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## Patterson interpretation of the seminvariant vectors and seminvariant moduli. The multiple implication function as a superposition structure.

By František Pavelčík, *Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University,* 842 15 *Bratislava, Czechoslovakia*

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### Abstract

Seminvariant vector and modulus give conditions for the possible reflections of a superposition structure with atomic positions related to the multiple implication function. This concept naturally leads to the $\Sigma_1$ formula.

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The concept of seminvariant vector and modulus was introduced in fundamental direct-method papers by Hauptman & Karle (1953, 1956, 1959; Karle & Hauptman, 1961). The seminvariant vectors and moduli have been tabulated either for primitive cells (*International Tables for X-ray Crystallography*, 1974) or for conventional cells (Giacovazzo, 1974).

On the other hand, the multiple implication function (MIF) published under a variety of names by Simpson, Dobrott & Lipscomb (1965), Ellison & Levy (1965), Hamilton (1965), Mighell & Jacobson (1963) and Pavelčík (1986),

$$Q(\mathbf{r}) = \left[\min_{i=1}^{s} (1/m_i) P(\mathbf{r} - \hat{\mathbf{S}}_i \mathbf{r})\right]^{1/2}, \qquad (1)$$

can be regarded as a general approach to the interpretation of the Patterson function, $P(\mathbf{r})$, on the basis of symmetry; $m_i$ is the multiplicity of the symmetry interaction (Simpson, Dobrott & Lipscomb, 1965), $P(\mathbf{r} - \hat{S}_i \mathbf{r})$ is the implication function (Buerger, 1959), $\hat{S}$ is the symmetry operator and $s$ is the number of space-group operators excluding those of centring. The symmetry of the MIF was studied by Zimmermann (1988) and the procedure for the generation of the MIF symmetry was developed by Pavelčík (1988, 1990).

The important property of the MIF is that its unit-cell volume is a fraction of the crystal cell volume (in some cubic groups both types of volumes coincide as a limiting case). In the polar groups the unit cell has infinitesimal thickness in the polar directions so that plane or line cells are obtained. The extreme case is the $P1$ space group where the MIF cell is reduced to a single point. The MIF described in the crystal unit-cell axes has non-standard centring points which coincide with permissible translations of the cell origin (equivalent origins, $\mathbf{t}_o$) (Pavelčík, 1990).

For the idealized Patterson function (with $\delta$-function peaks), the MIF gives the complete structure but without distinguishing the equivalent origins. In other words, the idealized MIF can be regarded as a superposition of crystal structures shifted by permissible origin translations ($O$ is the number of equivalent origins):

$$Q(\mathbf{r}) = \sum_{o=1}^{O} \rho(\mathbf{r} + \mathbf{t}_o). \qquad (2)$$

In polar groups, the $\mathbf{t}_o$ are infinitesimal quantities in polar directions and integration should be carried out so that a projection of the structure is obtained.

If the atomic positions are known, the $Q(\mathbf{r})$ can be calculated by

$$\begin{aligned} Q(\mathbf{r}) &= (1/V) \sum_{o=1}^{O} \sum_{\mathbf{H}} F_{\mathbf{H}} \exp[-2\pi i \mathbf{H} . (\mathbf{r} + \mathbf{t}_o)] \\ &= (1/V) \sum_{\mathbf{H}} F_{\mathbf{H}} \exp(-2\pi i \mathbf{H} . \mathbf{r}) \\ &\quad \times \left[\sum_{o=1}^{O} \exp(-2\pi i \mathbf{H} . \mathbf{t}_o)\right]. \end{aligned} \qquad (3)$$

An analysis of the individual non-standard centring types shows that the sum in square brackets is either zero or $O$ depending on $\mathbf{H}$. This means that in the superposition structure, in comparison to the crystal, some reflections are present and some systematically absent. The condition defining possible reflections is just seminvariant vector and seminvariant modulus. Equation (3) can be rewritten as

$$Q(\mathbf{r}) = (O/V) \sum_{\mathbf{H} \in \mathbf{H}^s} F_{\mathbf{H}} \exp(-2\pi i \mathbf{H} . \mathbf{r}), \qquad (4)$$

where $\mathbf{H}^s$ belongs to the structure seminvariant reflections. For example, in space group $P\bar{1}$, the seminvariant vector is $(h, k, l)$, the seminvariant modulus $(2, 2, 2)$ and the possible reflections for the MIF superposition structure are those with $h = 2n$, $k = 2n$, $l = 2n$; in space group $P2_1$, the seminvariant vector is $(h, k, l)$, the seminvariant modulus $(2, 0, 2)$ and possible reflections are $h = 2n$, $k = 0$, $l = 2n$.

Because $Q(\mathbf{r})$ can be calculated directly from $|F|^2$ [(1)], three possible applications are offered for crystal structure determination:

(i) An inverse Fourier transform of $Q(\mathbf{r})$ could lead to one-phase structure seminvariants applicable in direct methods. The same approach was proposed for a single Harker section by Ardito, Cascarano, Giacovazzo & Luić [1985; see also Cascarano, Giacovazzo & Luić (1984) and Burzlaff (1984)] and was tested on a heavy-atom structure with good results. But instead of a full Fourier transform, the largest peaks of a Harker section were used in the actual procedure. The method suggested here has the advantage of combining information from all Harker regions.

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(ii) Cascarano, Giacovazzo, Luić, Pifferi & Spagna (1987) tested successfully the possibility of refining a representative of a subset of atomic positional vectors compatible with Harker vectors on the basis of seminvariant reflections only. This approach is equally well applicable to the peaks of the MIF and represents a promising way to eliminate false peaks of the MIF.

(iii) A repeated Fourier calculation, according to (4), using experimental $|F_o|$ and the phase obtained from the peak positions of $Q(\mathbf{r})$ could lead to the superposition structure. The latter possibility is currently under experimental verification.

In the less-favourable case, when using the symmetry sum function (Pavelčík, 1989) and the rough approximation that the square of $Q(\mathbf{r})$ is proportional to the MIF superposition structure (equal-atom case), the inverse Fourier transform is

$$\begin{aligned} F_{\mathbf{H}\in\mathbf{H}^s} &\simeq C \int_V Q^2(\mathbf{r}) \exp(2\pi i \mathbf{H}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{r} \\ &= C \int_V \sum_{i=1}^{s} \sum_{\mathbf{K}} |F_{\mathbf{K}}|^2 \exp[-2\pi i \mathbf{K}\,.\,(\mathbf{r}-\mathbf{R}_i\mathbf{r}-\mathbf{t}_i) \\ &\quad \times \exp(2\pi i \mathbf{H}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{r} \\ &= C \sum_{i=1}^{s} \sum_{\mathbf{K}} |F_{\mathbf{K}}|^2 \exp(2\pi i \mathbf{K}\,.\,\mathbf{t}_i) \\ &\quad \times \int_V \exp[-2\pi i \mathbf{K}(\mathbf{I}-\mathbf{R}_i)\mathbf{r}] \exp(2\pi i \mathbf{H}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{r}. \qquad (5) \end{aligned}$$

The integral has non-zero value only if $\mathbf{K}(\mathbf{I}-\mathbf{R}_i)=\mathbf{H}$, so that

$$F_{\mathbf{H}\in\mathbf{H}^s} \simeq C \sum_{i=1}^{s} \sum_{\mathbf{K}} |F_{\mathbf{K}}|^2 \exp(2\pi i \mathbf{K}\,.\,\mathbf{t}_i) \qquad (6)$$

and the summation is over all $\mathbf{K}=\mathbf{H}(\mathbf{I}-\mathbf{R}_i)^{-1}$. $\mathbf{R}_i$ is the rotational matrix and $\mathbf{t}_i$ is the translation vector. Obviously, (6) is only an alternative form of the $\sum_1$ formula (for a review see Hašek, 1977). The fully comparable result can be obtained for the point and origin-removed Patterson calculated with $|E|^2-1$ as coefficients.

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