preferred to express the seminvariant as $(2h + 4k + 3l)$ rather than $(h - k, l)$.

The 6 equivalent origins are correctly given as $(0,0,0)$, $(0,0,\frac{1}{2})$, $(\frac{1}{3},\frac{2}{3},0)$, $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$, $(\frac{2}{3},\frac{1}{3},0)$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$. It looks as if one needed to specify the origin in two directions, *i.e.* along the z axis and in the xy plane. However, it is only necessary to specify the origin in one direction, along the line passing through $(0,0,0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. All the six permissible origins lie on this line since they are generated by the successive addition of $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ to $(0,0,0)$. The origin is uniquely specified through the fixation of the phase of one reflection which will take on different phase values in the six permissible origins, each differing by $2\pi/6$.

The only reflections which do not take on different values in the six permissible origins are those which have $(2h + 4k + 3l) = n6$. This proves the seminvariant vector to be $(2h + 4k + 3l)$ and the seminvariant modulus to be 6.

In the tables given by Hauptman & Karle (1956) and Karle (1974) the type should be $3P6$, not $3P32$. In the notation of Giacovazzo (1974) the H–K group is $(2h + 4k + 3l)P6$. In all tables the seminvariant phases should be Φ_{hkl} where $(2h + 4k + 3l) \equiv 6$. The permitted values for semi-independent phases are $\|6\|$, except for $\|2\|$ for $h + 2k = n3$ and $\|3\|$ for l even. The number of phases linearly semi-independent to be specified is 1.

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Acta Cryst. (1978). A**34**, 827–828

A discussion of the solution for the best rotation to relate two sets of vectors.

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(*Received* 3 *April* 1978; *accepted* 13 *April* 1978)

A method is discussed for obtaining the best proper rotation to relate two sets of vectors.

The simple procedure for obtaining the best rotation to relate two sets of vectors described in an earlier paper (Kabsch, 1976) has been used in processing oscillation films (Kabsch, 1977), for the determination of non-crystallographic symmetry elements (Kabsch, Gast, Schulz & Leberman, 1977), and for a comparison of macromolecules. In the last application an improper rotation was sometimes obtained from the procedure (Nyburg & Yuen, 1977). The purpose of this communication is to show how a best proper rotation can always be obtained from the procedure.

Let $\mathbf{x}_n$ and $\mathbf{y}_n$ ($n = 1, \ldots, N$) be two given vector sets and w_n the weights corresponding to each pair $\mathbf{x}_n$, $\mathbf{y}_n$. All possible orthogonal matrices $\mathbf{U}$ for which the function

$$E = \tfrac{1}{2} \sum_n w_n (\mathbf{U}\mathbf{x}_n - \mathbf{y}_n)^2 \qquad (1)$$

has an extremal point must obey [see equation (9) of Kabsch, 1976]

$$\mathbf{U}(\mathbf{S} + \mathbf{L}) = \mathbf{R}. \qquad (2)$$

Writing x_{nk} and y_{nk} for the kth components of the vectors $\mathbf{x}_n$ and $\mathbf{y}_n$ the matrices $\mathbf{R}$ and $\mathbf{S}$ are defined as

$$\mathbf{R} = (r_{ij}) = (\sum_n w_n y_{ni} x_{nj}) \qquad (3)$$

$$\mathbf{S} = (s_{ij}) = (\sum_n w_n x_{ni} x_{nj}). \qquad (4)$$

$\mathbf{L} = (l_{ij})$ is a symmetric matrix of Lagrange multipliers which is determined from the equation

$$(\mathbf{S} + \mathbf{L})(\mathbf{S} + \mathbf{L}) = \tilde{\mathbf{R}}\mathbf{R}. \qquad (5)$$

$\tilde{\mathbf{R}}\mathbf{R}$ is a known symmetric positive definite matrix whose positive eigenvalues μ_k and eigenvectors $\mathbf{a}_k$ can be determined by standard procedures. The general solution of (5) is of the form

$$(\mathbf{S} + \mathbf{L}) = (s_{ij} + l_{ij}) = (\sum_k a_{ki} a_{kj} \cdot \sigma_k \sqrt{\mu_k}), \qquad (6)$$

where a_{ki} denotes the ith component of $\mathbf{a}_k$ and the arbitrary quantities σ_k can only assume the values ± 1. If an eigenvalue μ_k is degenerate the eigenvector $\mathbf{a}_k$ of $\tilde{\mathbf{R}}\mathbf{R}$ cannot be determined uniquely. However, $\mathbf{S} + \mathbf{L}$ will not be affected by this ambiguity if all its eigenvalues of the magnitude $\sqrt{\mu_k}$ have identical signs. The final construction of all orthogonal matrices $\mathbf{U} = (u_{ij})$ for which E assumes an extremal point is given by

$$u_{ij} = \sum_k b_{ki} a_{kj}, \qquad (7)$$

where b_{ki} is the ith component of the vector

$$\mathbf{b}_k = \mathbf{U}\mathbf{a}_k = \mathbf{U}(\mathbf{S} + \mathbf{L})\mathbf{a}_k/(\sigma_k \sqrt{\mu_k}) = \mathbf{R}\mathbf{a}_k/(\sigma_k \sqrt{\mu_k}). \qquad (8)$$

The residual E at each extremal point is

$$\begin{aligned} E &= \tfrac{1}{2} \sum_n w_n (\mathbf{U}\mathbf{x}_n - \mathbf{y}_n)^2 = \tfrac{1}{2} \sum_n w_n (\mathbf{x}_n^2 + \mathbf{y}_n^2) \\ &\quad - \sum_n w_n \mathbf{y}_n \cdot (\mathbf{U}\mathbf{x}_n) \\ &= \tfrac{1}{2} \sum_n w_n (\mathbf{x}_n^2 + \mathbf{y}_n^2) - \sum_n w_n [\sum_k (\mathbf{b}_k \cdot \mathbf{y}_n)(\mathbf{x}_n \cdot \mathbf{a}_k)] \\ &= \tfrac{1}{2} \sum_n w_n (\mathbf{x}_n^2 + \mathbf{y}_n^2) - \sum_k \mathbf{b}_k \cdot (\mathbf{R}\mathbf{a}_k) \\ &= \tfrac{1}{2} \sum_n w_n (\mathbf{x}_n^2 + \mathbf{y}_n^2) - \sum_k \sigma_k \sqrt{\mu_k}. \end{aligned} \qquad (9)$$

The maximum of E is obtained if all σ_k are -1. The minimum of E is obtained if all σ_k are $+1$, which agrees with the result of Kabsch (1976).

It has also been shown in Kabsch (1976) that $\mathbf{S} + \mathbf{L}$ must be positive definite at the minimum of E. Hence, from (2) the determinants of the two matrices, $\mathbf{U}$ and $\mathbf{R}$, must have the same signs.

In the case that $\det(\mathbf{R}) > 0$, the orthogonal matrix $\mathbf{U}$ corresponding to the minimum of E will be a proper rotation. In the case that $\det(\mathbf{R}) < 0$, an improper rotation will be obtained at the minimum of E (Nyburg & Yuen, 1977). From (9), the smallest residual E corresponding to a best true rotation is then obtained if $\sigma_1 = \sigma_2 = +1$ and $\sigma_3 = -1$ assuming that μ_3 is the smallest eigenvalue of $\tilde{\mathbf{R}}\mathbf{R}$ (three-dimensional vector space). Note that if the smallest eigenvalue is degenerate a best rotation cannot be determined uniquely in the case $\det(\mathbf{R}) < 0$.

Finally, it might be worth mentioning that this procedure can be generalized to find a best unitary matrix to relate two sets of vectors in the complex finite-dimensional vector space.

Summarizing the above results, the following procedure for obtaining a best proper rotation in a three-dimensional vector space is suggested.

(*a*) Remove any translation between the two given vector sets $\mathbf{x}_n$, $\mathbf{y}_n$ and determine $E_0 = \frac{1}{2}\sum_n w_n(\mathbf{x}_n^2 + \mathbf{y}_n^2)$ and $\mathbf{R}$.

(*b*) Form $\tilde{\mathbf{R}}\mathbf{R}$, determine eigenvalues μ_k and the mutually orthogonal eigenvectors $\mathbf{a}_k$ and sort so that $\mu_1 \geq \mu_2 \geq \mu_3$. Set $\mathbf{a}_3 = \mathbf{a}_1 \times \mathbf{a}_2$ to be sure to have a right-handed system.

(*c*) Determine $\mathbf{Ra}_k$ ($k = 1, 2, 3$), normalize the first two vectors to obtain $\mathbf{b}_1$, $\mathbf{b}_2$ and set $\mathbf{b}_3 = \mathbf{b}_1 \times \mathbf{b}_2$. This will also take care of the case $\mu_2 > \mu_3 = 0$.

(*d*) Form $\mathbf{U}$ according to (7) to obtain the best rotation. Set $\sigma_3 = -1$ if $\mathbf{b}_3.(\mathbf{Ra}_3) < 0$, otherwise $\sigma_3 = +1$. The residual error is then $E = E_0 - \sqrt{\mu_1} - \sqrt{\mu_2} - \sigma_3\sqrt{\mu_3}$.

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Acta Cryst. (1978). A**34**, 828–829

A test for rigid-body vibrations, based on a generalization of Hirshfeld's 'rigid-bond' postulate.

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(*Received* 5 *April* 1978; *accepted* 12 *May* 1978)

A simple test for the validity of the rigid-body model for molecular vibrations in crystals is proposed.

Since bond-stretching vibrations for atoms other than hydrogen and deuterium are normally of much smaller amplitude than other vibrations (bond-bending, torsional, rigid-body translational and rotational oscillations), the mean-square vibrational amplitudes of a pair of bonded atoms should be equal along the bond direction, even though they may be widely different in other directions. As Hirshfeld (1976) has pointed out, this provides a necessary (although by no means sufficient) condition that thermal ellipsoids derived by X-ray analysis represent genuine vibrational ellipsoids. If the condition is seriously violated, the U_{ij} values may be suspected of being contaminated by charge-density deformation contributions or absorption or other systematic errors.

Hirshfeld's 'rigid-bond' postulate can be expressed in a more general (though somewhat weaker) form as a 'rigid-body' postulate and used as a simple test for the validity of the rigid-body model of any molecule for which U_{ij} values are available. Since rigidity implies that *all* distances within a body remain invariant, all pairs of atoms in a rigid molecule can be regarded as being connected by virtual bonds. Hence the equality condition should hold for all such pairs of atoms as well as it does for bonded pairs. Conversely, when the data satisfy the rigid-bond test, gross violation of the equality condition for certain pairs of non-bonded atoms within a molecule should indicate that the rigid-body model is inappropriate for the molecule in question and might also provide some hints about the nature of the internal motions within the molecule.

With these ideas in mind, we have calculated mean-square vibrational amplitudes $z^2_{A,B}$ in the AB direction for all pairs of atoms in several molecules from U_{ij} values obtained by conventional least-squares refinement. We find that the condition $\Delta_{A,B} = z^2_{A,B} - z^2_{B,A} \sim 0$ is obeyed well in cases where least-squares analysis of the vibration tensors in terms of rigid-body $\mathbf{T}$, $\mathbf{L}$ and $\mathbf{S}$ tensors (Schomaker & Trueblood, 1968) leads to good agreement between U_{ij}(obs.) and U_{ij}(calc.) values. This is hardly surprising, since the condition $\Delta_{A,B} = 0$ is obeyed *exactly* for the rigid-body model.

More interesting are examples where the rigid-body analysis leads to poor agreement between U_{ij}(obs.) and U_{ij}(calc.). We discuss here one illustrative example in detail, that of 3-phenyl-3-benzyl-*N*-methylsuccinimide (Fig. 1), the crystal structure of which has recently been determined (at 100 K) in our laboratory. The $z^2_{A,B}$ values for the $21.20/2$ directions between all pairs of C, N and O atoms are

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