One can thus arrive at the set of Heesch groups noting to what the given aspect groups belongs.

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References

DONNAY, G., CORLISS, L. M., DONNAY, J. D. H., ELLIOTT, N. & HASTINGS, J. M. (1958). *Phys. Rev.* **112**, 1917–1923.
DONNAY, J. D. H. (1967). *Trans. Amer. Cryst. Assoc.*, **3**, 74–95.
DONNAY, J. D. H. & DONNAY, G. (1959). *C. R. Acad. Sci. Paris*, **248**, 3317–3319.
HEESCH, H. (1930). *Z. Kristallogr.* **73**, 325–345.
LOMONT, J. S. (1959). *Applications of Finite Groups*. New York: Academic Press.
OPECHOWSKI, W. & GUCCIONE, R. (1965). *Magnetism*, Vol. IIA. Edited by G. T. RADO & H. SUHL. New York: Academic Press.
RIEDEL, E. P. & SPENCE, R. D. (1960). *Physica*, **26**, 1174–1184.
SHUBNIKOV, A. V. (1951). *Simmetrija i antisimmetrija konečnykh figur.* (Symmetry and antisymmetry of finite figures). Moscow: Nauka.
SHUBNIKOV, A. V. & BELOV, N. V. (1964). *Colored Symmetry*. New York: Pergamon Press.
SPENCE, R. D. & VAN DALEN, P. A. (1968). *Acta Cryst.* A**24**, 494–497.
SUMBERG, D. A., DAYANIDHI, K. K., PARKER, P. M. & SPENCE, R. D. (1972). *Acta Cryst.* **28**, 338.

Acta Cryst. (1973). A**29**, 306

On the use of unit-weight matrices in the least-squares determination of rigid-body vibration tensors.

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The transformation laws for the weighting and covariance matrices of the components of the atomic vibration tensors are derived. It is shown that the use of unit-weight matrices in the least-squares determination of the rigid-body vibration tensors **TLS** from the atomic vibration components leads to incompatible results when the **TLS** parameters are refined in different Cartesian coordinate systems. Numerical results for some molecules showed that the differences in the obtained components of **TLS** usually lie within the range of two standard deviations. If the covariances of the atomic vibration components are taken into account in some simple form the incompatibilities vanish.

The components of the rigid-body vibration tensors **TLS** are usually determined from the components of the atomic vibration tensors U_r by means of the least-squares method. In the majority of cases a Cartesian coordinate system and unit weights for the components U_r^{ik} are used. With the structure of lithium succinate (Klapper & Küppers, 1973) we first noticed that the principal components of the libration tensor **L** were not uniquely determined when it was refined in two different Cartesian coordinate systems and unit weights were employed. The differences found between the respective principal components could not be ascribed to rounding-off errors. In this paper we shall give further examples where this happens.

Discrepancies of this type arise because the unit matrix as weighting matrix does not transform into the unit matrix under rotation of axes. In an earlier paper (Scheringer, 1966*a*) – hereafter referred to as SCHE – we stated the transformation law without proof for the 6×6 weighting matrices of the components U_r^{ik} when the base vectors were transformed. Hirshfeld & Shmueli (1972) have recently derived the transformation law for the respective 6×6 covariance matrices by reducing it to the transformation law of a 4th rank tensor. In this paper we want to show first how the transformation law can be obtained simply from the basic equations of the least-squares method.

In SCHE we showed that the weighting matrix for the refinement of the parameters **TLS** should be the normal matrix M of a structure-factor least-squares refinement of the components U_r^{ik}. The covariance matrix C is then proportional to M^{-1}. We now assume that in the last cycle of the structure-factor refinement we have only refined the $6n$ independent components U_r^{ik} of the n atoms of the (nearly) rigid molecule, *i.e.* we neglect all covariances to other types of parameters. Then M and C consist of n^2 6×6 blocks. We define the change of the coordinate system by the transformation

$$\mathsf{X}' = \mathsf{A}\mathsf{X} \tag{1}$$

of the (contravariant) components of a vector X in direct space. Then the (contravariant) components U_r^{ik} of the rth atom transform according to

$$\mathsf{U}_r' = \mathsf{A}\mathsf{U}_r\mathsf{A}^T, \tag{2a}$$

(Scheringer, 1966*b*). If we now arrange the 6 independent components U_r^{ik} in a 6×1 column matrix V_r in the sequence 11, 22, 33, 12, 13, 23 then, by rearranging the terms in equation (2*a*), it can be shown that the transformation law

$$\mathsf{V}_r = \mathsf{L}\mathsf{V}_r \tag{2b}$$

corresponds to the law (2*a*). The elements of the 6×6 matrix L are given in SCHE. (Formally, L is obtained by reducing the 9×9 outer product $\mathsf{A}\times\mathsf{A}$ to a 6×6 matrix). The transformation laws (2*a*) and (2*b*) also hold for the shifts ε_r^{ik} of the components U_r^{ik}. Let the normal equations for refining the components U_r^{ik} from diffraction data in the two coordinate systems be

$$\mathsf{M}\varepsilon = \mathsf{N}\ , \quad \mathsf{M}'\varepsilon' = \mathsf{N}', \tag{3}$$

where ε and ε' are the $6n\times 1$ column matrices of the shifts. Let G be a $6n\times 6n$ block-diagonal matrix with 6×6 blocks L. Then we obtain from equation (2*b*)

$$\varepsilon'=\mathsf{G}\varepsilon\,,\quad \varepsilon=\mathsf{G}^{-1}\varepsilon'\,. \tag{4}$$

From equations (3) and (4) we obtain

$$\mathsf{G}^{T-1}\mathsf{M}\mathsf{G}^{-1}\varepsilon'=\mathsf{G}^{T-1}\mathsf{N}\,, \tag{5}$$

and hence for the weighting matrices

$$\mathsf{M}'=\mathsf{G}^{T-1}\mathsf{M}\mathsf{G}^{-1}, \tag{6}$$

and for the covariance matrices

$$\mathsf{C}'=\mathsf{G}\mathsf{C}\mathsf{G}^{T}. \tag{7}$$

Since G is 6×6 block-diagonal, equations (6) and (7) imply that for any 6×6 block of M and C that refers to two atoms r and s

$$\mathsf{M}'_{66}=\mathsf{L}^{T-1}\mathsf{M}_{66}\mathsf{L}^{-1}, \tag{8}$$

and

$$\mathsf{C}'_{66}=\mathsf{L}\mathsf{C}_{66}\mathsf{L}^{T}, \tag{9}$$

cf. SCHE (9). The equations (6) to (9) represent the transformation laws for weighting and covariance matrices of the thermal data U_r^{ik}. The equations are valid for any type of transformation (1) and are not restricted to orthogonal ones ($\mathsf{A}^T=\mathsf{A}^{-1}$).

Usually the full $6n\times 6n$ covariance matrices are not used for the refinement of the **TLS** parameters. Thus it is of interest to use approximate matrices in Cartesian coordinate systems which remain invariant under rotation of axes, *i.e.* we should postulate $\mathsf{M}'=\mathsf{M}$ and $\mathsf{C}'=\mathsf{C}$ if $\mathsf{A}^T=\mathsf{A}^{-1}$. One such invariant (non-diagonal) weighting matrix M_{66}, which is likely to apply to the components U_r^{ik} as data, is the matrix Q_r of SCHE (8). Hirshfeld & Shmueli (1972) showed that there are invariant 6×6 covariance matrices which are characterized by two parameters S and η and which can be derived from isotropic Cartesian tensors of 4th rank. The weighting matrix Q_r of SCHE (8) can be shown to correspond to the invariant covariance matrix with $S=Z_r^{-2}$ (Z_r = number of electrons of atom r) and $\eta=-\frac{1}{4}$.

The main point which concerns the unit matrix as a weighting (covariance) matrix is that it does not transform into the unit matrix for orthogonal transformations (1), *i.e.* if $\mathsf{M}=\mathsf{C}=\mathsf{E}$ then $\mathsf{M}'\neq\mathsf{E}$, $\mathsf{C}'\neq\mathsf{E}$ for $\mathsf{A}^T=\mathsf{A}^{-1}$. This follows from the fact that, for $S=1$, no value of η can be found which reduces Hirshfeld & Shmueli's matrix (1) to the unit matrix. Hence the parameters **TLS** will always attain incompatible values when they are refined in different Cartesian coordinate systems and unit weights are employed. However, Hirshfeld & Shmueli found with an example that the results obtained with unit weights did not significantly differ from those obtained with invariant weighting (covariance) matrices.

Initially, several examples of the transformation (9) for $\mathsf{C}_{66}=\mathsf{E}$ were computed and the unit matrix was found to be considerably altered by the transformation. In one example the diagonal elements of the transformed matrix C'_{66} attained values between 1·65 and 0·63, the off-diagonal elements in the upper left 3×3 block took values up to $-0{\cdot}37$, and the remaining off-diagonal elements took values up to $-0{\cdot}27$. These elements of the transformed unit matrix correspond, in order of magnitude, to those of a covariance matrix with $\eta=0$ and a monoclinic angle of 110° [Hirshfeld & Shmueli, 1972, equation (2)].

In order to study to what extent the non-invariance of the unit matrix influences the results of the refinement, we have refined the parameters **TLS** of 11 molecules with unit weights in 6 different Cartesian coordinate systems. Each system is characterized by 3 Eulerian angles φ, θ, ψ (for their definition see Margenau & Murphy, 1965, p. 354). Positional and thermal parameters of the atoms were transformed to the rotated systems. For the refinement of the **TLS** parameters a modified version of Schomaker & Trueblood's (1968) program was used. The results for 6 molecules are given in Table 1. Since the trend of the deviations

Table 1. *Principal components L_1, L_2, L_3 and estimated standard deviations $\sigma(L_i)$ [in (°)^2] of the libration* **L** *as determined from refinements of the* **TLS** *parameters in six different Cartesian coordinate systems*

Each system is described by three Eulerian angles φ, θ, ψ, which have the following values (in °): system I (0,0,0); II (0,45,45); III (30,90,60); IV (45,60,0); V (90,60,30); VI system of principal components L_i (angles not computed). $\Delta_{\max}$ is the maximum deviation found between any two respective components in different coordinate systems.

	I	II	III	IV	V	VI	$\Delta_{\max}$	$\sigma(L_i)$
Lithium succinate (Klapper & Küppers, 1973)	89·7	75·6	81·3	85·0	79·8	79·7	14·2	12·2
	0·5	0·2	0·2	− 1·5	0·1	− 1·8	2·3	1·3
	−14·9	−12·6	−12·5	−13·6	−12·5	−12·0	2·9	2·9
Dichlorodulcitol (Simon & Sasvári, 1971)	10·3	10·8	11·0	12·4	10·3	10·3	2·1	0·9
	8·7	8·9	9·5	9·7	9·2	9·6	1·0	1·5
	4·4	4·5	4·5	4·5	4·0	4·8	0·8	0·8
Dibromodulcitol (Simon & Sasvári, 1971)	13·2	14·6	11·7	17·7	16·0	16·2	4·3	4·5
	5·7	4·2	7·9	5·7	4·1	3·8	3·8	2·8
	− 3·3	0·5	− 3·9	− 0·7	− 3·1	− 2·1	4·4	3·4
Ammonium oxalate perhydrate (Pedersen, 1972)	88·2	94·2	87·4	90·6	92·6	83·7	10·5	10·8
	11·1	11·0	10·5	11·1	10·8	10·9	0·6	0·8
	− 4·1	− 9·9	− 1·9	− 7·3	− 7·5	0·3	10·2	10·7
Lidocain hydrohexafluoroarsenate (Hanson, 1972)	178·5	179·2	164·2	170·6	166·3	165·2	15·0	17·7
	93·4	93·1	102·8	87·2	92·6	92·1	15·6	17·6
	46·3	45·0	46·3	35·0	34·2	34·5	12·1	16·8
Azobisisobutyronitrile (Argay & Sasvári, 1971)	34·9	34·2	34·2	35·6	35·5	33·8	1·8	2·8
	8·8	8·8	8·2	8·8	9·0	8·7	0·8	1·2
	2·4	1·4	2·0	2·6	1·0	1·5	1·6	1·6

is much the same for all **TLS** components, we have only listed the principal components L_i of the libration tensor, and their standard deviations. Also, the maximum deviations found between any two respective components in different systems are listed under the heading $\Delta_{\max}$. Although these maximum deviations attain values up to 30% of the largest principal component L_i of a given molecule, only once do they exceed two standard deviations. As can be seen from Table 1 the trend of the values of $\Delta_{\max}(L_i)$ and $\sigma(L_i)$ is much the same. The $\sigma(L_i)$ are computed from standard statistical formulae, but they do, of course, not only contain statistical errors of the observed components U_r^{ik}, but also systematic experimental errors and insufficiencies of the rigid-body model. That insufficiencies of the rigid-body model do indeed influence the standard deviations $\sigma(L_i)$ can be seen from the fact that in those cases where a negative value of L_i was computed, $\sigma(L_i)$ is fairly large.

To sum up:

(1) There is a definite influence of the choice of the (Cartesian) coordinate system – or, equally, of the choice of the weighting system – upon the values obtained for the components of **TLS**, but the variation of the results will rarely exceed two standard deviations. Thus in most cases this impact does not seem to cause much trouble. In this sense we can confirm Hirshfeld & Shmueli's (1972) conclusion.

(2) The variation of the results obtained in different (Cartesian) coordinate systems is more or less proportional to the magnitude of the calculated standard deviation, no matter what the reason for a possible large value of the standard deviation may be. Hence not only the choice of the coordinate system – or the choice of the weighting matrix – but also the standard of the **TLS** refinement has an effect on the scattering of the final values of the parameters **TLS**.

(3) In order to obtain (and publish) unique results the use of a covariance (weighting) matrix, which remains invariant under changes of the coordinate system, is recommended. Simple covariance matrices in a Cartesian system are obtained either with $\eta=0$, which is diagonal, or with $\eta=-\frac{1}{4}$, which is not diagonal but can be better defended on physical grounds.

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References

ARGAY, G. & SASVÁRI, K. (1971). *Acta Cryst.* **B27**, 1851–1858.

HANSON, A. W. (1972). *Acta Cryst.* **B28**, 672–679.

HIRSHFELD, F. L. & SHMUELI, U. (1972). *Acta Cryst.* **A28**, 648–652.

KLAPPER, H. & KÜPPERS, H. (1973). *Acta Cryst.* **B29**. 21–26.

MARGENAU, H. & MURPHY, G. M. (1965). *Die Mathematik für Physik und Chemie.* Frankfurt, Zürich: Deutsch.

PEDERSEN, B. F. (1972). *Acta Cryst.* **B28**, 746–754.

SCHERINGER, C. (1966*a*). *Acta Cryst.* **20**, 319–320.

SCHERINGER, C. (1966*b*). *Acta Cryst.* **20**, 316–319.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

SIMON, K. & SASVÁRI, K. (1971). *Acta Cryst.* **B27**, 806–815.

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To find the largest sphere which can be inscribed between four others.

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An algorithm is given for determining the radius of a sphere inscribed in the cavity between four different spheres arbitrarily separated.

When considering the packing of atoms and molecules in a crystal it is often necessary to calculate the sizes of the cavities remaining in the structure. This question can be paraphrased as: find the radius of the sphere inscribed in the cavity between four tangent spheres.

If the four spheres are also mutually tangent, then the problem has an elegant solution in terms of the curvatures α, β, γ and δ (the reciprocals of the radii) of the four known spheres and the curvature ε of the inscribed (or circumscribed) sphere. These are related by $(\alpha+\beta+\gamma+\delta+\varepsilon)^2=3(\alpha^2+\beta^2+\gamma^2+\delta^2+\varepsilon^2)$. In N dimensions the general relationship $N(\sum\alpha^2)=(\sum\alpha)^2$ has been proved by Coxeter (1952).

If, however, the four spheres 1, 2, 3 and 4 are not mutually tangential but have radii r_1, r_2, r_3, and r_4 and their centres at distances d_{12}, d_{13}, *etc.* apart, no formula has been found in the literature and recourse to a computational procedure was necessary.

Five points, the centres of the five spheres, define four vectors, **12**, **13**, **14** and **15**. These four vectors involve 10 distances between the five points which would be sufficient to define a simplex (generalized tetrahedron) in four dimensions. The four-dimensional volume V of this simplex is given by a determinantal equation:

$$-(96)^2V^2=\begin{vmatrix} 0 & d_{12}^2 & d_{13}^2 & d_{14}^2 & d_{15}^2 & 1 \\ d_{12}^2 & 0 & d_{23}^2 & d_{24}^2 & d_{25}^2 & 1 \\ d_{13}^2 & d_{23}^2 & 0 & d_{34}^2 & d_{35}^2 & 1 \\ d_{14}^2 & d_{24}^2 & d_{34}^2 & 0 & d_{45}^2 & 1 \\ d_{15}^2 & d_{25}^2 & d_{35}^2 & d_{45}^2 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 0 \end{vmatrix}\,.$$

If our figure is not four-dimensional, but is degenerate and three-dimensional, as real configurations of atoms of course are, then this determinant will be zero. This relationship then enables us to find (from a quadratic equation) any one of the ten distances d_{ij} in terms of the others.

This can be used for at least two purposes. The first is: given the three distances of a point P from three fixed points A, B and C (at given distances from each other) and also the corresponding three distances of a point Q from the same three points, find the distance PQ. The two solu-