

Refinement of R_2 and R_1 : A Physical Interpretation

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Least-squares refinement of $R_2 = \sum |I_1 - I_2|^2$, where I_1 and I_2 are, for example, the observed and calculated intensities for a crystal structure, is equivalent to obtaining a least-squares fit between the Patterson syntheses for the observed intensities and the model structure. Least-squares refinement of $R'_1 = \sum |F_1 - F_2|^2$ is equivalent to obtaining a least-squares fit between the calculated electron density and that obtained from a Fourier series based on the observed structure factors; R'_1 approximates to the usual residual $R_1 = \sum ||F_1| - |F_2||^2$ when the model is good and refinement is approaching completion. Inclusion of weights in the residuals is equivalent to distorting the Patterson or electron-density synthesis to be fitted by modifying the amplitudes of the Fourier coefficients by factors proportional to the square roots of the weights.

It is generally accepted that all methods of refinement lead to much the same parameters; this has been discussed, for example, by Cochran (1948, 1951) and Cruickshank (1952). Although the parameters are much the same, they are not identical: different methods may lead to different biases or different variances. Wilson (1973) collected the conditions under which refinements in R_1 and R_2 (as defined in the abstract) would lead to the same results, to the first order of approximation. It was later shown (Wilson, 1974; Lomer & Wilson, 1975) that, even when the conditions of the 1973 paper were satisfied, refinement of the scaling factor in different ways would ordinarily lead to different values. So far, other parameters have not been treated with as high a degree of approximation.

The physical meaning of the refinement process does not seem to be well known. Refinement of

$$R_2 = \sum |I_1 - I_2|^2 \quad (1)$$

to give a minimum with respect to the adjustable parameters corresponds exactly to obtaining the best fit, in the least-squares sense, between the Patterson synthesis based on the observed intensities and that based on the intensities calculated from the model. Refinement of

$$R'_1 = \sum |F_1 - F_2|^2 \quad (2)$$

corresponds similarly to the best fit, in the least-squares sense, between the observed and calculated electron densities. The residual (2) is not that usually considered:

$$R_1 = \sum ||F_1| - |F_2||^2, \quad (3)$$

but approximates to it when the model is good and refinement is approaching completion. These results are probably simple corollaries of the Riesz-Fischer

theorem for finite trigonometrical series (see, for example, Hardy & Rogosinski, 1944), but it is convenient to derive them in an elementary fashion in one dimension. It is easy to generalize to three dimensions.

Calculation

Suppose that $f(x)$ is a periodic function of period unity (*e.g.* the electron density) and that $g(x)$ is a model of it with adjustable parameters (*e.g.* a set of atoms with adjustable positions, temperature factors, *etc.*). The mean-square difference between f and g is

$$\int_0^1 |f - g|^2 dx \quad (1)$$

$$= \int_0^1 (f - g)(f^* - g^*) dx. \quad (2)$$

In the example f and g will be real, aside from the effects of dispersion, but it does no harm to keep the expressions general. The expression (2) will be a minimum with respect to some parameter r of the model g if its derivative with respect to r is zero, that is, if

$$-\int_0^1 g'[f^* - g^*] dx - \int_0^1 (g')^* [f - g] dx = 0, \quad (3)$$

which reduces to

$$\int_0^1 [g^* g' + g(g')^*] dx = \int_0^1 [f^* g' + f(g')^*] dx, \quad (4)$$

where primes denote differentiation with respect to the parameter r . Refinement is complete when equations like (4) are satisfied for all the adjustable parameters.

Any reasonable periodic function can be represented by a Fourier series

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$$f(x) = \sum_{h=-\infty}^{\infty} F_h \exp(2\pi ihx) \quad (5)$$

where

$$F_h = \int_0^1 f(x) \exp(-2\pi ihx) dx, \quad (6)$$

and similarly for $g(x)$. In the example F_h will be the observed structure factors including their signs or phases, and G_h the calculated. The residual R'_1 is given by

$$R'_1 = \sum_h |F_h - G_h|^2 = \sum_h (F_h - G_h)(F_h^* - G_h^*), \quad (7)$$

and will be a minimum when its derivative with respect to r is zero. Differentiation gives, since G_h is the function of r ,

$$-\sum_h G'_h [F_h^* - G_h^*] - \sum_h (G_h^*)' [F_h - G_h] = 0, \quad (8)$$

which reduces to

$$\sum_h [G_h^* G'_h + G_h (G_h^*)'] = \sum_h [F_h^* G'_h + F_h (G_h^*)']. \quad (9)$$

It is readily shown that (9) is, term by term, the same as (4). In the first term of (4) replace g by its Fourier components, obtaining

$$\begin{aligned} \int_0^1 g^* g' dx &= \int_0^1 \left[\sum_h G_h^* \exp(-2\pi ihx) \right] \\ &\times \left[\sum_k G'_k \exp(2\pi ikx) \right] dx \\ &= \sum_{h,k} G_h^* G'_k \int_0^1 \exp[2\pi i(k-h)x] dx. \end{aligned} \quad (10)$$

The integral on the right is zero unless $h=k$, when it has the value unity, so that

$$\int_0^1 g^* g' dx = \sum_h G_h^* G'_h, \quad (11)$$

which is the first term of (9). The other terms may similarly be shown to be equal. Minimization of the residual R'_1 thus leads to exactly the condition required to give the best fit, in the least-squares sense, between the electron density, as represented by all observed structure factors, and the model chosen to represent the structure. The residual R'_1 , given by (7), is not the same as the residual R_1 ordinarily used in structure refinement, as the latter is based on $|F_h|$ and $|G_h|$. However, towards the end of the refinement of a structure with a good model, F_h and G_h will have the same sign if the structure is centrosymmetric, or nearly equal phases if non-centrosymmetric, so that one would expect that refinement in R_1 is very nearly equivalent to a least-squares fit between the real and the model electron densities. Refinement of R_2 , given by

$$R_2 = \sum_h (I_h - H_h)^2, \quad (12)$$

where I_h and H_h are the observed and calculated intensities, is analogously seen to be equivalent to obtaining the best fit, in the least-squares sense, between the Patterson density, as represented by the observed intensities, and the Patterson density of the model chosen to represent the structure. In this case no qualifications are necessary, since I and H are necessarily real and of determinate sign.

Effect of weights

In most crystallographic applications it is necessary to give zero weight to reflexions that have not been measured, because they were outside the limiting sphere, or were obscured by part of the apparatus, or were affected by *Umweganregung* or severe extinction. (Reflexions measured as zero or negative within the limits of statistical fluctuation do not come into this category, and should be included in the least-squares refinement.) In addition to this necessary zero weighting, it is common to include other weights, based on counting statistics and other estimates of the variance of the observation. Tracing the above argument backwards shows that refinement of the residual is then equivalent to obtaining the best fit, in the least-squares sense, between a fictitious model and a fictitious electron (Patterson) density in which each coefficient of the Fourier series is multiplied by the square root of the weight. If the model is perfect (in the sense that it has the same functional form as the true density, and differs from it only in that the adjustable parameters have to be determined) this will not matter, and the parameters will be unbiased estimates of the true parameters, though different weights will give different variances. If the model is defective, however, the estimates will be biased in the direction of fitting the fictitious density, distorted by the weights and termination-of-series effects, rather than being unbiased estimates of the true parameters. Least-squares refinement of a residual, though it makes working with a partial data set easier, does not entirely avoid the bias associated with termination-of-series *etc.* effects if the model is defective. Analogy with the result for the scaling factor (Lomer & Wilson, 1975) suggests that even statistical fluctuations† may bias results of refinement in R_1 . Use of weights proportional to I^{-1} (approximately corresponding to counting statistics as the only source of variance) turns refinement of R_2 into something closely resembling refinement of R_1 (unweighted).

The actual result obtained by Cochran (1948) was that refinement in R'_1 with weights equal to the reciprocal of the atomic scattering factor of the atom whose positional coordinates were being sought gives the coordinates of the maximum of the electron

† Note added in proof: In a paper now submitted for publication it is shown that weights depending explicitly on I_h produce bias in refinements in R_2 .

density as represented by a Fourier series with the observed structure factors as coefficients. This is a very interesting result, but it should be noted that the criterion for atomic position (maximum of electron density) is different from that of obtaining a least-squares fit for the entire electron density map, and that different weighting is required for atoms of differing atomic number. One would expect the least-squares fit to give a better estimate of the atomic positions, but in some applications it could be that the position of the maximum electron density is the focus of interest. Cruickshank (1952) has obtained results similar to Cochran's for the relation between peaks in a Patterson synthesis and refinement in a suitably weighted R_2 .

These reflexions were stimulated by the problem of locating the halogen atoms in Cd analogues of apatite (Sudarsanan, Wilson & Young, 1972; a full account is in preparation). I am indebted to Professor R. A. Young for stimulating discussions and to Professor D. W. J. Cruickshank, Dr David Harker and Profes-

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Coincidence-Site Lattices

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The possibility that two arbitrary lattices, 1 and 2, have a coincidence-site lattice (CSL) in common is examined. Let \mathbf{T} be the 3×3 matrix that maps a basis of lattice 1 onto a basis of lattice 2 and let $|\mathbf{T}|$ be the absolute value of its determinant. It may be assumed that $|\mathbf{T}| \geq 1$. There is a CSL if, and only if, \mathbf{T} is rational. The main result is that the density ratio, Σ_2 , of coincidence points to points of lattice 2 is equal to the least positive integer n such that $n\mathbf{T}$ and $n|\mathbf{T}|\mathbf{T}^{-1}$ are integral matrices. A basis for the CSL can be determined quickly if lattices 1 and 2 are related by a rotation.

Density of coincidence sites

The coincidence-site lattice model of a grain boundary considers the lattices that correspond to the crystals on both sides of the boundary (for example see Brandon, Ralph, Ranganathan & Wald, 1964). Working with this model we have to find out whether the metric properties of the lattices and their observed relative orientation are such that the two lattices, which we shall call 1 and 2, have vectors in common. If there are common vectors, they will form either a linear, a planar, or a spatial lattice. In the last case we shall speak of a coincidence-site lattice (CSL) and shall denote by Σ_1 (or Σ_2) the ratio of the volumes of primitive cells for the CSL and for lattice 1 (or 2). Σ_1 and Σ_2 are positive integers. Let the vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ form a basis of lattice 1 (*i.e.* $\mathbf{b}_1, \mathbf{b}_2$, and \mathbf{b}_3 span a primitive cell of lattice 1) and let $\mathbf{b}'_1, \mathbf{b}'_2, \mathbf{b}'_3$ be a basis of

lattice 2. We can write

$$\begin{aligned} \mathbf{b}'_1 &= t_{11}\mathbf{b}_1 + t_{12}\mathbf{b}_2 + t_{13}\mathbf{b}_3 \\ \mathbf{b}'_2 &= t_{21}\mathbf{b}_1 + t_{22}\mathbf{b}_2 + t_{23}\mathbf{b}_3 \\ \mathbf{b}'_3 &= t_{31}\mathbf{b}_1 + t_{32}\mathbf{b}_2 + t_{33}\mathbf{b}_3, \end{aligned}$$

or, introducing matrix notation,

$$\mathbf{b}' = \mathbf{T}\mathbf{b},$$

where

$$\mathbf{b}' = \begin{pmatrix} \mathbf{b}'_1 \\ \mathbf{b}'_2 \\ \mathbf{b}'_3 \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \\ \mathbf{b}_3 \end{pmatrix}$$

and \mathbf{T} is a 3×3 matrix. Let $|\mathbf{T}|$ be the absolute value of the determinant of \mathbf{T} . We shall call a matrix 'rational' if all its nine elements are rational numbers and 'integral' if all its nine elements are integers. In the Appendix we shall prove the following two theorems.