The first term in the braces is easily calculated as follows. By the differentiation of equation (A-2), one gets

$$\frac{\mathrm{d}^2}{\mathrm{d}\zeta^2}\varphi(p)=\varphi''(p)\left(\frac{\mathrm{d}p}{\mathrm{d}\zeta}\right)^2+\varphi'(p)\frac{\mathrm{d}^2p}{\mathrm{d}\zeta^2}=-1\,. \qquad \text{(A-5)}$$

Since $\varphi'(p)$ is zero at the point $p=p_0$, one obtains

$$\left(\frac{\mathrm{d}p}{\mathrm{d}\zeta}\right)_{p=p0}=\left[\frac{-1}{\varphi''(p_0)}\right]^{1/2}. \qquad \text{(A-6)*}$$

By the use of this relation, the first term of (A-4) gives equation (28).

The second term can be calculated with similar procedures. By the differential manipulation, one gets

$$\frac{\mathrm{d}^2}{\mathrm{d}\zeta^2}\left(A_h(p)\frac{\mathrm{d}p}{\mathrm{d}\zeta}\right)=A_h''(p)\left(\frac{\mathrm{d}p}{\mathrm{d}\zeta}\right)^3$$

$$+3A_h'(p)\frac{\mathrm{d}p}{\mathrm{d}\zeta}\frac{\mathrm{d}^2p}{\mathrm{d}\zeta^2}+A_h(p)\frac{\mathrm{d}^3p}{\mathrm{d}\zeta^3}\,. \qquad \text{(A-7)}$$

The derivatives $(\mathrm{d}^2p/\mathrm{d}\zeta^2)_{p=p0}$ and $(\mathrm{d}^3p/\mathrm{d}\zeta^3)_{p=p0}$ can be successively determined from the relations derived by differentiating equation (A-5). Inserting these into (A-7), one obtains

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\zeta^2}\left(A(p)\frac{\mathrm{d}p}{\mathrm{d}\zeta}\right)\right]_{p=p0}=\left\{-\left(\frac{1}{\varphi''}\right)^{1/2}\left[-\frac{A_h''}{\varphi''}\right.\right.$$

$$\left.\left.+\frac{A_h'\varphi^{(3)}}{(\varphi'')^2}-\frac{5A_h(\varphi^{(3)})^2}{12(\varphi'')^3}+\frac{A_h\varphi^{(4)}}{4(\varphi'')^2}\right]\right\}_{p=p0} \qquad \text{(A-8)}$$

where $\varphi^{(3)}$ and $\varphi^{(4)}$ imply $\mathrm{d}^3\varphi/\mathrm{d}p^3$ and $\mathrm{d}^4\varphi/\mathrm{d}p^4$ respectively. With this result, the second term of (A-4) gives equations (34).

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[*] As to the arguments on the phase angle of the expression $[\;]^{1/2}$, see Jeffereys & Jeffereys (1956), p. 505.

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Largest Likely Values of Residuals

By A. J. C. Wilson

Department of Physics, University of Birmingham, Birmingham B15 2TT, England

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The value of the residual $R_2=\langle(I_1-I_2)^2\rangle/\langle I_1^2\rangle$, where I_1 and I_2 are the intensities of reflexion for two unrelated structures having the same symmetry and containing the same atoms, has the value $1-\Sigma_4/(2\Sigma^2-\Sigma_4)$ for non-centrosymmetric structures and $\frac{4}{3}-2\Sigma_4/3(\Sigma^2-\Sigma_4)$ for centrosymmetric; the corresponding values for $R_1=\langle(F_1-F_2)^2\rangle/\langle F_1^2\rangle$ are approximately $2(1-\pi/4)\simeq0{\cdot}43$ and $2(1-2/\pi)\simeq0{\cdot}73$. More complex expressions are derived for hyper- and sesquisymmetric structures. If a residual with a scaling factor, such as $S_2=\langle(I_1-EI_2)^2\rangle/\langle I_1^2\rangle$, is used, and the scaling factor E is refined by least-squares, the value of E obtained is about $\frac{1}{2}$ or $\frac{1}{3}$, instead of the true value unity.

Introduction

Lenstra (1974) has considered the values of the residual

$$R_2=\frac{\sum(I_1-I_2)^2}{\sum I_1^2} \qquad (1)$$

$$=\frac{\langle(I_1-I_2)^2\rangle}{\langle I_1^2\rangle}\,, \qquad (2)$$

where, in Lenstra's application, I_1 represents the intensity of the *hkl* reflexion from a correct structure and I_2 represents the corresponding intensity calculated for a structure that is incomplete or in some way incorrect. Wilson (1969) had earlier considered the case in which the structures differed only through the misplacement of a single atom, and still earlier (Wilson, 1950) the case where the structures were entirely unrelated, except that they consisted of the same atoms and had the same symmetry; in this first paper the less convenient residual

$$R=\frac{\sum|F_1-F_2|}{\sum F_1}\,, \tag{3}$$

where the F's are the magnitudes of the structure amplitudes, was used. Lenstra states that for an entirely incorrect structure R_2 should be about 1·00, but gives no detailed discussion of the effect of symmetry. The present note obtains expressions for R_2 which depend explicitly on certain types of symmetry, crystallographic and non-crystallographic, and discusses more briefly a third residual,

$$R_1=\frac{\sum(F_1-F_2)^2}{\sum F_1^2}\,, \tag{4}$$

that is frequently used (Wilson, 1973). With unfortunate inconsistency Wilson (1969) has used the symbol R_1 also for

$$Q_1=\frac{\sum|I_1-I_2|}{\sum I_1}\,. \tag{5}$$

A paper by Parthasarathy & Parthasarathi (1972) contains several results relevant to the problem of largest likely values, though they are not entirely easy to pick out from among the authors' very general calculations.

Largest likely values of R_2

The form of R_2, in which all quantities are real and positive, is much easier to manipulate than those of R or R_1, which require taking the moduli of quantities that may be negative or complex. The values of R_2 can thus be obtained without the use of probability distribution functions, and require only the sums of powers of the atomic scattering factors, as in the variance calculations of Wilson (1951, 1952) and Rogers & Wilson (1953). Equation (2) may be written

$$R_2=\frac{\langle[(I_1-A_1)-(I_2-A_2)+(A_1-A_2)]^2\rangle}{\langle[(I_1-A_1)+A_1]^2\rangle}\,, \tag{6}$$

where A_1 and A_2 are the mean values of I_1 and I_2. On squaring and averaging this becomes

$$R_2=\frac{\operatorname{var}(I_1)-2\operatorname{cov}(I_1,I_2)+\operatorname{var}(I_2)+(A_1-A_2)^2}{\operatorname{var}(I_1)+A_1^2}\,, \tag{7}$$

where var and cov are the variance and covariance. Equation (7) is quite general; in the particular case of unrelated arrangements of the same atoms

$$A_1=A_2=\Sigma\,, \tag{8}$$

where Σ is the sum of the squares of the atomic scattering factors (Wilson, 1942),

$$\operatorname{cov}(I_1,I_2)=0, \tag{9}$$

$$\operatorname{var}(I_1)\ =\operatorname{var}(I_2)\,, \tag{10}$$

and equation (6) becomes

$$R_2=\frac{2\operatorname{var}(I)}{\operatorname{var}(I)+\Sigma^2}\,. \tag{11}$$

For non-centrosymmetric and centrosymmetric structures with all atoms in general positions the values of var (I) have been given by Wilson (1951), so that

$$(1)R_2=\frac{2\,\Sigma^2-2\,\Sigma_4}{2\,\Sigma^2-\Sigma_4} \tag{12}$$

$$=1-\frac{\Sigma_4}{2\,\Sigma^2-\Sigma_4}\,, \tag{13}$$

$$(\bar{1})R_2=\frac{4\,\Sigma^2-6\,\Sigma_4}{3\,\Sigma^2-3\,\Sigma_4} \tag{14}$$

$$=\tfrac{4}{3}-\frac{2\,\Sigma_4}{3(\Sigma^2-\Sigma_4)}\,, \tag{15}$$

where Σ_4 is the sum of the fourth powers of the atomic scattering factors. Ordinarily Σ_4 is small compared with Σ^2, so that $(1)R_2$ has a value close to that given by Lenstra, but $(\bar{1})R_2$ is about 1·3.

Hypersymmetry and sesquisymmetry

The variance of I is increased by non-crystallographic symmetry (Lipson & Woolfson, 1952; Wilson, 1952; Rogers & Wilson, 1953; Wilson, 1956); the papers cited should be consulted for the nomenclature and symbolism. If n is the degree of hypersymmetry and p that of sesquisymmetry,

$$(n,p)\operatorname{var}(I)=[2+(3^n2^{-n+1}-3)/p]\Sigma^2-3^n\Sigma_4 \tag{16}$$

[Wilson, 1956; equation (105)],

$$(n,p)R_2=\frac{4+2(3^n2^{-n+1}-3)/p-2\times3^n\Sigma_4/\Sigma^2}{3+(3^n2^{-n+1}-3)/p-3^n\Sigma_4/\Sigma^2}\,. \tag{17}$$

For $p=1$; $n=0,1$; this reduces to equations (13) and (15). For large n it approaches

$$(\infty,p)R_2=2\,, \tag{18}$$

and for large p

$$(n,\infty)R_2=\tfrac{4}{3}-\frac{2\times3^{n-1}\Sigma_4/\Sigma^2}{3-3^n\Sigma_4/\Sigma^2}\,; \tag{19}$$

here the main term is the same as in the expression for the centrosymmetric case.

Atoms in special positions

Atoms in special positions, on the other hand, reduce the variance. Hauptmann & Karle (1952) give an expression equivalent to var $(I)+\Sigma^2$ for the case where some of or all the centres of symmetry in a centrosymmetric space group are occupied, and undoubtedly other results concerning special positions are scattered in the extensive literature on direct methods. However, atoms in such special positions are likely to be correctly placed in any trial structure, so that the term cov (I_1,I_2) in equation (7) cannot be neglected. It may be quicker, if R_2 is wanted in any particular case, to calculate var (I) and cov(I_1,I_2) by methods like those of Wilson

(1951) and Lenstra (1974), rather than to search the voluminous literature for incidental relevant results.

Largest likely values of R_1

On squaring equation (4) the expression for the residual R_1 becomes

$$R_1 = \frac{\langle F_1^2\rangle - 2\langle F_1F_2\rangle + \langle F_2^2\rangle}{\langle F_1^2\rangle} \tag{20}$$

and, for unrelated structures consisting of the same atoms,

$$\langle F_2^2\rangle = \langle F_1^2\rangle = \langle F^2\rangle\,, \tag{21}$$

$$\langle F_1F_2\rangle = \langle F\rangle^2\,, \tag{22}$$

$$R_1 = 2\left[1 - \frac{\langle F\rangle^2}{\langle F^2\rangle}\right]. \tag{23}$$

The second term in equation (23) is the test ratio ϱ introduced by Wilson (1949), and has the value $\pi/4$ for a non-centrosymmetric crystal and $2/\pi$ for a centrosymmetric crystal. Thus

$$(1)R_1 = 2(1-\pi/4) \sim 0{\cdot}43\,, \tag{24}$$

and

$$(\bar{1})R_1 = 2(1-2/\pi) \sim 0{\cdot}73\,. \tag{25}$$

For hypersymmetric crystals

$$\varrho_n = 2^{3n-2}\pi^{-2n+1} \tag{26}$$

[Rogers & Wilson, 1953; equation (34)], so that

$$(n)R_1 = 2(1-\varrho_n) \tag{27}$$

$$= 2 - 2^{3n-1}\pi^{-2n+1}\,, \tag{28}$$

reducing to (24) and (25) for $n=0, 1$.

The above expressions for ϱ_n contain only the leading term; corrections depending on Σ_4 and possibly higher moments are to be expected. Those for $(1)R_1$ could be obtained from equation (79) of Hauptmann & Karle. Expressions for

$$R_m = \frac{\sum (F_1^m - F_2^m)^2}{\sum F_1^{2m}} \tag{29}$$

(Wilson, 1973) of the same order of accuracy as equation (28) could readily be obtained from expressions given by Rogers & Wilson if desired; the expressions for sesquicentric structures given by Wilson (1956) permit the evaluation of R_m only for even values of m.

Problems of scaling

In many actual cases there will be a problem of scaling, since, for example, I_1 may be a set of relative measured intensities, and I_2 a set of calculated intensities. The proper procedure would appear to be to multiply I_2 by a scaling factor, a function of $\sin^2\theta$ if necessary, so that for each range of $\sin^2\theta$

$$\langle I_1\rangle = \langle I_2\rangle\,. \tag{30}$$

Often, however, a scaling factor E is included in the refinement process as an adjustable parameter, so that the residual corresponding to R_2 is

$$S_2 = \frac{\sum (I_1 - EI_2)^2}{\sum I_1^2}\,. \tag{31}$$

The condition for minimum S_2, as a function of E, is

$$E = \langle I_1I_2\rangle / \langle I_2^2\rangle\,, \tag{32}$$

giving

$$(S_2)_{\min} = 1 - \langle I_1I_2\rangle^2 / \langle I_1^2\rangle\,\langle I_2^2\rangle\,. \tag{33}$$

The value of S_2, with the scaling factor adjusted by refinement, is therefore always less than unity, whereas all that can be said about R_2 when properly scaled is that it must be less than two. If I_1 and I_2 are unrelated the scaling factors given by equation (32) are ridiculously small:

$$(1)E = \Sigma^2/(2\,\Sigma^2 - \Sigma_4) \sim \tfrac{1}{2}\,, \tag{34}$$

$$(\bar{1})E = \Sigma^2/3(\Sigma^2 - \Sigma_4) \sim \tfrac{1}{3}\,, \tag{35}$$

instead of the true value of unity. The corresponding values of the residual are

$$(1)\ (S_2)_{\min} = 1 - \Sigma^4/(2\,\Sigma^2 - \Sigma_4)^2 \tag{36}$$

$$\sim 0{\cdot}75\,, \tag{37}$$

$$(\bar{1})\ (S_2)_{\min} = 1 - \Sigma^4/9(\Sigma^2 - \Sigma_4)^2 \tag{38}$$

$$\sim 0{\cdot}89\,. \tag{39}$$

A similar calculation for the analogue of R_1 gives a scaling factor ϱ, the test ratio already mentioned, and $(S_1)_{\min} = 1 - \varrho^2$. Thus

$$(1)\ (S_1)_{\min} = 1 - \pi^2/16 \sim 0{\cdot}38\,, \tag{40}$$

$$(\bar{1})\ (S_1)_{\min} = 1 - 4/\pi^2 \sim 0{\cdot}55\,. \tag{41}$$

Similar but smaller effects of refining scaling parameters for nearly correct, instead of entirely incorrect, structures are discussed elsewhere (Wilson, 1974; T. R. Lomer & A. J. C. Wilson, in preparation).

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