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The Calculation of ε Associated with Normalized Structure Factors, *E*

By James M. Stewart

Chemistry Department, University of Maryland, College Park, Md. 20742, *U.S.A.*

and Jerome Karle

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375, *U.S.A.*

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A method is presented for the convenient computation of the quantity ε used for obtaining the values of normalized structure factor magnitudes from structure factor amplitudes. ε has the value of unity for general reflections but can take on integral values which differ from unity for special classes of reflections. The method is based on the application of rotation operators which are easily formed from knowledge of the equivalent positions for the space group of interest. Only general positions are considered. Proof is given here for the procedure which has been used heuristically in the program system titled XRAY72.

The normalized structure factor, E, the form of the structure factor which has found widespread application in procedures for phase determination, is defined by

$$E_{\mathbf{h}}=F_{\mathbf{h}}/(\varepsilon_{\mathbf{h}}\sum_{j=1}^{N}f_{j\mathbf{h}}^{2})^{1/2} \tag{1}$$

where the $F_{\mathbf{h}}$ are the crystal structure factors placed on an absolute scale and corrected for thermal motion. The vector $\mathbf{h}=(h,k,l)$ labels the plane in the crystal associated with a particular reflection, $f_{j\mathbf{h}}$ is the atomic scattering factor of the jth atom in a crystal unit cell containing N atoms and the quantity epsilon as a function of $\mathbf{h}$, ε_h, is an integer whose value depends upon the point-group symmetry and the reflection class. It is the objective of this note to present a simple rule for determining the values of $\varepsilon_{\mathbf{h}}$ appropriate to the various space groups. In particular, it will be seen that the rule is well suited for computation on a digital computer.

A method for obtaining $\varepsilon_{\mathbf{h}}$ has been described by Wilson (1950). It is based upon a consideration of the effect on the statistics of classes of intensities by individual symmetry elements of the space group of interest. This approach has not been conveniently programmed for a digital computer.

A second method for evaluating $\varepsilon_{\mathbf{h}}$ follows from the definition (Karle & Hauptman, 1956)

$$\varepsilon_{\mathbf{h}}=\frac{m_2^0(\mathbf{h})+m_0^2(\mathbf{h})}{n}, \tag{2}$$

where n is the symmetry number of the space group, $m_i^k(\mathbf{h})$ is a moment for which the indices i and k are labels,

$$m_i^k(\mathbf{h})=\int_0^1\int_0^1\int_0^1 \xi^i\eta^k\mathrm{d}x\mathrm{d}y\mathrm{d}z\,, \tag{3}$$

$\xi^i\equiv\xi^i(x,y,z;\,\mathbf{h})$ and $\eta^k\equiv\eta^k(x,y,z;\,\mathbf{h})$ are the ith power of the real part and the kth power of the imaginary part, respectively, of the contribution of an atom to the structure factor as defined in the *International Tables for X-ray Crystallography* (1965). The definition given by (2) serves for the centrosymmetric case ($m_0^2=0$), for pure imaginary reflections ($m_2^0=0$) and also for the general noncentrosymmetric case ($m_2^0=m_0^2\neq 0$). The evaluation of the appropriate integrals for the individual space groups presents no difficulty. However, the moment integrals can be evaluated in general for all the space groups in terms of the symmetry number and the number of equivalent reflections which become identical for special conditions on h,k,l, the components of $\mathbf{h}$. This evaluation affords the basis for a simple rule for the evaluation of $\varepsilon_{\mathbf{h}}$ which is well suited for computation on a digital computer.

The rule is: ε_{hkl} is the number of times the transformed vector, $\mathbf{h}_t\equiv(h,k,l)_t$, is identical to a given reflection, $\mathbf{h}\equiv(h,k,l)$, under all the distinct pure rotational symmetry operations $\mathbf{R}$ of the space group; $\mathbf{h}_t=\mathbf{hR}_t$.

The pure rotational symmetry group with elements $\mathbf{R}$, the crystallographic point group, is the quotient subgroup of the space group by the translational subgroup. The set of all symmetry elements in the pure rotational symmetry group which leave $\mathbf{h}$ fixed is a subgroup called the isotropy subgroup. In these terms, the rule is: ε_{hkl} is the number of elements in the isotropy subgroup for the vector $\mathbf{h}$ in the pure rotational symmetry group of the space group.

One way to achieve the implementation of this rule is to form the set of distinct vectors obtained from the application of all the distinct rotational symmetry operations, $\mathbf{R}$, of the space group to a general choice of vector (h,k,l). This is followed by specialization of (h,k,l) and the observation of the number of initially distinct vectors which become equivalent. The latter is the value of $\varepsilon_{\mathbf{h}}$ for the particular specialization of the (h,k,l). This view of the rule is inherent in its proof which is presented below.

Reflection multiplicity is a contrasting concept which should be distinguished from the rule for $\varepsilon_{\mathbf{h}}$. The reflection multiplicity is the number of distinct vectors obtained from **h** by applying all the distinct rotational symmetry operations **R** of the space group; $\mathbf{h}_t = \mathbf{h}\mathbf{R}_t$.

Proof of rule for $\varepsilon_{\mathbf{h}}$

The proof of the rule for the evaluation of $\varepsilon_{\mathbf{h}}$ follows from the general evaluation of (2) by means of the definition (3). There are some considerations which facilitate the proof:

1. Instead of viewing ξ and η as the condensed trigonometric forms of the real and imaginary parts, respectively, of the contributions from an atom to the structure factor as listed in *International Tables*, ξ and η are viewed in terms of a sum of individual terms, one from each equivalent atomic position in the unit cell.

2. The moment integrals in (2) involve ξ^2 and η^2 in the integrand of (3). In squaring the sum of terms referred to in consideration 1, the only contributions to (3) derive from the squares of the distinct individual terms. The cross terms formed from distinct contributors integrate to zero.

3. Since translational quantities occur in the arguments of the individual cosine and sine terms of ξ and η respectively, because of the possible presence of glide planes and screw axes, it is necessary to make some further statements concerning how this affects the concepts of distinct terms under rotational operations. When the arguments of the individual cosines and sines are identical except for translational parts, extinction occurs unless all the translational parts are equal to integers which multiply 2π and hence may be omitted from the arguments. The value of $\varepsilon_{\mathbf{h}}$ where **h** characterizes a space-group extinction is meaningless. In other cases when the arguments of the individual cosines and sines differ independently of the translational parts, they are distinct because of the rotational parts of the symmetry operators, and the translational parts are superfluous to this categorization. It is for these reasons that we need concern ourselves only with the rotational parts of the symmetry operators to determine how many terms are equivalent and how many are distinct in ξ and η and for formulating the rule for the computation of $\varepsilon_{\mathbf{h}}$, as given above.

4. If there are p identical vectors generated by $(h,k,l)_t = (h,k,l)\mathbf{R}_t$ under all the distinct rotational symmetry operations **R** of the space group, there will be n/p distinct vectors, each occurring p times, where n is the symmetry number of the space group. The quantity n/p is the reflection multiplicity defined above. The reflection multiplicity, n/p, follows from the number of identical vectors generated, p, and the group properties of the rotational symmetry operators.

Noncentrosymmetric case

For the qth atom in a general position in the unit cell,

$$\xi_{q\mathbf{h}} = \sum_{j=1}^{N} \cos 2\pi\mathbf{h} \,.\, \mathbf{r}_{qj} \tag{4}$$

and

$$\eta_{q\mathbf{h}} = \sum_{j=1}^{N} \sin 2\pi\mathbf{h} \,.\, \mathbf{r}_{qj} \tag{5}$$

where the sum ranges over the n equivalent atomic positions of the space group of interest. As noted, the translational parts in (4) and (5) are to be ignored and if these sums are squared, as required by (3), the contributions to (3) derive only from the squares of the distinct terms remaining in (4) and (5) after summing the identical ones (p of them). The cross terms integrate to zero in (3). There are then n/p distinct squared cosine terms and corresponding squared sine terms in $\xi^2_{q\mathbf{h}}$ and $\eta^2_{q\mathbf{h}}$ respectively, each having a weight of p^2. Since $\cos^2 x + \sin^2 x = 1$, it follows from (2) and (3) that

$$\varepsilon_{\mathbf{h}} = \frac{p^2(n/p)}{n} = p\,. \tag{6}$$

This completes the proof of the rule for the noncentrosymmetric case.

Centrosymmetric case

In the centrosymmetric case $\eta_{q\mathbf{h}} = 0$ and therefore $m_0^2 = 0$. Each cosine term in $\xi_{q\mathbf{h}}$, before identical ones are summed, has a coefficient of 2 and there are $n/2$ such. After summing p identical ones there would be $n/2p$ distinct ones from rotational operations, each with a coefficient of $2p$. The contribution from a squared cosine function after integration in (3) is $\frac{1}{2}$. It follows from (2) and (3) that

$$\varepsilon_{\mathbf{h}} = \frac{4p^2(n/2p)}{2n} = p\,. \tag{7}$$

This completes the proof of the rule for the centrosymmetric case. The proof for pure imaginary reflections is comparable.

Evidently, the foregoing proof is valid for atoms in general positions. This evaluation of $\varepsilon_{\mathbf{h}}$ is inherent in the work of Wilson (1950), Hauptman & Karle (1953) and Bertaut (1959). In the case that a significant proportion of the scattering matter in a crystal occupies special positions in the unit cell, values for ε obtained by the rule stated here would not be valid and the values for the normalized structure factors derived for the various subsets of indices for the space group should be treated with some caution. Depending upon how much information is at hand concerning the occupation of special positions, it might be possible to estimate the uncertainties that are introduced.

The rule for finding $\varepsilon_{\mathbf{h}}$ may be stated mathematically, as indicated by (6) and (7), in the form $\varepsilon_{\mathbf{h}} = p$. This rule is valid for centered space groups as well as primitive ones. When applied to centered cells, p is determined by considering the n distinct rotation operators associated with the n equivalent coordinate triples which are independent of the translations that form the centered cell. Here the quantity n is again the number of equivalent points that would be found for general positions in the primitive unit cell. These statements are evident from the nature of the transformation between primitive and centered cells.

Examples

The following examples serve to illustrate the application of $\varepsilon_{\mathbf{h}}=p$, as it was first applied heuristically in the XRAY72 system of crystallographic computer programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). By inspection of the coordinates of the equivalent points in a primitive space group (or the set of coordinates independent of the centering translations in a centered space group), it is possible to list the independent rotation operators, $\mathbf{R}$. The multiplications $(h,k,l)\mathbf{R}_t$ may then be carried out to give the various $(h,k,l)_t$ which, on specialization, give the proper values for ε.

$P2_1/c$

$$\begin{array}{ccc} & x,y,z; & x,\tfrac{1}{2}-y,z+\tfrac{1}{2}; \\ \mathbf{R}: & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \end{array}$$

$$\begin{array}{ccc} & -x,y+\tfrac{1}{2},\tfrac{1}{2}-z; & -x,-y,-z \\ \mathbf{R}: & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}; & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \end{array}$$

$\mathbf{h}_t$: $h,k,l;\ h,\bar{k},l;\ \bar{h},k,\bar{l};\ \bar{h},\bar{k},\bar{l}$

Class	hkl	$hk0$	$h0l$	$0kl$	$h00$	$0k0$	$00l$
ε	1	1	2	1	2	2	2

The values for ε follow from the specialization of the $\mathbf{h}_t$ and application of the rule $\varepsilon_{\mathbf{h}}=p$.

$Aba2$

$\mathbf{h}_t$: $h,k,l;\ \bar{h},\bar{k},l;\ \bar{h},k,l;\ h,\bar{k},l$

Class	hkl	$hk0$	$h0l$	$0kl$	$h00$	$0k0$	$00l$
ε	1	1	2	2	2	2	4

$P4_12_12$

$\mathbf{h}_t$: $h,k,l;\ k,h,\bar{l};\ \bar{h},k,l;\ \bar{k},\bar{h},\bar{l};\ \bar{k},h,l;\ \bar{h},k,\bar{l};\ k,\bar{h},l;\ h,\bar{k},\bar{l}$

Class	$hh0$	$h00$	$0k0$	$00l$
ε	2	2	2	4

For all other classes, $\varepsilon=1$.

$P6_3/mmc$

$\mathbf{h}_t$: $\pm(h,k,l;\ k,\bar{h}+\bar{k},l;\ \bar{h}+\bar{k},h,l;\ \bar{k},\bar{h},l;\ h+k,\bar{k},l;$
$\bar{h},h+k,l;\ h,k,\bar{l};\ k,\bar{h}+\bar{k},\bar{l};\ \bar{h}+\bar{k},h,\bar{l};\ \bar{k},\bar{h},\bar{l};$
$h+k,\bar{k},\bar{l};\ \bar{h},h+k,\bar{l})$

Class	hkl	$h00$	$0k0$	$00l$	$hk0$	$h0l$	$0kl$
ε	1	4	4	12	2	2	2

Class	$hh0$	$h\bar{h}0$	hhl	$h\bar{h}l$
ε	4	4	2	2

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