Acta Cryst. (1974). A**30**, 848

On the standard deviation of dihedral angle.

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(*Received* 26 *March* 1974; *accepted* 11 *June* 1974)

Expressions for derivatives of a dihedral angle with respect to positional parameters of the atoms involved are presented and their use with the propagation-of-error formula, in evaluating the standard deviation of a dihedral angle, is indicated. The expressions derived are valid in oblique and orthogonal frames of reference. The approach outlined provides a greater flexibility in accounting for atomic positional variances and covariances than other treatments of the dihedral angle so far proposed. Inclusion of covariances of symmetry-related atoms in the equations presented is indicated.

Several expressions for the variance of a dihedral angle have been published (P. J. Huber in Huber-Buser & Dunitz, 1961; Stanford & Waser, 1972; Waser, 1973). These expressions are given in terms of the bond distances and angles defining the dihedral angle and in one case an equation utilizing components of the angle-defining vectors has also been presented (Stanford & Waser, 1972). With the exception of the relevant expression in Waser's (1973) article the above equations are based on the assumption of isotropic variances of atomic coordinates. On the other hand, Waser's equation [equation (49); Waser, 1973] contains in a symbolic form functions of full covariance matrices of the distances and angles involved and may be expressed in an oblique system of coordinates. It seems, however, that in practice intermediate approximations may be preferable to the assumption of isotropic variances or to the use of a full covariance matrix. Thus, it may be desired to employ available standard deviations of atomic coordinates, when they are evidently anisotropic, or to take into account some of the covariances, when correlation coefficients are large, in such a calculation. Moreover, construction of special Cartesian systems for this calculation (*e.g.* Stanford & Waser, 1972) either necessitates a transformation of the covariances to such a system or makes the assumption of isotropic variances imperative. In order to avoid these limitations, derivatives of the dihedral angle with respect to the relevant fractional atomic coordinates are presented and their use with the propagation-of-error formula is indicated.

It is also attempted to achieve a simple presentation of the results and to this end tensor algebra (*e.g.*, Patterson, 1959) is being employed, including the repeated-index summation convention.

The dihedral angle or, as often called, the torsional angle is given by

$$\tau=\cos^{-1}\frac{(\mathbf{u}\times\mathbf{v})\,.\,(\mathbf{v}\times\mathbf{w})}{|\mathbf{u}\times\mathbf{v}|\,|\mathbf{v}\times\mathbf{w}|} \tag{1}$$

as can be readily seen by an inspection of Fig. 1. Equation (1) can be rewritten, using the usual representation of a scalar product of two vector products, as

$$\tau=\cos^{-1}\frac{A}{(BC)^{1/2}} \tag{2}$$

where

$$\begin{aligned} A&=(\mathbf{u}\,.\,\mathbf{v})\,(\mathbf{v}\,.\,\mathbf{w})-(\mathbf{u}\,.\,\mathbf{w})\,(\mathbf{v}\,.\,\mathbf{v})\\ B&=(\mathbf{u}\,.\,\mathbf{u})\,(\mathbf{v}\,.\,\mathbf{v})-(\mathbf{u}\,.\,\mathbf{v})^2\\ C&=(\mathbf{v}\,.\,\mathbf{v})\,(\mathbf{w}\,.\,\mathbf{w})-(\mathbf{v}\,.\,\mathbf{w})^2. \end{aligned} \tag{3}$$

This representation of the scalar product of vector products is well known to be valid in orthogonal Cartesian systems and, as pointed out by Patterson (1959) and shown in the Appendix, it is in fact completely general.

In order to evaluate the estimated standard deviation of τ with the aid of the propagation-of-error formula [equations (8)–(11) below] we require the derivatives of τ with respect to the coordinates of the atoms involved as well as, in the general case, the covariances of these coordinates. Expressing the vectors, which define τ, in terms of their contravariant components, we have

$$\begin{aligned} u&=u^k\mathbf{a}_k\,, & u^k&=x^k{}_{(2)}-x^k{}_{(1)}\\ v&=v^k\mathbf{a}_k\,, & v^k&=x^k{}_{(3)}-x^k{}_{(2)}\\ w&=w^k\mathbf{a}_k\,, & w^k&=x^k{}_{(4)}-x^k{}_{(3)} \end{aligned} \tag{4}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ denote the unit-cell vectors **a**, **b** and **c** respectively and $x^k_{(m)}$ is the kth component of the position vector of atom m. The required derivatives are therefore

$$\begin{aligned} \frac{\partial\tau}{\partial x^s_{(1)}}&=-\frac{\partial\tau}{\partial u^s}\,, & \frac{\partial\tau}{\partial x^s_{(3)}}&=\frac{\partial\tau}{\partial v^s}-\frac{\partial\tau}{\partial w^s}\\ \frac{\partial\tau}{\partial x^s_{(2)}}&=\frac{\partial\tau}{\partial u^s}-\frac{\partial\tau}{\partial v^s}\,, & \frac{\partial\tau}{\partial x^s_{(4)}}&=\frac{\partial\tau}{\partial w^s} \end{aligned} \tag{5}$$

where, upon differentiating (2),

$$\begin{aligned} \frac{\partial\tau}{\partial u^s}&=K\left(\frac{\partial A}{\partial u^s}-\frac{A}{2B}\frac{\partial B}{\partial u^s}\right)\\ \frac{\partial\tau}{\partial v^s}&=K\left(\frac{\partial A}{\partial v^s}-\frac{A}{2B}\frac{\partial B}{\partial v^s}-\frac{A}{2C}\frac{\partial C}{\partial v^s}\right)\\ \frac{\partial\tau}{\partial w^s}&=K\left(\frac{\partial A}{\partial w^s}-\frac{A}{2C}\frac{\partial C}{\partial w^s}\right) \end{aligned} \tag{6}$$

with $K=-1/[(BC)^{1/2}\sin\tau]$.

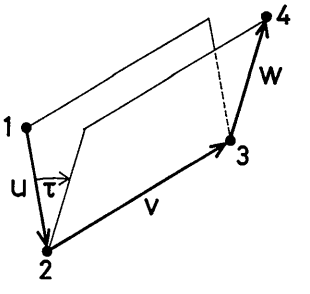

Fig. 1. A schematic representation of the dihedral angle. The angle τ is defined here as the angle formed between the unit normals $\mathbf{u}\times\mathbf{v}/|\mathbf{u}\times\mathbf{v}|$ and $\mathbf{v}\times\mathbf{w}/|\mathbf{v}\times\mathbf{w}|$ to the planes passing through atoms 123 and 234 respectively. The sign of τ is the sign of the triple product $(\mathbf{u}\times\mathbf{v})\,.\,\mathbf{w}$.

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Noting that, *e.g.*, $\mathbf{u} \cdot \mathbf{v} = u^i v^j g_{ij} = u^i v_i$, where $g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$ is the metric tensor of the crystal lattice and $v_i = g_{ij} v^j$ are the covariant components of $\mathbf{v}$, we obtain the derivatives of A, B and C with respect to u^s, v^s and w^s as given below

$$\begin{aligned}
\frac{\partial A}{\partial u^s} &= v_s h_{23} - w_s h_{22} & \frac{\partial B}{\partial u^s} &= 2(u_s h_{22} - v_s h_{12}) \\
\frac{\partial A}{\partial v^s} &= u_s h_{23} + w_s h_{12} - 2 v_s h_{13} & \frac{\partial B}{\partial v^s} &= 2(v_s h_{11} - u_s h_{12}) \qquad (7) \\
\frac{\partial A}{\partial w^s} &= v_s h_{12} - u_s h_{22} & \frac{\partial C}{\partial v^s} &= 2(v_s h_{33} - w_s h_{23}) \\
& & \frac{\partial C}{\partial w^s} &= 2(w_s h_{22} - v_s h_{23})
\end{aligned}$$

where $h_{11} = \mathbf{u} \cdot \mathbf{u}$, $h_{22} = \mathbf{v} \cdot \mathbf{v}$, $h_{33} = \mathbf{w} \cdot \mathbf{w}$, $h_{12} = \mathbf{u} \cdot \mathbf{v}$, $h_{23} = \mathbf{v} \cdot \mathbf{w}$ and $h_{13} = \mathbf{u} \cdot \mathbf{w}$.

Thus, if the atomic position vectors are given in terms of their fractional (contravariant) components, the covariant components of $\mathbf{u}$, $\mathbf{v}$ and $\mathbf{w}$ have to be evaluated with the aid of the metric tensor while if an orthogonal Cartesian system is employed, equations (7) can be used as they stand. A definition of the directions of $\mathbf{u}$, $\mathbf{v}$ and $\mathbf{w}$ other than that given in Fig. 1 and equations (4) will result in a modification of equations (5) only.

We can now summarize the expressions for $\sigma^2(\tau)$, the variance of a dihedral angle, which correspond to the various approximation levels mentioned in the introduction:

$$\sigma^2(\tau) = \sum_{k=1}^{4} \sum_{s=1}^{3} \left(\frac{\partial \tau}{\partial x^s_{(k)}} \right)^2 \sigma^2(k) \qquad (8)$$

$$\sigma^2(\tau) = \sum_{k=1}^{4} \sum_{s=1}^{3} \left(\frac{\partial \tau}{\partial x^s_{(k)}} \right)^2 \sigma^2(x^s_{(k)}) \qquad (9)$$

$$\sigma^2(\tau) = \sum_{k=1}^{4} \sum_{s=1}^{3} \sum_{q=1}^{3} \frac{\partial \tau}{\partial x^s_{(k)}} \frac{\partial \tau}{\partial x^q_{(k)}} \operatorname{cov}(x^s_{(k)}, x^q_{(k)}), \qquad (10)$$

$$\sigma^2(\tau) = \sum_{k=1}^{4} \sum_{n=1}^{4} \sum_{s=1}^{3} \sum_{q=1}^{3} \frac{\partial \tau}{\partial x^s_{(k)}} \frac{\partial \tau}{\partial x^q_{(n)}} \operatorname{cov}(x^s_{(k)}), x^q_{(n)}) \,. \qquad (11)$$

Equations (8), (9), (10) and (11) are forms of the propagation-of-error formula corresponding to the assumptions of isotropic atomic positional variances, diagonal covariance matrix, atom-block diagonal covariance matrix and a full covariance matrix respectively, thus covering all cases of practical importance.

For the sake of completeness, we indicate how the most general case, *i.e.* equation (11) including positions of one or more symmetry related atoms, can be formulated in practice. Equation (11) can be rewritten as a sum of quadratic forms

$$\sigma^2(\tau) = \sum_{k=1}^{4} \sum_{n=1}^{4} \mathbf{p}^T_{(k)i} \mathbf{C}_{(kn)} \mathbf{p}_{(n)j} \qquad (12)$$

where

$$p_{(k)s} = \frac{\partial \tau}{\partial x^s_{(k)}}, \quad C^{sq}_{(kn)} = \operatorname{cov}(x^s_{(k)}, \; x^q_{(n)})$$

and i,j are indicators denoting the serial numbers of the space-group operations by which the current positions of atoms k,n respectively were generated. In general, the 3×3 covariance matrix relating atoms k and n is then given by

$$\mathbf{C}_{(kn)} = \mathbf{P}_i \mathbf{C}^0_{(kn)} \mathbf{P}^T_j \qquad (13)$$

where $\mathbf{P}_i$ and $\mathbf{P}_j$ are the corresponding rotation matrices and $\mathbf{C}^0_{(kn)}$ is the available covariance matrix related to the reference asymmetric unit. This can be readily shown using the methods of Sands (1966). Of course, the matrix $\mathbf{C}_{(kn)}$ will usually have one of the following forms: $\mathbf{C}^0$, $\mathbf{PC}^0$, $\mathbf{C}^0\mathbf{P}^T$ or $\mathbf{PC}^0\mathbf{P}^T$ unless more than one non-trivial symmetry operation is involved. In the case of equation (10), *i.e.* neglecting covariances involving different atoms, only the forms $\mathbf{C}^0$ and $\mathbf{PC}^0\mathbf{P}^T$ will appear.

Analogous expressions for the variances of an interatomic distance and an angle defined by two interatomic vectors can be easily derived using tensor and vector notations which appear, in many cases, to combine conciseness, generality and suitability for computer programming.

A numerical test carried out with equations (9) and (10) suggests that the effect of including covariances is similar to that observed in calculations of standard deviations of distances and angles, the discrepancies being sometimes as large as 20–25% of the values given by (9). The example concerned a monoclinic structure with x–z correlation coefficients of the order of 0·3, but no symmetry-related atoms were involved in the calculation.

I wish to thank Mr W. Polder and Dr A. J. Wagner for the data used in the test calculation and Rietje Vaillant for typing the manuscript.

APPENDIX

We wish to show that the relation

$$(\mathbf{u} \times \mathbf{v}) \cdot (\mathbf{w} \times \mathbf{z}) = (\mathbf{u} \cdot \mathbf{w})(\mathbf{v} \cdot \mathbf{z}) - (\mathbf{u} \cdot \mathbf{z})(\mathbf{v} \cdot \mathbf{w}) \qquad (A1)$$

is valid in an oblique system of coordinates. Representing the pairs of vectors $\mathbf{u},\mathbf{v}$ and $\mathbf{w},\mathbf{z}$ in terms of their contravariant and covariant components respectively, we have

$$\mathbf{u} \times \mathbf{v} = V e_{ijk} u^j v^k \mathbf{a}^i \equiv \mathbf{G} \qquad (A2)$$

$$\mathbf{w} \times \mathbf{z} = V^{-1} e^{lmn} w_m z_n \mathbf{a}_l \equiv \mathbf{H} \qquad (A3)$$

where V is the volume of the unit cell, $\mathbf{a}^1,\mathbf{a}^2,\mathbf{a}^3$ are the reciprocal vectors $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ respectively and $e_{ijk}(e^{ijk})$, known as the Levi–Civita tensor, equals $+1, -1$ or zero according as ijk are a cyclic permutation of 123, a non-cyclic permutation of 123 or any two indices are equal respectively.

Since $\mathbf{a}^i \cdot \mathbf{a}_l = \delta^i_l$ and making use of the well-known relation

$$e_{ijk} e^{lmn} = \delta^m_j \delta^n_k - \delta^n_j \delta^m_k \,, \qquad (A4)$$

the scalar product of $\mathbf{G}$ and $\mathbf{H}$ readily reduces to

$$\begin{aligned}
\mathbf{G} \cdot \mathbf{H} &= u^m w_m v^n z_n - u^m z_m v^n w_n \\
&= (\mathbf{u} \cdot \mathbf{w})(\mathbf{v} \cdot \mathbf{z}) - (\mathbf{u} \cdot \mathbf{z})(\mathbf{v} \cdot \mathbf{w}) \qquad (A5)
\end{aligned}$$

which was to be shown. The proof is far more tedious if a different representation of $\mathbf{u}$, $\mathbf{v}$, $\mathbf{w}$ and $\mathbf{z}$ is chosen.

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