SHORT COMMUNICATIONS

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Clarification of discussion on constrained refinement.

By P. F. PRICE, *Institute Max von Laue–Paul Langevin, 156X Centre de Tri,* 38042 *Grenoble CEDEX, France and School of Physics, University of Melbourne, Parkville, Victoria* 3052, *Australia**

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Pawley's [*Acta Cryst.* (1976), A**32**, 921–922] disproof of the C & D method of applying constraints in crystallographic refinements [Chesick & Davidon (1975). *Acta Cryst.* A**31**, 586–591] is incorrect. Nevertheless, the C & D method *is* incorrect. Both the method and its disproof clearly fail for the particular case of linear least-squares with linear constraints. The method can be corrected in this case but not for the non-linear case.

Pawley (1976) (P2) recently criticized a method (Chesick & Davidon, 1975) (C & D) of applying constraints alternative to the strict constraints described by Pawley (1972) (P1). C & D suggested that each cycle of least-squares refinement should be unconstrained and the constraint applied to the parameter shifts. Pawley's criticisms were (i) that the C & D procedure loses the economic advantage of a much reduced cycle time and the ability to make use of computers with restricted storage capacity, (ii) that the programming involved is probably no simpler than with the P1 method, (iii) that the two methods converge to different parameter values and (iv) that the result obtained by the C & D procedure is probably not significantly different from that obtained by doing the constraining averages on the result of an unconstrained refinement.

The purpose of this note is to clarify the question behind criticism (iii). While agreeing with P2 regarding the result, we point out that Pawley's argument is incorrect. Pawley confuses a particular *method* of finding a minimum of the least-squares residual with the properties of the minimum itself.

While the C & D procedure is, of course, designed for non-linear problems and Pawley's 'disproof' of it had non-linear problems in mind, both the method and the disproof make no assumptions about the necessity of non-linearity. Thus, if both the method and its disproof are invalid for linear problems, they will be generally invalid for non-linear problems.

Many texts on least squares (*e.g.* Hamilton, 1964) have a section on linear least squares with linear constraints, with equations explicitly writing the final constrained parameters in terms of the final unconstrained parameters, the constraint matrix and vector, and the covariance matrix of the unconstrained parameters. The resulting constrained parameters are different from those which would be obtained from the application of C & D equation (4). This is most easily seen from the geometrical formulation of least squares (Price, 1978). In this approach least-squares estimation consists of projecting the *observed vector*, $\mathbf{y}^{\rm obs}$, a vector in n-dimensional *measurement space*, into the *calculated vector*, $\hat{\mathbf{y}}^{\rm calc}$, a vector in m-dimensional *fit-space*, this being a subspace of *measurement space*. A set of l independent linear constraints results in the *constrained fit-space* being an $(m-l)$ dimensional subspace of the unconstrained fit-space. The linearity of the problem results in these fit-spaces being vector spaces. The least squares with constraints problem then becomes finding $\hat{\mathbf{y}}_c^{\rm calc}$, the projection of $\mathbf{y}^{\rm obs}$ into the constrained fit-space. Since all these spaces are vector spaces this problem is equivalent to first projecting $\mathbf{y}^{\rm obs}$ into the unconstrained fit-space and then projecting this projection into the constrained fit-space. All calculated vectors $\mathbf{y}^{\rm calc}$ and $\mathbf{y}_c^{\rm calc}$ are related to parameter values, $\boldsymbol{\theta}$ and $\boldsymbol{\theta}_c$ by the design matrices, $\mathbf{T}$ and $\mathbf{T}_c$

$$\mathbf{y}^{\rm calc} = \mathbf{T}\boldsymbol{\theta} \tag{1}$$

$$\mathbf{y}_c^{\rm calc} = \mathbf{T}_c\boldsymbol{\theta}_c. \tag{2}$$

Thus, the second projection can just as well be done in *parameter space* as in fit-space. First, however, we must find the correct *least-squares metric tensor* for parameter space. In measurement or fit-space this metric tensor is the weight matrix $\mathbf{W} = \mathbf{V}^{-1}$ with $\mathbf{V}$ the variance matrix of the observations. As shown by the following arguments, in parameter space it is $\mathbf{V}_{\boldsymbol{\theta}}^{-1}$, the inverse of the variance matrix of the parameters, which is known to be (Hamilton, 1964)

$$\mathbf{V}_{\boldsymbol{\theta}}^{-1} = \mathbf{T}^t\mathbf{W}\mathbf{T}, \tag{3}$$

where the superscript t refers to the transpose of a matrix.

The projection in fit-space is achieved by minimizing

$$S = \|\hat{\mathbf{y}}^{\rm calc} - \hat{\mathbf{y}}_c^{\rm calc}\|_y^2 = (\hat{\mathbf{y}}^{\rm calc} - \hat{\mathbf{y}}_c^{\rm calc})^t\mathbf{W}(\hat{\mathbf{y}}^{\rm calc} - \hat{\mathbf{y}}_c^{\rm calc}) \tag{4}$$

with respect to $\hat{\mathbf{y}}_c^{\rm calc}$. Since (1) applies to all vectors in the unconstrained fit-space we have $\hat{\mathbf{y}}^{\rm calc} = \mathbf{T}\hat{\boldsymbol{\theta}}$ and $\hat{\mathbf{y}}_c^{\rm calc} = \mathbf{T}\hat{\boldsymbol{\theta}}_c$. Substitution in (4) gives

$$S = (\hat{\boldsymbol{\theta}} - \hat{\boldsymbol{\theta}}_c)^t(\mathbf{T}^t\mathbf{W}\mathbf{T})(\hat{\boldsymbol{\theta}} - \hat{\boldsymbol{\theta}}_c)$$

which by (3) is

$$S = (\hat{\boldsymbol{\theta}} - \hat{\boldsymbol{\theta}}_c)^t\mathbf{V}_{\boldsymbol{\theta}}^{-1}(\hat{\boldsymbol{\theta}}_c) \equiv \|\hat{\boldsymbol{\theta}} - \hat{\boldsymbol{\theta}}_c\|_{\boldsymbol{\theta}}^2. \tag{5}$$

In these expressions $\|\mathbf{x}\|_y$ (or $\|\mathbf{x}\|_{\boldsymbol{\theta}}$) means the length of $\mathbf{x}$ as measured by the metric tensor $\mathbf{W}$ (or $\mathbf{V}_{\boldsymbol{\theta}}^{-1}$) in fit-space (or parameter space). Thus minimization of (4) is equivalent to minimization of (5). Expression (5) is a *weighted* version of C & D equation (4).

For linear least squares and linear constraints we have thus shown that the C & D procedure [minimization of the

* Present address.

unweighted residual by their equation (4)] is incorrect and that, while the constrained parameters can be obtained from the unconstrained parameters, this requires the minimization of the weighted residual (5) or equivalently, by the application of the usual equations (Hamilton, 1964).

Since there is a procedure for finding the constrained parameters from the unconstrained parameters we have also shown, by counter-example, that Pawley's disproof is incorrect. His argument rests on the lack of an inverse to his equation (1):

$$P_i = f_i(\{p_j\}) .$$

Here the $\{P_i\}$ are the 'usual structure parameters' and the $\{p_j\}$ form 'the set of parameters in the constrained configuration'. There are two interpretations we can give this equation: firstly, that any constrained configuration (specified by the parameters $\{p_j\}$) can be described in terms of the original parameters $\{P_i\}$; and secondly, that for any given set of data, if a constrained refinement results in parameters $\{p_j\}$, then an unconstrained refinement will result in parameters $\{P_i\}$ as given by the function f_i. The first interpretation is a true statement, but in fact there is an inverse to the equation since it is generally 1–1. The inverse is defined only on a subspace (the range of the function), of parameter space. It is apparent from Pawley's arguments subsequent to his equation (1), however, that he intends the second interpretation. Now in this case the equation is patently incorrect, as there does not exist such a function f, even in the linear least-squares, linear-constraints case. There are many different sets of data which will result in the same set of constrained parameters but different values for the unconstrained parameters. This is because of the dimensionality of the two parameter spaces. However, as we have shown above (and as shown by Hamilton, 1964) the *inverse* to the equation does exist for the case of linear least squares with linear constraints.

When the function to be fitted is non-linear in the parameters we cannot rule out the possibility of an inverse to Pawley's equation (1) from dimensionality arguments. However, since fit-space is no longer flat, we cannot say that the projection of **y** into constrained fit-space is necessarily the same as the result obtained by first projecting **y** into the unconstrained fit-space and then projecting this projection into the constrained fit-space. In addition we cannot equate expressions (4) and (5), *i.e.* we cannot even do the latter projection in parameter space. Thus the C & D method [with their equation (4) replaced with (5) above] is invalid for non-linear problems. (The P1 method does not, of course, suffer from these restrictions.)

Aside from these rigorous objections we suspect that the C & D method is likely to be slowly convergent. Algorithms for non-linear least-squares generally only become rapidly convergent when the parameters approach the final values. The C & D method results in the starting parameters for every cycle being held some distance away from the final values. It is not obvious that true convergence will ever be reached.

With reference to P2, we would also like to point out that the many different methods of minimizing a sum of squares generally lead to different parameter shifts even when converging to the same minimum. The argument that two procedures with differing parameter shifts must converge to different minima is incorrect.

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The effect of bonding electrons on molecular dimensions as determined by X-rays.*

By L. M. PANT, *National Chemical Laboratory, Poona* 411008, *India*

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The central-bond shortening in disubstituted benzenes having an electron-withdrawing group and an electron-releasing group in *para* positions is well known. However, even in several disubstituted benzenes having electron-withdrawing groups in both *para* positions, X-ray analysis shows a central-bond shortening. In monosubstituted benzenes, the middle bonds and the bonds farthest from the substituent show bond shortenings which cannot be accounted for by librational motion alone. It is pointed out that these apparent shortenings are caused by the asymmetry of the charge distribution around the C atoms bonded to the H atoms. This charge asymmetry is to a large extent an artifact of the refinement procedure.

The shortening of the central bonds in disubstituted benzenes having an electron-withdrawing group and an electron-releasing group in *para* positions is well known. However, the central-bond shortening has also been observed, although generally to a lesser extent, in several disubstituted benzenes having electron-withdrawing groups in both *para* positions, *e.g.* in *p*-nitroacetophenone (Kim, Boyko & Carpenter, 1973), *α-p*-nitrobenzaldoxime (Bachechi & Zambonelli, 1973), *anti*-4-nitro-*N*-methylbenzaldoxime (Bachechi & Zambonelli, 1975) and in several other structures; these structures were all determined at room temperature by X-

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