 \) and Many

The \( n \)-th moment of \( y_Q \) can be obtained from (29) and (30) by using (C-2) as

\[ \langle y_Q^n \rangle_C = \frac{2^{n/2}}{\sqrt{\pi}} \Gamma \left( \frac{n+1}{2} \right) = W_C(n), \text{ say} \] (36)

\[ \langle y_Q^n \rangle_A = \Gamma \left( n/2 + 1 \right) = W_A(n), \text{ say} \] (37)

Here we have used the notation \( W_C(n) \) and \( W_A(n) \) to emphasise the fact that they denote the \( n \)-th moment of the normalised structure amplitude for Wilson's distributions for centrosymmetric and non-centrosymmetric crystals respectively.
From (31) we obtain

$$\langle y_p^n \rangle_1 = \int_0^\infty y_p^n \delta(y_p - 1) \, dy_p = 1$$

(38)

where we have used the property of the Dirac delta function given in (B-19). From (32), we obtain

$$\langle y_p^n \rangle_2 = \frac{\sqrt{2}}{2\pi} \int_0^{\sqrt{2}} y_p^n (2 - y_p^2)^{-1/2} \, dy_p$$

$$= \left( \frac{2^n}{\pi} \right)^{1/2} \frac{\Gamma\left( \frac{n+1}{2} \right)}{\Gamma\left( \frac{n}{2} + 1 \right)} = \frac{W_c(n)}{W_A(n)}$$

(39)

to obtain which we have used the substitution $y_p^2 = 2x$ and the result in (A-6). It is evident that

$$\langle y_p^n \rangle_M = \langle y_p^n \rangle_{MC} = \langle y_q^n \rangle_C = \left( \frac{2^n}{\pi} \right)^{1/2} \frac{\Gamma\left( \frac{n+1}{2} \right)}{\Gamma\left( \frac{n}{2} + 1 \right)} = W_C(n)$$

(40)

$$\langle y_p^n \rangle_{MA} = \langle y_q^n \rangle_A = \Gamma\left( \frac{n}{2} + 1 \right) = W_A(n)$$

(41)

The values of the first few moments of $y_p$ in the various cases are given in Table 1. It may be noted that the values of $\langle y_p^n \rangle$ for $n = 0$ are all unity, thereby showing that the PDF's of $y_p$ in (31) to (35) are in the normalised form.

* In this section subscript to the expectation symbol denotes the number of atoms in the $P$-group
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* This column proves that the PDF's of \( y_p \) in the various cases are in the normalised form.