Acta Cryst. (1954). **7**, 517

The maximum probable value of the reliability index for a hypercentric structure. By A. S. Douglas, *Mathematical Laboratory, Cambridge, England*, and M. M. Woolfson, *Crystallograpic Laboratory, Cavendish Laboratory, Cambridge, England*

(*Received* 11 *March* 1954 *and in revised form* 19 *March* 1954)

It has been shown by Wilson (1950) that the maximum probable value of the reliability index for a completely incorrect structure is

$$R = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|} \quad (1)$$

$$= 2-4\frac{\langle G(F)\rangle}{\langle|F|\rangle}, \quad (2)$$

where

$$G(F) = \int_0^F FP(F)dF\,, \quad (3)$$

$P(F)$ is the probability distribution of $|F|$, and the angle brackets indicate average values. For the acentric and centric distributions he obtained the values $R_0 = 2-\sqrt{2} = 0{\cdot}586$ and $R_1 = 2\sqrt{2}-2 = 0{\cdot}828$ respectively.

Rogers & Wilson (1953) have discussed qualitatively the values of R_n to be expected for incorrect hypersymmetric structures. They concluded that

$$2 > R_{n>1} > R_1 = 0{\cdot}828\,, \quad (4)$$

and that, therefore, large values of R for trial hypersymmetric structures are less discouraging than they would be for simple centrosymmetric or non-centrosymmetric structures. The values of R would be expected to drop rapidly on refinement, though they would probably not reach such low final values (cf. Phillips, Rogers & Wilson, 1950). Rogers & Wilson, however, were unable to calculate any numerical values of $R_{n>1}$. The simplest hypersymmetric distribution ($n = 2$, called hypercentric by Lipson & Woolfson (1952), and bicentric by Rogers & Wilson) is of fairly common occurrence, and the purpose of this note is to show that $R_2 = 1{\cdot}010$ for an incorrect structure with this intensity distribution.

From equation (12) of Rogers & Wilson we have

$$G_n(F) = (2^n/\pi^{2n-1}\Sigma)^{\frac{1}{2}}\int_0^F\int_0^{\frac{1}{2}\pi}\ldots\int_0^{\frac{1}{2}\pi}\exp\left[-F^2\sec^2\varphi_2\ldots\sec^2\varphi_n/2^n\Sigma\right]\sec\varphi_2\ldots\sec\varphi_n d\varphi_2\ldots d\varphi_n F dF$$

$$= (2^{3n-2}\Sigma/\pi^{2n-1})^{\frac{1}{2}}-(2^{3n-2}\Sigma/\pi^{2n-1})^{\frac{1}{2}}\int_0^{\frac{1}{2}\pi}\ldots\int_0^{\frac{1}{2}\pi}\exp\left[-F^2\sec^2\varphi_2\ldots\sec^2\varphi_n/2^n\Sigma\right]\cos\varphi_2\ldots\cos\varphi_n d\varphi_2\ldots d\varphi_n\,, \quad (5)$$

$$\langle G_n(F)\rangle = \int_0^\infty G_n(F)P_n(F)dF$$

$$= (2^{3n-2}\Sigma/\pi^{2n-1})^{\frac{1}{2}}-(2^{2n-1}/\pi^{2n-1})\int_0^\infty\int_0^{\frac{1}{2}\pi}\ldots\int_0^{\frac{1}{2}\pi}\exp\left[-F^2\{\sec^2\varphi_2\ldots\sec^2\varphi_n+\sec^2\varphi_2'\ldots\sec^2\varphi_n'\}/2^n\Sigma\right]$$

$$\times\cos\varphi_2\ldots\cos\varphi_n\sec\varphi_2'\ldots\sec\varphi_n' d\varphi_2\ldots d\varphi_n d\varphi_2'\ldots d\varphi_n' dF \quad (6)$$

$$= (2^{3n-2}\Sigma/\pi^{2n-1})^{\frac{1}{2}}-(2^{5n-4}\Sigma/\pi^{4n-3})^{\frac{1}{2}}\int_0^{\frac{1}{2}\pi}\ldots\int_0^{\frac{1}{2}\pi}\{\cos^2\varphi_2\ldots\cos^2\varphi_n+\cos^2\varphi_2'\ldots\cos^2\varphi_n'\}^{-\frac{1}{2}}$$

$$\times\cos^2\varphi_2\ldots\cos^2\varphi_n d\varphi_2\ldots d\varphi_n d\varphi_2'\ldots d\varphi_n'\,. \quad (7)$$

This integral may be simplified on noting that it has the same value if φ and φ' are interchanged, and thus it is equal to half the sum of itself and the integral formed by the interchange. Equation (7) becomes, therefore,

$$\langle G_n(F)\rangle = (2^{3n-2}\Sigma/\pi^{2n-1})^{\frac{1}{2}}$$

$$-(2^{5n-6}\Sigma/\pi^{4n-3})^{\frac{1}{2}}\int_0^{\frac{1}{2}\pi}\ldots\int_0^{\frac{1}{2}\pi}\{\cos^2\varphi_2\ldots\cos^2\varphi_n$$

$$+\cos^2\varphi_2'\ldots\cos^2\varphi_n'\}^{\frac{1}{2}}d\varphi_2\ldots d\varphi_n d\varphi_2'\ldots d\varphi_n'\,. \quad (8)$$

There seems to be no general method of evaluating the $(2n-2)$-fold integral in this equation, but for $n = 2$ we have applied Gregory's formula and find that

$$\int_0^{\frac{1}{2}\pi}\int_0^{\frac{1}{2}\pi}\{\cos^2\varphi+\cos^2\varphi'\}^{\frac{1}{2}}d\varphi d\varphi' = 2{\cdot}3640\,. \quad (9)$$

Equation (32) of Rogers & Wilson gives

$$\langle|F|\rangle = 4\pi^{-\frac{3}{2}}\Sigma^{\frac{1}{2}} \quad (10)$$

for $n = 2$, so that, from equation (2) above,

$$R_2 = 2-4+4\pi^{-1}\times 2{\cdot}3640$$
$$= 1{\cdot}010\,. \quad (11)$$

It is therefore probable that for a trial structure with a hypercentric intensity distribution a value of R as high as 0·6 would be significant, and the refined structure would have a higher reliability index than is usually expected.

We are indebted to Dr A. J. C. Wilson for suggestions leading to a generalization of the mathematics, and to the Department of Scientific and Industrial Research for financial assistance.

References

Lipson, H. & Woolfson, M. M. (1952). *Acta Cryst.* **5**, 680.

Phillips, D. C., Rogers, D. & Wilson, A. J. C. (1950). *Acta Cryst.* **3**, 398.

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

Wilson, A. J. C. (1950). *Acta Cryst.* **3**, 397.