

Covariances of Thermal Parameters and their Effect on Rigid-Body Calculations

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An isotropic approximation is developed for the covariance matrix of atomic vibration components in an arbitrary coordinate system. The effect of alternative treatments of these covariances on derived rigid-body vibration parameters is illustrated by a numerical comparison. Serious errors may result from neglect of the correlations between different components of the vibration tensors \mathbf{U} if these are referred to non-orthogonal axes.

Atomic vibration parameters deduced from crystallographic studies are often regarded, if at all, mainly as input data for the derivation of related quantities, such as the parameters of rigid-body molecular motion (Cruickshank, 1956; Schomaker & Trueblood, 1968) or of other kinds of postulated behaviour (*e.g.* Busing & Levy, 1964). If a specified model of vibrational behaviour is assumed to account fully for the observed atomic motions, the relevant amplitudes can be obtained more directly through the introduction of appropriate constraints in the crystallographic refinement model (Pawley, 1964, 1971). But crystallographers more commonly refine their structures without such constraints, leaving the atomic vibration parameters so derived to be tested subsequently for compatibility with whatever model or models may suggest themselves.

However, it seems that in the application of this two-stage procedure, the need to take proper account of the statistical correlations among the several atomic vibration components (Scheringer, 1966) may be inadequately recognized. Since these atomic parameters U^{ij} are all derived jointly from the same set of experimental data, it is certainly inappropriate, and may sometimes be severely misleading, to disregard their covariances when they are used for the subsequent derivation of molecular vibration parameters. It is therefore pertinent to examine when such neglect is likely to cause trouble, which are the important covariances, and how these may be included.

The explicit inclusion of the full covariance matrix should pose no problem when the entire study is performed by a single team, provided a suitable computer routine is available that accepts a non-diagonal weight matrix. Difficulties may arise, however, when one group attempts to fit a vibration model to atomic thermal parameters published by a distant laboratory (*e.g.* Burns, Ferrier & McMullan, 1967, 1968; Schomaker & Trueblood, 1968; Forder, 1971), since published reports, while they customarily include estimated

variances of the least-squares parameters, never record their covariances.

In such a situation the lack of published covariances may seem to justify the naive assumption of a diagonal covariance matrix. Unfortunately, such an assumption can lead to quite spurious conclusions, especially if the atomic vibration tensors \mathbf{U} are referred to non-orthogonal crystal axes. At the very least it may be advisable to transform the U^{ij} to an orthogonal coordinate system, in which the neglect of covariances is likely to cause less trouble (see below). But even such a transformation requires some approximations since ignorance of the covariances, in the non-orthogonal system, precludes the explicit evaluation even of the diagonal variances in any chosen orthogonal system.

A better approximation, of rather wide applicability, may be derived quite simply. In general we can safely neglect the variances of the atomic *coordinates*, since these are almost invariably too small to influence the molecular vibration parameters appreciably. Second, we can usually neglect the covariances between vibration parameters of crystallographically independent atoms. Thus, we assume the covariance matrix of the least-squares parameters to consist effectively of separate 6×6 atomic blocks, comprising the covariances among the several components U^{ij} of each atom. (Nevertheless, if a vibrating unit assumed in our model spans two or more asymmetric units and our computer routine demands the explicit introduction of the parameters of symmetry-related atoms, then the covariances of these must likewise be included explicitly.) When no contrary information is available about the form of these blocks, a reasonable assumption is that the variances and covariances are isotropic, *i.e.* that the covariance $\text{cov}(U_{\mathbf{p}}, U_{\mathbf{q}})$ between the mean square vibration amplitudes in directions \mathbf{p} and \mathbf{q} depends only on the angle between these two directions. With this assumption, the 21 independent elements of the 6×6 atomic covariance matrix are determined by two

independent quantities. These may conveniently be taken as S , the (isotropic) variance of the mean square amplitude U ; and η , the correlation coefficient between mutually perpendicular mean-square amplitudes. In a Cartesian coordinate system, the atomic covariance matrix then has the form (see, e.g., Jeffreys, 1961)

$$\begin{array}{ccccccc}
 & U_{(0)}^{11} & U_{(0)}^{22} & U_{(0)}^{33} & U_{(0)}^{12} & U_{(0)}^{23} & U_{(0)}^{13} \\
 U_{(0)}^{11} & S & & & & & \\
 U_{(0)}^{22} & \eta S & S & & & & \\
 U_{(0)}^{33} & \eta S & \eta S & S & & & \\
 U_{(0)}^{12} & 0 & 0 & 0 & \frac{1-\eta}{2} S & & \\
 U_{(0)}^{23} & 0 & 0 & 0 & 0 & \frac{1-\eta}{2} S & \\
 U_{(0)}^{13} & 0 & 0 & 0 & 0 & 0 & \frac{1-\eta}{2} S
 \end{array} \quad (1)$$

To obtain the corresponding covariances in a non-orthogonal system, we may make use of the fact that the covariance matrix of the tensor components U^{ij} transforms, under a change of axes, as the outer product (Margenau & Murphy, 1943) of the tensor U^{ij} with itself. We may thus rewrite the 6×6 matrix (1) above as a fourth-rank tensor, having the 81 totally contravariant components

$$\gamma_{(0)}^{ijkl} = \text{cov}(U_{(0)}^{ij}, U_{(0)}^{kl}).$$

This tensor can then be transformed to any other coordinate system by standard, if tedious, tensor algebra. To obtain the most general form in an arbitrary crystallographic axial system we may transform, for example, to triclinic axes oriented with the \mathbf{a}^* and \mathbf{b} directions parallel, respectively, to the x and y axes of the original Cartesian system. This transformation converts the tensor $\gamma_{(0)}^{ijkl}$ into

$$\gamma^{i'j'k'l'} = \gamma_{(0)}^{ijkl} B_i^{i'} B_j^{j'} B_k^{k'} B_l^{l'},$$

where the postfactor matrix \mathbf{B} is given by

$$\mathbf{B} = \begin{bmatrix} 1 & \cos \gamma^* & \cos \beta^* \\ 0 & \rho & 0 \\ 0 & \sigma & \sin \beta^* \end{bmatrix}$$

with

$$\begin{aligned}
 \rho &= (1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \\
 &\quad \times \cos \beta^* \cos \gamma^*)^{1/2} / \sin \beta^*, \\
 \sigma &= (\cos \alpha^* - \cos \beta^* \cos \gamma^*) / \sin \beta^*.
 \end{aligned}$$

After transformation the new tensor γ can be compressed back to yield the symmetric 6×6 covariance matrix of the transformed vibration components U^{ij} .

Alternatively, the initial matrix (1), as it stands, can be multiplied twice (rather than four times) by a 6×6 transformation matrix derivable from the elements of \mathbf{B} , as shown by Scheringer (1966).

By either route, the general form of the isotropic covariance matrix is found to be matrix (2) (Table 1).

In accordance with Cruickshank's (1956) original definition of U^{ij} , we have taken the transformed reference axes \mathbf{a}_i to be dimensionless, being related to the crystal axes \mathbf{a}_i by the simple proportionality

$$\mathbf{a}_1 = |a^*| \mathbf{a}, \quad \mathbf{a}_2 = |b^*| \mathbf{b}, \quad \mathbf{a}_3 = |c^*| \mathbf{c}$$

(Hirshfeld & Rabinovich, 1966; Cruickshank, 1971). If, instead, the atomic vibration parameters are chosen as

$$\beta^{ij} = |a^i| |a^j| U^{ij},$$

so that the temperature factor has the form

$$\exp(-2\pi^2 h_i h_j \beta^{ij})$$

rather than

$$\exp(-2\pi^2 h_i h_j |a^i| |a^j| U^{ij})$$

then every element γ^{ijkl} of the covariance matrix (2) above must be multiplied by the corresponding factor $|a^i| |a^j| |a^k| |a^l|$.

This isotropic covariance matrix (2), which simplifies materially if any of the reference axes are orthogonal, may be used in several ways. If the complete covariance matrix is available from the least-squares refinement, comparison with the standard matrix above will show how closely the least-squares results support the assumption of isotropic covariances. If only the diagonal variances are available, these may be examined similarly and, if the indicated assumption seems appropriate, may be used to provide estimates of the quantities S and η for evaluation of the full covariance matrix. Finally, if even the variances are lacking, plausible estimates of S and η may still be found for insertion in subsequent computations. Since only relative values of S for the several atoms are required, it suffices to assume, for example, that these vary inversely with the square of the atomic number Z . An appropriate value for η , valid under many circumstances, may be deduced from a statistical argument given by Scheringer (1966).

This argument assumes that the diffraction data, from which the vibration parameters have been derived, are distributed, in quantity and quality, isotropically in reciprocal space. It further supposes that the atomic vibration tensors themselves are approximately isotropic. In an orthogonal coordinate system (which may be adopted for the present argument whether or not

Table 1. The general form of the isotropic covariance matrix [matrix (2)].

	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
U^{11}	S					
U^{22}	$S[(1-\eta)\cos^2\gamma^* + \eta]$	S				
U^{33}	$S[(1-\eta)\cos^2\beta^* + \eta]$	$S[(1-\eta)\cos^2\alpha^* + \eta]$	S			
U^{12}	$S\cos\gamma^*$	$S\cos\gamma^*$	$S[(1-\eta)\cos\alpha^*\cos\beta^* + \eta\cos\gamma^*]$	$S\left[\frac{1-\eta}{2} + \frac{1+\eta}{2}\cos^2\gamma^*\right]$		
U^{23}	$S[(1-\eta)\cos\beta^*\cos\gamma^* + \eta\cos\alpha^*]$	$S\cos\alpha^*$	$S\cos\alpha^*$	$S\left[\frac{1-\eta}{2}\cos\beta^* + \frac{1+\eta}{2}\cos\alpha^*\cos\gamma^*\right]$	$S\left[\frac{1-\eta}{2} + \frac{1+\eta}{2}\cos^2\alpha^*\right]$	
U^{13}	$S\cos\beta^*$	$S[(1-\eta)\cos\alpha^*\cos\gamma^* + \eta\cos\beta^*]$	$S\cos\beta^*$	$S\left[\frac{1-\eta}{2}\cos\alpha^* + \frac{1+\eta}{2}\cos\beta^*\cos\gamma^*\right]$	$S\left[\frac{1-\eta}{2}\cos\gamma^* + \frac{1+\eta}{2}\cos\alpha^*\cos\beta^*\right]$	$S\left[\frac{1-\eta}{2} + \frac{1+\eta}{2}\cos^2\beta^*\right]$

(sym.)

it conforms to the conventional unit cell for a particular crystal) each atomic thermal-parameter block of the least-squares normal matrix is then found to be approximately proportional to

$$\begin{bmatrix} 3 & & & & & \\ 1 & 3 & & & & \\ 1 & 1 & 3 & & & \\ 0 & 0 & 0 & 4 & & \\ 0 & 0 & 0 & 0 & 4 & \\ 0 & 0 & 0 & 0 & 0 & 4 \end{bmatrix} \quad (\text{sym.})$$

This can be inverted to yield a matrix that is approximately proportional to the corresponding 6×6 block of the covariance matrix. The latter is seen to have the form, in an orthogonal coordinate system,

$$\begin{bmatrix} S & & & & & \\ -\frac{1}{4}S & S & & & & \\ -\frac{1}{4}S & -\frac{1}{4}S & S & & & \\ 0 & 0 & 0 & \frac{5}{8}S & & \\ 0 & 0 & 0 & 0 & \frac{5}{8}S & \\ 0 & 0 & 0 & 0 & 0 & \frac{5}{8}S \end{bmatrix} \quad (\text{sym.})$$

Comparing with expression (1), we find that the quantity η takes the value

$$\eta = -\frac{1}{4}$$

under the indicated statistical assumptions. This, then, is the recommended value to be substituted in expression (2), for an arbitrary coordinate system, when no better information is available.

The significance of these general arguments is best illustrated by a concrete example. Accordingly, the following results demonstrate the effect on computed rigid-body parameters of alternative assumptions about the variances and covariances of the input atomic vibration components U^{ij} . The reported computations all begin with the same atomic parameters, obtained by least-squares refinement of benzothieno benzothiophene disulphone, (Goldberg & Shmueli, 1971). The molecule occupies a general position in space group $P2_1/c$ and the monoclinic β angle is 116.8° . Six alternative computations were performed to fit a 'best' set of molecular rigid-body parameters to the 120 independent vibration components U^{ij} of the 20 non-hydrogen atoms in the molecule. For each computation, Table 2 presents the calculated components of the molecular translation and libration tensors \mathbf{T} and \mathbf{L} , as well as the coordinates x_i of the origin of the libration tensor measured from the molecular centre of mass. All quantities are referred to a Cartesian coordinate system defined by the molecular principle moments of inertia.

The agreement attained between input and calculated values of U^{ij} was virtually identical for all six computations. A simple measure of this agreement is provided by the root-mean-square weighted discrepancy

$$r = [\sum w(\Delta U)^2 / \sum w]^{1/2},$$

Table 2. Rigid-body parameters derived for test molecule with alternative assumed covariances of input atomic U^{ij}

Translation components T_{ij} , in $\text{\AA}^2 \times 10^{-4}$, libration components L_{ij} , in $\text{rad}^2 \times 10^{-4}$, coordinates x_i of libration origin, in \AA , all referred to molecular inertial axes. Last column lists estimated standard deviations, in the same units, derived from calculation 3.

Calculation Model	1 T,L,S	2 T,L,x	3/5 T,L,x	4 T,L,x	6 T,L,x	σ
Coordinate axes	Orthogonal	Orthogonal	Orthog/Monocl.	Monoclinic	Monoclinic	
Covariance matrix	Unit matrix	Unit matrix	Isotropic $\eta = -\frac{1}{4}$	Unit matrix	Isotropic $\eta = 0$	
T_{11}	328	330	333	327	332	15
T_{22}	270	268	267	266	270	18
T_{33}	260	259	235	158	247	24
T_{12}	-1	-2	-3	-4	-3	11
T_{23}	-11	-11	-11	-4	-11	16
T_{13}	24	21	19	15	20	13
L_{11}	35	33	39	44	35	4
L_{22}	10	11	12	22	12	2
L_{33}	20	20	20	21	20	2
L_{12}	-3	-3	-4	-5	-4	2
L_{23}	-3	-4	-4	-3	-4	2
L_{13}	5	3	2	1	3	2
x_1	0.58	0.54	0.57	0.45	0.52	0.11
x_2	1.02	1.08	1.01	1.02	1.04	0.09
x_3	0.02	-0.11	-0.10	-0.04	-0.13	0.14

where w is the statistical weight

$$w \propto 1/\sigma^2(U^{ij})$$

assigned to the input value of U^{ij} . Values of r for the several computations fall consistently between 0.0051 and 0.0053 \AA^2 . For comparison, estimates of $\sigma(U^{ij})$ from the crystallographic least-squares matrix were mainly in the range 0.002 to 0.003 \AA^2 . A quantity analogous to r but based on the full weight matrix leads to estimates of the standard deviations of the derived rigid-body parameters if it is assumed that the weight matrix used is an appropriate one and that the molecule in fact behaves as a rigid body. Such estimates, derived from computation 3, are listed in the last column of Table 2. They provide a yardstick against which to gauge the differences among the several computations.

The first computation, reported in column 1, was based on the three-tensor model of Schomaker & Trueblood (1968). The input atomic vibration tensors were first transformed to the inertial axes and, in this coordinate system, all 120 quantities U^{ij} were assigned unit weights, zero correlations. A linear least-squares calculation determined 6 components of the symmetric tensor \mathbf{T} , 6 of \mathbf{L} , and 8 of the screw tensor \mathbf{S} . These three tensors were then referred to a new origin, having the listed coordinates x_i , chosen to make \mathbf{S} symmetric and the trace of \mathbf{T} minimal. Referred to this new origin, none of the calculated components of \mathbf{S} differed significantly from zero and their values are omitted from Table 2.

That the symmetrized tensor \mathbf{S} is indeed of negligible significance is confirmed by the second computation. Here, the input data were treated in exactly the same way but the rigid-body computation was based on Cruickshank's (1956) two-tensor model, in which \mathbf{S} is constrained to zero. However, the coordinates x_i of the

centre of libration were treated as freely adjustable parameters (Hirshfeld, Sandler & Schmidt, 1963). The results, reported in column 2, as well as the r.m.s. discrepancy r , are scarcely distinguishable from those of the previous computation, indicating that for this structure the 15-parameter \mathbf{T} , \mathbf{L} , \mathbf{x} model may be safely substituted for the more elaborate 20-parameter \mathbf{T} , \mathbf{L} , \mathbf{S} model of Schomaker & Trueblood (1968). For simplicity, all remaining comparisons are limited to the \mathbf{T} , \mathbf{L} , \mathbf{x} model.

Column 3 reports a calculation in which the unit covariance matrix was replaced by the more defensible expression (1), with $\eta = -\frac{1}{4}$, all 20 atoms being again weighted equally. The results differ but slightly from those of the two previous calculations. We conclude that in an orthogonal coordinate system neither the neglect of the perpendicular correlations η nor the assignment of equal variances to mixed and unmixed components U^{ij} —neglecting the factor $(1-\eta)/2$ in expression (1)—is of serious consequence. The latter approximation implies variances that, while not quite isotropic, are nevertheless highly symmetric, with equal minima in the directions of the three coordinate axes.

The last three calculations were performed in the non-orthogonal crystal axial system. All quantities were transformed, after computation, to the molecular inertial axes for direct comparison with the previous results. In column 4 are results obtained with a unit covariance matrix, as for computations 1 and 2. Here, however, such a covariance matrix is highly unsuitable because of the very oblique monoclinic β angle. The results, accordingly, differ from those of all previous calculations, producing an unreasonably anisotropic translation tensor \mathbf{T} and anomalously large values of the libration components L_{11} and L_{22} .

In the next computation the variance matrix was taken from expression (2), as simplified by the mono-

clinic symmetry, with $\eta = -\frac{1}{4}$. The results, not tabulated separately, exactly duplicated those of column 3, confirming that the matrices (1) and (2) define strictly corresponding covariances in the two coordinate systems. They also verify that the rigid-body computation yields identical results in different coordinate systems provided the covariances of the input parameters are specified concordantly.

A final computation, reported in column 6, assumed $\eta = 0$ instead of $-\frac{1}{4}$ in expression (2). The results are substantially identical with those of the previous calculation, supporting the earlier indication (comparison of columns 2 and 3) that neglect of the perpendicular correlations η makes no great difference.

These numerical comparisons appear to justify the following generalizations:

(a) The use of the covariance matrix given by expression (2) yields results that are strictly independent of the coordinate system in which the atomic vibration components U^{ij} are expressed.

(b) Neglect of all covariances and equal weighting of U^{ii} and U^{ij} ($i \neq j$), while not strictly justifiable, are both relatively harmless approximations in an orthogonal axial system.

(c) The most serious error to be avoided is the neglect of those covariances that arise in a non-orthogonal system, regardless of the value assigned to η , because of the obliquity of the reference axes.

(d) The agreement between observed and calculated values of U^{ij} , as measured by the r.m.s. discrepancy r , cannot be relied upon to distinguish between a good and a bad weight matrix.

The calculations reported above pertain to a structure whose experimental thermal parameters fit the rigid-molecule hypothesis rather poorly, having been chosen to emphasize the effects of alternative weighting procedures. Similar calculations have been performed on the data for 1,4,5,8-tetraoxadecalin (Fuchs, Goldberg & Shmueli, 1972), whose thermal parameters conform closely to the rigid-body model. In this structure, changes in the assumed covariance matrix, based on alternative choices of unit-cell axes differing widely in obliquity, had relatively little effect on the derived rigid-body parameters. In general, the sensitivity of

the rigid-body parameters to the weighting procedure adopted is likely to depend, not only on the magnitudes of the discrepancies between experimental and calculated U^{ij} , but also on the relative contributions to these discrepancies of random experimental errors, systematic errors, intramolecular vibrations, and other deficiencies in our refinement model.

Our discussion is not meant to imply that an isotropic covariance matrix is always appropriate or, for that matter, that we may invariably neglect statistical correlations between the thermal parameters of different atoms in the asymmetric unit. What is suggested is that, in the absence of complete information, such an approximation is often less dangerous than various alternatives having even less physical justification.

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