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On the Refinement on Profile, Background and Net Intensities

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Abstract

The raw data obtained with a single-crystal diffractometer are typically integrated profile and background intensities. All linear combinations of these data items, and in particular net intensities and total backgrounds, are equivalent observations. However, net intensities may be negative, in apparent contradiction with basic physics. Backgrounds are generally discarded from the list of observations once they have been subtracted from the profile intensities. In a crystal structure refinement on *all* observations, structural parameters including scale, extinction and possibly others, as well as individual background intensities, are refined on the observed profile intensities and on the observed background intensities. It is shown that, in such a refinement, the structural parameters are determined exclusively by the net intensities as in traditional least squares, whereas calculated backgrounds depend on the difference between observed and calculated net intensities. Negative net intensities are therefore not in contradiction with physics or with the structural model, and should be retained unaltered in the data set.

Introduction

In a typical single-crystal diffraction experiment, the observations are, for the ith reflection, the integrated intensity Q_i^{obs} measured by scanning over the reflection profile, and the backgrounds L_i^{obs} and H_i^{obs} measured respectively on the low-angle and high-angle sides of the Bragg peak. The net intensity P_i^{obs} and total background intensity B_i^{obs} are

$$\begin{aligned} P_i^{obs} &= Q_i^{obs} - l_i L_i^{obs} - h_i H_i^{obs}, \\ B_i^{obs} &= l_i L_i^{obs} + h_i H_i^{obs}, \end{aligned} \tag{1}$$

l_i and h_i being the ratios of the time spent on the profile scan to the time spent on the measurement of the low- or high-angle background, respectively. If Q_i^{obs} is of the same order of magnitude as B_i^{obs}, the net intensity P_i^{obs} may be negative. It is still customary in some laboratories to discard such measurements or set $P_i^{obs} = 0$ since the calculation of the observed structure amplitude $|F_i^{obs}|$ requires the calculation of the square root of the intensity. French & Wilson (1978) have proposed a method for obtaining $|F_i^{obs}|$ based on Bayesian statistics. Hirshfeld & Rabinovich (1973) recommend refinement on $|F_i^{obs}|^2$ and inclusion of the negative values in the refinement since these are perfectly valid observations and discarding them or altering them in any way results in a bias. However, objections may be raised that negative net intensities appear to be contradictory to the refined model since $|F_i^{calc}|^2$ is always positive and the model is thus incapable of reproducing the observations irrespective of the values of its parameters.

The problem of negative net intensities arises since P_i^{obs} is not directly observed, but derived from the original observations. In this paper, we propose a refinement on the directly observed intensities, *both* profile *and* background, which cannot be negative. It will be shown that such a refinement is equivalent to the scheme of Hirshfeld & Rabinovich (1973).

Transformed observations

In the following, vectors are assumed to be column vectors, line vectors are identified by the superscript symbol T for transposed. Let the vector $\mathbf{o}$ with components o_j $(1 \le j \le J)$ represent a set of observations. A linear model $\mathbf{Av} = \mathbf{c} \simeq \mathbf{o}$ with N adjustable parameters v_n $(1 \le n \le N)$ assembled in the vector $\mathbf{v}$ relates the observations to the corresponding calculated quantities c_j assembled in the vector $\mathbf{c}$. In a least-squares refinement, the parameters v_n are optimized by minimizing the weighted deviance $D_w = \mathbf{d}^T\mathbf{Wd}$ where $\mathbf{W}$ is a general weight matrix, and $\mathbf{d} = \mathbf{o} - \mathbf{c}$ the vector of deviates. For minimum-variance weights, the inverse $\mathbf{S} = \mathbf{W}^{-1}$ is the variance-covariance matrix of the observations. The normal equations are then

$$\mathbf{A}^T\mathbf{WAv} = \mathbf{A}^T\mathbf{Wo}. \tag{2}$$

We now discuss the effect of a linear transformation of the observations represented by the invertible matrix $\mathbf{R}$ transforming the vectors $\mathbf{o}$ and $\mathbf{c}$ into $\mathbf{o}' = \mathbf{Ro}$ and $\mathbf{c}' = \mathbf{Rc}$, respectively. If the matrix $\mathbf{S}$ exists, it transforms as the variance-covariance matrix of the

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observations o_j, $\mathbf{S}' = \mathbf{RSR}^T$, and the new weight matrix is therefore $\mathbf{W}' = \mathbf{S}'^{-1} = (\mathbf{R}^T)^{-1}\mathbf{WR}^{-1}$. We adopt this transformation rule also for non-invertible matrices $\mathbf{W}$ where $\mathbf{S}$ does not exist. The model relating observed to calculated quantities becomes $\mathbf{A}'\mathbf{v} = \mathbf{c}' \simeq \mathbf{o}'$, and the new design matrix is therefore $\mathbf{A}' = \mathbf{RA}$. Using these properties, it is easily shown that the normal equations and the weighted deviance are invariant under the transformation $\mathbf{R}$;

$$D'_w = \mathbf{d}'^T\mathbf{W}'\mathbf{d}' = \mathbf{d}^T\mathbf{R}^T(\mathbf{R}^T)^{-1}\mathbf{WR}^{-1}\mathbf{Rd} = \mathbf{d}^T\mathbf{Wd} = D_w, \quad (3)$$

$$\mathbf{A}'^T\mathbf{W}'\mathbf{A}' = \mathbf{A}^T\mathbf{WA}, \qquad \mathbf{A}'^T\mathbf{W}'\mathbf{o}' = \mathbf{A}^T\mathbf{Wo}.$$

Therefore, all sets of quantities derived from the original observations by a non-singular matrix $\mathbf{R}$ serve equally well as observations.

In practice, cases arise where $\mathbf{R}$ is rectangular. As examples we would mention the derivation of net counts as in (1), the calculation of mean intensities from a set of symmetry-equivalent reflections, and the use of the integrated intensity $Q_i^{\rm obs}$ rather than the complete profile. It can be seen that a rectangular transformation matrix $\mathbf{R}_{\rm rect}$ corresponds to a refinement on a subset of the data. The case of the non-invertible $\mathbf{R}_{\rm rect}$ may be assimilated into the treatment given in the paragraph above applicable only to an invertible square $\mathbf{R}$ in the following way. The rectangular $\mathbf{R}_{\rm rect}$ is augmented to an invertible matrix $\mathbf{R}$ by adding additional (arbitrary) transformation equations. The observations defined by these additional equations are then excluded from the refinement by setting their diagonal and off-diagonal weights in the transformed weight matrix $\mathbf{W}'$ to zero. The resulting matrices $\mathbf{W}'_{\rm subset}$ and $\mathbf{W}_{\rm subset} = (\mathbf{R}^T)\mathbf{W}'_{\rm subset}\mathbf{R}$ are singular. This argument shows that $P_i^{\rm obs}$ or $|F_i^{\rm obs}|^2$ may serve as observations.

Transformed variables

A linear transformation of the variables represented by the matrix $\mathbf{T}$ transforming $\mathbf{v}$ into $\mathbf{v}'' = \mathbf{Tv}$ permits the structure of the normal-equations matrix to be changed. The latter transforms as a second-rank tensor. In terms of the new variables $\mathbf{v}''$, the model is $\mathbf{A}''\mathbf{v}'' = \mathbf{A}''\mathbf{Tv} = \mathbf{Av} = \mathbf{c}$, thus $\mathbf{A}'' = \mathbf{AT}^{-1}$. The new normal-equations matrix and vector are therefore

$$\mathbf{A}''^T\mathbf{WA}'' = (\mathbf{T}^T)^{-1}[\mathbf{A}^T\mathbf{WA}]\mathbf{T}^{-1}; \qquad \mathbf{A}''^T\mathbf{Wo} = (\mathbf{T}^T)^{-1}[\mathbf{A}^T\mathbf{Wo}]. \quad (4)$$

Below, the setting-up of the normal equations is facilitated by a transformation of the *observations* such that subsets of the (transformed) observations depend only on subsets of the variables. A change of the *variables* will be used to transform the normal-equations matrix into a block-diagonal one easier to invert.

Background refinement

The model relating the raw observations of a diffraction experiment to derived parameters is

$$Q_i^{\rm calc} = P_i(\nu_m) + l_iL_i + h_iH_i \simeq Q_i^{\rm obs}, \quad (5a)$$

$$L_i^{\rm calc} = L_i \simeq L_i^{\rm obs}, \quad (5b)$$

$$H_i^{\rm calc} = H_i \simeq H_i^{\rm obs}, \quad (5c)$$

where ν_m are adjustable parameters describing the crystal structure, the scale factor, secondary extinction and possibly other physical quantities. L_i and H_i are also variable parameters, adjusted to the observations by the restraint equations (5b and 5c). If i ranges from 1 to I and m from 1 to M, (5) represents a model with $J = 3I$ equations and $N = 2I + M$ parameters. For the least-squares adjustment of the $Q_i^{\rm calc}$, $L_i^{\rm calc}$ and $H_i^{\rm calc}$ to the corresponding observations, we admit non-zero off-diagonal terms of the weight matrix corresponding to the observed items of one reflection $Q_i^{\rm obs}$, $L_i^{\rm obs}$ and $H_i^{\rm obs}$ whose weights are given by the invertible 3×3 matrix

$$\mathbf{W}_i = \begin{bmatrix} w(Q_i) & w(Q_iL_i) & w(Q_iH_i) \\ w(Q_iL_i) & w(L_i) & w(L_iH_i) \\ w(Q_iH_i) & w(L_iH_i) & w(H_i) \end{bmatrix},$$

$$\mathbf{W}_i^{-1} = \mathbf{S}_i = \begin{bmatrix} s(Q_i) & s(Q_iL_i) & s(Q_iH_i) \\ s(Q_iL_i) & s(L_i) & s(L_iH_i) \\ s(Q_iH_i) & s(L_iH_i) & s(H_i) \end{bmatrix}. \quad (6)$$

Off-diagonal terms of the weight matrix corresponding to data items of different reflections are assumed to be zero. For minimum-variance weights, the inverse matrix $\mathbf{S}_i$ is the variance-covariance matrix of the three data items. The weighted deviance becomes

$$D_w = \sum_{i=1}^{I} \mathbf{d}_i^T\mathbf{W}_i\mathbf{d}_i,$$

$$\mathbf{d}_i^T = (Q_i^{\rm obs} - Q_i^{\rm calc}, L_i^{\rm obs} - L_i^{\rm calc}, H_i^{\rm obs} - H_i^{\rm calc}). \quad (7)$$

A suitable transformation of the raw data facilitates the task of compiling the normal-equations matrix and vector. The transformed observations we use are the net intensities $P_i^{\rm obs}$ of (1), and two linear combinations of $L_i^{\rm obs}$ and $H_i^{\rm obs}$ symbolized respectively by $Y_i^{\rm obs}$ and $Z_i^{\rm obs}$ chosen in such a way that the off-diagonal weights $w(P_iZ_i) = w(Y_iZ_i) = 0$, implying that the correlations of $Z_i^{\rm obs}$ with the other types of data vanish;

$$Y_i^{\rm obs} = \left[l_i + \frac{w(Q_iL_i)}{w(Q_i)}\right]L_i^{\rm obs} + \left[h_i + \frac{w(Q_iH_i)}{w(Q_i)}\right]H_i^{\rm obs}, \quad (8a)$$

$$Z_i^{\rm obs} = -K_i[h_is(H_i) + l_is(L_iH_i) - s(Q_iH_i)]L_i^{\rm obs} + K_i[l_is(L_i) + h_is(L_iH_i) - s(Q_iL_i)]H_i^{\rm obs},$$

$$K_i^{-2} = s(L_i)s(H_i) - s(L_iH_i). \quad (8b)$$

This choice results in a considerable simplification of the algebra. Y_i^{obs} is related to the sum of the background measurements and Z_i^{obs} is related to their difference. The variables L_i and H_i are replaced by Y_i and Z_i defined by (8) analogously to Y_i^{obs} and Z_i^{obs}. These transformations will result in a normal-equations matrix composed of two blocks where the Z_i depend only on the Z_i^{obs}. The weight matrix $\mathbf{W}_i'$ for P_i^{obs}, Y_i^{obs} and Z_i^{obs} is

$$w(P_i) = w(P_iY_i) = w(Q_i), \tag{9a}$$

$$w(Y_i) = w(Q_i)s(P_i)[s(P_i) - 1/w(Q_i)]^{-1}, \tag{9b}$$

$$w(Z_i) = [s(P_i) - 1/w(Q_i)]^{-1}, \tag{9c}$$

$$w(P_iZ_i) = w(Y_iZ_i) = 0. \tag{9d}$$

The inverse of $\mathbf{W}_i'$ is

$$\begin{aligned} s(P_i) &= (1, -l_i, -h_i)\mathbf{S}_i(1, -l_i, -h_i)^T \\ &= s(Q_i) + l_i^2 s(L_i) + h_i^2 s(H_i) - 2l_i s(Q_iL_i) \\ &\quad -2h_i s(Q_iH_i) + 2l_ih_i s(L_iH_i), \end{aligned} \tag{10a}$$

$$s(Y_i) = s(Z_i) = -s(P_iY_i) = s(P_i) - 1/w(Q_i), \tag{10b}$$

$$s(P_iZ_i) = s(Y_iZ_i) = 0. \tag{10c}$$

The non-linear function $P_i^{calc}(\nu_m)$ is linearized in the usual way by retaining the first term of a Taylor expansion calculated at approximate values ν_m^0. The refined variables are then M increments δ_m of ν_m, I increments y_i of Y_i and I parameters Z_i. The new model is thus

$$P_i^{calc} = P_i^0 + \sum_{m=1}^{M} p_{im}\delta_m \simeq P_i^{obs}, \tag{11a}$$

$$Y_i^{calc} = Y_i = Y_i^0 + y_i \simeq Y_i^{obs}, \tag{11b}$$

$$Z_i^{calc} = Z_i \simeq Z_i^{obs}, \tag{11c}$$

where $p_{im} = (\partial P_i/\partial \nu_m)^0$, P_i^0 and Y_i^0 are calculated with approximate parameter values at the start of the refinement cycle. The y_i are introduced instead of the Y_i because the off-diagonal weight $w(P_iY_i) = w(Q_i)$ of (9a) hardly ever vanishes. Therefore, the resulting normal-equations matrix possesses off-diagonal elements correlating δ_m and Y_i (or y_i). These elements vanish if the variable y_i is replaced by y_i';

$$\begin{aligned} y_i' &= y_i + [w(P_iY_i)/w(Y_i)] \sum_{m=1}^{M} p_{im}\delta_m \\ &= y_i + \{1 - [w(Q_i)s(P_i)]^{-1}\}(P_i^{calc} - P_i^0), \end{aligned} \tag{12a}$$

$$Y_i^{calc} - Y_i^0 = -[w(P_iY_i)/w(Y_i)] \sum_{m=1}^{M} p_{im}\delta_m + y_i', \tag{12b}$$

using (11a) and (9). The normal-equations matrix and vector corresponding to (11) and (12b) are easily compiled. Replacement of the variables L_i and H_i by y_i' and Z_i results in a blocked $(M+2I)$-dimensional matrix and decomposes the least-squares problem (5) into $1+2I$ independent sets of normal equations, one of dimension M and $2I$ of dimension 1:

$$\begin{aligned} \sum_{m=1}^{M} \delta_m \left\{ \sum_{i=1}^{I} p_{im}p_{in}/s(P_i) \right\} \\ = \sum_{i=1}^{I} p_{in}(P_i^{obs} - P_i^0)/s(P_i), \quad n = 1, \ldots, M, \end{aligned} \tag{13a}$$

$$\begin{aligned} y_i' = \{1 - [w(Q_i)s(P_i)]^{-1}\}(P_i^{obs} - P_i^0) \\ + (Y_i^{obs} - Y_i^0), \quad i = 1, \ldots, I, \end{aligned} \tag{13b}$$

$$Z_i^{calc} = Z_i^{obs}, \; i = 1, \ldots, I. \tag{13c}$$

Equation (13a) represents a refinement of the structural parameters ν_m on the net intensities P_i^{obs} with weights calculated by the inverse of (10a), minimum-variance weights being the inverse variances of P_i^{obs}. From (13b), (12a) and (11b), Y_i^{calc} is obtained in terms of P_i^{calc}. Using (13c) and inverting (8), one can calculate L_i^{calc} and H_i^{calc} and finally the total background B_i^{calc} is obtained from (1):

$$Y_i^{obs} - Y_i^{calc} = -\{1 - [w(Q_i)s(P_i)]^{-1}\}(P_i^{obs} - P_i^{calc}), \tag{14}$$

$$B_i^{obs} - B_i^{calc} = [s(P_iB_i)/s(P_i)](P_i^{obs} - P_i^{calc}), \tag{15}$$

$$\begin{aligned} s(P_iB_i) = -l_i^2 s(L_i) - h_i^2 s(H_i) - 2l_ih_i s(L_iH_i) \\ + l_i s(Q_iL_i) + h_i s(Q_iH_i). \end{aligned} \tag{16}$$

For minimum-variance weights, $s(P_iB_i)$ is the covariance of P_i^{obs} and B_i^{obs}. Calculating the deviance D_w from (7) with $\mathbf{d}_i'^T = (P_i^{obs} - P_i^{calc}, Y_i^{obs} - Y_i^{calc}, Z_i^{obs} - Z_i^{calc})$ and $\mathbf{W}_i'$ from (9), and introducing (13c) and (14), one gets

$$D_w = \sum_{i=1}^{I} [s(P_i)]^{-1}(P_i^{obs} - P_i^{calc})^2. \tag{17}$$

Concluding remarks

Equations (13a) and (17) show that the solution of the least-squares problem (5) is equivalent to a refinement on net intensities, be they positive or negative. A clear theoretical justification is thus provided of the recommendation of Hirshfeld & Rabinovich (1973). The dubious practice of refining on $|F_i^{obs}|$ with reflections of negative net intensity removed or transformed is seen to be a vogue without foundation. The essential component of this justification is the refinement of *all* variables necessary to model the *complete* set of observations of the experiment. This is an important general principle even if it turns out that in the present case the numerical calculation may be simplified to the conventional treatment and that it is in fact unnecessary to evaluate the unknown background variables explicitly. There is a very close mathematical parallel to the refinement of heavy-

atom coordinates in non-centrosymmetric isomorphs of proteins as revealed by Bricogne (1984). From (13*c*) and (14), it is evident that (13*a*), (15) and (17) are also obtained by using only a subset of observations composed of P_i^{obs} and the total backgrounds B_i^{obs}.

The fraction of $P_i^{obs} - P_i^{calc}$ which is attributed to the background intensity according to (15) increases with decreasing ratio of peak-to-background intensity. As expected, it reaches large values for very weak Bragg reflections. The covariance of P_i^{obs} and B_i^{obs} is normally a negative quantity. Thus, if $P_i^{calc} \gtrless P_i^{obs}$, then $B_i^{calc} \lessgtr B_i^{obs}$. In the following example, we assume that the variances of the observed intensities are derived from Poisson statistics, $s(Q_i) = Q_i^{obs}$, $s(L_i) = L_i^{obs}$, $s(H_i) = H_i^{obs}$ and $s(Q_iL_i) = s(Q_iH_i) = s(L_iH_i) = 0$. We also assume $l_i = h_i = 2$. In terms of the ratio of integrated intensity to total background $g_i = Q_i^{obs}/(l_iL_i^{obs} + h_iH_i^{obs})$, one obtains

$$B_i^{obs} - B_i^{calc} = -[2/(g_i+2)](P_i^{obs} - P_i^{calc}).$$

The fractions of $P_i^{obs} - P_i^{calc}$ attributed to the background are 2, 17, 67 and 100% for $g_i = 100$, 10, 1 and 0, respectively. Negative net intensities imply $g_i < 1$.

The model for the background intensities that we have used might be described as the *independent background* model, in which each and every reflection has its own independent variable parameters quantifying both the low-and high-angle backgrounds. A large number of variable parameters results but the total background is readily estimated using (15). Alternatively, the background might be represented by some more elaborate model in terms of a few variable global parameters. There is a risk of introducing additional modelling error, but the number of variables is considerably reduced. Once a suitable model has been found, it is easily introduced in (5) and the setting up of the corresponding normal equations is straightforward. However, we note that the structural parameters ν_m and the parameters describing the background are correlated and should be refined together. We do not recommend fitting the background intensities to their observed values first and then subtracting the resulting calculated backgrounds from the integrated scan intensities to obtain net intensities since the errors of such net intensities are correlated.

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SHORT COMMUNICATIONS

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A computational method for obtaining stationary solutions in RHEED and REM.

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Abstract

The application of the multislice approach of Cowley & Moodie [*Acta Cryst.* (1959), **12**, 353-359] to reflection high-energy electron diffraction (RHEED) may suffer from edge effects which continuously degrade the edge of the unit cell and prevent stationary solutions from being obtained for RHEED. The reason for this is that it is difficult to simulate a tilted infinite plane wave for the beam geometry of RHEED in a finite unit cell. It is shown that this can be done with a simple edge-patching method. It is then possible to obtain an infinitely convergent stationary solution for an arbitrary surface in RHEED within a finite unit cell.

The arrangement of the artificial supercell for the simulation of RHEED patterns (Peng & Cowley, 1986) using the Cowley-Moodie multislice approach (Cowley & Moodie, 1959) is similar to that used for the simulation of profile images in high-resolution electron microscopy (HREM). The unit cell is split into two parts, the first is a vacuum and the second contains atoms that comprise the crystal surface. The difference is that, for profile imaging, the incident plane wave is not tilted as much and illuminates the whole unit cell, while for the simulation of RHEED it is more tilted and only illuminates the vacuum part of the unit cell. If we have a propagator with a fixed slice thickness and an empty phase grating, the result of each iteration is simply to add a constant phase term to the initial incident wave function, which resulted from the convolution of the incident-wave function with a fixed propagation function. This phase term can be easily calculated either analytically or numerically. For the simulation of RHEED patterns, the phase grating in the edge area of the vacuum part of each unit cell is empty since the surface potential exponentially decays to near zero into the vacuum. Therefore, in this edge

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