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Constraining a recent paper.

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A recent paper concerning the application of constraints in crystallographic refinements is criticized. It is suggested that the method of applying constraints put forward by Chesick & Davidon [*Acta Cryst.* (1975), A31, 586–591] is of very limited validity and has all the economic disadvantages of an unconstrained refinement.

It is good to see a growing interest in the use of constraint procedures in structure refinement. Any paper which makes the method more readily understood or more readily programmed should be welcomed.

A method of applying constraints alternative to the strict constraints described by Pawley (1972) has been recently advocated by Chesick & Davidon (1975) (C & D). They suggest that each cycle of least-squares refinement should be unconstrained and the constraint should be applied to the parameter shifts. This procedure loses the economic advantage of a much reduced cycle time and the ability to make use of computers with restricted storage capacity, contrary to the authors' claims. A further claim is that the method is easier to program as the researcher does not have to write down and program the extra differentials required. Indeed this is a considerable part of the effort in applying constraints, but this has to be compared with the effort of implementing the extra task of their equation (4) which determines the constraints on the parameter shifts. It should be noticed that equation (4) involves position parameters and therefore positional constraints only, so that when further constraints are to be used, such as on temperature factors or site occupancies, the equation becomes invalid. Each parameter needs a metric for such an equation; only when all parameters have the same metric can equation (4) be used. It would be easy to argue that implementation of equation (4) is no simpler than programming differentials whereupon the C & D procedure loses any of the advantages advocated for it.

Next we must investigate whether the result of the C & D procedure has any of the true advantages of the constraint method. Strict constraint demands a certain relation between the usual structure parameters $\{P_l\}$ which thereby reduces the dimension of parameter space. Let us call the set of parameters in the constrained configuration $\{p_j\}$. The two parameter sets are related by a transformation,

$$P_l = f_l(\{p_j\}), \tag{1}$$

for which there is no inverse because the parameter space dimension is being altered. These equations contain all the information which is to be included in the refinement plus any hypothesis to be tested. If constraints are being used to test hypotheses then both the constrained and the unconstrained result are required for the appropriate statistical test.

A least-squares matrix and vector are set up with components

$$m_{ij} = \sum_{\mathbf{h}} w_{\mathbf{h}} \frac{\partial F_{\mathbf{h}}}{\partial p_i} \frac{\partial F_{\mathbf{h}}}{\partial p_j} \quad v_j = \sum_{\mathbf{h}} w_{\mathbf{h}} \Delta F_{\mathbf{h}} \frac{\partial F_{\mathbf{h}}}{\partial p_j} \tag{2}$$

where $w_{\mathbf{h}}$ is the weight for the reflexion with indices $\mathbf{h}$, $\Delta F_{\mathbf{h}} = F_{\mathbf{h}}^{\rm obs} - F_{\mathbf{h}}^{\rm calc}$, $F_{\mathbf{h}}^{\rm calc}$ is written $F_{\mathbf{h}}$ and the differentials are found using

$$\frac{\partial F_{\mathbf{h}}}{\partial p_j} = \sum_l \frac{\partial F_{\mathbf{h}}}{\partial P_l} f_{lj}, \; f_{lj} = \frac{\partial P_l}{\partial p_j}. \tag{3}$$

The unconstrained refinement uses

$$M_{lj} = \sum_{\mathbf{h}} w_{\mathbf{h}} \frac{\partial F_{\mathbf{h}}}{\partial P_l} \frac{\partial F_{\mathbf{h}}}{\partial P_j}, \; V_j = \sum_{\mathbf{h}} w_{\mathbf{h}} \Delta F_{\mathbf{h}} \frac{\partial F_{\mathbf{h}}}{\partial P_j}, \tag{4}$$

from which we see

$$m_{lj} = \sum_{kl} f_{kl} f_{lj} M_{kl}, \; v_j = \sum_k f_{kj} V_k. \tag{5}$$

The shift to be applied each cycle is $\Delta\mathbf{p} = \mathbf{m}^{-1}\mathbf{v}$ whereas the C & D procedure uses a constrained version of $\Delta\mathbf{P} = \mathbf{M}^{-1}\mathbf{V}$. The first question to be answered is: do the two procedures give the same shift $\Delta\mathbf{p}$? The negative answer is due ultimately to the fact that (1) has no inverse. This is equivalent to saying that the constrained version of $\Delta\mathbf{P}$, let us say constr ($\Delta\mathbf{P}$), is not well defined. If the two methods were identical, then

$$\Delta\mathbf{p} = (\tilde{\mathbf{f}}\mathbf{M}\mathbf{f})^{-1}\tilde{\mathbf{f}}\mathbf{V} = \text{constr}\,(\mathbf{M}^{-1}\mathbf{V}), \tag{6}$$

where the components of $\mathbf{f}$ are given in (3). The matrix $\mathbf{f}$ has no inverse, so we cannot write

$$(\tilde{\mathbf{f}}\mathbf{M}\mathbf{f})^{-1}\tilde{\mathbf{f}}\mathbf{V} = \mathbf{f}^{-1}\mathbf{M}^{-1}\tilde{\mathbf{f}}^{-1}\tilde{\mathbf{f}}\mathbf{V} = \mathbf{f}^{-1}\mathbf{M}^{-1}\mathbf{V} \tag{7}$$

which would give us the required function

$$\text{constr}\,(\mathbf{M}^{-1}\mathbf{V}).$$

The procedures must consequently be different, so the validity of the C & D procedure rests on this difference. As the two procedures cannot lead to exactly the same shifts in $\{p_l\}$ then they will converge to different minima. This is evident if we consider a cycle starting at the final minimum for one of the procedures. The suggested shift for this procedure must be everywhere zero as the starting point is a minimum. Now if the same starting point is used for the other procedure, the shifts, being different from those of the first procedure, must be non-zero. The question therefore arises: by how much do the shifts differ between the two procedures?

A related question which is more easily answered is: does the C & D procedure produce a result significantly different from that obtained by doing the constraining averages on the result of an unconstrained refinement? If the answer is 'no', then the C & D procedure has no advantage over unconstrained refinement. The argument presented in what follows suggests the answer, 'probably not'. Let us take as a starting point for the C & D procedure the minimum found by applying strict constraints. In one cycle the computer will calculate a shift towards the unconstrained result, and if the success factor $S = 100\%$ then the final result of the C & D procedure will be simply

equivalent to unconstrained refinement followed by judicious averaging – and we reject this as being of no advantage. Thus the efficacy of the C & D procedure rests on the difficulty of going from the constrained to the unconstrained result in one cycle; the more difficult this is the nearer the C & D procedure is to strict constraints. A rough guess for a value of S would be in excess of 70%: the one cycle mentioned finds more than 70% of the total shift. With a value as high as this the usefulness of the C & D procedure is in grave doubt.

Table 1. *R_w for pyrazole*

		R_w
Constraint (*a*)*	best value	254
Constraint (*b*)*	after 1 cycle	243
	after 2 cycles	241
Unconstrained	after 1 cycle	229
	after 2 cycles	228

* See Pawley (1972).

In all the cases in my experience this figure has been in excess of 70%. An example, the first to hand in my files, is given by pyrazole. The residual $R_w=\sum_{\mathbf{h}} w_{\mathbf{h}}(\Delta F_{\mathbf{h}})^2$ varied as in Table 1 where R_w improved by $S=90\%$ in the first cycle after removing the constraints.

If their procedure is to be established as worthwhile, Chesick & Davidon should perform detailed calculations to compare the results of their method with the strictly constrained and the unconstrained results.

References

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A solution for the best rotation to relate two sets of vectors.

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A simple procedure is derived which determines a best rotation of a given vector set into a second vector set by minimizing the weighted sum of squared deviations. The method is generalized for any given metric constraint on the transformation.

In various crystallographic situations the problem arises of finding a best rotation to fit a given atomic arrangement to approximately measured coordinates. Examples have been given by McLachlan (1972) and Diamond (1976). Diamond determines the best unconstrained transformation between the two sets of coordinates and factorizes it into a symmetric and an orthogonal matrix. McLachlan finds a best rotation between the two sets of coordinates by an iterative process. The analysis below shows that a direct solution is also possible, despite the non-linear character of the problem.

Let $\mathbf{x}_n$ and $\mathbf{y}_n$ $(n=1,2,\ldots,N)$ be two given vector sets and w_n the weight corresponding to each pair $\mathbf{x}_n,\mathbf{y}_n$. The problem is then to find an orthogonal matrix $\mathsf{U}=(u_{ij})$ which minimizes the function

$$E=\tfrac{1}{2}\sum_n w_n(\mathsf{U}\mathbf{x}_n-\mathbf{y}_n)^2 \qquad (1)$$

subject to the constraints

$$\sum_k u_{ki}u_{kj}-\delta_{ij}=0 \qquad (2)$$

where the δ_{ij} are the elements of the unit matrix. A translation, if admitted, can always be removed from the problem by shifting the centroids of the vector sets to the origin.

Introducing a symmetric matrix $\mathsf{L}=(l_{ij})$ of Lagrange multipliers an auxiliary function (see, for example, Brand, 1958)

$$F=\tfrac{1}{2}\sum_{i,j} l_{ij}\Big(\sum_k u_{ki}u_{kj}-\delta_{ij}\Big) \qquad (3)$$

is constructed and added to E to form the Lagrangian function

$$G=E+F. \qquad (4)$$

Since for each different condition (2) an independent number l_{ij} is available, the constrained minimum of E is now included among the free minima of G. A free minimum of G can only occur where

$$\frac{\partial G}{\partial u_{ij}}=\sum_k u_{ik}\Big(\sum_n w_n x_{nk}x_{nj}+l_{kj}\Big)-\sum_n w_n y_{ni}x_{nj}=0 \qquad (5)$$

and

$$\frac{\partial^2 G}{\partial u_{mk}\partial u_{ij}}=\delta_{mi}\Big(\sum_n w_n x_{nk}x_{nj}+l_{kj}\Big) \qquad (6)$$

are the elements of a positive definite matrix. x_{nk} and y_{nk} are the kth components of the vectors $\mathbf{x}_n$ and $\mathbf{y}_n$.

Let

$$r_{ij}=\sum_n w_n y_{ni}x_{nj} \qquad (7)$$

and

$$s_{ij}=\sum_n w_n x_{ni}x_{nj} \qquad (8)$$

be the elements of a matrix $\mathsf{R}=(r_{ij})$ and a symmetric matrix $\mathsf{S}=(s_{ij})$, respectively. For $i=m=1$ from equation (6), a minimum of the Lagrangian function G requires that $\mathsf{S}+\mathsf{L}$ is positive definite, and – by rewriting equation (5) – that

$$\mathsf{U}\,.\,(\mathsf{S}+\mathsf{L})=\mathsf{R}. \qquad (9)$$