

1. GENERAL RELATIONSHIPS AND TECHNIQUES

$$v^i \mathbf{a}_i = (v_k g^{ik}) \mathbf{a}_i = v_k \mathbf{a}^k.$$

Hence

$$\mathbf{a}^k = g^{ik} \mathbf{a}_i \quad (1.1.4.13)$$

and, similarly,

$$\mathbf{a}_k = g_{ik} \mathbf{a}^i. \quad (1.1.4.14)$$

(iii) The tensors g_{ij} and g^{ij} are symmetric, by definition.

(iv) It follows from (1.1.4.11) and (1.1.4.12) or (1.1.4.13) and (1.1.4.14) that the matrices of the direct and reciprocal metric tensors are mutually inverse, *i.e.*

$$\begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}^{-1} = \begin{pmatrix} g^{11} & g^{12} & g^{13} \\ g^{21} & g^{22} & g^{23} \\ g^{31} & g^{32} & g^{33} \end{pmatrix}, \quad (1.1.4.15)$$

and their determinants are mutually reciprocal.

1.1.4.4. Examples

There are numerous applications of tensor notation in crystallographic calculations, and many of them appear in the various chapters of this volume. We shall therefore present only a few examples.

(i) The (squared) magnitude of the diffraction vector $\mathbf{h} = h_i \mathbf{a}^i$ is given by

$$|\mathbf{h}|^2 = \frac{4 \sin^2 \theta}{\lambda^2} = h_i h_j g^{ij}. \quad (1.1.4.16)$$

This concise relationship is a starting point in a derivation of unit-cell parameters from experimental data.

(ii) The structure factor, including explicitly anisotropic displacement tensors, can be written in symbolic matrix notation as

$$F(\mathbf{h}) = \sum_{j=1}^N f_{(j)} \exp(-\mathbf{h}^T \boldsymbol{\beta}_{(j)} \mathbf{h}) \exp(2\pi i \mathbf{h}^T \mathbf{r}_{(j)}), \quad (1.1.4.17)$$

where $\boldsymbol{\beta}_{(j)}$ is the matrix of the anisotropic displacement tensor of the j th atom. In tensor notation, with the quantities referred to their natural bases, the structure factor can be written as

$$F(h_1 h_2 h_3) = \sum_{j=1}^N f_{(j)} \exp(-h_i h_k \beta_{(j)}^{ik}) \exp(2\pi i h_i x_{(j)}^i), \quad (1.1.4.18)$$

and similarly concise expressions can be written for the derivatives of the structure factor with respect to the positional and displacement parameters. The summation convention applies only to indices denoting components of vectors and tensors; the atom subscript j in (1.1.4.18) clearly does not qualify, and to indicate this it has been surrounded by parentheses.

(iii) Geometrical calculations, such as those described in the chapters of Part 3, may be carried out in any convenient basis but there are often some definite advantages to computations that are referred to the natural, non-Cartesian bases (see Chapter 3.1). Usually, the output positional parameters from structure refinement are available as contravariant components of the atomic position vectors. If we transform them by (1.1.4.11) to their covariant form, and store these covariant components of the atomic position vectors, the computation of scalar products using equations (1.1.4.9) or (1.1.4.10) is *almost as efficient as it would be if the coordinates were referred to a Cartesian system*. For example, the right-hand side of the vector identity (1.1.3.5), which is employed in the computation of dihedral angles, can be written as

$$(A_i C^i)(B_k D^k) - (A_i D^i)(B_k C^k).$$

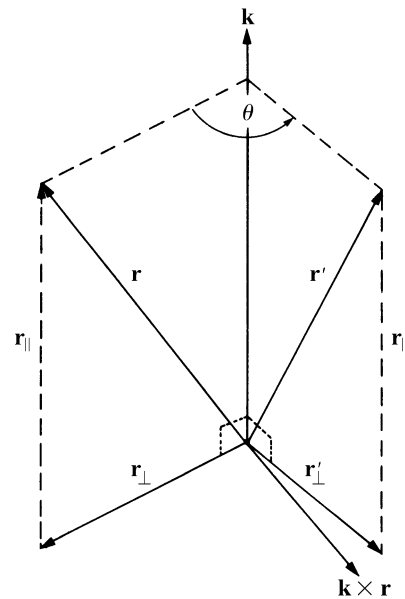


Fig. 1.1.4.1. Derivation of the general expression for the rotation operator. The figure illustrates schematically the decompositions and other simple geometrical considerations required for the derivation outlined in equations (1.1.4.22)–(1.1.4.28).

This is a typical application of reciprocal space to ordinary direct-space computations.

(iv) We wish to derive a tensor formulation of the vector product, along similar lines to those of Chapter 3.1. As with the scalar product, there are several such formulations and we choose that which has both vectors, say \mathbf{u} and \mathbf{v} , and the resulting product, $\mathbf{u} \times \mathbf{v}$, referred to a covariant basis. We have

$$\begin{aligned} \mathbf{u} \times \mathbf{v} &= u^i \mathbf{a}_i \times v^j \mathbf{a}_j \\ &= u^i v^j (\mathbf{a}_i \times \mathbf{a}_j). \end{aligned} \quad (1.1.4.19)$$

If we make use of the relationships (1.1.3.3) between the direct and reciprocal basis vectors, it can be verified that

$$\mathbf{a}_i \times \mathbf{a}_j = V e_{kij} \mathbf{a}^k, \quad (1.1.4.20)$$

where V is the volume of the unit cell and the antisymmetric tensor e_{kij} equals +1, -1, or 0 according as kij is an even permutation of 123, an odd permutation of 123 or any two of the indices kij have the same value, respectively. We thus have

$$\begin{aligned} \mathbf{u} \times \mathbf{v} &= V e_{kij} u^i v^j \mathbf{a}^k \\ &= V g^{lk} e_{kij} u^i v^j \mathbf{a}_l, \end{aligned} \quad (1.1.4.21)$$

since by (1.1.4.13), $\mathbf{a}^k = g^{lk} \mathbf{a}_l$.

(v) *The rotation operator.* The general formulation of an expression for the rotation operator is of interest in crystal structure determination by Patterson techniques (see Chapter 2.3) and in molecular modelling (see Chapter 3.3), and another well known crystallographic application of this device is the derivation of the translation, libration and screw-motion tensors by the method of Schomaker & Trueblood (1968), discussed in Part 8 of Volume C (*IT C*, 1999) and in Chapter 1.2 of this volume. A digression on an elementary derivation of the above seems to be worthwhile.

Suppose we wish to rotate the vector \mathbf{r} , about an axis coinciding with the unit vector \mathbf{k} , through the angle θ and in the positive sense, *i.e.* an observer looking in the direction of $+\mathbf{k}$ will see \mathbf{r} rotating in the clockwise sense. The vectors \mathbf{r} , \mathbf{k} and the rotated (target) vector \mathbf{r}' are referred to an origin on the axis of rotation (see Fig. 1.1.4.1). Our purpose is to express \mathbf{r}' in terms of \mathbf{r} , \mathbf{k} and θ by a general vector

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formula, and represent the components of the rotated vectors in coordinate systems that might be of interest.

Let us decompose the vector \mathbf{r} and the (target) vector \mathbf{r}' into their components which are parallel (\parallel) and perpendicular (\perp) to the axis of rotation:

$$\mathbf{r} = \mathbf{r}_{\parallel} + \mathbf{r}_{\perp} \quad (1.1.4.22)$$

and

$$\mathbf{r}' = \mathbf{r}'_{\parallel} + \mathbf{r}'_{\perp}. \quad (1.1.4.23)$$

It can be seen from Fig. 1.1.4.1 that the parallel components of \mathbf{r} and \mathbf{r}' are

$$\mathbf{r}_{\parallel} = \mathbf{r}'_{\parallel} = \mathbf{k}(\mathbf{k} \cdot \mathbf{r}) \quad (1.1.4.24)$$

and thus

$$\mathbf{r}_{\perp} = \mathbf{r} - \mathbf{k}(\mathbf{k} \cdot \mathbf{r}). \quad (1.1.4.25)$$

Only a suitable expression for \mathbf{r}'_{\perp} is missing. We can find this by decomposing \mathbf{r}'_{\perp} into its components (i) parallel to \mathbf{r}_{\perp} and (ii) parallel to $\mathbf{k} \times \mathbf{r}_{\perp}$. We have, as in (1.1.4.24),

$$\mathbf{r}'_{\perp} = \frac{\mathbf{r}_{\perp}}{|\mathbf{r}_{\perp}|} \left(\frac{\mathbf{r}_{\perp}}{|\mathbf{r}_{\perp}|} \cdot \mathbf{r}'_{\perp} \right) + \frac{\mathbf{k} \times \mathbf{r}_{\perp}}{|\mathbf{k} \times \mathbf{r}_{\perp}|} \left(\frac{\mathbf{k} \times \mathbf{r}_{\perp}}{|\mathbf{k} \times \mathbf{r}_{\perp}|} \cdot \mathbf{r}'_{\perp} \right). \quad (1.1.4.26)$$

We observe, using Fig. 1.1.4.1, that

$$|\mathbf{r}'_{\perp}| = |\mathbf{r}_{\perp}| = |\mathbf{k} \times \mathbf{r}_{\perp}|$$

and

$$\mathbf{k} \times \mathbf{r}_{\perp} = \mathbf{k} \times \mathbf{r},$$

and, further,

$$\mathbf{r}'_{\perp} \cdot \mathbf{r}_{\perp} = |\mathbf{r}_{\perp}|^2 \cos \theta$$

and

$$\mathbf{r}'_{\perp} \cdot (\mathbf{k} \times \mathbf{r}_{\perp}) = \mathbf{k} \cdot (\mathbf{r}'_{\perp} \times \mathbf{r}_{\perp}) = |\mathbf{r}_{\perp}|^2 \sin \theta,$$

since the unit vector \mathbf{k} is perpendicular to the plane containing the vectors \mathbf{r}_{\perp} and \mathbf{r}'_{\perp} . Equation (1.1.4.26) now reduces to

$$\mathbf{r}'_{\perp} = \mathbf{r}_{\perp} \cos \theta + (\mathbf{k} \times \mathbf{r}) \sin \theta \quad (1.1.4.27)$$

and equations (1.1.4.23), (1.1.4.25) and (1.1.4.27) lead to the required result

$$\mathbf{r}' = \mathbf{k}(\mathbf{k} \cdot \mathbf{r})(1 - \cos \theta) + \mathbf{r} \cos \theta + (\mathbf{k} \times \mathbf{r}) \sin \theta. \quad (1.1.4.28)$$

The above general expression can be written as a linear transformation by referring the vectors to an appropriate basis or bases. We choose here $\mathbf{r} = x^j \mathbf{a}_j$, $\mathbf{r}' = x'^i \mathbf{a}_i$ and assume that the components of \mathbf{k} are available in the direct and reciprocal bases.

If we make use of equations (1.1.4.9) and (1.1.4.21), (1.1.4.28) can be written as

$$x'^i = k^i(k_j x^j)(1 - \cos \theta) + \delta_j^i x^j \cos \theta + V g^{im} e_{mpj} k^p x^j \sin \theta, \quad (1.1.4.29)$$

or briefly

$$x'^i = R_j^i x^j, \quad (1.1.4.30)$$

where

$$R_j^i = k^i k_j (1 - \cos \theta) + \delta_j^i \cos \theta + V g^{im} e_{mpj} k^p \sin \theta \quad (1.1.4.31)$$

is a matrix element of the rotation operator \mathbf{R} which carries the vector \mathbf{r} into the vector \mathbf{r}' . Of course, the representation (1.1.4.31) of \mathbf{R} depends on our choice of reference bases.

If all the vectors are referred to a Cartesian basis, that is three orthogonal unit vectors, the direct and reciprocal metric tensors reduce to a unit tensor, there is no difference between covariant and contravariant quantities, and equation (1.1.4.31) reduces to

$$R_{ij} = k_j k_i (1 - \cos \theta) + \delta_{ij} \cos \theta + e_{ipj} k_p \sin \theta, \quad (1.1.4.32)$$

where all the indices have been taken as subscripts, but the summation convention is still observed. The relative simplicity of (1.1.4.32), as compared to (1.1.4.31), often justifies the transformation of all the vector quantities to a Cartesian basis. This is certainly the case for any extensive calculation in which covariances of the structural parameters are not considered.

1.1.5. Transformations

1.1.5.1. Transformations of coordinates

It happens rather frequently that a vector referred to a given basis has to be re-expressed in terms of another basis, and it is then required to find the relationship between the components (coordinates) of the vector in the two bases. Such situations have already been indicated in the previous section. The purpose of the present section is to give a general method of finding such relationships (transformations), and discuss some simplifications brought about by the use of mutually reciprocal and Cartesian bases. We do not assume anything about the bases, in the general treatment, and hence the tensor formulation of Section 1.1.4 is not appropriate at this stage.

Let

$$\mathbf{r} = \sum_{j=1}^3 u_j(1) \mathbf{c}_j(1) \quad (1.1.5.1)$$

and

$$\mathbf{r} = \sum_{j=1}^3 u_j(2) \mathbf{c}_j(2) \quad (1.1.5.2)$$

be the *given* and *required* representations of the vector \mathbf{r} , respectively. Upon the formation of scalar products of equations (1.1.5.1) and (1.1.5.2) with the vectors of the second basis, and employing again the summation convention, we obtain

$$u_k(1) [\mathbf{c}_k(1) \cdot \mathbf{c}_l(2)] = u_k(2) [\mathbf{c}_k(2) \cdot \mathbf{c}_l(2)], \quad l = 1, 2, 3 \quad (1.1.5.3)$$

or

$$u_k(1) G_{kl}(12) = u_k(2) G_{kl}(22), \quad l = 1, 2, 3, \quad (1.1.5.4)$$

where $G_{kl}(12) = \mathbf{c}_k(1) \cdot \mathbf{c}_l(2)$ and $G_{kl}(22) = \mathbf{c}_k(2) \cdot \mathbf{c}_l(2)$. Similarly, if we choose the basis vectors $\mathbf{c}_l(1)$, $l = 1, 2, 3$, as the multipliers of (1.1.5.1) and (1.1.5.2), we obtain

$$u_k(1) G_{kl}(11) = u_k(2) G_{kl}(21), \quad l = 1, 2, 3, \quad (1.1.5.5)$$

where $G_{kl}(11) = \mathbf{c}_k(1) \cdot \mathbf{c}_l(1)$ and $G_{kl}(21) = \mathbf{c}_k(2) \cdot \mathbf{c}_l(1)$. Rewriting (1.1.5.4) and (1.1.5.5) in symbolic matrix notation, we have

$$\mathbf{u}^T(1) \mathbf{G}(12) = \mathbf{u}^T(2) \mathbf{G}(22), \quad (1.1.5.6)$$

leading to

$$\mathbf{u}^T(1) = \mathbf{u}^T(2) \{ \mathbf{G}(22) [\mathbf{G}(12)]^{-1} \}$$

and

$$\mathbf{u}^T(2) = \mathbf{u}^T(1) \{ \mathbf{G}(12) [\mathbf{G}(22)]^{-1} \}, \quad (1.1.5.7)$$

and

$$\mathbf{u}^T(1) \mathbf{G}(11) = \mathbf{u}^T(2) \mathbf{G}(21), \quad (1.1.5.8)$$