Results and discussion

The performance of the new translation functions was tested on various known structures. Some examples are given in Table 1.

The results show that the new functions Q'_s are less powerful than Q_s. In all given examples the highest peak in Q_s gives the correct position of the fragment, whereas for some of the examples peak number 2 or 3 in Q'_s gives the correct position. The new functions Q'_s, however, are very useful if Q_s leads to an ambiguous result. An example is given in Table 2, in which the second peak in Q_s is ruled out because this peak does not occur in Q'_s.

An observation, made by Doesburg & Beurskens (1983), is also valid for Q'_s: one-dimensional searches (for mirror or glide planes) are slightly more reliable than two-dimensional searches (symmetry axis) and far more so than a search for a center of symmetry.

The new translation functions are incorporated in the *DIRDIF* program package (Beurskens *et al.*, 1984), with negligeable increase in core and CPU requirements.

References

ARGOS, P. & ROSSMANN, M. G. (1980). *Theory and Practice of Direct Methods in Crystallography*, edited by M. F. C. LADD & R. A. PALMER, p. 382. New York: Plenum Press.

BEURSKENS, P. T., BEURSKENS, G. & VAN DEN HARK, TH. E. M. (1976). *Cryst. Struct. Commun.* **5**, 241–246.

BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G., PARTHASARATHI, V., BRUINS SLOTT, H. J. & HALTIWANGER, R. C. (1984). Program system *DIRDIF*. Tech. Rep. 1984/1. Crystallography Laboratory, Univ. of Nijmegen.

BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G., GOULD, R. O. & PARTHASARATHI, V. (1982). In *Conformation in Biology*, edited by R. SRINIVASAN & R. H. SARMA, pp. 389–406. New York: Adenine Press.

DOESBURG, H. M. & BEURSKENS, P. T. (1983). *Acta Cryst.* A**39**, 368–376.

DOESBURG, H. M., NOORDIK, J. H. & BEURSKINS, P. T. (1982). *Z. Kristallogr.* **161**, 279–288.

NOORDIK, J. H., BEURSKENS, P. T., OTENHEIJM, H. C. J., HERSCHEID, J. D. M. & TIJHUIS, M. W. (1978). *Cryst. Struct. Commun.* **7**, 669–677.

VELDEN, G. P. M. VAN DER & NOORDIK, J. H. (1980). *Cryst. Mol. Struct.* **10**, 83–92.

Acta Cryst. (1984). A**40**, 703–704

Orientation Matrix Refinement During Four-Circle Diffractometer Data Collection

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Abstract

Crystal movement, detected during data collection, requires the orientation matrix to be modified, so that reflection positions can be correctly predicted. If the unit cell is assumed to remain unchanged, the necessary modification is a small rotation of the matrix, *viz* premultiplication by an orthogonal matrix. This rotation is easily calculated from the observed positions of two or more centred reflections, by the application of quaternion algebra.

Introduction

Crystal movement (slippage) during single-crystal intensity data collection is a recognized problem in structure determination. It is usually monitored by the periodic measurement of a number of standard reflections. Changes in the intensities of these may indicate crystal movement, various forms of instrument instability or radiation damage to the crystal. If profile analysis techniques are employed in the data collection, changes in profile shape or position of the reflection peaks may also suggest movement.

Most commercial diffractometer control programs include a routine for re-establishing the orientation matrix and then continuing with the data collection, possibly repeating the last batch of reflections. This routine may be entered when standard reflection measurements show a significant change in orientation or at regular intervals as a precaution. The normal method is that described by Vandlen & Tulinsky (1971). Reflections contained in a list are centred and the orientation matrix is refined from the positions found. This refinement is generally an unconstrained refinement of the nine elements of the matrix (Tichý, 1970; Shoemaker & Bassi, 1970), which effectively changes the unit-cell parameters too.

The major drawback of this method is the time consumed by the centring routine, which can be particularly slow on machines not equipped with special hardware such as half-shutters (beam splitters). The

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routine also involves a lot of driving and if the movement continues during this process the exercise may be in vain.

An alternative is to assume that the unit cell remains constant and only the crystal orientation has changed. In this case, the nine parameters to be determined are effectively reduced to three, describing a small rotation of the orientation matrix. Fewer reflections are needed in order to update the matrix by this method and data collection can be resumed with minimum time loss.

Method

Suppose we have a list of N reflections with indices given by the vectors $\mathbf{h}_i$ ($i = 1$ to N). On the basis of the current orientation matrix **A**, we calculate reciprocal-space coordinates on the φ-axis system, $\mathbf{x}_i = \mathbf{A}\mathbf{h}_i$: see Clegg (1984) for the notation and axis definitions. The reflections are centred, giving corresponding observed coordinates $\mathbf{y}_i$. In order to update the orientation matrix we must now apply an orthogonal rotation matrix **R**, which gives the best fit of the vectors **x** to the observations **y**: $\mathbf{A}' = \mathbf{R}\mathbf{A}$.

The problem of finding the best rotation to relate two sets of vectors has been addressed with particular application to the comparison of two molecular structures and various solutions have been proposed (Kabsch, 1976, 1978; McLachlan, 1982). The application of quaternion algebra gives a rapid linear solution. A description of some of the properties of quaternions and their application for comparing two molecular structures are given by Mackay (1984). The main difference in the application here is that both the observations $\mathbf{y}_i$ (centred reflections) and the corresponding calculated vectors $\mathbf{x}_i$ are already based on the same reciprocal-space axes, so no transformation of coordinates to new centre-of-gravity origins is made.

Using the notation of Mackay (1984), we wish to find the rotation angle θ and the direction cosines l, m, n of the rotation axis. Writing t for $\tan(\theta/2)$, x_a, x_b, x_c and y_a, y_b, y_c for the **x** and **y** coordinates of each calculated and observed reciprocal-lattice point, respectively, we obtain three simultaneous linear equations for each reflection, $3N$ in all:

$$\begin{aligned} mt(y_c + x_c) \quad & -nt(y_b + x_b) = (y_a - x_a) \\ -lt(y_c + x_c) \quad & +nt(y_a + x_a) = (y_b - x_b) \\ lt(y_b + x_b) \quad & -mt(y_a + x_a) \quad = (y_c - x_c). \end{aligned}$$

The $3N$ equations are solved by the usual least-squares method, to give values of lt, mt and nt, from which θ, l, m and n are calculated ($l^2 + m^2 + n^2 = 1$). It makes little difference in practice whether the refinement is carried out unweighted with the **x** and **y** vectors unmodified or whether the vectors are normalized to unity and their lengths used as weights in the refinement. A positive value of θ is always obtained from the square root of $\tan^2(\theta/2)$, but no ambiguity is involved, because the signs of l, m and n automatically define the correct sense of the rotation axis.

From θ, l, m and n, the required rotation matrix **R** is given by equation (1) of Mackay (1984):

$$\mathbf{R} = \begin{pmatrix} l^2d + c & mld + ns & nld - ms \\ lmd - ns & m^2d + c & nmd + ls \\ lnd + ms & mnd - ls & n^2d + c \end{pmatrix},$$

where $s = \sin\theta$, $c = \cos\theta$ and $d = 1 - \cos\theta$. The orientation matrix **A** is updated ($\mathbf{A}' = \mathbf{R}\mathbf{A}$) and data collection continues.

This method requires a minimum of two reflections, but there is no maximum limit to the number. For convenience, the same reflections may be used as standard reflections for monitoring the data collection and as reflections for updating the orientation matrix.

The same method may be used for establishing a preliminary orientation matrix from a known unit cell (possibly from photographic investigation) and as few as two indexed and centred reflections: the rotation to be determined need not be small, and the initial **A** matrix can be set up from the cell parameters for any arbitrary orientation. With two reflections, this is equivalent to the method of Busing & Levy (1976) (where the orientation matrix is called **UB**), except that the two reflections are assigned equal weight, rather than arbitrarily ascribing all the measurement error effectively to one reflection.

It should be stressed that any automatic orientation-checking routine assumes that the crystal remains reasonably centred in the X-ray beam. If this is not the case, subsequent measurements are invalid. The method described here additionally assumes that the unit cell remains unchanged if the crystal slips. It is a development of the method used in our diffractometer control program system for a number of years (Clegg, 1981) and is incorporated in the form described here in the program version currently being developed.

References

BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457–464.

CLEGG, W. (1981). *Acta Cryst.* A**37**, C313–C314.

CLEGG, W. (1984). *Methods and Applications in Crystallographic Computing*, edited by T. ASHIDA & S. HALL. Oxford Univ. Press. In the press.

KABSCH, W. (1976). *Acta Cryst.* A**32**, 922–923.

KABSCH, W. (1978). *Acta Cryst.* A**34**, 827–828.

MACKAY, A. L. (1984). *Acta Cryst.* A**40**, 165–166.

MCLACHLAN, A. D. (1982). *Acta Cryst.* A**38**, 871–873.

SHOEMAKER, D. P. & BASSI, G. (1970). *Acta Cryst.* A**26**, 97–101.

TICHÝ, K. (1970). *Acta Cryst.* A**26**, 295–296.

VANDLEN, R. L. & TULINSKY, A. (1971). *Acta Cryst.* B**27**, 437–442.