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Probability Distribution Connected with Structure Amplitudes of Two Related Crystals. VI. On the Significance of the Parameter σ_A*

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The physical significance of the parameter σ_A appearing in the various expressions of the earlier parts is discussed.

Introduction

In the previous part of this series we considered the problem of the probability distribution of the observed and calculated structure amplitudes for the general case when the latter include a part (P out of N atoms) of the structure, which might have finite errors in their coordinates. The various distributions and related expressions are all characterized by a single parameter represented by $\sigma_A=\sigma_1 D_P$ where σ_1 $(=\sigma_P/\sigma_N)$ is the ratio of the root mean square contribution to the intensity from the P atoms to that from all the N-atoms and $D_P=\langle\cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_{Pj}\rangle$, $\mathbf{H}$ being the reciprocal vector and $\Delta\mathbf{r}_{Pj}$ the errors in the coordinates of the P-atoms.

The purpose of this paper is to show that there exists a simple physical interpretation of the parameter σ_A apart from what is implicit in its definition, namely that it is the product of the two quantities σ_1 and D_P. This result follows from a detailed study of the problem of correlation functions and their properties, particularly as applied to structure factors. These are being reported elsewhere (Srinivasan & Chandrasekharan, 1966). We shall present here briefly only one particular result in so far as it pertains to the results discussed in the earlier parts.

Evaluation of the real correlation

Two quantities were defined in the earlier parts (Srinivasan, Sarma & Ramachandran (1963); (Srinivasan & Ramachandran, 1965) namely $\langle Z\rangle$ and $\langle Z^c\rangle$ which are the expectation values of the products of the normalized structure amplitudes concerned ($Z=y_N y_P$ and $Z^c=y_N y_P^c$). These are in the nature of correlation functions and in fact they may be described as amplitude correlations† since they are measures of the correlation between the structure amplitudes concerned. They are related to a well known statistical parameter, namely the coefficient of linear correlation and the relations are readily worked out (Srinivasan, 1961). One might consider more generally the correlation between the actual structure factors. Consider first the pair of structure factors* F_N and F_P. We have taken for convenience F_P, that is the case when the errors in the coordinates of the P-atoms are all zero. The real correlation, denoted by C_R, between such a pair is defined, for the non-centrosymmetric case by (see Srinivasan & Chandrasekharan, 1966):

$$C_R=\left\langle\frac{|F_N|}{\sigma_N}\frac{|F_P|}{\sigma_P}\cos\,(\alpha_N-\alpha_P)\right\rangle$$
$$=\langle|E_N|\,|E_P|\cos(\alpha_N-\alpha_P)\rangle\,, \quad (1)$$

where for convenience we have used

$$E_N=F_N/\sigma_N\,,\quad E_P=F_P/\sigma_P\,, \quad (2)$$

which may be termed normalized structure factors, σ_N and σ_P being the root mean square values of the structure amplitudes $|F_N|$ and $|F_P|$ respectively. In (1) σ_N and σ_P denote the phase angles of F_N and F_P respectively.

The definition of C_R for the centrosymmetric case is readily made and follows in fact from (1) for the non-centrosymmetric case. It is given by

$$C_R=\langle|E_N|\,|E_P|s\rangle=\langle E_N E_P\rangle\,, \quad (3)$$

where s stands for the relative sign of E_N with respect to E_P; *i.e.* $s=+1$ when E_N and E_P have the same sign and $s=-1$ when they have opposite signs.

The evaluation of C_R is fairly straightforward once the necessary joint probability distributions are worked out. A detailed account and rigorous proof of the results following such a procedure are given in the paper cited earlier (Srinivasan & Chandrasekharan, 1965). However, it is also possible to obtain some of these results by a simplified method based on physical arguments which nevertheless leads to the same results. We shall adopt here only this method since it would suffice for our purpose.

Consider first the centrosymmetric case. We can write

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† This term is preferred (see Srinivasan & Chandrasekharan, 1965) to the term direct correlation used earlier by Srinivasan (1961).

* The notation used here follows closely that used in earlier parts.

$$F_N = 2\sum_{i=1}^{N/2} f_{Ni} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Ni} , \quad (4),$$

and writing F_N in terms of the two components F_P, F_Q,

$$F_N = F_P + F_Q = 2\sum_{j}^{P/2} f_{Pj} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pj} + 2\sum_{k}^{Q/2} f_{Qk} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Qk} . \quad (5)$$

Since we require the quantity $\langle E_N E_P \rangle$ let us first evaluate $\langle F_N F_P \rangle$. It is readily shown from equation (5) that

$$\langle F_N F_P \rangle = \Big\langle \Delta \Big\{ \sum_{i=1}^{P/2} f_{Pi}^2 \cos^2 2\pi \mathbf{H} \cdot \mathbf{r}_{Pi} + \sum_{i \neq j}^{P/2} \sum^{P/2} f_{Pi} f_{Pj} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pi} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pj} + \sum_{i}^{P/2} \sum_{k}^{Q/2} f_{Pi} f_{Qk} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pi} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Qk} \Big\} \Big\rangle . \quad (6)$$

On averaging, the second and third terms within the curly brackets on the right hand side of equation (6) vanish, while the first term alone gives a finite contribution whose value is easily seen to be

$$\tfrac{1}{2} \sum_{i}^{P/2} f_{Pi}^2 = \tfrac{1}{4} \sum_{i}^{P} f_{Pi}^2 = \sigma_P^2 / 4$$

giving

$$\langle F_N F_P \rangle = \sigma_P^2 .$$

Thus, we see

$$\langle E_N E_P \rangle = \frac{1}{\sigma_N \sigma_P} \langle F_N F_P \rangle = \sigma_1 . \quad (7)$$

Thus, the average value of the product of the normalized structure factors E_N and E_P is the same as the ratio of the root mean square contribution to the intensity from the P-atoms to that from all the N-atoms. Conversely in view of the earlier definition (3) σ_1 may also be interpreted as the real correlation between the normalized structure factors E_N and E_P.

An exactly similar result can be shown for the noncentrosymmetric case also, namely the C_R defined by (1) reduces to σ_1. We omit the proof here.

Correlation in the presence of errors

The extension of the above result to the general case when the P-atoms have finite errors $\Delta\mathbf{r}_{Pj}$ is made readily. One has to take in (1) and (3) F_P^c instead of F_P. Here again for simplicity we consider the centrosymmetric case:

$$F_P^c = 2\sum_{j=1}^{P/2} f_{Pj} \cos 2\pi \mathbf{H} \cdot (\mathbf{r}_{Pj} + \Delta\mathbf{r}_{Pj}) . \quad (8)$$

We now evaluate $\langle F_N F_P^c \rangle$ where F_N is the same as defined earlier (4) and F_P^c is given by (8). Thus

$$\langle F_N F_P^c \rangle = \langle (F_P + F_Q) F_P^c \rangle = \langle F_P F_P^c + F_Q F_P^c \rangle . \quad (9)$$

It is easy to see that the second term, which involves interactions of the P- and Q-atoms, will vanish on averaging, since the two sets of atoms are completely independent. Expanding the first term using equation (5) and equation (8) we get

$$\langle F_P F_P^c \rangle = \Big\langle 4 \sum_{i=1}^{P/2} \sum_{j=1}^{P/2} f_{Pi} f_{Pj} \times \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pi} \cos 2\pi \mathbf{H} \cdot (\mathbf{r}_{Pj} + \Delta\mathbf{r}_{Pj}) \Big\rangle \quad (10)$$

$$= \Big\langle 4 \sum_{i=1}^{P/2} \sum_{j=1}^{P/2} f_{Pi} f_{Pj} \times (\cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pi} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pj} \cos 2\pi \mathbf{H} \cdot \Delta\mathbf{r}_{Pj} - \cos 2\pi \mathbf{H} \cdot \mathbf{r}_{Pi} \sin 2\pi \mathbf{H} \cdot \mathbf{r}_{Pj} \sin 2\pi \mathbf{H} \cdot \Delta\mathbf{r}_{Pj}) \Big\rangle . \quad (11)$$

The second term on the right hand side of equation (11) will tend to zero on averaging, by virtue of the fact that the quantities $\mathbf{r}_{Pi}$, $\mathbf{r}_{Pj}$, $\Delta\mathbf{r}_{Pj}$ are all as likely to be positive as negative and hence a mixed product of cosine and sine functions of these will also be as often positive as negative so that its mean will be zero. Also, in the term that remains only terms of the type $i=j$ survive. So also, since $\mathbf{r}_{Pj}$ are much larger compared with $\Delta\mathbf{r}_{Pj}$ for any given $\mathbf{H}$, we can replace the product of the first two cosine functions by its average value, namely $\langle \cos^2 2\pi \mathbf{H} \cdot \mathbf{r}_{Pj} \rangle = \frac{1}{2}$ for a particular value of $\mathbf{H}$. Hence, the first term gives $\sigma_P^2 \cos 2\pi \mathbf{H} \cdot \Delta\mathbf{r}_{Pj}$ so that $\langle F_N F_P^c \rangle = \langle \sigma_P^2 \cos 2\pi \mathbf{H} \cdot \Delta\mathbf{r}_{Pj} \rangle$. Thus, the correlation between the normalized structure factors E_N and E_P^c reduces to $\langle E_N E_P^c \rangle = \sigma_1 \langle \cos 2\pi \mathbf{H} \cdot \Delta\mathbf{r}_{Pj} \rangle = \sigma_A$.

Thus, in the presence of errors, the quantity σ_1 becomes replaced by $\sigma_A = \sigma_1 D_P$, which is to be anticipated in the light of the earlier results obtained in part V (Srinivasan & Ramachandran, 1965; see also Srinivasan & Chandrasekharan, 1966).

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