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The distribution of phase angles for structures containing heavy atoms. II. A modification of the normal heavy-atom method for non-centrosymmetrical structures.

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Introduction

The expected distribution of the phase angles of a set of structure factors about the phase angles calculated on the basis of only some of the atoms in the unit cell was considered for a simple triclinic case in an earlier communication (Sim, 1957). The present paper is concerned with the distribution law which applies to the phase angle α of a single structure factor F when $|F|$, $|F_H|$, and α_H are known, $|F_H|$ and α_H being values for the structure amplitude and phase angle calculated on the basis of only some of the atoms in the unit cell.

Luzzati (1953) has discussed the relationship between the true electron-density distribution ϱ and the electron-density distribution ϱ' calculated from the observed structure amplitudes $|F|$ with phase angles α_H, and his results show that the resolution in ϱ' of the remaining atoms of the structure, i.e. the atoms which were not used in calculating α_H, is less favourable in the non-centrosymmetrical than in the centrosymmetrical case. Woolfson (1956) has shown for the centrosymmetrical case that improved resolution of these remaining atoms can be obtained by calculating a Fourier series with coefficients $S_H\{(2P_+ - 1)|F| - |F_H|\}$, where S_H is the sign of F_H and P_+ is the probability that F and F_H have the same sign. P_+ is given by

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2} \tanh (|FF_H|/\Sigma_L) ,$$

where

$$\Sigma_L = \sum_{i=1}^{n} f_i^2$$

is a summation over the remaining atoms.

Vand & Pepinsky (1957) have discussed the related problem of improving the efficiency of refinement by the Fourier method of a centrosymmetrical crystal structure and recommend a weighting system for the structure amplitudes which is related to Woolfson's system.

In the present paper it is shown that by weighting the observed structure amplitudes in a suitable manner improved resolution of the remaining atoms in the structure can be obtained also in the non-centrosymmetrical case of the heavy-atom method.

Phase-angle distribution

For fixed values of $|F_H|$ and α_H the joint probability of obtaining a structure factor with amplitude $|F|$ between $|F|$ and $|F| + d|F|$ and with $(\alpha - \alpha_H)$ between ξ and $\xi + d\xi$ is

$$p(|F|, \xi)d|F|d\xi = |F|(\pi\Sigma_L)^{-1} \exp [-(|F|^2 + |F_H|^2)/\Sigma_L] \times \exp (2|F||F_H| \cos \xi/\Sigma_L)d|F|d\xi .$$

The probability of obtaining a value of $|F|$ between $|F|$ and $|F| + d|F|$ is in this case

$$p(|F|)d|F| = 2|F|(\Sigma_L^{-1}) \exp [-(|F|^2 + |F_H|^2)/\Sigma_L] \times I_0(2|F||F_H|/\Sigma_L)d|F| ,$$

where I_0 is the modified zero-order Bessel function (Watson, 1922, p. 77). The probability of $(\alpha - \alpha_H)$ lying between ξ and $\xi + d\xi$ for a structure factor with fixed values of $|F|$, $|F_H|$ and α_H is then

$$p(\xi)d\xi = p(|F|, \xi)d|F|d\xi/p(|F|)d|F| ,$$
$$= \exp (X \cos \xi)d\xi/2\pi I_0(X) ,$$

where

$$X = 2|F||F_H|/\Sigma_L .$$

A similar expression used in a different context has been derived by Cochran (1955).

The probability that $(\alpha - \alpha_H)$ lies between the limits $\pm\xi$ is then given by

$$P(\xi) = \int_{-\xi}^{+\xi} p(\xi)d\xi .$$

Values of $P(\xi)$ for various values of X and ξ are listed in Table 1. The results indicate that the larger the value of X the more likely $|\alpha - \alpha_H|$ is to be small, and conversely the smaller the value of X the more likely $|\alpha - \alpha_H|$ is to be large. When $X = 5$, for example, the probability that α is within $\pm 20°$ of α_H is 0·549, whereas when $X = 1$ the probability is only 0·234.

Table 1. *Values of* $P(\xi)$

		ξ (°)									
		0	20	40	60	80	100	120	140	160	180
	0	0·000	0·111	0·222	0·333	0·444	0·556	0·667	0·778	0·889	1·000
	1	0·000	0·234	0·442	0·609	0·733	0·821	0·883	0·930	0·967	1·000
	2	0·000	0·346	0·621	0·798	0·896	0·946	0·971	0·984	0·993	1·000
X	3	0·000	0·431	0·737	0·896	0·961	0·985	0·994	0·997	0·999	1·000
	4	0·000	0·496	0·811	0·944	0·985	0·996	0·999	0·999	1·000	1·000
	5	0·000	0·549	0·862	0·969	0·994	0·999	0·999	1·000	1·000	1·000

Table 2. *Values of the weighting factor* W *as a function of* $X = 2|F||F_H|/\Sigma_L$.

		X									
	0	0·25	0·50	0·75	1·0	1·5	2·0	3·0	4·0	5·0	∞
W	0	0·157	0·308	0·443	0·561	0·738	0·850	0·952	0·982	0·992	1·000

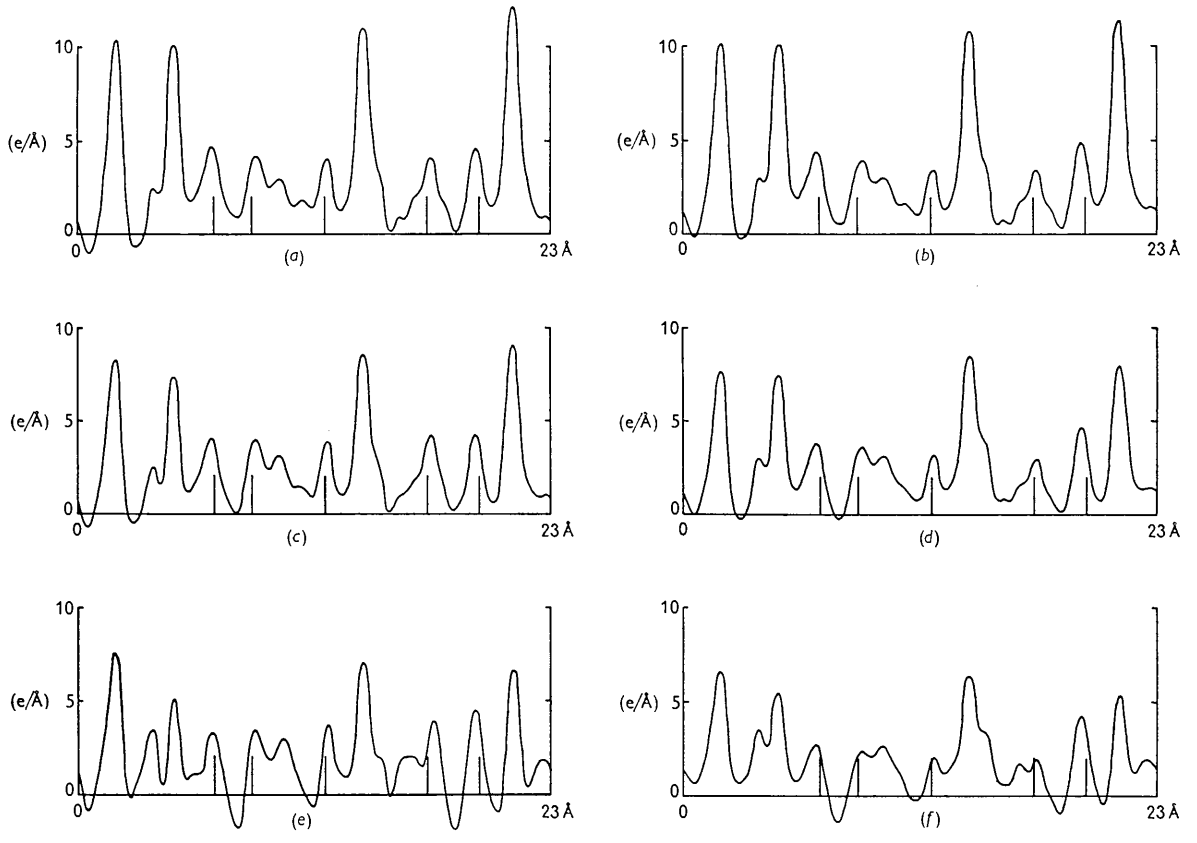

Fig. 1. The functions shown are

(a) ϱ'' for $r=1{\cdot}5$ (b) ϱ' for $r=1{\cdot}5$
(c) ϱ'' for $r=1{\cdot}0$ (d) ϱ' for $r=1{\cdot}0$
(e) ϱ'' for $r=0{\cdot}5$ (f) ϱ' for $r=0{\cdot}5$

The true positions of the 'unknown' atoms are indicated by vertical lines.

A modified Fourier series

In Woolfson's treatment of the centrosymmetrical case of the heavy-atom method the coefficients used in his modified Fourier series are $S_H\{(2P_+-1)|F|-|F_H|\}$, i.e., the sign of F_H is adopted and each structure amplitude $|F|$ is weighted by a factor which has a value between 0 and 1. When it is most uncertain that F and F_H have the same sign the weighting factor is very small and as the probability that F and F_H have the same sign increases so also does the weighting factor.

A similar treatment of the non-centrosymmetrical case seems desirable to improve the resolution of the atoms which were not included in the calculation of α_H: when it is probable that $|\alpha-\alpha_H|$ is large the structure amplitude $|F|$ should be weighted by a factor which is small and, on the other hand, when it is probable that $|\alpha-\alpha_H|$ is small the weighting factor should be large, approaching its limiting value of 1. If the weighting factor to be applied to a structure amplitude is denoted by W then obviously W should be a function of $P(\xi)$. A suitable weighting system is defined by

$$W=2P(90°)-1\,,$$

for when $|\alpha-\alpha_H|$ is likely to be large X is small and $2P(90°)-1$ approaches 0, and when $|\alpha-\alpha_H|$ is likely to be small X is large and $2P(90°)-1$ approaches 1. Values of the weighting factor as a function of X are listed in Table 2.

In the initial stages of a structure refinement the absolute scale of the observed $|F|$ values, determined for example by means of a Wilson plot, is often not known with great accuracy, an error of perhaps $\pm 20\%$ being possible. Accordingly it was decided in the present work not to compute a difference distribution such as used by Woolfson but to calculate directly a Fourier series in which the weighted structure amplitudes $W|F|$ are used as coefficients with phase angles α_H.

The example considered is a one-dimensional structure with 9 atoms. In the calculation of the structure amplitudes $|F|$ all 9 atoms were used but in the calculation of the phase angles α_H only 4 of the atoms were used. We have

$$F_H(h)=\sum_{j=1}^{4} f_H \exp\,(2\pi i h x_H)_j$$

$$F(h)=\sum_{j=1}^{4} f_H \exp\,(2\pi i h x_H)_j+\sum_{j=5}^{9} f_L \exp\,(2\pi i h x_L)_j\,.$$

The atomic form factors f_L used for the 5 atoms not included in the calculation of α_H were those given by

Hoerni & Ibers (1954) for carbon, modified by a temperature factor $B=3{\cdot}0$. The form factors f_H for the 4 atoms determining α_H were deduced from the relation

$$r = \Sigma_H/\Sigma_L = (f_H/f_L)(4/5)^{\frac{1}{2}} ,$$

r being assigned values of 0·5, 1·0 and 1·5 in turn. Values of $|F|$, $|F_H|$ and α_H were calculated for $h \leq 30$ and the appropriate values of W obtained by interpolation in Table 2.

Electron-density distributions ϱ' and ϱ'' were calculated for the three values of r: ϱ' was calculated from the structure amplitudes $|F|$ with phase angles α_H and ϱ'' was calculated from the suitably scaled weighted structure amplitudes $kW|F|$ with phase angles α_H, the same $F(0)$ term being used in each series and the scale factor k being defined by

$$\sum_{h=1}^{30} |F| = k \sum_{h=1}^{30} W|F| .$$

A fair comparison of the two distributions can then be made directly. The resultant distributions are shown in Fig. 1, and an examination of this shows the improved resolution in ϱ'', especially at the lowest value of r, of the atoms which make no contribution to α_H.

In order to provide a quantitative measure of the improvement a comparison was made of the average peak heights of the known atoms, that is, those contributing to α_H, and the unknown atoms in the weighted and unweighted Fourier series of Fig. 1. Values of $\overline{(\varrho W/\varrho U)_H}$ and $\overline{(\varrho W/\varrho U)_L}$, the ratios of the average peak height in the weighted series to the average peak height in the unweighted series of the known and unknown atoms, respectively, were calculated for the various values of r and are listed in Table 3. The results show that the average peak height of an unknown atom is increased considerably more in the weighted series than is the peak height of a known atom. The greatest improvement in resolution is associated with the smallest value of r, in agreement with Woolfson's conclusions concerning the centrosymmetrical case.

Table 3. *Comparison of the average peak heights in the weighted and unweighted Fourier series*

r	$\overline{(\varrho W/\varrho U)_H}$	$\overline{(\varrho W/\varrho U)_L}$
0·5	1·11	1·42
1·0	1·05	1·13
1·5	1·03	1·08

In view of these results it would appear that there is a greater possibility of recognizing the structure in the weighted than in the unweighted series and it would seem worthwhile, therefore, in the application of the heavy-atom method to non-centrosymmetrical structures, particularly when the parameter r is small, to weight each structure amplitude according to the function tabulated in Table 2 rather than to include indiscriminately each structure amplitude at its face value.

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The structure of the compounds of iodine with 1,4 diselenane and 1,4 dithiane.*

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A long term project in these laboratories has been the investigation of the structures of compounds of the type R_2SeX_2 and R_2TeX_2 where X is one of the halogens. The previously reported studies have involved only dichlorides and dibromides and the structures have, in all cases, involved nearly linear X–Se–X and X–Te–X axial bonds in molecules with pseudo trigonal bipyramidal structures (see Christofferson, Sparks & McCullough, 1958, for references to earlier studies). Preliminary studies on several iodides in the tellurium series showed these to be structurally complex. In contrast, the iodides of 1,4 diselenane and 1,4 dithiane proved to be crystallographically simple. Work on these compounds indicated that they are molecular complexes, rather than true diiodides. This unexpected result gave added interest to the study and prompted this preliminary report.

Crystallographic data for the isomorphous compounds are given in Table 1. Due to the presence of only two molecules per unit cell in $P2_1/c$, the molecules are required to be centrosymmetric. Satisfactory trial structures were obtained by means of Patterson summations on (010) and (100) and Fourier summations on these faces of the unit cells in the two compounds gave the positional parameters listed in Table 2. Although approximate carbon positions were indicated in the two-dimensional summations, reliable parameters must await the three-dimensional refinement of the structures now in progress. A projection of the structure of the selenium

Table 1. *Crystallographic data*

	$C_4H_8S_2.2\,I_2$	$C_4H_8Se_2.2\,I_2$
a (Å)	6·83	6·88
b (Å)	6·39	6·33
c (Å)	16·78	17·68
β (°)	117° 30′	118° 30′
$\varrho_{obs.}$ (g.cm^{-3})	—	3·4
$\varrho_{calc.}$ (g.cm^{-3})	3·22	3·53

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