Acta Cryst. (1966). **20**, 143

Weighting functions for use in the early stages of structure analysis when a part of the structure is known.*

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(*Received* 8 *March* 1965 *and in revised form* 13 *July* 1965)

The use of weighting schemes to improve the efficiency of a Fourier synthesis or that of the convergence of refinement of a structure by the least-squares method is now well recognized. Thus, it was suggested by Woolfson (1956) that when the positions of a few atoms (say P out of a total of N atoms) in a structure are known, a Fourier synthesis with weighted terms $W|F_N|e^{i\alpha_P}$ would reveal the unknown atoms better than the usual synthesis with terms $|F_N|e^{i\alpha_P}$ where $|F_N|$ is the structure amplitude corresponding to the entire structure [*i.e.* corresponding to the N atoms, whose position vectors may be denoted by $\mathbf{r}_j (j=1 \text{ to } N)$] and α_P is the phase of the contribution from the known P atoms. From probability arguments he showed that the function† W_C for a centrosymmetric crystal was of the form

$$W_C = \tanh X \tag{1}$$

where

$$X = |F_N|\,|F_P|/\sigma_N^2\,(1-\sigma_1^2) \tag{2}$$

and

$$\sigma_N^2 = \sum_{j=1}^{N} f_j^2\,, \quad \sigma_P^2 = \sum_{i=1}^{P} f_i^2\,, \quad \sigma_1^2 = \sigma_P^2/\sigma_N^2\,.$$

In the absence of the 'true' structure amplitudes $|F_N|$ of the structure, they may be replaced in (2) above by the observed structure amplitudes $|F_o|$ and this necessarily involves a certain amount of approximation, which is not serious if the observational errors are negligible. However, in order to be more specific, we shall still use $|F_N|$ in (2) and also in our subsequent discussions. It is convenient to recast (2) in terms of the normalized structure amplitudes $y_N = |F_N|/\sigma_N$, $y_P = |F_P|/\sigma_P$.

Thus, (2) can be written

$$X = \sigma_1 y_N y_P/(1-\sigma_1^2)\,. \tag{3}$$

The weighting function† for a non-centrosymmetric crystal was worked out by Sim (1960) to be

$$W_A = I_1(2X)/I_0(2X) \tag{4}$$

where $I_0(X)$ and $I_1(X)$ are Bessel functions with imaginary argument of order zero and one respectively. In (4) X is the same as defined in (3).

The problem of improving the efficiency of convergence of refinement of a structure when all the atoms are known but their positions are in error was first investigated by Qurashi & Vand (1953). This was improved upon by Vand & Pepinsky (1957) who approached the problem from probability considerations applying the statistical results of Luzzati (1952). The form of the weighting function obtained by them for a centrosymmetric crystal is

$$W_C = \tanh Y \tag{5}$$

where

$$Y = D_N|F_N|\,|F_N^c|/\sigma_N^2(1-D_N^2)\,. \tag{6}$$

Here again, in order to be more specific, we have used $|F_N|$, which may be replaced by the observed structure amplitudes, involving the approximation mentioned earlier. In (6) above $|F_N^c|$ corresponds to the calculated structure amplitudes corresponding to finite errors $\Delta\mathbf{r}_j$ in the coordinates of the N atoms and D_N stands for

$$\langle \cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_j\rangle_N \tag{7}$$

where $\mathbf{H}$ is the reciprocal vector, and the subscript N (7) denotes that the average is over the N atoms. It may be mentioned in this connexion that in the derivation of the results (5), (6) the usual conditions of Wilson statistics are to be satisfied, *i.e.* the number of atoms N is fairly large, and also that they are similar and randomly distributed in the structure. In terms of the normalized structure amplitudes $y_N = |F_N|/\sigma_N$, $y_N^c = |F_N^c|/\sigma_N$ (6) can be written

$$Y = D_N y_N y_N^c/(1-D_N^2)\,. \tag{8}$$

The result has been extended to the non-centrosymmetric case by Mazumdar (1964) who has shown that the weighting function is of the form

$$W_A = I_1(2Y)/I_0(2Y) \tag{9}$$

where Y is as defined in (8).

Obviously in applying the weighting functions (5) or (9) a knowledge is required of the value of D_N which depends on the magnitude of the errors $\Delta\mathbf{r}_j$. This may be obtained from a study of the variation of the reliability index with Bragg angle θ, as has been suggested by Luzzati (1952). Improved methods for the same purpose are also available for the centrosymmetric case (Vand & Pepinsky, 1957) and the non-centrosymmetric case (Mazumdar, 1964).

Although it is implicit in the derivation of Woolfson and Sim it should be pointed out that their weighting functions are strictly valid only if the assumed positions of the known P atoms have no errors. The question now arises as to the nature of the weighting function to be used when only a part (P) of the atoms is known *and* these atoms have, in addition, errors $\Delta\mathbf{r}_j$ in their coordinates. It might be noticed first that the two individual cases discussed earlier are but limiting ones of this general case. In particular, the weighting functions may be seen to be strikingly similar in form for the two cases (compare (1) and (4) with (5) and (9) respectively). Thus, when only a part of the atoms is used in the structure factor calculations and these atoms have no errors in their coordinates, the parameter σ_1 enters the expression (3), while if all the atoms are used and these have finite errors in their coordinates, the parameter $D_N = \langle \cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_j\rangle_N$ enters (8) and its role is thus exactly similar to that of σ_1.

The answer to the general case turns out to be simple and it follows from the theory of the distribution of the observed and calculated structure factors which has been considered recently (Srinivasan & Ramachandran, 1965) for the above situation. It turns out that the form of the mathematical results for the normalized structure factors is the same as that for the two individual cases above, with the only difference that a parameter $\sigma_A = \sigma_1 D_P$ takes the place of σ_1 or

* Contribution no. 171 from the Centre of Advanced Study in Physics, University of Madras.

† The subscripts C and A will be used to denote centrosymmetric and non-centrosymmetric (acentric) cases respectively.

D_N in the individual cases. In consequence the weighting functions for the general case can be simply written down as follows.† Thus, for a centrosymmetric crystal it is given by

$$W_C = \tanh U \tag{10}$$

and for a non-centrosymmetric crystal, by

$$W_A = I_1(2U)/I_0(2U) \tag{11}$$

where

$$U = \sigma_A y_N y_P^c/(1-\sigma_A^2) \tag{12}$$

and

$$\sigma_A = \sigma_1 \langle \cos 2\pi \mathbf{H} \,.\, \Delta \mathbf{r}_j \rangle_P = \sigma_1 D_P \,. \tag{13}$$

It may be verified that when $P=N$, $\sigma_1=1$ so that expressions (10) and (11) reduce to (8) and (9) respectively. On the other hand when the errors are all zero, $D_P=1$ so that $\sigma_A=\sigma_1$ and expressions (10) and (11) reduce to (3) and (4) respectively. Thus, when finite errors exist in the coordinates of the known P atoms the effective value gets reduced from σ_1 to $\sigma_1 D_P$ since D_P is always less than unity.

In order to be able to apply (8) and (11) in practice, a knowledge is required of the parameter σ_A. Methods of obtaining this from the experimental data have been suggested and are discussed in the paper cited above (Srinivasan & Ramachandran, 1965). It involves mainly the evaluation of one or both of two parameters $\langle R_1 \rangle$ and Z^c which have been termed the normalized reliability index and the amplitude correlation respectively and are given by

$$R_1 = \frac{\Sigma ||F_N| - |F_P^c|/\sigma_1|}{\Sigma |F_N|} \tag{14}$$

$$\langle Z^c \rangle = \frac{\Sigma |F_N|\,|F_P^c|}{(\Sigma |F_N|^2\, \Sigma |F_P^c|^2)^{\frac{1}{2}}} \,. \tag{15}$$

† For a formal proof of the results see Srinivasan & Chandrasekharan (1965).

Both R_1 and $\langle Z^c \rangle$ as a function of σ_A are available (Srinivasan & Ramachandran, 1965). It may be pointed out that since σ_A involves D_P it is strongly dependent on the Bragg angle θ, and hence the evaluation of the parameters R_1 and $\langle Z^c \rangle$ has to be done over a narrow region in the reciprocal space within which θ can be assumed to be constant. One could thus obtain σ_A as a function of θ which could then be used in (12).

It may be pointed out, however, that although theoretically the correct weighting functions to be used when the known atoms have errors in their atomic coordinates are given by (10) and (11), from the point of view of practical efficiency it becomes important, before applying these functions, to refine the coordinates of the known P atoms so as to minimize the errors in them. This is obvious from the nature of the functions. The larger the value of σ_A the larger will be the values of W, the maximum value of σ_A for any given σ_1 being σ_1 which would correspond to no errors in the positions of the P atoms. Preliminary refinement of the known atoms would ensure a value of σ_A as close to σ_1 as possible.

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Acta Cryst. (1966). **20**, 144

Dispersion of the strain optical ratios in cubic crystals.

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(*Received* 19 *July* 1965)

With the experimental set-up shown in Fig. 1, we have studied the variation of the strain-optical ratios P_{12}/P_{11} and $P_{44}/P_{11}+P_{12}$ for a few cubic crystals in the wavelength range 2500–6000 Å. Light from a 400-watt Hanovia arc after passing through an adjustable horizontal slit S is collimated by the lens L_1. The collimated beam then enters the crystal C under investigation, a double image prism D and finally the quartz prism Q of a medium quartz spectrograph. When the length of the slit is suitably adjusted, the prominent lines of the mercury spectrum are recorded as two sets of horizontal lines, one above the other, on the photographic plate placed at PP (Fig. 1; see also Fig. 2). The crystal rests on the ultrasonic transducer T and when suitably excited a longitudinal standing wave is set up in it. This results in each spectral line being split up into a number of diffraction orders giving rise to the familiar Hiedemann pattern. Mueller (1938; see also Bergmann & Fues, 1936) has shown, on theoretical grounds, that the ratio of the intensities of the corresponding diffraction lines of the mth order in the two polarized sets has the value $B_m^0 = R^{2m}$, where B_m^0 is the limiting ratio of intensities when the sound amplitude is reduced to zero; and $R = P_{12}/P_{11}$ or $P_{11}+P_{12}-2P_{44}/P_{11}+P_{12}+2P_{44}$ depending on the direction of propagation of sound in the crystal along [100] or [110] respectively and the light beam travelling in a direction normal to that of sound along a cube axis.

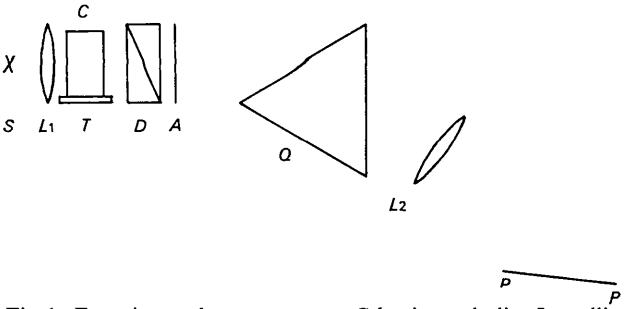

Fig. 1. Experimental arrangement. S horizontal slit, L_1 collimator lens, C crystal specimen, T transducer, D double image prism, A analyser, Q quartz prism, L_2 camera lens, PP photographic plate.