3.1. Distances, angles, and their standard uncertainties

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3.1.1. Introduction

A crystal structure analysis provides information from which it is possible to compute distances between atoms, angles between interatomic vectors, and the uncertainties in these quantities. In Cartesian coordinate systems, these geometric computations require the Pythagorean theorem and elementary trigonometry. The natural coordinate systems of crystals, though, are determined by symmetry, and only in special cases are the basis vectors (or coordinate axes) of these systems constrained to be of equal lengths or mutually perpendicular.

It is possible, of course, to transform the positional parameters of the atoms to a Cartesian system and perform the subsequent calculations with the transformed coordinates. Along with the coordinates, the transformations must be applied to anisotropic thermal factors, variance–covariance matrices and other important quantities. Moreover, leaving the natural coordinate system of the crystal sacrifices the simplified relationships imposed by translational and point symmetry; for example, if an atom has fractional coordinates x^1, x^2, x^3, an equivalent atom will be at $1 + x^1$, x^2, x^3, *etc*.

Fortunately, formulation of the calculations in generalized rectilinear coordinate systems is straightforward, and readily adapted to computer languages (Section 3.1.12 illustrates the use of Fortran for such calculations). The techniques for these computations are those of tensor analysis, which provides a compact and elegant notation. While an effort will be made to be self-sufficient in this chapter, some proficiency in vector algebra is assumed, and the reader not familiar with the basics of tensor analysis should refer to Chapter 1.1 and Sands (1982*a*).

3.1.2. Scalar product

The scalar product of vectors **u** and **v** is defined as

$$\mathbf{u} \cdot \mathbf{v} = uv \cos\varphi, \tag{3.1.2.1}$$

where u and v are the lengths of the vectors and φ is the angle between them. In terms of components,

$$\mathbf{u} \cdot \mathbf{v} = (u^i \mathbf{a}_i) \cdot (v^j \mathbf{a}_j) \tag{3.1.2.2}$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v^j \mathbf{a}_i \cdot \mathbf{a}_j \tag{3.1.2.3}$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v^j g_{ij}. \tag{3.1.2.4}$$

In all equations in this chapter, the convention is followed that summation is implied over an index that is repeated once as a subscript and once as a superscript in an expression; thus, the right-hand side of (3.1.2.4) implies the sum of nine terms

$$u^1 v^1 g_{11} + u^1 v^2 g_{12} + \ldots + u^3 v^3 g_{33}.$$

The g_{ij} in (3.1.2.4) are the components of the metric tensor [see Chapter 1.1 and Sands (1982*a*)]

$$g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j. \tag{3.1.2.5}$$

Subscripts are used for quantities that transform the same way as the basis vectors $\mathbf{a}_i$; such quantities are said to transform covariantly. Superscripts denote quantities that transform the same way as coordinates x^j; these quantities are said to transform contravariantly (Sands, 1982*a*).

Equation (3.1.2.4) is in a form convenient for computer evaluation, with indices i and j taking successively all values from 1 to 3. The matrix form of (3.1.2.4) is useful both for symbolic manipulation and for computation,

$$\mathbf{u} \cdot \mathbf{v} = \boldsymbol{u}^T \boldsymbol{g} \boldsymbol{v}, \tag{3.1.2.6}$$

where the superscript italic T following a matrix symbol indicates a transpose. Written out in full, (3.1.2.6) is

$$\mathbf{u} \cdot \mathbf{v} = (u^1 u^2 u^3) \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix} \begin{pmatrix} v^1 \\ v^2 \\ v^3 \end{pmatrix}. \tag{3.1.2.7}$$

If $\boldsymbol{u}$ is the column vector with components u^1, u^2, u^3, $\boldsymbol{u}^T$ is the corresponding row vector shown in (3.1.2.7).

3.1.3. Length of a vector

By (3.1.2.1), the scalar product of a vector with itself is

$$\mathbf{v} \cdot \mathbf{v} = (v)^2. \tag{3.1.3.1}$$

The length of **v** is, therefore, given by

$$v = (v^i v^j g_{ij})^{1/2}. \tag{3.1.3.2}$$

Computation of lengths in a generalized rectilinear coordinate system is thus simply a matter of evaluating the double summation $v^i v^j g_{ij}$ and taking the square root.

3.1.4. Angle between two vectors

By (3.1.2.1) and (3.1.2.4), the angle φ between vectors **u** and **v** is given by

$$\varphi = \cos^{-1}[u^i v^j g_{ij}/(uv)]. \tag{3.1.4.1}$$

An even more concise expression of equations such as (3.1.4.1) is possible by making use of the ability of the metric tensor $\boldsymbol{g}$ to convert components from contravariant to covariant (Sands, 1982*a*). Thus,

$$v_i = g_{ij} v^j, \quad u_j = g_{ij} u^i, \tag{3.1.4.2}$$

and (3.1.2.4) may be written succinctly as

$$\mathbf{u} \cdot \mathbf{v} = u^i v_i \tag{3.1.4.3}$$

or

$$\mathbf{u} \cdot \mathbf{v} = u_i v^i. \tag{3.1.4.4}$$

With this notation, the angle calculation of (3.1.4.1) becomes

$$\varphi = \cos^{-1}[u^i v_i/(uv)] = \cos^{-1}[u_i v^i/(uv)]. \tag{3.1.4.5}$$

The summations in (3.1.4.3), (3.1.4.4) and (3.1.4.5) include only three terms, and are thus equivalent in numerical effort to the computation in a Cartesian system, in which the metric tensor is represented by the unit matrix and there is no numerical distinction between covariant components and contravariant components.

Appreciation of the elegance of tensor formulations may be enhanced by noting that corresponding to the metric tensor **g** with components g_{ij} there is a contravariant metric tensor $\mathbf{g}^*$ with components

$$g^{ij} = \mathbf{a}^i \cdot \mathbf{a}^j. \tag{3.1.4.6}$$

The $\mathbf{a}^i$ are contravariant basis vectors, known to crystallographers as reciprocal axes. Expressions parallel to (3.1.4.2) may be written, in which $\mathbf{g}^*$ plays the role of converting covariant components to contravariant components. These tensors thus express mathematically the crystallographic notions of crystal space and reciprocal space [see Chapter 1.1 and Sands (1982*a*)].

references