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Testing the Hypothesis 'No Remaining Systematic Error' in Parameter Determination

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Abstract

Beu, Musil & Whitney [*Acta Cryst.* (1962), **15**, 1292–1301; *Acta Cryst.* (1963), **16**, 1241–1242] proposed a maximum-likelihood method of estimating the lattice parameters of cubic, tetragonal and hexagonal crystals, and a method of testing the hypothesis that systematic errors had been satisfactorily accounted for. The use of maximum likelihood is unnecessary, and open to some objection. The argument is therefore rewritten in the more familiar least-squares form, and is generalized to cover the remaining crystal systems. Only if systematic errors are absent is it legitimate to estimate standard deviations of parameters from the differences of observed and calculated Bragg angles. With minor modifications the results are applicable to structural parameters also.

1. Introduction

1.1. *Maximum likelihood versus least squares*

1.1.1. Beu, Musil & Whitney (1962, 1963; Beu & Whitney, 1967) have proposed a maximum-likelihood method of estimating lattice parameters, and Price (1979) has proposed one for estimating structural parameters. Advantages over the usual 'least-squares' methods are claimed for each application. Maximum-likelihood methods depend fundamentally on a knowlege of, or on an assumption about, the exact form of the distribution function of the statistical fluctuations and other random errors, and are thus more model-dependent than the method of least squares, which requires little more than that the second moments of the random fluctuations be finite. Price based his calculation on the assumption that the fluctuations in intensity had a Poisson distribution, though he recognized that the actual distribution, after correction for background, would be neither Poisson nor Gaussian (Wilson, 1978, 1980). Beu, Musil & Whitney assumed a Gaussian (normal) distribution of the errors in angle measurement, possibly without realizing, and certainly without emphasizing, that under this assumption the maximum-likelihood and the least-squares estimate are practically equivalent (see, for example, Hamilton, 1964, pp. 37–42, or Bard, 1974, p. 63). Both least-squares and maximum-likelihood estimates are likely to be biased, especially when the variance of the fluctuations had to be deduced from the observations, not being known *a priori*; a proposal for reducing the bias in least-squares estimates of structural parameters has been made by Wilson (1976). Price has not investigated the bias in parameters obtained by his method, but the results of Wilson suggest, though they do not prove, that the bias is likely to be about half of that given by the usual 'least-squares' refinements. The advantages of maximum-likelihood methods have been reviewed by Edwards (1972).

1.1.2. Objections, other than the necessity of knowing or assuming the distribution function of the random errors of measurement, have been raised against methods based on likelihood. The most important of these, in the present application, has been emphasized by Mandel (1979). For large numbers of 'degrees of freedom' the distribution of the likelihood ratio is asymptotically the same as that of χ^2, but it has been shown to deviate from that of χ^2 when the number is small (Good, Gover & Mitchell, 1970). In lattice-parameter determination, especially for cubic crystals, the number of observations, and hence the number of degrees of freedom, is small – in some applications made by Beu and his colleagues it has been as low as one or two. Another objection, probably not relevant in the present context, is that in some circumstances the method of maximum likelihood fails to find an estimate, though other estimators succeed (Rao, 1973, p. 355, gives a simple but rather artificial example).

1.1.3. The important advance in the proposals of Beu, Musil & Whitney thus does not lie in the use of the maximum-likelihood method, but in the emphasis on testing for the adequacy of the correction for systematic errors before lattice parameters are calculated. In view of the theoretical difficulties associated with the likelihood ratio – lack of knowledge of the distribution of random errors in the measurement of Bragg angles and lack of knowledge of the distribution of the likelihood ratio for small numbers of degrees of freedom (§2.1.2) – it seems worth while to

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rewrite their argument in least-squares form, a form that is in any case more familiar in crystallography.

1.2. *Systematic errors not detected*

1.2.1. It must be pointed out that certain systematic errors would not be detected by either procedure. As Beu, Musil & Whitney emphasize, the Bragg angles calculated from equation (2) below depend only on the ratio of the wavelength λ and the spacing d, so that all measurements made with a single emission line will be self-consistent, even if the assumed wavelength were grossly in error. The same self-consistency would be exhibited by all systematic errors equivalent to a wavelength error (those whose angle-dependence is proportional to $\tan\theta$). For the conventional diffractometer the summaries given by Wilson (1963, pp. 69–81; 1970, pp. 34–35, 143; 1974, p. 469 *etc.*) suggest that the self-consistent category would include absorption in the specimen, filters *etc.*; part of the axial divergence; refraction (wavelength change only); variation of quantum-counting efficiency; and, for peaks but not for centroids, dispersion-plus-Lorenz factor. A different list would apply for energy-dispersive diffractometers (Wilson, 1973), but their precision is not yet great enough for the question to be of much interest.

1.2.2. Perhaps a further disclaimer should be made. Although Beu, Musil & Whitney describe their test as one of 'no remaining systematic errors', it is really one of 'any remaining systematic errors are small compared with the random errors'. More precise angle measurements might reveal unforeseen systematic errors, or the need to take into account systematic errors previously regarded as negligible.

2. The residual *R*

2.1. *General discussion*

2.1.1. In the application to lattice-parameter determination the quantity to be minimized is the sum of the squares of the differences between the observed Bragg angles and those calculated from the lattice parameter in the cubic case, or the lattice parameters in systems of lower symmetry, with appropriate weights. The residual to be minimized is thus:

$$R = \sum_i w_i(\varphi_i - \theta_i)^2, \tag{1}$$

where φ_i is the observed Bragg angle and θ_i is the Bragg angle calculated from

$$\lambda = 2d_i \sin\theta_i; \tag{2}$$

θ_i is thus a function of the lattice parameters entering into d_i, the ith interplanar spacing. In the cubic case

$$d_i = a(h^2 + k^2 + l^2)^{-1/2}, \tag{3}$$

where a is the lattice parameter and hkl are the Miller indices; formulae for the less symmetrical crystal systems are to be found in *International Tables for X-ray Crystallography* (1959) and in most elementary texts (for example, Wilson, 1970, p. 73). The residual R is thus a function of the single parameter a for cubic crystals and up to six parameters ($abc\alpha\beta\gamma$) for crystals of lower symmetry. Provided that the number, say n, of lines measured is greater than the number, say m, of parameters to be determined, R can be minimized by standard methods and least-squares estimates of the parameters found.

2.1.2. Under the hypothesis to be tested, the observed angles φ_i have been corrected for all systematic errors, so that the differences between the φ_i's and the θ_i's are due only to the random errors of measurement. The weight w_i, according to usual statistical practice, should be chosen as the reciprocal of the variance of the corresponding φ_i, say σ_i^2, so that equation (1) for the residual becomes

$$R = \sum_{i=1}^{n} (\varphi_i - \theta_i)^2/\sigma_i^2, \tag{4}$$

the sum of n variables. If the angles θ_i were the true Bragg angles each of the n variables would have the mean value unity. In theory the sum could have any value between zero and infinity, though very large values would be unlikely. The expected value would be

$$R = \sum_{i=1}^{n} 1 = n. \tag{5}$$

In practice, when the lattice parameters are chosen to minimize R they are slightly influenced by the actual errors in determining the φ_i's, in such direction as to make the expected value of each term somewhat less than unity, and a little calculation shows that the reduction is 1 for each parameter determined (Hamilton, 1964, p. 130, footnote; a longer derivation by elementary methods is given in §3.3.3). The expected value of $R_{\min}$ is thus $n-1$ for cubic crystals, $n-2$ for tetragonal or hexagonal (including rhombohedral), $n-3$ for orthorhombic, $n-4$ for monoclinic, and $n-6$ for triclinic, say

$$E(R_{\min}) = n - m \tag{6}$$

in general.

2.2. *Variance of R_{min} when the error distribution is normal*

2.2.1. The expectation value of $R_{\min}$, $n-m$, does not depend on any assumption about the distribution function of the random experimental errors in the determination of φ_i. The variance of $R_{\min}$ does, however, depend on the exact distribution of the errors of measurement. For a normal distribution (as assumed by Beu, Musil & Whitney) it is easily found to be

$$\sigma_R^2 = 2(n - m). \qquad (7)$$

Its value if the distribution is not normal is discussed in §3.3. The probability of getting a random deviation of $2\sigma_R$ or more from the expected value is a few per cent, so that values of $R_{\min}$ up to

$$(R_{\min})_{\text{critical}} = E(R_{\min}) + 2\sigma_R \qquad (8)$$

$$= n - m + 2[2(n - m)]^{1/2} \qquad (9)$$

are not unlikely to arise by chance, but larger values are progressively less likely, and if large values are found they indicate that some systematic error has not been accounted for – if the remanent systematic error in φ_i is δ_i there will be an additional component of about

$$R_{\text{syst}} = \sum_{i=1}^{n} \delta_i^2/\sigma_i^2 \qquad (10)$$

in $R_{\min}$. The systematic errors act in the direction to increase $R_{\min}$, whatever the sign of the actual error δ_i.

2.2.2. Some critical values of $R_{\min}$ calculated from equation (9) for various values of $(n - m)$ given in the second column of Table 1, and the corresponding critical values recommended by Beu, Musil & Whitney for their likelihood statistic are given in the third column. They argue that values as large as those given in the table can happen quite frequently through random error, so that (though we may have our private suspicions) if $R_{\min}$ is less than that given in the appropriate line of the table, we cannot reject the hypothesis that systematic errors have been eliminated, either experimentally or by the application of appropriate corrections. On the other hand, values very much larger are more and more improbable, so that if $R_{\min}$ much exceeds the appropriate value we can be practically certain that systematic errors are still present.

Table 1. *Some values of R corresponding to a deviation of* $2\sigma_R$ *greater than chance expectation*

(For the third column see § 2.2.2.)

$n - m$	$n - m + 2[2(n - m)]^{1/2}$	5% critical value of χ^2
1	3·83	3·84
2	6·00	5·99
3	7·90	7·82
4	9·66	9·49
5	11·32	11·07
6	12·93	12·59
7	14·48	14·07
8	16·00	15·51
9	17·49	16·92
10	18·94	18·31

3. Variance of $R_{\min}$ when the error distribution is non-normal

3.1. *Criterion for rejecting the hypothesis*

3.1.1. The preceding discussion has left open two questions: how probable is a random deviation of $2\sigma_R$ above the expected value of $R_{\min}$, and what is the expected value of σ_R when it is *not* assumed that the random errors in measuring the Bragg angles φ_i have a normal distribution? The Bienaymé–Tchebycheff inequality (Cramér, 1945, p. 183) gives an upper limit of 25% for the probability of a deviation of 2σ without regard to direction, whatever the distribution function, with lower values for continuous unimodal distributions. As only positive deviations are of interest for the present purpose, and as the distribution of $R_{\min}$, though obviously skew (and very so for small values of $n - m$), is almost certainly continuous and unimodal, one may reasonably assume that the probability of a deviation of 2σ in the positive direction is not greater than 5 to 10%. (If $R_{\min}$ had a normal distribution, which it can not, even if the errors in φ_i have, the probability would be 2·3%.) The answer to the second question is complicated; as the following discussion shows, it is necessary to know the fourth moment of the distribution of the random errors in φ_i, as well as the second moment σ_i^2, in order to obtain σ_R. The reduced fourth moment (fourth moment about the mean divided by σ_i^4) for the errors in φ_i will be denoted by μ_i, and its excess over 3 by

$$\gamma_i = \mu_i - 3. \qquad (11)$$

(There is some difference in nomenclature; the word 'excess' always refers to γ, but 'kurtosis' is used sometimes for γ, as in Cramér, but also for μ, particularly in the USA.)

3.1.2. For the normal distribution μ is 3 and γ is zero, but in general they must be determined by appropriate theory or experiment. Related calculations have been made by Hsu (1938), Rao (1952), Abrahams (1969), and others, but with different ends in view and with assumptions about σ_i and μ_i, so that their results cannot be taken over directly. The general case of $m > 1$ involves complicated algebra, and is given later (§3.3). The simple case $m = 1$ (cubic crystals) follows.

3.2. *Variance of* $R_{\min}$ *for cubic crystals*

3.2.1. On the assumption of no remaining systematic errors, equation (4) can be written

$$R = \sum_{i=1}^{n} (\varepsilon_i - A_i a)^2/\sigma_i^2, \qquad (12)$$

where ε_i is the random error in the measurement of φ_i,

$$A_i = \partial\theta_i/\partial a \tag{13}$$

evaluated at the current value of the lattice parameter a, and α is the amount by which the current value of a differs from that required to minimize R in the presence of the random errors ε_i. (As usual in least-squares procedures, successive approximations with corrected current values of a may be necessary.) Differentiating equation (12) with respect to α and equating to zero gives

$$\alpha = \sum_i \frac{A_i\,\varepsilon_i}{\sigma_i^2} \Big/ \sum_i \frac{A_i^2}{\sigma_i^2} \tag{14}$$

and hence

$$R_{\min} = \sum_{i=1}^{n} \frac{\varepsilon_i^2}{\sigma_i^2} - \frac{\sum\limits_{i,j} \dfrac{A_i A_j\,\varepsilon_i\,\varepsilon_j}{\sigma_i^2\,\sigma_j^2}}{\sum\limits_i \dfrac{A_i^2}{\sigma_i^2}}. \tag{15}$$

The expected value of each term in the first summation is unity, giving n in all. Most of the terms in the numerator of the second term have the expected values zero, but those with $i = j$ have the expected value $\sum A_i^2/\sigma_i^2$, so that the expected value of the second term is unity, the numerator and the denominator being equal. The expected value of $R_{\min}$ is thus

$$E(R_{\min}) = n - 1, \tag{16}$$

confirming equation (6) for the cubic case of $m = 1$. The denominator of the second term of equation (15) occurs frequently, so that it is convenient to define a quantity D by

$$D = \sum_i A_i^2/\sigma_i^2. \tag{17}$$

3.2.2. The square of $R_{\min}$, required for calculating its variance, is then

$$R_{\min}^2 = \sum_{i,j} \frac{\varepsilon_i^2\,\varepsilon_j^2}{\sigma_i^2\,\sigma_j^2} - 2D^{-1} \sum_{i,j,k} \frac{A_i A_j\,\varepsilon_i\,\varepsilon_j\,\varepsilon_k^2}{\sigma_i^2\,\sigma_j^2\,\sigma_k^2} + D^{-2} \sum_{i,j,k,l} \frac{A_i A_j A_k A_l\,\varepsilon_i\,\varepsilon_j\,\varepsilon_k\,\varepsilon_l}{\sigma_i^2\,\sigma_j^2\,\sigma_k^2\,\sigma_l^2}. \tag{18}$$

The terms on the right are essentially of three kinds. (i) If any ε occurs to the first power the expectation value of that term is zero. (ii) If any ε occurs to the second power only the expectation value of ε^2/σ^2 is unity. (iii) If any ε occurs to the fourth power the expectation value of ε^4/σ^4 is μ. Most of the terms in second and third summations vanish because of (i): those that survive have i, j, k, l equal in pairs or quartets. On careful reduction one obtains

$$E(R_{\min}^2) = n^2 - 1 + \sum_i (\mu_i - 3)\,(1 - D^{-1}A_i^2/\sigma_i^2)^2, \tag{19}$$

and

$$\sigma_R^2 = \mathrm{Var}(R_{\min}) = E(R_{\min}^2) - E^2(R_{\min}) \tag{20}$$

$$= 2(n-1) + \sum_i (\mu_i - 3)\,(1 - D^{-1}A_i^2/\sigma_i^2)^2. \tag{21}$$

If all the μ's are equal to three (as would happen if the errors in all the φ's had normal distributions), the summation vanishes and equation (21) reduces to the appropriate special case of equation (7). If A^2/σ^2 has much the same value for all reflexions, the final term within the parentheses in equation (21) will have the approximate value n^{-1}, so that, approximately,

$$\sigma_R^2 = 2(n-1) + (1 - 2n^{-1} + n^{-2}) \sum_i (\mu_i - 3) \tag{22}$$

$$= 2(n-1) + (1 - 2n^{-1} + n^{-2}) \sum_i \gamma_i. \tag{23}$$

It will be seen that σ_R does not approach the 'normal' value $2(n-1)$, even asymptotically for large n, unless γ_i has the normal value of zero for all reflexions.

3.2.3. I have not found any empirical studies of the normality of the distribution of the random errors in angle measurement. Langford (1973) persuaded several observers to make repeated measurements of the same film; a preliminary survey of the raw data accumulated by him suggests that γ might vary with the observer. Values in the range between 1 and -1 were obtained, giving variations of up to 50% in the value of σ_R^2. It is possible, however, that the apparent variation is due only to statistical fluctuation, as no information is available about the variance of γ.

3.3. *Variance of R_{min} in the general case*

3.3.1. When there are m parameters to be determined, equation (12) for the residual becomes

$$R = \sum_{i=1}^{n} \left\{\varepsilon_i - \sum_{p=1}^{m} A_{ip}\,\alpha_p\right\}^2 \Big/ \sigma_i^2, \tag{24}$$

where

$$A_{ip} = \partial\theta_i/\partial a_p, \tag{25}$$

evaluated at the current value of the parameter a_p, α_p is the amount by which a_p differs from the value required to minimize R, and the other symbols have the same significance as in equation (12). Expanding the square in equation (24) gives

$$R = \sum_{i=1}^{n} \frac{\varepsilon_i^2}{\sigma_i^2} - 2\sum_{p=1}^{m} \alpha_p \left\{\sum_{i=1}^{n} \frac{A_{ip}\,\varepsilon_i}{\sigma_i^2}\right\} + \sum_{p,q=1}^{m} \alpha_p\,\alpha_q \left\{\sum_{i=1}^{n} \frac{A_{ip}\,A_{iq}}{\sigma_i^2}\right\}. \tag{26}$$

To facilitate manipulation, define

$$R_0 = \sum_i \frac{\varepsilon_i^2}{\sigma_i^2}, \tag{27}$$

$$c_p = \sum_i \frac{A_{ip}\,\varepsilon_i}{\sigma_i^2}, \tag{28}$$

$$b_{pq} = \sum_i \frac{A_{ip}A_{iq}}{\sigma_i^2}. \tag{29}$$

Then

$$R = R_0 - 2\sum_p c_p \alpha_p + \sum_{p,q} b_{pq}\,\alpha_p\,\alpha_q. \tag{30}$$

The following expectation values, needed later, are readily found:

$$E(R_0) = n, \tag{31}$$

$$E(R_0^2) = n(n-1) + \sum_{i=1}^{n} \mu_i \tag{32}$$

$$= n(n+2) + \sum_i (\mu_i - 3), \tag{33}$$

$$E(c_p) = 0, \tag{34}$$

$$E(c_p\,c_q) = b_{pq}, \tag{35}$$

$$E(R_0\,c_p\,c_q) = (n-1)b_{pq} + \sum_i \frac{A_{ip}A_{iq}\mu_i}{\sigma_i^2} \tag{36}$$

$$= (n+2)b_{pq} + \sum_i \frac{A_{ip}A_{iq}(\mu_i - 3)}{\sigma_i^2}, \tag{37}$$

and

$$E(c_p\,c_q\,c_r\,c_s) = b_{pq}\,b_{rs} + b_{pr}\,b_{qs} + b_{ps}\,b_{qr} + \sum_i \frac{A_{ip}A_{iq}A_{ir}A_{is}(\mu_i - 3)}{\sigma_i^4}. \tag{38}$$

3.3.2. Differentiating equation (30) with respect to α_k gives the m normal equations for minimum R:

$$\sum_{p=1}^{m} b_{pk}\,\alpha_p = c_k, \quad k = 1, 2, \ldots, m. \tag{39}$$

These can be solved by the usual determinantal method (see, for example, Aitken 1939, pp. 55–56). Form the determinant

$$D = \begin{vmatrix} b_{11} & b_{12} & \cdots & b_{1m} \\ b_{21} & b_{22} & \cdots & b_{2m} \\ \cdots & \cdots & \cdots & \cdots \\ b_{m1} & b_{m2} & \cdots & b_{mm} \end{vmatrix} \tag{40}$$

and let B_{pq} be the co-factor of b_{pq}. Then

$$a_k = \sum_{p=1}^{m} B_{pk}\,c_p/D, \quad k = 1, 2, \ldots, m, \tag{41}$$

where c_p is given by equation (28).

3.3.3. The minimum residual could be found by substituting these values of α_k in equation (30), but it is easier to use equations (39) to eliminate the quadratic terms $\alpha_p\,\alpha_q$ first. Multiplying each of the equations (39) by α_k and adding for all values of k gives

$$\sum_{p,q} b_{pq}\,\alpha_p\,\alpha_q = \sum_p c_p\,\alpha_p, \tag{42}$$

where on the left k as summation index has been replaced by q, and on the right by p. This substitution, obviously, does not change the value of the summations, and makes them look like those in equation (30). Substitution of this result in equation (30) and rearranging gives

$$\sum_{p=1}^{m} c_p\,\alpha_p = R - R_0. \tag{43}$$

Since the values of α_p in equations (39) and (43) must be self-consistent, the value of $R_{\min}$ is given by the vanishing of the determinant

$$\begin{vmatrix} R_{\min} - R_0 & c_1 & c_2 & \cdots & c_m \\ c_1 & b_{11} & b_{12} & \cdots & b_{1m} \\ c_2 & b_{21} & b_{22} & \cdots & b_{2m} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ c_m & b_{m1} & b_{m2} & \cdots & b_{mm} \end{vmatrix}. \tag{44}$$

Expanding in terms of the co-factors of the elements of the first row and column gives

$$D(R_{\min} - R_0) + \sum_{p,q} c_p\,c_q\,B_{pq} = 0. \tag{45}$$

The expectation value of $R_{\min}$ is, on making use of equations (31) and (35),

$$E(R_{\min}) = n - D^{-1}\sum_{p,q} b_{pq}\,B_{pq}, \tag{46}$$

or, since the summation of $b_{pq}\,B_{pq}$ over either p or q gives D, and then summation over the other gives mD,

$$E(R_{\min}) = n - m, \tag{47}$$

verifying equation (6). It will be noticed that there has been no assumption about the distribution of the errors in measuring the angles φ_i, other than that they have a finite variance.

3.3.4. Squaring equation (45) gives

$$D^2\,E(R_{\min}^2) = D^2\,R_0^2 - 2DR_0\sum_{p,q} c_p\,c_q\,B_{pq} + \sum_{p,q,r,s} c_p\,c_q\,c_r\,c_s\,B_{pq}\,B_{rs}, \tag{48}$$

which becomes, on taking expectation values from equations (33)–(38),

$$D^2 E(R^2_{\min}) = D^2 n(n+2) + D^2 \sum_i (\mu_i - 3)$$
$$- 2(n+2)D \sum_{p,q} b_{pq} B_{pq}$$
$$- 2D \sum_{i,p,q} (\mu_i - 3) \frac{A_{ip} A_{iq} B_{pq}}{\sigma_i^2}$$
$$+ \sum_{p,q,r,s} (b_{pq} b_{rs} + b_{pr} b_{qs}$$
$$+ b_{ps} b_{qr}) B_{pq} B_{rs}$$
$$+ \sum_{i,p,q,r,s} (\mu_i - 3) \frac{A_{ip} A_{iq} A_{ir} A_{is} B_{pq} B_{rs}}{\sigma_i^4}. \quad (49)$$

Unless μ_i is the same for all i, the terms in μ_i do not simplify further. The double sum over p,q in the second line gives, as before, mD. In the third line the terms involving $b_{pq} b_{rs}$ are the expansion of $m^2 D^2$ in terms of co-factors. Most of the sums involving $b_{pr} b_{qs}$ and $b_{ps} b_{qr}$ are expansions in false co-factors, and therefore vanish, but enough survive to give $2mD^2$. Subtracting

$$E^2(R_{\min}) = n^2 - 2mn + m^2, \quad (50)$$

as given by equation (47), one has finally for the variance of $R_{\min}$

$$\sigma_R^2 = 2(n-m) + \sum_i (\mu_i - 3)$$
$$- 2D^{-1} \sum_{i,p,q} (\mu_i - 3) \frac{A_{ip} A_{iq} B_{pq}}{\sigma_i^2}$$
$$+ D^{-2} \sum_{i,p,q,r,s} (\mu_i - 3) \frac{A_{ip} A_{iq} A_{ir} A_{is} B_{pq} B_{rs}}{\sigma_i^4}. \quad (51)$$

The first term is that expected for a normal distribution, for which the others vanish ($\mu = 3$). If μ is constant but not equal to 3, say $\mu = 3 + \gamma$, the second term reduces to $n\gamma$ and the third to $-2m\gamma$, but there is no significant simplification of the fourth. The fourth seems, however, to be smaller than the third by a factor of about m/n, so that, to some approximation,

$$\sigma_R^2 = 2(n-m) + \gamma(n-2m)$$
$$+ \text{term of the order of } \gamma m^2/n, \quad (52)$$

a reasonable generalization of equation (23) for the one-parameter case. Equation (51) can be written, without approximation, as

$$\sigma_R^2 = 2(n-m)$$
$$+ \sum_i (\mu_i - 3) \left\{ 1 - D^{-1} \sum_{p,q} \frac{a_{ip} A_{iq} B_{pq}}{\sigma_i^2} \right\}^2, \quad (53)$$

a generalization of equation (21). It would be easier to evaluate than equation (51) in an actual case.

3.4. *Variance and covariance of the parameters*

The expected value of the correction to the current value of the kth parameter is zero after a sufficient number of cycles of refinement, as is seen from equations (41) and (34). Its variance is

$$E(\alpha_k^2) = D^{-2} \sum_{pq} B_{pk} B_{qk} E(c_p c_q) \quad (54)$$

$$= D^{-2} \sum_{pq} B_{pk} B_{qk} b_{pq}, \quad (55)$$

by equation (35). Equation (55), considered as a sum over p, is an expansion in false co-factors unless $q = k$, when it is a true expansion of D. One thus obtains the familiar formula

$$\sigma^2(\alpha_k) = B_{kk}/D. \quad (56)$$

The covariance of the kth and lth parameter is, similarly,

$$\operatorname{cov}(\alpha_k, \alpha_l) = B_{kl}/D. \quad (57)$$

4. Effect of systematic errors

Most treatments of the method of least squares dismiss systematic errors with a sentence or two about the necessity of avoiding them. It is easy to include them formally in the preceding development; if each φ_i is subject to a systematic error δ_i as well as a random error ε_i, equations (24)–(30) and (39)–(45) are changed only by the substitution of $\varepsilon_i + \delta_i$ for ε_i wherever it occurs. The expectation values, equations (31)–(38) and (46) onwards, however, become more complicated. It is easy to show that

$$E(R_0) = n + \sum_i \delta_i^2/\sigma_i^2, \quad (58)$$

$$E(c_p) = \sum_i A_{ip} \delta_i/\sigma_i^2 \quad (59)$$

$$\equiv \Gamma_p, \text{ say}, \quad (60)$$

$$E(c_p c_q) = b_{pq} + \Gamma_p \Gamma_q, \quad (61)$$

so that

$$E(R_{\min}) = n - m + \sum_i \delta_i^2/\sigma_i^2$$
$$- D^{-1} \sum_{pq} B_{pq} \Gamma_p \Gamma_q. \quad (62)$$

The first two terms in equation (62), $n - m$, are the expectation value of $R_{\min}$ under the hypothesis of no remanent systematic error, as given by equation (47). The third term is the naive expectation of the increase in R caused by systematic errors, as given by equation

(10), and the fourth is the reduction in it caused by the attempts of the process to minimize R. It can, of course, be calculated for any known or postulated set of systematic errors, but it is not easy to see its physical significance. In the one-parameter (cubic) case it cancels exactly with the third term if δ_l is proportional to $\tan\theta_l$. The expected value of $R_{\min}$ is independent of such a systematic error, as foreseen by Beu, Musil & Whitney (§1.2.1 above). With a little more calculation it can be shown that the parts of the third and fourth terms corresponding to the scale factor for the linear dimensions a,b,c cancel for such an error even in the general case, though R remains sensitive to the axial ratios and the angles α, β, γ. Presumably systematic errors can never produce a nett negative effect on $E(R_{\min})$, though I have not found or been able to devise a general proof of this.

The expression for the variance of $R_{\min}$ in the presence of systematic errors is complicated, and involves the skewness as well as the excess of the distribution of random errors in the angle measurements. Fortunately it is not needed for testing the hypothesis that any remaining systematic errors are not large compared with the random errors (§5.2.1). The expected value of the kth parameter is given by

$$E(\alpha_k) = D^{-1} \sum_p B_{pk} \Gamma_p, \quad (63)$$

instead of zero, from equations (41) and (60). Its variance, however, remains

$$\sigma^2(\alpha_k) = B_{kk}/D, \quad (64)$$

the terms in the δ's cancelling, and the covariance remains

$$\mathrm{cov}\,(\alpha_k, \alpha_l) = B_{kl}/D. \quad (65)$$

However, although the form of equations (63) and (64) is the same as that of (56) and (57), the numerical values will be different – one hopes only slightly – because the derivatives A_{lp} [equation (25)] entering into b_{pq} [equation (29)] and hence the co-factors B_{pq} will be evaluated at values of the parameters biased by amounts given, on the average, by equation (63).

5. Implications

5.1. *Choice of method*

5.1.1. The preceding discussion shows that the method of maximum likelihood has no significant advantages over the method of least squares in the determination of parameters, and in fact has disadvantages, particularly when the number of degrees of freedom is small. The necessity of assuming an error-distribution function, and the uncertainty about the distribution of the likelihood ratio for small $n - m$, outweigh its apparent attractiveness. Even if a normal distribution of errors is assumed, the paper of Good, Gover & Mitchell (1970) shows that the distribution of R [equation (4)] is closer to that of the χ^2 distribution than the distribution of the likelihood ratio.

5.1.2. If the distribution is not normal, the method of least squares requires no alteration in the estimation of the parameters and their standard deviations. To test for significant remanent systematic errors the only additional information needed is the 'excess' of the error distribution. For the likelihood method a knowledge of the full error distribution is required.

5.2. *Estimation of parameters*

5.2.1. If systematic errors are present the standard deviation in the parameters, given by equation (64), may be quite small even if the parameters themselves are in error by the amounts given by equation (63). It is, therefore, of considerable importance to test for remanent systematic errors before calculating the parameters. A statistical test, of course, can never give certainty; it is always possible for $R_{\min}$ to have its expected value, or be even less, if in the particular set of measurements the random errors happen to be more or less equal and opposite to the systematic. It is also possible for $R_{\min}$ to exceed its expected value by $3\sigma_R$, or even $4\sigma_R$, if in the particular set of measurements the random errors happen to be particularly large, although the systematic errors have been fully corrected. The 5% critical value of χ^2, as used by Beu, Musil & Whitney, or the $2\sigma_R$ criterion used in §2.2.1 (almost equivalent if the errors have a normal distribution), is a reasonable practical compromise between a too frequent false reassurance when systematic errors are present, and a too frequent false alert when they are absent. The latter will occur about once in 20 sets of measurements, and there is perhaps a similar probability that the systematic errors, as defined by R_{syst} in equation (10), amount to about $4\sigma_R$, but are partially obscured by random fluctuations.

5.2.2. Suppose that the observed value of $R_{\min}$ is

$$R_{\min} = n - m + k\sigma_R, \quad (66)$$

and that we attribute the excess above $n - m$ to R_{syst}:

$$R_{\mathrm{syst}} = \sum_i \delta_i^2/\sigma^2 = k\sigma_R. \quad (67)$$

The average value of δ^2/σ^2 is then

$$(\delta^2/\sigma^2)_{\mathrm{av}} = k\sigma_R/n, \quad (68)$$

which is, for a normal distribution of errors,

$$(\delta^2/\sigma^2)_{\mathrm{av}} = 2^{1/2}k(n - m)^{1/2}/n, \quad (69)$$

or, for the general case, to the approximation of equation (52),

$$(\delta^2/\sigma^2)_{\mathrm{av}} = k\{(2 + \gamma)n - 2(1 + \gamma)m\}^{1/2}/n. \quad (70)$$

The root-mean-square value of the remanent systematic error is thus indicated to be

$$(\delta/\sigma)_{\rm r.m.s.} = k^{1/2}\{(2+\gamma)/n\}^{1/4} \times \{1-2(1+\gamma)m/(2+\gamma)n\}^{1/4}. \quad (71)$$

For values of n and m in the lattice-parameter range this is approximately unity, and it decreases slowly with increasing n. Some examples are:

n	m	γ	$(\delta/\sigma)_{\rm r.m.s.}$
3	1	−1	1·07
3	1	0	0·97
3	1	1	1·15
6	1	0	1·03
1000	100	0	0·29

all for $k = 2$.

5.3. *Estimation of standard deviations*

It has been assumed throughout that the standard deviations of the angle measurements are known, either from repeated observations (film methods) or from the counting statistics (counter methods; see, for example, Wilson, 1967). The quantities B_{pq} are then determinate. It is possible to estimate them instead by including the σ_i as parameters in the least-squares refinement, with a large increase in n and m, or to assume that their ratios are known and use the value of $R_{\rm min}$ to estimate their absolute values (see, for example, Hamilton, ch. 4). These least-squares estimates are legitimate only if the systematic errors are known to be negligible, and the preceding paragraph has shown that in the lattice-parameter range the sensitivity of statistical tests is limited; remanent systematic errors of the same order as the random errors being at the limit of detectability. If standard deviations, as such, are what is wanted, therefore, least-squares estimates of them based on $R_{\rm min}$ are somewhat dubious. However, as indicating error limits, estimates based on $R_{\rm min}$ are conservative in the sense that they over-estimate the standard deviations by including with them some part of the systematic errors.

5.4. *Structural parameters*

The preceding discussion has concentrated on the determination of lattice parameters, but no assumptions have been made that make it inapplicable to structural parameters. Any useful results could, therefore, be taken over immediately. In structure determination n is usually large and large compared with m, so that in the structure-parameter range statistical tests for systematic error are more sensitive, with $(\delta/\sigma)_{\rm r.m.s.} = 0{\cdot}3$ being at about the limit of detectability (last line of §5.2.2).

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