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**A new type of inequality relationship between unitary structure factors.\*** By EDWARD W. HUGHES,  
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Although it is generally recognized that the inequality method is not by itself of sufficient power to permit the solution of structures of more than moderate complexity, interest in the subject continues and many examples of its use in the complete or partial solution of structures are now recorded. Recently Bouman (1956) has published a theoretical examination in which he claims to have set forth a method for finding all possible inequality relationships. This claim is perhaps justified if restricted to relationships in closed form, but the derivation outlined briefly below shows that one can obtain other relationships which might conceivably be of some usefulness in some situations.

We begin by seeking the expansion of  $|\cos 2\pi x|$  in a Fourier series of cosines. By the usual method for evaluating coefficients in such series one obtains

$$|\cos 2\pi x| = (2/\pi) \left\{ 1 - 2 \sum_1^{\infty} [(-1)^n / (4n^2 - 1)] \cos 2\pi n x \right\}.$$

Now substitute  $\mathbf{H} \cdot \mathbf{r}_j$  for  $x$ , multiply by  $2q_j$ , twice the fraction of the total scattering power on the  $j$ th atom at  $\mathbf{r}_j$ , and sum over the  $j$ 's. Noting that in space group PI

$$2 \sum_1^{N/2} q_j = 1 \quad \text{and} \quad 2 \sum_1^{N/2} q_j \cos 2\pi \mathbf{H} \cdot \mathbf{r}_j = U_{\mathbf{H}},$$

we see that

$$2 \sum_1^{N/2} q_j |\cos 2\pi \mathbf{H} \cdot \mathbf{r}_j| = (2/\pi) \left\{ 1 - 2 \sum_1^{\infty} [(-1)^n / (4n^2 - 1)] U_{2n\mathbf{H}} \right\}.$$

If we now move the absolute-value bar on the left outside the summation sign, the quantity on the left may become smaller and equals  $|U_{\mathbf{H}}|$ . We thus have shown that

$$|U_{\mathbf{H}}| \leq (2/\pi) \left\{ 1 - 2 \sum_1^{\infty} [(-1)^n / (4n^2 - 1)] U_{2n\mathbf{H}} \right\}.$$

With the first few terms written out explicitly and rearranged, we get

$$(3\pi/4)|U_{\mathbf{H}}| - 3/2 \leq U_{2\mathbf{H}} - (3/15)U_{4\mathbf{H}} + (3/35)U_{6\mathbf{H}} - (3/63)U_{8\mathbf{H}} \dots,$$

which can be compared with the corresponding Harker & Kasper (1948) inequality

$$2U_{\mathbf{H}}^2 - 1 \leq U_{2\mathbf{H}}.$$

Higher orders in the series are usually of little importance because the coefficients decrease rapidly with increasing  $n$  and so if  $U_{4\mathbf{H}}$  is negligibly small, terms above  $U_{2\mathbf{H}}$  can be neglected in comparing the two formulas. It then appears that for a range of  $U_{\mathbf{H}}$  values between about 0.28 and 0.90, the new expression sets a lower

limit on  $U_{2\mathbf{H}}$  that is higher by up to 0.20 than that of the Harker-Kasper equation, and thus is more likely to fix the sign of  $U_{2\mathbf{H}}$ . Above and below this range the limit set is lower, but the largest difference is in the lower range of  $|U_{\mathbf{H}}|$  for which signs usually cannot be established by either inequality. This is shown graphically by Fig. 1, which plots the upper and lower limits of each

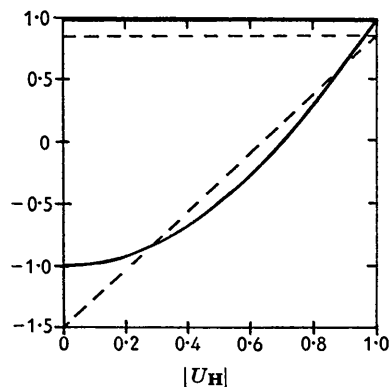


Fig. 1. Upper and lower limits of inequalities plotted against  $|U_{\mathbf{H}}|$ . Solid line: Harker-Kasper inequality; dashed line: series inequality.

inequality against  $|U_{\mathbf{H}}|$ . If  $U_{4\mathbf{H}}$  and other higher terms are not negligible in the series form, the two forms together might make a useful combination.

Since  $|\cos 2\pi x| \leq 1$ , we also have

$$2 \sum_1^{N/2} q_j |\cos 2\pi x_j| \leq 1.$$

This puts an upper limit of unity on the original series. In the rearranged form this upper limit becomes  $(3\pi/4) - 3/2 = 0.8562$ , indicated by a dashed line on Fig. 1. If  $U_{2\mathbf{H}}$  and higher orders are large, this upper limit might establish a sign relationship.

By analogous methods other inequalities can be established for series of unitary structure factors. In deriving these one sometimes requires the expansion of  $|\sin 2\pi x|$ , which is

$$|\sin 2\pi x| = (2/\pi) \left\{ 1 - 2 \sum_1^{\infty} [1 / (4n^2 - 1)] \cos 2\pi n x \right\}.$$

For example, using both expansions one can obtain

$$|U_{\mathbf{H} \pm \mathbf{K}}| \leq (4/\pi^2) \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} [(\mp 1)^{n+m} / (4n^2 - 1)(4m^2 - 1)] \times [U_{(n+m)\mathbf{H} + (n-m)\mathbf{K}} + U_{(n-m)\mathbf{H} + (n+m)\mathbf{K}}].$$

When both  $n$  and  $m$  differ from zero the coefficients of the series are quite small so that the  $n = \pm 1, m = 0$

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and  $n = 0$ ,  $m = \pm 1$  terms are most important. They yield, on the right,  $U_{\mathbf{H}+\mathbf{K}}$  and  $U_{\mathbf{H}-\mathbf{K}}$ , so this series inequality is closely related to the well known 'sum and difference' inequality of Harker & Kasper.

The validity of the derivation requires that  $q_j$  shall be a positive constant. This in turn requires that the atoms shall all have a common shape factor multiplied by their appropriate magnitude factors and that the

shape factor shall have a Fourier transform that is positive within the range of the data required to make the series effectively converge.

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*Acta Cryst.* (1957). **10**, 377

**Note on the sign determination by optical-transform methods.** By TOKUNOSUKÉ WATANABÉ and MASAMOTO OTSUKA, *Department of Physics, Osaka University, Osaka, Japan*

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It is reported (Lipson & Taylor, 1951; Hanson, Lipson & Taylor, 1953; Lipson & Cochran, 1953; Pinnock & Taylor, 1955) that the signs of the structure factors for a given arrangement of atoms may be quickly determined by means of optical-transform methods. They state that in optical-transform of a centrosymmetrical structure (1) the positive and negative regions are separated by nodal lines, and (2) by adding an extra hole at the centre of symmetry of a structure, the positive regions of the original transform are enhanced and the negative regions are depressed. These criteria have been proved powerful in solving a number of organic structures.

It has become common to use a mask in which some holes are displaced by a lattice translation in order to avoid overlapping, or several holes are placed at integral multiples of lattice translations in order to give appropriate weights to the scattering factors for particular atoms. As the number of such holes increases, the whole transform will become so modulated that criterion (1) will no longer be applicable, and that intensities only at reciprocal-lattice points will have a significant meaning.

Let us confine ourselves to the intensities of the optical transform at reciprocal-lattice points. In this case, criterion (2) must be used with caution, as will be explained in the following.

The Fourier transform of a centrosymmetrical structure consisting of holes of equal size can be given by

$$F(R) = f(R)g(R), \quad (1)$$

where  $f(R)$  is the Fourier transform of a single hole and  $g(R)$  is the geometrical structure factor  $\sum_i \exp 2\pi i r_i R$ ,  $r_i$  being the positional vector of the  $i$ th hole and  $R$  a vector in reciprocal space.

When an extra hole is added at the centre of symmetry of the same structure, the transform will become

$$F'(R) = f(R)\{1+g(R)\}. \quad (2)$$

Since both  $f(R)$  and  $g(R)$  are real, the increment in intensity is proportional to

$$F'(R)^2 - F(R)^2 = f(R)^2\{1+2g(R)\}. \quad (3)$$

Hence, the regions for which  $g(R) > -\frac{1}{2}$  are enhanced and those for which  $g(R) < -\frac{1}{2}$  are depressed. It follows that intensities weaker than  $\frac{1}{4}f(R)^2$  are always enhanced so that signs of their corresponding Fourier coefficients cannot be determined.

The sign determination can be extended to those weak reflexions  $> \frac{1}{4}f(R)^2$  in the following way. Prepare three photographs which correspond to the following three quantities:

$$A = f(R)^2g(R)^2, \quad (4)$$

$$B = f(R)^2\{1+g(R)\}^2, \quad (5)$$

$$C = f(R)^2\{1+g(R)^2\}. \quad (6)$$

$A$  is the optical transform of a given centrosymmetrical structure.  $B$  is the optical transform of the same structure plus an extra hole added at the centre.  $C$  is the superposition of  $A$  and the optical transform of a single hole, and can be prepared by exposing the mask of the structure and a single hole in succession. By subtracting  $C$  from  $B$ , we get

$$B - C = 2f(R)^2g(R). \quad (7)$$

The sign of (7) is exactly the same as that given by (1). Thus the original transform is positive if  $B$  is stronger than  $C$ , and is negative if  $B$  is weaker than  $C$ . This criterion can be applied throughout the whole optical transform observed at reciprocal-lattice points.

Further improvement can be made by comparing  $B$  with  $D$ , which is another photograph corresponding to the optical transform defined by

$$D = f(R)^2\{-1+g(R)\}^2. \quad (8)$$

$D$  can be prepared by exposing the mask of the structure and a central hole, the latter being covered with mica which retards the phase of the incident light by  $\pi$ . The difference in intensity between  $B$  and  $D$  is

$$B - D = 4f(R)^2g(R), \quad (9)$$

which is twice as much in magnitude as that given by (7).

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