X-RAY INTENSITY STATISTICS OF APPROXIMATELY CENTROSYMMETRIC STRUCTURES*

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ABSTRACT

The joint probability distribution of X-ray structure factors of a non-centrosymmetric structure (true structure) and that of a centrosymmetric structure (assumed model) from which it deviates slightly, are given. These are characterised by a parameter $D = < \cos 2 \pi H . \triangle r_j >$ where $\triangle r_j$ are the deviations of the N atoms from the centrosymmetric arrangement. The limiting forms of the distribution for $D = 0$, and $D = 1$ are respectively the acentric and centric distributions of Wilson. Intermediate values of D characterise different degrees of centrosymmetry of the structure. The parallelism of the results to another 'approximately centrosymmetric' situation (Srinivasan, *Indian J. Pure Appl. Phys.*, 1965, 3, 187), is pointed out.

1. INTRODUCTION

In a series of papers from this laboratory (Ramachandran *et al.*, 1963 ; Srinivasan *et al.*, 1963 *a*, *b* ; 1964 ; Srinivasan and Ramachandran, 1965 *a*, *b* ; 1966 ; Srinivasan and Chandrasekharan, 1966 ; Parthasarathy and Srinivasan, 1967) the statistical distribution of a pair of structure factors have been considered. The results obtained therein have been shown to be applicable to different stages of crystal structure refinement as well as for testing of isomorphism between a pair of crystals. The probability distributions established were for a pair of structure factors, F_N and $F_P{}^c$ where F_N corresponds to the true structure containing N atoms and $F_P{}^c$ to the assumed model containing a part (P atoms) of the structure whose coordinates $r_{Pj}{}^c$ differ from the true $r_{Pj}{}^c$ by $\triangle r_{Pj}$ Broadly, two cases have been considered so far namely (*a*) when both F_N and $F_P{}^c$ are non-centrosymmetric (case I) and (*b*) when both F_N and $F_P{}^c$ are centrosymmetric (case II). The various results that have been deduced are thus applicable to a crystal structure which is known to be either non-centrosymmetric or centrosymmetric as the case may be.

The possibility that $F_P{}^c$ could correspond to a centrosymmetric model while F_N is non-centrosymmetric (we shall refer to this as case III) and *vice versa* (case IV) was not considered earlier since it was thought that this might not have immediate practical application. It has however been realised now that these cases are also of interest since they could lead to distributions for pseudosymmetric structures.† Consider for simplicity the case $P = N$. It is possible to imagine a structure which is in reality non-centrosymmetric while the assumed model is centrosymmetric. Following the basic problem posed for cases I and II, we postulate that the N atoms of the true structure are related to the N atoms of the assumed model through the given set of errors $\triangle r_{Nj}$. Since the assumed model is centrosymmetric for the present case, this would mean that the true model could better be described as "approximately centrosymmetric". Thus one would expect that as $\triangle r_{Nj}$ tend to zero the distribution would tend to be a centric one while when $\triangle r_{Nj}$ tend to be large the distribution would tend to the acentric one. For intermediate values of $\triangle r_{Nj}$ the distribution can be taken to represent different degrees of centrosymmetry of a non-centrosymmetric structure.

It would appear that the statistics of such a situation was first considered by Luzzati (1953) who applied his earlier analysis (1952) to the above problem and worked out theoretically the values to be expected for a type of discrepancy index involving F_N and $F_N{}^c$ which would enable one to use the results to deduce $\langle|\triangle r_{Nj}|\rangle$ for a practical case. His treatment of the problem is brief and is restricted to the statement of a few results. Recently this aspect of the problem has been considered in this laboratory in detail following the type of analysis done for cases I and II. The purpose of this paper is to outline briefly some of the main steps involved in deducing the distributions and the possible application of these to develop other statistical criteria. Most of these could be deduced following the same procedures as for cases I and II and in conjunction with Luzzati's treatment (1953).

It may be mentioned that the problem of this type of degree of centrosymmetry of a non-centrosymmetric structure was also recently considered in this laboratory (Srinivasan and Vijayalakshmi, 1972 *a*, *b* ; Srinivasan *et al.*, 1974 ; Srinivasan, Swaminathan and Chacko, 1972) and the present

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† Following Srinivasan (1965 *a*) we use this term pseudosymmetry in a very general sense to denote the presence of any non-crystallographic symmetry property associated with the "asymmetric part" or "crystallographic unit" so as to invalidate the basic Wilson conditions.

analysis forms, in part, an extension of the above studies.

2. Basic Probability Distributions

Let r_{Nj} denote the true coordinates of the structure which is approximately centrosymmetric. These may be considered to have been obtained by giving random and independent displacements Δr_{Nj} to the coordinates of a perfectly centrosymmetric assumed model. It is assumed that the shifts Δr_{Nj} and $\Delta r_{Nj'}$ for the atoms j and j' which are related by centrosymmetry are random and independent where $n = N/2$. We denote by F_N and $F_N{}^c$ the structure factors of the true and assumed structures. It is also assumed that both the true and assumed structures satisfy the ideal Wilson conditions, namely, they contain large number of similar atoms randomly distributed in the unit cell.

The establishment of conditional distribution $P(F_N; F_N{}^c)$ follows closely the steps given earlier (*e.g.*, *see* Appendix 1 of Srinivasan and Chandrasekharan, 1966) and is not detailed here.‡ The conditional distribution $P(F_N, F_N{}^c)$ takes the form

$$P(F_N; F_N{}^c) = \frac{1}{\pi \sigma_N{}^2 (1 - D^2)} \exp - \left[\frac{|F_N|^2 - D^2 |F_N{}^c|^2 - 2D |F_N| |F_N{}^c| \cos \alpha}{\sigma_N{}^2 (1 - D^2)}\right] \quad (1)$$

where $D = \langle \cos 2\pi H \cdot \Delta r_{Nj} \rangle$, $\sigma_N{}^2 = \sum_{j=1}^{N} f_j{}^2$

and α is the angle between F_N and $F_N{}^c$. The joint distribution $P(|F_N|, \alpha; F_N{}^c)$ for a given $F_N{}^c$ is

$$P(|F_N|, \alpha; F_N{}^c) = \frac{|F_N|}{\pi \sigma_N{}^2 (1 - D^2)} \exp - \left[\frac{|F_N|^2 - D^2 |F_N{}^c|^2 - 2D |F_N| |F_N{}^c| \cos \alpha}{\sigma_N{}^2 (1 - D^2)}\right] \quad (2)$$

where $\alpha = \alpha_N - \alpha_N{}^c$. In terms of normalised variables $y_N = |F_N|/\sigma_N$, $y_N{}^c = |F_N{}^c|/\sigma_N$ we have

$$P(y_N, \alpha; y_N{}^c) = \frac{y_N}{(1 - D^2)} \exp - \left[\frac{y_N{}^2 - D^2 y_N{}^{c2} - 2D y_N y_N{}^c \cos \alpha}{(1 - D^2)}\right] \quad (3)$$

$$P(y_N; y_N{}^c) = \frac{2 y_N}{(1 - D^2)} \exp - \left[\frac{y_N{}^2 - D^2 y_N{}^{c2}}{1 - D^2}\right] I_0 \left[\frac{2D y_N y_N{}^c}{1 - D^2}\right] \quad (4)$$

‡ The number of atoms in the model and true structure are denoted here by N while in the paper cited (Srinivasan and Chandrasekharan, 1966) it was denoted by P. Also the only other difference is that $F_N{}^c$ now corresponds to a centrosymmetric model.

It is important to note that while F_N has both amplitude and phase, $F_N{}^c$ is real since it corresponds to a centrosymmetric model. Thus assuming a centric distribution for $P(y_N{}^c)$

$$P(y_N{}^c) = \sqrt{2/\pi} \exp - (y_N{}^{c2}/2) \quad (5)$$

the joint distribution $P(y_N, y_N{}^c)$ is readily deduced to be

$$P(y_N, y_N{}^c) = \sqrt{2/\pi} \frac{2 y_N}{(1 - D^2)} \exp - \left[\frac{2 y_N{}^2 + (1 - D^2) y_N{}^{c2}}{2(1 - D^2)}\right] I_0 \left[\frac{2D y_N y_N{}^c}{(1 - D^2)}\right] \quad (6)$$

The distribution of α for a given $|F_N|$, $|F_N{}^c|$ will be useful. This is given by

$$P(\alpha; |F_N|, |F_N{}^c|) = \frac{1}{2\pi} \frac{\exp \left[\dfrac{2D |F_N| |F_N{}^c| \cos \alpha}{\sigma_N{}^2 (1 - D^2)}\right]}{I_0 \left[\dfrac{2D |F_N| |F_N{}^c|}{\sigma_N{}^2 (1 - D^2)}\right]} \quad (7)$$

So also, the actual distribution of phases, α can be deduced from (3) by substituting for $P(y_N{}^c)$ corresponding to centric distribution and integrating over y_N and $y_N{}^c$. The expression is not given here.

3. Discussion of the Results

The above results form the basis for working out a number of statistical results of interest. For instance the availability of the joint distributions $P(y_N, y_N{}^c)$ enables us to study distributions of variables such as the difference $y_d = (y_N - y_N{}^c)$ (and also product, quotient, etc.). These will be considered in detail in a later paper. However, we shall deduce here one interesting result concerning the distribution $P(y_N)$ alone. Thus integration over $y_N{}^c$ in (6) leads to the marginal distribution $P(y_N)$ to be

$$P(y_N) = \frac{2 y_N}{\sqrt{1 - D^4}} \exp - [y_N{}^2/(1 - D^4)] \, I_0 \left[\frac{D^2 y_N{}^2}{1 - D^4}\right] \quad (8)$$

This may be compared with the probability distribution of the normalised amplitude for another situation of "an approximately centrosymmetric structure" considered earlier in the literature (Srinivasan, 1965 *a*, *b*). This deals with the case of a non-centrosymmetric structure (space group $P1$) containing a centrosymmetric and a non-centrosymmetric group. The distribution for such a case turns out to be§

$$P(y_N) = \frac{2 y_N}{\sqrt{1 - \sigma_1{}^4}} \exp - [y_N{}^2/(1 - \sigma_1{}^4)] \, I_0 \left[\frac{\sigma_1{}^2 y_N{}^2}{1 - \sigma_1{}^4}\right] \quad (9)$$

§ Although Srinivasan (1965 *a*) gave for this case $P(y_N)$ as an integral his expression can be reduced using standard integral tables (Gradshteyn *et al.*, 1965) to the above form.

where σ_1^2 stands for the ratio of the mean square amplitudes corresponding to the centric group to that of the entire structure. A comparison of (8) with (9) shows that the final distributions are identical in form except for the appearance of D in (8) in place of σ_1 in (9). The parallel roles of σ_1 and D are now obvious. Thus the two limits $D=0$ (or $\sigma_1=0$) and $D=1$ (or $\sigma_1=1$) correspond to acentric and centric distributions. Intermediate values of D (or σ_1) correspond to different degrees of centrosymmetry. Thus D (or σ_1) may be taken as a quantitative measure of the degree of centrosymmetry of the structure. In fact it may be pointed out that Srinivasan *et al.* (1972) suggested earlier the use of D for this purpose and the present results only supply a sound theoretical justification for the same. The curves of $P(y_N)$ given as a function of σ_1^2 in the earlier paper (Srinivasan, 1965 *a, b*) are applicable here.

It may be mentioned that D can be estimated in practice by working out some of the statistical parameters connected with y_N. For instance, the moments or variance of y_N can be worked out which turn out to be functions of D. However, these may not be very sensitive especially when $\triangle r_{Nj}$ are small. It seems preferable to turn to other statistical parameters involving quantities y_N and y_N^c such as say the difference $y_d = y_N - y_N^c$. Since it measures the deviation of y_N from that of the assumed model, this and other related parameters such as reliability indices based on it may be expected to be more sensitive.

We may also mention here that since y_N **and** y_N^c now involve non-centrosymmetric and centrosymmetric combination, distributions connected with pair such as say the quotients y_N/y_N^c, y_N^c/y_N need not show symmetry properties such as were associated with these variables for cases I and II. These aspects as well as statistics for case IV are under detailed investigation and will be reported later.

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