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Symmetry Considerations with respect to Space-Group Extinctions and Weights in Intensity Statistics

BY ANGELO GAVEZZOTTI AND CARLO M. GRAMACCIOLI

Istituto di Chimica Fisica e Centro CNR, Università di Milano, via Saldini 50, 20133 *Milano, Italy*

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A simple method is given for obtaining information about extinction and weight in the intensity statistics of an *hkl* reflexion. For this purpose, space-group transformations are directly applied; contrary to what seems to be a widespread view, weights are not directly correlated to extinctions.

In many recent crystallographic programs (see, for instance, *Crystallographic Computing,* 1969) there is a marked tendency toward deriving symmetry information directly from symmetry operations, *i.e.* from the rotation matrices and translation vectors of each particular space group. In our programs, written in Fortran IV for computers such as the IBM 7040 and the UNIVAC 1106, we found it particularly useful to adopt a straightforward procedure in order to obtain information about extinction, equivalence between reflexions, and statistical weights of the various $F_{\mathbf{h}}$'s directly from space-group transformations, without the help of trigonometric expressions. A similar problem was solved by Bertaut (1956; see also Bertaut & Waser, 1957). However, since our procedure seems to us to be more practical for computer application we are just giving a brief survey of it. In this survey, we are omitting the argument concerning equivalence between reflexions, because our method closely follows that proposed by Patterson (1952) and Brown (1971) and no further comment is thought to be necessary.

A structure factor $F_{\mathbf{h}}$ can be written as

$$F_{\mathbf{h}}=\sum_{i=1}^{N} f_i(\mathbf{h}) \exp 2\pi i(\mathbf{h}^T\mathbf{x}_i)=\sum_{i=1}^{N}\mathbf{f}_i(\mathbf{h})$$

where $\mathbf{f}_i(\mathbf{h})=f_i(\mathbf{h}) \exp 2\pi i(\mathbf{h}^T\mathbf{x}_i)$.

When symmetry elements are present in the cell, some $\mathbf{f}_i$ are related to each other by symmetry. For instance, if $\mathbf{x}_j=\mathbf{M}\mathbf{x}_i+\mathbf{t}$, it will always be:

$$f_j(\mathbf{h})=f_i(\mathbf{M}^T\mathbf{h})\,.$$

In fact, let us write $f_i(\mathbf{h})=f_i^0(\mathbf{h})T_i(\mathbf{h})$, where $f_i^0(\mathbf{h})$ is the scattering factor and $T_i(\mathbf{h})$ the temperature factor for the ith atom. Considering that $f_i^0(\mathbf{h})=f_i^0(\mathbf{M}^T\mathbf{h})$, the proof is trivial when $T_i(\mathbf{h})$ is isotropic. If $T_i(\mathbf{h})$ is anisotropic, as for instance in the case of the usual six-parameter temperature factor, since $\mathbf{B}_j=\mathbf{M}\mathbf{B}_i\mathbf{M}^T$, $T_i(\mathbf{M}^T\mathbf{h})=\mathbf{h}^T\mathbf{M}\mathbf{B}_i\mathbf{M}^T\mathbf{h}$ and $T_j(\mathbf{h})=\mathbf{h}^T\mathbf{B}_j\mathbf{h}=\mathbf{h}^T\mathbf{M}\mathbf{B}_i\mathbf{M}^T\mathbf{h}$ $=T_i(\mathbf{M}^T\mathbf{h})$. For more sophisticated calculations of $F_{\mathbf{h}}$'s, which use tensors of higher rank, such as the expansion proposed by Johnson (1969, 1970), a similar procedure can be applied, ending up with the same result. Therefore we have:

$$\mathbf{f}_j(\mathbf{h})=f_i(\mathbf{M}^T\mathbf{h}) \exp 2\pi_i(\mathbf{h}^T\mathbf{M}\mathbf{x}i+\mathbf{h}^T\mathbf{t})$$
$$=\mathbf{f}_i(\mathbf{M}^T\mathbf{h}) \exp 2\pi i(\mathbf{h}^T\mathbf{t})\,.$$

For some reflexions where $\mathbf{h}=\mathbf{M}^T\mathbf{h}$, then, the phase difference between $\mathbf{f}_j$ and $\mathbf{f}_i$ will be equal to $2\pi\mathbf{h}^T\mathbf{t}$, *i.e.* this will be independent of the particular atomic coordinates in the structure. Let us now consider the subgroup formed by the various symmetry operations connected with the powers of $\mathbf{M}$. For any of these, if $\mathbf{h}^T\mathbf{M}=\mathbf{h}^T$, we have $\mathbf{h}^T\mathbf{M}^n=\mathbf{h}^T\mathbf{M}\mathbf{M}^{n-1}=\mathbf{h}^T\mathbf{M}^{n-1}=\mathbf{h}^T$, *i.e.* the phase difference will also be independent of the particular atomic coordinates. Consequently, this subgroup will give rise to a subset of $\mathbf{f}_j$'s in the expression for $F_{\mathbf{h}}$, each one differing from the next only in phase and by precisely $2\pi\mathbf{h}^T\mathbf{t}$. If $\mathbf{h}^T\mathbf{t}$ is fractional, this will cause the $\mathbf{f}_j$'s to be either opposite ($\mathbf{h}^T\mathbf{t}=\frac{1}{2}$) or situated like vectors connecting the centre to the corners of a regular polygon; their sum will accordingly be zero. If, in addition to this subgroup other symmetry elements are present, they may be arranged into sets, each of them corresponding to multiplication of a new element by all operations in the subgroup of the powers of $\mathbf{M}$; the number of components in each of these sets is still the order of the subgroup. For instance, if a symmetry operation exists such as

$$\mathbf{x}_j=\mathbf{N}\mathbf{x}_i+\mathbf{q}\,,$$

where $\mathbf{N}\neq\mathbf{M}^k$, in addition we must have operations of the kind

$$\mathbf{x}_{jn}=\mathbf{M}^n(\mathbf{N}\mathbf{x}_i+\mathbf{q})+\sum_{i=1}^{n}\mathbf{M}^{n-i}\mathbf{t}\,.$$

Since

$$\mathbf{h}^T\mathbf{x}_{jn}=\mathbf{h}^T\mathbf{N}\mathbf{x}_i+\mathbf{h}^T\mathbf{q}+n\mathbf{h}^T\mathbf{t}=\mathbf{h}^T\mathbf{x}_j+n\mathbf{h}^T\mathbf{t}\,,$$

$\mathbf{f}_{jn}$ will have a phase difference of $2\pi n\mathbf{h}^T\mathbf{t}$ with respect to $\mathbf{f}_j$. For each set, then, the same arguments can be applied, resulting in a total of zero if $\mathbf{h}^T\mathbf{t}$ is fractional. In practice, for a given reflexion, if *any* operation exists for which $\mathbf{h}^T=\mathbf{h}^T\mathbf{M}$ and $\mathbf{h}^T\mathbf{t}$ is fractional, the reflexion is extinct, because we can apply our considerations to the subgroup formed by the powers of this operation. If $\mathbf{h}^T\mathbf{t}$ is integral, and p is the number of operations (including the identity operation) for which $\mathbf{h}^T=\mathbf{h}^T\mathbf{M}$,

this means that in each subset all vectors $\mathbf{f}_j$ are parallel to each other (the difference in phase being a multiple of 2π) and the average intensity of such reflexions is higher than for 'ordinary' reflexions. It will be:

$$\langle F^2\rangle = \sum_{i=1}^{N/p} p^2 f_i^2 = p \sum_{i=1}^{N} f_i^2 \qquad \text{(Wilson, 1950).}$$

Therefore, p corresponds to the statistical weight ['pwys' according to Rogers (1965) or 'poids statistique' according to Bertaut (1955, 1956)] of this reflexion, a coefficient which is important in obtaining Wilson plots and normalized structure factors.

In this respect, there seems to be some disagreement in the literature about the right value of p for some space groups. According to some authors, including Karle & Karle (1966), the normalized structure factor is *defined* as $E_h^2 = F_h^2/\varepsilon \sum f_i^2$, where ε should be 'a number which corrects for space-group extinctions'. According to Rogers (1965) and Bertaut (1955) we have: $z = E^2 = F^2/p \sum f_i^2$, from which it seems obvious to consider $p = \varepsilon$. However, p is different from unity even in cases when no extinctions are present: for instance, just to take an example as reported by Bertaut, in $h00$ reflexions of space-group $Pmmm$, $p = 4$, and there are no extinctions. If we *define* $E = F/\langle F^2\rangle$, in agreement with all authors, including Hauptman & Karle (1953), who defined it for the first time, remembering that $\langle F^2\rangle = p\sum f_i^2$, the inconsistency of the later definition by Karle & Karle (1966) appears evident. As a matter of fact, the great majority of structures treated by direct methods contain extinctions due to glide planes or screw axes, and very often the value of $\varepsilon = p$, calculated on the basis of extinctions, happens to be correct (consider, for instance, the space groups $P2_1/c$ or $P2_12_12_1$).

As an example of the application of our method, we shall consider the space group $P4_12_12$, whose symmetry transformations are represented by the following matrices and vectors:

$$\left|\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix}\right|, \left|\begin{matrix}0\\0\\0\end{matrix}\right| \quad (1); \qquad \left|\begin{matrix}-1&0&0\\0&-1&0\\0&0&1\end{matrix}\right|, \left|\begin{matrix}0\\0\\\frac{1}{2}\end{matrix}\right| \quad (2);$$

$$\left|\begin{matrix}0&-1&0\\1&0&0\\0&0&1\end{matrix}\right|, \left|\begin{matrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{4}\end{matrix}\right| \quad (3); \qquad \left|\begin{matrix}0&1&0\\-1&0&0\\0&0&1\end{matrix}\right|, \left|\begin{matrix}\frac{1}{2}\\\frac{1}{2}\\\frac{3}{4}\end{matrix}\right| \quad (4);$$

$$\left|\begin{matrix}0&1&0\\1&0&0\\0&0&-1\end{matrix}\right|, \left|\begin{matrix}0\\0\\0\end{matrix}\right| \quad (5); \qquad \left|\begin{matrix}0&-1&0\\-1&0&0\\0&0&-1\end{matrix}\right|, \left|\begin{matrix}0\\0\\\frac{1}{2}\end{matrix}\right| \quad (6);$$

$$\left|\begin{matrix}-1&0&0\\0&1&0\\0&0&-1\end{matrix}\right|, \left|\begin{matrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{4}\end{matrix}\right| \quad (7); \qquad \left|\begin{matrix}1&0&0\\0&-1&0\\0&0&-1\end{matrix}\right|, \left|\begin{matrix}\frac{1}{2}\\\frac{1}{2}\\\frac{3}{4}\end{matrix}\right| \quad (8).$$

For $00l$ reflexions, the transformations (2) and (3) afford the restrictions $l = 2n$ and $l = 4n$ respectively. For $h00$ reflexions, the transformation (8) affords the restriction $h = 2n$. Note that transformation (7) should afford the restriction $k = 2n$ for $0k0$ reflexions, which is a redundant one since $0k0$ and $h00$ reflexions are equivalent in this space group. Non-extinct $00l$ reflexions have their statistical weight enhanced by transformations (1), (2), (3), (4), that is, $p = 4$; $h00$ reflexions have $p = 2$ [transformations (1) and (8)]. Special reflexions of the $hh0$ type have $p = 2$ [transformation (5)].

Non-primitive space groups deserve special mention. In such cases, the identity matrix, appearing with a non-zero translation vector, offers an explanation of the so-called lattice extinctions. For instance, in space group $C2$ the transformations are:

$$\left|\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix}\right|, \left|\begin{matrix}0\\0\\0\end{matrix}\right| \quad (1); \qquad \left|\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix}\right|, \left|\begin{matrix}\frac{1}{2}\\\frac{1}{2}\\0\end{matrix}\right| \quad (2);$$

$$\left|\begin{matrix}-1&0&0\\0&1&0\\0&0&-1\end{matrix}\right|, \left|\begin{matrix}0\\0\\0\end{matrix}\right| \quad (3); \qquad \left|\begin{matrix}-1&0&0\\0&1&0\\0&0&-1\end{matrix}\right|, \left|\begin{matrix}\frac{1}{2}\\\frac{1}{2}\\0\end{matrix}\right| \quad (4).$$

Here, the transformation (2) affords the restriction $h + k = 2n$ on hkl reflexions (lattice extinctions). Transformation (4) affords the redundant restriction $k = 2n$ for $0k0$ reflexions.

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