

## LETTERS TO THE EDITOR

Contributions of a scientific nature intended for this section should be submitted to the Editor or any of the Co-Editors of *Acta Crystallographica* or *Journal of Applied Crystallography*.

*J. Appl. Cryst.* (1993). **26**, 142–143

## Hazards of oblique coordinate systems: a reminder

BY KENNETH W. MUIR AND PAUL R. MALLINSON

*Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland*

(Received 28 October 1992; accepted 4 November 1992)

**Abstract.** A reminder is given that ignoring correlations between fractional coordinates in an oblique coordinate system can lead to inaccuracies in the estimation of standard deviations of bond lengths and other derived quantities. Methods based on a paper by Templeton [*Acta Cryst.* (1959), **12**, 771–773] are suggested to make approximate allowance for the effect when the parameter variance matrix is unavailable.

Accounts of the derivation from the results of a diffraction analysis of the standard deviations of bond lengths and other quantities of scientific interest are widely available (see, for example, Dunitz, 1979). To recapitulate some well known results: if  $l = f(\mathbf{p})$  is a scalar function of  $n$  parameters,  $p_i$ , for which the corresponding standard deviations are  $\sigma_i$ , then  $\sigma(l)$ , the standard deviation of  $l$ , is given by

$$\sigma^2(l) = \sum_{i=1}^n \sum_{j=1}^n (\partial f / \partial p_i) (\partial f / \partial p_j) \sigma_i \sigma_j r_{ij} = \mathbf{d}^T \boldsymbol{\lambda} \mathbf{d}, \quad (1)$$

where  $r_{ij}$  is the correlation coefficient between parameters  $p_i$  and  $p_j$ ,  $\boldsymbol{\lambda}$  is the variance matrix with  $\lambda_{ij} = \sigma_i \sigma_j r_{ij}$  and the elements of the  $n$ -fold vector  $\mathbf{d}$  are the partial derivatives  $(\partial f / \partial p_i)$ . If  $l$  is a bond length, the parameters of interest consist of up to six cell dimensions and six fractional coordinates. Full-matrix least-squares refinement of the fractional coordinates automatically generates all the elements of  $\boldsymbol{\lambda}$  which involve coordinate variances and covariances (indeed, this is one reason for its widespread use); an independent least-squares process is usually employed to obtain the unit-cell dimensions and their variances and covariances. So far as we are aware, *ORFFE* (Busing & Levy, 1961) was the first crystallographic program which applied (1) without approximations. Modern crystallographic program systems should be expected to apply (1) rigorously and some do. However, the covariances between the cell parameters are often ignored in practice; indeed, these quantities are often not readily ac-

cessible with commercial diffractometer software. Sometimes, the contributions from the cell-parameter variances are also disregarded.

A different problem is posed if  $l$  and  $\sigma(l)$  have to be calculated only from the  $p_i$  and  $\sigma_i$  because information about the off-diagonal elements of  $\boldsymbol{\lambda}$  is unavailable. This will usually be the case if the data for the calculation are taken from a published structure. While it is desirable that such a calculation should give an answer as close as possible to that obtained by rigorous application of (1), it is also inevitable that it will involve some approximation. It often seems to be the case that all correlation effects between the atomic parameters are ignored in such circumstances. We wish to remind users and writers of crystallographic programs that failure to allow for correlations between fractional coordinates in oblique unit cells may lead to significant error in  $\sigma(l)$  and also to point out that approximate correction for such correlations is straightforward.

In any crystal structure with an oblique coordinate system, the fractional coordinates of an atom,  $x_1, x_2, x_3$ , are not statistically independent. In an elegant analysis of the problem, Templeton (1959) has shown that, provided the positional error of the atom is isotropic, the correlation coefficients  $r_{23}, r_{13}$  and  $r_{12}$  can be approximated as  $\cos \alpha^*$ ,  $\cos \beta^*$  and  $\cos \gamma^*$ . This approximation is used in our local geometry program *GEOM* (Mallinson & Muir, 1985) when the full variance matrix is unavailable.

As an illustration of the circumstances in which it is desirable to allow for correlations between different fractional coordinates of the same atom, we have recently examined a triclinic structure with  $a = 11.470$  (2),  $b = 12.645$  (3),  $c = 13.027$  (3) Å,  $\alpha = 118.18$  (1),  $\beta = 90.26$  (2),  $\gamma = 92.37$  (2)°. The C and H atoms are chemically bonded with parameters:

	$x$	$y$	$z$
C	0.0143 (3)	0.1370 (3)	0.9617 (3)
H	-0.0196 (30)	0.1064 (30)	1.0051 (30)

The C–H bond length is 0.907 Å and its standard deviation, calculated from the full variance matrix, is 0.034 Å.

Recalculation of this standard deviation from the data given above yields 0.034 Å provided Templeton's approximation for coordinate correlation is applied. If no allowance is made for correlation a standard deviation of 0.045 Å is obtained. In this case, the standard deviations of the cell parameters make only a negligible contribution to the bond-length standard deviation and both atoms have nearly isotropic positional errors; the large difference between  $\alpha^* = 61.78$  and  $90^\circ$  causes most of the trouble. Although in this example the bond-length standard deviation is overestimated by more than 30%, Templeton (1959) has shown that, in general, over- or underestimation of the derived standard deviation may occur when coordinate correlation is disregarded.

For programs which apply (1) in full, the remedy is obvious but laborious: the off-diagonal elements of  $\lambda$  which refer to correlations between coordinates of the same atom should be set to  $\sigma_i \sigma_j r_{ij}$  where  $r_{ij}$  is the cosine of the appropriate reciprocal-cell angle, as suggested by Templeton (1959). However, many programs designed primarily to deal with data from published structure analyses use only the diagonal elements of  $\lambda$ . To modify such programs, two approaches are possible, depending on the program design.

(1) Some programmers prefer to calculate derived quantities and their errors directly from the metric tensor,  $g$ , and the fractional coordinates since the derivative expressions required in the estimation of  $\sigma(l)$  are easily obtained. *PARST* is a typical and widely used example of this approach and has the advantage that its author has given a clear and detailed description of its algorithms (Nardelli, 1983). For an interatomic distance defined by the vector of differences in fractional coordinates  $\mathbf{x} = \mathbf{y} - \mathbf{z}$  of length  $l = (\mathbf{x}^T \mathbf{g} \mathbf{x})^{1/2}$ , the  $3 \times 3$  variance matrix for  $x_1, x_2, x_3$  is constructed by adding the variance matrices for the two sets of atomic fractional coordinates:

$$\lambda_{ij} = [\sigma(y_i)\sigma(y_j) + \sigma(z_i)\sigma(z_j)]r_{ij} \quad (2)$$

and the required partial-derivative vector  $\mathbf{d} = l^{-1} \mathbf{g} \mathbf{x}$ . The correction to the bond-length variance [equation (8) of Nardelli (1983)] is then

$$2(d_1 d_2 \lambda_{12} + d_1 d_3 \lambda_{13} + d_2 d_3 \lambda_{23}) \quad (3)$$

(2) For calculations of the type discussed there is something to be said for the alternative approach of transforming into an orthogonal coordinate system. Correlations between different coordinates of the same atom need be taken into account only in the transformation of the positional errors from crystallographic to orthogonal axes. Correlations between orthogonal coordinates of the same atom can be ignored in subsequent calculations of derived quantities and their standard deviations. This greatly simplifies the expressions for standard deviations of bond angles and torsion angles (Dunitz, 1979). It is, however, difficult to allow exactly for the variances of the cell parameters in such calculations which are therefore most useful when, as is often the case, the contributions of the cell-parameter errors to the variances of derived quantities is negligible. Nardelli (1983) suggests an approximation to allow for this source of error.

Dunitz (1979) gives a lucid and detailed discussion of the transformation from crystallographic to orthogonal axes. His equation (5.30),  $\mathbf{X} = \beta^T \mathbf{x}$ , allows the orthogonal coordinates,  $\mathbf{X}$ , to be calculated from the fractional coordinates  $\mathbf{x}$ . The standard deviations of the orthogonal coordinates can be obtained as the square roots of the diagonal elements of  $\mathbf{S}$ , where  $\mathbf{S} = \beta^T \lambda \beta$ . Here the symmetrical  $3 \times 3$  variance matrix for the fractional coordinates of each atom,  $\lambda$ , is constructed from  $\lambda_{ii} = \sigma^2(x_i)$  and  $\lambda_{ij} = \sigma(x_i)\sigma(x_j)r_{ij}$  where the correlation coefficients,  $r_{ij}$ , are again the cosines of the angles of the reciprocal cell, as suggested by Templeton (1959).

More generally, we wish to suggest that authors of structural papers should routinely consider whether any approximations they have made could adversely affect the values of the standard deviations they publish. This check is especially important if the calculations are made without access to the parameter-variance matrix.

## References

- BUSING, W. R. & LEVY, H. A. (1961) *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, pp. 140–145. Oxford: Pergamon.
- DUNITZ, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, pp. 225–265. Cornell Univ. Press.
- MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–97.
- TEMPLETON, D. H. (1959). *Acta Cryst.* **12**, 771–773.