

Relation between Parameters derived by R_1 , R_2 , and R_n Refinements

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Parameters estimated by minimizing $R_n = \sum_{hkl} w_n F^n - G^n)^2$, where F is the observed structure factor of the hkl reflexion, G that calculated on the basis of a model structure with adjustable parameters, and the w_n are weights, are (i) unbiased estimates of the true parameters only if the F 's are fully corrected for systematic error and the model is free from functional defects; (ii) equivalent only if the weights are assigned so that $w_n F^{2n-2}$ is the same for all n (aside from arbitrary proportionality constants independent of hkl); and (iii) of minimum variance if w_2 is inversely proportional to the variance of F^2 .

Introduction

Various residuals are used in the least-squares refinement of crystal-structure parameters; the commonest are

$$R_1 = \sum_{hkl} w_1 (F - G)^2 \quad (1)$$

and

$$R_2 = \sum_{hkl} w_2 (F^2 - G^2)^2, \quad (2)$$

where F is the magnitude of the observed hkl structure factor, G that of the calculated, and the w 's are weights. It is sometimes asked whether refinement by use of these two residuals leads to parameter estimates that are equivalent in all respects, and, if not, what the relation is between the estimates. The answers are implicit in well-known statistical results (see, for example, Hamilton, 1964), which are here brought together explicitly.

The observed and calculated structure factors may differ for five reasons:

(i) Statistical fluctuations in the counting rates measured (or the equivalent if densitometric methods are used).

(ii) Other random experimental errors.

(iii) Systematic experimental errors.

(iv) Defects in the model from which the calculated structure factors are derived.

(v) Incomplete refinement of the parameters.

In the present context (i) and (ii) need not be distinguished; both are 'random'. Similarly, (iii) and (iv) need not be distinguished; it is purely a matter of convenience or convention whether, for example, incomplete allowance for absorption is regarded as a systematic error in the measurements, or as a failure to account for absorption properly in calculating the intensity that ought to be observed if the postulated

model is correct. For the present purposes, therefore, we may speak briefly of 'random errors', 'defects in the model', and 'incomplete refinement'. Defects in the atomic scattering factors, regarded as at least partly random by Shoemaker (1968), are here classified as 'defects in the model'.

In any particular case the following conditions may or may not be satisfied:

Condition *A*. The weights are chosen so that w_1 is proportional to $w_2 F^2$ for all reflexions.

Condition *B*. The observations are fully corrected for systematic error and the model is correct in its functional form (though some adjustable parameters are to be evaluated from the observations).

Condition *C*. The weights w_2 are inversely proportional to the variances of F^2 .

The answers to the questions posed in the first paragraph are then:

1. If condition *A* is satisfied, refinements in R_1 and R_2 lead to parameters having the same values and the same standard deviations.

2. If condition *B* is satisfied the two estimates of the parameters are unbiased, but may differ in value and standard deviation unless *A* is also satisfied.

3. If condition *C* is satisfied the parameters obtained by refinement in R_2 have a smaller standard deviation than would be given by any other choice of weights; refinement in R_1 has this property if condition *A* is also satisfied.

4. If *B* is not satisfied the parameters obtained by refinement are biased; the bias differs for R_1 and R_2 unless condition *A* is satisfied.

Calculation

For simplicity let us consider a one-dimensional problem involving a single parameter x . Differentiating equation (1) and equating to zero gives as the condition for minimum R_1

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$$\sum w_1(F-G)G' = 0, \quad (3)$$

where

$$G' = \frac{\partial G}{\partial x} \quad (4)$$

for short. Similarly, equation (2) gives as the condition for minimum R_2

$$\sum w_2(F^2 - G^2)GG' = 0. \quad (5)$$

In a nearly refined structure F and G will be nearly equal, and need to be distinguished only when they subtract from one another, not when they add. Equation (5) may therefore be written

$$\sum w_2F^2(F-G)G' = 0. \quad (6)$$

Equations (3) and (6) are identical, and thus lead to parameters with identical properties, only if w_1 is proportional to w_2F^2 , or in other words only if condition A is satisfied. Statement 1 thus follows.

In view of the three sources of difference between the observed and calculated structure factors we may write

$$G = F + \sigma + \delta + G'(x - x_0) + \dots, \quad (7)$$

where σ is the statistical *etc.* random error, δ is the effect on G of defects in the model, G' is the derivative of G with respect to x , evaluated at the current trial value of x , and x_0 is the true value of the parameter being estimated. Like F and G , σ and δ are functions of hkl . Equation (3) now gives as the next R_1 estimate of x

$$x_1 = x_0 - \frac{\sum w_1\sigma G'}{\sum w_1(G')^2} - \frac{\sum w_1\delta G'}{\sum w_1(G')^2} + \dots, \quad (8)$$

whereas equation (6) gives as the next R_2 estimate of x

$$x_2 = x_0 - \frac{\sum w_2\sigma F^2 G'}{\sum w_2F^2(G')^2} - \frac{\sum w_2\delta F^2 G'}{\sum w_2F^2(G')^2} + \dots \quad (9)$$

These estimates become identical, as they must, if condition A is satisfied. Since the mean value of σ is zero the expected values of the parameters are

$$x_1 = x_0 - \frac{\sum w_1\delta G'}{\sum w_1(G')^2} + \dots \quad (10)$$

and

$$x_2 = x_0 - \frac{\sum w_2\delta F^2 G'}{\sum w_2F^2(G')^2} + \dots \quad (11)$$

The estimates x_1 and x_2 thus include biasing terms dependent on the effects of defects in the model, and statements 2 and 4 follow.

Statement 3 is, of course, a commonplace of statistical theory as far as R_2 is concerned.

Generalization to R_n

The results derived in the preceding section are easily generalized to refinement by use of the residual

$$R_n = \sum_{hkl} w_n(F^n - G^n)^2. \quad (12)$$

Condition A is that w_n should be proportional to w_2F^{4-2n} for all reflexions, and R_1 is replaced by R_n in statements 1, 3 and 4.

Effect of weak reflexions

The linear expansion used in equation (7) depends on the assumption that the structure factor is either actually linear in the errors (improbable) or large compared with the errors (true for most reflexions in most cases). The same assumption underlies the usual relation between the variances of F and F^2 :

$$W(F) = W(F^2)/(2F)^2. \quad (13)$$

Since the relation between F and F^2 is markedly non-linear for small F , one may wonder whether equation (13) is sufficiently accurate for statement 3 to be plausible for refinement in R_1 . This can be checked numerically for the part of the variance arising from statistical fluctuations in the counting rates, since these have a Poisson distribution. Calculations kindly arranged by Professor H. E. Daniels have shown that as far as these are concerned equation (13) holds within 1% for accumulated counts as low as 5. One may expect, therefore, that equation (13) will be of sufficient accuracy for crystallographic applications, as many more than 5 counts are normally accumulated for each intensity measurement.

Many crystallographers omit F 's that are smaller than some predetermined size, and one referee of this paper has suggested that this practice may introduce a bias, since there will be a tendency to omit weak reflexions for which σ in equation (7) is negative but to include those for which it is positive, and thus $\langle\sigma\rangle$ will not be zero. The author agrees, but has no useful recommendation to make about the treatment of reflexions with negative measured intensity.* The effect is likely to be more important for scaling factors and temperature factors (for which G' will also have a bias toward one sign) than for positional parameters.

Example

An example of the effect of inconsistent weighting (non-fulfilment of condition A) applied to an incorrect model (non-fulfilment of condition B) was noticed in the course of an attempted refinement of the structure of a synthetic apatite (Sudarsanan, Wilson & Young, 1972). The example may be idealized as follows. An

* Note added in proof:—This problem is discussed in a current paper by Hirshfeld & Rabinovich (1973).

atomic site is only partially occupied, but the partial occupancy is not recognized, and refinement is carried out in the usual way in both R_1 and R_2 with unit weights in each case. The temperature parameters found were too large to be reasonable for the halogen atom in question, and larger for R_2 than for R_1 . As pointed out by another referee, this suggests that deliberately carrying out two refinements with different weighting schemes might reveal the presence of significant but unsuspected defects in the model or systematic errors in the measurements.

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The Crystal and Molecular Structure of Bis-(2,4-dithiobiureto)nickel(II) Diperchlorate–Ethanol, $\text{Ni}(\text{HDTB})_2(\text{ClO}_4)_2 \cdot \text{EtOH}$

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The crystal structure was determined by Patterson and Fourier methods and refined by least-squares calculations using counter data (1363 reflexions), with anisotropic temperature factors for non-hydrogen atoms and positional parameters for hydrogen atoms, to a final $R=0.075$. The crystals are monoclinic, space group $P2_1/c$, $a=4.990$ (6), $b=20.026$ (11), $c=19.713$ (9) Å, $\beta=93.70$ (5)°, $Z=4$. The structure consists of four equivalent layers per unit cell, parallel to the xz plane, each containing the four constituents $\text{Ni}(\text{HDTB})_2 \cdot 2\text{ClO}_4 \cdot \text{EtOH}$ of the asymmetric and stoichiometric unit. The nickel atom is planar-coordinated to four sulphur atoms. In the cationic complex $\text{Ni}(\text{HDTB})_2^{2+}$ the interatomic distances and angles are very similar to those of the neutral complex $\text{Ni}(\text{DTB})_2$, except that the S–C and C–N bond distances are respectively shorter and longer, and the bond angles S–C–N (terminal) and N(terminal)–C–N(central) are respectively higher and lower than in the neutral complex. Average bond distances: Ni–S = 2.162, S–C = 1.645, C–N(central) = 1.38, C–N(terminal) = 1.37 Å. The perchlorate ions (average Cl–O = 1.40 Å) and the ethanol molecule (C–C = 1.53, C–O = 1.41 Å) are linked to each other and to the complex molecules by several intermolecular hydrogen bonds. Each central NH group of the complex is linked to an oxygen atom of the perchlorate ions by the shortest observed hydrogen bonds (O···H distances = 1.86 and 1.88 Å). Another eleven intermolecular hydrogen bonds have O···H distances of 2.09–2.48 Å, and seven intramolecular hydrogen bonds have N···H distances of 2.23–2.51 Å.

Introduction

The ligand 2,4-dithiobiuret (HDTB) could possibly chelate *via* two sulphur or two nitrogen atoms or *via* a sulphur and a nitrogen atom, in each case to form a six-membered ring. It generally acts as a uninegative donor in neutral solution or as a neutral donor in acidic solution. The crystal and molecular structure of its square planar neutral complexes $\text{Pd}(\text{DTB})_2$ (Girling & Amma, 1968) and $\text{Ni}(\text{DTB})_2$ (Luth, Hall, Spofford & Amma, 1969) showed an S, S coordination of the ligand to the metal. The crystal structure of the addition compound $\text{Ni}(\text{DTB})_2 \cdot \text{glycol}$ (Pignedoli, Peyronel & Antolini, 1972) showed several hydrogen bonds between the

glycol and the complex molecules having a definite influence on their molecular structures.

The crystal and molecular structure of the cationic complex $\text{Ni}(\text{HDTB})_2(\text{ClO}_4)_2 \cdot \text{EtOH}$ has now been determined in order to investigate (a) the class of the metal–ligand bonds, (b) the structural differences between the coordinated neutral ligand in this complex and the uninegative ligand in the neutral complex, (c) the hydrogen-bond system in this ionic structure.

Experimental

The compound was prepared by cooling very slowly a warm ethanolic solution of the reagents containing