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ABSTRACT

In a polar space group the magnitudes of the covariances of pairs of coordinates in a polar direction depend upon the way in which the origin is defined. With the assumption that one coordinate difference is as accurate as another, it is shown that the covariance is half the variance if the origin is defined by one of n equal atoms. With this result it is shown that if all n atoms are shifted according to the diagonal approximation in the method of least squares, the shifts are larger than the correct values by the factor $n/(n-1)$. The variance of a coordinate difference is overestimated by this same factor in the diagonal approximation. Covariances are also calculated for the case of the origin at the center of gravity of n equal atoms and for the case of unequal atoms with the origin at a heavy atom.

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INTRODUCTION

In the refinement of a crystal structure by the method of least squares, the structure is constrained by an assumption of symmetry, for example by the mathematical form of the structure factor. In the 162 non-polar space groups, the form of the structure factor determines the relation of the origin to the symmetry elements in all three dimensions. However, in the 68 space groups of the 10 polar crystallographic point groups (Table I) the location of the origin with respect to a polar dimension is not implied by the form of the structure factor. In these polar space groups the origin may be defined by one, two, or three extra constraints on the coordinates according to the number of polar dimensions. Otherwise, the least-squares matrix is singular and no unique solution is determined. In this paper some deductions are made concerning the form of the constrained matrix and concerning the accuracy of the diagonal approximation.

Table I

Polar crystallographic point groups

Point group	Number of space groups	Number of polar dimensions
1, C_1	1	3
m, C_s	4	2
2, C_2	3	1
mm2, C_{2v}	22	1
4, C_4	6	1
4mm, C_{4v}	12	1
3, C_3	4	1
3m, C_{3v}	6	1
6, C_6	6	1
6mm, C_{6v}	4	1

METHOD OF LEAST SQUARES

It is convenient to represent the normal equations of the method of least squares[1,2] as follows:

$$\underset{\sim}{M}\ \underset{\sim}{E} = \underset{\sim}{D}, \qquad \underset{\sim}{E} = \underset{\sim}{M}^{-1}\ \underset{\sim}{D}\ . \tag{1}$$

The elements of the column matrix $\underset{\sim}{E}$ are the shifts e_i of the parameters u_i. The elements of the column matrix $\underset{\sim}{D}$ are:

$$d_i = \sum w\ \frac{\partial |F|}{\partial u_i}\ (|F_o| - |F_c|). \tag{2}$$

The elements of the square matrix $\underset{\sim}{M}$ are:

$$m_{ij} = \sum w\ \frac{\partial |F|}{\partial u_i}\ \frac{\partial |F|}{\partial u_j}\ . \tag{3}$$

The elements of the inverse matrix $\underset{\sim}{M}^{-1}$ are proportional to the variances and covariances of the parameters.

ORIGIN AT ONE OF $\underline{n}$ EQUAL ATOMS

A simple method of choosing the origin is to assign an arbitrary value, such as zero, to the appropriate coordinates of one of the atoms. This constraint may be applied to the matrix $\underset{\sim}{M}$ simply by deleting the row and column corresponding to a coordinate which is assigned an arbitrary value. Such a coordinate obviously has no variance, nor is there any covariance of it with any other parameter.

This method introduces a strong correlation among the errors of the coordinates of the other atoms in a polar direction. Let us assume that the coordinate difference of one pair of atoms is determined by the data as accurately as that of another pair. This assumption seems to be reasonably realistic for a structure of equal atoms with three-dimensional data and without strong asymmetry of vibration. Let x_i be a coordinate in a polar direction.

Then, if $\underline{x}_0$ is the coordinate of the origin atom,

$$\sigma^2 \, (x_0 - x_i) = \sigma^2 \, (x_i) \; ; \tag{4}$$

$$\sigma^2 \, (x_i - x_j) = \sigma^2 \, (x_i) + \sigma^2 \, (x_j) - 2 \, \text{cov} \, (x_i x_j) \; ; \tag{5}$$

$$\therefore \; \text{cov} \, (x_i x_j) = 1/2 \, \sigma^2 \, (x_i) \; . \tag{6}$$

Therefore, in this case the matrix $\underset{\sim}{M}{}^{-1}$ has large off-diagonal elements. Consider just that part of the matrix which pertains to the coordinates in the polar direction. This matrix $\underset{\sim}{P}{}^{-1}$ has $\underline{n}$-1 rows and columns, if there are $\underline{n}$ atoms in the asymmetric unit. Except for a numerical factor, it is of the form:

$$(P^{-1})_{ij} = \begin{cases} 1, & i = j \; ; \\ 1/2, & i \neq j \; . \end{cases} \tag{7}$$

In the absence of correlation with respect to other parameters, for example due to inclination of axes,[3] the matrix $\underset{\sim}{P}{}^{-1}$ can be factored out of $\underset{\sim}{M}{}^{-1}$ and considered separately. It is easy to show by the rule of matrix multiplication that the inverse of $\underset{\sim}{P}{}^{-1}$ is of the form:

$$(P)_{ij} = \begin{cases} 2 \, (n\text{-}1)/n, & i = j \; ; \\ -2/n, & i \neq j \; , \end{cases} \tag{8}$$

where $\underline{n}$ again is the number of atoms. It is noticed that the off-diagonal elements of $\underset{\sim}{P}$ become small compared to the diagonal elements as the number of atoms becomes large. However, they diminish too slowly to be neglected in the inversion.

With these matrices, it is possible to investigate the accuracy of the "diagonal approximation," in which off-diagonal elements are neglected. A coordinate shift from the full matrix is, with $\underline{K}$ a constant:

$$e_i = K \, (d_i + 1/2 \sum_{j \neq i} d_j) = \frac{K}{2} \, (d_i + \sum_1^{n-1} d_j) \; . \tag{9}$$

The same coordinate shift in the diagonal approximation is:

$$\epsilon_i = \frac{Kn}{2(n-1)} \, d_i \tag{10}$$

If the origin atom also is shifted in the diagonal approximation, its shift is:

$$\epsilon_0 = \frac{Kn}{2(n-1)} \, d_0 = -\frac{Kn}{2(n-1)} \sum_1^{n-1} d_j \, , \tag{11}$$

since:

$$\sum_0^{n-1} d_j = 0 \, . \tag{12}$$

Eliminating the d_i and $\Sigma \, d_j$ from (9), (10), and (11) yields:

$$e_i = \frac{n-1}{n} \, (\epsilon_i - \epsilon_0) \tag{13}$$

This result means that in the diagonal approximation, if the shifts are multiplied by the factor $(n-1)/n$ and if the origin atom is also shifted, the result is the same as if the full matrix had been used. If the origin atom is not shifted, the convergence may be very slow in the diagonal approximation.

This effect of polar symmetry in the structure of sulfamide,[4] in space group Fdd2, contributed to Trueblood's choice of a partial-shift factor of one-half.[5] It may have influenced other workers similarly. On the other hand, failure of the above assumptions and the approximation of neglecting higher derivatives in deriving the normal equations allow other sources of error in shifts. The experience of Lipscomb's group[6] seems to demand partial shifts even in centric space groups.

A similar analysis of the variances is straightforward. In the diagonal approximation, with the origin atom considered also to be variable and with all covariances taken as zero, the variance of $(x_i - x_j)$ is calculated to be larger than the correct amount by the factor $n/(n-1)$. The standard deviation, of course, is wrong by the square root of this factor.

ORIGIN AT THE CENTER OF GRAVITY OF $\underline{n}$ EQUAL ATOMS

A more symmetrical way of defining the origin for a structure of equal atoms is to assign an arbitrary coordinate to the center of gravity of the $\underline{n}$ atoms. This is perhaps most conveniently done by the method of Lagrangian multipliers or "adjustment by correlates";[2] then the auxiliary condition is that the sum of the appropriate coordinates be a specified constant. Analysis reveals, with the same assumptions as before, that the variance of a coordinate is $(\underline{n}-1)/2\underline{n}$ as much as when the origin is placed at one atom. In this case the correlation of two coordinates is negative, with correlation coefficient $-1/(\underline{n}-1)$. These values, naturally, lead to the same result as before for the variance of $(\underline{x}_i - \underline{x}_j)$. These results concerning the variances and covariances are summarized in Table II.

Table II

Variances and covariances for $\underline{n}$ equal atoms			
Constraint	$\sigma^2 (\underline{x}_i)$	cov $(\underline{x}_i \ \underline{x}_j)$	$\sigma^2 (\underline{x}_i - \underline{x}_j)$
$\underline{x}_0 = 0$	σ^2	$\frac{1}{2} \sigma^2$	σ^2
$\displaystyle\sum_0^{n-1} \underline{x}_i = 0$	$\frac{\underline{n}-1}{2\underline{n}} \sigma^2$	$-\frac{1}{2\underline{n}} \sigma^2$	σ^2
diagonal approximation, no constraint	$\frac{\underline{n}}{2(\underline{n}-1)} \sigma^2$	0	$\frac{\underline{n}}{\underline{n}-1} \sigma^2$

In the above discussion, it is assumed that no other sources of correlation are present. In general, in point groups 1 and $\underline{m}$, the polar axes will be oblique to each other, and complications will arise from the additional correlation caused by that circumstance. If the polar axes are nearly orthogonal, then the above results may be applied without serious error to each group of coordinates for a polar direction (that is, the $\underline{x}$ coordinates separately from the $\underline{y}$ and $\underline{z}$ coordinates).

The situation is complicated for polar rhombohedral crystals if the rhombohedral unit cell is chosen, because there is correlation among the errors of all pairs of variable coordinates. I have not analyzed this problem since it can be evaded by use of a hexagonal coordinate system.

UNEQUAL ATOMS

If the structure contains both heavy and light atoms, then the heavy atoms in general are more accurately located by the data. The above discussion is expected to apply reasonably well to the heavy atoms, disregarding the light atoms, if the difference in scattering power is substantial. To investigate the light atoms, assume that one heavy-light coordinate difference is as accurate as another. If the origin is specified by a coordinate x_0 of a heavy atom and if x_h and x_ℓ represent coordinates of heavy and light atoms respectively, then one can calculate as before:

$$\sigma^2 (x_\ell - x_0) = \sigma^2 (x_\ell) \; ; \tag{14}$$

$$\sigma^2 (x_\ell - x_h) = \sigma^2 (x_\ell) + \sigma^2 (x_h) - 2 \text{ cov } (x_\ell \; x_h) \; ; \tag{15}$$

$$\therefore \; \text{cov } (x_\ell \; x_h) = \frac{1}{2} \sigma^2 (x_h) \; . \tag{16}$$

This covariance corresponds to a correlation coefficient of

$$r (x_\ell \; x_h) = \frac{1}{2} \frac{\sigma (x_h)}{\sigma (x_\ell)} \; . \tag{17}$$

I have not found a theoretical prediction for the correlation between errors of coordinates of two light atoms under these circumstances, but one is tempted to guess that it will be of the order of the square of the above ratio of standard deviations. It is not an important question, since the "noise" of the matrix from other effects is likely to obscure these small terms.

A test of Equation (17) with experimental data is provided by Hardgrove's study in this laboratory of the structure of cis-1,2-dibromo-benzocyclobutene.[7] The asymmetric unit in space group Pna2$_1$ contains two bromine atoms, eight carbon atoms, and six hydrogen atoms. With one bromine atom determining the origin, the correlation of errors of the other bromine z coordinate and carbon z coordinates was found to range from 0.05 to 0.22, with an average value of 0.13. The value predicted by Equation (17) is 0.10.

ACKNOWLEDGMENT

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