

Variations and Covariances of Coordinates in Polar Crystal Systems*

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Relationships between positional variances and covariances that refer to different choices of origin are presented, and the situation is considered in which the uncertainties in the positioning of atoms are direction-independent and the only covariance terms are those that arise from polar aspects and non-orthogonality of the coordinate axes and from symmetry. Covariance terms can often be made small by placing the origin at a suitable centroid.

In polar space groups the origin of at least one coordinate axis cannot be related to the positions of symmetry elements,† and since by diffraction methods only the differences of the coordinates of the various atoms can be determined, the origin of such an axis must be related to the coordinates themselves. Coordinates relative to such an origin are not linearly independent. There must therefore exist relationships among the variances and covariances of coordinates along polar axes, and the covariances between such coordinates cannot all be zero.‡ Moreover, such variances and covariances will depend on the way in which the origin is defined (Templeton, 1960). However, this situation is inherent to the method used to determine the coordinates, which in principle can be referred to any independent origin. We shall assume below that, by suitable measurements or on theoretical grounds, the variances and covariances between atomic coordinates relative to an independent origin are known, and shall examine the effect upon them of relating the origin to the coordinates. In particular, we shall examine the

case in which interatomic covariances referred to independent origin are all zero. The results will be extended to covariances between the coordinates of the same atom along different (and generally) inclined axes, assuming the atomic variance-covariance tensor to be isotropic. Covariances between coordinates of symmetry-related atoms will also be considered. In order to gauge the accuracy of atomic positions intuitively, covariance terms should be as small as possible, and we shall see that for this purpose a suitable centroid should be selected as origin.

Covariances for a polar coordinate axis

Let then the variances and covariances of the coordinates ξ^j of the atoms j ($j=1, 2, \dots, N$) along a polar coordinate axis, relative to an independent origin, be known and consider two alternative ways of fixing the origin relative to the ξ^j : (1) the origin is placed at one of the atoms, arranged to be atom N ; and (2) the origin is chosen at a centroid, defined as a weighted average of the ξ^j . In the first case

$$x^j = \xi^j - \xi^N \quad (1)$$

is the coordinate of atom j relative to an origin at atom N , and we have (see, e.g., Sands, 1966) for $j \neq N$, $k \neq N$, $j \neq k$

$$\sigma^2(x^j) = \sigma^2(\xi^j) + \sigma^2(\xi^N) - 2 \text{cov}(\xi^j, \xi^N) \quad (2)$$

$$\text{cov}(x^j, x^k) = \text{cov}(\xi^j, \xi^k) + \sigma^2(\xi^N) - \text{cov}(\xi^j, \xi^N) - \text{cov}(\xi^k, \xi^N) \quad (3)$$

$$\sigma^2(x^N) = \text{cov}(x^j, x^N) = 0 \quad (4)$$

For the second choice of origin we introduce suitable normalized weights p_j , $\sum p_j = 1$, in terms of which the centroid coordinate is

$$\bar{\xi} = \sum p_j \xi^j \quad (5)$$

Let the coordinates relative to $\bar{\xi}$ be designated by X^j ,

$$X^j = \xi^j - \sum p_n \xi^n \quad (6)$$

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† There is ambiguity regarding the concepts of polar and non-polar space and point groups. With the definition just given and here adopted, polar point groups are also those in which a piezoelectric effect may be achieved by hydrostatic pressure alone (see e.g., *International Tables for X-ray Crystallography*, 1952). On the other hand, a broader physical definition of a polar direction requires only that the direction and its opposite are not related by symmetry. For example, in point group 32 the directions of the twofold axes are polar in the broader sense, as are all other directions, except that of the threefold axis. Indeed, piezoelectric polarization in 32 may be achieved by torsion or anisotropic compression. Nevertheless, 32 is a non-polar point group in the sense used here, because there is no direction in which the origin cannot be related to symmetry elements, and mere hydrostatic pressure cannot produce a piezoelectric effect.

‡ For non-polar coordinate axes the locations of the symmetry elements, to which the origin may be tied, are in the end also defined in terms of atomic positions. In this case it is the variances and covariances of symmetry-linked coordinates that are by necessity related, because the symmetry relationships among the coordinates are unavoidably used in the diffraction method. The covariances between coordinates of unrelated atoms may, however, all be zero.

This transformation leads to the relationship

$$\text{cov}(X^j, X^k) = \text{cov}(\xi^j, \xi^k) - \sum_n p_n \text{cov}(\xi^j, \xi^n) - \sum_m p_m \text{cov}(\xi^k, \xi^m) + \sum_{n,m} p_n p_m \text{cov}(\xi^n, \xi^m) \quad (7)$$

where 'diagonal' terms represent variance terms, such as $\text{cov}(X^j, X^j) \equiv \sigma^2(X^j)$. As a check we note that because of

$$\bar{X} = \sum p_n X^n = 0 \quad (8)$$

the variances and covariances of the variables X^j must satisfy the N equations

$$\sum_n p_n \text{cov}(X^j, X^n) = 0 \quad j = 1, 2, \dots, N \quad (9)$$

while no such restrictions apply to the terms $\text{cov}(\xi^j, \xi^n)$. Indeed the relationships (9) are satisfied identically by the covariances expressed by (7). Note that (2) and (3) are special cases of (7), for the situation that $p_N = 1$, $p_j = 0, j \neq N$, in which the relationships (9) reduce to (4). [Also if the same constant is added to all of the terms $\text{cov}(\xi^j, \xi^k)$, none of the terms $\text{cov}(x^j, x^k)$ or $\text{cov}(X^j, X^k)$ is affected].

Consider now the special situation in which

$$\sigma^2(\xi^j) = s_j^2 \quad (10)$$

$$\text{cov}(\xi^j, \xi^k) = 0 \quad j \neq k. \quad (11)$$

Then for coordinates referred to an origin at atom N , and for $j \neq N, k \neq N, j \neq k$,

$$\sigma^2(x_j) = s_j^2 + s_N^2 \quad (12)$$

$$\text{cov}(x^j, x^k) = s_N^2. \quad (13)$$

Note that all covariances have the same value, except those that are zero because they involve atom N . For the second choice of origin, the terms defined by (10) and (11) inserted into (7) yield

$$\sigma^2(X^j) = (1 - 2p_j)s_j^2 + \sum p_n^2 s_n^2 \quad (14)$$

$$\text{cov}(X^j, X^k) = -p_j s_j^2 - p_k s_k^2 + \sum p_n^2 s_n^2 \quad j \neq k. \quad (15)$$

These values satisfy (9), and they reduce to (12) and (13) when $p_N = 1, p_j = 0, j \neq N$.

Grouping of atoms

To obtain a feeling for these results it is instructive to consider a situation in which all atoms of a given kind are associated with the same values of s_j^2 and of p_j . Let each group of atoms of the same kind be referred to by a Greek index, $\lambda = 1, 2, \dots, \nu$, there being ν groups. The λ th group then contains N_λ atoms, for all of which s_j^2 is equal to s_λ^2 and p_j is equal to p_λ , with $\sum N_\lambda p_\lambda = 1$. The results, some of which have been reported by Templeton (1960), are collected in Table 1, in which ν refers to the last group of atoms, while λ, μ , and α may refer to any of the groups. Note that when the origin is chosen at atom N , all covariance terms are equal, as is already clear from (13). When the origin is at a centroid related to just the last group, the covariance between a coordinate in this group and one in any of the other groups is zero.* Moreover, when the number N_ν of atoms defining the origin is very large (or when there is only one kind of atom), $\sigma^2(X^\lambda)$ approaches s_λ^2 (including the case $\lambda = \nu$), while all covariances approach zero.

Covariances of coordinates along different directions

Up to this point we have considered just one direction. What then are the covariances between coordinates along different directions, one or both of which may be polar? Let ξ^{rj} and ξ^{rk} be the respective coordinates of atoms j and k relative to the crystallographic axes \mathbf{a}_r and \mathbf{a}_t , and relative to an independent origin. First, let both \mathbf{a}_r and \mathbf{a}_t be polar, so that the origin must be defined in both directions in terms of the coordinates,

* This is analogous to the situation of a non-polar axis, where the origin is, in essence, referred to each and all groups of symmetry-related atoms, and all covariances between different groups may be zero.

Table 1. Groups of atoms with equal positional variances and weights

	ν kinds of atoms	One kind of atom	Remarks
Origin at atom N			
$\sigma^2(x^\nu)$	$2s_\nu^2$	$2s^2$	(1)
$\sigma^2(x^\lambda)$	$s_\lambda^2 + s_\nu^2$		
$\text{cov}(x^\lambda, x^\mu)$	$s_\nu^2 [= \frac{1}{2}\sigma^2(x^\nu)]$	$s^2 [= \frac{1}{2}\sigma^2]$	(1, 2)
Origin at centroid			
	Centroid related to all atoms	Centroid related to last group of atoms ($p_\nu = 1/N_\nu, p_\alpha = 0, \alpha \neq \nu$)	
$\sigma^2(X^\lambda)$	$(1 - 2p_\lambda)s_\lambda^2 + \sum N_\alpha p_\alpha^2 s_\alpha^2$	$\lambda = \nu \quad s_\nu^2(N_\nu - 1)/N_\nu$ $\lambda \neq \nu \quad s_\lambda^2 + s_\nu^2/N_\nu$	$s^2(N - 1)/N$
$\text{cov}(X^\lambda, X^\mu)$	$-p_\lambda s_\lambda^2 - p_\mu s_\mu^2 + \sum N_\alpha p_\alpha^2 s_\alpha^2$	$\lambda = \nu, \mu = \nu \quad -s_\nu^2/N_\nu$ $\lambda = \nu, \mu \neq \nu \quad \left. \begin{array}{l} 0 \\ \lambda \neq \nu, \mu = \nu \end{array} \right\}$ $\lambda \neq \nu, \mu \neq \nu \quad s_\nu^2/N_\nu$	$-s^2/N$ (2)

(1) Terms related to atom N are all zero.

(2) $\text{cov}(X^\lambda, X^\mu)$ with $\lambda = \mu$ refers to two different atoms in the same group and not to the variance $\sigma^2(X^\lambda)$.

when diffraction methods are used. Placing the origin at atom N , the new coordinates are

$$x^{rj} = \xi^{rj} - \xi^{rN} \quad (16)$$

in the direction \mathbf{a}_r , and similar equations apply to the direction \mathbf{a}_t . The covariance between x^{rj} and x^{tk} is then given by an equation similar to (3),

$$\begin{aligned} \text{cov}(x^{rj}, x^{tk}) &= \text{cov}(\xi^{rj}, \xi^{tk}) - \text{cov}(\xi^{rj}, \xi^{tN}) \\ &\quad - \text{cov}(\xi^{rN}, \xi^{tk}) + \text{cov}(\xi^{rN}, \xi^{tN}). \end{aligned}$$

When the origin is placed at a centroid defined in both direction in analogy to (5), we have for the new coordinates

$$X^{rj} = \xi^{rj} - \sum_n p_n \xi^{rn} \quad (17)$$

in the direction \mathbf{a}_r , and a similar equation for the direction \mathbf{a}_t . The covariance between X^{rj} and X^{tk} is given by an equation like (7),

$$\begin{aligned} \text{cov}(X^{rj}, X^{tk}) &= \text{cov}(\xi^{rj}, \xi^{tk}) - \sum_n p_n \text{cov}(\xi^{rj}, \xi^{tn}) \\ &\quad - \sum_m p_m \text{cov}(\xi^{rm}, \xi^{tk}) + \sum_{n,m} p_n p_m \text{cov}(\xi^{rn}, \xi^{tm}). \end{aligned}$$

Next, let only \mathbf{a}_r be polar, so that only in this direction is it required to relate the origin to the atomic coordinates. In effect we operate with independent coordinates ξ^{tk} in direction \mathbf{a}_t , and with dependent coordinates, x^{rj} or X^{rj} defined by (16) or (17), in direction \mathbf{a}_r . For the covariances we obtain

$$\text{cov}(x^{rj}, \xi^{tk}) = \text{cov}(\xi^{rj}, \xi^{tk}) - \text{cov}(\xi^{rN}, \xi^{tk}) \quad (18)$$

and

$$\text{cov}(X^{rj}, \xi^{tk}) = \text{cov}(\xi^{rj}, \xi^{tk}) - \sum_n p_n \text{cov}(\xi^{rn}, \xi^{tk}). \quad (19)$$

The value $j = N$ is excluded in (18), and $\text{cov}(x^{rN}, \xi^{tk}) = 0$; moreover, $\sum_j p_j \text{cov}(X^{rj}, \xi^{tk}) = 0$. When both \mathbf{a}_r and \mathbf{a}_t are non-polar, there is no need to relate the origin to the coordinates in these directions.

As an example we shall consider the case in which the positional variance-covariance tensor is isotropic, and there are no covariances between coordinates of different atoms, relative to an independent origin. In other words, the variance-covariance tensor for the coordinates ξ is

$$\text{cov}(\xi^{rj}, \xi^{tk}) = g^{rt} \delta_{jk} s_j^2 \quad (20)$$

with $g^{rt} = \mathbf{b}^r \cdot \mathbf{b}^t$ (see e.g., Templeton, 1959; Waser, 1973). When both \mathbf{a}_r and \mathbf{a}_t are polar, and the origin is fixed at atom N ,

$$\text{cov}(x^{rj}, x^{tk}) = g^{rt} (\delta_{jk} s_j^2 + s_N^2) \quad (21)$$

for $j \neq N, k \neq N$; terms with $j = N$ and/or $k = N$ are zero. With the origin fixed at the centroid

$$\text{cov}(X^{rj}, X^{tk}) = g^{rt} [(\delta_{jk} - p_j) s_j^2 - p_k s_k^2 + \sum_n p_n^2 s_n^2]. \quad (22)$$

Terms with $r = t$ and $j = k$ in (21) or (22) represent variances. When both \mathbf{a}_r and \mathbf{a}_t are non-polar, (20) needs no change, and when one of these axes is polar and the other is not, all covariance terms associated with them are zero, because two such axes are always at right angles, so that $g^{rt} = 0$.

Symmetry-induced variances and covariances

Variances and covariances arising by symmetry have been discussed, for example, by Sands (1966), and we shall restrict ourselves to modifications that arise for polar coordinate axes. In eight of the ten point groups in which this situation arises (2, $mm2$, 4, $4mm$, 3, $3m$, 6, $6mm$), there is only one polar coordinate axis, the principal axis of rotation. Atoms related by rotation or screw axes in this direction occur therefore in groups of N_λ , when N_λ may be equal to the order of the principal axis or to an integral divisor of this order (including unity). In the direction at issue, all of the related atoms have coordinates that are equal to each other or differ by fixed fractions of the unit-cell edge, and the variances and covariances between all these N_λ coordinates are equal to each other. That is, for an arbitrary origin

$$\text{cov}(\xi^{rj}, \xi^{rk}) = g^{rr} \delta_{\lambda\mu} \sigma_\lambda^2 \quad (23)$$

where r refers to the direction of the principal axis, while λ and μ refer to groups of symmetry-related atoms; j refers to any one of the N_λ atoms associated with group λ and k to any one of the N_μ atoms associated with group μ . We now position the origin at a centroid, for the definition of which we associate all atoms in any given group, denoted by α , with the same weight p_α . It follows from (7) and (23) that

$$\begin{aligned} \text{cov}(X^{r\lambda}, X^{r\mu}) &= g^{rr} [(\delta_{\lambda\mu} - N_\lambda p_\lambda) \sigma_\lambda^2 \\ &\quad - N_\mu p_\mu \sigma_\mu^2 + \sum_\alpha N_\alpha^2 p_\alpha^2 \sigma_\alpha^2]. \quad (24) \end{aligned}$$

Here the indices λ and μ in $\text{cov}(X^{r\lambda}, X^{r\mu})$ refer to any atoms in the respective groups λ and μ . In particular, $\text{cov}(X^{r\lambda}, X^{r\lambda})$ represents any of the covariances between two different atoms in group λ and also includes the variances of the atoms in that group; all of these quantities are equal to each other. The variances of atoms for which N_α is 1, which are therefore not related to others by the rotation axis concerned because they lie on it, must of course be included in the sum over α .

The remaining point groups associated with polar coordinate axes are 1 and m . In the space group associated with the first of these, $P1$, there are no symmetry-related atoms, all three coordinate axes are polar, and the situation is as discussed in the preceding section. In space groups associated with m , atoms may either be related by mirror planes (unless they lie on one of them) or by glide planes. There are two polar coordinate axes parallel to these planes, and the equation analogous to (23) is

$$\text{cov}(\xi^{rj}, \xi^{sk}) = g^{rs} \delta_{\lambda\mu} \sigma_\lambda^2. \quad (25)$$

The indices r and s refer to the two polar coordinate axes, and the meanings of j, k, λ , and μ are as described for (23). For two atoms related by a mirror or a glide plane the equation analogous to (24) is then

$$\text{cov}(X^{r\lambda}, X^{s\mu}) = g^{rs} [(\delta_{\lambda\mu} - 2p_\lambda)\sigma_\lambda^2 - N_\mu p_\mu \sigma_\mu^2 + \sum N_\alpha^2 p_\alpha^2 \sigma_\alpha^2] \quad (26)$$

because $N_\lambda = 2$, while N_μ and the N_α 's may be either 1 or 2.

Relationships among atoms associated with the translation group do not affect our developments. Let us consider, in particular, space groups with centered lattices, and let the number of translation-related atoms in the unit cell be h . Then all values of the N_α are larger by a factor h , and those of all p_α smaller by a factor $1/h$, relative to a situation in which the unit cell is primitive, because $\sum N_\alpha p_\alpha = 1$. Since (24) and (26) contain only products of the form $N_\alpha p_\alpha$, both are invariant to the value of h .

Minimization of covariances

An intuitive understanding of positional variances is facilitated by small values of covariance terms, and approximate computations of variances and covariances of derived quantities based on positional uncertainties (*e.g.* Stanford & Waser, 1970; Waser, Marsh & Cordes, 1973) are simplified when positional covariances can be neglected. For polar coordinate axes, covariances associated with different atoms are in general smaller, when they refer to an origin chosen at a centroid rather than when the origin is at a specific atom; and if the origin is at a specific atom, these terms are smaller when the atom is of high rather than low scattering power.

The reduction of variances and covariances, from values associated with an origin at atom N to values appropriate to an origin at a centroid, can be performed

by relationships analogous to (7) or to (19). For example, when both \mathbf{a}_r and \mathbf{a}_t are polar,

$$\begin{aligned} \text{cov}(X^{rj}, X^{tk}) &= \text{cov}(x^{rj}, x^{tk}) - \sum_n p_n \text{cov}(x^{rj}, x^{tn}) \\ &\quad - \sum_m p_m \text{cov}(x^{rm}, x^{tk}) + \sum_{n,m} p_n p_m \text{cov}(x^{rn}, x^{tm}) \end{aligned} \quad (27)$$

where any term on the right is zero when one of the indices j, k, n , or m is equal to N . A suitable first choice for the weights p_j is $Z_j^2 / \sum Z_n^2$ for X-ray diffraction, where the Z_j are atomic numbers, or analogous expressions for neutron or other types of diffraction methods. The resulting reduced variances σ_j^2 may then be used to redefine the weights to be proportional to $1/\sigma_j^2$, a procedure that may be repeated until the weights have become stationary. This refinement of the weights presupposes that the uncertainties in the atomic positions are at least approximately isotropic, permitting a reasonable averaging over different directions in the choice of the σ_j^2 . The different sets of variance and covariance terms that are based on different choices of origin are, of course, mathematically equivalent, and in computations that utilize all variance and covariance terms the choice of origin makes no difference.

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