

ever, can be detected in two ways. First, the reflections  $h'k'l'$  with  $k' = 2n$  are present only if  $l' = 2n$ . This condition is not required by any space group and indicates the presence of twins. Secondly, the ratio of the intensities of reflections  $h'k'l'$  and  $h', k', h' + l'$  (or  $h'k'l'$  and  $h', k', -h' - l'$ ) is constant (see Table 3). This result indicates that the sample is formed by at least two distinct individuals rather than being a single crystal.

By increasing the chromium content in  $\text{VO}_2$ , the values of  $a$  and  $2c$  become closer and the obliquity associated with the laws (201) and (20 $\bar{1}$ ) decreases. It is therefore reasonable to expect that these laws become more frequent with increasing amount of chromium in the sample. The results obtained in the present study seem to confirm this deduction. In fact, while the value of ratio (1) indicates that in  $\text{VO}_2 + 0.5$  at.% Cr only 11% of the total volume of the sample belongs to the individuals twinned with laws (201) and (20 $\bar{1}$ ), in  $\text{VO}_2 + 2.5$  at.% Cr about 40% of the total volume belongs to these individuals. Twins in which only the laws (201) and (20 $\bar{1}$ ) are operative are, therefore, more probable in samples of  $\text{VO}_2$  with a high chromium content. In these cases, unless twinning is detected, the systematic extinctions will inevitably lead to erroneous space groups.

*Note added in proof:* N.m.r. measurements, obtained while this paper was in press, seem to indicate that the

symmetry of the  $M_3$  phase is lower than  $2/m$  (H. Lauenrois & T. M. Rice, private communication). For the sample of  $\text{VO}_2 + 0.5$  at.% Cr, therefore, the operation (010) (or  $[010]_{180^\circ}$ ) may become a possible twin operation with vanishingly small obliquity (twinning by high-order merohedry, Friedel, 1964). This twinning, if present, cannot be detected by X-ray measurements at room temperature and it has no bearing on the interpretation of the other twins. All the conclusions obtained in the paper remain, therefore, unchanged.

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## Dyadics and the Variances and Covariances of Molecular Parameters, Including those of Best Planes\*

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Expressions are derived for the variances and covariances of molecular parameters by combining the error propagation equation and the formalism of Gibbs' dyadics. The resulting formulas concern bond angles, bond vectors and distances, torsion angles, the parameters that describe the best plane fitted to a set of atoms, and the dihedral angle between two such planes. All results include covariance terms between the coordinates of different atoms, an important example being the torsion angle defined by atoms related by a twofold axis. An Appendix concerns the transformation properties of covariance matrix elements.

In this paper a general method is developed for obtaining the variances and covariances of molecular parameters, such as bond and torsion angles, from the positional covariance matrices of the atoms defining these parameters. Substantial use is made of the del operator, vectors, and dyadics (e.g., Gibbs & Wilson, 1929; Wills, 1931; Zachariassen, 1944; Patterson,

1959). Dyadics are relatively unfamiliar, and matrices or tensors might have been employed instead. However, the use of dyadics places the cross product at our disposal, which will prove fruitful. Instead of the customary covariance matrix of the atomic coordinates we shall introduce a covariance dyadic, a procedure that is justified in an Appendix. In turn, some of our results are in the form of covariance dyadics rather than of covariance matrices. We shall first investigate

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parameters concerning two and three atoms, such as bond vectors, bond angles, and the angles of orientation of a vector normal to the plane through three atoms. Parameters related to more than three atoms follow, such as torsion angles and the parameters that describe the best plane fitted to a set of atoms by the method of least-squares. Covariance terms between the coordinates of different atoms are included in our results, as well as the simplifications that result from isotropic positional variances and no covariance among different atoms.

### Variance and covariance matrices and dyadics

Consider a typical structural molecular parameter  $A$  ( $\mathbf{r}^s, \mathbf{r}^t, \dots$ ), such as a bond distance or a bond angle,<sup>†</sup> which depends on the positions  $\mathbf{r}^s, \mathbf{r}^t, \dots$  of the atoms defining it, which we label  $s, t, \dots$ . Let the uncertainties in the positions of an atom, such as atom  $s$ , be described by the (symmetrical) covariance matrix<sup>‡</sup> [ $\mathbf{C}^{ss}$ ] with the elements  $C_{ij}^{ss}$ , where the subscripts  $i$  and  $j$  refer to the three coordinate axes, which may, but need not be, Cartesian.<sup>§</sup> The diagonal elements ( $i=j$ ) of [ $\mathbf{C}^{ss}$ ] are the variances of the coordinates  $x_i^s$  of atom  $s$ , and the off-diagonal terms ( $i \neq j$ ) are the covariances between  $x_i^s$  and  $x_j^s$ , coordinates that refer to different axes. When the covariance matrix [ $\mathbf{C}^{ss}$ ] is isotropic and the coordinate system Cartesian, the off-diagonal terms of [ $\mathbf{C}^{ss}$ ] vanish; the diagonal terms are all equal to the (scalar) positional variance  $\sigma_s^2$  for atom  $s$ , so that

$$[\mathbf{C}^{ss}] = (\sigma_s^2) [\mathbf{I}] \quad \text{or} \quad C_{ij}^{ss} = (\sigma_s^2) \delta_{ij} \quad (1)$$

where [ $\mathbf{I}$ ] is the unit matrix, with components  $\delta_{ij}$  (see also Appendix). The covariance between the coordinates  $x_i^s$  and  $x_j^t$  of different atoms is described by the matrix [ $\mathbf{C}^{st}$ ] with the elements  $C_{ij}^{st}$ . An important cause of such covariances are symmetry relations (Sands, 1966).

The variance  $\sigma^2(A)$  of  $A$  is given by the propagation-of-error equation

$$\sigma^2(A) = \sum_{s,t} \frac{\partial A}{\partial x_i^s} C_{ij}^{st} \frac{\partial A}{\partial x_j^t} \quad (2)$$

Here and in later equations we use the customary convention that all indices occurring twice, on different symbols, must be summed over (here  $i$  and  $j$ ); the indices  $s$  and  $t$  extend over all atoms concerned in the definition of  $A$ . For two different molecular parameters

<sup>†</sup> The word 'bond' as used here and later does not imply the existence of a chemical bond, but merely refers to a relationship between the atoms considered and a distance, an angle, or another parameter.

<sup>‡</sup> Matrices are denoted by bold-face capital letters in brackets, [ $\mathbf{C}$ ], vectors by bold-face lower-case letters,  $\mathbf{r}, \xi$ , and dyadics by bold-face capital letters,  $\mathbf{C}, \Gamma$ .

<sup>§</sup> By 'Cartesian' we imply right angles between, and equal unit lengths along, the three axes, in conformance with widespread usage.

$A$  and  $B$ , such as two distances or an angle and a distance, the covariance is,

$$\text{cov}(A, B) = \sum_{s,t} \frac{\partial A}{\partial x_i^s} C_{ij}^{st} \frac{\partial B}{\partial x_j^t} \quad (3)$$

Turning to vectorial quantities, the covariance matrix [ $\Gamma(\mathbf{p})$ ] of a molecular parameter  $\mathbf{p}$  contains variance as well as covariance terms of the components  $p_i$ ,

$$\Gamma_{ii}(\mathbf{p}) = \sigma^2(p_i) \quad (4a)$$

and

$$\Gamma_{ij}(\mathbf{p}) = \Gamma_{ji}(\mathbf{p}) = \text{cov}(p_i, p_j) \quad (4b)$$

for which

$$\Gamma_{mn}(\mathbf{p}) = \sum_{s,t} \frac{\partial p_m}{\partial x_i^s} C_{ij}^{st} \frac{\partial p_n}{\partial x_j^t} \quad (5)$$

For two vectorial parameters  $\mathbf{p}$  and  $\mathbf{q}$  the covariance matrix, [ $\Gamma(\mathbf{p}, \mathbf{q})$ ], has the elements

$$\Gamma_{mn}(\mathbf{p}, \mathbf{q}) = \text{cov}(p_m, q_n) = \sum_{s,t} \frac{\partial p_m}{\partial x_i^s} C_{ij}^{st} \frac{\partial q_n}{\partial x_j^t} \quad (6)$$

This matrix is not symmetric in general, its transpose being [ $\Gamma(\mathbf{q}, \mathbf{p})$ ]. Finally, the covariance matrix between a scalar parameter  $A$  and a vectorial parameter  $\mathbf{p}$  is rectangular ( $1 \times 3$ ) rather than square,

$$\Gamma_n(A, \mathbf{p}) = \text{cov}(A, p_n) = \sum_{s,t} \frac{\partial A}{\partial x_i^s} C_{ij}^{st} \frac{\partial p_n}{\partial x_j^t} \quad (7)$$

Extension to variances and covariances of tensor components, such as temperature parameters  $B_{ij}^{st}$ , is possible also.

Considerable simplification of the equations is achieved by using dyadics and the *del* operator  $\nabla$ , defined in terms of Cartesian unit vectors  $\mathbf{i}, \mathbf{j}, \mathbf{k}$ , along the  $x, y, z$  axes,\* by

$$\nabla_s \equiv \mathbf{i} \frac{\partial}{\partial x^s} + \mathbf{j} \frac{\partial}{\partial y^s} + \mathbf{k} \frac{\partial}{\partial z^s} \quad (8)$$

Moreover, we define positional covariance dyadics  $\mathbf{C}^{st}$  by combining the elements of the covariance matrices [ $\mathbf{C}^{st}$ ], appropriate to the Cartesian coordinate system chosen, with the vectors  $\mathbf{i}, \mathbf{j}, \mathbf{k}$ :

$$\mathbf{C}^{st} \equiv \sum_i \sum_j C_{ij}^{st} \mathbf{i} \mathbf{j} \quad (9)$$

where both sums extend over the vector triple  $\mathbf{i}, \mathbf{j}, \mathbf{k}$ . While a Cartesian coordinate frame has been used in (8) and (9), both  $\nabla_s$  and  $\mathbf{C}^{st}$  are independent of the coordinate system. If the positional covariance matrix [ $\mathbf{C}^{st}$ ] refers to a general crystallographic (rectilinear) coordinate system with axes  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ , an equivalent definition of the dyadic  $\mathbf{C}^{st}$  is

$$\mathbf{C}^{st} \equiv \bar{C}_{ij}^{st} \mathbf{a}_i \mathbf{a}_j \quad (10)$$

double summation over  $i$  and  $j$  being implied. This relationship is justified in the Appendix, where  $\nabla$  is also expressed in terms of crystallographic quantities. Note that the matrix [ $\mathbf{C}^{st}$ ] is the transpose of [ $\mathbf{C}^{st}$ ]

\* The symbols  $x, y, z$  and  $x_1, x_2, x_3$  are used interchangeably.

whereas the dyadics  $C^{ts}$  and  $C^{st}$  are what is called conjugate, that is, their antecedents and consequents are interchanged.

The definitions (8) and (9) permit us to write (2) in the form

$$\sigma^2(A) = \sum_{s,t} \nabla_s A \cdot C^{st} \cdot \nabla_t A \quad (11)$$

The dots on the right side of (11) imply respective scalar multiplication of the antecedents and the consequents of  $C^{st}$  by the vector  $\nabla_s A$  (representing the gradient of  $A$ ), the result being identical with (2). Equation (3) can be given a similar form

$$\text{cov}(A, B) = \sum_{s,t} \nabla_s A \cdot C^{st} \cdot \nabla_t B \quad (12)$$

The operator  $\nabla_s$  may also be applied to a vector, such as  $\mathbf{p}$ . The result,  $\nabla_s \mathbf{p}$ , is a dyadic that is, in general, not symmetrical, and it must be noted that it is the antecedents of  $\nabla_s$  in  $\nabla_s \mathbf{p}$  that must be multiplied with  $C^{st}$ . This is automatic when  $\nabla_s \mathbf{p}$  is used as post factor. As prefactor the conjugate dyadic  $\overleftarrow{\nabla_s \mathbf{p}}$  must be used, so that, e.g. in  $\overleftarrow{\nabla_s \mathbf{p}} \cdot C^{st}$ , it is again the antecedents of  $\nabla_s \mathbf{p}$  that are scalarly multiplied with the antecedents of  $C^{st}$ . The equations analogous to (7), (5), and (6) are then

$$\Gamma(A, \mathbf{p}) = \sum_{s,t} \nabla_s A \cdot C^{st} \cdot \nabla_t \mathbf{p} \quad (13)$$

$$\Gamma(\mathbf{p}) = \sum_{s,t} \overleftarrow{\nabla_s \mathbf{p}} \cdot C^{st} \cdot \nabla_t \mathbf{p} \quad (14)$$

$$\Gamma(\mathbf{p}, \mathbf{q}) = \sum_{s,t} \overleftarrow{\nabla_s \mathbf{p}} \cdot C^{st} \cdot \nabla_t \mathbf{q} \quad (15)$$

Note that  $\Gamma(\mathbf{q}, \mathbf{p})$  is the dyadic that is conjugate to  $\Gamma(\mathbf{p}, \mathbf{q})$ .

### Some results of applying the del operator

Application of  $\nabla_s$  to the vector  $\mathbf{r}_s$  with components  $x_i^s$  yields the idemfactor or unit dyadic, which we shall denote by  $\mathbf{I}$  and which is the analog of a unit matrix

$$\nabla_s \mathbf{r}_s = \mathbf{I} = \mathbf{ii} + \mathbf{jj} + \mathbf{kk} \quad (16)$$

(More general expressions of  $\mathbf{I}$  are given in the Appendix.) Similarly,  $\nabla_s$  applied to the length  $r_s$  of  $\mathbf{r}_s$  yields

$$\nabla_s r_s = \hat{\mathbf{f}}_s \equiv \mathbf{r}_s / r_s \quad (17)$$

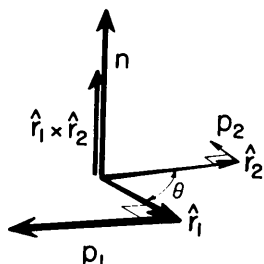


Fig. 1. Angle  $\theta$  between two unit vectors  $\hat{\mathbf{r}}_1$  and  $\hat{\mathbf{r}}_2$ .

where the circumflex implies unit length so that  $\hat{\mathbf{f}}_s$  is a unit vector in the direction of  $\mathbf{r}_s$ . Moreover,

$$\nabla_s \hat{\mathbf{f}}_s = \frac{1}{r_s} (\mathbf{I} - \hat{\mathbf{f}}_s \hat{\mathbf{f}}_s) \quad (18)$$

which may be proved by applying the product rule to  $\mathbf{r}_s = r_s \hat{\mathbf{f}}_s$ :

$$\nabla_s \mathbf{r}_s = \mathbf{I} = r_s \nabla_s \hat{\mathbf{f}}_s + \hat{\mathbf{f}}_s \hat{\mathbf{f}}_s$$

The factor  $(1/r_s)$  in (18) is a scale factor, which is equal to unity when  $\mathbf{r}_s$  itself happens to be of unit length. [The essential difference between (16) and (18) is that  $\hat{\mathbf{f}}_s$  of (18) is of constant length.]  $\nabla_s \hat{\mathbf{f}}_s$  is a uniplanar dyadic with its antecedents and consequents in a plane perpendicular to  $\hat{\mathbf{f}}_s$ , as may be seen with coordinate axes chosen so that  $\mathbf{k} = \hat{\mathbf{f}}_s$ , and  $\mathbf{i}$  and  $\mathbf{j}$  perpendicular to  $\hat{\mathbf{f}}_s$ ; in this system  $\mathbf{I} - \hat{\mathbf{f}}_s \hat{\mathbf{f}}_s = \mathbf{ii} + \mathbf{jj}$ .

The following rules are important in the manipulation of  $\nabla$ , the sequence of symbols often being crucial:

$$\nabla(ab) = (\nabla b)a + (\nabla a)b$$

$$\nabla(\mathbf{a} \cdot \mathbf{b}) = (\nabla \mathbf{a}) \cdot \mathbf{b} + (\nabla \mathbf{b}) \cdot \mathbf{a}$$

$$\nabla(\mathbf{a} \times \mathbf{b}) = (\nabla \mathbf{a}) \times \mathbf{b} - (\nabla \mathbf{b}) \times \mathbf{a}$$

Note that in the first equation the quantities on both sides are dyadics, in the second, vectors, and in the third, again dyadics.

Aside from vectors we are interested in angles, such as the angle  $\theta$  enclosed by two vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$  (Fig. 1), so that  $\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2 = \cos \theta$ , where  $\hat{\mathbf{r}}_i = \mathbf{r}_i / r_i$ . We shall need the quantities  $\nabla_1 \theta$  and  $\nabla_2 \theta$ , where the subscripts of  $\nabla$  refer to the arrow ends of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . Inspection of the geometry involved, or use of (18) on  $\theta = \cos^{-1}(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2)$ , yields

$$\nabla_1 \theta = -(1/r_1) \mathbf{n} \times \hat{\mathbf{r}}_1 \equiv \mathbf{p}_1 / r_1 \quad (19a)$$

where  $\mathbf{n}$  is a unit vector along  $\mathbf{r}_1 \times \mathbf{r}_2$  (Fig. 1) so that  $\hat{\mathbf{r}}_1 \times \hat{\mathbf{r}}_2 = \mathbf{n} \sin \theta$ , while  $\mathbf{p}_1$  is a unit vector in the plane of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , perpendicular to  $\mathbf{r}_1$ , and pointing in the direction of increased values of  $\theta$ . Similarly,

$$\nabla_2 \theta = (1/r_2) \mathbf{n} \times \hat{\mathbf{r}}_2 \equiv \mathbf{p}_2 / r_2 \quad (19b)$$

where  $\mathbf{p}_2$ , perpendicular to  $\mathbf{r}_2$  and in the plane of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , points again in the direction of increased  $\theta$  values. If we also consider variation at the other ends of the unit vectors that define  $\theta$ , applying the  $\nabla$  operator to  $\mathbf{r}_1$  and  $\mathbf{r}_2$  at the common tail ends, we find

$$\begin{aligned} \nabla_0 \theta &= (1/r_1) \mathbf{n} \times \hat{\mathbf{r}}_1 - (1/r_2) \mathbf{n} \times \hat{\mathbf{r}}_2 \\ &= -(\mathbf{p}_1 / r_1 + \mathbf{p}_2 / r_2) \end{aligned} \quad (19c)$$

so that  $\nabla_0 \theta + \nabla_1 \theta + \nabla_2 \theta = 0$ .

### Variations and covariances of vectors and distances

It is instructive to apply these developments to a few simple situations. Consider first the vector  $\mathbf{a} = \mathbf{r}_B - \mathbf{r}_A$  going from atom  $A$  to atom  $B$ . Then, since  $\nabla_A \mathbf{a} = -\mathbf{I}$  and  $\nabla_B \mathbf{a} = \mathbf{I}$ , we obtain from (14)

$$\Gamma(\mathbf{a}) = C^{AA} + C^{BB} - C^{AB} - C^{BA} \quad (20)$$

Similarly, since  $\nabla a = \hat{\mathbf{a}}$ , the chain rule of differentiation applied to (20) yields

$$\sigma^2(a) = \hat{\mathbf{a}} \cdot \Gamma(\mathbf{a}) \cdot \hat{\mathbf{a}} = \hat{\mathbf{a}} \cdot \mathbf{C}^{AA} \cdot \hat{\mathbf{a}} + \hat{\mathbf{a}} \cdot \mathbf{C}^{BB} \cdot \hat{\mathbf{a}} - 2\hat{\mathbf{a}} \cdot \mathbf{C}^{AB} \cdot \hat{\mathbf{a}} \quad (21)$$

where we have used the equality of  $\hat{\mathbf{a}} \cdot \mathbf{C}^{BA} \cdot \hat{\mathbf{a}}$  and  $\hat{\mathbf{a}} \cdot \mathbf{C}^{AB} \cdot \hat{\mathbf{a}}$ . The meaning of the terms on the right of (21) is that of 'components' of the dyadics concerned, in the direction of the vector  $\mathbf{a}$ . For example,  $\hat{\mathbf{a}} \cdot \mathbf{C}^{AB} \cdot \hat{\mathbf{a}}$  is the diagonal element  $C_{33}^{AB}$  of  $[\mathbf{C}^{AB}]$  in a Cartesian coordinate system in which the vector  $\mathbf{k}$  is equal to  $\hat{\mathbf{a}}$  while  $\mathbf{i}$  and  $\mathbf{j}$  are perpendicular to  $\hat{\mathbf{a}}$ . In this coordinate system the quantities  $(1/a^2) \Gamma_{ij}(\mathbf{a})$  with  $i, j=1$  or  $2$  are the variances and covariances of the angles that describe the direction of  $\mathbf{a}$  in planes containing, respectively, the vectors  $\mathbf{i}$  and  $\mathbf{k}$ , and  $\mathbf{j}$  and  $\mathbf{k}$ , while the quantities  $(1/a) \Gamma_{ij}(\mathbf{a})$  with  $i=3$  and  $j \neq 3$ , or with  $i \neq 3$  and  $j=3$  describe the covariances between these angles of orientation and the length  $a$ . More details about covariance dyadics of this kind are given in the later discussion of the orientation of plane normals. In oblique coordinate systems, or in Cartesian coordinate systems in which  $\mathbf{k}$  is not parallel to  $\mathbf{a}$ , the relationship between matrix elements and quantities such as  $\hat{\mathbf{a}} \cdot \mathbf{C} \cdot \hat{\mathbf{a}}$  is more complicated than just described, as is discussed in the Appendix.

For isotropic positional variances of the atoms and no interatomic covariance, the variance of  $a$  is  $\sigma_A^2 + \sigma_B^2$ , the variances of the angles describing the direction of  $\mathbf{a}$  are  $(\sigma_A^2 + \sigma_B^2)/a^2$ , and the covariances between these angles and the distance  $a$  vanish.

Let the position of a third atom  $C$  be given by  $\mathbf{r}_C$ , and introduce a vector  $\mathbf{b} = \mathbf{r}_C - \mathbf{r}_B$  going from atom  $B$  to atom  $C$ . Since  $\nabla_b \mathbf{b} = -\mathbf{I} = -\nabla_c \mathbf{b}$ , the covariance dyadic  $\Gamma(\mathbf{a}, \mathbf{b})$  of  $\mathbf{a}$  and  $\mathbf{b}$  is

$$\Gamma(\mathbf{a}, \mathbf{b}) = \mathbf{C}^{AB} - \mathbf{C}^{AC} - \mathbf{C}^{BB} + \mathbf{C}^{BC}. \quad (22)$$

As a check, the relationship

$$\Gamma(\mathbf{a} + \mathbf{b}) = \Gamma(\mathbf{a}) + \Gamma(\mathbf{b}) + \Gamma(\mathbf{a}, \mathbf{b}) + \Gamma(\mathbf{b}, \mathbf{a})$$

is found to be satisfied. Moreover, since  $\nabla a = \hat{\mathbf{a}}$  and  $\nabla b = \hat{\mathbf{b}}$ , the covariance between the distances  $a$  and  $b$  is

$$\text{cov}(a, b) = \hat{\mathbf{a}} \cdot \Gamma(\mathbf{a}, \mathbf{b}) \cdot \hat{\mathbf{b}} \quad (23)$$

which represents, so to speak, the interaction between the direction  $\hat{\mathbf{a}}$  and  $\hat{\mathbf{b}}$  as described by  $\Gamma(\mathbf{a}, \mathbf{b})$ . In the isotropic case

$$\text{cov}(a, b) = -\sigma_B^2(\hat{\mathbf{a}} \cdot \hat{\mathbf{b}}) = \sigma_B^2 \cos \varphi \quad (24)$$

where  $\varphi = \angle ABC$ ; that is,  $\varphi$  is the angle between  $-\mathbf{a}$  and  $\mathbf{b}$ . These results in their most general form were derived by Sands (1966; see also Cruickshank, 1959).

### Variances and covariances involving bond angles

We shall next consider the angles  $\alpha$ ,  $\beta$ , and  $\gamma$  defined by three atoms  $A$ ,  $B$ , and  $C$ , located at the endpoints of the vectors  $\mathbf{r}_A$ ,  $\mathbf{r}_B$ , and  $\mathbf{r}_C$  (Fig. 2). The interatomic vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are defined by  $\mathbf{c} = \mathbf{r}_B - \mathbf{r}_A$  and two

equations obtained from this one by the simultaneous cyclic permutations of  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  and  $A$ ,  $B$ ,  $C$ .

When  $\nabla_B(\alpha)$  is formed, the result is

$$\nabla_B(\alpha) = (1/c)\mathbf{p}_c \quad (25a)$$

with  $\mathbf{p}_c = \mathbf{n} \times \hat{\mathbf{c}}$ , where  $\mathbf{n} = (\hat{\mathbf{c}} \times \hat{\mathbf{b}})/\sin \alpha$ ; by vector algebra it also follows that  $\mathbf{p}_c = (\hat{\mathbf{b}} + \hat{\mathbf{c}} \cos \alpha)/\sin \alpha = -(\hat{\mathbf{a}} + \hat{\mathbf{c}} \cos \beta)/\sin \beta$ . The unit vector  $\mathbf{p}_c$  is in the plane  $ABC$ , perpendicular to  $\mathbf{c}$ , and points away from  $B$ . Similarly

$$\nabla_C(\alpha) = (1/b)\mathbf{p}_b \quad (25b)$$

and

$$\begin{aligned} \nabla_A(\alpha) &= -(1/c)\mathbf{p}_c - (1/b)\mathbf{p}_b \\ &= -(1/bc)(b\mathbf{p}_c + c\mathbf{p}_b) \end{aligned} \quad (25c)$$

where  $\mathbf{p}_b = \mathbf{n} \times \hat{\mathbf{b}} = (\hat{\mathbf{a}} + \hat{\mathbf{b}} \cos \gamma)/\sin \gamma = -(\hat{\mathbf{c}} + \hat{\mathbf{b}} \cos \alpha)/\sin \alpha$  is a unit vector in the plane  $ABC$ , perpendicular to  $\mathbf{b}$ , and points away from  $B$ . Considerations involving geometry (Fig. 2) and vector algebra reveal that  $-(b\mathbf{p}_c + c\mathbf{p}_b)$  is a vector of length  $a$ , directed from  $A$  to the center of the circle through  $A$ ,  $B$ ,  $C$ . The direction of this vector is not unexpected, because the variation of  $\alpha$  is zero when the position of  $A$  is varied tangentially to the circumscribed circle, in the plane  $ABC$ , or in a direction perpendicular to that plane; the gradient of  $\alpha$  is perpendicular to these two directions. If  $\mathbf{e}_A = (-\cos \gamma \hat{\mathbf{b}} + \cos \beta \hat{\mathbf{c}})/\sin \alpha$  denotes the unit vector pointing from  $A$  to the center of this circle, we have

$$a\mathbf{e}_A + c\mathbf{p}_b + b\mathbf{p}_c = 0 \quad (26)$$

and in terms of  $\mathbf{e}_A$ , (25c) becomes

$$\nabla_A(\alpha) = (a/bc)\mathbf{e}_A \quad (27)$$

and  $\nabla_A(\alpha) + \nabla_B(\alpha) + \nabla_C(\alpha) = 0$ .

We are now in a position to express the variance of  $\alpha$  by using (11), (25a, b) and (27):

$$\begin{aligned} \sigma^2(\alpha) &= \frac{a^2}{b^2 c^2} \mathbf{e}_A \cdot \mathbf{C}^{AA} \cdot \mathbf{e}_A + \frac{1}{c^2} \mathbf{p}_c \cdot \mathbf{C}^{BB} \cdot \mathbf{p}_c \\ &+ \frac{1}{b^2} \mathbf{p}_b \cdot \mathbf{C}^{CC} \cdot \mathbf{p}_b + \frac{2}{bc} \mathbf{p}_c \cdot \mathbf{C}^{BC} \cdot \mathbf{p}_b \\ &+ \frac{2a}{bc^2} \mathbf{e}_A \cdot \mathbf{C}^{AC} \cdot \mathbf{p}_b + \frac{2a}{bc^2} \mathbf{e}_A \cdot \mathbf{C}^{AB} \cdot \mathbf{p}_c. \end{aligned} \quad (28)$$

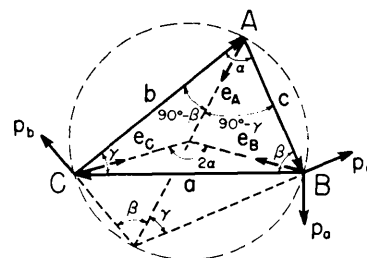


Fig. 2. Angles and vectors defined by three atoms  $A$ ,  $B$ , and  $C$ .

For isotropic positional variances the three 'atomic' terms are replaced by  $\sigma_A^2$ ,  $\sigma_B^2$ , and  $\sigma_C^2$ .

By cyclic permutation, (25a, b) and (27) can be extended to the angles  $\beta$  and  $\gamma$ . The results yield variances for these angles and, together with (12), covariances among them, such as for  $\alpha$  and  $\beta$ :

$$\begin{aligned} \text{cov}(\alpha, \beta) &= \frac{a}{bc^2} \mathbf{e}_A \cdot \mathbf{C}^{AA} \cdot \mathbf{p}_c + \frac{b}{ac^2} \mathbf{p}_c \cdot \mathbf{C}^{BB} \cdot \mathbf{e}_B \\ &+ \frac{1}{ab} \mathbf{p}_b \cdot \mathbf{C}^{CC} \cdot \mathbf{p}_a + \frac{1}{ac} (\mathbf{p}_c \cdot \mathbf{C}^{BC} \cdot \mathbf{p}_a + \mathbf{p}_b \cdot \mathbf{C}^{CB} \cdot \mathbf{e}_B) \\ &+ \frac{1}{bc} (\mathbf{e}_A \cdot \mathbf{C}^{AC} \cdot \mathbf{p}_a + \mathbf{p}_b \cdot \mathbf{C}^{CA} \cdot \mathbf{p}_c) \\ &+ \frac{1}{c^2} (\mathbf{e}_A \cdot \mathbf{C}^{AB} \cdot \mathbf{e}_B + \mathbf{p}_c \cdot \mathbf{C}^{BA} \cdot \mathbf{p}_c) \end{aligned} \quad (29)$$

where  $\mathbf{e}_B = (-\cos \alpha \hat{\mathbf{c}} + \cos \gamma \hat{\mathbf{a}}) / \sin \beta$  is a unit vector pointing from atom  $B$  to the center of the circumscribed circle, and  $\mathbf{p}_a = \mathbf{n} \times \hat{\mathbf{a}}$  is in the plane of the atoms considered, perpendicular to  $\mathbf{a}$ , and points away from  $A$ . In the isotropic case and if no interatomic covariance scalar products such as  $\mathbf{e}_A \cdot \mathbf{p}_c$  turn up, all of which equal  $-\cos \gamma$ , as shown by closer analysis (see Fig. 2), the result is

$$\text{cov}(\alpha, \beta) = -\cos \gamma \left( \frac{a\sigma_A^2}{bc^2} + \frac{b\sigma_B^2}{ac^2} + \frac{\sigma_C^2}{ab} \right).$$

Equation (28) is well known in absence of correlations among atomic positions (see *e.g.* Cruickshank, 1959; Darlow, 1960), while relationships equivalent to (28) and (29), in terms of variances and covariances between the distances  $a$ ,  $b$ , and  $c$ , were given by Sands (1966).

For the covariance between an angle and a bond vector, such as between  $\alpha$  and  $\mathbf{b}$ , we obtain

$$\Gamma(\alpha, \mathbf{b}) = \sum_{s,t} \nabla_s(\alpha) \cdot \mathbf{C}^{st} \cdot \nabla_t \mathbf{b}. \quad (30)$$

Noting that  $\nabla_A \mathbf{b} = \mathbf{I}$ ,  $\nabla_B \mathbf{b} = 0$ , and  $\nabla_C \mathbf{b} = -\mathbf{I}$ , we obtain

$$\begin{aligned} \Gamma(\alpha, \mathbf{b}) &= \frac{a}{bc} \mathbf{e}_A \cdot (\mathbf{C}^{AA} - \mathbf{C}^{AC}) \\ &+ \frac{1}{c} \mathbf{p}_c \cdot (\mathbf{C}^{BA} - \mathbf{C}^{BC}) + \frac{1}{b} \mathbf{p}_b \cdot (\mathbf{C}^{CA} - \mathbf{C}^{CC}) \end{aligned} \quad (31)$$

where  $\Gamma(\alpha, \mathbf{b})$  is a vector representing a  $1 \times 3$  covariance matrix. In the isotropic case and no covariance between atoms (31) takes the form

$$\Gamma(\alpha, \mathbf{b}) = \frac{a}{bc} \mathbf{e}_A \sigma_A^2 - \frac{1}{b} \mathbf{p}_b \sigma_C^2 \quad (32)$$

which indicates that the correlation described is along  $\mathbf{e}_A$  for atom  $A$  and along  $-\mathbf{p}_b$  for atom  $C$ .

To obtain  $\text{cov}(\alpha, b)$  we multiply (31) from the right by  $\nabla b = \hat{\mathbf{b}}$ ,

$$\begin{aligned} \text{cov}(\alpha, b) &= \Gamma(\alpha, \mathbf{b}) \cdot \hat{\mathbf{b}} = \frac{a}{bc} \mathbf{e}_A \cdot (\mathbf{C}^{AA} - \mathbf{C}^{AC}) \cdot \hat{\mathbf{b}} \\ &+ \frac{1}{c} \mathbf{p}_c \cdot (\mathbf{C}^{BA} - \mathbf{C}^{BC}) \cdot \hat{\mathbf{b}} + \frac{1}{b} \mathbf{p}_b \cdot (\mathbf{C}^{CA} - \mathbf{C}^{CC}) \cdot \hat{\mathbf{b}}. \end{aligned} \quad (33)$$

In the isotropic case the second term vanishes; we also find that  $\mathbf{e}_A \cdot \hat{\mathbf{b}} = -\sin \beta = -(b/a) \sin \alpha$  (see Fig. 2), and

$$\text{cov}(\alpha, b) = -(\sin \alpha / c) \sigma_A^2. \quad (34)$$

Similar considerations lead to

$$\begin{aligned} \text{cov}(\beta, b) &= \frac{1}{c} \mathbf{p}_c \cdot (\mathbf{C}^{AA} - \mathbf{C}^{AC}) \cdot \hat{\mathbf{b}} \\ &+ \frac{b}{ac} \mathbf{e}_B \cdot (\mathbf{C}^{BA} - \mathbf{C}^{BC}) \cdot \hat{\mathbf{b}} \\ &+ \frac{1}{a} \mathbf{p}_a \cdot (\mathbf{C}^{CA} - \mathbf{C}^{CC}) \cdot \hat{\mathbf{b}} \rightarrow \frac{\sin \alpha}{c} \sigma_A^2 + \frac{\sin \gamma}{a} \sigma_C^2 \\ \text{cov}(\gamma, b) &= \frac{1}{c} \mathbf{p}_b \cdot (\mathbf{C}^{AA} - \mathbf{C}^{AC}) \cdot \hat{\mathbf{b}} \\ &+ \frac{1}{a} \mathbf{p}_a \cdot (\mathbf{C}^{BA} - \mathbf{C}^{BC}) \cdot \hat{\mathbf{b}} \\ &+ \frac{c}{ab} \mathbf{e}_C \cdot (\mathbf{C}^{CA} - \mathbf{C}^{CC}) \cdot \hat{\mathbf{b}} \rightarrow -\frac{\sin \gamma}{a} \sigma_C^2 \end{aligned}$$

where the expressions at the ends of the arrows pertain to the isotropic case and no interatomic covariance. The covariances for angles are related, as are those for angles and distances, because  $\alpha + \beta + \gamma = 180^\circ$ ; *e.g.*

$$\sigma^2(\alpha) + \text{cov}(\alpha, \beta) + \text{cov}(\alpha, \gamma) = 0$$

and

$$\text{cov}(\alpha, b) + \text{cov}(\beta, b) + \text{cov}(\gamma, b) = 0.$$

### The plane through three atoms

To investigate the covariances that concern the orientation of a plane through the three atoms  $A$ ,  $B$ ,  $C$  (Fig. 2), we introduce the vector  $\mathbf{q} = \mathbf{b} \times \mathbf{a} = \mathbf{c} \times \mathbf{b} = \mathbf{a} \times \mathbf{c} = F\hat{\mathbf{q}}$  where  $\hat{\mathbf{q}}$  is a unit vector perpendicular to the plane considered. The length of  $\mathbf{q}$ , denoted by  $F$ , is twice the area of the triangle  $ABC$ ,  $F = ab \sin \gamma = bc \sin \alpha = ca \sin \beta$  ( $0 < \alpha, \beta, \gamma < 180^\circ$ ). In Fig. 2,  $\mathbf{q}$  is perpendicular to the plane of the drawing and points toward the viewer. Our goal is to find and analyze the covariance dyadic  $\Gamma(\mathbf{q})$ . Since the length of  $\mathbf{q}$  is  $F$ , we expect the component of  $\Gamma(\mathbf{q})$  in the direction of  $\mathbf{q}$  to be  $\sigma^2(F)$ . Perpendicular to  $\mathbf{q}$ ,  $\Gamma(\mathbf{q})$  should contain the variances and covariances of the angles describing the direction of  $\mathbf{q}$  (and thereby the orientation of the plane  $ABC$ ).

We find that  $\nabla_A \mathbf{q} = \mathbf{I} \times \mathbf{a}$ , while analogous results hold for  $\nabla_B \mathbf{q}$  and  $\nabla_C \mathbf{q}$ . Dyadics of the kind  $\mathbf{I} \times \mathbf{a}$  can be expressed alternatively by introducing an arbitrary

unit vector  $\mathbf{n}$  perpendicular to  $\mathbf{a}$ , and the unit vector  $\mathbf{p}_a = \mathbf{n} \times \hat{\mathbf{a}}$  that is perpendicular to both, whence  $\mathbf{I} = \hat{\mathbf{a}}\hat{\mathbf{a}} + \mathbf{nn} + \mathbf{p}_a\mathbf{p}_a$ . Execution of the cross products in  $\mathbf{I} \times \mathbf{a}$  then yields

$$\mathbf{I} \times \mathbf{a} = a(\mathbf{np}_a - \mathbf{p}_a\mathbf{n}) = \mathbf{a} \times \mathbf{I} = -\widetilde{\mathbf{I} \times \mathbf{a}} \quad (35a)$$

where  $\widetilde{\mathbf{I} \times \mathbf{a}}$  is the dyadic conjugate to  $\mathbf{I} \times \mathbf{a}$ . It also follows that

$$\widetilde{\mathbf{I} \times \mathbf{a}} \cdot \mathbf{I} \times \mathbf{a} = a^2(\mathbf{nn} + \mathbf{p}_a\mathbf{p}_a). \quad (35b)$$

Other aspects of  $\mathbf{I} \times \mathbf{a}$  are the equivalent forms of the scalar products with an arbitrary vector  $\mathbf{p}$

$$\begin{aligned} \mathbf{I} \times \mathbf{a} \cdot \mathbf{p} &\equiv \mathbf{I} \cdot \mathbf{a} \times \mathbf{p} \equiv \mathbf{a} \times \mathbf{p} \equiv \mathbf{p} \cdot \widetilde{\mathbf{I} \times \mathbf{a}} \\ \mathbf{p} \cdot \mathbf{I} \times \mathbf{a} &\equiv \mathbf{p} \times \mathbf{I} \cdot \mathbf{a} \equiv \mathbf{p} \times \mathbf{a} \equiv \widetilde{\mathbf{I} \times \mathbf{a}} \cdot \mathbf{p}. \end{aligned} \quad (35c)$$

Combinations that include the arbitrary dyadic  $\mathbf{C}$  may be reduced in a similar way:

$$\begin{aligned} \mathbf{p} \cdot \widetilde{\mathbf{I} \times \mathbf{a}} \cdot \mathbf{C} &= \mathbf{a} \times \mathbf{p} \cdot \mathbf{C} \\ \mathbf{C} \cdot \mathbf{I} \times \mathbf{a} \cdot \mathbf{p} &= \mathbf{C} \cdot \mathbf{a} \times \mathbf{p}. \end{aligned} \quad (35d)$$

Using some of these results and noting also that *e.g.*  $\widetilde{\nabla_A \mathbf{q}} = -\mathbf{a} \times \mathbf{I}$ , we find from (14)

$$\Gamma(\mathbf{q}) = \sum_A \sum_B -\mathbf{a} \times \mathbf{I} \cdot \mathbf{C}^{AB} \cdot \mathbf{I} \times \mathbf{b} \quad (36)$$

where the two sums range individually over all three atoms, and in each term the three vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are associated respectively with  $A$ ,  $B$ , and  $C$  in the manner exhibited by the term shown.

Turning for a moment to isotropic positional variances and setting  $\mathbf{n}$  equal to  $\hat{\mathbf{q}}$  in (35b) and in similar relationships for  $\mathbf{b}$  and  $\mathbf{c}$ , we find upon combination with (36)

$$\Gamma(\mathbf{q}) = \sigma^2(F)\hat{\mathbf{q}}\hat{\mathbf{q}} + a^2\sigma_A^2\mathbf{p}_a\mathbf{p}_a + b^2\sigma_B^2\mathbf{p}_b\mathbf{p}_b + c^2\sigma_C^2\mathbf{p}_c\mathbf{p}_c \quad (37)$$

with

$$\sigma^2(F) = a^2\sigma_A^2 + b^2\sigma_B^2 + c^2\sigma_C^2. \quad (38)$$

The coefficient of the dyad  $\hat{\mathbf{q}}\hat{\mathbf{q}}$  in (37) is the variance of the length  $F$  of  $\mathbf{q}$ , that is, of twice the area of the triangle  $ABC$ . The unit vector  $\mathbf{p}_a = \hat{\mathbf{q}} \times \hat{\mathbf{a}}$  is in the plane  $ABC$ , perpendicular to  $\mathbf{a}$ , and points away from  $A$ . The definitions and orientations of  $\mathbf{p}_b$  and  $\mathbf{p}_c$  are similar (Fig. 2). The portion of (37) not related to  $\hat{\mathbf{q}}\hat{\mathbf{q}}$  is therefore a planar dyadic, associated with the plane  $ABC$  perpendicular to  $\mathbf{q}$ . As shown below, it is just the diadic  $\Gamma(\hat{\mathbf{q}})$  that describes the orientation of  $\mathbf{q}$ , except for a factor  $1/F^2$ .

To extract  $\Gamma(\hat{\mathbf{q}})$  from (37) we consider  $\hat{\mathbf{q}}$  as a function of  $\mathbf{q}$  and note that  $\nabla(\hat{\mathbf{q}}) = (1/q)(\mathbf{I} - \hat{\mathbf{q}}\hat{\mathbf{q}})$ , so that

$$\Gamma(\hat{\mathbf{q}}) = (1/q^2)(\mathbf{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}) \cdot \Gamma(\mathbf{q}) \cdot (\mathbf{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}). \quad (39)$$

The portion of  $\Gamma(\mathbf{q})$  associated with the direction of  $\mathbf{q}$  is annihilated by this operation, with the result that

$$\Gamma(\hat{\mathbf{q}}) = \frac{\sigma_A^2}{h_a^2} \mathbf{p}_a\mathbf{p}_a + \frac{\sigma_B^2}{h_b^2} \mathbf{p}_b\mathbf{p}_b + \frac{\sigma_C^2}{h_c^2} \mathbf{p}_c\mathbf{p}_c \quad (40)$$

where  $h_a, h_b, h_c$  are the altitudes in the triangle  $ABC$  perpendicular on the sides  $a, b, c$  respectively, that is,  $h_a = F/a$ , etc.

To obtain  $\Gamma(\hat{\mathbf{q}})$  for the anisotropic general situation we combine (39) with (36) and note by use of (35a) that *e.g.*

$$(\mathbf{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}) \cdot \mathbf{a} \times \mathbf{I} = -a\mathbf{p}_a\mathbf{q}.$$

The final result is

$$\Gamma(\hat{\mathbf{q}}) = \sum_A \sum_B (1/h_a)\mathbf{p}_a\hat{\mathbf{q}} \cdot \mathbf{C}^{AB} \cdot \hat{\mathbf{q}}(1/h_b)\mathbf{p}_b \quad (41)$$

where the summation is analogous to that employed in (36),  $h_a$  and  $\mathbf{p}_a$  being associated with  $A$ ,  $h_b$  and  $\mathbf{p}_b$  with  $B$ , and  $h_c$  and  $\mathbf{p}_c$  with  $C$ . We see that this expression is entirely analogous to (40) and that the uncertainty in the direction of  $\hat{\mathbf{q}}$  is affected only by the atomic positional uncertainties in a direction perpendicular to the plane  $ABC$ .

To give  $\Gamma(\hat{\mathbf{q}})$  in component form, we introduce a right-handed Cartesian coordinate system with  $\mathbf{k} = \hat{\mathbf{q}}$ , and  $\mathbf{i}$  and  $\mathbf{j}$  perpendicular to  $\mathbf{k}$ , in which  $\alpha_x$  and  $\alpha_y$  are the directional cosines of  $\mathbf{a}$  relative to  $\mathbf{i}$  and  $\mathbf{j}$ , and similarly  $\beta_x, \beta_y$  and  $\gamma_x, \gamma_y$  those of  $\mathbf{b}$  and  $\mathbf{c}$ . Then  $\mathbf{p}_a$  has the directional cosines  $-\alpha_y, +\alpha_x$ , and those of  $\mathbf{p}_b$  and  $\mathbf{p}_c$  are  $-\beta_y, +\beta_x$ , and  $-\gamma_y, +\gamma_x$ . In addition, let  $\varphi_y$  be the angle of rotation about  $\mathbf{j}$  that describes the orientation of  $\mathbf{q}$  in the plane  $\mathbf{i}, \mathbf{k}$ , such as  $\varphi_y = 90^\circ$  relative to  $\mathbf{i}$ . Let  $\varphi_x$  be the similar angle about  $\mathbf{i}$ , in the plane  $\mathbf{j}, \mathbf{k}$ . Then  $\sigma^2(\varphi_y) = \Gamma_{11}(\hat{\mathbf{q}}) = \mathbf{i} \cdot \Gamma(\hat{\mathbf{q}}) \cdot \mathbf{i}$ ;  $\text{cov}(\varphi_x, \varphi_y) = \Gamma_{12}(\hat{\mathbf{q}}) = \mathbf{i} \cdot \Gamma(\hat{\mathbf{q}}) \cdot \mathbf{j}$ ; and  $\sigma^2(\varphi_x) = \Gamma_{22}(\hat{\mathbf{q}})$ . We obtain for these variances and covariances

$$\sigma^2(\varphi_y) = \sum_A \sum_B (\alpha_y/h_a)(\beta_y/h_b)C_{33}^{AB} \quad (42a)$$

$$\text{cov}(\varphi_x, \varphi_y) = \sum_A \sum_B -(\alpha_x/h_a)(\beta_y/h_b)C_{33}^{AB} \quad (42b)$$

$$\sigma^2(\varphi_x) = \sum_A \sum_B (\alpha_x/h_a)(\beta_x/h_b)C_{33}^{AB} \quad (42c)$$

where  $C_{33}^{AB}$  is the same as  $\hat{\mathbf{q}} \cdot \mathbf{C}^{AB} \cdot \hat{\mathbf{q}}$ , etc. Both sums are over all atoms, and  $\alpha$  and  $h_a$  are associated with  $A$ , etc.

### The variance of the torsion angle

Among the different possibilities of atomic arrangements of four atoms and the quantities associated with them, we shall consider only the torsion angle in a chain of 'bonded' atoms  $XABY$  (Fig. 3). We introduce the vectors  $\mathbf{q}_x = \mathbf{b} \times \mathbf{a}$  and  $\mathbf{q}_y = \mathbf{c} \times \mathbf{b}$ , which are analogous to the earlier vector  $\mathbf{q}$ . The angle enclosed by  $\mathbf{q}_x$  and  $\mathbf{q}_y$  is the torsion angle  $\tau$ , about  $\mathbf{b}$ , for which  $\cos \tau = \hat{\mathbf{q}}_x \cdot \hat{\mathbf{q}}_y$  and

$$\sin \tau = (\hat{\mathbf{a}} \times \hat{\mathbf{b}} \cdot \hat{\mathbf{c}}) / \sin \alpha \sin \beta \quad (43)$$

which also defines the sign of  $\tau$  (see *e.g.* Dunitz, 1968; Marsh & Waser, 1970).

The gradient dyadics of  $\mathbf{q}_\alpha$  and  $\mathbf{q}_\beta$  are

$$\begin{aligned} \nabla_X \mathbf{q}_\alpha &= \mathbf{I} \times \mathbf{b} & \nabla_A \mathbf{q}_\beta &= \mathbf{I} \times \mathbf{c} \\ \nabla_A \mathbf{q}_\alpha &= \mathbf{I} \times \mathbf{u} & \nabla_B \mathbf{q}_\beta &= \mathbf{I} \times \mathbf{v} \\ \nabla_B \mathbf{q}_\alpha &= \mathbf{I} \times \mathbf{a} & \nabla_Y \mathbf{q}_\beta &= \mathbf{I} \times \mathbf{b} \end{aligned} \quad (44)$$

where  $\mathbf{u} = -\mathbf{a} - \mathbf{b}$  and  $\mathbf{v} = -\mathbf{b} - \mathbf{c}$ . The following are then typical terms of the covariance dyadics that concern  $\mathbf{q}_\alpha$  and  $\mathbf{q}_\beta$ :

$$\begin{aligned} -\Gamma(\mathbf{q}_\alpha) &= \mathbf{b} \times \mathbf{I} \cdot \mathbf{C}^{XX} \cdot \mathbf{I} \times \mathbf{b} + \mathbf{b} \times \mathbf{I} \cdot \mathbf{C}^{XA} \cdot \mathbf{I} \times \mathbf{u} \\ &\quad + \mathbf{u} \times \mathbf{I} \cdot \mathbf{C}^{AX} \cdot \mathbf{I} \times \mathbf{b} + \dots \\ -\Gamma(\mathbf{q}_\beta) &= \mathbf{c} \times \mathbf{I} \cdot \mathbf{C}^{AA} \cdot \mathbf{I} \times \mathbf{c} + \mathbf{c} \times \mathbf{I} \cdot \mathbf{C}^{AB} \cdot \mathbf{I} \times \mathbf{v} \\ &\quad + \mathbf{v} \times \mathbf{I} \cdot \mathbf{C}^{BA} \cdot \mathbf{I} \times \mathbf{c} + \dots \\ -\Gamma(\mathbf{q}_\alpha, \mathbf{q}_\beta) &= \mathbf{b} \times \mathbf{I} \cdot \mathbf{C}^{XA} \cdot \mathbf{I} \times \mathbf{c} + \mathbf{b} \times \mathbf{I} \cdot \mathbf{C}^{XB} \cdot \mathbf{I} \times \mathbf{v} \\ &\quad + \mathbf{b} \times \mathbf{I} \cdot \mathbf{C}^{XY} \cdot \mathbf{I} \times \mathbf{b} + \dots \end{aligned} \quad (45)$$

The variation of the torsion angle  $\tau$  relative to  $\mathbf{q}_\alpha$  and  $\mathbf{q}_\beta$  can be found from (19a) and (19b), where we put  $\mathbf{f}_1 = \hat{\mathbf{q}}_\alpha$ ,  $\mathbf{f}_2 = \hat{\mathbf{q}}_\beta$ , and  $\mathbf{n} = \hat{\mathbf{b}}$ , resulting in

$$\nabla \mathbf{q}_\alpha(\tau) = \hat{\mathbf{p}}_1 / q_\alpha = -(\hat{\mathbf{b}} \times \hat{\mathbf{q}}_\alpha) / q_\alpha \quad (46a)$$

and

$$\nabla \mathbf{q}_\beta(\tau) = \hat{\mathbf{p}}_2 / q_\beta = (\hat{\mathbf{b}} \times \hat{\mathbf{q}}_\beta) / q_\beta. \quad (46b)$$

These equations result in

$$\begin{aligned} \sigma^2(\tau) &= \frac{1}{q_\alpha^2} \mathbf{p}_1 \cdot \Gamma(\mathbf{q}_\alpha) \cdot \mathbf{p}_1 + \frac{2}{q_\alpha q_\beta} \mathbf{p}_1 \cdot \Gamma(\mathbf{q}_\alpha, \mathbf{q}_\beta) \cdot \mathbf{p}_2 \\ &\quad + \frac{1}{q_\beta^2} \mathbf{p}_2 \cdot \Gamma(\mathbf{q}_\beta) \cdot \mathbf{p}_2. \end{aligned} \quad (47)$$

The combination of (45) and (47) leads to expressions such as  $\mathbf{p}_1 \cdot \mathbf{b} \times \mathbf{I} \cdot \mathbf{C}^{XA} \cdot \mathbf{I} \times \mathbf{c} \cdot \mathbf{p}_2 = \mathbf{p}_1 \times \mathbf{b} \cdot \mathbf{C}^{XA} \cdot \mathbf{c} \times \mathbf{p}_2$ . By vector algebra the needed pre- and postfactors can be transformed into

$$\begin{aligned} \mathbf{p}_1 \times \mathbf{a} &= a \cos \alpha \hat{\mathbf{q}}_\alpha & \mathbf{b} \times \mathbf{p}_2 &= -b \hat{\mathbf{q}}_\beta \\ \mathbf{p}_1 \times \mathbf{b} &= -b \hat{\mathbf{q}}_\alpha & \mathbf{c} \times \mathbf{p}_2 &= c \cos \beta \hat{\mathbf{q}}_\beta \\ \mathbf{p}_1 \times \mathbf{u} &= (b - a \cos \alpha) \hat{\mathbf{q}}_\alpha & \mathbf{v} \times \mathbf{p}_2 &= (b - c \cos \beta) \hat{\mathbf{q}}_\beta. \end{aligned} \quad (48)$$

With  $q_\alpha = ab \sin \alpha$  and  $q_\beta = bc \sin \beta$ , the final result for  $\sigma^2(\tau)$  turns out to be

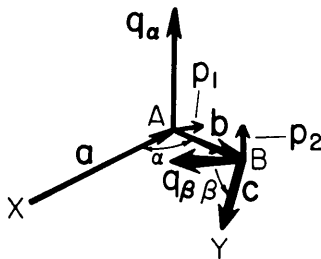


Fig. 3. Angles and vectors defined by a chain  $XABY$  of four atoms.

$$\begin{aligned} \sigma^2(\tau) &= \frac{XX_{\alpha\alpha}}{a^2 \sin^2 \alpha} - \frac{2XY_{\alpha\beta}}{ac \sin \alpha \sin \beta} + \frac{YY_{\beta\beta}}{c^2 \sin^2 \beta} \\ &\quad + \frac{2}{ab \sin \alpha} \left\{ -\frac{b-a \cos \alpha}{a \sin \alpha} XA_{\alpha\alpha} + \cot \beta XA_{\alpha\beta} \right. \\ &\quad \left. - \cot \alpha XB_{\alpha\alpha} + \frac{b-c \cos \beta}{c \sin \beta} XB_{\alpha\beta} \right\} \\ &\quad + \frac{2}{bc \sin \beta} \left\{ \frac{b-a \cos \alpha}{a \sin \alpha} YA_{\beta\alpha} - \cot \beta YA_{\beta\beta} \right. \\ &\quad \left. \times \cot \alpha YB_{\beta\alpha} - \frac{b-c \cos \beta}{c \sin \beta} YB_{\beta\beta} \right\} \\ &\quad + \frac{1}{b^2} \left\{ \left( \frac{b-a \cos \alpha}{a \sin \alpha} \right)^2 AA_{\alpha\alpha} + \frac{2(b-a \cos \alpha)}{a \sin \alpha} \right. \\ &\quad \left. \times \cot \beta (-AA_{\alpha\beta} + AB_{\alpha\alpha}) + \cot^2 \beta AA_{\beta\beta} \right. \\ &\quad \left. - \frac{2}{ac \sin \alpha \sin \beta} [(b-a \cos \alpha)(b-c \cos \beta) AB_{\alpha\beta} \right. \\ &\quad \left. + \cot \alpha \cot \beta BA_{\alpha\beta}] + \cot^2 \alpha BB_{\alpha\alpha} \right. \\ &\quad \left. + \frac{2(b-c \cos \beta)}{c \sin \beta} \cot \alpha (BA_{\beta\beta} - BB_{\beta\alpha}) \right. \\ &\quad \left. + \left( \frac{b-c \cos \beta}{c \sin \beta} \right)^2 BB_{\beta\beta} \right\}. \end{aligned} \quad (49)$$

We have used abbreviations such as  $XA_{\alpha\beta}$  to denote  $\hat{\mathbf{q}}_\alpha \cdot \mathbf{C}^{XA} \cdot \hat{\mathbf{q}}_\beta$ . Note that  $AB_{\alpha\beta}$  and  $BA_{\alpha\beta}$  are not the same quantities while *e.g.*  $AB_{\alpha\beta}$  and  $BA_{\beta\alpha}$  are, because  $\mathbf{C}^{AB}$  and  $\mathbf{C}^{BA}$  are conjugate dyadics. When all positional atomic variances are isotropic and there are no covariances between different atoms, 'atomic' terms such as  $AA_{\alpha\alpha}$  and  $AA_{\beta\beta}$  become equal to  $\sigma_A^2$  and  $AA_{\alpha\beta}$  to  $\sigma_A^2(\hat{\mathbf{q}}_\alpha \cdot \hat{\mathbf{q}}_\beta) = \sigma_A^2 \cos \tau$ , while 'interaction' terms such as  $AB_{\alpha\alpha}$  are zero. The result is an equation published earlier (P. J. Huber in Huber-Buser & Dunitz, 1961; Stanford & Waser, 1971).

An interesting case of covariance is that caused among atomic positions by symmetry. Let, for example, atoms  $X$  and  $Y$  and atoms  $A$  and  $B$  be related by a twofold axis. Equation (49) can then be simplified by the methods described by Sands (1966) (note that the twofold axis relates  $\mathbf{q}_\alpha$  and  $-\mathbf{q}_\beta$ ), with the result

$$\begin{aligned} \sigma^2(\tau) &= \frac{4XX_{zz}}{a^2 \sin^2 \alpha} + \frac{8}{ab \sin \alpha} \left\{ -\frac{b-a \cos \alpha}{a \sin \alpha} XA_{\alpha\alpha} \right. \\ &\quad \left. + \cot \alpha XA_{\alpha\beta} \right\} + \frac{4}{b^2} \left\{ \left( \frac{b-a \cos \alpha}{a \sin \alpha} \right)^2 AA_{\alpha\alpha} \right. \\ &\quad \left. - \frac{2(b-a \cos \alpha)}{a \sin \alpha} \cot \alpha AA_{\alpha\beta} + \cot^2 \alpha AA_{\beta\beta} \right\} \\ &\quad \rightarrow \frac{4\sigma_X^2}{a^2 \sin^2 \alpha} + \frac{4\sigma_A^2}{b^2} \left\{ \left( \frac{b-a \cos \alpha}{a \sin \alpha} \right)^2 \right. \\ &\quad \left. - \frac{2(b-a \cos \alpha)}{a \sin \alpha} \cot \alpha \cos \tau + \cot^2 \alpha \right\}. \end{aligned} \quad (50)$$

It can be seen that if  $\sigma^2(\tau)$  had been calculated without the covariances of symmetry-related atoms, the result would have been too small by a factor of 2, or the standard deviation by a factor of  $\sqrt{2}$ .

### The best plane through a set of atoms

To treat the best plane through  $N$  atoms ( $N \geq 3$ ) we proceed from the results described by Schomaker, Waser, Marsh & Bergman (1959), except that we use dyadics instead of matrices, so that the metric tensor does not appear explicitly. We begin with a summary of the pertinent results of that paper. The equation of a plane at a distance  $d$  from the origin is

$$\mathbf{r} \cdot \mathbf{m} = d \quad (51)$$

where  $\mathbf{m}$  is a unit vector perpendicular to the plane. Let the atoms to which such a plane is to be fitted have the positions  $\mathbf{r}^s$ ,  $s = 1, 2, \dots, N$ , and let the weights  $w_s$  be attached to them. These weights may be chosen inversely proportional to  $\mathbf{m} \cdot \mathbf{C}^{ss} \cdot \mathbf{m}$ , the positional variances perpendicular to the plane, or in any other suitable way. The distance of atom  $s$  from the plane is  $\mathbf{r}^s \cdot \mathbf{m} - d$ , and  $\mathbf{m}$  and  $d$  must by definition of the best plane satisfy the condition that the weighted sum of the squares of these distances is a minimum:

$$S = \sum w_s (\mathbf{r}^s \cdot \mathbf{m} - d)^2 \equiv [w(\mathbf{r} \cdot \mathbf{m} - d)^2] = \text{min}. \quad (52)$$

We are using here and later the Gaussian bracket,  $[\ ]$ , to indicate summation over all atoms. [An  $\mathbf{r}$  in such a bracket refers to a positional vector  $\mathbf{r}^s$ , rather than being an arbitrary vector as in (51).] The solution to the problem posed by (52), with the subsidiary condition that  $|\mathbf{m}| = 1$ , leads to

$$d = \mathbf{m} \cdot \langle \mathbf{r} \rangle \quad (53)$$

where

$$\langle \mathbf{r} \rangle = [w\mathbf{r}]/[w] \quad (54)$$

is the centroid of the weighted atomic positions, and the symbol  $\langle \ \rangle$  denotes the weighted average. Moreover,  $\mathbf{m}$  is a solution of the equation

$$\mathbf{A} \cdot \mathbf{m} = \lambda \mathbf{m} \quad (55)$$

where

$$\mathbf{A} = [w\mathbf{R}\mathbf{R}] \equiv \sum w_s \mathbf{R}^s \mathbf{R}^s \quad (56)$$

and  $\mathbf{R}^s = \mathbf{r}^s - \langle \mathbf{r} \rangle$ ;  $\lambda$  is the smallest eigenvalue of the determinantal equation

$$||\mathbf{A} - \lambda \mathbf{I}|| = 0. \quad (57)$$

By the relationship

$$\lambda = \mathbf{m} \cdot \mathbf{A} \cdot \mathbf{m} = [w(\mathbf{m} \cdot \mathbf{R})(\mathbf{R} \cdot \mathbf{m})] = [w(\mathbf{m} \cdot \mathbf{R})^2] = S_{\text{min}} \quad (58)$$

$\lambda$  is the minimum value of the sum of the weighted squares of the distances.

If  $\nabla_t$  is the del operator relative to  $\mathbf{r}^t$ , then  $\nabla_t \langle \mathbf{r} \rangle = (w_t/[w])\mathbf{I}$ , and

$$\nabla_t \mathbf{R}^k = (\delta_{tk} - w_t/[w])\mathbf{I}. \quad (59)$$

Applying  $\nabla_t$  to (53) yields

$$\nabla_t d = \nabla_t \mathbf{m} \cdot \langle \mathbf{r} \rangle + w_t \mathbf{m} / [w] \quad (60)$$

where  $\nabla_t \mathbf{m}$  is yet to be related to known quantities. One equation for  $\nabla_t \mathbf{m}$  follows from applying  $\nabla_t$  to  $\mathbf{m} \cdot \mathbf{m} = 1$ ,

$$\nabla_t \mathbf{m} \cdot \mathbf{m} = 0 \quad (61)$$

so that the consequents of  $\nabla_t \mathbf{m}$  must be perpendicular to  $\mathbf{m}$ . From (58) and (59)

$$\begin{aligned} \nabla_t \lambda = \nabla_t \sum w_s (\mathbf{m} \cdot \mathbf{R}^s)^2 &= 2 \nabla_t \mathbf{m} \cdot \sum w_s \mathbf{R}^s (\mathbf{R}^s \cdot \mathbf{m}) \\ &+ 2 w_t \mathbf{m} \{ (\mathbf{m} \cdot \mathbf{R}^t) - \sum w_s (\mathbf{R}^s \cdot \mathbf{m}) \}. \end{aligned}$$

The first term on the far right equals, by (56) and (55),  $2 \nabla_t \mathbf{m} \cdot \mathbf{A} \cdot \mathbf{m} = 2 \lambda \nabla_t \mathbf{m} \cdot \mathbf{m}$ , which is zero, by (61). The second term in the brace also vanishes, because  $[w\mathbf{R}] = 0$ . Hence

$$\nabla_t \lambda = 2 w_t (\mathbf{m} \cdot \mathbf{R}^t) \mathbf{m} \quad (62)$$

where  $(\mathbf{m} \cdot \mathbf{R}^t)$  is the distance of atom  $t$  from the plane. The gradient  $\nabla_t \lambda$  has therefore the direction  $\mathbf{m}$  and is not affected by a change of  $\mathbf{m}$  through variation of  $\mathbf{r}^t$ .

Another relationship for  $\nabla_t \mathbf{m}$  follows from using  $\nabla_t$  on both sides of (55). Operating with  $\nabla_t$  on  $\mathbf{A} \cdot \mathbf{m} = \sum w_s \mathbf{R}^s (\mathbf{R}^s \cdot \mathbf{m})$  yields, after some manipulation

$$\nabla_t (\mathbf{A} \cdot \mathbf{m}) = \nabla_t \mathbf{m} \cdot \mathbf{A} + w_t \{ \mathbf{m} \mathbf{R}^t + (\mathbf{m} \cdot \mathbf{R}^t) \mathbf{I} \}. \quad (63)$$

For the right side of (55) we obtain, using (62)

$$\nabla_t (\lambda \mathbf{m}) = 2 w_t (\mathbf{m} \cdot \mathbf{R}^t) \mathbf{m} \mathbf{m} + \lambda \nabla_t \mathbf{m}. \quad (64)$$

Equating (63) and (64) yields the following equation for  $\nabla_t \mathbf{m}$ :

$$\nabla_t \mathbf{m} \cdot (\mathbf{A} - \lambda \mathbf{I}) = w_t \{ (\mathbf{m} \cdot \mathbf{R}^t) (2 \mathbf{m} \mathbf{m} - \mathbf{I}) - \mathbf{m} \mathbf{R}^t \}. \quad (65)$$

The dyadic  $(\mathbf{A} - \lambda \mathbf{I})$  is planar, since  $\lambda$  has been specifically chosen to this end, being the eigenvalue for which  $\mathbf{m}$  is an eigenvector of  $\mathbf{A}$ . Equation (65) can be solved for  $\nabla_t \mathbf{m}$  only in the plane orthogonal to  $\mathbf{m}$ , but that is all that is required, because  $\nabla_t \mathbf{m}$  is itself a planar dyadic, by (61). We select a coordinate system with  $\mathbf{k} = \mathbf{m}$ , choosing  $\mathbf{i}$  and  $\mathbf{j}$  in such a way that  $\mathbf{A}$  has only terms in  $\mathbf{ii}$ ,  $\mathbf{jj}$ ,  $\mathbf{kk}$ . The directions  $\mathbf{i}$  and  $\mathbf{j}$  correspond to normals on the planes called by Schomaker *et al.* (1959) the 'worst' and the 'intermediate' planes. If  $X^s$ ,  $Y^s$ , and  $Z^s$  are the components of  $\mathbf{R}^s$ , we find

$$\mathbf{A} - \lambda \mathbf{I} = [w(X^2 - Z^2)]\mathbf{ii} + [w(Y^2 - Z^2)]\mathbf{jj}. \quad (66)$$

Equations (65) and (61) can now be solved for  $\nabla_t \mathbf{m}$  in terms of the coefficients of all dyads that involve  $\mathbf{i}$ ,  $\mathbf{j}$ , and  $\mathbf{k}$ , with the result

$$\nabla_t \mathbf{m} = -w_t \left\{ \frac{Z^t \mathbf{ii} + X^t \mathbf{ki}}{[w(X^2 - Z^2)]} + \frac{Z^t \mathbf{jj} + Y^t \mathbf{kj}}{[w(Y^2 - Z^2)]} \right\}. \quad (67)$$

The numerators on the right side of (67) can be expressed in terms of the second moments of the atom positions relative to the centroid,  $\langle X^2 \rangle$ ,  $\langle Y^2 \rangle$ , and  $\langle Z^2 \rangle$ , defined by equations of the form

$$\langle X^2 \rangle = [wX^2]/[w], \quad (68)$$



in terms of which

$$\nabla_t \mathbf{m} = \frac{w_t}{[w]} \left\{ \frac{Z^t \mathbf{i} + X^t \mathbf{k}}{\langle X^2 \rangle - \langle Z^2 \rangle} (-\mathbf{i}) + \frac{Z^t \mathbf{j} + Y^t \mathbf{k}}{\langle Y^2 \rangle - \langle Z^2 \rangle} (-\mathbf{j}) \right\}. \quad (69)$$

It is instructive to consider the details of the right side of (69). The factor  $w_t/[w]$  is the weight associated with atom  $t$ , normalized to 1. With the abbreviations

$$\begin{aligned} \xi^t &= \frac{Z^t \mathbf{i} + X^t \mathbf{k}}{\langle X^2 \rangle - \langle Z^2 \rangle} \\ \eta^t &= \frac{Z^t \mathbf{j} + Y^t \mathbf{k}}{\langle Y^2 \rangle - \langle Z^2 \rangle} \end{aligned} \quad (70)$$

we have

$$\nabla_t \mathbf{m} = (w_t/[w]) \{ \xi^t (-\mathbf{i}) + \eta^t (-\mathbf{j}) \}. \quad (71)$$

If the position of atom  $t$  is changed by  $d\mathbf{r}^t$ , the change  $d\mathbf{m}$  of  $\mathbf{m}$  is given by

$$d\mathbf{m} = d\mathbf{r}^t \cdot \nabla_t \mathbf{m} = -(w_t/[w]) \{ (\xi^t \cdot d\mathbf{r}^t) \mathbf{i} + (\eta^t \cdot d\mathbf{r}^t) \mathbf{j} \}. \quad (72)$$

The upper right portion of Fig. 4 illustrates a situation in which  $d\mathbf{r}^t$  is in the  $x, z$  plane, so that  $d\mathbf{m} = -(w_t/[w]) \xi^t \cos \theta d\mathbf{r}^t$ . Note that when atom  $t$  is moved in the direction  $+\mathbf{k}$ , the orientation of the best plane changes so as to tilt  $\mathbf{m}$  towards the left; the direction of  $d\mathbf{m}$  is then  $-\mathbf{i}$ . When atom  $t$  is moved in the direction  $+\mathbf{i}$ , the orientation of the plane is affected in a similar way, but the effect is less by a factor  $Z^t/X^t$  than is the effect of a motion in the direction  $+\mathbf{k}$ ,  $Z^t$  and  $X^t$  acting as respective lever arms. The factor  $(\langle X^2 \rangle - \langle Z^2 \rangle)^{-1}$  in  $\xi^t$  shows the stabilizing influence of a large value of  $\langle X^2 \rangle$  and a small value of  $\langle Z^2 \rangle$  on the orientation of the plane. In the  $yz$  plane the situation is analogous.

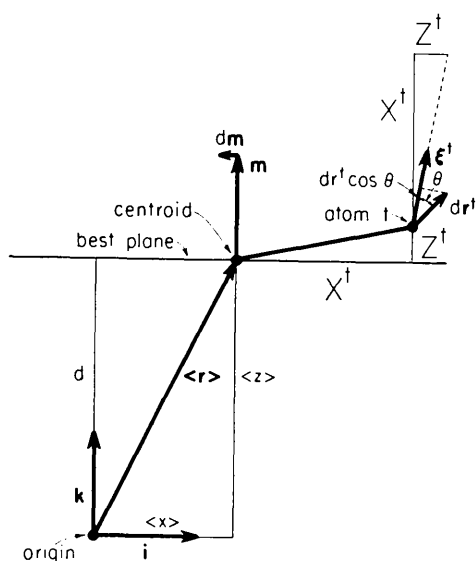


Fig. 4. Effect of the change of an atomic position on the parameters of a best plane.

As already stated,  $\nabla_t \mathbf{m}$  is a planar dyadic; the plane of its antecedents is extended by  $\xi^t$  and  $\eta^t$ , and the  $xy$  plane is the plane of its consequents. For atoms for which  $Z^t$  is zero,  $\nabla_t \mathbf{m}$  is axial (or almost axial when  $Z^t \ll X^t, Y^t$ ), the direction of the antecedent being  $\mathbf{k}$  and that of the consequent  $-(X^t/\langle X^2 \rangle) \mathbf{i} - (Y^t/\langle Y^2 \rangle) \mathbf{j}$ .

Returning to (60), (69), and (71), we find

$$\nabla_t d = \frac{w_t}{[w]} \{ \mathbf{k} - \langle x \rangle \xi^t - \langle y \rangle \eta^t \}. \quad (73)$$

The change in  $d$  caused by a change  $d\mathbf{r}^t$  in  $\mathbf{r}^t$  is given by

$$d\mathbf{r}^t \cdot \nabla_t d = (w_t/[w]) \{ dz^t - \langle x \rangle d\mathbf{r}^t \cdot \xi^t - \langle y \rangle d\mathbf{r}^t \cdot \eta^t \}.$$

The first term represents the direct effect of the change, as can be seen by tracing the origin of this term, or directly by noting that the other terms vanish when  $\langle x \rangle = \langle y \rangle = 0$ , so that the centroid lies on the  $z$  axis. The other terms come about because changes of orientation of the plane cause changes in  $d$  that are proportional to the lever arms  $\langle x \rangle$  and  $\langle y \rangle$ , as can be seen in Fig. 4 for the case that  $d\mathbf{r}^t$  is in the  $xz$  plane.

In terms of the vectors  $\xi^t$  and  $\eta^t$  we find the following formulas for the covariances involving  $\mathbf{m}$  and  $d$ :

$$\begin{aligned} \Gamma(\mathbf{m}) &= \frac{1}{[w]^2} \sum_s \sum_t w_s w_t \{ (\xi^s \cdot \mathbf{C}^{st} \cdot \xi^t) \mathbf{ii} \\ &+ (\xi^s \cdot \mathbf{C}^{st} \cdot \eta^t) (\mathbf{ij} + \mathbf{ji}) + (\eta^s \cdot \mathbf{C}^{st} \cdot \eta^t) \mathbf{jj} \}. \end{aligned} \quad (74)$$

The coefficients of  $\mathbf{ii}$  and  $\mathbf{jj}$  represent the respective variances of the angles  $\varphi$ , and  $\varphi_x$  describing the orientation of the plane normal  $\mathbf{m}$  (or of the components  $m_x$  and  $m_y$  of  $\mathbf{m}$ ), as discussed for the case of three atoms in connection with equations (42). The coefficient of  $\mathbf{ij}$  or  $\mathbf{ji}$  contains the covariance between  $\varphi_x$  and  $\varphi_y$ . The main contributions to  $\Gamma(\mathbf{m})$  are from the components of the atomic positional variances that are perpendicular to the plane considered, but there are also small contributions from these variances in other directions. Detailed analysis shows that for a plane through three atoms the present approach yields the same results for the variances and covariance of  $\varphi_x$  and  $\varphi_y$  as is given by (42a, b, c), provided that unit weights for the three atoms are used; note also that all  $Z^t$  are zero for three atoms. Variances and covariances of other angles that describe the direction of  $\mathbf{m}$  are discussed in the Appendix.

For the variance of  $d$  the result is

$$\begin{aligned} \sigma^2(d) &= \frac{1}{[w]^2} \sum_s \sum_t w_s w_t \{ (\mathbf{k} - \langle x \rangle \xi^s \\ &- \langle y \rangle \eta^s) \cdot \mathbf{C}^{st} \cdot (\mathbf{k} - \langle x \rangle \xi^t - \langle y \rangle \eta^t) \} \end{aligned} \quad (75)$$

where the direct contributions by the atomic positional variances and covariances are manifest in the terms with  $\mathbf{k}$ , while the other terms represent indirect contributions through the variance of  $\mathbf{m}$ . The indirect contributions vanish when  $\langle x \rangle$  and  $\langle y \rangle$  happen to be zero, that is, when the centroid of the points lies on

the  $z$  axis, but these terms can also completely overshadow the direct contributions.

Finally, the covariance between  $d$  and  $\mathbf{m}$  is described by

$$\Gamma(d, \mathbf{m}) = \frac{1}{[w]^2} \sum_s \sum_t w_s w_t \{ (-\mathbf{k} + \langle x \rangle \xi^s + \langle y \rangle \eta^s) \cdot \mathbf{C}^{st} \cdot \xi^t \mathbf{j} + \{ (-\mathbf{k} + \langle x \rangle \xi^s + \langle y \rangle \eta^s) \cdot \mathbf{C}^{st} \cdot \eta^t \} \mathbf{j} \}, \quad (76)$$

where the coefficient of  $\mathbf{i}$  is  $\text{cov}(d, \varphi_y)$  and that of  $\mathbf{j}$  is  $\text{cov}(d, \varphi_x)$ . For the case of isotropic positional variances and no covariances between different atoms, explicit formulas for the covariances among  $\mathbf{m}$  and  $d$  were recently published, together with two numerical examples (Waser, Marsh & Cordes, 1973).

The foregoing developments may be applied to the standard deviation of the dihedral angle  $\theta$  between two 'best' planes. To distinguish the two planes we shall use primes for all quantities associated with the second plane. The angle  $\theta$  is defined by the two plane normals  $\mathbf{m}$  and  $\mathbf{m}'$ , and its variance can be derived from the quantities  $\Gamma(\mathbf{m})$ ,  $\Gamma(\mathbf{m}')$ , and  $\Gamma(\mathbf{m}, \mathbf{m}')$ , the first of which is given by (74) and the second by a similar expression, in which all quantities have primes; the formula for  $\Gamma(\mathbf{m}, \mathbf{m}')$  is [in slightly more compact form than (74)]

$$\Gamma(\mathbf{m}, \mathbf{m}') = \frac{1}{[w][w']} \sum_s \sum_{t'} w_s w_{t'} (\mathbf{i} \xi^s + \mathbf{j} \eta^s) \times \mathbf{C}^{st'} \cdot (\xi^{t'} \mathbf{i}' + \eta^{t'} \mathbf{j}'). \quad (77)$$

The index  $s$  runs over all atoms in the first plane and the index  $t'$  over all atoms in the second plane; some atoms may be common to both planes. To find  $\sigma^2(\theta)$  we proceed as in (47) and shall need products such as  $\mathbf{p} \cdot \Gamma(\mathbf{m}, \mathbf{m}') \cdot \mathbf{p}'$ , where  $\mathbf{p}$  and  $\mathbf{p}'$  are unit vectors analogous to the vectors  $\mathbf{p}_1$  and  $\mathbf{p}_2$  introduced in connection with equations (19). In terms of the vectors  $\mathbf{k}$  and  $\mathbf{k}'$  of the orthogonal coordinate systems associated with the two planes

$$\begin{aligned} \mathbf{p} &= \mathbf{k} \cot \theta - (\mathbf{k}' / \sin \theta) \\ \mathbf{p}' &= \mathbf{k}' \cot \theta - (\mathbf{k} / \sin \theta). \end{aligned}$$

It turns out that in the required scalar products the parts of  $\mathbf{p}$  and  $\mathbf{p}'$  associated with  $\cot \theta$  make no contribution, because of orthogonality, with the result that

$$\sigma^2(\theta) = (1/\sin \theta)^2 \{ \mathbf{k}' \cdot \Gamma(\mathbf{m}) \cdot \mathbf{k}' + \mathbf{k} \cdot \Gamma(\mathbf{m}') \cdot \mathbf{k} + 2\mathbf{k} \cdot \Gamma(\mathbf{m}, \mathbf{m}') \cdot \mathbf{k}' \}.$$

Explicit formulas for the isotropic case and zero interatomic covariances, as well as a numerical example, are available (Waser, Marsh & Cordes, 1973). When the two planes are related by a twofold axis the situation is analogous to that described for torsion angles. That is, if all symmetry-induced covariances between different atoms are simply ignored, the resulting  $\sigma^2(\theta)$  is too small by a factor of 2.

I wish to thank Robert S. Deverill, Richard E. Marsh, and Richard H. Stanford Jr for helpful discussions.

## APPENDIX

### Covariance matrices, tensors and dyadics

In this Appendix we briefly consider the relationship between the components of a covariance matrix and the corresponding tensor and dyadic. Let the covariance matrix of the coordinates of an atom in two different coordinate frames  $\mathbf{a}_i$  and  $\bar{\mathbf{a}}_r$  ( $i, r = 1, 2, 3$ ) be  $[\mathbf{C}]$  and  $[\bar{\mathbf{C}}]$  with the respective elements  $C^{ij}$  and  $\bar{C}^{rs}$ . Let the transformation between the two coordinate sets  $x^i$  and  $\bar{x}^r$  be

$$x^i = t_r^i \bar{x}^r$$

to which the transformation of the axes is contragredient

$$\bar{\mathbf{a}}_r = t_r^i \mathbf{a}_i.$$

The matrix elements  $C^{ij}$  and  $\bar{C}^{rs}$  are then related by a propagation-of-error formula of the form (5)

$$C^{ij} = \frac{\partial x_i}{\partial \bar{x}_r} \frac{\partial x_j}{\partial \bar{x}_s} \bar{C}^{rs} = t_r^i t_s^j \bar{C}^{rs}$$

which shows that the matrix elements  $C^{ij}$  are the contravariant components\* of a tensor (which is the reason for the upper indices in  $C^{ij}$  and  $x^i$ , a usage that we restrict to this Appendix). It follows that the covariance dyadic

$$\mathbf{C} \equiv C^{ij} \mathbf{a}_i \mathbf{a}_j = t_r^i t_s^j \bar{C}^{rs} \mathbf{a}_i \mathbf{a}_j = \bar{C}^{rs} \bar{\mathbf{a}}_r \bar{\mathbf{a}}_s$$

has the same form for different axes of reference, which justifies its introduction. The same considerations apply to covariances between the coordinates of different atoms, or between the components of the same vector or of two different vectors. The coefficients  $C^{ij}$  are called contravariant nonionic components of the dyadic  $\mathbf{C}$ . Such dyadics may also be given in terms of mixed or of covariant† components, in combination with reciprocal vectors  $\mathbf{b}^m$ :

$$\mathbf{C} = C_m^i \mathbf{a}_i \mathbf{b}^m = C_m^i \mathbf{b}^m \mathbf{a}_i = C_{nm} \mathbf{b}^n \mathbf{b}^m$$

where  $C_m^i = g_{mj} C^{ij}$ ,  $C_m^i = g_{mj} C^{ji}$ ,  $C_{nm} = g_{ni} g_{mj} C^{ij}$ ,  $g_{nm} = \mathbf{a}_n \cdot \mathbf{a}_m$ . When  $C^{ij} = C^{ji}$ , as e.g. for the covariances between the coordinates of an atom, then  $C_m^i = C^i_m$  and  $C_{nm} = C_{mn}$ . For isotropic positional variances,  $C^{ij} = g^{ij} \sigma^2$ ,  $C_m^i = \delta_{im} \sigma^2$  and  $C_{nm} = g_{nm} \sigma^2$ , where  $g^{ij} = \mathbf{b}^i \cdot \mathbf{b}^j$  (see e.g. Templeton, 1959). This implies that the identity dyadic is of the form  $\mathbf{I} = \mathbf{a}_i \mathbf{b}^i = \mathbf{b}^i \mathbf{a}_i = g^{ij} \mathbf{a}_i \mathbf{a}_j = g_{ij} \mathbf{b}^i \mathbf{b}^j$ . In terms of the crystallographic coordinates  $x^i$  associated with the axes  $\mathbf{a}_i$ ,  $\nabla$  has the form  $\nabla = \mathbf{b}^i \partial / \partial x^i$ .

\* The same transformation properties are found when the positional covariance matrix is recognized as being the inverse of the matrix  $[\mathbf{V}]$  in the exponent  $-\frac{1}{2} V_{ij} x^i x^j$  of the multivariate Gaussian that describes the positional uncertainty of a given atom. As indicated, e.g., by Cerrini [1971, especially equations (2) and (3)], it follows that  $[C^{ij}] = [V_{ij}]^{-1}$  transforms in a contravariant manner.

† The confluence of ideas from different fields leads at times to juxtapositions of quite unrelated meanings of the same word as those of 'covariance'.

Suppose then that the quantity  $\mathbf{n} \cdot \mathbf{C} \cdot \mathbf{m}$  is needed, where  $\mathbf{n} = v^i \mathbf{a}_i$  and  $\mathbf{m} = \mu^i \mathbf{a}_i$  are unit vectors with the contravariant components  $v^i$  and  $\mu^i$ . We find

$$\mathbf{n} \cdot \mathbf{C} \cdot \mathbf{m} = v^i (\mathbf{a}_i \cdot \mathbf{a}_s) C^{st} (\mathbf{a}_t \cdot \mathbf{a}_j) \mu^j = v^i \mu^j g_{is} g_{jt} C^{st}.$$

We may also use the covariant components of the covariance tensor, or indeed the covariant components of  $\mathbf{n}$  and  $\mathbf{m}$  (e.g.,  $v_s = g_{is} v^i$ ), in terms of which

$$\mathbf{n} \cdot \mathbf{C} \cdot \mathbf{m} = v^i \mu^j C_{ij} = v_i \mu_j C^{ij} = v_i \mu^j C^i_j.$$

A related transformation problem concerns the angles  $\varphi_x$  and  $\varphi_y$  that describe the orientation of the normal  $\mathbf{m}$  of a best plane. Suppose that the direction of  $\mathbf{m}$  is characterized by angles of rotation  $\varphi_u$  and  $\varphi_v$  about unit vectors  $\mathbf{u}$  and  $\mathbf{v}$  other than  $\mathbf{i}$  and  $\mathbf{j}$ , but also perpendicular to  $\mathbf{m}$ , and that we wish to know the variances and covariance of these angles. Let  $\chi$  be the angle between  $\mathbf{u}$  and  $\mathbf{i}$ ,  $\psi$  the angle between  $\mathbf{v}$  and  $\mathbf{i}$ , and  $\Delta = \psi - \chi$  the angle between  $\mathbf{u}$  and  $\mathbf{v}$  (Fig. 5). Now although finite rotations cannot be considered to behave like vectors, in part because the sequence may be important when rotations are combined, it is possible to consider infinitesimal rotations as components of vectors, when terms of higher order than the first are neglected (e.g., Goldstein, 1950, pp. 124 ff.). For example, the changes  $\delta\varphi_x$  and  $\delta\varphi_y$  of  $\varphi_x$  and  $\varphi_y$  can be combined into the vector

$$\boldsymbol{\varepsilon} = \delta\varphi_x \mathbf{i} + \delta\varphi_y \mathbf{j}.$$

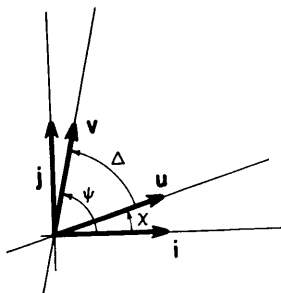


Fig. 5. Axes for specifying the orientation of a plane normal.

Then, using the transformation equations between the frames  $\mathbf{i}, \mathbf{j}$  and  $\mathbf{u}, \mathbf{v}$  and the fact that  $\boldsymbol{\varepsilon} = \delta\varphi_u \mathbf{u} + \delta\varphi_v \mathbf{v}$ , we find that

$$\sigma^2(\varphi_u) = \{\sin^2 \psi \sigma^2(\varphi_x) - 2 \sin \psi \cos \psi \text{cov}(\varphi_x, \varphi_y) + \cos^2 \psi \sigma^2(\varphi_y)\} / \sin^2 \Delta$$

$$\sigma^2(\varphi_v) = \{\sin^2 \chi \sigma^2(\varphi_x) - 2 \sin \chi \cos \chi \text{cov}(\varphi_x, \varphi_y) + \cos^2 \chi \sigma^2(\varphi_y)\} / \sin^2 \Delta$$

$$\text{cov}(\varphi_x, \varphi_y) = -\{\sin \psi \sin \chi \sigma^2(\varphi_x) - (\sin \psi \cos \chi + \cos \psi \sin \chi) \text{cov}(\varphi_x, \varphi_y) + \cos \psi \cos \chi \sigma^2(\varphi_y)\} / \sin^2 \Delta.$$

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