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The Probability Distribution of X-ray Intensities. VII. Some Sesquisymmetric Distributions

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It has been shown that parallel repetition of a motif through non-crystallographic symmetry, in addition to crystallographic centrosymmetry $\bar{1}$, leads to a set of intensity distributions (hypercentric distributions) whose variance is greater than that of the familiar centric distribution. If now further crystallographic symmetry is present, such as *m* or *mm*, the variance is reduced to a value intermediate between that of the centric (V_1) and that of the appropriate hypercentric distribution (V_n). If the multiplicity of the asymmetric unit is $2p$, the variance is in fact

$$V_n^{(p)} = V_1 + p^{-1}(V_n - V_1)\,.$$

Series for determining numerical values of the sesquicentric distributions are discussed.

[The following note is closely related to the fifth paper of this series (Rogers & Wilson, 1953), and in order to avoid much repetition of discussion and references it has been written as if it formed part of it. The numbered paragraphs should be read inserted in numerical order in the earlier paper.]

1·3·1.—If, in addition to centres of symmetry, the space group contains other elements of symmetry, molecules directly related by the crystallographic centres of symmetry are parallel in pairs, but those related only by other symmetry elements are not, in general, parallel. (Molecules not parallel in space may have parallel projections.) The fringe systems of the parallel pairs will be partially obliterated by the unrelated additive fringe systems of other pairs, and the dispersion of the intensity distribution will be reduced to a value somewhere between that of the centric distribution and that of the hypercentric distribution appropriate to a single pair. Such distributions may perhaps be termed 'sesquicentric', and expressions for their variance are derived in § 5·3·3 below. There will be analogous 'sesquiparallel' distributions, but their practical importance is not obvious at present.

5·3·2. *Series expansions*: errata.—In equation (96) of Rogers & Wilson (1953) μ_2^3 is misprinted as μ_3^2, and three signs are misprinted in equation (97). This should read

$$\begin{aligned} P_n(F) = \Sigma^{-\frac{1}{2}}\{&\Phi(\Sigma^{-\frac{1}{2}}F) \\ &+(3^{n-1}2^{-n-2}-\tfrac{1}{8}-3^{n-1}2^{-3}\Sigma_4/\Sigma^2)\Phi^{\mathrm{IV}}(\Sigma^{-\frac{1}{2}}F) \\ &+[3^{-1}2^{-n-3}(5^{n-1}-3^n)+\tfrac{1}{24}-2^{-4}(5^{n-1}-3^{n-1})\Sigma_4/\Sigma^2 \\ &\quad+3^{-2}5^{n-1}2^{n-2}\Sigma_6/\Sigma^3]\Phi^{\mathrm{VI}}(\Sigma^{-\frac{1}{2}}F)+\ldots\}\,. \end{aligned} \tag{97}$$

5·3·3. *Variance of sesquicentric distributions.*—Suppose that the space group requires $2p$ asymmetric units (p pairs related by the crystallographic symmetry centres) in the unit cell. The ith atom of the jth pair, together with those related to it by all centres of symmetry, will contribute an amount

$$2^n f_i \cos(2\pi\mathbf{s}\cdot\mathbf{r}_{i,j})\cos\psi_{2,j}\ldots\cos\psi_{n,j}$$

to the structure amplitude, as in equation (87) above. The contribution of the ith atom and those related to it by all symmetry elements is then

$$\xi_i = 2^n f_i\left[\sum_{j=1}^{p}\cos\theta_{i,j}\cos\psi_{2,j}\ldots\cos\psi_{n,j}\right], \tag{98}$$

where $\theta_{i,j}$ has been written for $2\pi\mathbf{s}\cdot\mathbf{r}_{i,j}$. Considered as a function of i, this is a random variable, and for the general reflexions terms with the same value of i but different j are uncorrelated. (Projections must be considered separately according to their actual symmetry, and coincidence of atoms in projection or non-primitiveness of the projected cell allowed for.) Averaging over the regions of reciprocal space for which the ψ's are constant gives the following values for the second and fourth central moments:

$$\begin{aligned} \mu_{n,2}^{(p,i)} &= 2^{2n}f_i^2\left\langle\left[\sum_{j=1}^{p}\cos\theta_{i,j}\cos\psi_{2,j}\ldots\cos\psi_{n,j}\right]^2\right\rangle \\ &= 2^{2n-1}f_i^2\left[\sum_{j=1}^{p}\cos^2\psi_{2,j}\ldots\cos^2\psi_{n,j}\right], \end{aligned} \tag{99}$$

$$\begin{aligned} \mu_{n,4}^{(p,i)} &= 2^{4n}f_i^4\left\langle\left[\sum_{j=1}^{p}\cos\theta_{i,j}\cos\psi_{2,j}\ldots\cos\psi_{n,j}\right]^4\right\rangle \\ &= 3\,.\,2^{4n-3}f_i^4\left[\sum_{j=1}^{p}\cos^4\psi_{2,j}\ldots\cos^4\psi_{n,j}\right] \\ &\quad+3\,.\,2^{4n-1}f_i^4\left[\sum_{j=1}^{p}\sum_{k>j}^{p}\cos^2\psi_{2,j}\ldots\cos^2\psi_{n,j} \right.\\ &\quad\left.\times\cos^2\psi_{2,k}\ldots\cos^2\psi_{n,k}\right]. \end{aligned} \tag{100}$$

Substitution in the first part of equations (91) and (92) gives for the whole cell

$$\mu^{(p)}_{n,2} = p^{-1}2^{n-1}\left[\sum_{j=1}^{p}\cos^2\psi_{2,j}\ldots\cos^2\psi_{n,j}\right]\Sigma\,, \tag{101}$$

$$\begin{aligned}\mu^{(p)}_{n,4} = &-3p^{-1}2^{3n-3}\left[\sum_{j=1}^{p}\cos^4\psi_{2,j}\ldots\cos^4\psi_{n,j}\right]\Sigma_4\\ &+3p^{-2}2^{2n-2}\left[\sum_{j=1}^{p}\sum_{k=1}^{p}\cos^2\psi_{2,j}\ldots\cos^2\psi_{n,j}\right.\\ &\left.\times\cos^2\psi_{2,k}\ldots\cos^2\psi_{n,k}\right]\Sigma^2. \end{aligned}\tag{102}$$

On now averaging over all reciprocal space (all values of the ψ's),

$$\langle\mu^{(p)}_{n,2}\rangle = \Sigma\,, \tag{103}$$

as it should,

$$\langle\mu^{(p)}_{n,4}\rangle = 3^n2^{-n+1}p^{-1}\Sigma^2+3p^{-1}(p-1)\Sigma^2-3^n\Sigma_4\,, \tag{104}$$

and the variance is (first part of equation (95))

$$V^{(p)}_n = [2+(3^n2^{-n+1}-3)/p]\Sigma^2-3^n\Sigma_4\,. \tag{105}$$

The correction term in Σ_4 is unaffected by the additional symmetry elements. The main term in Σ^2 can be written

$$V^{(p)}_n = V_1+(V_n-V_1)/p; \tag{106}$$

that is, the variance is increased over that of the centric distribution by one-pth of the excess variance of the n-centric distribution. Note that for $n = 1$ (centric distribution) the variance is independent of p, in agreement with (though not proving) the statement in § 1·3 that crystallographic symmetry leads only to the acentric or the centric distribution.

Values of the specific variance $v \equiv V/\Sigma^2$ are given in Table 4 for a few values of n and p. The variance goes up very rapi lly with increasing n, but for fixed n it decreases rather rapidly to the centric value 2 as p increases.

Table 4. *Specific variance* $v^{(p)}_n$

p	$n = 1$	$n = 2$	$n = 3$	$n = 4$
1	2	$3\frac{1}{2}$	$5\frac{3}{4}$	$9\frac{1}{8}$
2	2	$2\frac{3}{4}$	$3\frac{7}{8}$	$5\frac{9}{16}$
3	2	$2\frac{1}{2}$	$3\frac{1}{4}$	$4\frac{3}{8}$
4	2	$2\frac{3}{8}$	$2\frac{15}{16}$	$3\frac{25}{32}$
...	...	...	...	...
∞	2	2	2	2

5·3·4. *Series expansions of sesquicentric distributions.*—The important terms in the sixth moment (first part of equation (93) above) are

$$\begin{aligned}\mu^{(p)}_{n,6} &= 15\mu^{(p)}_{n,2}\mu^{(p)}_{n,4}-30[\mu^{(p)}_{n,2}]^3\\ &= 15p^{-3}2^{3n-3}\left[\sum_{j,k,l=1}^{p}\cos^2\psi_{2,j}\ldots\cos^2\psi_{n,j}\right.\\ &\quad\left.\times\cos^2\psi_{2,k}\ldots\cos^2\psi_{n,k}\cos^2\psi_{2,l}\ldots\cos^2\psi_{n,l}\right]\Sigma^3\,, \end{aligned}\tag{107}$$

where only the leading term has been kept. On averaging over all reciprocal space

$$\begin{aligned}\langle\mu^{(p)}_{n,6}\rangle = [&3p^{-2}5^n2^{-n+1}+15p^{-2}(p-1)3^n2^{-n+1}\\ &+15p^{-2}(p-1)(p-2)]\Sigma^3\,, \end{aligned}\tag{108}$$

and the series expansion for the distribution becomes

$$\begin{aligned}P^{(p)}_n(F) = \Sigma^{-\frac{1}{2}}\Big\{&\Phi(\Sigma^{-\frac{1}{2}}F)+\frac{3^n2^{-n+1}-3}{4!p}\Phi^{\mathrm{IV}}(\Sigma^{-\frac{1}{2}}F)\\ &+\frac{3.5^n2^{-n+}\ -15.3^n2^{-n+1}+30}{6!p^2}\Phi^{\mathrm{VI}}(\Sigma^{-\frac{1}{2}}F)\\ &+\ldots\Big\}, \end{aligned}\tag{109}$$

where all correction terms in Σ_4 and Σ_6 have been omitted. To a crude first approximation, therefore, the pth sesquicentric distribution is equal to the centric distribution increased by one-pth of the difference between the n-centric distribution and the centric distribution. For $n = 1$ the coefficients of Φ^{IV} and Φ^{VI} vanish.

5·3·5.—The analysis of §§ 5·3·3–4 is valid, *mutatis mutandis*, if p represents (i) half the multiplicity of the general position in the space group, or (ii) the number of independent non-crystallographically centrosymmetric molecules in the asymmetric unit, or (iii) the product of (i) and (ii).

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Reference

Rogers, D. & Wilson, A. J. C. (1953). *Acta Cryst.* **6**, 439.