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# Accuracy of Bond Distances in Oblique Coordinate Systems†

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If $\sigma(x)$ is the standard deviation of an atomic coordinate, the standard deviation of position of that atom in the direction of the corresponding reciprocal axis is $a\sigma(x)\cos \mathbf{aa}^*$, where $\mathbf{aa}^*$ is the angle between the direct and reciprocal axes. When this standard deviation is independent of direction, the statistical correlation coefficient of two coordinates of the atom is given by the cosine of the angle between the corresponding reciprocal axes. In the method of least squares, if the standard deviation of a coordinate is calculated with neglect of cross terms, it tends to be low by the factor $\cos \mathbf{aa}^*$. It is shown that crystallographic independence does not imply statistical independence.

## Introduction

The distance $l$ between two atoms in a crystal is a function of the coordinates $x_1, y_1, z_1, x_2, y_2, z_2$ of the two atoms and the dimensions $a, b, c, \alpha, \beta, \gamma$ of the unit cell. The variance of $l$ is given by an expression (Arley & Buch, 1950):

$$\sigma^2(l) = \left[\frac{\partial l}{\partial x_1}\sigma(x_1)\right]^2 + \ldots + 2\frac{\partial l}{\partial x_1}\frac{\partial l}{\partial y_1}\sigma(x_1)\sigma(y_1)r(x_1, y_1) + \ldots \quad (1)$$

where there is a term of the first kind for each variable and a term of the second kind for each pair of variables. The factor $\sigma(x_1)\sigma(y_1)r(x_1, y_1)$ is the covariance of $x_1$ and $y_1$, and $r(x_1, y_1)$ is the correlation coefficient. The correlation coefficient is zero if the two variables are statistically independent. It has one of the extreme values $+1$ or $-1$ if the two variables are related by symmetry (except in hexagonal coordinates, where sometimes a coordinate is a function of two other coordinates). Ordinarily the coordinates determined by X-ray diffraction, when expressed as fractions of the unit cell, are independent of the cell dimensions. It is commonly assumed (though not necessarily true, as shown below) that coordinates of two crystallographically independent atoms are statistically independent. It is well known that in oblique coordinate systems two different coordinates of an atom are not in general statistically independent of each other. Their correlation is related in a simple way to the angles of the reciprocal lattice, as shown below, when certain conditions are satisfied.

## Correlation due to inclination of axes

In the following discussion it is assumed that no correlation occurs between coordinates of different atoms, and no consideration is given to errors in the unit-cell dimensions. The variance of position of an atom, $p^2$, is defined as the sum of the six terms in (1) corresponding to the three coordinates of that atom and the three cross terms between them. The variance defined in this way is a function of the direction of $\mathbf{l}$, and it depends on the coordinates of the second atom only to the extent that they define this direction and thereby the values of the derivatives. When $\mathbf{l}$ lies in the direction of $\mathbf{a}^*$, the derivatives with respect to $y$ and $z$ vanish, and

$$p = a \cos \mathbf{aa}^* \sigma(x) = \sigma(x)/a^* \quad (2)$$

where $\mathbf{aa}^*$ represents the angle between the direct and reciprocal $a$ axes. For monoclinic crystals, $\cos \mathbf{aa}^* = \sin \beta$. When $p$ is independent of the direction of $\mathbf{l}$, the error is isotropic. Errors are frequently found to be approximately isotropic when reasonably symmetrical samples of three-dimensional data are used. If $p$ is isotropic and the axes are orthogonal, it is readily shown from (1), or by a simple symmetry consideration, that the covariance of two coordinates of the same atom is zero. The correlation for oblique axes can be derived by the following method, suggested by Waser (1958), again with isotropic $p$.

Let the unit-cell axes be $\mathbf{a}_i (i=1, 2, 3)$ and the reciprocal axes be $\mathbf{b}_i$. Let the coordinates of an atom be $x_i$ in the coordinate system of $\mathbf{a}_i$, and $X_i$ in a system of unit orthogonal axes $\mathbf{e}_i$. The coordinates in the two systems are related by a linear transformation

$$x_i = \sum_j t_{ij} X_j \, . \quad (3)$$

The same transformation relates the reciprocal axes to the unit vectors (*International Tables for X-ray Crystallography*, 1952):

$$\mathbf{b}_i = \sum_j t_{ij} \mathbf{e}_j \, . \quad (4)$$

By the definition of the scalar product,

$$\mathbf{b}_i \cdot \mathbf{b}_j = \sum_k t_{ik} t_{jk} \, . \quad (5)$$

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In the orthogonal system,

$$\operatorname{cov}(X_i, X_j) = \delta_{ij} p^2 \tag{6}$$

where cov means variance if $i=j$ and covariance otherwise, and $\delta_{ij}$ is the Kronecker delta. By the rule for calculation of variances and covariances of linearly related variables (Arley & Buch, 1950)

$$\operatorname{cov}(x_i, x_j) = \sum_{mn} t_{im} t_{jn} \operatorname{cov}(X_m, X_n)\,. \tag{7}$$

Substituting (6) in (7) one obtains

$$\begin{aligned}\operatorname{cov}(x_i, x_j) &= p^2 \sum_m t_{im} t_{jm} \\ &= p^2(\mathbf{b}_i \cdot \mathbf{b}_j)\,. \end{aligned} \tag{8}$$

From (8) and the definition of $r$,

$$\begin{aligned} r(x_i, x_j) &= (\mathbf{b}_i \cdot \mathbf{b}_j)[(\mathbf{b}_i \cdot \mathbf{b}_i)(\mathbf{b}_j \cdot \mathbf{b}_j)]^{-\frac{1}{2}} \\ &= \cos \alpha_{ij}^* \end{aligned} \tag{9}$$

where $\alpha_{ij}^*$ is a reciprocal cell angle. More explicitly, in conventional notation:

$$r(y, z) = \cos \alpha^* \tag{9a}$$

$$r(x, z) = \cos \beta^* \tag{9b}$$

$$r(x, y) = \cos \gamma^*\,. \tag{9c}$$

This result has also been derived by trigonometry by requiring that (1) give an isotropic $p$ in the plane of two reciprocal axes (Templeton, 1958).

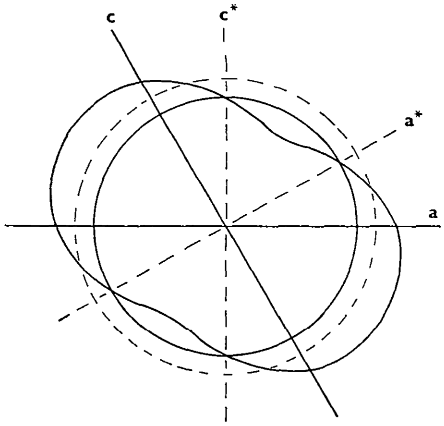

Fig. 1. Variance of position with and without correlation, as explained in the text.

To illustrate the magnitude of the effects of correlation, there is plotted in Fig. 1 the angular dependence of $p$ for a monoclinic $\beta = 120°$. The solid circle represents the isotropic $p$ corresponding to $r = \frac{1}{2}$. The curve shows the dependence of $p$ for independent coordinates, or no correlation. The latter curve would be appropriate, for example, when $x$ and $z$ were obtained from independent projections. Note that the curves coincide in the directions of the reciprocal axes. The broken circle is drawn with radius $a\sigma(x)$ to show the effect of omitting the factor $\cos \mathbf{aa}^*$.

The variances and covariances of coordinates are themselves subject to experimental uncertainty. Therefore when the error is reasonably isotropic it may be better (and certainly is simpler) to assume an isotropic error by some average of the various determinations, than to calculate the error by (1).

### Method of least squares

In the method of least squares, one derives a matrix $\mathbf{M}$ of elements:

$$m_{ij} = \sum w \frac{\partial F}{\partial x_i} \frac{\partial F}{\partial x_j}\,. \tag{10}$$

The inverse of $\mathbf{M}$ is $\mathbf{M}^{-1}$ with elements $n_{ij}$. If the discrepancies $\Delta = F_o - F_c$ represent random errors, then the variances and covariances of coordinates are:

$$\operatorname{cov}(x_i, x_j) = n_{ij} \sum w \Delta^2 / (u - v) \tag{11}$$

where $u - v$ is the excess of data over the number of variables. Sometimes the complete matrix $\mathbf{M}$ is not available, and the variance is approximated by using $1/m_{ii}$ in place of $n_{ii}$ in (11). The standard deviation calculated in this way will be called $s(x_i)$. According to Sparks (1958), experimental data suggest that $s(x)$ is less than $\sigma(x)$ by a factor similar to $\cos \mathbf{aa}^*$. It is shown below that this is true when the errors are isotropic and the only correlation is that among coordinates of a single atom because of the inclination of the axes. The latter restriction permits $\mathbf{M}$ to be factored into matrices of order $3 \times 3$, which can be considered one at a time.

From (8) and (11):

$$n_{ij} = K(\mathbf{b}_i \cdot \mathbf{b}_j) \tag{12}$$

where

$$K = p^2(u - v) / \sum w \Delta^2. \tag{13}$$

The inverse of the matrix with elements $\mathbf{b}_i \cdot \mathbf{b}_j$ is the matrix with elements $\mathbf{a}_i \cdot \mathbf{a}_j$. Therefore,

$$m_{ij} = K^{-1}(\mathbf{a}_i \cdot \mathbf{a}_j)\,. \tag{14}$$

Thus,

$$\begin{aligned} s(x_i)/\sigma(x_i) &= (m_{ii} n_{ii})^{-\frac{1}{2}} \\ &= (a_i b_i)^{-1} \\ &= \cos \mathbf{a}_i \mathbf{b}_i\,. \end{aligned} \tag{15}$$

This result indicates the importance of distinguishing $\sigma(x)$ and $s(x)$ in reporting experimental results. From (2) and (15),

$$p = a s(x)\,, \tag{16}$$

and the correct result is obtained (to the extent that the above assumptions are valid) if cross terms are ignored in the matrix $\mathbf{M}$ and if the cosine factor in (2) is also omitted. Apparently this procedure has been followed by some workers. Fortunately the effect of these factors is small for angles near 90°, however the calculation is made.

## Crystallographic and statistical independence

Crystallographic independence does not necessarily imply statistical independence of coordinates. The values of coordinates and their covariances depend on how the origin is defined. On the other hand, interatomic vectors and their variances should be independent of the choice of origin. As an example, consider a structure consisting of three atoms in a unit cell of no symmetry. If the origin is defined as the location of the first atom, then the variance of position of that atom is zero. Assume that the $x$ coordinates of the other two atoms, and the variances of these coordinates, are determined as well as possible from the data. Then, if these coordinates are statistically independent,

$$\sigma(x_1-x_2) < \sigma(x_3-x_2)\ .$$

This inequality can be reversed by placing the origin at the third atom. Therefore, it must be concluded that the coordinates are not statistically independent in this case when the origin is chosen in this way. If the data are such that $(x_1-x_2)$, $(x_3-x_2)$, and $(x_1-x_3)$ are equally well determined, then it follows by substitution in (1) that $r(x_2, x_3)=\frac{1}{2}$ with the origin at the first atom.

Other methods of choice of origin lead to other results for the covariances, but I have not made a general analysis of the problem.

I thank Dr R. A. Sparks for his suggestion concerning $s(x)$. The proofs involving the scalar products borrow heavily from an unpublished manuscript by Prof. J. Waser, and I thank him for permission to use these relations. I also thank Prof. K. N. Trueblood for helpful discussions.

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# Untersuchung kolloider Systeme auf Partikelgrösse und Polydispersität mit Hilfe der Röntgenkleinwinkelstreuung

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With the object of testing the theory small angle X-ray scattering (filtered Cu radiation) was observed on polydisperse systems (Carbon Black, Gold Sol, Polystyrene Latex) of varying grades of packing density. Using the method of discussion proposed by Hosemann (1939, 1950) the average particle radius $\bar{\bar{x}}$ and the degree of polydisperseness $g$ were determined for samples of different compaction. Electron microscope pictures of the samples were also taken and discussed statistically. Both $\bar{\bar{x}}$ and $g$ values checked with the X-ray values to within 6% in the case of latex and gold, whereas carbon black values differed. The effects of non-spherical particle shape, of multiple scattering and of in-phase scattering by different particles ('Liquids Maxima') are discussed and evaluated in the paper.

Aus der Röntgenkleinwinkelstreuung lassen sich Aussagen sowohl über die Grösse und Gestalt der Bausteine eines inhomogenen Systems als auch über die Grössenverteilung und Abstandsverhältnisse in kolloiden Dimensionen machen. Guinier (1939*a*, *b*) zeigte, dass bei monodispersen Systemen hoher Verdünnung (Gas) die Röntgenkleinwinkelstreuung die interferenzfreie Überlagerung der Streubilder der einzelnen Partikel ist. Durch Einführen einer maxwellartigen Grössenverteilung der Partikelradien konnte Hosemann (1939*a*, *b*) aus dem Röntgenkleinwinkeldiagramm Aussagen sowohl über die Grösse der Partikel als auch über ihre Grössenverteilung gewinnen.

Geht man zu dichtgepackten Systemen (Flüssigkeiten und hochpolymere Festkörper) über, so werden die Abstandsverhältnisse geordneter und im Streubild erscheinen ein oder mehrere sogenannte Flüssigkeitsringe, die Aufschluss über einen mittleren Abstand, der zwischen benachbarten Bausteinen am häufigsten vorkommt, geben. Während dieser Einfluss bei monodispersen Systemen beachtlich wird, zeigte Hosemann (1950*a*, *b*), dass die Komponente der Flüssigkeits-