

Short Communications

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Comments on Gruber's algorithm. By G. M. WOLTEN, *Aerospace Corporation Laboratories, El Segundo, California, U. S. A.*

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Gruber's algorithm [Gruber, B. (1970) *Acta Cryst.* A26, 622] for determining the symmetry and stacking properties of Bravais-lattice planes can be applied to problems in reciprocal space.

Gruber (1970) has published an interesting algorithm for determining the symmetry and stacking properties of Bravais-lattice planes.

It would seem that the algorithm can be applied to problems in reciprocal space as well, with useful results as follows. The normal to the direct lattice plane (hkl) is the reciprocal axis $[hkl]^*$. From reciprocity, it follows that the normal to the reciprocal lattice plane (uvw)^{*} is the direct space zone axis $[uvw]$. Thus, by supplying uvw instead of hkl , and reciprocal lattice parameters instead of direct ones the algorithm will determine the size and shape of recip-

rocal lattice planes as seen on precession photographs or on thin-crystal electron diffraction patterns.

The second of the worked-out examples in Gruber's paper contains a misprint. In the value for t_3 , the ratio $\frac{2}{3}$ should read $\frac{1}{3}$.

The author has programmed the algorithm in Fortran. Copies of the program may be obtained upon request.

Reference

GRUBER, B. (1970). *Acta Cryst.* A26, 622.

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The standard deviation of the torsion angle. By R. H. STANFORD JR and JÜRIG WASER, *Gates and Crellin Laboratories of Chemistry,* California Institute of Technology, Pasadena, California 91109, U.S.A.*

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Formulas are derived for calculating a torsion angle and its standard deviation. The positions of the four atoms defining the torsion angle are assumed to be uncorrelated and the positional standard deviations are assumed to be isotropic.

Given a sequence of four (usually bonded) atoms, 1, 2, 3, and 4, whose positions are uncorrelated, and the isotropic standard deviations of their positions, formulas are derived for the torsion angle about the line between atoms 2 and 3 and its standard deviation.

The position of each atom can be represented by:

$$\mathbf{r}_n = x_n \mathbf{i} + y_n \mathbf{j} + z_n \mathbf{k} \quad (n = 1, 2, 3 \text{ or } 4), \quad (1)$$

where x_n, y_n, z_n are the orthogonalized coordinates of atom n , and \mathbf{i}, \mathbf{j} , and \mathbf{k} are the usual Cartesian unit vectors. The variances of the atomic positions are assumed to be isotropic, that is

$$\sigma^2(x_n) = \sigma^2(y_n) = \sigma^2(z_n) = \sigma_n^2. \quad (2)$$

Define the interatomic vectors:

$$\mathbf{r}_{mn} = \mathbf{r}_n - \mathbf{r}_m. \quad (3)$$

Then, a vector normal to the plane defined by atoms 1, 2, and 3 is:

$$\mathbf{t}_1 = \mathbf{r}_{21} \times \mathbf{r}_{23}; \quad (4)$$

and a vector normal to the plane defined by atoms 2, 3, and 4 is:

$$\mathbf{t}_2 = \mathbf{r}_{32} \times \mathbf{r}_{34}. \quad (5)$$

The angle between these normals is the torsion angle, τ , about the line between atoms 2 and 3, and

$$\cos \tau = \mathbf{t}_1 \cdot \mathbf{t}_2 / t_1 t_2. \quad (6)$$

(The conventional sign of τ is discussed later.)

Substitution of (1) and (3) into (4) and (5) yields:

$$\mathbf{t}_l = a_l \mathbf{i} + b_l \mathbf{j} + c_l \mathbf{k} \quad (l = 1 \text{ or } 2), \quad (7)$$

where the coefficients a_l, b_l, c_l are given under 'general coordinates' in Table 1,

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Table 1. Components of the vector normals in the general and special coordinate systems

	General coordinates	Special coordinates
a_1	$y_1(z_3 - z_2) + y_2(z_1 - z_3) + y_3(z_2 - z_1)$	$Y_1 Z_3$
b_1	$x_1(z_2 - z_3) + x_2(z_3 - z_1) + x_3(z_1 - z_2)$	0
c_1	$x_1(y_3 - y_2) + x_2(y_1 - y_3) + x_3(y_2 - y_1)$	0
a_2	$y_2(z_4 - z_3) + y_3(z_2 - z_4) + y_4(z_3 - z_2)$	$Y_4 Z_3$
b_2	$x_2(z_3 - z_4) + x_3(z_4 - z_2) + x_4(z_2 - z_3)$	$-X_4 Z_3$
c_2	$x_2(y_4 - y_3) + x_3(y_2 - y_4) + x_4(y_3 - y_2)$	0

Substituting t_1 and t_2 from (7) into (6) gives:

$$\cos \tau = \frac{a_1 a_2 + b_1 b_2 + c_1 c_2}{t_1 t_2} \quad (8)$$

or

$$|\tau| = \cos^{-1} \left(\frac{a_1 a_2 + b_1 b_2 + c_1 c_2}{t_1 t_2} \right). \quad (8')$$

The variance of τ is then given by

$$\sigma^2(\tau) = \frac{1}{\sin^2 \tau} \sigma^2(\cos \tau), \quad (9)$$

where

$$\sigma^2(\cos \tau) = \sum_i \sum_j \frac{\partial(\cos \tau)}{\partial q_i} \frac{\partial(\cos \tau)}{\partial q_j} \text{cov}(q_i, q_j). \quad (10)$$

The quantities q_i and q_j represent the parameters x_n , y_n , and z_n ($n=1$ to 4) and $\text{cov}(q_i, q_j)$ is the covariance of q_i and q_j . It has been our experience that with good three-dimensional data the covariance matrix of each atom is usually, for all practical purposes, isotropic [*i.e.* in a Cartesian system the matrix is diagonal and of the form (2)]. Moreover, there are seldom significant correlations among different atoms, unless they are related by symmetry, which case we exclude here. If we, therefore, assume that the parameters are independent,

$$\text{cov}(q_i, q_j) = \begin{cases} 0 & q_i \neq q_j \\ \sigma^2(q_i) & q_i = q_j \end{cases}$$

and (10) reduces to:

$$\sigma^2(\cos \tau) = \sum_i \left(\frac{\partial(\cos \tau)}{\partial q_i} \right)^2 \sigma^2(q_i). \quad (11)$$

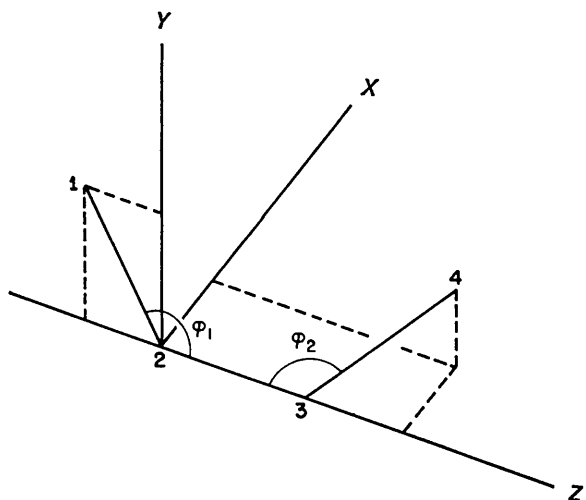


Fig. 1. Right-handed coordinate system.

Multiplication of (8) by $t_1 t_2$, taking partial derivatives, and rearranging yields:

$$t_1 t_2 \frac{\partial(\cos \tau)}{\partial q_m} = a_1 \frac{\partial a_2}{\partial q_m} + a_2 \frac{\partial a_1}{\partial q_m} + b_1 \frac{\partial b_2}{\partial q_m} + b_2 \frac{\partial b_1}{\partial q_m} + c_1 \frac{\partial c_2}{\partial q_m} + c_2 \frac{\partial c_1}{\partial q_m} - \cos \tau \left(t_1 \frac{\partial t_2}{\partial q_m} + t_2 \frac{\partial t_1}{\partial q_m} \right), \quad (12)$$

where

$$t_1 = (a_1^2 + b_1^2 + c_1^2)^{1/2} \quad (13)$$

and

$$\frac{\partial t_1}{\partial q_m} = \frac{1}{t_1} \left(a_1 \frac{\partial a_1}{\partial q_m} + b_1 \frac{\partial b_1}{\partial q_m} + c_1 \frac{\partial c_1}{\partial q_m} \right). \quad (14)$$

The final expressions can be simplified by choosing a special right-handed coordinate system to bring atom 2 to the origin, atom 3 to the k axis, and atom 1 into the plane of j and k , choosing the directions of j and k so as to make Y_1 and Z_3 positive. The new coordinates then become:

$$\begin{aligned} X_1 &= 0, Y_1 > 0, Z_1 \\ X_2 &= Y_2 = Z_2 = 0 \\ X_3 &= Y_3 = 0, Z_3 > 0 \\ X_4, Y_4, Z_4 & \end{aligned}$$

The coefficients a_1, a_2, \dots in (7) for this new set of axes are also given in Table 1. The derivatives appearing in (12) and (14) are shown in matrix form in Table 2 for the special coordinate system. Note that some of the derivatives are not zero, even though they would have vanished if straightforward derivatives of the expressions for a_1, a_2, \dots in the special coordinate system (see Table 1) had been taken. In other words, the complete expressions involving the symbolic coordinates must be retained during differentiation.

Table 2. Derivatives of the components in the special coordinate system of the normal vectors which appear in equations (12) and (14)

	$\partial a_1/$	$\partial b_1/$	$\partial c_1/$	$\partial a_2/$	$\partial b_2/$	$\partial c_2/$
∂X_1	0	$-Z_3$	0	0	0	0
∂Y_1	Z_3	0	0	0	0	0
∂Z_1	0	0	0	0	0	0
∂X_2	0	$Z_3 - Z_1$	Y_1	0	$Z_3 - Z_4$	Y_4
∂Y_2	$Z_1 - Z_3$	0	$-X_1$	$Z_4 - Z_3$	0	$-X_4$
∂Z_2	$-Y_1$	0	0	$-Y_4$	X_4	0
∂X_3	0	Z_1	$-Y_1$	0	Z_4	$-Y_4$
∂Y_3	$-Z_1$	0	X_1	$-Z_4$	0	X_4
∂Z_3	Y_1	0	0	Y_4	$-X_4$	0
∂X_4	0	0	0	0	$-Z_3$	0
∂Y_4	0	0	0	Z_3	0	0
∂Z_4	0	0	0	0	0	0

Finally, equation (9) takes the form:

$$\begin{aligned} \sigma^2(\tau) &= \frac{\sigma_1^2}{Y_1^2} + \frac{\sigma_2^2}{Z_3^2} \left[\frac{(Z_3 - Z_1)^2}{Y_1^2} \right. \\ &\quad \left. - \frac{2(Z_3 - Z_1)(Z_3 - Z_4) \cos \tau}{Y_1(X_4^2 + Y_4^2)^{1/2}} + \frac{(Z_3 - Z_4)^2}{(X_4^2 + Y_4^2)} \right] \\ &\quad + \frac{\sigma_3^2}{Z_3^2} \left[\frac{Z_1^2}{Y_1^2} - \frac{2Z_1 Z_4 \cos \tau}{Y_1(X_4^2 + Y_4^2)^{1/2}} \right. \\ &\quad \left. + \frac{Z_4^2}{(X_4^2 + Y_4^2)} \right] + \frac{\sigma_4^2}{(X_4^2 + Y_4^2)}. \quad (15) \end{aligned}$$

Fig. 1 shows that the various coordinates in (15) can be replaced as follows:

$$\begin{aligned} Y_1 &= r_{12} \sin \varphi_1 & Z_1 &= r_{12} \cos \varphi_1 \\ Z_3 &= r_{23} & Z_4 &= r_{23} - r_{34} \cos \varphi_2 \\ (X_4^2 + Y_4^2)^{1/2} &= r_{34} \sin \varphi_2, \end{aligned}$$

where r_{mn} is the distance between atoms m and n . Equation (15) for the variance of the torsion angle, τ , then becomes:

$$\begin{aligned} \sigma^2(\tau) &= \frac{\sigma_1^2}{r_{12}^2 \sin^2 \varphi_1} + \frac{\sigma_2^2}{r_{23}^2} \left[\left(\frac{r_{23} - r_{12} \cos \varphi_1}{r_{12} \sin \varphi_1} \right)^2 \right. \\ &\quad \left. - 2 \left(\frac{r_{23} - r_{12} \cos \varphi_1}{r_{12} \sin \varphi_1} \right) \cot \varphi_2 \cos \tau + \cot^2 \varphi_2 \right] \\ &\quad + \frac{\sigma_3^2}{r_{23}^2} \left[\cot^2 \varphi_1 - 2 \left(\frac{r_{23} - r_{34} \cos \varphi_2}{r_{34} \sin \varphi_2} \right) \cot \varphi_1 \cos \tau \right. \\ &\quad \left. + \left(\frac{r_{23} - r_{34} \cos \varphi_2}{r_{34} \sin \varphi_2} \right)^2 \right] + \frac{\sigma_4^2}{r_{34}^2 \sin^2 \varphi_2}. \end{aligned} \quad (16)$$

Use of the special coordinates in (8') leads to the torsion angle:

$$|\tau| = \cos^{-1} \frac{Y_4}{(X_4^2 + Y_4^2)^{1/2}}. \quad (17)$$

The convention of the 'right-hand rule' (Klyne & Prelog, 1960) is used to fix the sign of τ . In order to determine the

sign, in a right-handed system with $Y_1 > 0$ and $Z_3 > 0$, it is necessary only to examine X_4 . The sign of τ is the sign of $-X_4$.

For the purpose of programming a computer to calculate the standard deviation of the torsion angle, equation (15) seems most appropriate. If, however, the six structural parameters are known, then equation (16) would be more suitable.

The function-and-error program of Busing & Levy (1961) included a provision for calculating the dihedral angle and its standard error for two planes each defined by three atoms. The torsion-angle calculation is a special case in which two atoms are common to both planes. In this program the standard error is calculated from the full covariance matrix, and the necessary derivatives are evaluated by numerical differentiation.

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Normal probability plot analysis of small samples.* By WALTER C. HAMILTON, *Chemistry Department, Brookhaven National Laboratory, Upton, New York, U.S.A.* and S. C. ABRAHAMS, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.*

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In using normal probability plots for comparing two sets of crystallographic data [Abrahams, S. C. & Keve, E. T. (1971), *Acta Cryst.* **A27**, 157] note should be taken of the fact that the expected values of normal order statistics are not given exactly by the percentage points of the normal distribution. This becomes an important consideration only for small samples. Tables of expected ranked exact moduli of normal observations, for sample sizes to 41, are presented: these are useful for half-normal probability plots.

Differences between independent measurements or calculated values of the same i th crystallographic quantity, $\Delta_i = F(1)_i - F(2)_i$, are readily analyzed by the normal probability plot method (Abrahams & Keve, 1971) in terms of the pooled standard deviation $\sigma_i = [\sigma^2 F(1)_i + \sigma^2 F(2)_i]^{1/2}$. A plot of the j ranked values of the weighted deviations Δ_i/σ_i (where $i=1$ refers to the largest Δ_i/σ_i) against the expected values $\xi(i|j)$ should result in a scatter of points about a straight line of unit slope that passes through the origin. If the weighted deviations are drawn from a normal distribution, a reasonable assumption for a crystallographic experiment, then the expected values for large j are given approximately by the percentage points X_i of the normal distribution, with

$$P(X_i) = \frac{1}{\sqrt{2\pi}} \int_{-X_i}^{X_i} \exp(-\alpha^2/2) d\alpha = |(j-2i+1)/j| \quad (1)$$

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For small values of j , especially for $j < 50$, the deviations between the values given by equation (1) and the exact values as tabulated by Harter (1961) become appreciable, especially at the extremes of the array. Four examples are given in Table 1. The exact values should always be used for small samples.

If the sign of Δ_i is without significance, as in comparison of two sets of position parameters, the half-normal probability plot should be used (Abrahams & Keve, 1971). For large samples, the expected values may again be obtained from the percentage points of the normal distribution, with $P(X_i) = (2j-2i+1)/2j$.† For j small, these approximate values are appreciably in error, and the exact values should be used. The expected value of the i th largest modulus of

† The expression given for this quantity in Abrahams & Keve (1971) is misprinted as $(2i+1)/2j$; it should have read $(2i-1)/2j$, where $i=1$ refers to the smallest observation. For consistency with the full-normal case notation, we use the expression above, where $i=1$ refers to the largest observation.