A new method for origin specification

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Abstract

A new method for origin specification is described. The method makes easy the choice of reflections for the origin specification.

1. Introduction

Origin specification was almost perfectly solved by Hauptman & Karle (1953, 1956, 1959) and Karle & Hauptman (1961). Their results were tabulated in *International Tables for X-Ray Crystallography* (1974), Vol. Ⅳ. Giacovazzo (1974) proposed a new scheme to make the Hauptman-Karle Tables. He (1980) explained his method in detail in *Direct Methods in Crystallography*. Hovmöller (1981) gave a general rule for origin specification.

As seen from Homöller (1981), these methods depend essentially on trial and error method for choosing starting sets of reflections. A new method, which starts from very simple reflections and the value of the determinant of the indices of the reflections can be fixed, is proposed. Primitive sets can easily be obtained by this method.

2. Permissible origins and translations

A structure factor is ordinarily expressed by the sum of the products of scattering factors and trigonometric functions as follows,

$$F(h) = \Sigma f_i \exp(2\pi i h r_i) = \Sigma f_j \xi_j(h), \tag{2.1}$$

where the trigonometric functions $\xi_j(h)$ are formed by the symmetrically equivalent atoms with the j th atom and may be real or complex. This expression is somewhat inconvenient to discuss the origin problem, since there is no room to express the positions of the atoms, so that the expression of the structure factor is modified to the following form,

$$F(h,., r_i,.) = \Sigma f_i \xi_i(h,., r_i,.). \tag{2.2}$$

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There are positions which do not change the forms of the trigonometric functions, thus

$$F(h,., r_i-r_0,.) = \Sigma f_i \xi_i(h,., r_i-r_0,.). \quad (2.3)$$

The positions r_0 s can be new origins, and they are called permissible origins or permissible (origin) translations.

Permissible origins of a space group are given by the positions satisfying the following equation for all the rotations (in wide sense) of the corresponding point group,

$$Rr_0 \equiv r_0(mod.\ 1), \quad (2.4)$$

where 1 is the vector with components 1. The permissible origins of a space group are the positions of multiplicity 1, which are listed in *International Tables for Crystallography* (1983), Vol. A. The permissible origins satisfy the following relation,

$$\exp(2\pi ih(Rr_i+t-r_0)) = \exp(2\pi ihR(r_i-r_0)). \quad (2.5)$$

In the case of non-primitive lattices, the lattices should be transformed to primitive ones. Then, equation (2. 5) is valid for non-primitive lattice cases. As the results of numerical calculation, the types of space groups required for the lattices to be transformed to primitive lattices are turned out to be only $3P_24$ and $3P_32$. This fact can be seen also from *International Tables*. The other space groups with non-primitive lattices can be treated by not transforming the representations of symmetry operations.

If two positions r_1 and r_2 satisfy equation (2. 5), then the addition and the subtraction of the position vectors also satisfy the equation. In general, a linear combination of the vectors satisfying equation (2, 5) satisfies also equation (2, 5). Hence, there are independent vectors in the vectors satisfying equation (2, 5). Acoording to the concise definition of seminvariant by Giacovazzo (1980) is that the phase (of a structure factor) is a structure seminvariant if its value is unchanged when the origin is moved by the allowed translations. The condition that the phases are unchanged for all allowed translations is satisfied if the phases are unchanged for all the independent ones among the allowed translations. Although there are many selections of the independent vectors, the seminvariant is uniquely determined from these sets of the independent vectors. Hence, the independent vectors with the most simple form are convenient for obtaining seminvariants, so that independent vectors mean that the independent vectors with the most simple form in the position vector of the permissible origins in this article.

3. Choice of reflections

The i th component of a permissible origin, r_0, can be expressed by a fraction (m_i/n) with a common denominator n in any cases. The value of hr_0 multiplied by n satisfies

$$hm_1+km_2+1m_3 \equiv c(mod.\ n), \quad (3.1)$$

where $0 \leq m_1, m_2, m_3, c < n$. If a permissible origin, r_0, is assumed to be known, the choice of reflections to specify the origin becomes to search the reciprocal lattice vectors satisfying equation (3. 1).

There is very useful theorem for solving equation (3. 1).

Theorem: If the greatest common measure (G. C. M.) of integers $a_1, a_2, \ldots, a_n$ is d, there are integers $x_1, x_2, \ldots, x_n$ satisfying following equation,

$$a_1x_1+a_2x_2+ \ldots +a_nx_n = d, \tag{3. 2}$$

and if $d = 1$, then the integers $x_1, x_2, \ldots, x_n$ are prime to one another.

Since, the G. C. M. of m_1, m_2 and m_3 can be assumed to be 1, if a vector h satisfies equation (3. 1) for $c = 1$, then vectors satisfying equation (3. 1) for $c \neq 1$ are ch. Vectors satisfying equation (3. 1) for $c = 1$ can be obtained as the sum of a special solution of equation (3. 1) for $c = 1$ and the general solution of (3. 1) for $c = 0$. Then, vectors which are special solutions of equation (3. 1) can specify the origins.

For example, when $r_0 = (2/3, 1/3, 0)$, then the vector (0 1 0) satisfies equation (3. 1) for $c = 1$, and the vector (1 1 0) satisfies equation (3. 1) for $c = 0$, hence the vector (1 2 0) satisfies also equation (3. 1) for $c = 1$.

When the number of the independent permissible origins are p, the reflections to specify the origin can be obtained by solving p equations of the form of equation (3. 1). But, the value of the determinant of the matrix formed by the indices of the reflections thus obtained are not necessarily non-zero. For example, reflections (1 0 2), (0 1 1) and (1 −1 1) satisfy $h \equiv 1$, $k \equiv 1$ and $l \equiv 1$, respectively, but the value of the determinant is 0.

The reason that the reflections in the above example can not specify the origin is unsuitable choice of the solutions $h \equiv 0$, $k \equiv 0$ and $l \equiv 0$. This defect can be avoided by forming an equation for the linear combination with coefficients 1 of all independent vectors for $c_i = 0$. Seminvariants are obtained from the p equation with $c_i = 0$.

For example, three vectors for the types $1P$ and $1P222$ can be obtained by the following three equations,

$$h \equiv 1(mod.\ 2),$$
$$k \equiv 1(mod.\ 2),$$
$$l \equiv 1(mod.\ 2),$$

and one equation,

$$h+k+l \equiv 0(mod.\ 2).$$

We can chose special solutions (1 0 0), (0 1 0) and (0 0 1) for the above three equations. The three reflections to specify the origins are given by the following forms,

$$(1+h\ k\ l),\ (h\ 1+k\ l) \text{ and } (h\ k\ 1+l), \tag{3. 3}$$

where $h+k+l = 2n$ (n is an integer). The seminvariants are given by

$h \equiv 0(mod.\ 2)$,

$k \equiv 0(mod.\ 2)$,

$l \equiv 0(mod.\ 2)$.

The value of the determinant of the matrix composed of a diagonal matrix with the three elements a, b and c and of a matrix consisting of the column submatrices with the same elements h, k and l is $abc+hbc+akc+abl$. Hence, the value of the determinant of the matrix formed by indices given by equation (3. 3) is $1+2n$. For example, the vectors (1 1 1), (0 2 1) and (0 1 2) satisfy the above equations. The determinant of the matrix formed by the indices is 3. We can easily choose primitive sets of reflections by setting $h+k+l=0$.

When the value of the determinant is 1 for $p=3$, i. e. $h+k+l=0$, the three reciprocal vectors obtained thus can span the reciprocal lattice.

Since the products of odd numbers and even numbers are even and the products of odd numbers and odd numbers are odd, another set of reflections can be obtained from a set of reflections sufficient to specify origin by multiplying the same odd numbers to the indices of the reflections. For example, if the three reflections (1 1 1), (0 2 1) and (0 1 2) can specify the origins, then the reflections (3 3 3), (0 2 1) and (0 3 6) can also specify the origins.

The above method for $p=3$ can be extended easily to the cases of $p<3$. For example, the independent permissible origins are (0, 0, 1/2) and (2/3, 1/3, 0) for type $3P32$. Then, the equations for $c_i=1$ are:

$2h+k \equiv 1(mod.\ 3)$,

$l \equiv 1(mod.\ 2)$.

The special solutions of these equations are (0 1 0) and (0 0 1), respectively. The equation for $c_i=0$ becomes

$2(2h+k)+3l \equiv 0(mod.\ 6)$.

The reflection (1 1 −2) satisfies this equation. Hence, the two reflections (1 2 −2) and (1 1 −1) can specify the origins.

There are other cases that independent vectors are continuous. Types $1P202$ and $1P220$ are for the case of one continuous element. The invariant positions given in *International Tables for Crystallography* (1983), Vol. A are:

$1P202$: (0, y, 0); (0, y, 1/2); (1/2, y, 0); (1/2, y, 1/2).

$1P220$: (0, 0, z); (0, 1/2, z); (1/2, 0, z); (1/2, 1/2, z).

It is impossible to choose independent vectors from these positions, so that the invariant vectors for these space groups should be deduced from the positions and the independent vectors should be:

$1P202$: (0, y, 0); (1/2, 0, 0); (0, 0, 1/2).

$1P220$: (0, 0, z); (1/2, 0, 0); (0, 1/2, 0).

The equations for $c_i = 1 (i = 2 \text{ and } 3)$ in the case of $1P202$ are:

$$h \equiv 1 (mod.\ 2),$$
$$l \equiv 1 (mod.\ 2).$$

Special solutions of the equations are (1 0 0) and (0 0 1). In addition, $ky = \theta$, where θ is an arbitrary number. The value of k is set to be 1 for unique determination of y. The equation for $c_i = 0$ is:

$$h+l \equiv 0 (mod.\ 2).$$

The vectors obtained are:

$(1+h\ 0\ l)$, $(0\ 1\ 0)$ and $(h\ 0\ 1+l)$,

or

$(1+h\ 0\ l)$, $(h\ 1\ l)$ and $(h\ 0\ 1+l)$,

where $h+l = 2n$ (for the determinant to be 1, $h+l = 0$). Not only the first triple of vectors can specify the origin, but also the second one does.

In the case of the two continuous elements for $p = 2$, the type $1P020$ and the permissible origin $(x,\ 1/2,\ z)$, to choose two reflections corresponding to the independent vectors with continuous elements is quite analogous to the case of one continuous element. That is, the reflections to specify the origin are:

$(1+h\ 0\ l)$, $(0\ 1\ 0)$ and $(h\ 0\ 1+l)$;

or

$(1+h\ 0\ l)$, $(h\ 1\ l)$ and $(h\ 0\ 1+l)$;

where $h+l = 2n$ (for the determinant to be 1, $h+l = 0$).

4. Remarks

The merits of this method is to be able to know the values of the determinants formed from the indices of the reflections and that the primitive set of reflections can be obtained easily without calculation of the value of determinant. The other methods, for example the method of Hovmöller (1981), choose possible reflections to specify the origin and reduce the indices and calculate the determinant. If the values are non-zero, the trial successes.

If it is allowed to calculate the value of the determinant, the choice of reflections becomes very wide. For example, the reflections (1 0 0), (0 1 1) and (1 0 1) are special solutions of the first example. The value of the determinant is 1. We can obtain various reflections by adding the elements to even numbers of h, k and l by reversing procedure of the ordinary reducing,

or by adding the numbers h, k and l under the condition $h+k+l=2n$, where n is an arbitrary integer.

Centric reflections are obtained by the reflections $(1\ a\ 0)$, $(0\ 1\ b)$ and $(c\ 0\ 1)$ or $(1\ 0\ a)$, $(b\ 1\ 0)$ and $(0\ c\ 1)$. The determinant of the both cases is $1+abc$. Hence, the value of the determinant to be 1, the value of abc becomes 0, and the value to be -1, the value of abc becomes -2.

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