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References

Bochner, S. & Chandrasekharan, K. (1949). *Fourier Transforms*. Princeton: Princeton University Press.
Gillis, J. (1948*a*). *Acta Cryst.* **1**, 76.
Gillis, J. (1948*b*). *Acta Cryst.* **1**, 174.
Goedkoop, J. A. (1950). *Acta Cryst.* **3**, 374.
Harker, D. & Kasper, J. S. (1947). *J. Chem. Phys.* **15**, 882.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Karle, J. & Hauptmann, H. (1950). *Acta Cryst.* **3**, 181.
MacGillavry, C. H. (1950). *Acta Cryst.* **3**, 214.
Viervoll, H. & Ögrim, O. (1949). *Acta Cryst.* **2**, 277.
Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.
Zussman, J. (1951). *Acta Cryst.* **4**, 72.

Acta Cryst. (1952). **5**, 65

A Relation between the Signs of Structure Factors*

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By considering the extent to which a partial Fourier series, which contains as coefficients only a few of the larger structure factors, will represent the electron density in a crystal structure, and using the relations between the structure factors of an electron distribution and those of the square of this distribution, a probable relation between the signs of structure factors is deduced. The relation is suggested by the form of Sayre's equality, and is also related to Harker–Kasper inequalities.

1. Introduction

Relations between the magnitudes and phases of structure factors have been given by Harker & Kasper (1948), Karle & Hauptmann (1950) and Goedkoop (1950). All are based on the fact that the electron density in crystals is everywhere positive, and is approximately a superposition of spherically symmetric atoms of the same shape. An equality relation between structure factors, derived by Sayre (1952), is based on the fact that when a crystal contains equal atoms which are resolved from one another, the operation of squaring the electron density leaves it unchanged, in the sense that it is still composed of equal atoms in the same positions as before.

In this paper we shall use one of Sayre's results to show that the conditions fulfilled by a partial Fourier series lead to a very simple probable relation between the signs of structure factors. The relation is suggested by the form of Sayre's equality, and is also related to Harker–Kasper inequalities.

2. An exact condition satisfied by a partial series

Corresponding to the electron density

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{-\infty}^{+\infty} F(\mathbf{h}) \cos 2\pi\mathbf{h}\,.\,\mathbf{r}, \tag{1}$$

let

$$\rho_p(\mathbf{r}) = \frac{1}{V}\sum_{1}^{p} F(\mathbf{h}) \cos 2\pi\mathbf{h}\,.\,\mathbf{r}, \tag{2}$$

where the partial series (2) involves only p coefficients, which are not chosen from any particular region of the reciprocal lattice. By dividing the F's by the factor $\hat{f}$ (Harker & Kasper, 1948), (1) may be made to represent a distribution composed of point atoms.

Putting $F_s = F/\hat{f}$,

$$\sigma(\mathbf{r}) = \frac{1}{V}\sum_{-\infty}^{+\infty} F_s(\mathbf{h}) \cos 2\pi\mathbf{h}\,.\,\mathbf{r}, \tag{3}$$

and correspondingly

$$\sigma_p(\mathbf{r}) = \frac{1}{V}\sum_{1}^{p} F_s(\mathbf{h}) \cos 2\pi\mathbf{h}\,.\,\mathbf{r}. \tag{4}$$

Hence

$$\int_V \sigma\sigma_p\, dV = \frac{1}{V}\sum_{1}^{p} F_s^2. \tag{5}$$

Let $(\sigma_p)_j$ denote the value of σ_p at the centre of the jth atom. The value of $\int \sigma\, dV$, where the integral is now

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* A preliminary account of this work has already been given (Pepinsky & Cochran, 1951). Computations on X-RAC were carried out under contract N6o.n.r.–26916, T.O. 16 with the Office of Naval Research.

taken only over a volume in the immediate neighbourhood of the centre of the jth atom, is Z_j, the atomic number of this atom. Therefore, from (5),

$$\sum_{j=1}^{N} Z_j(\sigma_p)_j = \frac{1}{V}\sum_{1}^{p} F_s^2. \tag{6}$$

If we now consider

$$\sigma_p' = \frac{1}{V}\left\{\sum_{1}^{q} F_s(\mathbf{h})\cos 2\pi\mathbf{h}.\mathbf{r} - \sum_{q+1}^{p} F_s(\mathbf{h})\cos 2\pi\mathbf{h}.\mathbf{r}\right\}, \tag{7}$$

we find

$$\sum_{j=1}^{N} Z_j(\sigma_p')_j = \frac{1}{V}\left\{\sum_{1}^{q} F_s^2 - \sum_{q+1}^{p} F_s^2\right\} < \sum_{j=1}^{N} Z_j(\sigma_p)_j. \tag{8}$$

Thus, although σ_p does not satisfy any general condition such as non-negativity, (6) shows that the sum of its weighted values at atomic centres is a known positive quantity, while (8) shows that the correct choice of signs, as in (4), gives a greater value for this sum than any other sign combination such as (7).

To find the extent to which σ_p will resemble the crystal structure, we consider the case where all the atoms are equal. Then, from (6),

$$F(0)\,\overline{(\sigma_p)_j} = \frac{1}{V}\sum_{1}^{p} F_s^2, \tag{9}$$

where $\overline{(\sigma_p)_j}$ is the average value of σ_p at atomic centres. Now from (4),

$$\overline{\sigma_p},\ \text{defined as}\ \left\{\frac{1}{V}\int_V \sigma_p^2 dV\right\}^{\frac{1}{2}},$$

can be shown to be equal to

$$\frac{1}{V}\left\{\sum_{1}^{p} F_s^2\right\}^{\frac{1}{2}}, \tag{10}$$

and the structure will be recognizable to the extent that $\overline{(\sigma_p)_j} \gg \overline{\sigma_p}$. From (9) and (10) this condition is

$$\left\{\sum_{1}^{p} F_s^2\right\}^{\frac{1}{2}} \gg F(0),$$

or

$$\left\{\sum_{1}^{p} U^2\right\}^{\frac{1}{2}} \gg 1, \tag{11}$$

where $U = F/\{F(0)f\}$ is the unitary structure factor for point atoms.

3. A condition probably satisfied by a partial series

We now consider the case where σ_p involves only a few independent terms, say t. The number of terms in the series (4) will however be $p = tn$, where n is the symmetry number. The condition (11) is then

$$\sqrt{(nt)}\,\overline{U} > 1, \tag{12}$$

where $\overline{U}$ is the root-mean-square value of the t unitary structure factors involved. Equation (12) is already satisfied for $n=4$, $t=4$, $\overline{U}=0{\cdot}5$, which are practical orders of magnitude. The fact that, with quite a small number of terms, σ_p may already have values at atomic centres which are positive, and greater than the average magnitude elsewhere, suggests that the correct choice of signs will generally be that which causes σ_p to make greater excursions in the positive than in the negative direction. This is the case to the greatest extent when

$$\int_V \sigma_p^3 dV\ \text{is maximum positive.} \tag{13}$$

This result can be expressed in terms of the F's as follows.

It has been pointed out by Sayre (1952) that when the electron density is given by (1), the Fourier coefficients of the corresponding series for ρ^2 are

$$G(\mathbf{h}) = \frac{1}{V}\sum_{\mathbf{h}'} F(\mathbf{h}')F(\mathbf{h}+\mathbf{h}'). \tag{14}$$

The coefficients of σ_p^2 are therefore

$$G_s(\mathbf{h}) = \frac{1}{V}\sum_{\mathbf{h}'} F_s(\mathbf{h}')F_s(\mathbf{h}+\mathbf{h}'), \tag{15}$$

where it is understood that the summation in (15) involves only the p terms included in (4), and not all terms, as in (14).

Writing (13) as

$$\int_V \sigma_p\sigma_p^2 dV\ \text{is maximum positive,} \tag{16}$$

we find that this is satisfied when

$$\sum_{1}^{p} F_s(\mathbf{h})\,G_s(\mathbf{h})\ \text{is maximum positive.} \tag{17}$$

When the number of terms in (4) is small, to each $G_s(\mathbf{h})$ there will generally correspond, at most, one product $F_s(\mathbf{h}')F_s(\mathbf{h}+\mathbf{h}')$, so that (17), and therefore (13), is satisfied if each $F_s(\mathbf{h})$ and $G_s(\mathbf{h})$ have the same sign, or, from (15), if

$$s(\mathbf{h}) = s(\mathbf{h}')\,s(\mathbf{h}+\mathbf{h}'), \tag{18}$$

where $s(\mathbf{h})$ denotes the sign of $F(\mathbf{h})$.

It is particularly interesting to consider the situation when (4) involves only three independent terms, of indices $(\mathbf{h})$, $(\mathbf{h}')$ and $(\mathbf{h}+\mathbf{h}')$. The above considerations would lead us to expect from (12) that equation (18) will hold with increasing probability the more $\sqrt{(3n)}\,\overline{U}$ exceeds unity. Taking $n=4$, this gives $\overline{U} > \sim 0{\cdot}3$.

4. A connexion with Harker–Kasper inequalities

When the Harker–Kasper inequalities enable a sign determination to be made, it is always as given by (18). To prove this, we consider the most general Harker–Kasper inequality, as given by MacGillavry (1950). We adapt MacGillavry's notation so that the result applies to unitary structure factors with no imaginary component:

$$\begin{aligned} |\,U(\mathbf{h}) \pm U(\mathbf{h}')\,|^2 \leqslant \frac{1}{n}\sum_{K=0}^{n-1} \{&U(\mathbf{h}.(\phi_K - I))\exp[2\pi i(\mathbf{h}.\mathbf{t}_K)] \\ &+ U(\mathbf{h}'.(\phi_K - I))\exp[2\pi i(\mathbf{h}'.\mathbf{t}_K)] \\ &\pm 2U(\mathbf{h}-\mathbf{h}'.\phi_K)\exp[-2\pi i(\mathbf{h}'.\mathbf{t}_K)]\} \end{aligned} \tag{19}$$

(MacGillavry, 1950, §3). Now the product $s(\mathbf{h})\,s(\mathbf{h}')\,U(\mathbf{h}')$ has the same sign as $U(\mathbf{h})$, so that

$$|\,U(\mathbf{h})+s(\mathbf{h})\,s(\mathbf{h}')\,U(\mathbf{h}')\,|^2 \qquad (20)$$

is the maximum value of the left-hand side of the inequality, and when (20) replaces $|\,U(\mathbf{h})\pm U(\mathbf{h}')\,|^2$, $s(\mathbf{h})\,s(\mathbf{h}')$ replaces $\pm$ on the right-hand side of (19). When the left-hand side has its maximum value, the inequality can only prove a term on the right-hand side to be positive; for instance,

$s(\mathbf{h})\,s(\mathbf{h}')\,U(\mathbf{h}-\mathbf{h}'.\phi_K)\exp[-2\pi i(\mathbf{h}'.\mathbf{t}_K)]$ is positive,

or, since $s(\mathbf{h}')=s(-\mathbf{h}')$,

$s(\mathbf{h})\,s(\mathbf{h}')\,U(\mathbf{h}+\mathbf{h}'.\phi_K)\exp[2\pi i(\mathbf{h}'.\mathbf{t}_K)]$ is positive. (21)

We note that the vector index of U in (21) is the sum of the index of a term $U(\mathbf{h})$ appearing on the left-hand side of (19) and the index of a term $U(\mathbf{h}'.\phi_K)$ which is related by symmetry to the other, $U(\mathbf{h}')$, appearing on the left-hand side. Also $\exp[2\pi i(\mathbf{h}'.\mathbf{t}_K)]$ is the phase of $U(\mathbf{h}'.\phi_K)$ relative to that of $U(\mathbf{h}')$, or, since the U's are entirely real,

$$\exp[2\pi i(\mathbf{h}'.\mathbf{t}_K)]=s(\mathbf{h}')\,s(\mathbf{h}'.\phi_K).$$

Hence (21) becomes

$s(\mathbf{h})\,s(\mathbf{h}')\,U(\mathbf{h}+\mathbf{h}'.\phi_K)\,s(\mathbf{h}')\,s(\mathbf{h}'.\phi_K)$ is positive,

which requires

$$s(\mathbf{h})=s(\mathbf{h}'.\phi_K)\,s(\mathbf{h}+\mathbf{h}'.\phi_K),$$

and this is identical with (18).

5. Experimental test of the relation between signs of structure factors

We now show that (18) is true in a large number of instances when inequalities impose no limitation.

Example 1

Glutamine, $C_5O_3N_2H_{10}$. $a=16{\cdot}0$, $b=7{\cdot}8$, $c=5{\cdot}1$ Å. Space group $P2_12_12_1$ (Penfold, unpublished data). Of the 163 independent $F(hk0)$'s within the limiting circle of copper radiation, 37 have $|\,U\,|>0{\cdot}2$. Using only these 37 terms, there are 135 instances in which independent checks of (18) can be made. The table shows the number of cases in which (18) holds, the value of $\overline{U}$ being the average over the three terms involved, as in (12):

Value of $\overline{U}$	0·20 to 0·24	0·25 to 0·29	0·30 to 0·34	0·35 to 0·39	
(18) holds in	7	43	38	19	instances
(18) fails in	4	12	5	0	instances

	0·40 to 0·44	
(18) holds in	7	instances
(18) fails in	0	instances

In this case Harker–Kasper inequalities can be used to determine the signs of three terms, while those of ten others can be obtained in terms of a and b, where $a=\pm1$, $b=\pm1$. The scale of the U's was obtained by the statistical method of Wilson (1942). Subsequent comparison with calculated values showed that the magnitudes of low-index U's were overestimated by about 20%. When the correct values are used, practically all the inequality relations used are in fact satisfied by either choice of sign! The projection of the glutamine structure on (001) was obtained directly from the $|F(hk0)|$'s by application of inequalities as mentioned above, then by relation (18), and finally by a slight modification of the equality

$$f(\sin\theta)\,F(kh0)=\frac{1}{A}\sum_{h'k'}F(h'k'0)\,F(h+h',k+k',0),$$

derived by Sayre (1952). Details will be published later.

Example 2

Guanine hydrochloride monohydrate,

$$C_5ON_5H_5.H_2O.HCl.$$

$a=19{\cdot}3$, $b=9{\cdot}94$, $c=5{\cdot}0$ Å; $\beta=107°\,54'$. Space group $P2_1/a$ (Broomhead, 1951). Of the 242 independent $F(hk0)$'s within the limiting circle of copper radiation, 35 have $|\,U\,|>0{\cdot}2$. Checks of (18), involving these 35 terms, were made in 66 instances. The results are shown below:

Value of $\overline{U}$	0·21 to 0·23	0·24 to 0·26	0·27 to 0·29	0·30 to 0·34	
(18) holds in	9	24	19	9	instances
(18) fails in	3	2	0	0	instances

In this case inequalities require no sign relationships whatsoever. These results are in general agreement with the conclusions of §3, except that in the second example (18) holds to an even greater extent than might have been expected from the considerations of that section. This can be explained as due to the fact that the condition

$$\int_V \sigma_p^3\,dV \text{ is maximum positive,}$$

which leads to (18), is necessarily satisfied to a greater extent when the structure contains a region of high electron density, in this case the chlorine atom.

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References

Broomhead, J. M. (1951). *Acta Cryst.* **4**, 92.
Goedkoop, J. A. (1950). *Acta Cryst.* **3**, 374.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Karle, J. & Hauptmann, H. (1950). *Acta Cryst.* **3**, 181.
MacGillavry, C. H. (1950). *Acta Cryst.* **3**, 214.
Pepinsky, R. & Cochran, W. (1951). *Phys. Rev.* **83**, 226.
Sayre, D. (1952). *Acta. Cryst.* **5**, 60.
Wilson, A. J. C. (1942). *Nature, Lond.*, **150**, 152.